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Ordering and polytypism in $A^{II}_3B^{V}_2$ crystals

G.P.Chuiko, N.L.Don, V.V.Ivchenko

Laboratory of the Solid State Theory, Department of General and Applied Physics, Kherson State Technical University, 24 Berislavske Shosse, 73008 Kherson, Ukraine

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The ordering processes of stoichiometric vacancies within cationic sublattices were considered for Zn_3P_2, Cd_3P_2, Zn_3As_2, Cd_3As_2. It has been shown that two different types of ordering are possible in these crystals: positional and orientational. Typical energies for the first of them have been estimated to be 78, 71, 66 and 62 meV, respectively. It has been found that the mutual transformations of tetragonal phases could be interpreted as standard transitions between different polytypes.

Рассмотрены процессы упорядочения стехиометрических вакансий в катионных подрешетках Zn_3P_2, Cd_3P_2, Zn_3As_2, Cd_3As_2. Показано, что в этих кристаллах возможны два разнородных типа упорядочения: позиционное и ориентационное. Оценены характерные энергии первого из них: 78, 71, 66 и 62 мэВ, соответственно. Выяснено, что взаимные превращения тетрагональных фаз можно интерпретировать как стандартные переходы между различными политипами.

The materials of the general chemical formula $A^{II}_3B^{V}_2$ are remarkable for the variety of crystalline forms. They have its anion sublattices in the close proximity to the standard *FCC* packing. Their cations occupy only three quarters of the tetrahedral voids between the anions [1–3]. Their cationic sublattices contain exactly one quarter of vacancies which may be recognized even as stoichiometric. Different arrangement ways of these vacancies determine the key features of all the crystalline forms. The fully disordered phases have, for example, a cubic symmetry. The partially ordered crystals demonstrate a tetragonal symmetry both with the center of symmetry and without it [1–3]. Such rebuilding of the tetragonal phases is associated with the polymorphism [1–4]. Other sources [5–7] were pointing out, however, that polymorphous modifications should be distinguished by the following factors:

- by different coordinating numbers;
- by various arrangement motives of cations in voids under conditions of the packing type invariance as well as of the coordination numbers of anions;
- by the presence of a small turn of some structural groups;
- by rotation of separate molecules or radicals;
- by distinctions in fundamental properties.

Several experimental confirmations exist only for the second point of the above list. Therefore, distinctions in the arrangement motives of cations are the only and important argument for the polymorphism supporters. It has been pointed out in [7] however, that a substance can be often crystallized in forms for which lattice parameters are invariable in two spatial directions but vary in the third one. The packing distinctions in such crystals may be observable only within second coordination spheres. That is why many authors consider such "one-dimensional polymorphism" as its special case, i.e. the polytypism. The properties of polytypes are not so sharply different physically and chemically as for various po-

lymorphous modifications [7]. In particular, it has been pointed out [8, 9] that the polytypic transformations are special cases of the "order-disorder" type transitions. Consequently, they are either the second order phase transitions of the, or are quite like thereto [10–12]. Only two types of transitions between polytypes are considered as standard ones [7]:

- the transitions with the change of number of non-equivalent layered packages, but without the change of the structure of any package;
- the transitions without the change of number of non-equivalent layered packages, but with the change of structures of the part of packages.

Thus, the transformations attracting our attention belong to the "order-disorder" type. They do not change the packing as well as the coordination numbers anions and seem to be the second order phase transitions [1–4, 10–12]. Those transitions are accompanied only by insignificant changes of physical properties [1, 3, 13–16] and a small lattice deformations in the main crystal axis direction [15, 17–19]. Such a set of the features allows to suppose that at least a part of these crystalline forms would be worthy of the recognizing as polytypes. So three main aims of this work are as follows. We are going to investigate the arrangement motives of the vacancies and thus to verify the above supposition. We intend also to revise the concepts [2, 10, 11, 18–20, 22] of the interrelations between these crystalline forms. The structural analysis will allow to propose a simple model for the "order-disorder" type transformations in these compounds as well as to evaluate their typical energies.

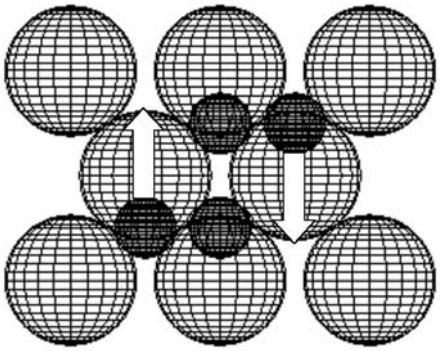

Fig. 1. A cubic fragment of antitype Ag_2O_3: projection on the (110)-plane. Two white arrows show the possible transitions inside united voids from one cations position to another possible one.

Table 1 presents all currently known crystalline forms of the $A^{II}_3B^V_2$ compounds. Let us start the analysis with the high temperature cubic β-phase. A model of a structure fragment of the β modification is presented in Fig. 1. The cations occupy "randomly" only six of eight tetrahedral voids between the anions, both vacant voids being located strictly along one of four spatial diagonals of the cubic fragment [22]. This model is known as the lattice of anti – Ag_2O_3 type [21, 22]). Here and on, the prefix "anti" means solely the place interchange between the cations and anions. The symmetry of every fragment is $Pn3m$–O^4_h. More exactly, it is the symmetry of a structure consisting of identical fragments belonging to one of four possible types. The disordered cubic phase should be generally a truly random mixture of the four fragment types. Each of those differs from others by the spatial orientation of the vacant void

Table 1. Description of crystalline forms

Description of crystalline form	List of compounds	Notes
β-phase; cubic space group is either $Fm3m$–O^3_h or $Pn3m$–O^4_h ; (number of atoms per a cell) $z = 10$	Zn_3P_2, Cd_3P_2, Zn_3As_2, Cd_3As_2,	Disordered, high-temperature phase
α″-phase; tetragonal space group $P4_1mnc$–D^{15}_{4h}; $z = 40$	Zn_3P_2, Cd_3P_2, Zn_3As_2, Cd_3As_2	The lattice is some-what compressed along the main axis. It has been observed only as an epitaxial layer Zn_3As_2
α′-phase; tetragonal space group $P4_1nbc$–D^{11}_{4h}; $z = 160$	Zn_3As_2, Cd_3As_2	The lattice are some stretched; a symmetry centre is present
α-phase; tetragonal space group $I4_1cd$–C^{12}_{4v}; $z = 160$	Zn_3As_2, Cd_3As_2	The lattice is more stretched; low temperature phase without symmetry centre

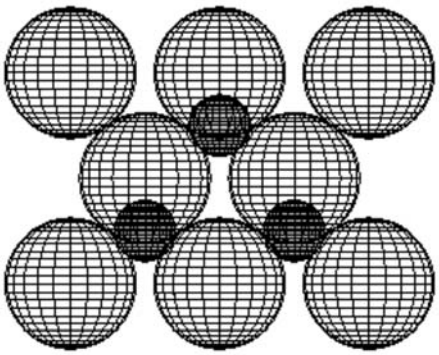

Fig. 2. A cubic fragment of sphalerite type (*s*): projection on the (110)-plane.

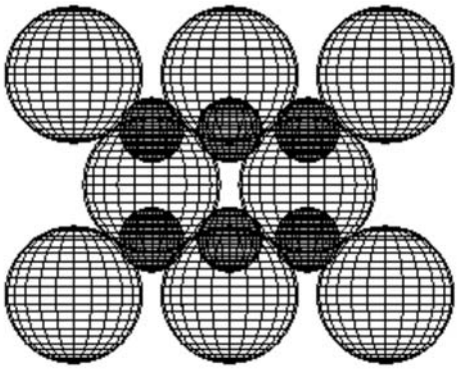

Fig. 3. A cubic fragment of fluorite type (*f*): the projection on the (110)-plane.

pair. Therefore, the direct extrapolation from the fragment symmetry to the whole structure is invalid.

The anion to cation radius ratio in the figures corresponds to the mean point of the range $r_a/r_c \approx (1.9 \div 2.4)$ [5]. The radii ratio to the lattice parameters of the fragments is also shown nearly right in the figures, at least for average magnitudes (0.186 nm and 0.194 nm for $P^{(3-)}$ and $As^{(3-)}$ ions [5] to (0.58÷0.64 nm [1–3, 21], respectively). These figures show clearly that the neighboring tetrahedral voids of opposite sorts are intersected in pairs and as a result form the combined voids with two possible and equivalent positions for the cations. From four such voids in each fragment, some two are filled fully, whereas two others, only by half. The arrows in Fig. 1 show transitions of two cations from one possible position to another inside both semifilled combined voids. Therefore, just two concerted transitions of the cations provide the transformation of the fragment type.

An alternative model images the same structure as a random mixture of the cubic fragments of two types. These are fragments of the sphalerite type, or ZnS, and of the fluorite type, or anti–CaF_2 [2]. Both (as *s*,*f*) are presented in Figs. 2, 3 being denoted as s_1 and s_2, respectively. Both the above-mentioned sphalerite cells $V(s_1,s_2)$ are linked together by the inversion operation in the cell symmetry center. Any of four combined voids is filled with the cations only by half in a sphalerite-like fragment. Its symmetry is $F\bar{4}3m$–T_d^2. The small cube of cations inside the fluorite type cell may be presented as a combination of two mutually inverted tetrahedrons. All combined voids are filled fully within the fragments of the type of fluorite. The fragment symmetry is $Fm3m$–O_h^5. The absence of the long range order and the presence of two types of the sphalerite-like cells in the structure can create the illusion of the central symmetry. Perhaps that is why this phase has been described the spatial symmetry group of the fluorite [2, 19, 20], while the symmetry of the sphalerite fragments is a half lower.

Now let the partially ordered α″ phases be considered. It is more convenient to consider the structure of this crystalline form in the same coordinates as those used for α, α′-phases. For this purpose, it is sufficient to transform the primitive elementary cell into a non-primitive cell with the additional site in the basis center and the double number of atoms. The following simple relation relates the basic translations of the extended elementary cell (EEC [23]) to those of the primitive cell:

$$\begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix} = \begin{pmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_0 \\ \mathbf{b}_0 \\ \mathbf{c}_0 \end{pmatrix}. \qquad (1)$$

In the EEC coordinate system, the crystalline structure of the α″ modification can be presented as a sequence of two non-equivalent layered packages alternating along the main axis — *X*,*Y*. Every package consists of four atomic layers. Each package contains two different layers of the closely packed anions (α, β) alternated by two layers of cations (*A*,*B*), so that: $X = \alpha A \beta B$. The atomic layers, as well as the layered packages, are normal to the main crystal axis. It is possible to present the structure of each package by two methods. The first method uses four types of anti–Ag_2O_3 cells as the package fragments [1, 21, 24]. This fragments may be denoted as 1, 2, 3, 4 in

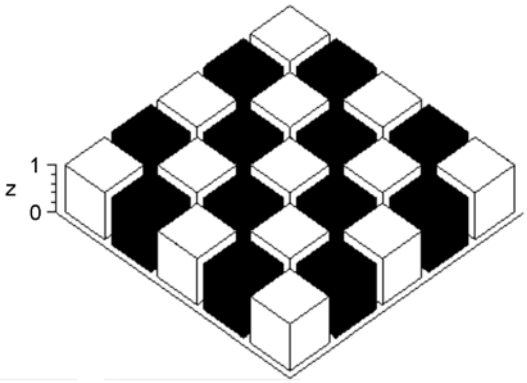

Fig. 4. The model of a basic package (X) for α''-phase. The fragments of fluorite type (f) are black, the sphalerite type fragments ones (s), white.

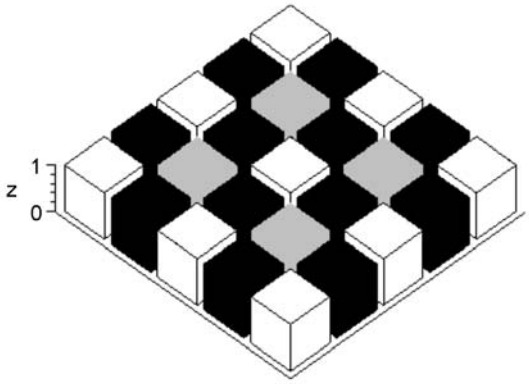

Fig. 5. The model of basic package (X) for α, α'-phases. White and grey cubes symbolize two kinds of sphalerite fragments (s_1, s_2).

clockwise direction starting from a corner of the small cube of the cations. Then the package X contains the fragments of 2 and 4 types organized in a chess order. The package Y is the same "chess-board" but consisting of 1 and 3 type fragments. The second way to representation of these packages is described in [2, 20, 24]. Each package is an alternation of only two cubic fragments of sphalerite and fluorite types,which are organized like a chess-board. Their combination within limits of a package is shown in Fig. 4 (s, f as white and black cubes).

The two different fragments of the sphalerite type (s_1, s_2) are indistinguish — able both in this package and in the whole structure. This means that each of such fragments may be either of the s_1 type or of the s_2 one at equal probability. Otherwise, all of them must belong to one and the same sort (e.g. s_1). There are no other options compatible with the saving of the phase structure. The layered packages X and Y are though non-equivalent, but compatible by means of translations. In fact, the package X is transformed to the package Y, and vice versa, by the partial translations $\boldsymbol{n}_a = (\boldsymbol{a} + \boldsymbol{c})/2$ and $\boldsymbol{n}_b = (\boldsymbol{b} + \boldsymbol{c})/2$ in the EEC coordinate systems. This corresponds to the shift vectors in the coordinate system of the primitive cell: $\boldsymbol{n}_a = (\boldsymbol{a}_0 - \boldsymbol{b}_0 + \boldsymbol{c}_0)/2$ and $\boldsymbol{n}_b = (\boldsymbol{a}_0 + \boldsymbol{b}_0 + \boldsymbol{c}_0)/2$. The packages have identical structures and are compatible with one another by shift vectors n_a or n_b. The ordering in the α''-phase structure may be similar to the ordering of components in a binary alloy. The ordering of two types of atoms in such alloy corresponds to the ordering of positions of fragments of two types: s and f. All the coordinating numbers are conserved here.

Really, $z = 6$ both for the fragments (as though of "atoms"), and for the vacancies in relation to the cations. In other words, the transition $\alpha'' \leftrightarrow \beta$ can be considered as a positional kind of the "order-disorder" transformations within limits of first coordination spheres of two types fragments: s and f. Each of them operates as a structural unit. It has been noted [2] that "a place transposition" of two neighboring different type fragments $s \leftrightarrow f$ corresponded to transitions of four cations into the nearest tetrahedral voids.

Now let the low temperature and ordered α, α'-phases be considered. The unit cells of these phases must contain four layered packages as it follows from Table 1. The reason therefor is the doubled number of atoms in cells and the doubled lattice parameter along the main crystal axis direction. Let be noted also that the number of packages does not change at the low-temperature transformations $\alpha' \leftrightarrow \alpha$. The structure of all packages also demonstrates some changes in the $\alpha'' \leftrightarrow \alpha'$ transformations. The package X, being the main structural element of the α, α' phases, is similar at first glance to that presented in Fig. 4. However, layered packages of the low-temperature phases consist of cells of not two but three types (Fig. 5). These are the same cells of the fluorite type (the black cubes) and two types of the sphalerite cells (they are shown in white and gray colors). The sphalerite-like cells of two different types (s_1, s_2) alternate regularly along the crystalline directions [110] and [1$\bar{1}$0]. Therefore, six black cubes (fragments f) form the first coordination sphere for white or gray cubes (fragments s_1, s_2). Each fragment of this couple is included only in the second

coordination sphere of the other. The transitions $\alpha' \leftrightarrow \alpha''$ have to be recognized as the "order-disorder" type ones like the transitions $\alpha'' \leftrightarrow \beta$. The only distinction is that here we deal with an orientation ordering within second coordination spheres of the sphalerite type fragments. This result was unknown up to now, and it induces to consider α''-phases as structures with the orientation disorder in second coordination spheres, although and organized positionally in the first ones.

The layered packages of other three types can be got by the already known translations of the X package presented in Fig. 5 according to the following rules:

$$X + \boldsymbol{n}_a = \overline{Y};\ \ X + \boldsymbol{n}_b = Y;\ \ X + \boldsymbol{n}_a + \boldsymbol{n}_b = \overline{X} \quad (2)$$

Here, $\boldsymbol{n}_a = \boldsymbol{a}/2 + \boldsymbol{c}/4$ and $\boldsymbol{n}_b = \boldsymbol{b}/2 + \boldsymbol{c}/4$ are the same shift vectors as mentioned above for the α'' phase, but both are being written down for the twice-higher unit cell. The structures of all considered tetragonal phases by symbols of packages as follows: α''-phase (D_{4h}^{15}–$P4_2/nmc$). This structure consists of only two layered packages (Fig. 4) compatible by any shift vector of the set ($\boldsymbol{n}_a$, $\boldsymbol{n}_b$), i.e.:

$$...XY/XY/XY.... \quad (3)$$

here

$$X + \left\{ \begin{array}{c} \boldsymbol{n}_a \\ \boldsymbol{n}_b \end{array} \right\} = Y. \quad (4)$$

The shift vector between different packages takes one of values from this set of translations in a random fashion.

α'-Phase (D_{4h}^{11}–$P4_1/nbc$). This phase structure consists of four packages of type different from the previous structure (see Fig. 5) and is imaged as:

$$../XYX\overline{Y}/XYX\overline{Y}/XYX\overline{Y}.... \quad (5)$$

Thus, the shift vectors between packages (2) are ordered in each unit cell as follows:

$$.../X(\boldsymbol{n}_b)Y(\boldsymbol{n}_b)X(\boldsymbol{n}_a)\overline{Y}(\boldsymbol{n}_a)/X... \rightarrow \quad (6)$$
$$\rightarrow .../X(\boldsymbol{n}_b\boldsymbol{n}_b\boldsymbol{n}_a\boldsymbol{n}_a)/X....$$

The packages (3, 4) and (5, 6) differ only in every fourth layered package ($\overline{Y} = Y + (\boldsymbol{a} + \boldsymbol{b})/2$). Nevertheless, such a minor change of the packing manner results in ordering of both the shift vectors between packages and two different sorts of the sphalerite type fragments.

α-Phase ($C_{4v}^{12} - I4_1cd$). This structure consists of the same packages that α' modification but they are arranged in a slightly other order:

$$.../XY\overline{X}\overline{Y}/XY\overline{X}\overline{Y}/XY\overline{X}\overline{Y}/.... \quad (7)$$

The shift vectors between packages in this phase are also regular but demonstrate a bit another organization manner:

$$.../X(\boldsymbol{n}_b)Y(\boldsymbol{n}_a)\overline{X}(\boldsymbol{n}_b)\overline{Y}(\boldsymbol{n}_a)/... \rightarrow \quad (8)$$
$$\rightarrow .../X(\boldsymbol{n}_b\boldsymbol{n}_a\boldsymbol{n}_b\boldsymbol{n}_a)/....$$

For the α''-phases, as well as in the case of the α, α' phase structure, we did not take into account small tetragonal distortions of lattices and some displacements of atoms from their ideal positions [1–4, 17].

In the structure of the β phases and α'' ones, the sphalerite cells of two types (s_1, s_2) are not distinguished. This means that the $\beta \rightarrow \alpha''$ transformation results in the ordering of only two types of the quite different fragments, i.e. their positions within of the first coordination spheres. It is possible to interpret the α''-phase structure to be similar to an ordered binary alloy with the AB composition (here $A = s$, $B = f$) with a positionally ordered fragments at the critical temperature. Under the "quasi-chemical" approximation [18], at the limiting $T \rightarrow T_c$ the ordering process activation energy of the alloy structure units A and B at the coordination number $z_1 = 6$ has the form

$$\varepsilon_1 = 2\ln(3/2)k_0T_{c1} \approx 0.81093 \cdot k_0T_{c1}. \quad (9)$$

The calculation results are presented in Table 2.

The orientation ordering in the subsystem of the sphalerite type fragments (s_1, s_2) arises up in the second coordination spheres of the fragments at another coordination number, $z_2 = 12$. This ordering type is observable in the transitions of $\alpha'' \leftrightarrow \alpha'$ type.

Table 2. The temperatures of "order-disorder" transitions and typical energies of the positional ordering, calculated from (9)

Compound	T_{c1}, K	T_{c2}, K	ε_1, eV
Zn_3P_2	1118	–	0.078
Cd_3P_2	1010	–	0.071
Zn_3As_2	945	–	0.066
Cd_3As_2	876	739	0.062

Evaluations of its energy result in the relation $\varepsilon_2 < \varepsilon_1$.

Systems having the more than of one kind of disorder, including the crystals of $A^{II}_3B^V_2$ group, are known a long ago [23]. These materials demonstrate two different mechanisms of the ordering, see Table 2. At $(z_2\varepsilon_2)/(z_1\varepsilon_1) << 1$, an orientation disorder shall arise with the increasing of temperature as the first one. A position disorder appears at a higher temperature point. Perhaps cadmium arsenide (Cd_3As_2) corresponds to such a behavior, although the $(T_{c1} \div T_{c2})$ interval is rather narrow. At $(T_{c1} \approx T_{c2})$, $z_2\varepsilon_2/z_1\varepsilon_1 \sim 1$ [23], and it seems to be a more realistic condition for our materials.

Such a kind of systems can be observed both in the equilibrium state relative to all the parameters of order as well as in the "frozen", non-equilibrium state relative to one of them. We suppose that such a situation is most probable for the α'' phase of zinc and cadmium phosphides (Zn_3P_2, Cd_3P_2). The orientation ordering in these materials does not occur or occurs extraordinarily slowly. There have been investigated samples of Cd_3P_2, namely, the sublimated crystals "frozen" from $T = 900$ K, as well as annealed at $T = 600$ K [24]. The materials of both groups were identical in crystalline structure accordingly to the X-ray diffraction data. However, they had different parameters of spin-lattice relaxation that were shown by the NMR on P^{31} isotopes nuclei. Consequently, the crystal lattices of "frozen" and annealed samples were not equivalent in all respects, despite of the full identity of all crystal parameters.

The α'' phase crystals of Zn_3As_2 and Cd_3As_2 as well as strained epytaxial layers (Zn_3As_2) can be considered as position-ordered systems with an orientation disorder. Thus, the transitions $\alpha'' \rightarrow \alpha'$ are similar to the standard polytypic transformations. Indeed, in this case, we deal with a transformation of the two-package structure in the four-package one, but without any substantial change of both the structure and the symmetry of the basic package. The $\alpha' \rightarrow \alpha$ transitions are the second type of standard polytypic transformations, mentioned in introduction. In fact, these occur without a change of the package number, but with an insignificant structure change in one quarter of them. Both transformations belong to the "order-disorder" type.

Moreover, the phase transition with the loss of the positional order, that is typical of all considered compounds, belongs to this type. It is to note that the evaluations of typical positional ordering energy values (see Table 2) are only somewhat higher than typical elastic deformation energies of the lattices which have been estimated in [15]. Therefore, the small tetragonal deformation, which we did not take into account, can be the reason of a considerable anisotropy in the frequency of the cation transitions inside the united voids, both of those occurring in the package plane and of others taking place in the normal direction (along the main axis), for example. This problem seems to be worth of a separate consideration,.

To conclude, results of the analysis and discussions allow us to formulate the following conclusions. The crystalline lattices of all modifications the $A^{II}_3B^V_2$ group compounds can be presented as superstructures built of cubic fragments of three types. One of those is the fluorite type of and two other are belong to the sphalerite type (according to [2, 18]). The high-temperature cubic β-phases of these materials demonstrate simultaneously disorders both in position and in orientation of the fragments. The positional order arises in the transitions $\beta \rightarrow \alpha''$ from the high temperature cubic phase into the tetragonal one. This positional order appears within the first coordination sphere of the fragments of essentially different types (the fluorite type and any phalerite type). Typical positional ordering energy values exceed only slightly the evaluations of typical energy of the tetragonal deformation of the α'' phase lattices. The orientation order arises in the mutual transformations of the tetragonal phases. The orientation ordering appears within the second coordination spheres of the different sphalerite type fragments. Various tetragonal phases of these materials can be recognized as polytypes, and their mutual transformations, as polytypic transitions.

All the above statements are presented for discussion for the first time, except for the first that has been cited in [2, 18].

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Впорядкування та політипія у кристалах $A_3^{II}B_2^{V}$

Г.П.Чуйко, Н.Л.Дон, В.В.Івченко

Розглянуто процеси впорядкування стехіометричних вакансій у катіонних підгратках Zn_3P_2, Cd_3P_2, Zn_3As_2, Cd_3As_2. Показано, що у цих кристалах можливі два відмінних типи впорядкування: позиційний та орієнтаційний. Оцінено характерні енергії першого з них: відповідно 78, 71, 66 і 62 меВ. З'ясовано, що взаємні перетворення тетрагональних фаз можна інтерпретувати як стандартні переходи між різними політипами.