

The Occurrence of Rhombic Prisms in Some Structures

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An ideal rhombic prism is defined as two regular trigonal prisms sharing a square face. In terms of such rhombic prisms, the structures of CrB and α -PdCl₂, U₃Si₂ and Au₃Zn, CoCa₃ and PdS are easily described. A network of rhombic prisms, with cubic symmetry, is also used to describe the structures of CoAs₃, Sc(OH)₃, WAl₁₂, and NaMn₇O₁₂.

Introduction

It is a well-known fact that in a structure built up of centered polyhedra there are also empty polyhedra of the same or a different kind between the centered ones. In the ReO₃ structure (1), the ReO₆ octahedra are joined by corner-sharing. The interstices, in the form of cubic octahedra, are empty. In the related perovskite structure (2), the cubic octahedra are filled with large cations. Another example is the Al(OH)₃ structure (3), in which the close-packed layers of Al(OH)₆ octahedra are separated by empty trigonal prisms (17). In this work we have studied relationships between structures in which a special kind of eight-coordination occurs, the rhombic prism coordination. An ideal rhombic prism, as demonstrated in Fig. 1, is built up of two regular trigonal prisms sharing a square face and the rhombic prisms may be filled or empty. If the prism is filled, there is an atom at the center of the square face.

CrB and α -PdCl₂

In the CrB structure (4), every boron atom is situated at the center of a regular trigonal prism of chromium atoms. These prisms share four faces, two square and the two triangular ones, with other prisms. The infinite layers

formed are separated by square pyramids and stacked in the way shown in Fig. 2. In the upper part of the figure, two boron atoms are shown.

In the α -PdCl₂ structure (5), on the other hand, each palladium atom is surrounded by four chlorine atoms in a square at a close distance, and four other chlorine atoms further away, altogether making a rhombic prism. The chromium atom packing in CrB is identical with the chlorine atom packing in α -PdCl₂. The only difference between these two structures is the position of the central atoms, boron and palladium, respectively. If one-half of the boron atoms are removed and the rest are shifted into the center of a rhombic prism, an isostructural configuration with the α -PdCl₂ structure is obtained. The fine lines in the lower part of Fig. 2 indicate, as they do in Figs. 3 and 4, rhombic prisms instead of pairs of trigonal prisms.

U₃Si₂ and Au₃Zn

In the structure of the alloy U₃Si₂ (6), the silicon atoms are situated at the center of regular trigonal prisms of uranium atoms. The prisms share one square face and the trigonal faces with other prisms. The rhombic column made in this way shares edges with other rhombic columns. In the network thus created there are square tunnels in which the

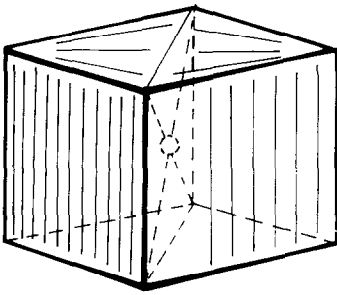
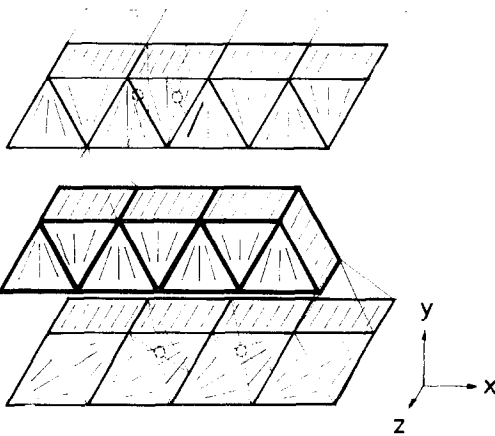
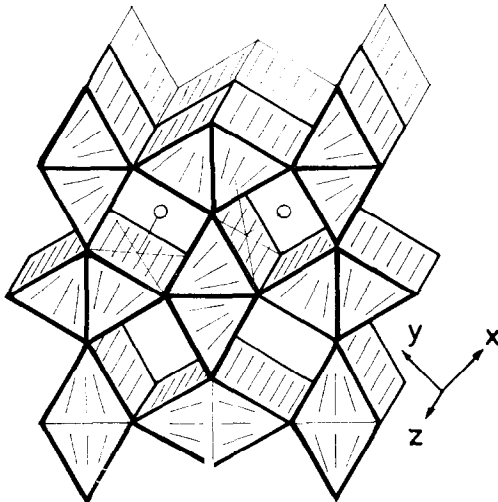
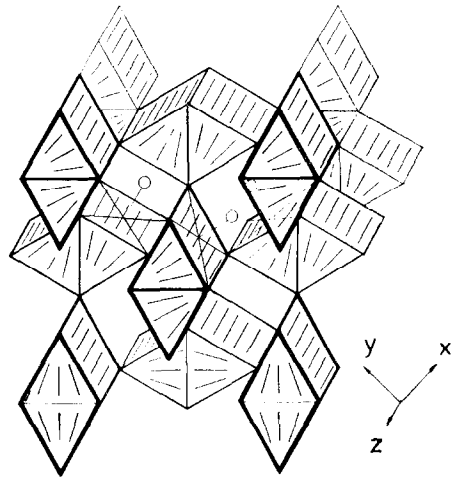


FIG. 1. A rhombic prism.

FIG. 2. The structure of CrB (or α -PdCl₂).FIG. 3. The structure of U₃Si₂ (or Au₃Zn).

remaining uranium atoms are situated. Figure 3 shows two such uranium atoms. The structure of Au₃Zn (7) can be split up into sheets

FIG. 4. The structure of CoGa₃ (or PdS).

of zinc-centered rhombic prisms. Every sheet is one prism high and the rhombic prisms have the same positions in the *ab* plane as the pairs of regular trigonal prisms in the U₃Si₂ structure. The sheets in Au₃Zn are repeated by a translation of $\frac{1}{2}(b+c)$.

CoGa₃ and PdS

The CoGa₃ structure (8) is rather similar to the U₃Si₂ structure. Here again there are pairs of regular trigonal prisms sharing a square face. The centers of the prisms are occupied by cobalt atoms. However, in the CoGa₃ structure, every such pair of trigonal prisms shares corners with other pairs of prisms, creating a network, as shown in Fig. 4. In analogy with the U₃Si₂ structure, the remaining gallium atoms are placed in the square tunnels. The network of the sulfur atoms in PdS (9) has the same geometry as the network of gallium atoms in CoGa₃, but the pairs of trigonal prisms are replaced by Pd-centered rhombic prisms of sulfur atoms. Although the remaining palladium atoms are not situated corresponding to the Ga atoms in CoGa₃, the two structures are quite similar.

Framework with Cubic Symmetry

We noticed that in stacking ideal rhombic prisms in the way shown in Fig. 5 a framework

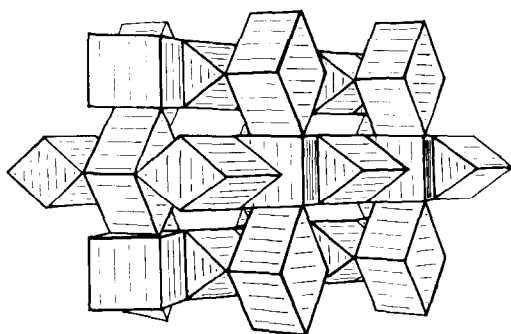


FIG. 5. A network of rhombic prisms with cubic symmetry.

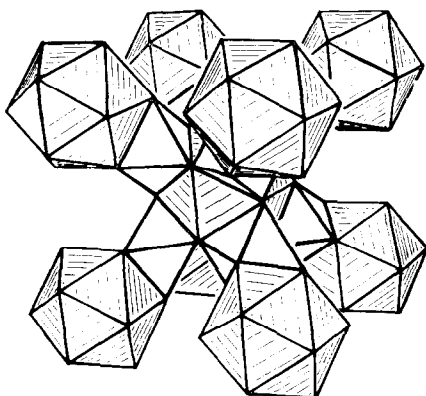


FIG. 6. The interstices in the rhombic prism network.

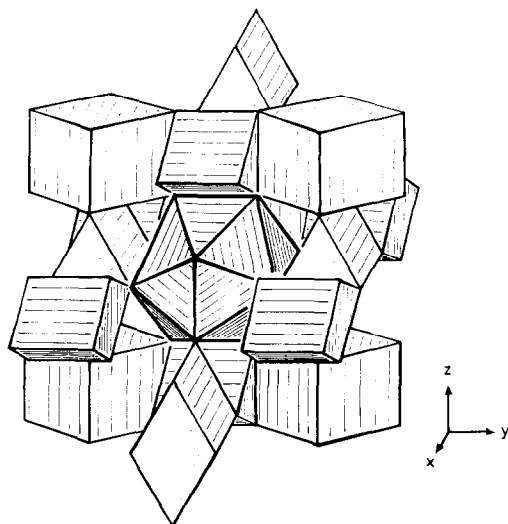


Fig. 7. The edge-sharing between one icosahedron and the rhombic prisms. Two prisms in the front are omitted.

with cubic symmetry is obtained. In this framework there are two kinds of holes, small ones with slightly distorted octahedral geometry, and bigger ones shaped as almost perfect icosahedra. These two kinds of interstices share faces, as shown in Fig. 6. The rhombic prism network in Fig. 5 shares edges with the network in Fig. 6. In Fig. 7, the edge-sharing between one icosahedron and the surrounding rhombic prisms is described. By filling up the centers of these three kinds of polyhedra in the framework with atoms, some known structures are obtained.

Framework with Filled Octahedra

In the structure of CoAs_3 (skutterudite; 10-12) and related compounds, there are square As_4 groups. These square As_4 groups can be thought of as the middle square in the rhombic prisms of our framework. Then the cobalt atoms are situated in the octahedral interstices. Another structure similar to CoAs_3 is the $\text{Sc}(\text{OH})_3$ structure (13). The corners of the rhombic prisms are occupied by OH^- ions, and the octahedral interstices contain the Sc^{3+} ions.

These two structures can be described using our rhombic prism framework with filled octahedra, while the rhombic prisms and the icosahedra are empty.

Framework with Filled Icosahedra

According to Adam and Rich (14) each tungsten atom in the alloy WAl_{12} is surrounded by 12 aluminium atoms in the shape of an icosahedron. The structure of WAl_{12} is of cubic symmetry and the tungsten atoms are placed in $0,0,0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The icosahedra are separated by empty octahedra at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, etc. The framework created in this way is the same as the framework of interstices in our rhombic prism net, shown in Fig. 6.

In the WAl_{12} structure, our rhombic prism framework has filled icosahedra, while the rhombic prisms and the octahedra are empty.

Framework with Filled Octahedra, Icosahedra, and Rhombic Prisms

In the cubic $\text{NaMn}_7\text{O}_{12}$ structure (15) there are sodium atoms at 0,0,0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Each sodium atom is surrounded by 12 oxygen atoms in the shape of an icosahedron. Between these icosahedra there are Mn^{4+} and low-spin Mn^{3+} atoms at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, etc., surrounded by oxygen octahedra. That leads to a structure as the one shown in Fig. 6, in this case with filled icosahedra and filled octahedra. The high-spin Mn^{3+} atoms are situated at the centers of the rhombic prisms in the framework shown in Fig. 5. The $\text{NaMn}_7\text{O}_{12}$ structure can thus be described using our rhombic prism framework with filled octahedra, icosahedra, and rhombic prisms.

In Table I, parameters for two networks, one with ideal rhombic prisms and one with ideal octahedra and icosahedra are given. It is obvious that the structure of $\text{NaMn}_7\text{O}_{12}$, with the high-spin Mn^{3+} in the rhombic prisms, is best represented by the rhombic prism network. The structures of $\text{Sc}(\text{OH})_3$ and WAl_{12} seem to be intermediate between the two ideal networks.

TABLE I^a

	<i>y</i>	<i>z</i>
Parameters of a framework of ideal rhombic prisms; Fig 5	0.183	0.317
Parameters of a framework of ideal icosahedra + ideal octahedra (16); Fig. 6	0.191	0.309
Observed parameters		
COAs ₃ (10)	0.15	0.35
CoP ₃ (11)	0.1453	0.3482
Sc(OH) ₃ (13)	0.182	0.307
WAl ₁₂ (14)	0.184	0.309
NaMn ₇ O ₁₂ (15)	0.1828	0.3132

^aThe observed parameters are given for the atoms in position (24 *g*) of *Im*3 (18).

The deviations observed for the parameters of the skutterudite structure, here represented by CoAs₃ and CoP₃, are explained by strong As-As, or P-P bonds, giving the structure of the characteristic As₄ or P₄ groups.

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References

1. K. MEISEL, *Z. Anorg. Allg. Chem.* **207**, 121 (1932).
2. H. D. MEGAW, *Proc. Phys. Soc.* **58**, 133 (1946).
3. H. D. MEGAW, *Z. Kristallogr.* **87**, 185 (1934).
4. R. W. G. WYCKOFF, "Crystal Structures," 2nd ed., Chap. 3, p. 130, Interscience, New York
5. R. W. G. WYCKOFF, "Crystal Structures," 2nd ed., Chap. 4, p. 344, Interscience, New York (1968).
6. R. W. G. WYCKOFF, "Crystal Structures," 2nd ed., Chap. 5A, p. 32, Interscience, New York (1968).
7. K. SCHUBERT, "Kristallstrukturen zweikomponentiger Phasen," p. 105, Springer-Verlag, Berlin (1964).
8. K. SCHUBERT, "Kristallstrukturen zweikomponentigen Phasen," p. 301, Springer-Verlag, Berlin (1964).
9. R. W. G. WYCKOFF, "Crystal Structures," 2nd ed., Chap. 3, p. 142, Interscience, New York (1968).
10. I. OFTEDAL, *Z. Kristallogr.* **66**, 517 (1928).
11. S. RUNDQVIST AND N.-O. ERSSON, *Ark. Kemi* **30**, 103 (1968).
12. W. B. PEARSON, "The Crystal Chemistry and Physics of Metals and Alloys," pp. 223, 699, Wiley-Interscience, New York (1972).
13. K. SCHUBERT AND A. SEITZ, *Z. Anorg. Chemie* **256**, 226 (1948).
14. J. ADAM AND J. B. RICH, *Acta Crystallogr.* **7**, 813 (1954).
15. M. MAREZIO, P. D. DERNIER, J. CHENAVASS, AND J. O. JOUBERT, *J. Solid State Chem.* **6**, 16 (1973).
16. "International Tables for X-ray Crystallography," Vol. II, p. 49, Kynoch Press, Birmingham (1967).
17. S. ANDERSSON, private communication.
18. "International Tables for X-ray Crystallography," Vol. III, p. 314, Kynoch Press, Birmingham (1967).