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Second Edition
Inorganic Chemistry

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Preface

Given the increasing quantity of knowledge in all areas of science, the imparting of this knowledge must necessarily concentrate on general principles and laws while details must be restricted to important examples. A textbook should be reasonably small, but essential aspects of the subject may not be neglected, traditional foundations must be considered, and modern developments should be included. This introductory text is an attempt to present inorganic structural chemistry in this way. Compromises cannot be avoided; some sections may be shorter, while others may be longer than some experts in this area may deem appropriate.

Chemists predominantly think in illustrative models: they like to “see” structures and bonds. Modern bond theory has won its place in chemistry, and is given proper attention in Chapter 10. However, with its extensive calculations it corresponds more to the way of thinking of physicists. Furthermore, albeit the computational results have become quite reliable, it often remains difficult to understand structural details. For everyday use, simple models such as those treated in Chapters 8, 9 and 13 are usually more useful to a chemist: “The peasant who wants to harvest in his lifetime cannot wait for the \textit{ab initio} theory of weather. Chemists, like peasants, believe in rules, but cunningly manage to interpret them as occasion demands” (H.G. \textsc{von Schnering} [112]).

This book is mainly addressed to advanced students of chemistry. Basic chemical knowledge concerning atomic structure, chemical bond theory and structural aspects is required. Parts of the text are based on a course on inorganic crystal chemistry by Prof. H. Bärnighausen at the University of Karlsruhe. I am grateful to him for permission to use the manuscript of his course, for numerous suggestions, and for his encouragement. For discussions and suggestions I also thank Prof. D. Babel, Prof. K. Dehnicke, Prof. C. Elschenbroich, Prof. D. Reinen and Prof. G. Weiser. I thank Prof. T. Fässler for supplying figures of the electron localization function and for reviewing the corresponding section. I thank Prof. S. Schlecht for providing figures and for reviewing the chapter on nanostructures. I thank Ms. J. Gregory and Mr. P. C. Weston for reviewing and correcting the English version of the manuscript.

In this second edition the text has been revised and new scientific findings have been taken into consideration. For example, many recently discovered modifications of the elements have been included, most of which occur at high pressures. The treatment of symmetry has been shifted to the third chapter and the aspect of symmetry is given more attention in the following chapters. New sections deal with quasicrystals and other not strictly crystalline solids, with phase transitions and with the electron localization function. There is a new chapter on nanostructures. Nearly all figures have been redrawn.

Ulrich Müller

Marburg, Germany, April 2006
1 Introduction

Structural chemistry or stereochemistry is the science of the structures of chemical compounds, the latter term being used mainly when the structures of molecules are concerned. Structural chemistry deals with the elucidation and description of the spatial order of atoms in a compound, with the explanation of the reasons that lead to this order, and with the properties resulting therefrom. It also includes the systematic ordering of the recognized structure types and the disclosure of relationships among them.

Structural chemistry is an essential part of modern chemistry in theory and practice. To understand the processes taking place during a chemical reaction and to render it possible to design experiments for the synthesis of new compounds, a knowledge of the structures of the compounds involved is essential. Chemical and physical properties of a substance can only be understood when its structure is known. The enormous influence that the structure of a material has on its properties can be seen by the comparison of graphite and diamond: both consist only of carbon, and yet they differ widely in their physical and chemical properties.

The most important experimental task in structural chemistry is the structure determination. It is mainly performed by X-ray diffraction from single crystals; further methods include X-ray diffraction from crystalline powders and neutron diffraction from single crystals and powders. Structure determination is the analytical aspect of structural chemistry; the usual result is a static model. The elucidation of the spatial rearrangements of atoms during a chemical reaction is much less accessible experimentally. Reaction mechanisms deal with this aspect of structural chemistry in the chemistry of molecules. Topotaxy is concerned with chemical processes in solids, in which structural relations exist between the orientation of educts and products. Neither dynamic aspects of this kind are subjects of this book, nor the experimental methods for the preparation of solids, to grow crystals or to determine structures.

Crystals are distinguished by the regular, periodic order of their components. In the following we will focus much attention on this order. However, this should not lead to the impression of a perfect order. Real crystals contain numerous faults, their number increasing with temperature. Atoms can be missing or misplaced, and dislocations and other imperfections can occur. These faults can have an enormous influence on the properties of a material.
2 Description of Chemical Structures

In order to specify the structure of a chemical compound, we have to describe the spatial distribution of the atoms in an adequate manner. This can be done with the aid of chemical nomenclature, which is well developed, at least for small molecules. However, for solid-state structures, there exists no systematic nomenclature which allows us to specify structural facts. One manages with the specification of structure types in the following manner: ‘magnesium fluoride crystallizes in the rutile type’, which expresses for MgF$_2$ a distribution of Mg and F atoms corresponding to that of Ti and O atoms in rutile. Every structure type is designated by an arbitrarily chosen representative. How structural information can be expressed in formulas is treated in Section 2.1.

Graphic representations are useful. One of these is the much used valence-bond formula, which allows a succinct representation of essential structural aspects of a molecule. More exact and more illustrative are perspective, true-to-scale figures, in which the atoms are drawn as balls or — if the always present thermal vibrations are to be expressed — as ellipsoids. To achieve a better view, the balls or ellipsoids are plotted on a smaller scale than that corresponding to the effective atomic sizes. Covalent bonds are represented as sticks. The size of a thermal ellipsoid is chosen to represent the probability of finding the atom averaged over time (usually 50 % probability of finding the center of the atom within the ellipsoid; cf. Fig. 2.1b). For more complicated structures the perspective image can be made clearer with the aid of a stereoscopic view (cf. Fig. 7.5, p. 56). Different types of drawings can be used to stress different aspects of a structure (Fig. 2.1).

Quantitative specifications are made with numeric values for interatomic distances and angles. The interatomic distance is defined as the distance between the nuclei of two atoms.
in their mean positions (mean positions of the thermal vibration). The most common method to determine interatomic distances experimentally is X-ray diffraction from single crystals. Other methods include neutron diffraction from crystals and, for small molecules, electron diffraction and microwave spectroscopy with gaseous samples. X-ray diffraction determines not the positions of the atomic nuclei but the positions of the centers of the negative charges of the atomic electron shells, because X-rays are diffracted by the electrons of the atoms. However, the negative charge centers coincide almost exactly with the positions of the atomic nuclei, except for covalently bonded hydrogen atoms. To locate hydrogen atoms exactly, neutron diffraction is also more appropriate than X-ray diffraction for another reason: X-rays are diffracted by the large number of electrons of heavy atoms to a much larger extent, so that the position of H atoms in the presence of heavy atoms can be determined only with low reliability. This is not the case for neutrons, as they interact with the atomic nuclei. (Because neutrons suffer incoherent scattering from H atom nuclei to a larger extent than from D atom nuclei, neutron scattering is performed with deuterated compounds.)

2.1 Coordination Numbers and Coordination Polyhedra

The coordination number (c.n.) and the coordination polyhedron serve to characterize the immediate surroundings of an atom. The coordination number specifies the number of coordinated atoms; these are the closest neighboring atoms. For many compounds there are no difficulties in stating the coordination numbers for all atoms. However, it is not always clear up to what limit a neighboring atom is to be counted as a closest neighbor. For instance, in metallic antimony every Sb atom has three neighboring atoms at distances of 291 pm and three others at distances of 336 pm, which is only 15% more. In this case it helps to specify the coordination number by 3+3, the first number referring to the number of neighboring atoms at the shorter distance.

Stating the coordination of an atom as a single number is not very informative in more complicated cases. However, specifications of the following kind can be made: in white tin an atom has four neighboring atoms at a distance of 302 pm, two at 318 pm and four at 377 pm. Several propositions have been made to calculate a mean or ‘effective’ coordination number (e.c.n. or ECoN) by adding all surrounding atoms with a weighting scheme, in that the atoms are not counted as full atoms, but as fractional atoms with a number between 0 and 1; this number is closer to zero when the atom is further away. Frequently a gap can be found in the distribution of the interatomic distances of the neighboring atoms: if the shortest distance to a neighboring atom is set equal to 1, then often further atoms are found at distances between 1 and 1.3, and after them follows a gap in which no atoms are found. According to a proposition of G. Brunner and D. Schwarzenbach an atom at the distance of 1 obtains the weight 1, the first atom beyond the gap obtains zero weight, and all intermediate atoms are included with weights that are calculated from their distances by linear interpolation:

\[
e\text{c.n.} = \frac{\sum_i (d_g - d_i)}{(d_g - d_1)}
\]

- \(d_1\) = distance to the closest atom
- \(d_g\) = distance to the first atom beyond the gap
- \(d_i\) = distance to the \(i\)-th atom in the region between \(d_1\) and \(d_g\)

For example for antimony: taking \(3 \times d_1 = 291\), \(3 \times d_i = 336\) and \(d_g = 391\) pm one obtains e.c.n. = 4.65. The method is however of no help when no clear gap can be discerned.
A mathematically unique method of calculation considers the domain of influence (also called Wirkungsbereich, VORONOI polyhedron, WIGNER-SEITZ cell, or DIRICHLET domain). The domain is constructed by connecting the atom in question with all surrounding atoms; the set of planes perpendicular to the connecting lines and passing through their midpoints forms the domain of influence, which is a convex polyhedron. In this way, a polyhedron face can be assigned to every neighboring atom, the area of the face serving as measure for the weighting. A value of 1 is assigned to the largest face. Other formulas have also been derived, for example,

\[
E\text{CoN} = \sum_i \exp[1 - (d_i/d_1)^n]
\]

\(n = 5 \text{ or } 6\)

\(d_i = \text{distance to the } i\text{-th atom}\)

\(d_1 = \text{shortest distance or assumed standard distance}\)

With this formula we obtain ECoN = 6.5 for white tin and ECoN = 4.7 for antimony.

The kind of bond between neighboring atoms also has to be considered. For instance, the coordination number for a chlorine atom in the CCl₄ molecule is 1 when only the covalently bonded C atom is counted, but it is 4 (1 C + 3 Cl) when all atoms ‘in contact’ are counted. In the case of molecules one will tend to count only covalently bonded atoms as coordinated atoms. In the case of crystals consisting of monoatomic ions usually only the anions immediately adjacent to a cation and the cations immediately adjacent to an anion are considered, even when there are contacts between anions and anions or between cations and cations. In this way, an I⁻ ion in LiI (NaCl type) is assigned the coordination number 6, whereas it is 18 when the 12 I⁻ ions with which it is also in contact are included. In case of doubt, one should always specify exactly what is to be included in the coordination sphere.

The coordination polyhedron results when the centers of mutually adjacent coordinated atoms are connected with one another. For every coordination number typical coordination polyhedra exist (Fig. 2.2). In some cases, several coordination polyhedra for a given coordination number differ only slightly, even though this may not be obvious at first glance; by minor displacements of atoms one polyhedron may be converted into another. For example, a trigonal bipyramid can be converted into a tetragonal pyramid by displacements of four of the coordinated atoms (Fig. 8.2, p. 71).

Larger structural units can be described by connected polyhedra. Two polyhedra can be joined by a common vertex, a common edge, or a common face (Fig. 2.3). The common atoms of two connected polyhedra are called bridging atoms. In face-sharing polyhedra the central atoms are closest to one another and in vertex-sharing polyhedra they are furthest apart. Further details concerning the connection of polyhedra are discussed in chapter 16.

The coordination conditions can be expressed in a chemical formula using a notation suggested by F. MACHATSCHKI (and extended by several other authors; for recommendations see [35]). The coordination number and polyhedron of an atom are given in brackets in a right superscript next to the element symbol. The polyhedron is designated with a symbol as listed in Fig. 2.2. Short forms can be used for the symbols, namely the coordination number alone or, for simple polyhedra, the letter alone, e.g. t for tetrahedron, and in this case the brackets can also be dropped. For example:

\[
\text{Na}^{[6]}\text{Cl}^{[6]} \quad \text{or} \quad \text{Na}^{[6]}\text{Cl}^{[6]} \quad \text{or} \quad \text{Na}^{6}\text{Cl}^{6}
\]

\[
\text{Ca}^{[8]}\text{F}_2^{[4]} \quad \text{or} \quad \text{Ca}^{[8]}\text{F}_2^{[4]} \quad \text{or} \quad \text{Ca}^{4}\text{F}_2^{4}
\]
2.1 Coordination Numbers and Coordination Polyhedra

2: linear arrangement \([2l]\)

2: angular arrangement \([2n]\)

3: triangle \([3l]\)

4: square \([4l] \text{ or } [s]\)

4: tetrahedron \([4l] \text{ or } [t]\)

5: trigonal bi-pyramid \([5by]\)

5: tetragonal pyramid \([5y]\)

6: octahedron \([6o] \text{ or } [o]\)

6: trigonal prism \([6p]\)

7: capped trigonal prism \([6p1c]\)

8: cube \([8cb] \text{ or } [cb]\)

8: square antiprism \([8acb]\)

8: dodecahedron \([8do] \text{ or } [do]\)

9: triply-capped trigonal prism \([6p3c]\)

12: anticuboctahedron \([12aco] \text{ or } [aco]\)

12: cuboctahedron \([12co] \text{ or } [co]\)

Fig. 2.2
The most important coordination polyhedra and their symbols; for explanation of the symbols see page 6
Fig. 2.3
Examples for the connection of polyhedra.
(a) Two tetrahedra sharing a vertex.
(b) Two tetrahedra sharing an edge.
(c) Two octahedra sharing a vertex.
(d) Two octahedra sharing a face. For two octahedra sharing an edge see Fig. 1

For more complicated cases an extended notation can be used, in which the coordination of an atom is expressed in the manner $A^{[m,n,p]}$. For $m$, $n$, and $p$ the polyhedra symbols are taken. Symbols before the semicolon refer to polyhedra spanned by the atoms $B$, $C$..., in the sequence as in the chemical formula $A_aB_bC_c$. The symbol after the semicolon refers to the coordination of the atom in question with atoms of the same kind. For example perovskite:

$$\text{Ca}^{[12co]}\text{Ti}^{[6o]}\text{O}_3^{[4t,2l;8p]}$$

(cf. Fig. 17.10, p. 203)

Since Ca is not directly surrounded by Ti atoms, the first polyhedron symbol is dropped; however, the first comma cannot be dropped to make it clear that the $12co$ refers to a cuboctahedron formed by 12 O atoms. Ti is not directly surrounded by Ca, but by six O atoms forming an octahedron. O is surrounded in planar (square) coordination by four Ca, by two linearly arranged Ti and by eight O atoms forming a prism.

In addition to the polyhedra symbols listed in Fig. 2.2, further symbols can be constructed. The letters have the following meanings:

- $l$: collinear
- $t$: tetrahedral
- $o$: octahedral
- $n$: not collinear
- $s$: square
- $p$: prismatic
- $y$: pyramidal
- $cb$: cubic
- $a$: anti-
- $b$: bipyramidal
- $FK$: Frank–Kasper polyhedron (Fig. 15.5)

For example: $[3n]$ = three atoms not coplanar with the central atom as in NH$_3$; $[12p]$ = hexagonal prism. When lone electron pairs in polyhedra vertices are also counted, a symbolism in the following manner can be used: $[\psi - 4t]$ (same meaning as $[3n]$), $[\psi - 6o]$ (same as $[5y]$), $[2\psi - 6o]$ (same as $[4t]$).

When coordination polyhedra are connected to chains, layers or a three-dimensional network, this can be expressed by the preceding symbols $\frac{1}{\infty}$, $\frac{2}{\infty}$ or $\frac{3}{\infty}$, respectively. Examples:

$$\text{Na}_3\text{Cl}^{[6]}\quad \text{Ti}^{[6]}\text{O}_2^{[3]}\quad \text{C}^{[3]}\text{(graphite)}$$

To state the existence of individual, finite atom groups, $\frac{0}{\infty}$ can be set in front of the symbol. For their further specification, the following less popular symbols may be used:
2.2 Description of Crystal Structures

In a crystal atoms are joined to form a larger network with a periodical order in three dimensions. The spatial order of the atoms is called the crystal structure. When we connect the periodically repeated atoms of one kind in three space directions to a three-dimensional grid, we obtain the crystal lattice. The crystal lattice represents a three-dimensional order of points; all points of the lattice are completely equivalent and have the same surroundings. We can think of the crystal lattice as generated by periodically repeating a small parallelepiped in three dimensions without gaps (Fig. 2.4; parallelepiped = body limited by six faces that are parallel in pairs). The parallelepiped is called the unit cell.

Fig. 2.4
Primitive cubic crystal lattice. One unit cell is marked
The unit cell can be defined by three basis vectors labeled \( \mathbf{a}, \mathbf{b}, \) and \( \mathbf{c} \). By definition, the crystal lattice is the complete set of all linear combinations \( \mathbf{t} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}, u, v, w \) comprising all positive and negative integers. Therefore, the crystal lattice is an abstract geometric construction, and the terms ‘crystal lattice’ and ‘crystal structure’ should not be confounded. The lengths \( a, b, \) and \( c \) of the basis vectors and the angles \( \alpha, \beta, \) and \( \gamma \) between them are the lattice parameters (or lattice constants; \( \alpha \) between \( b \) and \( c \) etc.). There is no unique way to choose the unit cell for a given crystal structure, as is illustrated for a two-dimensional example in Fig. 2.5. To achieve standardization in the description of crystal structures, certain conventions for the selection of the unit cell have been settled upon in crystallography:

1. The unit cell is to show the symmetry of the crystal, i.e. the basis vectors are to be chosen parallel to symmetry axes or perpendicular to symmetry planes.

2. For the origin of the unit cell a geometrically unique point is selected, with priority given to an inversion center.

3. The basis vectors should be as short as possible. This also means that the cell volume should be as small as possible, and the angles between them should be as close as possible to 90°.

4. If the angles between the basis vectors deviate from 90°, they are either chosen to be all larger or all smaller than 90° (preferably \( > 90° \)).

A unit cell having the smallest possible volume is called a primitive cell. For reasons of symmetry according to rule 1 and contrary to rule 3, a primitive cell is not always chosen, but instead a centered cell, which is double, triple or fourfold primitive, i.e. its volume is larger by a corresponding factor. The centered cells to be considered are shown in Fig. 2.6.
Aside from the conventions mentioned for the cell choice, further rules have been developed to achieve standardized descriptions of crystal structures [36]. They should be followed to assure a systematic and comparable documentation of the data and to facilitate the inclusion in databases. However, contraventions of the standards are rather frequent, not only from negligence or ignorance of the rules, but often for compelling reasons, for example when the relationships between different structures are to be pointed out.

Specification of the lattice parameters and the positions of all atoms contained in the unit cell is sufficient to characterize all essential aspects of a crystal structure. A unit cell can only contain an integral number of atoms. When stating the contents of the cell one refers to the chemical formula, i.e. the number of ‘formula units’ per unit cell is given; this number is usually termed \( Z \). How the atoms are to be counted is shown in Fig. 2.7.

**Fig. 2.7**

The way to count the contents of a unit cell for the example of the face-centered unit cell of NaCl: 8 Cl\(^-\) ions in 8 vertices, each of which belongs to 8 adjacent cells makes \( 8/8 = 1 \); 6 Cl\(^-\) ions in the centers of 6 faces belonging to two adjacent cells each makes \( 6/2 = 3 \). 12 Na\(^+\) ions in the centers of 12 edges belonging to 4 cells each makes \( 12/4 = 3 \); 1 Na\(^+\) ion in the cube center, belonging only to this cell. Total: 4 Na\(^+\) and 4 Cl\(^-\) ions or four formula units of NaCl (\( Z = 4 \)).

### 2.3 Atomic Coordinates

The position of an atom in the unit cell is specified by a set of **atomic coordinates**, i.e. by three coordinates \( x, y \) and \( z \). These refer to a coordinate system that is defined by the basis vectors of the unit cell. The unit length taken along each of the coordinate axes corresponds to the length of the respective basis vector. The coordinates \( x, y \) and \( z \) for every atom within the unit cell thus have values between 0.0 and <1.0. The coordinate system is **not** a Cartesian one; the coordinate axes can be inclined to one another and the unit lengths on the axes may differ from each other. Addition or subtraction of an **integral** number to a coordinate value generates the coordinates of an equivalent atom in a different unit cell. For example, the coordinate triplet \( x = 1.27, y = 0.52 \) and \( z = -0.10 \) specifies the position of an atom in a cell neighboring the origin cell, namely in the direction \(+a\) and \(-c\); this atom is equivalent to the atom at \( x = 0.27, y = 0.52 \) and \( z = 0.90 \) in the origin cell.

Commonly, only the atomic coordinates for the atoms in one **asymmetric unit** are listed. Atoms that can be ‘generated’ from these by symmetry operations are not listed. Which symmetry operations are to be applied is revealed by stating the **space group** (cf. Section 3.3). When the lattice parameters, the space group, and the atomic coordinates are known, all structural details can be deduced. In particular, all interatomic distances and angles can be calculated.

The following formula can be used to calculate the distance \( d \) between two atoms from the lattice parameters and atomic coordinates:
2 DESCRIPTION OF CHEMICAL STRUCTURES

\[ d = \sqrt{(a\Delta x)^2 + (b\Delta y)^2 + (c\Delta z)^2 + 2bc\Delta y\Delta z \cos \alpha + 2ac\Delta x\Delta z \cos \beta + 2ab\Delta x\Delta y \cos \gamma} \]

\[ \Delta x = x_2 - x_1, \Delta y = y_2 - y_1 \text{ and } \Delta z = z_2 - z_1 \] are the differences between the coordinates of the two atoms. The angle \( \omega \) at atom 2 in a group of three atoms 1, 2 and 3 can be calculated from the three distances \( d_{12}, d_{23} \) and \( d_{13} \) between them according to the cosine formula:

\[ \cos \omega = -\sqrt{\frac{d_{13}^2 - d_{12}^2 - d_{23}^2}{2d_{12}d_{23}}} \]

When specifying atomic coordinates, interatomic distances etc., the corresponding standard deviations should also be given, which serve to express the precision of their experimental determination. The commonly used notation, such as \( \sigma = 0.004 \text{ pm} \) states a standard deviation of 4 units for the last digit, \textit{i.e.} the standard deviation in this case amounts to 0.4 pm. Standard deviation is a term in statistics. When a standard deviation \( \sigma \) is linked to some value, the probability of the true value being within the limits \( \pm \sigma \) of the stated value is 68.3\%. The probability of being within \( \pm 2\sigma \) is 95.4\%, and within \( \pm 3\sigma \) is 99.7\%. The standard deviation gives no reliable information about the trueness of a value, because it only takes into account statistical errors, and not systematic errors.

2.4 Isotypism

The crystal structures of two compounds are \textit{isotypic} if their atoms are distributed in a like manner and if they have the same symmetry. One of them can be generated from the other if atoms of an element are substituted by atoms of another element without changing their positions in the crystal structure. The absolute values of the lattice dimensions and the interatomic distances may differ, and \textit{small} variations are permitted for the atomic coordinates. The angles between the crystallographic axes and the relative lattice dimensions (axes ratios) must be similar. Two isotypic structures exhibit a one-to-one relation for all atomic positions and have coincident geometric conditions. If, in addition, the chemical bonding conditions are also similar, then the structures also are \textit{crystal-chemical isotypic}.

The ability of two compounds which have isotypic structures to form mixed crystals, \textit{i.e.} when the exchange process of the atoms can actually be performed continuously, has been termed \textit{isomorphism}. However, because this term is also used for some other phenomena, it has been recommended that its use be discontinued in this context.

Two structures are \textit{homeotypic} if they are similar, but fail to fulfill the aforementioned conditions for isotypism because of different symmetry, because corresponding atomic positions are occupied by several different kinds of atoms (substitution derivatives) or because the geometric conditions differ (different axes ratios, angles, or atomic coordinates). An example of substitution derivatives is: C (diamond)–ZnS (zinc blende)–Cu3SbS4 (famatinite). The most appropriate method to work out the relations between homeotypic structures takes advantage of their symmetry relations (\textit{cf.} Chapter 18).

If two ionic compounds have the same structure type, but in such a way that the cationic positions of one compound are taken by the anions of the other and vice versa (‘exchange of cations and anions’), then they sometimes are called ‘antitypes’. For example: in Li2O the Li\textsuperscript{+} ions occupy the same positions as the F\textsuperscript{-} ions in CaF\textsubscript{2}, while the O\textsuperscript{2-} ions take the same positions as the Ca\textsuperscript{2+} ions; Li2O crystallizes in the ‘anti-CaF\textsubscript{2} type’. 

2.5 Problems

2.1 Calculate effective coordination numbers (e.c.n.) with the formula given on page 3 for:
(a) Tellurium, \(4 \times d_1 = 283 \text{ pm}, 2 \times d_2 = 349 \text{ pm}, d_3 = 444 \text{ pm};\)
(b) Gallium, \(1 \times d_1 = 247 \text{ pm}, 2 \times d_2 = 270 \text{ pm}, 2 \times d_3 = 274 \text{ pm}, 2 \times d_4 = 279 \text{ pm}, d_g = 398 \text{ pm};\)
(c) Tungsten, \(8 \times d_1 = 274.1 \text{ pm}, 6 \times d_2 = 316.5 \text{ pm}, d_g = 447.6 \text{ pm}.\)

2.2 Include specifications of the coordination of the atoms in the following formulas:
(a) FeTiO\(_3\), Fe and Ti octahedral, O coordinated by 2 Fe and by 2 Ti in a nonlinear arrangement;
(b) CdCl\(_2\), Cd octahedral, Cl trigonal-nonplanar;
(c) MoS\(_2\), Mo trigonal-prismatic, S trigonal-nonplanar;
(d) Cu\(_2\)O, Cu linear, O tetrahedral;
(e) PtS, Pt square, S tetrahedral;
(f) MgCu\(_2\), Mg Frank-Kasper polyhedron with c.n. 16, Cu icosahedral;
(g) Al\(_2\)Mg\(_3\)Si\(_3\)O\(_12\), Al octahedral, Mg dodecahedral, Si tetrahedral;
(h) UCl\(_3\), U tricapped trigonal-prismatic, Cl 3-nonplanar.

2.3 Give the symbols stating the kind of centering of the unit cells of CaC\(_2\) (Fig. 7.6, heavily outlined cell), K\(_2\)PtCl\(_6\) (Fig. 7.7), cristobalite (Fig. 12.9), AuCu\(_3\) (Fig. 15.1), K\(_2\)NiF\(_4\) (Fig. 16.4), perovskite (Fig. 17.10).

2.4 Give the number of formula units per unit cell for:
CsCl (Fig. 7.1), ZnS (Fig. 7.1), TiO\(_2\) (rutile, Fig. 7.4), ThSi\(_2\) (Fig. 13.1), ReO\(_3\) (Fig. 16.5), \(\alpha\)-ZnCl\(_2\) (Fig. 17.14).

2.5 What is the I–I bond length in solid iodine? Unit cell parameters: \(a = 714, b = 469, c = 978 \text{ pm}, \alpha = \beta = \gamma = 90^\circ\). Atomic coordinates: \(x = 0.0, y = 0.1543, z = 0.1174\); A symmetrically equivalent atom is at \(-x, -y, -z\).

2.6 Calculate the bond lengths and the bond angle at the central atom of the I\(_7^-\) ion in RbI\(_3\). Unit cell parameters: \(a = 1091, b = 1060, c = 665.5 \text{ pm}, \alpha = \beta = \gamma = 90^\circ\). Atomic coordinates: I(1), \(x = 0.1581, y = 0.1543, z = 0.5461\); I(2), \(x = 0.3772, y = 0.5461\); I(3), \(x = 0.5753, y = 0.1543, z = 0.7348\).

In the following problems the positions of symmetrically equivalent atoms (due to space group symmetry) may have to be considered; they are given as coordinate triplets to be calculated from the generating position \(x, y, z\). To obtain positions of adjacent (bonded) atoms, some atomic positions may have to be shifted to a neighboring unit cell.

2.7 MnF\(_2\) crystallizes in the rutile type with \(a = b = 487.3 \text{ pm}, c = 331.0 \text{ pm}\). Atomic coordinates: Mn at \(x = y = z = 0\); F at \(x = y = 0.3050, z = 0\). Symmetrically equivalent positions: \(-x, -y, z\); \(0.5-x, 0.5+y, 0.5; 0.5-x, 0.5+y, 0.5\). Calculate the two different Mn–F bond lengths (< 250 pm) and the F–Mn–F bond angle referring to two F atoms having the same \(x\) and \(y\) coordinates and \(z\) differing by 1.0.

2.8 WOB\(_3\) is tetragonal, \(a = b = 900.2 \text{ pm}, c = 393.5 \text{ pm}, \alpha = \beta = \gamma = 90^\circ\). Calculate the W–Br, W=O and O–W bond lengths and the O=W–Br bond angle. Make a true-to-scale drawing (1 or 2 cm per 100 pm) of projections on to the \(ab\) and the \(ac\) plane, including atoms up to a distance of 300 pm from the \(z\) axis and covering \(z = -0.5\) to \(z = 1.6\). Draw atoms as circles and bonds (atomic contacts shorter than 300 pm) as heavy lines. What is the coordination polyhedron of the W atom?

Atomic coordinates:

\[
\begin{array}{ccc}
W & 0.0 & 0.0 & 0.0779 \\
O & 0.0 & 0.0 & 0.529 \\
Br & 0.2603 & 0.0693 & 0.0
\end{array}
\]

Symmetrically equivalent positions:
\(-x, -y, z; -y, x, z; y, -x, z\)

2.9 Calculate the Zr–O bond lengths in baddeleyite (ZrO\(_2\)), considering only interatomic distances shorter than 300 pm. What is the coordination number of Zr?

Lattice parameters: \(a = 514.5, b = 520.7, c = 531.1 \text{ pm}, \beta = 99.23^\circ, \alpha = \gamma = 90^\circ\).

Atomic coordinates:

\[
\begin{array}{ccc}
Zr & 0.2758 & 0.0411 & 0.2082 \\
O(1) & 0.0703 & 0.3359 & 0.3406 \\
O(2) & 0.5577 & 0.2549 & 0.0211
\end{array}
\]

Symmetrically equivalent positions:
\(-x, 0.5+y, 0.5-z; x, 0.5-y, 0.5+z; -x, -y, z\).
3 Symmetry

The most characteristic feature of any crystal is its symmetry. It not only serves to describe important aspects of a structure, but is also related to essential properties of a solid. For example, quartz crystals could not exhibit the piezoelectric effect if quartz did not have the appropriate symmetry; this effect is the basis for the application of quartz in watches and electronic devices. Knowledge of the crystal symmetry is also of fundamental importance in crystal structure analysis.

In order to designate symmetry in a compact form, symmetry symbols have been developed. Two kinds of symbols are used: the Schoenflies symbols and the Hermann–Mauguin symbols, which are also called international symbols. Historically, Schoenflies symbols were developed first; they continue to be used in spectroscopy and to designate the symmetry of molecules. However, since they are less appropriate for describing the symmetry in crystals, they are now scarcely used in crystallography. We therefore discuss primarily the Hermann–Mauguin symbols. In addition, there are graphical symbols which are used in figures.

3.1 Symmetry Operations and Symmetry Elements

A symmetry operation transfers an object into a new spatial position that cannot be distinguished from its original position. In terms of mathematics, this is a mapping of an object onto itself that causes no distortions. A mapping is an instruction by which each point in space obtains a uniquely assigned point, the image point. ‘Mapping onto itself’ does not mean that each point is mapped exactly onto itself, but that after having performed the mapping, an observer cannot decide whether the object as a whole has been mapped or not.

After selecting a coordinate system, a mapping can be expressed by the following set of equations:

\[
\begin{align*}
\tilde{x} &= W_{11}x + W_{12}y + W_{13}z + w_1 \\
\tilde{y} &= W_{21}x + W_{22}y + W_{23}z + w_2 \\
\tilde{z} &= W_{31}x + W_{32}y + W_{33}z + w_3
\end{align*}
\]  

(3.1)

\((x, y, z)\) coordinates of the original point; \((\tilde{x}, \tilde{y}, \tilde{z})\) coordinates of the image point

A symmetry operation can be repeated infinitely many times. The symmetry element is a point, a straight line or a plane that preserves its position during execution of the symmetry operation. The symmetry operations are the following:

1. **Translation** (more exactly: symmetry-translation). Shift in a specified direction by a specified length. A translation vector corresponds to every translation. For example:
3.1 Symmetry Operations and Symmetry Elements

Strictly speaking, a symmetry-translation is only possible for an infinitely extended object. An ideal crystal is infinitely large and has translational symmetry in three dimensions. To characterize its translational symmetry, three non-coplanar translation vectors $a$, $b$ and $c$ are required. A real crystal can be regarded as a finite section of an ideal crystal; this is an excellent way to describe the actual conditions.

As vectors $a$, $b$ and $c$ we choose the three basis vectors that also serve to define the unit cell (Section 2.2). Any translation vector $t$ in the crystal can be expressed as the vectorial sum of three basis vectors, $t = ua + vb + wc$, where $u$, $v$ and $w$ are positive or negative integers.

Translational symmetry is the most important symmetry property of a crystal. In the Hermann–Mauguin symbols the three-dimensional translational symmetry is expressed by a capital letter which also allows the distinction of primitive and centered crystal lattices (cf. Fig. 2.6, p. 8):

- $P = \text{primitive}$
- $A$, $B$ or $C = \text{base-centered in the bc, ac or ab plane, respectively}$
- $F = \text{face-centered (all faces)}$
- $I = \text{body-centered (from innenzentriert in German)}$
- $R = \text{rhombohedral}$

2. Rotation about some axis by an angle of $360/N$ degrees. The symmetry element is an $N$-fold rotation axis. The multiplicity $N$ is an integer. After having performed the rotation $N$ times the object has returned to its original position. Every object has infinitely many axes with $N = 1$, since an arbitrary rotation by $360^\circ$ returns the object into its original position. The symbol for the onefold rotation is used for objects that have no symmetry other than translational symmetry. The Hermann–Mauguin symbol for an $N$-fold rotation is the number $N$; the Schoenflies symbol is $C_N$ (cf. Fig. 3.1):

<table>
<thead>
<tr>
<th>Hermann–Mauguin symbol</th>
<th>Schoenflies symbol</th>
<th>graphical symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>onefold rotation axis</td>
<td>1</td>
<td>$C_1$</td>
</tr>
<tr>
<td>twofold rotation axis</td>
<td>2</td>
<td>$C_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>threefold rotation axis</td>
<td>3</td>
<td>$C_3$</td>
</tr>
<tr>
<td>fourfold rotation axis</td>
<td>4</td>
<td>$C_4$</td>
</tr>
<tr>
<td>sixfold rotation axis</td>
<td>6</td>
<td>$C_6$</td>
</tr>
</tbody>
</table>
3. **Reflection.** The symmetry element is a *reflection plane* (Fig. 3.2).

Hermann–Mauguin symbol: \(m\). Schoenflies symbol: \(\sigma\) (used only for a detached plane).

Graphical symbols:

- reflection plane perpendicular to the plane of the paper
- reflection plane parallel to the plane of the paper

4. **Inversion.** ‘Reflection’ through a point (Fig. 3.2). This point is the symmetry element and is called *inversion center* or *center of symmetry*.

Hermann–Mauguin symbol: \(\bar{1}\) (‘one bar’). Schoenflies symbol: \(i\). Graphical symbol: \(\circ\)

5. **Rotoinversion.** The symmetry element is a *rotoinversion axis* or, for short, an *inversion axis*. This refers to a *coupled* symmetry operation which involves two motions: take a rotation through an angle of \(360/\mathcal{N}\) degrees immediately followed by an inversion at a point located on the axis (Fig. 3.3):

- Hermann–Mauguin symbol
- graphical symbol

\[
\begin{align*}
\bar{1} & \quad \circ \quad \text{identical with an inversion center} \\
\frac{2}{m} & \quad \triangle \quad \text{identical with a reflection plane perpendicular to the axis} \\
\frac{3}{3} & \quad \Phi \quad \text{identical with a reflection plane parallel to the axis} \\
\mathcal{C}_4 & \quad \Phi \quad \text{identical with a reflection plane parallel to the axis} \\
\mathcal{C}_5 & \quad \Phi \quad \text{identical with a reflection plane parallel to the axis} \\
\mathcal{C}_6 & \quad \Phi \quad \text{identical with a reflection plane parallel to the axis}
\end{align*}
\]
If $N$ is an even number, the inversion axis automatically contains a rotation axis with half the multiplicity. If $N$ is an odd number, automatically an inversion center is present. This is expressed by the graphical symbols. If $N$ is even but not divisible by 4, automatically a reflection plane perpendicular to the axis is present.

A **rotoreflection** is a coupled symmetry operation of a rotation and a reflection at a plane perpendicular to the axis. Rotoreflection axes are identical with inversion axes, but the multiplicities do not coincide if they are not divisible by 4 (Fig. 3.3). In the Hermann–Mauguin notation only inversion axes are used, and in the Schoenflies notation only rotoreflection axes are used, the symbol for the latter being $S_N$.

**6. Screw rotation.** The symmetry element is a *screw axis*. It can only occur if there is translational symmetry in the direction of the axis. The screw rotation results when a rotation of $360/N$ degrees is coupled with a displacement parallel to the axis. The Hermann–Mauguin symbol is $N_M$ (‘$N$ sub $M$’); $N$ expresses the rotational component and the fraction $M/N$ is the displacement component as a fraction of the translation vector. Some screw axes are right or left-handed. Screw axes that can occur in crystals are shown in Fig. 3.4. Single polymer molecules can also have non-crystallographic screw axes, e.g. $10_3$ in polymeric sulfur.

**7. Glide reflection.** The symmetry element is a *glide plane*. It can only occur if translational symmetry is present parallel to the plane. At the plane, reflections are performed, but every reflection is coupled with an immediate displacement parallel to the plane. The Hermann–Mauguin symbol is $a, b, c, n, d$ or $e$, the letter designating the direction of the glide referred to the unit cell. $a, b$ and $c$ refer to displacements parallel to the basis vectors $a, b$ and $c$, the displacements amounting to $\frac{1}{2}a, \frac{1}{2}b$ and $\frac{1}{4}c$, respectively. The glide planes $n$ and $d$ involve displacements in a diagonal direction by amounts of $\frac{1}{4}$ and $\frac{1}{4}$ of the translation vector in this direction, respectively. $e$ designates two glide planes in one another with two mutually perpendicular glide directions (Fig. 3.5).

### 3.2 Point Groups

A geometric object can have several symmetry elements simultaneously. However, symmetry elements cannot be combined arbitrarily. For example, if there is only one reflection plane, it cannot be inclined to a symmetry axis (the axis has to be in the plane or perpendicular to it). Possible combinations of symmetry operations excluding translations are called **point groups**. This term expresses the fact that any allowed combination has one unique
Screw axes and their graphical symbols. The axes $3_1, 4_1, 6_1,$ and $6_2$ are right-handed; $3_2, 4_3, 6_5,$ and $6_4$ are the corresponding left-handed screw axes.

**Fig. 3.4**

Point (or one unique axis or plane) which is common to all the symmetry elements. Point groups strictly fulfill the conditions set by group theory in mathematics. The symmetry operations are the elements that make up the group.

When two symmetry operations are combined, a third symmetry operation can result automatically. For example, the combination of a twofold rotation with a reflection at a plane perpendicular to the rotation axis automatically results in an inversion center at the site where the axis crosses the plane. It makes no difference which two of the three symmetry operations are combined ($2, m$ or $\bar{1}$), the third one always results (Fig. 3.6).

**Hermann–Mauguin Point-group Symbols**

A Hermann–Mauguin point-group symbol consists of a listing of the symmetry elements that are present according to certain rules in such a way that their relative orientations can
3.2 Point Groups

Fig. 3.5
Top left: perspective illustration of a glide plane. Other images: printed and graphical symbols for glide planes perpendicular to $a$ and $c$ with different glide directions. $z = \text{height of the point in the unit cell}$

Fig. 3.6
The combination of a twofold rotation and a reflection at a plane perpendicular to the rotation axis results in an inversion

also be recognized. In the full Hermann–Mauguin symbol all symmetry elements, with few exceptions, are listed. However, because they are more compact, usually only the short Hermann–Mauguin symbols are cited; in these, symmetry axes that result automatically from mentioned symmetry planes are not expressed; symmetry planes which are present are not omitted.

The following rules apply:

1. The orientation of symmetry elements is referred to a coordinate system $xyz$. If one symmetry axis is distinguished from the others by a higher multiplicity ('principal axis') or when there is only one symmetry axis, it is set as the $z$ axis.

2. An inversion center is mentioned only if it is the only symmetry element present. The symbol then is $\overline{T}$. In other cases the presence or absence of an inversion center can be recognized as follows: it is present and only present if there is either an inversion axis with odd multiplicity ($\overline{N}$, with $N$ odd) or a rotation axis with even multiplicity and a reflection plane perpendicular to it ($N/m$, with $N$ even).

3. A symmetry element occurring repeatedly because it is multiplied by another symmetry operation is mentioned only once.
4. A reflection plane that is perpendicular to a symmetry axis is designated by a slash, e.g. \(2/m\) (‘two over \(m\’) = reflection plane perpendicular to a twofold rotation axis. However, reflection planes perpendicular to rotation axes with odd multiplicities are not usually designated in the form \(3/m\), but as inversion axes like \(\bar{6}; \ 3/m\) and \(\bar{6}\) express identical facts.

5. The mutual orientation of different symmetry elements is expressed by the sequence in which they are listed. The orientation refers to the coordinate system. If the symmetry axis of highest multiplicity is twofold, the sequence is \(x–y–z\), i.e. the symmetry element in the \(x\) direction is mentioned first etc.; the direction of reference for a reflection plane is *normal* to the plane. If there is an axis with a higher multiplicity, it is mentioned first; since it coincides by convention with the \(z\) axis, the sequence is different, namely \(z–x–d\). The symmetry element oriented in the \(x\) direction occurs repeatedly because it is being multiplied by the higher multiplicity of the \(z\) axis; the bisecting direction between \(x\) and its next symmetry-equivalent direction is the direction indicated by \(d\). See the examples in Fig. 3.7.

6. Cubic point groups have four threefold axes (3 or \(\bar{3}\)) that mutually intersect at angles of 109.47°. They correspond to the four body diagonals of a cube (directions \(x+y+z\), \(-x+y-z\), \(-x-y+z\) and \(x-y-z\), added vectorially). In the directions \(x\), \(y\), and \(z\) there are axes 4, 4, or 2, and there can be reflection planes perpendicular to them. In the six directions \(x+y\), \(x–y\), \(x+z\), … twofold axes and reflection planes may be present. The sequence of the reference directions in the Hermann–Mauguin symbols is \(z\), \(x+y+z\), \(x+y\). The occurrence of a 3 in the second position of the symbol (direction \(x+y+z\)) gives evidence of a cubic point group. See Fig. 3.8.
Figures 3.8 and 3.9 list point group symbols and illustrate them by geometric figures. In addition to the short Hermann–Mauguin symbols the Schoenflies symbols are also listed. Full Hermann–Mauguin symbols for some point groups are:

<table>
<thead>
<tr>
<th>Short</th>
<th>Full</th>
<th>Short</th>
<th>Full</th>
</tr>
</thead>
<tbody>
<tr>
<td>mmm</td>
<td>2/m 2/m 2/m</td>
<td>3m</td>
<td>3 2/m</td>
</tr>
<tr>
<td>4/mmm</td>
<td>4/m 2/m 2/m</td>
<td>m 3m</td>
<td>4/m 3 2/m</td>
</tr>
<tr>
<td>6/mmm</td>
<td>6/m 2/m 2/m</td>
<td>m 3</td>
<td>2/m m</td>
</tr>
</tbody>
</table>


**Schoenflies Point-group Symbols**

The coordinate system of reference is taken with the vertical principal axis (z axis). Schoenflies symbols are rather compact — they designate only a minimum of the symmetry elements present in the following way (the corresponding Hermann–Mauguin symbols are given in brackets):

\[ C_i = \text{an inversion center is the only symmetry element} \ [\overline{1}] \]
\[ C_s = \text{a reflection plane is the only symmetry element} \ [m] \]
\[ C_N = \text{an N-fold rotation axis is the only symmetry element} \ [N] \]
\[ C_{Ni} (N \text{ odd}) = \text{an N-fold rotation axis and an inversion center} \ [\overline{N}] \]
\[ D_N = \text{perpendicular to an N-fold rotation axis there are N twofold rotation axes} \ [N2] \text{ if the value of } N \text{ is odd}; \ [\mbox{N}22] \text{ if } N \text{ is even}. \]
\[ C_{Nh} = \text{there is one N-fold (vertical) rotation axis and one horizontal reflection plane} \ [N/m] \]
\[ C_{Nv} = \text{an N-fold (vertical) rotation axis is at the intersection line of } N \text{ vertical reflection planes} \ [Nm] \text{ if the value of } N \text{ is odd}; \ [NmN] \text{ if } N \text{ is even}. \ C_{ovv} = \text{symmetry of a cone} \ [\infty m] \]
\[ D_{Nh} = \text{in addition to an N-fold (vertical) rotation axis there are } N \text{ horizontal twofold axes, } N \text{ vertical reflection planes and one horizontal reflection plane} \ [\overline{N}2/m] \text{ if } N \text{ is odd}; \ [N/m2/m2/m] \text{, for short } N/mm, \text{ if } N \text{ is even}. \ D_{ovh} = \text{symmetry of a cylinder} \ [\infty/m2/m, \text{ for short } \infty/mm \text{ or } \overline{m}]. \]
\[ D_{Nd} = \text{the N-fold vertical rotation axis contains a } 2N \text{-fold rotoreflection axis, } N \text{ horizontal twofold rotation axes are situated at bisecting angles between } N \text{ vertical reflection planes} \ [\overline{M}2m] \text{ with } M = 2 \times N]. \ S_{mz} \text{ has the same meaning as } D_{Nd} \text{ and can be used instead, but it has gone out of use}. \]
\[ S_N = \text{there is only an N-fold (vertical) rotoreflection axis (cf. Fig. 3.3). The symbol } S_N \text{ is needed only if } N \text{ is divisible by 4. If } N \text{ is even but not divisible by 4, } C_{2i} \text{ can be used instead, e.g. } C_{5i} = S_{10}. \text{ If } N \text{ is odd, the symbol } C_{Nh} \text{ is commonly used instead of } S_N, \text{ e.g. } C_{3h} = S_3. \]
\[ T_d = \text{symmetry of a tetrahedron} \ [\overline{4}3m] \]
\[ O_h = \text{symmetry of an octahedron and of a cube} \ [4/m\overline{3}2/m, \text{ short } m\overline{3}3]. \]
\[ T_h = \text{symmetry of an octahedron without fourfold axes} \ [2/m\overline{3}, \text{ short } m\overline{3}3]. \]
\[ I_h = \text{symmetry of an icosahedron and of a pentagonal dodecahedron} \ [2/m\overline{3}5, \text{ short } m\overline{3}5]. \]
\[ O, T \text{ and } I = \text{as } O_h, T_h \text{ and } I_h, \text{ but with no reflection planes} \ [432, 23 \text{ and } 235, \text{ respectively}]. \]
\[ K_h = \text{symmetry of a sphere} \ [2/m\overline{3}, \text{ short } m\overline{3}]. \]

**3.3 Space Groups and Space-group Types**

Symmetry axes can only have the multiplicities 1, 2, 3, 4 or 6 when translational symmetry is present in three dimensions. If, for example, fivefold axes were present in one direction, the unit cell would have to be a pentagonal prism; space cannot be filled, free of voids, with prisms of this kind. Due to the restriction to certain multiplicities, symmetry operations can only be combined in a finite number of ways in the presence of three-dimensional translational symmetry. The 230 possibilities are called space-group types (often, not quite correctly, called the 230 space groups).
The Hermann–Mauguin symbol for a space-group type begins with a capital letter $P$, $A$, $B$, $C$, $F$, $I$ or $R$ which expresses the presence of translational symmetry in three dimensions and the kind of centering. The letter is followed by a listing of the other symmetry elements according to the same rules as for point groups; the basis vectors $a$, $b$ and $c$ define the coordinate system (Fig. 3.11). If several kinds of symmetry elements exist in one direction (e.g. parallel 2 and 2$_1$ axes), then only one is mentioned; as a rule, the denomination of mirror planes has priority over glide planes and rotation axes over screw axes.

The 230 space-group types are listed in full in *International Tables for Crystallography*, Volume A [48]. Whenever crystal symmetry is to be considered, this fundamental tabular work should be consulted. It includes figures that show the relative positions of the symmetry elements as well as details concerning all possible sites in the unit cell (cf. next section).

In some circumstances the magnitudes of the translation vectors must be taken into account. Let us demonstrate this with the example of the trirutile structure. If we triplicate the unit cell of rutile in the $c$ direction, we can occupy the metal atom positions with two kinds of metals in a ratio of 1 : 2, such as is shown in Fig. 3.10. This structure type is known for several oxides and fluorides, e.g. ZnSb$_2$O$_6$. Both the rutile and the trirutile structure belong to the same space-group **type** $P4_2/mnm$. Due to the triplicated translation vector in the $c$ direction, the density of the symmetry elements in trirutile is less than in rutile. The total number of symmetry operations (including the translations) is reduced to $\frac{1}{3}$. In other words, trirutile has a symmetry that is reduced by a factor of three. A structure with a specific symmetry *including* the translational symmetry has a specific space group; the space-group type, however, is independent of the special magnitudes of the translation vectors. Therefore, rutile and trirutile do not have the same space group. Although space group and space-group type have to be distinguished, the same symbols are used for both. However, this does not cause any problems since the specification of a space group is only used to designate the symmetry of a specific structure or a specific structure type, and this always involves a crystal lattice with definite translation vectors.

![Fig. 3.10](image)

Unit cells of the rutile and the trirutile structures. The positions of the twofold rotation axes have been included.

*P4$_2$/m2$_1$/n2$_1$/m (short P4$_2$/mnm)*
If an atom is situated on a center of symmetry, on a rotation axis or on a reflection plane, then it occupies a special position. On execution of the corresponding symmetry operation, the atom is mapped onto itself. Any other site is a general position. A special position is connected with a specific site symmetry which is higher than 1. The site symmetry at a general position is always 1.
Molecules or ions in crystals often occupy special positions. In that case the site symmetry may not be higher than the symmetry of the free molecule or ion. For example, an octahedral ion like SbCl$_6^-$ can be placed on a site with symmetry 4 if its Sb atom and two trans Cl atoms are located on the fourfold axis; a water molecule, however, cannot be placed on a fourfold axis.

The different sets of positions in crystals are called Wyckoff positions. They are listed for every space-group type in *International Tables for Crystallography*, Volume A, in the following way (example space-group type Nr. 87, I4/m):

<table>
<thead>
<tr>
<th>Multiplicity, Wyckoff letter, Site symmetry</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 i 1</td>
<td>(0,0,0) + (1/4,1/4,1/4) +</td>
</tr>
<tr>
<td>(2) x, y, z</td>
<td>(3) y, x, z</td>
</tr>
<tr>
<td>(4) y, x, z</td>
<td>(8) y, x, z</td>
</tr>
<tr>
<td>8 h m</td>
<td>x, y, 0</td>
</tr>
<tr>
<td>(5) x, y, z</td>
<td>(6) x, y, z</td>
</tr>
<tr>
<td>(7) y, x, 0</td>
<td>(8) y, x, z</td>
</tr>
<tr>
<td>8 g 2</td>
<td>0, 1/2, z</td>
</tr>
<tr>
<td>(2) x, y, 0</td>
<td>(3) y, x, z</td>
</tr>
<tr>
<td>(4) y, x, 0</td>
<td></td>
</tr>
<tr>
<td>8 f T</td>
<td>0, 1/2, 1/2</td>
</tr>
<tr>
<td>(5) x, y, z</td>
<td>(6) x, y, z</td>
</tr>
<tr>
<td>(7) y, x, z</td>
<td>(8) y, x, z</td>
</tr>
<tr>
<td>4 e 4</td>
<td>0, 0, z</td>
</tr>
<tr>
<td>(5) x, y, z</td>
<td>(6) x, y, z</td>
</tr>
<tr>
<td>(7) y, x, z</td>
<td>(8) y, x, z</td>
</tr>
<tr>
<td>4 d 4</td>
<td>0, 1/2, 1/2</td>
</tr>
<tr>
<td>(5) x, y, z</td>
<td>(6) x, y, z</td>
</tr>
<tr>
<td>(7) y, x, z</td>
<td>(8) y, x, z</td>
</tr>
<tr>
<td>4 c 2/m</td>
<td>0, 1/2, 0</td>
</tr>
<tr>
<td>(5) x, y, z</td>
<td>(6) x, y, z</td>
</tr>
<tr>
<td>(7) y, x, z</td>
<td>(8) y, x, z</td>
</tr>
<tr>
<td>2 b 4/m</td>
<td>0, 1/2, 0</td>
</tr>
<tr>
<td>(5) x, y, z</td>
<td>(6) x, y, z</td>
</tr>
<tr>
<td>(7) y, x, z</td>
<td>(8) y, x, z</td>
</tr>
<tr>
<td>2 a 4/m</td>
<td>0, 0, 0</td>
</tr>
<tr>
<td>(5) x, y, z</td>
<td>(6) x, y, z</td>
</tr>
<tr>
<td>(7) y, x, z</td>
<td>(8) y, x, z</td>
</tr>
</tbody>
</table>

In crystallography it is a common practice to write minus signs on top of the symbols; $\bar{x}$ means $-x$. The meaning of the coordinate triplets is: to a point with the coordinates $x, y, z$ the following points are symmetry-equivalent:

$-x, -y, z; -x, y, z; y, -x, z$ etc.;

in addition, all points with $+((1/2, 1/2, 1/2)$, *i.e.* $1/2 + x, 1/2 + y, 1/2 + z; 1/2 - x, 1/2 - y, 1/2 + z; 1/2 - y, 1/2 + x, 1/2 + z$ etc.

The coordinate triplets are just a shorthand notation for mappings according to equation (3.1).

The Wyckoff symbol is a short designation; it consists of a numeral followed by a letter, for example 8f. The cipher 8 states the multiplicity, that is, the number of symmetry-equivalent points in the unit cell. The f is an alphabetical label (a, b, c, . . .) according to the sequence of the listing of the positions; a is always the position with the highest site symmetry.

A (crystallographic) orbit is the set of all points that are symmetry equivalent to a point. An orbit can be designated by the coordinate triplet of any of its points. If the coordinates of a point are fixed by symmetry, for example $0, 1/2, 1/4$, then the orbit and the Wyckoff position are identical. However, if there is a free variable, for example $z$ in $0, 1/2, z$, the Wyckoff position comprises an infinity of orbits. Take the points $0, 1/2, 0.2478$ and $0, 1/2, 0.3629$: they designate two different orbits; both of them belong to the same Wyckoff position 8g of the space group I4/m. Each of these points belongs to an orbit consisting of an infinity of points (don’t get irritated by the singular form of the words ‘Wyckoff position’ and ‘orbit’).
3.5 Crystal Classes and Crystal Systems

A well-grown crystal exhibits a macroscopic symmetry which is apparent from its faces; this symmetry is intimately related to the pertinent space group. Due to its finite size, a macroscopic crystal can have no translational symmetry. In addition, due to the conditions of crystal growth, it hardly ever exhibits a perfect symmetry. However, the ideal symmetry of the crystal follows from the symmetry of the bundle of normals perpendicular to its faces. This symmetry is that of the point group resulting from the corresponding space group if translational symmetry is removed, screw axes are replaced by rotation axes, and glide planes are replaced by reflection planes. In this way the 230 space-group types can be correlated with 32 point groups which are called crystal classes. Examples of some space-group types and the crystal classes to which they belong are:

<table>
<thead>
<tr>
<th>space-group type</th>
<th>crystal class</th>
</tr>
</thead>
<tbody>
<tr>
<td>full symbol</td>
<td>short symbol</td>
</tr>
<tr>
<td>P 121/c1</td>
<td>P21/c</td>
</tr>
<tr>
<td>C2/m2/c21/m</td>
<td>Cmcm</td>
</tr>
<tr>
<td>P63/m2/m2/c</td>
<td>P63/mmc</td>
</tr>
</tbody>
</table>

In general: the P, A, B, C, F, I or R of the space group symbol is removed, the subscript numbers are removed, and a, b, c, d, e or n are replaced by m.

A special coordinate system defined by the basis vectors a, b and c belongs to each space group. Depending on the space group, certain relations hold among the basis vectors; they serve to classify seven crystal systems. Every crystal class can be assigned to one of these crystal systems, as listed in Table 3.1. The existence of the corresponding symmetry elements is relevant for assigning a crystal to a specific crystal system. The metric parameters of the unit cell alone are not sufficient (e.g. a crystal can be monoclinic even if α = β = γ = 90°).

<table>
<thead>
<tr>
<th>crystal system (abbreviation)</th>
<th>crystal classes</th>
<th>metric parameters of the unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>triclinic (a)</td>
<td>1; T</td>
<td>a ≠ b ≠ c; α ≠ β ≠ γ ≠ 90°</td>
</tr>
<tr>
<td>monoclinic (m)</td>
<td>2; m; 2/m</td>
<td>a ≠ b ≠ c; α = γ = 90°, β ≠ 90°</td>
</tr>
<tr>
<td>(or α = β = 90°, γ ≠ 90°)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>orthorhombic (o)</td>
<td>2 2 2; mmm2; mmm</td>
<td>a ≠ b ≠ c; α = β = γ = 90°</td>
</tr>
<tr>
<td>tetragonal (t)</td>
<td>4; 4/m; 4 2 2; 4mm; 4/m 2/m; 4/m mmm</td>
<td>a = b ≠ c; α = β = γ = 90°</td>
</tr>
<tr>
<td>trigonal (h)</td>
<td>3; 3 2; 3/m; 3m</td>
<td>a = b ≠ c; α = β = γ = 90°, γ = 120°</td>
</tr>
<tr>
<td>hexagonal (h)</td>
<td>6; 6/m; 6 2 2; 6mm; 6/m 2/m; 6/m mm</td>
<td>a = b ≠ c; α = β = γ = 90°, γ = 120°</td>
</tr>
<tr>
<td>cubic (c)</td>
<td>2 3; m 3; 4 3 2; 4 3 2 m 3</td>
<td>a = b = c; α = β = γ = 90°</td>
</tr>
</tbody>
</table>
3.6 Aperiodic Crystals

Normally, solids are crystalline, i.e. they have a three-dimensional periodic order with three-dimensional translational symmetry. However, this is not always so. Aperiodic crystals do have a long-distance order, but no three-dimensional translational symmetry. In a formal (mathematical) way, they can be treated with lattices having translational symmetry in four- or five-dimensional ‘space’, the so-called superspace; their symmetry corresponds to a four- or five-dimensional superspace group. The additional dimensions are not dimensions in real space, but have to be taken in a similar way to the fourth dimension in space-time. In space-time the position of an object is specified by its spatial coordinates \(x, y, z\); the coordinate \(t\) of the fourth dimension is the time at which the object is located at the site \(x, y, z\).

We distinguish three kinds of aperiodic crystals:

1. Incommensurately modulated structures;
2. Incommensurate composite crystals;
3. Quasicrystals.

Incommensurately modulated structures can be described with a three-dimensional periodic average structure called approximant. However, the true atomic positions are shifted from the positions of the approximant. The shifts follow one or several modulation functions. An example is the modification of iodine that occurs at pressures between 23 and 28 GPa (iodine-V). The three-dimensional approximant is a face-centered structure in the orthorhombic space group \(Fmmm\) (cf. Fig. 11.1, upper right, p. 104). In the incommensurately modulated structure the atoms are shifted parallel to \(b\) and follow a sine wave along \(c\) (Fig. 11.1, lower right). Its wave length is incommensurate with \(c\), i.e. there is no rational numeric ratio with the lattice parameter \(c\). The wave length depends on pressure; at 24.6 GPa it is 3.89\(c\). In this case the description is made with the three-dimensional space group \(Fmmm\) with an added fourth dimension; the translation period of the axis in the fourth dimension is 3.89\(c\). The corresponding four-dimensional superspace group obtains the symbol \(Fmmm/B400q3/00s0\) with \(q1 = 0.257 = 1/3.89\).

One of the structures of this kind that has been known for a long time is that of \(\gamma-Na2CO3\). At high temperatures sodium carbonate is hexagonal (\(\alpha-Na2CO3\)). It contains carbonate ions that are oriented perpendicular to the hexagonal \(c\) axis. Upon cooling below 481 °C, the \(c\) axis becomes slightly tilted to the \(ab\) plane, and the hexagonal symmetry is lost; the symmetry now is monoclinic (\(\beta-Na2CO3\), space group \(C2/m\)). \(\gamma-Na2CO3\) appears at temperatures between 332°C and –103°C. In the mean, it still has the structure of \(\beta-Na2CO3\). However, the atoms are no longer arranged in a straight line along \(c\), but follow a sine wave. In this case, the symbol of the superspace group is \(C2/m(q10q3)0s\). \(q1\) and \(q3\) are the reciprocal values of the components of the wave length of the modulation wave given as multiples of the lattice parameters \(a\) and \(c\); they depend on pressure and temperature. Below –103°C the modulation wave becomes commensurate with a wave length of \(6a + 3c\). This structure can be described with a normal three-dimensional space group and a correspondingly enlarged unit cell.

In X-ray diffraction, modulated structures reveal themselves by the appearance of satellite reflections. In between the intense main reflections which correspond to the structure of the approximant, weaker reflections appear; they do not fit into the regular pattern of the main reflections.
An incommensurate composite crystal can be regarded as the intergrowth of two periodic structures whose periodicities do not match with one another. The compound \((\text{LaS})_{1.14}\text{TaS}_2\) offers an example. It consists of alternating stacked layers of the compositions LaS and TaS\(_2\). Periodical order is present in the stacking direction. Parallel to the layers, their translational periods match in one direction, but not in the other direction. The translation vectors \(a\) are 581 pm in the LaS layer and 329 pm in the TaS\(_2\) layer (Fig. 3.12). The chemical composition results from the numerical ratio \(581/329 = 1.766\): \((\text{LaS})_{2/1.766}\text{TaS}_2\) (the number of La atoms in a layer fraction of length 581 pm is twice that of the Ta atoms in 329 pm).

Quasicrystals exhibit the peculiarity of noncrystallographic symmetry operations. Most frequent are axial quasicrystals with a tenfold rotation axis. In addition, axial quasicrystals with five-, eight- and twelvefold rotation axes and quasicrystals with icosahedral symmetry have been observed. Axial quasicrystals have periodic order in the direction of the axis and can be described with the aid of five-dimensional superspace groups. Thus far, all observed quasicrystals are alloys. Generally, they have a complicated composition comprising one to three transition metals and mostly an additional main group element (mainly Mg, Al, Si or Te). In three-dimensional space, their structures can be described as nonperiodic tilings. At least two kinds of tiles are needed to attain a voidless filling of space. A well-known tiling is the PENROSE tiling. It has fivefold rotation symmetry and consists of two kinds of rhomboid tiles with rhombus angles of \(72°/108°\) and \(36°/144°\) (Fig. 3.13).

The X-ray diffraction pattern of a quasicrystal exhibits noncrystallographic symmetry. In addition, the number of observable reflections increases more and more the more intense the X-ray radiation is or the longer the exposure time is (in a similar way to the number of stars visible in the sky with a more potent telescope).
Several kinds of intermediate states exist between the state of highest order in a crystal having translational symmetry in three dimensions and the disordered distribution of particles in a liquid. Liquid crystals are closest to the liquid state. They behave macroscopically like liquids, their molecules are in constant motion, but to a certain degree there exists a crystal-like order.

In plastic crystals all or a part of the molecules rotate about their centers of gravity. Typically, plastic crystals are formed by nearly spherical molecules, for example hexafluorides like SF$_6$ or MoF$_6$ or white phosphorus in a temperature range immediately below the melting point. Such crystals often are soft and can be easily deformed.

The term plastic crystal is not used if the rotation of the particles is hindered, i.e. if the molecules or ions perform rotational vibrations (librations) about their centers of gravity with large amplitudes; this may include the occurrence of several preferred orientations. Instead, such crystals are said to have orientational disorder. Such crystals are annoying during crystal structure analysis by X-ray diffraction because the atoms can hardly be located. This situation is frequent among ions like BF$_4^-$, PF$_6^-$ or N(CH$_3$)$_4^+$. To circumvent difficulties during structure determination, experienced chemists avoid such ions and prefer heavier, less symmetrical or more bulky ions.

Orientation disorder is also present if a molecule or part of a molecule occupies two or more different orientations in the crystal, even without performing unusual vibrations. For example, tetraethylammonium ions often occupy two orientations that are mutually rotated by 90°, in such a way that the positions of the C atoms of the methyl groups coincide, but the C atoms of the CH$_2$ groups occupy the vertices of a cube around the N atom, with two occupation probabilities.
Plastic crystals and crystals with orientational disorder still fulfill the three-dimensional translational symmetry, provided a mean partial occupation is assumed for the atomic positions of the molecules whose orientations differ from unit cell to unit cell (‘split positions’).

Crystals having stacking faults lack translational symmetry in one direction. Such crystals consist of layers that are stacked without a periodic order. Usually, only a few positions occur for the layers, but their sequence is statistical. For example, if we have two layers in positions A and B in a closest-packing of spheres and the following (third) layer again takes the position A with 100% probability, the result is an ordered hexagonal closest-packing of spheres (stacking sequence ABAB…, cf. Fig. 14.1, p. 151). However, if the probability is only 90% and the third layer may adopt a position C with 10% probability, the result is a stacking disorder. Essentially, i.e. by 90%, the packing still corresponds to a hexagonal closest-packing of spheres, but on an average there is a stacking fault every ten layers:

\[
\]

Metallic cobalt exhibits this phenomenon, and so do layered silicates and layered halides like CdI₂ or BiI₃. In X-ray diffraction, stacking faults cause the appearance of diffuse streaks (continuous lines in the diffraction pattern).

If the stacking faults occur only rarely (say, every 10⁵ layers on average), the result is a polysynthetic twinned crystal (cf. Fig. 18.8, p. 223). Depending on the frequency of the stacking faults, there is a smooth transition between crystals with stacking faults and polysynthetic twinning.

Among crystals with stacking faults the lack of a periodic order is restricted to one dimension; this is called a one-dimensional disorder. If only a few layer positions occur and all of them are projected into one layer, we obtain an averaged structure. Its symmetry can be described with a space group, albeit with partially occupied atomic positions. The real symmetry is restricted to the symmetry of an individual layer. The layer is a three-dimensional object, but it only has translational symmetry in two dimensions. Its symmetry is that of a layer group; there exist 80 layer-group types.

A two-dimensional disorder results when rod-like polymeric molecules are mutually shifted with statistical frequency. Translational symmetry then only exists in the direction of the molecules, and not in the transverse directions. The rod is a three-dimensional object with one-dimensional translational symmetry. Its symmetry is that of a rod group. Layer groups and rod groups are subperiodic groups. They are listed in detail in International Tables for Crystallography, Volume E.

Structures with one- or two-dimensional disorder are also called order–disorder structures (OD structures).

A solid that has no translational symmetry at all is said to be amorphous. Glasses are amorphous solids that behave like liquids with very high viscosity. The viscosity decreases with increasing temperature, i.e. the material softens, but it has no melting point.

### 3.8 Problems

3.1 Give the Hermann–Mauguin symbols for the following molecules or ions:

- H₂O
- HCCl₃
- BF₃ (triangular planar)
- XeF₄ (square planar)
- ClSF₅
- SF₆
- cis-SbF₄Cl²⁻
- trans-N₂F₂
- B(OH)₃ (planar)
- Co(NO₂)₆²⁻
3.2 Plots of the following molecules or ions can be found on pp. 132, 133 and 146. State their Hermann–Mauguin symbols.
Si\(_4\text{sq}^2\), As\(_4\text{sq}\), P\(_4\text{sq}\), Sn\(_5\text{sq}^2\), As\(_4\text{sq}^2\), As\(_4\text{sq}^4\), P\(_6\text{sq}^2\), As\(_7\text{sq}^3\), P\(_11\text{sq}^2\), Sn\(_9\text{sq}^2\), Bi\(_8^{2+}\).

3.3 What Hermann–Mauguin symbols correspond to the linked polyhedra shown in Fig. 16.1 (p. 166)?

3.4 What symmetry elements are present in the HgO chain shown on page 13? Does its symmetry correspond to a point group, rod group, layer group or space group?

3.5 Find out which symmetry elements are present in the structures of the following compounds. Derive the Hermann–Mauguin symbol of the corresponding space group (it may be helpful to consult *International Tables for Crystallography*, Vol. A).
Tungsten bronzes M\(_x\)WO\(_3\) (Fig. 16.6, p. 172); CaC\(_2\) (Fig. 7.6, heavily outlined cell, p. 57); CaB\(_6\) (Fig. 13.13, p. 145).

3.6 State the crystal classes and crystal systems to which the following space groups belong:
(a) P\(_2_1\text{b}1\text{c}2_1\text{a}\); (b) I\(_4\text{adm}\); (c) R\(_3\text{m}\); (d) P\(_63\text{m}\); (e) P\(_63\text{2}2\); (f) P\(_2_1\text{2}_1\text{2}_1\); (h) F\(_\text{dd}2\); (i) F\(_\text{m}5\text{m}\).

3.7 Rutile (TiO\(_2\), Fig. 3.10) crystallizes in the space group P\(_4_2\text{mnm}\) (Nr. 136 in *International Tables for Crystallography*, Vol. A). The atomic coordinates are: Ti 0, 0, 0; O 0.303, 0.303, 0. Which Wyckoff positions are occupied by the atoms? How many atoms are in one unit cell? What are the site symmetries of the atoms?

3.8 What is the point group of the Penrose tiling (Fig. 3.13) if it consists of one layer of tiles? What is the point group if two layers are stacked with their midpoints one on top of the other, the second layer being rotated by 180°?
4 Polymorphism and Phase Transitions

4.1 Thermodynamic Stability

When the free enthalpy of reaction $\Delta G$ for the transformation of the structure of a compound to any other structure is positive, then this structure is thermodynamically stable. Since $\Delta G$ depends on the transition enthalpy $\Delta H$ and the transition entropy $\Delta S$, and $\Delta H$ and $\Delta S$ in turn depend on pressure and temperature, a structure can be stable only within a certain range of pressures and temperatures. By variation of the pressure and/or the temperature, $\Delta G$ will eventually become negative relative to some other structure and a phase transition will occur. This may be a phase transition from a solid to another solid modification, or it may be a transition to another aggregate state.

According to the thermodynamic relations

$$\Delta G = \Delta H - T\Delta S \quad \text{and} \quad \Delta H = \Delta U + p\Delta V \quad (4.1)$$

the following rules can be given for the temperature and pressure dependence of thermodynamically stable structures:

1. With increasing temperature $T$ structures with a low degree of order will be favored. Their formation involves a positive transition entropy $\Delta S$ and the value of $\Delta G$ then depends mainly on the term $T\Delta S$. For instance, among hexahalides such as MoF$_6$ two modifications are known in the solid state, one having molecules with well-defined orientations and the other having molecules rotating about their centers of gravity within the crystal. Since the order is lower for the latter modification, it is the thermodynamically stable one at higher temperatures. In the liquid state, the order is even lower and it is the lowest in the gaseous state. Raising the temperature will thus lead to melting and finally to evaporation of the substance.

2. Higher pressures $p$ favor structures that occupy a lower volume, i.e. that have a higher density. As their formation involves a decrease in the volume (negative $\Delta V$), $\Delta H$ will attain a negative value. For instance, diamond (density 3.51 g cm$^{-3}$) is more stable than graphite (density 2.26 g cm$^{-3}$) at very high pressures.

4.2 Kinetic Stability

A thermodynamically unstable structure can exist when its conversion to some other structure proceeds at a negligible rate. In this case we call the structure metastable, inert or kinetically stable. Since the rate constant $k$ depends on the activation energy $E_a$ and the temperature according to the ARRHENIUS equation,

$$k = k_0 e^{-E_a/RT}$$

we have kinetic stability whenever a negligibly low $k$ results from a large ratio $E_a/RT$. At sufficiently low temperatures any structure can be stabilized kinetically. Kinetic stability is
4.3 Polymorphism

Molecules having the same composition but different structures are called isomers. The corresponding phenomenon for crystalline solids is called 

**polymorphism**. The different structures are the *modifications* or *polymorphic forms*. Modifications differ not only in the spatial arrangement of their atoms, but also in their physical and chemical properties. The structural differences may comprise anything from minor variations in the orientation of molecules up to a completely different atomic arrangement.

Different modifications of a compound are frequently designated by lower case Greek letters $\alpha$, $\beta$, ..., e.g. $\alpha$-sulfur, $\beta$-sulfur, or by roman numerals, e.g. tin-I, tin-II etc. Polymorphic forms of minerals have in many cases been given trivial names, like $\alpha$-quartz, $\beta$-quartz, tridymite, cristobalite, coesite, keatite, and stishovite for SiO$_2$ forms.

More systematic (but not always unambiguous) is the designation by PEARSON symbols; their use is recommended by IUPAC (International Union of Pure and Applied Chemistry). A PEARSON symbol consists of a lower case letter for the crystal system (cf. the abbreviations in Table 3.1, p. 24), an upper case letter for the kind of centering of the lattice (cf. Fig. 2.6, p. 8) and the number of atoms in the unit cell. Example: sulfur-$oF128$ is orthorhombic, face centered and has 128 atoms per unit cell ($\alpha$-sulfur).

Polymorphic forms with structures having different stacking sequences of like layers are called *polytypes*.

Which polymorphic form of a compound is formed depends on the preparation and crystallization conditions: method of synthesis, temperature, pressure, kind of solvent, cooling or heating rate, crystallization from solution, fusion or gas phase, and presence of seed crystals are some of the factors of influence.

When a compound that can form several modifications crystallizes, first a modification may form that is thermodynamically unstable under the given conditions; afterwards it converts to the more stable form (OSTWALD step rule). Selenium is an example: when elemental selenium forms by a chemical reaction in solution, it precipitates in a red modification that consists of Se$_8$ molecules; this then converts slowly into the stable, gray form that consists of polymeric chain molecules. Potassium nitrate is another example: at room temperature $\beta$-KNO$_3$ is stable, but above 128 °C $\alpha$-KNO$_3$ is stable. From an aqueous solution at room temperature $\alpha$-KNO$_3$ crystallizes first, then, after a short while or when triggered by the slightest mechanical stress, it transforms to $\beta$-KNO$_3$.

The nucleation energy governs which modification crystallizes first. This energy depends on the surface energy. As a rule, nucleation energy decreases with decreasing surface energy. The modification having the smallest nucleation energy crystallizes first. As
the surface energy depends sensitively on the adsorption of extraneous particles, the sequence of crystallization of polymorphic forms can be influenced by the presence of foreign matter.

### 4.4 Phase Transitions

**Definition:** A phase transition is an event which entails a discontinuous (sudden) change of at least one property of a material.

Generally, a phase transition is triggered by an external stress which most commonly is a change in temperature or pressure. Properties that can change discontinuously include volume, density, specific heat, elasticity, compressibility, viscosity, color, electric conductivity, magnetism and solubility. As a rule, albeit not always, phase transitions involve structural changes. Therefore, a phase transition in the solid state normally involves a change from one to another modification.

If a modification is unstable at every temperature and every pressure, then its conversion into another modification is irreversible; such phase transitions are called **monotropic**. **Enantiotropic** phase transitions are reversible; they proceed under equilibrium conditions ($\Delta G = 0$). The following considerations are valid for enantiotropic phase transitions that are induced by a variation of temperature or pressure.

The first derivatives of the free enthalpy $G = U + pV - TS$ are

$$\frac{\partial G}{\partial T} \bigg|_p = -S \quad \text{and} \quad \frac{\partial G}{\partial p} \bigg|_T = V$$

If one of these quantities experiences a discontinuous change, *i.e.* if $\Delta S \neq 0$ or $\Delta V \neq 0$, then the phase transition is called a first-order transition according to *Ehrenfest*. It is accompanied by the exchange of conversion enthalpy $\Delta H = T \Delta S$ with the surroundings.

First-order phase transitions exhibit hysteresis, *i.e.* the transition takes place some time after the temperature or pressure change giving rise to it. How fast the transformation proceeds also depends on the formation or presence of sites of nucleation. The phase transition can proceed at an extremely slow rate. For this reason many thermodynamically unstable modifications are well known and can be studied in conditions under which they should already have been transformed.

In a second-order phase transition, volume and entropy experience a continuous variation, but at least one of the second derivatives of $G$ exhibits a discontinuity:

$$\frac{\partial^2 G}{\partial T^2} \bigg|_p = -\frac{\partial S}{\partial T} \bigg|_p = -\frac{1}{T} \frac{\partial H}{\partial T} \bigg|_p = -\frac{C_p}{T} \quad \text{and} \quad \frac{\partial^2 G}{\partial p^2} \bigg|_T = \frac{\partial V}{\partial p} \bigg|_T = -V \kappa$$

$C_p$ is the specific heat at constant pressure, $\kappa$ is the compressibility at constant temperature. The conversion process of a second-order phase transition can extend over a certain temperature range. If it is linked with a change of the structure (which usually is the case), this is a continuous structural change. There is no hysteresis and no metastable phases occur. A transformation that almost proceeds in a second-order manner (very small discontinuity of volume or entropy) is sometimes called ‘weakly first order’.

Solid-state phase transitions can be distinguished according to *Buerger* in the following manner:
1. **Reconstructive phase transitions**: Chemical bonds are broken and rejoined; the reconstruction involves considerable atomic movements. Such conversions are always first-order transitions.

2. **Displacive phase transitions**: Atoms experience small shifts; if at all, only intermolecular bonds (e.g. hydrogen bonds) are broken and rejoined, but no primary chemical bonds. The transition may be but need not be a second-order transition.

3. **Order–disorder transitions**: Different atoms that statistically occupy the same position become ordered or vice versa. Usually this is a second-order transition.

An example of a continuous structural change is the second-order phase transition of calcium chloride (Fig. 4.1). At higher temperatures it is tetragonal (rutile type). When cooled, a mutual rotation of the coordination octahedra starts at 217 °C. As soon as the slightest rotation has taken place, the symmetry can no longer be tetragonal; at 217 °C a symmetry reduction occurs, the symmetry is ‘broken’. The orthorhombic space group $P\overline{4}2_{1}mnm$ of the low-temperature modification has fewer symmetry operations than the space group $P4_{2}/mnm$ of the rutile type; $P\overline{4}2_{1}mnm$ is a subgroup of $P4_{2}/mnm$. For second-order phase transitions it is mandatory that there is a group–subgroup relation between the two space groups. For more details see Chapter 18.

With the aid of an order parameter one can follow the changes taking place during a second-order phase transition. A quantity that experiences changes during the phase transition and which becomes zero at the critical temperature $T_{C}$ (or the critical pressure) can be chosen as the order parameter. $T_{C}$ is the temperature at which the phase transition sets in and the symmetry is broken. For example, for CaCl$_{2}$ the rotation angle of the octahedra or the ratio $\eta = (b-a)/(b+a)$ of the lattice parameters can be used as the order parameter. According to L"ANDAU theory, below $T_{C}$ the order parameter changes according to a power function of the temperature difference $T_{C}-T$:

$$\eta = A \left( \frac{T_{C}-T}{T_{C}} \right)^{\beta}$$

$A$ is a constant and $\beta$ is the critical exponent which adopts values from 0.3 to 0.5. Values around $\beta = 0.5$ are observed for long-range interactions between the particles; for short-range interactions (e.g. magnetic interactions) the critical exponent is closer to $\beta \approx 0.33$. As shown in the typical curve diagram in Fig. 4.2, the order parameter experiences its most relevant changes close to the critical temperature; the curve runs vertical at $T_{C}$. 

**Fig. 4.1**
Rotation of the coordination octahedra during the second-order phase transition of CaCl$_{2}$

CaCl$_{2}$, $> 217^\circ$C (rutile type), $P4_{2}/mnm$

$\begin{align*}
a &= b &= 637.9 \text{ pm, } c &= 419.3 \text{ pm at 247}^\circ\text{C} \\
a &= 625.9 \text{ pm, } b &= 644.4 \text{ pm, } c &= 417.0 \text{ pm}
\end{align*}$

CaCl$_{2}$, $17^\circ$C, $P\overline{4}nm$

$\begin{align*}
\end{align*}$
4 POLYMORPHISM AND PHASE TRANSITIONS

4.5 Phase Diagrams

For phases that are in equilibrium with one another, the GIBBS phase law holds:

\[ F + P = C + 2 \]

\( F \) is the number of degrees of freedom, i.e. the number of variables of state such as temperature and pressure that can be varied independently, \( P \) is the number of phases and \( C \) is the number of components. Components are to be understood as independent, pure substances (elements or compounds), from which the other compounds that eventually occur in the system can be formed. For example:

1. For pure water (one component, \( C = 1 \)) \( F + P = 3 \) holds. When three phases are simultaneously in equilibrium with each other, e.g. vapor, liquid and ice, or vapor and two different modifications of ice, then \( F = 0 \); there is no degree of freedom, the three phases can coexist only at one fixed pressure and one fixed temperature (‘triple point’).

2. In the system iron/oxygen (\( C = 2 \)), when two phases are present, e.g. \( \text{Fe}_3\text{O}_4 \) and oxygen, pressure and temperature can be varied (\( F = 2 \)). When three phases are in equilibrium, e.g. \( \text{Fe}, \text{Fe}_2\text{O}_3\) and \( \text{Fe}_3\text{O}_4 \), only one degree of freedom exists, and only the pressure or the temperature can be chosen freely.

A phase diagram in which pressure is plotted vs. temperature shows the existence ranges for the different phases of a system comprising only one component. Fig. 4.3 displays the phase diagram for water, in which the ranges of existence of liquid water and ten different modifications of ice are discernible, the latter being designated by Roman numerals. Within each of the marked fields only the corresponding phase is stable, but pressure and temperature can be varied independently (2 degrees of freedom). Along the delimiting lines two phases can coexist, and either the pressure or the temperature can be varied, whereas the other one has to adopt the value specified by the diagram (one degree of freedom). At triple points there is no degree of freedom, pressure and temperature have fixed values, but three phases are simultaneously in equilibrium with each other.

In phase diagrams for two-component systems the composition is plotted vs. one of the variables of state (pressure or temperature), the other one having a constant value. Most common are plots of the composition vs. temperature at ambient pressure. Such phase diagrams differ depending on whether the components form solid solutions with each other or not or whether they combine to form compounds.
Fig. 4.3
Phase diagram for 
H₂O. Dashed lines 
have not been verified 
experimentally. 
Additional metastable 
phases are ice Ic in the 
low-temperature 
section of ice Ih and 
ice IV and ice XII 
within the region of 
ice V.

Not shown: region of gaseous H₂O at pressures below 22 MPa. The line delimiting the liquid and ice VII continues up 
to at a triple point at 43 GPa and 1370 °C; at this triple point it probably meets the line delimiting ice VII and ice X. The 
melting point continues to move upward until approximately 2150 °C at 90 GPa

The phase diagram for the antimony/bismuth system, in which mixed crystals (solid solutions) are formed, is shown in Fig. 4.4. Crystalline antimony and bismuth are isotypic, and Sb and Bi atoms can occupy the atomic positions in any proportion. The upper part 
of the diagram corresponds to the range of existence of the liquid phase, i.e. a liquid 
solution of antimony and bismuth. The lower part corresponds to the range of existence 
of the mixed crystals. In between is a range in which liquid and solid coexist. On the 
upper side it is delimited by the liquidus curve, and on the lower side by the solidus 
curve. At a given temperature, the liquid and the solid that are in equilibrium with one 
another have different compositions. The compositions can be read from the cross-points 
of the horizontal straight line marking the temperature in question with the solidus and 
the liquidus curves. Upon cooling an Sb/Bi melt with a composition corresponding to the 
point marked A in Fig. 4.4, crystallization begins when the temperature marked by the 
horizontal arrow is reached. The composition of the mixed crystals that form is that of 
point B — the mixed crystals have a higher Sb content than the melt.

The potassium/caesium phase diagram is an example of a system involving the forma- 
tion of mixed crystals with a temperature minimum (Fig. 4.4). The right and left halves 
of the diagram are of the same type as the diagram for antimony/bismuth. The minimum 
corresponds to a special point for which the compositions of the solid and the liquid are 
the same. Other systems can have the special point at a temperature maximum.

Limited formation of mixed crystals occurs when the two components have different 
structures, as for example in the case of indium and cadmium. Mixed crystals containing 
much indium and little cadmium have the structure of indium, while those containing little 
indium and much cadmium have the cadmium structure. At intermediate compositions a 
gap is observed, i.e. there are no homogeneous mixed crystals, but instead a mixture of 
crystals rich in indium and crystals rich in cadmium is formed. This situation can even
occur when both of the pure components have the same structure, but mixed crystals may not have any arbitrary composition. Copper and silver offer an example; the corresponding phase diagram is shown in Fig. 4.5.

The phase diagram for aluminum/silicon (Fig. 4.5) is a typical example of a system of two components that form neither solid solutions (except for very low concentrations) nor a compound with one another, but are miscible in the liquid state. As a special feature an acute minimum is observed in the diagram, the eutectic point. It marks the melting point of the eutectic mixture, which is the mixture which has a lower melting point than either of the pure components or any other mixture. The eutectic line is the horizontal line that passes through the eutectic point. The area underneath is a region in which both components coexist as solids, i.e. in two phases.

A liquid solution of aluminum and silicon containing an amount-of-substance fraction of 40% aluminum and having a temperature of 1100 °C corresponds to point A in Fig. 4.5. Upon cooling the liquid we move downwards in the diagram (as marked by the arrow). At the moment we reach the liquidus line, pure silicon begins to crystallize. As a consequence, the composition of the liquid changes as it now contains an increasing fraction of aluminum; this corresponds to a leftward movement in the diagram. There the crystal-
lization temperature for silicon is lower. According to the amount of crystallizing silicon, the temperature for the crystallization of further silicon decreases more and more until finally the eutectic point is reached, where both aluminum and silicon solidify. The term *incongruent solidification* serves to express the continuous change of the solidification temperature.

When the two components form compounds with each other, more complicated conditions arise. Fig. 4.6 shows the phase diagram for a system in which the two components, magnesium and calcium, form a compound, CaMg$_2$. At the composition CaMg$_2$ we observe a maximum which marks the melting point of this compound. On the left there is a eutectic point, formed by the components Mg and CaMg$_2$. On the right there is another eutectic point with the components Ca and CaMg$_2$. Both the left and right parts of the phase diagram in Fig. 4.6 correspond to the phase diagram of a simple eutectic system as in Fig. 4.5.

The system H$_2$O/HF exhibits an even more complicated phase diagram, as three compounds occur: H$_2$O-HF, H$_2$O-2 HF and H$_2$O-4 HF. In these compounds H$_3$O$^+$, HF and F$^-$ particles are joined with each other in different ways via hydrogen bridges. For two of the compounds we find maxima in the phase diagram (Fig. 4.6), in a similar way as for the compound CaMg$_2$. However, there is no maximum at the composition H$_2$O-2 HF and no eutectic point between H$_2$O-2 HF and H$_2$O-HF; we can only discern a kink in the liquidus line, the *peritectic point*. The expected maximum is ‘covered’ (dashed line). The horizontal line running through the kink is called the *peritectic line*. The solids of composition H$_2$O-HF and H$_2$O-4 HF show congruent melting, *i.e.* they have definite melting temperatures according to the maxima in the diagram. The solid with the composition H$_2$O-2 HF, however, shows incongruent melting: at $-78^\circ$C it decomposes to solid H$_2$O-HF and a liquid with a higher HF content. In addition, the compound H$_2$O-2 HF experiences a phase transition at $-103^\circ$C from a ‘high-temperature’ to a low-temperature modification; in the diagram this is expressed by the horizontal line at this temperature.

Phase diagrams give valuable information about the compounds that can form in a system of components. These compounds can then be prepared and studied. For the experimental determination of phase diagrams the following methods are used. In *differential thermal analysis* (DTA) a sample of a given composition is heated or cooled slowly
together with a thermally indifferent reference substance, and the temperatures of both substances are monitored continuously. When a phase transition occurs in the sample, the enthalpy of conversion is freed or absorbed and therefore a temperature difference shows up between the sample and the reference, thus indicating the phase transition. In X-ray phase studies an X-ray diffraction pattern is recorded continuously while the sample is being cooled or heated; when a phase transition occurs, changes in the diffraction pattern show up.

4.6 Problems

4.1 The densities of some SiO₂ modifications are: α-quartz 2.65 g cm⁻³, β-quartz 2.53 g cm⁻³, β-tridymite 2.27 g cm⁻³, β-cristobalite 2.33 g cm⁻³, vitreous SiO₂ 2.20 g cm⁻³. Should it be possible to convert β-cristobalite to some of the other modifications by applying pressure?

4.2 Silica glass is formed when molten SiO₂ is cooled rapidly. It experiences slow crystallization. Will the rate of crystallization be higher at room temperature or at 1000 °C?

4.3 BeF₂, like quartz, has a polymeric structure with F atoms linking tetrahedrally coordinated Be atoms; BF₃ is monomeric. When cooling the liquid down to solidification, which of the two is more likely to form a glass?

4.4 Is the conversion α-KNO₃ → β-KNO₃ (cf. p. 31) a first- or second-order phase transition?

4.5 CaO experiences a phase transition form the NaCl type to the CsCl type at a pressure of 65 GPa (images in Fig. 7.1, p. 53). What kind of a transformation is this?

4.6 Will ice at a temperature of −10°C melt if pressure is applied to it? If so, will it refreeze if the pressure is increased even more? Which modification would have to form?

4.7 Can water at 40 °C be made to freeze? If so, what modification(s) of ice will form?

4.8 What will happen when a solution of HF and water containing an amount-of-substance fraction of 40 % HF is cooled from 0 °C to −100 °C?

4.9 As shown in Fig. 12.11 (p. 126), upon heating at ambient pressure, β-quartz will experience phase transitions to β-tridymite and then to β-cristobalite at 870 °C and 1470 °C, respectively. Is it feasible to achieve a direct interconversion β-quartz ⇌ β-cristobalite by temperature variation at high pressure?
5 Chemical Bonding and Lattice Energy

5.1 Chemical Bonding and Structure

Which spatial arrangement of atoms results in a stable or metastable structure depends decisively on the distribution of their electrons.

For noble gases the electronic configuration of a single atom is thermodynamically stable at normal conditions. Merely by packing the atoms closer together to form a liquid or a solid a small amount of van der Waals energy can still be released. The condensation and crystallization enthalpies being rather small, the magnitude of $\Delta G$ is governed already at relatively low temperatures by the term $T\Delta S$, and correspondingly the melting and boiling points are low.

For all other elements the electronic configuration of a single atom does not correspond to a thermodynamically stable state at normal conditions. Only at very high temperatures do single atoms occur in the vapor phase. At more ordinary temperatures atoms have to be linked to produce stable structures.

The electrons in an aggregate of atoms can only exist in certain definite energy states, just as in a single atom. These states are expressed mathematically by the eigenvalues of wave functions $\psi$. The wave functions result theoretically as solutions of the Schrödinger equation for the complete set of all constituent atoms. Although the exact mathematical solution of this equation poses insurmountable difficulties, we do have a well-founded knowledge about wave functions and thus about electrons in atomic systems. The knowledge is based on experimental data and on mathematical approximations that by now have become quite reliable; we will discuss this more broadly in Chapter 10.

To begin with, we will restrict ourselves to the simplified scheme of two extreme kinds of chemical bonding, namely ionic and covalent bonds. However, we will also allow for intermediate states between these two extremes and we will consider the coexistence of both bonding types. As far as is relevant, we will also take into account the weaker ion–dipole, dipole–dipole and dispersion interactions.

The (localized) covalent bond is distinguished by its short range of action, which usually extends only from one atom to the next. However, within this range it is a strong bond. A near order arises around an atom; it depends on the one hand on the tight interatomic bonds and on the other hand on the mutual repulsion of the valence electrons and on the space requirements of the bonded atoms.\(^1\) When atoms are linked to form larger structures, the near order can result in a long-range order in a similar way as the near order around a brick propagates to a long-range order in a brick wall.

In a nonpolymer molecule or molecular ion a limited number of atoms are linked by covalent bonds. The covalent forces within the molecule are considerably stronger than

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\(^1\)Frequently, directionality is a property attributed to the covalent bond which supposedly is taken to be the cause of the resulting structures. However, as the success of the valence electron pair repulsion theory shows, there exists no need to assume any orbitals directed apriori. The concept of directed orbitals is based on calculations in which hybridization is used as a mathematical aid. The popular use of hybridization models occasionally has created the false impression that hybridization is some kind of process occurring prior to bond formation and committing stereochemistry.
all forces acting outwards. For this reason, when molecular structures are being considered, one commits only a small error when one acts as if the molecule would occur by itself and had no surroundings. Common experience as well as more detailed studies by KITAEV and calculations with force fields show that bond lengths and angles in molecules usually only undergo marginal alterations when the molecules assemble to a crystal. Only conformation angles are influenced more significantly in certain cases. Many properties of a molecular compound can therefore be explained from the molecular structure.

This is not equally valid for macromolecular compounds, in which a molecule consists of a nearly unlimited number of atoms. The interactions with surrounding molecules cannot be neglected in this case. For instance, for a substance consisting of thread-like macromolecules, it makes a difference to the physical properties whether the molecules are ordered in a crystalline manner or whether they are tangled.

Crystalline macromolecular substances can be classified according to the kind of connectivity of the covalently linked atoms as chain structures, layer structures and framework structures. The chains or layers may be electrically uncharged molecules that interact with each other only by VANDERWAALS forces, or they can be polyanions or polycations held together by intervening counter-ions. Framework structures can also be charged, the counter-ions occupying cavities in the network. The structure of the chain, layer or framework depends to a large extent on the covalent bonds and the resulting near order around each atom.

On the other hand, the crystal structures of ionic compounds with small molecular ions depend mainly on how space can be filled most efficiently by the ions, following the principle of cations around anions and anions around cations. Geometric factors such as the relative size of the ions and the shape of molecular ions are of prime importance. More details are given in Chapter 7.

5.2 Lattice Energy

**Definition:** Lattice energy is the energy released when one mole of a crystalline compound is assembled at a temperature of 0 K from its infinitely separated components.

In this sense, components are taken to be:

- for molecular compounds: the molecules
- for ionic compounds: the ions
- for metals: the atoms
- for pure elements, excluding molecular species such as H₂, N₂, S₈ etc.: the atoms

For compounds that cannot be assigned uniquely to one of these substance classes, the specification of a lattice energy makes sense only if the kind of components is defined. Should SiO₂ be composed from Si and O atoms or from Si⁺⁺ and O²⁻ ions? For polar compounds like SiO₂, lattice energy values given in the literature usually refer to a composition formed from ions. Values calculated under this assumption should be considered with caution as the neglected covalent bonds are of considerable importance. Even in the case of an assembly from ions conditions are not always clear: should Na₂SO₄ be assembled from Na⁺ and SO₄²⁻ ions or from Na⁺, S⁶⁺ and O²⁻ ions?
Lattice Energy of Molecular Compounds

The lattice energy $E$ of a molecular compound corresponds to the energy of sublimation at 0 K. This energy cannot be measured directly, but it is equal to the enthalpy of sublimation at a temperature $T$ plus the thermal energy needed to warm the sample from 0 K to this temperature, minus $RT$. $RT$ is the amount of energy required to expand one mole of a gas at a temperature $T$ to an infinitely small pressure. These amounts of energy, in principle, can be measured and therefore the lattice energy can be determined experimentally in this case. However, the measurement is not simple and is subject to various uncertainties.

The following four forces acting between molecules contribute to the lattice energy of a crystal consisting of molecules:

1. The dispersion forces (LONDON forces) which are always attractive.
2. The repulsion due to the interpenetration of the electron shells of atoms that come together too closely.
3. For molecules with polar bonds, i.e. for molecules having the character of dipoles or multipoles, the electrostatic interaction between the dipoles or multipoles.
4. The zero point energy which always is present even at absolute zero temperature.

The zero point energy follows from quantum theory, according to which atoms do not cease to vibrate at the absolute zero point. For a DEBYE solid (that is, a homogeneous body of $N$ equal particles) the zero point energy is

$$E_0 = \frac{9}{8} \hbar \nu_{\text{max}}$$

$\nu_{\text{max}}$ is the frequency of the highest occupied vibrational state in the crystal. For molecules with a very small mass and for molecules that are being held together via hydrogen bridges, the zero point energy makes a considerable contribution. For H$_2$ and He it even amounts to the predominant part of the lattice energy. For H$_2$O it contributes about 30 %, and for N$_2$, O$_2$ and CO about 10 %. For larger molecules the contribution of the zero point energy is marginal.

The dispersion force between two atoms results in the dispersion energy $E_D$, which is approximately proportional to $r^{-6}$, $r$ being the distance between the atoms:

$$E_D = \frac{C}{r^6}$$

The dispersion energy between two molecules results approximately from the sum of the contributions of atoms of one molecule to atoms of the other molecule.

For the repulsion energy $E_A$ between two atoms that come together too closely an exponential function is usually taken:

$$E_A = B e^{-\alpha r}$$

Another, equally appropriate approximation is:

$$E_A = B' r^{-n}$$

with values $n$ ranging between 5 and 12 (BORN repulsion term).

For molecules with low polarity like hydrocarbons, electrostatic forces have only a minor influence. Molecules with highly polar bonds behave as dipoles or multipoles and exhibit corresponding interactions. For instance, hexahalide molecules like WF$_6$ or WCl$_6$ are multipoles, the halogen atoms bearing a negative partial charge $-q$, while the metal
atom has a positive charge $+6q$; the partial charge $q$ has some value between zero and one, but its exact amount is not usually known. Although the forces exerted by a multipole only have appreciable influence on close-lying molecules, they can contribute significantly to the lattice energy. The electrostatic or Coulomb energy $E_C$ for two interacting atoms having the charges $q_i$ and $q_j$ is:

$$E_C = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j e^2}{r} \quad (5.1)$$

$q_i, q_j$ being given in units of the electrical unit charge $e = 1.6022 \times 10^{-19} \text{ C. } \varepsilon_0 = \text{electric field constant} = 8.859 \times 10^{-12} \text{ C}^2\text{J}^{-1}\text{m}^{-1}$.

Overall, the lattice energy $E$ can thus be calculated according to the following approximation:

$$E = N_A \sum (E_D + E_A + E_C + E_0) = N_A \sum_{i,j} \left[ -C_{ij}r_{ij}^6 + B_{ij} \exp(-\alpha_{ij}r_{ij}) + \frac{q_i q_j e^2}{4\pi\varepsilon_0 r_{ij}} + \frac{9}{8}h\nu_{\text{max}} \right] \quad (5.2)$$

The choice of the signs gives a negative value for the lattice energy, corresponding to its definition as energy that is released upon formation of the crystal. The atoms of one molecule are counted with the index $i$, while all atoms of all other molecules in the crystal are counted with the index $j$. In this way the interaction energy of one molecule with all other molecules is calculated. The lattice energy per mole results from multiplication by Avogadro’s number $N_A$. $r_{ij}$ is the distance between the atoms $i$ and $j$, $q_i$ and $q_j$ are their partial charges in units of the electric unit charge. $B_{ij}$, $\alpha_{ij}$ and $C_{ij}$ are parameters that have to be determined experimentally; they are optimized to reproduce the measured sublimation enthalpies at 300 K correctly. As the contributions of the terms in equation (5.2) decrease with growing distances $r_{ij}$, sufficient accuracy can be obtained by considering only atoms up to some upper limit for $r_{ij}$. The summation can then be performed rather quickly with a computer.

Values for the partial charges of atoms can be derived from quantum mechanical calculations, from the molecular dipole moments and from rotation–vibration spectra. However, often they are not well known. If the contribution of the Coulomb energy cannot be calculated precisely, no reliable lattice energy calculations are possible.

Fig. 5.1

Potential functions for the interaction energies due to repulsive and to dispersion forces between two atoms as a function of the interatomic distance.
5.2 Lattice Energy

Parameters $B_{ij}$, $\alpha_{ij}$ and $C_{ij}$ for light atoms have been listed by Gavezzotti [63]. Examples of the resulting potential functions are shown in Fig. 5.1. The minimum point in each graph corresponds to the interatomic equilibrium distance between two single atoms. In a crystal shorter distances result because a molecule contains several atoms and thus several attractive atom–atom forces are active between two molecules, and because attractive forces with further surrounding molecules cause an additional compression. All attractive forces taken together are called Van der Waals forces.

Generally, increasing molecular size, heavier atoms and more polar bonds contribute to an increased lattice energy of a molecular crystal. Typical values are: argon 7.7 kJ mol$^{-1}$/Å$^1$; krypton 11.1 kJ mol$^{-1}$/Å$^1$; organic compounds 50 to 150 kJ mol$^{-1}$/Å$^1$.

Lattice Energy of Ionic Compounds

In a molecule the partial charges of all atoms add up to zero and therefore the repulsive and the attractive electrostatic forces between two molecules are more or less balanced. Only the uneven distribution of the charges causes a certain electrostatic contribution to the lattice energy. For a polyatomic ion, however, the partial charges do not add up to zero, but to the value of the ionic charge. As a consequence, strong electrostatic interactions are present between ions, their contributions amounting to the main part of the lattice energy. Numerical values for sodium chloride illustrate this:

$$ E = -787 \text{ kJ mol}^{-1} $$

The calculation of the lattice energy can be performed with the aid of equation (5.2). In the case of monatomic ions the charges $q$ take the values of the ionic charges. Crystals consisting of monoatomic ions like Na$^+$ or Cl$^-$ have simple and symmetrical structures, which are useful for the summation according to equation (5.2). Let us take the structure of NaCl as an example. If we designate the shortest distance Na$^+$–Cl$^-$ in the crystal by $R$, then all other interionic distances can be given as multiples of $R$. Which multiples occur follows from simple geometric considerations on the basis of the structure model of NaCl (cf. Fig. 7.1, p. 53). For a Na$^+$ ion within the crystal the Coulomb energy turns out to be:

$$ E_C = \frac{N_A}{4\pi\varepsilon_0} \sum_j \frac{q_i q_j e^2}{r_{ij}} $$

The terms in parentheses result as follows:

1. $-6$, because the Na$^+$ ion is surrounded by 6 Cl$^-$ ions with charge $-1$ at a distance $r = R$ in a first sphere.
2. $+12/\sqrt{2}$, because the Na$^+$ ion is surrounded by 12 Na$^+$ ions with charge $+1$ at a distance $R\sqrt{2}$ in a second sphere.
3. $-8/\sqrt{3}$, because there are 8 Cl$^-$ ions at a distance $R\sqrt{3}$. 

$$ E = \frac{N_A e^2}{4\pi\varepsilon_0 R} \left( -\frac{6}{1} + \frac{12}{\sqrt{2}} - \frac{8}{\sqrt{3}} + \frac{6}{\sqrt{4}} - \frac{24}{\sqrt{5}} + \ldots \right) $$

(5.3)
Extending the series given in parentheses to infinite length, it sums to the value $-A = -1.74756$. For short, we can write:

$$E_C = -\frac{N_Ae^2}{4\pi\varepsilon_0R}$$  \hspace{1cm} (5.4)

The quantity $A$ is called the MADELUNG constant. By comparison of equation (5.1) with equation (5.4) we can see that more energy is liberated by combining the ions into a crystal than by forming one mole of separate ion pairs (assuming equal interionic distances $r = R$; in fact, for a single ion pair $r < R$, so that the energy gain actually does not quite attain the factor $A$).

The same constant $A$ can also be used when ions with higher charges are involved, as long as the structure type is the same:

$$E_C = -|q_1||q_2|\frac{N_Ae^2}{4\pi\varepsilon_0R}$$

$|q_1|$ and $|q_2|$ are the absolute values of the ionic charges as multiples of the electric unit charge. The MADELUNG constant is independent of the ionic charges and of the lattice dimensions, but it is valid only for one specific structure type. Table 5.1 lists the values for some simple structure types.

<table>
<thead>
<tr>
<th>structure type</th>
<th>$A$</th>
<th>structure type</th>
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<tbody>
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<td>CsCl</td>
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<td>CaF$_2$</td>
<td>5.03879</td>
</tr>
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<td>NaCl</td>
<td>1.74756</td>
<td>TiO$_2$ (rutile)</td>
<td>4.816</td>
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<td>CdI$_2$</td>
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</tbody>
</table>

MADELUNG constants only cover the coulombic part of the lattice energy provided that the values of the charges $q_1$ and $q_2$ are known. A complete separation of charges between anions and cations yielding integer values for the ionic charges is met quite well only for the alkali metal halides. When some covalent bonding is present, partial charges must be assumed. The magnitudes of these partial charges are not usually known. In this case absolute values for the coulombic part of the lattice energy cannot be calculated. For ZnS, TiO$_2$, CdCl$_2$ and CdI$_2$ differing polarities have to be assumed, so that the values listed in Table 5.1 do not follow the real trend of the lattice energies. Nevertheless, MADELUNG constants are useful quantities; they can serve to estimate which structure type should be favored energetically by a compound when the Coulomb energy is the determining factor.

### 5.3 Problems

5.1 Derive the first four terms of the series to calculate the MADELUNG constant for CsCl (Fig. 7.1).

5.2 Calculate the contribution of the Coulomb energy to the lattice energy of:

(a) CsCl, $R = 356$ pm;
(b) CaF$_2$, $R = 236$ pm;
(c) BaO (NaCl type), $R = 276$ pm.
6 The Effective Size of Atoms

According to wave mechanics, the electron density in an atom decreases asymptotically towards zero with increasing distance from the atomic center. An atom therefore has no definite size. When two atoms approach each other, interaction forces between them become more and more effective.

Attractive are:

- The ever present dispersion force (LONDON attraction).
- Electronic interactions with the formation of bonding molecular orbitals (orbital energy) and the electrostatic attraction between the nuclei of atoms and electrons. These two contributions cause the bonding forces of covalent bonds.
- Electrostatic forces between the charges of ions or the partial charges of atoms having opposite signs.

Repulsive are:

- The electrostatic forces between ions or partially charged atoms having charges of the same sign.
- The electrostatic repulsion between the atomic nuclei.
- The mutual electrostatic repulsion of the electrons and the PAULI repulsion between electrons having the same spin. The PAULI repulsion contributes the principal part of the repulsion. It is based on the fact that two electrons having the same spin cannot share the same space. PAULI repulsion can only be explained by quantum mechanics, and it eludes simple model conceptions.

The effectiveness of these forces differs and, furthermore, they change to a different degree as a function of the interatomic distance. The last-mentioned repulsion force is by far the most effective at short distances, but its range is rather restricted; at somewhat bigger distances the other forces dominate. At some definite interatomic distance attractive and repulsive forces are balanced. This equilibrium distance corresponds to the minimum in a graph in which the potential energy is plotted as a function of the atomic distance (‘potential curve’, cf. Fig. 5.1, p. 42).

The equilibrium distance that always occurs between atoms conveys the impression of atoms being spheres of a definite size. In fact, in many cases atoms can be treated as if they were more or less hard spheres.

Since the attractive forces between the atoms differ depending on the type of bonding forces, for every kind of atom several different sphere radii have to be assigned according to the bonding types. From experience we know that for one specific kind of bonding the atomic radius of an element has a fairly constant value. We distinguish the following radius types: VAN DER WAALS radii, metallic radii, several ionic radii depending on the ionic charges, and covalent radii for single, double and triple bonds. Furthermore, the values vary depending on coordination numbers: the larger the coordination number, the bigger is the radius.
6.1 Van der Waals Radii

In a crystalline compound consisting of molecules, the molecules usually are packed as close as possible, but with atoms of neighboring molecules not coming closer than the sums of their Van der Waals radii. The shortest commonly observed distance between atoms of the same element in adjacent molecules is taken to calculate the Van der Waals radius for this element. Some values are listed in Table 6.1. A more detailed study reveals that covalently bonded atoms are not exactly spherical. For instance, a halogen atom bonded to a carbon atom is flattened to some degree, i.e. its Van der Waals radius is shorter in the direction of the extension of the C–halogen bond than in transverse directions (cf. Table 6.1). If the covalent bond is more polar, as in metal halides, then the deviation from the spherical form is less pronounced. The kind of bonding also can have some influence; for example, carbon atoms in acetylenes have a slightly bigger radius than in other compounds.

Distances that are shorter than the sums of the corresponding listed values of the Van der Waals radii occur when there exist special attractive forces. For example, in a solvated ion the distances between the ion and atoms of the solvent molecules cannot be calculated with the aid of Van der Waals radii. The same applies in the presence of hydrogen bonding.

### Table 6.1: Van der Waals radii/pm

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6.2 Atomic Radii in Metals

The degree of cohesion of the atoms in metals is governed by the extent to which occupation of bonding electron states outweighs antibonding states in the electronic energy bands (cf. Section 10.8). Metals belonging to groups in the left part of the periodic table have few valence electrons; the numbers of occupied bonding energy states are low. Metals in the right part of the periodic table have many valence electrons; a fraction of them has to be accommodated in antibonding states. In both cases we have relatively weak metallic bonding. When many bonding but few antibonding states are occupied, the resulting bond forces between the metal atoms are large. This is valid for the metals belonging to the central part of the block of transition elements. Atomic radii in metals therefore decrease from...
### 6.3 Covalent Radii

Covalent radii are derived from the observed distances between covalently bonded atoms of the same element. For example, the C–C bond length in diamond and in alkanes is 154 pm; half of this value, 77 pm, is the covalent radius for a single bond at a carbon atom having coordination number 4 (sp$^3$ C atom). In the same way we calculate the covalent radii for chlorine (100 pm) from the Cl–Cl distance in a Cl$_2$ molecule, for oxygen (73 pm) from the O–O distance in H$_2$O$_2$ and for silicon (118 pm) from the bond length in elemental silicon. If we add the covalent radii for C and Cl, we obtain 77 + 100 = 177 pm; this value corresponds rather well to the distances observed in C–Cl compounds. However, if we add the covalent radii for Si and O, 118 + 73 = 191 pm, the value obtained does not agree satisfactorily with the distances observed in SiO$_2$ (158 to 162 pm). Generally we must state: the more polar a bond is, the more its length deviates to lower values compared with the sum of the covalent radii. To take this into account, SHOMAKER and STEVENSON derived the following correction formula:

$$d(AX) = r(A) + r(X) - c|\varepsilon(A) - \varepsilon(X)|$$

$d(AX)$ = bond length, $r(A)$ und $r(X)$ = covalent radii of the atoms A and X, $\varepsilon(A)$ and $\varepsilon(X)$ = electronegativities of A and X.

The correction parameter $c$ depends on the atoms concerned and has values between 2 and 9 pm. For C–X bonds no correction is necessary when X is an element of the 5th,

| Table 6.2: Atomic radii in metals/pm. All values refer to coordination number 12, except for the alkali metals (c.n. 8), Ga (c.n. 1+6), Sn (c.n. 4+2), Pa (c.n. 10), U, Np and Pu |
|---|---|
| Li | 152 | Be | 112 |
| Na | 186 | Mg | 160 |
| K | 230 | Ca | 197 | Sc | 162 | Ti | 146 | V | 134 | Cr | 128 | Mn | 137 | Fe | 126 | Co | 125 | Ni | 125 | Cu | 128 | Zn | 134 | Ga | 135 |
| Rb | 247 | Sr | 215 | Y | 180 | Zr | 160 | Nb | 146 | Mo | 139 | Tc | 135 | Ru | 134 | Rh | 134 | Pd | 137 | Ag | 144 | Cd | 151 | In | 167 | Sn | 154 |
| Cs | 267 | Ba | 222 | La | 187 | Hf | 158 | Ta | 146 | W | 139 | Re | 137 | Os | 135 | Ir | 136 | Pt | 139 | Au | 144 | Hg | 151 | Tl | 171 | Pb | 175 |
| Ce | 182 | Pr | 182 | Nd | 182 | Pm | 181 | Sm | 180 | Eu | 204 | Gd | 179 | Tb | 178 | Dy | 177 | Ho | 176 | Er | 175 | Tm | 174 | Yb | 193 | Lu | 174 |
| Th | 180 | Pa | 161 | U | 156 | Np | 155 | Pu | 159 | Am | 173 | Cm | 174 | Bk | 170 | Cf | 169 | Es | 160 | Fm | 174 | Md | 174 | No | 174 | Lr | 174 |

the alkali metals up to the metals of the groups six to eight, and then they increase. Superimposed on this sequence is the general tendency of decreasing atomic sizes observed in all periods from the alkali metals to the noble gases, which is due to the increasing nuclear charge (Table 6.2). For intermetallic compounds the ratio of the total number of available valence electrons to the number of atoms (the ‘valence electron concentration’) is a decisive factor affecting the effective atomic size.
6th or 7th main groups, except for N, O and F. The influence of bond polarity also shows up in the fact that the bond lengths depend on the oxidation states; for instance, the P–O bonds in P₄O₆ (164 pm) are longer than in P₄O₁₀ (160 pm; sum of the covalent radii 183 pm). Deviations of this kind are larger for ‘soft’ atoms, i.e. for atoms that can be polarized easily.

Calculated bond lengths also are uncertain when it is not known to exactly what degree multiple bonding is present, what influence lone electron pairs exercise on adjacent bonds, and to what extent the ionic charge and the coordination number have an effect. The range of Cl–O bond lengths illustrates this: HOCl 170 pm, ClO⁻² 156 pm, ClO⁻³ 149 pm, ClO⁻⁴ 143 pm, HOClO₃ one at 164 and three at 141 pm, ClO₂ 147 pm, ClO⁺² 131 pm. Problems related to bond lengths are also dealt with on pages 60 and 67 – 71.

6.4 Ionic Radii

The shortest cation–anion distance in an ionic compound corresponds to the sum of the ionic radii. This distance can be determined experimentally. However, there is no straightforward way to obtain values for the radii themselves. Data taken from carefully performed X-ray diffraction experiments allow the calculation of the electron density in the crystal; the point having the minimum electron density along the connection line between a cation and an adjacent anion can be taken as the contact point of the ions. As shown in the example of sodium fluoride in Fig. 6.1, the ions in the crystal show certain deviations from spherical shape, i.e. the electron shell is polarized. This indicates the presence of some degree of covalent bonding, which can be interpreted as a partial backflow of electron density from the anion to the cation. The electron density minimum therefore does not necessarily represent the ideal place for the limit between cation and anion.

The commonly used values for ionic radii are based on an arbitrarily assigned standard radius for a certain ion. In this way, a consistent set of radii for other ions can be

![Fig. 6.1](image)

**Fig. 6.1**
Experimentally determined electron density \( \rho \) (multiples of \( 10^{-6} \text{e}^{-}/\text{pm}^3 \)) in crystalline sodium fluoride [68]). Left: plane of intersection through adjacent ions; right: electron density along the connecting line Na⁺—F⁻ and marks for the ionic radii values according to Table 6.3
6.4 Ionic Radii

Several tables have been published, each of which was derived using a different standard value for one ionic radius (ionic radii by Goldschmidt, Pauling, Ahrens, Shannon). The values by Shannon are based on a critical evaluation of experimentally determined interatomic distances and on the standard radius of 140 pm for the O\(^{2-}\) ion with sixfold coordination. They are listed in Tables 6.3 and 6.4.

Ionic radii can also be used when considerable covalent bonding is involved. The higher the charge of a cation, the greater is its polarizing effect on a neighboring anion, i.e., the covalent character of the bond increases. Nevertheless, arithmetically one can still assume a constant radius for the anion and assign a radius for the cation that will yield the correct interatomic distance. A value like \(r(\text{Nb}^{5+}) = 64\) pm therefore does not imply the existence of a Nb\(^{5+}\) ion with this radius, but means that in niobium(V) compounds the bond length between an Nb atom and a more electronegative atom X can be calculated as the sum of \(r(\text{Nb}^{5+})\) plus the anionic radius of X. However, the values are not completely independent of the nature of X; for instance, the values given in Table 6.4 cannot be used readily for sulfur compounds; for this purpose another set of slightly different ionic radii has been derived [70]. Conversely, one can deduce the oxidation states of the atoms from observed bond lengths.

Ionic radii of soft (easily polarized) ions depend on the counter-ion. The H\(^-\) ion is an example; its radius is 130 pm in MgH\(_2\), 137 pm in LiH, 146 pm in NaH and 152 pm in KH.

The ionic radii listed in Tables 6.3 and 6.4 in most cases apply to ions which have coordination number 6. For other coordination numbers slightly different values have to be taken. For every unit by which the coordination number increases or decreases, the ionic radius increases or decreases by 1.5 to 2%. For coordination number 4 the values are approximately 4% smaller, and for coordination number 8 about 3% greater than for coordination number 6. The reason for this is the mutual repulsion of the coordinated ions.

**Table 6.3:** Ionic radii for main group elements according to Shannon [69], based on \(r(\text{O}^{2-}) = 140\) pm. Numbers with signs: oxidation states. All values refer to coordination number 6 (except c.n. 4 for N\(^{3-}\)).

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**Table 6.4:** Ionic radii for transition metals and non-transition metals.

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the effect of which increases when more of them are present. The size of the coordinated ions also has some influence: a cation that is surrounded by six small anions appears to be slightly smaller than the same cation surrounded by six large anions because in the latter case the anions repel each other more. To account for this, a correction function was derived by Pauling [73]. When covalent bonding is involved, the ionic radii depend to a larger extent on the coordination number. For instance, increasing the coordination number from 6 to 8 entails an increase of the ionic radii of lanthanoid ions of about 13%, and for Ti$^{3+}$ and Pb$^{4+}$ of about 21%. An ionic radius decrease of 20 to 35% is observed when the coordination number of a transition element decreases from 6 to 4.

### Table 6.4: Ionic radii for transition elements according to Shannon [69], based on $r(O^{2-}) = 140$ pm. Numbers with signs: oxidation states; ls = low spin, hs = high spin; roman numerals: coordination numbers if other than 6

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<td>73</td>
<td>72</td>
<td>71</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.5 Problems

6.1 In the following tetrahedral molecules the bond lengths are:
\( \text{SiF}_4 \) 155 pm; \( \text{SiCl}_4 \) 202 pm; \( \text{SiI}_4 \) 243 pm.
Calculate the halogen–halogen distances and compare them with the \textsc{van der Waals} distances. What do you conclude?

6.2 Use ionic radii to calculate expected bond lengths for:
Molecules \( \text{WF}_6 \), \( \text{WCl}_6 \), \( \text{PCl}_5 \), \( \text{PBr}_5 \), \( \text{SbF}_6 \), \( \text{MnO}_4^- \);
Solids (metal atom has c.n. 6) \( \text{TiO}_2 \), \( \text{ReO}_3 \), \( \text{EuO} \), \( \text{CdCl}_2 \).
7 Ionic Compounds

7.1 Radius Ratios

In an energetically favorable packing of cations and anions only anions are directly adjacent to a cation and vice versa. In this way, the attractive forces between ions of opposite charges outweigh the repulsive forces between ions of like charges. Packing many ions together into a crystal frees an amount of energy which is larger by the factor $A$ than in the formation of separate ion pairs (assuming equal interionic distances $R$). $A$ is the MADELUNG constant discussed in Section 5.2 (p. 43), which has a definite value for a given crystal structure type. One might now think that the structure type having the largest MADELUNG constant for a given chemical composition should always be favored. However, this is not the case.

The stability of a certain structure type depends essentially on the relative sizes of cations and anions. Even with a larger MADELUNG constant a structure type can be less stable than another structure type in which cations and anions can approach each other more closely; this is so because the lattice energy also depends on the interionic distances [cf. equation (5.4), p. 44]. The relative size of the ions is quantified by the *radius ratio* $r_M/r_X$, $r_M$ being the cation radius and $r_X$ the anion radius. In the following the ions are taken to be hard spheres having specific radii.

For compounds of the composition $MX$ ($M =$ cation, $X =$ anion) the CsCl type has the largest MADELUNG constant. In this structure type a $\text{Cs}^+$ ion is in contact with eight $\text{Cl}^-$ ions in a cubic arrangement (Fig. 7.1). The $\text{Cl}^-$ ions have no contact with one another. With cations smaller than $\text{Cs}^+$ the $\text{Cl}^-$ ions come closer together and when the radius ratio has the value of $r_M/r_X = 0.732$, the $\text{Cl}^-$ ions are in contact with each other. When $r_M/r_X < 0.732$, the $\text{Cl}^-$ ions remain in contact, but there is no more contact between anions and cations. Now another structure type is favored: its MADELUNG constant is indeed smaller, but it again allows contact of cations with anions. This is achieved by the smaller coordination number 6 of the ions that is fulfilled in the NaCl type (Fig. 7.1). When the radius ratio becomes even smaller, the zinc blende (sphalerite) or the wurtzite type should occur, in which the ions only have the coordination number 4 (Fig. 7.1; zinc blende and wurtzite are two modifications of ZnS).

The geometric considerations leading to the following values are outlined in Fig. 7.2:

<table>
<thead>
<tr>
<th>$r_M/r_X$</th>
<th>coordination number and polyhedron</th>
<th>structure type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&gt; 0.732$</td>
<td>8 cube</td>
<td>CsCl</td>
</tr>
<tr>
<td>0.414 to 0.732</td>
<td>6 octahedron</td>
<td>NaCl</td>
</tr>
<tr>
<td>$&lt; 0.414$</td>
<td>4 tetrahedron</td>
<td>zinc blende</td>
</tr>
</tbody>
</table>

The purely geometric approach we have considered so far is still too simple. The really determining factor is the lattice energy, the calculation of which is somewhat more...
Fig. 7.1
The three most important structure types for ionic compounds of composition MX. Compared to their effective sizes, the ions have been drawn to a smaller scale.

Fig. 7.2
Calculation of the limiting radius ratios $r_{M}/r_{X}$

- CsCl type
  - $r_{M} + r_{X} = r_{X}\sqrt{3}$
  - $r_{M}/r_{X} = \sqrt{3} - 1 = 0.732$

- NaCl type
  - $r_{M} + r_{X} = r_{X}\sqrt{2}$
  - $r_{M}/r_{X} = \sqrt{2} - 1 = 0.414$

- zinc blende type
  - $r_{M} + r_{X} = r_{X} \cdot \frac{1}{2}\sqrt{6}$
  - $r_{M}/r_{X} = \frac{1}{2}\sqrt{6} - 1 = 0.225$

complicated. If we only take into account the electrostatic part of the lattice energy, then the relevant magnitude in equation (5.4) is the ratio $A/R$ ($A = \text{MADELUNG constant}, R = \text{shortest cation–anion distance}$). Fig. 7.3 shows how the electrostatic part of the lattice energy depends on the radius ratio for chlorides. The transition from the NaCl type to the zinc blende type is to be expected at the crossing point of the curves at $r_{M}/r_{X} \approx 0.3$ instead of $r_{M}/r_{X} = 0.414$. The transition from the NaCl type to the CsCl type is to be expected at $r_{M}/r_{X} \approx 0.71$. The curves were calculated assuming hard Cl$^{-}$ ions with $r_{\text{Cl}^{-}} = 181$ pm. If, in addition, we take into account the increase of the ionic radius for an increased coordination number, then we obtain the dotted line in Fig. 7.3 for the CsCl type. As a consequence, the CsCl type should not occur at all, as the dotted line always runs below
The electrostatic part of the lattice energy for chlorides crystallizing in the CsCl, NaCl and zinc blende type as a function of the radius ratio.

The line for the NaCl type. However, the CsCl type does occur when heavy ions are involved; this is due to the dispersion energy, which has a larger contribution in the case of the CsCl type. Table 7.1 lists the structure types actually observed for the alkali metal halides.

Table 7.1: Radius ratios and observed structure types for the alkali metal halides

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.57</td>
<td>0.77</td>
<td>0.96</td>
<td>0.88</td>
<td>0.80</td>
</tr>
<tr>
<td>Cl</td>
<td>0.42</td>
<td>0.56</td>
<td>0.76</td>
<td>0.84</td>
<td>0.92</td>
</tr>
<tr>
<td>Br</td>
<td>0.39</td>
<td>0.52</td>
<td>0.70</td>
<td>0.78</td>
<td>0.85</td>
</tr>
<tr>
<td>I</td>
<td>0.35</td>
<td>0.46</td>
<td>0.63</td>
<td>0.69</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Twelve anions can be arranged around a cation when the radius ratio is 0.95 to 1.00. However, unlike the three structure types considered so far, geometrically the coordination number 12 does not allow for any arrangement which has cations surrounded only by anions and anions only by cations simultaneously. This kind of coordination therefore does not occur among ionic compounds. When \( r_M/r_X \) becomes larger than 1, as for RbF and CsF, the relations are reversed: in this case the cations are larger than the anions and the contacts among the cations determine the limiting radius ratios; the same numerical values and structure types apply, but the inverse radius ratios have to be taken, i.e. \( r_X/r_M \).

The zinc blende type is unknown for truly ionic compounds because there exists no pair of ions having the appropriate radius ratio. However, it is well known for compounds with considerable covalent bonding even when the zinc blende type is not to be expected according to the relative sizes of the atoms in the sense of the above-mentioned considerations. Examples are CuCl, AgI, ZnS, SiC, and GaAs. We focus in more detail on this structure type in Chapter 12.

In the structure types for compounds MX so far considered, both anions and cations have the same coordination numbers. In compounds MX₂ the coordination number of the cations must be twice that of the anions. The geometric considerations concerning
the relations of radius ratios and coordination polyhedra are the same. First of all, two structure types fulfill the conditions and are of special importance (Fig. 7.4):

<table>
<thead>
<tr>
<th>( r_M/r_X )</th>
<th>coordination number and polyhedron</th>
<th>structure type</th>
<th>examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 0.732</td>
<td>8 cube</td>
<td>fluorite</td>
<td>SrF(_2), BaF(_2), EuF(_2), SrCl(_2), BaCl(_2), ThO(_2)</td>
</tr>
<tr>
<td>0.414 to 0.732</td>
<td>6 octahedron</td>
<td>rutile</td>
<td>MgF(_2), FeF(_2), ZnF(_2), SiO(_2)^*, SnO(_2), RuO(_2)</td>
</tr>
<tr>
<td></td>
<td>3 triangle</td>
<td></td>
<td>stishovite</td>
</tr>
</tbody>
</table>

When the positions of cations and anions are interchanged, the same structure types result for the CsCl, NaCl and zinc blende type. In the case of the fluorite type the interchange also involves an interchange of the coordination numbers, i.e. the anions obtain coordination number 8 and the cations 4. This structure type sometimes is called ‘anti-fluorite’ type; it is known for the alkali metal oxides (Li\(_2\)O, ... , Rb\(_2\)O).

The structure types discussed so far have a favorable arrangement of cations and anions and are well suited for ionic compounds consisting of spherical ions. However, their occurrence is by no means restricted to ionic compounds. The majority of their representatives are found among compounds with considerable covalent bonding and among intermetallic compounds.

Several additional, more complicated structure types are known for ionic compounds. For example, according to the radius ratio, one could expect the rutile type for strontium iodide (\( r_{\text{Sr}^{2+}}/r_{\text{I}^-} = 0.54 \)). In fact, the structure consists of \( \text{Sr}^{2+} \) ions with a coordination number of 7 and anions having two different coordination numbers, 3 and 4.

### 7.2 Ternary Ionic Compounds

When three different kinds of spherical ions are present, their relative sizes are also an important factor that controls the stability of a structure. The PbFCl type is an example having anions packed with different densities according to their sizes. As shown in Fig. 7.5, the Cl\(^-\) ions form a layer with a square pattern. On top of that there is a layer of F\(^-\) ions, also with a square pattern, but rotated through 45°. The F\(^-\) ions are situated above the edges of the squares of the Cl\(^-\) layer (dotted line in Fig. 7.5). With this arrangement the F\(^-\)–F\(^-\) distances are smaller by a factor of 0.707 (= \( \frac{1}{\sqrt{2}} \)) than the Cl\(^-\)–Cl\(^-\) distances; this matches the ionic radius ratio of \( r_{\text{F}^-}/r_{\text{Cl}^-} = 0.73 \). An F\(^-\) layer contains twice as many ions as a Cl\(^-\) layer. Every Pb\(^{2+}\) ion is located in an antiprism having as vertices four F\(^-\) and four
How to view the stereo picture: the left picture is to be viewed with the right eye, and the right one with the left eye. It requires some practice to orient the eyes crosswise for this purpose. As an aid, one can hold a finger tip halfway between the figure and the eyes. Aim at the finger tip and move the finger towards the paper or away from it until the images in the center merge to one image. Then focus the image without turning the eyes.

Cl⁻ ions that form two square faces of different sizes. Pb²⁺ ions are located under one half of the squares of the F⁻ ions; an equal number of Pb²⁺ ions are situated above the other half of the squares, which in turn form the base faces of further antiprisms that are completed by another layer of Cl⁻ ions. In this way, the total number of Pb²⁺ ions is the same as the number of F⁻ ions; the number of Cl⁻ ions also is the same because there are two Cl⁻ layers for every F⁻ layer. Together, these layers form a slab that is limited by Cl⁻ ions on either side. In the crystal these slabs are stacked with staggered adjacent Cl⁻ layers. As a consequence, the coordination sphere of each Pb²⁺ ion is completed by a fifth Cl⁻ ion (dashed in Fig. 7.5).

Numerous compounds adopt the PbFCl structure. These include, apart from fluoride chlorides, oxide halides MOX (M = Bi, lanthanoids, actinoids; X = Cl, Br, I), hydride halides like CaHCl and many compounds with metallic properties like ZrSiS or NbSiAs.

Further ternary compounds for which the relative sizes of the ions are an important factor for their stability are the perovskites and the spinels, which are discussed in Sections 17.4 and 17.6.

7.3 Compounds with Complex Ions

The structures of ionic compounds comprising complex ions can in many cases be derived from the structures of simple ionic compounds. A spherical ion is substituted by the complex ion and the crystal lattice is distorted in a manner adequate to account for the shape of this ion.

Rod-like ions like CN⁻, C₅⁻ or N₅⁻ can substitute the Cl⁻ ions in the NaCl type when all of them are oriented parallel and the lattice is stretched in the corresponding direction. In CaC₂ the acetylide ions are oriented parallel to one of the edges of the unit cell; as a consequence, the symmetry is no longer cubic, but tetragonal (Fig. 7.6). The hyperoxides KO₂, RbO₂ and CsO₂ as well as peroxides like BaO₂ crystallize in the CaC₂ type. In CsCN and NaN₃ the cyanide and azide ions, respectively, are oriented along one of the space diagonals of the unit cell, and the symmetry is rhombohedral (Fig. 7.6).

The structure of calcite (CaCO₃) can be derived from the NaCl structure by substituting the Cl⁻ ions for CO₃²⁻ ions. These are oriented perpendicular to one of the space diago-
Fig. 7.6
The structures of CaC$_2$ and NaN$_3$ (stereo views).
Heavy outlines: body-centered tetragonal unit cell of CaC$_2$. Dashed line at NaN$_3$: direction of the elongation of the NaCl cell.

Fig. 7.7
The structures of CaCO$_3$ (calcite) and K$_2$PtCl$_6$. The section of the calcite structure shown does not correspond to the unit cell (as can be seen from the orientations of the CO$_3^{2-}$ groups on opposite edges).

By substituting the Ca$^{2+}$ ions in the CaF$_2$ type for PtCl$_6^{2-}$ ions and the F$^{-}$ ion for K$^+$ ions, one obtains the K$_2$PtCl$_6$ type (Fig. 7.7). It occurs among numerous hexahalo salts. In this structure type each of a group of four PtCl$_6^{2-}$ ions has one octahedron face in contact with one K$^+$ ion, which therefore has coordination number 12. How this structure can be regarded as derived from the perovskite type with a close packing of Cl and K particles is discussed on p. 204.
7.4 The Rules of Pauling and Baur

Important structural principles for ionic crystals, which had already been recognized in part by V. Goldschmidt, were summarized by L. Pauling in the following rules.

First rule: Coordination polyhedra
A coordination polyhedron of anions is formed around every cation. The cation–anion distances are determined by the sum of the ionic radii, and the coordination number of the cation by the radius ratio.

Second rule: The electrostatic valence rule
In a stable ionic structure the valence (ionic charge) of each anion with changed sign is exactly or nearly equal to the sum of the electrostatic bond strengths to it from adjacent cations. The electrostatic bond strength is defined as the ratio of the charge on a cation to its coordination number.

Let \( a \) be the coordination number of an anion. Of the set of its \( a \) adjacent cations, let \( n_i \) be the charge on the \( i \)-th cation and \( k_i \) its coordination number. The electrostatic bond strength of this cation is:

\[
s_i = \frac{n_i}{k_i} \tag{7.1}\]

The charge \( z_j \) of the \( j \)-th anion is:

\[
z_j \approx -p_j = -\sum_{i=1}^{a} s_i = -\sum_{i=1}^{a} \frac{n_i}{k_i} \tag{7.2}\]

The rule states that the electrostatic charges in an ionic crystal are balanced locally around every ion as evenly as possible.

Example 7.1
Let the cation \( \text{M}^{2+} \) in a compound \( \text{MX}_2 \) have coordination number 6. Its electrostatic bond strength is \( s = 2/6 = \frac{1}{3} \). The correct charge for the anion, \( z = -1 \), can only be obtained when the anion has the coordination number \( a = 3 \).

Example 7.2
Let the cation \( \text{M}^{4+} \) in a compound \( \text{MX}_4 \) also have coordination number 6; its electrostatic bond strength is \( s = 4/6 = \frac{2}{3} \). For an anion \( \text{X}^- \) having coordination number \( a = 2 \) we obtain \( \sum s_i = \frac{2}{3} + \frac{2}{3} = \frac{4}{3} \); for an anion with \( a = 1 \) the sum is \( \sum s_i = \frac{2}{3} \). For other values of \( a \) the resulting \( p_j \) deviate even more from the expected value \( z = -1 \). The most favorable structure will have anions with \( a = 2 \) and with \( a = 1 \), and these in a ratio of 1:1, so that the correct value for \( z \) results in the mean.

The electrostatic valence rule usually is met rather well by polar compounds, even when considerable covalent bonding is present. For instance, in calcite (\( \text{CaCO}_3 \)) the \( \text{Ca}^{2+} \) ion has coordination number 6 and thus an electrostatic bond strength of \( s(\text{Ca}^{2+}) = \frac{1}{3} \). For the C atom, taken as \( \text{C}^{2+} \) ion, it is \( s(\text{C}^{2+}) = \frac{4}{3} \). We obtain the correct value of \( z \) for the oxygen atoms, considering them as \( \text{O}^{2-} \) ions, if every one of them is surrounded by one C and two Ca particles, \( z = -[2s(\text{Ca}^{2+}) + s(\text{C}^{2+})] = -[2 \cdot \frac{1}{3} + \frac{4}{3}] = -2 \). This corresponds to the actual structure. \( \text{NaNO}_3 \) and \( \text{YBO}_3 \) have the same structure; in these cases the rule also is fulfilled when the ions are taken to be \( \text{Na}^+, \text{N}^{5+}, \text{Y}^{3+}, \text{B}^{3+} \) and \( \text{O}^{2-} \). For the numerous silicates no or only marginal deviations result when the calculation is performed with metal ions, \( \text{Si}^{4+} \) and \( \text{O}^{2-} \) ions.
The electrostatic valence rule has turned out to be a valuable tool for the distinction of the particles $O_2^-$, $OH^-$ and $OH_2$. Because H atoms often cannot be localized reliably by X-ray diffraction, which is the most common method for structure determination, $O_2^-$, $OH^-$ and $OH_2$ cannot be distinguished unequivocally at first. However, their charges must harmonize with the sums $p_j$ of the electrostatic bond strengths of the adjacent cations.

### Example 7.3

Kaolinite, $Al_2Si_2O_5(OH)_4$ or “$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$”, is a sheet silicate with Al atoms in octahedral and Si atoms in tetrahedral coordination; the corresponding electrostatic bond strengths are:

- $s(Al^{3+}) = \frac{3}{6} = 0.5$
- $s(Si^{4+}) = \frac{4}{4} = 1.0$

The atoms in a sheet are situated in planes with the sequence $O(1)$–Al–$O(2)$–Si–$O(3)$ (cf. Fig. 16.21e, p. 183). The particles $O(2)$, which are shared by octahedra and tetrahedra, have c.n. 3 ($2 \times Al, 1 \times Si$), the other $O$ particles have c.n. 2. We calculate the following sums of electrostatic bond strengths:

- $O(1): \quad p_1 = 2 \cdot s(Al^{3+}) = 2 \cdot 0.5 = 1$
- $O(2): \quad p_2 = 2 \cdot s(Al^{3+}) + 1 \cdot s(Si^{4+}) = 2 \cdot 0.5 + 1 = 2$
- $O(3): \quad p_3 = 2 \cdot s(Si^{4+}) = 2 \cdot 1 = 2$

Therefore, the OH$^-$ ions must take the $O(1)$ positions and the $O_2^-$ ions the remaining positions.

### Third rule: Linking of polyhedra

An ionic crystal can be described as a set of linked polyhedra. The electrostatic valence rule allows the deduction of the number of polyhedra that share a common vertex, but not how many vertices are common to two adjacent polyhedra. Two shared vertices are equivalent to one shared edge, three or more common vertices are equivalent to a shared face. In the four modifications of $TiO_2$, rutile, high-pressure $TiO_2$ ($\alpha$-PbO$_2$ type), brookite, and anatase, the Ti atoms have octahedral coordination. As required by the electrostatic valence rule, every O atom is shared by three octahedra. In rutile and high-pressure $TiO_2$, every octahedron has two common edges with other octahedra, in brookite there are three and in anatase four shared edges per octahedron. The third rule states in what way the kind of polyhedron linkage affects the stability of the structure:

*The presence of shared edges and especially of shared faces in a structure decreases its stability; this effect is large for cations with high charge and low coordination number.*

The stability decrease is due to the electrostatic repulsion between the cations. The centers of two polyhedra are closest to each other in the case of a shared face and they are relatively distant when only one vertex is shared (cf. Fig. 2.3, p. 6, and Table 16.1, p. 167). According to this rule, rutile and, at high pressures, the modification with the $\alpha$-PbO$_2$ type, brookite, and anatase, are the most stable forms of $TiO_2$. Numerous compounds crystallize in the rutile type and some in the $\alpha$-PbO$_2$ type, whereas scarcely any examples are known for the brookite and the anatase structures.

Exceptions to the rule are observed for compounds with low polarity, *i.e.* when covalent bonds predominate. Fluorides and oxides (including silicates) usually fulfill the rule, whereas it is inapplicable to chlorides, bromides, iodides, and sulfides. For instance, in metal trifluorides like $FeF_3$ octahedra sharing vertices are present, while in most other trihalides octahedra usually share edges or even faces.
In some cases a tendency exactly opposite to the rule is observed, i.e. decreasing stability in the sequence face-sharing > edge-sharing > vertex-sharing. This applies when it is favorable to allow the atoms in the centers of the polyhedra to come close to one another. This is observed when the metal atoms in transition metal compounds have d electrons and tend to form metal–metal bonds. For example, TiBr₃, TiI₃, ZrBr₃ and ZrI₃ form columns consisting of octahedra sharing opposite faces, with metal atoms forming M–M bonds in pairs between adjacent octahedra (cf. Fig. 16.10, p. 175).

Fourth rule: Linking of polyhedra having different cations

In a crystal containing different cations, those with large charge and small coordination number tend not to share polyhedron elements with each other, i.e. they tend to keep as far apart as possible.

Silicates having an O : Si ratio larger than or equal to 4 are orthosilicates, i.e. the SiO₄ tetrahedra do not share atoms with each other, but with the polyhedra about the other cations. Examples: olivines, M₂SiO₄ (M = Mg²⁺, Fe²⁺) and garnets, M₃M₂[SiO₄]₃ (M = Mg²⁺, Ca²⁺, Fe²⁺; M⁺ = Al³⁺, Y³⁺, Cr³⁺, Fe³⁺).

The extended electrostatic valence rules

Two additional rules, put forward by W. H. Baur, deal with the bond lengths d(MX) in ionic compounds:

The distances d(MX) within the coordination polyhedron of a cation M vary in the same manner as the values p_j corresponding to the anions X [cf. equation (7.2)], and

For a given pair of ions the average value of the distances d(MX) within a coordination polyhedron, d(MX), is approximately constant and independent of the sum of the p_j values received by all the anions in the polyhedron. The deviation of an individual bond length from the average value is proportional to \( \Delta p_j = p_j - \bar{p} \) (\( \bar{p} \) = mean value of the \( p_j \) for the polyhedron). Therefore, the bond lengths can be predicted from the equation:

\[
d(MX(j)) = d(MX) + b\Delta p_j
\]

(7.3)

\( d(MX) \) and \( b \) are empirically derived values for given pairs of M and X in a given coordination.

Example 7.4

In baddeleyite, a modification of ZrO₂, Zr⁴⁺ has coordination number 7 in the sense of the formula ZrO₃/₃O₄/₄; i.e. there are two kinds of O²⁻ ions, O(1) with c.n. 3 and O(2) with c.n. 4. The electrostatic valence strength of a Zr⁴⁺ ion is:

\[ s = \frac{4}{7} \]

For O(1) and O(2) we calculate:

\[
O(1): \quad p_1 = 3 \cdot \frac{4}{7} = 1.714 \quad O(2): \quad p_2 = 4 \cdot \frac{4}{7} = 2.286
\]

We expect shorter distances for O(1); the observed mean distances are:

\[
d(Zr–O(1)) = 209 \text{ pm} \quad \text{and} \quad d(Zr–O(2)) = 221 \text{ pm}
\]

The average values are:

\[
d(ZrO) = \frac{1}{7}(3 \cdot 209 + 4 \cdot 221) = 216 \text{ pm} \quad \text{and} \quad \bar{p} = \frac{1}{7}(3 \cdot 1.714 + 4 \cdot 2.286) = 2.041
\]

With \( b = 20.4 \text{ pm} \) the actual distances can be calculated according to equation (7.3).
Table 7.2 lists values for $d(MX)$ and $b$ that have been derived from extensive data. They can be used to calculate the bond lengths in oxides, usually with deviations of less than $\pm 2$ pm from the actual values.

**Table 7.2:** Some average values $d(MO)$ and parameters $b$ for the calculation of bond lengths in oxides according to equation (7.3) [74]

<table>
<thead>
<tr>
<th>bond state</th>
<th>c.n.</th>
<th>$d(MO)$ / pm</th>
<th>$b$ / pm</th>
<th>bond state</th>
<th>c.n.</th>
<th>$d(MO)$ / pm</th>
<th>$b$ / pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li–O</td>
<td>+1</td>
<td>4</td>
<td>198</td>
<td>Si–O</td>
<td>+4</td>
<td>4</td>
<td>162</td>
</tr>
<tr>
<td>Na–O</td>
<td>+1</td>
<td>6</td>
<td>244</td>
<td>P–O</td>
<td>+5</td>
<td>4</td>
<td>154</td>
</tr>
<tr>
<td>Na–O</td>
<td>+1</td>
<td>8</td>
<td>251</td>
<td>S–O</td>
<td>+6</td>
<td>4</td>
<td>147</td>
</tr>
<tr>
<td>K–O</td>
<td>+1</td>
<td>8</td>
<td>285</td>
<td>Ti–O</td>
<td>+4</td>
<td>6</td>
<td>197</td>
</tr>
<tr>
<td>Mg–O</td>
<td>+2</td>
<td>6</td>
<td>209</td>
<td>Ti–O</td>
<td>+4</td>
<td>6</td>
<td>197</td>
</tr>
<tr>
<td>Ca–O</td>
<td>+2</td>
<td>8</td>
<td>250</td>
<td>V–O</td>
<td>+5</td>
<td>4</td>
<td>172</td>
</tr>
<tr>
<td>B–O</td>
<td>+3</td>
<td>3</td>
<td>137</td>
<td>Cr–O</td>
<td>+3</td>
<td>6</td>
<td>200</td>
</tr>
<tr>
<td>B–O</td>
<td>+3</td>
<td>4</td>
<td>148</td>
<td>Fe–O</td>
<td>+2</td>
<td>6</td>
<td>214</td>
</tr>
<tr>
<td>Al–O</td>
<td>+3</td>
<td>4</td>
<td>175</td>
<td>Fe–O</td>
<td>+3</td>
<td>6</td>
<td>201</td>
</tr>
<tr>
<td>Al–O</td>
<td>+3</td>
<td>6</td>
<td>191</td>
<td>Zn–O</td>
<td>+2</td>
<td>4</td>
<td>196</td>
</tr>
</tbody>
</table>

### 7.5 Problems

7.1 Use ionic radius ratios (Tables 6.3 and 6.4) to decide whether the CaF$_2$ or the rutile type is more likely to be adopted by: NiF$_2$, CdF$_2$, GeO$_2$, K$_2$S.

7.2 In garnet, Mg$_3$Al$_2$Si$_3$O$_{12}$, an O$^{2-}$ ion is surrounded by 2 Mg$^{2+}$, 1 Al$^{3+}$ and 1 Si$^{4+}$ particle. There are cation sites having coordination numbers of 4, 6 and 8. Use Pauling’s second rule to decide which cations go in which sites.

7.3 YIG (yttrium iron garnet), Y$_3$Fe$_5$O$_{12}$, has the same structure as garnet. Which are the appropriate sites for the Y$^{3+}$ and Fe$^{3+}$ ions? If the electrostatic valence rule is insufficient for you to come to a decision, take ionic radii as an additional criterion.

7.4 In crednerite, Cu$^{2+}$Mn$^{6+}$O$_2$, every oxygen atom is surrounded by 1 Cu and 3 Mn. Can the electrostatic valence rule help to decide whether the oxidation states are Cu$^{+}$ and Mn$^{3+}$, or Cu$^{2+}$ and Mn$^{3+}$?

7.5 Silver cyanate, AgNCO, consists of infinite chains of alternating Ag$^+$ and NCO$^-$ ions. Ag$^+$ has c.n. 2 and only one of the terminal atoms of the cyanate group is part of the chain skeleton, being coordinated to 2 Ag$^+$. Decide with the aid of Pauling’s second rule which of the cyanate atoms (N or O) is the coordinated one. (Decompose the NCO$^-$ to N$^{3-}$, C$^4+$ and O$^{2-}$).

7.6 In Rb$_2$V$_3$O$_8$ the Rb$^+$ ions have coordination number 10; there are two kinds of vanadium ions, V$^{4+}$ with c.n. 5 and V$^{5+}$ with c.n. 4, and four kinds of O$^{2-}$ ions. The mutual coordination of these particles is given in the table, the first value referring to the number of O$^{2-}$ ions per cation, the second to the number of cations per O$^{2-}$ ion (the sums of the first numbers per row and of the second numbers per column correspond to the c.n.s).

<table>
<thead>
<tr>
<th>O(1)</th>
<th>O(2)</th>
<th>O(3)</th>
<th>O(4)</th>
<th>c.n.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb$^+$</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>V$^{4+}$</td>
<td>1</td>
<td>1</td>
<td>4;1</td>
<td>–</td>
</tr>
<tr>
<td>V$^{5+}$</td>
<td>–</td>
<td>2;1</td>
<td>1;2</td>
<td>1;1</td>
</tr>
</tbody>
</table>

Calculate the electrostatic bond strengths of the cations and determine how well the electrostatic valence rule is fulfilled. Calculate the expected individual V–O bond lengths using data from Table 7.2 and the values $d(V^{4+}O) = 189$ pm and $b(V^{4+}O) = 36$ pm.
8 Molecular Structures I: Compounds of Main Group Elements

Molecules and molecular ions consist of atoms that are connected by covalent bonds. With few exceptions, molecules and molecular ions only exist when hydrogen or elements of the fourth to seventh main groups of the periodic table are involved (the exceptions are molecules such as Li₂ in the gas phase). These elements tend to attain the electron configuration of the noble gas that follows them in the periodic table. For every covalent bond in which one of their atoms participates, it gains one electron. The \(8-N\) rule holds: an electron configuration corresponding to a noble gas is attained when the atom takes part in \(8-N\) covalent bonds; \(N = \) main group number = 4 to 7 (except for hydrogen).

Usually a molecule consists of atoms with different electronegativities, and the more electronegative atoms have smaller coordination numbers (we only count covalently bonded atoms as belonging to the coordination sphere of an atom). The more electronegative atoms normally fulfill the \(8-N\) rule; in many cases they are 'terminal atoms', i.e. they have coordination number 1. Elements of the second period of the periodic table almost never surpass the coordination number 4 in molecules. However, for elements of higher periods this is quite common, the \(8-N\) rule being violated in this case.

The structure of a molecule depends essentially on the covalent bond forces acting between its atoms. In the first place, they determine the constitution of the molecule, that is, the sequence of the linkage of the atoms. The constitution can be expressed in a simple way by means of the valence bond formula. For a given constitution the atoms arrange themselves in space according to certain principles. These include: atoms not bonded directly with one another may not come too close (repulsion of interpenetrating electron shells); and the valence electron pairs of an atom keep as far apart as possible from each other.

8.1 Valence Shell Electron-Pair Repulsion

The structures of numerous molecules can be understood and predicted with the valence shell electron-pair repulsion theory (VSEPR theory) of Gillespie and Nyholm. In the first place, it is applicable to compounds of main group elements. The special aspects concerning transition group elements are dealt with in Chapter 9. However, transition group elements having the electron configurations \(d^0\), high-spin \(d^5\), and \(d^{10}\) generally can be treated in the same way as main group elements; the \(d\) electrons need not be taken into account in these cases.

In order to apply the theory, one first draws a valence bond formula with the correct constitution, including all lone electron pairs. This formula shows how many valence electron pairs are to be considered at an atom. Every electron pair is taken as one unit (orbital). The electron pairs are being attracted by the corresponding atomic nucleus, but they exercise a mutual repulsion. A function proportional to \(1/r^n\) can be used to approximate the
repulsion energy between two electron pairs; \( r \) is the distance between the centers of gravity of their charges, and \( n \) has some value between 5 and 12. \( n = 1 \) would correspond to a purely electrostatic repulsion. In fact, the contribution of the Pauli repulsion between electrons having the same spin is more important (cf. p. 45), and with \( n = 6 \) one obtains good agreement with experimental data.

The next step is to consider how the electron pairs have to be arranged to achieve a minimum energy for their mutual repulsion. If the centers of the charge of all orbitals are equidistant from the atomic nucleus, every orbital can be represented by a point on the surface of a sphere. The problem thus amounts to deducing what distribution of the points on the sphere corresponds to a minimum for the sum \( \sum (1/r_i^n) \), covering all distances \( r_i \) between the points. As a result, we obtain a definite polyhedron for every number of points (Fig. 8.1). The resulting polyhedron is independent of the value of the exponent \( n \) only for 2, 3, 4, 6, 8, 9, and 12 points. For five points the trigonal bipyramid is only slightly more favorable than the square pyramid. A model to visualize the mutual arrangement of the orbitals about a common center consists of tightly joined balloons; the pressure in the balloons simulates the value of \( n \).

\[
\begin{align*}
2 & \quad \text{linear arrangement} \\
3 & \quad \text{triangle} \\
4 & \quad \text{tetrahedron} \\
5 & \quad \text{trigonal bipyramid} \\
6 & \quad \text{square pyramid} \\
8 & \quad \text{square antiprism} \\
9 & \quad \text{triplly capped trigonal prism} \\
12 & \quad \text{icosahedron}
\end{align*}
\]
Molecules having no lone electron pairs at the central atom and having only equal atoms bonded to this atom usually have structures that correspond to the polyhedra shown in Fig. 8.1.

Some polyhedra have vertices that are not equivalent in the first place. In any case, non-equivalent points always result when the corresponding orbitals belong to bonds with atoms of different elements or when some of the points represent lone electron pairs. In these cases the charge centers of the orbitals have different distances from the atomic center. A charge center that is closer to the atomic nucleus also has shorter distances to the remaining orbitals and thus exerts stronger repulsions on them. In the balloon model an electron pair close to the atomic nucleus corresponds to a larger balloon. This has important consequences for the molecular structure. The following aspects have to be taken into account:

1. A lone electron pair is under the direct influence of only one atomic nucleus, and its charge center therefore is located significantly closer to the nucleus than the centers of bonding electron pairs. Lone electron pairs are especially effective sterically in the following manner:

- If the polyhedron has non-equivalent vertices, a lone electron pair will take the position that is most distant from the remaining electron pairs. At a trigonal bipyramid these are the equatorial positions. In SF$_4$ and in ClF$_3$ the lone electron pairs thus take equatorial positions, and fluorine atoms take the two axial positions (cf. Table 8.1).
- Two equivalent lone electron pairs take those positions which are farthest apart. In an octahedron two lone electron pairs thus have the $trans$ configuration, as for example in XeF$_4$.
- Due to their stronger repulsion lone electron pairs press other electron pairs closer together. The more lone electron pairs are present, the more this effect is noticeable, and the more the real molecular shape deviates from the ideal polyhedron. For larger central atoms the charge centers of bonding electron pairs are more distant from each other, their mutual repulsion is reduced and the lone electron pairs can press them together to a larger extent. The following bond angles exemplify this:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond Angle</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>109.5°</td>
<td>&gt; 109.5°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>107.3°</td>
<td>&gt; 107.3°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH$_2$</td>
<td>104.5°</td>
<td>&gt; 104.5°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH$_4$</td>
<td>109.5°</td>
<td>&gt; 109.5°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PH$_3$</td>
<td>93.5°</td>
<td>&gt; 93.5°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SH$_3$</td>
<td>92.3°</td>
<td>&gt; 92.3°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeH$_4$</td>
<td>109.5°</td>
<td>&gt; 109.5°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsH$_3$</td>
<td>92.0°</td>
<td>&gt; 92.0°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SeH$_2$</td>
<td>91.0°</td>
<td>&gt; 91.0°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnH$_4$</td>
<td>109.5°</td>
<td>&gt; 109.5°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SbH$_3$</td>
<td>91.5°</td>
<td>&gt; 91.5°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TeH$_2$</td>
<td>89.5°</td>
<td>&gt; 89.5°</td>
</tr>
</tbody>
</table>

If only an unpaired electron is present instead of an electron pair, its influence is reduced, for example:

\[ \text{O=N=O}^+ \]

180°

\[ \text{N}^{\text{III}} \]

134°

\[ \text{O}^- \]

115°
Table 8.1: Molecular structures of compounds $AX_nE_m$. $A =$ main group element, $E =$ lone electron pair

<table>
<thead>
<tr>
<th>composition</th>
<th>structure</th>
<th>angle XAX</th>
<th>examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$AX_2E$</td>
<td><img src="image1" alt="Structure" /></td>
<td>$&lt; 120^\circ$</td>
<td>$\text{SnCl}_2(\text{g}), \text{GeBr}_2(\text{g})$</td>
</tr>
<tr>
<td>$AX_3E_2$</td>
<td><img src="image2" alt="Structure" /></td>
<td>$&lt; 109,5^\circ$</td>
<td>$\text{H}_2\text{O}, \text{F}_2\text{O}, \text{Cl}_2\text{O}, \text{H}_2\text{S}, \text{H}_2\text{N}^-$</td>
</tr>
<tr>
<td>$AX_2E_3$</td>
<td><img src="image3" alt="Structure" /></td>
<td>$180^\circ$</td>
<td>$\text{XeF}_2, \text{I}_3^-$</td>
</tr>
<tr>
<td>$AX_3E$</td>
<td><img src="image4" alt="Structure" /></td>
<td>$&lt; 109,5^\circ$</td>
<td>$\text{NH}_3, \text{NF}_3, \text{PH}_3, \text{PCl}_3, \text{OH}_3^+, \text{SCl}_3^-, \text{SnCl}_3^-$</td>
</tr>
<tr>
<td>$AX_3E_2$</td>
<td><img src="image5" alt="Structure" /></td>
<td>$&lt; 90^\circ$</td>
<td>$\text{ClF}_3$</td>
</tr>
<tr>
<td>$AX_4E$</td>
<td><img src="image6" alt="Structure" /></td>
<td>$&lt; 90^\circ$ and $&lt; 120^\circ$</td>
<td>$\text{SF}_4$</td>
</tr>
<tr>
<td>$AX_4E_2$</td>
<td><img src="image7" alt="Structure" /></td>
<td>$90^\circ$</td>
<td>$\text{XeF}_4, \text{BrF}_4, \text{ICl}_4^-$</td>
</tr>
<tr>
<td>$AX_5E$</td>
<td><img src="image8" alt="Structure" /></td>
<td>$&lt; 90^\circ$</td>
<td>$\text{SbCl}_5^-, \text{SF}_5^-, \text{BrF}_5$</td>
</tr>
<tr>
<td>$AX_5E_2$</td>
<td><img src="image9" alt="Structure" /></td>
<td>$72^\circ$</td>
<td>$\text{XeF}_5^-$</td>
</tr>
</tbody>
</table>

By definition, the coordination number includes the adjacent atoms, and lone electron pairs are not counted. On the other hand, now we are considering lone pairs as occupying polyhedron vertices. To take account of this, we regard the coordination sphere as including the lone pairs, but we designate them with a $\psi$, for example: $\psi_2$-octahedral = octahedron with two lone electron pairs and four ligands.
2. Decreasing electronegativity of the ligand atoms causes the charge centers of bonding electron pairs to shift toward the central atom; their repulsive activity increases. Ligands having low electronegativity therefore have a similar influence, albeit less effective, as lone electron pairs. Correspondingly the bond angles in the following pairs increase:

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{F}_2\text{O}$</td>
<td>103.2°</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>104.5°</td>
</tr>
<tr>
<td>$\text{NF}_3$</td>
<td>102.1°</td>
</tr>
<tr>
<td>$\text{NH}_3$</td>
<td>107.3°</td>
</tr>
</tbody>
</table>

However, bond angles cannot be understood satisfactorily by considering only the electron-pair repulsion because they also depend on another factor:

3. **The effective size of the ligands.** In most cases (unless the central atom is very large) the ligands come closer to each other than the corresponding van der Waals distance; the electron shells of the ligand atoms interpenetrate one another and additional repulsive forces become active. This is especially valid for large ligand atoms. Within a group of the periodic table decreasing electronegativities and increasing atom sizes go hand in hand, so that they act in the same sense. The increase of the following bond angles is due to both effects:

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{HCl}_3$</td>
<td>110.8°</td>
</tr>
<tr>
<td>$\text{HCCl}_3$</td>
<td>110.4°</td>
</tr>
<tr>
<td>$\text{HCBr}_3$</td>
<td>110.8°</td>
</tr>
<tr>
<td>$\text{HCl}_3$</td>
<td>113.0°</td>
</tr>
<tr>
<td>$\text{PF}_3$</td>
<td>97.8°</td>
</tr>
<tr>
<td>$\text{PCl}_3$</td>
<td>100.1°</td>
</tr>
<tr>
<td>$\text{PBr}_3$</td>
<td>101.0°</td>
</tr>
<tr>
<td>$\text{PI}_3$</td>
<td>102°</td>
</tr>
</tbody>
</table>

When the electronegativity and the size of the ligand atoms have opposing influence, no safe predictions can be made:

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{F}_2\text{O}$</td>
<td>103.2°</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>104.5°</td>
</tr>
</tbody>
</table>

Sometimes the opposing influence of the two effects is just balanced. For example, the steric influence of chlorine atoms and methyl groups is often the same (the carbon atom of a methyl group is smaller, but it is less electronegative than a chlorine atom):  

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cl}_2\text{O}$</td>
<td>110.8°</td>
</tr>
<tr>
<td>$\text{Me}_2\text{O}$</td>
<td>111°</td>
</tr>
<tr>
<td>$\text{PCl}_3$</td>
<td>100.1°</td>
</tr>
<tr>
<td>$\text{PMe}_3$</td>
<td>99.1°</td>
</tr>
</tbody>
</table>

4. A **pre-existing distortion** is found when certain bond angles deviate from the ideal values of the corresponding polyhedron for geometric reasons. In this case the remaining angles adapt themselves. Forced angle deviations result mainly in small rings. For example:

The bridging chlorine atoms (2 lone electron pairs) should have bond angles smaller than 109.5° but larger than 90°. The angle at the metal atom in the four-membered ring is forced to a value under 90°; it adopts 78.6°. The outer, equatorial Cl atoms now experience a reduced repulsion, so that the angle between them is enlarged from 90° to 101.2°. Due
to this distortion the axial Cl atoms should be inclined slightly outwards; however, as the Nb–Cl bonds in the ring are longer and their charge centers therefore are situated farther away from the centers of the niobium atoms, they are less repulsive, and the axial Cl atoms are inclined inwards. The increased Nb–Cl distances in the ring are a consequence of the higher coordination number (2 instead of 1) at the bridging Cl atoms (cf. point 6).

5. **Multiple bonds** can be treated as ring structures with bent bonds. The distortions dealt with in the preceding paragraph must be taken into account. For example, in ethylene every C atom is surrounded tetrahedrally by four electron pairs; two pairs mediate the double bond between the C atoms via two bent bonds. The tension in the bent bonds reduces the angle between them and decreases their repulsion toward the C–H bonds, and the HCH bond angle is therefore bigger than $109.5^\circ$.

![Diagram of ethylene molecule](image)

Usually, it is more straightforward to treat double and triple bonds as if they form a single orbital that is occupied by four and six electrons, respectively. The increased repulsive power of this orbital corresponds to its high charge. In this way, the structure of the ethylene molecule can be considered as having triangularly coordinated C atoms, but with angles deviating from $120^\circ$; the two angles between the double bond and the C–H bonds will be larger than $120^\circ$, and the H–C–H will be smaller than $120^\circ$.

Molecules like OPCl$_3$ and O$_2$SCL$_2$ used to be (and often continue to be) formulated with double bonds, in violation of the octet rule at the P or S atom. This would require the participation of $d$ orbitals of these atoms; however, this is not the case according to more recent quantum mechanical calculations. The formulae with formal charges seem to be closer to the true conditions, and if the more electronegative atom obtains a negative formal charge, this qualitatively corresponds to the actual charge distribution.

![Diagram of OPCl$_3$ and O$_2$SCL$_2$](image)

To estimate the bond angles it does not matter which kind of formula one uses. A double bond as well as an excess negative charge act repulsively on the other bonds. In any case, one expects a tetrahedral OPCl$_3$ molecule, but with widened OPCl angles. In O$_2$SCL$_2$ the OSO angle will be the largest. In Table 8.2 some examples are listed; they also show the influence of electronegativity and atomic size.

6. **Bond lengths** are affected like bond angles. The more electron pairs are present, the more they repel each other and the longer the bonds become. The increase in bond length with increasing coordination number is also mentioned in the discussion of ionic radii (p. 49). For example:

\[
\text{distance Sn–Cl: } \quad \text{SnCl}_4 \quad 228 \text{ pm } \quad \text{Cl}_4\text{Sn(OPCl}_3\text{)}_2 \quad 233 \text{ pm}
\]

The polarity of bonds indeed has a much more marked influence on their lengths. With increasing negative charge of a particle the repulsive forces gain importance. Examples:

\[
\text{distance Sn–Cl: } \quad \text{Cl}_4\text{Sn(OPCl}_3\text{)}_2 \quad 233 \text{ pm } \quad \text{SnCl}_6^{2-} \quad 244 \text{ pm}
\]
Table 8.2: Bond angles in degrees for some molecules having multiple bonds. X = singly, Z = double bonded ligand atom

<table>
<thead>
<tr>
<th></th>
<th>Z</th>
<th>Z</th>
<th>Z</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>(planar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
<td></td>
<td>A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>XAX</td>
<td>XAX</td>
<td>XAX ZAZ</td>
<td>XAX XAZ</td>
<td></td>
</tr>
<tr>
<td>F₂C=O</td>
<td>107.7</td>
<td>F₃P=O</td>
<td>101.3</td>
<td>F₅SO₂</td>
</tr>
<tr>
<td>Cl₂C=O</td>
<td>111.3</td>
<td>Cl₃P=O</td>
<td>103.3</td>
<td>Cl₂SO₂</td>
</tr>
<tr>
<td>Br₂C=O</td>
<td>112.3</td>
<td>Br₃P=O</td>
<td>105.4</td>
<td></td>
</tr>
<tr>
<td>Me₂C=O</td>
<td>112.4</td>
<td>Me₃P=O</td>
<td>104.1</td>
<td>Me₂SO₂</td>
</tr>
</tbody>
</table>

The bond between two atoms of different electronegativities is polar. The opposite partial charges of the atoms cause them to attract each other. A change in polarity affects the bond length. This can be noted especially when the more electronegative atom participates in more bonds than it should have according to the $8-N$ rule: contrary to its electronegativity it must supply electrons for the bonds, its negative partial charge is lowered or even becomes positive, and the attraction to the partner atom is decreased. This effect is conspicuous for bridging halogen atoms, as can be seen by comparison with the non-bridging atoms:

Niobium pentachloride mentioned on page 66 is another example. The BAUR rules also express these facts (cf. p. 60).

7. Influence of a partial valence shell. Atoms of elements of the third period, such as Si, P, and S, and of higher periods can accommodate more than four valence electron pairs in their valence shell (hypervalent atoms). In fact, most main group elements only tolerate a maximum of six electron pairs (for example the S atom in SF₆). Compounds having more than six valence electron pairs per atom are known only for the heavy elements, the iodine atom in IF₇ being an example. Obviously an increased repulsion between the electron pairs comes into effect when the bond angles become smaller than 90°; this would have to be the case for coordination numbers higher than six. However, crowding electron pairs down to angles of 90° is possible without large resistance (cf. hydrogen compounds listed on page 64; note the marked jump for the angles between the second and third periods).
8.1 Valence Shell Electron-Pair Repulsion

If the central atom can still take over electrons and if a ligand has lone electron pairs, then these tend to pass over to the central atom to some degree. In other words, the electron pairs of the ligand reduce their mutual repulsion by shifting partially towards the central atom. This applies especially for small ligand atoms like O and N, particularly when high formal charges have to be allocated to them. For this reason terminal O and N atoms tend to form multiple bonds with the central atom, for example:

\[
\begin{align*}
\text{HO} & \quad \text{S} & \quad \text{OH} \\
\text{instead of} & \quad \text{HO} & \quad \text{S} & \quad \text{OH}
\end{align*}
\]

In the case of the molecule of sulfuric acid the left resonance formula would indeed require the participation of \(d\) orbitals at the sulfur atom; according to recent theoretical calculations this is not justified (for \(\text{H}_2\text{SO}_4\) the formal charges even seem to reflect the real charge distribution quite well). However, the resonance formula with the formal charges can also explain the bond lengths and angles: the negative charges at the O atoms cause a mutual repulsion of these atoms and an angle widening; simultaneously the S–O bonds are shortened due to the \(S^{2-}\)–O\(^{2-}\) attraction.

A similar explanation can be given for the larger Si–O–Si bond angles as compared to C–O–C. Electron density is given over from the oxygen atom into the valence shells of the silicon atoms, but not of the carbon atoms, in the sense of the resonance formulas:

\[
\begin{align*}
\text{Si} & \quad \text{O} & \quad \text{Si} & \quad \leftrightarrow & \quad \text{Si} & \quad \text{O} & \quad \text{Si} \\
\text{C} & \quad \text{O} & \quad \text{C}
\end{align*}
\]

Examples:

\[
\begin{align*}
\text{angle SIOSi} & \quad \text{angle COC} \\
\text{O(SiH}_3\text{)_2} & \quad 144^\circ & \quad \text{O(CH}_3\text{)_2} & \quad 111^\circ \\
\text{\(\alpha\)-quartz} & \quad 142^\circ & \quad \text{O(C}_6\text{H}_5\text{)_2} & \quad 124^\circ \\
\text{\(\alpha\)-cristobalite} & \quad 147^\circ
\end{align*}
\]

That the COC angle is larger in diphenyl ether than in diethyl ether can be explained by the electron acceptor capacity of the phenyl groups. When two strongly electron-accepting atoms are bonded to an oxygen atom, the transition of the lone electron pairs can go so far that a completely linear group of atoms M=O=M results, as for example in the \([\text{Cl}_3\text{FeOFeCl}_3]^{2-}\) ion.

The electron transition and the resulting multiple bonds should reveal themselves by shortened bond lengths. In fact, bridging oxygen atoms between metal atoms in a linear arrangement exhibit rather short metal–oxygen bonds. Because of the high electronegativity of oxygen the charge centers of the bonding electron pairs will be located more towards the side of the oxygen atom, \textit{i.e.} the bonds will be polar. This can be expressed by the following resonance formulas:

\[
[\text{Cl}_3\text{Fe} \equiv \text{O} \equiv \text{FeCl}_3] \leftrightarrow \text{Cl}_3\text{Fe} \quad \left[\text{O} \equiv \text{FeCl}_3\right]^{2-}
\]

The lowest formal charges result when both formulas have equal weight. In the case of bridging fluorine atoms the ionic formula should be more important to achieve lower formal charges, \textit{e.g.}:

\[
[\text{F}_5\text{Sb} \equiv \text{F} \equiv \text{SbF}_5] \leftrightarrow \text{F}_5\text{Sb} \quad \left[\text{F} \equiv \text{SbF}_5\right]^{-}
\]
In fact, bridging fluorine atoms usually exhibit bond angles between 140 and 180° and rather long bonds. The significance of the right formula, representing weak interactions between the central F⁻ ion and two SbF₅ molecules, also shows up in the chemical reactivity: fluorine bridges are cleaved easily.

**Restrictions**

The consideration of the mutual valence electron-pair repulsion as a rule results in correct qualitative models for molecular structures. In spite of the simple concept the theory is well founded and compatible with the more complicated and less illustrative MO theory (Chapter 10). The results often are by no means inferior to those of sophisticated calculations. Nevertheless, in some cases the model fails. Examples are the ions SbBr₆²⁻, SeBr₆²⁻, and TeCl₆²⁻, which have undistorted octahedral structures, although the central atom still has a lone electron pair. This electron pair is said to be ‘stereochemically inactive’, although this is not quite true, because its influence still shows up in increased bond lengths. This phenomenon is observed only for higher coordination numbers (≥ 6), when the central atom is a heavy atom and when the ligands belong to a higher period of the periodic table, i.e. when the ligands are easily polarized. The decreasing influence of the lone electron pairs can also be seen by comparing the solid-state structures of AsI₃, SbI₃ and BiI₃. AsI₃ forms pyramidal molecules (bond angles 100.2°), but in the solid they are associated in that three iodine atoms of adjacent molecules are coordinated to an arsenic atom. In all, the coordination is distorted octahedral, with three intramolecular As–I lengths of 259 pm and three intermolecular lengths of 347 pm. In BiI₃ the coordination is octahedral with six equal Bi–I distances (307 pm). SbI₃ takes an intermediate position (3 × 287 pm, 3 × 332 pm).

The theory also cannot explain the ‘trans-influence’ that is observed between ligands that are located on opposite sides of the central atom on a straight line, as for two ligands in trans arrangement in octahedral coordination. The more tightly one ligand is bonded to the central atom, as evidenced by a short bond, the longer is the bond to the ligand in the trans position. Particularly multiple bonds are strongly effective in this way. This can also be noted in the reactivity: the weakly bonded ligand is easily displaced. On the other hand, a lone electron pair usually does not cause a lengthened bond of the ligand trans to it; on the contrary, this bond tends to be shorter (distances in pm):

Note how the bond angles show the repulsive action of the multiple bonds and of the lone electron pair.

Transition metal compounds with ligands of low electronegativity also show deviations, in spite of a d⁰ electron configuration. For example, W(CH₃)₆ does not have the expected octahedral structure, but is trigonal-prismatic.

In one respect the valence shell electron-pair repulsion theory is no better (and no worse) than other theories of molecular structure. Predictions can only be made when the constitution is known, i.e. when it is already known which and how many atoms are joined
Table 8.3: Axial and equatorial bond lengths /pm for trigonal-bipyramidal distribution of the valence electrons

<table>
<thead>
<tr>
<th>AX₅</th>
<th>AX₆</th>
<th>AX₅eq</th>
<th>AX₄E</th>
<th>AX₆eq</th>
<th>AX₃E₂</th>
<th>AX₆eq</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF₅</td>
<td>158</td>
<td>153</td>
<td>SF₄</td>
<td>165</td>
<td>155</td>
<td>ClF₃</td>
</tr>
<tr>
<td>AsF₅</td>
<td>171</td>
<td>166</td>
<td>SeF₄</td>
<td>177</td>
<td>168</td>
<td>BrF₃</td>
</tr>
<tr>
<td>PCl₅</td>
<td>212</td>
<td>202</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

to each other. For example, it cannot be explained why the following pentahalides consist of so different kinds of molecules or ions in the solid state: SbCl₅ monomeric, (NbCl₅)₂ dimeric, (PaCl₅)ₙ polymeric, PCl₅⁺PCl₆⁻ ionic, PBr₄ Br⁻ ionic; PCl₂F₃ monomeric, AsCl₄⁺AsF₆⁻ (= AsCl₂F₃) ionic, SbCl₄⁺[F₄ClSb–F–SbClF₄]⁻ (= SbCl₂F₃) ionic.

8.2 Structures with Five Valence Electron Pairs

The features described in the preceding section can be studied well with molecules for which five valence electron pairs are to be considered. As they also show some peculiarities, we deal with them separately. The favored arrangement for five points on a sphere is the trigonal bipyramid. Its two axial and three equatorial positions are not equivalent, a greater repulsive force being exercised on the axial positions. Therefore, lone electron pairs as well as ligands with lower electronegativities prefer the equatorial sites. If the five ligands are of the same kind, the bonds to the axial ligands are longer (in other words, the covalent radius is larger in the axial direction). Cf. Table 8.3.

The molecular parameters for CH₃PF₄ and (CH₃)₂PF₃ illustrate the influence of the lower electronegativity of the methyl groups and the corresponding increased repulsive effect of the electron pairs of the P–C bonds:

Energetically, the tetragonal pyramid is almost as favorable as the trigonal bipyramid. With a bond angle of 104° between the apical and a basal position the repulsion energy is only 0.14 % more when a purely coulombic repulsion is assumed; for the PAULI repulsion the difference is even less. Furthermore, the transformation of a trigonal bipyramid to a tetragonal pyramid requires only a low activation energy; as a consequence, a fast exchange of positions of the ligands from one trigonal bipyramid to a tetragonal pyramid and on to a differently oriented trigonal bipyramid occurs (‘BERRY rotation’, Fig. 8.2). This explains why only a doublet peak is observed in the ¹⁹F-NMR spectrum of PF₅ even
at low temperatures; the doublet is due to the P–F spin-spin coupling. If the fast positional exchange did not occur, two doublets with an intensity ratio of 2 : 3 would be expected.

The tetragonal pyramid is often favored when one double bond is present, especially with compounds of transition metals having a \(d^0\) configuration. Molecules or ions such as \(\text{O=CrF}_4\), \(\text{O=WCl}_4\) (as monomers in the gas phase), \(\text{O=TiCl}_2^+\) and \(\text{S=NbCl}_4^-\) have this structure. However, \(\text{O=SF}_4\) has a trigonal-bipyramidal structure with the oxygen atom in an equatorial position.

Very low energy differences also result for different polyhedra with higher coordination numbers, including coordination number 7. In these cases the electron pair repulsion theory no longer allows reliable predictions.

8.3 Problems

8.1 What structures will the following molecules have according to VSEPR theory?
- \(\text{BeCl}_2\) (g), \(\text{BF}_3\), \(\text{PF}_3\), \(\text{BrF}_3\), \(\text{TeCl}_3^+\), \(\text{XeF}_3^+\), \(\text{GeBr}_4\), \(\text{AsCl}_4^+\), \(\text{SbF}_4\), \(\text{ICl}_4^-\), \(\text{BrF}_4^+\), \(\text{TiBr}_4\), \(\text{SbCl}_5\), \(\text{SnCl}_5^-\), \(\text{TeF}_5^-\), \(\text{CISF}_5\), \(\text{O}_5^-\), \(\text{Cl}_5^-\), \(\text{S}_2^\text{2-}\), \(\text{O}_2\text{ClF}_3\), \(\text{O}_2\text{ClF}_2^-\), \(\text{OCIF}_4\), \(\text{O}_3\text{BrF}\), \(\text{O}_3\text{XeF}_2\).

8.2 The following dimeric species are associated via two bridging halogen atoms. What are their structures?
- \(\text{Be}_2\text{Cl}_4\), \(\text{Al}_2\text{Br}_6\), \(\text{I}_2\text{Cl}_6\), \(\text{As}_2\text{Cl}_2^2\), \(\text{Ta}_2\text{I}_{10}\).

8.3 What structure is to be expected for \(\text{H}_2\text{C}^-\text{SF}_4\)?

8.4 Arrange the following molecules in the order of increasing bond angles.
(a) \(\text{OF}_2\), \(\text{SF}_2\), \(\text{SCl}_2\), \(\text{S}_3^-\), \(\text{S}_3^{2-}\);
(b) Angle \(\text{H–N–H}\) in \(\text{H}_3\text{CNH}_2\), \(\text{[(H}_3\text{C)}_2\text{NH}_2]^+\);
(c) Angle \(\text{F}_{\text{ax}}^-\text{P–F}_{\text{ax}}^+\) in \(\text{PCl}_2\text{F}_3\), \(\text{PCl}_3\text{F}_2\).

8.5 There are two bridging chlorine atoms in \(\text{Al}_2\text{Cl}_6\). Give the sequence of increasing bond lengths and bond angles and estimate approximate values for the angles.

8.6 Which of the following species should have the longer bond lengths?
- \(\text{SnCl}_3^-\) or \(\text{SnCl}_5^-\);
- \(\text{PF}_5\) or \(\text{PF}_6^+\);
- \(\text{SnCl}_6^{2-}\) or \(\text{SbCl}_6^-\).

8.7 Which of the following species are the most likely to violate the VSEPR rules?
- \(\text{SbF}_5^{2-}\), \(\text{BiBr}_5^{2-}\), \(\text{TeI}_6^-\), \(\text{ClF}_5\), \(\text{IF}_7\), \(\text{IF}_8^-\).
9 Molecular Structures II: Compounds of Transition Metals

9.1 Ligand Field Theory

The mutual interaction between bonding electron pairs is the same for transition metal compounds as for compounds of main group elements. All statements concerning molecular structure apply equally. However, nonbonding valence electrons behave differently. For transition metal atoms these generally are d electrons that can be accommodated in five d orbitals. In what manner the electrons are distributed among these orbitals and in what way they become active stereochemically can be judged with the aid of ligand field theory. The concept of ligand field theory is equivalent to that of the valence shell electron-pair repulsion theory: it considers how the d electrons have to be distributed so that they attain a minimum repulsion with each other and with the bonding electron pairs. In its original version by H. Bethe it was formulated as crystal field theory; it considered the electrostatic repulsion between the d electrons and the ligands, which were treated as point-like ions. After the success of the valence shell electron-pair repulsion theory it appears more appropriate to consider the interactions between nonbonding d electrons and bonding electron pairs; thus the same notions apply for both theories. This way, one obtains qualitatively correct structural statements with relatively simple models. The more exact molecular orbital theory draws the same conclusions.

The relative orientations of the regions with high charge density of d electrons and of bonding electrons about an atom can be described with the aid of a coordinate system that has its origin in the center of the atom. Two sets of d orbitals are to be distinguished (Fig. 9.1): the first set consists of two orbitals oriented along the coordinate axes, and the second set consists of three orbitals oriented toward the centers of the edges of a circumscribed cube.

Octahedral Coordination

If an atom has six ligands, then the mutual repulsion of the six bonding electron pairs results in an octahedral coordination. The positions of the ligands correspond to points on the axes of the coordinate system. If nonbonding electrons are present, these will prefer the orbitals \( d_{xy}, d_{yz} \) and \( d_{xz} \) because the regions of high charge density of the other two d orbitals are especially close to the bonding electron pairs (Fig. 9.1). The three orbitals favored energetically are termed \( t_{2g} \) orbitals (this is a symbol for the orbital symmetry; the \( t \) designates a triply degenerate state); the other two are \( e_g \) orbitals (\( e = \) doubly degenerate; from German entartet = degenerate). Cf. the diagram in the margin on the next page.

\[ \text{The terms crystal field theory and ligand field theory are not used in a uniform way. As only interactions between adjacent atoms are being considered, without referring to crystal influences, the term crystal field theory does not seem adequate. Some authors consider certain electronic interactions (like } \pi \text{ bonds) as part of ligand field theory, although they originate from MO theory.} \]
Fig. 9.1
Orientation of the regions of high electron density for $3d$ orbitals.
True-to-scale drawings of areas with constant value for the wave functions. The dots on the circumscribed cubes mark the directions of preferential orientation of the 'partial clouds'.

The energy difference between the occupation of a $t_{2g}$ and an $e_g$ orbital is termed $\Delta_o$. The value of $\Delta_o$ depends on the repulsion exercised by the bonding electron pairs on the $d$ electrons. Compared to a transition metal atom the bonded ligand atoms are usually much more electronegative. The centers of charge of the bonding electron pairs are much closer to them, especially when they are strongly electronegative. Therefore, one can expect a decreasing influence on the $d$ electrons and thus a decrease of $\Delta_o$ with increasing ligand electronegativity. Decreasing $\Delta_o$ values also result with increasing sizes of the ligand atoms; in this case the electron pairs are distributed over a larger space so that the difference of their repulsive action on a $t_{2g}$ and an $e_g$ orbital is less marked. In the presence of multiple bonds between the metal atom and the ligands, as for example in metal carboxyls, the electron density of the bonds is especially high and their action is correspondingly large. $\Delta_o$ is a value that can be measured directly with spectroscopic methods: by photoexcitation of an electron from the $t_{2g}$ to the $e_g$ level we have $\Delta_o = h\nu$. The spectrochemical series is obtained by ordering different ligands according to decreasing $\Delta_o$:

$$\text{CO} > \text{CN}^- > \text{PR}_3 > \text{NO}_2^- > \text{NH}_3 > \text{NCS}^- > \text{H}_2\text{O} > \text{RCO}_2^- \approx \text{OH}^-$$
$$> \text{F}^- > \text{NO}_3^- > \text{Cl}^- \approx \text{SCN}^- > \text{S}_2^- > \text{Br}^- > \text{I}^-$$

When two or three nonbonding electrons are present, they will occupy two or three of the $t_{2g}$ orbitals (HUND’s rule). This is more favorable than pairing electrons in one orbital because the pairing requires that the electrostatic repulsion between the two electrons be overcome. The energy necessary to include a second electron in an already occupied orbital is called the electron pairing energy $P$. When four nonbonding electrons are present, there are two alternatives for the placement of the fourth electron. If $P > \Delta_o$, then it will be an $e_g$ orbital and all four electrons will have parallel spin: we call this a high-spin complex. If $P < \Delta_o$, then it is more favorable to form a low-spin complex leaving the $e_g$ orbitals unoccupied and having two paired electrons:
In a high-spin \( d^4 \) complex only one of the two \( e_g \) orbitals is occupied. If it is the \( d_{z^2} \) orbital then it exerts a strong repulsion on the bonding electrons of the two ligands on the \( z \) axis. These ligands are forced outwards; the coordination octahedron suffers an elongation along the \( z \) axis. This effect is known as the Jahn–Teller effect. Instead of the \( d_{z^2} \) orbital the \( d_{x^2-y^2} \) orbital could have been occupied, which would have produced elongations along the \( x \) and \( y \) axes. However, a higher force is needed to stretch four bonds; stretching only two bonds is energetically more favorable, and consequently only examples with octahedra elongated in one direction are known.

The Jahn–Teller effect is always to be expected when degenerate orbitals are unevenly occupied with electrons. In fact, it is observed for the following electronic configurations:

- \( d^4 \) high-spin, Examples: Cr(II), Mn(III)
- \( d^9 \) low-spin, Examples: Cu(II)
- \( d^7 \) low-spin, Examples: Ni(III)

A Jahn–Teller distortion should also occur for configuration \( d^1 \). However, in this case the occupied orbital is a \( t_{2g} \) orbital, for example \( d_{xy} \); this exerts a repulsion on the ligands on the axes \( x \) and \( y \) which is only slightly larger than the force exerted along the \( z \) axis. The distorting force is usually not sufficient to produce a perceptible effect. Ions like TiF\(_6^{3-}\) or MoCl\(_6^{3-}\) show no detectable deviation from octahedral symmetry.

Not even the slightest Jahn–Teller distortion and therefore no deviation from the ideal octahedral symmetry are to be expected when the \( t_{2g} \) and \( e_g \) orbitals are occupied evenly. This applies to the following electronic configurations:

- \( d^0 \), \( d^3 \), \( d^5 \) high-spin, \( d^6 \) low-spin, \( d^8 \) and \( d^{10} \). However, for configuration \( d^8 \), octahedral coordination occurs only rarely (see below, square coordination).

If there are different kinds of ligands, those which have the smaller influence according to the spectrochemical series prefer the positions with the stretched bonds. For example, in the \([\text{CuCl}_4(\text{OH}_2)_2]^{2-}\) ion two of the Cl atoms take the positions in the vertices of the elongated axis of the coordination polyhedron.

**Tetrahedral Coordination**

We can imagine the four ligands of a tetrahedrally coordinated atom to be placed in four of the eight vertices of a cube. The orbitals \( d_{xy} \), \( d_{yz} \) and \( d_{xz} \) (\( t_2 \) orbitals), which are oriented toward the cube edges, are closer to the bonding electron pairs than the orbitals \( d_{x^2-y^2} \) and \( d_{z^2} \).
Fig. 9.2

JAHN–TELLER distortions of tetrahedral complexes.

The arrows indicate the directions of displacement of the ligands due to repulsion by the nonbonding \( d \) electrons. The spheres on the cube edges mark the centers of gravity of the charges of the \( t_2 \) orbitals; a gray sphere means occupation by one electron more than a white sphere.

If the \( t_2 \) orbitals are occupied unevenly, JAHN–TELLER distortions occur. For configuration \( d^4 \), one of the \( t_2 \) orbitals is unoccupied; for \( d^9 \), one has single occupation and the rest double. As a consequence, the ligands experience differing repulsions, and a flattened tetrahedron results (Fig. 9.2). Typical bond angles are, for example in the \( \text{CuCl}_2^- \) ion, \( 116^\circ \) and \( 106^\circ \).

For the configurations \( d^3 \) and \( d^8 \) one \( t_2 \) orbital has one electron more than the others; in this case an elongated tetrahedron is to be expected; however, the deformation turns out to be smaller than for \( d^4 \) and \( d^9 \), because the deforming repulsion force is being exerted by only one electron (instead of two; Fig. 9.2). Since the deformation force is small and the requirements of the packing in the crystal sometimes cause opposite deformations, observations do not always conform to expectations. For example, \( \text{NiCl}_2^- \) \( (d^8) \) has been observed to have undistorted, slightly elongated or slightly flattened tetrahedra depending on the cation. For uneven occupation of the \( e \) orbitals distortions could also be expected, but the effect is even smaller and usually it is not detectable; \( \text{VCl}_4 \) \( (d^1) \) for example has undistorted tetrahedra.

Square Coordination

When the two ligands on the \( z \) axis of an octahedral complex are removed, the remaining ligands form a square. The repulsion between bonding electrons on the \( z \) axis ceases for the \( d_{z^2} \), the \( d_{xz} \), and the \( d_{yz} \) electrons. Only one orbital, namely \( d_{z^2-\gamma^2} \), still experiences a strong repulsion from the remaining bond electrons and is energetically unfavorable (Fig. 9.3). Square coordination is the preferential coordination for \( d^8 \) configuration, as for \( \text{Ni(II)} \) and especially for \( \text{Pd(II)}, \text{Pt(II)}, \text{and Au(III)} \), in particular with ligands that cause a strong...
9.2 Ligand Field Stabilization Energy

When ligands approach a central atom or ion, the following energetic contributions become effective:

- Energy gain (freed energy) by the formation of covalent bonds.
- Energy expenditure due to the mutual repulsion of the bonding electron pairs and due to the repulsion between ligands that approach each other too closely.
- Energy expenditure due to the repulsion exerted by bonding electron pairs on non-bonding electrons of the central atom.

Ligand field theory mainly considers the last contribution. For this contribution the geometric distribution of the ligands is irrelevant as long as the electrons of the central atom have a spherical distribution; the repulsion energy is always the same in this case. All half and fully occupied electron shells of an atom are spherical, namely \( d^5 \) high-spin and \( d^{10} \) (and naturally \( d^0 \)). This is not so for other \( d \) electron configurations.

In order to compare the structural options for transition metal compounds and to estimate which of them are most favorable energetically, the ligand field stabilization energy (LFSE) is a useful parameter. This is defined as the difference between the repulsion energy of the bonding electrons toward the \( d \) electrons as compared to a notional repulsion energy that would exist if the \( d \) electron distribution were spherical.

In an octahedral complex a \( d_{z^2} \) electron is oriented toward the ligands (the same applies for \( d_{x^2-y^2} \)); it exercises more repulsion than if it were distributed spherically. Compared to this imaginary distribution it has a higher energy state. On the other hand, a \( d_{xy} \) electron is lowered energetically: it is being repelled less than an electron with spherical distribution. The principle of the weighted mean holds: the sum of the energies of the raised and the lowered states must be equal to the energy of the spherical state. Since there are two raised and three lowered states for an octahedron, the following scheme results:
The energy level diagrams in Fig. 9.3 have been drawn according to the principle of the weighted mean energy. They show how the energy levels are placed relative to the level of the notional state of a spherical $d$ electron distribution. They do not represent absolute energy values, as the absolute level of the notional state also depends on the other energy contributions mentioned above. Even when the central atoms and the ligands are the same, the level of the notional state differs on an absolute scale for different ligand arrangements, i.e. the different term schemes are shifted mutually.

Table 9.1 lists the values for the ligand field stabilization energies for octahedral and tetrahedral complexes. The values are given as multiples of $\Delta_o$ and $\Delta_t$. In Fig. 9.4 the values have been plotted; the curves also show the influence of the other energy contributions for $3d$ elements. In the series from Ca$^{2+}$ to Zn$^{2+}$ the ionic radii decrease and the bond energies increase; correspondingly the curves run downwards from left to right. The dashed lines apply for the notional ions with spherical electron distributions. The actual energy values for the truly spherical electron distributions $d^0$, $d^5$ high-spin and $d^{10}$ are situated on these lines. Due to the decreasing ionic radii octahedral complexes become less stable than tetrahedral complexes toward the end of the series (because of increasing repulsive forces between the bonding electron pairs and due to the more crowded ligand atoms); for this reason the dashed line for octahedra bends upwards at the end. The ligand field stabilization energy is the reason for the occurrence of two minima in the curves for high-spin complexes. The minima correspond to the configurations $d^3$ and $d^8$ for octahedral and

\[
\begin{align*}
E & \quad e_g \quad \frac{3}{2}\Delta_o \quad \text{energy level for (notional) spherical distribution of } d \text{ electrons} \\
& \quad \frac{3}{2}\Delta_o \quad \text{tetrahedra, high-spin} \\
t_{2g} & \quad \frac{3}{2}\Delta_o \quad \text{octahedra, high-spin} \\
& \quad \frac{3}{2}\Delta_o \quad \text{octahedra, low-spin} \\
& \quad \frac{3}{2}\Delta_o \quad \text{tetrahedra, high-spin} \\
\end{align*}
\]

\[
\begin{array}{c|c|c|c|c|c|c|c|c|c|c}
\text{number of } d & 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\
\hline
\text{octahedra, high-spin} & \text{electron distribution} \times \text{energy} / \Delta_o \\
\hline
\frac{3}{2}\Delta_o & e_g & 0 & 1 \times \frac{3}{5} & 2 \times \frac{3}{5} & 2 \times \frac{3}{5} & 2 \times \frac{3}{5} & 2 \times \frac{3}{5} & 3 \times \frac{3}{5} & 4 \times \frac{3}{5} \\
-\frac{3}{2}\Delta_o & t_{2g} & 0 & -1 \times \frac{3}{5} & -2 \times \frac{3}{5} & -3 \times \frac{3}{5} & -3 \times \frac{3}{5} & -4 \times \frac{3}{5} & -5 \times \frac{3}{5} & -6 \times \frac{3}{5} & -6 \times \frac{3}{5} & -6 \times \frac{3}{5} \\
\text{sum = LFSE} / \Delta_o & 0 & -\frac{2}{5} & -\frac{1}{5} & -\frac{2}{5} & -\frac{3}{5} & 0 & -\frac{2}{5} & -\frac{3}{5} & -\frac{2}{5} & -\frac{3}{5} & 0 \\
\hline
\text{octahedra, low-spin} & \text{electron distribution} \times \text{energy} / \Delta_o \\
\hline
\frac{3}{2}\Delta_o & e_g & 0 & 1 \times \frac{3}{5} & 2 \times \frac{3}{5} & 2 \times \frac{3}{5} & 2 \times \frac{3}{5} & 2 \times \frac{3}{5} & 3 \times \frac{3}{5} & 4 \times \frac{3}{5} \\
-\frac{3}{2}\Delta_o & t_{2g} & 0 & -1 \times \frac{3}{5} & -2 \times \frac{3}{5} & -3 \times \frac{3}{5} & -3 \times \frac{3}{5} & -4 \times \frac{3}{5} & -5 \times \frac{3}{5} & -6 \times \frac{3}{5} & -6 \times \frac{3}{5} & -6 \times \frac{3}{5} \\
\text{sum = LFSE} / \Delta_o & 0 & -\frac{2}{5} & -\frac{1}{5} & -\frac{2}{5} & -\frac{3}{5} & 0 & -\frac{2}{5} & -\frac{3}{5} & -\frac{2}{5} & -\frac{3}{5} & 0 \\
\hline
\text{tetrahedra, high-spin} & \text{electron distribution} \times \text{energy} / \Delta_t \\
\hline
\frac{3}{2}\Delta_o & t_2 & 0 & 1 \times \frac{3}{5} & 2 \times \frac{3}{5} & 3 \times \frac{3}{5} & 3 \times \frac{3}{5} & 3 \times \frac{3}{5} & 4 \times \frac{3}{5} & 5 \times \frac{3}{5} & 6 \times \frac{3}{5} \\
-\frac{3}{2}\Delta_o & e & 0 & -1 \times \frac{3}{5} & -2 \times \frac{3}{5} & -3 \times \frac{3}{5} & -3 \times \frac{3}{5} & -4 \times \frac{3}{5} & -4 \times \frac{3}{5} & -4 \times \frac{3}{5} & -4 \times \frac{3}{5} \\
\text{sum = LFSE} / \Delta_t & 0 & -\frac{2}{5} & -\frac{1}{5} & -\frac{2}{5} & -\frac{3}{5} & 0 & -\frac{2}{5} & -\frac{3}{5} & -\frac{2}{5} & -\frac{3}{5} & 0
\end{array}
\]
9.2 Ligand Field Stabilization Energy

Relative ligand field stabilization energies for $3d$ ions.

Thick lines: octahedral field; thin lines: tetrahedral field; dashed lines: energies for (notional) spherical $d$ electron distributions

to $d^2$ and $d^7$ for tetrahedral complexes. The stabilization energies are less for tetrahedral ligand fields, since generally $\Delta_o > \Delta_t$ (in Fig. 9.4 $\Delta_t = \frac{3}{2}\Delta_o$ was assumed). For octahedral low-spin complexes there is only one minimum at $d^6$.

For high-spin compounds only rather small stabilization differences result between octahedral and tetrahedral coordination for the configurations $d^7$ and $d^8$ (Fig. 9.4). $Co^{2+}$ shows a tendency to tetrahedral coordination, whereas this tendency is overcompensated for $Ni^{2+}$ by the larger ligand field stabilization for octahedra, so that $Ni^{2+}$ prefers octahedral coordination. Here the different locations of the maxima of the ligand field stabilization energies takes effect (Table 9.1): it is largest for tetrahedra at configuration $d^7$ ($Co^{2+}$) and for octahedra at $d^8$ ($Ni^{2+}$). With increasing ligand sizes the tendency toward tetrahedral coordination becomes more marked; in other words, the octahedral arrangement becomes relatively less stable; in Fig. 9.4 this would be expressed by an earlier upwards bending of the thick dashed line. $Fe^{2+}$ and $Mn^{2+}$ also form tetrahedral complexes with larger ligands like $Cl^-$ or $Br^-$.

In Fig. 9.4 the additional stabilization by the Jahn–Teller effect has not been taken into account. Its inclusion brings the point for the (distorted) octahedral coordination for $Cu^{2+}$ further down, thus rendering this arrangement more favorable.

The ligand field stabilization is expressed in the lattice energies of the halides $MX_2$. The values obtained by the Born–Haber cycle from experimental data are plotted vs. the $d$ electron configuration in Fig. 9.5. The ligand field stabilization energy contribution is no more than 200 kJ mol$^{-1}$, which is less than 8% of the total lattice energy. The ionic radii also show a similar dependence (Fig. 9.6; Table 6.4, p. 50).
According to the preceding statements certain coordination polyhedra occur preferentially for compounds of transition metals, depending on the central atom, the oxidation state, and the kind of ligand. The general tendencies can be summarized as follows:

The series of 3d elements from scandium to iron as well as nickel preferably form octahedral complexes in the oxidation states I, II, III, and IV. Octahedra and tetrahedra are known for cobalt, and tetrahedra for zinc and copper(I). Copper(II) \( (d^9) \) forms JAHN-TELLER distorted octahedra and tetrahedra. With higher oxidation states (= smaller ionic radii) and larger ligands the tendency to form tetrahedra increases. For vanadium(V), chromium(VI) and manganese(VII) almost only tetrahedral coordination is known (VF\(_5\) is an exception). Nickel(II) low-spin complexes \( (d^8) \) can be either octahedral or square.

Among the heavier 4d and 5d elements, tetrahedral coordination only occurs for silver, cadmium, and mercury and when the oxidation states are very high as in MoO\(_4^2^-\), ReO\(_4^2^-\) or OsO\(_4\). Octahedra are very common, and higher coordination numbers, especially 7, 8, and 9, are not unusual, as for example in ZrO\(_2\) (c.n. 7), Mo(CN)\(_8^{4-}\) or LaCl\(_3\) (c.n. 9). A special situation arises for the electronic configuration \( d^8 \), namely for Pd(II), Pt(II), Ag(III), and Au(III), which almost always have square coordination. Pd(0), Pt(0), Ag(I), Au(I), and Hg(II) \( (d^{10}) \) frequently show linear coordination (c.n. 2). In Table 9.2 the most important coordination polyhedra are summarized with corresponding examples.
Table 9.2 Most common coordination polyhedra for coordination numbers 2 to 6 for transition metal compounds

<table>
<thead>
<tr>
<th>polyhedron</th>
<th>c.n.</th>
<th>electron config.</th>
<th>central atom</th>
<th>examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear arrangement</td>
<td>2</td>
<td>$d^{10}$</td>
<td>Cu(I), Ag(I), Au(I), Hg(II)</td>
<td>Cu$_2$O, Ag(CN)$_2^-$, AuCN$^+$, AuCl$_2^-$, HgCl$_2$, HgO$^+$</td>
</tr>
<tr>
<td>triangle</td>
<td>3</td>
<td>$d^{10}$</td>
<td>Cu(I), Ag(I), Au(I), Hg(II)</td>
<td>Cu(CN)$_2^-$, Ag$_2$Cl$_5^-$, Au(PPh$_3$)$_3^+$, HgI$_3$</td>
</tr>
<tr>
<td>square</td>
<td>4</td>
<td>$d^8$</td>
<td>Ni(II), Pd(II), Pt(II), Au(III)</td>
<td>Ni(CN)$_4^{2-}$, PdCl$_5^-$, PtH$_4^{2-}$, Pt(NH$_3$)$_2$Cl$_2$, AuCl$_4^-$</td>
</tr>
<tr>
<td>tetrahedron</td>
<td>4</td>
<td>$d^4$</td>
<td>Ti(IV), V(V), Cr(VI), Mo(VI), Mn(VII), Re(VII), Ru(VII), Os(VIII)</td>
<td>TiCl$_4$, VO$_4^{2-}$, CrO$_3^-$, CrO$_4^{2-}$, MoO$_4^{2-}$, WO$_4^{2-}$, Mn$_3$O$_7$, ReO$_7^-$, RuO$_4^-$, OsO$_4^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^1$</td>
<td>V(IV), Cr(V), Mn(VI), Ru(VII)</td>
<td>VCl$_4$, CrO$_3^-$, MnO$_4^{2-}$, RuO$_4^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^5$</td>
<td>Mn(II), Fe(III)</td>
<td>MnBr$_2^-$, Fe$_2$Cl$_6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^6$</td>
<td>Fe(II)</td>
<td>FeCl$_4^{2-}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^7$</td>
<td>Co(II)</td>
<td>CoCl$_2^{2-}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^8$</td>
<td>Ni(II)</td>
<td>NiCl$_4^{2-}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^9$</td>
<td>Cu(II)</td>
<td>CuCl$_3^{2-}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^{10}$</td>
<td>Ni(0), Cu(I), Zn(II), Hg(II)</td>
<td>Ni(II), Cu(CN)$_3^{2-}$, Zn(CN)$_3^{2-}$</td>
</tr>
<tr>
<td>square pyramid</td>
<td>5</td>
<td>$d^4$</td>
<td>Ti(IV), V(V), Nb(V), Mo(VI), W(VI), V(IV), Cr(V), Mo(V), W(V), V(IV), Cr(V), Mo(V), W(V)</td>
<td>TiOCl$_4^{2-}$, VOF$_4^-$, NbSCl$_4^-$, MoNCl$_4^-$, WNCI$_4^-$, VO(NCS)$_2^{2-}$, CrOCl$_4^-$, MoOCl$_4^-$, WSCl$_7^-$, Re(VI)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^1$</td>
<td>V(IV), Cr(V), Mo(V), W(V), Re(VI)</td>
<td>VCl$_4$, CrCl$_3^-$, MoCl$_3^-$, WCl$_3^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^2$</td>
<td>Os(VI)</td>
<td>OsNCl$_4^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^3$</td>
<td>Mn(III), Re(III)</td>
<td>MnCl$_2^{2-}$, Re$_2$Cl$_8$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^7$</td>
<td>Co(II)</td>
<td>Co(CN)$_3^{2-}$</td>
</tr>
<tr>
<td>trigonal bipyramid</td>
<td>5</td>
<td>$d^4$</td>
<td>V(IV)</td>
<td>VCl$_3$(NMe$_3$)$_2$</td>
</tr>
<tr>
<td>octahedron</td>
<td>6</td>
<td>$d^8$</td>
<td>Fe(0)</td>
<td>Fe(CO)$_5$</td>
</tr>
</tbody>
</table>

* endless chain † Jahn–Teller distorted

### 9.4 Isomerism

Two compounds are *isomers* when they have the same chemical composition but different molecular structures. Isomers have different physical and chemical properties.

**Constitution isomers** have molecules with different constitutions, i.e. the atoms linked with one another differ. For example:

\[
\begin{align*}
\text{S} & \quad \text{F} \\
\text{F} & \quad \text{S}
\end{align*}
\]

\[
\begin{align*}
\text{S} & \quad \text{S} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{S}
\end{align*}
\]

\[
\begin{align*}
\text{As} & \quad \text{As} \\
\text{S} & \quad \text{S} \\
\text{S} & \quad \text{S}
\end{align*}
\]

\[
\begin{align*}
\text{S} & \quad \text{S} \\
\text{As} & \quad \text{As} \\
\text{S} & \quad \text{S}
\end{align*}
\]

\[
\begin{align*}
\text{S} & \quad \text{S} \\
\text{S} & \quad \text{S} \\
\text{S} & \quad \text{S}
\end{align*}
\]
Transition metal complexes in particular show several kinds of constitution isomers, namely:

*Bonding isomers*, differing by the kind of ligand atom bonded to the central atom, for example:

\[
\begin{align*}
\text{Ph}_3\text{As} & \quad \text{AsPh}_3 \\
\text{Pt} & \quad \text{Pt} \\
\text{N}=\text{C} & \quad \text{S} \\
\text{S} & \quad \text{C}=\text{N} \\
\text{S} & \quad \text{C} = \text{N} \\
\text{S} & \quad \text{S}
\end{align*}
\]

Further ligands that can be bonded by different atoms include OCN⁻ and NO₂⁻. Cyanide ions always are linked with their C atoms in isolated complexes, but in polymeric structures as in Prussian blue they can be coordinated via both atoms (Fe–C≡N—Fe).

*Coordination isomers* occur when complex cations and complex anions are present and ligands are exchanged between anions and cations, for example:

\[
\begin{align*}
\text{[Cu(NH}_3\text{)}_4\text{][PtCl}_4]_2 & \quad \text{[Pt(NH}_3\text{)}_4\text{][CuCl}_4]_2} \\
\text{[Pt(NH}_3\text{)}_4\text{][PtCl}_6] & \quad \text{[Pt(NH}_3\text{)}_4\text{Cl}_2][\text{PtCl}_4]}
\end{align*}
\]

Further variations are:

*Hydrate isomers*, e.g. \([\text{Cr(OH}_2\text{)}_6\text{]}\text{Cl}_3\), \([\text{Cr(OH}_2\text{)}_5\text{Cl}]\text{Cl}_2\cdot\text{H}_2\text{O}\), \([\text{Cr(OH}_2\text{)}_4\text{Cl}_2]\text{Cl}_2\cdot2\text{H}_2\text{O}\)

*Ionization isomers*, e.g. \([\text{Pt(NH}_3\text{)}_4\text{][Br}_2]\), \([\text{Pt(NH}_3\text{)}_4\text{][Br}_3]\text{Cl}_2\)

*Stereo isomers* have the same constitution, but a different spatial arrangement of their atoms; they differ in their *configuration*. Two cases have to be distinguished: geometric isomers (diastereomers) and enantiomers.

*Geometric isomers* occur as *cis*–*trans* isomers in compounds with double bonds like in \(\text{N}_2\text{F}_2\) and especially when coordination polyhedra have different kinds of ligands. The most important types are square and octahedral complexes with two or more different ligands (Fig. 9.7). To designate them in more complicated cases, the polyhedron vertices are numbered alphabetically, for example *abf*-tri aqua-*cde*-tribromoplatinum(IV) for mer-[PtBr3(OH2)3]⁺. No geometric isomers exist for tetrahedral complexes. With other
Table 9.3: Number of possible geometric isomers depending on the number of different ligands (designated by A, B, C, ...) for some coordination polyhedra (excluding chelate complexes). Of every pair of enantiomers only one representative was counted.

<table>
<thead>
<tr>
<th>polyhedron</th>
<th>ligands</th>
<th>total number</th>
<th>chiral number</th>
<th>polyhedron</th>
<th>ligands</th>
<th>total number</th>
<th>chiral number</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetrahedron</td>
<td>unrestricted</td>
<td>1</td>
<td>ABCD</td>
<td>octahedron</td>
<td>AB₅</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>square</td>
<td>AB₃</td>
<td>1</td>
<td>0</td>
<td></td>
<td>A₂B₄</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>A₂B₂</td>
<td>2</td>
<td>0</td>
<td></td>
<td>A₂B₃</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>ABC₂</td>
<td>2</td>
<td>0</td>
<td></td>
<td>ABC₄</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>ABCD</td>
<td>3</td>
<td>0</td>
<td></td>
<td>A₂B₂C₃</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>trigonal</td>
<td>AB₄</td>
<td>2</td>
<td>0</td>
<td></td>
<td>A₂B₂C₂</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>bipyramid</td>
<td>A₂B₃</td>
<td>3</td>
<td>0</td>
<td></td>
<td>ABCD₃</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>ABC₃</td>
<td>4</td>
<td>0</td>
<td></td>
<td>ABC₂D₂</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>AB₂C₂</td>
<td>5</td>
<td>1</td>
<td></td>
<td>ABCDE₂</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>ABCD₂</td>
<td>7</td>
<td>3</td>
<td></td>
<td>ABCDEF</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>ABCDE</td>
<td>10</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

coordination polyhedra the number of possible isomers increases with the number of different ligands (Table 9.3); however, usually only one or two of them are known.

Enantiomers have structures of exactly the same kind and yet are different. Their structures correspond to mirror images. In their physical properties they differ only with respect to phenomena that are polar, i.e. that have some kind of a preferred direction. This especially includes polarized light, the polarization plane of which experiences a rotation when it passes through a solution of the substance. For this reason enantiomers have also been called optical isomers. In their chemical properties enantiomers differ only when they react with a compound that is an enantiomer itself.

The requirement for the existence of enantiomers is a chiral structure. Chirality is solely a symmetry property: a rigid object is chiral if it is not superposable by pure rotation or translation on its image formed by inversion. Such an object contains no rotoinversion axis (or rotoreflection axis; cf. Section 3.1). Since the reflection plane and the inversion center are special cases of rotoinversion axes (2 and 1), they are excluded.

A chiral object and the opposite object formed by inversion form a pair of enantiomorphs. If an enantiomorph is a molecular entity, it is called an enantiomer. An equimolar mixture of enantiomers is a racemate.

In crystals, in addition, no glide planes may occur. Rotation axes and screw axes are permitted. As a consequence, only 65 out of the 230 space-group types may occur; these are called Sohncke space-group types after L. SOHNCKE who was the first to describe them. Among the 65 SOHNCKE space group types there are 11 enantiomorphic pairs which have only one kind of right- or left-handed screw axis (e.g. P₄₁ and P₄₃). Only these 22 space-group types are chiral themselves. The remaining 43 SOHNCKE space-group types do permit chiral crystal structures, but their space groups are not chiral.¹

The great majority of known chiral compounds are naturally occurring organic substances, their molecules having one or more asymmetrically substituted carbon atoms (stereogenic atoms). Chirality is present when a tetrahedrally coordinated atom has

¹In literature, SOHNCKE space-group types are often termed ‘chiral space groups’, which is not correct. Most chiral molecular compounds do not crystallize in a chiral (enantiomorphic) space group. For details see [86].
known inorganic enantiomers are mainly complex compounds, mostly with octahedral coordination. In Table 9.3 ligand combinations are listed for which chiral molecules are possible. Well known chiral complexes are chelate complexes, some examples being shown in Fig. 9.8. The configuration of trichelate complexes like [Co(H₂N(CH₂)₂NH₂)₃]³⁺ can be designated by Δ or Λ: view the structure along the threefold rotation axis, as shown in Fig. 9.8; if the chelate groups are oriented like the turns of a right-handed screw, then the symbol is Δ.

9.5 Problems

9.1 State which of the following octahedral high-spin complexes should be JAHN–TELLER distorted.
\[ \text{TiF}_6^{2-}, \text{MoF}_6, [\text{Cr(OH}_2)_6]^{2+}, [\text{Mn(OH}_2)_6]^{2+}, [\text{Mn(OH}_2)_6]^{3+}, \text{FeCl}_6^{2-}, [\text{Ni(NH}_3)_6]^{2+}, [\text{Cu(NH}_3)_6]^{2+}. \]

9.2 State which of the following tetrahedral complexes should be JAHN–TELLER distorted, and what kind of a distortion it should be.
\[ \text{CrCl}_4^{2-}, \text{MnCl}_4^{2-}, \text{FeCl}_4^{2-}, \text{NiBr}_4^{2-}, \text{CuBr}_4^{2-}, \text{Cu(CN)_4}^{2-}, \text{Zn(NH}_3)_4^{2+}. \]

9.3 Decide whether the following complexes are tetrahedral or square.
\[ \text{Co(CO)}_4, \text{Ni(PF}_3)_4, \text{PtCl}_2(\text{NH}_3)_2, \text{Pt(NH}_3)_4^{2+}, \text{Cu(OH)}_2^{2-}, \text{Au}_2\text{Cl}_6 \text{ (dimeric via chloro bridges).} \]

9.4 What are the point groups of the complexes shown in Fig. 9.8 and why are they chiral?

9.5 How many isomers do you expect for the following complexes?
(a) PtCl₂(NH₃)₂; (b) ZnCl₂(NH₃)₂; (c) [OsCl₄F₂]²⁻; (d) [CrCl₃(OH₂)₃]³⁻; (e) Mo(CO)₅OR₂.

---

*In organic stereochemistry the terms ‘center of chirality’ or ‘center of asymmetry’ are often used; usually they refer to an asymmetrically substituted C atom. These terms should be avoided since they are contradictions in themselves: a chiral object by definition has no center (the only kind of center existing in symmetry is the inversion center).
Molecular orbital (MO) theory currently offers the most accurate description of the bonding within a molecule. The term orbital is a neologism reminiscent of the concept of an orbiting electron, but it also expresses the inadequacy of this concept for the precise characterization of the behavior of an electron. Mathematically an electron is treated as a standing wave by the formulation of a wave function $\psi$. For the hydrogen atom the wave functions for the ground state and all excited states are known exactly; they can be calculated as solutions of the SCHRÖDINGER equation. Hydrogen-like wave functions are assumed for other atoms, and their calculation is performed with sophisticated approximation methods.

The wave function of an electron corresponds to the expression used to describe the amplitude of a vibrating chord as a function of the position $x$. The opposite direction of the motion of the chord on the two sides of a vibrational node is expressed by opposite signs of the wave function. Similarly, the wave function of an electron has opposite signs on the two sides of a nodal surface. The wave function is a function of the site $x, y, z$, referred to a coordinate system that has its origin in the center of the atomic nucleus.

Wave functions for the orbitals of molecules are calculated by linear combinations of all wave functions of all atoms involved. The total number of orbitals remains unaltered, i.e. the total number of contributing atomic orbitals must be equal to the number of molecular orbitals. Furthermore, certain conditions have to be obeyed in the calculation; these include linear independence of the molecular orbital functions and normalization. In the following we will designate wave functions of atoms by $\chi$ and wave functions of molecules by $\psi$. We obtain the wave functions of an $\text{H}_2$ molecule by linear combination of the 1s functions $\chi_1$ and $\chi_2$ of the two hydrogen atoms:

$$
\psi_1 = \frac{1}{2} \sqrt{2} (\chi_1 + \chi_2) \\
\psi_2 = \frac{1}{2} \sqrt{2} (\chi_1 - \chi_2)
$$

bonding  \hspace{2cm}  antibonding
Compared to an H atom, electrons with the function $\psi_1$ are less energetic, and those with the function $\psi_2$ are more energetic. When the two available electrons ‘occupy’ the molecular orbital $\psi_1$, this is energetically favorable; $\psi_1$ is the wave function of a bonding molecular orbital. $\psi_2$ belongs to an antibonding molecular orbital; its occupation by electrons requires the input of energy.

When calculating the wave functions for the bonds between two atoms of different elements, the functions of the atoms contribute with different coefficients $c_1$ and $c_2$:

$$\psi_1 = c_1 \chi_1 + c_2 \chi_2$$  \hspace{1cm} (10.1)

$$\psi_2 = c_2 \chi_1 - c_1 \chi_2$$  \hspace{1cm} (10.2)

The probability of finding an electron at a site $x, y, z$ is given by $\psi^2$. Integrated over all space, the probability must be equal to 1:

$$1 = \int \psi^2 dV = \int |c_1 \chi_1 + c_2 \chi_2|^2 dV = c_1^2 + c_2^2 + 2c_1 c_2 S_{12}$$  \hspace{1cm} (10.3)

$S_{12}$ is the overlap integral between $\chi_1$ and $\chi_2$. The term $2c_1 c_2 S_{12}$ is the overlap population; it expresses the electronic interaction between the atoms. The contributions $c_1^2$ and $c_2^2$ can be assigned to the atoms 1 and 2, respectively.

Equation (10.3) is fulfilled when $c_1^2 \approx 1$ and $c_2^2 \approx 0$; in this case the electron is localized essentially at atom 1 and the overlap population is approximately zero. This is the situation of a minor electronic interaction, either because the corresponding orbitals are too far apart or because they differ considerably in energy. Such an electron does not contribute to bonding.

For $\psi_1$ the overlap population $2c_1 c_2 S_{12}$ is positive, and the electron is bonding; for $\psi_2$ it is negative, and the electron is antibonding. The sum of the values $2c_1 c_2 S_{12}$ of all occupied orbitals of the molecule, the MULLIKEN overlap population, is a measure of the bond strength or bond order (b.o.):

$$\text{b.o.} = \frac{1}{2}[\text{(number of bonding electrons)} - \text{(number of antibonding electrons)}]$$

Despite the given formula, the calculation of the bond order is not always clear in the case of the occupation of orbitals having only a minor bonding or minor antibonding effect; should they be counted or not? Nevertheless, the bond order is a simple and useful concept.† In valence-bond formulas it corresponds to the number of bonding lines.

Orbitals other than $s$ orbitals can also be combined to give bonding, antibonding or nonbonding molecular orbitals. Nonbonding are those orbitals for which bonding and antibonding components cancel each other. Some possibilities are shown in Fig. 10.1. Note the signs of the wave functions. A bonding molecular orbital having no nodal surface is a $\sigma$ orbital; if it has one nodal plane parallel to the connecting line between the atomic centers it is a $\pi$ orbital, and with two such nodal planes it is a $\delta$ orbital. Antibonding orbitals usually are designated by an asterisk "*".

†Chemists very successfully use many concepts in a more intuitive manner, although they generally tend not to define their concepts clearly (like the bond order), and to ignore definitions if they happen not to be convenient.
10.2 Hybridization

In order to calculate the orbitals for a methane molecule, the four 1s functions of the four hydrogen atoms and the functions 2s, 2px, 2py and 2pz of the carbon atom are combined to give eight wave functions, four of which are bonding and four of which are antibonding. The four bonding wave functions are:

\[
\psi_1 = \frac{c_1}{2}(s + p_x + p_y + p_z) + c_2\chi_{H1} + c_3(\chi_{H2} + \chi_{H3} + \chi_{H4})
\]
\[
\psi_2 = \frac{c_1}{2}(s + p_x - p_y - p_z) + c_2\chi_{H2} + c_3(\chi_{H3} + \chi_{H4} + \chi_{H1})
\]
\[
\psi_3 = \frac{c_1}{2}(s - p_x + p_y - p_z) + c_2\chi_{H3} + c_3(\chi_{H4} + \chi_{H1} + \chi_{H2})
\]
\[
\psi_4 = \frac{c_1}{2}(s - p_x - p_y + p_z) + c_2\chi_{H4} + c_3(\chi_{H1} + \chi_{H2} + \chi_{H3})
\]

\(\psi_1, \psi_2, \ldots\) are wave functions of the CH4 molecule, s, px, py and pz designate the wave functions of the C atom, and \(\chi_{H1}, \chi_{H2}, \ldots\) correspond to the H atoms. Among the coefficients \(c_1, c_2\) and \(c_3\), one is negligible: \(c_3 \approx 0\).

Formulated as in the preceding paragraph, the functions are not especially illustrative. They do not correspond to the idea a chemist associates with the formation of a bond between two atoms: in his or her imagination the atoms approach each other and their atomic orbitals merge into a bonding molecular orbital. To match this kind of mental picture it is expedient to start from atomic orbitals whose spatial orientations correspond to the orientations of the bonds of the molecule that is formed. Such orbitals can be obtained by hybridization of atomic orbitals. Instead of calculating the molecular orbitals of the methane molecule in one step according to the equations mentioned above, one proceeds in two steps. First, only the wave functions of the C atom are combined to give \(sp^3\) hybrid orbitals:

\[
\chi_1 = \frac{1}{2}(s + p_x + p_y + p_z)
\]
\[
\chi_2 = \frac{1}{2}(s + p_x - p_y - p_z)
\]
\[
\chi_3 = \frac{1}{2}(s - p_x + p_y - p_z)
\]
\[
\chi_4 = \frac{1}{2}(s - p_x - p_y + p_z)
\]
The functions $\chi_1$ to $\chi_4$ correspond to orbitals having preferential alignments oriented towards the vertices of an circumscribed tetrahedron. Their combinations with the wave functions of four hydrogen atoms placed in these vertices yield the following functions, the insignificant coefficient $c_3$ being neglected:

$$
\psi_1 = c_1\chi_1 + c_2\chi_{H1}
$$
$$
\psi_2 = c_1\chi_2 + c_2\chi_{H2}
$$

etc.

$\psi_1$ corresponds to a bonding orbital that essentially involves the interaction of the C atom with the first H atom; its charge density $\psi_1^2$ is concentrated in the region between these two atoms. This matches the idea of a localized C–H bond: The electron pair of this orbital is assigned to a bond between these two atoms and symbolized by a dash in the valence bond formula.

To be more exact, every bond is a ‘multi-center bond’ with contributions of the wave functions of all atoms. However, due to the charge concentration in the region between two atoms and because of the inferior contributions $\chi_{H2}$, $\chi_{H3}$, and $\chi_{H4}$, the bond can be taken to a good approximation to be a ‘two-center-two-electron bond’ (2c2e bond) between the atoms C and H1. From the mathematical point of view the hybridization is not necessary for the calculation, and in the usual molecular orbital calculations it is not performed. It is, however, a helpful mathematical trick for adapting the wave functions to a chemist’s mental picture.

For molecules with different structures different hybridization functions are appropriate. An infinity of hybridization functions can be formulated by linear combinations of $s$ and $p$ orbitals:

$$
\chi_i = \alpha_is + \beta_ip_x + \gamma_ip_y + \delta_ip_z
$$

The coefficients must be normalized, i.e. $\alpha_i^2 + \beta_i^2 + \gamma_i^2 + \delta_i^2 = 1$. Their values determine the preferential directions of the hybrid orbitals. For example, the functions

$$
\chi_1 = 0.833s + 0.32(p_x + p_y + p_z)
$$
$$
\chi_2 = 0.32s + 0.547(p_x - p_y - p_z)
$$
$$
\chi_3 = 0.32s + 0.547(-p_x + p_y - p_z)
$$
$$
\chi_4 = 0.32s + 0.547(-p_x - p_y + p_z)
$$

define an orbital $\chi_1$ having contributions of 69 % ($= 0.833^2 \times 100 \%$) $s$ and 31 % $p$ and three orbitals $\chi_2$, $\chi_3$ and $\chi_4$, each with contributions of 10 % $s$ and 90 % $p$. They are adequate to calculate the wave functions for a molecule $|AX_3\rangle$ that has a lone electron pair ($\chi_1$) with a larger $s$ contribution and bonds with larger $p$ orbital contributions as compared to $sp^3$ hybridization. The corresponding bond angles are between 90° and 109.5°, namely 96.5°.

To derive the values of the coefficients $\alpha_i$, $\beta_i$, $\gamma_i$, and $\delta_i$ so that the bond energy is maximized and the correct molecular structure results, the mutual interactions between the electrons have to be considered. This requires a great deal of computational expenditure. However, in a qualitative manner the interactions can be estimated rather well: that is exactly what the valence shell electron-pair repulsion theory accomplishes.
10.3 The Electron Localization Function

Wave functions can be calculated rather reliably with quantum-chemical approximations. The sum of the squares of all wave functions $\psi_i$ of the occupied orbitals at a site $x, y, z$ is the electron density $\rho(x, y, z) = \sum \psi_i^2$. It can also be determined experimentally by X-ray diffraction (with high expenditure). The electron density is not very appropriate to visualize chemical bonds. It shows an accumulation of electrons close to the atomic nuclei. The enhanced electron density in the region of chemical bonds can be displayed after the contribution of the inner atomic electrons has been subtracted. But even then it remains difficult to discern and to distinguish the electron pairs.

Redress can be obtained by the electron localization function (ELF). It decomposes the electron density spatially into regions that correspond to the notion of electron pairs, and its results are compatible with the valence shell electron-pair repulsion theory. An electron has a certain electron density $\rho_1(x, y, z)$ at a site $x, y, z$; this can be calculated with quantum mechanics. Take a small, spherical volume element $\Delta V$ around this site. The product $n_1(x, y, z) = \rho_1(x, y, z)\Delta V$ corresponds to the number of electrons in this volume element. For a given number of electrons the size of the sphere $\Delta V$ adapts itself to the electron density. For this given number of electrons one can calculate the probability $w(x, y, z)$ of finding a second electron with the same spin within this very volume element. According to the PAULI principle this electron must belong to another electron pair. The electron localization function is defined with the aid of this probability:

$$\text{ELF}(x, y, z) = \frac{1}{1 + [c - w(x, y, z)]^2}$$

$c$ is a positive constant that is arbitrarily chosen as to yield ELF = 0.5 for a homogeneous electron gas.

The properties of the thus defined function are:

- ELF is a function of the spatial coordinates $x, y, z$.
- ELF adopts values between 0 and 1.
- In a region where an electron pair is present, where therefore the probability of coming across a second electron pair is low, ELF adopts high values. Low values of ELF separate the regions of different electron pairs.
- The symmetry of ELF corresponds to the symmetry of the molecule or crystal.

ELF can be visualized with different kinds of images. Colored sections through a molecule are popular, using white for high values of ELF, followed by yellow–red–violet–blue–dark blue for decreasing values; simultaneously, the electron density can be depicted by the density of colored points. Contour lines can be used instead of the colors for black and white printing. Another possibility is to draw perspective images with iso surfaces, i.e. surfaces with a constant value of ELF. Fig. 10.2 shows iso surfaces with ELF = 0.8 for some molecules; from experience a value of ELF = 0.8 is well suited to reveal the distribution of electron pairs in space.

On the one hand, Fig. 10.2 exhibits iso surfaces around the fluorine atoms; on the other hand the lone electron pairs at the central atoms can be discerned quite well. The space requirement of one lone pair is larger than that of the four electron pairs at one of the more electronegative fluorine atoms. The three lone pairs at the chlorine atom of ClF$_2$ add up to a rotation-symmetrical torus.
10.4 Band Theory. The Linear Chain of Hydrogen Atoms

In a solid that cannot be interpreted on the basis of localized covalent bonds or of ions, the assessment of the bonding requires the consideration of the complete set of molecular orbitals of all involved atoms. This is the subject of band theory, which offers the most comprehensive concept of chemical bonding. Ionic bonding and localized covalent bonds result as special cases. The ideas presented in this chapter are based on the intelligible exposition by R. Hoffmann [87], the reading of which is recommended for a deeper insight into the subject. To begin with, we consider a linear chain of $N + 1$ evenly spaced hydrogen atoms. By the linear combination of their $1s$ functions we obtain $N + 1$ wave functions $\psi_{k'}; k' = 0, \ldots, N$. The wave functions have some similarity to the standing waves of a vibrating chord or, better, with the vibrations of a chain of $N + 1$ spheres that are connected by springs (Fig. 10.3). The chain can adopt different vibrational modes that differ in the number of vibrational nodes; we number the modes by sequential numbers $k'$ corresponding to the number of nodes. $k'$ cannot be larger than $N$, as the chain cannot adopt more nodes than spheres. We number the $N + 1$ spheres from $n = 0$ to $n = N$. Every sphere vibrates with a certain amplitude:

$$A_n = A_0 \cos \frac{k'n}{2N}$$

Each of the standing waves has a wavelength $\lambda_{k'}$:

$$\lambda_{k'} = \frac{2Na}{k'}$$

$a$ is the distance between two spheres. Instead of numbering the vibrational modes with sequential numbers $k'$, it is more convenient to use wave numbers $k$:

$$k = \frac{2\pi}{\lambda_{k'}} = \frac{\pi k'}{Na}$$

In this way one becomes independent of the number $N$, as the limits for $k$ become $0$ and $\pi/a$. Contrary to the numbers $k'$ the values for $k$ are not integral numbers.
The k-th wave function of the electrons in a chain of hydrogen atoms results in a similar way. From every atom we obtain a contribution $\chi_n \cos nka$, i.e. the 1s function $\chi_0$ of the $n$-th atom of the chain takes the place of $A_0$. All atoms have the same function $\chi$, referred to the local coordinate system of the atom, and the index $n$ designates the position of the atom in the chain. The $k$-th wave function is composed of contributions of all atoms:

$$\psi_k = \sum_{n=0}^{N} \chi_n \cos nka$$

A wave function composed in this way from the contributions of single atoms is called a BLOCH function [in texts on quantum chemistry you will find this function being formulated with exponential functions $\exp(inka)$ instead of the cosine functions, since this facilitates the mathematical treatment].

The number $k$ is more than just a simple number to designate a wave function. According to the DE BROGLIE equation, $p = \hbar / \lambda$, every electron can be assigned a momentum $p$ ($\hbar =$ PLANCK’S constant). $k$ and the momentum are related:

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{\hbar}$$
At the lower limit of the summation in equation (10.4) at \( k = 0 \) the cosine function always has the value 1, \( i.e. \psi_0 = \sum \chi_n \). At the upper limit \( k = \pi/a \) the cosine terms in the sum of equation (10.4) alternately have the values +1 and -1, \( i.e. \psi_{\pi/a} = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \ldots \). If we denote an H atom that contributes to the sum with +\( \chi \) by ○ and one that contributes with -\( \chi \) by ●, then this corresponds to the following sequences in the chain of atoms:

\[
\begin{align*}
\psi_0 & : \quad \psi = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \ldots \\
\psi_{\pi/a} & : \quad \psi = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \ldots
\end{align*}
\]

\( \psi_0 \) of the chain resembles the bonding molecular orbital of the \( \text{H}_2 \) molecule. At \( \psi_{\pi/a} \) there is a node between every pair of atoms, and the wave function is completely antibonding. Every wave function \( \psi_k \) is related to a definite energy state. Taking \( 10^6 \) H atoms in the chain we thus have the huge number of \( 10^6 \) energy states \( E(k) \) within the limits \( E(0) \) and \( E(\pi/a) \). The region between these limits is called an energy band or a band for short. The energy states are not distributed evenly in the band. Fig. 10.4 shows on the left a scheme of the band in which every line represents one energy state; only 38 instead of \( 10^6 \) lines were drawn. In the center the band structure is plotted, \( i.e. \) the energy as a function of \( k \); the curve is not really continuous as it appears but consists of numerous tightly crowded dots, one for each energy state. The curve flattens out at the ends, showing a denser sequence of the energy levels at the band limits. The density of states (DOS) is shown at the right side; DOS \( \cdot dE = \) number of energy states between \( E \) and \( E + dE \). The energy levels in the lower part of the band belong to bonding states, and in the upper part to antibonding states.

The band width or band dispersion is the energy difference between the highest and the lowest energy level in the band. The band width becomes larger when the interaction among the atoms increases, \( i.e. \) when the atomic orbitals overlap to a greater extent. A smaller interatomic distance \( a \) causes a larger band width. For the chain of hydrogen atoms a band width of 4.4 eV is calculated when adjacent atoms are separated by 200 pm, and 39 eV results when they move up to 100 pm.

According to the Pauli principle two electrons can adopt the same wave function, so that the \( N \) electrons of the \( N \) hydrogen atoms take the energy states in the lower half of the band, and the band is said to be ‘half occupied’. The highest occupied energy level

\*\( 10^6 \) atoms with interatomic distances of 100 pm can be accommodated in a chain of 0.1 mm length
10.5 The Peierls Distortion

The model of the chain of hydrogen atoms with a completely delocalized (metallic) type of bonding is outlined in the preceding section. Intuitively, a chemist will find this model rather unreal, as he or she expects the atoms to combine in pairs to give H₂ molecules. In other words, the chain of equidistant H atoms is expected to be unstable, so it undergoes a distortion in such a way that the atoms approach each other in pairs. This process is called Peierls distortion (or strong electron–phonon coupling) in solid-state physics:

\[
\begin{array}{c}
\cdots \text{H} \cdots \text{H} \cdots \text{H} \cdots \text{H} \cdots \text{H} \\
\downarrow \\
\text{H} - \text{H} \quad \text{H} - \text{H} \quad \text{H} - \text{H}
\end{array}
\]

The very useful chemist’s intuition, however, is of no help when the question arises of how hydrogen will behave at a pressure of 500 GPa. Presumably it will be metallic then.

Let us consider once more the chain of hydrogen atoms, but this time we put it together starting from H₂ molecules. In the beginning the chain then consists of H atoms, and electron pairs occur between every other pair of atoms. Nevertheless, let us still assume equidistant H atoms. The orbitals of the H₂ molecules interact with one another to give a

\[\psi_0 = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \ldots\]

\[\psi_{\pi/a} = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \ldots\]
band. As the repeating unit, \(i.e.\) the lattice constant in the chain, is now doubled to \(2a\), the \(k\) values only run from \(k = 0\) to \(k = \pi/(2a)\). Instead, we have two branches in the curve for the band energy (Fig. 10.6). One branch begins at \(k = 0\) and has a positive slope; it starts from the bonding molecular orbitals of the \(H_2\), all having the same sign for their wave functions. The second branch starts at \(k = 0\) with the higher energy of the antibonding \(H_2\) orbital and has a negative slope. The two branches meet at \(k = \pi/(2a)\).

As a result, the same band structure must result for the \(H\) atom chain, irrespective of whether it is based on the wave functions of \(N\) \(H\) atoms or of \(N/2\) \(H_2\) molecules. In fact, the curve of Fig. 10.4 coincides with the curve of Fig. 10.6. The apparent difference has to do with the doubling of the lattice constant from \(a\) to \(d' = 2a\). As we see from equation (10.4), the same wave functions \(\psi_k\) result for \(k = 0\) and for \(k = 2\pi/a\), the same ones for \(k = \pi/a\) and for \(k = 3\pi/a\), etc. Whereas the curve in Fig. 10.4 runs steadily upwards from \(k = 0\) to \(k = \pi/a\), in Fig. 10.6 it only runs until \(k = \pi/(2a) = \pi/d'\), then it continues upwards from right to left. We can obtain the one plot from the other by folding the diagram, as shown in the lower part of Fig. 10.6. The folding can be continued: triplication of the unit cell requires two folds, etc.

Up to now we have assumed evenly spaced \(H\) atoms. If we now allow the \(H\) atoms to approach each other in pairs, a change in the band structure takes place. The corresponding movements of the atoms are marked by arrows in Fig. 10.6. At \(k = 0\) this has no consequences; at the lower (or upper) end of the band an energy gain (or loss) occurs for the atoms that approach each other; it is compensated by the energy loss (or gain) of the atoms moving apart. However, in the central part of the band, where the \(H\) atom chain has
its Fermi limit, substantial changes take place. The upper branch of the curve shifts upwards, and the lower one downwards. As a result a gap opens up, and the band splits (Fig. 10.7). For the half-filled band the net result is an energy gain. Therefore, it is energetically more favorable when short and long distances between the H atoms alternate in the chain. The chain no longer is an electrical conductor, as an electron must overcome the energy gap in order to pass from one energy state to another.

The one-dimensional chain of hydrogen atoms is merely a model. However, compounds do exist to which the same kind of considerations are applicable and have been confirmed experimentally. These include polyene chains such as polyacetylene. The $p$ orbitals of the C atoms take the place of the $1s$ functions of the H atoms; they form one bonding and one antibonding $\pi$ band. Due to the Peierls distortion the polyacetylene chain is only stable with alternate short and long C–C bonds, that is, in the sense of the valence bond formula with alternate single and double bonds:

Polyacetylene is not an electrical conductor. If it is doped with an impurity that either introduces electrons into the upper band or removes electrons from the lower band, it becomes a good conductor.

The Peierls distortion is a substantial factor influencing which structure a solid adopts. The driving force is the tendency to maximize bonding, i.e. the same tendency that forces H atoms or other radicals to bond with each other. In a solid, that amounts to shifting the density of states at the Fermi level, in that bonding states are shifted towards lower and antibonding states towards higher energy values. By opening up an energy gap the bands become narrower; within a band the energy levels become more crowded. The extreme case is a band that has shrunk to a single energy value, i.e. all levels have the same energy. This happens, for example, when the chain of hydrogen atoms consists of widely separated $H_2$ molecules; then we have separate, independent $H_2$ molecules whose energy levels all have the same value; the bonds are localized in the molecules. Generally,
the band width is a measure for the degree of localization of the bonds: a narrow band represents a high degree of localization, and with increasing band width the bonds become more delocalized. Since narrow bands can hardly overlap and are usually separated by intervening gaps, compounds with essentially localized bonds are electrical insulators.

When the atoms are forced to move closer by the exertion of pressure, their interaction increases and the bands become wider. At sufficiently high pressures the bands overlap again and the properties become metallic. The pressure-induced transition from a nonmetal to a metal has been shown experimentally in many cases, for example for iodine and other nonmetals. Under extremely high pressures even hydrogen should become metallic (metallic hydrogen is assumed to exist in the interior of Jupiter).

The Peierls distortion is not the only possible way to achieve the most stable state for a system. Whether it occurs is a question not only of the band structure itself, but also of the degree of occupation of the bands. For an unoccupied band or for a band occupied only at values around \( k = 0 \), it is of no importance how the energy levels are distributed at \( k = \pi/\alpha \). In a solid, a stabilizing distortion in one direction can cause a destabilization in another direction and may therefore not take place. The stabilizing effect of the Peierls distortion is small for the heavy elements (from the fifth period onward) and can be overcome by other effects. Therefore, undistorted chains and networks are observed mainly among compounds of the heavy elements.

## 10.6 Crystal Orbital Overlap Population (COOP)

At the end of Section 10.1 the Mulliken overlap population is mentioned as a quantity related to the bond order. A corresponding quantity for solids was introduced by R. Hoffmann: the crystal orbital overlap population (COOP). It is a function that specifies the bond strength in a crystal, all states being taken into account by the Mulliken overlap populations \( 2\langle c_i c_j S_{ij} \rangle \). Its calculation requires a powerful computer; however, it can be estimated in a qualitative manner by considering the interactions between neighboring atomic orbitals, such as shown in Fig. 10.8. At \( k = 0 \) all interatomic interactions are bonding. At \( k = \pi/\alpha \) they are antibonding for directly adjacent atoms, but they are bonding

![Figure 10.8](image)

**Fig. 10.8**
Density of states (DOS) and crystal overlap population (COOP) for a chain of equidistant H atoms
between every other atom, albeit with reduced contributions due to the longer distance. At \( k = \pi/(2a) \) the contributions between every other atom are antibonding, and those of adjacent atoms cancel each other. By also taking into account the densities of states one obtains the COOP diagram. In it net bonding overlap populations are plotted to the right and antibonding ones to the left. By marking the FERMI level it can be discerned to what extent bonding interactions predominate over antibonding interactions; they correspond to the areas enclosed by the curve below the FERMI level to the right and left sides.

Even in more complicated cases it is possible to obtain a qualitative idea. We choose the example of planar PtX_4^{2-} units that form a chain with Pt–Pt contacts. This kind of a structure is found for K_2Pt(CN)_4 and its partially oxidized derivatives like K_2Pt(CN)_4Cl_{0.3}:

![Diagram showing Pt–Pt interactions in a polymeric chain](image)

We will consider only the Pt–Pt interactions within the chain in the following. Fig. 10.9

![Diagram showing formation of bands and corresponding band structure and density of states](image)
shows the orientations of the relevant atomic orbitals at \( k = 0 \) and \( k = \pi/a \). Aside from \( d \) orbitals one \( p \) orbital is also taken into account. At the lower left is plotted the sequence of the energy states of the molecular orbitals of the monomeric, square complex (cf. Fig. 9.3, p. 77). The sketch to its right indicates how the energy levels fan out into bands when the \( \text{PtX}_2^{2-} \) ions are joined to a chain. The bands become wider the more intensely the orbitals interact with one another. With the aid of the orbital representations in the upper part of the figure the differences can be estimated: the orbitals \( d_{z^2} \) and \( p_z \) are oriented towards each other, and produce the widest bands; the interaction of the orbitals \( d_{xy} \) and \( d_{yz} \) is lower, and for \( d_{xy} \) and \( d_{x^2-y^2} \) it is rather small (the band width for \( d_{x^2-y^2} \) is slightly larger than for \( d_{xy} \) because of the inflation of \( d_{x^2-y^2} \) due to its interaction with the ligands). The central plot shows the band structure, and the one on the right the density of states.

The DOS diagram results from the superposition of the densities of states of the different bands (Fig. 10.10). The \( d_{xy} \) band is narrow, its energy levels are crowded, and therefore it has a high density of states. For the wide \( d_{z^2} \) band the energy levels are distributed over a larger interval, and the density of states is smaller. The COOP contribution of every

---

**Fig. 10.10**

Top: DOS contributions of the different bands of a \( \text{PtX}_2^{2-} \) chain and their superposition to give the total density of states.

Bottom: COOP contributions of the different bands and their superposition to give the crystal orbital overlap population.
10.7 Bonds in Two and Three Dimensions

In principle, the calculation of bonding in two or three dimensions follows the same scheme as outlined for the chain extended in one dimension. Instead of one lattice constant \(a\), two or three lattice constants \(a\), \(b\) and \(c\) have to be considered, and instead of one sequential number \(k\), two or three numbers \(k_x\), \(k_y\) and \(k_z\) are needed. The triplet of numbers \(\mathbf{k} = (k_x, k_y, k_z)\) is called wave vector. This term expresses the relation with the momentum of the electron. The momentum has vectorial character, its direction coincides with the direction of \(\mathbf{k}\); the magnitudes of both are related by the de Broglie relation [equation (10.5)]. In the directions \(a\), \(b\) and \(c\) the components of \(\mathbf{k}\) run from 0 to \(\pi/a\), \(\pi/b\) and \(\pi/c\), respectively. As the direction of motion and the momentum of an electron can be reversed, we also allow for negative values of \(k_x\), \(k_y\) and \(k_z\), with values that run from 0 to \(-\pi/a\) etc. However, for the calculation of the energy states the positive values are sufficient, since according to equation (10.4) the energy of a wave function is \(E(\mathbf{k}) = E(-\mathbf{k})\).

The magnitude of \(\mathbf{k}\) corresponds to a wave number \(2\pi/\lambda\) and therefore is measured with a unit of reciprocal length. For this reason \(\mathbf{k}\) is said to be a vector in a ‘reciprocal space’ or ‘\(k\) space’.* This is a ‘space’ in a mathematical sense, i.e. it is concerned with vectors in a coordinate system, the axes of which serve to plot \(k_x\), \(k_y\) and \(k_z\). The directions of the axes run perpendicular to the delimiting faces of the unit cell of the crystal.

The region within which \(\mathbf{k}\) is considered \((-\pi/a \leq k_x \leq \pi/a\) etc.) is the first Brillouin zone. In the coordinate system of \(k\) space it is a polyhedron. The faces of the first Brillouin zone are oriented perpendicular to the directions from one atom to the equivalent atoms in the adjacent unit cells. The distance of a face from the origin of the \(k\) coordinate system is \(\pi/s\), \(s\) being the distance between the atoms. The first Brillouin zone for a cubic-primitive crystal lattice is shown in Fig. 10.11; the symbols commonly given to certain points of the Brillouin zone are labeled. The Brillouin zone consists of a very large number of small cells, one for each electronic state.

The pictures in Fig. 10.12 give an impression of how \(s\) orbitals interact with each other in a square lattice. Depending on the \(k\) values, i.e. for different points in the Brillouin zone, different kinds of interactions result. Between adjacent atoms there are only bonding

*Compared to the reciprocal space commonly used in crystallography, the \(k\) space is expanded by a factor \(2\pi\), otherwise the construction for both is the same.
Fig. 10.11
First Brillouin zone for a cubic-primitive crystal lattice. The points $X$ are located at $k = \pi/a$ in each case.

Fig. 10.12
Combination of $s$ orbitals (top) and $p$ orbitals in a square net and the resulting band structure (bottom).
interactions at $\Gamma$, and only antibonding interactions at $M$; the wave function corresponding to $\Gamma$ therefore is the most favorable one energetically, and the one corresponding to $M$ the least favorable. At $X$ every atom has two bonding and two antibonding interactions with adjacent atoms, and its energy level is intermediate between those of $\Gamma$ and $M$. It is hardly possible to visualize the energy levels for all of the BRILLOUIN zone, but one can plot diagrams that show how the energy values run along certain directions within the zone. This has been done in the lower part of Fig. 10.12 for three directions ($\Gamma \rightarrow X, X \rightarrow M$ and $\Gamma \rightarrow M$).

$p_z$ orbitals that are oriented perpendicular to the square lattice interact in the same way as the $s$ orbitals, but the $\pi$-type interactions are inferior and correspondingly the band width is smaller. For $p_x$ and $p_y$ orbitals the situation is somewhat more complicated, because $\sigma$ and $\pi$ interactions have to be considered between adjacent atoms (Fig. 10.12). For example, at $\Gamma$ the $p_x$ orbitals are $\sigma$-antibonding, but $\pi$-bonding. At $X$ $p_x$ and $p_y$ differ most, one being $\sigma$ and $\pi$-bonding, and the other $\sigma$ and $\pi$-antibonding.

In a cubic-primitive structure ($\alpha$-polonium, Fig. 2.4, p. 7) the situation is similar. By stacking square nets and considering how the orbitals interact at different points of the BRILLOUIN zone, a qualitative picture of the band structure can be obtained.

### 10.8 Bonding in Metals

The density of states for the elements of a long period of the periodic table can be sketched roughly as in Fig. 10.13. Due to the three-dimensional structures the more accurate consideration will no longer yield the simple DOS curves with two peaks as for a linear chain, but yields instead more or less complicated curves with numerous peaks. We will not go into the details here; in Fig. 10.13 merely a rectangle represents the DOS curve of each band. In each case the lower part of a band is bonding, and the upper part is antibonding. Correspondingly, the COOP diagram shows a contribution to the right and to the left side for every band. The $p$ band has more antibonding than bonding contributions so that its left side predominates. In the series potassium, calcium, scandium, ... we add a valence electron from element to element, and the FERMI limit climbs; the FERMI limit is marked to the right side of the figure for some valence electron counts. As can be seen, at first

![Fig. 10.13](image)

**Fig. 10.13**
Schematic sketch of the density of states and the crystal orbital overlap population for metals.
bonding states are occupied and therefore the bond strength increases for the metals from potassium to chromium. For the seventh to tenth valence electrons only antibonding states are available, and so the bond strengths decrease from chromium to nickel. The next electrons (Cu, Zn) are weakly bonding. With more than 14 valence electrons the total overlap population for a metallic structure becomes negative; structures with lower coordination numbers become favored.

The outlined sketch is rather rough, but it correctly shows the tendencies, as can be exemplified by the melting points of the metals (values in °C):

<table>
<thead>
<tr>
<th>Metal</th>
<th>K</th>
<th>Ca</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>63</td>
<td>839</td>
<td>1539</td>
<td>1667</td>
<td>1915</td>
<td>1900</td>
<td>1244</td>
<td>1535</td>
<td>1495</td>
<td>1455</td>
<td>1083</td>
<td>420</td>
</tr>
</tbody>
</table>

In reality there are subtle deviations from this simple picture. The energy levels shift somewhat from element to element, and different structure types have different band structures that become more or less favorable depending on the valence electron concentration. Furthermore, in the COOP diagram of Fig. 10.13 the $s-p$, $s-d$ and $p-d$ interactions were not taken into account, although they cannot be neglected. A more exact calculation shows that only antibonding contributions are to be expected from the eleventh valence electron onwards.

### 10.9 Problems

10.1 What changes should occur in the band structure and the DOS diagrams (Fig. 10.4) when the chain of H atoms is compressed?

10.2 What would the band structure of a chain of $p$ orbitals oriented head-on (Fig. 10.5) look like after a PEIERLS distortion?

10.3 What changes should occur in the band structure of the square net (Fig. 10.12) when it is compressed in the $x$ direction?
11 The Element Structures of the Nonmetals

According to the $8-N$ rule (Chapter 8) an atom $X$ of an element of the $N$-th main group of the periodic table will participate in $8-N$ covalent bonds ($N = 4$ to $7$):

$$b(XX) = 8 - N$$

In addition, as a rule, the principle of maximal connectivity holds for elements of the third and higher periods: the $8-N$ bonds usually are bonds to $8-N$ different atoms, and multiple bonds are avoided. For carbon, however, being an element of the second period, the less connected graphite is more stable than diamond at normal conditions. At higher pressures the importance of the principle of maximal connectivity increases; then, diamond becomes more stable.

11.1 Hydrogen and the Halogens

Hydrogen, fluorine, chlorine, bromine and iodine consist of molecules $X_2$, even when in the solid state. In solid hydrogen, rotating $H_2$ molecules take an arrangement as in a hexagonal-closet packing of spheres. In $\alpha$-F$_2$ the F$_2$ molecules are packed in hexagonal layers; the molecules are oriented perpendicular to the layer, and the layers are stacked in the same way as in cubic closest-packing. Above 45.6 K up to the melting point (53.5 K) the modification $\beta$-F$_2$ is stable in which the molecules rotate about their centers of gravity.

The molecules in crystalline chlorine, bromine and iodine are packed in a different manner, as shown in Fig. 11.1. The rather different distances between atoms of adjacent molecules are remarkable. If we take the van der Waals distance, such as observed in organic and inorganic molecular compounds, as reference, then some of the intermolecular contacts in the $b$-$c$ plane are shorter, whereas they are longer to the molecules of the next plane. We thus observe a certain degree of association of the halogen molecules within the $b$-$c$ plane (dotted in Fig. 11.1, top left). This association increases from chlorine to iodine. The weaker attractive forces between the planes show up in the plate-like habit of the crystals and in their easy cleavage parallel to the layers. Similar association tendencies are also observed for the heavier elements of the fifth and sixth main groups.

The packing can be interpreted as a cubic closest-packing of halogen atoms that has been severely distorted by the covalent bonds within the molecules. By exerting pressure the distortion is reduced, i.e. the different lengths of the contact distances between the atoms approximate each other (Fig. 11.1). For iodine a continuous approximation is observed with increasing pressure, then at 23 GPa an abrupt phase transition takes place yielding the incommensurately modulated crystal structure of iodine-V. Such a structure cannot be described as usual with a three-dimensional space group (Section 3.6, p. 25). The four-dimensional superspace group is in this case $Fmmm(00q_3)000$ with $q_3 = 0.257$ at 24.6 GPa. The structure can thus be described with a three-dimensional approximant (mean structure) in the orthorhombic space group $Fmmm$, but the atoms are displaced and obey a sine wave along $c$. The wave length of the wave is $c/q_3 = c/0.257 = 3.89c$. 

Inorganic Structural Chemistry, Second Edition  Ulrich Müller
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The structure of iodine at four different pressures.

The outlined face-centered unit cell in the 30-Gpa figure corresponds to that of a (distorted) cubic closest-packing of spheres. At 24.6 GPa four unit cells of the face-centered approximant structure are shown; the structure is incommensurately modulated, the atomic positions follow a sine wave with a wave length of 3.89 × 89/2. The amplitude of the wave is exaggerated by a factor of two.

Dependence of the twelve interatomic contact distances on pressure

The amplitude of the wave is parallel to b and amounts to 0.053b. The interatomic distances differ from atom to atom within an interval of 286 to 311 pm.

When pressure exceeds 28 GPa, the modulation disappears and a distorted cubic closest-packing of spheres is obtained (iodine-II). The distortion of the sphere packing decreases when the pressure is increased. A transformation to a tetragonal distorted packing of spheres (iodine-III) takes place at approximately 37.5 GPa, and finally the packing becomes undistorted cubic at 55 GPa (iodine-IV). With increasing pressure the energy gap between the fully occupied valence band and the unoccupied conduction band decreases. The energy gap disappears already at about 16 GPa, i.e. a transition from an insulator to a metallic conductor takes place even though molecules are still present at this pressure. Iodine thus actually becomes a metal, and at high pressures it also adopts the structure of a closest packing of spheres that is typical for metals, albeit at first in a distorted manner. A comparable transition to a metal is also expected to occur for hydrogen; the necessary pressure (not yet achieved experimentally) could amount to 450 GPa.
11.2 Chalcogens

Oxygen in the solid state consists of O₂ molecules. From 24 K to 43.6 K they are packed as in α-F₂. Under pressure (5.5 GPa) this packing is also observed at room temperature. Below 24 K the molecules are slightly tilted against the hexagonal layer. From 43.6 K up to the melting point (54.8 K) the molecules rotate in the crystal as in β-F₂. Under pressure oxygen becomes metallic at approximately 100 GPa, but it remains molecular.

No element shows as many different structures as sulfur. Crystal structures are known for the following forms: S₆, S₇ (four modifications), S₈ (three modifications), S₁₀, S₆ • S₁₀, S₁₁, S₁₂, S₁₃, S₁₄, S₁₅, S₁₈ (two forms), S₂₀, S₂₀ (Fig. 11.2). Many of them can be separated by chromatography from solutions that were obtained by extraction of quenched
sulfur melts; they can also be prepared by specific chemical synthesis. Quenched sulfur melts also yield polymeric forms; the structure of one of these has been determined. All mentioned sulfur forms consist of rings or chains of S atoms, every sulfur atom being bonded to two other sulfur atoms in accordance with the $8 - N$ rule. The S–S bond lengths usually are about 206 pm, but they show a certain scatter (±10 pm). The S–S–S bond angles are between 101 and 110° and the dihedral angles between 74 and 100°. As a consequence, a sequence of five atoms can adopt one of two arrangements:

Only the cisoid arrangement occurs in the smaller rings $S_6$, $S_7$, and $S_8$, the dihedral angles being forced to adapt themselves (74.5° for $S_6$, 98° for $S_8$). $S_6$ has chair conformation, and the $S_8$ conformation is called crown-form (Fig. 11.2). $S_7$ can be imagined to be formed from $S_8$ by taking out one S atom. Larger rings require the presence of cisoid and transoid groups in order to be free of strain. In $S_{12}$ cisoid and transoid groups alternate. Helical chains result when there are only transoid groups; the dihedral angle determines how many turns it takes to reach another atom directly above of an atom on a line parallel to the axis of the helix. In one form of polymer sulfur it takes ten atoms in three turns (screw axis 103; cf. Section 3.1).

In orthorhombic $\alpha$-sulfur, the modification stable at normal conditions, $S_8$ rings are stacked to form columns. Consecutive rings are not stacked one exactly above another (as in a roll of coins), but in a staggered manner so that the column looks like a crank shaft (Fig. 11.3). This arrangement allows for a dense packing of the molecules, with columns in two mutually perpendicular directions. The columns of one direction are placed in the recesses of the perpendicular ‘crank shafts’. In $S_8$ and in $S_{12}$ the rings are stacked exactly one above another, and the rolls are bundled parallel to each other. In the structures a

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*Dihedral angle = angle between two planes. For a chain of four atoms it is the angle between the planes through the atoms 1,2,3 and 2,3,4.*
11.3 Elements of the Fifth Main Group

For solid nitrogen five modifications are known that differ in the packing of the N₂ molecules. Two of them are stable at normal pressure (transition temperature 35.6 K); the others exist only under high pressure. At pressures around 100 GPa a phase transition with a marked hysteresis takes place, resulting in a non-molecular modification. It presumably corresponds to the α-arsenic type. Electrical conductivity sets in at 140 GPa.

Selenium forms three known modifications that consist of Se₈ rings. The stacking of the rings differs from that of the S₈ modifications in that they resemble coin rolls, but the rings are tilted. There also exists a modification that is isotypic with S₆, consisting of Se₆ molecules. The thermodynamically stable form of selenium, α-selenium or Se-I, consists of helical chains having three Se atoms in every turn (Fig. 11.4). The chains are bundled parallel in the crystal. Every selenium atom has four adjacent atoms from three different chains at a distance of 344 pm. Together with the two adjacent atoms within the chain at a distance of 237 pm, a strongly distorted octahedral 2+4 coordination results. The Se∥Se distance between the chains is significantly shorter than expected from the Van der Waals distance. For high-pressure modifications of selenium see Section 11.4.

Tellurium crystallizes isotypic to α-selenium. As expected, the Te–Te bonds in the chain (283 pm) are longer than in selenium, but the contact distances to the atoms of the adjacent chains are nearly the same (Te∥Te 349 pm). The shortening, as compared to the Van der Waals distance, is more marked and the deviation from a regular octahedral coordination of the atoms is reduced (cf. Table 11.1, p. 111). By exerting pressure all six distances can be made to be equal (cf. Section 11.4).

Two modifications are known for polonium. At room temperature α-polonium is stable; it has a cubic-primitive structure, every atom having an exact octahedral coordination (Fig. 2.4, p. 7). This is a rather unusual structure, but it also occurs for phosphorus and antimony at high pressures. At 54 °C α-Po is converted to β-Po. The phase transition involves a compression in the direction of one of the body diagonals of the cubic-primitive unit cell, and the result is a rhombohedral lattice. The bond angles are 98.2°.

A universally valid principle can be discerned: *in the solid state molecules tend to pack as tightly as possible.*

Universally valid principle can be discerned: *in the solid state molecules tend to pack as tightly as possible.*

**Fig. 11.4**
Structure of α-selenium. Left: side view of a helix with 3/2 screw symmetry. Right: view along the helices; the unit cell and the coordination about one atom are plotted.

Universally valid principle can be discerned: *in the solid state molecules tend to pack as tightly as possible.*

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Two modifications are known for **polonium.** At room temperature α-polonium is stable; it has a cubic-primitive structure, every atom having an exact octahedral coordination (Fig. 2.4, p. 7). This is a rather unusual structure, but it also occurs for phosphorus and antimony at high pressures. At 54 °C α-Po is converted to β-Po. The phase transition involves a compression in the direction of one of the body diagonals of the cubic-primitive unit cell, and the result is a rhombohedral lattice. The bond angles are 98.2°.
Phosphorus vapor consists of tetrahedral $P_4$ molecules, and at higher temperatures also of $P_2$ molecules ($P\equiv P$ bond length 190 pm). White phosphorus forms by condensation of the vapor; it also consists of $P_4$ molecules. Liquid phosphorus normally consists of $P_4$ molecules, but at a pressure of 1 GPa and 100 °C polymeric liquid phosphorus is formed which is not miscible with liquid $P_4$.

By irradiation with light or by heating it to temperatures above 180 °C, white phosphorus is transformed to red phosphorus. Its tint, melting point, vapor pressure and especially its density depend on the conditions of preparation. Usually, it is amorphous or microcrystalline, and it is rather laborious to grow crystals.

Platelets of HITTORF’s (violet) phosphorus slowly crystallize together with fibrous red phosphorus at temperatures around 550 °C. Single crystals of HITTORF’s phosphorus were obtained by slow cooling (from 630 to 520 °C) of a solution in liquid lead. Both modifications consist of polymeric tubes with a pentagonal cross-section; the tubes are composed of cages of the same shape as in $As_4S_4$ and $As_4S_5$, being connected via $P_2$ dumbbells (Fig. 11.5). In fibrous phosphorus the tubes are interconnected to parallel pairs. In HITTORF’s phosphorus they are connected crosswise to grids; pairs of grids are interlocked
but not bonded with each other. According to the $8-N$ rule every P atom is bonded with three other atoms. Despite its complicated structure, the linking principle of these modifications occurs frequently in the structural chemistry of phosphorus compounds. Building units that correspond to fragments of the tubes are known among the polyphosphides and polyphosphanes (cf. p. 133). Similar tubes also occur in P$_{15}$Se and P$_{19}$Se.

The compound (CuI)$_3$P$_{12}$ can be obtained from the elements at 550°C. It contains chains of polymeric phosphorus that can be isolated when the copper iodide is extracted with an aqueous solution of potassium cyanide. The molecules consist of P$_8$ cages that are joined via P$_4$ squares (Fig. 11.5, top). Another variety can be obtained in a similar way from (CuI)$_3$P$_{12}$; its chains consist of P$_{10}$ cages and P$_2$ dumbbells.

Black phosphorus only forms under special conditions (high pressure, crystallization from liquid bismuth or prolonged heating in the presence of Hg); nevertheless, it is the thermodynamically stable modification at normal conditions. It consists of layers having six-membered rings in the chair conformation. Pairs of rings are connected like the rings in cis-decalin (Fig. 11.6). The layer can also be regarded as a system of interconnected zigzag lines that alternate in two different planes. Within the layer every P atom is bonded to three other P atoms at distances of 222 and 224 pm. The atomic distances between the layers (2/359 pm; 1/380 pm) correspond to the van der Waals distance. Certain structural features of black phosphorus are also found among the polyphosphides (cf. Fig. 13.2, p. 133).

Arsenic modifications with the structures of white and black phosphorus have been described. However, only gray (metallic, rhombohedral) $\alpha$-arsenic is stable. It consists of layers of six-membered rings in the chair conformation that are connected with each other in the same way as in trans-decalin (Fig. 11.7). In the layer the atoms are situated alternately in an upper and a lower plane. The layers are stacked in a staggered manner such that over and under the center of every ring there is an As atom in an adjacent layer. In this way every As atom is in contact with three more atoms in addition to the three atoms to which it is bonded within the layer; it has a distorted octahedral 3 + 3 coordination. The As–As bond length in the layer is 252 pm; the distance between adjacent atoms of different layers is 312 pm and thus is considerably shorter than the van der Waals distance (370 pm).

The structures of antimony and bismuth correspond to that of gray arsenic. With increasing atomic weight the distances between adjacent atoms within a layer and between layers become less different, i.e. the coordination polyhedra deviate less from a regular octahedron. This effect is enhanced under pressure (cf. next section).
The description of the structures of P, As, Sb, and Bi as layer structures and of Se and Te as chain structures neglects the presence of bonding interactions between the layers and chains. These interactions gain importance for the heavier atoms (Table 11.1). For example, the interlayer distances between adjacent atoms for Sb and Bi are only 15% longer than the intralayer distances; the actual deviation from the $\alpha$-polonium structure is rather small. Furthermore, As, Sb, and Bi show metallic conductivity. The bonding interactions can be understood using band theory: starting from the $\alpha$-Po structure, a Peierls distortion takes place that enhances three bonds per atom (Fig. 11.8). The same applies to tellurium and selenium, two bonds per atom being enhanced.
11.4 Elements of the Fifth and Sixth Main Groups under Pressure

Crystal structure determinations from very small samples have become possible due to the high intensities of the X-rays from a synchrotron. Very high pressures can be exerted on a small sample situated between two anvils made from diamond. In this way, our knowledge of the behavior of matter under high pressures has been widened considerably. Under pressure the elements of the fifth and sixth main groups exhibit rather unusual structures. A synopsis of the structures that occur is given in Fig. 11.9.

Under normal conditions an atom in elemental tellurium has coordination number 2 + 4. It has been known for a long time that pressure causes the interatomic distances to approximate each other until finally every tellurium atom has six equidistant neighboring atoms at 297 pm; the structure (now called Te-IV) corresponds to β-polonium. However, before this is attained, two other modifications (Te-II and Te-III) that are out of the ordinary appear at 4 GPa and 7 GPa. Te-II contains parallel, linear chains that are mutually shifted in such a way that each Te atom has, in addition to its two neighboring atoms within the chain

---

**Table 11.1**: Distances between adjacent atoms and bond angles in structures of the α-As, α-Se, α-Po and β-Po type. $d_1 =$ bond distance, $d_2 =$ shortest interatomic distance between layers or chains; distances in pm, angles in degrees

<table>
<thead>
<tr>
<th>structure type</th>
<th>$d_1$</th>
<th>$d_2$</th>
<th>$d_2/d_1$</th>
<th>angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (~10 GPa) α-As</td>
<td>213</td>
<td>327</td>
<td>1.54</td>
<td>105</td>
</tr>
<tr>
<td>P (~12 GPa) α-Po</td>
<td>238</td>
<td>238</td>
<td>1.00</td>
<td>90</td>
</tr>
<tr>
<td>As α-As</td>
<td>252</td>
<td>312</td>
<td>1.24</td>
<td>96.6</td>
</tr>
<tr>
<td>As (25 GPa) α-Po</td>
<td>255</td>
<td>255</td>
<td>1.00</td>
<td>90</td>
</tr>
<tr>
<td>Se α-Se</td>
<td>237</td>
<td>344</td>
<td>1.45</td>
<td>103.1</td>
</tr>
<tr>
<td>Sb α-As</td>
<td>291</td>
<td>336</td>
<td>1.15</td>
<td>95.6</td>
</tr>
<tr>
<td>Te α-Se</td>
<td>283</td>
<td>349</td>
<td>1.23</td>
<td>103.2</td>
</tr>
<tr>
<td>Te-IV (11.5 GPa) β-Po</td>
<td>295</td>
<td>295</td>
<td>1.00</td>
<td>102.7</td>
</tr>
<tr>
<td>Bi α-As</td>
<td>307</td>
<td>353</td>
<td>1.15</td>
<td>95.5</td>
</tr>
<tr>
<td>Po α-Po</td>
<td>337</td>
<td>337</td>
<td>1.00</td>
<td>90</td>
</tr>
<tr>
<td>Po β-Po</td>
<td>337</td>
<td>337</td>
<td>1.00</td>
<td>98.2</td>
</tr>
</tbody>
</table>

---

**Fig. 11.9**
Ranges of stabilities of the elements of the fifth and sixth main groups in dependence on pressure at room temperature.
- $cP =$ cubic primitive (α-Po);
- $hP =$ hexagonal primitive;
- $cl =$ body-centered cubic packing of spheres
Fig. 11.10
Four body-centered unit cells of the incommensurately modulated structure of tellurium-III.
Short bonds are drawn black, long bonds open; two more long contacts along \( a = 392 \) pm are not shown.
In the direction \( b \) the atoms follow a sine wave having a wave length of \( 3.742 \times b \)

(310 pm), two closer (286 – 299 pm) and four more distant neighboring atoms (331 – 364 pm). Te-III has an incommensurately modulated structure in which every tellurium atom has six neighboring atoms at distances of 297 to 316 pm and six more distant ones at 368 to 392 pm; these distances vary slightly from atom to atom (Fig. 11.10). Finally, at 27 GPa tellurium transforms to a body-centered cubic arrangement, which is a typically metallic structure (Te-V). Sulfur forms at least five high-pressure modifications; one of them (> 80 GPa) has the \( \beta \)-polonium structure.

Under pressure black phosphorus transforms first to a modification that corresponds to gray arsenic. At an even higher pressure this is converted to the \( \alpha \)-polonium structure. Then follows a hexagonal-primitive structure, which has also been observed for silicon under pressure (p. 122), but that hardly ever occurs otherwise. Above 262 GPa phosphorus is body-centered cubic; this modification becomes superconducting below 22 K.

Arsenic also adopts the \( \alpha \)-polonium structure at 25 GPa and becomes body-centered cubic at the highest pressures. The rather unusual Bi-III structure appears intermittently between these two modifications.

This bismuth-III structure is also observed for antimony from 10 to 28 GPa and for bismuth from 2.8 to 8 GPa. At even higher pressures antimony and bismuth adopt the body-centered cubic packing of spheres which is typical for metals. Bi-III has a peculiar incommensurate composite crystal structure. It can be described by two intergrown partial structures that are not compatible metrically with one another (Fig. 11.11). The partial structure 1 consists of square antiprisms which share faces along \( c \) and which are connected by tetrahedral building blocks. The partial structure 2 forms linear chains of atoms that run along \( c \) in the midst of the square antiprisms. In addition, to compensate for the

Fig. 11.11
The incommensurate composite structure of bismuth-III

Partial structure 1
Space group \( I4/mcm \)
\[ a = b = 851.8 \text{ pm} \]
\[ c_1 = 416.4 \text{ pm} \]
\[ c_1/c_2 = 1.309 \]
(at 6.8 GPa)

Partial structure 2
Space group \( I4/mmm \)
\[ a = b = 851.8 \text{ pm} \]
\[ c_2 = 318.0 \text{ pm} \]
differing distances between the atoms of the chains and the surrounding antiprisms, both partial structures are incommensurately modulated. The atoms of the chains are slightly displaced along $c$, those of the antiprisms perpendicular to $c$.

As a summary, one can state the following tendencies: the larger the atomic number, the lower is the pressure needed to attain a typically metallic structure. Intermediate between the non-metallic and the metallic structures, peculiar structures appear that cannot be integrated in the common chemical models.

11.5 Carbon

Graphite is the modification of carbon which is stable under normal conditions. It has a structure consisting of planar layers (Fig. 11.12). Within the layer each C atom is bonded covalently with three other C atoms. Every atom contributes one $p$ orbital and one electron to the delocalized $\pi$ bond system of the layer. This constitutes a half-filled band, so we have a metallic state with two-dimensional electrical conductivity. Between the layers weak van der Waals forces are the essential attractive forces. The bonds within the layers have a length of 142 pm and the distance from layer to layer is 335 pm. The high electric conductivity therefore only exists parallel to the layers, and not perpendicular to them. The layers are stacked in a staggered manner; half of the atoms of one layer are situated exactly above atoms of the layer below, and the other half are situated over the ring centers (Fig. 11.12). Three layer positions are possible, $A$, $B$ and $C$. The stacking sequence in normal (hexagonal) graphite is $ABAB\ldots$, but frequently a more or less statistical layer sequence is found, in which regions of the predominating sequence $ABAB\ldots$ are separated by regions with the sequence $ABC$. This is called a one-dimensional disorder, i.e. within the layers the atoms are ordered, but in the direction of stacking the periodic order is missing.

Graphite forms intercalation compounds with alkali metals. They have compositions such as LiC$_6$, LiC$_{12}$, LiC$_{18}$ or KC$_8$, KC$_{24}$, KC$_{36}$, KC$_{48}$. Depending on the metal content they have colors extending from a golden luster to black. They are better electric conductors than graphite. The alkali metal ions are intercalated between every pair of graphite layers in KC$_8$ (first stage intercalation), between every other pair in KC$_{24}$ (second stage) etc. (Fig. 11.13). The metal atoms turn over their valence electrons to the valence band of the graphite. The possibility of the reversible electrochemical intercalation of Li$^+$ ions into graphite in varying amounts is taken advantage of in the electrodes of lithium ion batter-

![Fig. 11.12](#)  
Structure of graphite (stereo image)  
R  
L
**Fig. 11.13**

Left: arrangement of the K\(^+\) ions relative to an adjacent graphite layer in KC\(_8\); in KC\(_{24}\) a K\(^+\) ion layer only contains two thirds as many ions, they are disordered and highly mobile.

Right: stacking sequence of graphite layers and K\(^+\) ions in KC\(_8\) and KC\(_{24}\)

A different kind of intercalation compound is those with metal chlorides MCl\(_n\) (M = nearly all metals; n = 2 to 6) and some fluorides and bromides. The intercalated halide layers have structures that essentially correspond to the structures in the pure compounds; for example, intercalated FeCl\(_3\) layers have the same structure as in pure FeCl\(_3\), as shown on the front cover.

Carbon in its different forms such as pit-coal, coke, charcoal, soot etc., is in principle graphite-like, but with a low degree of ordering. It can be microcrystalline or amorphous; OH groups and possibly other atom groups are bonded at the edges of the graphite layer fragments. Many species of carbon have numerous pores and therefore have a large inner surface; for this reason they can adsorb large quantities of other substances and act as catalysts. In this respect crystalline graphite is less active. Carbon fibers that can be made, for example, by pyrolysis of polycrylonitrile fibers, consist of graphite layers that are oriented parallel to the fiber direction.

**Fullerenes** are modifications of carbon that consist of cage-like molecules. They can be obtained by setting up an electric arc between two graphite electrodes in a controlled atmosphere of helium and condensing the evaporated carbon, and then recrystallizing it from magenta-colored benzene solution. The main product is the fullerene C\(_{60}\), called buckminsterfullerene. The C\(_{60}\) molecule has the shape of a soccer ball, consisting of 12 pentagons and 20 benzene-like hexagons (Fig. 11.14). Second in yield from this preparation is C\(_{70}\), which has 12 pentagons and 25 hexagons and a shape reminiscent of a peanut. Cages with other sizes can also be produced, but they are less stable (they may have any even number of C atoms, beginning at C\(_{32}\)). Independent of its size, a fullerene molecule always has twelve pentagons.

In crystalline C\(_{60}\) the molecules have a face-centered cubic arrangement, i.e. they are packed as in a cubic closest-packing of spheres; as they are nearly spherical, the molecules spin in the crystal. The crystals are as soft as graphite. Similar to the intercalation com-
In the compound R$_3$C$_6$, potassium atoms can be enclosed; they occupy the cavities between the C$_{60}$ balls. With all cavities occupied (tetrahedral and octahedral interstices if the C$_{60}$ balls are taken as closest-packed spheres), the composition is K$_3$C$_{60}$. This compound has metallic properties and becomes superconducting when cooled below 18 K. Even more potassium can be intercalated; in K$_6$C$_{60}$ the C$_{60}$ molecules have a body-centered cubic packing.

**Carbon nanotubes** can be made from graphite in an electric arc or by laser ablation. These tubes are tangled. Catalyzed pyrolysis of gaseous hydrocarbons at temperatures of 700 to 1100 °C is a method to produce ordered arrays of carbon nanotubes on appropriate carrier materials. For example, single-walled nanotubes with a diameter of 1.4 nm are obtained by pyrolysis of acetylene in the presence of ferrocene at 1100 °C; pyrolysis of benzene in the presence of Fe(CO)$_5$ yields multi-walled nanotubes. Nanotubes consist of bent graphite-like layers; they can be as long as 0.1 mm (Fig. 11.15). As a rule, the tubes are closed at their ends by half a fullerene sphere; these caps can be removed with ultrasound in a suspension of a strong acid. The six-membered rings can have different orientations relative to the tube axis (Fig. 11.15); this has influence on the electric conductivity. Multilayered nanotubes consist of tubes arranged concentrically around each other.

The structures of diamond, silicon, germanium and tin are discussed in Chapter 12.
11.6 Boron

Boron is as unusual in its structures as it is in its chemical behavior. Sixteen boron modifications have been described, but most of them have not been well characterized. Many samples assumed to have consisted only of boron were possibly boron-rich borides (many of which are known, e.g. YB$_{66}$). An established structure is that of rhombohedral $\alpha$-B$_{12}$ (the subscript number designates the number of atoms per unit cell). The crystal structures of three further forms are known, tetragonal $\alpha$-B$_{50}$, rhombohedral $\beta$-B$_{105}$ and rhombohedral $\beta$-B$_{320}$, but probably boron-rich borides were studied. $\alpha$-B$_{50}$ should be formulated B$_{48}$X$_2$. It consists of B$_{12}$ icosahedra that are linked by tetrahedrally coordinated X atoms. These atoms are presumably C or N atoms (B, C and N can hardly be distinguished by X-ray diffraction).

The outstanding building unit in all modifications of boron that have been described is the B$_{12}$ icosahedron, which also is present in the anionic closo-borane B$_{12}$H$_{12}^-$. The twelve atoms of an icosahedron are held together by multicenter bonds; according to MO theory, 13 bonding orbitals occupied by 26 electrons should be present; 10 valence electrons are left over. In the B$_{12}$H$_{12}^-$ ion 14 additional electrons are present (12 from the H atoms, 2 from the ionic charge), which amounts to a total of 24 electrons or 12 electron pairs; these are used for the 12 covalent B–H bonds that are oriented radially outwards from the icosahedron. In elemental boron the B$_{12}$ icosahedra are linked with one another by such radial bonds, but for 12 bonds only 10 valence electrons are available; therefore, not all of them can be normal two-center two-electron bonds.

In $\alpha$-B$_{12}$ the icosahedra are arranged as in a cubic closest-packing of spheres (Fig. 11.16). In one layer of icosahedra every icosahedron is surrounded by six other icosahedra that are linked by three-center two-electron bonds. Every boron atom involved contributes an average of $\frac{2}{3}$ electrons to these bonds, which amounts to $\frac{2}{3} \cdot 6 = 4$ electrons per icosahedron. Every icosahedron is surrounded additionally by six icosahedra of the two adjacent layers, to which it is bonded by normal B–B bonds; this requires 6 electrons per icosahedron. In total, this adds up exactly to the above-mentioned 10 electrons for the inter-icosahedron bonds.
Fig. 11.16
Structure of rhombohedral \( \alpha \)-B\(_{12} \). The icosahedra in the layer section shown are connected with each other by 3e2e-bonds. One icosahedron of the next layer is shown.
12 Diamond-like Structures

12.1 Cubic and Hexagonal Diamond

Diamond, silicon, germanium and (gray) α-tin (stable below 13 °C) are isotypic. Diamond consists of a network of carbon atoms with four covalent bonds per atom. Starting from a layer of gray arsenic (cf. Fig. 11.7), all As atoms can be thought of as being substituted by C atoms; each of these can participate in a fourth bond that is oriented perpendicular to the layer. Relative to any one of the chair conformation rings of the layer the bonds within the layer take equatorial positions; the remaining bonds correspond to axial positions that are directed alternately upwards and downwards from the layer. In graphite fluoride (CF)$_x$ every axial position is occupied by a fluorine atom. In diamond the axial bonds serve to link the layers with each other (Fig. 12.1). Thereby new six-membered rings are formed that can have either a chair or a boat conformation, depending on how the joined layers are positioned relative to each other. If in projection the layers are staggered, then all resulting rings have a chair conformation; this is the arrangement in normal, cubic diamond. In hexagonal diamond the layers in projection are eclipsed, and the new rings have a boat conformation. Hexagonal diamond occurs very seldom as the mineral lonsdaleite; it has been found in meteorites.

The unit cell of cubic diamond corresponds to a face-centered packing of carbon atoms. Aside from the four C atoms in the vertices and face centers, four more atoms are present in the centers of four of the eight octants of the unit cell. Since every octant is a cube having four of its eight vertices occupied by C atoms, an exact tetrahedral coordination results for the atom in the center of the octant. The same also applies to all other atoms — they are all symmetry-equivalent. In the center of every C–C bond there is an inversion center. As in alkanes the C–C bonds have a length of 154 pm and the bond angles are 109.47°.

12.2 Binary Diamond-like Compounds

By substituting alternately the carbon atoms in cubic diamond by zinc and sulfur atoms, one obtains the structure of zinc blende (sphalerite). By the corresponding substitution in hexagonal diamond, the wurtzite structure results. As long as atoms of one element are allowed to be bonded only to atoms of the other element, binary compounds can only have a 1:1 composition. For the four bonds per atom an average of four electrons per atom are needed; this condition is fulfilled if the total number of valence electrons is four times the number of atoms. Possible element combinations and examples are given in Table 12.1.
Fig. 12.1
Structure of cubic (left) and hexagonal (right) diamond. Top row: connected layers as in α-As. Central row: the same layers in projection perpendicular to the layers. Bottom: unit cells; when the light and dark atoms are different, this corresponds to the structures of zinc blende (sphalerite) and wurtzite, respectively.

Table 12.1: Possible element combinations for the ZnS structure types

<table>
<thead>
<tr>
<th>combination</th>
<th>examples, zinc blende type</th>
<th>examples, wurtzite type</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV IV</td>
<td>β-SiC</td>
<td>SiC</td>
</tr>
<tr>
<td>III V</td>
<td>BP, GaAs, InSb</td>
<td>AlN, GaN</td>
</tr>
<tr>
<td>II VI</td>
<td>BeS, CdS, ZnSe</td>
<td>BeO, ZnO, CdS (high temp.)</td>
</tr>
<tr>
<td>I VII</td>
<td>CuCl, CuBr, AgI</td>
<td>CuCl (high temp.), β-AgI</td>
</tr>
</tbody>
</table>

The GRIMM–SOMMERFELD rule is valid for the bond lengths: if the sum of the atomic numbers is the same, the interatomic distances are the same. For example:

\[
\begin{align*}
\text{MX} & \quad Z(M) + Z(X) & \quad d(M-X) \\
\text{GeGe} & \quad 32 + 32 = 64 & \quad 245.0 \text{ pm} \\
\text{GaAs} & \quad 31 + 33 = 64 & \quad 244.8 \text{ pm} \\
\text{ZnSe} & \quad 30 + 34 = 64 & \quad 244.7 \text{ pm} \\
\text{CuBr} & \quad 29 + 35 = 64 & \quad 246.0 \text{ pm}
\end{align*}
\]

The sections of the structures of zinc blende and wurtzite shown in Fig. 12.2 correspond to the central row of Fig. 12.1 (projections perpendicular to the arsenic-like layers).
Behind every sulfur atom there is a zinc atom bonded to it the direction of view. The zinc atoms within one of the arsenic-like layers are in one plane and form a hexagonal pattern (dotted in Fig. 12.2); the same applies to the sulfur atoms on top of them. The position of the pattern is marked by an A. In wurtzite the hexagonal pattern of the following atoms is staggered relative to the first pattern; the atoms of this position B are placed over the centers of one half of the dotted triangles. Atoms over the centers of the remaining triangles (position C) do not occur in wurtzite, but they do occur in zinc blende. If we designate the positions of the planes containing the Zn atoms by A, B, and C, respectively, and the corresponding planes of the S atoms by $\alpha$, $\beta$, and $\gamma$, then the following stacking sequences apply to the planes:

- Zinc blende: $A\alpha B\beta C\gamma \ldots$
- Wurtzite: $A\alpha B\beta \ldots$

Other stacking sequences than these are also possible, for example $A\alpha B\beta A\alpha C\gamma \ldots$ or statistical sequences without periodic order. More than 70 stacking varieties are known for silicon carbide, and together they are called \( \alpha \)-SiC. Structures that can be considered as stacking variants are called polytypes. We deal with them further in the context of closest-sphere packings (Chapter 14).

Several of the binary diamond-like compounds have industrial applications because of their physical properties. They include silicon carbide and cubic boron nitride (obtainable from graphite-like BN under pressure at 1800 °C); they are almost as hard as diamond and serve as abrasives. SiC is also used to make heating devices for high-temperature furnaces as it is a semiconductor with a sufficiently high conductivity at high temperatures, but also is highly corrosion resistant and has a low thermal expansion. Yellow CdS and red CdSe are excellent color pigments, and ZnS is used as a luminophore in cathode ray displays. The III–V compounds are semiconductors with electric properties that can be adapted by variation of the composition and by doping; light-emitting diodes and photovoltaic cells are made on the basis of GaAs.

### 12.3 Diamond-like Compounds under Pressure

The diamond-type structure of \( \alpha \)-tin is stable at ambient pressure only up to 13 °C; above 13 °C it transforms to \( \beta \)-tin (white tin). The transition $\alpha$-$\text{Sn} \rightarrow \beta$-$\text{Sn}$ can also by achieved below 13 °C by exerting pressure. Silicon and germanium also adopt the structure of \( \beta \)-Sn at higher pressures. The transformation involves a considerable increase in density (for Sn +21%). The \( \beta \)-Sn structure evolves from the $\alpha$-Sn structure by a drastic compression
in the direction of one of the edges of the unit cell (Fig. 12.3). In this way two atoms that previously were further away in the direction of the compression become neighbors to an atom; together with the four atoms that were already adjacent in $\alpha$-Sn, a coordination number of 6 results. The regular coordination tetrahedron of $\alpha$-Sn is converted to a flattened tetrahedron with Sn–Sn distances of 302 pm; the two atoms above and below the flattened tetrahedron are at a distance of 318 pm. These distances are longer than in $\alpha$-Sn (281 pm). Although $\beta$-Sn forms from $\alpha$-Sn by the action of pressure and has a higher density, the transformation involves an increase of the interatomic distances.

Generally, the following rules apply for pressure-induced phase transitions:

**Pressure–coordination rule** by A. Neuhaus: *with increasing pressure an increase of the coordination number takes place.*

**‘Pressure–distance paradox’** by W. Kleber: *When the coordination number increases according to the previous rule, the interatomic distances also increase.*

Further examples where these rules are observed are as follows. Under pressure, some compounds with zinc blende structure, such as AlSb and GaSb, transform to modifications that correspond to the $\beta$-Sn structure. Others, such as InAs, CdS, and CdSe, adopt the NaCl structure when compressed, and their atoms thus also attain coordination number 6. Graphite (c.n. 3, C–C distance 141.5 pm, density 2.26 g cm$^{-3}$) $\rightarrow$ diamond (c.n. 4, C–C 154 pm, 3.51 g cm$^{-3}$).

The rules are also reflected in the behavior of silicon and germanium at even higher pressures. Fig. 12.4 shows which other structure types are observed. Silicon adopts a complicated variety of structures at high pressures. However, in general, the higher the...
Table 12.2: High-pressure modifications of silicon

<table>
<thead>
<tr>
<th>structure type</th>
<th>c.n.: d/ pm(^d)</th>
<th>range of stability</th>
<th>space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-I diamond</td>
<td>4: 235</td>
<td>&lt; 10.3 GPa</td>
<td>Fd(\bar{3}m)</td>
</tr>
<tr>
<td>Si-II β-Sn</td>
<td>6: 248</td>
<td>10.3 – 13.2 GPa</td>
<td>I(<em>4)</em>/amd</td>
</tr>
<tr>
<td>Si-XI</td>
<td>6 + 2: 253</td>
<td>13.2 – 15.6 GPa</td>
<td>Imma</td>
</tr>
<tr>
<td>Si-V hexagonal-primitive</td>
<td>8: 251</td>
<td>15.6 – 38 GPa</td>
<td>P6(_3/mmm)</td>
</tr>
<tr>
<td>Si-VI</td>
<td>10: 248; 11: 249</td>
<td>38 – 42 GPa</td>
<td>Cmce</td>
</tr>
<tr>
<td>Si-VII Mg(^{**})</td>
<td>12: 248</td>
<td>42 – 79 GPa</td>
<td>P6(_3/mmc)</td>
</tr>
<tr>
<td>Si-X Cu(^\dagger)</td>
<td>12: 248</td>
<td>&gt; 79 GPa</td>
<td>Fm(\bar{3}m)</td>
</tr>
</tbody>
</table>

\(^{\dagger}\) c.n. = coordination number, \(d\) = mean value of the bond lengths
** hexagonal closest-packing of spheres
\(^\dagger\) cubic closest-packing of spheres

pressure, the higher is the coordination number of the atoms (Table 12.2). At very high pressures the pressure–distance paradox becomes nearly imperceptible.

Si-XI, which is the next modification formed under pressure after Si-II, can be described as a compressed variant of the β-tin type. The structure is compressed in the direction of one of the diagonals of the \(a\–b\) plane. As a consequence, the two bonds drawn as open bonds in Fig. 12.3 are shortened to 275 pm, whereas the other six bonds approximately keep their lengths. The coordination polyhedron is a distorted hexagonal bipyramid (Si-XI, Fig. 12.5). From this, with further increase in pressure, an undistorted hexagonal bipyramid results in a simple, hexagonal-primitive structure (Si-V, Fig. 12.6). Then, a major rearrangement follows at 38 GPa. In the Si-VI structure obtained one can discern two kinds of alternating layers. One kind of layer has a slightly corrugated square pattern with atoms of coordination number 10; the other kind of layer consists of squares and rhombs and has atoms of coordination number 11 (layers at \(x = \frac{1}{2}\) and \(x = 1\), Fig. 12.6). Finally, at the highest pressures, silicon forms closest packings of spheres with atoms of coordination number 12.

In addition, silicon adopts a number of metastable structures that can be obtained, depending on pressure, by rapid release of the pressure: from Si-II, Si-XII is formed, and from this Si-III; upon heating, Si-III transforms to the hexagonal diamond structure (Si-IV). Si-III has a peculiar structure with a distorted tetrahedral coordination of its atoms. The atoms are arranged to interconnected right- and left-handed helices (Fig. 12.7). The structure being cubic, the helices run in the directions \(a\), \(b\) as well as \(c\). Si-VIII and Si-IX

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Fig. 12.5

Change of the coordination polyhedron of a silicon atom at increasing pressures; same perspective as for the atom in the dashed octant of Fig. 12.3. Si–Si distances in pm

Si-II, 12 GPa
Si-XI, 15 GPa
Si-V, 20 GPa
12.4 Polynary Diamond-like Compounds

Fig. 12.6
Hexagonal-primitive packing of Si-V; one unit cell is outlined. Si-VI; only atomic contacts within the layers parallel to the \( b-c \) plane have been drawn; Numbers: \( x \) coordinates

Fig. 12.7
The metastable cubic structures of Si-III and Ge-IV (stereo image)

are obtained from Si-XI upon sudden release of pressure. All high-pressure modifications of silicon are metallic.

Germanium forms the same kinds of modifications as silicon at similar conditions (Fig. 12.4). Tin, however, does not exhibit this diversity; \( \beta \)-tin transforms to a body-centered cubic packing of spheres at 45 GPa. Lead already adopts a cubic closest-packing of spheres at ambient pressure.

12.4 Polynary Diamond-like Compounds

Of the numerous ternary and polynary diamond-like compounds we deal only with those that can be considered as superstructures of zinc blende. A superstructure is a structure that, while having the same structural principle, has an enlarged unit cell. When the unit cell of zinc blende is doubled in one direction (\( c \) axis), different kinds of atoms can occupy the doubled number of atomic positions. All the structure types listed in Fig. 12.8 have the tetrahedral coordination of all atoms in common, except for the variants with certain vacant positions.

\( \text{CuFeS}_2 \) (chalcopyrite) is one of the most important copper minerals. Red \( \beta \)-\( \text{Cu}_2\text{HgI}_4 \) and yellow \( \beta \)-\( \text{Ag}_2\text{HgI}_4 \) (CdGa\(_2\)S\(_4\) type) are thermochromic: they transform at 70 °C and 51 °C, respectively, to modifications having different colors (black and orange); in these the atoms and the vacancies have a disordered distribution.

Aside from the superstructures mentioned, other superstructures with other enlargement factors for the unit cell are known, as well as superstructures of wurtzite. Defect structures,
i.e. structures with vacancies, are known with ordered and disordered distributions of the vacancies. \( \gamma \)-Ga\(_2\)S\(_3\), for example, has the zinc blende structure with statistically only two thirds of the metal positions occupied by Ga atoms.

### 12.5 Widened Diamond Lattices. SiO\(_2\) Structures

Take elemental silicon (diamond structure) and insert an oxygen atom between every pair of silicon atoms; in this way, every Si–Si bond is replaced by an Si–O–Si group and every Si atom is surrounded tetrahedrally by four O atoms. The result is the structure of cristobalite. The SiO\(_4\) tetrahedra are all linked by common vertices. As there are twice as many Si–Si bonds than Si atoms in silicon, the composition is SiO\(_2\). Cristobalite is one of the polymorphic forms of SiO\(_2\); it is stable between 1470 and 1713 \( \text{AE} \) and is metastable at lower temperatures. It occurs as a mineral. The oxygen atoms are situated to the side of the Si···Si connecting lines, so that the Si–O–Si bond angle is 147°. The structure model shown in Fig. 12.9, left side, however, is only a snapshot. Above 250 °C the tetrahedra perform coupled tilting vibrations that on average result in a higher symmetry, with O atoms exactly on the Si–Si connecting lines (Fig. 12.9, right); the large ellipsoids show the vibration. When cooled below \( \sim \)240 °C the vibrations ‘freeze’ (\( \rightarrow \) \( \alpha \)-cristobalite; the \( \alpha \) \( \rightarrow \) \( \beta \) transition temperature depends on the purity of the sample).

The insertion of the oxygen atoms widens the silicon lattice considerably. A relatively large void remains in each of the four vacant octants of the unit cell. In natural cristobalite they usually contain foreign ions (mainly alkali and alkaline earth metal ions) that probably stabilize the structure and allow the crystallization of this modification at temperatures far below the stability range of pure cristobalite. To conserve electrical neutrality, probably one Si atom per alkali metal ion is substituted by an Al atom. The substitution of Si

\[ ^* \text{Al and Si can hardly be distinguished by X-ray structure analysis owing to the nearly equal number of electrons} \]
12.5 Widened Diamond Lattices. SiO₂ Structures

by Al atoms in an SiO₂ framework with simultaneous inclusion of cations in voids is a very common phenomenon; silicates of this kind are called aluminosilicates. The mineral carnegieite, Na[AlSiO₄], has a cristobalite structure in which half of the Si atoms have been substituted by Al atoms and all voids have been occupied by Na⁺ ions. The Loewenstein rule has been stated for aluminosilicates: AlO₄ tetrahedra tend not to be linked directly with each other; the group Al–O–Al is avoided.

Tridymite is another form of SiO₂ which is stable between 870 and 1470 °C, but it can also be maintained in a metastable state at lower temperatures and occurs as a mineral. Its structure can be derived from that of hexagonal diamond in the same way as that of cristobalite from cubic diamond. In this case the oxygen atoms are also situated to the side of the Si⋯Si connecting lines and the Si–O–Si bond angles are approximately 150°. At temperatures below 380 °C several variants occur that differ in the kind of mutual tilting of the SiO₄ tetrahedra. Tridymite also encloses larger voids that can be occupied by alkali or alkaline earth ions. The anionic framework of some aluminosilicates corresponds to the tridymite structure, for example in nepheline, Na₃K[AlSiO₄]₄.

Quartz is the modification of SiO₂ that is stable up to 870 °C, with two slightly different forms, α-quartz occurring below and β-quartz above 573 °C. We discuss the quartz structure here, although it cannot be derived from one of the forms of diamond. Nevertheless, quartz also consists of a network of SiO₄ tetrahedra sharing vertices, but with smaller voids than in cristobalite and tridymite (this is manifested in the densities: quartz 2.65, cristobalite 2.33, tridymite 2.27 g cm⁻³). As shown in Fig 12.10, the tetrahedra form helices, and in a given crystal these are all either right-handed or left-handed. Right-handed and left-handed quartz can also be intergrown in a well-defined manner, forming twinned crystals (‘Brazilian twins’). Due to the helical structure quartz crystals are optically active and have piezoelectric properties (Section 19.2). Quartz crystals are produced industrially by hydrothermal synthesis. For this purpose quartz powder is placed in one end of a closed vial at 400 °C, while a seed crystal is placed at the opposite end at 380 °C; the vial is filled with an aqueous alkaline solution that is maintained liquid by a pressure of 100 MPa. The quartz powder slowly dissolves while the seed crystal grows.

The phase diagram for SiO₂ is shown in Fig. 12.11. The transition between α- and β-quartz only requires minor rotations of the SiO₄ tetrahedra, the linkage pattern remaining unaltered (Fig. 18.9, p. 224); this transition takes place rapidly. The other transitions, on the other hand, require a reconstruction of the structure, Si–O bonds beinguntied and rejoined; they proceed slowly and thus render possible the existence of the metastable mod-
The structure of $\alpha$-quartz, space group $P\overline{3}21$. Only SiO$_4$ tetrahedra are shown. Numbers designate the heights of the Si atoms in the tetrahedron centers as multiples of $\frac{1}{3}$ of the unit cell height. The symbols $\uparrow$ for 3$_2$ screw axes mark the axes of the helical chains. The slight tilting of the tetrahedra relative to the direction of view (c axis) vanishes in $\beta$-quartz (stereo image).

Coesite and stishovite are stable only at high pressures, but they are metastable at ambient temperature and pressure. Coesite also consists of a framework of SiO$_4$ tetrahedra sharing vertices. Stishovite, however, has the rutile structure, i.e. silicon atoms having coordination number 6. Further metastable modifications are quartz glass (supercooled melt), moganite, keatite and fibrous SiO$_2$ with the SiS$_2$ structure (Fig. 16.27, p. 189).

Further compounds that occur with the structure types of SiO$_2$ are H$_2$O and BeF$_2$. Ice normally crystallizes in the hexagonal tridymite type (ice I$_h$), the oxygen atoms occupying the Si positions of tridymite while the hydrogen atoms are placed between two oxygen atoms each. An H atom is shifted towards one of the O atoms so that it belongs to one H$_2$O molecule and participates in a hydrogen bridge to another H$_2$O molecule. Metastable ice I$_c$ crystallizes from the gas phase at temperatures below $-140^\circ$C; it has a cubic structure like cristobalite. Eleven further modifications can be obtained under pressure, some of

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**Fig. 12.11**
Phase diagram for SiO$_2$. In addition, modifications of the $\alpha$-PbO$_2$ and CaCl$_2$ type occur at pressures above 35 MPa.
which correspond to other SiO₂ modifications (e.g. keatite; see the phase diagram of H₂O, Fig. 4.3, p. 35).

In the same way as the zinc blende structure is derived from diamond by the alternating substitution of C atoms by Zn and S atoms, the Si atoms in the SiO₂ structures can be substituted alternately by two different kinds of atoms. Examples include AlPO₄, MnPO₄, and ZnSO₄. The cristobalite and tridymite structures with filled voids also are frequently encountered. Examples in addition to the above-mentioned aluminosilicates Na[AlSiO₄] and Na₂K[Al₂SiO₇] are K[FeO₂] and MILLON’s base, [NH₄]⁺OH⁻⋅H₂O.

The large voids in the network of cristobalite can also be filled in another way, namely by a second network of the same kind that interpenetrates the first. Cuprite, Cu₂O, has this structure. Take a cristobalite structure in which the Si positions are occupied by O atoms that are linked via Cu atoms having coordination number 2. As the bond angle at a Cu atom is 180°, the packing density is even less than in cristobalite itself. Two exactly equal networks of this kind interpenetrate each other, one being shifted against the other (Fig. 12.12). The two networks ‘float’ one within the other; there are no direct bonds between them. This kind of a structure is possible when tetrahedrally coordinated atoms are held at a distance from each other by linear linking groups like −Cu− or −Ag− (in isotypic Ag₂O). Cyanide groups between tetrahedrally coordinated zinc atoms, Zn–CN−Zn, act in the same way as spacers in Zn(CN)₂, which has the same structure as Cu₂O (with metal atom positions interchanged with the anion positions).

**Fig. 12.12**
The structure of Cu₂O (cuprite). Eight unit cells are shown; they correspond to one unit cell of cristobalite if only one of the two networks is present. The gray network has no direct bonds to the black network (stereo image).

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### 12.6 Problems

12.1 The bond length in β-SiC is 188 pm. For which of the following compounds would you expect longer, shorter or the same bond lengths?
- BeO, BeS, BN, BP, AlN, AlP.

12.2 Stishovite is a high-pressure modification of SiO₂ having the rutile structure. Should it have longer or shorter Si–O bond lengths than quartz?

12.3 Whereas AgCl has the NaCl structure, AgI has the zinc blende structure. Could you imagine conditions under which both compounds would have the same structure?

12.4 What is the coordination number of the iodine atoms in β-Cu₂HgI₄?

12.5 If well-crystallized Hg₂C could be made, what structure should it have?
13 Polyanionic and Polycationic Compounds. Zintl Phases

The compounds dealt with first in this chapter belong to the normal valence compounds; these are compounds that fulfill the classical valence concept of stable eight-electron shells. They include not only the numerous molecular compounds of nonmetals, but also compounds made up of elements from the left side with elements from the right side of the ZINTL line. The ZINTL line is a delimiting line that runs in the periodic table of the elements between the third and the fourth main groups. According to the classical concepts, such compounds consist of ions, for example NaCl, K2S, Mg2Sn, Ba3Bi2. Judging by the composition, however, in many cases the octet rule seems to be violated as, for example, in CaSi2 or NaP. This impression is erroneous: the octet rule is still being fulfilled; the formation of covalent bonds renders it possible. In CaSi2 the Si atoms are joined in layers as in gray arsenic (Si and As are isoelectronic), and in NaP the phosphorus atoms form helical chains analogous to polymeric sulfur (P and S are isoelectronic). Whether a compound fulfills the octet rule can only be decided when its structure is known.

13.1 The Generalized 8–N Rule

The octet principle can be expressed as a formula by the generalized 8–N rule according to E. Moosler & W. B. Pearson. We restrict our considerations to binary compounds, and presuppose the following:

1. Let X be an element of the fourth to seventh main groups of the periodic table, i.e. an element that tends to attain the electronic configuration of the following noble gas by taking up electrons (the heavy elements of the third main group may also be included). An X atom has \( e(X) \) valence electrons.

2. The electrons needed to fill up the electron octet at X are supplied by the more electropositive element M. An M atom has \( e(M) \) valence electrons.

The composition being \( M_mX_x \), \( 8x \) electrons are required in order to achieve the octet shells for the \( x \) X atoms:

\[
m \cdot e(M) + x \cdot e(X) = 8x
\]  
(13.1)

If covalent bonds exist between M atoms, then not all of the \( e(M) \) electrons of M can be turned over to X, and the number \( e(M) \) in equation (13.1) must be reduced by the number \( b(MM) \) of covalent bonds per M atom. If the M atoms retain nonbonding electrons (lone electron pairs as for Ti\(^{4+}\)), then \( e(M) \) must also be reduced by the number \( E \) of these electrons. On the other hand, the X atoms require fewer electrons if they take part in covalent bonds with each other; the number \( e(X) \) can be increased by the number \( b(XX) \) of covalent bonds per X atom:

\[
m[e(M) - b(MM) - E] + x[e(X) + b(XX)] = 8x
\]  
(13.2)
13.1 The Generalized $8 - N$ Rule

By rearrangement of this equation we obtain:

$$\frac{m \cdot e(M) + x \cdot e(X)}{x} = 8 + \frac{m[b(MM) + E] - x \cdot b(XX)}{x}$$  \hspace{1cm} (13.3)$$

We define the valence electron concentration per anion, $\text{VEC}(X)$, as the total number of all valence electrons in relation to the number of anionic atoms:

$$\text{VEC}(X) = \frac{m \cdot e(M) + x \cdot e(X)}{x}$$  \hspace{1cm} (13.4)$$

By substituting equation (13.3) into equation (13.4) and solving for $b(XX)$ we obtain:

$$b(XX) = 8 - \text{VEC}(X) + \frac{m}{x}[b(MM) + E]$$  \hspace{1cm} (13.5)$$

Equation (13.5) represents the generalized $8 - N$ rule. Compared to the simple $8 - N$ rule (p. 62), it is enlarged by the term $\frac{m}{x}[b(MM) + E]$, and $\text{VEC}(X)$ has taken the place of the main group number $N$. The following specialized cases are of importance:

1. Elements. For pure elements that belong to the right side of the ZINTL line, we have $m = 0$, $\text{VEC}(X) = e(X) = N$, and equation (13.5) becomes:

$$b(XX) = 8 - \text{VEC}(X) = 8 - N$$  \hspace{1cm} (13.6)$$

This is none other than the simple $8 - N$ rule. For example, in sulfur ($N = 6$) the number of covalent bonds per S atom is $b(SS) = 8 - N = 2$.

2. Polyanionic compounds. Frequently, the $M$ atoms lose all their valence electrons to the $X$ atoms, i.e. no cation–cation bonds occur and no nonbonding electrons remain at the cations, $b(MM) = 0$ and $E = 0$. Equation (13.5) then becomes:

$$b(XX) = 8 - \text{VEC}(X)$$  \hspace{1cm} (13.7)$$

This once again is the $8 - N$ rule, but only for the anionic component of the compound. For example: $\text{Na}_2\text{O}_2$; $\text{VEC(O)} = 7$; $b(\text{OO}) = 8 - 7 = 1$, there is one covalent bond per O atom.

By comparing equations (13.6) and (13.7) we can deduce:

The geometric arrangement of the atoms in a polyanionic compound corresponds to the arrangement in the structures of the elements of the fourth to seventh main groups when the number of covalent bonds per atom $b(XX)$ is equal. According to this concept, put forward by E. ZINTL and further developed by W. KLEMM and E. BUSMANN, the more electronegative partner in a compound is treated like that element which has the same number of electrons. This statement is therefore a specialized case of the general rule according to which isoelectronic atom groups adopt the same kind of structures.

3. Polycationic compounds. Provided that no covalent bonds occur between the anionic atoms, $b(XX) = 0$, equation (13.5) becomes:

$$b(MM) + E = \frac{x}{m}[\text{VEC}(X) - 8]$$  \hspace{1cm} (13.8)$$

When applying this equation, note that for the calculation of $\text{VEC}(X)$ according to equation (13.4) all valence electrons have to be considered, including those that take part in $M$–$M$ bonds.

For example: $\text{Hg}_2\text{Cl}_2$; $e(\text{Hg}) = 2$; $\text{VEC(Cl)} = 9$; $b(\text{HgHg}) = 1$ [when the 10 $d$ electrons of an Hg atom are also considered as being valence electrons, then $\text{VEC(Cl)} = 19$, $E = 10$, $b(\text{HgHg}) = 1$].
4. Simple ionic compounds, *i.e.* compounds having no covalent bonds, \( b(\text{MM}) = b(\text{XX}) = E = 0 \). Equation (13.5) becomes:

\[
\text{VEC}(X) = 8
\]

which is the octet rule.

We now can classify compounds according to the values of VEC(X). Since \( b(\text{MM}), E \) and \( b(\text{XX}) \) cannot adopt negative values, VEC(X) in equation (13.7) must be smaller than 8, and in equation (13.8) it must be greater than 8. We thus deduce the criterion:

<table>
<thead>
<tr>
<th>VEC(X)</th>
<th>Polyanionic</th>
<th>Simple ionic</th>
<th>Polycationic</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt; 8)</td>
<td>Polyanionic</td>
<td>Simple ionic</td>
<td>Polycationic</td>
</tr>
<tr>
<td>(= 8)</td>
<td>Simple ionic</td>
<td>Simple ionic</td>
<td>Polycationic</td>
</tr>
<tr>
<td>(&gt; 8)</td>
<td>Polycationic</td>
<td>Simple ionic</td>
<td>Polycationic</td>
</tr>
</tbody>
</table>

As VEC(X) is easy to calculate according to equation (13.4), we can quickly estimate the kind of bonding in a compound, for example:

<table>
<thead>
<tr>
<th>Polycationic</th>
<th>Polyaniotic</th>
<th>Simple Ionic</th>
</tr>
</thead>
<tbody>
<tr>
<td>VEC(X)</td>
<td>VEC(X)</td>
<td>VEC(X)</td>
</tr>
<tr>
<td>Ti₂S</td>
<td>14</td>
<td>Ca₃Si₃</td>
</tr>
<tr>
<td>MoCl₂</td>
<td>10</td>
<td>Sr₂Sb₃</td>
</tr>
<tr>
<td>Cs₁₁O₃</td>
<td>9½</td>
<td>CaSi</td>
</tr>
<tr>
<td>GaSe</td>
<td>9</td>
<td>KGe</td>
</tr>
<tr>
<td>Mg₂Sn</td>
<td>8</td>
<td>Na₃P</td>
</tr>
<tr>
<td>Sr₂Sb₃</td>
<td>6½</td>
<td>InBi</td>
</tr>
<tr>
<td>Mg₂Sn</td>
<td>8</td>
<td>KGe</td>
</tr>
</tbody>
</table>

As we can see from the last entry in this table, we have deduced only a *rule*. In InBi there are Bi–Bi contacts and it has metallic properties. Further examples that do not fulfill the rule are LiPb (Pb atoms surrounded only by Li) and K₈Ge₄₆. In the latter, all Ge atoms have four covalent bonds; they form a wide-meshed framework that encloses the K⁺ ions (Fig. 16.26, p. 188); the electrons donated by the potassium atoms are not taken over by the germanium, and instead they form a band. In a way, this is a kind of a solid solution, with germanium as ‘solvent’ for K⁺ and ‘solvated’ electrons. K₈Ge₄₆ has metallic properties. In the sense of the \(8–N\) rule the metallic electrons can be ‘captured’: in K₈Ga₈Ge₃₈, which has the same structure, all the electrons of the potassium are required for the framework, and it is a semiconductor. In spite of the exceptions, the concept has turned out to be very fruitful, especially in the context of understanding the ZINTL phases.

### 13.2 Polyanionic Compounds, Zintl Phases

Table 13.1 lists some binary polyanionic compounds, arranged according to the valence electron concentration per anion atom. Only compounds with integral values for VEC(X) are listed. In agreement with the above-mentioned rule, in fact structures like those of pure elements with the corresponding numbers of valence electrons occur for the anionic components. However, the variety of structures is considerably larger than for the pure elements. For example, three-bonded atoms occur not only in the layer structures as in phosphorus and arsenic, but also in several other connection patterns (Fig. 13.1). This seems reasonable, since the anionic grid has to make allowance for the space requirements of the cations. CaSi₂, for example, has layers \((\text{Si}^-)_{\infty}\) as in arsenic; the Ca²⁺ ions are located between the layers. SrSi₂, however, has a network structure in which helical chains with fourfold screw symmetry are interconnected; each Si atom has three bonds. Under pressure, both CaSi₂ and SrSi₂ are transformed to the \(\alpha\)-ThSi₂ type, with yet another kind of network of three-bonded Si atoms. Contrary to expectations based on the \(8–N\) rule, the
Table 13.1: Examples of polyanionic compounds which have integral valence electron concentrations per anion atom

<table>
<thead>
<tr>
<th>Example</th>
<th>VEC(X)</th>
<th>b(XX)</th>
<th>structure of the anion part</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$S$_2$</td>
<td>7</td>
<td>1</td>
<td>S$_2^-$ pairs as in Cl$_2$</td>
</tr>
<tr>
<td>FeS$_2$</td>
<td>7</td>
<td>1</td>
<td>S$_2^-$ and AsS$_3^-$ pairs</td>
</tr>
<tr>
<td>NiP</td>
<td>7</td>
<td>1</td>
<td>P$_2^{4-}$ pairs</td>
</tr>
<tr>
<td>CaSi</td>
<td>6</td>
<td>2</td>
<td>zigzag chains</td>
</tr>
<tr>
<td>LiAs</td>
<td>6</td>
<td>2</td>
<td>helical chains</td>
</tr>
<tr>
<td>CoAs$_3$</td>
<td>6</td>
<td>2</td>
<td>four-membered As$_4^{4-}$ rings</td>
</tr>
<tr>
<td>InP$_3$</td>
<td>6</td>
<td>2</td>
<td>P$_6^{12-}$ rings (chair) as in S$_6$</td>
</tr>
<tr>
<td>CaSi$_2$</td>
<td>5</td>
<td>3</td>
<td>undulated layers as in α-As</td>
</tr>
<tr>
<td>SrSi$_2$</td>
<td>5</td>
<td>3</td>
<td>interconnected helical chains</td>
</tr>
<tr>
<td>K$_4$Ge$_4$</td>
<td>5</td>
<td>3</td>
<td>Ge$_4^{4-}$ tetrahedra as in P$_4$</td>
</tr>
<tr>
<td>CaC$_2$</td>
<td>5</td>
<td>3</td>
<td>C$_2^{2-}$ pairs as in N$_2$</td>
</tr>
<tr>
<td>NaTl</td>
<td>4</td>
<td>4</td>
<td>diamond-like</td>
</tr>
<tr>
<td>SrGa$_2$</td>
<td>4</td>
<td>4</td>
<td>graphite-like</td>
</tr>
</tbody>
</table>

Fig. 13.1
Sections of the structures of some polysilicides with three-bonded Si atoms. In the stereo image for SrSi$_2$, the positions of the 4$_3$ screw axes of the cubic space group $P4_332$ are shown.
Si atoms in α-ThSi₂ do not have pyramidal coordination, but planar coordination; in SrSi₂ the coordination is nearly planar. The Si atoms in the α-ThSi₂ type are located in the centers of trigonal prisms formed by the cations.

The calculation of VEC(X) for many compounds results in non-integral numbers. According to equation (13.7) fractional numbers then also result for the number b(XX) of covalent bonds. This happens when structurally different atoms occur in the anion. The following examples help to illustrate this:

Na₂S₃: with VEC(X) = \( \frac{22}{3} \) we obtain \( b(XX) = \frac{4}{3} \). This is due to the chain structure of the \( S^{2-}_3 \) ion. For the two terminal atoms we have \( b(XX) = 1 \), and for the central one \( b(XX) = 2 \); the average is \( (2 \times 1 + 2)/3 = \frac{4}{3} \). For unbranched chains with specific lengths as in polysulfides \( S^{2-}_n \), \( 6 < VEC(X) < 7 \) holds as long as no multiple bonds occur. When there are multiple bonds, \( VEC(X) \leq 6 \) is possible, e.g. \( VEC(N) = 5.33 \) for the azide ion, \( \text{N} = \text{N} = \text{N} \). Ba₃Si₄: VEC(X) = \( \frac{11}{7} \), \( b(XX) = \frac{5}{7} \). An average value of \( 2\frac{1}{2} \) covalent bonds per Si atom results when half of the Si atoms are bonded with two covalent bonds, and the other half with three covalent bonds. This corresponds to the real structure.

The number of negative charges of the anion can also be counted in the following way: an atom of the \( N \)-th main group that participates in \( 8-N \) covalent bonds obtains a formal charge of zero; for every bond less than \( 8-N \) it obtains a negative formal charge. A four-bonded silicon atom thus obtains a formal charge of 0, a three-bonded one obtains \( 1 \) and a two-bonded one obtains \( 2 \). The sum of all formal charges is equal to the ionic charge.*

Sometimes rather complicated structures occur in the anionic part of a structure. For example, approximately 50 different binary polyphosphides are known only for the alkali and alkaline earth metals, which, in part, also adopt different modifications. In addition, there are more than 120 binary polyphosphides of other metals. Fig. 13.2 conveys an impression of how manifold the structures are.

Apart from simple chains and rings, cages like those in sulfides such as \( \text{As}_4\text{S}_4 \) and \( \text{P}_2\text{S}_3 \) (and others) have been observed; every P atom that substitutes an S atom is to be taken as a \( \text{P}^\ominus \). Layer structures can be regarded as sections of the structures of black phosphorus or arsenic. Other structures correspond to fragments of the structure of fibrous red phosphorus. The diversity in polyarsenides, polyantimonides and polysilicides is just as complicated. In addition, several different kinds of anions can be present simultaneously. For example, \( \text{Ca}_2\text{As}_3 \) or rather \( \text{Ca}_8[\text{As}_4][\text{As}_8] \) contains unbranched chain-like \( \text{As}^{5-}_4 \) and \( \text{As}^{10-}_8 \) ions.

Atoms which are assigned negative formal charges in fact bear negative charges, as can be recognized in the overall structures; these atoms are those which are coordinated to the cations. For example, in \( \text{NaP}_3 \) there are four neutral P atoms for each \( \text{P}^\ominus \). The neutral atoms form ribbons of connected rings having chair conformation. The ribbons are interconnected by individual \( \text{P}^\ominus \) atoms (Fig. 13.2, bottom). Only these \( \text{P}^\ominus \) atoms are in close contact with the \( \text{Na}^+ \) ions.

Binary polyanionic compounds can frequently be synthesized directly from the elements. In some cases, intact cage-like anions can be extracted from the solids when a complexing ligand is offered for the cation. For example, the \( \text{Na}^+ \) ions of \( \text{Na}_5\text{Sn}_3 \) can be captured by cryptand molecules, giving \( \text{[NaCrypt}^+\text{]}_2\text{Sn}^{2-}_5 \). Cryptands like \( \text{N}(\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4)_3\text{N} \) enclose the alkali metal ion.

---

*The signs of formal charges should always be encircled, \( \ominus \) and \( \oplus \), and the signs of ionic charges should never be encircled.
13.2 Polyanionic Compounds, Zintl Phases

Fig. 13.2
Examples of the anionic structures in polyphosphides, polyarsenides and polyantimonides.
For comparison, recall the structures of red and black phosphorus and of arsenic (pp. 108, 109 and 110).
Stereo image for NaP₅

p⁴⁻ in Sr₂P₂
As₄⁴⁻ in CoAs₃
As₆⁻ in Sr₃As₄
(X⁻)ₙ in NaP, KAs, KSB
(P⁻)ₙ in KP₁₅
X₇⁻/₃ in Na₃P₇, Cs₃As₇
P₁₁⁻ in Na₃P₁₁
(X₂⁻)ₙ in CaP₃, SrAs₃

Stereo image for NaP₅
For some of the cage-like anions the kind of bonding is consistent with the preceding statements, but for some others they do not seem to apply. The ionic charges of As$_3^{3-}$ or P$_{11}^{3-}$ correspond exactly to the numbers of two-bonded P$^{2+}$ or As$^{3+}$ atoms (Fig. 13.2). For Sn$_5^{2-}$ this is not so clear. The 22 valence electrons of the Sn$_5^{2-}$ ion could be accommodated in exact agreement with the octet rule according to the formula given in the margin. However, calculations with the electron localization function show that lone electron pairs are also present at the equatorial atoms; therefore, only six electron pairs remain for the bonds. This corresponds to the number expected according to the WADE rules, as for boranes ($n + 1$ multibonded bonds in a $closo$ cluster with $n = 5$ vertices, cf. p. 144). We will deal with the bonding in such cluster compounds in Section 13.4.

**Zintl Phases**

Many of the compounds presented in the preceding paragraphs belong to the **Zintl phases**. This is a class of compounds consisting of an electropositive, cationic component (alkali metal, alkaline earth metal, lanthanoid) and an anionic component of main group elements of moderate electronegativity. The anionic part of the structure fulfills the simple concept of normal valence compounds. Nevertheless, the compounds are not salt-like, but have metallic properties, especially metallic luster. However, they are not ‘full-value’ metals; instead of being metallic-ductile, many of them are brittle. As far as the electrical properties have been studied, mostly semiconductivity has been found. There are many analogies with the half-metallic elements: in the structures of germanium, $\alpha$-tin, arsenic, antimony, bismuth, selenium and tellurium the $8–N$ rule can be discerned; although these elements can be considered to be normal valence compounds, they show metallic luster, but they are brittle and are semiconductors or moderate metallic conductors.

The classic example of a ZINTL phase is the compound NaTl which can be interpreted as Na$^+\cdot$Tl$^-\cdot$; its thallium partial structure has the diamond structure (Fig. 13.3). In NaTl the Tl–Tl bonds are significantly shorter than the contact distances in metallic thallium (324 instead of 343 pm, albeit with a reduced coordination number). Although the valence electron concentration is the same, the Ga$^-$ particles in SrGa$_2$ do not form a diamond-like structure, but layers as in graphite (AlB$_2$ type; AlB$_2$ itself does not fulfill the octet rule). MgB$_2$, which becomes superconducting below 39 K, has the same structure. All compounds listed in Table 13.1 with the exception of Li$_2$S$_2$ and CaC$_2$ are ZINTL phases (recall the golden luster of pyrite, FeS$_2$). The number of known ZINTL phases is enormous.
Polyanionic Compounds that do not Fulfill the Octet Rule

The generalized $8-N$ rule can hold only as long as the atoms of the more electronegative element fulfill the octet principle. Especially for the heavier non-metals it is quite common for this principle not to be fulfilled. The corresponding atoms are termed hypervalent. The polyhalides offer an example. Among these the polyiodides show the largest variety. They can be regarded as association products of $\text{I}_2$ molecules and $\text{I}^-$ ions, with a weakened bond in the $\text{I}_2$ molecules and a relatively weak bond between the $\text{I}_2$ and $\text{I}^-$ (Fig. 13.5). The structures fulfill the GILLESPIE–NYHOLM rules.
According to MO theory, a three-center four-electron bond accounts for the bonding. The central, hypervalent iodine atom in the $I^-_3$ ion has an $s$ orbital, two $p$ orbitals perpendicular to the molecular axis and one $p$ orbital in the molecular axis. The last-mentioned $p$ orbital interacts with the corresponding $p$ orbitals of the neighboring atoms. The situation is just as in the chain of atoms having $p$ orbitals joined head-on (Fig. 10.5, p. 93), but the chain consists of only three atoms. The result is one bonding, one nonbonding and one antibonding molecular orbital. Two electron pairs have to be placed in these three orbitals. The bonding orbital causes a bond between all three atoms, but it is relatively weak, since it must join three atoms. The two electron pairs correspond to the two bond lines in the valence-bond formula (Fig. 13.5). The valence-bond formula does not show that the bonds are weaker than normal single bonds (bond order $\frac{1}{2}$), but with the aid of the GILLESPIE–NYHOLM rules it yields the correct (linear) structure.

The GILLESPIE–NYHOLM rules usually can also be applied to other polyanionic compounds with hypervalent atoms. As an example, some polytellurides are depicted in Fig. 13.6. The $Te^{6-}_5$ ion is square like the $BrF_4^-$ ion.

In Li$_2$Sb we can assume $Sb^{2-}$ particles with seven valence electrons. Therefore, we expect $Sb^{2-}_2$ dumbbells (isoelectronic with $I_2$) and observance of the octet rule. In fact, such dumbbells are present in the structure (Sb–Sb bond length 297 pm); however, this applies only to half of the Sb atoms. The other half form linear chains of Sb atoms (Sb–Sb distance 326 pm). For the bonds in the chain we assume a band according to Fig. 10.5 (p. 93); every Sb atom contributes to this band with one $p$ orbital and one electron. With one electron per Sb atom the band is half-occupied, and therefore it is bonding. The
remaining six electrons occupy the $s$ orbital and the other two $p$ orbitals of the Sb atom and act as nonbonding lone electron pairs. In the mean we have one bonding electron per Sb–Sb bond, which corresponds to a bond order of $\frac{1}{2}$, just as in an $I_3^-$ ion. We draw the conclusion: **Seven valence electrons per atom are needed for a linear chain of main-group atoms.** To express this with a valence-bond formula, we can use bonding dots instead of bonding lines (this does not mean that there are unpaired electrons).

The GILLESPIE–NYHOLM rules can be applied with the aid of this formulation. The occurrence of both kinds of building blocks in Li$_2$Sb, chains and dumbbells, shows that in this case the PEIERLS distortion contributes only a minor stabilization and is partially overridden by other effects. The PEIERLS distortion cannot be suppressed that easily with lighter elements.

The formation of linear chains can be extended to two dimensions. Parallel $\scriptstyle \frac{1}{\infty}$Sb$^{2-}$ chains lying side by side can be joined to a square net. One more singly occupied $p$ orbital per Sb atom is needed. Formally, an oxidation, $\scriptstyle \frac{1}{\infty}$Sb$^{2-} \rightarrow \frac{2}{\infty}$Sb$^{-}$, has to take place. Six valence electrons per atom are needed for the square net. Nets of this kind occur, for example, in YbSb$_2$ (with Yb$^{2+}$). Starting from the square nets, another formal oxidation, $\scriptstyle \frac{2}{\infty}$Sb$^{-} \rightarrow \frac{3}{\infty}$Sb, yields the primitive-cubic polonium-type structure, which is known as a high-pressure modification of arsenic. Therefore, five electrons per atom are needed for this structure. Remarkably, polonium itself has one electron per atom too many for its structure.

### 13.3 Polycationic Compounds

The number of known polycationic compounds of main group elements is far less than that of polyanionic compounds. Examples include the chalcogen cations S$_4^{2+}$, S$_8^{2+}$, Se$_{10}^{2+}$ and Te$_6^{4+}$ that are obtained when the elements react with Lewis acids under oxidizing conditions. The ions S$_4^{2+}$, Se$_4^{2+}$ and Te$_4^{2+}$ have a square structure that can be assumed to have a $6\pi$ electron system.

The structures of S$_8^{2+}$ and Se$_8^{2+}$ can be interpreted with the $8-N$ rule: a bond is generated across an S$_8$ ring, resulting in two atoms having three bonds and one positive formal charge each (Fig. 13.7). The new bond is remarkably long (289 pm as compared to 203 pm for the other bonds), but the occurrence of abnormally long S–S bonds is also known for some other sulfur compounds. Several varieties are known of Te$_4^{4+}$ ions, in which triply bonded Te$^{8+}$ and uncharged Te atoms are discernible. The structure of the Te$_3$S$_3^{2+}$ and Te$_6^{4+}$ ions can also be understood in terms of the $8-N$ rule. Te$_6^{4+}$ can be described as a trigonal-pyramidal structure in which one prism edge has been strongly elongated; according to the $8-N$ rule, this edge would not be considered to be a bond. However, some weak bonding interaction must still be present, otherwise the structure would not be as it is. The $8-N$ rule is somewhat too simple, just as it is too simple to understand elemental tellurium. For the trigonal-prismatic Bi$_5^{3+}$ ion, one could formulate a simple valence bond formula as given on page 134 for the isoelectronic Sn$_3^{2-}$ ion (without lone electron pairs at the equatorial atoms). However, for the square-antiprismatic Bi$_5^{2+}$ ion this is not possible. In this case multicenter bonds are needed, such as are used to describe the bonding in cluster compounds. In a broader sense numerous cluster compounds can be considered to be polycationic compounds; due to their variety we deal with them next in a section of their own.
138 POLYANIONIC AND POLYCATIONIC COMPOUNDS. ZINTL PHASES

Fig. 13.7
Structures of some polycations. Interatomic distances in pm. Short contacts to neighboring Te$_2^+$ ions are present in Te$_8$[WCl$_6$]$_2$, Te$_8^+$ in Te$_8$[WCl$_6$]$_2$, Te$_8^+$ (polymeric) in Te$_8$[Bi$_4$Cl$_{14}$]

13.4 Cluster Compounds

Links between atoms serve to compensate for the lack of the electrons which are necessary to attain the electron configuration of the next noble gas in the periodic table. With a common electron pair between two atoms each of them gains one electron in its valence shell. As the two electrons link two ‘centers’, this is called a two-center two-electron bond or, for short, 2c2e bond. If, for an element, the number of available partner atoms of a different element is not sufficient to fill the valence shell, atoms of the same element combine with each other, as is the case for polyanionic compounds and for the numerous organic compounds. For the majority of polyanionic compounds a sufficient number of electrons is available to satisfy the demand for electrons with the aid of 2c2e bonds. Therefore, the generalized 8—N rule is usually fulfilled for polyanionic compounds.

For more electropositive elements, which have an inferior number of valence electrons in the first place, and which in addition have to supply electrons to a more electronegative partner, the number of available electrons is rather small. They can gain electrons in two ways: first, as far as possible, by complexation, i.e. by the acquisition of ligands; and second, by combining their own atoms with each other. This can result in the formation of clusters. A cluster is an accumulation of three or more atoms of the same element or of similar elements that are directly linked with each other. If the accumulation of atoms yields a sufficient number of electrons to allow for one electron pair for every connecting line between two adjacent atoms, then each of these lines can be taken to be a 2c2e bond just as in a common valence bond (LEWIS) formula. Clusters of this kind have been called electron precise.

For low values of the valence electron concentration (VEC< 4 for main group elements), covalent 2c2e bonds are not sufficient to overcome the electron deficiency. We have the case of ‘electron-deficient compounds’. For these, relief comes from multicenter bonds. In a three-center two-electron bond (3c2e) three atoms share an electron pair. An even larger number of atoms can share one electron pair. With increasing numbers of

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1In recent times, in chemistry it has become a fatuous habit to call atoms ‘centers’. See comments on page 247.
atoms sharing the same electron pair, each atom is less tightly bonded. The electron pair in a $3c2e$ bond essentially is located in the center of the triangle defined by the three atoms:

The location of electrons linking more than three atoms cannot be illustrated as easily. The simple, descriptive models must give way to the theoretical treatment by molecular orbital theory. With its aid, however, certain electron counting rules have been deduced for cluster compounds that set up relations between the structure and the number of valence electrons. A bridge between molecular-orbital theory and vividness is offered by the electron-localization function (*cf.* p. 89).

Completely closed, convex, single-shell clusters are called *closo* clusters; their atoms form a polyhedron. If the polyhedron has only triangular faces, it is also called a *deltahedron*. Depending on the number of available electrons, we can distinguish four general bonding types for *closo* clusters:

1. Electron precise clusters with exactly one electron pair per polyhedron edge;
2. Clusters with one $3c2e$ bond for every triangular face;
3. Clusters that satisfy the W ADE rules discussed on page 144;
4. Clusters not matching any of these patterns.

**Electron Precise Clusters**

Molecules such as $P_4$ and the polyanionic clusters such as $Si_3^{4-}$ or $As_3^{3-}$ that are discussed in Section 13.2 are representatives of electron precise closo clusters. Organic cage molecules like tetrahedrane ($C_4R_4$), prismane ($C_6H_6$), cubane ($C_8H_8$), and dodecahedrane ($C_{20}H_{20}$) also belong to this kind of cluster.

Numerous clusters with electron numbers that account for exactly one electron pair per polyhedron edge are also known for the more electron-rich transition group elements (beginning with group six). In addition, every cluster atom obtains electrons from coordinated ligands, with a tendency to attain a total of 18 valence electrons per atom. The easiest way to count the number of electrons is to start from uncharged metal atoms and uncharged ligands. Ligands such as $NH_3$, $PR_3$, and $CO$ supply two electrons. Nonbridging halogen atoms, $H$ atoms and groups such as $SiR_3$ supply one electron (for halogen atoms this amounts to the same as assuming a $Hal^-$ ligand that makes available two electrons, but that had previously obtained an electron from a metal atom). A $\mu_2$-bridging halogen atom supplies three electrons (one as before plus one of its lone electron pairs), and a $\mu_3$-bridging halogen atom five. Table 13.2 lists how many electrons are to be taken into account for some ligands.

The electrons supplied by the ligands and the valence electrons of the $n$ metal atoms of an $M_n$ cluster are added to a total electron number $g$. The number of $M$–$M$ bonds (polyhedron edges) then is:

\[
\begin{align*}
\text{main group element clusters:} & \quad b = \frac{1}{2}(8n - g) \\
\text{transition element clusters:} & \quad b = \frac{1}{2}(18n - g)
\end{align*}
\]
Table 13.2: Number of electrons supplied by ligands to metal atoms in complexes when the metal atoms are considered to be uncharged.

$\mu_1$ = terminal ligand, $\mu_2$ = ligand bridging two atoms, $\mu_3$ = ligand bridging three atoms; int = interstitial atom inside a cluster

<table>
<thead>
<tr>
<th>ligand</th>
<th>electrons</th>
<th>ligand</th>
<th>electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>$\mu_1$ 1</td>
<td>NR$_3$</td>
<td>$\mu_1$ 2</td>
</tr>
<tr>
<td>H</td>
<td>$\mu_2$ 1</td>
<td>NCR</td>
<td>$\mu_1$ 2</td>
</tr>
<tr>
<td>H</td>
<td>$\mu_3$ 1</td>
<td>NO</td>
<td>$\mu_1$ 3</td>
</tr>
<tr>
<td>CO</td>
<td>$\mu_1$ 2</td>
<td>PR$_3$</td>
<td>$\mu_1$ 2</td>
</tr>
<tr>
<td>CO</td>
<td>$\mu_2$ 2</td>
<td>OR</td>
<td>$\mu_1$ 1</td>
</tr>
<tr>
<td>CS</td>
<td>$\mu_1$ 2</td>
<td>OR</td>
<td>$\mu_2$ 3</td>
</tr>
<tr>
<td>CR$_2$</td>
<td>$\mu_1$ 2</td>
<td>OR$_2$</td>
<td>$\mu_1$ 2</td>
</tr>
<tr>
<td>$\eta^2$-C$_2$R$_4$</td>
<td>$\mu_1$ 2</td>
<td>O, S, Se, Te</td>
<td>$\mu_1$ 0</td>
</tr>
<tr>
<td>$\eta^2$-C$_2$R$_2$</td>
<td>$\mu_1$ 2</td>
<td>O, S, Se, Te</td>
<td>$\mu_2$ 2</td>
</tr>
<tr>
<td>$\eta^5$-C$_5$R$_5$</td>
<td>$\mu_1$ 5</td>
<td>O, S, Se, Te</td>
<td>$\mu_3$ 4</td>
</tr>
<tr>
<td>$\eta^6$-C$_6$R$_6$</td>
<td>$\mu_1$ 6</td>
<td>O, S</td>
<td>int 6</td>
</tr>
<tr>
<td>C</td>
<td>int 4</td>
<td>F, Cl, Br, I</td>
<td>$\mu_1$ 1</td>
</tr>
<tr>
<td>SiR$_3$</td>
<td>$\mu_1$ 2</td>
<td>F, Cl, Br, I</td>
<td>$\mu_2$ 3</td>
</tr>
<tr>
<td>N, P</td>
<td>int 5</td>
<td>Cl, Br, I</td>
<td>$\mu_3$ 5</td>
</tr>
</tbody>
</table>

This mode of calculation has been called the ‘EAN rule’ (effective atomic number rule). It is valid for arbitrary metal clusters (closo and others) if the number of electrons is sufficient to assign one electron pair for every M–M connecting line between adjacent atoms, and if the octet rule or the 18-electron rule is fulfilled for main group elements or for transition group elements, respectively. The number of bonds $b$ calculated in this way is a limiting value: the number of polyhedron edges in the cluster can be greater than or equal to $b$, but never smaller. If it is equal, the cluster is electron precise.

Since an M atom gains one electron per M–M bond, the calculation can also be performed in the following way: the total number $g$ of valence electrons of the cluster must be equal to:

- **main group element clusters:** $g = 7n_1 + 6n_2 + 5n_3 + 4n_4$ (13.11)
- **transition element clusters:** $g = 17n_1 + 16n_2 + 15n_3 + 14n_4$ (13.12)

$n_1, n_2, n_3,$ and $n_4$ are the numbers of polyhedron vertices at which 1, 2, 3 or 4 polyhedron edges (M–M bonds) meet, respectively. Polyhedra with five or more edges per vertex are generally not electron precise (for this reason no numbers $n_5, n_6, \ldots$ occur in the equations). Therefore, the expected valence electron numbers for some simple polyhedra are:

<table>
<thead>
<tr>
<th>polyhedron</th>
<th>main group elements</th>
<th>transition group elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>triangle</td>
<td>18</td>
<td>48</td>
</tr>
<tr>
<td>tetrahedron</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>trigonal bipyramid</td>
<td>22</td>
<td>72</td>
</tr>
<tr>
<td>octahedron</td>
<td>–</td>
<td>84</td>
</tr>
<tr>
<td>trigonal prism</td>
<td>30</td>
<td>90</td>
</tr>
<tr>
<td>cube</td>
<td>40</td>
<td>120</td>
</tr>
</tbody>
</table>

No value is given for the octahedron in the list for the main group elements, because their
13.4 Cluster Compounds

Octahedral clusters do not fit into the scheme of electron precise clusters. This is explained below for Tl$_6^{6-}$ (p. 146). As an exercise, one could calculate the numbers for some of the polyanionic compounds in Section 13.2. Further examples include:

\[ \text{Os}_3(\text{CO})_{12} \quad 3 \text{Os} \quad 3 \times 8 = 24 \\
12 \text{CO} \quad 12 \times 2 = 24 \\
g = \frac{3 \times 8 + 12 \times 2}{48} = 16n_2 \\
b = \frac{1}{2}(18 \times 3 - 48) = 3 \]

\[ \text{Ir}_4(\text{CO})_{12} \quad 4 \text{Ir} \quad 4 \times 9 = 36 \\
12 \text{CO} \quad 12 \times 2 = 24 \\
g = \frac{4 \times 9 + 12 \times 2}{60} = 15n_3 \\
b = \frac{1}{2}(18 \times 4 - 60) = 6 \]

\[ [\text{Os}_6(\text{CO})_{18}\text{P}]^- \quad 6 \text{Os} \quad 6 \times 8 = 48 \\
18 \text{CO} \quad 18 \times 2 = 36 \\
\text{P} \quad 5 \\
\text{charge} = 1 \\
g = \frac{6 \times 8 + 18 \times 2}{90} = 15n_3 \\
b = \frac{1}{2}(18 \times 6 - 90) = 9 \]

\[ [\text{Mo}_6\text{Cl}_{14}]^{2-} \quad 6 \text{Mo} \quad 6 \times 6 = 36 \\
8 \mu_3-\text{Cl} \quad 8 \times 5 = 40 \\
6 \mu_1-\text{Cl} \quad 6 \times 1 = 6 \\
\text{charge} = 2 \\
g = \frac{6 \times 6 + 8 \times 5 + 6 \times 1}{84} = 14n_4 \\
b = \frac{1}{2}(18 \times 6 - 84) = 12 \]

The cluster mentioned last, [Mo$_6$Cl$_{14}$]$^{2-}$, also occurs in MoCl$_2$. It consists of an Mo$_6$ octahedron inscribed in a Cl$_8$ cube; each of the eight Cl atoms of the cube is situated on top of one of the octahedron faces and is coordinated to three molybdenum atoms (Fig. 13.8). The formula [Mo$_6$Cl$_8$]$^{4+}$ applies to this unit; in it, every Mo atom is still short of two electrons it needs to attain 18 valence electrons. They are supplied by the six Cl$^-$ ions bonded at each octahedron vertex. This also applies to MoCl$_2$, but there are only four Cl$^-$ per cluster; however, two of them act as bridging ligands between clusters, corresponding to the formula [Mo$_6$Cl$_8$]Cl$_2$/Cl$_{14}$/2 (Fig. 13.8).

The situation is very similar in the CHEVREL phases. These are ternary molybdenum chalcogenides A$_x$[Mo$_6$X$_8$] (A = metal, X = S, Se) that have attracted much attention because of their physical properties, especially as superconductors. The ‘parent compound’ is PbMo$_6$S$_8$; it contains Mo$_6$S$_8$ clusters that are linked with each other in such a way that the free coordination sites of one cluster are occupied by sulfur atoms of adjacent clusters (Fig. 13.9). The electric properties of CHEVREL phases depend on the number of valence electrons. With 24 electrons per cluster (one electron pair for each edge of the
Fig. 13.8
Top: two representations of the $[\text{Mo}_6\text{Cl}_8]^{4+}$ cluster and the structure of the $[\text{Mo}_6\text{Cl}_{14}]^{2-}$ ion. Bottom: array of $\text{Mo}_6\text{Cl}_8$ clusters linked via chlorine atoms to a layer in $\text{Mo}_6\text{Cl}_{12}$.

Fig. 13.9
Association of $\text{Mo}_6\text{S}_8$ clusters in the CHEVREL phase $\text{PbMo}_6\text{S}_8$ (stereo image).

R

L
13.4 Cluster Compounds

Mo$_6$ octahedron) the cluster is electron-precise, the valence band is fully occupied and the compounds are semiconductors, as, for example, (Mo$_3$Ru$_2$)Se$_8$ (it has two Mo atoms substituted by Ru atoms in the cluster). In PbMo$_6$S$_8$ there are only 22 electrons per cluster; the ‘electron holes’ facilitate a better electrical conductivity; below 14 K it becomes a superconductor. By incorporating other elements in the cluster and by the choice of the electron-donating element A, the number of electrons in the cluster can be varied within certain limits (19 to 24 electrons for the octahedral skeleton). With the lower electron numbers the weakened cluster bonds show up in trigonally elongated octahedra.

If electrons are added to an electron precise cluster, cleavage of bonds is to be expected according to equation (13.9) or (13.10); for every additional electron pair $g$ increases by 2 and $b$ decreases by 1. The Si$_4^-$ ion presented on p. 132 is an example; it can be thought of having been formed from a tetrahedral Si$_4^4^-$ by the addition of two electrons. Another example is Os$_3$(CO)$_{12}$(SiCl$_3$)$_2$ with a linear Os–Os–Os group; by attaching two SiCl$_3$ groups to triangular Os$_3$(CO)$_{12}$, two more electrons are supplied, and one Os–Os bond has to be cleaved.

However, certain polyhedra allow the inclusion of another electron pair without cleavage of any bond. This applies especially to octahedral clusters which should have 84 valence electrons according to equation (13.12), but they frequently have 86 electrons. The additional electron pair assumes a bonding action as a six-center bond inside the octahedron. An octahedral cluster with 86 valence electrons fulfills the WADE rule discussed below.

Clusters with 3c2e Bonds

If there are not enough electrons for all of the polyhedron edges, 3c2e bonds on the triangular polyhedron faces can be the next best solution to compensate for the lack of electrons. This solution is only possible for deltahedra that have no more than four edges (and faces) meeting at any vertex. These include especially the tetrahedron, trigonal bipyramid and octahedron.

For example, the bonding in B$_4$Cl$_4$ can be interpreted in the following way: every boron atom takes part in four bonds, one 2c2e B–Cl bond and three 3c2e bonds on the faces of the B$_4$ tetrahedron. In this way every boron atom attains an electron octet. Eight of the valence electrons take part in the multicenter bonds; the other eight are needed for the B–Cl bonds.

In the Nb$_6$Cl$_{18}^{12+}$ ion the octahedral Nb$_6$ cluster can be assumed to have eight 3c2e bonds on its eight octahedron faces. A chlorine atom bonded with two Nb atoms is situated next to each octahedron edge. This makes twelve Cl atoms in an Nb$_6$Cl$_{12}^{12+}$ unit. The remaining six Cl$^-$ ions are terminally bonded to the octahedron vertices (Fig. 13.10). The number of valence electrons is:

\[
\begin{align*}
6 \text{ Nb} & \quad 6 \times 5 = 30 \\
12 \mu_2^+\text{-Cl} & \quad 12 \times 3 = 36 \\
6 \mu_1^-\text{-Cl} & \quad 6 \times 1 = 6 \\
\text{charge} & \quad 4
\end{align*}
\]

12 of these 76 electrons are needed for the bonds with the $\mu_1^-\text{-Cl}$ atoms. Four electrons are needed for every Cl atom on top of an octahedron edge, altogether $4 \times 12 = 48$. 76 − 12 − 48 = 16 electrons remain for the Nb$_6$ skeleton, i.e. exactly one electron pair per octahedron face.
For each Nb atom the situation is the same as in the Mo$_6$Cl$_{24}^{2-}$ ion: the metal atom is surrounded by five Cl atoms and is involved in four metal–metal bonds in the cluster. However, the MCl$_5$ unit is rotated with respect to the octahedron: Cl atoms on top of the Mo$_6$ octahedron faces become Cl atoms on top of the Nb$_6$ octahedron edges, and the bonding electron pairs switch over from the edges to the faces. In both cases the valence electrons for a metal atom add up to 18. In Nb$_6$Cl$_{14}$ the Nb$_6$Cl$_{12}^{2+}$ clusters are associated via intervening chlorine atoms, similar to Mo$_6$Cl$_{12}$.

Just as the Mo$_6$X$_8$ units in the CHEVREL phases tolerate a certain lack of electrons (e.g. 20 instead of 24 skeleton electrons), clusters with M$_6$X$_{12}$ units which have fewer than 16 skeleton electrons are also possible. For example, in Zr$_6$I$_{12}$ there are only 12 skeleton electrons, and Sc$_7$Cl$_{12}$ = Sc$_3^+[\text{Sc}_6\text{Cl}_{12}]^{3-}$ has only nine.

Wade Clusters

K. WADE has put forward some rules that relate the composition of a cluster to the number of its valence electrons. The rules were first derived for boranes. To calculate the wave functions of a closo cluster with $n$ atoms, the coordinate systems of all $n$ atoms are oriented with their $z$ axes radially to the center of the polyhedron. The contribution of the $s$ orbitals can be estimated best by combining them with the $p_z$ orbitals to form $sp$ hybrid orbitals. One of the two $sp$ orbitals of an atom points radially to the center of the cluster, the other one radially outwards. The latter is used for bonding with external atoms (e.g. with the H atoms of the B$_6$H$_{2n}$ ion). The $n$ $sp$ orbitals pointing inwards combine to give one bonding and $n-1$ nonbonding or antibonding orbitals. The orbitals $p_x$ and $p_y$ of every atom are oriented tangentially to the cluster and combine to give $n$ bonding and $n$ antibonding orbitals (Fig. 13.11). Altogether, we obtain $n+1$ bonding orbitals for the cluster skeleton. From this follows the WADE rule: a stable closo cluster requires $2n+2$ skeleton electrons. This is a smaller number of electrons than that required for an electron precise cluster or for a cluster with 3c2e bonds, with one exception: a tetrahedral cluster with 3c2e bonds on its four faces requires only 8 electrons, whereas it should have 10 electrons according to the WADE rule; the WADE rule does not apply to tetrahedra. In fact, closo-boranes with the composition B$_n$H$_{2n}^{2-}$ are known only for $n \geq 5$. For a trigonal bipyramid it makes no difference whether one assumes 3c2e bonds on the six faces or $n + 1 = 6$ electron pairs according to the WADE rule.

According to calculations with the electron localization function (ELF) the electron pairs of the B$_n$H$_{2n}^{2-}$ cluster are essentially concentrated on top of the octahedron edges and faces (Fig. 13.12).
For the triply degenerate orbitals \( t_{2g} \) and \( t_{1u} \) only one of each is plotted; for each of them, two further, equal orbitals exist which are oriented along the other two octahedron axes. Right: energy sequence of the seven occupied bonding orbitals.

The closo-boranes \( B_nH_{2n}^2^- \) \((5 \leq n \leq 12)\) and the carboranes \( B_nC_2H_{n+2} \) are showpieces for the mentioned WADE rule. Further examples include the \( B_{12} \) icosahedra in elemental boron (Fig. 11.16) and certain borides such as \( CaB_6 \). In \( CaB_6 \), \( B_6 \) octahedra are linked with each other via normal \( 2c2e \) bonds (Fig. 13.13). Six electrons per octahedron are required for these bonds; together with the \( 2n + 2 = 14 \) electrons for the octahedron skeleton this adds up to a total of 20 valence electrons. The boron atoms supply \( 3 \times 6 = 18 \) of them, and calcium the remaining two.

WADE stated some further rules for open clusters that are interpreted as deltahedra with missing vertices. They are of special importance for boranes:

- **nido** cluster: one missing polyhedron vertex, \( n + 2 \) bonding skeleton orbitals;
- **arachno** cluster: two missing vertices, \( n + 3 \) bonding skeleton orbitals;
- **hypho** cluster: three missing vertices, \( n + 4 \) bonding skeleton orbitals.

The WADE rules can be applied to ligand-free cluster compounds of main-group elements. If we postulate one lone electron pair pointing outwards on each of the \( n \) atoms, then \( g - 2n \) electrons remain for the polyhedron skeleton \((g = \text{total number of valence elec-} \)

---

**Fig. 13.11**
Combinations of atomic orbitals that result in bonding molecular orbitals in an octahedral cluster such as \( B_6H_{26}^- \).

\( a_{1g} \) six radial \( sp \)

\( t_{2g} \) four tangential \( p \)

\( t_{1u} \) two \( sp \) and four \( p \)

---

**Fig. 13.12**
Electron localization function for \( B_6H_{26}^- \) (only valence electrons, without regions around the H atoms), shown as iso-surface with ELF = 0.80. (Reprinted from *Angewandte Chemie* [97] with permission from Wiley-VCH)

**Fig. 13.13**
The structure of \( CaB_6 \)
trons; Fig. 13.14). The calculation also works if some of the atoms bear ligands (instead of lone pairs) and others have no ligands but lone electron pairs. Examples:

<table>
<thead>
<tr>
<th>Cluster Type</th>
<th>$n$</th>
<th>$g$</th>
<th>$g - 2n$</th>
<th>Cluster Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$_5^2-$, Bi$_5^{3+}$</td>
<td>5</td>
<td>22</td>
<td>12</td>
<td>= $2n + 2$</td>
</tr>
<tr>
<td>Tl$_6^6-$</td>
<td>6</td>
<td>26</td>
<td>14</td>
<td>= $2n + 2$</td>
</tr>
<tr>
<td>Sn$_9^4-$, Bi$_9^{5+}$</td>
<td>9</td>
<td>40</td>
<td>22</td>
<td>= $2n + 4$</td>
</tr>
<tr>
<td>Bi$_8^{2+}$</td>
<td>8</td>
<td>38</td>
<td>22</td>
<td>= $2n + 6$</td>
</tr>
<tr>
<td>As$_2$B$_4$Cl$_4$</td>
<td>6</td>
<td>26</td>
<td>14</td>
<td>= $2n + 2$</td>
</tr>
</tbody>
</table>

The examples should not give the misleading impression that bonding in clusters is a clear and simple matter. Next to many examples for which the WADE rules work well, they do not do so in many other cases, or additional assumptions have to be made.

KTl does not have the NaTl structure because the K$^+$ ions are too large to fit into the interstices of the diamond-like Tl$^-$ framework. It is a cluster compound K$_6$Tl$_6$ with distorted octahedral Tl$_6^6-$ ions. A Tl$_6^6-$ ion could be formulated as an electron precise octahedral cluster, with 24 skeleton electrons and four $2c2e$ bonds per octahedron vertex. The thallium atoms then would have no lone electron pairs, the outside of the octahedron would have nearly no valence electron density, and there would be no reason for the distortion of the octahedron. Taken as a closo cluster with one lone electron pair per Tl atom, it should have two more electrons. If we assume bonding as in the B$_6$H$_{12}^2-$ ion (Fig. 13.11), but occupy the $t_{2g}$ orbitals with only four instead of six electrons, we can understand the observed compression of the octahedra as a JAHN–TELLER distortion. Clusters of this kind, that have less electrons than expected according to the WADE rules, are known with gallium, indium and thallium. They are called hypoelectronic clusters; their skeleton electron numbers often are $2n$ or $2n - 4$.

B$_8$Cl$_8$ has a dodecahedral B$_8$ closo-skeleton with $2n = 16$ electrons. In this case, the WADE rule neither can be applied, nor can it be interpreted as an electron precise cluster nor as a cluster with $3c2e$ bonds. B$_4$(BF$_3$)$_6$ has a tetrahedral B$_4$ skeleton with a radially bonded BF$_2$ ligand at each vertex, but it has two more BF$_2$ groups bonded to two tetrahedron edges. In such cases the simple electron counting rules fail.

WADE also extended the application of his rules to transition metal clusters; the further extension by D. M. P. MINGOS mainly concerns the bonding in metal carbonyl and metal phosphane clusters, i.e. organometallic compounds (WADE–MINGOS rules); these are beyond the scope of this book.
Clusters with Interstitial Atoms

Clusters derived from metals which have only a few valence electrons can relieve their electron deficit by incorporating atoms inside. This is an option especially for octahedral clusters which are able to enclose a binding electron pair anyway. The interstitial atom usually contributes all of its valence electrons to the electron balance. Nonmetal atoms such as H, B, C, N, and Si as well as metal atoms such as Be, Al, Mn, Fe, Co, and Ir have been found as interstitial atoms.

Transition metals of groups 3 and 4 form many octahedral clusters that are isostructural with those of the less electron-deficient elements of the following groups, but they contain additional atoms in their centers (Fig. 13.15). Starting from the above-mentioned Nb$_6$Cl$_{14}$ (Fig. 13.10), we can substitute the niobium atoms by zirconium atoms; the number of available electrons is then reduced by six. This loss can partly be compensated by introducing a carbon atom in the Zr$_6$ octahedron. Despite the slightly inferior number of electrons the cluster in Zr$_6$CCl$_{14}$ is stable due to some changes in the bonding. The more electronegative atom in the center of the cluster pulls electron density inwards, thus weakening the Zr–Zr bonds to some extent, but stronger bonding interactions with the C atom emerge.

On the other hand, the metal–metal bonds are strengthened when the interstitial atom is a metal atom. Nb$_6$F$_{15}$, for example, consists of Nb$_6$F$_{12}$ clusters of the same kind as in the Nb$_6$Cl$_{12}^{2+}$ unit; they are linked by all six of their vertices via bridging fluorine atoms, forming a network. Th$_6$FeBr$_{15}$ has the same kind of structure, but with an additional Fe atom in the octahedron center (Fig. 13.15). Nb$_6$F$_{15}$ has one electron less than required for the eight 3c2e bonds; in Th$_6$Br$_{15}$ a further six electrons are missing. The intercalated Fe atom ($d^8$) supplies these seven electrons; the eighth electron remains with the Fe atom.

Even the extremely electron-deficient alkali metals can form clusters when interstitial atoms contribute to their stabilization. Compounds of this kind are the alkali metal suboxides such as Rb$_9$O$_2$; it has two octahedra sharing a common face, and each is occupied by one O atom (Fig. 13.16). However, the electron deficiency is so severe that metallic bonding is needed between the clusters. In a way, these compounds are metals, but not with single metal ions as in the pure metal Rb$^+$e$^-$, but with a constitution [Rb$_9$O$_2$]$^{5+}$(e$^-$)$_5$, essentially with ionic bonding in the cluster.

---

**Fig. 13.15**
Cluster unit with an interstitial atom in compounds such as Zr$_6$CCl$_{14}$ and Th$_6$FeBr$_{15}$

**Fig. 13.16**
Cluster in Rb$_9$O$_2$
I contrast to cages like $\text{B}_{12}\text{X}_{12}^{2-}$ or $\text{C}_{60}$, clusters with similar sizes consisting of metal atoms are not stable if they are hollow; the bonds at their surfaces are too weak. However, they can be stabilized by interstitial atoms, even if the interstitial atoms do not contribute with their electrons. Such clusters are called endohedral. Examples are the icosahedral clusters $\left[\text{Pt}@\text{Pb}_{12}\right]^{2-}$ and $\left[\text{Cd}@\text{Tl}_{12}\right]^{12-}$ with a Tl$^{14-}$ cage. The atom mentioned before the @ sign is the enclosed, endohedral atom. These clusters fulfill the WADE rule for closo clusters if one assumes a neutral Pt atom and a Cd$^{2+}$ ion.

$\left[\text{Pd}@\text{Bi}_{10}\right]^{4+}$ is an example of an arachno cluster in the compound $\left[\text{Pd}@\text{Bi}_{10}\right]^{4+}\left(\text{BiBr}_3\right)_4$. It has $2n+6$ skeleton electrons if one assumes one lone electron pair per Bi atom and a neutral Pd atom. The Bi atoms form a pentagonal antiprism which is the same as an icosahedron with two missing vertices.

Endohedral closo clusters can be regarded as intermediate stations on the way to the structures of metals. In a closest packing of spheres an atom is surrounded by 12 other atoms; that adds up to 13 atoms. With an additional covering of atoms, the total number of atoms is 55. A corresponding cluster is known in $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$; the envelope of ligands prevents the condensation to the bulk metal. Metal clusters of different sizes can be stabilized by external ligands; as a rule, the metal atom arrangement corresponds to a section of the structure of the pure metal. Examples are: $\left[\text{Al}_{69}\text{R}_{18}\right]^{3-}$, $\left[\text{Al}_{77}\text{R}_{20}\right]^{2-}$, $\left[\text{Ga}_{19}\text{R}_{6}\right]^{-}$, $\left[\text{Ga}_{84}\text{R}_{20}\right]^{4-}$ with $\text{R} = \text{N(SiMe}_3\text{)}_2$ or $\text{C(SiMe}_3\text{)}_3$.

### Condensed Clusters

Another possibility for relieving the electron deficiency consists of joining clusters to form larger building blocks. Among the known condensed clusters the majority consist of $\text{M}_6\text{X}_8$ octahedra linked with each other. When joining $\text{M}_6\text{X}_8$ or $\text{M}_6\text{X}_{12}$ units in such a way that metal atoms ‘merge’ with one another, some of the $\text{X}$ atoms have to be ‘merged’ also.

Fig. 13.17 shows a possibility for the condensation of $\text{M}_6\text{X}_8$ clusters. Merging trans vertices of octahedra to a linear chain requires that opposite faces of the $\text{X}_8$ cubes also merge; every $\text{X}$ atom is thus shared by two cubes. The resulting composition is $\text{M}_3\text{X}_4$. The relative arrangement of chains bundled in parallel allows the coordination of $\text{X}$ atoms of one chain to the octahedra vertices of four adjacent chains, in a similar way as in the CHEVREL phases. Compounds with this structure are known with $\text{M} = \text{Ti, V, Nb, Ta, Mo}$ and $\text{X} = \text{S, Se, Te, As, Sb}$, e.g. $\text{Ti}_3\text{Te}_4$. They have 12 ($\text{Ti}_3\text{Te}_4$) to 18 ($\text{Mo}_5\text{As}_4$) skeleton electrons per octahedron. Eight of the electrons form four $2e2e$ bonds at the four equatorial
edges of the octahedron; the remaining electrons are oriented along the other octahedron edges, and their interaction in the chain direction results in metallic energy bands.

Chains with the composition $M_2M_4X_8/2 = M_4X_4$ are the result of the condensation of $M_4X_8$ clusters by merging opposite octahedron edges. They are known for lanthanoid halides like Gd$_2$Cl$_3$; they have additional halogen atoms placed between the chains (Fig. 13.18). The clusters may contain interstitial atoms. For example, Sc$_4$BCl$_6$ has chains like Gd$_2$Cl$_3$ with a boron atom enclosed in each octahedron.

The cluster condensation can be carried on: the chains of octahedra sharing edges can be joined to double-strands and finally to layers of octahedra (Fig. 13.18). Every layer consists of metal atoms in two planes arranged in the same way as two adjacent layers of atoms in a closest-packing of spheres. This is simply a section from a metal structure. The X atoms occupy positions between the metal layers and act as ‘insulating’ layers. Substances like ZrCl that have this structure have metallic properties in two dimensions.

**Fig. 13.18**
Condensation of $M_6X_8$ clusters by sharing octahedra edges to yield chains in Gd$_2$Cl$_3$, double-strands in Sc$_7$Cl$_{10}$ and layers in ZrCl. Every metal atom of Gd$_2$Cl$_3$ and Sc$_7$Cl$_{10}$ is also coordinated to a chlorine atom of a neighboring chain.

### 13.5 Problems

**13.1** Use the extended $8-N$ rule to decide whether the following compounds are polyanionic, polycationic or simple ionic.

(a) Be$_2$C; (b) Mg$_2$C$_5$; (c) ThC$_2$; (d) Li$_2$Si; (e) In$_4$Se$_3$; (f) KSB; (g) Nb$_3$Cl$_8$; (h) TiS$_2$.

**13.2** Which of the following compounds should be ZINTL phases?

(a) Y$_5$Si$_3$; (b) CaSi; (c) CaO; (d) K$_3$As$_7$; (e) NbF$_4$; (f) LaNi$_5$.

**13.3** Draw valence bond formulas for the following ZINTL anions.

(a) Al$_2$Te$_6^6$; (b) [SnSb$_3$]$^{3-}$; (c) [SnSb]$^{2-}$; (d) [SiF$_5$]$^{2-}$; (e) P$_2^{2-}$.

**13.4** State which of the following clusters is electron precise, may have 3e2e bonds or fulfills the WADE rule for closo clusters.

(a) B$_{10}$C$_2$H$_{12}$ (icosahedron); (b) Re$_6$(µ$_3$-S)$_4$(µ$_3$-Cl)$_4$µ$_1$-Cl$_6$ (octahedron);
(c) Pt$_4$(µ$_3$-H)$_4$(µ$_1$-H)$_4$(PR$_3$)$_4$ (tetrahedron); (d) Os$_5$(CO)$_{16}$ (trigonal bipyramid);
(e) Rh$_6$(CO)$_{16}$ (octahedron).
14 Packings of Spheres. Metal Structures

Metals are materials in which atoms are held together by multicenter bonds. The entire set of atoms in a crystal contributes to the multicenter bonds; the valence electrons are delocalized throughout the crystal. More details are given in Chapter 10. The bonding forces act evenly on all atoms: usually there are no prevalent local forces that cause some specific atomic arrangement around an atom in such a way as in a molecule. In what way the atoms arrange themselves in a metallic crystal depends first on how a most dense packing can be achieved geometrically. However, second, the electronic configuration and the valence electron concentration do have some influence; they determine which of several possible packing variants will actually occur. In principle, band structure calculations can allow us to differentiate these variants.

If atoms are considered as hard spheres, the packing density can be expressed by the space filling $SF$ of the spheres. It is:

$$SF = \frac{4\pi}{3V} \sum_i Z_i r_i^3$$  \hspace{1cm} (14.1)

$V$ = volume of the unit cell

$r_i$ = radius of the $i$-th kind of sphere

$Z_i$ = number of spheres of the $i$-th kind in the unit cell

If only one kind of sphere is present and all dimensions are referred to the diameter of one sphere, i.e. if we set the diameter to be 1 and the radius to be $r = \frac{1}{2}$, we obtain:

$$SF = \frac{\pi}{6} \cdot \frac{Z}{V} = 0.5236 \frac{Z}{V}$$

14.1 Closest-packings of Spheres

In order to fill space in the most economical way with spheres of equal size, we arrange them in a closest-packing of spheres. The closest arrangement of spheres in a plane is a hexagonal layer of spheres (Fig. 14.1). In such a layer every sphere has six adjacent spheres; six voids remain between a sphere and its six adjacent spheres. The distance from one void to the next void is exactly the same as that between the centers of two adjacent spheres. Let us denote the position of the sphere centers by $A$ as in Fig. 14.1, and the positions of the voids by $B$ and $C$. The closest stacking of layers requires that a layer in the position $A$ be followed by a layer having its spheres in hollows on top of either the voids $B$ or the voids $C$. Altogether, there exist three possible layer positions in a closest stack of hexagonal layers; a layer can only be followed by another layer in a different position ($A$ cannot be followed by $A$ etc.).

The layer sequence $ABCABC...$ is marked by arrows in Fig. 14.1. In this sequence all arrows point in the same direction. In a sequence $ABA$ one arrow would point in one direction, and the next arrow would point in the opposite direction. If we designate the direction $A \to B = B \to C = C \to A$ by + and $A \leftarrow B = B \leftarrow C = C \leftarrow A$ by −, we can characterize the stacking sequence by a sequence of + and − signs (HÄGG, 1943). The
14.1 Closest-packings of Spheres

symbolism can be abbreviated according to ZHDANOV by a sequence of numbers, with every number specifying how many equal signs are side by side; only the numbers of one periodically repeating unit are given. Another frequently used symbolism is that by JAGODZINSKI: a layer having its two adjacent layers in different positions (e.g. the layer $B$ in the sequence $ABC$), is designated by $c$ (for cubic); if its two adjacent layers have the same position (e.g. $B$ in the sequence $ABA$), the symbol is $h$ (for hexagonal).

Although the number of possible stacking sequences is infinitely large, predominantly only the following two are observed:

<table>
<thead>
<tr>
<th>Stacking Sequence</th>
<th>HÄGG Symbol</th>
<th>ZHDANOV Symbol</th>
<th>JAGODZINSKI Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>cubic closest-packing (c.c.p.)</td>
<td>...ABCABC...</td>
<td>$\infty$</td>
<td>$c$</td>
</tr>
<tr>
<td>hexagonal closest-packing (h.c.p.)</td>
<td>...+++-+-...</td>
<td>11</td>
<td>$h$</td>
</tr>
</tbody>
</table>

Cubic closest-packing is also called copper type and hexagonal closest-packing is also called magnesium type. In the cubic closest-packing the spheres have a face-centered cubic (f.c.c.) arrangement (Fig. 14.2); the stacking direction of the hexagonal layers is perpendicular to either of the body diagonals across the cube. The coordination number of every sphere is 12 for both packings. The coordination polyhedron is a cuboctahedron for cubic closest-packing; a cuboctahedron can be regarded either as a truncated cube or as a truncated octahedron (cf. Fig. 2.2, p. 5). The coordination polyhedron for hexagonal closest-packing is an anticuboctahedron; it results when two opposite triangular faces of a cuboctahedron are mutually rotated by 30°.

More complicated stacking sequences occur less frequently. Some have been observed among the lanthanoids:

<table>
<thead>
<tr>
<th>Stacking Sequence</th>
<th>JAGODZINSKI</th>
<th>ZHDANOV</th>
</tr>
</thead>
<tbody>
<tr>
<td>La, Pr, Nd, Pm</td>
<td>...ABAC...</td>
<td>$hc$</td>
</tr>
<tr>
<td>Sm</td>
<td>...ABACACBCB...</td>
<td>$hhc$</td>
</tr>
</tbody>
</table>

The $hc$ packing is called double-hexagonal closest-packing of spheres. Gadolinium to thulium as well as lutetium form hexagonal closest-packings of spheres. The proportion of $h$ layers hence increases with increasing number of $f$ electrons. The electronic configuration controls the kind of packing adopted; the influence of the $4f$ shell decreases with the atomic number. Being in the interior of an atom, with increasing nuclear charge the $f$ shell experiences a stronger contraction than the $5d$ and the $6s$ shells, i.e. the lanthanoid contraction shows up to a higher degree inside the atoms than can be seen in the atomic radii. The influence of the $f$ electrons also expresses itself in the behavior of the lanthanoids...
under pressure. When compressed, the outer shells are squeezed more than the inner ones, and the $f$ electrons gain influence resulting in structures with more $c$ layers:

<table>
<thead>
<tr>
<th></th>
<th>normal pressure</th>
<th>high pressure</th>
<th>higher pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>La, Pr, Nd</td>
<td>$hc$</td>
<td>$c$</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>$hhc$</td>
<td>$hc$</td>
<td>$c$</td>
</tr>
<tr>
<td>Gd, Tb, Dy, Ho, Tm</td>
<td>$h$</td>
<td>$hhc$</td>
<td>$hhc$</td>
</tr>
</tbody>
</table>

Finally, the influence of the electronic configuration also shows up in the exceptions: europium and ytterbium, having $4f$ shells ‘prematurely’ half and completely filled, respectively, have structures which do not follow the sequence of the other metals (Table 14.2, p. 155; configuration for Eu $4f^76s^2$ instead of $4f^65d^16s^2$, for Yb $4f^{14}6s^2$ instead of $4f^{13}5d^16s^2$. These elements also have irregular atomic radii, cf. Table 6.2, p. 47). There is also an irregularity at the beginning of the series, since cerium adopts a cubic closest-packing.

The number of different possible stacking variants increases with increasing numbers of hexagonal layers in one periodically repeating slab of layers:

<table>
<thead>
<tr>
<th>number of layers per slab:</th>
<th>2 3 4 5 6 7 8 9 10 11 12 20</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of stacking variants:</td>
<td>1 1 1 1 2 3 6 7 16 21 43 4625</td>
</tr>
</tbody>
</table>

The notable predominance of simple stacking forms is an expression of the *symmetry principle*:

*Among several feasible structure types those having the highest symmetry are normally favored.*

We discuss the reasons for and the importance of this principle in more detail in Section 18.2. The frequent observance of the *principle of most economic filling of space, i.e. of purely geometric aspects*, is also remarkable: of the 95 elements with known struc-
14.2 Body-centered Cubic Packing of Spheres

In the solid state, 46 adopt closest packings at ambient conditions. If we include low- and high-temperature and high-pressure modifications, closest-packings of spheres occur among 101 modifications of 75 elements.

Aside from the ordered stacking sequences we have considered so far, a more or less statistical sequence of hexagonal layers can also occur. Since there is some kind of an ordering principle on the one hand, but on the other hand the periodical order is missing in the stacking direction, this is called an order–disorder (OD) structure with stacking faults. In this particular case, it is a one-dimensionally disordered structure, since the order is missing only in one dimension. When cobalt is cooled from 500 °C it exhibits this kind of disorder.

The space filling is the same for all stacking variants of closest-packings of spheres. It amounts to \( \pi / (3\sqrt{2}) = 0.7405 \) or 74.05 %. That no packing of spheres can have a higher density was claimed in 1603 by J. KEPLER. However, conclusive proof was not furnished until 1998. Spheres surrounding a central sphere icosahedrally are not in contact with one another, i.e. there is slightly more space than for twelve neighboring spheres. However, icosahedra cannot be packed in a space-filling manner. Some nonperiodic packings of spheres have been described that have densities close to the density of closest-packings of spheres. Because no packing of spheres can have a higher density, one should not say ‘close’ packing, but closest packing.

14.2 Body-centered Cubic Packing of Spheres

The space filling in the body-centered cubic packing of spheres is less than in the closest packings, but the difference is moderate. The fraction of space filled amounts to \( \frac{1}{8}\pi \sqrt{3} = 0.6802 \) or 68.02 %. The reduction of the coordination number from 12 to 8 seems to be more serious; however, the difference is actually not so serious because in addition to the 8 directly adjacent spheres every sphere has 6 further neighbors that are only 15.5 % more distant (Fig. 14.3). The coordination number can be designated by \( 8 + 6 \).

Corresponding to its inferior space filling, the body-centered cubic packing of spheres is less frequent among the element structures. None the less, 15 elements crystallize with this structure. As tungsten is one of them, the term tungsten type is sometimes used for this kind of packing.

The mentioned number of elements refers to ambient conditions. If we also include the modifications adopted by some elements at low and high temperatures and at high pres-
Table 14.1: Numbers of structures of the elements known until 2006 in the solid state at different conditions

<table>
<thead>
<tr>
<th>nonmetals †</th>
<th>closest-packings of spheres ‡</th>
<th>body-centered cubic</th>
<th>other metal structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>ambient pressure</td>
<td>55</td>
<td>4 ‡</td>
<td>–</td>
</tr>
<tr>
<td>high pressure</td>
<td>4</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>metals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>up to 400 K</td>
<td>2</td>
<td>51</td>
<td>15</td>
</tr>
<tr>
<td>high temperature</td>
<td>–</td>
<td>7</td>
<td>23</td>
</tr>
<tr>
<td>high pressure</td>
<td>–</td>
<td>31</td>
<td>8</td>
</tr>
<tr>
<td>total</td>
<td>61</td>
<td>101</td>
<td>53</td>
</tr>
</tbody>
</table>

† including Si, Ge, As, Sb, Te. All temperature ranges
‡ including slightly distorted variants
‡ noble gases

At high pressures, we obtain the statistics given in Table 14.1. As can be seen, the additional structures at high pressures are mainly closest-packings of spheres and ‘exotic’ metal structures. At high temperatures the body-centered packing becomes more important. This is in accordance with the GOLDSCHMIDT rule:

Increased temperatures favor structures with lower coordination numbers.

### 14.3 Other Metal Structures

The crystal structures of most metals correspond to the above-mentioned packings of spheres (with certain distortions in some cases; Table 14.2). Some metals, however, show structure types of their own: Ga, Sn, Bi, Po, Mn, Pa, U, Np, and Pu. For Sn, Bi, and Po refer to pp. 121, 109 and 107. Gallium has a rather unusual structure in which every Ga atom has coordination number \( 1 + 6 \); one of the seven adjacent atoms is significantly closer than the others (\( 1 \times 244 \text{ pm}, 6 \times 270 \text{ to } 279 \text{ pm} \)). This has been interpreted as a metal structure consisting not of single atoms, but of Ga–Ga pairs with a covalent bond. The notably low melting point of gallium (29.8 °C) shows this structure to be not especially stable; it seems to be only an ‘expedient’. There also seems to be no optimal structure for Mn, U, Np, and Pu, as these elements form a remarkable number of polymorphic forms with rather peculiar structures. For example, the unit cell of \( \alpha \)-Mn, the modification stable at room temperature, contains 58 atoms with four different kinds of coordination polyhedra having coordination numbers 12, 13, and 16.

A remarkable number of unusual structures are observed at high pressures, especially among the alkali and alkaline earth metals (Fig. 14.4). For example, caesium is first transformed from a body-centered cubic packing to a cubic closest-packing at 2.3 GPa, which is not surprising. However, at increasing pressures, three modifications follow with atoms having coordination numbers of 8 – 11, then 8 and then 10 – 11; finally, at 70 GPa, a closest (double-hexagonal) packing of spheres reappears. An electron transition from the 6s to the 5d band is the assumed reason for this behavior. Some of the caesium modifications are also adopted by rubidium; in addition, rubidium exhibits an incommensurate composite structure between 16 and 20 GPa which is similar to that of bismuth-III.
(Fig. 11.11, p. 112). Incommensurate structures related to bismuth-III are also observed for strontium and barium. Magnesium, calcium and strontium are remarkable in that they transform from the normal closest-packing of spheres to a body-centered packing upon exertion of pressure. Even more remarkable is the following decrease of the coordination number to 6 for calcium and strontium (Ca-III, α-Po type; Sr-III, β-tin type).

Table 14.2: The element structures of the metals at ambient conditions

<table>
<thead>
<tr>
<th></th>
<th>h</th>
<th>c</th>
<th>hc</th>
<th>i</th>
<th>BR</th>
<th>/BA</th>
<th>/BB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li i</td>
<td>Be h</td>
<td>Na i</td>
<td>Mg h</td>
<td>K i</td>
<td>Ca c</td>
<td>Sc h</td>
<td>Ti h</td>
</tr>
<tr>
<td>V i</td>
<td>Cr i</td>
<td>Mn h</td>
<td>Fe i</td>
<td>Co h</td>
<td>Ni c</td>
<td>Cu c</td>
<td>Zn h*</td>
</tr>
<tr>
<td>hcc</td>
<td>cchh</td>
<td>h</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The solid noble gases also adopt closest-packings of spheres at low temperatures: Ne… Xe c; helium becomes solid only under pressure (depending on pressure, c, h or i)

14.4 Problems

14.1 State the JAGONDZINSKI and the ZHDANOV symbols for the closest-packings of spheres with the following stacking sequences:
   (a) ABABC; (b) ABABACAC.

14.2 State the stacking sequence (by A, B and C) for the closest-packings of spheres with the following JAGONDZINSKI or ZHDANOV symbols:
   (a) hcc; (b) cchh; (c) 221.
**Fig. 14.4**

Regions of stability for the structure types of the alkali and alkaline earth metals in dependence on pressure at room temperature.

- $h$ = hexagonal closest-packing;
- $c$ = cubic closest-packing;
- $hc = $ double-hexagonal closest-packing;
- $i = $ body-centered cubic; $cP =$ cubic primitive ($\alpha$-Po);
- $^* =$ slightly distorted; Cs-IV: c.n. = 8, arrangement as the Th atoms in ThSi$_2$ (Fig. 13.1, p. 131)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Structure Type</th>
<th>Stability Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>$i$</td>
<td>$c$ Li-IV, $I\bar{4}3d$, c.n. 11</td>
</tr>
<tr>
<td>Na</td>
<td>$i$</td>
<td>$c$</td>
</tr>
<tr>
<td>K</td>
<td>$i$</td>
<td>$c$ Bi-III$^*$</td>
</tr>
<tr>
<td>Rb</td>
<td>$i$</td>
<td>$c$ Cs-IV Cs-V, c.n. 10, 11</td>
</tr>
<tr>
<td>Cs</td>
<td>$i$</td>
<td>$c$ Cs-IV Cs-V, c.n. 10, 11</td>
</tr>
<tr>
<td>Mg</td>
<td>$h$</td>
<td>$i$</td>
</tr>
<tr>
<td>Ca</td>
<td>$c$</td>
<td>$i$ $cP$ $^*$</td>
</tr>
<tr>
<td>Sr</td>
<td>$c$</td>
<td>$i$ Sn $^<em>$     Bi-III$^</em>$</td>
</tr>
<tr>
<td>Ba</td>
<td>$i$</td>
<td>$h^<em>$ Bi-III$^</em>$</td>
</tr>
</tbody>
</table>
15 The Sphere-packing Principle for Compounds

The geometric principles for the packing of spheres do not only apply to pure elements. As might be expected, the sphere packings discussed in the preceding chapter are also frequently encountered when similar atoms are combined, especially among the numerous alloys and intermetallic compounds. Furthermore, the same principles also apply to many compounds consisting of elements which differ widely.

15.1 Ordered and Disordered Alloys

Different metals can very frequently be mixed with each other in the molten state, \( i.e. \) they form homogeneous solutions. A solid solution is obtained by quenching the liquid; in the disordered alloy obtained this way, the atoms are distributed randomly. When cooled slowly, in some cases solid solutions can also be obtained. However, it is more common that a segregation takes place, in one of the following ways:

1. The metals crystallize separately (complete segregation).
2. Two kinds of solid solutions crystallize, a solution of metal 1 in metal 2 and vice versa (limited miscibility).
3. An alloy with a specific composition crystallizes; its composition may differ from that of the liquid (formation of an intermetallic compound). The composition of the liquid can change during the crystallization process and further intermetallic compounds with other compositions may crystallize.

The phase diagram shows which of these possibilities applies and whether intermetallic compounds will eventually form (cf. Section 4.5, p. 34).

The tendency to form solid solutions depends mainly on two factors, namely the chemical relationship between the elements and the relative size of their atoms.

Two metals that are chemically related and that have atoms of nearly the same size form disordered alloys with each other. Silver and gold, both crystallizing with cubic closest-packing, have atoms of nearly equal size (radii 144.4 and 144.2 pm). They form solid solutions (mixed crystals) of arbitrary composition in which the silver and the gold atoms randomly occupy the positions of the sphere packing. Related metals, especially from the same group of the periodic table, generally form solid solutions which have any composition if their atomic radii do not differ by more than approximately 15%; for example Mo + W, K + Rb, K + Cs, but not Na + Cs. If the elements are less similar, there may be a limited miscibility as in the case of, for example, Zn in Cu (amount-of-substance fraction of Zn maximally 38.4%) and Cu in Zn (maximally 2.3% Cu); copper and zinc additionally form intermetallic compounds (cf. Section 15.4).

When the atoms differ in size or when the metals are chemically different, structures with ordered atomic distributions are considerably more likely. Since the transition from a
disordered to an ordered state involves a decrease in entropy, and since the transition only takes place when \( \Delta G = \Delta H - T \Delta S \leq 0 \), the transformation enthalpy \( \Delta H \) must be negative. The ordered structure therefore is favored energetically; the amount of its lattice energy is larger.

An ordered distribution of spheres of different sizes always allows a better filling of space; the atoms are closer together, and the attractive bonding forces become more effective. As for the structures of other types of compound, we observe the validity of the principle of the most efficient filling of space. A definite order of atoms requires a definite chemical composition. Therefore, metal atoms having different radii preferentially will combine in the solid state with a definite stoichiometric ratio: they will form an intermetallic compound.

Even when complete miscibility is possible in the solid state, ordered structures will be favored at suitable compositions if the atoms have different sizes. For example: copper atoms are smaller than gold atoms (radii 127.8 and 144.2 pm); copper and gold form mixed crystals of any composition, but ordered alloys are formed with the compositions AuCu and AuCu\(_3\) (Fig. 15.1). The degree of order is temperature dependent; with increasing temperatures the order decreases continuously. Therefore, there is no phase transition with a well-defined transition temperature. This can be seen in the temperature dependence of the specific heat (Fig. 15.2). Because of the form of the curve, this kind of order–disorder transformation is also called a \( \Lambda \) type transformation; it is observed in many solid-state transformations.

### 15.2 Compounds with Close-packed Atoms

As in ionic compounds, the atoms in a binary intermetallic compound show a tendency, albeit less pronounced, to be surrounded by atoms of the other kind as far as possible. However, it is not possible to fulfill this condition simultaneously for both kinds of atoms if they form a closest-packed arrangement. For compositions MX\(_n\) with \( n < 3 \) it cannot be fulfilled for either the M or the X atoms: in every case every atom has to have some adjacent atoms of the same kind. Only with a higher content of X atoms, beginning with MX\(_3\) (\( n \geq 3 \)), are atomic arrangements possible in which every M atom is surrounded solely by X atoms; the X atoms, however, must continue to have other X atoms as neighbors.

Usually, the composition of the compound is fulfilled in all of the hexagonal layers. This facilitates a rational classification of the extensive data: it is only necessary to draw a sketch of the atomic arrangement in one layer and to specify the stacking sequence.

![Fig. 15.1](image1)
The structures of the ordered alloys AuCu and AuCu\(_3\). At higher temperatures they are transformed to alloys which have all atomic positions statistically occupied by the Cu and Au atoms.
Variation of the specific heat $C_p$ with temperature of AuCu$_3$ (A-type transformation).

The most important structure types of this kind are the following (M atoms dark gray in the figures; positions of M atoms in the following layer marked by black circles):

1. MX$_3$ structures with hexagonal arrangement of M atoms in one layer

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Zhdanov Symbol</th>
<th>Jagodzinski Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuCu$_3$</td>
<td>∞</td>
<td>c</td>
</tr>
<tr>
<td>SnNi$_3$</td>
<td>11</td>
<td>h</td>
</tr>
</tbody>
</table>

2. MX$_3$ structures with rectangular arrangement of M atoms

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Zhdanov Symbol</th>
<th>Jagodzinski Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiAl$_3$</td>
<td>∞</td>
<td>c</td>
</tr>
<tr>
<td>TiCu$_3$</td>
<td>11</td>
<td>h</td>
</tr>
</tbody>
</table>

3. MX structures with alternating strings of equal atoms

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Zhdanov Symbol</th>
<th>Jagodzinski Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuCu</td>
<td>∞</td>
<td>c</td>
</tr>
<tr>
<td>AuCd</td>
<td>11</td>
<td>h</td>
</tr>
<tr>
<td>TaRh</td>
<td>33</td>
<td>hcc</td>
</tr>
</tbody>
</table>

Because strings of the same atoms come to be adjacent when these layers are stacked, alternating layers of atoms of one kind each are formed. These layers are planar in AuCu; they are inclined relative to the plane of the paper; in the unit cell (Fig. 15.1) they are parallel to the base plane. The layers of equal atoms are undulated in the other two structure types.
15.3 Structures Derived of Body-centered Cubic Packing (CsCl Type)

Disordered alloys may form when two metals are mixed if both have body-centered cubic structures and if their atomic radii do not differ by much (e.g. K and Rb). The formation of ordered alloys, however, is usually favored; at higher temperatures the tendency towards disordered structures increases. Such an arrangement can even be adopted if metals are combined which do not crystallize with body-centered cubic packings themselves, on condition of the appropriate composition. β-Brass (CuZn) is an example; below 300 °C it has a CsCl structure, but between 300 °C and 500 °C a Λ type transformation takes place resulting in a disordered alloy with a body-centered cubic structure.

The CsCl type offers the simplest way to combine atoms of two different elements in the same arrangement as in body-centered cubic packing: the atom in the center of the unit cell is surrounded by eight atoms of the other element in the vertices of the unit cell. In this way each atom only has adjacent atoms of the other element. This is a condition that cannot be fulfilled in a closest-packing of spheres (cf. preceding section).

Although the space filling of the body-centered cubic sphere packing is somewhat inferior to that of a closest-packing, the CsCl type thus turns out to be excellently suited for compounds with a 1:1 composition. Due to the occupation of the positions 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ with different kinds of atoms, the structure is not body-centered.

We presented the CsCl type in Chapter 7 as an important structure type for ionic compounds. Its importance, however, is by no means restricted to this class of compounds: only about 12 out of more than 200 compounds with this structure are salt-like (e.g. CsI, TlBr), although at higher temperatures or higher pressures there are some 15 more (e.g. NaCl, KCl at high pressure; TICN at high temperature with rotating CN$^{-}$ ions). More than 200 representatives are intermetallic compounds, e.g. MgAg, CaHg, AlFe and CuZn.

Superstructures of the CsCl type result when the unit cell of the CsCl structure is multiplied and the atomic positions are occupied by different kinds of atoms. If we double the cell edges in all three dimensions, we obtain a cell that consists of eight subcells, each of which contains one atom in its center (Fig. 15.3). The 16 atoms in the cell can be subdivided into four groups of four atoms each; each group has a face-centered arrangement. Depending on how we distribute atoms of different elements among these four groups, we obtain different structure types, as listed in Fig. 15.3. The list includes possibilities with certain vacant atomic positions (marked with the SCHOTTKY symbol $\square$ in the table). This option reduces the space filling; however, as long as the positions $a$ and $b$ are occupied by different kinds of atoms than the positions $c$ and $d$, each atom still has only atoms of a different kind as nearest neighbors. Consequently, the structure types are adequate for ionic compounds, including ZINTL phases with simple ‘anions’ such as As$^{3-}$, Sb$^{3-}$ or Ge$^{4-}$.

The following series shows that the mentioned structure types are adopted by all kinds of compounds from purely ionic to purely metallic:

<table>
<thead>
<tr>
<th>Fluorite type and variants</th>
<th>Fe$_3$Al type and variants</th>
<th>W type</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_2$Ca Li$_2$O Li$_2$Te LiMgAs Mg$_2$Sn</td>
<td>Cu$_3$Sb Cu$_2$MnAl Fe$_3$Al</td>
<td>Fe</td>
</tr>
<tr>
<td>ionic</td>
<td>ionic</td>
<td>metallic</td>
</tr>
</tbody>
</table>
When covalent bonds favor neighbors of the same element, the positions \(c\) and \(d\) can also be occupied by atoms of the same kind as in \(a\) or \(b\). This applies to diamond and to the ZINTL phase NaTl; NaTl can be regarded as a network of Tl\(^-\) particles that form a diamond structure which encloses Na\(^+\) ions (cf. Fig. 13.3, p. 134).

### 15.4 Hume–Rothery Phases

HUMER–ROTHERY phases (brass phases, ‘electron compounds’) are certain alloys with the structures of the different types of brass (brass = Cu–Zn alloys). They are classical examples of the structure-determining influence of the valence electron concentration (VEC) in metals. VEC = (number of valence electrons)/(number of atoms). A survey is given in Table 15.1.

\(\alpha\)-Brass is a solid solution of zinc in copper which has the structure of copper; the atoms statistically occupy the positions of the cubic closest-packing of spheres. In \(\beta\)-brass,
which is obtained by quenching the melt, the atoms also have a random distribution, and the packing is body-centered cubic. The composition is not exactly CuZn; this phase is stable only if the fraction of zinc atoms amounts to 45 to 48%. The γ phase also has a certain range of compositions from Cu₅Zn₆ to Cu₅Zn₉. The γ-brass structure can be described as a superstructure of the body-centered cubic packing with tripled lattice constants, so that the unit cell has a volume enlarged by a factor \(3^3 = 27\). However, the cell only contains 52 instead of \(2 \times 27 = 54\) atoms; there are two vacancies. The distribution of the vacancies is ordered. There are four kinds of positions for the metal atoms in a ratio of \(3:2:2:6\), but a random distribution may occur to some extent. In Cu₅Zn₈ the distribution is \(3\text{Cu} : 2\text{Cu} : 2\text{Zn} : 6\text{Zn}\). A brass sample with a composition outside of the mentioned ranges consists of a mixture of the two neighboring phases.

Because of the permitted composition ranges, alloys with rather different compositions can adopt the same structure, as can be seen by the examples in Table 15.1. The determining factor is the valence electron concentration, which can be calculated as follows:

<table>
<thead>
<tr>
<th>Alloys</th>
<th>(\frac{1+2}{2} = \frac{3}{2} = \frac{21}{14})</th>
<th>(\frac{5+16}{13} = \frac{21}{13})</th>
<th>(\frac{1+6}{4} = \frac{7}{4} = \frac{21}{12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgZn</td>
<td>Cu₅Zn₈</td>
<td>Cu₉Al₄</td>
<td>Na₃Pb₈</td>
</tr>
<tr>
<td>Cu₃Al</td>
<td>(\frac{3+3}{4} = \frac{6}{4} = \frac{21}{14})</td>
<td>(\frac{9+12}{13} = \frac{21}{13})</td>
<td>(\frac{3+4}{4} = \frac{7}{4} = \frac{21}{12})</td>
</tr>
<tr>
<td>Cu₅Sn</td>
<td>(\frac{5+4}{6} = \frac{9}{6} = \frac{21}{14})</td>
<td>(\frac{31+32}{39} = \frac{21}{13})</td>
<td>(\frac{5+9}{8} = \frac{14}{8} = \frac{21}{12})</td>
</tr>
</tbody>
</table>

A theoretical interpretation relating the valence electron concentration and the structure was put forward by H. Jones. If we start from copper and add more and more zinc, the valence electron concentration increases. The added electrons have to occupy higher energy levels, i.e. the energy of the Fermi limit is raised and comes closer to the limits of the first Brilliouin zone. This is approached at about VEC = 1.36. Higher values of the VEC require the occupation of antibonding states; now the body-centered cubic lattice becomes more favorable as it allows a higher VEC within the first Brilliouin zone, up to approximately VEC = 1.48.

### 15.5 Laves Phases

The term LAVES phases is used for certain alloys with the composition MM′₂, the M atoms being bigger than the M′ atoms. The classical representative is MgCu₂; its structure is shown in Fig. 15.4. It can be regarded as a superstructure of the CsCl type as in Fig. 15.3, with the following occupation of the positions \(a\), \(b\), \(c\), and \(d\):

\[
\begin{align*}
  a: & \text{Mg} & b: & \text{Cu}_4 & c: & \text{Mg} & d: & \text{Cu}_4 \\
\end{align*}
\]
We thus have placed a tetrahedron of four Cu atoms instead of a single atom in the position \( b \); the same kind of Cu tetrahedron then also results at the position \( d \). The magnesium atoms by themselves have the same arrangement as in diamond.

In addition to this cubic LAVES phase, a variant with magnesium atoms arranged as in hexagonal diamond exists in the MgZn\(_2\) type, and further polytypes are known.

The copper atoms of the MgCu\(_2\) type are linked to a network of vertex-sharing tetrahedra (Fig. 15.4), so that every Cu atom is linked with six other Cu atoms. If we assume an electron distribution according to the formula \( \text{Mg}^{2+}(\text{Cu}^-) \), every copper atom attains a valence electron concentration of \( \text{VEC}(	ext{Cu}) = \frac{1}{2}(1 \cdot 2 + 2 \cdot 11) = 12 \). Taking equation (13.7) from p. 129, adapted to transition metals as \( b(\text{X}) = 18 - \text{VEC(M)} \), we calculate \( b(\text{X}) = 18 - 12 = 6 \) bonds per Cu atom. In other words, by linking Cu particles this way, copper attains the electron configuration of the next noble gas. MgCu\(_2\), in a way, fulfills the rules for a ZINTL phase. Nevertheless, LAVES phases customarily are not considered to be ZINTL phases; some 170 intermetallic compounds having the MgCu\(_2\) structure are known, and most of them do not fulfill ZINTL’s valence rule (e.g. CaAl\(_2\), YCo\(_2\), LiPt\(_2\)).

The space filling in the MgCu\(_2\) type can be calculated with the aid of equation (14.1) (p. 150); the geometric relations follow from the bottom image in Fig. 15.4: the four Cu spheres form a row along the diagonal of length \( a\sqrt{2} \), therefore \( r(\text{Cu}) = \frac{1}{8}\sqrt{2}a \); two Mg
spheres along the space diagonal of the unit cell are at a distance of \( \frac{1}{4}\sqrt{3}a \), therefore \( r(\text{Mg}) = \frac{1}{8}\sqrt{3}a \). The ideal radius ratio is therefore

\[
\frac{r(\text{Mg})}{r(\text{Cu})} = \frac{\sqrt{3}}{2} = 1.225
\]

and the space filling is

\[
\frac{4}{3} \pi \frac{1}{a^3} \left[ 8 \left( \frac{1}{8}\sqrt{3}a \right)^3 + 16 \left( \frac{1}{8}\sqrt{2}a \right)^3 \right] = 0.710
\]

(the unit cell contains 8 Mg and 16 Cu atoms). The space filling of 71.0 % is somewhat inferior to that in a closest-packing of spheres (74.1 %). The coordination of the atoms is the following:

- Mg: c.n. 16, 4 Mg at a distance of \( \frac{1}{8}\sqrt{2}a \) and 12 Cu at a distance of \( \frac{1}{8}\sqrt{11}a \);
- Cu: c.n. 12, 6 Cu at a distance of \( \frac{1}{8}\sqrt{8}a \) and 6 Mg at a distance of \( \frac{1}{8}\sqrt{11}a \).

The coordination polyhedra are FRANK–KASPER polyhedra. These are polyhedra with equal or different triangular faces, and at least five triangles meeting at every vertex. Such polyhedra allow for the coordination numbers 12, 14, 15, and 16. Fig. 15.5 shows the two FRANK–KASPER polyhedra occurring in MgCu_2. FRANK–KASPER polyhedra and the corresponding high coordination numbers are known among numerous intermetallic compounds.

The sketched model assuming hard spheres has a flaw: the sum of the atomic radii of Mg and Cu is smaller than the shortest distance between these atoms:

\[
r(\text{Mg}) + r(\text{Cu}) = \frac{1}{8}(\sqrt{3} + \sqrt{2})a = 0.393a
\]

\[
d(\text{Mg–Cu}) = \frac{1}{8}\sqrt{11}a = 0.415a
\]

Whereas the Mg atoms are in contact with each other and the Cu atoms are in contact with each other, the Cu partial structure ‘floats’ inside the Mg partial structure. The hard sphere model proves to be insufficient to account for the real situation: atoms are not really hard. The principle of the most efficient filling space should rather be stated as the principle of achieving the highest possible density. Indeed, this shows up in the actual densities of the LAVES phases; they are greater than the densities of the components (in some cases up to 50 % more). For example, the density of MgCu_2 is 5.75 g cm\(^{-3}\), which is 7% more than the mean density of 5.37 g cm\(^{-3}\) for 1 mole Mg + 2 moles Cu. Therefore,

![Fig. 15.5](image)

**Fig. 15.5**

FRANK–KASPER polyhedra in MgCu_2. The polyhedron around an Mg atom (c.n. 16) is composed of 12 Cu atoms and of four Mg atoms that form a tetrahedron by themselves; the Cu atoms form four triangles that are opposed to the Mg atoms. The polyhedron around a Cu atom (c.n. 12) is an icosahedron in which two opposite faces are occupied by Cu atoms.
the atoms have a denser packing in MgCu₂ than in the pure elements, the atoms are effectively smaller. According to the hard sphere model, MgCu₂ should not be formed at all, as its space filling of 71% is inferior to that of both magnesium and copper, both of which crystallize with closest-packings of spheres (74% space filling).

It is mainly the Mg atoms that are affected by the compression of the atoms. The increase in density is the expression of the gain in lattice energy due to stronger bonding forces between the different kinds of atoms. These bonding forces have polar contributions since LAVES phases of this type experience a higher compression when the difference in the electronegativities of the atoms is higher. The polarity is an argument in favor of regarding LAVES phases in a similar way as ZINTL phases. More insight into the kind of bonding has been obtained by band structure calculations, which also allow the distinction of the electron counts at which the cubic MgCu₂ or the hexagonal MgZn₂ type is favored.

15.6 Problems

15.1 Use Table 14.2 to decide whether the following pairs of metals are likely to form disordered alloys of arbitrary composition with each other.
(a) Mg/Ca; (b) Ca/Sr; (c) Sr/Ba; (d) Lu/Ac; (e) Ti/Mn; (f) Ru/Os; (g) Pr/Nd; (h) Eu/Gd.

15.2 Draw a section of each of the structure types presented on p. 159 corresponding to a plane running in the vertical direction of the figure and perpendicular to the plane of the paper.

15.3 What structure types result when the atomic positions in Fig. 15.3 are occupied in the following manner (A, B, C and D refer to chemical elements)?
(a) a A, b A, c □, d B; (b) a A, b B, c C, d □; (c) a A, b A, c C, d D.

15.4 How is it possible that both Ag₅Zn₈ and Cu₉Al₄ have the γ-brass structure even though their compositions differ?

15.5 Can an icosahedron be considered to be a FRANK–KASPER polyhedron?
The immediate surroundings of single atoms can be rationalized quite well with the aid of coordination polyhedra, at least when the polyhedra show a certain degree of symmetry to a good approximation. The most important polyhedra are presented in Fig. 2.2 (p. 5). Larger structural entities can be regarded as a system of linked polyhedra. Two polyhedra can be linked by sharing a common vertex, a common edge or a common face, i.e. they share one, two or three (or more) common bridging atoms (Fig. 2.3, p. 6).

Depending on the kind of polyhedron and the kind of linking, the resulting bond angles at the bridging atoms have a definite value or values confined within certain limits. The bond angle is fixed by geometry in the case of face-sharing polyhedra. The bond angle can be varied within certain limiting values for vertex-sharing and in some cases for edge-sharing polyhedra by mutually rotating the polyhedra (Fig. 16.1; cf. also Fig. 16.18, p. 181). The values of the bond angles are listed in Table 16.1; they refer to undistorted tetrahedra and octahedra, and it is assumed that the closest contact of any two atoms corresponds to the distance of two adjacent atoms within a polyhedron. Distortions occur frequently and allow for an additional range of angles. Distortions may involve differing lengths of the polyhedron edges, but they may also come about by shifting the central atom out of the polyhedron center, thus changing the bond angles at the central atom and the bridging atoms even when the polyhedron edges remain constant.
Table 16.1: Bond angles at the bridging atoms and distances between the central atoms M of linked tetrahedra and octahedra (disregarding possible distortions). The distances are given as multiples of the polyhedron edge length

<table>
<thead>
<tr>
<th>Polyhedron</th>
<th>Bond Angles (°)</th>
<th>Linking by</th>
<th>M–M Distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedron</td>
<td>102.1 to 180°</td>
<td>vertices</td>
<td>0.95 to 1.22</td>
</tr>
<tr>
<td></td>
<td>66.0 to 70.5°</td>
<td>edges</td>
<td>0.66 to 0.71</td>
</tr>
<tr>
<td></td>
<td>38.9°</td>
<td>faces</td>
<td>0.41</td>
</tr>
<tr>
<td>Octahedron</td>
<td>131.8 to 180°</td>
<td>vertices</td>
<td>1.29 to 1.41</td>
</tr>
<tr>
<td></td>
<td>90°</td>
<td>edges</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>70.5°</td>
<td>faces</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Distortions of coordination polyhedra can often be interpreted according to the Gillespie–Nyholm rules and by taking into account the electrostatic forces. For example, a mutual repulsion of the Fe atoms can be perceived in the two edge-sharing tetrahedra of the (FeCl$_3$)$_2$ molecule; it can be ascribed to their positive partial charges. These Fe–Cl distances to the bridging atoms thus become longer than the remaining Fe–Cl bonds. The Cl atoms adjust their positions by a slight deformation of the tetrahedra. If the bridging atoms have a more negative partial charge than the terminal atoms, they counterbalance this kind of distortion since they exert a stronger attraction towards the central atoms which now only experience a decreased shift from the polyhedron centers. (FeSCL$_2^{2-}$, which is iso-electronic with (FeCl$_3$)$_2$, is an example (Fig. 16.2); in order to compare the electrostatic forces, in a simplified manner one can assume the existence of ions Fe$^{3+}$, Cl$^-$ and S$^{2-}$).

The way in which polyhedra will join depends on several factors, which include:

1. Chemical composition. Only very definite patterns of linking polyhedra are consistent with a given composition.
2. The nature of the bridging atoms. They tend to attain certain bond angles and tolerate only bond angles within certain limits. Bridging sulfur, selenium, chlorine, bromine, and iodine atoms (having two lone electron pairs) favor angles close to 100°. This angle is compatible with vertex-sharing tetrahedra and with edge-sharing octahedra; however, examples with smaller angles among edge-sharing tetrahedra and face-sharing octahedra are known. Bridging oxygen and fluorine atoms allow for angles up to 180°; frequently observed values are in the range 130° to 150°.
3. Bond polarity. Very polar bonds do not harmonize with edge-sharing polyhedra and

![Fig. 16.2](image_url)

Two edge-sharing tetrahedra showing only minor distortions in the Fe$_2$S$_2$Cl$_4^{2-}$ ion and two more distorted tetrahedra in the Fe$_2$Cl$_6$ molecule. The distortions can be ascribed mainly to the electrostatic repulsion between the Fe atoms. Bond lengths in pm
especially with face-sharing polyhedra because of the increased electrostatic repulsion between the central atoms (Pauling’s third rule, p. 59). Central atoms in high oxidation states therefore favor vertex-sharing. If there are two kinds of central atom, those with the higher oxidation state will avoid having their polyhedra linked with one another (Pauling’s fourth rule).

4. Interactions between the central atoms of the linked polyhedra. When a direct bond between the central atoms is advantageous, they tend to come close together. This favors edge-sharing or face-sharing arrangements. For example, the face-sharing of two octahedra in the $[\text{W}_2\text{Cl}_9]^{3-}$ ion renders the formation of a $\text{W}≡\text{W}$ triple bond possible; in this way every tungsten atom gains electrons in addition to its electronic configuration $d^3$ and the electrons supplied by the ligands, thus attaining noble gas configuration (18 valence electrons).

With our present knowledge, we often cannot understand, let alone predict, the more profound details concerning the kind of linking. Why does BiF$_5$ form linear, polymeric chains, SbF$_5$ tetrameric molecules and AsF$_5$ monomeric molecules? Why are there chloro and not sulfur bridges in (WSCl$_4$)$_2$? Why does no modification of TiO$_2$ exist which has the quartz structure?

The composition of a compound is intimately related to the way of linking the polyhedra. An atom X with coordination number c.n.(X) that acts as a common vertex to this number of polyhedra makes a contribution of $1/c.n.(X)$ to every polyhedron. If a polyhedron has $n$ such atoms, this amounts to $n/c.n.(X)$ for this polyhedron. This can be expressed with NigglI formulae, as shown in the following sections. To specify the coordination polyhedra, the formalism presented at the end of Section 2.1 and in Fig. 2.2 (p. 5) is useful.

### 16.1 Vertex-sharing Octahedra

A single octahedral molecule has the composition MX$_6$. Two octahedra with a common vertex can be regarded as a unit MX$_6$ to which a unit MX$_5$ has been added, so that the composition is M$_2$X$_{11}$. If the addition of MX$_5$ units is continued, one obtains chain-like or ring-like molecules of composition (MX$_5$)$_n$ (Fig. 16.3). In these, every octahedron has four terminal atoms and two atoms that act as common vertices to other octahedra, corresponding to the NigglI formula MX$_{4/1}$X$_{2/2}$. If the two bridging vertices of every octahedron are mutually in trans positions, the result is a chain; it can either be entirely straight as in BiF$_5$, with bond angles of 180° at the bridging atoms, or it can have a zigzag shape as in the CrF$_2^-$ ion, with bond angles between 132° and 180° (usually 132° to 150° for fluorides). If the two bridging vertices of every octahedron are in cis positions, a large number of geometrical arrangements are possible. Among these, zigzag chains as in CrF$_5$ and tetrameric molecules as in (NbF$_5$)$_4$ are of importance. Again, the bond angles at the bridging atoms can have values from 132° to 180°. In pentafluorides, the frequent occurrence of angles of either 132° or 180° has to do with the packing of the molecules in the crystal: these two values result geometrically when the fluorine atoms for themselves form a hexagonal or a cubic closest-packing of spheres, respectively.
16.1 Vertex-sharing Octahedra

Fig. 16.3
Some possibilities for joining octahedra via common vertices to form MX$_5$ chains and rings

(this is discussed in more detail in Chapter 17). The most important linking patterns for pentafluorides, pentafluoro anions and oxotetrahalides are:

<table>
<thead>
<tr>
<th>octahedron configuration</th>
<th>bond angle at bridging atom approx.</th>
<th>examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>rings (MF$_5$)$_4$</td>
<td>cis</td>
<td>180°</td>
</tr>
<tr>
<td>rings (MF$_5$)$_4$</td>
<td>cis</td>
<td>132°</td>
</tr>
<tr>
<td>linear chains</td>
<td>trans</td>
<td>180°</td>
</tr>
<tr>
<td>zigzag chains</td>
<td>trans</td>
<td>150°</td>
</tr>
<tr>
<td>zigzag chains</td>
<td>cis</td>
<td>180°</td>
</tr>
<tr>
<td>zigzag chains</td>
<td>cis</td>
<td>152°</td>
</tr>
</tbody>
</table>

The layer shown in the left part of Fig. 16.4 represents the most important way to join octahedra by sharing four vertices each; the composition is MX$_4 = MX_{2/1}X_{4/2}$ or
MX₄ layer of vertex-sharing octahedra, and the packing of such layers in the K₂NiF₄ type. The packing in SnF₄ is obtained by leaving out the K⁺ ions and shifting the layers towards each other in such a way that every octahedron apex of one layer comes to be between four apexes of the next layer.

Layers of this kind occur among some tetrafluorides such as SnF₄ and PbF₄ as well as in the anions of Tl[AlF₄] and K₂[NiF₄]. The K₂NiF₄ type has been observed in a series of fluorides and oxides: K₂MF₄ with M = Mg, Zn, Co, Ni; Sr₂MO₄ with M = Sn, Ti, Mo, Mn, Ru, Rh, Ir, and some others. The preference of K⁺ and Sr²⁺ has to do with the sizes of these cations: they just fit into the hollow between four F or O atoms of the non-bridging octahedron vertices (Fig. 16.4). Larger cations such as Cs⁺ or Ba²⁺ fit if the octahedra are widened because of large central atoms, as for example in Cs₂UO₄ or Ba₂PbO₄. The composition A₂MX₄ is fulfilled when all the hollows between the octahedron apexes on either side of the [MX₄]₂⁻ layer are occupied with Aⁿ⁺ ions. In the stacking of this kind of layer, the Aⁿ⁺ ions of one layer are placed exactly above the X atoms of the preceding layer. Every Aⁿ⁺ ion then has coordination number 9 (four of the bridging atoms in the layer, the four X atoms of the surrounding octahedron apexes and the one X atom of the next layer); the coordination polyhedron is a capped square antiprism.

If we stack MX₄ layers with octahedron apex on top of octahedron apex and amalgamate the apexes with each other, the result is the network of the ReO₃ structure with connections in three dimensions (Fig. 16.5). In this structure every octahedron shares all of its vertices with other octahedra; the bond angles at the bridging atoms are 180°. The centers of eight octahedra form a cube which corresponds to the unit cell. There is a rather large cavity in the center of the unit cell. This cavity can be occupied by a cation, which gives the perovskite type (perovskite = CaTiO₃); this structure type is rather frequent among compounds of the compositions AMF₃ and AMO₃, and because of its importance we discuss it separately (Section 17.4, p. 202).
16.1 Vertex-sharing Octahedra

Fig. 16.5
Top: framework of octahedra sharing all vertices = ReO$_3$ type.
Center and bottom: by rotating the octahedra, the ReO$_3$ type is converted to the VF$_3$, RhF$_3$ and calcite type. The unit cell of the VF$_3$ type is spanned by the threefold rotation axes running through the octahedra drawn in light gray.

ReO$_3$

VF$_3$, FeF$_3$, R$_3$c

RhF$_3$; FeF$_3$ (9 GPa)

CaO$_3$C (calcite)

The degree of space filling of the ReO$_3$ type can be increased by rotating the octahedra about the direction of one of the space diagonals of the cubic unit cell (Fig. 16.5). Thereby the large cavity in the ReO$_3$ cell becomes smaller, the octahedra come closer to each other, and the bond angles at the bridging atoms decrease from 180$^\circ$ to 132$^\circ$. Once this value is reached, we have the RhF$_3$ type, in which the F atoms are arranged as in a hexagonal closest-packing. A number of trifluorides crystallize with structures between these two extreme cases, with bond angles of about 150$^\circ$ at the F atoms: GaF$_3$, TiF$_3$, VF$_3$, CrF$_3$, FeF$_3$, CoF$_3$, and others. Some of them, such as ScF$_3$, are near to the ReO$_3$ type; others, such as MoF$_3$, are nearer to the hexagonal closest-packed structure. The mutual rotation of the octahedra can be continued to a ‘superdense’ sphere packing which contains groups which
have three squeezed atoms each. This corresponds to the structure of calcite (CaCO₃); the carbon atom of the carbonate ion is located in the center between three squeezed O atoms.

The described rotation of the octahedra can actually be performed. At ambient pressure \( (p = 10^{-4} \text{ GPa}) \), the octahedra of FeF₃ are turned by 17.0°, as compared to ReO₃. As listed in the table in the margin, they rotate under high pressure up to nearly 30°, which corresponds to the ideal RhF₃ type. Simultaneously, the lattice parameter \( a \) is reduced, whereas \( c \) shows only minor changes.

The LiSbF₆ type results when the sites of the metal atoms in the VF₃ type are occupied alternately by atoms of two different elements; this structure type is frequent among compounds AMF₆, e.g. ZnSnF₆. Similarly, two kinds of metal atoms can alternate in the metal positions of RhF₃ packing; this applies to PdF₃ (and PtF₃), which has to be regarded as Pd²⁺Pd⁴⁺F₆ or Pd²⁺[PdF₆]⁺⁻, as can be seen by the different Pd–F bond lengths of 217 pm (Pd²⁺) and 190 pm (Pd⁴⁺).

WO₃ occurs in a greater variety of modifications, all of which are distorted forms of the ReO₃ type (with W atoms shifted from the octahedron centers and with varying W–O bond lengths). In addition, a form exists that can be obtained by dehydrating WO₃·\( \frac{1}{4} \)H₂O; its framework is shown in Fig. 16.6. This also consists of vertex-sharing octahedra, with W–O–W bond angles of 150°. This structure is remarkable because of the channels it contains. These channels can be occupied by potassium ions in varying amounts, resulting in compositions KₓWO₃ ranging from \( x = 0 \) to \( x = 0.33 \) (rubidium and caesium ions can also be included). These compounds are termed hexagonal tungsten bronzes. Cubic tungsten bronzes have the ReO₃ structure with partial occupation of the voids by Li⁺ or Na⁺, i.e. they are intermediate between the ReO₃ type and the perovskite type. Tetragonal tungsten bronzes are similar to the hexagonal bronzes, but have narrower four and five-sided channels that can take up Na⁺ or K⁺ (Fig. 16.6). Tungsten bronzes are metallic conductors, and have metallic luster and colors that go from gold to black, depending on composition. They are very resistant chemically and serve as industrial catalysts and as pigments in ‘bronze colors’.

### Table: Observed octahedron rotation angles for FeF₃

<table>
<thead>
<tr>
<th>( p )/GPa</th>
<th>( a )/pm</th>
<th>( c )/pm</th>
<th>angle/°</th>
</tr>
</thead>
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<tr>
<td>10⁻⁴</td>
<td>521</td>
<td>1332</td>
<td>17.0</td>
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<tr>
<td>1.5</td>
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<td>21.7</td>
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<tr>
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</tr>
<tr>
<td>6.4</td>
<td>476</td>
<td>1348</td>
<td>28.2</td>
</tr>
<tr>
<td>9.0</td>
<td>470</td>
<td>1349</td>
<td>29.8</td>
</tr>
</tbody>
</table>

Fig. 16.6

Linking of the octahedra in hexagonal and tetragonal tungsten bronzes MₓWO₃.

In the direction of view, the octahedra are arranged one on top of the other with common vertices. The channels in this direction contain varying amounts of alkali metal ions.
16.2 Edge-sharing Octahedra

Two octahedra sharing one edge correspond to the composition \((\text{MX}_5)_2\) or \((\text{MX}_4/1\text{X}_2/2)_2\). This is the kind of structure common among pentahalides and ions \([\text{MX}_5]^{2-}\) when \(X = \text{Cl}, \text{Br} \) or I:

\[
\begin{align*}
(\text{SbCl}_5)_2 & \quad (\text{NbCl}_5)_2 & \quad (\text{TaCl}_5)_2 & \quad (\text{MoCl}_5)_2 & \quad (\text{WCl}_5)_2 & \quad (\text{ReCl}_5)_2 & \quad (\text{OsCl}_5)_2 & \quad (\text{UCl}_5)_2 \\
< -54^\circ \text{C} & \quad (\text{NbBr}_5)_2 & \quad (\text{TaBr}_5)_2 & \quad (\text{MCl}_4)_2 & \quad (\text{WBr}_5)_2 & \quad (\text{WeBr}_5)_2 & \quad (\text{UBr}_5)_2 & \quad (\text{PaBr}_5)_2 \\
(\text{NbI}_5)_2 & \quad (\text{TaI}_5)_2 & \quad (\text{MCl}_4)_2 & \quad (\text{WCl}_5)_2 & \quad (\text{OsCl}_5)_2 & \quad (\text{OsBr}_5)_2 & \quad (\text{PaI}_5)_2
\end{align*}
\]

There are some exceptions in which the metal atoms are not coordinated octahedrally: SbCl\(_5\) (monomeric above \(-54^\circ \text{C}\)), PCl\(_5\) (ionic PCl\(_4^+\)PCl\(_5^-\)), and PBr\(_5\) (ionic PBr\(_4^+\)Br\(^-\)). \((\text{MX}_5)_2\) molecules can be packed very efficiently in such a way that the X atoms for themselves form a closest-packing of spheres.

If the linking is continued to form a string of edge-sharing octahedra, the resulting composition is \(\text{MX}_2/1\text{X}_4/2\), i.e. \(\text{MX}_4\). Every octahedron then has two common edges with other octahedra in addition to two terminal X atoms. If the two terminal X atoms have a mutual trans arrangement, the chain is linear (Fig. 16.7). This kind of chain occurs among tetrachlorides and tetraiodides if metal–metal bonds form in pairs between the M atoms of adjacent octahedra; the metal atoms are then shifted from the octahedron centers in the direction of the corresponding octahedron edge, and the octaheda experience some distortion. Examples are NbCl\(_4\), NbI\(_4\), WCl\(_4\). The same kind of chain, but with metal atoms in the octahedron centers, has been observed for OsCl\(_4\).

If the two terminal X atoms of an octahedron in an MX\(_4\) chain have a cis arrangement, the chain can have a large variety of configurations. The most frequent one is a zigzag chain (Fig. 16.7); known examples include ZrCl\(_4\), TcCl\(_4\), PtCl\(_4\), PtI\(_4\), and UI\(_4\). Chains with other configurations are rare; ZrI\(_4\) is such an exception. Six edge-sharing octahedra can also join to form a ring (Fig. 16.7), but this kind of a structure is known for only one modification of MoCl\(_4\).

By linking edge-sharing octahedra to form a layer as in Fig. 16.8, all X atoms act as bridging agents, and every one of them simultaneously belongs to two octahedra. This kind of layer encloses voids that have an octahedral shape (see also the figure on the cover). The composition of the layer is \(\text{MX}_3\) \((\text{MX}_6/2)\). Numerous trichlorides, tribromides and triiodides and also some trihydroxides are composed of layers of this kind. The layers

---

**Fig. 16.7**

Some configurations of chains with composition MX\(_4\) consisting of edge-sharing octahedra
are stacked in such a way that the X atoms themselves form a closest-packing of spheres, namely:

**BiI$_3$ type**: hexagonal closest-packing of X atoms  
FeCl$_3$, CrBr$_3$, Al(OH)$_3$ (bayerite) and others

**AlCl$_3$ type**: cubic closest-packing of X atoms  
YCl$_3$, CrCl$_3$ (high temperature) and others

The same kind of layers also occur in a second modification of Al(OH)$_3$, hydrargillite (gibbsite), but with a stacking in which adjacent O atoms of two layers are exactly one on top of the other; they are joined via hydrogen bridges.

The CdCl$_2$ and the CdI$_2$ type are also layer structures (Fig. 16.9; because there exist numerous stacking variants of CdI$_2$, some authors prefer the term Cd(OH)$_2$ type instead of CdI$_2$ type). The octahedra in the layer share six edges each. The structure of the layer is the same as in an MX$_3$ layer if the voids in the MX$_3$ layer were occupied by M atoms. Every halogen atom is shared by three octahedra (MX$_{6/3}$). The stacking variants of the layers are:

**CdI$_2$ type** (Cd(OH)$_2$ type): hexagonal closest-packing of X atoms  
MgBr$_2$, TiBr$_2$, VBr$_2$, CrBr$_2$†, MnBr$_2$, FeBr$_2$, CoBr$_2$, NiBr$_2$, CuBr$_2$†  
MgI$_2$, CaI$_2$, PbI$_2$, TiI$_2$, VI$_2$, CrI$_2$†, MnI$_2$, FeI$_2$, CoI$_2$  
Mg(OH)$_2$, Ca(OH)$_2$, Mn(OH)$_2$, Fe(OH)$_2$, Co(OH)$_2$, Ni(OH)$_2$, Cd(OH)$_2$  
SnS$_2$, TiS$_2$, ZrS$_2$, NbS$_2$, PtS$_2$  
TiSe$_2$, ZrSe$_2$, PtSe$_2$  
Ag$_2$F, Ag$_2$O (F and O in the octahedron centers)

**CdCl$_2$ type**: cubic closest-packing of X atoms  
MgCl$_2$, MnCl$_2$, FeCl$_2$, CoCl$_2$, NiCl$_2$  
Cs$_2$O (O in the octahedron centers)

† distorted by Jahn–Teller effect
Among hydroxides such as Mg(OH)$_2$ (brucite) and Ca(OH)$_2$ the packing of the O atoms deviates from an ideal hexagonal closest-packing in that the layers are somewhat flattened; the bond angles M–O–M in the layer are larger than the ideal 90° for undistorted octahedra (e.g. 98.5° in Ca(OH)$_2$).

### 16.3 Face-sharing Octahedra

Two octahedra sharing a common face correspond to a composition M$_2$X$_9$ (Fig. 16.10). This structure is known for some molecules, for example Fe$_2$(CO)$_9$, and especially for some ions with trivalent metals. In some cases, the reason for the face-sharing is the presence of metal–metal bonds, for example in the [W$_2$Cl$_9$]$^{3-}$ ion; its small magnetic moment suggests a W≡W bond (cf. the structure shown on p. 168). The [Cr$_2$Cl$_9$]$^{3-}$ ion has the same structure, but nevertheless, it exhibits the paramagnetism that is to be expected for the electron configuration $d^3$; [Mo$_2$Cl$_9$]$^{3-}$ is intermediate in its behavior. The bond angles at the bridging atoms also reflect these differences: 58° in [W$_2$Cl$_9$]$^{3-}$, 77° in [Cr$_2$Cl$_9$]$^{3-}$.
[M2X9]3− ions are also known among compounds which have no metal–metal bonding, for example [Tl2Cl9]3− or [Bi2Br9]3−. The occurrence of this kind of ion often depends on the counter-ion, i.e. the packing in the crystal is an important factor. For example, Cs+ ions and Cl− ions, being of comparable size, allow close packing and facilitate the occurrence of these double octahedra. They also occur with large cations such as P(C6H5)4.

If opposite faces of the octahedra are used to continue their linking, the result is a strand of composition MX3 (Fig. 16.10). Strands of this kind occur among some trihalides of metals with an odd number of d electrons. Between pairs of adjacent octahedra metal–metal bonds occur: β-TiCl3, ZrI3 (d1), MoBr3 (d3), RuCl3, RuBr3 (d5). Anionic strands of the same kind are also known in compounds such as Cs[NiCl3] or Ba[NiO3]; again, the comparable sizes of the cations Cs+ and Ba2+ and the anions Cl− and O2−, respectively, facilitate close packing.

### 16.4 Octahedra Sharing Vertices and Edges

Units (MX5)2 can be joined via common vertices to form double strands as shown in Fig. 16.11. Since every octahedron still has two terminal atoms, the composition MX5X2Z2 or MX3Z results, the atoms in the common vertices being designated by Z. The same structure also results when two parallel strands of the BiF5 type are joined via common edges. Compounds such as NbOCl3, MoOBr3 or WO3 have this kind of structure, with oxygen atoms taking the positions of the common vertices.

In rutile every O atom is common to three octahedra, as expressed by the formula TiO6/3. As can be seen in Fig. 16.12, linear strands of edge-sharing octahedra are present, as in compounds MX4. Parallel strands are joined by common octahedron vertices. Compared with the layers of the CdI2 type, the number of common edges is reduced, namely two instead of six per octahedron. According to Pauling’s third rule (p. 59), this favors the rutile type for electrostatic reasons. Compounds MX2 with octahedrally coordinated M atoms therefore prefer the rutile type to the CdCl2 or CdI2 type if they are very polar: among dioxides and difluorides the rutile type is very common, examples being GeO2, SnO2, CrO2, MnO2, and RuO2 as well as MgF2, FeF2, CoF2, NiF2, and ZnF2.

In rutile the metal atoms in a strand of edge-sharing octahedra are equidistant. In some dioxides, however, alternating short and long M–M distances occur, i.e. the metal atoms are shifted in pairs from the octahedron centers towards each other. This phenomenon occurs (though not always) when the metal atoms still have d electrons and thus can engage
Strands of edge-sharing octahedra running parallel to \( c \) are joined with each other in rutile and \( \alpha\text{-PbO}_2 \) via common vertices in metal–metal bonds, for example in the low-temperature modifications of VO\(_2\), NbO\(_2\), MoO\(_2\), and WO\(_2\) (the high-temperature forms have the normal rutile structure).

The zigzag chains of edge-sharing octahedra that occur among compounds MX\(_4\) can also be joined by common vertices, resulting in the \( \alpha\text{-PbO}_2 \) type (Fig. 16.12). This structure type is less frequent.

Octahedra linked in different ways often occur when different kinds of metal atom are present. Li\(_2\)ZrF\(_6\) offers an example. The Li and the F atoms are arranged in layers of the same kind as in BiI\(_3\). The layers are joined by single ZrF\(_6\) octahedra which are placed below and on top of the voids of the layer (Fig. 16.13). The octahedra of the Li\(_2\)F\(_6\) layer share common edges with one another and they share vertices with the ZrF\(_6\) octahedra.

Numerous linking patterns, some of which are very complex, consisting mainly of octahedra sharing vertices and edges are known among polyvanadates, niobates, tantalates, molybdates, and tungstates. If only one of these elements occurs in the polyhedra, they are also called isopoly acids or isopoly anions. If additional elements also form part of the structures, they are called heteropoly acids; the additional atoms can be coordinated tetrahedrally, octahedrally, square-antiprismatically or icosahedrally. The dodecamolybdatophosphate \([PO_4Mo_{12}O_{36}]^{3-}\) is the classical example of this compound class; the precipitation of its ammonium salt serves as an analytical proof for phosphate ions. It has the KEGGIN structure: four groups consisting of three edge-sharing octahedra are
linked by common vertices, so that the twelve MoO₆ octahedra form a cage (Fig. 16.14). The tetrahedrally coordinated phosphorus atom is in the interior of the cage; it can be replaced by Al(III), Si(IV), As(V) and others. Octahedrally coordinated heteroatoms are found in the ions \([\text{EMo}_6\text{O}_{24}]^{2-}\), e.g. \([\text{TeMo}_6\text{O}_{24}]^{5-}\) \(\text{E} = \text{Te(VI)}, \text{I(VII)}, \text{Mn(IV)}\).

Some isopoly anions consist of a compact system of edge-sharing octahedra; a few examples are shown in Fig. 16.14. Oxygen atoms with high coordination numbers are situated in their interior; for example, the O atom at the center of the \([\text{W}_6\text{O}_{19}]^{2-}\) ion has coordination number 6. Other representatives with part of their octahedra sharing only vertices can have more or less large cavities in their interior, such as, for example, the \([\text{W}_{12}\text{O}_{42}]^{2-}\) ion. Isopoly anions are formed in aqueous solutions, depending on the pH value. Molybdate solutions, for example, contain MoO₄²⁻ ions at high pH values, \([\text{Mo}_7\text{O}_{24}]^{6-}\) ions at pH \(\approx 5\) and even larger aggregates in more acidic solutions. ‘Giant wheels’ can be obtained by reduction of part of the molybdenum atoms to Mo(IV), as in \(\text{H}_{48}\text{Mo}_{176}\text{O}_{536}\); the molecule consists of groups of vertex-sharing MoO₆ octahedra that share edges with pentagonal bipyramids, altogether forming a hoop with an inner diameter of 2.3 nm.
16.5 Octahedra Sharing Edges and Faces

The corundum structure (α-Al₂O₃) is the result of linking layers of the BiI₃ kind one on top of the other; the layers are mutually shifted as shown in Fig. 16.15. There are pairs of face-sharing octahedra and, in addition, every octahedron shares three edges within a layer and three vertices with octahedra from the adjacent layer to which it has no face-sharing connection. This structure type is adopted by some oxides M₂O₃ (e.g. Ti₂O₃, Cr₂O₃, α-Fe₂O₃).

Alternate layers can be occupied by two different kinds of metal atom, then every pair of the face-sharing octahedra contains two different metal atoms; this is the ilmenite type (FeTiO₃). Ilmenite is, along with perovskite, another structure type for the composition A⁺⁺M⁴⁺O₃. The space for the A²⁺ ion is larger in perovskite. Which structure type is preferred can be estimated with the aid of the ionic radius ratio:

\[ r(A^{2+})/r(O^{2-}) < 0.7 \quad \text{ilmenite} \]
\[ r(A^{2+})/r(O^{2-}) > 0.7 \quad \text{perovskite} \]

Another criterion for the same purpose is discussed on p. 203.

The **nickel arsenide type** (NiAs) is the result of linking layers of the kind as in cadmium iodide. Continuous strands of face-sharing octahedra perpendicular to the layers
arise from this connection. The same structure results when strands of the kind found in ZrI$_3$ are linked from all sides by common edges (Fig. 16.16). The nickel atoms in the octahedron centers form a primitive hexagonal lattice; every arsenic atom is surrounded by a trigonal prism of Ni atoms. Since the atoms in the face-sharing octahedra are quite close to one another, interactions must exist between them. This shows up in the electric properties: compounds with the NiAs structure are semiconductors or metallic conductors. Numerous representatives are known for this structure type: the metallic component is an element of the titanium to nickel groups, and Ga, Si, P, S, and their heavier homologous elements are adequate to substitute for the arsenic. Examples include TiS, TiP, CoS, and CrSb.

### 16.6 Linked Trigonal Prisms

In NiAs the Ni atoms form a network of trigonal prisms which contain the As atoms, and the Ni atoms have octahedral coordination. Metal atoms with trigonal-prismatic coordination are present in MoS$_2$. The S atoms form hexagonal planes with the stacking sequence AABBAABB... or AABBCC... (or some additional stacking variants). In every pair of congruent planes, e.g. AA, there are edge-sharing trigonal prisms which contain the Mo atoms and form a layer (Fig. 16.17). Between the layers, i.e. between sulfur atom planes having different positions, e.g. AB, the only attractive forces are weak VAN DER WAALS interactions. The MoS$_2$ layers can easily slip as in graphite; for this reason MoS$_2$ is used as a lubricant. Further similarities to graphite include the anisotropic electrical conductivity and the ability to form intercalation compounds, e.g. K$_{0.5}$MoS$_2$.

![Fig. 16.17](image)

Layer of edge-sharing trigonal prisms in MoS$_2$

### 16.7 Vertex-sharing Tetrahedra. Silicates

The linking of tetrahedra takes place predominantly by sharing vertices. Edge-sharing and especially face-sharing is considerably less frequent than among octahedra.

Two tetrahedra sharing a common vertex form a unit M$_2$X$_7$. This unit is known among oxides such as Cl$_2$O$_7$ and Mn$_2$O$_7$ and among several anions, e.g. S$_2$O$_7^{2-}$, Cr$_2$O$_7^{2-}$, P$_2$O$_7^{4-}$, Si$_2$O$_7^{6-}$ and Al$_2$Cl$_7^-$. Depending on the conformation of the two tetrahedra, the bond angle at the bridging atom can have values between 102.1° and 180° (Fig. 16.18).

A chain of vertex-sharing tetrahedra results when every tetrahedron has two terminal and two bridging atoms; the composition is MX$_{2/1}$X$_{2/2}$ or MX$_3$. The chain can be closed to form a ring as in [SO$_3$]$_3$, [PO$_3$]$^-$, [SiO$_3^{2-}$]$_3$ or [SiO$_3^{2-}$]$_6$. Endless chains have different shapes depending on the mutual conformation of the tetrahedra (Fig. 16.19). They occur especially among silicates, where the chain shape is also determined by the interactions...
16.7 Vertex-sharing Tetrahedra. Silicates

with the cations. In silicates of the composition MSiO₃ with octahedrally coordinated M²⁺ ions (M²⁺ = Mg²⁺, Ca²⁺, Fe²⁺, and others, ionic radii 50 to 100 pm), the coordination octahedra of the metal ions are arranged to form layers as in Mg(OH)₂. Thus the octahedra share edges, and their vertices are also shared with vertices of the SiO₂⁻⁻ chains corresponding to terminal O atoms of the chain; these O atoms thus link tetrahedra with octahedra. Different chain conformations occur, depending on the kind of cation, i.e. octahedron size (Fig. 16.19). Compounds of this kind such as enstatite, MgSiO₃, are termed pyroxenes if the silicate chain is a zweierkette, i.e. if the chain pattern repeats after two tetrahedra; pyroxenoids have more complicated chain forms, for example the dreierkette in wollastonite, CaSiO₃.

Linked tetrahedra in P₄O₁₀

Tetrahedra linked via three vertices correspond to a composition MX₁₁/₁X₆₃/₂ or MX₂₅ = M₂X₅. Small units consisting of four tetrahedra are known in P₄O₁₀, but most important are the layer structures in the numerous sheet silicates and aluminosilicates with anions of the compositions [Si₂O₅⁻⁻]∞ and [Al₂SiO₅³⁻⁻]∞. Because the terminal vertices of the single

*From the German zwei = two, drei = three, zweier = two-membered, dreier = three-membered, Kette = chain.

Fig. 16.19
Some forms of rings and chains of vertex-sharing tetrahedra in silicates. How the chain conformations adapt to the size of the cation octahedron is shown for two chains (the octahedron chain is a section of a layer)
Some arrangements of tetrahedra in sheet silicates. The lower image in each case represents a side view.

Sheet silicates are of frequent natural occurrence, the most important ones being clay minerals (prototype: kaolinite), talc (soapstone) and micas (prototype: muscovite). In these minerals the terminal O atoms of a silicate layer are bonded with octahedrally coordinated cations; these are mainly Mg$^{2+}$, Ca$^{2+}$, Al$^{3+}$ or Fe$^{2+}$. The octahedra are linked with each other by common edges, forming layers as in Mg(OH)$_2$ (≡ CdI$_2$) or Al(OH)$_3$ (≡ BiI$_3$). The number of terminal O atoms in the silicate layer is not sufficient to provide all of the O atoms for the octahedron layer, so the remaining octahedron vertices are occupied by additional OH$^-\)$ ions. Two kinds of linking between the silicate layer and the octahedron layer can be distinguished: in *cation-rich sheet silicates* an octahedron layer is linked with only one silicate layer on one of its sides, and the result is an octahedron–tetrahedron sheet;
in cation-poor sheet silicates there are tetrahedron-octahedron-tetrahedron sheets, an octahedron layer being linked to two silicate layers on either side (Fig. 16.21). Depending on whether the cation layer is of the Mg(OH)$_2$ or the Al(OH)$_3$ type, certain numerical relations result between the number of cations in the octahedron layer and the number of silicate tetrahedra; the number of OH$^-$ ions needed to complete the octahedra is also fixed by geometry. Additional cations may be intercalated between the sheets (Table 16.2).

The sheets consisting of tetrahedron-octahedron-tetrahedron layers in cation-poor sheet silicates are completely planar due to the symmetrical environment of the cation layer. If the sheets are electrically neutral as in talc, the attractive forces between them are weak; as a consequence, the crystals are soft and easy to cleave. The use of talc as powder, lubricating agent, polishing material and filling material for paper is due to these properties.

Micas are cation-poor sheet silicates consisting of electrically charged sheets that are held together by intercalated, unhydrated cations. For this reason the sheets cannot slip as in talc, but the crystals can be cleaved parallel to the sheets. The crystals usually form thin, stiff plates. Larger plates (in sizes from centimeters to meters) are used industrially because of their ruggedness, transparency, electrical insulating properties, and chemical and thermal resistance (muscovite up to approximately 500 °C, phlogopite, KMg$_3$(OH)$_2$[AlSi$_3$O$_{10}$], up to approximately 1000 °C).

Clay materials show a different behavior. They are either cation-poor or cation-rich sheet silicates. They can swell by taking up varying amounts of water between the sheets. If the intercalated cations are hydrated as in montmorillonite, they act as cation exchangers. Montmorillonite, especially when it has intercalated Ca$^{2+}$ ions, has thixotropic properties and is used to seal up drill holes. The effect is due to the charge distribution on
Table 16.2: Different kinds of sheet silicates

<table>
<thead>
<tr>
<th>cation layer</th>
<th>composition</th>
<th>examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>cation-rich sheet silicates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(OH)₃ type</td>
<td>M₂(OH)₄[T₂O₅]</td>
<td>kaolinite, Al₂(OH)₄[Si₂O₅]</td>
</tr>
<tr>
<td>Mg₂(OH)₄ type</td>
<td>M₃(OH)₄[T₂O₅]</td>
<td>chrysotile, Mg₃(OH)₄[Si₂O₅]</td>
</tr>
<tr>
<td>cation-poor sheet silicates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(OH)₃ type</td>
<td>M₂(OH)₂[T₄O₁₀]</td>
<td>pyrophyllite, Al₂(OH)₂[Si₄O₁₀]</td>
</tr>
<tr>
<td>Mg₂(OH)₄ type</td>
<td>M₃(OH)₂[T₄O₁₀]</td>
<td>talc (soapstone), Mg₃(OH)₂[Si₄O₁₀]</td>
</tr>
<tr>
<td>cation-poor sheet silicates with intercalations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(OH)₃ type</td>
<td>Aₙ[M₂(OH)₂[T₄O₁₀]]·nH₂O</td>
<td>muscovite, Kₙ[Al₂(OH)₂[AlSi₃O₁₀]</td>
</tr>
<tr>
<td>Mg₂(OH)₄ type</td>
<td>M₃(OH)₂[T₄O₁₀]</td>
<td>montmorillonite, Naₙ{Mg₃Al₂₋₄(OH)₂[Si₄O₁₀]}·nH₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>vermiculite, Mg₃(OH)₃[Si₄O₁₀]·nH₂O</td>
</tr>
</tbody>
</table>

T = tetrahedrally coordinated Al or Si
M = Mg²⁺, Ca²⁺, Al³⁺, Fe²⁺ etc.  A = Na⁺, K⁺, Ca²⁺ etc.

the crystal platelets: they bear a negative charge on the surface and a positive charge on the edges. In suspension they therefore orient themselves edge against surface, resulting in a jelly. Upon agitation the mutual orientation is disturbed and the mass is liquefied.

Swollen clay materials are soft and easy to mould. They serve to produce ceramic materials. High quality fire-clay has a high kaolinite content. Upon firing, the intercalated water is removed first at approximately 100 °C. Then, beginning at 450 °C, the OH groups are converted to oxidic O atoms by liberation of water, and after some more intermediate steps, mullite is formed at approximately 950 °C. Mullite is an aluminum aluminosilicate, Al₄O₁₀[Al₂Si₃O₁₀] with x ≈ 0.6 to 0.8.

Because the dimensions of an octahedron and a tetrahedron layer usually do not coincide exactly, the unilateral linking of the layers in cation-rich sheet silicates leads to tensions. If the dimensions do not deviate too much, the tension is relieved by slight rotations of the tetrahedra and the sheets remain planar. This applies to kaolinite, which has only Al³⁺ ions in the cation layer. With the larger Mg²⁺ ions the metric fit is inferior; the tension then causes a bending of the sheets. This can be compensated for by tetrahedron apexes periodically pointing to one side and then to the other side of the tetrahedron layer, as in antigorite (Fig. 16.22). If the bending is not compensated for, the sheets curl up to form tubes in the way shown in Fig. 16.22, corresponding to the structure of chrysotile, Mg₃(OH)₄[Si₂O₅]. Because the sheet only tolerates curvatures within certain limits, the tubes remain hollow and they cannot exceed some maximum diameter. The inner diameter in chrysotile is about 5 nm, the outer one 20 nm. The tubular building blocks explain the fibrous properties of chrysotile which used to be the most important asbestos mineral.

A layer of tetrahedra can be considered as being built up by linking parallel chains. That this is not a mere formalism is shown by the existence of intermediate stages. Two linked silicate chains result in a ribbon of the composition [Si₄O₁₁]ₙ; it has two kinds of tetrahedra, one kind being joined via three and the other kind via two vertices, [SiO₁/₁₂O₃/₁₂O₂/₁₂O₂/₁₂]³⁻. Silicates of this type are termed amphiboles. They are fibrous and also used to be used as asbestos.
16.7 Vertex-sharing Tetrahedra. Silicates

Fig. 16.22
Bent sheets of linked octahedron and tetrahedron layers in chrysotile and antigorite. Bottom: rolled sheets forming tubes in chrysotile

Linking Tetrahedra by All Four Vertices. Zeolites

Mercury iodide offers an example of a layer structure consisting of tetrahedra sharing all of their vertices (Fig. 16.23). Much more frequent are framework structures; they include the different modifications of SiO$_2$ and the aluminosilicates that are discussed in Section 12.5. Another important class of aluminosilicates are the zeolites. They occur as minerals, but are also produced industrially. They have structures consisting of certain polyhedra that are linked in such a way that hollows and channels of different sizes and shapes are present.

Fig. 16.24 shows the structure of the methylxotasiloxane, Me$_8$Si$_8$O$_{12}$, which can be made by hydrolysis of MeSiCl$_3$. Its framework is a cube of silicon atoms linked via oxygen
atoms placed on each cube edge. The O atoms are situated slightly to one side of the edges, thus allowing for a framework without tensions and bond angles of 109.5° at the Si atoms and of 148.4° at the O atoms. This framework has been drawn schematically in the rest of Fig. 16.24 as a simple cube. It is one of several possible building units occurring in zeolites; the place of the methyl groups is taken by O atoms which mediate the connection to other Si atoms. In addition to the cube, other polyhedra occur, some of which are shown in Fig. 16.24. Every vertex of these polyhedra is occupied by an Si or Al atom, and in the middle of each edge there is an O atom which joins two of the atoms in the vertices. In a zeolite four edges meet at every vertex, corresponding to the four bonds of the tetrahedrally coordinated atoms.

The linking pattern of two zeolites is shown in Fig. 16.24. They have the ‘β-cage’ as one of their building blocks, that is, a truncated octahedron, a polyhedron with 24 vertices and 14 faces. In the synthetic zeolite A (Linde A) the β-cages form a cubic primitive lattice, and are joined by cubes. β-Cages distributed in the same manner as the atoms in diamond and linked by hexagonal prisms make up the structure of faujasite (zeolite X).

The fraction of aluminum atoms in the framework is variable. For each of them there is one negative charge. As a whole, the framework is thus a polyanion; the cations...
occupy places in the hollows. This in principle applies also to other aluminosilicates, but the framework of the zeolites is much more open. This is the basis of the characteristic properties of the zeolites: they act as cation exchangers and absorb and release water easily. A zeolite that has been dehydrated by heating *in vacuo* is highly hygroscopic and can be used to remove water from solvents or gases. In addition to water, it can also absorb other molecules; the size and shape of the molecules relative to the size and shape of the hollow spaces in the zeolite determine how easily this occurs and how tightly the guest molecules are retained by the host framework. Different types of zeolite differ widely with regard to their hollows and channels, and they can be made to measure in order to take up certain molecules. This effect is applied for the selective separation of compounds, and therefore zeolites are also termed molecular sieves. For example, they can separate unbranched and branched alkanes, which is important for petroleum refineries. Even the separation of O\textsubscript{2} and N\textsubscript{2} is possible. The channels can also accommodate different molecules simultaneously, the shape of the channels forcing the molecules to adopt some definite mutual orientation. As a consequence, zeolites can act as selective catalysts. Synthetic zeolite ZSM-5, for example, serves to catalyze the hydrogenation of methanol to alkanes.

Zeolites are structurally related to colorless sodalite, Na\textsubscript{4}Cl[Al\textsubscript{3}Si\textsubscript{3}O\textsubscript{12}], and to deeply colored ultramarines. These have aluminosilicate frameworks that enclose cations but no water molecules (Fig. 16.25). Their special feature is the additional presence of anions in the hollows, e.g. Cl\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, S\textsubscript{2} or S\textsubscript{3}. The two last-mentioned species are colored radical ions (green and blue, respectively) that are responsible for the brilliant colors. The best-known representative is the blue mineral lapis lazuli, Na\textsubscript{4}S\textsubscript{x}[Al\textsubscript{3}Si\textsubscript{3}O\textsubscript{12}], which is also produced industrially and serves as color pigment.

**Fig. 16.25**
Sodalite and ultramarine framework

Framework silicates are also termed tectosilicates. Their common feature is the three-dimensional connection of tetrahedra sharing all four vertices. They are subdivided into:

1. Pyknolites, which have a framework with relatively small cavities that are filled with cations; for example: feldspars M\textsuperscript{+}[AlSi\textsubscript{3}O\textsubscript{8}] and M\textsuperscript{2+}[Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{8}\textsuperscript{2−}] such as K[AlSi\textsubscript{3}O\textsubscript{8}] (orthoclase, sanidine) or plagioclase, Ca\textsubscript{1−x}Na\textsubscript{x}[Al\textsubscript{2−x}Si\textsubscript{2+x}O\textsubscript{8}] which includes Na[AlSi\textsubscript{3}O\textsubscript{8}] (albite; x = 1) and Ca[Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{8}] (anorthite; x = 0). Feldspars, especially plagioclase, are by far the most abundant minerals in Earth’s crust.

2. Clathrasils, which have polyhedral cavities, but with windows that are too small to allow the passage of other molecules, so that enclosed ions or foreign molecules cannot escape. Examples are ultramarines and melanophlogite (SiO\textsubscript{2})\textsubscript{46}·8(N\textsubscript{2}, CO\textsubscript{2}, CH\textsubscript{4}).

3. Zeolites with polyhedral cavities which are connected by wide windows or channels that permit the diffusion of foreign ions or molecules.
The structural relationship between SiO₂ and H₂O (cf. Section 12.5) also shows up in the clathrates (inclusion compounds); they include clathrasils that enclose foreign molecules. Water forms analogous clathrate hydrates which consist of foreign molecules enclosed by a framework of H₂O molecules. As in ice, every O atom is surrounded by four H atoms. The structures are only stable in the presence of the enclosed molecules, otherwise the hollow, wide-meshed framework would collapse. The gas hydrates are among the best-known species of this kind. They have particles such as Ar, CH₄, H₂S or Cl₂ enclosed by a framework which has two dodecahedral and six larger tetrakaidecahedral (polyhedron with 14 faces) cavities per 46 molecules of H₂O (Fig. 16.26; the above-mentioned melanophlogite has the same structure). If all of the cavities are occupied, the composition is (H₂O)₄₆X₈ or X·5½H₂O; if only the larger cavities are occupied, as in the Cl₂ hydrate, the composition is (H₂O)₄₆(Cl₂)₂ or Cl₂·7½H₂O. Different frameworks with larger cavities form with larger foreign molecules. Examples include (CH₃)₃CNH₂·9½H₂O, HPF₆·6H₂O, and CHCl₃·17H₂O. Clathrates such as C₃H₈·17H₂O, which has a melting point of 8.5 °C, can crystallize from humid natural gas during cold weather and obstruct pipelines. (H₂O)₄₆(CH₄)₈ is stable at the pressures that exist in the oceans at depths below 600 m. There it occurs in huge amounts that surpass the deposits of natural gas; however, the extraction is not worthwhile because the energy needed for this purpose exceeds the combustion energy of the enclosed methane. The clathrate structure also occurs among the compounds Na₈Si₄₆, K₈Si₄₆, K₈Ge₄₆, and K₈Sn₄₆, the Si atoms taking the positions of the water molecules and thus having four bonds each. The alkali metal ions occupy the cavities, and their electrons contribute to a metallic electron gas.

16.8 Edge-sharing Tetrahedra

Two tetrahedra sharing one edge lead to the composition M₂X₆, as in Al₂Cl₆ (in the gaseous state or in solution) (Fig. 16.2, p. 167). Continuation of the linking using opposite edges results in a linear chain, with all X atoms having bridging functions. Chains of this kind are known in BeCl₂ and SiS₂ as well as in the anion of K[FeS₂] (Fig. 16.27).

If tetrahedra are joined via four of their edges, the resulting composition is MX₄/₄ or MX. This kind of linking corresponds to the structure of the red modification of PbO, in which O atoms occupy the tetrahedron centers and the Pb atoms the vertices (Fig. 16.28). This rather peculiar structure may be regarded as a consequence of the steric influence of...
the lone electron pair at the Pb(II) atom; if we include the electron pair, the coordination polyhedron of a lead atom is a square pyramid. The layer can be described as a checker board having O atoms at its cross-points; the Pb atoms are placed above the black and under the white fields of the board.

The CaF$_2$ structure can be regarded as a network of three-dimensionally linked, edge-sharing FCa$_4$ tetrahedra (cf. Fig. 17.3 b).

16.9 Problems

16.1 Take W$_4$O$_{16}^{8-}$ ions (Fig. 16.14) and pile them to form a column consisting of pairs of edge-sharing octahedra that alternate crosswise. What is the composition of the resulting column?

16.2 Take pairs of face-sharing coordination octahedra and join them by common vertices to form a chain, with every octahedron taking part in one common vertex not belonging to the shared face. What is the composition of the resulting chain?

16.3 What is the composition of a column of square antiprisms joined by common square faces?

16.4 Which of the following compounds could possibly form columns of face-sharing octahedra as in ZrI$_3$?

InF$_3$, InCl$_3$, MoF$_3$, MoI$_3$, TaS$_3^{2-}$

16.5 Take the network of vertex-sharing tetrahedra of the Cu atoms in MgCu$_2$ (Fig. 15.4) and assume that there is an additional atom inside of every tetrahedron. What structure type would this be?
17 Packings of Spheres with Occupied Interstices

The packing of polyhedral building blocks is mentioned repeatedly in Chapter 16, for example with respect to the difference between the CdCl$_2$ and CdI$_2$ types. These both consist of the same kind of layers of edge-sharing octahedra. The layers are stacked in such a way that the halogen atoms, taken by themselves, form a cubic closest-packing in the CdCl$_2$ type and a hexagonal closest-packing in the CdI$_2$ type. The metal atoms occupy octahedral interstices of the packing. Attention is focused in Chapter 16 on the linking of the polyhedra and on the corresponding chemical compositions, while the packing of the molecules or ions in the crystal is a secondary aspect. In this chapter we develop the same facts from the point of view of the general packing. We restrict the discussion mainly to the most important packing principle, that of the closest-packings of spheres.

That which applies to the cadmium halides also applies to many other compounds: a proportion of the atoms, taken by themselves, form a closest-packing, and the remaining atoms occupy interstices in this packing. The atoms forming the packing do not have to be the same, but they must have similar sizes, in the sense outlined in the Sections 15.1 and 15.2 concerning compounds with closest-packed atoms. In perovskite, CaTiO$_3$, for example, the calcium and the oxygen atoms together form a cubic closest-packing, and the titanium atoms occupy certain octahedral interstices. Due to the space requirements of the atoms in the interstices and to their bonding interactions with the surrounding atoms, the sphere packing frequently experiences certain distortions, but these are often surprisingly small. Moreover, it is possible to include atoms that are too large for the interstices if the packing is expanded; strictly speaking, the packing is then no longer a closest-packing (the spheres have no contact with each other), but their relative arrangement in principle remains unchanged.

17.1 The Interstices in Closest-packings of Spheres

Octahedral Interstices in the Hexagonal Closest-packing

Fig. 17.1(a) shows a section of two superimposed hexagonal layers in a closest-packing of spheres. This representation has the disadvantage that the spheres of layer A are largely concealed by the layer B. In all the following figures we will therefore use the representation shown in Fig. 17.1(b); it shows exactly the same section of the packing, but the spheres are drawn smaller. Of course, since the real size of the spheres is larger, the points of contact between the spheres can no longer be perceived, but we now gain an excellent impression of the sites of the octahedral interstices in the packing: they appear as the large holes surrounded by six spheres. The edges of two octahedra are plotted in Fig. 17.1(b); these two octahedra share a common edge. Fig. 17.1(c) represents a side view of a hexagonal closest-packing (looking towards the edges of the hexagonal layers); the two plotted octahedra share a common face. The two octahedra shown in Fig. 17.1(d) are next to each other at different heights, they share a common vertex.
From Fig. 17.1 we can see how adjacent octahedra are linked in a hexagonal closest-packing:

- face-sharing when the octahedra are located one on top of the other in the direction $c$;
- edge-sharing when they are adjacent in the $a$–$b$ plane;
- vertex-sharing when they are adjacent at different heights.

The bond angles at the bridging X atoms in the common octahedron vertices are fixed by geometry (angles M–X–M, M in the octahedron centers):

- $70.5^\circ$ for face-sharing;
- $90.0^\circ$ for edge-sharing;
- $131.8^\circ$ for vertex-sharing.

The number of octahedral holes in the unit cell can be deduced from Fig. 17.1(c): two differently oriented octahedra alternate in direction $c$, i.e. it takes two octahedra until the pattern is repeated. Hence there are two octahedral interstices per unit cell. Fig. 17.1(b) shows the presence of two spheres in the unit cell, one each in the layers $A$ and $B$. The number of spheres and of octahedral interstices are thus the same, i.e. there is exactly one octahedral interstice per sphere.

The size of the octahedral interstices follows from the construction of Fig. 7.2 (p. 53). There, it is assumed that the spheres are in contact with one another just as in a packing of spheres. A sphere with radius 0.414 can be accommodated in the hole between six octahedrally arranged spheres with radius 1.
From Fig. 17.1 we realize another fact. The octahedron centers are arranged in planes parallel to the $a\text{--}b$ plane, half-way between the layers of spheres. The position of the octahedron centers corresponds to the position $C$ which does not occur in the stacking sequence $ABAB\ldots$ of the spheres. We designate octahedral interstices in this position in the following sections by $\gamma$. By analogy, we will designate octahedral interstices in the positions $A$ and $B$ by $\alpha$ and $\beta$, respectively.

**Tetrahedral Interstices in the Hexagonal Closest-packing**

Fig. 17.2 shows sections of the hexagonal closest-packing in the same manner as in Fig. 17.1, but displaying tetrahedra made up of four spheres each. The tetrahedra share vertices in the $a\text{--}b$ plane. Pairs of tetrahedra share a common face in the stacking direction, and the pairs are connected with each other by common vertices. A pair can be regarded as a trigonal bipyramid. The center of the trigonal bipyramid is identical with the interstice between three atoms in the hexagonal layer; from the center, the axial atoms of the bipyramid are 41% more distant than the equatorial atoms. If we only consider the three equatorial atoms, the interstice is triangular; if we also take into account the axial atoms, it is trigonal-bipyramidal. The tetrahedral interstices are situated above and below this interstice. Within a pair of layers $AB$ a tetrahedron pointing upwards shares edges with three tetrahedra pointing downwards.

The bond angles $M\text{--}X\text{--}M$ at the bridging atoms between two occupied tetrahedra are:

- $56.7^\circ$ for face-sharing;
- $70.5^\circ$ for edge-sharing;
- $109.5^\circ$ for vertex-sharing.

As can be seen from Fig. 17.2(b), there is one tetrahedral interstice above and one below every sphere, i.e. there are two tetrahedral interstices per sphere.

According to the calculation of Fig. 7.2 (p. 53), a sphere with radius 0.225 fits into the tetrahedral hole enclosed by four spheres of radius 1.

**Fig. 17.2**

* Tetrahedra in hexagonal closest-packing:  
  (a) view of the hexagonal layers;  
  (b) view parallel to the hexagonal layers (stacking direction upwards)

**Octahedral and Tetrahedral Interstices in the Cubic Closest-packing**

In cubic closest-packing, consideration of the face-centered unit cell is a convenient way to get an impression of the arrangement of the interstices. The octahedral interstices are situated in the center of the unit cell and in the middle of each of its edges [Fig. 17.3(a)]. The octahedra share vertices in the three directions parallel to the unit cell edges. They share edges in the directions diagonal to the unit cell faces. There are no face-sharing octahedra.
17.1 The Interstices in Closest-packings of Spheres

Fig. 17.3
Face-centered unit cell of cubic closest-packing:
(a) with octahedral interstices (small spheres);
(b) with tetrahedral interstices

If we consider the unit cell to be subdivided into eight octants, we can perceive one tetrahedral interstice in the center of every octant [Fig. 17.3(b)]. Two tetrahedra share an edge when their octants have a common face. They share a vertex if their octants only have a common edge or a common vertex. There are no face-sharing tetrahedra.

There are four spheres, four octahedral interstices and eight tetrahedral interstices per unit cell. Therefore, their numerical relations are the same as for hexagonal closest-packing, as well as for any other stacking variant of closest-packings: one octahedral and two tetrahedral interstices per sphere. Moreover, the sizes of these interstices are the same in all closest-packings of spheres.

The bond angles $M-X-M$ at the bridging atoms between two polyhedra occupied by $M$ atoms are:

<table>
<thead>
<tr>
<th>Type of Polyhedron</th>
<th>Bond Angle $^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>edge-sharing octahedra</td>
<td>90.0</td>
</tr>
<tr>
<td>vertex-sharing octahedra</td>
<td>180.0</td>
</tr>
<tr>
<td>edge-sharing tetrahedra</td>
<td>70.5</td>
</tr>
<tr>
<td>vertex-sharing tetrahedra in octants with a common edge</td>
<td>109.5</td>
</tr>
<tr>
<td>vertex-sharing tetrahedra in octants with a common vertex</td>
<td>180.0</td>
</tr>
</tbody>
</table>

The hexagonal layers with the stacking sequence $ABCABC\ldots$ are perpendicular to the space diagonals of the unit cell. The layers in one pair of layers, say $AB$, have the same mutual arrangement as in Fig. 17.1(b). The position of the following layer $C$ is situated exactly over the octahedral interstices between $A$ and $B$. The pattern of the edge-sharing octahedra within one pair of layers is independent of the stacking sequence. The sequence of the positions of the octahedron centers in the stacking direction is $\gamma\gamma\ldots$ in the hexagonal closest-packing and it is $\gamma\alpha\beta\gamma\alpha\ldots$ in the cubic closest-packing (Fig. 17.4).

The crystallographic data for the two packings of spheres are summarized in Table 17.1.

Table 17.1: Crystallographic data of the hexagonal and cubic closest-packings of spheres. $+F$ means $+(\frac{1}{2}, \frac{1}{2}, 0), +(\frac{1}{2}, 0, \frac{1}{2}), +(0, \frac{1}{2}, \frac{1}{2})$ (face centering). Values given as 0 or fractional numbers are fixed by space-group symmetry (special positions).

<table>
<thead>
<tr>
<th>Packing</th>
<th>Space Group</th>
<th>Position of Centers of the Spheres</th>
<th>Centers of the Octahedral Voids</th>
<th>Centers of the Tetrahedral Voids</th>
<th>$c/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexagonal closest-packing</td>
<td>$P6_3/mmc$</td>
<td>$2a\equiv\frac{2}{3}, \frac{1}{3}, \frac{1}{3}; \frac{1}{2}, \frac{2}{3}, \frac{3}{4}$</td>
<td>$0, 0, 0$; $0, 0, \frac{1}{2}$</td>
<td>$4f\pm(\frac{2}{3}, \frac{1}{3}, 0, 0.625)$; $\pm(\frac{1}{2}, \frac{1}{2}, 0.125)$</td>
<td>$\frac{2}{3}\sqrt{6} = 1.633$</td>
</tr>
<tr>
<td>cubic closest-packing</td>
<td>$F\bar{m}3m$</td>
<td>$4a\equiv0, 0, 0$</td>
<td>$+F$; $0, 0, \frac{1}{2}$</td>
<td>$8c\equiv\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, \frac{1}{4}, \frac{3}{4}$</td>
<td>$+F$</td>
</tr>
</tbody>
</table>
17.2 Interstitial Compounds

The concept of intercalating atoms in the interstices between the spheres is not just an idea; with some elements it can actually be performed. The uptake of hydrogen by certain metals yielding metal hydrides is the most familiar example. During the absorption of the hydrogen the properties of the metal experience significant changes and usually phase transitions take place, i.e. the packing of the metal atoms in the final metal hydride is usually not the same as that of the pure metal. However, as a rule, it still is one of the packings typical for metals. For this reason the term interstitial hydrides has been coined. The hydrogen content is variable, it depends on pressure and temperature; we have to deal with nonstoichiometric compounds.

Interstitial hydrides are known for the transition metals (including lanthanoids and actinoids). Magnesium hydride can also be included, since magnesium can take up hydrogen under pressure up to the composition MgH₂; upon heating the hydrogen is released. The limiting composition is MH₃ for most of the lanthanoids and actinoids, otherwise it is MH₂ or less. In some cases the compounds are unstable for certain composition ranges (e.g. only cubic HoH₁.₉₅ to HoH₂.₂₄ and hexagonal HoH₂.₆₄ to HoH₃.₀₀ are stable).

The typical structure for the composition MH₂ is a cubic closest-packing of metal atoms in which all tetrahedral interstices are occupied by H atoms; this is the CaF₂ type. The surplus hydrogen in the lanthanoid hydrides MH₂ to MH₃ is placed in the octahedral interstices (Li₃Bi type for LaH₃ to NdH₃, cf. Fig. 15.3, p. 161).

The interstitial hydrides of transition metals differ from the salt-like hydrides of the alkali and alkaline-earth metals MH and MH₂, as can be seen from their densities. While the latter have higher densities than the metals, the transition metal hydrides have expanded metal lattices. Furthermore, the transition metal hydrides exhibit metallic luster and are semiconducting. Alkali metal hydrides have NaCl structure; MgH₂ has rutile structure.

The packing density of the H atoms is very high in all hydrogen-rich metal hydrides. For example, in MgH₂ it is 55 % higher than in liquid hydrogen. Years of efforts to develop a storage medium for hydrogen using magnesium have not met with success. The alloy LaNi₅ can also absorb and release hydrogen easily; it is used as electrode material in metal hydride batteries.

The carbides and nitrides of the elements Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Th, and U are considered to be typical interstitial compounds. Their compositions frequently correspond to one of the approximate formulas M₂X or MX. As a rule, they are nonstoichiometric compounds with compositions ranging within certain limits. This fact, the limitation to a
few similar structure types, and very similar properties show that the geometric packing conditions of the atoms have fundamental importance in this class of compounds.

The nitrides can be prepared by heating a metal powder in an N$_2$ or NH$_3$ atmosphere to temperatures above 1100$^\circ$C. The carbides form upon heating mixtures of the metal powders with carbon to temperatures of about 2200 $^\circ$C. Both the nitrides and carbides can also be made by chemical transport reactions by the VAN ARKEL–DE BOER method if the metal deposition takes place in an atmosphere of N$_2$ or a hydrocarbon. Their remarkable properties are:

- Very high hardness with values of 8 to 10 on the MOHS scale; in some cases they approach the hardness of diamond (e.g. W$_2$C).
- Extremely high melting points, for example (values in $^\circ$C):

<table>
<thead>
<tr>
<th>Metal</th>
<th>Melting Point $^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>3140</td>
</tr>
<tr>
<td>TiC</td>
<td>2950</td>
</tr>
<tr>
<td>TiN</td>
<td>2890</td>
</tr>
<tr>
<td>VC</td>
<td>2650</td>
</tr>
<tr>
<td>Zr</td>
<td>3530</td>
</tr>
<tr>
<td>ZrC</td>
<td>2980</td>
</tr>
<tr>
<td>ZrN</td>
<td>2600</td>
</tr>
<tr>
<td>NbC</td>
<td>3890</td>
</tr>
<tr>
<td>HfC</td>
<td>3300</td>
</tr>
<tr>
<td>HfN</td>
<td>3880</td>
</tr>
<tr>
<td>TaC</td>
<td>3400</td>
</tr>
</tbody>
</table>

Values for comparison: melting point of W 3420 $^\circ$C (highest melting metal), sublimation point of graphite approximately 3350 $^\circ$C.
- Metallic electrical conductivity, in some cases also superconductivity at low temperatures (e.g. NbC, transition temperature 10.1 K).
- High chemical resistance, except to oxidizing agents at high temperatures (such as atmospheric oxygen above 1000 $^\circ$C or hot concentrated nitric acid).

The intercalation of C or N into the metal thus involves an increased refractoriness with preservation of metallic properties.

The structures can be considered as packings of metal atoms which have incorporated the nonmetal atoms in their interstices. Usually, the metal atom packings are not the same as those of the corresponding pure metals. The following structure types have been observed:

- M$_2$C and M$_2$N hexagonal closest-packing of M atoms, C or N atoms in half of the octahedral interstices
- MC and MN cubic closest-packing of M atoms, C or N atoms in all octahedral interstices = NaCl type (not for Mo, W)
- MoC, MoN, WC, WN WC type

In the WC type the metal atoms do not have a closest-packing, but a hexagonal-primitive packing; the metal atoms form trigonal prisms that are occupied by the C atoms.

For the structures of M$_2$C and M$_2$N the question arises: is there an ordered distribution of occupied and unoccupied octahedral holes? There are several possibilities for an ordered distribution, some of which actually occur. For example, in W$_2$C occupied and unoccupied octahedral holes alternate in layers; this is the Cdl$_2$ type. In $\beta$-V$_2$N there are alternating layers in which the octahedral holes are one-third and two-thirds occupied.

The question of ordered distributions of occupied interstices is the subject of the following sections.

17.3 Structure Types with Occupied Octahedral Interstices in Closest-packings of Spheres

We focus attention here on the binary compounds MX$_n$, the X atoms being arranged in a closest-packed manner and the M atoms occupying the octahedral interstices. Since the
number of octahedral interstices coincides with the number of X atoms, exactly the fraction $1/n$ of them has to be occupied to ensure the correct composition. As outlined above, in the following we denote the positions of the layers of X atoms by $A$, $B$ and $C$, and the intermediate planes of octahedral interstices by $\alpha$ (between $B$ and $C$), $\beta$ (between $C$ and $A$) and $\gamma$ (between $A$ and $B$). Fractional numbers indicate the fraction of octahedral holes that are occupied in the corresponding intermediate plane; a completely unoccupied intermediate plane is marked by the SCHOTTKY symbol $\square$.

### Compounds MX

<table>
<thead>
<tr>
<th>structure type</th>
<th>stacking sequence</th>
<th>examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>$A\gamma B\alpha C\beta$</td>
<td>LiH, KF, AgCl, MgO, PbS, TiC, CrN</td>
</tr>
<tr>
<td>NiAs</td>
<td>$A\gamma B\gamma$</td>
<td>CrH, TiS, CoS, CoSb, AuSn</td>
</tr>
</tbody>
</table>

In both the NaCl and the NiAs structure types all octahedral interstices are occupied in a cubic closest-packing or hexagonal closest-packing, respectively. The coordination number is 6 for all atoms. In the NaCl type all atoms have octahedral coordination, and it does not matter whether the structure is regarded as a packing of Na$^+$ spheres with intercalated Cl$^-$ ions or vice versa. The situation is different for the NiAs type; only the arrangement of the As atoms is that of a closest-packing, while the nickel atoms in the octahedral interstices ($\gamma$ positions) are stacked one on top the other (Fig. 17.5). Only the nickel atoms have octahedral coordination; the coordination polyhedron of the arsenic atoms is a trigonal prism. The structure can also be considered as a primitive hexagonal lattice of Ni atoms; in this lattice the only occurring polyhedra are trigonal prisms, their number being twice the number of the Ni atoms. One half of these prisms are occupied by As atoms (cf. also Fig. 16.16, p. 179).

The above-mentioned examples show that the NaCl type occurs preferentially in salt-like (ionic) compounds, some oxides and sulfides, and the interstitial compounds discussed in the preceding section. For electrostatic reasons the NaCl type is well-suited for very polar compounds, since every atom only has atoms of the other element as closest neighbors. Sulfides, selenides, and tellurides, as well as phosphides, arsenides and antimonides, with NaCl structure have been observed with alkaline earth metals and with elements of the third transition metal group (MgS, CaS, …, MgSe, …, BaTe; ScS, YS, LnS, LnSe, LnTe; LnP, LnAs, LnSb with Ln = lanthanoid). However, with other transition metals, the NiAs type and its distorted variants are preferred. The Ni atoms in the face-sharing octahedra are rather close to each other (Ni–Ni distance 252 pm, just slightly longer than the Ni–As distance of 243 pm). This suggests the presence of bonding metal–metal interactions, particularly since this structure type only occurs if the metal atoms still have $d$ electrons available. The existence of metal–metal interactions is also supported by the following observations: metallic luster and conductivity, variable composition, and the dependence of the lattice parameters on the electronic configuration, for example:

<table>
<thead>
<tr>
<th>ratio $c/a$ of the hexagonal unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiSe</td>
</tr>
<tr>
<td>1.68</td>
</tr>
</tbody>
</table>

Even smaller $c/a$ ratios are observed for the more electron-rich arsenides and antimonides (e.g. 1.39 for NiAs). Since the ideal $c/a$ ratio of hexagonal closest-packing is 1.633, there is a considerable compression in the $c$ direction, *i.e.* in the direction of the closest contacts among the metal atoms.
The NiAs structure and distorted variants. The images for MnP and NiP show the same section as the image for NiAs in the upper left. Dashed: pseudohexagonal cells corresponding to the NiAs cell. Numbers: z coordinates (in the viewing direction).

The structure of MnP is a distorted variant of the NiAs type: the metal atoms also have close contacts with each other in zigzag lines parallel to the a–b plane, which amounts to a total of four close metal atoms (Fig. 17.5). Simultaneously, the P atoms have moved up to a zigzag line; this can be interpreted as a \( (P^-)_\infty \) chain in the same manner as in Zintl phases. In NiP the distortion is different, allowing for the presence of \( P_2 \) pairs (\( P_2^4 \)). These distortions are to be taken as Peierls distortions. Calculations of the electronic band structures can be summarized in short: 9–10 valence electrons per metal atom favor the NiAs structure, 11–14 the MnP structure, and more than 14 the NiP structure (phosphorus contributes 5 valence electrons per metal atom); this is valid for phosphides. Arsenides and especially antimonides prefer the NiAs structure also for the larger electron counts.

Compounds which have the NiAs structure often exhibit a certain phase width in that metal atom positions can be vacant. The composition then is \( M_{1-x}X \). The vacancies can have a random or an ordered distribution. In the latter case we have to deal with superstructures of the NiAs type; they are known, for example, among iron sulfides such as Fe\(_9\)S\(_{10}\) and Fe\(_{10}\)S\(_{11}\). If metal atoms are removed from every other layer, we have a continuous series from \( M_{1.0}X \) with the NiAs structure down to \( M_{0.5}X (= MX_2) \) with the CdI\(_2\) structure; phases of this kind are known for Co\(_{1-x}\)Te (CoTe: NiAs type; CoTe\(_2\): CdI\(_2\) type).

**Compounds MX\(_2\)**

In compounds MX\(_2\), half of the octahedral interstices are occupied. There are several possibilities for the distribution of occupied and vacant interstices in the intermediate planes:
1. Fully occupied and vacant intermediate planes alternate. In the occupied planes the octahedra share common edges (Fig. 16.9, p. 175).

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Stacking Sequence</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdCl₂</td>
<td>$A\gamma B\square C\beta A\square B\alpha C\square$</td>
<td>MgCl₂, FeCl₂, Cs₂O</td>
</tr>
<tr>
<td>CdI₂</td>
<td>$A\gamma B\square$</td>
<td>MgBr₂, PbI₂, SnS₂, Mg(OH)₂, Cd(OH)₂, Ag₂F</td>
</tr>
</tbody>
</table>

In addition, further polytypes exist, i.e. structures having other stacking sequences of the halogen atoms. Especially for CdI₂ itself a large number of such polytypes are now known; for this reason the term CdI₂ type is nowadays considered unfortunate, and the terms Mg(OH)₂ (brucite) or Cd(OH)₂ type are preferred by some authors. The H atoms of the hydroxides are oriented into the tetrahedral interstices between the layers, and do not act as H bridges. Botallackite, Cu₂(OH)₃Cl, has a structure like CdI₂, every other layer of the packing of spheres consisting of Cl atoms and OH groups (another modification with this composition is atacamite, which is mentioned below).

Distorted variants, similar to the distorted variants of the NiAs type, are known for the CdI₂ type. For example, ZrI₂ has a distorted CdI₂ structure in which the Zr atoms form zigzag chains. Therefore, every Zr atom is involved in two Zr–Zr bonds which is in accordance with the $d^2$ configuration of divalent zirconium.

2. The intermediate planes are alternately two-thirds and one-third occupied.

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Stacking Sequence</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon$-Fe₂N</td>
<td>$A\gamma_{1/3} B\gamma'_{1/3}$</td>
<td>$\beta$-Nb₂N, Li₂ZrF₆</td>
</tr>
</tbody>
</table>

The intermediate planes with two-thirds occupation have octahedra sharing edges with the honeycomb pattern as in BiI₃; the octahedra in the intermediate planes with one-third occupation are not directly connected with one another, but they have common vertices with octahedra of the adjacent layers. In Li₂ZrF₆ the Zr atoms are those in the intermediate plane with one-third occupation (cf. Fig. 16.13, p. 177).

3. The intermediate planes are alternately one-quarter and three-quarters occupied. This is the arrangement in atacamite, a modification of Cu₂(OH)₃Cl with the stacking sequence:

$A\gamma_{1/4} B\alpha_{3/4} C\beta_{1/4} A\gamma'_{3/4} B\alpha'_{1/4} C\beta'_{3/4}$.

4. Every intermediate plane is half occupied.

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Stacking Sequence</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂</td>
<td>$A\gamma_{1/2} B\gamma'_{1/2}$</td>
<td>CaBr₂, $\epsilon$-FeO(OH), Co₂C</td>
</tr>
<tr>
<td>$\alpha$-PbO₂</td>
<td>$A\gamma_{1/2} B\gamma'_{1/2}$</td>
<td>TiO₂ (high pressure)</td>
</tr>
<tr>
<td>$\alpha$-AlO(OH)</td>
<td>$A\gamma_{1/2} B\gamma'_{1/2}$</td>
<td>$\alpha$-FeO(OH) (goethite)</td>
</tr>
</tbody>
</table>

In CaCl₂ linear strands of edge-sharing octahedra are present, and the strands are joined by common octahedron vertices (Fig. 17.6). Marcasite is a modification of FeS₂ related to the CaCl₂ type, but distorted by the presence of S₂ dumbbells. The joining of adjacent S atoms to form dumbbells is facilitated by a mutual rotation of the octahedron strands (Fig. 17.6). Several compounds adopt this structure type, for example NiAs₂ and CoTe₂.

If the octahedron strands are rotated in the opposite direction, the rutile type results (Fig. 17.6). Due to this relation with the CaCl₂ type, a hexagonal closest-packing of O atoms has frequently been ascribed to the rutile type. However, the deviations from this kind of packing are quite significant. For one thing, every O atom is no longer in contact with twelve other O atoms, but only with eleven; moreover, the ‘hexagonal’ layers are considerably corrugated. By the formalism of group theory it is also not permissible to regard the tetragonal rutile as a derivative of the hexagonal closest-packing (cf. Section
17.3 Structure Types with Occupied Octahedral Interstices in Closest-packings of Spheres

In fact, the arrangement of the O atoms in rutile is that of a tetragonal close-packing of spheres. This is a packing filling space to 71.9%, which is only slightly less than in a closest-packing. Consider a ladder which has spheres at the joints of the rungs (Fig. 17.7). Set up such ladders vertical, but mutually rotated around the vertical axis in such a way that the spheres of one ladder come to be next to the gaps between the rungs of the adjacent ladders. In the packing obtained in this way every sphere has coordination number 11: 2 + 4 + 2 spheres from three neighboring ladders and 3 spheres within the ladder. The gaps between the rungs correspond to the octahedral interstices that are occupied by Ti atoms in rutile, and the ladders correspond to the strands of edge-sharing octahedra. Compared to a closest-packing of spheres (c.n. 12), the coordination number is reduced by 8%, but the space filling is reduced by only 3%; this gives an idea of why the rutile type is the preferred packing for highly polar compounds (dioxides, difluorides).

The similarity of the structures of rutile, CaCl$_2$ and marcasite also comes to light by comparison of their crystal structure data (Table 17.2). The space groups of CaCl$_2$ and marcasite (both $Pnmm$) are subgroups of the space group of rutile. The tetragonal sym-

Table 17.2: Crystal data of rutile, CaCl$_2$ and marcasite

<table>
<thead>
<tr>
<th></th>
<th>space group</th>
<th>$a$ (pm)</th>
<th>$b$ (pm)</th>
<th>$c$ (pm)</th>
<th>M atom</th>
<th>anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>rutile</td>
<td>$P4_2/mnm$</td>
<td>459.3</td>
<td>459.3</td>
<td>295.9</td>
<td>0 0 0</td>
<td>0.305 0.305 0</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>$Pnmm$</td>
<td>625.9</td>
<td>644.4</td>
<td>417.0</td>
<td>0 0 0</td>
<td>0.275 0.325 0</td>
</tr>
<tr>
<td>marcasite</td>
<td>$Pnmm$</td>
<td>444.3</td>
<td>542.4</td>
<td>338.6</td>
<td>0 0 0</td>
<td>0.200 0.378 0</td>
</tr>
</tbody>
</table>
metry of rutile is broken by the mutual rotation of the strands of octahedra (cf. p. 33 and Section 18.4).

α-PbO₂ is another structure which has mutually connected strands of edge-sharing octahedra; the strands have zigzag shape (Fig. 16.12, p. 177). Linear strands of edge-sharing octahedra as in CaCl₂, but which form edge-sharing double-strands, are present in diaspore, α-AlO(OH) (Fig. 17.8).

Compounds MX₃
In compounds MX₃, one-third of the octahedral interstices are occupied. Again, there are several possible distributions of vacant and occupied interstices in the intermediate planes:

1. Every third intermediate plane is fully occupied, and the others are unoccupied. The octahedra within the occupied planes share edges as in CdI₂. This is the structure of Cr₂AlC, in which the sequence of layers is:

\[ A_{Cr} \gamma B_{Cr} \square A_{Al} \square B_{Cr} \gamma A_{Cr} \square B_{Cr} \square \]

The carbon atoms take positions inside octahedra made up from only one kind of atom, those of the transition metal.
2. Every other intermediate plane is two-thirds occupied.

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Stacking Sequence</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AlCl}_3$</td>
<td>$A_{\gamma_{2/3}}B\square C_{\beta_{2/3}}A\square B\sigma_{2/3}\square$</td>
<td>YCl$_3$, CrCl$_3$ (high temperature)</td>
</tr>
<tr>
<td>$\text{BiI}_3$</td>
<td>$A_{\gamma_{2/3}}B\square$</td>
<td>FeCl$_3$, CrCl$_3$ (low temperature)</td>
</tr>
</tbody>
</table>

Both structure types have the same kind of layer of edge-sharing octahedra (Fig. 16.8). Among the trihalides with this kind of layer structure, stacking disorder is quite common, i.e. the stacking sequence of the hexagonal halogen-atom layers is not strictly $AB$ or $ABC$, but stacking faults occur frequently. This also applies to $\text{AlCl}_3$ and $\text{BiI}_3$ themselves. The frequency of the stacking faults depends on the growth conditions of the specific single crystal. For example, one crystal of $\text{BiI}_3$ that had been obtained by sublimation essentially had the hexagonal stacking sequence $hhh\ldots$, but in a random sequence one out of 16 layers was a c layer.

3. Every intermediate layer is one-third occupied.

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Stacking Sequence</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{RuBr}_3$</td>
<td>$A_{\gamma_{1/3}}B_{\gamma_{1/3}}$</td>
<td>$\beta\text{-TiCl}_3$, ZrI$_3$, MoBr$_3$</td>
</tr>
<tr>
<td>$\text{RhF}_3$</td>
<td>$A_{\gamma_{1/3}}B_{\gamma_{1/3}}$</td>
<td>IrF$_3$, PdF$_3$, TmCl$_3$</td>
</tr>
</tbody>
</table>

In the $\text{RuBr}_3$ type a succession of face-sharing octahedra form a strand in the c direction. The metal atoms in adjacent octahedra are shifted in pairs from the octahedron centers, forming metal–metal bonds (Fig. 16.10, p. 175). This seems to be the condition for the existence of this structure type, i.e. it only occurs with transition metals that have an odd-numbered $d$ electron configuration.

In the $\text{RhF}_3$ type all octahedra share vertices, and corresponding to the hexagonal closest-packing of the F atoms the Rh–F–Rh angles are approximately 132°. By mutual rotation of the octahedra the angle can be widened up to 180°, but then the packing is less dense. This has been observed for the $\text{VF}_3$ type (V–F–V angle approximately 150°), which occurs with some trifluorides (GaF$_3$, TiF$_3$, FeF$_3$ etc.; Fig. 16.5). In PdF$_3$ the Pd–F lengths in the octahedra alternate (217 and 190 pm) in accordance with the formula Pd$^{II}$Pd$^{IV}$F$_6$.

**Compounds $\text{M}_2\text{X}_3$**

Two-thirds of the octahedral interstices are occupied. In a way the possible structure types are the ‘inverse’ of the MX$_3$ structures, since in these two-thirds of the octahedral interstices are vacant. If we take an MX$_3$ type, clear the occupied interstices and occupy the vacant ones, the result is an $\text{M}_2\text{X}_3$ structure. The kind of linking between the occupied octahedra, however, is different. The arrangement of the vacant octahedral interstices of the $\text{RhF}_3$ type corresponds to the occupied interstices in corundum, Al$_2$O$_3$; its occupied octahedra share edges and faces (Fig. 16.15, p. 179). The layer sequence is:

$$A_{\gamma_{2/3}}B_{\gamma_{2/3}}A_{\gamma_{2/3}}B_{\gamma_{2/3}}A_{\gamma_{2/3}}B_{\gamma_{2/3}}$$

**Compounds $\text{MX}_4$, $\text{MX}_5$, and $\text{MX}_6$**

$\frac{1}{4}$, $\frac{1}{3}$, and $\frac{1}{6}$ of the octahedral interstices are occupied, respectively. There are various possibilities for the distribution of the occupied sites, and the specification of a layer sequence alone is not very informative. Fig. 17.9 shows some examples which also allow us to recognize an important principle concerning the packing of molecules: all octahedral interstices that immediately surround a molecule must be vacant, and then occupied interstices have to follow; otherwise either the molecules would be joined to polymeric assemblies or not all of the atoms of the sphere packing would be part of a molecule. These
statements may seem self-evident; however, they imply a severe restriction on the number of possible packing variants for a given kind of molecule. For tetrahalides consisting of chains of edge-sharing octahedra, we noted on page 173 that numerous chain configurations are conceivable. However, because of the packing necessities, some of them are not compatible with a closest-packing; no examples are known for them and it is unlikely that any will ever be observed.

17.4 Perovskites

Among the MX₄ compounds γ’-Fe₄N is a special case: its Fe atoms form a cubic closest-packing, and one-quarter of the octahedral interstices are occupied with N atoms. The occupied octahedra share vertices and form a framework; however, only three out of four Fe atoms take part in this framework; the fourth Fe atom is not bonded to an N atom.

This structure is nothing else than the perovskite type (CaTiO₃; Fig. 17.10). The Ca and O atoms jointly form the cubic closest-packing in an arrangement corresponding to the ordered alloy AuCu₃ (Fig. 15.1, p. 158). The atomic order in the hexagonal layers of spheres is that shown for AuCu₃ on page 159. Being a part of the packing of spheres, a Ca²⁺ ion has coordination number 12. The titanium atoms occupy one-quarter of the octahedral voids, namely those which are surrounded solely by oxygen atoms.

If the position of the Ca²⁺ ion is vacant, the remaining framework is that of the ReO₃
The analogy between ReO$_3$ and CaTiO$_3$ is not a mere formalism, since the partial occupation of the Ca positions with varying amounts of metal ions can actually be achieved, specifically in the case of the cubic tungsten bronzes, A$_x$WO$_3$ (A = alkali metal, $x = 0.3$ to 0.93). Their color and the oxidation state of the tungsten depend on the value of $x$; they have metallic luster, and with $x \approx 1$ they are gold-colored, with $x \approx 0.6$ red and with $x \approx 0.3$ dark violet.

In normal, cubic perovskite the closest-packed hexagonal CaO$_3$ layers have the stacking sequence $ABC\ldots$ or $c\ldots$ and the occupied octahedra only share vertices. The structural family of perovskites also includes numerous other stacking variants, with $c$ and $h$ layers in different sequences. At an $h$ layer the octahedra share faces. In a sequence like $chhc$, there is a group of three octahedra that share faces at the $h$ layers; this group is connected with other octahedra by vertex-sharing at the $c$ layers. The size of the groups of face-sharing octahedra depends on the nature of the metal atoms in the octahedra and especially on the ionic radius ratios. Fig. 17.11 shows some examples.

The ideal, cubic perovskite structure is not very common; even the mineral perovskite itself, CaTiO$_3$, is slightly distorted. SrTiO$_3$ is undistorted. As shown in Fig. 16.5 (p. 171), the ReO$_3$ type can be converted to a more dense packing by mutual rotation of the octahedra until a hexagonal closest-packing is obtained in the RhF$_3$ type. During the rotation the void in the center of the ReO$_3$ unit cell becomes smaller and finally becomes an octahedral interstice in the closest-packing of F atoms in the RhF$_3$ type. If this octahedral interstice is occupied, we have the ilmenite type (FeTiO$_3$). By an appropriate amount of rotation of the octahedra, the size of the hole can be adapted to the size of the A ion in a perovskite. In addition, some tilting of the octahedra allows a variation of the coordination number and coordination polyhedra. Distorted perovskites have reduced symmetry, which is important for the magnetic and electric properties of these compounds. Due to these properties perovskites have great industrial importance, especially the ferroelectric BaTiO$_3$. This is discussed in Chapter 19.

The **tolerance factor** $t$ for perovskites AMX$_3$ is a value that allows us to estimate the degree of distortion. Its calculation is performed using ionic radii, *i.e.* purely ionic bonding is assumed:

$$t = \frac{r(A) + r(X)}{\sqrt{2}[r(M) + r(X)]}$$

Geometry requires a value of $t = 1$ for the ideal cubic structure. In fact, this structure occurs if $0.89 < t < 1$. Distorted perovskites occur if $0.8 < t < 0.89$. With values less than
Fig. 17.11
Linking of the octahedra in different representatives of the structural family of the perovskites with different stacking sequences.

0.8, the ilmenite type is more stable (Fig. 16.15, p. 179). The hexagonal stacking variants such as depicted in Fig. 17.11 usually have \( t > 1 \). Since perovskites are not truly ionic compounds and since the result also depends on which values are taken for the ionic radii, the tolerance factor is only a rough estimate.

**Superstructures of the Perovskite Type**

If we enlarge the unit cell of perovskite by doubling all three edges, it is possible to occupy equivalent positions with atoms of different elements. Fig. 17.12 shows some representatives of the elpasolite family. In elpasolite, \( \text{K}_2\text{NaAlF}_6 \), the potassium and the fluoride ions jointly form the cubic closest-packing, *i.e.* \( \text{K}^+ \) and \( \text{F}^- \) take the Ca and O positions of perovskite. The one-to-one relation can be recognized by comparison with the doubled formula of perovskite, \( \text{Ca}_2\text{Ti}_2\text{O}_6 \). The comparison also shows the partition of the octahedral Ti positions into two sites for Na and Al. In kryolite, \( \text{Na}_3\text{AlF}_6 \), the \( \text{Na}^+ \) ions occupy two different positions, namely those of \( \text{Na}^+ \) and \( \text{K}^+ \) in elpasolite, *i.e.* positions with coordination numbers of 6 and 12. Since this is not convenient for ions of the same size, the lattice experiences some distortion.

‘High-temperature’ superconductors show superconductivity at temperatures higher than the boiling point of liquid nitrogen (77 K). Their structures are superstructures of
perovskite with copper atoms in the octahedral positions, and they are deficient in oxygen, ACuO_{3-δ}. Alkaline earth metal ions and trivalent ions (Y^{3+}, lanthanoids, Bi^{3+}, Tl^{3+}) occupy the A positions. A typical composition is YBa_2Cu_3O_{7-x} with x ≈ 0.04. Approximately \( \frac{2}{3} \) of the oxygen positions are vacant, in such a way that \( \frac{2}{3} \) of the Cu atoms have square-pyramidal coordination and \( \frac{1}{3} \) have square-planar coordination (Fig. 17.13). The structures of some other representatives of this compound class are considerably more complicated, and may exhibit disorder and other particularities.
17.5 Occupation of Tetrahedral Interstices in Closest-packings of Spheres

Coordination tetrahedra sharing faces would be present if all tetrahedral interstices in a hexagonal closest-packing were occupied. This would be an unfavorable arrangement for electrostatic reasons. On the other hand, the occupation of all tetrahedral interstices in cubic closest-packing results in an electrostatically favorable structure type: the CaF$_2$ type (F$^-$ ions in the interstices), which also is the structure of Li$_2$O (Li$^+$ in the interstices). The tetrahedra are linked by common edges and common vertices.

Taking out half of the atoms from the tetrahedral interstices of the CaF$_2$ type leaves the composition MX. Several structure types can arise, depending on the selection of the vacated interstices: the zinc blende type with a network of vertex-sharing tetrahedra, the PbO type with layers of edge-sharing tetrahedra, and the PtS type (Fig. 17.14). In PbO and PtS the metal atoms form the packing of spheres. PbO only has tetrahedra occupied by O atoms at the height $z = \frac{1}{4}$, and those in $z = \frac{3}{4}$ are vacant; the Pb atoms at $z \approx 0$ and $z \approx \frac{1}{2}$ and the O atoms together form a layer in which every Pb atom has square-pyramidal coordination (cf. Fig. 16.28, p. 189). The distribution of the atoms in PtS results in a planar coordination around a Pt atom. The packing is a compromise between the requirements of tetrahedral coordination for sulfur and square coordination for platinum. With a ratio $c/a = 1.00$ the sulfur atoms would have an undistorted tetrahedral coordination, but it would be rectangular at Pt atoms; with $c/a = 1.41$ the bond angles would be 90° at Pt, but also at S. The actual ratio is $c/a = 1.24$. HgI$_2$ and α-ZnCl$_2$ are examples of structures with cubic closest-packing of halogen atoms, having one-quarter of the tetrahedral interstices occupied. These tetrahedra share vertices, every tetrahedron vertex being common to two tetrahedra with bond angles of 109.5° at the bridging atoms. The HgI$_2$ structure corresponds to a PbO structure in which half of the O atoms have been removed and cations have been exchanged with anions (Fig. 17.14). There are layers, and all Hg atoms are at the same level within one layer (cf. also Fig. 16.23, p. 185).

If half of the atoms are removed from zinc blende, in the way shown in the right part of Fig. 17.14, the result is the α-ZnCl$_2$ structure. It has a framework of vertex-sharing tetrahedra. The zinc atoms form helices parallel to c. The c axis is doubled. By mutually rotating the tetrahedra, the lattice is widened and the bond angles at the bridging atoms become larger; the result is the cristobalite structure (Fig. 17.15). The face-centered unit cell shown in Fig. 12.9 (p. 125) is twice as big as the body-centered cell of Fig. 17.15; the axes a and b of the face-centered cell run diagonal to those of the body-centered cell.

SiS$_2$ offers another variant of the occupation of one-quarter of the tetrahedral interstices in a cubic closest-packing of S atoms. It contains strands of edge-sharing tetrahedra (Fig. 17.14).

The structure of wurtzite corresponds to a hexagonal closest-packing of S atoms in which half of the tetrahedral interstices are occupied by Zn atoms. In addition, any other stacking variant of closest-packings can have occupied tetrahedral interstices. Polytypes of this kind are known, for example, for SiC.

Tetrahedral molecules such as SnCl$_4$, SnBr$_4$, SnI$_4$, and TiBr$_4$ usually crystallize with a cubic closest-packing with $\frac{1}{8}$ of the tetrahedral interstices being occupied. Especially the lighter molecules like CCl$_4$ also exhibit modifications which have molecules rotating in the crystal; averaged over time, the molecules then appear as spheres, and adopt a body-centered cubic packing.
Relationships among the structures of CaF$_2$, PbO, PtS, ZnS, HgI$_2$, SiS$_2$, and α-ZnCl$_2$. In the top row all tetrahedral interstices (= centers of the octants of the cube) are occupied. Every arrow designates a step in which the number of occupied tetrahedral interstices is halved; this includes a doubling of the unit cells in the bottom row. Light hatching = metal atoms, dark hatching = non-metal atoms. The atoms given first in the formulas form the cubic closest-packing.

Whereas AlCl$_3$ and FeCl$_3$ have layer structures with octahedral coordination of the metal atoms in the solid state, they form dimeric molecules (two edge-sharing tetrahedra) in solution and in the gaseous state. Al$_2$Br$_6$, Al$_2$I$_6$ and the gallium trihalides, however, retain the dimeric structure even in the solid state. The halogen atoms form a hexagonal closest-packing in which $\frac{1}{5}$ of the tetrahedral interstices are occupied. Other molecules that consist of linked tetrahedra in many cases also are packed in the solid state according to the principle of closest-packings of spheres with occupied tetrahedral interstices, for example Cl$_2$O$_7$ or Re$_2$O$_7$. 
By mutual rotation of the tetrahedra the \( \alpha \)-ZnCl\(_2\) structure is converted to the cristobalite structure.

### 17.6 Spinels

Packings of spheres having occupied tetrahedral and octahedral interstices usually occur if atoms of two different elements are present, one of which prefers tetrahedral coordination, and the other octahedral coordination. This is a common feature among silicates (cf. Section 16.7). Another important structure type of this kind is the spinel type. Spinel is the mineral MgAl\(_2\)O\(_4\), and generally spinels have the composition AM\(_2\)X\(_4\). Most of them are oxides; in addition, there exist sulfides, selenides, halides and pseudohalides.

In the following, we start by assuming purely ionic structures. In spinel the oxide ions form a cubic closest-packing. Two-thirds of the metal ions occupy octahedral interstices, the rest tetrahedral ones. In a ‘normal’ spinel the A ions are found in the tetrahedral interstices and the M ions in the octahedral interstices; we express this by the subscripts \( T \) and \( O \), for example Mg\(_7\)[Al\(_2\)]\(_6\)O\(_4\). Since tetrahedral holes are smaller than octahedral holes, the A ions should be smaller than the M ions. Remarkably, this condition is not fulfilled in many spinels, and just as remarkable is the occurrence of ‘inverse’ spinels which have half of the M ions occupying tetrahedral sites and the other half occupying octahedral sites while the A ions occupy the remaining octahedral sites. Table 17.3 summarizes these facts and also includes a classification according to the oxidation states of the metal ions.

Arbitrary intermediate states also exist between normal and inverse spinels; they can be characterized by the degree of inversion \( \lambda \):

\[
\lambda = 0: \text{normal spinel} \quad \lambda = 0.5: \text{inverse spinel}
\]

The distribution of the cations among the tetrahedral and octahedral sites is then expressed

<table>
<thead>
<tr>
<th>oxidation state combination</th>
<th>normal spinels ( A_7[\text{M}_2]\text{O}_4 )</th>
<th>inverse spinels ( M_7[\text{AM}]\text{O}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>II, III</td>
<td>MgAl(_2)O(_4)</td>
<td>MgIn(_2)O(_4)</td>
</tr>
<tr>
<td>II, III</td>
<td>Co(_3)O(_4)</td>
<td>Fe(_3)O(_4)</td>
</tr>
<tr>
<td>IV, II</td>
<td>GeNi(_2)O(_4)</td>
<td>TiMg(_2)O(_4)</td>
</tr>
<tr>
<td>II, I</td>
<td>ZnK(_2)(CN)(_4)</td>
<td>NiLi(_2)F(_4)</td>
</tr>
<tr>
<td>VI, I</td>
<td>WNa(_3)O(_4)</td>
<td></td>
</tr>
<tr>
<td>Ionic radii:</td>
<td>Mg(^{2+}): 72 pm</td>
<td>Fe(^{2+}): 78 pm</td>
</tr>
<tr>
<td></td>
<td>Al(^{3+}): 54 pm</td>
<td>Fe(^{3+}): 65 pm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Co(^{2+}): 75 pm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
in the following way: \((\text{Mg}_{1-2\lambda}\text{Fe}_{2\lambda})_7[\text{Mg}_{2\lambda}\text{Fe}_{2(1-\lambda)}]_0\text{O}_4\). The value of \(\lambda\) is temperature dependent. For example, at room temperature \(\text{MgFe}_2\text{O}_4\) has \(\lambda = 0.45\) and thus is essentially inverse.

The difficulties in understanding the cation distributions and in explaining the occurrence of inverse spinels on the basis of ionic radii show how insufficient this kind of approach is. A somewhat better approach considers the electrostatic part of the lattice energy, the calculated MADELUNG constant being a useful quantity. For a II,III-spinel which has an undistorted packing of anions, the MADELUNG constant of the normal spinel is 1.6\% smaller than that of the inverse one, i.e. the inverse distribution is slightly more favorable. However, small distortions that commonly occur in most spinels (widening of the tetrahedral interstices) can reverse this. In fact, spinels are not purely ionic compounds and the consideration of electrostatic interactions alone is hardly adequate, although it does work quite well for spinels of main group elements. With transition metals, in addition, the considerations of ligand field theory have to be taken into account. To illustrate this, we take as examples the spinels \(\text{Mn}_3\text{O}_4, \text{Fe}_3\text{O}_4\) and \(\text{Co}_3\text{O}_4\). Except for \(\text{Co}(\text{III})\) these are made up of high-spin complexes. The relative ligand field stabilization energies are, expressed as multiples of \(\Delta_O\) (cf. Table 9.1, p. 78):

\[
\begin{align*}
\text{Mn}^{II}_2: & \quad \text{Fe}^{III}_2: \\
\text{Mn}^{II}: & \quad 0 & \quad \text{Fe}^{III}: & 0.27 \\
\text{Mn}^{III}: & \quad 2 \times 0.6 = 1.2 \\
\text{Fe}^{II}: & \quad 0.27 \\
\text{Fe}^{III}: & \quad 0.0 \\
\text{Co}^{II}: & \quad 0.53 \\
\text{Co}^{III}: & \quad 0.80 \\
\text{Co}^{III}: & \quad 0.27 \\
\text{Co}^{III}: & \quad 2 \times 2.4 = 4.80 \\
\end{align*}
\]

\(\Delta_T = \frac{4}{5}\Delta_O\) was taken for tetrahedral ligand fields. \(\text{Mn}_3\text{O}_4\) is a normal spinel, \(\text{Mn}^{II}_7[\text{Mn}^{III}_2]_0\text{O}_4\). If it were to be converted to an inverse spinel, half of the \(\text{Mn}^{III}\) atoms would have to shift from the octahedral to the tetrahedral environment, and this would imply a decreased ligand field stabilization for these atoms (Table 17.4); for the \(\text{Mn}^{II}\) atoms the shifting would make no difference. \(\text{Fe}_3\text{O}_4\) is an inverse spinel, \(\text{Fe}^{III}_7[\text{Fe}^{II}\text{Fe}^{III}]_0\text{O}_4\). For

![Table 17.4: Ligand field stabilization energies for Mn3O4, Fe3O4 and Co3O4. Values for high-spin complexes in all cases except for octahedral CoIII.](image-url)
the Fe\textsuperscript{III} atoms the exchange of positions would make no difference; for the Fe\textsuperscript{II} atoms it would be unfavorable \((0.4\Delta_O \rightarrow 0.27\Delta_O)\).

In the case of Co\textsubscript{3}O\textsubscript{4}, which is a normal spinel, Co\textsuperscript{II}[Co\textsuperscript{II}]	extsubscript{3}O\textsubscript{4}, the situation is different because octahedrally coordinated Co\textsuperscript{III} almost never occurs in high-spin complexes (its \(d^6\) configuration corresponds to the maximum of ligand field stabilization energy in the low-spin state). If Co\textsuperscript{3+} were to adopt a high-spin state in Co\textsubscript{3}O\textsubscript{4}, it should be an inverse spinel. However, in the low-spin state the normal spinel is favored (Table 17.4). In addition, the ionic radius has also an effect; it decreases in the series Mn\textsuperscript{2+}–Fe\textsuperscript{2+}–Co\textsuperscript{2+}–Ni\textsuperscript{2+}–Cu\textsuperscript{2+}–Zn\textsuperscript{2+} and therefore favors the tetrahedral coordination towards the end of the series. Co\textsuperscript{2+} generally shows a tendency towards tetrahedral coordination in its compounds. In Fig. 9.4 (p. 79) this influence of the ionic size is taken into account by having the dashed line bent for octahedral coordination; this line corresponds to the notional reference state (spherical distribution of the \(d\) electrons), relative to which the ligand field stabilization energy is defined. According to Fig. 9.4, Co\textsuperscript{2+} is more stable in a tetrahedral environment.

Fig. 17.16 shows the spinel structure. There are four Al\textsuperscript{3+} and four O\textsuperscript{2–} ions in the vertices of an Al\textsubscript{4}O\textsubscript{4} cube. Every Al\textsuperscript{3+} ion belongs to two such cubes, so that every cube is linked with four more cubes and every Al\textsuperscript{3+} ion has octahedral coordination. In addition, every O\textsuperscript{2–} ion belongs to an MgO\textsubscript{4} tetrahedron. Each of these tetrahedra shares vertices with four cubes. The cubic unit cell contains eight MgO\textsubscript{4} tetrahedra and eight Al\textsubscript{4}O\textsubscript{4} cubes. The metal ions, taken by themselves, have the same arrangement as in the cubic LAVES phase MgCu\textsubscript{2} (cf. Fig. 15.4, p. 163).

The coordination of an O\textsuperscript{2–} ion is three Al\textsuperscript{3+} ions within an Al\textsubscript{4}O\textsubscript{4} cube and one Mg\textsuperscript{2+} ion outside of this cube. This way it fulfills the electrostatic valence rule (Pauling’s second rule, cf. p. 58), i.e. the sum of the electrostatic bond strengths of the cations corresponds exactly to the charge on an O\textsuperscript{2–} ion:

\[
z(O) = -\left(3 \cdot \frac{3}{6} + 1 \cdot \frac{2}{4}\right) = -2
\]

\[
3 \text{Al}^{3+} + 1 \text{Mg}^{2+}
\]

The required local charge balance between cations and anions which is expressed in Pauling’s rule causes the distribution of cations and anions among the octahedral and tetrahedral interstices of the sphere packing. Other distributions of the cations are not compatible with Pauling’s rule.
The above-mentioned influence of the ligand field can be discerned when metal atoms with Jahn–Teller distortions are present in a spinel. Mn$_3$O$_4$ is an example: its octahedra are elongated, and the structure is no longer cubic but tetragonal. Other examples with tetragonal distortions are the normal spinels NiCr$_2$O$_4$ and CuCr$_2$O$_4$ (Ni and Cu in tetrahedral interstices); in NiCr$_2$O$_4$ the tetrahedra are elongated, and in CuCr$_2$O$_4$ they are compressed.

**Olivine** (Mg,Fe)$_2$SiO$_4$ is the most abundant mineral of the upper Earth’s mantle. Its oxygen atoms form a hexagonal closest-packing of spheres. One-eighth of the tetrahedral voids is occupied with Si atoms. Half of the octahedral voids are randomly occupied with Mg and Fe atoms. Therefore, the magnesium atoms occupy a different kind of void as compared to spinel. This accounts for the lower density of olivine, which is approximately 6% less. Olivine is transformed to a spinel by the exertion of pressure. This transformation takes place in the Earth’s mantle at a depth of 300 to 400 km, where a subduction zone is being forced under a continental plate. At the beginning, ‘lenses’ of spinel form; they have boundaries with the surrounding, yet untransformed olivine. Olivine and spinel can mutually slip at the boundaries. Therefore, the lenses are zones of instability which behave like cracks (they are called ‘anticracks’ because they have a higher density than the surrounding material). Such zones are the focuses of earthquakes.

**17.7 Problems**

17.1 Suppose the connection of tetrahedra shown in Fig. 17.2(a) were continued to form a layer. What would the composition be?

17.2 Why are the MX$_3$ strands shown in Fig. 16.10 compatible only with a hexagonal closest-packing of the X atoms?

17.3 What structure types would you expect for TiN, FeP, FeSb, CoS, and CoSb?

17.4 Why are CdI$_2$ and BiI$_3$ much more susceptible to stacking faults than CaBr$_2$ or RhF$_3$?

17.5 What fraction of the tetrahedral interstices are occupied in solid Cl$_2$O$_7$?

17.6 Decide whether the following compounds should form normal or inverse spinels using the ligand field stabilization energy as the criterion: MgV$_2$O$_4$, VMg$_2$O$_4$, NiGa$_2$O$_4$, ZnCr$_2$S$_4$, NiFe$_2$O$_4$. 
18 Symmetry as the Organizing Principle for Crystal Structures

18.1 Crystallographic Group–Subgroup Relations

A space group consists of a set of symmetry operations that always fulfills the conditions according to which a group is defined in mathematics. Group theory offers a mathematically clear-cut and very powerful tool for ordering the multitude of crystal structures according to their space groups. To this end we introduce some concepts without discussing group theory itself in detail. The following is rather an illustrative description of the facts than a strict mathematical treatment. However, this leads to no errors for our purpose. The exact mathematical treatment is rendered difficult due to the fact that space groups are infinite groups. For an exact treatment cf. [181].

A space group $G_1$ consists of a set of symmetry operations. If another space group $G_2$ consists of a subset of these symmetry operations, it is a subgroup of $G_1$; at the same time $G_1$ is a supergroup of $G_2$. The symmetry operations present in the space group $G_1$ multiply an atom which is placed in a general position by a factor $n_1$. A corresponding atom in the subgroup $G_2$ is multiplied by analogy by a factor $n_2$. Since $G_2$ possesses less symmetry operations than $G_1$, $n_1 > n_2$ holds. The fraction $n_1/n_2$ is the index of the symmetry reduction from $G_1$ to $G_2$. It always is an integer and serves to order space groups hierarchically. For example, when passing from rutile to trirutile (cf. the end of Section 3.3, p. 21), there is a symmetry reduction of index 3.

$G_2$ is a maximal subgroup of $G_1$ if there exists no space group that can act as intermediate group between $G_1$ and $G_2$. $G_1$ then is a minimal supergroup of $G_2$. The index of symmetry reduction from a group to a maximal subgroup always is a prime number or a prime number power. According to the theorem of C. HERMANN a maximal subgroup is either a translationengleiche or klassengleiche subgroup.\(^1\)

Translationengleiche subgroups have an unaltered translation lattice, i.e. the translation vectors and therefore the size of the primitive unit cells of group and subgroup coincide. The symmetry reduction in this case is accomplished by the loss of other symmetry operations, for example by the reduction of the multiplicity of symmetry axes. This implies a transition to a different crystal class. The example on the right in Fig. 18.1 shows how a fourfold rotation axis is converted to a twofold rotation axis when four symmetry-equivalent atoms are replaced by two pairs of different atoms; the translation vectors are not affected.

A space group and a klassengleiche subgroup belong to the same crystal class. The symmetry reduction takes place by the loss of translation symmetry, i.e. by enlargement of the unit cell or by the loss of centering of the unit cell. With the loss of translation symmetry the number of other symmetry operations is also reduced. Fig. 18.2 shows two examples. The example on the right side of Fig. 18.2 also shows how the enlargement of

\(^1\)Terms taken from German: translationengleiche = with the same translations; klassengleiche = of the same class.
18.1 Crystallographic Group–Subgroup Relations

Fig. 18.1
Examples for translationengleiche group–subgroup relations: left, loss of reflection planes; right, reduction of the multiplicity of a rotation axis from 4 to 2. The circles of the same type, ◯ and ●, designate symmetry-equivalent positions.

Fig. 18.2
Examples for klassengleiche group–subgroup relations: left, loss of centering including the loss of glide planes and twofold axes; right, enlargement of the unit cell including the symmetry reduction of reflection planes perpendicular to b to glide planes. Circles of the same type, ◯ and ●, refer to symmetry-equivalent positions.
the unit cell can cause the reduction of the symmetry of a reflection plane to a glide plane. In a similar way the symmetry of a rotation axis can be reduced to that of a screw axis when the cell enlargement is along the axis (cf. Problem 18.1, p. 225).

A special case of klassengleiche subgroups are the isomorphic subgroups. Group and subgroup belong to the same or the enantiomorphic space group type. Therefore, they have the same Hermann–Mauguin symbol or the symbol of the enantiomorphic space group type (e.g. $P\overline{3}_1$ and $P\overline{3}_2$). The subgroup has an enlarged unit cell. Rutile and trirutile offer an example (Fig. 3.10).

A suitable way to represent group–subgroup relations is by means of ‘family trees’ which show the relations from space groups to their maximal subgroups by arrows pointing downwards. In the middle of each arrow the kind of the relation and the index of the symmetry reduction are labeled, for example:

$t^2 = \text{translationengleiche subgroup of index 2}$
$k^2 = \text{klassengleiche subgroup of index 2}$
$i^3 = \text{isomorphic subgroup of index 3}$

In addition, if applicable, it is stated how the new unit cell emerges from the old one (base vectors of the subgroup given as vectorial sums of the base vectors of the preceding group; see Fig. 18.2). Sometimes it is also necessary to state an origin shift. This applies when, according to the conventions of International Tables for Crystallography [48], the origin of the subgroup has to be placed in a different position than the origin of the preceding space group. The origin shift is given as a triplet of numbers, for example $0, \frac{1}{2}, -\frac{1}{4} = \text{shift by } 0, \frac{1}{2}b, -\frac{1}{4}c$; $b$ and $c$ being the base vectors of the preceding space group.

18.2 The Symmetry Principle in Crystal Chemistry

In crystalline solids a tendency to form arrangements of high symmetry is observable. The symmetry principle, put forward in this form by F. LAVES, has been stated in a more exact manner by H. BÄRNIGHAUSEN:

1. In the solid state the arrangement of atoms shows a pronounced tendency towards the highest possible symmetry.

2. Counteracting properties of the atoms or atom aggregates may prevent the attainment of the highest possible symmetry, but in most cases the deviations from the ideal symmetry are only small (keyword pseudosymmetry).

3. During a phase transition or a reaction in the solid state which results in one or more products of lower symmetry, very often the higher symmetry of the starting material is indirectly preserved by the orientation of domains formed within the crystalline matrix.

Aspect 1 corresponds approximately to the formulation of G. O. BRUNNER:

Atoms of the same kind tend to be in equivalent positions.

This formulation gives a clue to the physical background of the symmetry principle: Given certain conditions such as chemical composition, the kind of chemical bonding, electronic configuration of the atoms, relative size of the atoms, pressure, temperature etc., for every kind of atom there exists one energetically most favorable spatial arrangement which all atoms of this kind tend to adopt. Like atoms are indistinguishable particles.
According to quantum mechanics, however, in a crystal they are only indistinguishable if they are symmetry equivalent; only then do they have the same surrounding.

As an example of the prevalence of high-symmetry structures, we can take the closest packings of spheres: only in the cubic and the hexagonal closest-packings of spheres are all atoms symmetry equivalent; in other stacking variants of closest-packings several non-equivalent atomic positions are present, and these packings only seldom occur.

The given conditions do not always allow for equivalent positions for all atoms. Take as an example the following conditions: composition MX₅, covalent M–X bonds, all X atoms bonded to M atoms. In this case all X atoms can only be equivalent if each set of five of them form a regular pentagon around an M atom (as for example in the XeF₅⁻ ion). If this is not possible for some reason, then there must be at least two non-equivalent positions for the X atoms. According to the symmetry principle the number of these non-equivalent positions will be as small as possible.

18.3 Structural Relationships by Group–Subgroup Relations

As was shown in various previous chapters, many structures of solids can be regarded as derivatives of simple, high-symmetry structure types. Let us recall some examples:

- Body-centered cubic sphere packing $\Rightarrow$ CsCl type $\Rightarrow$ superstructures of the CsCl type (Section 15.3)
- Diamond $\Rightarrow$ zinc blende $\Rightarrow$ chalcopyrite (Sections 12.2 and 12.4)
- Closest-packings $\Rightarrow$ closest-packings with occupied octahedral interstices (e.g. CdI₂ type, Section 17.3)

In all cases we start from a simple structure which has high symmetry. Every arrow ($\Rightarrow$) in the preceding examples marks a reduction of symmetry, i.e. a group–subgroup relation. Since these are well-defined mathematically, they are an ideal tool for revealing structural relationships in a systematic way. Changes that may be the reason for symmetry reductions include:

- Atoms of an element in symmetry-equivalent positions are substituted by several kinds of atoms. For example: CC (diamond) $\Rightarrow$ ZnS (zinc blende).
- Atoms are replaced by voids or voids are occupied by atoms. For example: hexagonal closest-packing $\Rightarrow$ CdI₂ type. If the voids are considered to be ‘zero atoms’, this can be considered as a ‘substitution’ of voids by atoms.
- Atoms of an element are substituted by atoms of another element that requires an altered kind of bonding. For example: KMgF₃ (perovskite type) $\Rightarrow$ CsGeCl₃ (lone electron pair at the Ge atom, Ge atom shifted from the octahedron center towards an octahedron face so that the three covalent bonds of an GeCl₃²⁻ ion are formed).
- Distortions due to the Jahn–Teller effect. For example: CdBr₂ (CdI₂ type) $\Rightarrow$ CuBr₂ (distorted CdI₂ type).
- Emergence of new interactions. For example: iodine (high pressure, metallic, packing of spheres) $\Rightarrow$ I₂ molecules (normal pressure).
- Distortions due to covalent bonds. For example: RuCl₃ (high temperature, hexagonal TiI₃ type) $\Rightarrow$ RuCl₃ (low temperature, orthorhombic, Ru–Ru bonds).
Phase transitions. Examples: BaTiO$_3$ ($> 120^\circ$C, cubic perovskite type) → BaTiO$_3$ ($< 120^\circ$C, tetragonal), cf. Fig. 19.5, p. 230; CaCl$_2$ ($> 217^\circ$C, rutile type) → CaCl$_2$ ($< 217^\circ$C), cf. Fig. 4.1, p. 33. For second-order phase transitions it is mandatory that there is a group–subgroup relation between the involved space groups (Section 18.4).

Structural relations can be presented in a clear and concise manner using family trees of group–subgroup relations as put forward by Bärnighausen. They can be set up with the aid of International Tables for Crystallography, Volume A1 [181], in which the maximal subgroups of every space group are completely listed. The top of the family tree (Bärnighausen tree) corresponds to the structure of highest symmetry, the aristotype (or basic structure), from which all other structures of a structure family are derived. The hettotypes (or derivative structures) are the structures that result by symmetry reduction.

Every space group listed in the family tree corresponds to a structure. Since the space group symbol itself states only symmetry, and gives no information about the atomic positions, additional information concerning these is necessary for every member of the family tree (Wyckoff symbol, site symmetry, atomic coordinates). The value of information of a tree is rather restricted without these data. In simple cases the data can be included in the family tree; in more complicated cases an additional table is convenient. The following examples show how specifications can be made for the site occupations. Because they are more informative, it is advisable to label the space groups with their full Hermann-Mauguin symbols.

Inspection of the atomic positions reveals how the symmetry is being reduced step by step. In the aristotype usually all atoms are situated in special positions, i.e. they have positions on certain symmetry elements, fixed values of the coordinates, and specific site symmetries. From group to subgroup at least one of the following changes occurs for each atomic position:

1. The site symmetry is reduced. Simultaneously, individual values of the coordinates $x$, $y$, $z$ may become independent, i.e. the atom can shift away from the fixed values of a special position.

2. Symmetry-equivalent positions split into several positions that are independent of one another.

**Diamond–Zinc Blende**

The group–subgroup relation of the symmetry reduction from diamond to zinc blende is shown in Fig. 18.3. Some comments concerning the terminology have been included. In both structures the atoms have identical coordinates and site symmetries. The unit cell of diamond contains eight C atoms in symmetry-equivalent positions (Wyckoff position 8a). With the symmetry reduction the atomic positions split to two independent positions (4a and 4c) which are occupied in zinc blende by zinc and sulfur atoms. The space groups are translationenungleiche: the dimensions of the unit cells correspond to each other. The index of the symmetry reduction is 2; exactly half of all symmetry operations is lost. This includes the inversion centers which in diamond are present in the centers of the C–C bonds.

The symmetry reduction can be continued. A (non-maximal) subgroup of $F\bar{4}3m$ is $I\bar{4}2d$ with doubled lattice parameter $c$. On the way $F\bar{4}3m \rightarrow I\bar{4}2d$ the Wyckoff position of the zinc atoms splits once more and can be occupied by atoms of two different elements.
That corresponds to the structure of chalcopyrite, CuFeS₂. Another tetragonal subgroup of \( F4_3m \) with doubled \( c \) axis is \( I4_2m \). It has the position \( 4c \) of zinc blende split into three positions, \( 2a, 2b \) and \( 4d \). Their occupation by atoms of three elements corresponds to the structure of stannite, FeSnCu₂S₄.

### The Relation between NiAs and MnP

The symmetry reduction to the mentioned hettotypes of diamond is necessary to allow the substitution of the C atoms by atoms of different elements. No splitting of Wyckoff positions, but a reduction of site symmetries in necessary to account for distortions of a structure. Let us consider once more MnP as a distorted variant of the nickel arsenide type (Fig. 17.5, p. 197). Fig. 18.4 shows the relations together with images of the structures.

The first step entails a loss of the hexagonal symmetry; a slight distortion of the lattice would suffice to this end. To meet the conventions, a \( C \)-centered cell has to be chosen for the orthorhombic subgroup. Due to the centering it is a \( \text{translationengleiche} \) subgroup, even though the size of the cell has been doubled. The corresponding cell transformation is mentioned in the middle of the group–subgroup arrow. The centering is removed in the second step, which corresponds to a loss of half of the translations. Therefore, it is a \( \text{klassengleiche} \) symmetry reduction of index 2.

The images in Fig. 18.4 display which symmetry elements are being lost in the two steps of the symmetry reduction. Among others, half of the inversion centers are removed in the second step. The removed inversion centers of the space group \( C2/m2/c2_1/m \) (for short \( Cmcm \)) are those of the Wyckoff positions \( 4a \) \((0,0,0)\) and \( 4b \) \((\frac{1}{2},0,0)\), while those of the Wyckoff position \( 8d \) \((\frac{1}{2},\frac{1}{2},0)\) are retained. Since the origin of the subgroup \( P2_1/m2_1/c2_1/n \) (short \( Pmcn \)) is supposed to be situated in an inversion center, this requires an origin shift by \(-\frac{1}{2},-\frac{1}{2},0\), as mentioned in the group–subgroup arrow. This shift means that \( \frac{1}{3},\frac{1}{3},0 \) have to be added to the coordinates. The necessary coordinate transformations are given between the boxes with the atomic coordinates.
By the addition of $\frac{1}{2}, \frac{1}{2}, 0$ to the coordinates listed in Fig. 18.4 for the space group $Cmcm$, we obtain ideal values for an undistorted structure in $Pmcn$. However, due to the missing distortion the symmetry would still be $Cmcm$. The space group $Pmcn$ is only attained by the shift of the atoms from the ideal positions. First of all, the deviations concern the $y$ coordinate of the Mn atom (0.214 instead of $\frac{1}{4}$) and the $z$ coordinate of the P atom (0.207 instead of $\frac{1}{4}$). These are rather small deviations, so we have good reasons to consider MnP as being a distorted variant of the NiAs type.

The relation between diamond and zinc blende shown above is a formal view. The substitution of carbon atoms by zinc and sulfur atoms cannot be performed in reality. The distortion of the NiAs structure according to Fig. 18.4, however, can actually be performed. This happens during phase transitions (Section 18.4). For example, MnAs exhibits this kind of phase transition at 125 °C (NiAs type above 125 °C, second-order phase transition; another transition takes place at 45 °C, cf. p. 238).

**Occupation of Octahedral Interstices in Hexagonal Closest-packing**

According to the discussion in Section 17.3, many structures can be derived from the hexagonal closest-packing of spheres by occupying a fraction of the octahedral interstices with other atoms. If the X atoms of a compound MX$_n$ form the packing of spheres, then the fraction $1/n$ of the octahedral interstices must be occupied. The unit cell of the
Section of the hexagonal closest-packing. Gray area:
Unit cell, space group $P6_3/m2/m2/c$.
Large cell: Base of the triple cell. The $z$ coordinates of the spheres refer to $\mathbf{e}' = c$.
The dots labeled ①, ②, and ③ mark six octahedral voids at $z = 0$ and $z = \frac{1}{2}$
(for $\mathbf{e}' = c$) and at $z = 0$ and $z = \frac{1}{3}$ ($\mathbf{e}' = 3c$).

Hexagonal closest-packing contains two octahedral interstices, so that only the fractions $\frac{1}{3}$ or $\frac{1}{2}$ of the octahedral interstices can be occupied without enlargement of the unit cell. Occupation of any other fraction requires an enlargement of the unit cell. In other words, only the compositions MX and MX$_2$ allow for structures without cell enlargement. Cell enlargement is equivalent to loss of translation symmetry, therefore *klassengleiche* group–subgroup relations must occur.

The aristotype can be considered to be either the packing of spheres itself, or the NiAs type which corresponds to the packing in which all octahedral interstices are occupied by Ni atoms (Wyckoff position 2$a$). In the aristotype these interstices are symmetry equivalent; subgroups result if the interstices are occupied only partially or by different kinds of atoms (or if the Ni atoms of NiAs are partially removed or substituted). By this procedure the sites of the interstices become non-equivalent.

$P6_3/m2/m2/c$, which is the space group of the hexagonal closest-packing of spheres, has only one maximal subgroup in which the position 2$a$ is split into two independent positions, namely $P32/m1$. If one of these positions is occupied and the other one remains vacant, this corresponds to the CdI$_2$ type.

Fig. 18.5 shows how the unit cell of the hexagonal closest-packing can be enlarged by a factor of three. The enlarged cell remains hexagonal or trigonal if the base vector $\mathbf{c}$ (viewing direction) is not changed. A rhombohedral cell results if $\mathbf{c}$ is also triplicated, together with a centering in $\frac{2}{3}, \frac{1}{3}, \frac{2}{3}$, and $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$. The volume of the cell itself then is nine times larger, but due to the centering the primitive cell is only three times larger. In both cases the primitive, enlarged cell contains six spheres (X atoms) and six octahedral holes. The composition M$_2$X$_6$ or MX$_3$ is the result of the occupation of two of the octahedral holes, the other four remaining vacant.

The Bärnighausen tree shown in Fig. 18.6 shows how the structures of some compounds MX$_3$ and M$_2$X$_6$ can be derived from a hexagonal closest-packing of spheres, taking the mentioned triplicated cells. The octahedral positions for each space group are represented by two or six small boxes instead of specifying numerical values. The boxes refer to the octahedral voids in the unit cell. The corresponding coordinates are given in the image at the top left. The positions of the octahedron centers are labeled by their Wyckoff letters;
Depending on which one of them is occupied, we obtain the structure types of BiI₃, leaving vacant 4c, corresponds to the RhF₃ type. The opposite, occupation of 4c, leaving vacant 2b, corresponds to corundum (α-Al₂O₃). Further splitting of the positions takes place at the next step, \( R\bar{3}2/c \rightarrow R\bar{3}3 \). Depending on which one of them is occupied, we obtain the structure types of BiI₃, ilmenite (FeTiO₃), WCl₆ and LiSbF₆.
Three structure types of composition MX$_3$ are mentioned in the left branch of Fig. 18.6. Hexagonal TiI$_3$ has strands of occupied face-sharing octahedra in the direction of c (gray boxes one on top of the other; cf. also Fig. 16.10, p. 175). OAg$_3$ has edge-sharing octahedra joined to layers as in the BiI$_3$ type (gray boxes side-by-side; cf. Fig. 16.8, p. 174). The occupied octahedra of NNi$_3$ share vertices.

The structures of TiI$_3$, OAg$_3$ and NNi$_3$ are followed by distorted variants with the same occupation patterns (lower part of the left branch). The symmetries are further reduced because in all three cases the atoms are shifted away from the octahedron centers; this is marked by the dots ●. The Ru atoms of RuBr$_3$ have shifted toward each other in pairs (Ru–Ru bonds). The P atoms of PI$_3$ have lone electron pairs. Each P atom has shifted toward an octahedron face parallel to +c; in this way the P atoms obtain three short P–I bonds and three long P···I contacts. A similar situation arises in crystalline trimethylamine, whose methyl groups form a hexagonal closest-packing. The N atoms are alternately shifted in the directions +c and −c out of the midpoints of the octahedra.

The crystal data compared to expected values assuming no distortions are summarized in Table 18.1. Inspection of the atomic coordinates reveals that the distortions of the packing of spheres are only marginal. As expected, the greatest deviations are observed for the molecular compounds PI$_3$ and NMe$_3$.

18.4 Symmetry Relations at Phase Transitions. Twinned Crystals

As discussed in Section 4.4 (p. 32), reconstructive phase transitions are always first-order transitions. The transformation begins at a nucleation site, which may be a site with a vacancy in the crystal. There, the movement of the atoms sets in and is followed by the growth of the nucleus and the reconstruction of the structure. Bonds of the old structure are broken and new bonds of the growing new structure are joined at the boundary between the two phases, while atoms perform the necessary diffusion. Group–subgroup relations between the space groups are of no importance in this kind of phase transition. Occasional speculations that assume a first-order phase transition to proceed via an intermediate common subgroup of the space groups concerned have no physical foundation whatsoever; it is not possible to assign a space group to the atomic arrangement along a phase boundary.

The situation is different for second-order phase transitions. These can only occur when the space group of the one phase is a (not necessarily maximal) subgroup of the space group of the other phase. Many displacive structure transformations are second-order transitions, in which atomic groups experience only small mutual motions. As an example, Fig. 4.1 (p. 33) shows the second-order phase transition of calcium chloride from the rutile type to the CaCl$_2$ type. All that happens is a mutual rotation of the strands of edge-sharing octahedra. This implies that the tetragonal symmetry cannot be retained; the symmetry is ‘broken’. The space group of the CaCl$_2$ type necessarily is a subgroup of the space group $P4_2/mn2/m$ of the rutile type. Since the crystal class changes from tetragonal to orthorhombic, the subgroup is translationengleiche. The corresponding relation is depicted in Fig. 18.7.

The lattice parameters $a$ and $b$ become different during the transition from the tetragonal to the orthorhombic structure. Either $a > b$ or $a < b$ results, depending on the direction of the rotation of the octahedra strands. During the phase transition both directions of rotation occur at random; domains appear, in which either $a > b$ or $a < b$. The obtained crystal is a twinned crystal or twin, consisting of intergrown domains. The twin domains are
### Table 18.1: Crystal data of structures mentioned in Fig. 18.6. The ideal coordinates would apply to an undistorted packing of spheres. Coordinate values fixed by symmetry are stated as 0 or fractional numbers, otherwise as decimal numbers

<table>
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<th>Structure</th>
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<th>c (pm)</th>
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<th>x</th>
<th>y</th>
<th>z</th>
<th>ideal coordinates</th>
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</table>

Interrelated by symmetry: their mutual orientation corresponds to a symmetry operation that has been lost during the symmetry reduction. Cf. aspect 3 of the symmetry principle mentioned on page 214.

**Definition:** An intergrowth of two or more macroscopic individuals of the same crystal species is a twin, if the orientation relations between the individuals conform to crystallographic laws. The individuals are called twin partners, twin components or twin domains.
The occurrence of twinned crystals is a widespread phenomenon. They may consist of individuals that can be depicted macroscopically as in the case of the ‘dovetail twins’ of gypsum, where the two components are mirror-inverted (Fig. 18.8). There may also be numerous alternating components which sometimes cause a streaky appearance of the crystals (polysynthetic twin). One of the twin components is converted to the other by some symmetry operation (twinning operation), for example by a reflection in the case of the dovetail twins. Another example is the ‘Dauphiné twins’ of quartz which are interconverted by a twofold rotation axis (Fig. 18.8). Threefold or fourfold axes can also occur as symmetry elements between the components; the domains then have three or four orientations. The twinning operation is not a symmetry operation of the space group of the structure, but it must be compatible with the given structural facts.

The formation of twins is to be expected if a phase transition takes place from a space group to another less symmetrical space group and if there occurs a translationengleiche group–subgroup relation. If it is a translationengleiche subgroup of index 2, the twin will consist of two kinds of domains, with index 3 three kinds and with index 4 four kinds of domains (indices higher than 4 do not occur among translationengleiche maximal subgroups). If the symmetry reduction entails several steps and there occur two translationengleiche steps, twins of twins may emerge. Among phase transitions induced by a change of temperature, as a rule, the high-temperature modification has the higher symmetry.

The Dauphiné twins of quartz are formed when quartz is transformed from its high-temperature form (β or high quartz, stable above of 573 °C) to the low-temperature form...
Group–subgroup relations and the emergence of twins in the phase transition $\beta$-quartz $\rightarrow \alpha$-quartz (Dauphiné twins). The space group of $\alpha$-quartz is a *translationengleiche* subgroup of index 2 of the space group of $\beta$-quartz, and twins are the result. During the symmetry reduction certain twofold axes are lost (the last 2 in the space group symbol $P\overline{6}_222$). These axes, present only in the higher symmetry space group, produce the twinning operation. If they were present, they would map an atom from the site $x, y, z$ to the sites $x, x - y, \frac{2}{3} - z; y - x, \frac{1}{3} - z$ and $-y, -x, -z$ in terms of the coordinate system of $P3_221$. Compare this with the atomic coordinates of the two twin components given in Fig. 18.9. Quartz crystals twinned in this manner are unsuitable as piezoelectric components for electronic devices, as the polar directions of the twins compensate each other. During the production of piezoelectric quartz the temperature must therefore never exceed 573 °C.

The symmetry reduction shown in Fig. 18.6 resulting in the space group of RuBr$_3$ ($P2_1/m2/m2/m$) includes a *translationengleiche* step of index 3. The structure deviates only slightly from the hexagonal TiI$_3$ type in the higher symmetrical space group $P6_3/m2c2/m$ (shifting of the Ru atoms from the octahedron centers), and at higher temperatures the higher symmetry is true. RuBr$_3$ that was prepared at higher temperatures and then cooled consists of twinned crystals with three components being mutually rotated by 120°, corresponding to the loss of the threefold symmetry during the step $P6_3/m2c2/m \rightarrow C2/m2c2/m$. In X-ray diffraction studies the X-ray reflections of the tree com-
ponents appear superimposed, so that they give the impression of hexagonal symmetry and the resulting Ru atom positions seem to be exactly in the octahedron centers. Unrecognized twins that feign a wrong symmetry can be a treacherous problem during structure determination and may cause erroneous results.

In addition to the formation of twins during phase transformations in the solid state, twins can also develop during the growth of crystals. The emergence of crystallization nuclei controls how growth twins will be intergrown. Group–subgroup relations are irrelevant in this case.

18.5 Problems

18.1 To solve the following problems it is useful to draw images of the symmetry axes in the way as in Fig. 3.4, p. 16.
(a) Let a space group (e.g. P\text{3}) have threefold rotation axes parallel to c. What kind of screw axes can remain when c triplicated?
(b) The space group P\text{3}1 has threefold screw axes parallel to c. Which screw axes remain in the maximal subgroup having c doubled?
(c) Let a space group (e.g. P\text{2}1) have twofold screw axes parallel to b. Can this space group have klassengleiche or isomorphic, maximal subgroups in which b has been increased by a factor of two or three?

18.2 Determine whether the following group–subgroup relations are translationengleiche, klassengleiche or isomorphic. If the unit cell of the subgroup is enlarged, this is stated within the arrow.
(a) Cmcm \rightarrow Pmcm;
(b) P2_1/c \rightarrow P\overline{1};
(c) Pbc\text{m} \rightarrow 2a,b,c \rightarrow P\text{bca};
(d) C\text{12}/m1 \rightarrow a,3b,c \rightarrow C\text{12}/m1;
(e) P6_3/m\text{cm} \rightarrow P6_\text{2}2\text{2};
(f) P2_1/m2_1/m2/n \rightarrow P\text{mm}2;
(g) P2_1/m2_1/m2/n \rightarrow P1\text{2}1/m1.

18.3 Set up the Bärnighausen tree for the relation between disordered and ordered AuCu\text{3}, including the relations between the Wyckoff positions (Fig. 15.1, p. 158). You will need International Tables for Crystallography [48], Volume A, and advantageously also Volume A1 [181]. Will ordered AuCu\text{3} form twins?

18.4 Set up the Bärnighausen tree for the relation between perovskite and elpasolite, including the relations between the Wyckoff positions (Fig. 17.10, p. 203 and Fig. 17.12, p. 205). Make use of International Tables, Volumes A and A1 [48, 181].

18.5 Set up the Bärnighausen tree for the relation between cubic BaTiO\text{3} (perovskite type, Fig. 17.10) and tetragonal BaTiO\text{3} (Fig. 19.5, p. 230). Remark: the subgroup is not maximal. Is it to be expected that the phase transition from the cubic to the tetragonal form will yield twins? Atomic coordinates for tetragonal BaTiO\text{3}: Ba, \frac{1}{2} \frac{1}{2} \frac{1}{2}; Ti, 0 0 0.020; O1, 0 0 0.474; O2, \frac{1}{2} 0 -0.012. Make use of International Tables, Volumes A and A1 [48, 181].

18.6 The phase transition from \alpha\text{-}tin to \beta\text{-}tin involves a change of space group F4_1/d\overline{3}2/m \rightarrow t3\rightarrow I4_1/a2/m2/d. Would you expect \beta\text{-}tin to form twins?

18.7 The phase transition of NaNO\text{2} at 164 \degree C from the paraelectric to the ferroelectric form involves a change of space group from I2/m2/m2/m to I\text{mm}2. Will the ferroelectric phase be twinned?
19 Physical Properties of Solids

The majority of the materials we use and handle every day are solid. We take advantage of their physical properties in manifold ways. The properties are intimately related to the structures. In the following we will deal only briefly with a few properties that are directly connected with some structural aspects. Many other properties such as electrical and thermal conductivity, optical transparency and reflectivity, color, luminescence etc. require the discussion of sophisticated theories that are beyond the scope of this book.

19.1 Mechanical Properties

In addition to specific properties of interest for a particular application of a material, its elasticity, compressive and tensile strength, deformability, hardness, wear-resistance, brittleness and cleavability also determine whether an application is possible. No matter how good the electric, magnetic, chemical or other properties are, a material is of no use if it does not fulfill mechanical requirements. These depend to a large extent on the structure and on the kind of chemical bonding. Mechanical properties usually are anisotropic, i.e. they depend on the direction of the applied force.

A framework of strong covalent bonds as in diamond results in high hardness and compressive strength. It also accounts for a high tensile strength; in this case it is sufficient if the covalent bonds are present in the direction of the tensile stress. Hardness can be determined in a qualitative manner by the MOHS scratch test: a material capable of scratching another is the harder of the two. Standard materials on the MOHS scale are talc at the lower end (hardness 1) and diamond (hardness 10) at the upper end. Talc is soft because its structure consists of electrically uncharged layers; only VAN DER WAALS forces act (cf. Fig. 16.21), and the layers can easily slide over each other. The same applies to graphite and MoS₂, which are used as lubricants. Crystals consisting of stiff parallel chain molecules have strong bonding forces in the chain direction and weak ones in perpendicular directions. They can be cleaved to form fiber bunches.

Ionic crystals have moderate to medium hardness, those incorporating highly charged ions being harder (e.g. NaCl hardness 2, CaF₂ hardness 4). Quartz with its network of polar covalent bonds is harder (hardness 7). The surfaces of materials with hardness below 7 become lusterless in everyday use because they continually suffer scratching from quartz particles in dust. The differing cohesion due to covalent and to ionic bonds in different directions is apparent in micas. Micas consist of anionic layers and intercalated cations. Within the layers atoms are held together by (polar) covalent bonds. Micas can easily be cleaved parallel to the layers, which allows the manufacture of plates with sizes of several square decimeters and a thickness of less than 0.01 mm.

Ionic crystals can be cleaved in certain directions. Fig. 19.1 shows why the exertion of a force results in cleavage: if two parts of a crystal experience a mutual displacement by a shearing force, ions of like charges come to lie side by side and repel each other. The displacement is easiest along planes which have the fewest cation–anion contacts. In
Fig. 19.1  
Shearing forces exerted on an ionic crystal (left) result in cleavage (right).

rock salt, for example, one encounters one Cl\(^{-}\) neighbor when looking from an Na\(^{+}\) ion in the direction parallel to an edge of the unit cell, two Cl\(^{-}\) neighbors if one looks in the direction diagonal to a face, and three Cl\(^{-}\) neighbors in the direction of a body diagonal. An NaCl crystal is most easily cleaved perpendicular to a cell edge.

Metals behave differently since the metal atoms are embedded in an electron gas. The attractive forces remain active even after mutual displacement of parts of a crystal has occurred. Metals therefore can be deformed without fracture.

Most ceramic materials are oxides (MgO, Al\(_2\)O\(_3\), ZrO\(_2\), silicates), though some are nitrides (BN, AlN, Si\(_3\)N\(_4\)) or carbides (B\(_4\)C, SiC, WC). Because of the short range of action of the chemical bonds, the material suffers a substantial loss of strength once a rupture has begun. The resulting brittleness is one of the most severe drawbacks of ceramic materials. This problem has been largely solved for one material, zirconium dioxide. ZrO\(_2\) adopts several modifications: at temperatures above 2370 °C it has the cubic CaF\(_2\) structure (Zr atoms with c.n. 8), between 1170 and 2370 °C it has a slightly distorted, tetragonal CaF\(_2\) structure (Zr coordination 4 + 4), and below 1170 °C baddeleyite is the stable form; this is a more distorted variant of the CaF\(_2\) type in which a Zr atom only has the coordination number 7. The tetragonal form can be stabilized down to room temperature by doping with a few percent of Y\(_2\)O\(_3\). Compared to the tetragonal modification, baddeleyite requires 7% more volume. For this reason pure ZrO\(_2\) is not appropriate as a high-temperature ceramic: it cracks during heating when the transition temperature of 1170 °C is reached. But it is precisely this volume effect which is taken advantage of in order to reduce the brittleness, thus rendering ZrO\(_2\) a high-performance ceramic material. Such material consists of ‘partially stabilized’ tetragonal ZrO\(_2\), i.e. it is maintained metastable in this modification by doping. The mechanical forces have their maximum at the tip of a crack, and this is where the crack propagates in common materials. In metastable tetragonal ZrO\(_2\), however, mechanical strain at the tip of a crack induces a transition to the baddeleyite form at this site, and by the volume expansion the crack is sealed.

19.2 Piezoelectric and Ferroelectric Properties

The Piezoelectric Effect

Within a crystal, consider an atom with a positive partial charge that is surrounded tetrahedrally by atoms with negative partial charges. The center of gravity of the negative charges is at the center of the tetrahedron. By exerting pressure on the crystal in an appropriate direction, the tetrahedron will experience a distortion, and the center of gravity of the negative charges will no longer coincide with the position of the positive central atom (Fig. 19.2); an electric dipole has developed. If there are inversion centers in the
Fig. 19.2
Explanation of the piezoelectric effect:
external pressure causes the deformation of a coordination tetrahedron, resulting in a shift of the centers of gravity of the electric charges.

- Structure, then for every tetrahedron there is another tetrahedron which has the exact opposite orientation; the electric fields of the dipoles compensate each other. If, however, all tetrahedra have the same orientation or some other mutual orientation that does not allow for a compensation, then the action of all dipoles adds up and the whole crystal becomes a dipole. Two opposite faces of the crystal develop opposite electric charges. Depending on the direction of the acting force, the faces being charged are either the two faces experiencing the pressure (longitudinal effect) or two other faces in a perpendicular or an inclined direction (transversal effect).

This described piezoelectric effect is reversible. If the crystal is introduced into an external electric field, it experiences a contraction or an elongation. Zinc blende, turmaline, ammonium chloride and quartz are examples. The effect is used in the quartz resonators that beat time in electronic watches and computers. The quartz resonator is a sheet cut from a quartz crystal in an appropriate direction. Metal coatings act as electrical contacts. Mechanical vibrations are induced in the quartz with the aid of electric pulses; these vibrations have an exactly defined frequency and produce a corresponding alternating electric field. Aside from quartz, Pb(Ti,Zr)O₃ (PZT) is mainly used; its properties can be controlled by the Ti/Zr ratio. It has a distorted perovskite structure (space group \(P_{4mm}\), Fig. 19.5, or \(R\bar{3}c\), depending on composition). Piezoelectric crystals serve whenever mechanical pulses are to be converted to electrical signals or vice versa, for example in seismometers, vacuum meters, acceleration meters, press keys, microphones or in the production of ultrasound.

Crystals can only be piezoelectric when they are non-centrosymmetric. In addition, they may not belong to the crystal class \(4\bar{3}2\). The effect is thus restricted to 20 out of the 32 crystal classes.

Ferroelectricity

In some crystalline substances the centers of gravity of positive and negative charges do not coincide in the first place, i.e. permanent dipoles are present. Concerning the electrical properties, the following cases can be distinguished.

A paraelectric substance is not polarized macroscopically because the dipoles are oriented randomly. However, they can be oriented by an external electric field (orientation polarization). The orientation is counteracted by thermal motion, i.e. the degree of polarization decreases with increasing temperature.

An electret is a crystal which has dipoles oriented permanently in one direction. The crystal therefore is a macroscopic dipole.
In a ferroelectric substance all dipoles are also oriented uniformly, but they can be re-oriented by an external electric field. A previously untreated crystal can be made up of domains, and the uniform orientation of the dipoles is fulfilled within a domain. It differs from domain to domain. As a whole, the dipole moments of different domains can compensate each other. If an increasing external electric field acts on the sample, those domains whose polarization corresponds to the direction of the electric field will grow at the expense of the remaining domains. The total polarization of the crystal increases (curve \( v \) in Fig. 19.3). Finally, if the external field is strong enough, the whole crystal is one large domain, and the polarization continues to increase only slightly with increasing electric field (curve \( s \); the continuing increase is due to the normal dielectric polarization which takes place in any substance by polarization of the electrons). If the external electric field is removed, a remanent polarization \( P_r \) remains, i.e. the crystal now is a macroscopic dipole. In order to remove the remanent polarization, an electric field \(-E_c\) with the opposite orientation to has to be applied; this is the coercive field. The value of \( P_s \), the spontaneous polarization, corresponds to the polarization within a domain.

Above a specific temperature, the Curie temperature, a ferroelectric substance becomes paraelectric since the thermal vibrations counteract the orientation of the dipoles. The coordinated orientation of the dipoles taking place during the ferroelectric polarization is a cooperative phenomenon. This behavior is similar to that of ferromagnetic substances, which is the reason for its name; the effect has to do nothing with iron (it is also called seignette or rochelle electricity).

The polarization induced by the electric field is considerably larger than in a nonferroelectric substance, and therefore the dielectric constants are much larger. \( \text{BaTiO}_3 \) in particular has practical applications in the manufacture of capacitors with large capacitance. Further examples include \( \text{SbSI, KH}_2\text{PO}_4 \), and \( \text{NaNO}_2 \), as well as certain substances which have a distorted perovskite structure such as \( \text{LiNbO}_3 \) and \( \text{KNbO}_3 \). Fig. 19.4 shows how all nitrite ions in sodium nitrite are oriented in one direction below 164 °C, thus producing a macroscopic dipole moment. It also shows how the differently oriented domains alternate as long as there has been no electric field to shift all the \( \text{NO}_2^- \) ions into the same orientation. Above the Curie temperature of 164 °C all \( \text{NO}_2^- \) ions are randomly oriented and \( \text{NaNO}_2 \) is paraelectric.

In sodium nitrite the ferroelectric polarization only occurs in one direction. In \( \text{BaTiO}_3 \) it is not restricted to one direction. \( \text{BaTiO}_3 \) has the structure of a distorted perovskite between 5 and 120 °C. Due to the size of the \( \text{Ba}^{2+} \) ions, which form a closest packing of spheres together with the oxygen atoms, the octahedral interstices are rather too large for
Fig. 19.4
Structure of NaNO$_2$ below and above the CURIE point. Bottom: domains in a ferroelectric crystal of NaNO$_2$.

Fig. 19.5

The titanium atoms, and these consequently do not occupy exactly the octahedron centers. The titanium atom in an octahedron is shifted towards one of the O atoms, the direction of the shift being the same for all octahedra of one domain (Fig. 19.5). The result is a polarization in the domain. The shift is similar for the W atoms in WOCl$_4$, which has square-pyramidal molecules associated to form a strand with alternating short and long W–O distances. Above the CURIE temperature of 120°C, BaTiO$_3$ has the cubic perovskite structure, with all titanium atoms occupying the octahedron centers. A considerably higher CURIE temperature (1470°C) and also a much larger polarization have been found for LiNbO$_3$.

No ferroelectricity is possible when the dipoles in the crystal compensate each other due to the crystal symmetry. All centrosymmetric, all cubic and a few other crystal classes are
Table 19.1: Crystal classes permitting ferroelectric crystals

<table>
<thead>
<tr>
<th>crystal class</th>
<th>direction of polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>arbitrary</td>
</tr>
<tr>
<td>2</td>
<td>parallel to the monoclinic axis</td>
</tr>
<tr>
<td>m</td>
<td>perpendicular to the monoclinic axis</td>
</tr>
<tr>
<td>mm2</td>
<td>parallel to the c axis</td>
</tr>
</tbody>
</table>

excluded. The allowed crystal classes are listed in Table 19.1. All ferroelectric materials also are piezoelectric.

Ferroelasticity is the mechanical analogon to ferroelectricity. A crystal is ferroelastic if it exhibits two (or more) differently oriented states in the absence of mechanical strain, and if one of these states can be shifted to the other one by mechanical strain. CaCl₂ offers an example (Fig. 4.1, p. 33). During the phase transition from the rutile type to the CaCl₂ type, the octahedra can be rotated in one or the other direction. If either rotation takes place in different regions of the crystal, the crystal will consist of domains having the one or the other orientation. By exerting pressure all domains can be forced to adopt only one orientation.

19.3 Magnetic Properties

An unpaired electron executes a spin about its own axis. The mechanical spin momentum is related to a spin vector which specifies the direction of the rotation axis and the magnitude of the momentum. The spin vector \( \mathbf{s} \) of an electron has an exactly defined magnitude:

\[
|s| = \frac{\hbar}{2\pi}\sqrt{s(s+1)} = \frac{\hbar}{4\pi}
\]

The spin quantum number \( s \) is used to characterize the spin. It can have only the one numerical value of \( s = \frac{1}{2} \). \( \hbar = 6.6262 \cdot 10^{-34} \text{ Js} = \text{PLANCK'S constant.} \)

The spin is associated with a magnetic moment, i.e. an electron behaves like a tiny bar magnet. An external magnetic field exerts a force on an electron, resulting in a precession of the electron about the direction of the magnetic field which is similar to the precession of a top; the rotation axis of the electron is thus inclined relative to the magnetic field. Quantum theory permits only two values for the inclination; they are expressed by the magnetic spin quantum number \( m_s \), which has the values of \( m_s = +s = +\frac{1}{2} \) or \( m_s = -s = -\frac{1}{2} \). The two inclinations are also called ‘parallel’ and ‘antiparallel’, although the spin vectors are not really exactly parallel or antiparallel to the magnetic field.

The magnetic moment of an isolated electron has a definite values of

\[
\mu_s = 2\mu_B\sqrt{s(s+1)} = 2\mu_B\sqrt{3} \\
\text{with} \quad \mu_B = \frac{e\hbar}{4\pi m_e} = 9.274 \cdot 10^{-24} \text{ JT}^{-1}
\]

\( e = \text{unit charge}, \ h = \text{PLANCK'S constant,} \ m_e = \text{mass of the electron;} \ 1 \text{ tesla is the unit of the magnetic flux density,} \ 1 \text{ T} = 1 \text{ V} \cdot \text{s} \cdot \text{m}^{-2} \)

\( \mu_B \) is termed the BOHR magneton. Magnetic moments are given as multiples of \( \mu_B \).
An electron orbiting in an atom is a circular electric current that is surrounded by a magnetic field. This also can adopt only certain orientations in an external magnetic field according to quantum mechanics. The state of an electron in an atom is characterized by four quantum numbers:

- Principal quantum number, \( n = 1, 2, 3, \ldots \)
- Orbital quantum number, \( l = 0, 1, 2, \ldots, n - 1 \)
- Magnetic quantum number, \( m_l = -l, \ldots, 0, \ldots + l \)
- Magnetic spin quantum number, \( m_s = -\frac{1}{2}, +\frac{1}{2} \)

Two electrons in an atom exert an influence on each other, \( i.e. \) their spins and their orbital angular momenta are coupled. Two electrons are termed paired if they coincide in all of their quantum numbers except the magnetic spin quantum number. In such an electron pair the magnetic moments of the electrons compensate each other. Unpaired electrons in different orbitals tend to orient their spins parallel and thus produce an accordingly larger magnetic field (HUND’s rule); they have the same magnetic spin quantum number and differ in some other quantum number.

Substances having only paired electrons are diamagnetic. When they are introduced into an external magnetic field, a force acts on the electrons, \( i.e. \) an electric current is induced. The magnetic field of this current is opposed to the external field (LENZ’s rule). As a result, the substance experiences a repulsion by the external magnetic field; the repulsive force is rather weak, but ever present.

In a paramagnetic substance unpaired electrons are present. Frequently the unpaired electrons can be assigned to certain atoms. When an external magnetic field acts on a paramagnetic substance, the magnetic moments of the electrons adopt the orientation of this field, the sample is magnetized and a force pulls the substance into the field. The magnetization can be determined quantitatively by measuring this force. Thermal motion of the atoms prevents a complete orientation, and higher temperatures therefore cause a smaller degree of magnetization.

The additional magnetic field produced by the orientation is a measure of the magnetization \( M \). It is proportional to the external magnetic field \( H \):

\[
M = \chi H
\]

The dimensionless proportionality factor \( \chi \) is the magnetic susceptibility. The magnetization and consequently also the susceptibility depend on the number of orientable particles in a given volume. A volume-independent, material-specific magnitude is the molar susceptibility \( \chi_{\text{mol}} \):

\[
\chi_{\text{mol}} = \chi V_{\text{mol}} = \chi_g M_{\text{mol}}
\]

\( V_{\text{mol}} \) is the molar volume, \( M_{\text{mol}} \) the molar mass and \( \chi_g = \chi / \rho \) the commonly specified mass susceptibility (\( \rho \) = density).

Taking the susceptibility, we can classify materials according to their magnetic properties in the following way:

\[
\begin{align*}
\chi_{\text{mol}} < 0 & \quad \text{diamagnetic} \\
\chi_{\text{mol}} > 0 & \quad \text{paramagnetic} \\
\chi_{\text{mol}} \gg 0 & \quad \text{ferromagnetic}
\end{align*}
\]
Paramagnetism

The temperature dependence of the molar susceptibility of a paramagnetic substance follows the CURIE–WEISS law (if the magnetic field is not too strong):

$$\chi_{\text{mol}} = \frac{C}{T - \Theta}$$ (19.3)

where \( T = \) absolute temperature, \( C = \) CURIE constant, and \( \Theta = \) WEISS constant.

A plot of the reciprocal of the measured susceptibility \( 1/\chi_{\text{mol}} \) vs. \( T \) is a straight line with slope \( 1/C \), and which crosses the abscissa at \( T = \Theta \) (Fig. 19.6). For \( \Theta = 0 \) the equation is simplified to the classic CURIE law \( \chi_{\text{mol}} = C/T \). Generally, values of \( \Theta \neq 0 \) are found when cooperative effects arise at low temperatures (ferro-, ferri- or antiferromagnetism). The straight line then has to be extrapolated from high to low temperatures (dashed lines in Fig. 19.6).

The following discussion is restricted to the case of a substance containing only one species of paramagnetic atoms (atoms with unpaired electrons). The \textit{magnetic moment} \( \mu \) is used to specify how magnetic an atom is. An increasing magnetic moment results in an increasing susceptibility; the quantitative relation is given by means of the CURIE constant:

$$C = \mu_0 \frac{N_A^2 \mu^2}{3R}$$ (19.4)

\( \mu_0 = \) magnetic field constant = \( 4\pi \times 10^{-7} \) V s A\(^{-1}\) m\(^{-1}\); \( N_A = \) AVOGADRO’s number, \( R = \) gas constant.

The solution of equation (19.4) and division of \( \mu \) by \( \mu_B \) yields the experimentally determined magnetic moment \( \mu_{\text{eff}} \) of a sample, expressed as a multiple of \( \mu_B \):

$$\mu_{\text{eff}} = \frac{\mu}{\mu_B} = \frac{1}{\mu_B} \sqrt{\frac{3R}{\mu_0 N_A^2 \chi_{\text{mol}}(T - \Theta) = 800 \sqrt{\chi_{\text{mol}} \frac{(T - \Theta)}{\text{mol}^{-1} \text{m}^3 \text{K}}}}$$ (19.5)

The coupling of the spins of the electrons in an atom is accounted for by adding their magnetic spin quantum numbers. Since they add up to zero for paired electrons, it is sufficient to consider only the unpaired electrons. The spins of \( n \) unpaired electrons add up according to HUND’s rule to a total spin quantum number \( S = \frac{1}{2} n \). The magnetic moment of these \( n \) electrons, however, is not the scalar sum of the single magnetic moments. The
spin momenta must be added vectorially, taking into account the particular directions they may adopt according to quantum theory. The addition of the spin momenta yields a total spin momentum with the magnitude:

\[ |S| = \frac{\hbar}{2\pi} \sqrt{S(S+1)} \]

which is related to a magnetic moment:

\[ \mu = 2\mu_B \sqrt{S(S+1)} \]  

(19.6)

In addition to the magnetism due to the electron spin, the magnetism of the orbital motion has to be considered. For this purpose the magnetic quantum numbers of the electrons are added to a \textit{resultant orbital quantum number} \( L = \sum m_l \), beginning with the highest magnetic quantum number. For example:

\[
\begin{align*}
\text{Cr}^{2+}: & \quad d^4 \quad \begin{array}{cccc}
\uparrow & \uparrow & \uparrow & \uparrow \\
1 & 2 & 3 & 4
\end{array} \\
& \quad l = 2; \quad L = +2 + 1 + 1 = 2; \quad S = 4 \times \frac{1}{2} = 2 \\
\text{Cu}^{2+}: & \quad d^9 \quad \begin{array}{ccccccc}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
1 & 2 & 3 & 4 & 5 & 6 & 7
\end{array} \\
& \quad l = 2; \quad L = +2 + 2 + 1 + 1 + 0 = 2; \quad S = \frac{9}{2}
\end{align*}
\]

Finally, the magnetic moments resulting from the spin and the orbital motion interact. This spin–orbit coupling is taken into account by the \textit{total angular momentum quantum number} \( J \) (Russell-Saunders coupling):

\[ J = L - S \] if the subshell is less than half-occupied, otherwise \( J = L + S \).

The corresponding magnetic moment is:

\[ \mu = g \mu_B \sqrt{J(J+1)} \]  

(19.7)

with \( g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \) (Landé factor)

\( L = 0 \) and \( S = 0 \) always hold for a fully occupied subshell. Therefore, the core electrons of an atom do not contribute to magnetism. \( L = 0 \) and \( g = 2 \) hold for half-filled subshells, resulting in a pure spin paramagnetism according to equation (19.6).

However, compounds of the lighter elements including the 3\textit{d} transition elements also show only a spin magnetism with nearly no contribution from orbital motion. Their orbits are strongly influenced by the ligand field and cannot orient themselves freely in a magnetic field. The ligand field quenches the contributions of the orbital angular momentum completely or partially. As shown in Table 19.2, the spin-only approximation according to equation (19.6) is fulfilled quite well for 3\textit{d} ions having electron configurations \( 3d^1 \) to \( 3d^5 \); a small amount of spin–orbit coupling is observed for the configurations \( 3d^6 \) to \( 3d^9 \).

The spin–orbit coupling generally cannot be neglected for compounds of the heavier 4\textit{d} transition metals and especially of the 5\textit{d} metals. This leads to large discrepancies between the spin-only and the observed values of the magnetic moments. The coupling depends on the electron configuration and for certain configurations also on temperature. Usually, it leads to reduced magnetic moments for \( d^1 \) to \( d^4 \) and to enhanced moments for \( d^5 \) to \( d^9 \) as compared to the spin-only value. For more details the specialist literature should be consulted.

The 4\textit{f} electrons of lanthanoid ions, being shielded by the fully occupied, spherical shells \( 5s \) and \( 5p \), experience almost no influence from the ligand field. In this case the orbit magnetism is fully effective. Good agreement is observed between experimental magnetic moments and values calculated from the Russell-Saunders coupling according to equation (19.7) (Table 19.2).
Table 19.2: Calculated values of $2\sqrt{S(S+1)}$ and $g\sqrt{J(J+1)}$ for some high-spin ions and comparison with experimental values $\mu_{\text{eff}} = \mu / \mu_B$

<table>
<thead>
<tr>
<th>Ion</th>
<th>$2\sqrt{S(S+1)}$</th>
<th>$\mu_{\text{eff}}$</th>
<th>$g\sqrt{J(J+1)}$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$^{3+}$</td>
<td>3$d^0$</td>
<td>0</td>
<td>0</td>
<td>Ce$^{3+}$</td>
</tr>
<tr>
<td>Ti$^{3+}$</td>
<td>3$d^1$</td>
<td>1.73</td>
<td>1.7 – 1.8</td>
<td>Pr$^{3+}$</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>3$d^2$</td>
<td>2.83</td>
<td>2.8 – 2.9</td>
<td>Nd$^{3+}$</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>3$d^3$</td>
<td>3.87</td>
<td>3.7 – 3.9</td>
<td>Sm$^{3+}$</td>
</tr>
<tr>
<td>Cr$^{2+}$, Mn$^{3+}$</td>
<td>3$d^4$</td>
<td>4.90</td>
<td>4.8 – 5.0</td>
<td>Eu$^{3+}$</td>
</tr>
<tr>
<td>Mn$^{2+}$, Fe$^{3+}$</td>
<td>3$d^5$</td>
<td>5.92</td>
<td>5.7 – 6.1</td>
<td>Gd$^{3+}$</td>
</tr>
<tr>
<td>Fe$^{2+}$, Co$^{3+}$</td>
<td>3$d^6$</td>
<td>4.90</td>
<td>5.1 – 5.7</td>
<td>Tb$^{3+}$</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>3$d^7$</td>
<td>3.87</td>
<td>4.3 – 5.2</td>
<td>Dy$^{3+}$</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>3$d^8$</td>
<td>2.83</td>
<td>2.8 – 3.0</td>
<td>Ho$^{3+}$</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>3$d^9$</td>
<td>1.73</td>
<td>1.7 – 2.0</td>
<td>Er$^{3+}$</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>3$d^{10}$</td>
<td>0</td>
<td>0</td>
<td>Yb$^{3+}$</td>
</tr>
</tbody>
</table>

*Deviation because the first excited state is only slightly above the ground state and a fraction of the atoms is always excited; $\mu_{\text{eff}} \to 0$ when $T \to 0$*

**Ferro-, Ferri- and Antiferromagnetism**

The term ferromagnetism reflects the fact that iron shows this effect, but it is by no means restricted to iron or iron compounds. Ferromagnetism is a cooperative phenomenon, *i.e.* many particles in a solid behave in a coupled manner. Paramagnetic atoms or ions exert influence on each other over extended regions.

In a ferromagnetic substance the magnetic moments of adjacent atoms orient themselves mutually parallel, and their action is added up. However, most materials that have not been treated magnetically exhibit no macroscopic magnetic moment. This is due to the presence of numerous domains (WEISS domains). In each domain the orientation of all spins is parallel, but it differs from domain to domain. An external magnetic field causes the growth of those domains oriented parallel with the magnetic field at the expense of the other domains. When the spins of all domains have been oriented, saturation has taken place. To achieve this state, a magnetic field with some minimum field strength is required; its magnitude is dependent on the material.

A hysteresis curve shows this kind of behavior; it is like the hysteresis of a ferroelectric material (Fig. 19.7). Starting with an untreated sample, an increasing magnetic field causes an increasing magnetization until saturation has been reached. After turning off the magnetic field, there is some loss of magnetization, but a remanent magnetization $R$ is retained. By reversing the magnetic field, the spins experience a reorientation. The minimum magnetic field required for this is the coercive force or coercive field $K$. Depending on the application, magnetic materials with different magnetic ‘hardness’ are required. For example, a permanent magnet in a direct-current electric motor must have a high coercive force in order to maintain its magnetization. Small coercive forces are required whenever frequent and fast remagnetizations are required, as for example in recording heads.

Above a critical temperature $T_C$, the CURIE temperature, a ferromagnetic material becomes paramagnetic, since thermal motion inhibits the parallel orientation of the magnetic moments. The susceptibility then follows the CURIE–WEISS law with a positive value of the WEISS constant, $\Theta > 0$ (Fig. 19.6).
The coupling of the magnetic moments of the atoms can also result in spins having opposite orientations; in this case the material is antiferromagnetic (Fig. 19.8). At very low temperatures its total magnetic moment is zero. With increasing temperature the thermal motion interferes with the antiparallel orientation of all particles and the magnetic susceptibility increases; at even higher temperatures, thermal motion increasingly causes a random distribution of the spin orientations and the magnetic susceptibility decreases again, as in a paramagnetic material. Therefore, an antiferromagnetic material exhibits a maximum susceptibility at a certain temperature, the Néel temperature.

The symmetry of antiferromagnetic crystals with the inclusion of the spin orientation can be described with the aid of black–white space groups (SHUBNIKOV groups, antisymmetry space groups). They are an extension of the space groups. Every point in space is distinguished to be either black or white. The common symmetry operations then can be coupled with a change of the color. In the Hermann–Mauguin symbol this is expressed by a prime ‘. For example, a twofold rotation that is coupled with a color change (or with a spin inversion) obtains the symbol $2'$. There exist 1191 black–white space group types.

In a ferrimagnetic material the situation is the same as in an antiferromagnetic material, but the particles bearing opposite magnetic moments occur in different quantities and/or their magnetic moments differ in magnitude. As a consequence, they do not compensate each other even at very low temperatures. The behavior in a magnetic field is like that of ferromagnetic materials.
Table 19.3: Coupling of the spin vectors related to cooperative magnetic effects

<table>
<thead>
<tr>
<th>Property</th>
<th>Spin orientation within a domain</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferromagnetism</td>
<td>↑↑</td>
<td>α-Fe, Ni, Gd; EuO (NaCl type)</td>
</tr>
<tr>
<td>Antiferromagnetism</td>
<td>↓↓</td>
<td>MnF₂, FeF₂ (rutile type)</td>
</tr>
<tr>
<td>Ferrimagnetism</td>
<td>↑↑</td>
<td>Fe₃O₄, NiFe₂O₄ (inverse spinels)</td>
</tr>
<tr>
<td></td>
<td>↑↑↑</td>
<td>Y₃Fe₅O₁₂ (garnet)</td>
</tr>
</tbody>
</table>

The order occurring among the spins of the atoms in the unit cell can be determined experimentally by neutron diffraction. Since a neutron itself has a spin and a magnetic moment, it is diffracted by an atom to an extent which depends on the orientation of the magnetic moment.

Different kinds of spin coupling are listed in Table 19.3.

What determines the way in which the spins couple? Parallel orientation always occurs when the corresponding atoms act directly on one another. This is the case in pure metals like iron or nickel, but also in EuO (NaCl type). Antiparallel orientation usually occurs when two paramagnetic particles interact indirectly by means of the electrons of an intermediate particle which itself is not paramagnetic; this is called superexchange mechanism. That is the case in the commercially important spinels and garnets.

In NiFe₂O₄, an inverse spinel Fe³⁺[Ni²⁺Fe³⁺]O₄, the spins of the octahedral sites are parallel with one another; the same applies to the tetrahedral sites (Fig. 19.8). The interaction between the two kinds of sites is mediated by superexchange via the oxygen atoms. High-spin states being involved, Fe³⁺ (d⁵) has five unpaired electrons, and Ni²⁺ (d⁸) has two unpaired electrons. The coupled parallel spins at the octahedral sites add up to a spin of \( S = \frac{5}{2} + \frac{3}{2} = \frac{8}{2} \). It is opposed to the spin of \( \frac{5}{2} \) of the Fe³⁺ particles at the tetrahedral sites. A total spin of \( S = 1 \) remains which is equivalent to two unpaired electrons per formula unit.

Garnet is an orthosilicate, Mg₃Al₂(SiO₄)₃, which has a complicated cubic structure. The structure is retained when all metal atoms are trivalent according to the following substitution:

\[ \text{octahedral site (c.n. 6)} \quad \text{dodecahedral site (c.n. 8)} \quad \text{tetrahedral site (c.n. 4)} \]

\[ \text{Mg₃Al₂Si₃O₁₂} \quad \text{Y₃Fe³⁺Fe³⁺O₁₂} \]

In yttrium iron garnet Y₃Fe₅O₁₂ (‘YIG’) a ferrimagnetic coupling (superexchange) is active between the octahedral and the tetrahedral sites. Since the tetrahedral sites are in excess, the magnetic moments do not compensate each other. The magnetic properties can be varied by substitution of yttrium by lanthanoids.

**Magnetic Materials of Practical Importance**

Iron is a material whose ferromagnetic properties have been applied for a long time. It becomes paramagnetic when heated above the Curie temperature of 766°C; this does
not involve a phase transition of the body-centered cubic structure (a phase transition to cubic closest-packing occurs at 906 °C). Being magnetically soft, iron and alloys of iron with silicon, cobalt or nickel are applied in electric motors and in transformers. Finely dispersed iron powder (‘iron pigment’) serves as magnetic material in data storage devices (since it is pyrophoric it is stabilized by plating it by evaporation with a Co–Cr alloy). A disadvantage of iron is its electrical conductivity; an alternating magnetic field induces electric eddy currents which cause energy losses by heating the iron. Using stacks of mutually insulated iron plates can decrease but not fully avoid the eddy currents.

Wherever there are no alternating magnetic fields, the electric conductivity causes no trouble, for example in certain applications of permanent magnets. Permanent magnets with especially high magnetization and coercivity are made of SmCo₅ or Sm₃Co₁₇.

Nearly no eddy current losses occur in electrically insulating magnetic materials. This is one of the reasons for the importance of oxidic materials, especially of spinels and garnets. Another reason is the large variability of the magnetic properties that can be achieved with spinels and garnets of different compositions. The tolerance of the spinel structure to substitution at the metal atom sites and the interplay between normal and inverse spinels allow the adaptation of the properties to given requirements.

Spinel ferrites are iron-containing spinels M²⁺Fe₂O₄. They are magnetically soft to medium hard. γ-Fe₂O₃ is a spinel with defective structure, Fe₇³⁺Fe₁₁⁺₂O₄; it is used as a storage medium (diskettes, recording tapes). Fe₃O₄ is applied in ‘magnetic liquids’ that are used to seal bearings against vacuum. These are suspensions of magnetic pigments in oil; in a magnetic field the pigment collects in the region with the most intense field and causes an increase in the density and viscosity of the liquid. Magnetically soft materials are needed in high-frequency electronics; manganese–zinc ferrites are most important for this purpose.

Hexagonal ferrites of the magnetoplumbite type serve as magnetic hard materials. They have high coercivities combined with low remanent magnetizations. They are used as nonconducting permanent magnets, for example in electric motors, generators, and closet locks. Structurally, they are related to spinels, but with some of the oxygen atoms substituted by larger cations like Ba²⁺ or Pb²⁺. The two main types are BaFe₁₂O₁₉ (‘M phase’) and Ba₂Zn₂Fe₁₂O₂₂ (‘Y phase’).

The Magnetocaloric Effect

A phase transition of a magnetic material can be connected with a change of the magnetic properties (magnetostructural phase transition). In some cases the phase transition can be induced by an external magnetic field. If the transformation is of first order and thus involves the exchange of an enthalpy of transformation with the surroundings, this phenomenon is called magnetocaloric effect.

MnAs exhibits this behavior. It has the NiAs structure at temperatures exceeding 125 °C. When cooled, a second-order phase transition takes place at 125 °C, resulting in the MnP type (cf. Fig. 18.4, p. 218). This is a normal behavior, as shown by many other substances. Unusual, however, is the reappearance of the higher symmetrical NiAs structure at lower temperatures after a second phase transition has taken place at 45 °C. This second transformation is of first order, with a discontinuous volume change ∆V and with enthalpy of transformation ∆H. In addition, a reorientation of the electronic spins occurs from a low-spin to a high-spin state. The high-spin structure (< 45°C) is ferromagnetic,
the low-spin structure is paramagnetic. The ferromagnetic structure can be stabilized by a magnetic field above 45 °C.

Refrigeration devices that take advantage of the magnetocaloric effect are being developed. For this purpose, there is a need for materials exhibiting a strong magnetocaloric effect at some desired temperature. Gd$_5$Si$_x$Ge$_{4-x}$ may be a candidate. Gd$_5$Si$_4$ and Gd$_5$Ge$_4$ have very similar structures, but they differ in a crucial minor detail. They consist of slabs in which cubes and pairs of trigonal prisms of Gd atoms are joined (Fig. 19.9). There is another Gd atom inside of every cube, and an Si$_2$ or Ge$_2$ dumbbell with a covalent Si–Si or Ge–Ge bond is placed inside of every pair of prisms. The slabs are stacked with a mutual shift. Further Si$_2$ or Ge$_2$ dumbbells are located at an angle in between the slabs. The last-mentioned dumbbells make the difference. Their Si–Si bond length measures 247 pm in Gd$_5$Si$_4$, which is consistent with a covalent bond. Taking a calculation according to the ZINTL rules, this corresponds to the formula Gd$_3^{3+}$(Si$_2^{6-}$)$_2e^-$. In Gd$_5$Ge$_4$, however, the Ge···Ge distance in these dumbbells amounts to 363 pm, which is too long for a bond. The ZINTL formula would be Gd$_3^{3+}$(Ge$_2^{6-}$)(Ge$_4^{4-}$)$_3e^-$. Although the assumption of Ge$^{4-}$ ions is not realistic. The difference entails marked differences in the properties: Gd$_5$Si$_4$ is fer-

![Fig. 19.9](image-url)
romagnetic below 6 °C; Gd₅Ge₄ becomes antiferromagnetic below the Néel temperature of −148 °C and ferromagnetic below 20 K.

Gd₅Si₂Ge₂ has a structure with short and long dumbbells. It crystallizes in the monoclinic space group P112₁/a (Fig. 19.9), which is a subgroup of Pnma, the orthorhombic space group of Gd₅Si₄ and Gd₅Ge₄. Si and Ge atoms have a random distribution in both kinds of dumbbells. Gd₅Si₂Ge₂ is ferrimagnetic below the Curie temperature of 26 °C, with a small magnetic moment. Upon cooling, a first-order phase transition takes place at 3 °C. Below this temperature, the atoms of the long dumbbells have moved up, such that all dumbbells now have short bonds as in Gd₅Si₄. The low-temperature form is ferromagnetic, with the full magnetic moment of the Gd³⁺ ions. This transition exhibits a strong magnetocaloric effect. Mixed crystals Gd₅SiₓGe₄₋ₓ with 0.2 < x < 0.5 show the same structure as Gd₅Si₂Ge₂ and the same properties; the transition temperature can be controlled by the value of x (the higher the Ge content, the lower is the transition temperature).
Materials that consist of particles or that have structural attributes (such as pores) with sizes of 2 to 1000 nanometers are called nanostructured or nanocrystalline materials. Since the diameter of an atom is approximately 0.2 to 0.3 nm, we are dealing with distances that comprise 8 to 5000 atoms. The properties of a material that consists of particles of this magnitude differ from those of the same material consisting of larger aggregates. A crystal measuring $1 \times 1 \times 1 \text{ mm}^3$ has a fraction of about $10^{-6}$ atoms at its surface; but it amounts to approximately 1% of the atoms if the size of the crystal is only $100 \times 100 \times 100 \text{ nm}^3$.

The surface is the most severe disturbance of the periodic order of a crystal. Atoms at the surface have a different bonding and differ electronically as compared to interior atoms. The properties of a nanostructured material are influenced to a large extent by the atoms at the surface. Mechanical, electric, magnetic, optical and chemical properties depend on the particle sizes and shapes. At even smaller sizes, in addition, quantum-mechanical effects become effective. If the color of luminescence of a semiconductor is red at a particle size of 8 nm, it becomes green at 2.5 nm. If one wants to achieve certain properties, the particles have to have a uniform size, shape and orientation.

The terminology is not yet homogeneous. The use of the prefix ‘nano’ spread out in the 1990s. Until then, the common term used to be mesoscopic structures, which continues to be used. According to a definition by IUPAC of 1985, the following classification applies to porous materials: microporous, $<2 \text{ nm}$ pore diameter; mesoporous, 2–50 nm; macroporous, $>50 \text{ nm}$.

Nanostructured materials are nothing new. Chrysotile fibers are an example (Fig. 16.22), as are bones, teeth and shells. The latter are composite materials made up of proteins and embedded hard, nanocrystalline, inorganic substances like apatite. Just as with the imitated artificial composite materials, the mechanical strength is accomplished by the combination of the components.

Chemists have been working for a long time with particles having sizes of nanometers. The novelty of recent developments concerns the ability to make nanostructured substances with uniform particle sizes and in regular arrays. In this way it becomes feasible to produce materials that have definite and reproducible properties that depend on the particle size. The development began with the discovery of carbon nanotubes by Iijima in 1991 (Fig. 11.15, p. 116).

Aside from the methods for the production of carbon nanotubes mentioned on page 115, a number of methods to make nanostructured materials have been developed. In the following we mention a selection.

In the LaMer process particles are grown from solution. The formation of crystallization nuclei and their growth are strictly separated. First, a large number of crystal nuclei are produced in a short interval of time from a supersaturated solution; then the crystals are allowed to grow slowly with avoidance of further nucleation from a solution which is only slightly supersaturated. Surfactants such as thiols or amines with long-chain alkyl groups can be used to influence the crystal growth. In this way, one can obtain spherical particles with uniform diameters of 3 to 15 nm.
In order to control the shape of the particles, the rate of growth of the crystal faces has to be controlled. Fast-growing crystal faces disappear after a while (Fig. 20.1). Ligands such as long-chain carbonic acids are deposited in a selective manner on certain crystal faces and suppress their growth, with the consequence that only these faces remain at the end. If the growth in the direction of the cube vertices of a cubic crystal is faster, one obtains a cube. If the growth of the faces of the cube is faster, one obtains an octahedron. If the rate of growth of both is the same, the result is a cuboctahedron. For example, nanocubes of silver can be made by the reduction of silver nitrate in alcoholic solution. These cubes can be used as a template to produce hollow gold boxes. This is done by the reaction with tetrachloroauric acid, HAuCl₄; gold precipitates on the surface of the cubes while the silver dissolves. One obtains gold nanoboxes in the form of empty cuboctahedra.

Nanowires of hexagonal cobalt can be grown by the selective adsorption of ligands on all crystal faces except the faces that become the sides of the wires.

Another method takes advantage of an oriented solidification from eutectic melts. The two components solidify simultaneously when a eutectic mixture is cooled (p. 36). A BRIDGMAN furnace serves to produce large single crystals. This is done by slowly drawing downward a crucible from the furnace (Fig. 20.2). The lower apex of the crucible cools first, giving rise to the formation of a crystallization nucleus, followed by the slow crystallization of the melt in the crucible. There is a narrow zone of supercooled melt between the crystal and the remaining melt on top of it. In the case of a eutectic mixture, the separation of the phases takes place by horizontal diffusion in the supercooled melt. Continuous single crystals form in the drawing direction. If one of the components has a small volume fraction, it solidifies in the form of parallel nanowires with uniform thickness, embedded in the other phase. For example, rhenium wires embedded in a single-crystal matrix of NiAl can be obtained from a eutectic melt of NiAl/Re. The result can be influenced by the temperature gradient and the drawing speed. The wires can be separated by complete or partial dissolution of the NiAl matrix with an acid. Electrochemical oxidation of the rhenium to perrhenate permits the removal of the rhenium, leaving behind a nanofilter of NiAl.

The anodic oxidation of sheet aluminum has been used for a long time to protect aluminum against corrosion by a well-adhering oxide layer. Porous oxide layers are formed if acid electrolytes are used that can redissolve the aluminum oxide (mostly sulfuric or phosphoric acid). A compact oxide layer is formed at the beginning of the electrolysis (Fig. 20.3). Simultaneously, the current decreases, due to the electric resistance of the oxide. Subsequently follows a process in which the oxide is redissolved by the acid, and the current increases until it reaches a steady state. The electrochemical oxidation continues to take place with formation of pores. At the end of a pore, where it has the largest curvature, the electric field has its largest gradient and the process of redissolution is fastest.
Therefore, there is no growth of the oxide layer at the base of a pore. Instead, the walls between the pores grow and become higher and higher. Depending on the electric tension and the kind of acid, a certain curvature results at the base of a pore. Finally, as a consequence, all pores have the same diameter and form a regular array. Pore diameters of 25 to 400 nm and pore depths of 0.1 mm can be achieved. The pore walls have the approximate composition AlOOH; they still contain anions of the electrolyte, and they are amorphous.

Porous aluminum oxide can be used as a template for the production of nanowires and nanotubes. For example, metals can be deposited on the pore walls by the following procedures: deposition from the gas phase, precipitation from solution by electrochemical reduction or with chemical reducing agents, or by pyrolysis of substances that have previously been introduced into the pores. Wires are obtained when the pore diameters are 25 nm, and tubes from larger pores; the walls of the tubes can be as thin as 3 nm. For example, nanowires and nanotubes of nickel, cobalt, copper or silver can be made by electrochemical deposition. Finally, the aluminum oxide template can be removed by dissolution with a base.

One can also take advantage of reactions with the pore walls. For example, if the pore walls of aluminum oxide are coated with Sn(SePh)_4, then they react with each other at
650 °C, and one obtains nanowires of SnO₂. If the same is done in a mesoporous template of silicon, the silicon acts as a reducing agent. Depending on temperature, the products are nanowires of SnSe or of tin (Fig. 20.4).

Surfactants, cyclodextrins or proteins can also be used as template materials. The molecules of surfactants consist of a long hydrophobic alkyl chain and a hydrophilic end group (–SO₃⁻, –CO₂⁻, –NR₃⁺). In aqueous solution they aggregate to micelles if the concentration exceeds a critical value. First, approximately spherical micelles are formed, which have the hydrophilic groups on the surface and the alkyl groups pointing inwards. At higher concentrations the micelles become rod-like and adopt a liquid-crystalline order similar to a hexagonal rod-packing (Fig. 20.5). When a solid product is prepared by a precipitation reaction from such a solution, it encloses the micelles. If the solid is cross-linked and sufficiently stable, the micelle molecules can be removed, for example by calcination.

As an example, take the manufacture of mesoporous silica (amorphous SiO₂) with uniformly sized pores. Rod-like micelles of alkyltrimethylammonium ions form in an aqueous solution of an alkyltrimethylammonium halide. The micelles have a positive electric
charge at their surfaces and arrange themselves parallel. The counter-ions are located in the aqueous solution between the micelles. Precipitation of silica is induced by slow hydrolysis of tetraethylorthosilicate, Si(OC₂H₅)₄, at pH ≈ 11 at 100 to 150 °C (hydrothermal conditions, i.e. under pressure). The enclosed micelles can be removed by calcination at 540 °C, and mesoporous silica (‘MCM-41’) is left. The pore size can be controlled by the length of the alkyl groups.

In mixtures of nonpolar solvents with little water, surfactants form spherical reverse micelles. They have a reversed orientation of the molecules with the hydrophilic groups in the interior and a drop of enclosed water in the middle. Starting from a precursor material, metal oxides in the form of uniform nanosized spheres can be obtained by hydrolysis under controlled conditions (pH, concentration, temperature). For example, titanium oxide spheres are obtained from a titanium alkoxide, Ti(OR)₄ + 2H₂O → TiO₂ + 4ROH.

Nanostructured materials have found several applications, and more are to be expected, for example:

Encapsulation in nanocontainers, which crack under pressure and set free an enclosed substance. This includes adhesives that become effective under pressure, or perfume that is freed upon rubbing.

Nanoparticles of TiO₂ in sun-ray filter cream remain adhered to the skin and do not migrate into wrinkles.

Water- and dirt-repelling coatings have nanoparticles pointing outwards. Water is in touch with the surface at only a few points; due to the surface tension it contracts to droplets which roll off (‘lotus effect’).

SiO₂ nanospheres are fused onto the surface of glass at 650 °C, resulting in a surface that reflects nearly no light.

Ferroelectric Pb(Ti,Zr)O₃ nanoparticles for electronic data storage.
21 Pitfalls and Linguistic Aberrations

In the literature and speech it is common to find incorrect, inaccurate, misleading or inane expressions. Below, some are listed which it is hoped you will never use.

Do not confuse crystal structure and crystal lattice. The crystal structure designates a regular array of atoms, the crystal lattice corresponds to an infinity of translation vectors (Section 2.2). The terms should not be mixed up either. There exists no ‘lattice structure’ and no ‘diamond lattice’, but a diamond structure.

Caesium chloride is not body-centered cubic, but cubic primitive. A structure is body centered only if for every atom in the position \(x, y, z\) there is another symmetry-equivalent atom in the position \(x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}\) in the unit cell. The atoms therefore must be of the same kind. It is unfortunate to call a cluster with an interstitial atom a ‘centered cluster’ because this causes a confusion of the well-defined term ‘centered’ with a rather blurred term. Do not say, the \(O_4\) tetrahedron of the sulfate ion is ‘centered’ by the sulfur atom.

Do not confuse symmetry operation and symmetry element (p. 12).
Do not confuse space group and space-group type (p. 20).
Do not call an achiral Sohncke space group (or space-group type) a ‘chiral space group’. Most chiral molecules do not crystallize in a chiral space group (p. 83).

Identical means ‘the very same’. Avoid the expression ‘identical atoms’ when you mean symmetry-equivalent or translationally equivalent atoms. It is impossible to lessen or to increase the term identical; ‘nearly identical’ is nonsense.

A crystal that consists of only one kind of atoms is not a ‘monoatomic crystal’; it consists of more than one atom.

A molecule does not contain ‘hydrogens’, ‘oxygens’ or ‘borons’, but hydrogen atoms, oxygen atoms or boron atoms.

Do not say ‘octahedrally coordinated complex’ if you mean an octahedrally coordinated atom in a complex compound. An ‘octahedrally coordinated complex’ could at best be a complex molecule that is surrounded by six other molecules.

Molecules with a planar coordination figure do not contain ‘planar atoms’. Further, ‘tetrahedral atoms’, ‘chiral atoms’ etc. are nonsense. A minimum of four atoms is required for a chiral structure.

‘One-dimensional structures’ do not exist. Structures are always three-dimensional. The term one-dimensional is acceptable to express specifically named, highly anisotropic properties, such as ‘one-dimensional conductivity’, ‘one-dimensional connection’ or ‘one-dimensional disorder’. The ‘dimensionality’ of a structure is a meaningless phrase.

A structure can be tetragonal or not. That is a clear yes-or-no case. When the symmetry of an orthorhombic structure is close to tetragonal, it is nonsense to talk of a ‘tertagonality’ of the structure.

The image of a single molecule, the structure of which has been determined by crystal structure analysis, shows a molecular structure, but not a ‘crystal structure’, an ‘X-ray structure’, or even worse an ‘X-ray’. The packing and the spatial arrangement of the molecules in a crystal are always an indispensable part of a crystal structure.
Stoichiometry is the discipline that deals with the amount relationships of the elements in compounds and during chemical reactions. It is not the amount relationship itself. A specific compound has no stoichiometry, but a composition.

Geometry is the science of bodies in space. It is a mathematical discipline, subdivided into subdisciplines such as Euclidean geometry, spherical geometry, analytical geometry etc., but it is never the property of an object. Analogous considerations are valid for architecture. A molecule has a structure, a constitution, a configuration, an atomic arrangement, a spatial arrangement, a shape, but no geometry and no architecture. ‘Molecular geometry’ or ‘coordination geometry’ could perhaps be used to designate a discipline that deals with the geometric conditions in molecules, but it should not be used to designate the spatial arrangement of atoms in a molecule. There exists neither a ‘tetrahedral geometry’ nor a ‘chiral geometry’, and the quantum-chemical calculation of a molecular structure is by no means a ‘geometry optimization’.

The idiomatic changes taking place in everyday life also affect the language used by chemists. This includes the spreading of certain fatuous expressions. One of them is the ‘center’ instead of atom. According to this, $10^{23}$ ‘centers’ are located in one gram of water, and a C$_{60}$ molecule has 60 ‘centers’, but none of them is in the center. Advocates in favor of the ‘center’ (if they happen to meditate on this in the first place) argue that only this is an expression which comprises atoms as well as monoatomic ions. That is wrong: ions (monoatomic ones) are atoms! They only have the special property of bearing an electric charge. ‘Excited centers’, ‘peripheral centers’, ‘tetrahedral zinc centers’ etc. are especially absurd terms.

Another superfluous vogue word is ‘self organization’ or ‘self assembly’, meaning a more or less ordered atomic or molecular association, crystal nucleation, or crystal growth. Whenever molecules become associated, this happens by itself. ‘Self organization’ has become one of the favorite expressions in the science of nanostructures. The terms ‘self organization’ or ‘self assembled’ can almost always be completely deleted without changing the sense of a text or making it even slightly less understandable or readable. A ‘self-assembled’ monolayer of molecules is just a monolayer of molecules; it goes without saying that the molecules have assembled and that they have done so by themselves.

Correct Use of Units of Measurement

Science cannot be performed without an accurate system of measurement, which is globally standardized and compulsory. Units and standards of measurement are agreed upon and harmonized on an international basis by the Bureau International des Poids et Mesures in Sèvres, France, and by the International Organization for Standardization in Geneva, Switzerland. The units and standards are then laid down in national laws. Nearly all countries have accepted the Système International d’Unités (SI units) as their system of measurement. This also applies to countries that had been accustomed to use British units like Australia, Canada, South Africa and the United States. In Britain, SI units are official from January 2010. The valid standards are available from the competent bureaus, for example:

- National Measurement Institute (Australia), www.measurement.gov.au
- National Institute of Standards and Technology (NIST, USA), www.physics.nist.gov/Pubs/SP811/

The specification of a value like $d = 235 \text{ pm}$ means: the distance $d$ amounts to 235 times 1 picometer. Arithmetically, this is a multiplication of the numerical value with
the unit. In tables and diagrams, it is common not to repeat the unit with every listed number. That means that the actual values have been divided by the unit. Therefore, the correct heading of a table or marking at a diagram axis reads: \(d/\text{pm}\) or \(d_{\text{pm}}\) or \(d\ \text{pm}^{-1}\). The frequently encountered notation ‘\(d [\text{pm}]\)’ is not in accordance with the SI standards. Brackets have a special meaning in the SI system, namely: ‘\([d]\) = pm’ means, ‘the selected unit for \(d\) is picometer’.

The use of non-SI units is strongly discouraged. For these units there often do not exist standards, and for historical reasons the same denomination may mean sundry units. For example, it is common practice in theoretical chemistry to state energy values in kilocalories. However, to convert a calorie to the SI unit Joule, there exist different conversion factors:

\[
1 \text{ cal} = 4.1868 \text{ J} \quad \text{('international calorie')}, \quad 1 \text{ cal} = 4.1855 \text{ J} \quad \text{('15° calorie')}, \quad 1 \text{ cal} = 4.184 \text{ J} \quad \text{('thermochemical calorie')}.
\]

Which one is applicable?

Some non-SI units are explicitly permitted. They include for crystallographic statements: 1 Å = 10\(^{-10}\) m = 100 pm and 1° = \(\pi/180\) rad (plane angle). The liter is also permitted (both abbreviations are official, L or l); 1 L = 1 dm\(^3\).

The much used term ‘molarity’ instead of amount-of-substance concentration (for short amount concentration or just concentration) is obsolete and should not be used. The same applies to specifications such as ‘0.5 \(M\)’ or ‘0.5 \(M\)’; the correct statement is \(c = 0.5 \text{ mol/L}\).

**Hints for the Publication of Data on Crystal Structures**

Crystal structure analysis by X-ray diffraction has become the most powerful tool for structure determination in chemistry. Certain rules should be observed for the documentation of the results, taking into account the standards common in crystallography. The most important information are the lattice parameters, the space group and all atomic coordinates. If the parameters of the thermal displacement of all atoms are not listed, at least one figure should show the corresponding ellipsoids, because unusual ellipsoids indicate flaws in the structure determination or the presence of special structural circumstances. Those who do not depict the ellipsoids are suspect of trying to conceal something. Even with scrupulous work, crystal structure determinations are not always free of flaws (wrong space groups are a frequent error, resulting in unreliable atomic coordinates).

Nowadays, most data are deposited in databases. Good-working databases are very helpful, but in a way treacherous. Due to the rapid development of computer and data storage technologies, data need uninterrupted attention in order to be saved reliably. The financial breakdown of a database, computer viruses and other events can lead to a total loss of the data. Data that have been stored on other media (like CDs) remain legible only for the few years of existence of devices that can process them. Therefore, results of structure determinations, especially the atomic coordinates, should be published on a durable material in a way that can be read without the need for machines, and they should remain generally accessible without the need for a license for a database. It is an absurdity that scientific results are accessible only against the annually repeated payment of license fees even though they have been elaborated nearly exclusively by the employment of public funds. Another problem is the incomplete inclusion of the data in the databases. The Inorganic Crystal Structure Database (ICSD) certainly is a very useful tool, but on the one side it is incomplete, and on the other side it contains many duplicates and unfortunately also many errors.
References

General Literature, Text Books


Collections of Molecular and Crystal Structure Data


*Inorganic Structural Chemistry, Second Edition* Ulrich Müller
© 2006 John Wiley & Sons, Ltd.

[29] *Cambridge Structural Database (CSD).* Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge, UK. Electronic database of crystal structures of organic and metalorganic compounds. [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).


**Literature to Individual Chapters**

**Chapter 2**


**Chapter 3**


**Chapter 4**


REFERENCES


Chapter 5


Chapter 6


Chapter 7


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Chapter 18

REFERENCES


Chapter 19


Chapter 20


Answers to the Problems

2.1 (a) 5.18; (b) 5.91; (c) 12.53.

2.2 (a) Fe$^{2+}$TiO$_3$ or Fe$^{6+}$TiO$_3$; (b) Ca$^{2+}$$\bar{D}_3$; (c) Mo$^{6+}$$C_2$$ \bar{S}_3$; (d) Cu$_2$$^{2+}$; (e) Pt$^{4+}S$ or Pt$^{4+}S'$; (f) Mg$^{16+}F$ or Cu$_2$$^{2+}$; (g) Al$^{3+}$$F$$_3$ or As$^{3+}$$C_3$; (b) U$^{6+}F$$_3$Cl$_3$$ ^{3+}$.

2.3 CaC$_2$, 2; K$_2$PtCl$_6$, 4; Hf$_2$, 2; Th$_2$, 2; ReO$_3$, 1; α-ZnCl$_2$, 4.

2.5 271.4 pm.

2.6 (1)–(2) 272.1 pm; (1)–(3) 250.0 pm; angle 178.4°.

2.7 210.2 and 213.2 pm; angle 101.8°.

2.8 W=O 177.5 pm; W…O 216.0 pm; W–Br 244.4 pm; angle O=W–Br 97.2°; the coordination polyhedron is a distorted octahedron (cf. Fig. 19.5, p. 230).

2.9 Zr–O(1), 205.1, 216.3 and 205.7 pm; Zr–O(2), 218.9, 222.0, 228.5 and 215.1 pm; c.n. 7.

3.1 H$_2$O, mm2; HCl, m; BF$_3$, $\bar{D}_3$; XeF$_4$, 4/m 2/m 2/m (for short 4/mmm); ClSF$_4$, 4/m; SF$_6$, 4/m $\bar{T}$2/m (short m.3); cis-SbF$_3$Cl$_2$, m 2 (trans-N$_2$F$_2$, 2/m; B(OH)$_3$, 6; Co(NO)$_2$Cl$_3$, 2/m 3 (short m.3).

3.2 Si$^{6+}$, m 2; As$_2$S$_3$, $\bar{T}$2/m; P$_4$S$_3$, 3/m; Sn$_2$S$_3$, $\bar{T}$2/m; As$^{6+}$, 1; As$_2$, 4/m 2/m 2/m (short 4/mmm); P$_4$S$_3$, $\bar{T}$2/m 1 (short m.3); As$_2$S$_3$, 3/m; P$_4$S$_3$, 3/m; Sn$_2$S$_3$, 4/m; Bi$^{2+}$, $\bar{S}$2/m.

3.3 Linked tetrahedra, 2/m 2/m 2/m (short mmm) and m 2; linked octahedra, 4/m 2/m 2/m (short mmm), $\bar{B}$2/m and 2.

3.4 Inferred to the direction of the chain: translation, 2, and one mirror plane through each O atom (the mirror planes are perpendicular to the direction of reference); the normal on the plane of the mirror: mirror plane and one 2 axis through each Hg atom; referred to the direction vertical in the plane of the paper: glide plane and one 2 axis through each O atom; one inversion center in every Hg atom. If we define a coordinate system a, b, c with a perpendicular to the plane and c = translation vector, the Hermann–Mauguin symbol is P(2/m 2/c)2/m; the parentheses designate the directions for which there is no translation symmetry. That is a rod group.

3.5 Hexagonal M$_x$WO$_3$, P 6/m 2/m 2/m (this is an idealized symmetry; the octahedra are slightly tilted and the real space group is P6$_3$22); tetragonal M$_x$WO$_3$, P 4/m 2/m 2/m (short P 4/m mm); CaC$_2$, I 4/m 2/m 2/m (short P 4/m mm); CaF$_2$, P 4/m $\bar{T}$2/m (short P m 3).

3.6 (a) 2/m 2/m 2/m (short mmm), orthorhombic; (b) 4/m mm, tetragonal; (c) $\bar{T}$2/m (short m 3), trigonal; (d) 2/m, monoclinic; (e) 6/m, hexagonal; (f) 6 2 2, hexagonal; (g) 2 2 2, orthorhombic; (h) m 2/m, orthorhombic; (i) 4/m $\bar{T}$2/m (short m 3), cubic.

3.7 Ti, 2a, mmm; O, 4f, m 2/m. There are 2 Ti and 4 O atoms in the unit cell (Z = 2).

3.8 One layer of tiles, $\bar{T}$02/m; two layers, $\bar{S}$2/m (short $\bar{S}$ m).

4.1 β-Cristobalite could be converted to α and β-quartz.

4.2 At 1000 °C recrystallization will be faster.

4.3 BeF$_2$.

4.4 First order (hysteresis observed).

4.5 The coordination numbers of the atoms increase from 6 to 8 in the NaCl → CsCl type conversion; therefore, it is a reconstructive phase transition which can only be a first-order transition.

4.6 At −10 °C, ice will melt at approximately 100 MPa and refloat at approximately 450 MPa, forming modification V. This will transform to ice VI at ~600 MPa, then to ice VIII at ~2.2 Ga and to ice VII at ~7.18 GPa.

4.7 Water will freeze at 40 °C at approximately 1.2 GPa forming modification VI. This will transform to ice VII at 2 GPa.

4.8 H$_2$O–HF will crystallize, then, in addition, H$_2$O will freeze at −72 °C.

4.9 At approximately 0.5 GPa β-quartz will transform directly to β-cristobalite.

5.1 $-\frac{1}{8} + \frac{6\sqrt{3}}{2} + 12\sqrt{3} - \frac{24\sqrt{3}}{\sqrt{10}}$.

5.2 (a) 687 kJ mol$^{-1}$; (b) 2965 kJ mol$^{-1}$; (c) 3517 kJ mol$^{-1}$.

6.1 F…F in SiF$_4$ 253 pm, van der Waals distance 294 pm; Cl…Cl in SiCl$_4$ 330 pm, van der Waals distance 350 pm; I…I in SiF$_4$ 397 pm, van der Waals distance 396 pm; in SiF$_4$ and SiCl$_4$ the halogen atoms are squeezed.

6.2 WF$_6$ 193, WCl$_6$ 241, PCl$_5$ 219, PBr$_5$ 234, SbF$_5$ 193, MnO$_2$ 166 pm; TiO$_2$ 201, ReO$_3$ 195, EuO 257, CdCl$_2$ 276 pm.

7.1 (a) Rutile; (b) rutile; (c) neither (GeO$_2$ is actually polymorphic, adopting the rutile and the quartz structures); (d) anti-CaF$_2$.

7.2 Mg$^{2+}$ c.n. 8, Al$^{3+}$ c.n. 6, Si$^{4+}$ c.n. 4 (interchange of the c.n. of Mg$^{2+}$ and Si$^{4+}$ would also fulfill PAULING’S rule, but c.n. 8 is rather improbable for Si$^{4+}$.)

7.3 Since all cations have the same charge (+3), the electrostatic valence rule is of no help. The larger Y$^{3+}$ ions will take the sites with c.n. 8.

7.4 No.

7.5 N is coordinated to Ag.

7.6 s(Rb$^+$) = $\frac{1}{10}$; $s(V^{4+}) = \frac{4}{5}$; $s(V^{5+}) = \frac{5}{4}$;

$p_1 = 1.20$; $p_2 = 2.25$; $p_3 = 2.70$; $p_4 = 1.55$;
\[ \overline{\nu(V^4^+)} = 2.04; \overline{\nu(V^{5^+})} = 2.19; \]

Expected bond lengths:
- \( V^{4^+} - O(1) \) 159 pm, \( V^{4^+} - O(2) \) 197 pm, \( V^{5^+} - O(2) \) 173 pm, \( V^{5^+} - O(3) \) 180 pm, \( V^{5^+} - O(4) \) 162 pm.

8.1 Linear: BeCl₂, Cl₃⁻; angular: O₃⁻ (radical), S₃⁻; trigonal planar: BF₃; trigonal pyramidal PF₃, TeCl₃⁻; T shaped: BrF₃, XeF₃⁻; square: PtCl₂(NH₃)₂(NO₂)₂, point group 1; square pyramidal: TeF₅⁻; trigonal pyramidal: SbCl₅⁻, O₂ClF₃ and O₃XeF₂ (O equatorial); square pyramidal: TeF₅⁻; octahedral: ClSF₅⁻.

8.2

\[
\begin{array}{c}
\text{Cl-Be-Cl} \\
\text{Be-Cl-Be} \\
\end{array}
\]

Ta₂I₁₀ like Nb₂Cl₁₀ (cf. p. 66).

8.3 Trigonal bipyramid, CH₃ group in equatorial position perpendicular to equatorial plane. Derive it from an octahedron with bent S=C bonds.

8.4 (a) SF₃ < SCl₂ < S₂⁻ < S⁻ ≈ OF₂; (b) H₃CNH₂ < \([\text{H}_2\text{C}_2\text{NH}_2]^{+}\); (c) PCl₁Fr < PCl₁F₂ (= 180°).

8.5 Bond lengths Al–Cl(terminal) < Al–Cl(bridge); angles Cl(bridge)–Al–Cl(bridge) ≈ 95° < Cl(bridge)–Al–Cl(terminal) ≈ 110° < Cl(terminal)–Al–Cl(terminal) ≈ 120°.

8.6 SnCl₇⁻; PF₆⁻; SnCl₆⁻.

8.7 BiBr₂⁻ and TeI₂⁻.

9.1 \([\text{Cr(OH)}_2]^{1+}, [\text{Mn(OH)}_2]^{3+}, [\text{Cu(NH)}_3]^{2+}\).

9.2 CrCl₄⁻ and NiBr₄⁻, elongated tetrahedra; CuBr₂⁻, flattened tetrahedron; FeCl₂⁻ could be slightly distorted.

9.3 Tetrahedral: Co(CO)₄⁻, Ni(PF₃)₄, Cu(OH)₂⁻ (distorted); square: PtCl₂(NH₃)₂, Pt(NH₄)₂⁺, Au₂Cl₆.

9.4 PtCl₂(NH₂)₂(NO₂)₂, point group 1; [Co(H₂N(CH₂)₂NH₂)₂]³⁺, point group 3 2; [Rh(SO₄)(NH₂)₂(H₂O)₂]⁻, point group 2; in all three cases no inversion axes are present (including \( m \) and \( T \)).

9.5 (a) 2; (b) 1; (c) 2; (d) 2; (e) 1.

10.1 The band will broaden and the DOS will decrease.

10.2 It would look like the right part of Fig. 10.7.

10.3 The s band, the \( p_y \) band and the \( p_z \) band will shift to lower energy values at \( \Gamma \) and \( X' \), and to higher values at \( X \) and \( M \).

12.1 Shorter, BeO, BN; equal, BeS, BP, AlN; longer, AlP.

12.2 Longer bonds.

12.3 Under pressure AgI could adopt the NaCl structure (it actually does).

12.4 3.

12.5 Hg₃C should have the Cu₂O structure.

13.1 (a) Simple ionic; (b) polyanionic; (c) polyanionic; (d) polyionic; (e) polycationic; (f) polyionic; (g) polycationic; (h) simple ionic.

13.2 (a), (b), (d).

13.3 (a) [Co(CO)₄]⁻, (b) Cu(NH₃)₂⁺, (c) 5, (d) 4, (e) 2, (f) 3.

13.4 (a) Wade (26 e⁻); (b) electron precise (84 e⁻); (c) 3c2e (56 e⁻); (d) electron precise (72 e⁻); (e) Wade (86 e⁻).

14.1 (a) hhcc or 41; (b) hhhe or 211.

14.2 (a) ABABC; (b) ABCABCBCAB; (c) ABCBABACAB.

15.1 (a) No (because of different structures); (b) yes; (c) no; (d) no; (e) yes; (f) yes; (g) yes; (h) no.

15.2

\[
\begin{array}{c}
\text{AuCu₃} \\
\text{SnNi₃} \\
\end{array}
\]

15.3 (a) CaF₂; (b) MgAgAs; (c) MgCu₂Al.

15.4 In both compounds each of the elements occupies two of the four different positions, but with different multiplicities: 3Cu:2Cu:Zn:6Zn and 3Cu:2Al:2Al:6Cu.

15.5 Yes.

16.1 WO₃.

16.2 MX₄; this is the structure of a form of ReCl₄.
16.3 MX₄.

16.4 MoI₃ and TaS₂⁻.

16.5 Cristobalite.

17.1 MX₂.
17.2 Face-sharing octahedra occur only in hexagonal closest-packing.

17.3 TiN, NaCl type; FeP, MnP type; FeSb, NiAs type; CoS, NiP type; CoSb, NiAs type.

17.4 In CaBr₂ and RhF₃ there is a three-dimensional linking of the octahedra; CdI₂ and BiI₃ consist of layers that can mutually be displaced.

17.5 One-seventh.

17.6 MgV₂O₄, normal; VMg₂O₄, inverse; NiGa₂O₄, inverse; ZnCr₂S₄, normal; NiFe₂O₄, inverse.

18.1 (a) 3₁ and 3₂. (b) 3₂. (c) 2₁ axes cannot be retained upon doubling of b; after enlargement by an odd number 2₁ axes remain possible; therefore, klassengleiche subgroups after triplication are possible.

18.2 (a) Klassengleiche; (b) translationengleiche; (c) klassengleiche; (d) isomorphic; (e) translationengleiche; (f) translationengleiche; (g) translationengleiche.

18.3

\[
\begin{array}{c|c|c|c}
F/432/m & \text{AuCu₃, Cu type} \\
AuCu₃ & 0 & 0 & 0 \\
k2 & 0 & \frac{1}{2} & \frac{1}{2} \\
P4/32/m & \text{AuCu₃, ordered} \\
AuCu₃ & 0 & 0 & 0 \\
\end{array}
\]

AuCu₃ will not form twins (k2 relation).

18.4

\[
\begin{array}{c|c|c|c|c|c}
P4/m32/m & \text{Ti:1a} & \text{Ca:1b} & \text{O:3d} \\
& m/3m & m/3m & 4/mmm \\
\text{perovskite} & 0 & \frac{1}{2} & 0 \\
0 & \frac{1}{2} & 0 \\
0 & \frac{1}{2} & 0 \\
\end{array}
\]

18.5

\[
\begin{array}{c|c|c|c|c|c|c|c}
P4/m32/m & \text{Ti:1a} & \text{Ba:1b} & \text{O:3d} \\
& m/3m & m/3m & 4/mmm \\
\text{BaTiO₃ cub.} & 0 & \frac{1}{2} & 0 \\
0 & \frac{1}{2} & 0 \\
\end{array}
\]

One can expect the formation of six kinds of domains, i.e. twins of triplet twins, due to the t3 and t2 subgroup relations.

18.6 \(\beta\)-Sn should form twinned crystals with domains in three orientations.

18.7 Twins with two kinds of domains will be formed (Fig. 19.4, p. 230).
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