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The Pyrochlore Structure and Its Relatives

HARRY NYMAN AND STEN ANDERSSON

Inorganic Chemistry 2, Chemical Center, University of Lund, P.O. Box 740, S-22007 Lund, Sweden

B. G. HYDE

Chemistry Department, University of Western Australia, Nedlands, Australia

AND M. O'KEEFFE

Department of Chemistry, Arizona State University, Tempe, Arizona

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The structures of pyrochlore, W_3Fe_3C, Sb_2O_3 (cub), $KTaWO_6 \cdot H_2O$, $RbNbTeO_6$, and $Mg_3Cr_2Al_{18}$ are discussed. Ideal atomic parameters are derived and compared with those observed.

Introduction

We have noticed that there are many metal alloy structure types, particularly those involving Al and/or some transition metals such as Fe and Ti, which contain three-dimensional arrays of metal atoms (frameworks) identical with the anion frameworks in some inorganic structures or with mixtures/intergrowths of them: a fact which seems not to have been previously pointed out, but which we believe to be useful in correlating and systematizing the mass of available, but largely uncorrelated, (nonmolecular) crystal structures. This is the more interesting in that it has been pointed out (O'Keeffe and Hyde, submitted for publication) that, in terms of the stacking of planar nets normal to the threefold axis, there are simple topological relationships between these well-known inorganic structure types: the oxides ReO_3, hexagonal tungsten bronze (*HTB*), $[a_{1/3}BX_3]$, and pyrochlore $[(Ay_{1/2})BX_3]$, and the sulfides such as Ln_3MgAlS_7.

In the present paper we will describe only the pyrochlore and related structures: oxide and metal alloy types. Other structure types will be the subject of subsequent papers.

Many of the structures concerned are noteworthy for containing icosahedral coordination polyhedra. These are generated by the juxtaposition of simpler, more familiar polyhedra, e.g., octahedra, in suitable groups.

Pyrochlores

The pyrochlore group of compounds includes many oxides, halides, and oxyhalides of different compositions. The pyrochlore structure has been described as an anion-deficient fluorite derivative, but is best compared with that of the hexagonal tungsten bronzes (*1*, *2*). The oxygen positions in the structure of cubic Sb_2O_3 were also shown (*3*) to be the same as the octahedral anion positions in pyrochlore. We now wish to report how the structures of W_3Fe_3C (a common alloy type = e.g., M_3Ti_3O), Co_2W_4C, $NiTi_2$, $Cr_4Al_{13}Si_4$, some oxides, and the lone pair structure of cubic Sb_2O_3 and those of $Mg_3Cr_2Al_{18}$, $ZrZn_{22}$, and VAl_{10} all can be

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related to and accurately derived from that of pyrochlore.

It was previously shown that a tetragonal packing of rods (symmetry $I4_1/amd$) was useful in describing a number of structures, including the pyrochlore type (*4*). The packing is shown in Fig. 1. In the plane of the drawing the rods are separated by $\sqrt{2}\times$ their diameter and, perpendicular to the plane, they are in contact. The rod interstitial position in this packing is a large octahedron, shown in the right-hand part of the figure. If each corner of this octahedron is substituted by two atoms, regularly spaced in the rods, a regular truncated tetrahedron is obtained, also shown in Fig. 1. If this truncated tetrahedron is centered, the well-known cubic Friauf–Laves phase ($MgCu_2$) is obtained. [An identical operation applied to the primitive cubic rod packing, $Pm3n$, results in the octahedron transforming to a nonregular icosahedron; and the resulting structure is exactly the Cr_3Si type (*5*)].

Atoms can now be placed along and in the rods to form the structure shown in Fig. 2, in which linear strings of corner-connected octahedra are also joined by corner-sharing. [Linear strings of the same sort occur elsewhere, for example in the structure of Re_3B = anti-$PuBr_3$, twinned c.c.p. (*6*)]. This framework of octahedra occurs in the pyrochlore structure. At the rod contacts there are groups of four octahedra sharing corners, and the structure can be described as being composed of such units (sharing corners). These groups of four octahedra share faces with another, central octahedron, which is empty in pyrochlore (Fig. 3).

The classical pyrochlore composition is $(Na,Ca)_2(Nb,Ti)_2(O,F)_6(O,F)$ $[=A_2B_2X_6Y]$. The space group is $Fd3m$, with the octahedral anions X in $48(f)$ and the octahedral cations

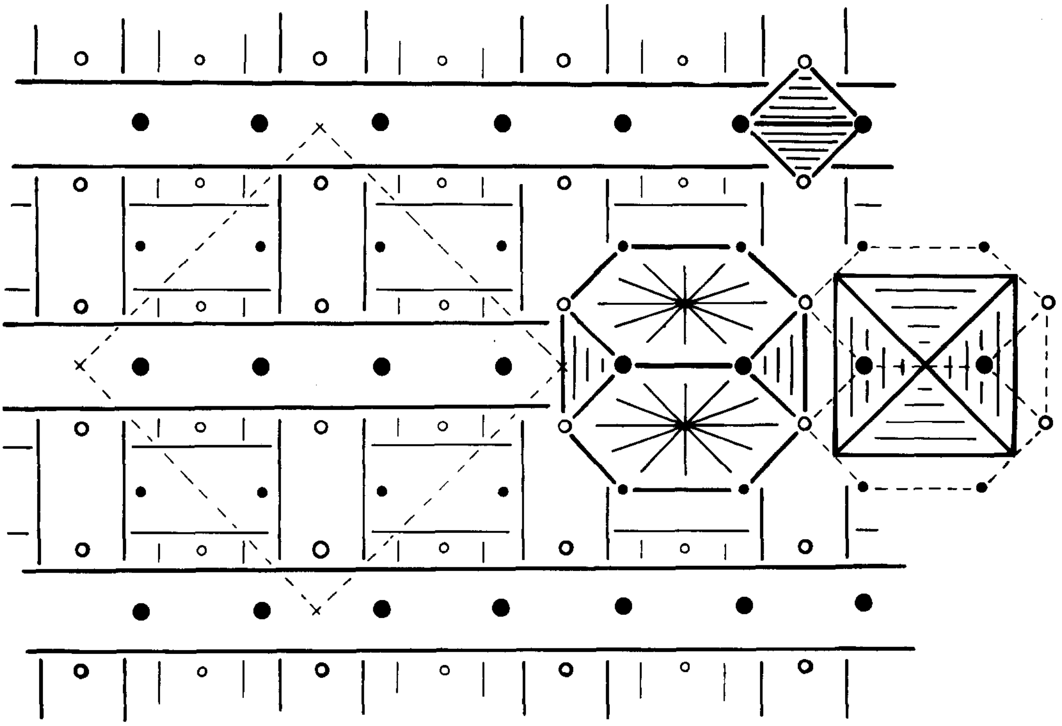

FIG. 1. A tetragonal packing of rods (four different levels). The big interstitial octahedron inscribed in a truncated tetrahedron is shown in the right part of the figure. The hatched lines indicate a tetragonal repeat unit.

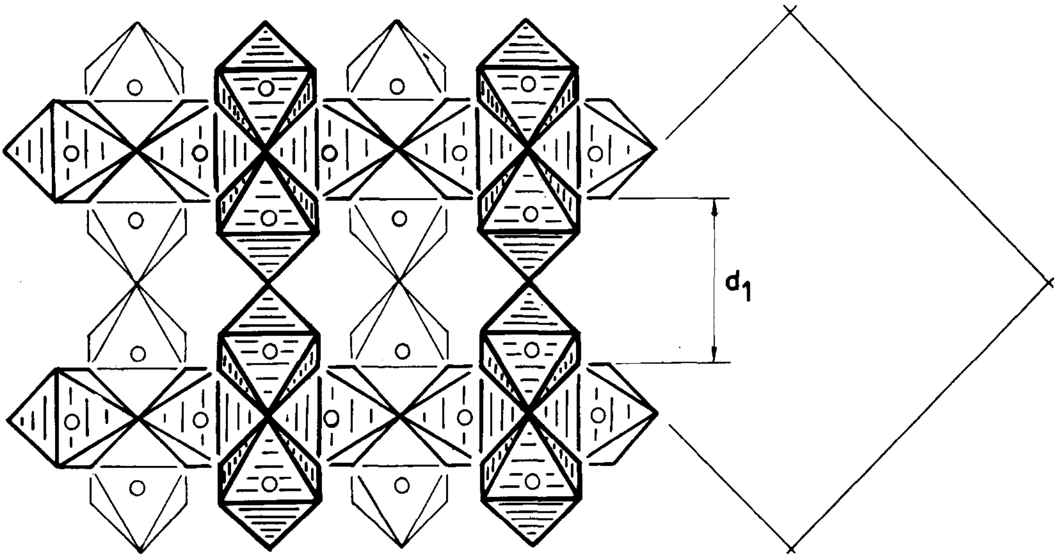

FIG. 2. The framework of octahedra in the pyrochlore structure.

B in 16(c). The A atoms are in 16 (d) and form a corner-connected array of tetrahedra, the Y atoms being at the centers of the tetrahedra, in 8(b) (Fig. 4), which corresponds to the idealized anti-cristobalite arrangement with composition $(Na,Ca)_2(O,F)$. [That of the octahedral framework is $2(Nb,Ti)(O,F)_3$.]

The coordination of the A atoms by anions is of interest: each A is at the center of a puckered hexagon (chair form) of six X atoms and, normal to the mean plane of this hexagon, by a pair of Y atoms. The coordination unit is therefore a (puckered) hexagonal bipyramid $[AX_6Y_2]$; the same unit as occurs in the α-UO_3 structure type $[UO_6O_2]$. These coordination polyhedra are corner-connected to form another three-dimensional framework, joined to the octahedral framework by common edges (the puckered hexagon).

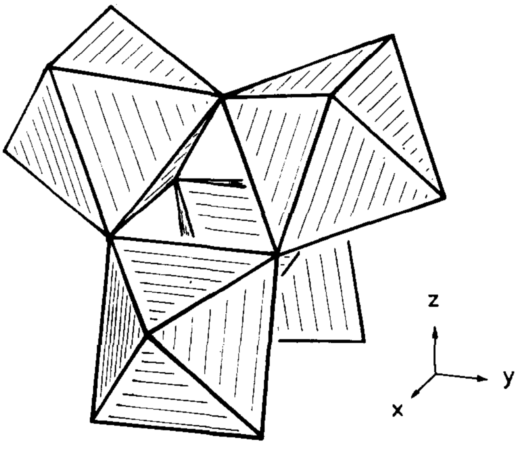

FIG. 3. The "pyrochlore unit." Four octahedra sharing corners.

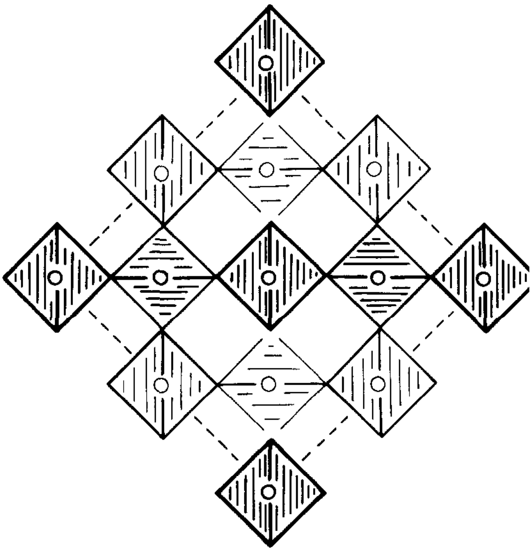

FIG. 4. An idealized anticristobalite structure. Open circles inside the tetrahedra indicate position 8(b).

TABLE I

SPACE GROUP *Fd*3*m*, ORIGIN AT 43*m*

Octahedral corner positions	48(*f*)	*x*,0,0
Octahedral central positions	16(*c*)	$\frac{1}{8},\frac{1}{8},\frac{1}{8}$
Inner tetrahedron	32(*e*)	*x*,*x*,*x*
Outer tetrahedron	16(*d*)	$\frac{5}{8},\frac{5}{8},\frac{5}{8}$

Center of inner tetrahedron; $x = \frac{1}{2},\frac{1}{2},\frac{1}{2}$, special case of 32(*e*) = 8(*b*).

Composition	*a* (Å)	[16(*d*)]	[16(*c*)]	[48(*f*)]	[32(*e*)]	[8(*b*)]	Reference
Pyrochlore	10.40	$(Na,Ca)_{16}$	$(Nb,Ti)_{16}$	$(O,F)_{48}$		$(O,F)_8$	2
W_3Fe_3C	11.09	Fe_{16}	C_{16}	W_{48}	Fe_{32}		10
Sb_2O_3	11.15			O_{48}	Sb_{32} E_{32}		3
$KTaWO_6 \cdot H_2O$	10.48	K_8	$(Ta,W)_{16}$	O_{48}		$(H_2O)_8$	2
$RbNbTeO_6$	10.25		$(Nb,Te)_{16}$	O_{48}		Rb_8	2

Space group $F\bar{4}3m$ (equivalent *Fd*3*m* positions in table head above)

		[16(*e*)]		[24(*f*)] +[24(*g*)]	[16(*e*)]	[4(*a*)]	
$Cr_4Al_{13}Si_4$	10.917	Si_{16}		Al_{48}	Cr_{16}	Al_4	11

The compounds $KTaWO_6 \cdot H_2O$ and $RbNbTeO_6$ have good ion-exchange properties, which reflects their structures. Both have pyrochlore structures. In the former $Y = H_2O$, in 8(*b*); B = (Ta,W) in 16(*c*); $X = 0$ in 48(*f*); and $A = K_{1/2}$, i.e., 8K atoms are randomly distributed over the 16(*d*) positions. In $RbNbTeO_6$ the *A* sites [16(*d*)] are empty; Nb and Te randomly occupy 16(*c*); and O is in 48(*f*).

The Structures of W_3Fe_3C, Co_2W_4C and $NiTi_2$

The cristobalite tetrahedra of Fig. 5 are centered by (*Y*) atoms in positions 8(*b*) of *Fd*3*m*. If these are replaced by smaller tetrahedra of atoms, inscribed in the larger ones but of reverse orientation [and with the centers of both coinciding with positions 8(*b*], the geometrical figure obtained is one central tetrahedron sharing all its faces with four surrounding tetrahedra: a tetra-capped tetrahedron or "stella quadrangula" (Fig. 8; by analogy with Kepler's polyhedron, the stella octangula, obtained by capping an octahedron with one atom outside each of its eight faces). The corners of the (smaller) central tetrahedra are in the 32(*e*) positions of *Fd*3*m*; the capping atoms are, as before, in 16(*d*). The octahedral, corner-connected framework is now interpenetrated by a framework of corner-connected stellae quadrangulae, which is shown in Fig. 9.

In the structure of W_3Fe_3C (with which many other alloys are isostructural, e.g., M_3Ti_3O with M = Co, Cu, or Fe) the Fe atoms

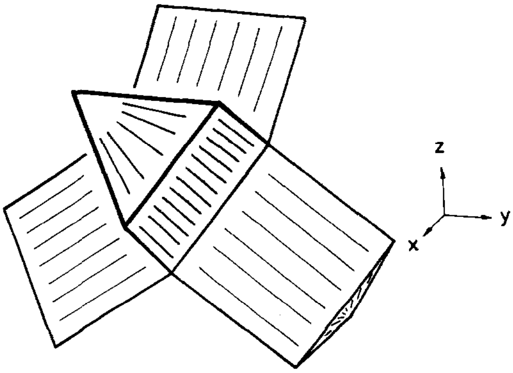

FIG. 5. Four trigonal prisms sharing triangular faces with a tetrahedron.

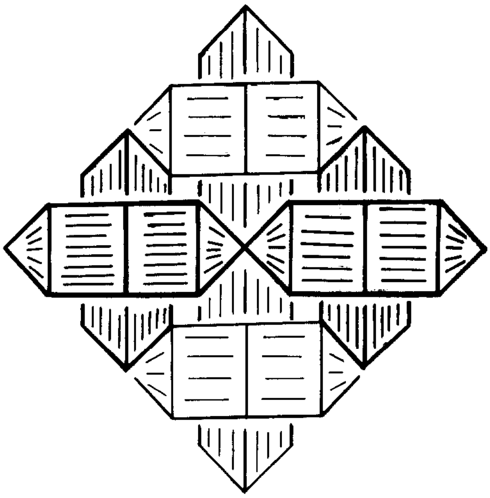

FIG. 6. A framework of trigonal prisms which can be placed in the cavities of pyrochlore.

form the array of stellae quadrangulae, i.e., both 16(*d*) and 32(*e*) are occupied by Fe; the 48(*f*) positions are occupied by W; and the 16(*c*) positions (at the centers of the W_6 octahedra) are occupied by C.

In the structure of Co_2W_4C the tungsten atoms occupy 48(*f*) and 16(*d*), and the Co atoms only 32(*e*). The C atoms are again in 16(*c*). $NiTi_2$ is very closely related, with Ti in place of the W in Co_2W_4C, Ni in place of Co, and the C sites empty.

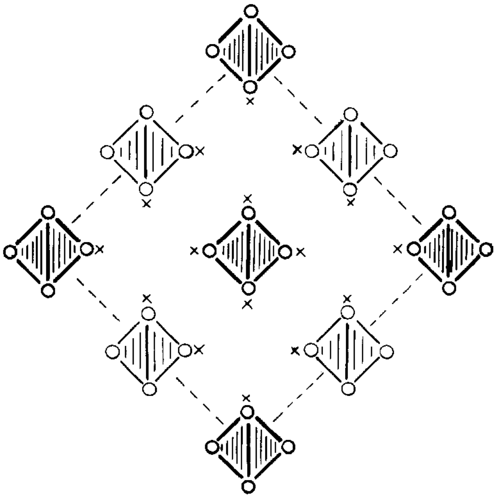

FIG. 7. The positions of the central tetrahedra of the framework shown in Fig. 6. If the tetrahedra are expanded to the crosses, the cristobalite structure shown in Fig. 4 is obtained.

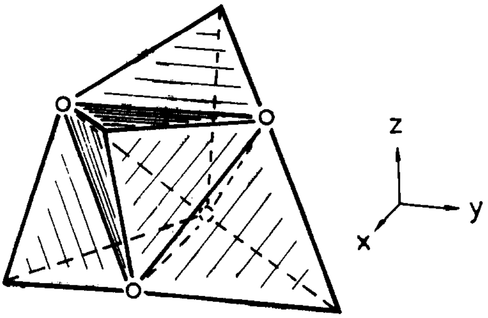

FIG. 8. A tetra-capped tetrahedron. One central tetrahedron sharing faces with four other tetrahedra.

The coordination of the 16(*d*) (=*A*) sites has now changed: The puckered hexagon of X[=48(*f*)] atoms remains but in place of the two axial *Y* [=8(*f*)] atoms there are now two triangles of 32(*e*) atoms. The axial direction is a $\bar{6}$ axis, and the coordination polyhedron (around *A*) is an icosahedron. Thus, interpenetrating the octahedral framework we now have a framework of icosahedra, joined by edge-sharing at the 32(*e*) positions, i.e., also sharing faces with the "central tetrahedron." The puckered hexagons are of course common

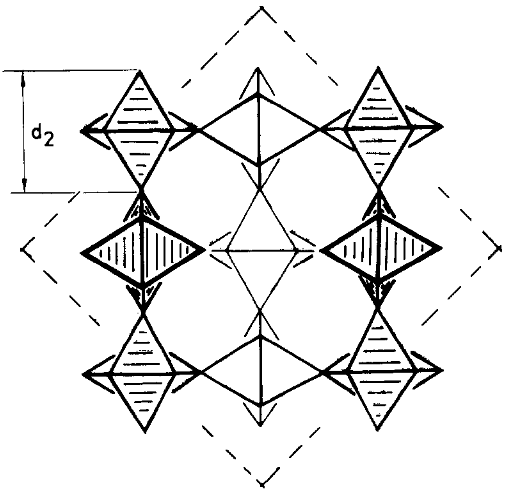

FIG. 9. Corner-sharing "stella quandrangular." One of the two interpenetrating frameworks of W_3Fe_3C.

to both frameworks, i.e., they correspond to shared edges between them.

The Cubic Sb_2O_3 Structure

The oxygen atoms are again in 48(*f*); the Sb atoms are in 32(*e*), with $x = 0.115$ [cf. W_3Fe_3C, where Fe in 32(*e*) has $x = 0.046$]. The Sb^{3+} in Sb_2O_3 is coordinated by three 48(*f*) atoms, all on one side of Sb (the nearest half of the puckered hexagon). And the lone pair of electrons on each Sb^{3+} must be pointing in the opposite (cubic space diagonal) direction, i.e., toward the 8(*f*) position. If, as we believe (*7*), the Sb–lone pair distance is 1.18 Å, then the center of the lone pair is at $x \doteq 0.054$ [also in 32(*e*)], which agrees well with the Fe coordinate in W_3Fe_3C. Again, as is frequently observed, the positions of both lone pairs and anions must be considered when structures of ns^2 elements are described and related to other structures.

In this case the puckered hexagonal bipyramids are defined by six 48(*f*) oxygens and two (axial) lone pairs of electrons. They are now isolated from each other and each contains *two* cations, one in each pyramid.

The Structure of $Cr_4Al_{13}Si_4$

This is an interesting intermediate case: In the corner-connected octahedral framework half the interstices have their 8(*f*) sites occupied and their 32(*e*) sites empty, and the other half have their 8(*f*) sites empty and their 32(*e*) sites occupied. The two possibilities alternate regularly along each cubic space diagonal, i.e., each cavity of one type is surrounded by four cavities of the other type (in a cubic ZnS type of arrangement). The space group is now $F\bar{4}3m$; the occupied positions are as follows (equivalent $Fd3m$ positions in parentheses): Al_4 in 4(*a*) [8(*b*)], Si_{16} in 16(*e*) [16(*d*)], Cr_{16} in 16(*e*) [32(*e*)], Al_{48} in 24(*f*) + 24(*g*) [48(*f*)]. [The 16(*c*) positions of $Fd3m$, now 16(*e*) of $F43m$, are not utilized.]

Thus, the structure consists of a corner-connected array of empty Al_6 octahedra (i.e., the common three-dimensional framework of corner-connected pyrochlore units) interpenetrated by a second array of corner-connected Si_4 tetrahedra, alternate tetrahedra being centered by an additional Al atom and by a smaller, central tetrahedron of Cr atoms. Put another way, this second framework is a corner-connected array of alternately, centered tetrahedra $AlSi_4$ and stellae quadrangulae Cr_4Si_4. The coordination of the Si (=*A*) atoms is, as before, a puckered hexagon, but now this has a single Al atom on one side and a triangle of Cr atoms on the other. The coordination number is 10 and the coordination polyhedron $SiAl_7Cr_3$ consists of a puckered hexagonal (mono-) pyramid sharing its hexagonal face with a half-icosahedron.

A Hypothetical Trigonal Prism Structure

If the octahedral framework is retained, the rod interstices can also be filled with trigonal prisms. These share one triangular face with the empty, central octahedron of the pyrochlore unit in Fig. 3, and one with a tetrahedron of [32(*e*)] atoms at the center of the void in the octahedral framework. Four prisms meet at the void center, sharing edges with each other, and all four faces of the central tetrahedron (Fig. 5). Only alternate voids can be filled in this way [only a half of the 32(*e*) sites can be occupied if the trigonal prisms are regular; otherwise the atoms are too close together], so that the space group is again $F\bar{4}3m$, rather than $Fd3m$, with the 48(*f*) positions of the latter split into 24(*f*) and 24(*g*) of the correct space group (with $x = 0.310$ and 0.560, respectively), the atoms forming the tetrahedra being 16(*e*) (with $x = 0.155$) as in the previous structure. The trigonal prism array is shown in Fig. 6 and the tetrahedra is shown in Fig. 7, where it is also shown how they easily may be changed to the corner-connected array of pyrochlore [i.e., to positions identical with 16(*d*) of $Fd3m$]. The trigonal prisms may therefore be said to be defined by three X atoms and three A atoms [in 24(f) or 24(g) and 16(e)]; there are 16 per unit cell and so, if each is centered by a Z atom, the stoichiometry of the prism array will be $Z_{16}A_{16}X_{24} = Z_{16}(A,X)_{40} = 8Z_2(A,X)_5$. To our knowledge no such structure exists. (But it is interesting that a small rotation of the tetrahedral units in Fig. 6—all in the same direction, and with a small translation parallel to the rotation axis which is the projection axis in the drawing, i.e., a screw operation—transforms the prism network to the structure of Fe_3P.) The two structures are very closely related. Furthermore, the {111} layers of this cubic trigonal prism structure (again ignoring the octahedra) are identical with the (0001) layers in hexagonal Fe_7C_3, Ru_7B_3, and Ln_3S_7 in Ln_3MgAlS_7, etc.—see the Introduction.

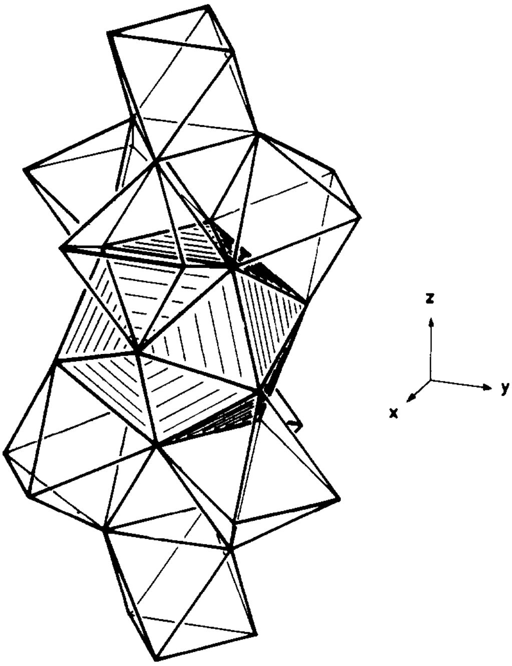

FIG. 10. Part of the $Mg_3Cr_2Al_{18}$ structure; an icosahedron created between two pyrochlore units.

The Structure of $Mg_3Cr_2Al_{18}$

This is also closely related to the pyrochlore structure, a fact which seems not to have previously been pointed out in its description (*8*). We imagine the octahedral framework of Fig. 2 to be "exploded" into isolated pyrochlore units by breaking their corner connections and translating them parallel to the cube edges. The unshared vertices then define truncated tetrahedra (cf. Fig. 1), and the structure consists of pyrochlore units joined via these truncated tetrahedra with which they share triangular faces (Fig. 11). (This corresponds to replacing each corner of a "large octahedron" by two atoms—see above.) The voids are now much larger and may be interpenetrated by an identical framework. In the resulting composite, pairs of pyrochlore units face each other; they are unconnected but have a common $\bar{6}$ axis. The space between them is an icosahedron (Figs. 10 and 12). They are not quite regular, the distortion being as in $Mg_3Cr_2Al_{10}$, in which the Al atoms are at the vertices of the octahedra (and truncated tetrahedra), in positions 96(g) and 48(f) of space group $Fd3m$, the Mg being in 16(d) and 8(b), and the Cr in 16(c). The Mg in 8(b) are at the centers of the Al_{12} truncated tetrahedra, those in 16(d) being just outside the hexagonal faces of these polyhedra. Truncated tetrahedra from the two (independent) frameworks

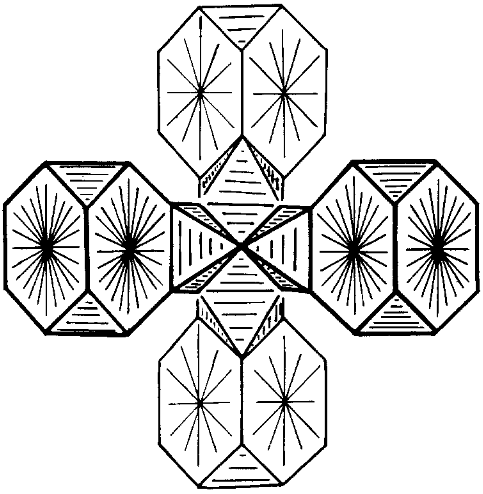

FIG. 11. Part of the $Mg_3Cr_2Al_{18}$ structure; one pyrochlore unit shares faces with four truncated tetrahedra.

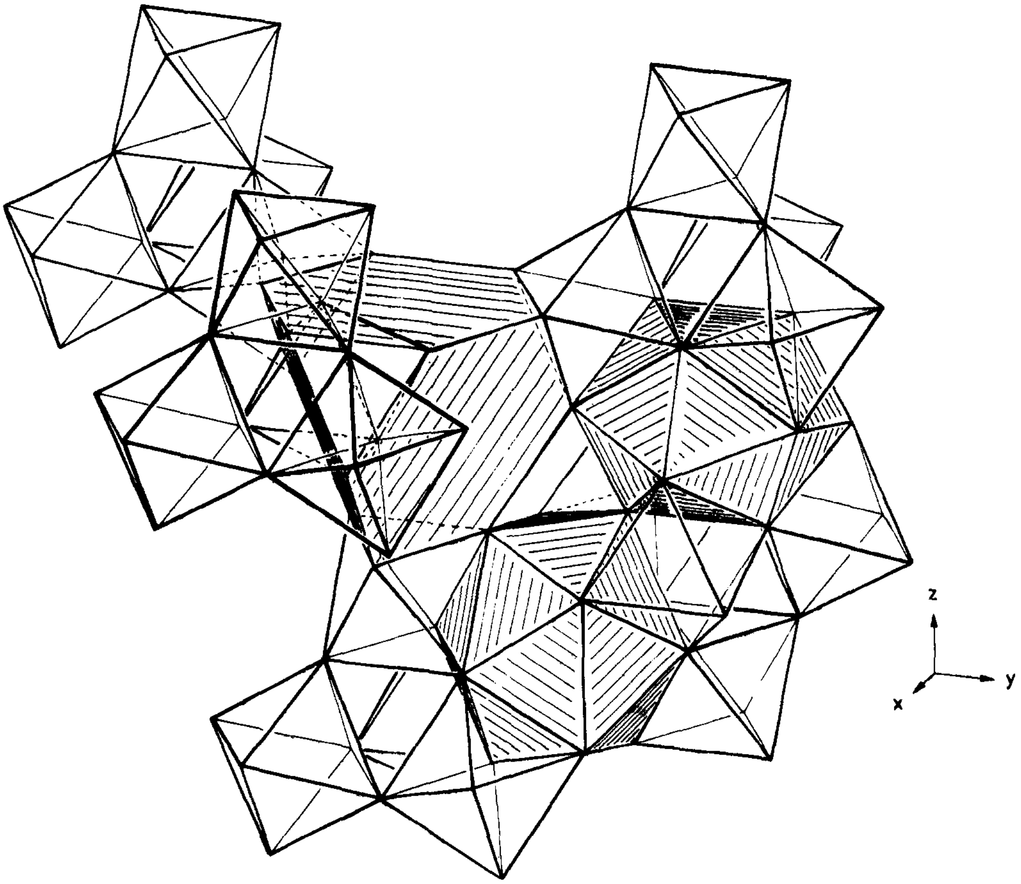

FIG. 12. Part of the $Mg_3Cr_2Al_{18}$ structure; four pyrochlore units sharing faces with a truncated tetrahedra. In the lower right part of the figure one pyrochlore unit from the other pyrochlore-truncated tetrahedra framework is inserted to show the creation of two icosahedra.

have hexagonal faces opposite each other, so that these latter Al atoms are actually at the centers of the intervening hexagonal prisms. The Cr atoms are at the centers of the Al_{12} icosahedra, and the octahedra (in the pyrochlore units) are empty.

There are two very similar structures. In VAl_{10} the Al atoms again occupy positions 96(*g*) and 48(*f*), but also the 16(*d*) position (in the hexagonal prisms); the V atoms are in 16(*c*), i.e., in the icosahedra. Surprisingly, the 8(*b*) positions (at the centers of the large truncated tetrahedral interstices) are said to be unoccupied. This is consistent with the observation that the measured density is "anomalously low" (*9*). In $ZrZn_{22}$ the 8(*b*) positions *are* occupied—by Zr, the Zn atoms being in 96(*g*) and 48(*f*) and 16(*d*) and also 16(*c*) at the centers of the icosahedra.

Calculation of Atomic Parameters

Pyrochlore

Octahedral structure. If d_1 is a distance given in Fig. 2, it is easy to find that

$$d_1 = e_{oct} \cdot \sqrt{3} \cdot \sin \tfrac{1}{2}\,\theta,$$

where e_{oct} is the octahedral edge, and θ is the dihedral angle in a tetrahedron. Further on, the size of the unit edge becomes

$$a_{cub} = \sqrt{2}(d_1 + e_{oct}).$$

The general expression to find the 48(*f*) parameters becomes

$$x = \frac{1}{2(\sqrt{3}\sin\frac{3}{2}\theta + 1)} = 0.1875.$$

Tetrahedral structure. If d_2 is a distance given in Fig. 7, again

$$d_2 = e_{\text{tetr}} \cdot \sqrt{3} \cdot \sin\tfrac{3}{2}\theta,$$

where e_{tetr} is the tetrahedral edge, and θ is the same as above.

$$a_{\text{cub}} = 2d\sqrt{2}.$$

The general expression to find the 32(*e*) parameter becomes

$$x = \frac{\sqrt{3}\sin\frac{3}{2}\theta - 1}{8 \cdot \sqrt{3}\sin\frac{3}{2}\theta} = 0.0500.$$

The metric size ratio between the two interpenetrating structures becomes

$$\frac{e_{\text{oct}}}{e_{\text{tetr}}} = \frac{2 \cdot \sqrt{3}\sin\frac{3}{2}\theta}{1 + \sqrt{3}\sin\frac{3}{2}\theta} = 1.25.$$

$Mg_3Cr_2Al_{18}$

Similarly as for pyrochlore, it is easy to find that

$$a_{\text{cub}} = e_{\text{oct}}(\sqrt{6}\sin\tfrac{3}{2}\theta + 2\sqrt{2})$$

and for the 96(*g*) position the parameters become:

$$x = \frac{\sqrt{2} \cdot e_{\text{oct}}}{2a_{\text{cub}}} = 0.068$$

$$z = \frac{e_{\text{oct}}(\sqrt{2} + \sqrt{3})}{2a_{\text{cub}}} = 0.303$$

and for 48(*f*) the parameter become

$$x = \frac{e_{\text{oct}} \cdot \sqrt{2}}{2a_{\text{cub}}} = 0.136.$$

The above calculations of parameters show, when compared with the observed ones below, that the descriptions of these structures are sound.

	Calculated parameters	Observed parameters	Reference
Pyrochlore (48 *f*)	$x = 0.187$	$x = 0.195$	*2*
Sb_2O_3 (48 *f*)	$x = 0.187$	$x = 0.186$	*3*
W_3Fe_3C (48 *f*)	$x = 0.187$	$x = 0.187$	*10*
W_3Fe_3C (32 *e*)	$x = 0.050$	$x = 0.046$	*10*
$Mg_3Cr_2Al_{18}$ (96 *g*)	$x = 0.068$	$x = 0.067$	*8*
	$z = 0.303$	$z = 0.300$	
$Mg_3Cr_2Al_{18}$ (48*f*)	$x = 0.136$	$x = 0.141$	*8*

Acknowledgment

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