# Crystal-Chemical Model of Atomic Interactions. 3. Convex Polyhedra with Regular Faces

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## Abstract

Convex polyhedra with regular faces were used for developing the crystal-chemical model of atomic interactions. Some examples of inorganic crystal structures with coordination polyhedra belonging to convex polyhedra with regular faces are considered. Only four polyhedra – tetrahedron, octahedron, trigonal bipyramid and cube (without due regard for displacement of some atomic groups as a whole) – are shown to be stable at any value of the atomic interaction potential.

## Introduction

It was shown in previous papers of this series (Aslanov, 1988) that atoms in crystals of a cubic system are placed at vertices of Platonic regular solids (PRS) and Archimedean semiregular solids (ASRS); however, many crystals of hexagonal systems contain the anticuboctahedron which is not included in PRS or ASRS. The $Th_3P_4$ structure is built of eight-vertex dodecahedra. This polyhedron does not belong to PRS or ASRS. There exist many structures containing coordination polyhedra with odd numbers of vertices – 5, 7, 9, 11 and so on. All these examples demanded the development of a crystal-chemical model of atomic interactions (CCMAI) described earlier (Aslanov, 1988).

## Zalgaller's convex polyhedra with regular faces

PRS's and ASRS's possess three important properties: (i) all their vertices are placed on a sphere; (ii) all their faces are regular polygons (triangles, squares and so on), so that all polyhedra edges have equal lengths; (iii) all polyhedral angles are congruent or symmetric. In accordance with Zalgaller's (1969) work, the second condition alone gives 92 convex polyhedra other than PRS's and ASRS's. All of them are listed in the book by Zalgaller (1969). The most widespread of Zalgaller's polyhedra (ZP) is a triangular orthobicupola or an anticuboctahedron (Fig. 1g) which is one of the ZP's inscribed into the sphere in such manner than the center of this sphere coincides with the ZP's center of gravity. Among all

the ZP's seven more polyhedra* have their centers at points coinciding with the centres of describing
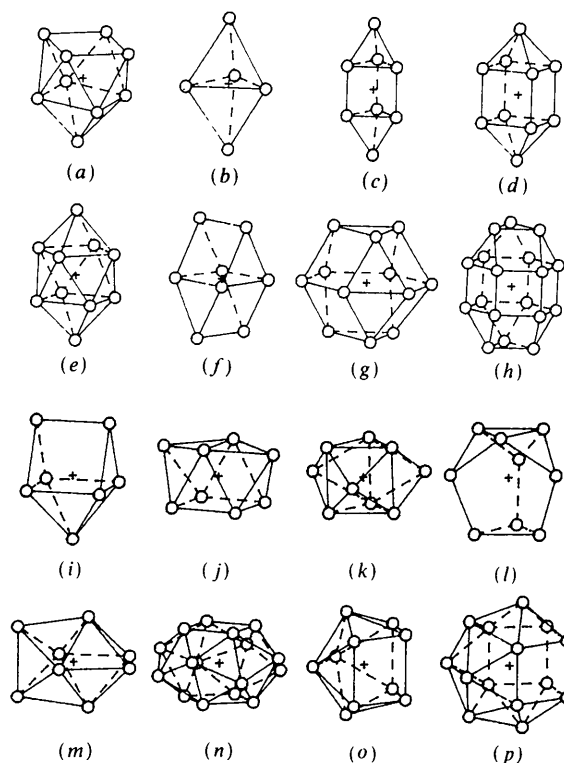
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Fig. 1. Zalgaller's polyhedra discussed in this paper. After the polyhedron name Zalgaller's (1969) number of this polyhedron is indicated. (a) Gyroelongated square pyramid (capped tetragonal antiprism), no. 10; (b) trigonal bipyramid, no. 12; (c) elongated triangular bipyramid (3,3-bicapped trigonal prism), no. 14; (d) elongated square bipyramid, no. 15; (e) gyroelongated square bipyramid (4,4-bicapped tetragonal antiprism), no. 17; (f) gyrobifastigium, no. 26; (g) triangular orthobicupola (anticuboctahedron), no. 27; (h) elongated triangular orthobicupola, no. 35; (i) augmented triangular prism (4-capped trigonal prism), no. 49; (j) biaugmented triangular prism (4,4-bicapped trigonal prism), no. 50; (k) triaugmented triangular prism (4,4,4-tricapped trigonal prism), no. 51; (l) tridiminished icosahedron, no. 63; (m) snub disphenoid (eight-vertex dodecahedron), no. 84; (n) snub square antiprism, no. 85; (o) sphenocorona, no. 86; (p) hebesphenomegacorona, no. 89.

spheres, but these polyhedra have no significance for crystal chemistry and are disregarded here. The wide spread of the anticuboctahedron in crystal structures is presumably due to two reasons: (i) the first and second conditions of the three mentioned above for PRS's and ASRS's are met; (ii) because of the specific space distribution of the 12 anticuboctahedron vertices the close packing of atoms is implemented. The other ZP's, inscribed into a sphere in such a way that the center of the sphere coincides with the polyhedron's center of gravity, have the following numbers of vertices: 24 [no. 37 – the Ashkinusean polyhedron (Ashkinuze, 1957)], 30 (no. 34), 60 and more (nos. 72-75, 80). Some crystal structures are considered below as examples indicative of the important role of ZP's for crystal-chemical analysis. As a rule, PRS's, ASRS's and ZP's are distorted in real crystal structures, say tetragonal (pentagonal and so on) faces are bent along diagonals. If such a bend exists in our examples, but is omitted from the figure to make the polyhedron clear, the value of the dihedral angle (d.a.) is put in brackets after the name of the polyhedron in the text. Dihedral angles less than 2° were ignored. Other distortions are visually demonstrated in the figures; that is why these facts are not pointed out in the text.

The crystal data for the compounds used as examples below are taken from Wyckoff's (1964) handbook, except for a few points specifically referenced.

## Discussion

Let us begin with the structure $LaF_3$. In accordance with widespread opinion, the coordination number (CN) of the lanthanum atom is 11 and the coordination polyhedron (CP) is a trigonal prism with caps above all its faces. There is no such polyhedron among the ZP's, but within the CCMAI framework this polyhedron should be considered as a sum of two coordination spheres (Fig. 2): in the first coordination sphere the fluorine atoms comprise a trigonal bipyramid (TB) with La–F distances of 2·36-2·43 Å, but the second coordination sphere represents a

trigonal prism (TP) with La–F distances 2·73 Å × 6. The CP's in the first and second coordination spheres are dual with respect to each other. TB is included in the set of ZP's, TP is one of the ASRS's. The third coordination sphere of the complex contains 12 lanthanum atoms distributed at the anticuboctahedron (ZP no. 27) vertices at distances 4·20-4·40 Å from the center of the complex (d.a. 3°). Any of the peripheral lanthanum atoms has exactly the same three coordination spheres. As a result, translational symmetry arises. This approach eliminates the problems in descriptions of the $LaF_3$ structure, which are inevitable when the distribution of fluorine atoms in the close packing of lanthanum atoms is considered.

One of the most widespread polyhedra is the tri-augmented triangular prism (ZP no. 51, Fig. 1k) or, in other words, the 4,4,4-tricapped trigonal prism (4,4,4-TTP). For instance, in the $PbCl_2$ structure (Fig. 3) the center of a complex coincides with the lead atom, and the first coordination sphere – 4,4,4-TTP – is formed by nine chlorine atoms. The interatomic Pb–Cl distances are within the range of 2·85-3·63 Å. The second coordination sphere consists of 12 lead atoms placed at the anticuboctahedron vertices at distances of 4·55-5·05 Å from the central lead atom (d.a. 4°). The 4,4,4-TTP in the first coordination sphere was found to be around yttrium atoms in the $YF_3$ and $Y(OH)_3$ structures, around the uranium atom in $UCl_3$, around the boron atom in $Re_3B$, around the phosphorus atom in $Ni_3P$, around the P(1) atom in $Fe_2P$ and around the S(2) atom in CuS. This CP exists in some structures in the second coordination sphere: in the olivine $Mg_2SiO_4$ structure (Birlie, Gibbs, Moore & Smith, 1968) the silicon atom is surrounded by oxygen atoms at the tetrahedron vertices in the first coordination sphere and by magnesium atoms at the 4,4,4-TTP vertices in the second coordination sphere.

Another polyhedron, rather typical of crystal structures, is the snub disphenoid or eight-vertex dodecahedron (ZP no. 84, Fig. 1m). For instance, the $ThCl_4$ structure (Fig. 4) consists of complexes with
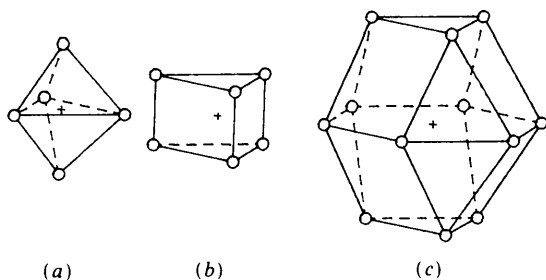


(a)          (b)          (c)

Fig. 2. The polyhedral structure of complexes in $LaF_3$ crystals. The center is occupied by an La atom. The atoms at polyhedra vertices are: (a) and (b) F; (c) La.
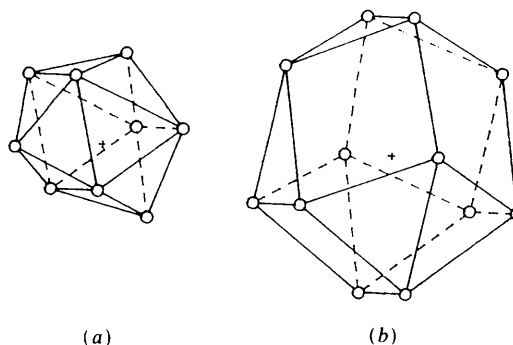


(a)          (b)

Fig. 3. The polyhedral structure of complexes in $PbCl_2$ crystals. The center is occupied by a Pb atom. The atoms at polyhedra vertices are: (a) Cl; (b) Pb.

the thorium atom at the center; eight chlorine atoms are in the first coordination sphere at eight-vertex dodecahedra vertices at Th–Cl distances of 2·46 Å × 4, 3·11 Å × 4; the four thorium atoms comprise a tetrahedron in the second coordination sphere with distances 4·64 Å × 4 from the center of the complex. This example shows that the eight-vertex dodecahedron has two groups of distances between the vertices and the polyhedron center: the short distances belong to vertices placed at the point of intersection of five edges, the long ones correspond to vertices where four edges cross each other. Thus, the eight-vertex dodecahedron cannot be inscribed into a sphere without distortions and, therefore, one of the conditions for potential-energy minimum mentioned above is not met. The potential energy of such a complex is not minimal despite the fact that all faces of this polyhedron are trianglar and all edges have equal lengths. Very often the crystal structures contain eight-vertex dodecahedra which have nearly equal distances between vertices and the center of a polyhedron, but different lengths of edges, i.e. the polyhedron topology (the numbers of vertices of two above-mentioned types and their mutual displacement) is preserved, but the polyhedron has distortions. Such eight-vertex dodecahedra were found in the first coordination spheres of a calcium atom in the sheelite structure (CaWO$_4$) and of a zirconium atom in the zircon structure (ZrSiO$_4$), as well as in the second coordination sphere of a titanium atom in the anatase (TiO$_2$) structure.

In the rutile (TiO$_2$) structure the titanium atom is placed at the center of a complex consisting of two coordination spheres (Fig. 5). The first coordination sphere contains the oxygen atoms only, which are at the octahedron vertices (the Ti–O distances are 2·13 Å × 4, 2·16 Å × 2); the second has ten titanium atoms placed at the elongated tetragonal bipyramid, vertices (ZP no. 15, Fig. 1d) at distances 3·55 Å × 2, 3·56 Å × 8 from the center of the complex. The elongated tetragonal bipyramid is the name of the ideal ZP, but this polyhedron is distorted in the rutile structure; it is compressed along the fourfold axis. So the rutile structure differs from the anatase structure in the second coordination sphere. The elongated
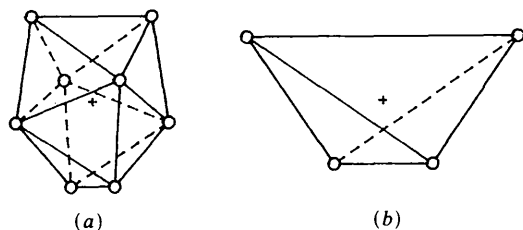
tetragonal bipyramids are found in the second coordination spheres of a tellurium atom in the tellurium dioxide structure, of an Ir(1) atom in the IrSe$_2$ structure, of a boron atom in the Re$_3$B structure, of an iron atom in the marcasite structure, of zirconium and silicon atoms in the zircon structure.

The elongated trigonal bipyramid (ZP no. 14, Fig. 1c) is a quite ordinary polyhedron in crystal structures. For instance, in the UCl$_3$ structure (Fig. 6) the uranium atom is at the center of the complex. Its first coordination sphere consists of nine chlorine atoms distributed at 4,4,4-TTP vertices, as mentioned above. The second coordination sphere is formed by eight uranium atoms fixed at vertices of the elongated trigonal bipyramid, i.e. the 3,3-bicapped trigonal prism (3,3-BTP) at distances 4·31 Å × 2 (caps) and 4·80 × 6 from the center of the complex. The same polyhedra were discovered in the second coordination spheres of Ir(2) in the IrSe$_2$ structure, of an aluminium atom in the AlOOH structure, and of O(1) in the Pb$_3$O$_4$ structure.

The Pb$_3$O$_4$ structure is formed by two mutually correlated complexes (Fig. 7). The Pb(1) atom is at the center of the first complex. Its first coordination sphere is an octahedron with oxygen atoms at the



Fig. 5. The polyhedral structure of complexes in rutile (TiO$_2$) crystals. The center is occupied by a Ti atom. The atoms at polyhedra vertices are: (a) oxygen; (b) Ti.



Fig. 4. The polyhedral structure of complexes in ThCl$_4$ crystals. The center is occupied by a Th atom. The atoms at polyhedra vertices are: (a) Cl; (b) Th.
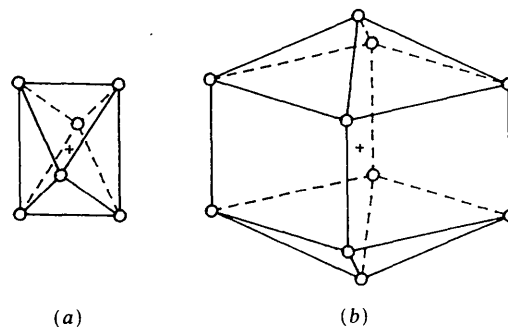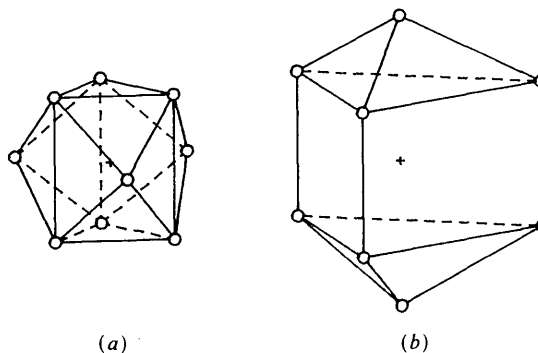


Fig. 6. The polyhedral structure of complexes in UCl$_3$ crystals. The center is occupied by a U atom. The atoms at polyhedra vertices are: (a) Cl; (b) U.

vertices at distances $2 \cdot 14 \text{ Å} \times 2$ [for O(2)] and $2 \cdot 17 \text{ Å} \times 4$ [for O(1)] from the central lead atom. The second coordination sphere contains ten lead atoms arranged as a gyroelongated square bipyramid (ZP no. 17, Fig. 1$e$), which is known in crystal chemistry as the 4,4-bicapped tetragonal antiprism (4,4-BTA). The distances from the lead atoms to the center of the complex are $3 \cdot 27 \text{ Å} \times 2$ (caps) for Pb(1) and $3 \cdot 71 \text{ Å} \times 8$ for Pb(2). The third coordination sphere consists of six O(2) atoms distributed at the octahedron vertices and removed at $3 \cdot 91 \text{ Å} \times 4$, $4 \cdot 08 \text{ Å} \times 2$ from the center. The other atoms are placed at a distance of no less than $5 \cdot 07 \text{ Å}$ from the center of the complex.

The third coordination sphere in the previous complex was taken into consideration because complexes of the second type are centered on O(2) atoms. The O(2) atom is surrounded by three lead atoms – Pb(1) 2·14, Pb(2) $2 \cdot 25 \text{ Å} \times 2$. The second coordination sphere has eight oxygen atoms at 3,3-BTP vertices (ZP no. 14, Fig. 1$c$). The distances of these atoms from the center of the complex are $3 \cdot 04 \text{ Å} \times 4$, $3 \cdot 12 \text{ Å} \times 2$ for O(1) and $3 \cdot 27 \text{ Å} \times 2$ for O(2) (caps). The third coordination sphere is a trigonal bipyramid (ZP no. 12) with five lead atoms at vertices placed at the following distances from the center of the second-type complex: $3 \cdot 63 \text{ Å} \times 2$ for Pb(2), $3 \cdot 91 \text{ Å} \times 2$ (apical) and $4 \cdot 08 \text{ Å}$ for Pb(1). The next closest atoms to the center of the complex are at a distance of $4 \cdot 54 \text{ Å}$.

In the $Pb_3O_4$ structure the atoms of the last coordination sphere of the second type of complex are the central atoms of the first type of complex and *vice versa*, which is quite an ordinary phenomenon in crystals of various substances. The Pb(2) atoms and O(1) do not form complexes and play an auxiliary role in the structure.
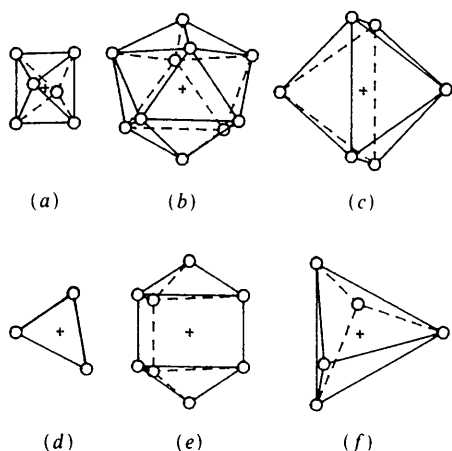
Some structures contain a coordination polyhedron as a gyrobifastigium (ZP no. 26, Fig. 1$f$). For example, in the NbP structure (Fig. 8) both niobium and phosphorus atoms contain this polyhedron in the first coordination spheres with Nb–P distances of $3 \cdot 29 \text{ Å} \times 8$. The second coordination sphere of a niobium (phosphorus) atom consists of niobium (phosphorus) atoms placed at vertices of the eight-vertex dodecahedra (ZP no. 84), distorted in such a way that this polyhedron could be inscribed into the sphere: the distances of the vertices of this polyhedron from the center of the complex are $3 \cdot 32 \text{ Å} \times 8$. The gyrobifastigium was found in the second coordination sphere of the tetrahedral Ni(1) cluster in the $Ni_3P$ structure (the nickel atoms are at the vertices of this polyhedron).

The $Cu_3As$ structure is remarkable because of the existence of different ZPs in it. It is worth mentioning that the $Cu_3As$ compound is intermetallic by character, and its structure has some peculiarities; *e.g.* the copper atom can be coordinated by another copper atoms. In the $Cu_3As$ structure (Fig. 9) three types of complexes can be singled out. In the first type of complex nine copper atoms form around an arsenic atom the rare CP the so-called tridiminished icosahedron (ZP no. 63, Fig. 1$l$, d.a. 12°). The As–Cu distances lie inside the $3 \cdot 39$–$3 \cdot 63 \text{ Å}$ interval. This polyhedron is slightly twisted around the threefold axis. The two other complexes have clusters at their centers. One of these clusters has four copper atoms at vertices of the distorted tetrahedron at distances of $2 \cdot 11 \text{ Å}$ from the center of the cluster. The first coordination sphere is the gyrobifastigium (ZP no. 26, d.a. 8°) consisting of four arsenic atoms ($2 \cdot 60 \text{ Å}$ from the center of the cluster) and four copper atoms in the equatorial plane ($2 \cdot 85 \text{ Å}$ from the center of the cluster). In the other cluster complex four copper atoms form a tetrahedron ($1 \cdot 54 \text{ Å}$ from the center of the cluster), and eight arsenic atoms are distributed at the eight-vertex dodecahedron vertices (ZP no. 84) with distances $2 \cdot 85 \text{Å} \times 4$ (vertices with five edges) and $3 \cdot 94 \text{ Å} \times 4$ from the center of the cluster. And, finally, the eight copper atoms are grouped in the distorted



*(a)*  *(b)*  *(c)*

*(d)*  *(e)*  *(f)*

Fig. 7. The polyhedral structure of complexes in $Pb_3O_4$ crystals. The first complex has a Pb atom at the center; the atoms at vertices are: ($a$) oxygen, ($b$) Pb; ($c$) oxygen. The second complex has an oxygen atom at the center; the atoms at the vertices are: ($d$) Pb; ($e$) oxygen; ($f$) Pb.
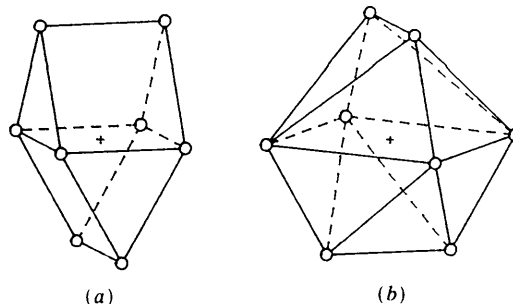


*(a)*  *(b)*

Fig. 8. The polyhedral structure of complexes in NbP crystals. The center is occupied by an Nb atom. The atoms at polyhedra vertices are: ($a$) P; ($b$) Nb.

gyrobifastigium (ZP no. 26, d.a. 15°). The distances from the center of the cluster are 3·34 Å × 4 and 3·94 Å × 4 (the equatorial plane). The specific feature of the latter complex is the fact that half of the atoms in the first coordination sphere lie farther (0·57 Å) from the center of the cluster than half of the atoms in the second coordination sphere, in spite of the fact that, on average, the distances from the center of the cluster to atoms differ noticeably in the first and second coordination spheres. This is one more peculiarity of intermetallic structures.

Quite a few structures have as CP a gyroelongated square pyramid (ZP no. 10, fig. 1a) or, in other words, the four-capped tetragonal antiprism (4-CTA). For instance, the lead atom in the PbFCl structure (Fig. 10) has this particular polyhedron in the first coordination sphere. The only square face is formed by fluorine atoms; the other vertices are filled with chlorine atoms. The Pb–F distances are 2·51 Å × 4,



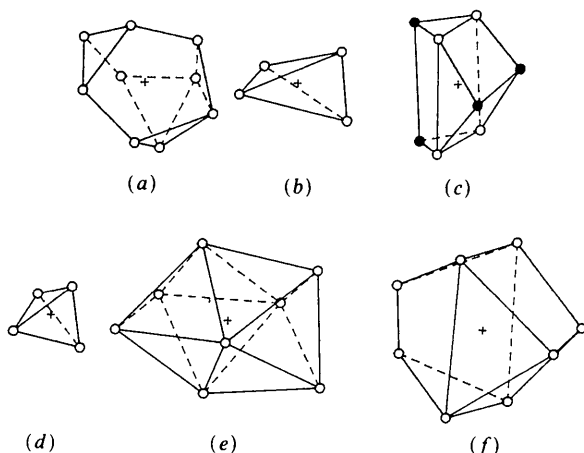(a)          (b)          (c)

(d)          (e)          (f)

Fig. 9. The polyhedral structure of complexes in Cu₃As crystals. The first complex has an As atom at the center; the atoms at vertices (a) are Cu. The second complex has a cluster (b) with Cu atoms at the center; the atoms at the vertices (c) are four As atoms (black circles) and four Cu atoms. The third complex has a cluster (d) with Cu atoms; the atoms at the vertices are: (e) As; (f) Cu.
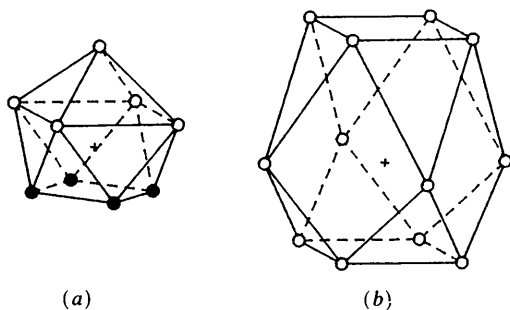


(a)                    (b)

Fig. 10. The polyhedral structure of complexes in PbFCl crystals. The center is occupied by a Pb atom. The atoms at polyhedra vertices are: (a) F (black circles) and Cl; (b) Pb.

the Pb–Cl ones are 3·10 Å × 4, 3·25 Å (a cap). The second coordination sphere consists of 12 lead atoms. Eight of these atoms are nearly at the same distance from the center of the complex: 4·10 Å × 4, 4·11 Å × 4, but the other four atoms are placed much farther, at 5·22 Å × 4. This deformation of the cuboctahedron is predetermined by the first coordination sphere which is responsible for the stratified character of the structure.

The $Ni_{12}P_5$ structure (Rundqvist & Larsson, 1959) consists of two types of correlated complexes (Fig. 11). Both complexes have phosphorus atoms at the centers. In the first type of complex the center coincides with a P(1) atom. The CP of this atom consists of 10 nickel atoms distributed at vertices of the sphenocorona (ZP no. 86, Fig. 1o). The P(1)–Ni distances are 2·21–2·60 Å. The second coordination sphere is a cuboctahedron (d.a. 6°). It has nine P(1) atoms and three P(2) atoms situated at 3·63–3·93 and 3·73–3·96 Å from the center of the complex, respectively. The center of the second type of complex is occupied by the P(2) atom. Its first coordination sphere is a slightly flattened cube with Ni(1) atoms at the vertices (the distances from the center are 2·25 Å × 8). The second coordination sphere is a cuboctahedron (d.a.f. 4°) with the P(1) atoms at the vertices, which are 3·37 Å × 8 and 3·96 Å × 4 from the center of the complex.

According to the description of this structure (Kripyakevich, 1977), the CP's of nickel atoms are defined as unusual ones. Presumably this is because of the fact that the $Ni_{12}P_5$ structure is formed by complexes with phosphorus atoms at their centers, but the nickel atoms are influenced by phosphorus ones. The $Ni_{12}P_5$ structure demonstrates the possibilities of CCMAI for correct description and classification of structures.

This idea can be confirmed by another example. Wyckoff (1964) pointed out that all three independent nickel atoms in the $Ni_3P$ structure (Fig. 12) have different coordinations and the distances between the central Ni atom and adjacent atoms grow so gradually that there is no possibility of determining CN's without knowing about the CP. The CCMAI has shown that the N₃P structure consists of three types of complexes and none of them has a nickel atom at

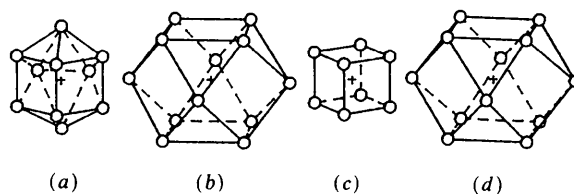

(a)          (b)          (c)          (d)

Fig. 11. The polyhedral structure of complexes in $Ni_{12}P_5$ crystals. The first complex has a P(1) atom at the center; the atoms at the vertices are (a) Ni; (b) P. The second complex has a P(2) atom at the center; the atoms at the vertices are (c) Ni; (d) P.

the center. The complexes of the first type form chains of tetrahedral clusters (Figs. 12b,d). The centers of clusters have two independent positions in the structure. These two positions are half of a c translation apart. The distances of the centers of the clusters from Ni(2) atoms at the vertices are 1·59 and 1·73 Å. The coordination spheres of these two clusters are tetrahedra (Figs. 12c,e) with phosphorus atoms at the vertices (the distances from the centers of the clusters are 2·29 and 2·21 Å, respectively). The nickel tetrahedra are dual with respect to phosphorus ones. The nickel tetrahedra have common edges joining them in chains running along the c axis.

The complex of the second type has a phosphorus atom at the center and the only coordination sphere has a nickel atom at 4,4,4-TTP vertices (ZP no. 51, Fig. 12a). The P–Ni distances are 2·21–2·34 Å for three Ni(3) atoms, 2·22 and 2·29 Å for two Ni(1) atoms, and 2·29–2·34 Å for four Ni(2) atoms. The complex of the third type consists of a tetrahedral cluster with Ni(1) atoms at the vertices [the distances from the center of the cluster to Ni(1) atoms are 1·61 Å × 4] and three coordination spheres. The center of this cluster coincides with the structure origin. The first coordination sphere is a tetrahedron with Ni(3) atoms at the vertices (the distances from the center of the cluster are 2·71 Å × 4). The second coordination sphere has eight nickel atoms distributed at the vertices of a distorted gyrobifastigium (ZP no. 26). The distances from the center of the cluster are 3·28 Å × 4 for Ni(2) (the equatorial plane) and 3·55 Å × 4 for Ni(1). The third coordination sphere contains eight phosphorus atoms at the vertices of a slightly distorted cube (the distances from the center of the cluster are 3·35 Å × 4 and 3·46 Å × 4).

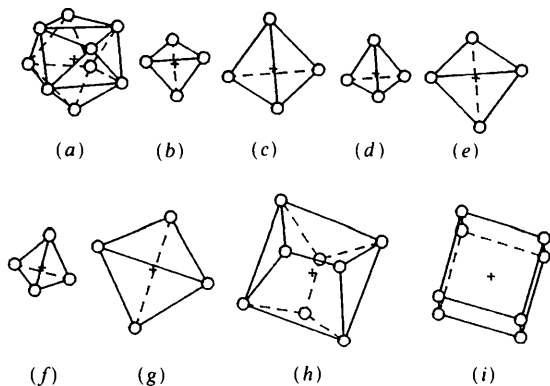One more ZP was found in the CdNi structure (Critchley & Jeffery, 1965) which possesses complexes of three types (Fig. 13). The center of the first type of complex is placed at a cadmium atom, which is surrounded by 14 nickel and cadmium atoms at the vertices of a hebesphenomegacorona (ZP no. 89, Fig. 1p). The distances from the center of the complex to atoms of the first coordination sphere are 2·77–2·85 Å for four Ni(1) atoms, 2·86 Å for two Ni(2) atoms and 2·97–3·17 Å for eight cadmium atoms. The center of the second type of complex is occupied by an Ni(1) atom. The only coordination sphere in this complex is an icosahedron with distances from the center of the complex of 2·44 Å × 3 for Ni(2), 2·54 Å × 3 for Ni(1), 2·77 Å × 3 and 2·85 Å × 3 for cadmium atoms. The third type of complex has an Ni(2) atom at its center and an icosahedral coordination sphere with distances from the center of the complex of 2·44 Å for Ni(1) atoms and 2·86 Å × 6 for cadmium atoms.

The $Ag_8Ca_3$ structure (Calvert & Rand, 1964) demonstrates one more ZP, i.e. the snub square antiprism (ZP no. 85, Fig. 1n), which is the CP of a calcium atom. The $Ag_8Ca_3$ structure (Fig. 14) is arranged as follows. The octahedral cluster consisting of six calcium atoms (all the distances from the center of the cluster to calcium atoms are 2·50 Å) is placed at the center of the complex. The first coordination sphere with 4·25 Å radius has Ag(1) atoms at the
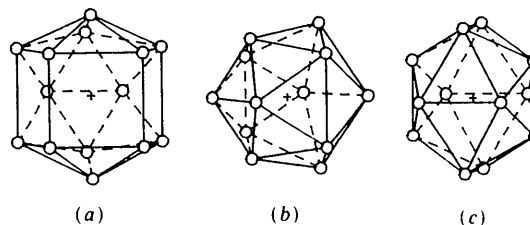


Fig. 13. The polyhedral structure of three complexes in CdNi crystals with (a) Cd, (b) Ni(1), (c) Ni(2) atoms at the centers, respectively, and both Ni and Cd atoms at the vertices.



Fig. 12. The polyhedral structure of complexes in $Ni_3P$ crystals: (a) CP of the phosphorus atom with Ni atoms at the vertices (complex II); (b), (d) the central clusters with Ni atoms (complex I); (c) the first coordination spheres with P atoms (complex I); (f) the central cluster with Ni atoms and its three coordination spheres: (g) Ni; (h) Ni; (i) P (complex III).



Fig. 14. The polyhedral structure of complexes in $Ag_8Ca_3$ crystals. The center is occupied by cluster (a) with Ca atoms. The atoms at polyhedra vertices are: (b) Ag(1); (c) Ag(2); (d) Ag(2); (e) Ag(2); (f) Ca; (g) CP of Ca atom.

vertices of a cube which is a dual polyhedron with respect to the central cluster. The second coordination sphere with 4·81 Å radius is formed by Ag(2) atoms distributed at cuboctahedron vertices. The third coordination sphere with 5·34 Å radius is a distorted rhombicuboctahedron with Ag(2) atoms at the vertices. The fourth coordination sphere with 7·25 Å radius has 24 Ag(2) atoms at the vertices of a truncated octahe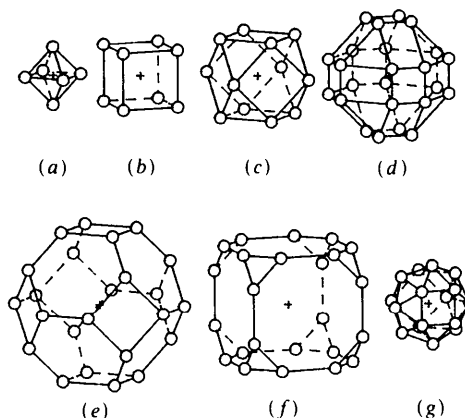dron. The fifth coordination sphere with 7·34 Å radius is a truncated cube with calcium atoms at the vertices. Each triangular face of the last polyhedron belongs to the central octahedral cluster, and this is a new starting point for development of the structure.

Some very interesting ZP's (no. 35, Fig. 1h) exist in the $MoS_2$ structure (Fig. 15). This is an elongated triangular orthobicupola. The $MoS_2$ structure has a cluster consisting of three molybdenum atoms and two sulfur atoms combined in a trigonal bipyramid (ZP no. 12). This five-atom cluster has in its first coordination sphere 18 sulfur atoms distributed at the vertices of the polyhedron mentioned. The distances from the center of the cluster to the vertices of the hexagonal-prismatic fragment are 3·49 Å. The other six sulfur atoms are 5·00 Å apart from the cluster of the cluster.

Two more ZP's will be considered below. These are taken from the $Gd_2S_2$ structure (Prewitt & Sleight, 1968) containing two correlated complexes (Fig. 16). The center of the first complex is occupied by the Gd(1) atom. The first coordination sphere has eight sulfur atoms at the vertices of a biaugmented triangular prism (ZP no. 50, Fig. 1j) or a 4,4-bicapped trigonal prism (4,4-BTP). The distances from the center of the complex to sulfur atoms are 2·75–3·06 Å. The second coordination sphere is a trigonal bipyramid (ZP no. 12) with five gadolinium atoms at the vertices (the distances from the center of the complex are 4·89–4·93 Å). The third coordination sphere is a trigonal prism with Gd(2) atoms at the

vertices; this is a dual polyhedron with respect to the previous CP. The distances from the center of the complex to the atoms in the third coordination sphere are 5·36 Å × 6.

In the second type of complex the seven sulfur atoms form an augmented triangular prism (ZP no. 49, Fig. 1i, d.a. 3°), which is known in crystal chemistry as a four-capped trigonal prism (4-CTP). The distances from the center of the complex to sulfur atoms are 2·75–2·92 Å. The second coordination sphere contains 13 gadolinium atoms which are 4·89–5·56 Å from the center. These atoms form some original combination of a cuboctahedron and an anticuboctahedron. As is well known, the cuboctahedron differs from the anticuboctahedron by a 60° rotation of a triangular face around a threefold axis. The polyhedron in the outer sphere of the second complex in the $Gd_2S_3$ structure has two vertices of these triangles which belong to both cuboctahedron (the black circles in Fig. 16f) and an anticuboctahedron (the arrowed circles in Fig. 16f). Such a polyhedron has edges of different length and, hence, it does not belong to PRS, ASRS or ZP. The two correlated complexes in the $Gd_2S_3$ structure yield together a minimal set of atoms which generates a translational symmetry.

The TlI structure provides the second example of a polyhedron which does not belong to PRS, ASRS or ZP. The thallium and iodine atoms have identical CP's, so let us take for a choice the complex with a thallium atom at the center (Fig. 17) and seven iodine atoms (ZP no. 49, Fig. 1i) in the first coordination sphere. The Tl–I distances are 3·35–3·86 Å. The polyhedron in the second coordination sphere is a combination (Fig. 17b) of half of a cuboctahedron with half of an eight-vertex dodecahedron which is



*(a)*          *(b)*          *(c)*

*(d)*          *(e)*          *(f)*

Fig. 16. The polyhedral structure of complexes in $Gd_2S_3$ crystals. The first complex has a Gd(1) atom at the center; the atoms at the vertices are (a) S; (b) Gd; (c) Gd. The second complex has a Gd(2) atom at the center; the atoms at the vertices are: (d) S (the quadrilateral faces are slightly bent along the diagonals); (e) Gd. (f) The same polyhedron as at (e), but in the other aspect.
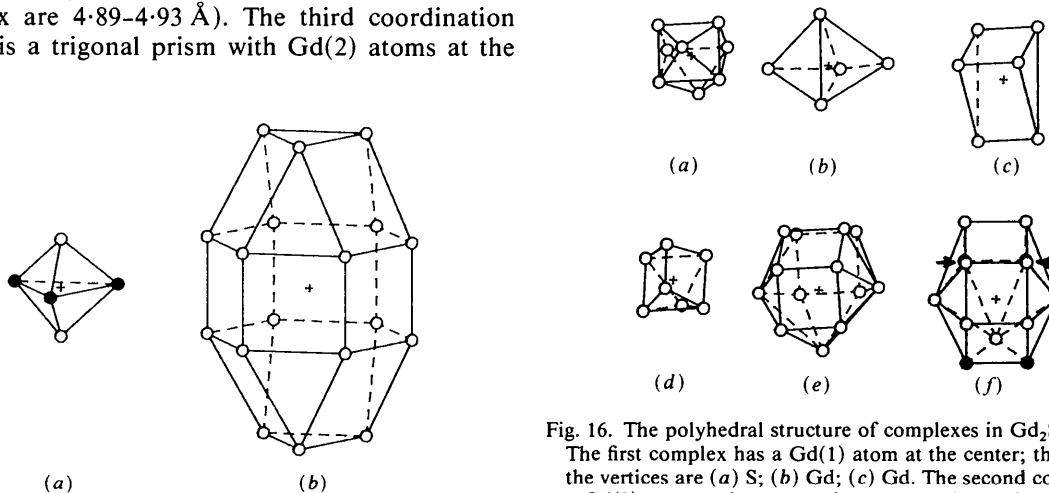


*(a)*                    *(b)*

Fig. 15. The polyhedral structure of complexes in $MoS_2$ crystals. The center is occupied by cluster (a) with three Mo atoms (black circles) and two S atoms; (b) the sulfur atoms are at the vertices.

Table 1. *The deviations of the ZP vertices from a sphere and numbers of vertices equidistant from the centers of polyhedra*

| Zalgaller's number and name of polyhedron | A(%) | Number of vertices equidistant from the centers of polyhedra (for groups of vertices) | | |
| --- | --- | --- | --- | --- |
| | | First | Second | Third |
| 10. Gyroelongated square pyramid | 22·93 | 4 | 5 | |
| 12. Trigonal bipyramid | 34·31 | 3 | 2 | |
| 14. Elongated triangular bipyramid | 53·14 | 6 | 2 | |
| 15. Elongated square bipyramid | 32·90 | 8 | 2 | |
| 17. Gyroelongated square bipyramid | 31·27 | 8 | 2 | |
| 26. Gyrobifastigium | 34·31 | 4 | 4 | |
| 27. Triangular orthobicupola | 0 | 12 | | |
| 35. Elongated triangular orthobicupola | 25·00 | 12 | 6 | |
| 49. Augmented triangular prism | 17·76 | 4 | 3 | |
| 50. Biaugmented triangular prism | 26·37 | 6 | 2 | |
| 51. Triaugmented triangular prism | 26·37 | 6 | 3 | |
| 63. Tridiminished icosahedron | 0 | 9 | | |
| 84. Snub disphenoid | 31·53 | 4 | 4 | |
| 85. Snub square antiprism | 22·52 | 8 | 8 | |
| 86. Sphenocorona | 18·90 | 4 | 2 | 4 |
| 89. Hebesphenomegacorona | 23·65 | 4 | 6 | 4 |

distorted in such a way that the vertices with five converging edges form a square. This square is a common part of the two parts of the polyhedron mentioned. The distances from the center of the complex to thallium atoms in the second sphere are 4·53–4·57 Å for four vertices of a cuboctahedron, 5·05 Å × 4 for four vertices common to two pieces of the CP, and 5·24 Å for the vertices of a distorted eight-vertex dodecahedron.

One can say, in conclusion, that the inorganic crystal structures consist of regular or distorted PRS's, ASRS's and ZP's, as a rule. The other types of CP are rare, such as, for instance, the two polyhedra discovered above, which are in fact combinations of ASRS's and ZP's.

ZP's with a large number of vertices have not been found in crystal structures, but ZP's with a number of vertices in the range 5–10 are widespread. The following ZP's were found in crystal structures: both 5-vertex polyhedra, all 8-vertex polyhedra, two 7-vertex polyhedra of the three known ones, three 9-vertex polyhedra of the four known, and three 10-



(a)         (b)

Fig. 17. The polyhedral structure of complexes in Tl1 crystals. The center is occupied by a Tl atom. The atoms at the vertices are (a) I, (b) Tl.

vertex polyhedra of the five known. There are ZP's which each include four different 11-, 12-, 14-, 16- and 18-vertex polyhedra, but only one representative of each of four such polyhedra have so far been recorded in crystal structures. ZP's with numbers of vertices of 20 and more have not yet been found.

As shown above, many ZP's cannot be inscribed into a sphere. The deviation of the vertices of a ZP from a sphere (the asphericity) is worth estimating. As a measure of ZP asphericity the following formula was used:

$$A = \frac{r_{max} - r_{min}}{(r_{max} + r_{min})/2} \times 100\%,$$

where $r_{max}$, $r_{min}$ are maximal and minimal distances from the polyhedron vertices to a point $O$ respectively; the point $O$ satisfies the condition that the difference $(r_{max} - r_{min})$ is minimal. Table 1 shows $A$ values for some ZP's and numbers of vertices equally remote from the point $O$, starting with the vertices nearest to the point $O$.

Table 1 supports the conclusion that ZP's with solely triangular faces – trigonal bipyramid (CN 5), eight-vertex dodecahedron (CN 8), 4,4,4-TTP (CN 9) – are the most widespread polyhedra in spite of their significant asphericities. A polyhedron with triangular faces has longest edges among polyhedra with identical number of vertices. Such a result supports an assertion about the strong influence of ligand repulsion over crystal structures.

The formation of different CP's is usually explained by distinctions between the potentials of the atomic interactions. But as was made clear, there are stable CP's in spite of rather general conditions for the potentials of the atomic interactions. These polyhedra are the tetrahedron, trigonal bipyramid, octahedron and cube (the appearance of the cube is prompted by the fact that the model under consideration does not take into account the possibility of the consistent
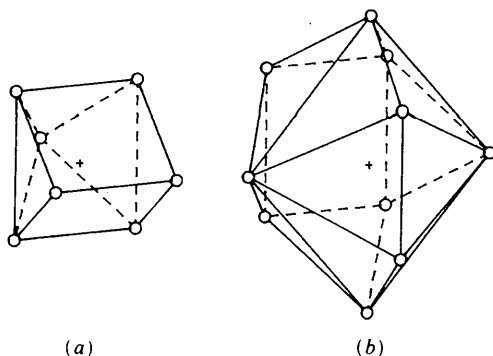
displacement of the atomic group), and only these. Tetrahedra and octahedra fill space without emptiness generating f.c.c or h.c.p. of atoms (ions) in crystals of inorganic substances. Presumably close packing of atoms is widespread in crystals because it does not depend on the potential of the atomic interactions. A proof of the stability of the four polyhedra mentioned above at any potential of the atomic interactions is given in the Appendix. For the cube the consistent displacement of atomic groups converts a cube into another polyhedron, for instance a tetragonal antiprism. The potential energy of the latter is lower than the potential energy of the former (Kepert, 1982), so the cube is not so important as the tetrahedron or octahedron.

The authors are grateful to Dr R. V. Galliulin for fruitful discussions of the subject.

## APPENDIX

We consider the following model of interaction of atoms forming a coordination polyhedron around some central atom. Let these atoms be placed in the vertices of a convex polyhedron inscribed into a sphere of fixed radius $r$, so that the action of each vertex on its neighbors is defined by a potential $f(\rho)$, where $\rho$ is the length of the edge connecting these vertices. Let the following conditions always be satisfied: $f'(\rho) < 0, f''(\rho) > 0$ (i.e. the force of repulsion increases when the points draw together). Call the polyhedron $f$ stable if every vertex of it is at a stable equilibrium position in the field of force defined by the actions of all its neighbors, i.e. by the action determined by the given potential $f = f(\rho)$.

### Theorem

The following and only the following convex polyhedra are $f$ stable for every atomic interaction potential (a.i.p.) $f$ satisfying the aforesaid conditions: (1) a tetrahedron; (2) an octahedron; (3) a cube; (4) a trigonal bipyramid inscribed into a sphere.

Let $M$ hereafter be a convex polyhedron inscribed into a sphere of radius $r$, $V(M)$ be the set of its vertices, $\rho(A, B)$ denote the distance between points $A$ and $B$, $a(M) = a$ be the length of the shortest edge of polyhedron $M$, and $s(M)$ denote the family of edges of $M$ having length equal to $a$ and the vertices incident to these edges.

The following statements may be easily verified:

### Lemma 1

Let $A_1 \in V(M)$. If all the edges incident to $A_1$ lie in a single half-space then the whole polyhedron $M$ lies in the same half-space.

### Lemma 2

If $A, B \in V(M)$ and $A \neq B$ then there exists a vertex $A \in V(M)$ such that it is connected to $A$ by an edge and $\rho(A', B) < \rho(A, B)$ (possibly $A' = B$).

### Lemma 3

If $A, B \in V(M)$ then $\rho(A, B) \geq a$, the equality holding only if $A$ and $B$ are connected by an edge.

Now let $U(X)$ be the potential produced by the vertices of $M$ which are connected to a vertex $A$. Let $U(X) = U_0(X) + U_1(X)$, where $U_0(X)$ is the potential produced by vertices belonging to $s(M)$ and $U_1(X)$ is the potential produced by the other connected vertices. Choose a rectangular Euclidean coordinate system such that its origin coincides with the center of the sphere, the $Oz$ axis passes through vertex $A$ and some of the vertices belonging to $s(M)$ and connected to $A$ lie in the $Oxz$ plane. Then the coordinates of any point $X$ on the sphere in the neighborhood of $A$ are $(x, y, [r^2 - x^2 - y^2]^{1/2})$, so that $U(X) = U(x, y)$ and the linear forms $dU_0, dU_1$ and quadratic forms $d^2U_0, d^2U_1$ of $dx, dy$ with $x = y = 0$ are defined.

### Lemma 4

If vertex $A$ is stable for any a.i.p. then $dU_0 = dU_1 = 0$ and $d^2U_0$ is non-negative for any a.i.p. Conversely, if $dU_0 = dU_1 = 0$ and the $dU_0$ and $dU_1$ forms are non-negatively defined, at least one of them being positively defined, then $A$ is a stable vertex.

### Proof

For any a.i.p. $f(\rho)$ and arbitrary $\varepsilon > 0$ one can choose the a.i.p. $\tilde{f}(\rho)$ such that $\tilde{f}'(\rho)$ and $\tilde{f}''(\rho)$ are negligibly small compared with $f'(a)$ and $f''(a)$, respectively, in the interval $[a + \varepsilon, +\infty]$ but $f(\rho) = \tilde{f}(\rho)$ in the interval $[a - \varepsilon, a + \varepsilon]$. This results in the first statement. The second statement follows from well-known theorems of mathematical analysis.

### Lemma 5

If polyhedron $M$ is stable for any a.i.p. then $a(M) \geq 2r/\sqrt{3}$. If there exists a vertex of $s(M)$ connected to exactly two vertices of $s(M)$ then $a(M) = r\sqrt{2}$.

### Proof

Let $(x, y_i, z_a)$ be the coordinates of the vertices $A_i$, $i = 1, \ldots, n$, belonging to $s(M)$ connected to vertex $A$. It is clear that $z_a = (2r^2 - a^2)/2r$. Then lemma 4 implies that $\sum x_i = \sum y_i = 0$. The simple calculation shows that the matrix of $d^2U_0$ has the following expansion: $dU_0 = [f''(a)/a^2]P_1 + [f'(a)/a]P_2$, where

$$P_1 = \begin{pmatrix} \sum x_i^2 & \sum x_i y_i \\ \sum x_i y_i & \sum y_i^2 \end{pmatrix}$$

$$P_2 = \begin{pmatrix} \sum (z_a/r - x_i^2/a^2) & -\sum (x_i y_i/a^2) \\ -\sum (x_i y_i/a^2) & \sum (z_a/r - y_i^2/a^2) \end{pmatrix}.$$

So far as $f''(a) > 0$, $f'(a) < 0$ and the ratio $|f''(a)|/|f'(a)|$ can be arbitrary, it is necessary that matrix $P_2$ be non-positively defined. Considering the cases $n = 2$ and $n > 2$ separately one can deduce the statements of the lemma required.

## Lemma 6

If vertex $A$ is incident to exactly three edges belonging to $s(M)$ and $A$ is stable for any a.i.p., then $a \geq 2r/\sqrt{3}$ and these edges form equal angles. Conversely, if vertex $A$ is incident only to the edges having length $a = a(M) \geq 2r/\sqrt{3}$, their number being equal to three and the angles formed by these edges being equal to each other, then $A$ is stable for every a.i.p.

### Proof

Let $A$ be stable for any a.i.p. Then $dU_0 = 0$ results in the equality of angles and $a \geq 2r/\sqrt{3}$ by lemma 5. Conversely, let the conditions stated in the lemma be satisfied. Then one can write $x_i = r_a \cos 2\pi(i-1)/3$, $y_i = r_a \sin 2\pi(i-1)/3$, $i = 1, 2, 3$, $r_a = (r^2 - z_a^2)^{1/2}$ (see the proof of lemma 5). Then a direct calculation shows that $dU = dU_0 = 0$, $P_1$ is positively defined, $P_2$ is a non-positively defined matrix, which implies that $d^2U = d^2U_0$ is a positively defined quadratic form.

## Lemma 7

If there exists a vertex of $M$ incident to exactly two edges belonging to $s(M)$ and $M$ is stable for any a.i.p., then $M$ is an inscribed trigonal bipyramid. Conversely, an inscribed trigonal bipyramid is stable for any a.i.p.

### Proof

By virtue of lemma 5 one has $a = r\sqrt{2}$. Denote by $A_1$ and $A_2$ two vertices connected to vertex $A$ satisfying the condition of the lemma. Then $A_1$ and $A_2$ have coordinates $(r, 0)$ and $(-r, 0)$ respectively. By virtue of lemma 3 every vertex of $M$ which is distinct from $A_1$ and $A_2$ lies in the $x = 0$ plane. Evidently, not more than three such vertices can lie in this plane, otherwise either the distance between a pair of them is greater than $a$, or $A$ is incident to four edges of length $a$, which is a contradiction. The equality $dU_0 = 0$ applied to the vertex $A$ (or $A_2$) implies that these three vertices in the $x = 0$ plane form a regular triangle. The converse statement follows from lemma 6 (for the 'poles') and from the calculation carried out in the proof of lemma 5 (for 'equatorial vertices').

## Lemma 8

If a polyhedron $M$ is stable for any a.i.p. then every vertex of $M$ is incident to not more than four edges of length $a$.

### Proof

It is clear that if vertex $A$ is connected to five vertices by edges of length $a$, then these vertices lie on a circle of radius $r_a = (r^2 - z_a^2)^{1/2} \leq a\sqrt{(2/3)}$, so that at least one of the distances between these vertices is less than or equal to $2r_a \sin(\pi/5) \leq a\sqrt{(2/3)} \sin(\pi/5) < 0.96a < a$ which is impossible.

## Lemma 9

If a polyhedron $M$ is stable for any a.i.p. and there exists a vertex of $M$ incident to four edges belonging to $s(M)$ then $M$ is an octahedron. Conversely, an octahedron is stable for any a.i.p.

### Proof

The second statement follows from lemma 5, since $a = r\sqrt{2} > 2r/\sqrt{3}$ for an octahedron. Suppose $M$ is stable for any a.i.p. and vertex $A$ is connected to vertices $A_1$, $A_2$, $A_3$, $A_4$ by edges belonging to $s(M)$. Then, obviously, the distances between these vertices are greater than or equal to $a$, so $a \leq r\sqrt{2}$. Suppose $a < r\sqrt{2}$ and the angle between $OAA_1$ and $OAA_2$ planes is less than or equal to $90°$. Consider two cases:

(1) Each of the vertices $A_1$ and $A_2$ is incident to four edges belonging to $s(M)$. One can see from lemma 5 applied to the vertex $A_1$ that one of these edges lies in the $OAA_1$ plane and does not coincide with edge $A_1A$. Let $B_1$ be the end of this edge. Similarly, let $B_2$ denote the end of the edge of length $a$ which lies on the $OAA_2$ plane, starts from $A_2$ and is distinct from $A_2A$. The calculation shows that $0 < \rho(B_1, B_2) < 2a\sqrt{6}/9 \approx 0.554a$, which is impossible in view of lemma 3.

(2) Vertex $A_1$ is incident to three edges. Let $C$ be the end of one of them which lies on the same side of the $OAA_1$ plane as the vertex $A_2$. Then one easily calculates that $0 < \rho(A_2, C) < a$, which is impossible as well.

So one has $a = r\sqrt{2}$, and $A_1$, $A_2$, $A_3$, $A_4$ are the vertices of a square lying in the $z = 0$ plane. Five vertices $A$, $A_1$, $A_2$, $A_3$, $A_4$ uniquely define the sixth vertex of an octahedron.

### Proof of the theorem

The stability of listed polyhedra follows from lemma 6 (a cube with $a = 2r/\sqrt{3}$ and a tetrahedron with $a > 2r/\sqrt{3}$), lemma 7 (an inscribed trigonal bipyramid) and lemma 9 (an octahedron). Conversely, let $M$ be a polyhedron which is stable for any a.i.p. In virtue of lemmas 7 and 9 one can suppose that every vertex (say $A$) of $s(M)$ is connected to three vertices (say $A_1$, $A_2$, $A_3$) by the edges of length $a$. Let the vertices $A_1$, $A_2$ and $C$ be chosen in the same way as in the proof of case 2 of lemma 9. Then either $C = A_2$ which results in a tetrahedron, or $\rho(A_2, C) = a$ and $a = 2r/\sqrt{3}$, i.e. $M$ is a cube. The theorem is proved.

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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