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Crystal structures of inorganic compounds with atomic defects

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Abstract. Main types of crystal structures with different atomic defects (point, volume, planar and linear) are considered using inorganic compounds as an example. The review presents the results of composite analysis of such real structures. Their symmetry, ordering, ways of description, nomenclature and the possibility of the diagnostics from diffraction patterns are discussed. The results of studies provide evidence that polymorphism is typical of real crystal structures. The bibliography includes 101 references.

I. Introduction

Crystalline compounds are generally chemically inhomogeneous because they contain impurities (atoms, ions, vacancies), which disrupt the three-dimensional periodicity of the host crystal structure. Numerous atomic defects are often distributed over the crystal rather uniformly. In these cases, systems are quasi-homogeneous and can be characterised by a single atomic structure, which is established by diffraction methods. The present review surveys such real crystal structures and the related views on isomorphism, polysomatism, solid solutions, mixed crystals and compounds with non-stoichiometric or variable compositions.

Extensive investigations of the real structures of chemically inhomogeneous crystals are currently underway both in Russia and abroad. In the last decades, new experimental analytical methods (synchrotron radiation, EXAFS spectroscopy, high-resolution electron microscopy, *etc.*) and powerful computer facilities have been developed and designed. Besides, a number of lines of theoretical research dealing with diffraction in quasi-homogeneous systems and their symmetry have been further elaborated. All these advances have provided a higher level of detailed information on real crystal structures. The amount of available information obtained by these methods has increased dramatically and fine details of the local structures of real crystals have been revealed. As a consequence, there is a common impression that each crystal has a unique structure and that it is impossible to characterise real crystal structures using precise mathematical laws. In addition, a number of complex structures with non-stoichiometric compositions, which could not be described by three-dimensionally periodic models, were studied by diffraction methods and it was reported that these structures can be used for the construction of new composite crystalline materials possessing useful properties.

The aim of the present review is to analyse the available data on real crystal structures of inorganic compounds with atomic defects. Initially, types of distortion of the long-range order in chemically inhomogeneous structures and their basic classification are considered. Then the characteristic features of the main structural types (symmetry, composite character, ordering, *etc.*), the accepted nomenclature and characteristic diffraction features are discussed using inorganic compounds as an example.

The need for such generalisations became apparent long ago. Researchers from different scientific schools often use different nomenclatures for the description of analogously organised real crystal structures, which hinders mutual understanding and does not allow one to obtain the general structural picture. In the present review, relationships between numerous real crystal structures with atomic defects are revealed on the basis of precise mathematical (symmetry) laws and ways of simplifying and generalising their nomenclature are proposed.

II. Main types of quasi-homogeneous structures

Let us consider types of distortions in the ideal three-dimensional long-range order caused by impurity atomic complexes of different sizes (Fig. 1): point (zero-dimensional), linear (one-dimensional), plane (two-dimensional) and volume (three-dimensional) defects.[1]

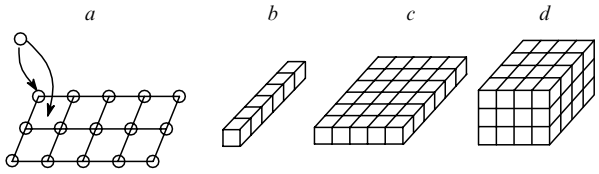


Figure 1. Types of atomic defects formed as a result of normal (*a*) and anomalous (*b* – *d*) isomorphous replacements;
(*a*) point (atom or complex), (*b*) linear (chain), (*c*) planar (layer), (*d*) volume (block) defects.

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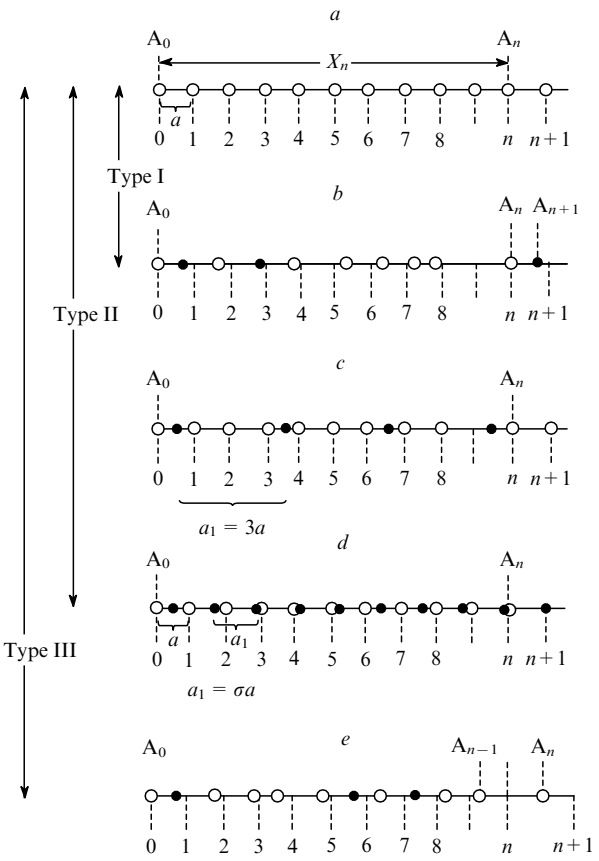


Figure 2. Types of atomic rows in crystal structures with atomic defects (main and impurity atoms are represented by empty and solid circles, respectively);[2]
(*a*) structures without impurity atoms; main atoms follow translational symmetry with the parameter *a*; (*b*) main and impurity atoms obey statistical translational symmetry with the parameter *a*; (*c*) main and impurity atoms follow different translational symmetries with the parameters *a* and a_1, respectively ($a_1 = na$, where *n* is an integer); (*d*) main and impurity atoms obey different translational symmetries with the parameters *a* and a_1, respectively ($a_1 = \sigma a$, where σ is an irrational number); (*e*) a non-periodic atomic distribution.

The insertion of impurity atoms, ions or vacancies into the ideal lattice of the host crystal gives rise to atomic point defects. Such structures contain rows of main and impurity atoms in addition to regular atomic rows along which an ideal translational symmetry with the lattice parameter *a* of the host crystal is retained (Fig. 2 *a*).[2] The atom distribution along such rows does not violate the statistical translational parameter, which is equal to the host crystal constant *a* (in real structures, close to *a*) (Fig. 2 *b*). This means that the distance X_n between the first (A_0) and *n*th (A_n) atoms in the row of *n* atoms approaches *na* when $n \to \infty$, whereas the distances between the adjacent atoms may substantially vary. Guinier [3] called this type of distortions in the long-range order the 'replacement disorder' and considered it as a manifestation of disorder of the first kind. This type of disorder is also associated with thermal vibrations of atoms due to which ideal atomic rows are wholly absent in real crystal structures.

Atomic volume defects appear in crystal structures if the distribution of atomic impurities obeys a three-dimensional translational symmetry, which differs from the symmetry of the host crystal. In this case, the structure necessarily has at least one direction along which the major and impurity structural units are distributed with different periodicities (Fig. 2 *c*,*d*). As a consequence, the crystal has the superperiods *na*. If the co-existing three-dimensional sublattices are essentially incommensurate (Fig. 2 *d*), the parameters of the common crystal lattice can reach several hundred angstroms.

The disorder of another type, *viz*., disorder of the second kind,[3] occurs in the host crystal structure, when the distribution of atomic impurities obeys a translational symmetry in less than three directions, *i.e*., when structural units in real crystal structures are distributed non-periodically along particular directions and only local regularities take place (Fig. 2 *e*). The difference between X_n and *na* increases with increasing *n*. However, the fluctuations of the distances between the adjacent atoms may be of the same order as those observed in the structures with the above-described types of disorder. Disorder of the second kind is typical of structures with atomic planar or linear defects. In the former case, the periodicity of the host crystal structure is distorted only in one direction. In the latter case, the periodicity is violated in two directions.

Hence, only three types of disorder can occur in chemically inhomogeneous structures under consideration. Correspondingly, three types of real crystal structures can be distinguished based on the translational symmetry retained in the crystal (see Fig. 2).[2,4]

In structures of type I (with atomic point defects), the three-dimensional lattice of the host crystal is statistically retained.

In structures of type II (with atomic volume defects), the disorder is associated with the fact that the major and impurity atoms obey different translational symmetries (Fig. 2 *c*, *d*). These structures are characterised by two or more three-dimensional sublattices (commensurate or incommensurate) or by a single three-dimensional lattice with superperiods, which are multiples of the lattice parameters of the host crystal.

Structures of type III (with atomic planar or linear defects) are periodic in less than three (in two or one) directions. These structures are characterised by two or more two-dimensional or one-dimensional sublattices (commensurate or incommensurate), which generally contain point defects.

III. Structures with atomic point defects (type I)

1. General views

Point defects, which do not disturb the three-dimensional statistical lattice, are present in virtually all crystals of both natural and synthetic origin. These defects occur due to continuous replacements of structural elements in the host crystal (atoms, ions, vacancies and their associates) as well as through other order–disorder processes. These crystal-chemical effects correspond to the modern views on isomorphism (see, for example, Ref. 5). Order–disorder transformations can be considered as a special case of isomorphism, *viz*., autoisomorphism, which is characterised by the redistribution of atoms and vacancies in the crystal structure. If the isomorphous replacement is accompanied by a change in the structural type of the crystal, this phenomenon is called isodimorphism.

The isomorphism and related problems were the subject of numerous reviews, including classical monographs by Russian scientists.[6–10] The morphological aspect of isomorphism, which was described by Mitscherlich [11] as a manifestation of the similarity in habits of crystals with different chemical compositions, is already a history. The crystal-chemical interpretation of this phenomenon, which assumes the similarity in the sizes of particles replacing each other as well as the similarity in some of their properties (Goldschmidt's rule), has also been essentially refined as the notion of the real crystal structures became deeper and more general. The history of evolution of these notions has been described in detail (see, for example, Ref. 12). It is common practice to consider quasi-homogeneous structures, which appear due to isomorphous replacements of different types, as solid solutions (replacement, insertion, subtractions, *etc*.). Besides, such systems are called mixed crystals, isomorphous mixtures, crystals, phases and compounds with variable compositions (see, for example, Refs 6, 10 and 13). The last-mentioned three terms

are less general because they do not take into account autoisomorphism.

2. Composite analysis. Way of description

Idealised structures of solid solutions consist of statistically alternating modules as 'unit cells', which correspond to the real or hypothetical end members of isomorphous (or isodimorphous) series (Fig. 3).[2] Consequently, crystal structures with atomic point defects are composed of at least two statistically alternating substructures, which are generally isostructural and differ only in composition. Hence, such real structures can be considered as composite structures. If vacancies serve as atomic point defects (Fig. 3 *b*), the corresponding real structures represent one of the possible forms of non-stoichiometry.[14] Due to local displacements induced by impurity atoms, the co-existing 'unit cells' undergo substantial local deformations (Fig. 4).[15]

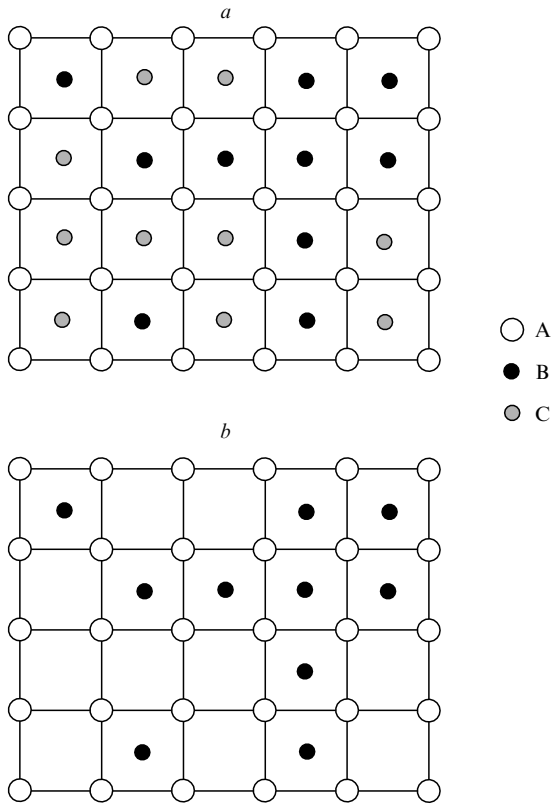


Figure 3. Schematic representation of the structures of the solid solutions $A(B_{0.5}C_{0.5})$ (*a*) and $A(B_{0.5}\square_{0.5})$ (*b*); empty cells represent vacancies in the positions of the atoms C.[2]

The relationship between the parameters of two 'unit cells' of solid solution (a_1, b_1, c_1 and a_2, b_2, c_2) can be described by the following matrix equation

$$A_2 = \sigma A_1, \qquad (1)$$

where $A_i = \begin{vmatrix} a_i \\ b_i \\ c_i \end{vmatrix}, i = 1, 2; \qquad \sigma = \begin{vmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{vmatrix}.$

In the general case, the components of the matrix σ are irrational due to local deformations. Since a system statistically retains the three-dimensional long-range order, the average relational matrix $\bar{\sigma}$ is always a unit matrix and the structure of a solid solution can be described by an averaged unit cell with a mixed occupancy of at least one crystallographic site. This means that the site is occupied in a particular ratio by at least two elements,

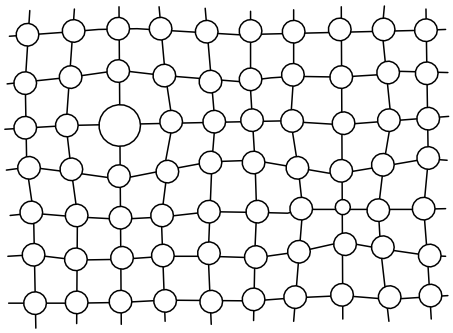


Figure 4. Local deformation of unit cells of a host crystal induced by impurity atoms.[15]

such as atoms, ions or vacancies. Partially vacant crystallographic sites are the necessary element in the crystal structures with non-stoichiometric compositions.

3. Symmetry

The symmetry of an average structure is statistically overestimated and is characterised by one of the space groups, *viz*., G_3^3. The parameters of a statistical three-dimensional periodic lattice are similar to those of the host crystal. It should be noted that the symmetry of the solid solution can be either higher or lower than the symmetry of the host crystal depending on the ordering of the distribution of impurity elements over regular point systems. If a solid solution is in the middle of an isomorphous (isodimorphous) series or it is formed through order–disorder processes, the notion of the host crystal loses its meaning. The symmetry of a solid solution can change both on crystal growth and in the course of its post-crystallisation transformations. Structural transformations can proceed either stepwise or continuously, both with changes (type I or II isodimorphism) and retention (type I or II polymorphism) of the overall composition of the crystal.[5, 16]

4. Chemical deformations of average structures

Changes in the composition of a solid solution as a result of isomorphous replacements lead to chemical deformations of the average crystal structure[9, 12] characterised by changes in the lattice constants, interatomic distances and bond angles. The mutual dependence between these changes enables one to study selected structural features of solid solutions on the basis of the crystal lattice parameters and interplanar distances (see, for example, the studies[17–20]).

Deformations of coordination polyhedra caused by changes in the chemical composition, temperature or pressure often show traits of similarity (primarily, in crystals with essentially ionic bonds).[9, 21, 22] Chemical deformations can be quantitatively characterised by the coefficient γ_a ($\%^{-1}$)

$$\gamma_a = \frac{1}{a}\frac{da}{dx},$$

which characterises the relative increment of a particular structural parameter *a* as the impurity concentration (x) is increased by 1%, by analogy with the thermal expansion coefficients.[9, 21]

Deformations of different nature can be quantitatively compared by calculating their mutual equivalents. For example, it is convenient to use the ratio γ_a/α [°C (at.%)$^{-1}$], where γ_a is the coefficient of chemical deformations and α is the thermal expansion coefficient, as the thermal equivalent of the chemical deformation of the structure (on the basis of the parameter *a* for a particular isomorphous replacement).[9]

Local displacements of atoms from ideal sites lead to deviations of both the lattice parameters and average interatomic distances in the solid solution from Vegard's rule, *i.e*., from the strictly additive behaviour,[23] which lies at the basis of the virtual

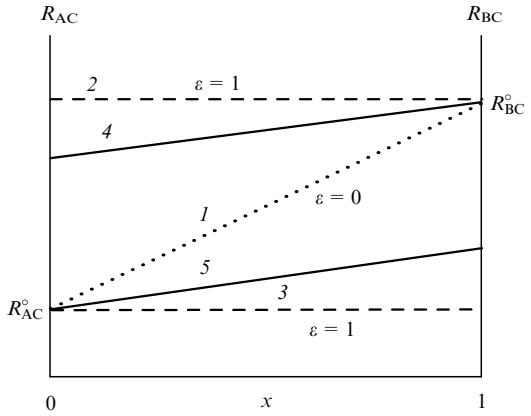


Figure 5. Changes in the B—C and A—C interatomic distances depending on the composition of the solid solution $(A_{1-x}B_x)C$ determined within the virtual crystal model (*1*) and bond length alternation model (*2*, *3*) and on the basis of experimental data (*4*, *5*) (after V S Urusov [23]); (*2* and *4*) R_{BC}; (*3* and *5*) R_{AC}.

crystal model (Fig. 5). These characteristics also do not obey the bond length alternation model according to which the bond lengths in a solid solution are equal to those in pure compounds (end members of the isomorphous series). These models are the hypothetical limiting cases. The actual parameters and interatomic distances in a solid solution are intermediate between the above-mentioned limiting values and the determination of these parameters is the subject of a special experimental study. The degree of structure relaxation of a solid solution can be characterised by the following parameter

$$\varepsilon = \frac{R_{BC} - R^{\circ}_{AC}}{R^{\circ}_{BC} - R^{\circ}_{AC}},$$

where R_{BC} are the bond lengths in the structure of the solid solution $(A_{1-x}B_x)C$, R°_{BC} and R°_{AC} are the bond lengths in the structures of the corresponding pure components.[23] Relaxation of the virtual crystal AC with a very small impurity BC approaches zero, whereas relaxation of the crystal with the bond-length alternation is maximum (equal to unity). In real structures of solid solutions, relaxation is incomplete ($0 < \varepsilon < 1$).

5. Short-range order

In crystals of compounds with ionic bonds, the electroneutrality condition requires that atomic defects be generated in pairs (Fig. 6), *viz*., a vacancy and the corresponding interstitial ion (Frenkel defect), two vacancies of opposite charges (Schottky defect) or two interstitial ions of opposite charges (antipode of the Schottky defect). The formation of defects is accompanied by migrations of the surrounding atoms. Atoms about the vacancies are shifted primarily toward the vacant lattice point, whereas interstitial ions, by contrast, push aside the adjacent atoms. Hence, the fulfilment of the electroneutrality condition for a solid solution primarily through a local charge compensation gives rise to a short-range order (appearance of block isomorphism [15]). In non-stoichiometric solid solutions, statistically distributed associates of atoms and vacancies (simple and complex clusters) whose compositions and structures differ from those of the host crystal can occur. Due to the presence of such defect complexes, impurity atoms in the host crystal structure can create coordination conditions typical of the structures of real or hypothetical end members of isomorphous (isodimorphous) series.[2] If several structural modifications of the compound can occur, the impurity atoms tend to give rise to the coordination typical of the modification that is the nearest to the phase of the host crystal in the phase diagram.[24] The possibility of the presence of statistically distributed cluster groups in the structure of a solid solution is often evidenced by unreasonably shortened interatomic distances.

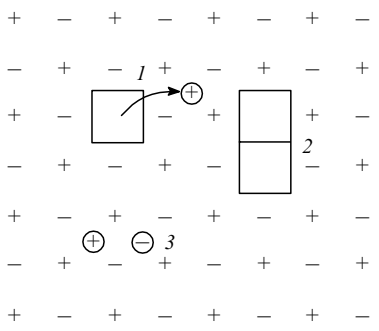


Figure 6. Point defects in the NaCl-type crystals.[15] (*1*) Frenkel defects, (*2*) Schottky defects, (*3*) antipode of the Schottky defect; vacancies and interstitial ions are indicated by squares and circles, respectively.

6. Diffraction patterns

Diffraction patterns of quasi-homogeneous structures with atomic point defects represent three-dimensional reciprocal lattices and differ from the patterns of ideal three-dimensionally periodic crystals only by generally insignificant effects of diffusion scattering associated with manifestations of a short-range order.

7. Ordering

The insertions of atomic point defects into an ideal three-dimensional lattice leads to lowering of the internal order of the system. If all symmetry elements, except for translations, are ignored, the crystal structure with these defects can be described as a combination of intersecting translationally equivalent atomic sublattices, into some of which impurity atoms are inserted. The larger is the portion of such statistical atomic sublattices, the lesser is the degree of internal order. It should be noted that crystal structures with atomic point defects are the most ordered form of the naturally occurring condensed state.

IV. Structures with atomic volume defects (type II)

1. General notions

Crystal structures with atomic volume defects (multilattice structures) were found among minerals and can be prepared under laboratory conditions by performing the synthesis in multicomponent systems. These structures show considerable promise in searching for new materials with useful properties. These structures are poorly studied primarily because of the fact that classical X-ray diffraction methods on the basis of three-dimensional space symmetry groups are not sufficiently efficient to solve superstructures (particularly, with large periods). Due to the design of special computer programs involving *N*-dimensional descriptions of superspace symmetry groups, considerable progress has been made in the determination of multilattice crystal structures in the last decade.

The structures under consideration can appear due to isomorphism, if atomic point defects are inserted into the host lattice in an ordered fashion. This is a way in which superstructures of ordered solid solutions are formed (Fig. 7). In such crystals, the co-existing sublattices are commensurate. Quasi-homogeneous systems with essentially incommensurate three-dimensional sublattices can occur, if the host crystal structure contains periodically distributed fragments (layers or columns) with other structures (Fig. 8). Frank-Kamenetskii [1, 10] related the formation of such structures to anomalous (lamellar) isomorphism (see Fig. 1). According to the modern notions, this is a manifestation of polysomatism.

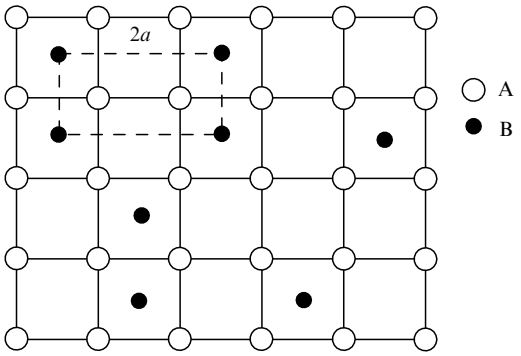


Figure 7. Schematic representation of the formation of a supercell (shown by dashed lines) of an ordered solid solution.[2]

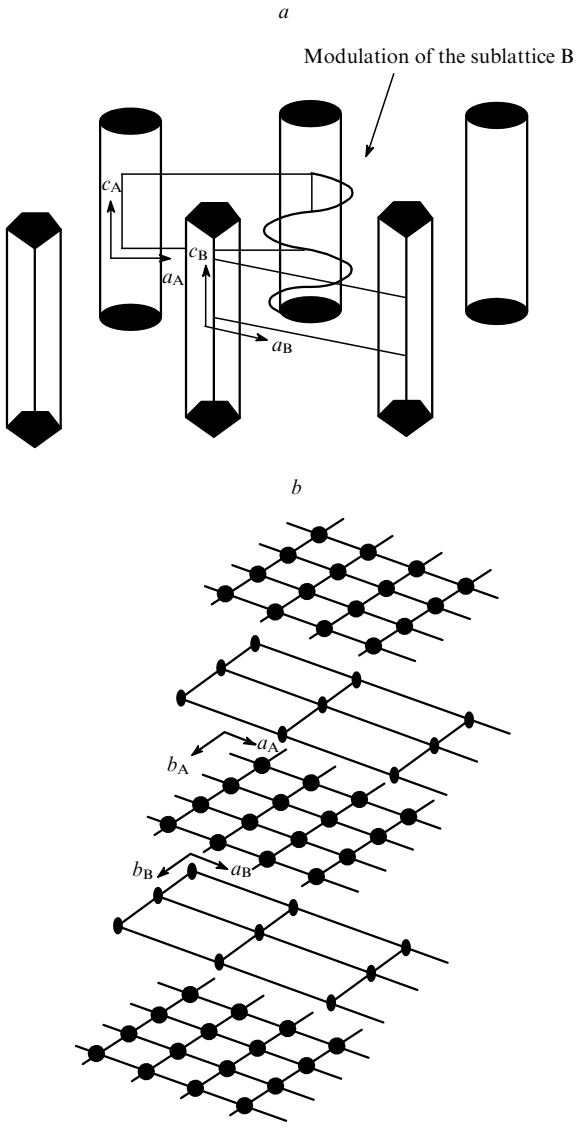


Figure 8. Schematic illustration of the packing of the two sublattices (A, B) in composite structures: column (*a*) and layer (*b*) (after P Coppens[25]). The appearance of a modulation of the sublattice B with the period of the sublattice A is exemplified by columnar structures.

The term 'polysomatism' was proposed by Thompson[26] for the description of the formation of complex mineral structures from fragments (modules) of different simpler (really occurring in nature) compounds. The commonly accepted extended concept of polysomatism (see, for example, Refs 27–30) is applied to various series of crystal structures consisting of modules of at least two types. Generally, modules (layers, columns or blocks) differ both in the structure and composition, but they can differ only in one of these parameters. Polysomatism is very widespread in nature and is often, along with isomorphism, responsible for non-stoichiometry of compounds. Apparently, the mechanisms of formation of members of polysomatic series (polysomes) can be described with the use of models developed for polytypes.[30] Polysomatic structural series are often described as homologous series.[31,32]

Crystal structures with incommensurate sublattices are typical of minerals and synthetic (both inorganic and organic) compounds. In nature, such structures most often occur in small amounts and in mixtures with other minerals. These structures are variously referred to as hybrids,[33] intergrowth structures,[34] misfit layered structures,[35–37] incommensurate ladder structures,[38–41] intercalates,[42] *etc*. Due to the structural similarity of multilattice compounds, they are assigned to one group and considered as composite structures.[25,43,44]

Composite structures were surveyed in the monograph[45] and reviews.[25,34–37,44] Unfortunately, data on the structures of this type containing more than two components are very scarce.

The minerals koenenite $[(Mg,Al)(OH)_2]_x[(Na,Ca,Mg)Cl_2]$ ($x \approx 1.78$)[46] and valleriite $[(Mg,Al,Fe)(OH)_2]_x[(Fe,Cu)_2S_2]$ ($x = 1.37-1.56$)[33,47] are examples of layered composite structures. In the crystal structures of these minerals, the brucite-like octahedral layers alternate with the NaCl-like layers or tetrahedral sulfide layers, respectively. Figure 9 shows the fragment of the composite layered structure of valleriite represented as polyhedra. The minerals cylindrite $[(Pb,Ag,Sn,Sb,Fe)S]_x.[(Sn,Sb,Fe)S_2]$ ($x \approx 1.38$),[48] cannizzarite $[(Pb,Bi)S]_x[(Pb,Bi)_2S_3]$ ($x \approx 1.70-1.71$)[49] and their synthetic analogues provide examples of layered composite structures characterised by superperiods of length >100 Å. Layered composite structures are known also for graphite intercalates exhibiting high conductivity,[42] for example, for $FeCl_3$-graphite.[50] Layered structures of superconducting bismuth cuprates $Bi_2Sr_2CuO_{6+x}$ and $Bi_2(Sr,Ca)_3Cu_2O_{8+x}$ can also be described as composite structures $[Bi_2Sr_2CuO_4][O]_y$ and $[Bi_2(Sr,Ca)_3Cu_2O_6][O]_y$ ($y \approx 2.2$), respectively.[51]

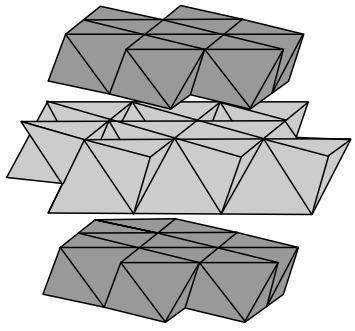


Figure 9. Fragment of the layer composite structure of valleriite.[35]

The known columnar composite structures are much less in number. For example, these structures are typical of the compounds $Ba_p(Fe_2S_4)_q$.[52] In the structures of these compounds, the chains of the edge-sharing Fe–S tetrahedra alternate with columns of barium ions. Composite structures containing zigzag chains as two-leg ladders occupy a special place. For example, the structures of $[M_2Cu_2O_3]_{0.714}[CuO_2]$ (M = Bi, Sr, Ca, Y or lanthanides)[39–41,53] (Fig. 10) contain the Cu_2O_3 layers composed of two-leg ladders, which alternate along the [010] direction with the layers consisting of the CuO_2 chains. If interactions between the ladders are ignored, these structures can be considered as columnar structures, which consist of two types of chains parallel to the [001] direction. One of these phases with composition $Sr_{0.4}Ca_{13.6}$.

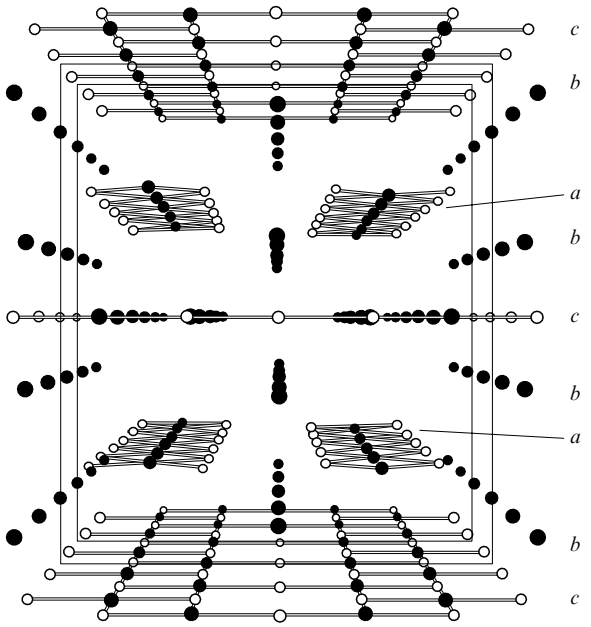


Figure 10. The composite structure of $[M_2Cu_2O_3]_{0.714}[CuO_2]$ (M = Bi, Sr, Ca);[41]
(*a*) layers of the CuO_2 chains, (*b*) layers of the cations M, (*c*) Cu_2O_3 layers built from two-leg ladders.

$.Cu_{24}O_{41+x}$ is transformed into the superconducting state at 9–12 K and 4.5 GPa.[54] Two-leg ladders are present also in numerous composite structures of intermetallides,[38] for example, in $[V]_{17}[Ge]_{31}$, $[Mo]_9[Ge]_{16}$, $[Re]_{17}[Ge]_{22}$, $[Te]_{17}[Si]_7$, *etc*. In these chimney-ladder structures (often with superperiods of length > 100 Å), chains of Group III and IV metals (ladders) are inserted into the channels of the frameworks of transition metals.

Frank-Kamenetskii [1] considered real crystal structures containing extended chemical defects as solid solutions. These views have been further developed in the study.[27] The authors of the cited study proposed that series of structures consisting of analogous modules be considered as fragmentary solid solutions composed not of individual atoms or ions but of structural fragments arranged with different degrees of order. In usual solid solutions, which are formed as a result of isomorphous replacements, the structures are changed due to variations in the chemical composition. By contrast, structural changes are responsible for the formation of fragmentary solid solutions, whereas variations in the composition are manifested only in relation to these structural changes. In the light of these concepts, crystal structures with atomic volume defects can be considered as ordered fragmentary solid solutions.

2. Composite analysis. Ways of description

Crystal structures with atomic volume defects (regardless of the commensurability of the co-existing sublattices) can always be described as superstructures (the lengths of the superperiods can reach hundreds of angstroms) or as composite structures consisting of two or more mutually penetrating three-dimensionally periodic substructures. Ionic-covalent bonds between atoms within substructures are often much stronger than those between atoms belonging to different substructures.[25] In many cases, the requirement of electroneutrality is ensured by variable-valence elements. The stronger are interactions between the substructures, the more substantial are mutual periodic distortions (modulations). Modulations of the sublattice B occur with the period of the co-existing sublattice A (see Fig. 8 *a*) and *vice versa*. Hence, composite structures of this type represent the most general case of modulated structures. If the co-existing sublattices are essentially incommensurate and the ratios between the volumes of the subcells deviate from integer values, the structures characterise one of the possible forms of manifestation of non-stoichiometry.[14, 25, 43]

The co-existence of different substructures in one crystal imposes certain conditions on the components of the matrix σ in Eqn (1). In the case under consideration, Eqn (1) describes the relations between the sublattice parameters.[25, 43]

If the composite structure consists of columns of two types parallel to the axis *c* (see Fig. 8 *a*), it is necessary to avoid their overlapping. Columns must fit together into an infinite array in the plane perpendicular to the column axis. For this purpose, the axes a_2 and b_2 are chosen in the planes a_1c_1 and b_1c_1, respectively. Hence, the minimum requirements for the commensurability of the parameters of the co-existing sublattices are determined by the following matrix

$$\sigma = \begin{vmatrix} n_1 & 0 & \sigma_{13} \\ 0 & n_2 & \sigma_{23} \\ 0 & 0 & \sigma_{33} \end{vmatrix}, \qquad (2)$$

where n are integers or rational fractions and σ are irrational values. Consequently, five basis vectors are required for the description of columnar composite structures.

In the case of layered composite structures (see Fig. 8 *b*), the parallel planes cannot overlap, and the minimum requirements for the space fitting of the co-existing sublattices are determined by the following matrix

$$\sigma = \begin{vmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{21} & \sigma_{22} & 0 \\ \sigma_{31} & \sigma_{32} & n \end{vmatrix}. \qquad (3)$$

Six basis vectors are required for the description of such structures. If the axes *a* and *b* of two sublattices can be chosen parallel to each other ($a_1 \| a_2$, $b_1 \| b_2$), the matrix (3) takes the form

$$\sigma = \begin{vmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ \sigma_{31} & \sigma_{32} & n \end{vmatrix}. \qquad (4)$$

In this case, four basis vectors are sufficient for the description of a layered composite structure.

Composite structures cannot be unambiguously classified according to the type of the matrix relating the co-existing sublattices. If the matrix σ is reduced to a diagonal form, the structure cannot be assigned to rod or layered structures (without considering the characteristic features of chemical interactions). For example, the structures of $[M_2Cu_2O_3]_{0.714}[CuO_2]$ (M = Bi, Sr, Ca, Y or lanthanides) [39–41, 53] (see Fig. 10) whose sublattices are related by a diagonal matrix can be considered as structures composed of either alternating layers perpendicular to the axis *b* or alternating columns (rods) parallel to the axis *c*. Besides, the structure identified according to the corresponding relational matrix as a rod structure can, in fact, contain a framework formed by one of the components through strong hydrogen or covalent bonds. In this case, the second component is located as a guest in the channels of the framework. For example, such guest–host structures are typical of urea-based complexes.[25]

3. Symmetry

Average structures of all substructures co-existing in the same crystal (without considering possible modulations) and the superstructure as a whole are characterised by the space groups G_3^3. The space group of the superstructure is determined by the intersection of the symmetry groups of the substructures at their given orientations. If sublattices co-existing in the same crystal are substantially incommensurate, the lengths of the superperiods can reach hundreds of angstroms. In this case, it is reasonable to consider the system as periodic in more than three directions (Fig. 11).[25] Then, taking into account mutual modulations whose periodicity is determined by the parameters of the co-existing sublattices (see Fig. 8 *a*), the symmetry of each of the substruc-

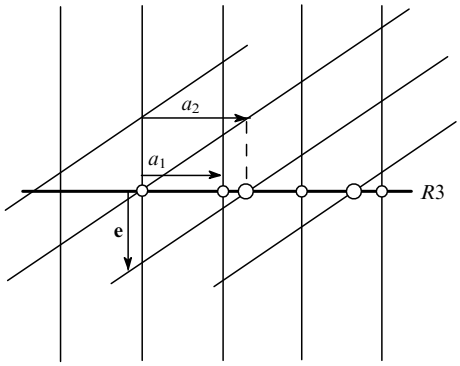


Figure 11. Schematic representation of a two-component composite crystal in the four-dimensional space.[25]
$R3$ is the three-dimensional space with two different periodicities a_1 and a_2, **e** is the unit vector. Lines in the fourth dimension are strings representing the atoms of two substructures without taking into account the modulations.

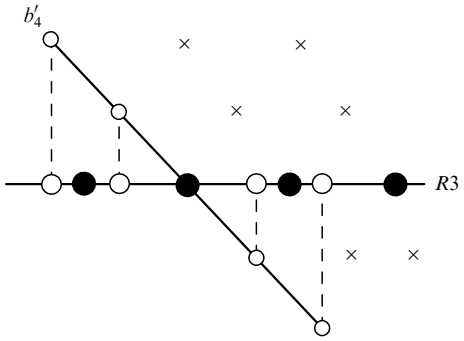


Figure 12. Schematic representation of the four-dimensional reciprocal space of a two-component composite crystal.[25]
$R3$ is the three-dimensional space with two sets of reflections with different periodicities, b'_4 is an additional coordinate axis. Main reflections of two sublattices are shown by circles. Satellite reflections are indicated by asterisks.

tures and the system as a whole can be characterised by the superspace groups G_{3+d}^{3+d} (Refs 25, 44). Composite structures with commensurate sublattices can also be described with the use of superspace symmetry groups (see Ref. 44 and other publications).

The theory of superspace groups, which has been extensively developed in the last decades, was considered in the studies [55–62] and the expressions for structure factors corresponding to these concepts were published in the studies.[44, 63]

4. Diffraction patterns

In the general case, the diffraction pattern of a composite crystal [25, 44] is very complicated due to overlapping of the diffraction patterns of all co-existing substructures. In such a pattern, there are the so-called main reflections among which are mixed reflections serving simultaneously as main reflections for one of substructures and as satellite reflections for another substructure. In addition, weak satellite reflections should be present, which are unambiguously indicative of the occurrence of modulations caused by interactions between the substructures. However, satellite reflections are often impossible to reveal by X-ray diffraction methods and mixed reflections are the only source of information on modulations of sublattices. Depending on the incommensurability of sublattices co-existing in the crystal, the diffraction pattern can be virtually indistinguishable from that of either an oriented intergrowth or an ideal three-dimensionally periodic crystal.

In the general case, $3 + d$ basis vectors are required for indexing diffraction patterns of a composite crystal (Fig. 12). The relationship between the parameters of two reciprocal sublattices a_1^*, b_1^*, c_1^* and a_2^*, b_2^*, c_2^* can be described by the following matrix equation: [25]

$$\mathrm{A}_2^* = (\sigma^{-1})^{\mathrm{T}}\mathrm{A}_1^* = \sigma^*\mathrm{A}_1^*, \tag{5}$$

where $\mathrm{A}_i^* = \begin{vmatrix} a_i^* \\ b_i^* \\ c_i^* \end{vmatrix}$, $i = 1, 2$; σ is the matrix from Eqn (1);

T is a transpose operation.

In the case of columnar composite structures for which the relationship between the sublattices is determined by the matrix (2), the matrix σ^* takes the form

$$\sigma^* = \begin{vmatrix} 1/n_1 & 0 & 0 \\ 0 & 1/n_2 & 0 \\ -\sigma_{13}(n_1\sigma_{33}) & -\sigma_{23}(n_2\sigma_{33}) & 1/\sigma_{33} \end{vmatrix}. \tag{6}$$

Hence, the axes a_1^* and b_1^* are parallel to the axes a_2^* and b_2^*, respectively (in the reciprocal space, the $hk0$ plane is common to both substructures), and the diffraction pattern can be described by four basis vectors ($d = 1$).

In the case of layered composite structures for which the relationship between the sublattices is determined by the matrix (4), the matrix σ^* takes the form

$$\sigma^* = \begin{vmatrix} 1/\sigma_{11} & 0 & -\sigma_{31}(n\sigma_{11}) \\ 0 & 1/\sigma_{22} & -\sigma_{32}(n\sigma_{22}) \\ 0 & 0 & 1/n \end{vmatrix}. \tag{7}$$

Here, only the axis c^* is common to both substructures, and the diffraction pattern is described by five basis vectors ($d = 2$).

5. Ordering

The appearance of superperiods decreases the homogeneity of the crystal structure. In different structures, the degree of ordering varies substantially and decreases with increasing incommensurability of the co-existing sublattices (with increasing volume of the unit cell characterising the superstructure). It should be remembered that structures with atomic volume defects virtually always contain atomic point defects as well. Therefore, structures of type II are characterised by lower degrees of internal ordering compared to those observed in the above-described structures of type I (usual solid solutions).

V. Structures with atomic planar and linear defects (type III)

1. General views. Probability-statistical models

Chemically inhomogeneous structures, which consist of modules (layers or columns) with different compositions alternating in a disordered fashion, are also rather widespread among natural and synthetic compounds. According to the results of high-resolution electron microscopy (see, for example, Refs 64 and 65), structures with two-dimensional defects represent one of the most widespread types of crystal inhomogeneity. Irregularly alternating modules can have either different or identical atomic structures. Structures of the first type are characteristic of members of polysomatic series, whereas structures of the second type are typical of intermediate compositions of isomorphous series. The weaker are interactions between atoms belonging to different modules, the more substantial is the deviation of the real crystal structure from a homogeneous three-dimensionally periodic structure. If the scale of structural inhomogeneity, *i.e.*, the maximum possible thickness of the packet of impurity modules, is smaller than the average size of the coherent scattering domains (CSDs) and if numerous defects are rather uniformly distributed over the crystal, interactions between alternating modules are

rather strong and the irregular structure is quasi-homogeneous. Such structures can be described within the framework of a single probability-statistical model whose parameters characterise the ratios between the co-existing one- or two-dimensional fragments and their distribution along directions that lose periodicity.

Probability-statistical models have been developed only for one-dimensionally disordered structures. The first of these models allowed one to describe only completely disordered layer packings without considering possible interactions between the layers.[66–68] Later on, it has been proposed that interlayer interactions be characterised by the factor of the short-range order R, which is equal to the number of layers responsible for the probability of the occurrence of a particular layer in the crystal.[69–72] More recently, the probability parameters were suggested for the description of the character of alternation of the layers at $R = 0$ or 1.[73–75] Probability-statistical models of irregular layered structures and the diffraction theory based on these models were generalised and developed in the studies.[76–78] Unfortunately, irregular mixed-layer structures studied with the use of probability-statistical models are few in number. Most of these structures were surveyed in the monograph [77] and reviews.[78–80] Examples of the application of these models to the description of irregular mixed-layer structures of chemically inhomogeneous crystals are given in Table 1.

Quasi-homogeneous structures with two- and one-dimensional defects can arise in the course of both crystal growth (in particular, in the course of formation of a composite zoning) and post-crystallisation changes, for example, upon decomposition of solid solutions or metosomatic replacements. Irregular mixed-layer structures are often generated in the course of transformations of layered silicates at high p and T.[81]

Disordered mixed-layer structures are typical of various natural and synthetic compounds, *viz*., silicates, sulfides, carbonates, graphite intercalates, perovskite-like cuprates and other oxides and hydroxides. Mixed-layer layered silicates (see Refs 66, 67, 77, 78 and other publications) were studied in most detail. Since the latter minerals are widespread in nature and very sensitive to changes in the thermodynamic conditions, they are successfully used as indicators of the geochemical conditions of formation. Their crystal structures are built from layers of different clay minerals, which are present in variable amounts (Fig. 13).[30] The interlayer space can be filled either with complexes of cations with water molecules or with potassium and sodium cations. Quasi-homogeneous structures with the maximum possible degree of short-range order are widespread among mixed-layer layered silicates. The structures with a very low degree of order were found among illite- and kaolinite-montmorillonites.[82] Probability-statistical models of irregular mixed-layer structures were applied also to the investigation of the chemical imperfection in the structures of non-stoichiometric perovskite-like cuprates $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1-3$)[80, 83, 84] (Fig. 14)

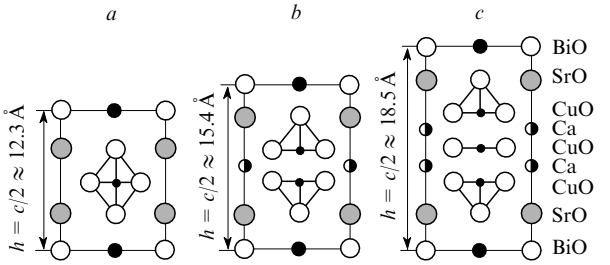


Figure 14. Crystal structures of members of the polysomatic series $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$.[80]
(*a*) Bi-2201, $n = 1$, $T_c \approx 20$K; (*b*) Bi-2202, $n = 2$, $T_c \approx 90$K; (*c*) Bi-2203, $n = 3$, $T_c \approx 110$K (T_c is the superconducting transition temperature, h is the height of the layer).

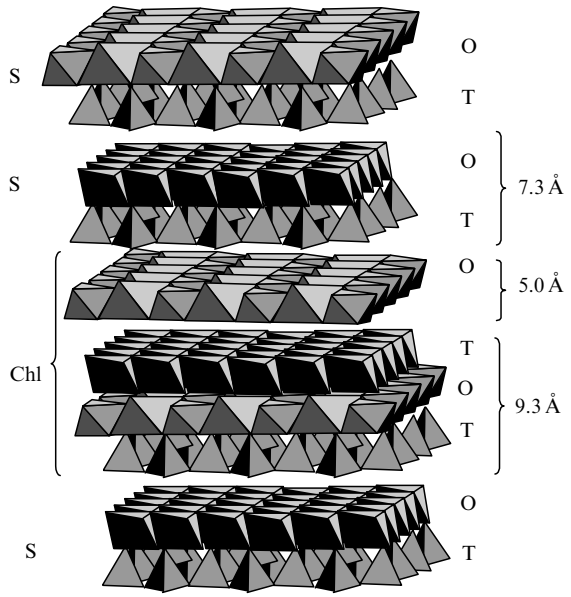


Figure 13. Diagrammatic structure of the chlorite/serpentine interlayering (S is serpentine, Chl is chlorite).[30]
Layers of tetrahedra (T) and octahedra (O) are shown.

and $YBa_2Cu_3O_x$ ($x = 6$, 7)[85] (Fig. 15). This approach made it possible to estimate the concentration and characteristic features of the distribution of impurity layers, which belong to phases with other n or differ from matrix layers due to the in-layer distribution of cations and vacancies (see Table 1). The relationships between the probability characteristics of the real structure, synthesis conditions and post-growth treatment of the crystals were revealed and their correlations with the average temperature and the width of the temperature range of the transformation into the superconducting state were found.[86, 87] Besides, probability-statistical models were successfully used in studies of the fine oscillatory zoning in crystals of garnets of the grossular-andradite series $Ca_3(Al,Fe)_2(SiO_4)_3$ (see Ref. 88) and the decomposition structure of the solid solution $(K,Na)(Ca,Na)_2(Mg,Fe)_5.(Si,Al)_8O_{22}(OH,F)_2$, *viz*., the calcium amphibole edenite.[89] Investigations of irregular structures formed as a result of layer isomorphism [79, 80] demonstrated that the common feature of these structures is a high degree of segregation of layers with the same

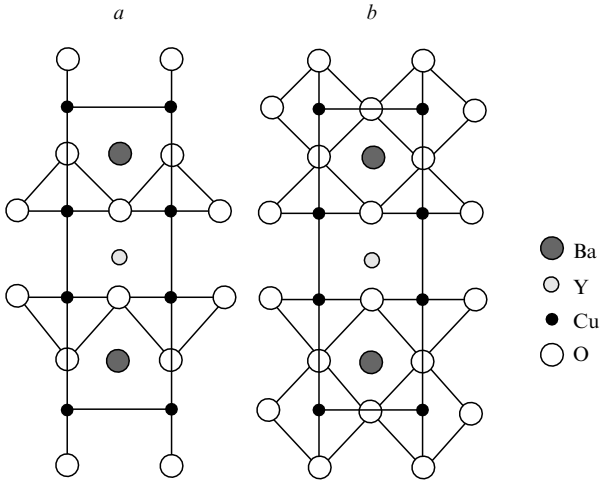


Figure 15. Crystal structures of the non-stoichiometric phases $YBa_2Cu_3O_x$.
$x = 6$ (*a*), 7 (*b*).

Table 1. Examples of the use of binary probability-statistical models ($R = 1$) for the description of irregular mixed-layer crystal structures of selected inorganic compounds.[80]

Compound	h_i /Å	Limits of variations in composition of layers	Probability-statistical parameters					
			M	W_i	P_{ii}	K_s	L /Å	l /Å
$Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1-3$)	15.45	$(Bi_{1.9-2.0}Cu_{0.1-0.0})(Sr_{1.7-2.0}Bi_{0.3-0.0})Ca_{1.0}Cu_{2.0}$	10	0.95	0.95	–	154	12
	12.15	$Bi_{2.0}(Sr_{1.5-2.0}Bi_{0.3-0.0}Ca_{0.2})Cu_{1.0}$		0.05	0.00			
$(Bi,Cu)_2(Sr,Bi)_2CaCu_2O_8$	15.38 – 15.57	$(Bi_{1.9-2.0}Cu_{0.1-0.0})(Sr_{1.6-1.9}Bi_{0.4-0.1})Ca_{1.0}Cu_{2.0}$	11 – 13	0.60 – 0.70	0.95 – 0.90	0.67 – 0.81	170 – 200	43 – 63
	15.55 – 15.25	$(Bi_{2.0-1.8}Cu_{0.0-0.2})(Sr_{1.9-1.3}Bi_{0.1-0.7})Ca_{1.0}Cu_{2.0}$		0.40 – 0.30	0.93 – 0.77			
$YBa_2Cu_3O_x$ ($x = 6, 7$)	11.67 – 11.71	$x = 6.70 - 7.00$	100 – 140	0.60 – 0.90	1.00	1.00	1170 – 1640	140 – 470
	11.72 – 11.69	$x = 6.85 - 6.70$		0.40 – 0.10	1.00			
$Ca_2(Al,Fe)_2(SiO_4)_3$ (garnets)	4.21	$Ca_3(Al_{0.70-0.65}Fe_{0.30-0.35})_2$	320 – 380	0.65 – 1.00	0.98 – 1.00	0.97 – 1.00	1350 – 1600	240 – 460
	4.23	$Ca_3(Al_{0.50-0.45}Fe_{0.50-0.55})_2$		0.35 – 0.00	0.99 – 1.00			
$(K,Na)(Ca,Na)_2(Mg,Fe)_5$.	9.03	$(K_{0.3}Na_{0.7})(Ca_{1.65}Na_{0.35})(Mg_{4.25}Fe_{0.75})$	60	0.85	0.98	0.88	540	70
$.(Si,Al)_8O_{22}(OH,F)_2$ (amphibole)	9.10	$(K_{0.7}Na_{0.3})Ca_{2.0}(Mg_{3.0}Fe_{2.0})$		0.15	0.90			

Note. h_i is the height of the layer of type i ($i = 1, 2$); M is the total number of layers in the coherent scattering domain (CSD); W_i is the portion of the layers of type i in CSD; P_{ii} is the conditional probability of the layers of type i following the layer of type i; K_s is the segregation coefficient; L is the average size of CSD along the normal to the layers; l is the maximum possible thickness of the packets of impurity layers.

composition. The above-considered results provide evidence that probability-statistical models show promise for the description of irregular mixed-layer structures in studies of the chemical inhomogeneity of layers in crystals regardless of their structural type.

Ribbon-chain silicates, which were called 'biopyriboles' by Thompson,[26,91] are commonly considered as a classical example of mixed-chain structures.[90] These compounds are members of a polysomatic series, which embraces structures from a chain silicate (pyroxene) to mica (biotite) and includes a ribbon silicate (amphibole). In the structures of biopyriboles (Fig. 16), columns of different widths, *viz*., multiple silicate chains, parallel to the axis *c* can irregularly alternate along the axis *b*. Such structures can also be described as structures composed of layers of different widths, which alternate in a disordered fashion along the axis *b*.

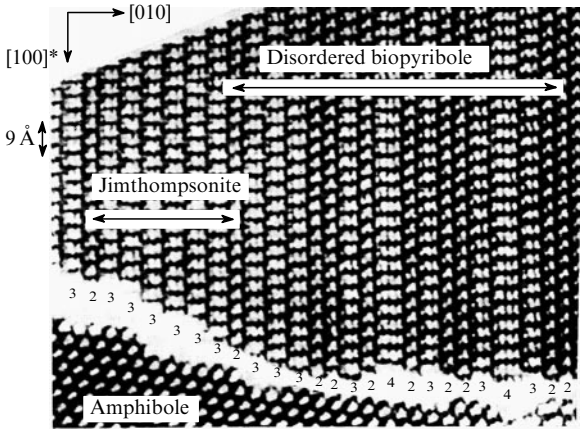


Figure 16. High-resolution TEM image of a biopyribole crystal. Numbers refer to the silicate chain multiplicity [(2) amphibole; (3) jimthompsonite, (4) quadruple-chain silicate].[30]

One would also expect that structures built from fibres (columns) with different compositions, which are several ten angstroms in thickness and are distributed in a disordered fashion, will be found among minerals and synthetic crystals with cylindrical lattices (serpentines, molybdenites, tochilinites, graphites and halloysites)[30,45] (Fig. 17). The disordered distribution of the corresponding modules (layers or columns) was often observed in the above-described incommensurate composite structures.[25,45,78]

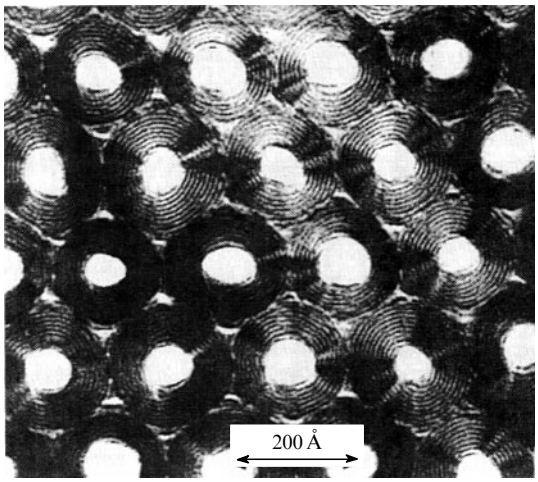


Figure 17. Electron-microscopy image of the cylindrical serpentine (chrysotile).[30]

In the light of the views discussed in Section IV, quasi-homogeneous structures with atomic plane and linear defects can be considered as representatives of a large group of fragmentary solid solutions. These irregular structures have not been adequately studied by diffraction methods not only due to the lack of statistical models for the quantitative description of one-dimensionally periodic systems but also because of a common practice to use probability-statistical models of irregular mixed-layer structures only for obtaining information on real structures of finely dispersed minerals with layered structures, primarily, of silicates. The application of statistical models enables one to substantially extend the possibilities of diffraction methods for studying layered structures of chemically inhomogeneous 'single crystals' of any structural type.[79,80] Such layered structures can be detected on a polarising microscope because the thicknesses of homogeneous zones are only several hundred angstroms.

2. Composite analysis

Quasi-homogeneous structures with atomic defects extended in one or two directions are also composite structures because they consist of two- or one-dimensionally periodic substructures with different structures and(or) compositions, which alternate with a certain degree of disorder. Interatomic interactions within substructures are much stronger that interactions between substructures. Taking into account that there are no restrictions on the ratios between the co-existing modules, these structures should be considered as yet another widespread structural form of non-stoichiometry.

In this case, the matrix σ, which characterises [according to Eqn (1)] the relations between the parameters of two- or one-dimensional sublattices co-existing in the same crystal, either has a dimensionality of 2×2 or is represented by one component, respectively. It is known that the necessary condition for a quasi-homogeneous mixed-layer structure to occur is the similarity of the structural motifs of the alternating layers (see, for example, Refs 30 and 80). Mixed-layer structures can be divided into three groups according to the ratio between the parameters of two-dimensional sublattices co-existing in the same crystal (according to the type of the matrix σ).[78] The first group includes structures with virtually identical sublattices (related by a unit matrix). The second group involves structures with commensurate sublattices related by diagonal matrices with integer components. The third group includes structures with incommensurate sublattices related by matrices with irrational coefficients. For example, structures of perovskite-like superconductors (containing alternating layers with different *n*), a series of mixed-layer silicates (chlorite-vermiculite, kaolinite-smectite, *etc*.), numerous mixed-layer structures formed as a results of layer isomorphism, *etc*. belong to the first group. The second group involves structures in which the unit cell of the layers of one type serves as a supercell of the layers of another type. These structures are typical, in particular, of some varieties of the mineral tochilinite $[Fe_{1-x}S]_2[(Mg,Al,Fe)(OH)_2]_n$ ($x = 0.08-0.28$, $n = 1.58-1.75$).[45] The third group includes disordered varieties of such minerals as koenenite, valleriite, cylindrite, *etc*. (examples of layered composite structures are cited in Section IV). The incommensurability of the layers in the crystal structures of these minerals is associated with their structural differences. However, this effect may also be a consequence of layer isomorphism. Examples are provided by irregular mixed-layer structures found in oceanic sediments (asbolanes).[92] The incommensurability of co-existing two-dimensional sublattices generally leads to substantial structural modulations in the layers.

Apparently, the same effects should be typical also of quasi-homogeneous structures built from columns alternating in a disordered fashion. However, these structures have not been adequately studied by diffraction methods.

3. Symmetry

Without considering modulations, the symmetry of two- or one-dimensionally periodic substructures is characterised by the

symmetry groups of layers G_2^3 or rods G_1^3, respectively. The determination and analysis of these groups were reported, for example, in the monograph.[93]

Two-component mixed-layer structures can be divided into two groups according to the symmetry of alternating layers.[45, 78] The first group includes structures consisting of alternating layers with hexagonal and trigonal symmetry. The second group involves structures built from alternating layers with hexagonal and tetragonal symmetry. Examples of the first group are provided by disordered varieties of valleriite and koenenite. The second group involves, for example, cylindrite and cannizzarite.

4. Diffraction patterns

The weaker are the interactions between the co-existing two- or one-dimensionally periodic substructures, the more similar is the diffraction pattern of the real crystal to a two- or one-dimensional reciprocal lattice, respectively. However, perturbations in the periodicity are most often insignificant and are manifested in the broadening, asymmetric shape, non-integer indices and weaker intensities of particular groups of diffraction reflections. The detection of these characteristic features presents a serious experimental problem, which becomes more complicated at lower concentrations of impurity modules disturbing the long-range order.

Diffraction patterns of irregular mixed-layer structures were discussed in the monographs [76, 77, 90] and reviews.[78–80] Analysis of basal reflections made it possible to distinguish three families of real structures characterised by different ratios between the heights of alternating layers.[78, 80]

1. The heights of layers with different structures differ substantially from each other (by several angstroms). Diffraction patterns of such structures are characterised primarily by non-integer values of basal reflections. If this effect is not observed at low concentrations of impurity layers, the asymmetry of the profiles of different reflections of a series, which is manifested to a variable extent and on different sides of reflections (and is often accompanied by broadening of some reflections), serves as a diagnostic indicator. These diffraction features are characteristic of members of different polysomatic series. Non-integer indices are often observed in diffraction patterns of mixed-layer silicates.

2. The heights of layers with different structures are multiple of each other. In this case, the positions of basal reflections generally correspond to integer indices, but their intensities can be changed in parallel with l. Such diffraction patterns are often difficult to distinguish from those of the corresponding structures with regular superperiods. For example, these patterns are typical of hypothetical mixed-layer structures (see Fig. 13) with the irregular alternation of 7 and 14 Å thick layers.

3. The heights of layers, which differ only in occupancies of crystallographic sites, are nearly identical (differ by only hundredths or tenths of angstroms). In this family, the asymmetry of reflection profiles (in the case of integer basal reflections), which is manifested on the same side and increases in parallel with the diffraction angle, serves as the major criterion for the occurrence of perturbation in the periodicity. These diffraction patterns are typical of intermediate members of isomorphous series and are also obtained for some layered silicates consisting of layers, which differ in the distribution of cations occupying octahedral positions.

5. Ordering

Real structures periodic in less than three directions are less homogeneous compared to all the structures described above. One-dimensionally periodic structures consisting of irregularly alternating columns are not only less ordered than irregular mixed-layer structures but also represent the least homogeneous real form of the crystalline state.

In addition, it should be remembered that the disordered alternation of two- or one-dimensionally periodic modules generally differs from the statistical distribution and tends to be either ordered or segregated. Hence, the degree of order within each of two subgroups, *viz*., the structures with planar and linear defects, varies substantially. The degree of order in the real structures under consideration is additionally reduced due to the insertions of atomic point defects and also due to the non-identity of the co-existing sublattices giving rise to mutual modulations.

VI. Conclusion

The present review surveys real crystal structures, which remain rather homogeneous (quasi-homogeneous) in spite of the presence of numerous atomic impurities (atoms, ions or vacancies). In the structural classification of condensed states (see, for example, Ref. 94), such systems occupy an intermediate place between ideal crystals and one-dimensional periodic structures (polymers and liquid crystals) according to the degree of order. In spaces of dimension m ($m \geqslant 3$), the main types of real structures, which are categorised according to the characteristic features of disorder induced by atomic impurities, are characterised by the symmetry groups G_n^m periodic in n dimensions ($m \geqslant n$, $n \geqslant 1$). Real structures of different types differ in the degree of internal order and, in most cases, are reliably identified from diffraction patterns. These real structures represent all possible structural forms of non-stoichiometry of compounds. In each of three structural types, the degree of order varies substantially and the boundaries between these types overlap.

Atomic impurities present in the structures of host crystals are nucleations of other (real or hypothetical) compounds.[13] Hence, the characteristic feature of the real crystals under considerations is their composite nature. Structures of types I and II consist of two or more three-dimensionally periodic substructures, which are distributed statistically or in an ordered fashion, respectively. Structures of type III are composed of two- or one-dimensionally periodic substructures alternating with different degrees of order. Consequently, real structures of the first type can be described by an average unit cell with mixed occupancies of certain crystallographic sites. Real structures of the second type (without considering mutual modulations) can be represented by two or more types of unit cells, which differ in the structure and(or) composition. Real structures of the third type can be described within the framework of probability-statistical models.

Due to the composite properties, quasi-homogeneous structures with atomic defects of different types can be considered as solid solutions (in essence, always fragmentary), because these compounds are characterised, first, by a rather uniform distribution of components over the bulk of the compound and, second, by the theoretical possibility to vary their ratio (in most cases, this possibility is realised). In principle, these chemically inhomogeneous crystals can be called mixed, if this rather uncertain and seemingly archaic notion is assigned a real structural meaning. It should be remembered that the boundary between composite quasi-homogeneous structures and crystal overgrowths, including epitaxial and syntaxial overgrowths, is substantially blurred.

Crystal structures with atomic defects surveyed in the present review are widespread among minerals and synthetic inorganic compounds (including new promising materials). The above-considered basic classification enables one to substantially simplify their nomenclature.

Taking into account the diversity and specificity of defects found in real crystal structures in exact agreement with their morphogenesis (see, for example, Ref. 80), Zorkii raised the question as to whether it is adequate to discuss the polymorphism of real crystalline substance.[95] The basic classification of crystal structures with atomic defects on the basis of symmetry (primarily, translational symmetry) [2, 4] allows one to state that such a phenomenon as polymorphism actually occurs. Analysis of thermodynamic and energy characteristics of the above-considered types of real crystal structures is beyond the scope of the present review. One can become acquainted with the energy theory of classical solid replacement solutions by reading the monographs

by Urusov[8,96] and publications of his colleagues (see, for example, Refs 97 and 98). The possibilities of the use of superspaces for calculations of the energies of incommensurate composite structures were discussed in the review.[25]

The polymorphism of amorphous compounds was studied.[99,100] The data published in the literature provide evidence that this phenomenon is typical of all structural forms of the condensed state.

Early in the 20th century, when discussing the real crystal structures, E S Fedorov wrote: 'When we dealt with perfect crystals, we operated with one of the most precise sciences of the mathematical field, the so-called theoretical crystallography. When our attention is directed to imperfections in the crystal formation, we go beyond the scope of this science and enter in the field of empirical sciences. There is no doubt that new areas of the science will be developed, which will allow one to study such phenomena using precise mathematical laws'.[101]

The data surveyed in the present review provide evidence that the accumulated knowledge enables one to make steps forward in this direction. The above-described basic classification on the symmetry basis can be considered as the starting point for developing the notion of the polymorphism of real crystals.

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