The second coordination sphere is a dodecahedron consisting of Th atoms. Th atoms of different trapezoids can be distinguished. Axes $\bar{4}$ of the dodecahedra built by P atoms pass along axis x for Th atoms of one trapezoid of the second coordination sphere and along axis y for Th atoms of another one, axis $\bar{4}$ of the central 'phosphorus' dodecahedron being directed along the z axis of the crystal. Axis $\bar{4}$ of the dodecahedron of Th atoms is also directed along the z axis but the dodecahedron of Th atoms (of the second coordination sphere) is rotated through an angle of 90° with respect to the P dodecahedron of the first coordination sphere. This process of 'expansion' of the crystal lattice may be continued infinitely.

Discussion

As follows from the examples considered above, the crystal-chemical model of atomic interactions is equally applicable to metals and intermetallic compounds, to substances with mainly ionic bonding, to covalent materials such as diamond, and to crystals with the van der Waals interactions (between inert-gas atoms). This is possible because the model takes into account the attraction between atoms and the mutual repulsion of filled electronic shells (skeletons) of atoms. The ability of the model to describe such a wide range of crystal structures should make it a universal tool for crystal-chemical analysis.

In conclusion it should be noted that the examples used in the present paper were dictated not only by the crystal systems but also by the models of crystal structures collected at the Chemical and Geological Departments of the Moscow State University. Such models were a substantial help in the determination of the coordination spheres and made our work much more successful.

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Crystal-Chemical Model of Atomic Interactions. 2. Hexagonal, Trigonal and Tetragonal Systems

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Abstract

The crystal-chemical model of atomic interactions suggested by Aslanov [*Acta Cryst.* (1988), B**44**, 449–458] has been verified on crystal structures of hexagonal, trigonal and tetragonal symmetry. The model includes the concept of close packing of spheres, but also explains the formation of structures with atomic arrangements deviating from closest packing. A reduction of crystal symmetry affects individual atomic interactions and the shape of coordination polyhedra in the first and subsequent coordination spheres.

Introduction

In the previous paper (Aslanov, 1988) it has been shown that atoms in a crystal structure which interact one with another arrange in the crystal around the

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central atom or a cluster and occupy the vertices of Platonic regular solids (PRS's), Archimedean semiregular solids (ASRS's) or polyhedra built from triangular faces alone, *e.g.*, an eight-vertex dodecahedron. The suggested model has been verified on cubic crystals characterized by isotropic atomic interactions. Twenty structure types have been derived, and the appearance of the translation symmetry in crystals has been explained. In the present paper the model is tested on 15 structure types of crystals belonging to the hexagonal, trigonal and tetragonal systems.*

Model verification

Hexagonal and trigonal systems

Two-layer hexagonal packing (h.c.p.; ...*ABAB*...) is typical for structures of numerous metals, *e.g.*, magnesium, and for the inert gas helium. The first coordination sphere of the central atom is built by neighboring atoms situated at the vertices of a hexagonal cuboctahedron not belonging to the ASRS's since its dihedral angles are of two different kinds. But the stability of such a polyhedron may be explained under the assumption that the curve of the pair-interaction energy for atoms in such a structure is less steep than for face-centered cubic (f.c.c.) crystals.

This curve runs between similar curves (Fig. 1) for f.c.c. [curve (*a*)] and b.c.c. [curve (*c*)] structures. In this case the contribution to the total crystal energy from interacting atoms having no direct contact in the structure increases. It concerns, in particular, the interaction of atoms located on opposite faces of the cuboctahedron. Such interactions do not necessarily give rise to the transformation of the polyhedron into a hexagonal cuboctahedron. They may simply flatten the cuboctahedron along the threefold axis thus bringing the opposite triangular faces of the cuboctahedron closer to one another (as is the case in the structure of mercury) or flatten it along the fourfold axis bringing closer the opposite square faces of the cuboctahedron (as is the case in In and γ-Mn structures). More often, however, another variant is encountered – all the vertices of the cuboctahedron remain on the sphere, whereas one of triangular faces rotates through 60°, thus transforming the cuboctahedron into its hexagonal analogue. The distances between the vertices of triangular faces forming the trigonal prism change upon rotation. Instead of six equal distances we now have three short and three long distances (Fig. 2). Short distances are observed along the edges of the trigonal prism parallel to the threefold axes, and long distances along the diagonals of rectangular faces. These distances are on the right-hand side of the minimum of the atomic interaction curve (the minimum corresponds to the shortest distance, *e.g.*, the distance between the atoms of the first coordination sphere and the central atoms). Since this portion of the curve is bent, the shortening of the distance may result in a decrease of the crystal energy which is much larger than the gain in the crystal energy caused by an increase of the distance (Fig. 2). This becomes more probable the steeper the

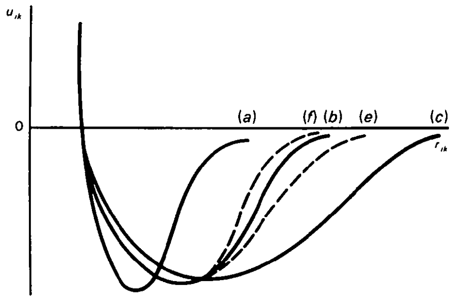

Fig. 1. Atomic interaction curves (arbitrary scale): (*a*) f.c.c., (*b*) h.c.p., (*c*) b.c.c., (*e*) structure of Zn or Cd, (*f*) structure of La (h.c.).

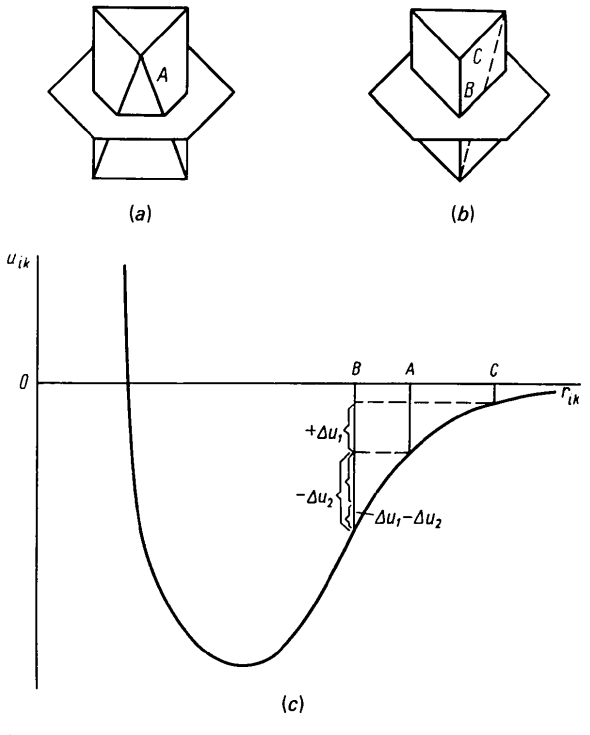

Fig. 2. The problem of variation in energy caused by the substitution of a cuboctahedron by its hexagonal analogue for a complex of 13 atoms. (*a*) Interatomic distances (*A*) in the trigonal antiprism which is a fragment of a cuboctahedron: (*b*) Short (*B*) and long (*C*) interatomic distances in a trigonal prism which is a fragment of a hexagonal cuboctahedron. (*c*) Δu_1 is an increase in the energy of pairwise interaction owing to an increase of interatomic distances from *A* to *C*, Δu_2 is a decrease in the energy of pairwise interaction owing to a decrease in interatomic distances from *A* to *B*, $(\Delta u_1-\Delta u_2)$ is the total change in the energy.

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* The data on space groups and atomic coordinates of the structures under consideration are taken from the *Metals Reference Book* (Smithells, 1976) and from Bokii (1954).

right-hand portion of the curve in Fig. 2 becomes (but in all the cases it is less steep than for an f.c.c. crystal). The interactions between the atoms of the second coordination sphere may turn out to be so weak that their contribution to the crystal energy will be insignificant. Indeed, the second coordination sphere in h.c.p. crystals is a distorted trigonal prism with the edge of a triangular face (90·00°) much larger than the edge parallel to the threefold axis (70·53°). In zinc and cadmium structures atoms interact presumably at distances larger than those known for other h.c.p. structures (the right-hand portion of the curve in Fig. 1 is flatter). As a result, the trigonal prism of the second coordination sphere is more similar to an ASRS, namely, in the cadmium structure the angle of a triangular face becomes as low as 85·26°, whereas the edges parallel to the threefold axis increase up to 78·47°. Such changes are accompanied by a distortion of the first coordination sphere in the cadmium structure (in comparison with h.c.p.). The edges inclined to the threefold axes of the hexagonal cuboctahedron increase from 60 to 63·11°. But a flatter atomic interaction curve for cadmium (zinc) in comparison with that for h.c.p. structures (Fig. 1) provides only an insignificant increase of the crystal energy caused by such an elongation.

The contribution which comes from atomic interactions in the second coordination sphere decreases the total energy of the crystal.

Hexagonal close packing may also be built by atoms of different kinds forming different layers, *e.g.*, two layers of S atoms and a third layer of Mo. In other words, the alternation of layers ...*ABABAB*... corresponds to the sequence of atoms ...MoSSMoSS.... As a result, we arrive at the MoS_2 structure.

Now consider the combinations of at least two coordination spheres in a way similar to that used in the previous paper (Aslanov, 1988). Let us assume that the first coordination sphere of the central atom is a tetrahedron (Fig. 3) and the second a hexagonal cuboctahedron which envelops the tetrahedron in the direction along the threefold axis and three symmetry planes passing along this axis. We thus arrive at the lonsdaleite structure – a hexagonal analogue of diamond. The same structure built by atoms of two different kinds corresponds to wurtzite (ZnS). For the latter structure it is not important which atom is placed at the center; what is important is that the different atoms alternate in subsequent coordination spheres, *e.g.*, a Zn atom in the center, S atoms in the first coordination sphere and Zn atoms in the second coordination sphere.

An important combination of coordination polyhedra around the central atom is that of a trigonal prism flattened along the 3 axis in the first coordination sphere with a hexagonal cuboctahedron in the second sphere (Fig. 4). Each atom of the second sphere builds its surroundings up to a trigonal prism in its first coordination sphere and to a hexagonal cuboctahedron in the second sphere. Such a sequence leads to a lattice of the ... *ABAC* ... or ch type. The representatives of this structure type (La, Pr, α-Nd) are seldom among the structures of simple substances.

If a structure of the La type consists of an equal number of atoms of two kinds, we arrive at the NiAs structure with Ni atoms filling the cubic layers and As atoms filling the hexagonal layers (...*ABAB*... ... chch ... ... NiAs NiAs ...). If the atomic ratio in a binary structure is 1:3, then one of four layers in the La structure is filled with one kind of atoms, whereas three other layers are occupied by atoms of the other kind. An example here is the α-UO_3 structure where one of the cubic layers (*A*) is occupied by U atoms. The structure is flattened along the sixfold axis; as a result, an octahedron of the first coordination sphere of the U atom is complemented by two O atoms lying above the centers of the opposite faces of the octahedron, thus forming a slightly distorted cube.

The structure of corundum (α-Al_2O_3) is also a derivative of the La type. Cubic layers *A* are occupied with Al atoms whereas hexagonal layers (*B* and *C*) are filled by O atoms, positions *A* being filled only partly, in accordance with the stoichiometry. In each cubic layer, Al atoms form graphite-like nets displaced with respect to one another, which can be understood by comparing the corundum structure with NiAs. Thus the corundum structure belongs to the NiAs structure type in which Ni atoms are replaced by Al, and O atoms are replaced by As. The closest contacts in the structure are observed for Ni atoms forming chains along the short edges of trigonal prisms. Since two-thirds of the metal

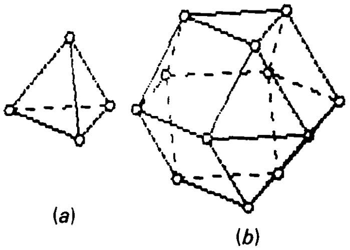

Fig. 3. The lonsdaleite structure: (*a*) and (*b*) are the first and second coordination spheres, respectively.

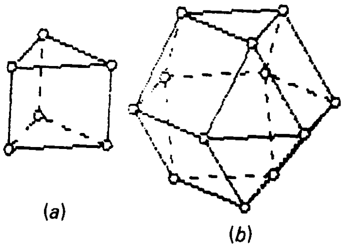

Fig. 4. The lanthanum structure: (*a*) and (*b*) are the first and second coordination spheres, respectively.

positions are occupied, each third position in the series $\ldots AA\textcircled{A}AA\textcircled{A}\ldots$ is vacant. This makes remaining pairs of atoms move towards empty trigonal prisms, and results in the corrugation of A layers. Vacancies in the corundum structure are arranged over the vertices of a rhombohedron whose edges are equal to the diagonal of the rectangular face of a trigonal prism (the first coordination sphere of As atoms in the NiAs structure). This rhombohedron in NiAs is very close to a cube, being only slightly elongated along the threefold axis. The presence of vacancies results in the 'compression' of the rhombohedral lattice along the threefold axis up to $\alpha = 55{\cdot}10°$ for corundum instead of $\alpha = 53{\cdot}76°$ for ideal hexagonal packing. This makes the rhombohedron even more similar to a cube. As shown by the corundum structure, the first coordination sphere of an O atom should not necessarily be a trigonal prism; it is sufficient to have only its fragment of four Al atoms.

The structure type of ilmenite, $FeTiO_3$, and $LiNbO_3$ (Wells, 1984) differs from corundum only by the arrangement of metal atoms (in the $FeTiO_3$ structure they form layers). A layer of Fe atoms alternates with a layer of Ti atoms to form a hexagonal arrangement. In the $LiNbO_3$ structure, Li atoms are arranged at the vertices of rhombohedra such as those occupied by vacancies in the α-Al_2O_3 structure, whereas Nb atoms occupy one-third of metal sites of the NiAs structure type and therefore are arranged at the vertices of rhombohedra such as those occupied by Li atoms and vacancies (small distortions of rhombohedra due to the corrugation of the layers of metal atoms can be neglected). If the ratio of metal to O atoms in the structure is 2:3, the La_2O_3 structure type is also possible. In the five-layered stack having cubic packing, O atoms form odd and La atoms even layers. The structure type of the stack is slightly distorted NaCl type, the distortions being caused by high coordination 'capacity' of the La atoms and the low electronic donor ability of the O atoms (Aslanov & Porai-Koshits, 1975). A five-layered stack is electrically neutral. The structure is built by imposition of the stacks one onto another as in cubic close packing.

So in all the examples mentioned both cation and anion layers should be considered together, rather than considering anion packing with cations in the holes.

Tetragonal system

It is convenient to begin the analysis of tetragonal structures with the simplest one – protactinium (Fig. 5). The reference structure for protactinium is b.c.c. type. Let us consider a b.c.c. structure with the a and b axes rotated around the c axis by 45°. The volume of the cell is doubled and the lattice is tetragonal face centered. In fact this is an f.c.c. lattice compressed along the fourfold c axis up to $c/a = 1/\sqrt{2}$. Further compression to $c/a = 1/\sqrt{3}$ gives the protactinium structure, where each atom has ten nearest neighbors and four atoms at a distance 22·5% longer. Thus, the coordination number in protactinium is 14 as in b.c.c. structures, but instead of the six distances in a b.c.c. structure to atoms of the second coordination sphere, each of which is 15% longer than the distance to atoms of the first coordination sphere, there are only four distances 22·5% longer than the shortest interatomic distance.

A somewhat different structure is possessed by PtS (Fig. 6): the first coordination sphere of Pt atoms (a square of S atoms) has no threefold axes in contrast to the second coordination sphere (a cuboctahedron of Pt atoms); this reduces the crystal symmetry to tetragonal.

The third example of a reduction in symmetry from cubic to tetragonal caused by individual features of the structure is chalcopyrite, $CuFeS_2$. Its unit cell is equivalent to two unit cells of the sphalerite type. All S atoms in chalcopyrite are surrounded by two Cu and two Fe atoms occupying the tetrahedron vertices, which results in doubling of the sphalerite-type unit cell.

The above examples – protactinium, PtS and $CuFeS_2$ – indicate that reduction of crystal symmetry to tetragonal may be associated with several factors.

Discussion

The crystal-chemical model of atomic interactions allows the determination of the conditions for the minimum potential energy of multiatomic systems without calculations of crystal energy. Firstly, the model takes into account pair interactions between atoms (the requirement for equality of edges for PRS's and ASRS's). These interactions seem to be decisive for the potential energy of a multiatomic system. Thus the

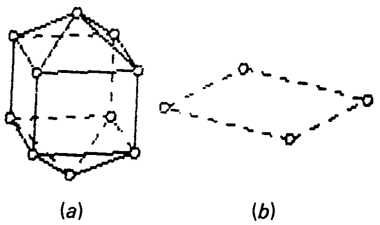

Fig. 5. The protactinium structure: (a) and (b) are two coordination spheres.

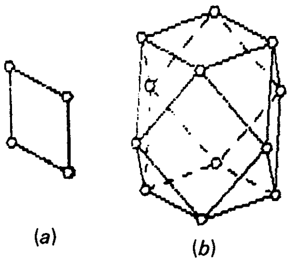

Fig. 6. The PtS structure: (a) S, (b) Pt.

melting enthalpy of elemental metal crystals does not exceed 5% of the atomization energy of the same crystals. In other words, the condensation of a gas into a liquid is responsible for the largest part of the energy of a multiatomic system. Since a liquid has no long-range order, this energy should be ascribed to pair atomic interactions. This also explains the successful structural calculations based on the minimization of the potential energy of crystals obtained by summing the energies of pair interactions (see references in Aslanov, 1988).

Secondly, the model takes account of multiatomic interactions in two different ways. On the one hand, it takes into consideration the interactions of each atom with all the other atoms of the coordination sphere under question (the requirement of symmetry or congruence of polyhedral angles for PRS's and ASRS's). On the other hand, it takes into account the conditions necessary for the appearance of the translation symmetry, which permits each atom of the crystal structure to be considered as the center of another central atom. The intersection of the coordination sphere of different central atoms provides the formation of a crystal structure. Thus the appearance of the crystal symmetry, including translation symmetry, follows from multiatomic interactions which make the potential energy of the system minimal.

The idea that crystal symmetry is a result of the minimization of the potential energy of a crystal is not new. Now we may add that the crystal symmetry also follows from numerous multiatomic rather than pair interactions (pair interactions are known for any condensed phase but neither in liquids nor in amorphous substances do they lead to the appearance of the long-range order). In other words, the model gives the solution to the problem of multiparticle interactions if the forces acting on them are of a central nature. Despite the fact that this solution is at the symmetry level, it is of interest not only for crystallography but also for other branches of science since it is the only known solution to this important problem.

Another important problem in which polyhedra can be used in the model in addition to the PRS's and ASRS's. We have already invoked a hexagonal analogue of a cuboctahedron and an eight-vertex dodecahedron in which atomic interactions are of two types depending on the number of polyhedral angles. For the latter polyhedron, the requirement for edges to be equal is replaced by the requirement for interatomic distances in the coordination sphere of a certain radius to be maximal, which unavoidably leads to polyhedra solely with triangular faces. Thus the coordination polyhedra should meet three important requirements: (i) they must have the maximum number of triangular faces for the given number of vertices, (ii) they must have the minimum number of groups with unequal edges, and (iii) they must have the minimum number of different (noncongruent) polyhedral angles. All three requirements are best met by a tetrahedron, an octahedron and an icosahedron. The systematic analysis of polyhedra with allowance for all these requirements is the subject of another paper, but we may mention here as an example a tricapped trigonal prism which should be the most favorable polyhedron among nonatops since all its faces are triangular, the edges form only two groups (those of the trigonal prism and those of the caps), and the polyhedral angles are also of only two kinds (the vertices of the trigonal prism and those of the caps).

Thus proceeding from general principles, the model permits one to explain the diversity of known structure types. It has all the advantages of close packing, but in addition it provides an explanation of structures with less-dense packing. In contrast to the theory of close packing of spheres, the suggested model does not use atomic or ionic radii but takes account of interatomic distances which affect the energy of pair interactions. Abandoning the atomic and ionic radii permits one to avoid many problems, *e.g.*, it becomes unimportant which ions form the framework of NaCl-type structures and which occupy the voids of such a framework if the structure is built by atoms of approximately equal ionic radii (*e.g.*, KF).

The further development of atomic interactions is essential for understanding layered structures similar to graphite. It seems that crystals of low or moderate symmetry may illustrate how individual features of atomic interactions can affect the crystal structures of various substances. The first results obtained in this direction are very promising.

The author is grateful to Dr L. I. Man who kindly translated this paper into English.

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