

The Archimedean Truncated Octahedron. II. Crystal Structures with Geometric Units of Symmetry $\bar{4}3m$

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Abstract

All geometric units in crystal structures of space groups $P\bar{4}3m$, $I\bar{4}3m$, $Pn3m$, $F\bar{4}3m$ and $Fd3m$ possess point group $\bar{4}3m$. These units may be vacant, or may contain one or more atoms. In units containing more atoms than one, the atoms form one or a collection of these polyhedra: tetrahedron, truncated tetrahedron, octahedron, cuboctahedron or truncated octahedron; the last two may be distorted. Therefore, a formula that lists the consecutive polyhedra starting from the center of the unit can be used for the tabulation of these crystal structures. Only structures of Cu_2O type are known in $Pn3m$ and typical structures of the other four space groups are tabulated.

Introduction

In part I (Chieh, 1979), geometric units were developed for the description and classification of all cubic crystal structures. This paper presents some applications of the geometric units to five space groups; all geometric units in them possess the point group $\bar{4}3m$. A concise notation is developed to represent a unit and used in the tabulation of crystal structures.

Formulation of geometric units in space groups $I\bar{4}3m$, $P\bar{4}3m$, $F\bar{4}3m$, $Pn3m$ and $Fd3m$

The centers of all geometric units for crystal structures of the space groups $P\bar{4}3m$ (T_d^1 , No. 215), $F\bar{4}3m$ (T_d^2 , No. 216), $I\bar{4}3m$ (T_d^3 , No. 217), $Pn3m$ (O_h^4 , No. 224) and $Fd3m$ (O_h^7 , No. 227) are special crystallographic site sets (site set for short) with the highest symmetry $\bar{4}3m$ (*International Tables for X-ray Crystallography*, 1969). Even for vacant units or those containing single atoms, the symmetry remains. The formulae for these types of unit are \square and E respectively, where E is the symbol of the element.

When a point moves away from the center of a geometric unit, the $\bar{4}3m$ symmetry requires that the N

equivalent points form a polyhedron with $\bar{4}3m$ as a subgroup symmetry. The possible polyhedra for the five space groups are shown in Fig. 1. Atoms in equivalent positions x, x, x ; x, \bar{x}, \bar{x} ; \bar{x}, x, \bar{x} ; and \bar{x}, \bar{x}, x form a tetrahedron (Fig. 1A and *a*). In extreme cases, the vertices lie on four of the eight hexagonal faces of the geometric unit; these atoms are then shared by two units. This polyhedron is represented by E_4 or $E_{0.5 \times 4}$. A truncated tetrahedron (Fig. 1B and *b*) is formed by atoms occupying site sets x, x, z etc. when $|x| > |z|$. If $|x| < |z|$, a distorted cuboctahedron (Fig. 1E and *e*) is formed and an undistorted one (Fig. 1D and *d*) results from special values for z . These three polyhedra are represented by E_{12} , $E_{12}(\text{dco})$ and $E_{12}(\text{co})$ respectively in the formulation. The cuboctahedron and other polyhedra present in crystal structures of these space groups are related to the octahedron (Fig. 1C and *c*) which possesses $m3m$ symmetry and itself is formed by atoms in a site set of $\pm x, 0, 0$; $0, \pm x, 0$; and $0, 0, \pm x$. Again, the vertices of an octahedron can lie on the square faces of a geometric unit; thus the atoms are shared by two units. Points of a general site set, x, y, z etc., form a distorted truncated octahedron (Fig. 1F''); however, an undistorted one (Fig. 1F) may result from special values of z . Atoms on the vertices of an Archimedean truncated octahedron (Fig. 1F''') are shared among four units and the special coordinates giving this semi-regular polyhedron depend only on lattice type. For a P or an I lattice, the coordinates are $\pm \frac{1}{4}, \pm \frac{1}{2}, 0$ etc. and for an F lattice they are $\pm \frac{1}{8}, \pm \frac{1}{4}, 0$ etc. For the latter cases, the atoms are shared by units A, C, B and D in $F\bar{4}3m$ and by two A plus two B in $Fd3m$. Atoms forming these polyhedra are represented by E_{24} , $E_{24}(\text{dto})$ and $E_{0.5 \times 24}$ respectively for truncated octahedron, distorted truncated octahedron and Archimedean truncated octahedron. The fractional numbers in the last formulation indicate that the atoms are shared. However, for crystal structures of $F\bar{4}3m$ and $Fd3m$, one may use $E_{24}(\text{ato})$ $E_{0.5 \times 24}(\text{ato})$ by assuming the atoms in the unit A .

For example, the geometric unit for Cu_5Zn_8 , a γ -brass, is $Zn_4Cu_4Cu_6Zn_{12}(\text{dco})$. The polyhedra are given in the ascending order of their distances from the

vertex to the center. Fig. 2 shows the constituent polyhedra of this unit.

Using either lattice-complex notations (Hellner, 1965; Hermann, 1960), or those given in the previous paper (Chieh, 1979), the units form simple, easily understandable patterns:

| space group | geometric notation | lattice complex |
|--------------|--------------------|-----------------|
| $I\bar{4}3m$ | A | I |
| $P\bar{4}3m$ | AB | PP' |
| $Pn3m$ | AA | I |
| $Fd3m$ | $AA\bar{B}\bar{B}$ | DD' |
| $F\bar{4}3m$ | $ACBD$ | $FF'F''F'''$ |

The geometric notation gives the unit(s) for one period along the body diagonal.

The lattice complex D is named after the diamond structure, and DD' represents two lattice complexes (D' being a D moved by $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). Obviously, AA in crystals of $Fd3m$ forms a D lattice complex and $\bar{B}\bar{B}$ forms the complement of D, D' .

Crystals of both space groups $I\bar{4}3m$ and $Pn3m$ have only one type of unit, but those of $P\bar{4}3m$ and $Fd3m$ consist of two. Crystals belonging to $F\bar{4}3m$ have four independent units.

Survey of crystal structures

We surveyed reported structures in these space groups and the typical ones are presented in tabular form.

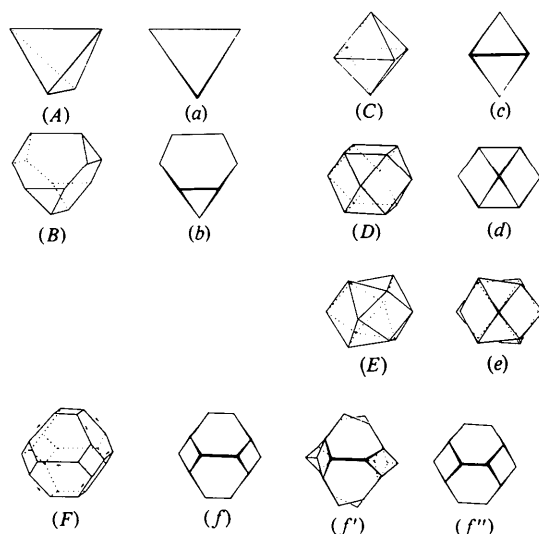


Fig. 1. Polyhedra formed by equivalent positions of space groups $I\bar{4}3m$, $Pn3m$, $P\bar{4}3m$, $Fd3m$ and $F\bar{4}3m$: (A) a tetrahedron, (a) a tetrahedron on (110) plane; (B) and (b) a truncated tetrahedron; (C) and (c) an octahedron; (D) and (d) a cuboctahedron; (E) and (e) a distorted cuboctahedron; (F) and (f) a truncated octahedron; (f') a distorted (along the arrows of F) truncated octahedron; (f'') an Archimedean truncated octahedron.

A-type crystal structures in $I\bar{4}3m$

Crystal structures of $I\bar{4}3m$, Table 1, can be divided into six groups. The first group consists of molecular compounds, many of them tetramers. For these compounds, units are also molecules, which pack in an I lattice as do the atoms in a b.c.c. structure.

In $Zn_4O_{13}B_6$, the boron atoms at the vertices of an Archimedean truncated octahedron are shared by three other neighboring units, $0.25 (= \frac{1}{4})$. Apparently, the B_6O_{12} ring does not exist as claimed by Smith, Garcia-Blanco & Rivoir (1964).

For compounds with the common formula Tl_3VS_4 , ($V = V, Ta$ or Sb and $S = S$ or Se), the tetrahedron VS_4 is embedded in a three-dimensional net of vertex-sharing octahedra, $Tl_{0.5 \times 6}$. A unit in $Cu_{12}AsS_{13}$ or $Cu_{12}SbS_{13}$ has a S-filled octahedron in the center when compared with those of Cu_3AsS_3 , Cu_3SbS_3 or Ag_3SbS_3 . The Cu atoms are shared by four units, like the B atoms in $Zn_4B_6O_{13}$.

Braun & Jeitschko (1978) reported a structure type for compounds with formula $Ln_6Ni_6P_{17}$ ($Ln = La, Ce, Pr$). The units of these compounds contain a portion similar to those in $Cu_{12}AsS_{13}$ or $Cu_{12}SbS_{13}$.

There are 11 γ -brass and 12 α -manganese structures reported for $I\bar{4}3m$. The units of the former start with a tetrahedron whereas those of the latter start with a single atom followed by a truncated tetrahedron. The outermost polyhedron of the units for both groups is a slightly distorted cuboctahedron. Even the unit of white phosphorus has the same collection of polyhedra as the α -manganese when P_4 is taken as a subunit (Sugawara, Sakamoto & Kanda, 1949).

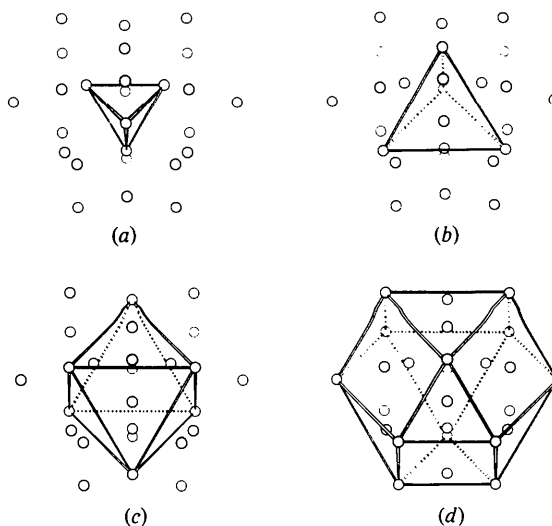


Fig. 2. A typical 26-atom γ -brass geometric unit, $Zn_4Cu_4Cu_6Zn_{12}(dco)$, consisting of two tetrahedra (a and b) followed by an octahedron, (c), and a distorted cuboctahedron (d).

AB crystal structures in $P\bar{4}3m$

For crystal structures in $P\bar{4}3m$, two units, *A* and *B*, are stacked alternately along $\langle 111 \rangle$ directions (Table 2). When *A* contains a molecule, unit *B* is designated as vacant. As in $I\bar{4}3m$ crystal structures, there is a group of molecular compounds with some tetramers.

The structures of $Zn(CN)_2$ and $Cd(CN)_2$ are three-dimensional networks. Units given for this group are based on an ideally ordered arrangement. Disordered CN groups would lead to $I\bar{4}3m$.

The formulae Cu_3VS_4 and Tl_3VS_4 are similar, but they belong to $P43m$ and $I\bar{4}3m$ respectively. These structures are compared in Fig. 3.

For the two minerals rhodizite, $CsBe_4Al_4O_{28}$, and pharmacosiderite, $Fe_4As_3O_{16} \cdot 5H_2O$, a cluster description was given by Taxer & Buerger (1967) and Buerger, Dollase & Garaycochea-Wittke (1967). Regardless of the boundary choice, the packing pattern is true.

Five *P* γ -brasses were reported. Both *A* and *B* units contain the same collection of polyhedra, but each has a unique distribution of atoms. The factors deciding the lattice type of a γ -brass have been discussed by Pearson, Brandon & Brizard (1976).

The *B* unit in $NiCd_5$ is similar to that of a γ -brass, but the *A* unit is different (Ljung & Westman, 1970).

 Cu_2O , an $A\bar{A}$ structure in $Pn3m$

Only Cu_2O , Ag_2O , Pb_2O and H_2O (ice VII) were reported for $Pn3m$. A unit contains $OM_{0.5 \times 4}$ where *M* is a metal or a hydrogen atom.

ACBD crystal structures in $F\bar{4}3m$

In zinc blende, units *A* and *C* contain an atom each, whereas *B* and *D* are interstitial spaces enclosed by S_4Zn_6 and Zn_4S_6 cages respectively, Fig. 4(a). Many binary and disordered ternary compounds share this

Table 1. *A*-type crystal structures of $I\bar{4}3m$

| Type | Compound | Geometric unit <i>A</i> | <i>a</i> (Å) | |
|---------------------|-----------------------|--|---------------------------------|------|
| Molecular compounds | SiF_4 | SiF_4 | 5.42 | |
| | $C(NO_2)_4$ | $C[NC_2]_4$ | 7.09 | |
| | $N_4C_6H_{12}$ | $N_4C_6H_{12}$ or $N_4[CH_2]_6$ | 7.029 | |
| | $(CH_3Li)_4$ | $Li_4C_4H_{12}$ | 7.24 | |
| | $[(CH_3)_4Pt]_4$ | $Pt_4(CH_3)_4(CH_3)_{12}$ | 10.145 | |
| | $[(CH_3)_3PtCl]_4$ | $Pt_4Cl_4(CH_3)_{12}$ | 10.55 | |
| | $[As(C_2H_5)_3Cu]_4$ | $Cu_4I_4As_4C_{0.5 \times 24}H(?)C_{12}H(?)$ | 13.148 | |
| | $[Pt(C_2H_5)_3CuI]_4$ | $Cu_4I_4Pt_4C_{0.5 \times 24}H(?)C_{12}H(?)$ | 13.08 | |
| | $Zn_4C_{13}B_6$ | $Zn_4O_{13}B_6$ | $OZn_4O_{12}B_{0.25 \times 24}$ | 7.48 |
| | Tl_3VS_4 | Tl_3VS_4 | $VS_4Tl_{0.5 \times 6}$ | 7.51 |
| $Cu_{12}As_4S_{13}$ | $Cu_{12}As_4S_{13}$ | $SCu_6As_4S_{12}Cu_{0.25 \times 24}$ | 10.232 | |
| | Cu_3AsS_3 | $Cu_6As_4S_{12}Cu_{0.25 \times 24}$ | 10.21 | |
| Polyfosfite | $La_6Ni_6P_{17}$ | $PLa_6P_{12}(co)$ | 10.168 | |
| γ -brass | Cu_7Zn_8 | $Zn_4Cu_4Cu_6Zn_{12}(dco)$ | 8.878 | |
| α -Mn | α -Mn | $MnMn_{12}Mn_4Mn_{12}(dco)$ | 8.9128 | |

Table 2. *AB* crystal structures of $P\bar{4}3m$

| Type | Compound | Geometric units <i>A</i> ; <i>B</i> | <i>a</i> (Å) |
|---------------------|------------------------------|--|--------------|
| Molecular compounds | CFe_4 | CFe_4 ; \square | 3.878 |
| | CBr_4 | CBr_4 ; \square | 5.68 |
| | CI_4 | CI_4 ; \square | 5.82 |
| | $[(CH_3)_3SiOK]_4$ | $O_4K_4Si_4(CH_3)_{12}$; \square | 8.844 |
| | $[(CH_3)_3SiORb]_4$ | $O_4Rb_4Si_4(CH_3)_{12}$; \square | 8.844 |
| | $[(CH_3)_3SiOCs]_4$ | $O_4Cs_4Si_4(CH_3)_{12}$; \square | 8.844 |
| $Zn(CN)_2$ | $Zn(CN)_2$ | ZnC_4 ; ZnN_4 | 5.91 |
| Cu_3VS_4 | Cu_3VS_4 | $VS_4Cu_{0.5 \times 6}$; \square | 5.3912 |
| Rhodizite | $CsBe_4Al_4O_{28}$ | $CsBe_4O_{12}$; $O_4Al_4Be_4O_{12}B_{0.5 \times 24}$ | 7.319 |
| Pharmacosiderite | $Fe_4As_3O_{16} \cdot 5H_2O$ | $O_4Fe_4O_{12}As_{0.5 \times 6}$; $(H_2O)_{0.5 \times 4}(H_2O)_{0.5 \times 6}$ | 7.9816 |
| γ -brass | Cu_9Al_4 | $Al_4Cu_4Cu_6Cu_{12}(dco)$; $Cu_4Cu_4Cu_6Al_{12}(dco)$ | 8.7023 |
| $NiCd_5$ | $NiCd_5$ | $(Ni_{24/5}Cd_{6/5})(oh)(Ni_{16/5}Cd_{4/5})Cd_{12}(dco)$; $Cd_4Cd_4Cd_6Cd_{12}(dco)$ | 9.7878 |

structure type. In HgAg_2I_4 , HgCu_2I_4 , CdIn_2Te_4 and HgIn_2Te_4 , the atoms are randomly displaced by about 0.25 \AA along the tetrahedral directions with respect to the zinc blende structure as a result of anharmonic vibration (Kasper & Browall, 1975).

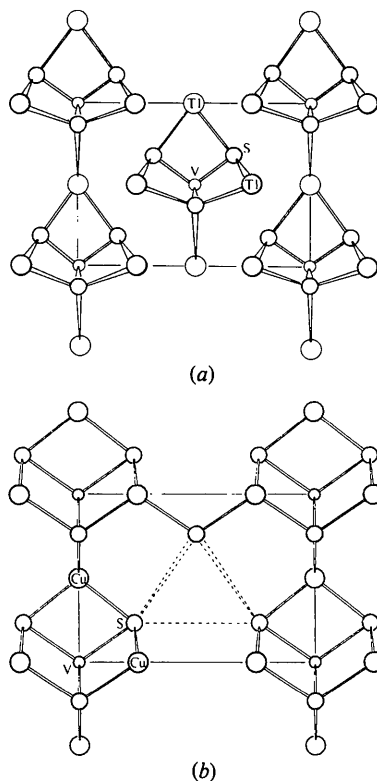


Fig. 3. Comparison of Tl_3VS_4 ($I\bar{4}3m$) and Cu_3VS_4 ($P\bar{4}3m$) structures.

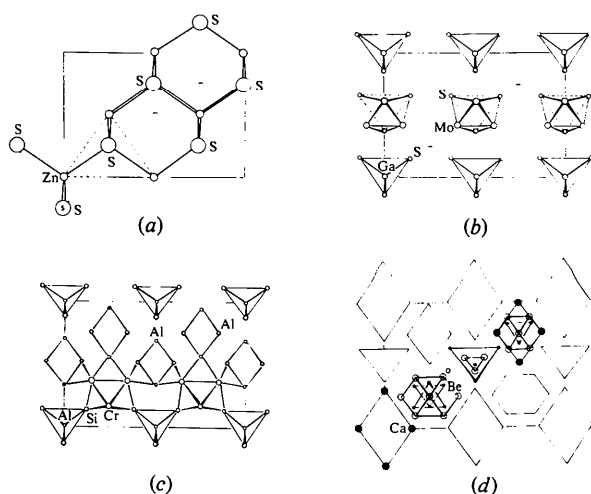


Fig. 4. Four $F\bar{4}3m$ crystal structures. (a) Zinc blende: Zn; S; \square ; \square . (b) GaMo_4S_8 structure: GaS_4 ; \square ; Mo_4S_4 ; \square . (c) $\alpha\text{-Al}_{13}\text{Cr}_4\text{Si}_4$ structure: AlSi_4 ; Cr_4 ; Al_6 ; Al_6 . (d) Calcium beryllate structure: Ca ; $\text{OBe}_4\text{Be}_4\text{O}_{12}(\text{dco})$; BeO_4Be_4 ; $\text{Be}_4\text{Ca}_6\text{O}_{12}(\text{dco})$.

The AgMgAs structure can be derived from the zinc blende structure by placing an atom in the vacant unit D , with B remaining vacant. Pearson (1967) lists many compounds with this structure. In $\beta\text{-Ni}_3\text{S}_2$, there is random distribution and partial occupancy (Line & Huber, 1963).

The compounds AuBe_5 , UCu_5 , CuNi_5 , PdBe_5 , and LuCu_5 have a common structure type, in which units B and D are corner-sharing tetrahedra. The following ternary compounds have similar structures: $\text{Cu}_3\text{Mn}_2\text{Al}$, Cu_4MnSn , Cu_4MgSn , Cu_4InMg .

In GaMo_4S_8 , two units are vacant, Fig. 4(b) (Perrin, Chevrel & Sergent, 1975).

The four units in $\alpha\text{-Al}_{13}\text{Cr}_4\text{Si}_4$ are AlSi_4 , Cr_4 , Al_6 and Al_6 ; they are not isolated identities but the content in each unit is easily comprehensible, Fig. 4(c) (Robinson, 1953).

$\text{CsM}(\text{OH}_2)\text{XO}_4$, with $X = \text{P}$, $M = \text{Fe}$, Co or Ni , or with $X = \text{As}$, $M = \text{Mn}$, Fe , Co or Ni was reported in $F\bar{4}3m$ (Ferrari, Tani & Bondati, 1956). However, $\text{CsMnPO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CsCdPO}_4 \cdot 6\text{H}_2\text{O}$ are hexagonal.

Compounds $\text{Co}(\text{NH}_3)_6(\text{BF}_4)_3$, $\text{Co}(\text{NH}_3)_6\text{SO}_4$ and $\text{Co}(\text{NH}_3)_6\text{SO}_4\text{Br}$ are isostructural (Okaya *et al.*, 1957). In these structures, the units contain individual ions. The compound $\{\text{Ru}(\text{NH}_3)_5\text{N}_2\}\text{Cl}_2$ is of the same type with the N_2 and NH_3 groups randomly distributed (Bottomley & Nyburg, 1968). The only molecular compound in $F\bar{4}3m$ is adamantane, $(\text{CH})_4(\text{CH}_2)_6$, the molecule of which has a shape similar to that of hexamethylenetetramine, $\text{N}_4(\text{CH}_2)_6$. Slight differences, CH vs N , cause them to crystallize in different space groups (Giacomello & Illuminati, 1945).

The structure of calcium beryllate, $\text{Ca}_{12}\text{Be}_{17}\text{O}_{29}$, was described as composed of rods of close-packed atoms running parallel to $\langle 110 \rangle$ directions, probably due to the densely packed B unit, Fig. 4(d) (Harris & Yakel, 1966).

Louisnathan & Gibbs (1972) described the structure of zunyite as composed of four clusters whereas Zagalskaya & Belov (1963) considered it composed of three: (1) the Si_5O_{16} tetrahedral silicate pentamers, (2) the $\text{Al}_{13}(\text{O}, \text{OH} \text{ or } \text{F})_{40}$ cluster and (3) the Cl anion. Cluster Si_5O_{16} consists of four C and one A units (Table 3) and it can be written $\text{SiO}_4\text{Si}_4\text{O}_{12}$. Because A and C units form a structure similar to the linkage of Zn and S atoms in zinc blende, their claimed pentamer is apparently not an isolated entity. Cluster $\text{Al}_{13}(\text{O}, \text{OH} \text{ or } \text{F})_{40}$ contains D plus some atoms of the B unit, $\text{AlO}_4\text{O}_{12}\text{Al}_{12}(\text{dco})\text{O}_4(\text{OH}, \text{F})_{24}(\text{dto})$. The Cl^- ion lies at the center of B inside an octahedron of O or OH .

Alloys $\text{Sn}_{11}\text{Cu}_{41}$, $\text{Sn}_3\text{Cu}_6\text{Ni}$, $\text{Sn}_2\text{Al}_2\text{Cu}_{12}$, $\text{Pt}_5\text{Hg}_{21}$, $\text{Ce}_5\text{Hg}_{21}$, $\text{Pu}_5\text{Hg}_{21}$ and $\text{Pt}_3\text{Zn}_{11}$ are γ -brasses with F cells (Booth, Brandon, Brizard, Chieh & Pearson, 1977). Each unit has a unique atom distribution on the same geometric arrangement.

Na_6Tl and Mg_6Pd structures are similar (Samson,

1972; Samson & Hansen, 1972). There are two 26-atom γ -brass-like units, B and C , in these and two other compounds, $\text{Ir}_7\text{Mg}_{44}$ and $\text{Rh}_7\text{Mg}_{44}$ (Westin & Edshammar, 1972).

The most complicated structure in $F\bar{4}3m$ is Cu_4Cd_3 with 1124 atoms per cell (Samson, 1966).

$A\bar{A}B\bar{B}$ crystal structures in $Fd\bar{3}m$

$Fd\bar{3}m$ crystal structures have two independent units compared with four in $F\bar{4}3m$, Table 4.

The diamond structure has the same network as zinc blende, Fig. 4(a), but consists of one element so that C and D units become \bar{A} and \bar{B} , thus leading to $Fd\bar{3}m$. The NaTl structure can be viewed as two interpenetrating diamond nets. Some ternary compounds, such as CuZrHg_2 , CuHfHg_2 , AlMgLi_2 and ZnMgLi_2 ,

as well as AlLi , CdLi , GaLi , InLi , ZnLi and InNa have the same structure.

Among the diverse structure types in $Fd\bar{3}m$, Cu_2Mg and spinel are of common occurrence (Bagshaw, 1976). In Cu_2Mg , Mg atoms have the same arrangement as the C in diamond. However, the Mg network interweaves with another one made up of corner-sharing tetrahedra ($\text{Cu}_{0.5\times 4}$), compare Figs. 4(a) and 5(a). Around each Mg is a truncated tetrahedron of Cu atoms, whereas within the adamantane-like cage Mg_4Mg_6 is a Cu_4 tetrahedron. The Cu_2Mg structure can be obtained from NaTl by replacing Tl by $\text{Cu}_{0.5\times 4}$ and Na by Mg. A random distribution of Au and Be in units A and C (Table 3) will make AuBe_5 a Laves phase. Pearson (1967) lists 226 alloys that have the Cu_2Mg structure. The major examples are alloys with lanthanides or actinides. Compounds with stoichi-

Table 3. $ACBD$ crystal structures of $F\bar{4}3m$

Superscripts p indicate partial occupancy.

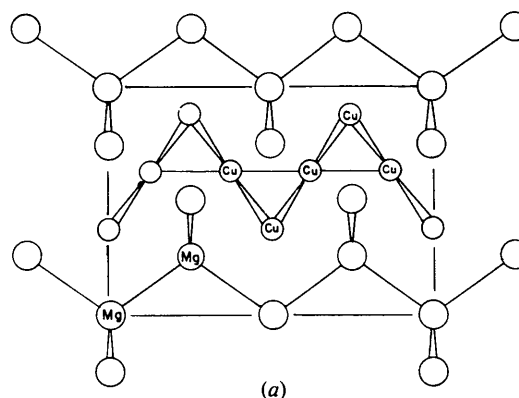
| Type | Compound | Geometric units A ; C ; B ; D | a (Å) |
|-------------------------------|---|---|---------|
| Zinc blende | ZnS | Zn; S; □; □ | 5.405 |
| | CuAsSe ₂ | (Cu,As); Se; □; □ | 5.75 |
| | CuGe ₂ P ₃ | (Cu,Ge); P; □; □ | 5.65 |
| | HgAg ₂ I ₄ | (Hg,Ag) _{3/4} ; I; □; □ | 6.35 |
| | AgAsMg | As; Ag; □; Mg | 6.254 |
| AuBe ₅ | β -Ni ₃ S ₂ | Ni _{0.64\times 4} ^p ; Ni _{0.64\times 4} ^p ; □; S ₄ | 5.22 |
| | AuBe ₅ | Au; Be; Be _{0.5\times 4} ; Be _{0.5\times 4} | 6.698 |
| Ionic and molecular compounds | GaMo ₄ S ₈ | GaS ₄ ; □; Mo ₄ S ₄ ; □ | 9.73 |
| | α -Al ₁₃ Cr ₄ Si ₄ | AlSi ₄ ; Cr ₄ ; Al ₆ ; Al ₆ | 10.917 |
| | CsMgAsO ₄ ·6H ₂ O | Mg(H ₂ O) ₆ ; AsO ₄ ; □; Cs | 10.178 |
| | Co(NH ₃) ₆ (BF ₄) ₃ | Co(NH ₃) ₆ ²⁺ ; BF ₄ ⁻ ; BF ₄ ⁻ ; BF ₄ ⁻ | 11.211 |
| | (NH ₄) ₃ AlF ₆ | AlF ₆ ³⁻ ; NH ₄ ⁺ ; NH ₄ ⁺ ; NH ₄ ⁺ | 9.12 |
| | C ₁₀ H ₁₀ | (CH) ₄ (CH ₂) ₆ ; □; □; □ | 9.426 |
| | Cu ₆ PS ₃ Br | (Br,S); (S,Br); P _{0.83} ^p S ₄ ; P _{0.15} ^p (Cu partially occupy several sites) | 9.728 |
| Calcium beryllate | Ca ₁₂ Be ₁₇ O ₂₉ | Ca ₆ ; OBe ₄ Be ₄ O ₁₂ (dco); BeO ₄ Be ₄ ; Be ₄ Ca ₆ O ₁₂ (dco) | 14.023 |
| | Zunyite | Al ₁₂ Si ₁₅ O ₂₀ F ₃ (OH) ₁₅ Cl | 13.86 |
| γ -Brass | Sn ₁₁ Cu ₄₁ | O ₁₂ (dco)Si ₄ ; SiO ₄ ; Cl(OH) ₆ ; AlO ₄ O ₁₂ ; Cu _{0.75\times 4} ^p Sn ₄ Cu ₆ Cu ₁₂ (dco); Cu ₄ Cu ₄ Cu ₆ Sn ₁₂ (dco); Cu ₄ Cu ₄ Cu ₆ Cu ₁₂ (dco); Cu ₄ Cu ₄ Sn ₆ Cu ₁₂ (dco) | 17.98 |
| | Na ₆ Tl | Na ₆ Tl ₄ Na ₁₂ Na ₁₂ (dco); Na ₄ Tl ₄ Na ₆ Na ₁₂ (dco); Na ₄ Na ₄ Tl ₆ Na ₁₂ (dco); Na _{0.94} ^p Na ₄ Na ₁₂ | 24.154 |
| Cubic alloys | Mg ₄₄ Ir ₇ | Mg ₄ Ir ₄ Mg ₆ Mg ₁₂ (dco); Mg ₆ Ir ₄ Mg ₁₂ (dco); Mg ₄ Mg ₁₂ Mg ₁₂ (dco); Mg ₄ Mg ₄ Ir ₆ Mg ₁₂ (dco); | 20.097 |
| | Sm ₁₁ Cd ₄₅ | SmCd ₄ Cd ₄ Cd ₆ Sm ₁₂ (dco); SmCd ₁₂ Cd ₄ Cd ₁₂ (dco); CdCd ₁₂ Sm ₄ Cd ₁₂ (dco); CdCd ₄ Sm ₄ Cd ₁₂ (dco) | 21.699 |
| | Cu ₄ Cd ₃ | Cd ₆ Cu ₄ Cd ₁₂ Cu ₁₂ (Cu,Cd) ₁₂ (dco)Cu ₁₂ (dco)Cd ₂₄ (dto); CdCu ₁₂ Cd ₄ Cu ₁₂ Cd ₄ Cd ₁₂ (dco)Cu ₁₂ ; Cu ₄ Cd ₄ Cd ₆ Cu ₁₂ (dco)Cu ₄ Cd ₁₂ Cu ₂₄ (dto)Cu ₁₂ ; Cu ₆ Cu ₄ (Cu,Cd) ₁₂ (dco),(Cu,Cd) ₁₂ (Cu,Cd) ₁₂ Cd ₁₂ Cu ₆ | 25.871 |

ometry different from Cu_2Mg adopt this structure by having disordered distributions. The following compounds can be added to Pearson's list: Co_2Cd , (Co or Fe) $_2\text{U}$, Cu_2Se , Fe_2Tb , Ni_2Ta , Zn_2Hf ; AlCrNi , AlCuZr , $\text{Al}_{50}\text{Cu}_{25}\text{Zr}_{25}$, AlNiZr , $\text{Co}_{2-x}\text{Ni}_x\text{Zr}$, CrNiZr , $\text{Cu}_{1.5}\text{Ge}_{0.5}\text{Li}$, $\text{Fe}_{2-x}\text{Ni}_x\text{Zr}$, MgLiZn .

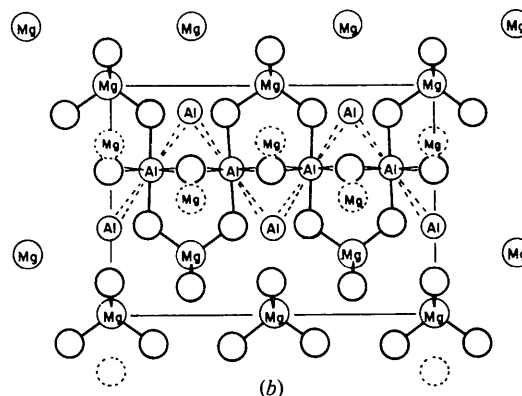
The controversy whether normal spinel Al_2MgO_4 belongs to $F\bar{4}3m$ or $Fd\bar{3}m$ indicates the close relationship between these space groups (Hwang, Heuer & Mitchell, 1973; Bacon, 1952; Zorina & Kritka, 1968; Mishra & Thomas, 1977). The metals, Mg and Al, are located in a framework similar to that of Cu_2Mg (compare Fig. 5a and b). However, the orientation of the MgO_4 tetrahedron in spinel is different from that of MgMg_4 in Cu_2Mg .

In inverse spinels, e.g. Ni_2CoO_4 , NiO_4 takes over the role of MgO_4 in Al_2MgO_4 instead of CoO_4 which would be present in a normal spinel. Between the two extremes, some compounds have partial inversions. Hundreds of compounds including some containing other group VI elements adopt this structure type (Kugimiya & Steinfink, 1968; Wells, 1975).

The pyrochlore-type structure $(\text{Ca}, \text{Na})_2\text{Nb}_2\text{O}_6\text{F}$ is common for compounds with stoichiometry $A_2B_2O_7$. This structure is related to Cu_2Mg or spinel but the A unit contains $\text{FNb}_{0.5 \times 4}\text{O}_6$. The position of the oxygen atom depends on the compound. Compounds adopting the pyrochlore-type structure are: (i) $M_2^2M_2^5O_7$; (ii) $M_2^3M_2^4O_7$ (the superscript indicates the group of M in the Periodic Table); (iii) compounds involving group VIIIb elements and lanthanides with formula $\text{Ln}_2M_2O_7$, where Ln = rare-earth elements and $M = \text{Ru}, \text{Ir}, \text{etc.}$;



(a)



(b)

Fig. 5. Two examples of $Fd\bar{3}m$ structures. (a) The Friauf-Laves structure: $\text{Mg}; (\text{Mg}); \text{Cu}_{0.5 \times 4}; (\text{Cu})_{0.5 \times 4}$. (b) The spinel structure: $\text{MgO}_4; (\text{MgO}_4); \text{Al}_{0.5 \times 4}; (\text{Al})_{0.5 \times 4}$.

Table 4. $A\bar{A}B\bar{B}$ crystal structures of $Fd\bar{3}m$

p = partial occupancy.

| Type | Compound | Geometric units $A; B$ | a (Å) |
|-------------------------------|--|--|---------|
| Diamond | C | C; □ | 3.57 |
| NaCl | NaCl | Na; Cl | 7.488 |
| Friauf-Laves | Cu_2Mg | $\text{Mg}; \text{Cu}_{0.5 \times 4}$ | 7.048 |
| Spinel | Al_2MgO_4 | $\text{MgO}_4; \text{Al}_{0.5 \times 4}$ | 8.075 |
| (inverse) | Ni_2CoO_4 | $\text{NiO}_4; (\text{Ni}, \text{Co})_{0.5 \times 4}$ | 9.427 |
| Pyrochlore | $(\text{Ca}, \text{Na})_{16}\text{Nb}_{16}\text{O}_{48}\text{F}_8$ | $\text{FNb}_{0.5 \times 4}\text{O}_6; (\text{Ca} \text{ or } \text{Na})_{0.5 \times 4}$ | 10.43 |
| | RbSbWO_6 | $\text{W}_{0.5 \times 4}\text{O}_6; (\text{Sb}, \text{Rb})(?)$ | 10.245 |
| | $\alpha\text{-Li}_2\text{MoO}_3$ | $\text{Li}_{0.5 \times 4}\text{O}_4; (\frac{1}{3}\text{Li}^{2/3}\text{Mo})_{0.5 \times 4}$ | 8.30 |
| η -Carbide | $\eta_1\text{-W}_3\text{Co}_3\text{C}$ | $\text{C}_{0.5 \times 4}\text{W}_6; \text{Co}_4\text{Co}_{0.5 \times 4}$ | 11.01 |
| | $\eta_2\text{-W}_4\text{Co}_2\text{C}$ | $\text{C}_{0.5 \times 4}\text{W}_6; \text{Co}_4\text{W}_{0.5 \times 4}$ | 11.210 |
| | CFe_6W_6 | $\text{CW}_6; \text{Fe}_{0.5 \times 4}\text{Fe}_4$ | 10.934 |
| Molecular and ionic compounds | $\text{Na}_3\text{MgCl}(\text{CO}_3)_2$ | $\text{Cl}_{0.5 \times 4}\text{Na}_6; \text{C}_4\text{O}_{12}\text{Mg}_{0.5 \times 4}$ | 14.02 |
| | $\text{Na}_6\text{Mg}_2\text{SO}_4(\text{CO}_3)_4$ | $\text{SO}_4\text{Na}_6; \text{C}_4\text{O}_{12}\text{Mg}_{0.5 \times 4}$ | 13.93 |
| | $\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$ | $\text{OZn}_4\text{O}_{12}\text{C}_6\text{C}_6\text{H}_{18}(?)$; □ | 16.45 |
| | $\text{H}_2[\text{Ta}_6\text{Cl}_{18}] \cdot 6\text{H}_2\text{O}$ | $\text{Ta}_6\text{Cl}_{12}\text{Cl}_6; \text{HH}_2\text{O}(?)$ | 19.92 |
| Faujasite | $\text{Na}_{57}\text{Si}_{135}\text{Al}_{57}\text{O}_{384}$ | $\text{O}_{12}(\text{dco})\text{O}_{12}\text{O}_{12}(\text{Si}, \text{Al})_{24}\text{O}_{0.5 \times 24}$; □ | 24.71 |
| Alloys with large cells | Mg_2Al_3 | $\text{Al}_4\text{Mg}_4\text{Mg}_6\text{Al}_{12}(\text{dco})\text{Al}_{0.5 \times 4}\text{Mg}_{12}\text{Al}_{12}(\text{dco})\text{Al}_{24}(\text{dto})$; $\text{MgAl}_{0.083 \times 12}^p\text{Al}_{0.167 \times 12}^p\text{Al}_{0.25 \times 12}(\text{dco})\text{Mg}_{0.5 \times 12}\text{Al}_{0.25 \times 12}\text{Al}_{0.5 \times 12}\text{Al}_4$; $\text{Mg}_{0.75 \times 12}^p(\text{dco})\text{Mg}_{12}\text{Al}_{0.25 \times 12}\text{Al}_{0.5 \times 12}\text{Mg}_4$ | 28.239 |
| | NaCd_2 | $\text{Cd}_4\text{Na}_4\text{Na}_6\text{Cd}_{12}(\text{dco})\text{Cd}_{0.5 \times 4}\text{Na}_{12}(\text{dco})\text{Cd}_{12}(\text{dco})$; $\text{NaNa}_{0.35 \times 4}\text{Cd}_{0.7 \times 12}^p\text{Cd}_{0.5 \times 4}\text{Na}_{12}(\text{dco})\text{Na}_{12}(\text{dco})\text{Cd}_{0.8 \times 12}^p(\text{dco})\text{Cd}_4$ | 30.56 |

(iv) a group of compounds with formula $AMWO_6$ or AM_2O_6 ($A = K, Rb, Cs; M = Nb, Ta$) [their structure is slightly different from that of $(Ca, Na)_2Nb_2O_6F$ in that K, Rb and Cs are randomly distributed in unit A , Table 4]; the F^- ions can be replaced by H_3O^+ , NH_4^+ or Ag^+ through ion exchange (Groult, Michel & Raneau, 1973); (v) fluorides of $MNiCrF_6$ type with $M = K$ and Rb .

The α - Li_2MoO_3 , Li_2TiO_3 and $Li_6Mo_6O_7$ structures have been considered to be related to the pyrochlores, although the oxygen atoms form a tetrahedron instead of an octahedron (Table 4) (Barblan, Brandenberger & Niggli, 1944).

Many ternary carbides, nitrides or oxides adopt the so-called η or η -like carbide structure, whose A unit is the same as that of the pyrochlores. If four Co atoms are inserted into the B unit of the Laves phase or spinel structures, the B unit of the η carbides results. The corner-sharing tetrahedra form two interpenetrating lattice complexes D and D' . This structural feature explains the hardness of these compounds. Some carbides with stoichiometries W_3Co_3C , W_4Co_2C and Al_2VTa_3C have this structure. Even non-carbides such as $NiTi_2$, Ag_2Zr_3Zn , Al_2Au_2Hf , Mn_3Ni_2Si and Ni_2V_3Si belong to this type.

A few molecular or ionic compounds belong to space group $Fd\bar{3}m$. $Na_3MgCl(CO_3)_2$ and $Na_6Mg_2SO_4(CO_3)_4$ are isotypic, with corner-sharing Mg tetrahedra enclosing the CO_3 groups in B , and six Na and a corner-sharing tetrahedron in A (Shiba & Watanabe, 1931). Unit A contains a molecule in $Zn_4O(CH_3COO)_6$ (Koyama & Saito, 1954) and an anion, $Ta_6Cl_{18}^{2-}$, in $H_2[Ta_6Cl_{18}] \cdot 6H_2O$ (Thaxton & Jacobson, 1971).

Faujasite, a zeolite whose cell constant ranges from 24.6 to 25.1 Å, has a complicated cubic structure. The atoms in the framework of the A unit can be divided into three layers. The first layer consists of two truncated tetrahedra, $O_{12}O_{12}$, and a distorted cuboctahedron, $O_{12}(dco)$. These O atoms are almost equally distant from the center of the A unit. On top of this layer is a slightly distorted truncated octahedron $(Si, Al)_{24}$. In the outermost layer are oxygen atoms forming another distorted truncated octahedron, $O_{0.5 \times 24}$, which is shared with an adjacent A unit. These cage-like units A and \bar{A} form a lattice complex D . Within the A unit, a site for trapping ions makes faujasite an excellent ion exchanger. The structures of divalent-copper-exchanged faujasites were reported by Maxwell & de Boer (1975). The B units are large connected empty spaces that provide channels for the passage of fluids.

Discussion

The method used for formulating geometric units presented here is economical for computer storage and

handling of massive structural data, especially for non-crystallographer users. For this purpose, the coordinates can be inserted after the polyhedron, such as $A_4(x)A_6(z)A_{12}(xy)$. This method also provides a systematic way of dissecting structures, which helps one to understand them (Fig. 2). Furthermore, the method led to the discovery that some crystallographers had misinterpreted their results. The systematic listing makes it easy to study the frequently occurring structure types. Units with γ -brass and α -Mn structures are common, indicating a high degree of geometric stability.

Only in five space groups can structures be built from geometric units of $43m$ symmetry. There are only a few reasonable ways of building such units for a structure with a known number of atoms per cell. Tables 1 through 4 give a summary of $43m$ units that have been reported in actual structures. A systematic study of these data provides clues for solving and predicting crystal structures.

Among the five space groups discussed, $Pn\bar{3}m$ is the least common with only one well characterized structure type. Molecular compounds are found in the other four space groups, most of them in $I\bar{4}3m$ and $P\bar{4}3m$, with adamantane in $F\bar{4}3m$ and $Zn_4O(CH_3CO_2)_6$ in $Fd\bar{3}m$.

The study of geometric construction gives an interesting relationship among structures. For example, $AgAsMg$, $NaTl$, etc. have been related to the networks in zinc blende and diamond. No known structure has both cages of the zinc blende filled as is the case in $NaTl$ in its relation to the diamond structure. Corner-sharing tetrahedra occupy the cages to give $AuBe_5$ and Cu_2Mg from the ZnS and diamond structures respectively.

As for units of γ -brasses and some complicated alloy structures with large cells, their centers contain: (i) a single atom followed by a 12-vertex-polyhedron (e.g. α -manganese, Table 1); (ii) a tetrahedron (γ -brasses); (iii) an octahedron (Cu_4Cd_3 , Table 3). In $Sm_{11}Cd_{45}$, Table 3, two of the four units are similar to those of γ -brass, with an additional atom in the center, whereas the other two are the same as those of α -Mn (Fornasini, Chabot & Parthé, 1978).

The outer cuboctahedra of the γ -brass and α -Mn are only slightly distorted. The same is true for the distorted truncated octahedra. Undistorted polyhedra require special values for the z coordinates, but better R values would be obtained if they were varied.

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