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Crystal-Chemical Model of Atomic Interactions. 1. The Cubic System

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Abstract

A crystal-chemical model of atomic interactions has been suggested to explain the diversity of inorganic structure types, their translational symmetry, and other basic characteristics. The model is based on the concepts of the minimum potential energy of a crystal and energy contributions to the total energy of a crystal which come not only from the first coordination sphere but also from the second, third and subsequent coordination spheres. The minimum potential energy is provided by coordination spheres in the shape of the Platonic regular solids or Archimedean semiregular solids and also by polyhedra having triangular faces. The model is applicable to materials with different types of chemical bonding – metals, nonmetals (diamond), ionic compounds and substances with van der Waals atomic interactions.

Introduction

The most general rule explaining the formation of crystals is the principle of maximum filling of space (Vainshtein, Fridkin & Indenbom, 1983) which says that if the forces acting on atoms or complex structure units of a crystal are of a central or almost central nature, then such atoms or units always tend to approach one another so that the number of admissible shortest contacts is maximal. We may also put it in another way: there is a trend to the maximum number of atoms or structural units in the unit volume v with distances r_{tj} between atoms (structure units) not shorter than standard admissible values $r_{\rm st}$:

$$n/v_{(r_{tj}>r_{\rm st})}\rightarrow \max.$$

This geometrical principle is, to some extent, a universal one since it corresponds to the minimum potential energy of the system. The energy U of a crystal may be determined rather accurately (with the exception of intermetallic compounds) if it is considered that the total potential energy is a sum of functions $u_{ik}(r_{ik})$ over all possible atomic pairs

$$U=\tfrac{1}{2}\sum_{i,k} u_{ik}(r_{ik}). \qquad (1)$$

The greater the number of atoms approaching one another up to equilibrium interatomic distances, *i.e.*, the more terms with maximum $u_{ik}(r_{ik})$ values in (1), the higher is the energy U.

The principle of the maximum filling of space is also known in its modified form as the principle of closest packing. It has been considered in detail for inorganic compounds by Belov (1947). However, the densest packing of spheres fails to explain not only the whole diversity of known structure types but even crystal structures of the simplest substances, *e.g.*, of transition metals from groups V and VI of the Periodic Table. These substances are characterized by body-centered cubic (b.c.c.) unit cells in which the density of space filling (68·01%) is essentially lower than that for the closest packing of spheres (74·05%).

The energy of crystal formation from melts may roughly be estimated from such experimentally determinable quantities as the enthalpy of crystal melting – the higher the melting enthalpy the higher the crystal energy.

Let us consider the melting enthalpy for 4*d* and 5*d* elements from Nd to Ag and from Ta to Au (Knunyants, 1983). The choice of this series of metals was dictated by several factors. Firstly, they show no phase transitions up to the melting point and secondly, electrons in these metals fill inner *d* shells and not outer electron shells, which 'smoothes' the difference in the individual properties of the atoms, in particular their metallic radii. Close atomic dimensions in these groups are a prerequisite for approximate equality of the energies of interaction between different pairs of atoms in a crystal under the condition that these energies are dependent mainly on interatomic distances. But one can clearly see three different groups of elements in the above two series with different types of crystal structures (Table 1). The first group includes the metals of groups V and VI of the Periodic Table which have b.c.c. structures. An increase of the melting enthalpy in the transition from group V to group VI may be explained by a decrease in the atomic radii of the metals (Wells, 1984). A further decrease of atomic radii in the transition to group VII should result in a still further increase of the melting enthalpy, but instead it drops, which may be ascribed to the change of the structure to an h.c.p. type. A jumpwise decrease of the melting enthalpy is also observed when an h.c.p. structure is transformed into an f.c.c. one. Note here that this jump is independent of the variations in atomic radii, which

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Table 1. *Melting enthalpies* (ΔH_m), *crystal structure types, metallic radii and unit-cell dimensions for transition metals*

		Nb	Mo	Tc	Ru	Rh	Pd	Ag
ΔH_m (kJ mol^{-1})		27·6	36	24	24	20·0	16·7	11·3
Crystal structure type		b.c.c.	b.c.c.	h.c.p.	h.c.p.	f.c.c.	f.c.c.	f.c.c.
Metallic radius (Å)		1·47	1·40	1·35	1·34	1·34	1·37	1·44
Unit-cell dimensions (Å)	*a*	3·294	3·140	2·74	2·70	3·80	3·88	4·08
	c			4·39	4·27			

		Ta	W	Re	Os	Ir	Pt	Au
ΔH_m (kJ mol^{-1})		34·7	61·5	33	31·8	26·0	20·0	12·5
Crystal structure type		b.c.c.	b.c.c.	h.c.p.	h.c.p.	f.c.c.	f.c.c.	f.c.c.
Metallic radius (Å)		1·47	1·47	1·37	1·35	1·36	1·39	1·44
Unit-cell dimensions (Å)	*a*	3·30	3·16	2·76	2·73	3·83	3·92	4·07
	c			4·45	4·31			

are almost the same for Ru and Rh as for Os and Ir. A further decrease in the melting enthalpy for Rh, Pd, Ag and Ir, Pt, Au seems to be due to a monotonic increase of atomic radii.

The crystal energy depends not only on the energies of pair interactions but also on the number of such interactions. It is the sum of such interactions which determines the total energy of the crystal. It is natural to expect that the melting enthalpy in b.c.c. structures with no close packing should be lower since the number of the shortest interatomic contacts is small (only eight in comparison with twelve in h.c.p. and f.c.c. structures). However, the experimental data contradict such a conclusion. The experimentally observed values of the melting enthalpy may be explained from the crystal structure standpoint if b.c.c. structures are taken to be formed by atoms which may interact within quite a large range of distances. This essentially increases the number of possible pairwise atomic interactions including those between the atoms of the second and perhaps of the following coordination spheres. Developing this hypothesis further, we should also assume that in h.c.p. structures the pair interactions occur in a more limited region around the central atoms whereas in f.c.c. structures the crystal energy is due mainly to the interactions between the atoms of the first coordination sphere.

As far as we know, there is no reliable information on the energy of pair interactions for the crystals listed in Table 1. But it may be assumed that the dependence of such an energy on the interatomic distances may be described by a Morse-like function (Fig. 1). Then the above hypothesis yields that the curves which describe the pair-interaction energies as a function of interatomic distance should have mild minima (*c*) for b.c.c. structures, in f.c.c. structures they should be steep (*a*), and in h.c.p. structures the profile should be of a type (*b*) intermediate between (*a*) and (*c*).

In recent years crystal structures of inorganic compounds have been calculated with molecular-mechanics methods (Parker, 1983; Parker, Catlow & Cormack, 1983; Catlow, Cormack & Theobald, 1984; Urusov & Dubrovinskii, 1985) by minimizing the total energy of the pair atomic interactions in crystals. For each pair of atoms the interaction energy is a function of interatomic distance and is described by Morse curves.

The minimization of the crystal energy in the atom–atom approximation is carried out with allowance for the interaction between the atom under consideration and all other atoms within a sphere of a radius of 30 or even 60 Å, with the center at the chosen atom (Urusov & Dubrovinskii, 1985). Therefore one should take into account not only the contributions to the total energy which come from the interaction between the chosen atom and the atoms from the first coordination sphere, but also the contributions due to the interactions with atoms from the subsequent coordination spheres. Such contributions should be either essential if the interaction of atoms in a crystal is described by curve (*c*) in Fig. 1 or nonessential if they are described by interactions of type (*a*) (Fig. 1). This fact shows that in the analysis of a crystal structure not only the first coordination sphere should be considered. Such an analysis should also include the second, third and perhaps subsequent coordination spheres. Below we suggest a method for such an analysis and illustrate it by several practical examples.

Description of the model

The minimum of the potential energy for a set of atoms included in a coordination sphere depends not only on its radius and the number of atoms in it, but also on the mutual positions of atoms inside the coordination sphere. Consider first the condition for the minimum of the potential energy for a group of atoms from one coordination sphere of arbitrary radius.

We define as central lines those lines passing through the central atom and any other atom of its coordination sphere. The potential energy of such a 'complex'* is minimal if the following conditions are met: (i) all central lines should form equal angles with the

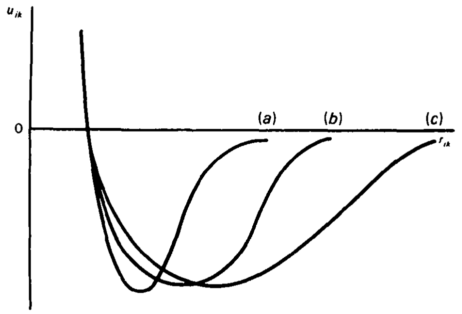

Fig. 1. Atomic interaction curves: (*a*) f.c.c., (*b*) h.c.p., (*c*) b.c.c.

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*The term 'complex' is conventional for crystals of elemental substances. We use it here for brevity implying that the distances from the central atom of such a complex to all the atoms of the coordination sphere are equal.

nearest central lines and (ii) all central lines should be equally surrounded by other central lines. Proceeding from these conditions, it is possible to find analytical expressions which allow one to examine the arrangement of central lines in the space. For crystals, the geometrical approach is more convenient. Then the above conditions may be reformulated.

Let us connect the centers of atoms/ligands by straight lines. We obtain a polyhedron inscribed into a sphere. The above conditions may then be formulated as follows: (i) all the edges of a polyhedron inscribed into a sphere should be equal and (ii) all the polyhedral angles of a polyhedron inscribed into a sphere should be congruent or symmetric. It follows from the second condition that each polyhedron may have only one type of polyhedral angles. These requirements are met by the Platonic regular solids (PRS's) and Archimedean semiregular solids (ASRS's) listed in Table 2. These polyhedra have been depicted by Wenninger (1971). The ASRS's include not only solids obtained by the truncation of a cube or an icosahedron but also of all prisms and antiprisms. However, not all of them should be taken into consideration since with an increase of the number m of sides of multiangular faces for such prisms and antiprisms the coordination polyhedron becomes thinner and flatter, transforming into a circumference for $m \to \infty$, thus losing sense as a coordination polyhedron. In addition to the above-mentioned solids one should also take into account the Archimedean–Ashkinusean semiregular solid (Ashkinuze, 1957). It should be noted that the maximum distances between the points on a sphere are obtained when all the faces of an inscribed polyhedron are triangular. For a coordination number of eight, a preferable polyhedron is a dodecahedron (Fig. 2) and not a cube or a tetragonal antiprism. This example shows that the PRS's and ASRS's should be supplemented with polyhedra whose shape may be established experimentally as a result of special investigation.

One more note about the shape of coordination polyhedra. In a series of ASRS's each antiprism has a corresponding prism; if a tetrahedron is considered as an antiprism built from two dumbbells, then a square should be considered as a prism corresponding to a tetrahedron. A square is necessary for the analysis of a number of structures. Two more figures are also necessary for such an analysis – an equilateral triangle and a dumbbell.

The PRS's and ASRS's with symmetry O_h can combine to form crystals, whereas those with symmetry I_h cannot make such combinations owing to the presence of fivefold axes. Nevertheless, polyhedra with symmetry I_h may form crystal fragments and the conditions of their existence should be a subject of special consideration. The combinations of the PRS's and ASRS's taken as coordination spheres result in a great diversity of space lattices, many of which correspond to real structures. At the beginning, we neglect the symmetry reduction associated with the anisotropy of atomic interactions in crystals, the different size of atoms and other factors, and verify our model on cubic crystals.

Table 2. *PRS's and ASRS's with symmetries T_d, O_h, I_h with the number of polyhedron vertices*

T_d	O_h	I_h
Tetrahedron 4	Octahedron 6	Icosahedron 12
Truncated tetrahedron 12	Cube 8	Dodecahedron 20
	Cuboctahedron 12	Icosidodecahedron 30
	Rhombicuboctahedron 24	Rhombicosidodecahedron 60
	Truncated cube 24	Truncated icosahedron 60
	Truncated octahedron 24	Truncated dodecahedron 60
	Snub cube 24	Snub dodecahedron 60
	Rhombitruncated cuboctahedron 48	Rhombitruncated icosidodecahedron 120

Model verification*

Thus, as has been shown, in order to evaluate the crystal energy one should take into account two factors – the number of atoms within each coordination sphere [the larger the number, the more terms in (1) and the lower the potential energy of the crystal] and the range of the atomic interactions in crystals, which affects the shape of curves shown in Fig. 1. For a small range of interactions [curve (*a*), Fig. 1 corresponds to f.c.c. structures] the minimum of the potential energy may be attained for the maximum number of neighbors (12 for identical atoms) in the first coordination sphere. Of all the PRS's and ASRS's the minimum interaction energy for atoms from the first coordination sphere may be expected for an icosahedron, since all its faces are triangular and therefore the distances between its vertices are maximal among all dodecagons of the PRS's and ASRS's. However, an undistorted icosahedron cannot form a three-dimensional crystal lattice since it has fivefold axes. Therefore in crystals a cuboctahedron consisting of six square and eight triangular faces turns out to be preferable. The third dodecatop, a truncated tetrahedron, consists of four

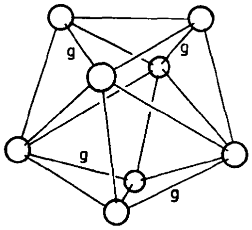

Fig. 2. An eight-vertex dodecahedron.

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*The data on space groups and atomic coordinates of the structures considered in this section are taken (with some exceptions) from *Metals Reference Book* (Smithells, 1976).

hexagonal and four triangular faces and therefore the interatomic distances in this dodecatop may turn out to be shorter than those corresponding to the minimum of curve (*a*) (Fig. 1) whereas the interaction energy may be higher than for a cuboctahedron. Thus for crystals the most favorable dodecatop is a cuboctahedron. This is found for f.c.c. structures.

Among simple substances, f.c.c. structures (in which any atom is surrounded by neighbors occupying the vertices of a cuboctahedron) are very common. These include numerous metals, *e.g.*, copper, and also all inert gases except helium. The contribution made by the second and distant coordination spheres to the total energy of a crystal with an f.c.c. structure may be rather modest in comparison with that made by the first one. Such a conclusion is drawn from the comparison of such a structure with b.c.c. ones common for metals (V, Nb, Ta, Mo, *etc.*).

The first coordination sphere in b.c.c. crystals is a cube, the second an octahedron. Together they form an equifacial semiregular polyhedron – a rhombidodecahedron – which is a dual cuboctahedron. Thus the third coordination sphere in b.c.c. structures, a cuboctahedron, is a logical continuation of the first two. A smaller number of neighbors (eight) in the first coordination sphere of b.c.c. structures should unavoidably yield a smaller contribution to the crystal energy as compared with f.c.c. structures. However, owing to the larger range of distances essential for atomic interactions [curve (*c*), Fig. 1], the first and second coordination spheres make the main contribution to the energy of a b.c.c. crystal. In b.c.c. structures the distances from the central atom to atoms of the first and second coordination spheres differ by approximately 15%, but the energies of atomic interaction between the central atom and atoms of the first and second coordination spheres are nearly the same. This follows from calculations performed by the pseudopotential method (Pick, 1967) and depicted in Fig. 3 for the lithium (b.c.c.) and aluminium (f.c.c.) crystals. Fig. 3 shows the compression of the two atomic interaction curves along the horizontal axis in aluminium crystals in comparison with the lithium curves. The relatively gentle and deep first minimum of the alkali atom interaction curve contains distances from the central atom to atoms of the first and second coordination spheres in b.c.c. structures. Energies of interaction of the central atom with atoms of the first and second coordination spheres differ a little from the energy at the first minimum of the curve. The total number of atoms in the first and second coordination spheres in b.c.c. structures is 14. This is two atoms more than in the first coordination sphere in f.c.c. structures and consequently there is a gain in the potential energy of the structure. This explains why the b.c.c. structure is stable. The first minimum in the Al-atom interaction curve is very narrow and the only possibility of obtaining a potential-energy minimum for the crystal is an f.c.c. structure with 12 atoms in the first coordination sphere.

The pseudopotential method is applicable to non-transition metals, but is difficult to apply to the transition metals. This is why the functions of the two atomic interactions are only known for a restricted number of simple solids, and here an approximation is used for illustration, *i.e.* the curves depicted in Fig. 1. This sort of function (potential Mie) has been successfully used in calculations of a number of properties of metals (Machlin, 1983).

To avoid misunderstanding it is worth mentioning that the sum of the atom–atom interactions is not equal to the potential energy of metallic crystals, but these interactions are influential in choosing between f.c.c., b.c.c. and h.c.p. types of structure (Pettifor, 1983).

Hexagonal and trigonal crystals are the subject of our next paper (Aslanov, 1988), where we consider the position of curve (*b*) in Fig. 1. Here we dwell only on the structure of polonium, which has a primitive cubic unit cell (the packing density of this structure is extremely low, only 52·36%). The first coordination sphere for any atom in the structure is an octahedron, the second a cuboctahedron. In diamond-like structures (possessed, in addition to diamond, by silicon, germanium and gray tin) the first coordination sphere is a tetrahedron, the second a cuboctahedron. These examples and some other structures which will be considered below demonstrate the role of the second coordination sphere in the formation of various crystals with minimum potential energy. However, the first coordination sphere in f.c.c. structures, and the second in b.c.c., polonium and diamond structures show one more important quality of crystal formation. Consider the central atom and the first coordination sphere of an

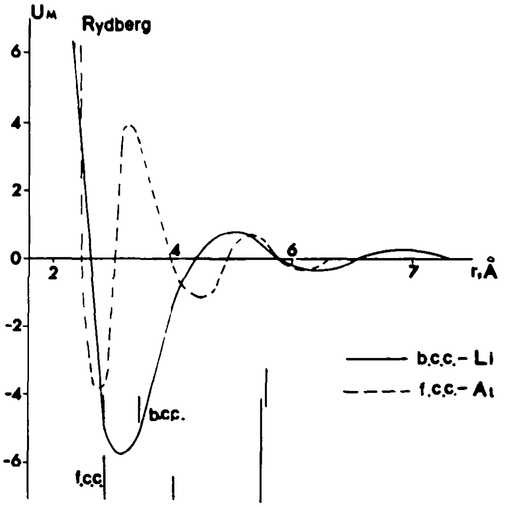

Fig. 3. Atomic interaction curves for lithium and aluminium, calculated by the pseudopotential method.

f.c.c. crystal of an elemental substance. Any of the twelve atoms forming the first coordination sphere is absolutely equivalent to the central atom and therefore in the process of crystallization the surroundings of any such atom will be built up to a cuboctahedron by the atoms of the liquid phase. On the crystal surface, this process repeats itself infinitely during growth, the cuboctahedra being shifted by an equal distance parallel to one another (Fig. 4), resulting in the formation of a three-dimensional crystal lattice characterized by translation symmetry. The strictly parallel shift of cuboctahedra is explained by the fact that a new cuboctahedron is not formed around each atom of the first coordination sphere. It is built up instead with the initial part of the cuboctahedron being a part of the central complex (five atoms including the central one) and having an orientation effect on the newly built cuboctahedron. Thus the translation symmetry results from a 'complex' of thirteen equivalent atoms experiencing both mutual attraction and repulsion. Thus taking into consideration the second and following coordination spheres permits the formation of different structure types for inorganic crystals and the translation symmetry of crystals to be explained.

For crystal structures in which the coordination number of the first coordination sphere is less than twelve (in the above examples coordination numbers were eight, six and four) the main role in the formation of translation symmetry is played by the second coordination spheres. Thus in the polonium and diamond structures each atom from the second coordination sphere becomes the center for the formation of new coordination spheres placed one into another. The cuboctahedron of the crystal nucleus (including the central atom and two coordination spheres) is shifted parallel to itself so that the atom of the second coordination sphere of the nucleus becomes central and the central atom of the crystal nucleus enters the second coordination sphere.

Body-centered crystals may start growing from the octahedron vertices (the second coordination sphere, Fig. 5). The central atom of the nucleus enters the second coordination sphere for any of the vertices of its second coordination sphere, and four adjacent vertices of the cube of the first coordination sphere of the crystal nucleus also enter the first coordination sphere of the atom at the octahedron vertex. Two coordination spheres forming around the octahedron vertex share five atoms with the initial complex which has an orientation effect and provides the strictly parallel shift of the coordination polyhedra and thus the translation symmetry. A b.c.c. crystal may also start growing from cube vertices if there are two coordination spheres, but then two coordination spheres around the cube vertex share only four atoms with the initial complex, which leads to the appearance of the translation symmetry in the crystal. The third coordination sphere, a cuboctahedron, makes the formation of a crystal structure even more energetically advantageous.

It should also be emphasized that in all the above examples the coordination polyhedra of the first sphere were included in the polyhedra of the second coordination sphere and those of the second sphere were included in the polyhedra of the third coordination sphere, *etc.*, so that all threefold axes of all the

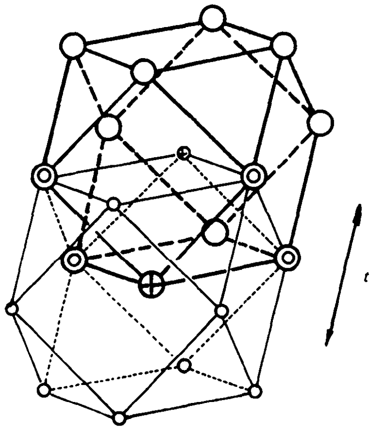

Fig. 4. An f.c.c. structure showing the appearance of translation symmetry in the process of crystal growth. The initial central atom is indicated by a cross in a small circle. Its first coordination sphere (a cuboctahedron) is depicted by large circles. The central atom of the first coordination sphere, around which the cuboctahedron is built, is depicted by a cross in a large circle. The atoms of its first coordination sphere are shown by small circles. Atoms shared by two 13-atom complexes consisting of the central atom and atoms occupying cuboctahedron vertices are depicted by double circles or by an encircled cross. *t* is a translation.

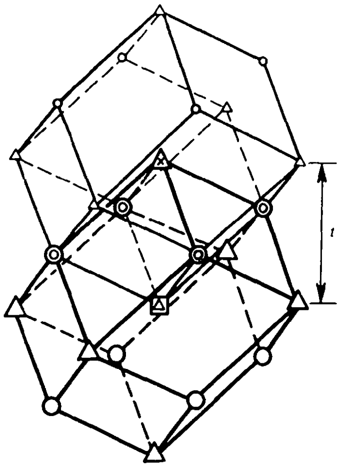

Fig. 5. The appearance of translation symmetry in b.c.c. crystals. The first coordination spheres of the initial and secondary complexes consist of small and large circles, the second coordination spheres are shown as small and large triangles. The central atoms of the initial and secondary complexes are denoted by a cross and a square, respectively. The rhombidodecahedron of the secondary complex is depicted by a solid line. *t* denotes the translation.

polyhedra coincided. This provided the minimum potential energy of interaction between the polyhedra of the first and second coordination spheres and the formation of a cubic crystal.

The above scheme for crystal formation from a nucleus built by the central atom and two coordination spheres* is applicable not only to simple elemental materials (metals, inert gases, nonmetals) but also to various compounds. Thus if the central atom and the atoms of the second coordination sphere in the polonium-type structure are of the same kind (say, metal) and those of the first coordination sphere are of another kind (nonmetal), we arrive at the NaCl structure type, the metal and nonmetal sites in the coordination spheres being interchangeable. In the diamond-type structure or in crystals with a b.c.c. structure the central atom and the second coordination sphere may be formed by metal (or, *vice versa*, nonmetal) atoms, whereas the first coordination sphere is formed by nonmetal (or metal) atoms. We then arrive at the sphalerite or CsCl structure types, respectively.

In the fluorite (CaF_2) structure the central Ca atom is surrounded by two coordination spheres – a cube of F atoms and a cuboctahedron of Ca atoms. In the same way, each Ca atom of the second coordination sphere tends to surround itself with two coordination spheres. As a result, a crystal nucleus is formed. The perovskite ($SrTiO_3$) structure has four coordination spheres around the central atom (Ti). The first one is an octahedron consisting of O atoms, the second a cube consisting of Sr atoms, and the third a truncated octahedron built from O atoms. These four coordination spheres embrace one unit cell and also, partly, six neighboring unit cells, thus forming a 'stack' of the structure, with orienting atoms predetermining the translation symmetry of the crystal. The ReO_3 structure type is very similar to that of perovskite. The only difference is that ReO_3 has no coordination sphere in the shape of a cube. In the perovskite-type structure the vertices of such a cube are occupied by Sr atoms. Both in perovskite and ReO_3 the octahedron and truncated-octahedron edges are equal to one another and are the shortest distances between the vertices of these two polyhedra, providing the minimum potential energy of the crystal. K_2PtCl_6 (Bokii, 1954) differs from the perovskite type by distant coordination spheres (Fig. 6). The first coordination sphere of the central Pt atom (an octahedron) is built by Cl atoms, the second sphere consisting of K atoms is a cube, the third is a truncated octahedron formed by Cl atoms, and the fourth is a cuboctahedron with the vertices occupied by Pt atoms. The fourth coordination sphere in K_2PtCl_6 completes the formation of the unit cell. Hence all four coordination spheres should necessarily be taken into account when explaining crystal formation. Each Pt atom of the fourth coordination sphere may be considered as the central one. The second, third, and fourth spheres exhibit an orienting effect on the formation of unit cells neighboring the initial one.

The unit cell of BiF_3-type crystals (Fig. 7) consists of the central Bi atom, the first coordination sphere is a cube of F(2) atoms at the site with T_d symmetry, the second is an octahedron with the F(1) atoms in the sites with O_h symmetry (vertices) and the third is a cuboctahedron of Bi atoms. Bi atoms from the third coordination sphere form the same coordination spheres as the central atom. This process occurs repeatedly during crystal growth.

The example considered below shows that any combinations of the PRS's and ASRS's are worth considering. In the Cu_2O structure (Bokii, 1954) the first coordination sphere (Fig. 8) of an O atom is a tetrahedron with Cu atoms at the vertices, the second is a truncated tetrahedron of Cu atoms and the third is a cube, the vertices of which are occupied by O atoms. At first glance, a tetrahedron and a cube do not match together since the vertices of a tetrahedron and a cube lie on one line with the central atom, thus making the packing rather loose. However, the experimental data confirm the existence of such a combination.

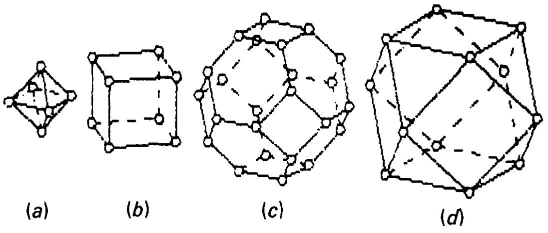

Fig. 6. The K_2PtCl_6 structure: (*a*) Cl, (*b*) K, (*c*) Cl, (*d*) Pt.

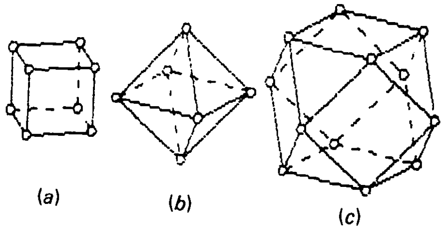

Fig. 7. The BiF_3 structure: (*a*) F(2), (*b*) F(1), (*c*) Bi.

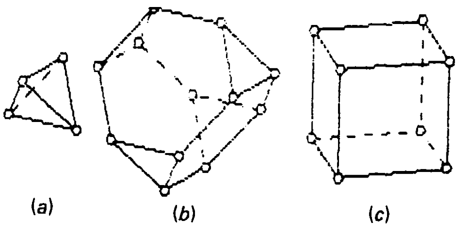

Fig. 8. The Cu_2O structure: (*a*) Cu, (*b*) Cu, (*c*) O.

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* One twelve-atom sphere in an f.c.c. crystal is the only exception to the general rule.

The sulvanite (Cu_3VS_4) structure (Fig. 9) may be represented by the following sequence of coordination spheres: a central V atom is surrounded in the first coordination sphere by S atoms occupying tetrahedron vertices; the vertices of the octahedron of the second sphere are occupied by Cu atoms; the third sphere is built by S atoms at the vertices of a truncated tetrahedron; the fourth sphere is formed by V atoms at the octahedron vertices. These coordination spheres are a good prerequisite for the development of a crystal structure.

In all the above examples the formation of structure types was initiated at the central atom. But there is another way of combining the PRS's and ASRS's – the initial point of a crystal nucleus is chosen to be the center of a cluster of atoms in the shape of a PRS or an ASRS. Thus in the spinel structure (Fig. 10) the central cluster consists of four Al and four O atoms occupying cube vertices in such a way that the Al and O atoms both form tetrahedra. The vertices of such a cluster occupied by Al atoms are surrounded by a truncated tetrahedron of O atoms, and a tetrahedron of O atoms from the initial cluster is surrounded by Mg atoms occupying tetrahedron vertices. The triangular faces of a truncated tetrahedron and the Al atoms of the initial cluster form half of a cube (the unit equivalent to the initial cluster) and therefore these cubes are built up from three Al atoms and one O atom, which results in the formation around Al_4O_4 cubes of coordination spheres built by truncated tetrahedra with O atoms at the vertices and tetrahedra of Mg atoms similar to the case of the cluster considered above. This procedure repeats itself until the whole space is filled and the translation symmetry appears. In Fig. 10 two more coordination spheres are drawn for clarity.

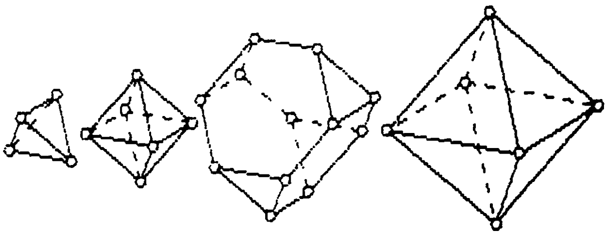


Fig. 9. The Cu_3VS_4 structure: (*a*) S, (*b*) Cu, (*c*) S, (*d*) V.

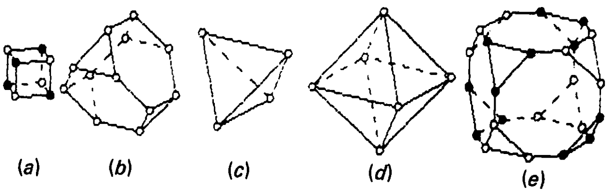


Fig. 10. The $MgAl_2O_4$ structure: (*a*) central cluster Al (filled circles) and O (open circles), (*b*) O, (*c*) and (*d*) Mg, (*e*) Al (filled circles) and O (open circles).

Another example of a structure with the central cluster is the Pt_3O_4 structure type (Bokii, 1954). The central cluster is an octahedron with Pt atoms at the vertices. The first coordination sphere is a cube of O atoms, the second is a cuboctahedron with the vertices occupied by Pt atoms. Each triangular face of the second coordination sphere is at the same time a face of an octahedron equivalent to the central cluster. Thus the translation symmetry appears to be due to the orientational effect of the second coordination sphere.

In the $Cr_{23}C_6$ structure (Fig. 11) the central cluster has the shape of an empty cube of Cr(3) atoms occupying the site with C_{3v} symmetry. The first coordination sphere of the cluster is an octahedron with C atoms at the vertices, the second sphere is a truncated octahedron formed by Cr(4) atoms in the sites with the C_{2v} symmetry, the third sphere is a cube of Cr(2) atoms in the sites with the T_d symmetry, the fourth sphere is an octahedron of Cr(1) atoms in the site with the O_h symmetry, the fifth sphere is built by two dual-truncated tetrahedra placed one into another with Cr(4) atoms at the vertices, the sixth sphere is a somewhat distorted truncated cube of Cr(3) atoms, and the seventh sphere is a truncated octahedron of C atoms.

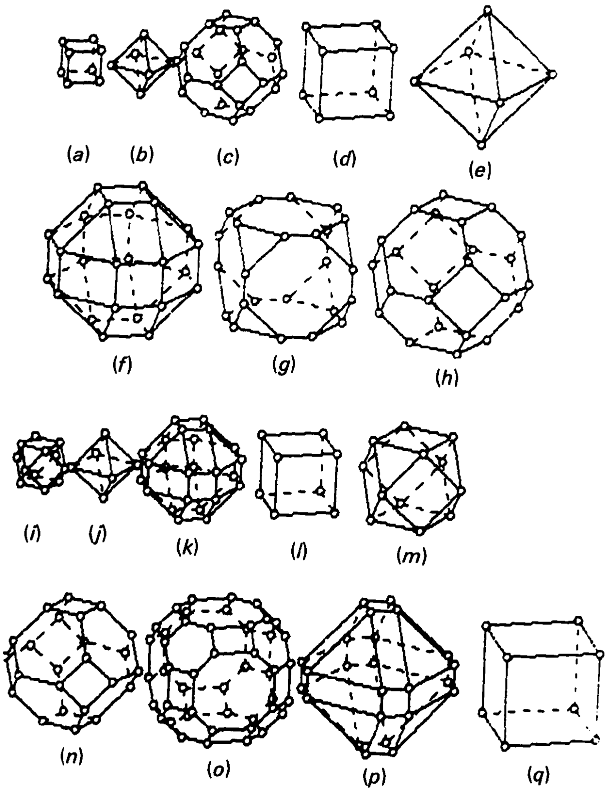


Fig. 11. The $Cr_{23}C_6$ structure: (*a*) central cluster Cr(3), (*b*) C, (*c*) Cr(4), (*d*) Cr(2), (*e*) Cr(1), (*f*) Cr(4), (*g*) Cr(3), (*h*) C. Another complex consists of central atom Cr(1) and coordination spheres: (*i*) Cr(4), (*j*) C, (*k*) Cr(3), (*l*) Cr(2), (*m*) Cr(4), (*n*) C, (*o*) Cr, (*p*) Cr(3), (*q*) Cr(1).

The edges of the fourth coordination sphere are those of the central cluster (an empty cube). Thus 16 atoms of the initial seven spheres are shared with the neighboring formation consisting of the central cluster and seven coordination spheres. There are twelve new centers for the formation of such clusters and their coordination spheres, corresponding to the number of cube edges. The crystal continues to grow just from such centers.

Another complex should be considered in this structure with central atom Cr(1). The first coordination sphere is a cuboctahedron with Cr(4) at the vertices, the second an octahedron of C atoms, the third two dual-truncated tetrahedra inserted one into another with Cr(3), the fourth a cube of Cr(2), the fifth sphere a cuboctahedron of Cr(4), the sixth a truncated octahedron of C atoms, the seventh a rhombitruncated cuboctahedron of Cr(4), the eighth a distorted rhombicuboctahedron of Cr(3), and the last sphere a cube of Cr(1).

The construction of structure types from the PRS's and ASRS's is applicable not only to metals and ionic substances but also to intermetallic compounds. The Cr_3Si type (Fig. 12) consists of a central Si atom, the first coordination sphere of Cr atoms is a distorted ('crystallographic') icosahedron which has lost its fivefold axes owing to deformation, the second coordination sphere is a cube with the vertices occupied by Si atoms. The crystal is then built up around the Si atoms of the second sphere in the same way as around the central atom. The third sphere is built from Cr atoms at the vertices of a crystallographic icosahedron that is less distorted than the icosahedron of the first coordination sphere – the edges of both icosahedra may be divided into two groups having different lengths, the edge ratio for the icosahedron of the first sphere is 1:6/8, whereas the same ratio for the icosahedron of the third sphere is 1:7/8. The fourth coordination sphere is an octahedron with Si atoms at the vertices.

In the Laves phases (β-$MgCu_2$), the central Mg atom is surrounded by a first coordination sphere (Fig. 13) of Cu atoms situated at the vertices of a truncated tetrahedron; the vertices of a double tetrahedron around the central atom are occupied by Mg atoms surrounded, in the same way as the central atom, with Cu atoms occupying the vertices of a truncated tetrahedron. Repeating the atoms in a similar fashion, it is possible to fill the unit cell and obtain the translation symmetry.

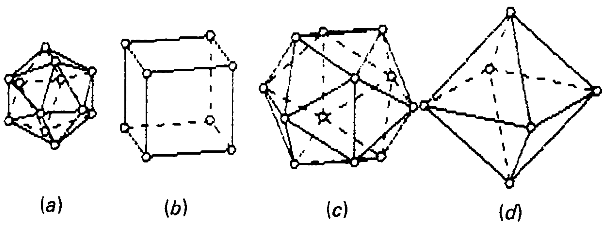

(a) (b) (c) (d)

Fig. 12. The Cr_3Si structure: (a) Cr, (b) Si, (c) Cr, (d) Si.

In the Ir_3Sn_7 structure (Fig. 14) an empty cluster in the shape of a cube with Sn atoms [Sn(2) in the site with C_{3v} symmetry] at the vertices has the first coordination sphere of Ir atoms situated at the vertices of an octahedron and the second coordination sphere of Sn atoms occupying the vertices of a truncated octahedron [Sn(1) in the position with symmetry D_{2d}]. The third coordination sphere is a cube of Sn(2) atoms, the fourth an octahedron of Ir atoms and the fifth a distorted truncated cube of Ir atoms. The further development of the structure occurs at the vertices of the unit cell just as was the case with its center.

An unusual coordination polyhedron may be constructed for the first coordination sphere of an Na atom in $NaZn_{13}$ (Fig. 15) – a snub cube of Zn(2) atoms in the site with C_s symmetry. The second coordination sphere of the Na atom is a cube with Zn(1) atoms occupying the vertices of the cube [the site of Zn(1) atoms has T_h symmetry]. Each atom of the second sphere is simultaneously the central atom of the cluster of Zn_{13} atoms in which a Zn atom, Zn(1), is surrounded by Zn(2) atoms occupying the vertices of an icosahedron, three of which are shared with the initial snub cube. The second and the third coordination spheres of the Zn(1) atom are icosahedra with Zn(2) atoms at the vertices,

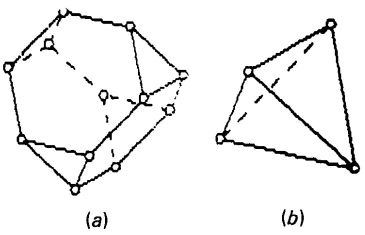
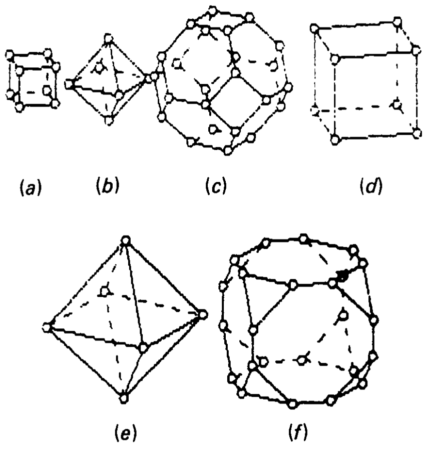

(a) (b)

Fig. 13. The β-$MgCu_2$ structure: (a) Cu, (b) Mg.


(a) (b) (c) (d)

(e) (f)

Fig. 14. The Ir_3Sn_7 structure: (a) central cluster Sn(2), (b) Ir, (c) Sn(1), (d) Sn(2), (e) Ir, (f) Ir.

the fourth sphere is cube of Na. These two complexes together give the translation symmetry. This process may be continued infinitely, which results in the appearance of the translation symmetry.

The $Mg_2Cu_6Al_5(Mg_2Zn_{11})$ structure (Fig. 16) may be represented as a combination of two types of complexes. The first type of complex is built by the central Al atom, Al(1), in the position with T_h symmetry and five coordination spheres. The first sphere is an icosahedron with Cu atoms at the vertices [Cu(2) atoms in the sites with C_s symmetry]. The second coordination sphere is a cube consisting of eight Al(3) atoms in the position with C_3 symmetry; the third sphere is a distorted icosahedron of 12 Mg atoms which supplement the cube to form a dodecahedron; the fourth coordination sphere is an icosahedron with Al(2) atoms at the position with C_{2v} symmetry at the vertices; the fifth sphere is a distorted truncated cube of Cu(1) atoms (the symmetry of position C_{2v}). The second type of complex has a cluster in the center – an octahedron with Cu(1) atoms at the vertices. Three Cu atoms of such a cluster are shared with a triangular face of the fifth coordination sphere of the first type of complex which results in a certain orientation of the complexes relative to one another. The first coordination sphere in the second type of complex is a cube of Al(3) atoms, the second a distorted icosahedron of Al(2) atoms. The latter together with Al(3) atoms of the first sphere may be interpreted as a distorted dodecahedron. The third sphere is an icosahedron of Mg atoms. These spheres complete the unit cell and fulfil the conditions necessary for the development of the structure.

In the $CoAs_3$ structure (Fig. 17) eight Co atoms and twelve As atoms form a cluster in the shape of a slightly distorted dodecahedron. Co atoms form a cubic fragment in the dodecahedron, each atom being shared by two dodecahedra, whereas As atoms enter only one dodecahedron. Therefore, Co atoms of the dodecahedral nucleus are built up with eight new dodecahedra at the vertices. The Co atoms interacting with one another form a primitive cubic cell.

The Th_3P_4 structure (Fig. 18) is of special interest. P atoms lie at the crossed threefold axes at equal distances from one another (one-quarter of the body diagonal of the cube). Each Th atom is surrounded by four threefold axes, the pairs of P atoms lying at the same distances from Th atoms. In other words, the coordination number of Th atoms is eight. The first coordination sphere of a Th atom is an eight-vertex dodecahedron in which threefold axes are directed along two *g*-type edges of four, forming each of two dihedra of the dodecahedron. Trapezoids of the dodecahedron are corrugated, with Th atoms lying on crystallographic axes $\bar{4}$, in accordance with the symmetry of a dodecahedron.

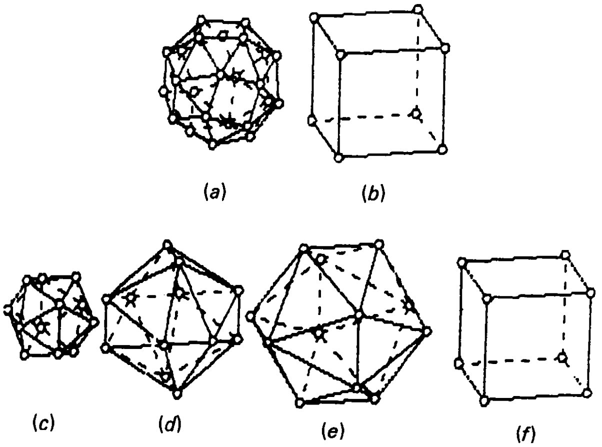


Fig. 15. The $NaZn_{13}$ structure: (*a*) Zn(2), (*b*) Zn(1), (*c*) Zn(2), (*d*) Zn(2), (*e*) Zn(2), (*f*) Na.

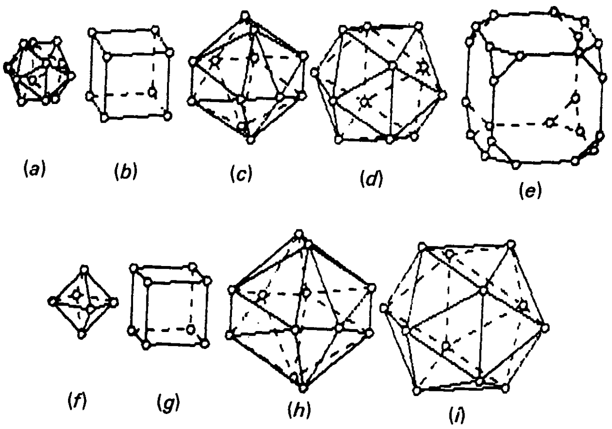


Fig. 16. The $Mg_2Cu_6Al_5$ structure. Complex I: (*a*) Cu(2), (*b*) Al(3), (*c*) Mg, (*d*) Al(2), (*e*) Cu(1). Complex II: (*f*) central cluster Cu(1), (*g*) Al(3), (*h*) Al(2), (*i*) Mg.

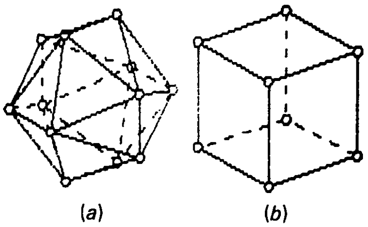


Fig. 17. The $CoAs_3$ structure: (*a*) As, (*b*) Co.

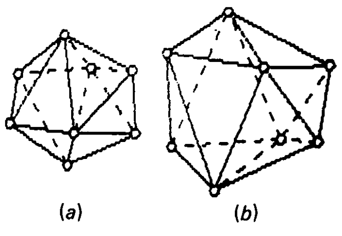


Fig. 18. The Th_3P_4 structure: (*a*) P, (*b*) Th.

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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