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Closest Packing in Dense Oxides: The Structure of a Polymorph of $Co_3(AsO_4)_2$

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Crystals of $Co_3(AsO_4)_2$ were grown from the melt of a mixture of $Co_2As_2O_7$ and As_2O_5. The crystals are isostructural with $Mg_3(AsO_4)_2$ and are tetragonal with $a = 6.858(2)$, $c = 18.872(5)$ Å, $Z = 6$, and space group $I\bar{4}2d$. A total of 1048 independent reflections were measured by diffractometer and used in the full-matrix refinement to a final R value of 0.069. The structure contains two distinct AsO_4 groups. Two of the cobalt ions are octahedrally coordinated and a third occupies a $\bar{4}$ site with four short and four long Co–O distances. The crystal structure of $Co_3(AsO_4)_2$ is not based on the continuous three-dimensional closest packing of oxygen atoms. Nevertheless the number of oxygen atoms per cubic centimeter is 5.4×10^{22}, which falls in the range of values for hexagonal and cubic closest packed structures. A better measure of the degree to which closest packing is achieved by a structure is suggested. It is based on an analysis of the polyhedra of oxygen atoms which surround each of the oxygen atoms in a structure and their relation to the polyhedra in ideally closest packed structures. In order to facilitate the analysis, polytopes of 11- and 12-vertex polyhedra were studied. A new decahexahedral 11-vertex polyhedron was found.

Introduction

The structures of several compounds of composition $M_3(XO_4)_2$ (where M is a divalent cation and $X = P$, As, or V) have been studied to date. The structures show a large variation in the packing of oxygen atoms and coordination of the cations and, despite the availability of a large body of information on cation–oxygen bond lengths and cation bonding tendencies, it is not possible to predict the structure of an unknown member of the series with any certainty. The structures of $Mg_3(VO_4)_2$ (*1*) and $Zn_3(VO_4)_2$ (*2*) are based on the cubic closest packing of oxygen atoms and are related to the spinel structure (*3*). The Zn^{2+} and Mg^{2+} ions occupy the octahedral sites and the V atoms occupy tetrahedral sites. A polymorph of $Co_3(AsO_4)_2$ has been studied by Krishnamachari and Calvo (*4*). They describe the structure as based on the hexagonal closest packing of oxygen atoms in a manner related to the structure of olivine (*5*).

The possibility that a particular compound might be based on a closest packed arrangement of oxygen atoms is dependent on the tendency of the cations to enter into octahedral coordination or tetrahedral coordination and the degree to which the M–O and X–O bonds approximate the ideal values for the octahedral and tetrahedral cavities in hexagonal and cubic closest packed arrangements of oxygen atoms. Therefore, $Cu_3(AsO_4)_2$ (*6*), with a large Jahn–Teller distortion, is not closest packed, but in $Co_3(AsO_4)_2$ the Co^{2+} ions are more

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likely to be octahedrally coordinated and the expected average Co–O distance of ca. 2.13 Å (*7*) is near the ideal value of 2.05 Å for the octahedral sites in an undistorted closest packed lattice with an O–O contact distance of 2.9 Å. In contrast, the average expected Ca–O distance is 2.40 Å or greater (*7*) and indeed the structure of $Ca_3(AsO_4)_2$ is not closest packed. Using these arguments one would expect the structure of $Mg_3(AsO_4)_2$ to also be closest packed, but this is not the case (*8*) and the aforementioned criteria for closest packing are therefore not in themselves adequate.

$Co_3(AsO_4)_2$ is also a member of the $n\mathrm{CoO} \cdot As_2O_5$ series of compounds. Studies of the $n\mathrm{CoO}\cdot As_2O_5$ system indicate that compounds corresponding to $n = \frac{1}{2}, 1, 2, 3,$ and 6 can be prepared (*9, 10*) and most of these structures have been determined. $\mathrm{CoO}\cdot As_2O_5$ is structurally similar to $PbSb_2O_6$ with a hexagonally closest packed arrangement of oxygen atoms (*10*). $6\mathrm{MgO}\cdot As_2O_5$ (*11*) and $6\mathrm{CoO}\cdot As_2O_5$ (*12*) are isostructural and their oxygen atoms are cubic closest packed. $3\mathrm{CoO}\cdot As_2O_5$ (*4*) was found to be monoclinic with an approximate hexagonally closest packed arrangement of oxygen atoms. The Co and As atoms occupy the octahedral and tetrahedral sites, respectively. A similar packing was found in the structure of $3{\cdot}84\mathrm{CoO}\cdot As_2O_5$ (*13*).

The compound reported here also has the stoichiometry of $3\mathrm{CoO}\cdot As_2O_5$ but was prepared inadvertently from a melt of $Co_2As_2O_7$ and As_2O_5, in the process of attempting to prepare crystals of $Co_2As_2O_7$ itself from incorrectly labeled commercial starting materials. The existence of this phase has also been reported by Krishnamachari and Calvo (*4*). The presence of polymorphism in the $n\mathrm{CoO}\cdot As_2O_5$ and $M_3(XO_4)_2$ series of compounds suggests that a knowledge of average M–O and X–O bond lengths will not be sufficient to predict the structure of any unknown compound.

Experimental

The crystals of $Co_3(AsO_4)_2$ were grown by Dr. E. Kostiner, University of Connecticut. They were prepared from the melt of a mixture of $Co_2As_2O_7$ and As_2O_5 under nitrogen in a closed platinum crucible at 1230°C, held for 4 hr, and cooled at 20°C/hr to 750°C. The formation of these crystals can be explained by the reaction:

$$3Co_2As_2O_7 \rightarrow 2Co_3(AsO_4) + As_2O_5.$$

An approximately rectangular shaped crystal of dimensions ($0.08 \times 0.08 \times 0.10$ mm) was mounted on a fiber. The crystals were found to be tetragonal with the systematic absences

$$h + k + l \neq 2n \qquad \text{for } (hkl)$$

and

$$2h + l \neq 4n \qquad \text{for } (hhl).$$

Therefore the space group is $I4md$ or $I\bar{4}2d$. The cell dimensions are $a = 6.858(2)$ Å and $c = 18.872(5)$ Å. The space group $I\bar{4}2d$ was chosen because of the similarity of the cell dimensions to those of $Mg_3(AsO_4)_2$ (*8*). Twenty-five reflections with $2\theta > 60°$ were centered at both positive and negative 2θ and were used to calculate accurate cell dimensions. The integrated intensities of 3500 reflections ($2\theta < 100°$) were obtained with a Picker FACS-I diffractometer using Mo$K\alpha$ radiation. The structure was then refined by the full-matrix least-squares method using the parameters of $Mg_3(AsO_4)_2$ as initial parameters. A total of 1048 unique reflections were used in the refinement after averaging over the symmetry equivalent reflections. The scattering factors were taken from Cromer and Mann (*14*). A series weighting scheme with $\omega = (1.7346 - 0.00333|F_o| + 0.000369|F_o|^2)^{-2}$ was used in the final cycles of least squares. The term in brackets is an approximation for $\sigma(|F_o|)$, calculated with the assumption that the best approximation for $\sigma(|F_o|)$ is the average value of $||F_o|-|F_c||$ in the range of $|F_o|$. The final agreement factors were $R=0.069$ and $R_\omega=0.073$. Table I, containing a list of observed and calculated structure factors, is available as supplementary material.[1] The final positional and thermal parameters are listed in Table II.

Description of the Structure

As noted earlier, $Co_3(AsO_4)_2$ is isostructural with $Mg_3(AsO_4)_2$ (*8*). A stereoscopic view of the structure is given in Fig. 1 (*15*). The oxygen atoms are represented either by the termination of stick bonds or the joining of two stick bonds at a vertex. When small volumes are viewed separately, the array of oxygen atoms appears hexagonally closest packed with the stack axes approximately parallel to the ⟨301⟩ family of directions. The deviations from closest packing are such that discontinuities in stacking appear between equivalent areas in adjacent unit cells. In other words, the translational symmetry does not tessellate small local areas of closest packing in order to create continuous three-dimensional

TABLE II

FRACTIONAL ATOMIC COORDINATES[a,b]

Atom	Site symmetry	x/a	y/b	z/c
Co(1)	8d	2435 (2)	2500	1250
Co(2)	8c	0	0	2277 (1)
Co(3)[c]	4b	0	0	5000
As(1)	8d	−3435 (2)	2500	1250
As(2)	4a	0	0	0
O(1)	16e	576 (11)	2072 (9)	435 (3)
O(2)	16e	4963 (11)	2898 (12)	1925 (3)
O(3)	16e	2208 (8)	5470 (9)	1016 (3)

THERMAL PARAMETERS[a,b,d]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	65 (4)	74 (4)	63 (4)	0	0	−2 (2)
Co(2)	83 (5)	65 (5)	60 (4)	−1 (2)	0	0
Co (3)	137 (22)	U_{11}	162 (18)	0	0	0
As(1)	63 (3)	63 (3)	58 (3)	0	0	−2 (2)
As(2)	57 (6)	U_{11}	51 (4)	0	0	0
O(1)	164 (23)	58 (16)	108 (18)	−5 (8)	−11 (9)	−8 (8)
O(2)	87 (19)	250 (31)	109 (17)	−11 (11)	11 (10)	−46 (9)
O(3)	107 (21)	56 (15)	130 (19)	−7 (6)	−36 (8)	−12 (7)

[a] $\times 10^4$.

[b] Numbers in parentheses are estimated standard deviations.

[c] Site of half occupancy.

[d] The temperature factor expression is $\exp\{-2\pi^2(a^{*2}h^2U_{11}+\cdots+2a^*b^*hkU_{12}+\cdots\}$.

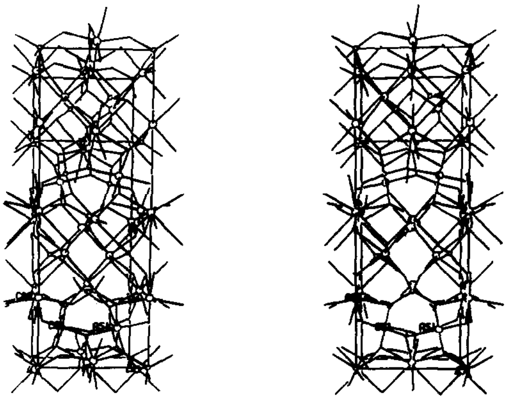

FIG. 1. Stereoscopic view of the packing of tetragonal $Co_3(AsO_4)_2$.

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[1] See NAPS Document No. 03507 for 16 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10017. Remit in advance for each NAPS Accession number. Institutions and organizations may use purchase orders when ordering. However, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are \$5.00. Microfiche are \$3.00. Outside of U.S. and Canada, postage is \$3.00 for a photocopy or \$1.50 for a fiche.

closest packing. The coordination polyhedra present in the structure consist of two independent CoO_6 octahedra with $C_2(2)$ symmetry, two independent AsO_4 tetrahedra, one with C_2 symmetry and one with $D_{2d}(\bar{4})$ symmetry, and a CoO_8 polyhedron with D_{2d} symmetry which may be formed by capping the four faces of a D_{2d} distorted tetrahedron with an outer tetrahedron and which is also known as the Hoard dodecahedron. The bond length to the inner tetrahedron is 2.265(9) and to the outer, 2.729(7) Å. The tendency of Co^{2+} to assume eight coordination is well documented (*16*). In the present case only one-half of the Co^{2+} sites of the dodecahedra are occupied.

The bonds and angles from all of the polyhedra are listed in Table III. The average Co–O distance in the octahedron around Co(1) is 2.092 Å and for the octahedron around Co(2), 2.108 Å. These bond lengths are slightly shorter than the averages for the three independent CoO_6 octahedra in the monoclinic modification of $Co_3(AsO_4)_2$ (*4*). Furthermore the spread of Co–O octahedral bond lengths here is 2.019 to 2.168 Å. In the monoclinic form it is 1.991 to 2.292 Å.

In order to understand the packing of the structure, many approaches are possible, depending on which features are to be emphasized. In $Mg_3(AsO_4)_2$ Krishnamachari and Calvo (*8*) have chosen to emphasize the connectivity of the aforementioned polyhedra. They separate the structure into sheets containing the vectors **a** + **b** and **c** and isolate edge sharing undulating strips of polyhedra within these sheets. It must be understood, however, that such a description is only a convenience in visualizing the structure because the amount of edge sharing between polyhedra in adjacent sheets is not significantly less than within the sheets.

We may emphasize the fourfold symmetry of the structure by separating it into sheets parallel to the basal plane of the tetragonal unit cell. Our discussion is in terms of the same polyhedra used by Krishnamachari and Calvo (*8*) and illustrated in their Fig. 1.

TABLE III

BOND DISTANCES (Å) AND ANGLES (°)[a]

Co(1)–O($1^{\mathrm{i,vi}}$)	2 × 2.019(6)
–O($2^{\mathrm{i,vi}}$)	2 × 2.168(7)
–O($3^{\mathrm{i,vi}}$)	2 × 2.090(6)
Co(2)–O($1^{\mathrm{v,vi}}$)	2 × 2.085(6)
–O($2^{\mathrm{x,xi}}$)	2 × 2.085(6)
–O($3^{\mathrm{v,vi}}$)	2 × 2.154(5)
Co(3)–O($2^{\mathrm{vii,viii,xiii,xii}}$)	4 × 2.265(8)
–O($3^{\mathrm{ix,x,xi,xii}}$)	4 × 2.729(6)
As(1)–O($2^{\mathrm{i,vi}}$)	2 × 1.703(6)
–O($3^{\mathrm{ii,v}}$)	2 × 1.686(6)
As(2)–O($1^{\mathrm{i,ii,iii,iv}}$)	4 × 1.688(6)

O(1^{i})–Co(1)–O(1^{vi})	101.7(3)
–O(2^{vi})	92.2(3) × 2
–O(3^{i})	86.2(2) × 2
–O(3^{vi})	88.4(2) × 2
O(2^{i})–Co(1)–O(2^{vi})	73.8(4)
–O(3^{i})	93.5(3) × 2
–O(3^{vi})	93.3(3) × 2
O(1^{v})–Co(2)–O(2^{xi})	105.0(3) × 2
–O(2^{xii})	91.1(3) × 2
–O(3^{v})	82.9(3) × 2
–O(3^{vi})	81.7(3) × 2
O(2^{xi})–Co(2)–O(2^{xii})	87.5(4)
–O(3^{vi})	90.8(3) × 2
O(3^{v})–Co(2)–O(3^{vi})	91.9(3)
O(2^{vii})–Co(3)–O(2^{viii})	122.7(4)
–O($2^{\mathrm{xiii,xiv}}$)	103.3(4) × 2
–O(3^{ix})	162.5(3)
–O(3^{x})	73.7(3)
–O(3^{xi})	76.0(3)
O(2^{viii})–Co(3)–O(3^{xii})	64.4(3)
–O($2^{\mathrm{xiii,xiv}}$)	103.3(4)
O(3^{ix})–Co(3)–O(3^{x})	90.7(3)
O(3^{x})–Co(3)–O(3^{xi})	119.6(3)
O(2^{i})–As(1)–O(2^{vi})	99.7(5)
–O(3^{ii})	112.7(3) × 2
O(2^{vi})–As(1)–O(3^{ii})	105.0(3) × 2
O(3^{ii})–As(1)–O(3^{v})	120.1(4)
O(1^{i})–As(2)–O(1^{ii})	121.8(4)
–O($1^{\mathrm{iii,iv}}$)	103.7(4) × 2
O(1^{ii})–As(2)–O($1^{\mathrm{iii,iv}}$)	103.7(4) × 2
O(1^{iii})–As(2)–O(1^{iv})	121.8(4)

[a] Symmetry operators: i, x, y, z; ii, $-x, -y, z$; iii, $-y, x, -z$; iv, $y, -x, -z$; v, $-x, \frac{1}{2}+y, \frac{1}{4}-z$; vi, $x, \frac{1}{2}-y, \frac{1}{4}-z$; vii, $y, \frac{1}{2}+x, \frac{1}{4}+z$; viii, $-y, \frac{1}{2}-x, \frac{1}{4}+z$; ix, $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$; x, $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$; xi, $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}-z$; xii, $\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}-z$; xiii, $\frac{1}{2}-x, y, \frac{3}{4}-z$; xiv, $\frac{1}{2}+x, -y, \frac{3}{4}-z$; xv, $\frac{1}{2}+y, x, \frac{3}{4}+z$; xvi, $\frac{1}{2}-y, -x, \frac{3}{4}+z$.

Identical but displaced sheets of polyhedra sit approximately at $z = 0, \frac{1}{4}, \frac{1}{2}$, and $\frac{3}{4}$. The sheets are square nets with repeat distance **a** and with Co(3)O_8 dodecahedra at the corners of the square net. These corners are joined in both directions by the octahedra around Co(2) which share polyhedral edges with two Co(3) dodecahedra each. At the center of the square of the net sits a tetrahedron around As(2), sharing one vertex with each of the four Co(2) octahedra surrounding it.

The sheets are separated by straight double ribbons of polyhedra at $z = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$, and $\frac{7}{8}$. Each successive plane of ribbons is rotated through 90°. The basic unit of the ribbons is an As(1) tetrahedron and a Co(1) octahedron sharing a common edge. This pair of polyhedra are joined to the next pair along the double ribbon by corner sharing with the polyhedron of opposite type in the next unit along the ribbon. Adjacent ribbons do not share either edges or corners. Each As(1) tetrahedron shares an edge with a Co(3) dodecahedron in the sheet above and with one in the sheet below the plane of the ribbon. The Co(1) octahedron shares an edge with a Co(3) dodecahedron above and below it and also with a Co(2) octahedron above and below it.

The unusual Co–O bonds to the Co^{2+} cation in the half-occupied Co(3) site were used in a bond strength calculation using the method of Brown and Wu (*17*). Each bond is assigned a "bond strength" in valence units (v.u.) given by $s = (R/R_1)^{-N}$ and the sum of bond strengths should approach the valence of the ion. Using values for R_1 and N given by Brown and Wu, the four oxygen atoms at a distance of 2.265 Å from the Co(3) ion contribute a total of 0.88 v.u. The four at 2.729 Å contribute 0.31 v.u. for a total of 1.19 v.u. The site is half occupied by a divalent cation and one might therefore expect a value of 1.00 vu. In order to test the applicability of the method to this structure we also calculated the sum of bond strengths for the other cations. We find for Co(1), Co(2), As(1), and As(2) the values 2.08, 1.97, 4.80, and 4.91 v.u., respectively, in better agreement with the formal charges on these cations.

Figure 2 shows that the thermal ellipsoids of the O(2) and O(3) atoms are highly anisotropic and that the long axes of the ellipsoids are along the direction of the Co(3)–O bonds. The O atom position is then assumed to be the average of two positions, one corresponding to an occupied Co(3) site and one corresponding to an unoccupied Co(3) site. The contribution of the Co(3)–O(3) bond strength (0.08 v.u.). based on this average O(3) position gives a total value of 1.95 v.u. for the O(3) atom, in good agreement with the values of 1.99 and 2.01 v.u. for the atoms O(1) and O(2). We conclude therefore that it is not correct to expect a total bond strength value for a partially occupied site equal to the average valency of the site.

Oxygen Packing

The calculated density of tetragonal $Co_3(AsO_4)_2$ is 5.10 g cm^{-3} and the calculated density of monoclinic $Co_3(AsO_4)_2$ is 5.19 g cm^{-3}. A difference of less than 2% is rather surprising considering the fact that one form appears to be closest packed and the other is clearly not. Another indicator of closest packing that might be considered is

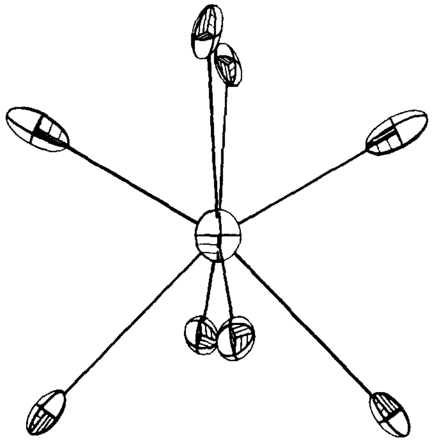

FIG. 2. Thermal ellipsoids of the oxygen atoms around the partially occupied site of the Co(3) atom.

the number of oxygen atoms per cm^3. Assuming an oxygen closest packing radius of 1.45 Å, ideal hexagonal and cubic closest packing contain 5.8×10^{22} oxygen atoms per cm^3. The values for tetragonal $Co_3(AsO_4)_2$, monoclinic $Co_3(As_2O_4)_2$ (*4*), $Co_{6.95}As_{3.62}O_{16}$ (*13*), and $6MgO \cdot As_2O_5$ (*11*) are 5.4, 5.5, 5.2, and 5.5×10^{22} oxygen atoms per cm^3, respectively. The latter three compounds are identified as being closest packed. It would appear, then, that a better indicator is needed. An analysis of the packing in terms of contact distances between oxygen atoms suggests itself but we are then left with the problem of deciding which pairs of oxygen atoms are in contact and which are not.

We therefore undertook to examine the geometry of the polyhedron of oxygen atoms which surrounds each individual oxygen atom in high density oxides. In such an approach, the effect of the cations is manifested only through the perturbations of the idealized closest packing of the oxygen atoms caused by their presence in the lattice.

A practical method of characterizing polyhedra in terms of polyhedral edge angles was first suggested by Porai-Koshits and Aslanov (*18*). The method has been discussed by several authors and has recently been expanded to include 9- and 10-vertex polyhedra (19). The oxygen polyhedra in hexagonal and cubic closest packed structures have 12 vertices. In non-closest-packed structures we might expect polyhedra with less than 12 vertices. It is therefore necessary to first extend this analysis to include 11- and 12- vertex polyhedra.

The results obtained probably have limited application outside of the present context because coordination numbers 11 and 12 are not common in discreet polyhedra and furthermore, 11-vertex polyhedra are particularly unstable toward the formation of the 12-vertex icosahedron. Therefore a brief discussion of 11- and 12- vertex polyhedra is presented here.

In lattice structures and alloys, the requirements of tessellation produce a large variety of low-symmetry, high-coordination polyhedra. A number of such polyhedra have recently been discussed by Bhandary and Girgis (*20*). They find two 11- vertex polyhedra, the pentacapped trigonal prism (PTP) with symmetry D_{3h} and an "11 verticon" with symmetry C_s. An 11-vertex polyhedron is clearly created by removing a vertex from an icosahedron, i.e., the monocapped pentagonal antiprism (MPAP), with symmetry C_{5v}. In order to establish the geometry of reference polyhedra (polytopes) we have used the method of Claxton and Benson (*21*), which varies the geometry of the reference polyhedron in order to minimize the energy of repulsion between ligands at the vertices of the polyhedron, written as $\sum R_{ij}^{-n}$ where R_{ij} is the separation of the ligands *i* and *j*. An important feature of the method is that symmetry once achieved in the variable polyhedron is never lost. It was therefore of considerable interest that wherever a low symmetry or random placement of vertices was used as a starting point (sometimes unintentionally) a new 11-vertex polyhedron of symmetry C_{2v} was nearly always generated. In a few cases the threefold symmetry of the PTP became "locked in" and the PTP was generated.

The new 11-vertex polyhedron has 16 triangular faces and we shall therefore refer to it as the decahexadron (DHH). Table IV lists

TABLE IV

RELATIVE REPULSIVE ENERGIES OF 11-VERTEX POLYHEDRA

n	MPAP	DHH	PTP
1	121.844	121.805	121.865
4	68.468	68.258	69.027
6	55.712	55.684	57.204
7	51.558	51.728	53.672
8	48.168	48.592	50.982
9	45.277	45.996	48.843
10	42.724	43.984	47.077

a measure of the energy of repulsion of the MPAP, DHH, and PTP for several values of the exponent n. The units are arbitrary and comparisons are valid only between polyhedra of equal n. For values of n less than 7, the DHH is the energetically favorable polyhedron. The PTP is the superior polyhedron for no values of n. Nevertheless, because of its high symmetry and its existence in alloy structures it must be considered as an important 11-vertex polyhedron. The three 11-vertex polyhedra are shown in Fig. 3.

The dihedral angles δ, between the pairs of planes forming each polyhedral edge, were calculated for all three polyhedra with a value of 6 assigned to the exponent n. The values of δ and the lengths of the associated edge for a polyhedron inscribed within a unit sphere are given in Table V. The labeling of the edges of the MPAP and DHH is shown in Fig. 4. The connectivity of a polyhedron intermediate between the two polytopes is given in Fig. 5. In the DHH, the equivalent edges are the b and c edges, the d and e edges, the f and g edges, the h and i edges, the k and l edges, and the n and o edges. In the MPAP, the a, b, and e edges are equivalent, as are the c, f, and h, the d, g, j, k, and n, and the i, m, and o edges. The l edges divide the pentagonal base of the MPAP into three triangles and have the value zero in the MPAP. They are therefore the most sensitive indicators of polyhedral type.

TABLE V

δ ANGLES AND EDGE LENGTHS FOR THE MPAP AND DHH WITH $n = 6$

	MPAP		DHH	
Edge	Length	δ (°)	Length	δ (°)
a	1.090	43.2	1.155	36.3
b	1.090	43.2	1.057	48.6
c	1.075	45.2	1.057	48.6
d	1.094	40.9	1.104	41.9
e	1.090	43.2	1.104	41.9
f	1.075	45.2	1.137	36.9
g	1.094	40.9	1.137	36.9
h	1.075	45.2	1.003	60.9
i	0.988	76.1	1.003	60.9
j	1.094	40.9	1.047	44.9
k	1.094	40.9	1.321	27.5
l	1.599	0	1.321	27.5
m	0.988	76.1	0.995	61.4
n	1.094	40.9	1.003	54.8
o	0.988	76.1	1.003	54.8

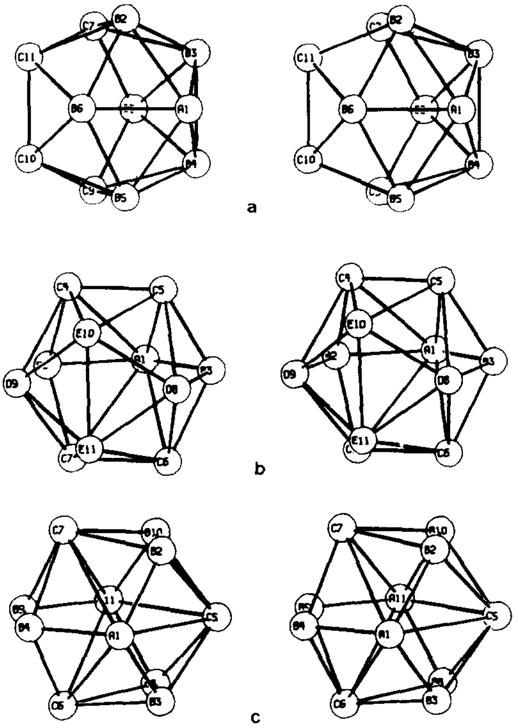

FIG. 3. Stereoscopic views of the (a) monocapped pentagonal antiprism (MPAP), (b) decahexahedron (DHH), and (c) pentacapped trigonal prism (PTP).

We will not attempt to relate the connectivity of the PTP with that of the aforementioned polytopes. However, we list here the δ angles for the four independent sets of edges of the PTP. Referring to Fig. 3c, the values for A-B edges, A-C edges, B-B edges, and B-C edges are 71.5, 6.2, 44.9, and 53.6°, respectively. In order to relate the PTP to the more familiar tricapped trigonal prism (TTP) we observe that the addition of the two A vertices to the TTP removes the edges,

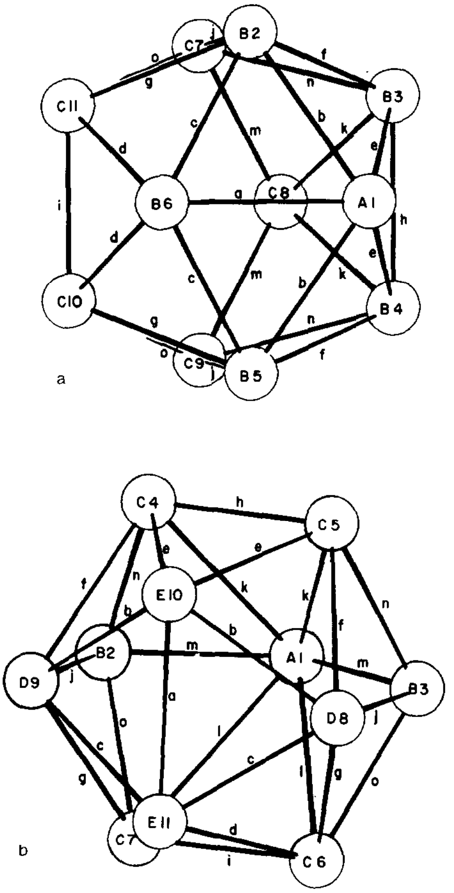

FIG. 4. Labeling of the edges of the (a) monocapped pentagonal antiprism and (b) the decahexahedron.

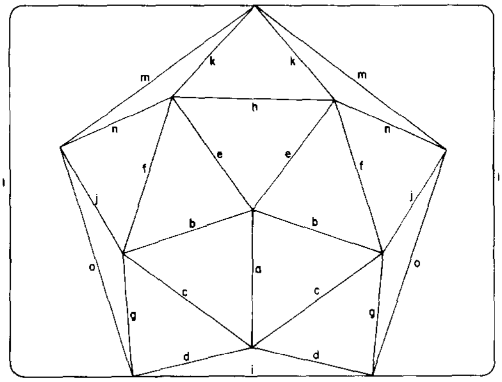

FIG. 5. Schematic representation of the connectivity of a general 11-vertex polyhedron intermediate between the MPAP and DHH.

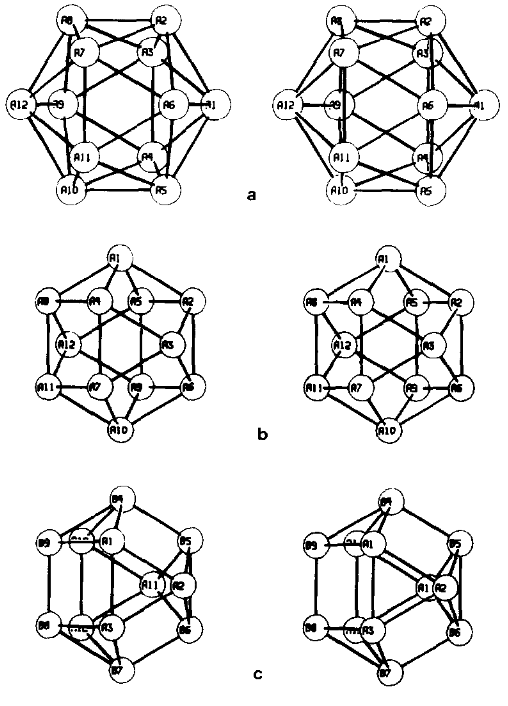

FIG. 6. Stereoscopic views of the (a) icosahedron, (b) the cuboctahedron (COH), and (c) the twinned cuboctahedron (TCOH).

B2-B3, B3-B4, B4-B2, B8-B9, B9-B10, B10-B8 which would exist in the TTP.

The 12-vertex polyhedron with maximum edge length in a unit sphere is the well-known regular polyhedron, the icosahedron. However, the icosahedron has fivefold symmetry and therefore does not pack well. Many structures exist which are based on icosahedra, particularly the higher borides (*22*), but they are not based on the closest packing of atoms. The polyhedron of oxygen atoms surrounding each oxygen atom in cubic closest packed and hexagonal closest packed structures are the cuboctahedron (COH) and the twinned cuboctahedron (TCOH). The advantage of icosahedral geometry is illustrated by the fact that the relative repulsive energies of the icosahedron, COH, and TCOH, with a negative exponent of 6 in the repulsion potential, are 70.6, 79.4, and 78.8, respectively. Figure 6 shows stereograms of the three 12- vertex polyhedra.

For the icosahedron and the COH all edges are equivalent for all values of the exponent n. The edge lengths are 1.052 and 1.000, respectively, for the icosahedron and COH inscribed in a unit sphere. The δ angles are 41.8 and 54.7°. The TCOH is formed by combining half of a COH with its mirror image. The polyhedron thus obtained corresponds to the packing of solid spheres: i.e., the $n = \infty$ case. If n is assigned a finite value four independent sets of edges are formed. Their lengths and δ angles are given in Table VI, for $n = 6$.

We must also establish a criterion for choosing the oxygen atoms surrounding a given oxygen atom which shall be considered as being part of the polyhedron to be analyzed, i.e., the near neighbors. We shall use the "difference in reciprocal distance concept" which has been suggested by Brunner (*23*). The rationale for the method in terms of Coulomb potential energy would seem to be as appropriate for repulsive potentials as for attractive potentials. A negative power of the interatomic distances greater than one would probably be more realistic and would provide sharper discrimination between those surrounding oxygen atoms which are or are not part of the appropriate polyhedron. We find in practice that the method as proposed by Brunner has the advantage that it is both adequate and easy to carry out.

TABLE VI

δ ANGLES AND EDGE LENGTHS FOR THE TCOH

Edge	δ (°)	Edge lengths
(a) B_5–B_6, B_7–B_8, B_9–B_4[a]	37.2	1.039
(b) All A–A	54.2	1.006
(c) All A–B	55.2	1.004
(d) B_4–B_5, B_6–B_7, B_8–B_9	71.6	0.960

[a] See Fig. 6c.

We now proceed to examine some representative structures using the procedures outlined above. The number of surrounding oxygen atoms belonging to the appropriate polyhedron were determined using the method of Brunner (*23*). The vertices of the polyhedron were moved along their radius vector to the surface of a unit sphere and the Porai-Koshits and Aslanov δ angles were calculated. Spinel ($MgAl_2O_4$) (*3*) was found to clearly contain 12-vertex polyhedra corresponding to the COH and the δ angles range from 52.0 to 57.2°, in excellent agreement with the expected value. In $BeAl_2O_4$, which is representative of the olivine structure (*3*), there are three independent oxygen atoms, two of which are on mirror planes. All are surrounded by 12-vertex TCOH. There are therefore nine independent δ_a angles which range from 36.2 to 40.4°. There are a total of 36 independent δ_b and δ_c angles which range from 49.5 to 59.0°. There are a total of nine independent δ_d angles which range from 67.0 to 71.7°. The agreement with the expected values for hexagonal closest packed structures is again excellent.

The structure of $Mg_{8.5}As_3O_{16}$ has four independent oxygen atoms in the space group $R\bar{3}m$ (8). The oxygen atoms are all surrounded by COH with δ angles ranging from 44.9 to 65.5°, which reflects the lower symmetry of the packing here compared to that in spinel but the structure is correctly identified as cubic closest packed.

$Co_{6.95}As_{3.62}O_{16}$ has three independent oxygen atoms in the space group *Pnma*. The polyhedron around each oxygen atom is a TCOH with δ_a between 32.4 and 43.4°, δ_b and δ_c between 45.4 and 62.3°, and δ_d between 62.8 and 71.7°. The distortions are larger than in olivine but the structure is based on the hexagonal closest packing of oxygen atoms.

We now turn to the monoclinic and tetragonal polymorphs of $Co_3(AsO_4)_2$. Table VII which is available as supplementary material[1], lists the relevant O–O distances for each of the independent oxygen atoms. The values of $(1/d_{n-1} - 1/d_n)$, multiplied by 1000, are also given for each atom.

Some unusually short O–O distances occur which correspond to edges of AsO_4 tetrahedra; and therefore some large values of the reciprocal function occur at low n. Nevertheless in all cases but one, a large increase in the value of 1000 $(1/d_{n-1} - 1/d_n)$ occurs at $n = 9$, 10, or 11. Even in the exception the maximum value of the function occurs at $n = 11$ although it is not distinctly larger than neighboring values. We find that all of the oxygen polyhedra in monoclinic $Co_3(AsO_4)_2$ have 11 vertices and the three polyhedra in tetragonal $Co_3(AsO_4)_2$ have 10, 11, and 9 vertices. Therefore neither is closest packed. The tetragonal form is, by inspection of the structure, clearly not closest packed. Based on the presence of roughly closest packed continuous planes of oxygen atoms, monoclinic, $Co_3(AsO_4)_2$ appears, by inspection, to be hexagonally closest packed. Nevertheless, the foregoing analysis would suggest that this is only a manifestation of the favorable relation between the translational symmetry and the local packing in that the former propagates the latter to give infinite planes of oxygen atoms which is a necessary but not then a sufficient condition for closest packing. The presence of the cations, particularly the tetrahedrally coordinated cations, is sufficient to condense the structures in such a manner that the oxygen atom density is similar to that in closest packed structures.

The question remains as to what kind of polyhedra are formed by the oxygen atoms surrounding each independent oxygen atom. In coordination polyhedra the force between the central atom and the vertices is attractive and between the vertices the force is repulsive, thus limiting the number of ways that energy efficient polyhedra can be formed. Here the force between the vertices and the central atom is repulsive and furthermore it tends to be small in comparison with other forces which we have not considered. We should then expect less tendency toward regularity in the polyhedra examined here than in coordination polyhedra.

This is indeed the situation we find in the polyhedra in the two polymorphs of $Co_3(AsO_4)_2$. Of the nine 11-vertex polyhedra in the two polymorphs of $Co_3(AsO_4)_2$, four have the connectivity of the intermediate 11-vertex polyhedron given in Fig. 5. These are the polyhedra around O(2) in tetragonal $Co_3(AsO_4)_2$ and O(14), O(21), and O(23) in monoclinic $Co_3(AsO_4)_2$. The four sets of δ_l values are given in Table VIII. None of these four polyhedra approach the geometry of the DHH or the MPAP even though they have the appropriate connectivity. None of the nine 11-vertex polyhedra have the connectivity of the PTP. The 10-vertex polyhedron around O(1) does not have the connectivity of the intermediate 10-vertex polyhedron. The 9-vertex polyhedron around O(3) is the exception in that it is a distorted monocapped square antiprism with a δ_a of 12° (*18*). In order to investigate the structure of the monoclinic form of $Co_3(AsO_4)_2$, further we added the 12th oxygen atom to each of the 11-vertex polyhedra and again examined the polyhedral geometry. The connectivities of both the original polyhedra formed in this way, and the polyhedra formed by reducing the latter to the surface of a unit sphere were neither TCOH or COH.

TABLE VIII

δ_l ANGLES FOR POLYHEDRA IN THE TWO POLYMORPHS OF $Co_3(AsO_4)_2$ WHICH HAVE THE CONNECTIVITY OF THE INTERMEDIATE 11-VERTEX POLYHEDRON

	δ_l (°)	
O(2) tetragonal)	10	52
O(14) (monoclinic)	6	40
O(21) (monoclinic)	3	42
O(23) (monoclinic)	8	40

TABLE IX

δ ANGLES FOR THREE DHH

Edges	δ(°)			
	Al(12)[a]	Al(17)	$Th(NO_3)_4 \cdot 3H_2O$[b]	$C_{23}H_{21}N_8O_{11}La$
a	3	3	20	55
b and c	52, 67, 71, 73	51, 70, 70, 74	44, 63	40, 42, 43, 46
d and e	30, 39, 50, 63	18, 40, 52, 68	39, 50	33, 36, 39, 41
f and g	1, 6, 23, 34	3, 9, 39, 42	30, 34	39, 39, 40, 42
h and i	39, 78	41, 80	57	69, 74
j	52, 71	50, 53	43	54, 55
k and l	23, 36, 45, 54	15, 34, 38, 41	15, 50	19, 25, 28, 29
m	20, 51	42, 59	54	65, 66
n and o	42, 69, 70, 76	39, 68, 71, 75	54, 67	48, 49, 51, 52

[a] The numbering scheme is as in the original paper (*24*).

[b] The polyhedron has symmetry C_2 (*25*).

In order to determine if an oxide should be designated as closest packed we suggest then a rather simple procedure. It is first necessary to determine if each oxygen atom contains 12 atoms in its surrounding sphere of oxygen atoms. Although more sophisticated procedures are available, the test used here seems both straightforward and adequate. Second, the degree to which those polyhedra approach either of the idealized TCOH or COH, as indicated by the δ parameters, determines both the type of closest packing and serves as a qualitative measure of the extent to which closest packing is achieved. Analysis of the polyhedra with less than 12 vertices is of less value in this regard but might in some cases shed light on the factors which influence the packing.

We are not aware of the existence in the literature of an 11-vertex polyhedron which has the full C_{2v} symmetry of the DHH. However, 11 vertex polyhedra do tend to have the connectivity of the DHH and two polyhedra in the α' phase of the vanadium aluminium system (*24*) and the discreet polyhedron in $Th(NO_3)_4 \cdot 3H_2O$ (*25*) are highly distorted DHH. Recently, however, Thomas *et al.* (*26*) have found a discreet polyhedron in the structure of trionitrato[2,6-diacetylpyridine-bis(benzoic acid [hydrazone)]lanthanum (III) ($C_{23}H_{21}N_8O_{11}La$) which is a DHH with δ parameters similar to those of the polytopal DHH with $n = 6$ in the repulsion potential and which approaches the C_{2v} symmetry of the DHH. The δ angles of these polyhedra are given in Table IX.

Spherical polar coordinates for the decahexahedron, monocapped pentagonal antiprism, pentacapped trigonal prism, icosahedron, cuboctahedron, and the twinned cuboctahedron, are available as supplementary material.

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