

The Archimedean Truncated Octahedron.

III. Crystal Structures with Geometric Units of Symmetry $m3m$

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Abstract

All geometric units in crystal structures of space groups $Im3m$ and $Pm3m$ and two out of the three types in those of $Fm3m$ have $m3m$ symmetry, whereas the remaining one of $Fm3m$ possesses $\bar{4}3m$ symmetry. Theoretically, a geometric unit of $m3m$ symmetry has atoms arranged as a collection of these possible polyhedra: octahedron, cube, cuboctahedron, truncated octahedron, truncated cube, small rhombicuboctahedron and rhombicuboctahedron. All these can be derived from truncations, sometimes repeated, of the pair of platonic solids, cube and octahedron, which possess $m3m$ symmetry. In reality, no known crystal structure has a geometric unit with a rhombicuboctahedron or a truncated cube. The close-packing requirement causes a complicated geometric unit to start (from the center) in one of the following ways: (i) a single atom followed by an octahedron, (ii) a single atom followed by a cube, (iii) an octahedron and (iv) a cube. The survey of structures indicates that polyhedra derived from an octahedron occur more frequently in real geometric units than those related to a cube.

Introduction

Part I (Chieh, 1979) introduced the concept of geometric units and their generality in cubic crystal structures. The application of this concept to crystal structures with geometric units of $\bar{4}3m$ symmetry was given in part II (Chieh, 1980). Only geometric units in $Im3m$, $Pm3m$ and $Fm3m$ have $m3m$ symmetry; they have one, two and three types of geometric units respectively. The geometric unit designated as C for structures of $Fm3m$ has $\bar{4}3m$ symmetry and a period along the $[111]$ consists of a sequence $ACB\bar{C}$, where \bar{C} is related to C by a center of symmetry. A similar period consists of A and AB respectively for structures of $Im3m$ and $Pm3m$.

In this paper, the concept of geometric units will be applied to the description of crystal structures of these three space groups.

Polyhedra in geometric units of $m3m$ symmetry

The polyhedra and their representations in geometric units of $m3m$ symmetry are given below with their types of coordinates in parentheses:

Octahedron	$E_6(x, k, k); E_{0.5 \times 6}(\frac{1}{2}, k, k);$
Cube	$E_8(x, x, x); E_{0.5 \times 8}(k, k, k);$
Cuboctahedron	$E_{12}(x, x, k);$
Truncated octahedron	$E_{24}(k, y, z); E_{0.5 \times 24}(x, x, k);$
	$E_{0.25 \times 24}(0, \frac{1}{4}, \frac{1}{2});$
Truncated cube	$E_{24}(tc)(x, x, z, \text{ when } x > z);$
Small rhombicuboctahedron	$E_{24}(sr)(x, x, z, \text{ when } x < z);$
Rhombicuboctahedron	$E_{48}(x, y, z).$

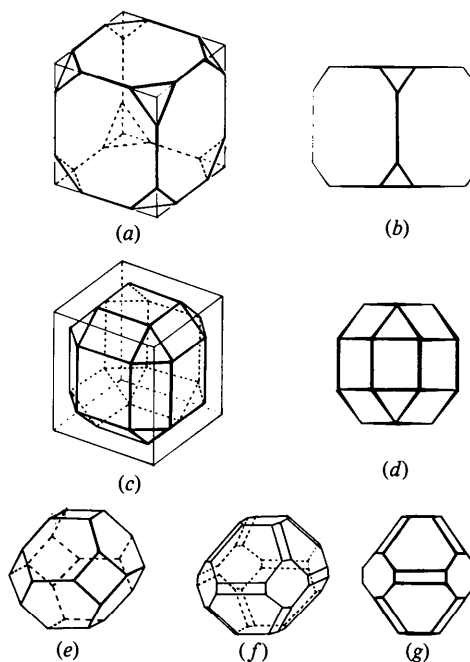


Fig. 1. (a) The derivation of a truncated cube, tc. (b) Truncated cube seen from a $[110]$. (c) A small rhombicuboctahedron, sr, from a cube. (d) A small rhombicuboctahedron, sr, seen from a $[110]$. (e) A truncated octahedron. (f) A rhombicuboctahedron. (g) A rhombicuboctahedron seen from a $[110]$.

The E 's in these formulas will be replaced by symbols of elements in the tabulation of structures and k 's in the coordinates represent special values such as 0, $\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$ in the appropriate space groups. The subscripts of 0.5 and 0.25 indicate atoms shared by 2 and 4 units respectively. The conditions such as $x < z$ refer to the absolute values of x and z from the centers of the geometric units.

The cube and octahedron, duals of each other, belong to $m3m$ symmetry. The three- and fourfold axes pass through the vertices of these polyhedra respectively, and the truncation of them results in polyhedra formed by some equivalent positions of these space groups. The truncated cube and small rhombicuboctahedron can both be derived from the cube, the former by cutting off the vertices and the latter by cutting off a roof-shaped ridge along the edges. This relationship and their views along a $[110]$ direction are shown in Figs. 1(a) to (d). The same process on an octahedron results in the formation of a truncated octahedron and, under special cases, an Archimedean truncated octahedron or a cuboctahedron; this has been discussed in part II and their views from a $[110]$ direction have already been given (Chieh, 1980).

Further truncation of an already truncated octahedron, Fig. 1(e), by cutting off the vertices will not give a configuration with equivalent vertices. The three edges around a vertex are not equivalent. The most general positions of x,y,z type form a polyhedron similar to a great rhombicuboctahedron (Williams, 1972) except that the faces are not necessarily regular polygons. For this reason, it is referred to as a rhombicuboctahedron. It can be derived from a truncated octahedron by cutting off a roof-shaped ridge from all edges between two hexagonal faces. This relationship can be understood by comparing Figs. 1(e) and 1(f). The view of the latter along a $[110]$ direction is shown in Fig. 1(g).

Survey of crystal structures having $m3m$ geometric units

Crystal structures consisting of all $m3m$ geometric units

Crystal structure types consisting of all $m3m$ geometric units are listed in Table 1. These are divided into A and AB types according to their repeating period in the $[110]$ direction. The Pearson (1967) symbols are included for easy reference.

The simplest A -type structure of $Im3m$ is the b.c.c. arrangement adopted by many elements. Next is the structure of Ge_7Ir_3 consisting of 20 atoms, a big jump, per geometric unit, which is composed of a cube, Ge_8 , and an octahedron, Ir_6 , embedded in the shared Archimedean truncated octahedron of $Ge_{0.25 \times 24}$. With

Table 1. Structures with all geometric units of $m3m$ symmetry

A-type structure of $Im3m$			a (Å)	Reference
Pearson symbol	Typical compound	Geometric unit A		
cI2	W	W (b.c.c.)	3.16	1
cI40	Ge_7Ir_3	$Ge_8Ir_6Ge_{0.25 \times 24}$	8.735	1
cI42	Nb_6F_{15}	$Nb_6F_{12}F_{0.5 \times 6}$	8.19	2
cI44	AB_3CA_3	$CA_6AB_{0.5 \times 8}AB_{12}$	9.81	3
cI52	$Ce_3Ni_8Si_2$	$Ce_3Si_{0.5 \times 8}Ni_{12}$	8.858	4
cI52	$Ba_4Sb_3LiO_{12}$	$LiO_8Ba_{0.5 \times 8}Sb_{0.5 \times 6}O_{0.25 \times 24}$	8.217	5
cI54	Sb_2Ti_7	$TiTi_6Sb_6Ti_{12}$	11.618	6
AB-type crystal structures of $Pm3m$			a (Å)	Reference
Pearson symbol	Typical compound	Geometric units A; B		
cP1	α -Po	Po; \square^*	3.359	1
cP2	CsCl	Cs; Cl	3.332	1
cP4	O_3Re	Re; $O_{0.5 \times 6}$	3.751	1
cP5	$CaTiO_3$	Ca; $TiO_{0.5 \times 6}$	3.800	1
cP6	NbO	$Nb_{0.5 \times 6}$; $O_{0.5 \times 6}$	4.2097	7
cP7	CaB_6	Ca; B_6	4.1522	1
	U_3S_3	$US_{0.5 \times 6}$; $U_{0.5 \times 6}$	5.505	8
cP8	AB_2CD_3	$AB_{0.5 \times 6}$; $CD_{0.5 \times 6}$	Hypothetical	9
cP16	$Fe_{13}Ge_3$	$FeFe_{0.5 \times 8}Ge_{0.5 \times 6}$; $FeFe_{0.5 \times 8}Fe_{0.5 \times 6}$	5.763	10
cP36	$BaHg_{11}$	$Hg_8Ba_{0.5 \times 6}Hg_{12}$; $HgHg_{12}$	9.600	1
cP45	$C_4H_2NiO_6$	$(C_4O)_{0.5 \times 6}$; $(H_2O)_2Ni_{0.5 \times 6}$	8.068	11
cP58	K_4LiFe_{24}	$ClK_4S_{0.5 \times 24}$; $LiS_4Fe_{24}(sr)$	10.358	12
cP64	$Pd_{17}Se_{15}$	$Pd_6Se_2Pd_{0.5 \times 6}$; $PdSe_6Pd_{24}Se_{12}$	10.606	13
cP70	$Fe_4[Fe(CN)_6]_3 \cdot 15H_2O$	$Fe(III)Fe(CN)_6$; $[Fe(II)(CN)_6][Fe(III)]_{0.5 \times 6}(p)$	10.166	14

* \square empty unit.

References: 1. Pearson (1967); 2. Shafer, Schnering, Niehues & Neider-Vahrenholz (1965); 3. Calvert & Raud (1964); 4. Gladyshevskij, Kripiakovic & Bodak (1966); 5. Jacobson, Collins & Fender (1974); 6. Stokhuyzen & Chieh (1977); 7. Anderson & Magnéli (1957); 8. Zumbush (1940); 9. Hypothesized by Hellner (1979); 10. Lecocq & Michel (1962); 11. Habenschuss & Gerstein (1974) (the compound is nickel squarate dihydrate, disordered); 12. Tani (1977); 13. Geller (1962); 14. Buser, Schwarzenbach, Peter & Ludi (1977) (p for partial occupancy).

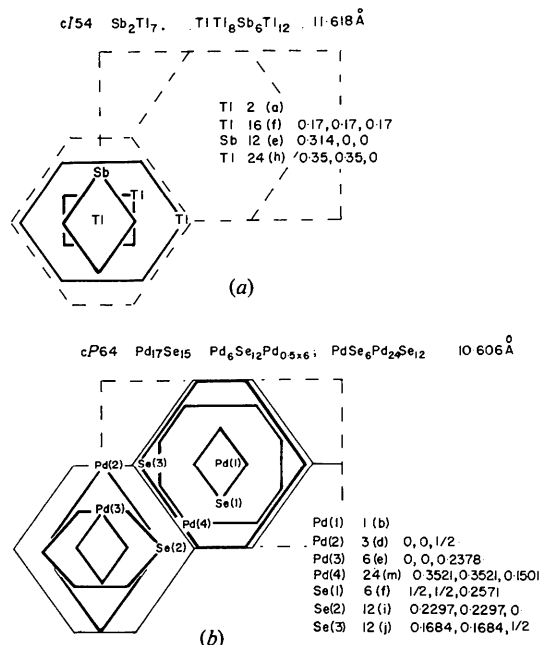


Fig. 2. Geometric units in Sb_2Ti_7 , (a) and $Pd_{17}Se_{15}$, (b).

a slight increase in number of atoms, the geometric units start with octahedra and for Sb_2Tl_7 there is an atom in the center of a cube, which is surrounded by an octahedron and a cuboctahedron consecutively. The last structure is shown in Fig. 2(a).

For structure-type identification, work-sheets such as those shown in Fig. 2 are useful. The headings consist of the entries for Table 1. The formulas for geometric units can be derived by putting down the profile of the polyhedra starting with the atom, whose coordinates are shown, on the grid sheet. It is noteworthy to mention that the profiles of most polyhedra have lines parallel to those of the profile of the geometric units.

For the AB -type crystal structures, the $CsCl$ type is widely known whereas the α -Po is not usually mentioned in fundamental texts, probably because of the notion that such an arrangement of spheres is not stable. There are two geometric arrangements of $cP7$ structures and no known $cP8$ structure, although such a hypothetical structure (Hellner, 1979) might be stable from the geometrical consideration. In fact, this is a superstructure of $NaCl$ written in the form $NaCl_3$; $ClNa_3$ and for mixed salts, the ordered superstructure is unfavorable because of its low entropy requirement. As one of the complicated structures of the AB type, the structure of $Pd_{17}Se_{15}$ is shown in Fig. 2(b). The octahedra, including one shared, the cuboctahedra and the small rhombicuboctahedron of both units are outlined.

The $AC\bar{B}C$ type crystal structures of $Fm\bar{3}m$

The geometric units A and B for space group $Fm\bar{3}m$ have symmetry $m\bar{3}m$ whereas the unit C belongs to $4\bar{3}m$, which has been discussed in part II (Chieh, 1980).

Table 2. $AC\bar{B}C$ -type crystal structures of $Fm\bar{3}m$

Pearson symbol	Typical compound	Geometrical units A ; C ; B	a (Å)	Reference
$cF4$	Cu	Cu; t ; o^* (f.c.c.)	3.6147	1
$cF20$	CD_4	CD_4 ; t ; o	5.96	15
$cF72$	C_6H_{12}	(C_6H_{12}) ; t ; o	8.61	16
$cF12$	CaF_2	Ca; F; o	5.462	1
$cF36$	K_2PtCl_6	$PtCl_6$; K; o	9.751	17
	D_2RuSr_2	RuD_6 ; Sr; o	7.60	18
$cF60$	Mn_2O_8	MnO_6 ; $OMn_{0.3 \times 6}$; o	8.381	18
$cF68$	Co_3S_8	CoS_4 ; Co_4 ; o	9.923	19
$cF75$	$[(CH_3)_4N]_2SnCl_6$	$SnCl_6$; $N(CH_3)_4$; o	12.853	20
$cF8$	$NaCl$	Na; t ; Cl	5.6280	1
$cF52$	UB_{12}	U; t ; B_{12}	7.4773	1
$cF16$	$AlCu_2Mn$	Al; Cu; Mn	5.949	1
	BiF_3	Bi; F; F	5.861	1
$cF14$	Cu_3Ge_2	Ge; Cu; Cu_3 (partial)	5.906	1
$cF40$	Ba_2CaWO_6	WO_6 ; Ba; Ca	8.390	21
$cF116$	C_6Cr_{23}	$CrCr_{12}$; Cr; Cr_6C_6	10.659	22
	$Mn_{23}Th_6$	Th_6 ; $Mn_4Mn_{0.3 \times 6}$; $MnMn_8$	12.523	22

* The tetrahedral and octahedral sites are indicated by t and o respectively to show the packing characteristics.

References (numbers continued from Table 1): 15. Press (1972); 16. Kahn, Fourné, André & Renaud (1973); 17. Williams, Dillin & Milligan (1973); 18. Moyer, Stanitski, Tanaka, Kay & Kleinberg (1971); 19. Kasper & Prener (1954); 20. Rajamani & Prewitt (1975); 21. Brill, Gearhart & Welsh (1974); 22. Steward & Rooksby (1951); 23. Fiedler, Stadelmaier & Simousen (1977).

The f.c.c. structure adopted by many elements or high-temperature disordered phases of molecular compounds, although consisting of identical species, features the C and B units with tetra- and octahedral sites (not holes) of the sphere-packing model. These features are indicated by t and o respectively in Table 2. Filling these sites results in CaF_2 , $NaCl$ and $AlCu_2Mn$ structure types and in this order is Table 2 arranged.

In neither the CaF_2 nor the K_2PtCl_6 are the contents of the C units of $4\bar{3}m$ symmetry, but the arrangement of the A (or B) units, Ca or $PtCl_6$, around C is tetrahedral. However, in $[(CH_3)_4N]_2SnCl_6$, the ions in the C units conform with the site symmetry, $4\bar{3}m$. The contents of the C units for structures of the $AlCu_2Mn$ group seldom conform with $4\bar{3}m$ symmetry. Only for the complicated structure $Mn_{23}Th_6$, containing 116 atoms per unit cell, does the content of the C unit agree with the site symmetry. For a comparison purpose, the geometric representations of C_6Cr_{23} and $Mn_{23}Th_6$ structures are shown in Fig. 3 in the same work-sheet format as those of Fig. 2.

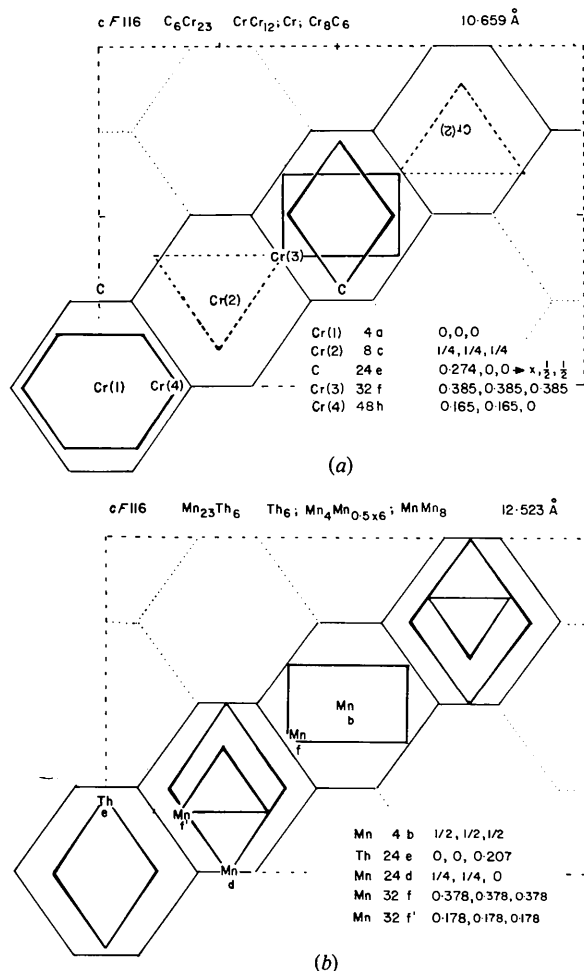


Fig. 3. Geometric representations of two complicated $cF116$ structures, C_6Cr_{23} and $Mn_{23}Th_6$.

Discussion

It is trivial to crystallographers that molecules or ions in the solid state are placed in sites of symmetry lower than their own. Thus polyhedra of $m\bar{3}m$ symmetry can be found in $\bar{4}3m$ geometric units and the reverse is not true. Theoretically, the cube and the octahedron can be present in geometric units of symmetry lower than $m\bar{3}m$, but only octahedron and truncated octahedron are found in real $\bar{4}3m$ geometric units as seen in the previous survey (Chieh, 1980). The cube and the small rhombicuboctahedron are present in $m\bar{3}m$ geometric units, for example those of Ge_7Ir_3 , Sb_2Tl_7 , $\text{Pd}_{17}\text{Se}_{15}$ and C_6Cr_{23} . However, the cube-related polyhedra are not as common as those related to the octahedron, as seen from Tables 1 and 2. The cuboctahedron, which is related to both the cube and the octahedron, is present in geometric units of both $m\bar{3}m$ and $\bar{4}3m$ symmetries; those in the latter are slightly distorted.

Few $\bar{4}3m$ geometric units having more than one atom in the $Fm\bar{3}m$ space group consist of or start (from the center) with a tetrahedron, but many for space groups $I\bar{4}3m$, $P\bar{4}3m$, $F\bar{4}3m$ and $Fd\bar{3}m$ begin with a tetrahedron (Chieh, 1980). In contrast, $m\bar{3}m$ geometric units consisting of more than one atom usually start with an octahedron or a cube. Some have an atom in the center followed by an octahedron, or in the case of Sb_2Tl_7 , a cube. Thus these are the clues for building models in cases where the structure to be analyzed is complicated.

Tables 1 and 2 not only list the surveyed structures, they correlate and organize the structures into families by symmetry. The geometric units in all the A -type structures form an I lattice complex; simply the units become more complicated as the number of atoms increases. The AB type structures can be associated with the familiar CsCl structure whereas the $AC\bar{B}\bar{C}$ structures are divided into four groups.

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