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Crystal-Chemical Model of Atomic Interactions. 4. Prognostic Ability: Crystals and Quasicrystals

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Abstract

The idea of structural ensembles is introduced in the framework of the crystal-chemical model of atomic interactions (CCMAI). The atomic ensemble is treated as a minimal portion of atoms, which predetermines the crystal structure. Inorganic crystal structures such as graphite, white tin, PbO are considered. It is supposed that both atoms and localized electron pairs form these structures. On the basis of CCMAI the hypothetical structure of icosahedral quasicrystals is worked out. In accordance with this hypothesis the initial cluster (or simply cluster) of the quasicrystal has a double-shell structure and each shell has an icosahedral form; the thickness of a shell is equal to the diameter of one atom; the number of atoms in one shell is $10n^2 + 2$, where n is the number of the shell. The quasicrystal has two subsystems of atoms. One of them consists of the central atoms of clusters and the atoms included in the first shells of clusters. The 13-atom icosahedral bodies form a crystal lattice with space group $Fd3$. All icosahedra of this atomic subsystem have a perfect form and all of them are perfectly oriented with respective to each other. The first atomic subsystem is responsible for the diffraction of electrons and X-rays. The second atomic subsystem includes atoms of the second shells of clusters. This subsystem has no translational symmetry, but it is partially ordered.

Introduction

In the previous papers in this series (Aslanov, 1988*a*, *b*; Aslanov & Markov, 1989) the crystal structures were considered as sets of coordination polyhedra. The atoms were assumed to be attracted to each other by different sorts of chemical bondings and mutually repelled by atomic electron shells.

Any theoretical model must have some prognostic ability. The discussion of the prognostic ability of CCMAI is the main purpose of this paper.

For the explanation of some crystal structures the widely known model of valence-shell electron-pair repulsion (VSEPR) is necessary (Gillespie, 1972). This model is intended for molecular structures with covalent bonds. Gillespie (1972) pointed out that the structures of ionic crystals are wholly defined by the packing of charged spheres, where the relative dimensions and charges of ions play the main role. On this assumption one can form the conclusion that the VSEPR model is not applicable to metallic structures and to crystals with van der Waals atomic interactions. CCMAI allows one to demonstrate the effect of electron pairs on crystal structures with ionic and metallic bonding. The crystal data considered below were taken from the book by Wyckoff (1964). Another topic of this paper is quasicrystals, a very delicate problem of advanced crystallography.

Crystals

First it is worth introducing the concept of structural ensemble into the crystal-chemical model of atomic interactions (CCMAI). The concept summarizes previous ideas (Aslanov, 1988*a*, *b*; Aslanov & Markov, 1989). A structural ensemble is a minimal set of atoms (i) consisting of the central atom (cluster) and its coordination spheres, (ii) having a minimum of potential energy of atomic interactions (iii) at the peripheral coordination sphere possessing the atoms (clusters) of the same sort as in the center, (iv) crossing similar ensembles in such a way that the common part of the pair of crossing ensembles consists of at least three atoms; these atoms do not lie in a straight line.

The first step of crystal-chemical analysis with CCMAI involves the isolation of Platonic regular solids (PRS), Archimedian semiregular solids (ASRS) or Zalgaller's polyhedra (ZP) which are the fragments of the structural ensemble. Of course the distance from the center of the structural ensemble

to the vertices of the polyhedra is a very important value, but it should be considered as an average, because some atoms of the inner coordination sphere in intermetallic compounds could lie farther from the center of the structural ensemble than certain atoms in the outer coordination sphere. This situation was met, for example, in the Cu_3As structure (Aslanov & Markov, 1989). Such an approach will be used throughout this paper.

The ensemble is equivalent to the monosphere complex in some structures, for instance in crystals with f.c.c. and h.c.p. lattices (Aslanov, 1988a, b), where the central atom has the only coordination sphere. The ensemble coincides with one multisphere complex in many structures, for example perovskite or K_2PtCl_6 (Aslanov, 1988a). But in many crystals such as Pb_3O_4, $Ni_{12}P_5$ or Ni_3P (Aslanov & Markov, 1989) the ensembles are formed by two or three complexes.

The concept of the structural ensemble is useful because it points out a minimal set of atoms and their spatial distribution which leads to a minimum of potential energy of the crystal structure as a whole. An ensemble is the only correct basis for the structure classification. The widespread extraction of layers and chains out of structures (for instance layers from hexagonal close packing of atoms or ions) is a method of description of structures that is inadequate to the nature of crystals. Three-dimensional structures such as crystals should not be formed by plane or one-dimensional elements, but by three-dimensional ones – such as structural ensembles. An ensemble and a crystal are uniquely inter-related. A crystal and its translational symmetry do not exist without the ensemble. That is why molecular ensembles exist in the molecular crystals, including protein crystals.

Even such a layer structure as graphite has ensembles. Generally speaking, the structures of two modifications of graphite need some special attention. One can try to select atoms for an ensemble as shown in Fig. 1(a): in both modifications the central atom

has three carbon atoms at the apices of the equilateral triangle in the first coordination sphere, and the second coordination sphere has a cuboctahedron or anticuboctahedron elongated parallel to a threefold axis. But this approach is not a satisfactory one. Firstly there is an arbitrary choice of cuboctahedron and anticuboctahedron in the second coordination sphere of both modifications. Secondly, in both modifications of graphite half of the atoms in each layer are opposite interatomic holes of neighbor layers, but the other half of the atoms (Fig. 1a) form columns to atoms resting against each other, and the columns are parallel to the main axis of the crystal. These structures should be unfavorable from an energetic point of view. But it is quite simple to explain the graphite structures by taking into consideration the localized electron pairs (LEP). One can think that the middle of the shortest interatomic intervals coincides with the centers of LEP which form a kagomé (3636) net inside the atomic layer (Fig. 1b). The stacking of layers gives anticuboctahedra in double-layer structures of graphite and cuboctahedra in triple-layer structures, which have LEP's at vertices of these polyhedra. Of course these polyhedra are elongated in the direction parallel to the threefold axis in accordance with the strong distinction between forces of the atomic interactions inside and between the layers.

One can suppose that the electronic shells of heavy atoms have dimensions comparable with the dimensions of the LEP's, and crystal structures are formed by both of them. This hypothesis allows one to realize unique structures of some simple substances, white tin for example. It is known (Bokii, 1954; Wells, 1984) that many properties of white tin are explained by the divalent state of atoms which is supposed to exist. In this case each atom can have two LEP's outside its core for connection with adjacent atoms, instead of the four LEP's in grey tin. For instance, the tin atoms can be connected by LEP's in infinite chains. The distance between a tin atom core and a LEP inside the chain is $1.58\,\text{Å} \times 2$, but the shortest distance between a tin atom core of one chain and a LEP of an adjacent chain is $3.02\,\text{Å} \times 4$. The shortest distance between the tin atom cores is $3.02\,\text{Å} \times 4$.

The crystal-structure analysis of white tin shows (Fig. 2) that it could be considered as a protactinium
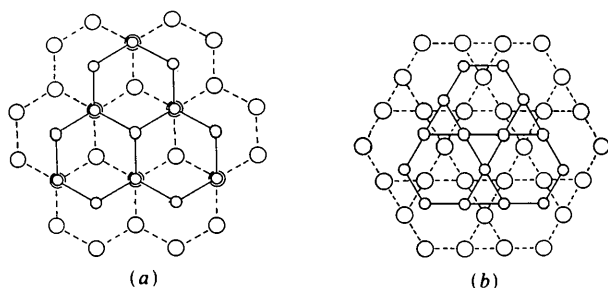

Fig. 1. The structure of double-layer graphite. (a) Two nets of atoms; the dotted line picks out the hexagonal section of an anticuboctahedron (cuboctahedron) in the second coordination sphere; atoms screening each other are depicted by double circles. (b) Two kagomé nets with LEP's at nodes; the structure consists of anticuboctahedra with LEP's at vertices; radii of circles are different for the two nets.
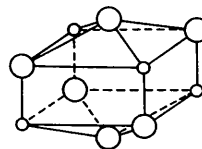

Fig. 2. Coordination polyhedron of the tin atom in the white tin structure; the bigger circles are LEP's the smaller ones are the tin atoms.

type of structure (Aslanov, 1988*b*) where the cores of atoms alternate with LEP's in rows along a fourfold axis. Both tin-atom cores (for small atoms) and LEP's have coordination number 10 and are surrounded by six LEP's and four tin atoms or four LEP's and six tin atoms for tin atoms and LEP's respectively. The coordination polyhedra are elongated square bipyramids which are one of the Zalgaller's polyhedra (ZP) discussed earlier (Aslanov & Markov, 1989). The coordination polyhedron in the white tin structure is compressed along a fourfold axis, perhaps because of the aspherical form of LEP. So the white tin structure should be considered as a packing of cores of atoms and LEP's connected in chains; this predetermines the peculiarities of the structure.

Another unique structure is the polonium one. The density of its packing is extraordinary low – 52·36% (primitive cubic cell). It is necessary to explain the existence of crystals with such a low density of packing. One can assume that in accordance with the position of polonium in the Mendeleev table of elements each atom has three LEP's which are placed in the same plane with the cores of the polonium atoms at angles 120° relative to each other. In this case the cores of atoms are distributed at the vertices of a primitive cubic cell, and LEP's are placed in the centers of square faces (Fig. 3). So the cores of atoms together with LEP's form a f.c.c. structure.

Both tin and polonium are on the diagonal border between metals and non-metals in the Mendeleev table. Gallium is on this border as well. The gallium structure is also unusual, as properties of gallium are very specific ones. For instance, the anisotropy of the atomic polarization factor is maximal for elements of the gallium group and for gallium it reaches 70% of average polarizability (Urusov, 1987). Morphology of the gallium crystals, grown from the melt, can be understood only if it is assumed that the crystallizing particles are Ga_2 molecules (Hartman, 1987). As each gallium atom has one unpaired $4p$ electron let us suppose that there is a LEP in the center of a Ga_2 molecule. As Hartman (1987) clarified, the centers of

Ga_2 molecules are disposed in the nodes of a face-centered orthorhombic lattice. So the LEP's form a distorted f.c.c. framework, with all its tetrahedral holes filled with gallium atoms. The gallium structure, with account taken of the LEP's, is a distorted CaF_2 type, where atoms of calcium and fluorine are replaced by LEP's and gallium atoms respectively.

The examples studied above give us indirect arguments in favor of the participation of LEP's in the structure formation. But there is direct structural proof that LEP's influence the structure of the red modification of PbO. The center of the complex is occupied by the lead atom. Its first coordination sphere looks unusual at first glance. It is a square with oxygen atoms at the corners; the center of the square does not coincide with the central atom of the complex (Fig. 4). The second coordination sphere has 12 lead atoms at the vertices of a distorted cuboctahedron remote from the center of the complex at 3·69 Å × 4, 3·85 Å × 4. Presumably the first coordination sphere contains LEP's of the lead atom (Naray-Szabo, 1969) so that the coordination polyhedron of the lead atom is a tetragonal pyramid, which is a ZP. This hypothesis is supported by the fact that the red modification of PbO is anti-isomorphic to the structure of LiOH, *i.e.* lithium atoms are placed in the oxygen-atom positions of the PbO structure and, conversely, the lead atoms occupy the positions of the oxygen atoms in the LiOH structure. In accordance with neutron diffraction experiments the LEP of an oxygen atom located between atoms of oxygen and hydrogen in the LiOH structure supplements four lithium atoms with the fifth vertex of a tetragonal pyramid.

The structure of the yellow modification of PbO differs from the red one mainly in the first coordination sphere of the lead atom (Fig. 5) which is formed by four oxygen atoms and a LEP of the central lead atom. The coordination polyhedron is a trigonal bipyramid. The distances from the center of the complex to the apical oxygen atoms are 2·48 Å × 2 and to the equatorial oxygen atoms 2·09 and 2·37 Å (the
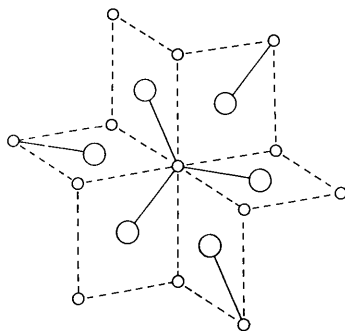

Fig. 3. Distribution of LEP's and atoms in the polonium structure; atoms are depicted by the small circles, the bigger circles are LEP's.
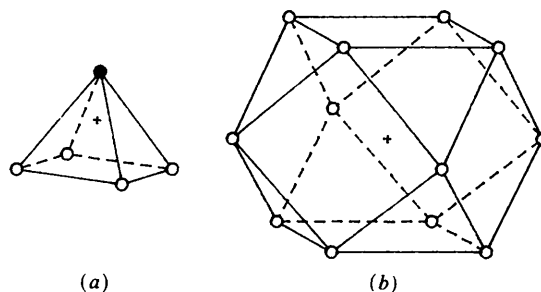

(a)   (b)

Fig. 4. Polyhedral structure of red modification of PbO. The lead atom is in the center of the ensemble; (a) four oxygen atoms (open circles) and LEP's (filled circle); (b) Pb.

third equatorial vertex is occupied by a LEP). The second coordination sphere is a cuboctahedron distorted more significantly than in the red modification: two quadrilateral faces are bent along diagonals, and the distances from the center of the complex to the vertices of the polyhedron are in a wider interval – 3·49–4·17 Å.

The compound Cu_2S has a very unusual structure. The symmetry of the crystal is hexagonal. Inside a hexagonal layer atoms are packed closely, but layers are stacked on each other so that a primitive hexagonal cell is formed. The density of packing is very low and an explanation for the stability of the structure should be proposed. Let us assume that any sulfide ion is surrounded by four LEP's distributed at the vertices of a tetrahedron. One of the threefold axes of each tetrahedron is parallel to a sixfold axis of the crystal. Let us assume also that three LEP's out of four from each sulfide ion are situated on one side of the atomic layer (let us say below the atomic layer) and are oriented in the way shown in Fig. 6. In this case LEP's form the kagomé net below the atomic layer (Fig. 6). The centers of hexagons in the kagomé net are filled by LEP's from a neighboring atomic layer. The upper part of this neighboring atomic layer has one LEP above each sulfide ion. These LEP's are situated between atoms of sulfur and copper on a straight line with these atoms. Such straight lines are parallel to the sixfold axis of the crystal. As a result LEP's form h.c.p. where a quarter of the tetrahedral holes are occupied by sulfur atoms and Cu(1) atoms, but a quarter of the octahedral holes are filled by Cu(2) atoms. The ensemble of the Cu_2S structure has LEP's in its center and two coordination spheres. In the first coordination sphere there are two Cu(2) atoms, a Cu(1) atom and an S at the corners of a rectangle. In the second coordination sphere 12 LEP's occupy the vertices of an anticuboctahedron. It is worth mentioning the fact that the LEP's in the Cu_2S structure are different. The center of the ensemble can be placed only at those which are on a straight line with atoms Cu(1) and S.

Comparing Fig. 1 and Fig. 6 and the descriptions of graphite structures and Cu_2S one finds that these two structures have common features: both Cu(2) and S atoms form together graphite-like layers which are stacked on each other like layers in β-graphite. But the Cu_2S and graphite structures have important distinctions: the carbon atoms are inside the LEP layer in the graphite structure and the atoms of the Cu_2S structure are between LEP layers in tetrahedral and octahedral holes.

Taking into consideration the differences in sizes between the carbon atoms on the one hand and the atoms of copper and sulfur on the other, one can conclude that the c axis of Cu_2S should be longer than the c axis of graphite. But the c axes of these crystals are nearly equal: 6·68 Å for Cu_2S and 6·70 Å for graphite. Presumably the lengths of the c axes of Cu_2S cells and graphite cells are predetermined by the layers of LEP's. The hypothesis about the existence of LEP layers explains the rather large shortest Cu(1)–S distances between atoms belonging to adjacent layers, i.e. half of the c axis, 3·35 Å, compared with the Cu(1)–S distance of 2·28 Å inside the atomic layer. The interactions of atoms inside the layers in these structures are quite different from the interlayer interactions. The a axes of Cu_2S crystals and graphite crystals are proportional to the shortest interatomic distances: 1·40 for C–C and 2·28 Å for

(a)

(b)

Fig. 6. The atomic layers of structure Cu_2S with account of supposed LEP. The small circles are the sulfur atoms; the bigger circles are the Cu(1) atoms; double circles are the Cu(2) atoms; crosses are LEP's distributed below the atomic layer; LEP's situated above the sulfur atoms are omitted. (a) Odd layer; (b) even layer.
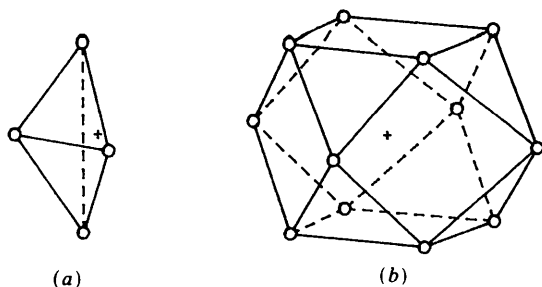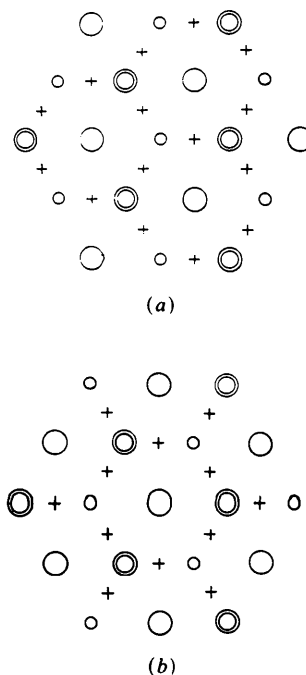

(a)   (b)

Fig. 5. Polyhedral structure of yellow modification of PbO. The lead atom is in the centre of the ensemble; (a) four oxygen atoms (the LEP is not depicted); (b) Pb.

Cu(2)–S (in the framework of the graphite-like net). Proceeding from the length of the a axis Cu_2S, 3·89 Å, the calculated value of the a axis of graphite is 2·39 Å; this is very close to the experimental value of 2·46 Å. Apparently, the atoms interact inside the atomic layer of Cu_2S, but the layers of LEP's are responsible for the organization of the atomic layers in three-dimensional structures.

The examples discussed above demonstrated the important role of LEP's in crystal structure formation. The CCMAI helps to reveal the participation of LEP's in some structures, i.e. it allows one to get results which one cannot yet obtain experimentally.

It is worth mentioning the pyrite structure (FeS_2) as it gives an example of a special property of an ensemble. The center of the ensemble is the atom of iron. The first coordination sphere with radius 2·26 Å×6 is an octahedron with sulfur atoms at the vertices (Fig. 7a). The second coordination sphere, of radius 3·82 Å, is a cuboctahedron (Fig. 7c) with atoms of iron. Between the first and second coordination sphere there are eight atoms of sulfur (Fig. 7b) remote from the center of the ensemble at 3·43 Å×6 and 3·61 Å×2. These atoms do not form any polyhedron of PRS, ASRS or ZP. They do not belong to this ensemble because all of them are parts of the first coordination spheres of the iron atoms placed in the second coordination sphere of the initial ensemble. In the pyrite structure ensembles cross each other only in the second coordination spheres but their first coordination spheres are only neighbors. Such a mutual penetration of ensembles inside each other is met in many types of structures.

The compound FeS_2 has two modification – pyrite and marcasite. The marcasite structure (Fig. 8) has the center of the ensemble at the iron atom. In the first coordination sphere the sulfur atoms are situated at the vertices of an octahedron (Fe–S distances are 2·23 Å×2 and 2·25 Å×4). In the second coordination sphere ten iron atoms form an elongated square bipyramid (ZP). The distances from the center of the ensemble to the vertices of a polyhedron in the second coordination sphere are 3·38 Å×2 (caps above the cube faces) and 3·89 Å×8. The marcasite structure is very similar to the rutile structure (Aslanov &

Markov, 1989); the shortest axis of the marcasite cell corresponds to the fourfold axis in the rutile structure.

Quasicrystals

The f.c.c. structures of simple substances have an important peculiarity. This type of structure can be considered as a sum of concentric shells around the central atom. Each shell has a cuboctahedral form. Sometimes this type of structure is compared to an onion (Teo & Sloane, 1985). The first shell has 12 atoms at the vertices of a cuboctahedron. The second shell contains 42 atoms which are at the vertices of the following polyhedra: octahedron (6 atoms), two truncated tetrahedra inserted in each other (24 atoms), cuboctahedron (12 atoms). The third and the other shells have cuboctahedral form and the number of atoms in each shell is $10n^2+2$, where n is the number of the shell (Teo & Sloane, 1985).

Thus the f.c.c. crystal structure has both a structural ensemble and a shell structure. These two aspects of crystal structure coexist in crystals with ensembles consisting of PRS's and ASRS's, for instance the b.c.c. structures. But not every crystal contains concentric shells. There are no such shells in crystals with ZP's in the atomic ensembles. For example, the h.c.p. structure has no shell structure as its structural ensemble contains an anticuboctahedron.

PRS's and ASRS's with I_h symmetry have the shell structures (Teo & Sloane, 1985), but the icosahedron is the most important polyhedron as it has only triangular faces and 12 atoms in the first coordination sphere. The existence of the icosahedral shell structure was proved experimentally for a giant cluster $[Pd_{561}L_{60}](OAL)_{180}$ (Vargaftik et al., 1985), where the cluster Pd_{561} has icosahedral form with $n = 5$. These clusters give 5–6 reflections on the electron diffraction patterns, i.e. they could be considered as small bodies with a regular distribution of atoms.

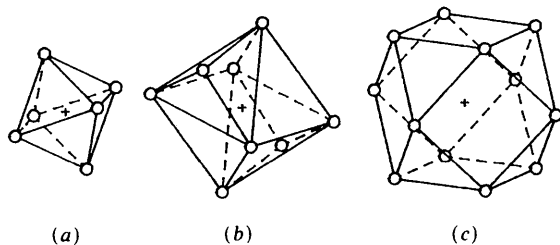It is known (Nepiiko, 1985; Gillet, 1977) that the gold solids grown by condensation of vapor on the

Fig. 7. Polyhedral purite structure (FeS_2). The atom of iron is at the center of the ensemble; at the vertices of polyhedra are (a) S; (b) S; (c) Fe.
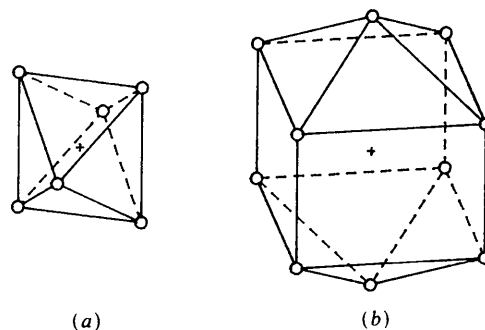

Fig. 8. Polyhedral marcasite structure (FeS_2). The atom of iron is at the center of the ensemble; at the vertices of polyhedra are (a) S; (b) Fe.

surface of an NaCl crystal have at first icosahedral or dodecahedral form instead of cuboctahedral. These particles rearrange into the f.c.c. structure if their dimensions approach 100–500 Å. The formation of icosahedral particles at the beginning of vapor condensation is quite natural as the icosahedron, compared with the cuboctahedron, is a perferable polyhedron in the first coordination sphere (Aslanov, 1988a). The first icosahedral shell predetermines the form of a solid particle. From now on we shall call it a cluster. Such an icosahedral cluster has no structural ensemble and hence translational symmetry. An icosahedron does not form an ensemble because the length of an icosahedral edge is not equal to the distance from the central atom to the atoms of the first shell and consequently a particle comprised of 13 atoms (one central atom and 12 atoms at the vertices of the icosahedron) has no fragment in the same particle.

The second and the third shells of the icosahedral cluster consist of PRS's and ASRS's exclusively (Fig. 9). In the second shell the atoms are distributed at the vertices of an icosahedron (12 atoms) and an icosadodecahedron (30 atoms). In the third shell there are an icosahedron (12 atoms), dodecahedron (20 atoms) and truncated icosahedron (60 atoms). Perhaps this fact promotes the formation of the multishell icosahedral cluster at the very beginning.

Three initial shells of icosahedral cluster together with the central atom form a regular set of atoms which has an important feature: it consists of 20 slightly distorted tetrahedral fragments. Each tetrahedral fragment has the f.c.c. structure compressed along a threefold axis which is normal to the faces

of shells, i.e. along the beam going from the center of the cluster. As a result of such deformation of the f.c.c. structure the distances between the atoms inside the shell are 1·052 times longer than the distances between the atoms of adjacent shells. This difference is sufficient for the realization of an icosahedral form of any shell.

Some details of the icosahedral cluster structure are worth paying attention to. Atoms 1 (Figs. 10a,b,c) have only one shortest contact with the atoms of the previous shell; atoms 2 and 3 (Figs. 10b,c) have two such contacts each, but atom 4 (Fig. 10c) has three shortest contacts. So only atom 4 in the third shell has an opportunity to become the center of another double-shell cluster, because the combination of atom 4 with three adjacent atoms of the previous shell composes a fragment of an icosahedron and hence atoms in position 4 give a maximal energetic effect.

Three atoms of the second shell of the initial cluster (atoms 2 in Fig. 10b) are involved in the construction of the first icosahedral shell around atom 4. The second shell around atom 4 is a fragmental one, unlike the second shell of the initial cluster, as the completion of the second shell is preserved by the initial double-shell cluster. The number of atoms 4 is 20 (number of vertices of dodecahedron). The formation of a double-shell cluster around each of these 20 atoms is impossible as atoms 4 are placed too close to each other. But the vertices of a dodecahedron can be combined in fours, forming perfect tetrahedra. The vertices of one of these tetrahedra become centers of double-shell clusters which in their turn are built up by double-shell clusters in the same way, so this process is endless.

The construction of a ball model clarified one detail: the second shell of the cluster consists of atoms 2 (Fig. 10b) only, but atoms 1 migrate from their positions into the first shell of four clusters attached around atoms 4. For further discussion it is worth noting that only twelve atoms 2 (Fig. 10b) of the initial cluster are incorporated in the first shells of
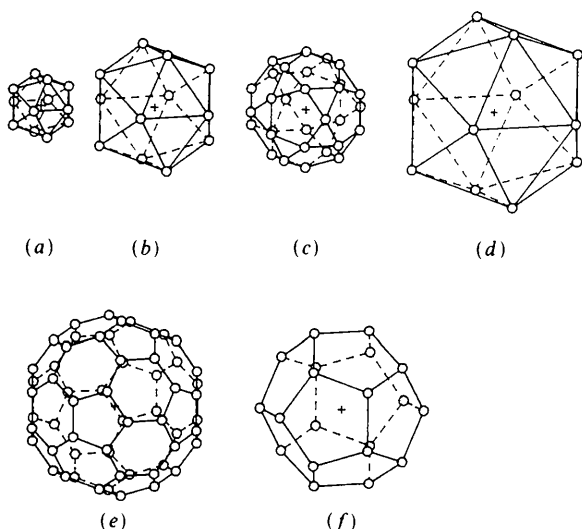

(a)   (b)   (c)   (d)

(e)   (f)

Fig. 9. Polyhedra included in first, second and third shells of the icosahedral cluster: (a) icosahedron in the first shell; (b) icosahedron in the second shell; (c) icosadodecahedron in the second shell; (d) icosahedron in the third shell; (e) truncated icosahedron in the third shell; (f) dodecahedron in the third shell.
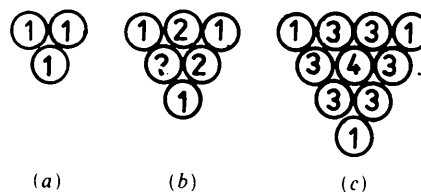

(a)   (b)   (c)

Fig. 10. Distribution of atoms in one of twenty triangular faces of an icosahedron in (a) the first, (b) the second and (c) the third shells of a quasicrystal. Atoms 1 (a, b, c) are placed at the vertices of icosahedra; atoms 2 (b) are at the vertices of an icosadodecahedron; atoms 3 and 4 (c) are at vertices of a truncated icosahedron and a dodecahedron, respectively. The superposition of layers (a), (b) and (c) on each other brings atom 4 (c) into the position which is equivalent to the position of the central atom (it is not depicted in the figure) which is below the center of a triangle with atoms 1 in the corners (a).

the attached clusters. The other 18 atoms 2 are aside from this process.

The icosahedra in the first shells of the central cluster and all attached clusters are precisely oriented with respect to each other; all axes of the central and of all attached clusters are parallel. This is caused by the orientation of atoms 1 (Fig. 10a) with respect to atoms 2 (Fig. 10b): two triangles formed by these atoms cross. Such a position of two triangles is predetermined by a double-shell structure of the clusters. For clarity let us imagine that atom 4 (Fig. 10c) is not in the third shell (or in the sixth, the ninth and so on) but it is in the fifth shell (or in the second, in the eighth, in the eleventh and so on). In this case three atoms of the previous shell (having the shortest contacts with atom 4) screen atoms 1 of the first shell. [If atom 4 is placed in the second shell, then atoms of the previous shell are atoms 1 of the first shell in Fig. 10(a).] As a result the elements of symmetry of the initial icosahedron are not parallel to the elements of symmetry of the attached icosahedron.

The icosahedra of the first shells in all clusters (both initial and attached ones) together with their central atoms form the diamond-like crystal structure (space group $Fd3$) where the central atoms of the clusters occupy the positions of carbon atoms in the diamond structure $[A(1)\ x = 0, y = 0, z = 0;\ A(2)\ x \simeq 0\cdot15,\ y = 0,\ z \simeq 0\cdot09]$. All 13-atom icosahedral complexes (parts of the double-shell clusters) form one of two subsystems of a quasicrystal (Fig. 11). This subsystem possesses translational symmetry and provides the diffraction of electrons and X-rays. The cell dimension of the first subsystem is 13·6 Å if the minimal parameter of the lattice, 2·38 Å, of the quasi-crystal Al_6CuLi_3 (van Smaalen, Bronsveld & de Boer, 1987) is a minimal interatomic distance. The value

Fig. 11. The orientation of the icosahedral clusters in the translationally symmetrical subsystem of the quasicrystal.

13·6 Å is close to half of the cell dimension (26·7 Å) for a cubic face-centered lattice found by Pauling (1985) for Al_6Mn (Shechtman, Blech, Gratias & Cahn, 1984) by the powder method. But all reflections with intensities 150-155 units (i.e. most powerful reflections) have only even indexes (Pauling, 1985). This means that there is a subcell with twice as small a parameter. Taking into consideration the discrepancy of chemical compositions of quasicrystals we conclude that the coincidence of the cell dimension with that of the subcell is satisfactory.

The second subsystem of the quasicrystal is formed by atoms incorporated in the second shells of clusters. This subsystem has no translational symmetry because only the initial double-shell cluster is complete, but any attached cluster has a part of the second shell. These parts of the different clusters are oriented in different ways depending on the side where a new cluster has been attached. The second atomic subsystem provides in a diffraction pattern reflections which are considered as proof of the point of view that quasicrystals have incommensurate structure. Any anisotropy of velocity of the quasicrystal growth changes the relation between quantities of clusters with different orientation of the fragments of the second shells. So a part of the diffraction pattern provided by the second subsystem of the quasicrystal depends on the conditions of preparation of a sample.

The model of a quasicrystal described contains ideal icosahedra; it has orientational order, but the translational symmetry in quasicrystals for two subsystems taken together is absent. This hypothesis differs from existing concepts which state either incommensurability of the quasicrystal structure (Bak, 1985; Long & Kuriyama, 1986) or multiple twinning of 20 cubic crystals (Pauling, 1985; Hua Mingjian, Li Chunzhi, Xu Jianming & Yan Minggao, 1988). Both approaches have arguments and counter-arguments, which is why some authors do not prefer any of these concepts (Bartges, Tosten, Howell & Ryba, 1987) or suggest a new theory (Coddens, 1988). So there is no commonly accepted idea about the structure of quasicrystals yet. It seems that the hypothesis described above meets all the requirements coming out of experimental facts.

Finally, it is necessary to note the fact that a quasicrystalline state is not restricted by the metastable phases with icosahedral structure. Presumably a protein globule is a sort of quasicrystal with orientational order of the peptide groups –C(O)–NH–, but without translational symmetry. Any peptide group has individual orientation and any protein globule has the same orientation for the peptide group (of course a certain protein should be considered). The environments of the peptide groups in peptide chains are different and this provides individual orientations of the peptide groups. It is clear that the so-called non-valent interactions are important for the protein chain
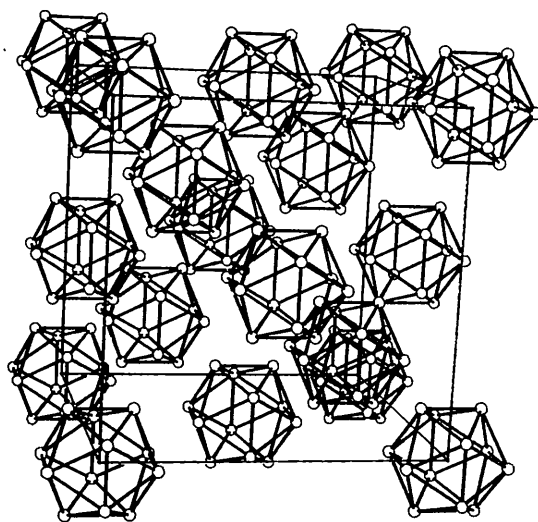
conformation as much as the second shells in the icosahedral quasicrystals are predeterminative for the orientation of icosahedra.

Concluding remarks

The fundamental idea of this paper is the concept of structural ensemble, *i.e.* the minimal set of atoms (molecules) containing all information about crystal structure. This ensemble is a center of growth of the crystal. This conforms with comprehensive views about the center of crystallization (Chernov, Givargizov, Bagdasarov, Kuznetzov, Demjanetz & Lobachov, 1983) as a set of a dozen (or so) atoms approximately.

Non-closely-packed structures are usually considered as a proof of direct bonds. The CCMAI allows one to explain the unusual non-closely-packed structures by taking into account LEP. Generally speaking the main conclusion following from CCMAI is a keystone for the theory of chemical structure: crystal and molecular structures are provided by basic principles of CCMAI, and not by supposed covalent bonds. Today the opinion is widely disseminated in the chemical literature that atomic orbitals orient adjacent atoms, thus determining the structures of molecules and crystals. Briefly, the principles of CCMAI control the structures of molecules and crystals, and the electronic structure and consequently chemical and physical properties of substances depend on molecular and crystal structure. This point of view allows one to realize why quantum chemistry methods, bond theory, pseudopotential theory and so on use experimental data on the crystal or molecular structures for calculation of properties of molecules and crystals, but are not capable of predicting their structure (if the 'trial and error' method is not taken into consideration). It is now obvious that structural chemistry has its own specific laws, but we are at the very beginning of the process of capturing these laws. This is evident from CCMAI and from a number of investigations where some conclusion about the important role of the mutual repulsion of atoms for structures of molecules (complexes) and crystals is drawn (Burdett, Hoffman & Fay, 1978; Kepert, 1982; Bartell & Barshad, 1984; Burdett, Hughbanks, Miller, Richardson & Smith, 1987; Feng Xi-Zhang, Guo Ao-Ling, Xu Ying-Ting, Li Xing-Fu & Sun Peng-Nian, 1987).

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