

THE CRYSTAL STRUCTURE OF MINERALS

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Summary

This chapter deals with the characterization of minerals from a crystallographic and crystal chemical point of view. Besides knowledge of the chemical composition, the crystal structure or at least some essential features must be known to define a mineral correctly. The chapter starts with an explanation of the symmetry elements. Crystallized matter is based on a periodic arrangement of the atoms which is defined by the translation lattice. As a consequence there are only strictly limited possibilities for the arrangement of symmetry elements in the (three-dimensional) space. The crystal systems (geometrical requirements of the crystal lattice), crystal classes (symmetry of the shape of a crystal) and space groups (symmetry of the atomic arrangement of a crystal) are discussed. An approach to modulated- and composite- (incommensurate-) structures as well as to quasi- and nano-crystals is given. The second part of the chapter accounts for crystal chemistry. The properties of a mineral are determined by the kind and geometrical arrangement of atoms or molecules within the crystal structure. As a consequence, the description of the environment of atoms (coordination) as well as the chemical interactions between them (chemical bonds), are of great value for understanding physical and chemical properties of minerals. In consideration of Pauling's rules some ideas for the stability of structure types are obtained. Finally, terms for the comparison of crystal structures are compiled and explained.

1. Introduction

Usually a chemical compound or a mineral is characterized by its chemical composition, *i.e.* the kind of atoms and their ratios. This allows us to establish a chemical formula. However, neither the chemical compound nor the mineral is unequivocally defined. Even if both, the kind and the ratio of atoms as well as their relative positions, are known for a compound, the distinct phase is correctly characterized. Many minerals have the same chemical composition but exhibit different crystal structures.

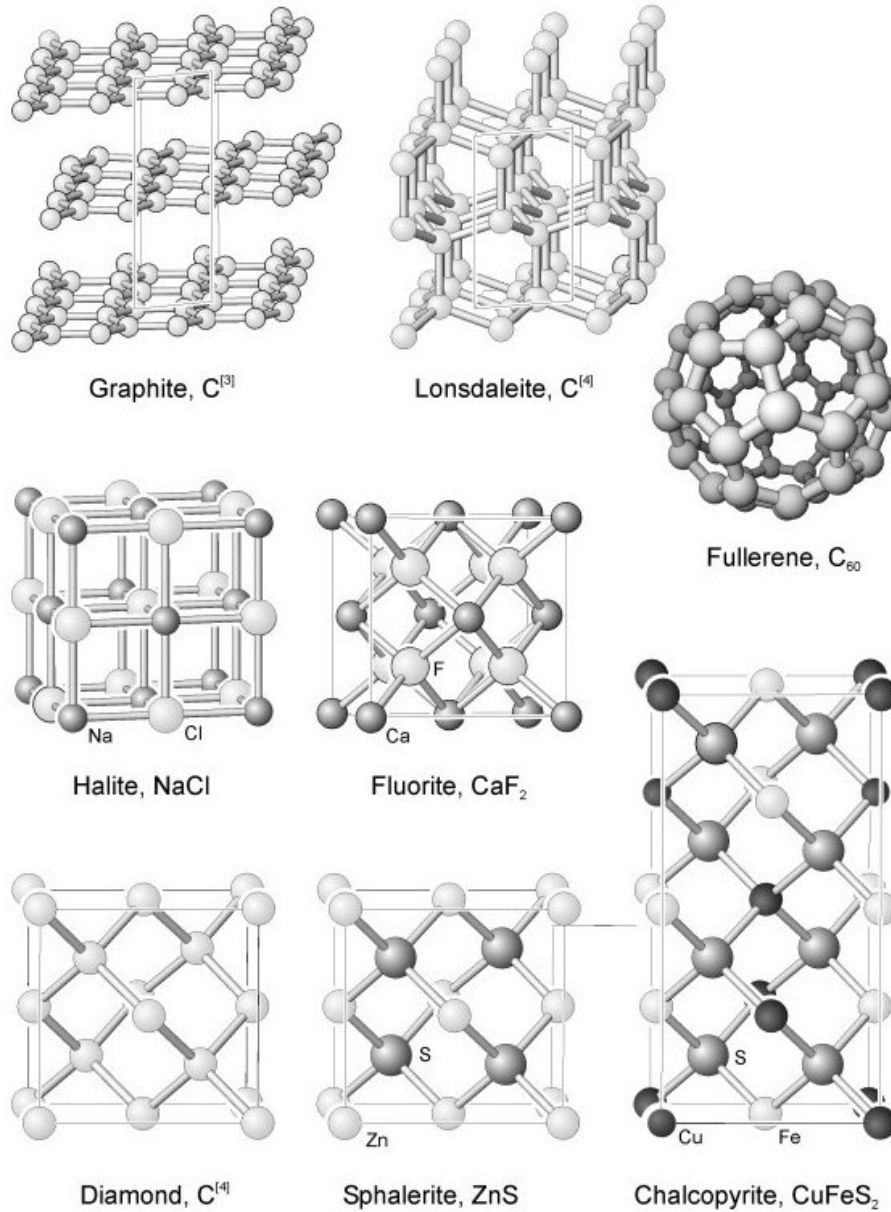


Figure 1: Some important crystal structures

Even the variety of crystal structures formed only by one chemical element is conspicuous. As an example serves carbon (see Figure 1): graphite and diamond are two well known minerals with quite different frequencies in occurrence, appearances, physical and chemical

properties and commercial values; in addition, lonsdaleite is a rare mineral related to diamond but with another symmetry. During the last decades of the 20th century molecules formed by football-like arrangements of 60, 70, or more carbon atoms were found and named fullerenes (bucky balls). In the meantime, similarly constructed tube-like arranged carbon atoms were also recognized (bucky tubes). Obviously they are wide spread in soot. This shows that a chemical compound (or a mineral) is not correctly defined if the kind and ratio of chemical elements are known (as derived from a chemical analysis); it is also necessary to characterize the atomic arrangement, *i.e.* the crystal structure. In the past, an increasing number of crystal-structure investigations were performed by scattering experiments with X-ray, neutron or electron radiation.

The physical properties of a compound reflect at least some features of the atomic arrangement as well as the symmetry of the crystal structure. Often it is overseen that the types of the chemical bonds present within a crystal image physical properties such as luster, color and transparency. Etching figures, inclusions, anisotropy of hardness, cleavage, electrical and thermal conductivity, elasticity, rate of growth, piezoelectricity or pyroelectricity as well as other electric and magnetic properties also reflect the symmetry of a crystal and the character of its chemical bonds. The different symmetry and composition of crystals cause a distinct optical behavior of compounds as used for distinction of minerals with the help of a polarizing microscope. Optically positive and negative crystals are related to mainly axial and planar arranged chemical bonds. As a consequence, the characterization of the crystal symmetry and knowledge of the crystal structure is a useful tool for studying physical and chemical properties of minerals.

2. Symmetry Elements

Macroscopically, an undamaged crystal which grew unobstructed shows conspicuous regularities: it is formed by plane faces intersecting in edges. Often it is observed that two faces or some edges are parallel to each other. Faces and edges may be arranged in a distinct regularity. Already Nils Steensen, a Dane (Latinized Nicolaus Steno, 1638 - 1686) considered equal angles between analogue faces of quartz crystals in 1669. In 1688 these observations were extended to other crystal species by Domenico Guglielmini (1655 - 1710). It was Jean Baptiste Louis Romé de l'Isle (1736 - 1790) who proposed in 1783 the law of constancy of interfacial angles which states that the angle between two faces is independent of the crystal's size. Therefore the angles are maintained during crystal growth if temperature and pressure are unchanged. As a consequence, under defined physical conditions the interfacial angles are characteristic for any crystalline species. Faces and edges are not arbitrarily arranged but may be repeated by mathematically defined operations. The regular repetition is described by the symmetry elements.

The regular shape of a crystal is a result of the atomic arrangement. As a consequence, the crystal structure is reflected in the crystal's habit. The habit of a crystal is its characteristic and common form defined by the regularly arranged faces. For many minerals, the crystal habit is so typical that it serves as a tool of identification. Already in the 18th century a crystal was thought to be formed from small sized regular bodies which are regularly arranged; they were called 'molécule intégrante' by René-Just Haüy (1743 - 1822). At least since experiments showed that X-rays are scattered by a crystal, the regular atomic construction of crystals was proved. The first X-ray scattering experiments were performed

by Walter Friedrich and Paul Knipping under the supervision of Max von Laue in 1912 (Max Theodor Felix von Laue, 1879 - 1960).

For the morphological description and for description of the atomic arrangement of a crystal three non-planar (and general not orthogonal) vectors **a**, **b**, and **c** with lengths of $a = |\mathbf{a}|$, $b = |\mathbf{b}|$, and $c = |\mathbf{c}|$ are used. The vectors are chosen parallel to existing or at least possible edges of the crystal. The vectors are oriented in a right-handed coordinate system with the angles α (between **b** and **c**), β (between **a** and **c**), and γ (between **a** and **b**). The crystallographic axes of coordinates (labeled a, b, c or sometimes x, y, z) are chosen parallel to **a**, **b**, and **c**. The regularity of a crystal is characterized by symmetry elements. These are mathematical operations which describe the repetition of a crystal's face, edge or corner (macroscopically) or an atom or molecule (on atomic scale) with respect to a point, a line or a plane. Moreover, symmetry elements can be applied to any motifs or objects. They are subdivided into "primary" and "secondary" symmetry elements. Primary symmetry elements are inversion, reflection or rotation. The successive execution (or the product) of two primary symmetry elements results in a new link between objects: One face or one atom or in general one motif is repeated after applying two different symmetry elements, *i.e.*, a secondary symmetry element. Combinations of the symmetry elements are possible: A distinct number of primary and / or secondary symmetry elements are present which operate separately as if they solely existed. Symmetry elements which are used to describe the morphological habit of a crystal are also found within the atomic arrangement. However the macroscopically observable symmetry elements are either maintained or modified due to translation. In detail, the symmetry elements are defined as follows:

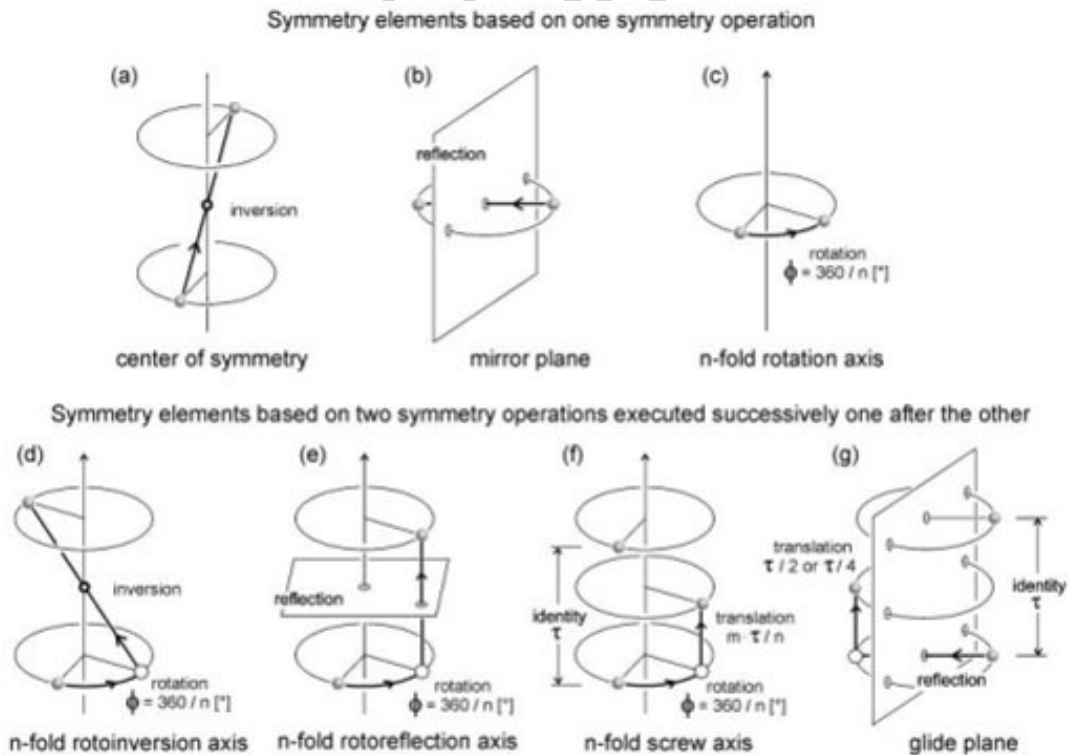


Figure 2: Repetition of two atoms according to symmetry elements. Symmetry elements based on one symmetry operation: (a) center of symmetry (inversion center); (b) mirror

plane; (c) rotation axis. Symmetry elements based on two symmetry operations executed successively one after the other (repetition according to a product of two symmetry elements): (d) rotoinversion axis (inversion axis); (e) rotoreflection axis; (f) screw axis; (g) glide plane

- (i) Identity (translation) (see Section 3.): A crystal is formed by a three-dimensional periodic lattice. Identical motifs (atoms, molecules) are repeated in equal amounts (translation period τ) in all directions of the three-dimensional space.
- (ii) Center of symmetry, also called an inversion center (Figure 2a): This primary symmetry operation defines the repetition of the motif with respect to a point, *i.e.* the inversion center (symbol $\bar{1}$; manner of speaking 'one bar'). An imaginary line can be passed from any point of a crystal, any atom in the crystal structure or any other object through the center of symmetry to an analogous point on the opposite side; the center of symmetry is located exactly in the middle between the symmetrically analogue pairs.
- (iii) Reflection plane, also called a mirror plane (Figure 2b): This primary symmetry operation defines the repetition of a motif with respect to a plane (symbol m). A mirror plane is an imaginary plane passed through a crystal or any other object dividing it in half so that each half is the mirror image of the other.
- (iv) Rotation axis (Figure 2c): This primary symmetry operation defines the repetition of a motif with respect to an n -fold rotation axis. After n times rotation of $360/n$ [$^{\circ}$] identity of the motif is obtained, $n \in \mathbb{N}$ (symbol n). Rotation includes identity: It is obvious that an object is repeated after a rotation of $360/1$ [$^{\circ}$] into itself (one-fold axis, symbol 1). An axis of symmetry is an imaginary line through a crystal or any other object about which it may be rotated and repeated into itself after a complete revolution.
- (v) Inversion axis, also called a axis of rotoinversion (Figure 2d): This secondary symmetry operation defines the repetition of a motif with respect to the product of an n -fold rotation around an axis and an inversion at a point centered at this axis (symbol \bar{n} ; manner of speaking 'n bar').
- (vi) Rotoreflection axis (Figure 2e): This secondary symmetry operation defines the repetition of a motif with respect to the product of a rotation around an n -fold axis and a reflection at a plane perpendicular to this axis (symbol \tilde{n}).
- (vii) Screw axis, also called a axis of rototranslation (Figure 2f): This secondary symmetry operation defines the repetition of a motif with respect to the product of a rotation around an n -fold axis and a translation parallel to this axis; the translation amounts $m \cdot \tau/n$ with τ being the translation period parallel to the n -fold axis and $1 \leq m < n$; $m, n \in \mathbb{N}$ (symbol n_m).
- (viii) Glide plane (Figure 2g): This secondary symmetry operation defines the repetition of a motif with respect to the product of a reflection on a mirror plane and a translation (glide vector) τ/m parallel to this plane where m is 2 or 4. The translation vector is

either parallel to a crystallographic axis, τ/m amounts $\mathbf{a}/2$ (symbol a , a -glide plane), $\mathbf{b}/2$ (symbol b , b -glide plane), $\mathbf{c}/2$ (symbol c , c -glide plane), or it is parallel to the diagonal of a face of the unit cell, τ/m amounts $(\mathbf{a}+\mathbf{b})/2$, $(\mathbf{a}+\mathbf{c})/2$, $(\mathbf{b}+\mathbf{c})/2$ (symbol n , n -glide plane). In some F or I centered cells (see Section 5) also glide planes with glide vectors of $(\mathbf{a}\pm\mathbf{b})/4$, $(\mathbf{a}\pm\mathbf{c})/4$, $(\mathbf{b}\pm\mathbf{c})/4$, or $(\mathbf{a}\pm\mathbf{b}\pm\mathbf{c})/4$ occur (symbol d , d -glide plane).

There are some symmetry elements which describe the same repetition. The repetition of any motif by a one-fold rotoinversion $\bar{1}$ is identical to the description as a repetition of the motif by a center of symmetry. The two-fold rotoinversion $\bar{2}$ causes a repetition of a motif which is identical to the repetition of the motif by a mirror plane perpendicular to the $\bar{2}$ axis. The repetition by a rotoreflection may alternatively be described by a rotoinversion which, by convention, is used.

The application of a symmetry element results in two or more congruent objects. However, the congruence may either be direct or opposite. In the first case, conventional movement or rotation maintains the sign of corresponding angles within the object (transformation according to two right hands by a rotation, screw axes or translation) with the result that the two motifs are identical. In the second case, the two objects behave like left and right hands; they are enantiomorphous with respect to each other. The two objects may be transformed into each other by an inversion, a reflection, a rotoinversion, or a glide plane.

Macroscopically, only the center of symmetry, rotation axes, rotoinversion axes (rotoreflection axes), and mirror planes are observable on a crystal. The atomic arrangement exhibits the center of symmetry as the crystal macroscopically does. The rotation axes and rotoinversion axes are either maintained in the crystal structure or modified by a glide component (screw axes or glide planes). These are verified macroscopically without the glide component (*i.e.*, as rotation axes and mirror planes). The reason is that the translation periods of crystals are roughly between 3 Å and 50 Å in minerals (the Ångström unit amounts to $1 \text{ Å} = 10^{-10} \text{ m} = 0.0001 \text{ μm} = 0.1 \text{ nm} = 100 \text{ pm}$; it is commonly used for the discussion of crystal structures notwithstanding that is no SI unit). With the best microscopes available we do not reach a magnification down to a level to image such a glide vector. There is a further essential difference between the symmetry of a crystal and that of the atomic arrangement: a crystal has only one symmetry center and neither collinear axes nor coplanar mirror planes occur. In contrast, the crystal structure exhibits series of symmetry elements arranged parallel to each other at equal distances due to translation.

3. Periodicity

Solid matter forming a three-dimensional periodic arrangement of atoms is called a 'crystal'. It is characterized by the periodic repetition of the motifs which are composed of atoms or molecules. Most minerals form crystals; there are only a few amorphous minerals. In amorphous compounds the atomic arrangement features only a short-range order, any long-range order is missing. One exception is naturally fused silica; the name of the mineral is lechatelierite. The silicon atoms are tetrahedrally coordinated by four oxygen atoms which are corner connected among each other, but neither the arrangement of the silicon atoms nor that of the oxygen atoms is periodic. Even calcedony or opal - often put to the amorphous

minerals because viewable crystals are unknown - are at least in parts fine grained varieties of quartz, opal is sometimes mixed with cristobalite and / or tridymite.

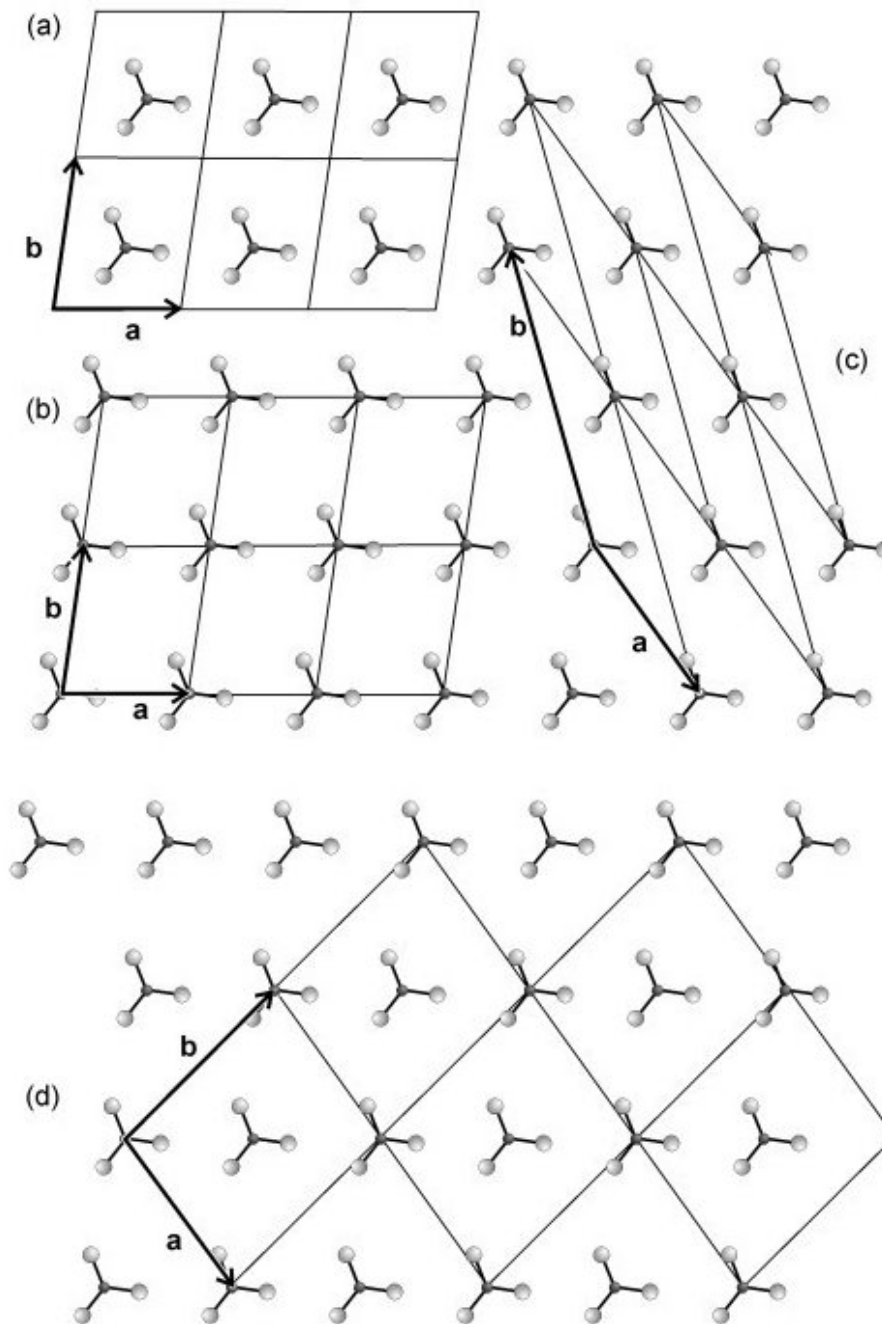


Figure 3: The repetition of a motif (a group of four atoms) in the two-dimensional space and four arbitrarily chosen translation lattices characterized by their unit cells. In (a) and (b) only the origin of the unit cell is shifted relative to each other. In (c) an uncommon (extremely flat) cell is represented. The lengths of the vectors **a** and **b** are unnecessarily long and define a so-called 'not reduced cell'. The unit cell chosen in (d) exhibits a doubled area which is unnecessarily large and involves two identical motifs. (It represents a centered cell.)

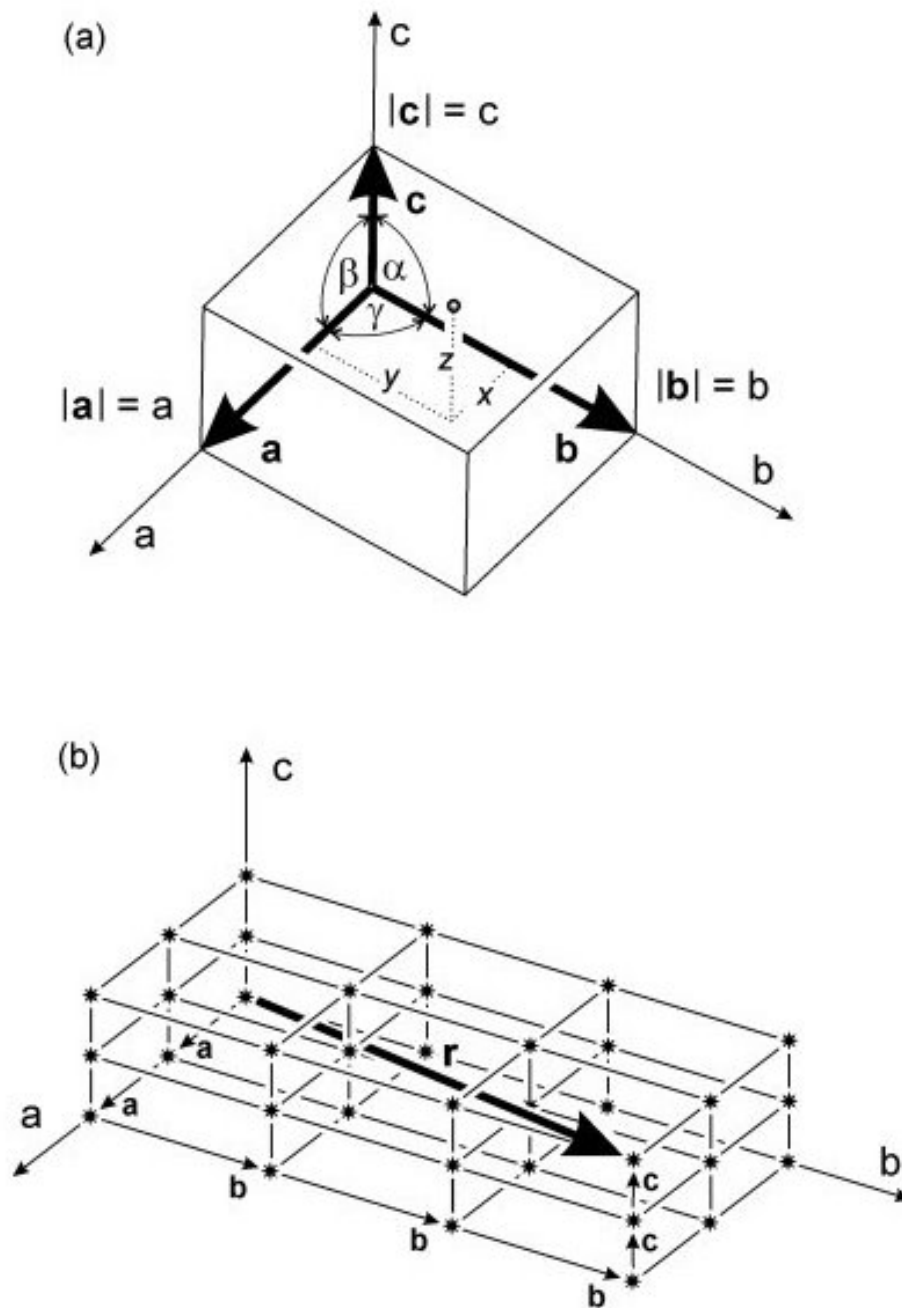


Figure 4: (a) A unit cell in the three-dimensional space characterized by the vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} parallel to the crystallographic axes a , b , and c . The lengths a , b , and c of the three vectors and the angles α , β , and γ between them are called 'cell parameters'. A point in the unit cell has the coordinates x , y , z . (b) A part of a three-dimensional lattice and a lattice vector $\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, u , v , and $w \in \mathbb{N}$ (here $[uvw]$ is $[232]$). The 'lattice points' are marked by asterisks.

A periodic structure consists of motifs (atoms or molecules) which are repeated by translation. Infinity of the repetition within a crystal is assumed. The translation lattice (or short lattice) images the periodicity of the structure. Figure 3 shows an example for the repetition of a motif within the two-dimensional space and four arbitrarily chosen lattices.

Each of these lattices defines a unit cell which may be used for the description of the same structure (*i.e.*, the motif and the direction and amount of its translation). It is to be considered that the lattice does not define the arrangement of atoms within the unit cell. In the two-dimensional space, the translation lattice is characterized by a parallelogram defined by two non-collinear translation vectors **a** and **b**. In the three-dimensional space the translation lattice is characterized by a parallelepiped defined by three non-coplanar vectors **a**, **b**, and **c** where $a = |\mathbf{a}|$, $b = |\mathbf{b}|$ and $c = |\mathbf{c}|$ and the angles α , β , and γ between them are called 'cell parameters' (Figure 4a).

The parallelogram as well as the parallelepiped is called 'unit cell' or simple 'cell'. The corners of the unit cell are called 'lattice points'. The lattice points do not necessarily represent atoms or other physical objects; *i.e.*, the origin of the lattice is not necessarily in an atom or in the center of an atomic group; it can be chosen arbitrarily. In two-dimensional space the lattice points are described by the translation vectors

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b}, \quad u \text{ and } v \in \mathbb{N}; \quad (1)$$

in three-dimensional space they are described by

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}, \quad u, v \text{ and } w \in \mathbb{N} \quad (2)$$

(Figure 4b). Note that $[uvw]$ is called the 'zone' (or more precisely zone axis) of a crystal which denotes the direction of an existing or possible edge of the crystal. However, there are international conventions for the choice of the unit cell with respect to the angles α , β , and γ (and the length of the edges of the unit cell). An example is shown in Figure 3. The common (reduced) cell for the lattice shown is that in Figure 3a and b. The cell selected in Figure 3c is unusual because of the extremely large angle γ accompanied by unnecessary large vectors **a** and **b**. The cell in Figure 3d is uncommon because its area is unnecessarily large since there are two identical motifs within the cell. In addition, there are international conventions for the choice of the origin of the lattice with respect to symmetry elements if present (as a reference serve the 'International Tables for Crystallography'). The coordinates x , y , and z of a point within the unit cell are referred to this non-unitary coordinate system and $0 \leq x, y, z < 1$. Thus the coordinates of an atom or of any point within the unit cell are dimension-less numbers.

In this context it is worthy to note that the principle of translation allows only one-, two-, three-, four-, and six-fold axes. In Figures. 5a to 5f it is shown that the two-dimensional space can be filled with triangles, the parallelogram (including rectangles and squares) and hexagons. In contrast, regular penta-, hepta-, octa-, nona-, deca-, ... -gons cannot fill planar space solely (see Figures. 5g and 5h as examples). As a consequence, five-, seven-, eight-, nine-, ten-, ... -fold axes are not compatible with crystallized materials.

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Bibliography

Buchanan, R.C., Park, T. (1997): *Materials crystal chemistry*. New York, Basel, Hongkong: Marcel Dekker, Inc. [Furnishes a thorough presentation of crystal structure development in compounds used in materials science and engineering providing a unique synthesis of bonding, symmetry, and crystallographic concepts].

Burdett, J.K. (1995): *Chemical bonding in solids*. New York, Oxford: Oxford University Press. [Examines how atoms in solids are bound together and how this determines the crystal structure and physical properties of materials].

Cheetham, A.K., Day, P. (eds.) (1992): *Solid state chemistry compounds*. Oxford: Clarendon Press. [Deals with the electronic structure and bonding in solids, and then focuses on several important classes of inorganic compounds].

Evarestov, R.A., Smirnov, V.P. (1997): *Site symmetry in crystals. Theory and application*. - Springer Series in Solid-State Sciences **108** (2. ed.) Berlin, Heidelberg, New York: Springer-Verlag. [A comprehensive account to the group-theoretical aspects of the site (local) symmetry approach to the study of crystalline solids].

Flack, H.D., Párkányi, L., Simon, K. (eds.) (1993): *Crystallographic Computing 6. A window on modern crystallography*. International Union of Crystallography. University Press: Oxford. [Subjects of topical interest in the state of crystallographic software are covered].

Giacovazzo, C., Monaco, H.L., Viterbo, D., Scordari, F., Gilli, G., Zanotti, G., Catti, M. (1992) *Fundamentals of Crystallography*. - International Union of Crystallography. Oxford: Oxford University Press. [Provides a comprehensive and accessible overview of modern crystallography and includes a rigorous treatment of theory and describes experimental applications in many fields].

Hahn, T. (ed.) (1995): *International Tables for Crystallography, Vol. A. Space group symmetry*. Dordrecht, Boston, London: Kluwer Academic Publishers. [A rigorous compilation of data, facts and literature related with all aspects of symmetry and crystal structure investigation].

Kostov, I., Kostov, R.I. (1999): *Crystal habits of minerals*. Sofia: Prof. Marin Drinov Academic Publishing House & Pensoft Publisher. [A comprehensive crystallographic overview on the morphology of minerals].

Lima-de-Faria, J. (1994): *Structural mineralogy, an introduction*. Dordrecht, Boston, London: Kluwer Academic Publishers. [A structural classification of minerals, based on the strength distribution and directional character of chemical bonds].

Merlino, St. (ed., 1997): *European Mineralogical Union Notes in Mineralogy. Vol. 1. Modular aspects of minerals*. Budapest: Eötvös University Press. [The wide range of modular problems in mineralogy is shown and the procedures to deal with them is indicated].

Meisel, A., Leonhardt, G., Szargan, R. (1989): *X-ray spectra and chemical binding*. In: Springer series in chemical physics **37**. Berlin, Heidelberg, New York, London, Paris, Tokyo, Hong Kong: Springer Verlag. [A general treatment of X-ray processes in matter; physical processes are combined with the interpretation of spectra from the perspective of chemistry to give a unified and rigorous presentation].

Schwarzenbach, D. (1997): *Crystallography*. Chichester, New York, Brisbane, Toronto, Singapore: John Wiley & Sons. [A comprehensive and practical guide to crystal structure investigation including physics, chemistry, molecular biology, materials science and mineralogy].

Senechal, M. (1990): *Crystalline symmetries. An informal mathematical introduction*. Bristol, Philadelphia, New York: Adam Hilger. [A guided tour through the maze of mathematical models and classifications that are

used to describe the symmetries of crystals].

Vainshtein, B.K. (1994): *Modern Crystallography, Vol. 1. Fundamentals of crystals. Symmetry and Methods of structural crystallography.* Berlin, Heidelberg, New York, London, Paris, Tokyo, Hong Kong, Barcelona, Budapest: Springer-Verlag. [Deals with general characteristics of crystalline matter, the principles of crystallography and its theoretical basis including aspects of symmetry of crystals and methods for analyzing the atomic structure of crystals].

Vainshtein, B.K., Fridkin, V.M., Indenbom, V.L. (1995): *Modern Crystallography, Vol. 2. Structure of crystals.* Berlin, Heidelberg, New York, London, Paris, Tokyo, Hong Kong, Barcelona, Budapest: Springer-Verlag. [Describes the ideal and real atomic structure of crystals as well as the electronic structures including fundamentals in chemical bonding between atoms, crystal chemistry and lattice energy].

Biographical Sketch

H. Effenberger is professor at the Institut für Mineralogie und Kristallographie at the Universität Wien, Austria. Fields of interest are related to the crystal chemistry of inorganic materials and minerals. Syntheses of chemical compounds are performed mainly under hydrothermal conditions. Structural investigations are related to the stereochemistry of divalent copper, the influence of the steric active lone-pair electrons of chemical elements as As^{3+} , Sb^{3+} , Se^{4+} , Te^{4+} , Tl^{1+} , Pb^{2+} , or Bi^{3+} , and the configuration of (short and / or symmetry restricted) hydrogen bonds. In addition, topological relations between crystal structures and structure types are studied. Furthermore, she is (co-)author of about one dozen of new minerals. A couple of minerals were re-investigated and re-defined with respect to their symmetry, cell metrics, and chemical or structural formula.

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