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On the Compound Coordination Polyhedron in $MnAl_6$ and Fe_2Al_5

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It is argued that the coordinations of Mn in $MnAl_6$ and of Fe in Fe_2Al_5 are close to an ideal, quasi-regular 10-fold coordination, as given by a compound polyhedron based on the icosahedron and the octahedron.

INTRODUCTION

The coordination of Mn in $MnAl_6$ and Fe in Fe_2Al_5 has been described by various authors (1, 2) as irregular. We show here that it is in fact a highly regular polyhedron belonging to the class of compound polyhedra, made up from partial icosahedra and octahedra. The positions of the aluminium atoms are reproduced with high accuracy by this idealization. The icosahedron may, with a reasonably good fit, be joined together with polyhedra containing squares in several different ways. The union along the threefold axis with a cube, yielding the classic 'Centaur' polyhedron, may be accomplished without any distortion of the partial polyhedra. The union along the twofold direction, yielding the polyhedron of this paper (Fig. 1a), requires an adjustment of the original polyhedra/polygons, half an icosahedron, and two squares.

THE COMPOUND POLYHEDRON IO_{10}

A compound polyhedron may be defined as the union of at least two fragments from simpler polyhedra. One well known example is the twinned cuboctahedron, the coordination polyhedron around Ba in $BaNiO_3$ (3), and another is the Edshammar polyhedron, the coordination polyhedron around As in Na_3As (4, 5). The compound polyhedron used in the structural descriptions in this paper is constructed as follows: Half an icosahedron shares four vertices, arranged as a golden rectangle (the ratio of the sides being $\tau:1$ ($\approx$1.61803)), with two squares. This ratio is very close to the ideal c/a value in hexagonal close packing ($\approx$1.63299), and hence the squares may be regarded as part of two octahedra, i.e., two quadratic pyramids sharing a triangular face (Fig. 1b). The discrepancy between the two rectangles to be fitted is thus less than 1%, and without loss of accuracy the icosahedron may be kept ideal, while the angle between the pyramid squares is adjusted slightly. The position at the center of the polyhedron is most easily determined as the center of the tetrahedron indicated in Fig. 1c. We denote the polyhedron IO_{10} (Icosahedron, Octahedra, 10 vertices).

$MnAl_6$

In the structure of $MnAl_6$ (6, 7) the Mn filled IO_{10} polyhedra form strings by edge-sharing along the c axis. The shared edge is a twofold axis of rotation in the structure and hence the string will alternatingly expose faces reminiscent of icosahedra and of twinned cuboctahedra. The strings are joined by the corner connection of polyhedra. The polyhedra are close to ideal; there is a contraction along c and an expansion in the ab plane, but if the unit cell is fixed the agreement between the positions in the real structure and the ideal positions of the IO_{10} polyhedron model is excellent. Table 1 shows the parameters of the real structure compared to those of the ideal IO_{10} model. Figure 2 shows the structure of $MnAl_6$ described by the IO_{10} polyhedron.

Fe_2Al_5

The structure of Fe_2Al_5 (8) may be regarded as a simple crystallographic shear of $MnAl_6$. The edge-sharing in the strings in that structure are then supplanted by face-sharing in Fe_2Al_5 (conf. Fig. 3c). A result of this 'compactification'

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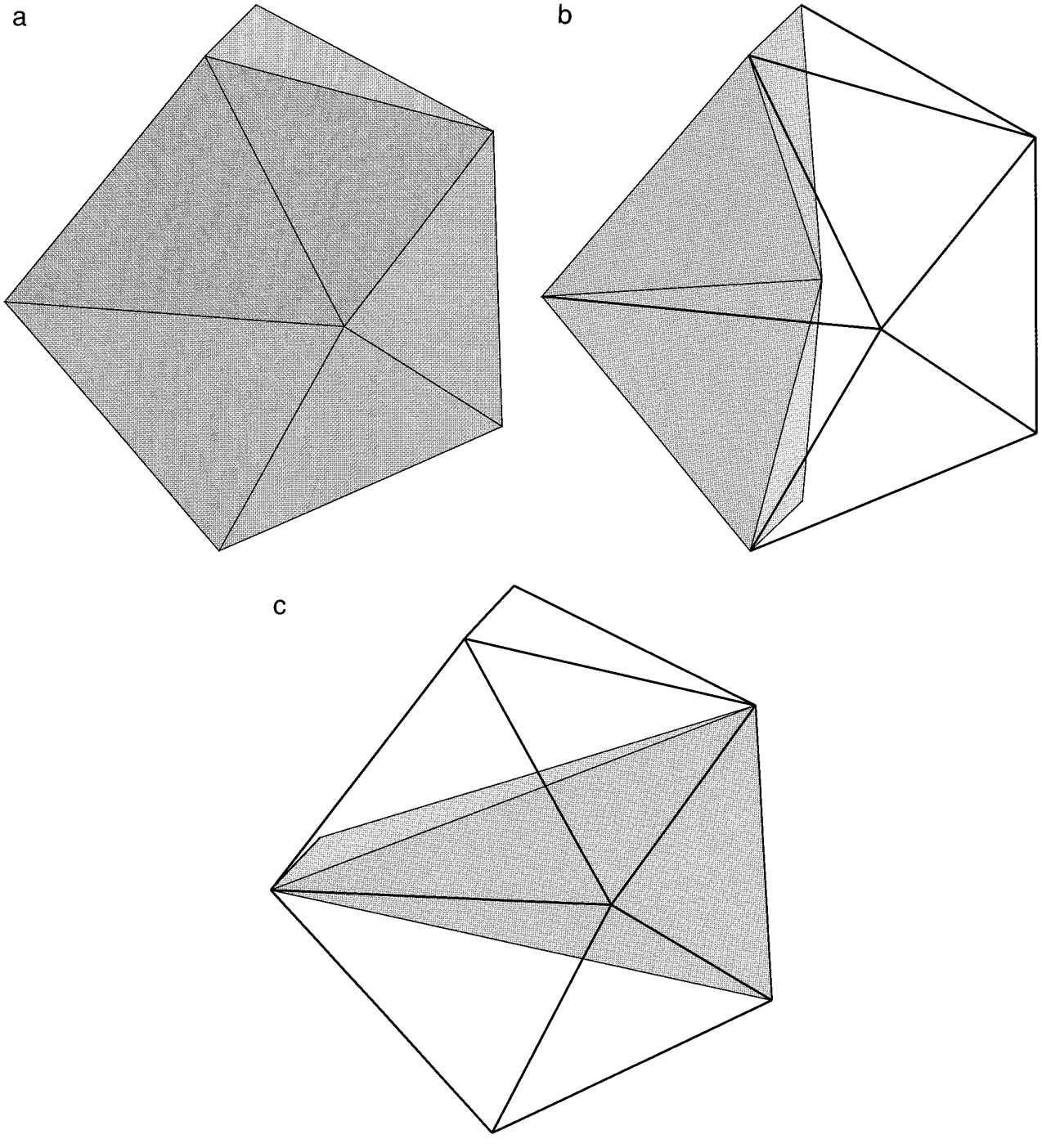

FIG. 1. (a) The IO_{10} polyhedron. (b) Highlighting the octahedra part; (c) Highlighting the central tetrahedron.

of the structure is that the ideal composition changes from 1:6 to 1:3 (the partial occupancy of one Al position due to close Al–Al contacts changes the composition slightly 1:2.5). In this structure there is edge-sharing as well as corner connection between the strings along *c*. Again, the polyhedra are close to ideal (see Table 2). Figure 3 shows the structure described by the IO_{10} polyhedron.

OTHER COMPOUNDS

In the structure of $CsCdI_3 \cdot H_2O$ (9) the coordination around Cs may also be described by a IO_{10} polyhedron. Here the deviations from ideality are more severe, the ligands being iodines and oxygens and the center-to-vertex distances hence varying widely. The description is still use-

TABLE 1
Atomic Parameters of $MnAl_6$

	Refined structure (6)			Ideal structure according to IO_{10}			Difference		
Atom	x	y	z	x	y	z	Δx	Δy	Δz
Mn	0	0.46	1/4	0	0.44	1/4	—	0.02	—
Al1	0.33	0	0	0.31	0	0	0.02	—	—
Al2	0	0.14	0.10	0	0.13	0.10	—	0.01	0.00
Al3	0.32	0.29	1/4	0.31	0.27	1/4	0.01	0.02	—

Note. Coordinates are given relative to the unit cell $a = 7.55$, $b = 6.50$, $c = 8.87$.

TABLE 2
Atomic Parameters of Fe_2Al_5 (No Refinement Available) Relative to the Unit Cell $a = 7.66$, $b = 6.39$, $c = 4.19$

	Structure (8)			Ideal structure according to IO_{10}			Difference		
Atom	x	y	z	x	y	z	Δx	Δy	Δz
Fe	0	1/3	1/4	0	1/3	1/4	—	—	—
Al1	0	0	0	0	0	0	—	—	—
Al2	0.18	0.65	1/4	0.18	0.69	1/4	0.00	0.04	—

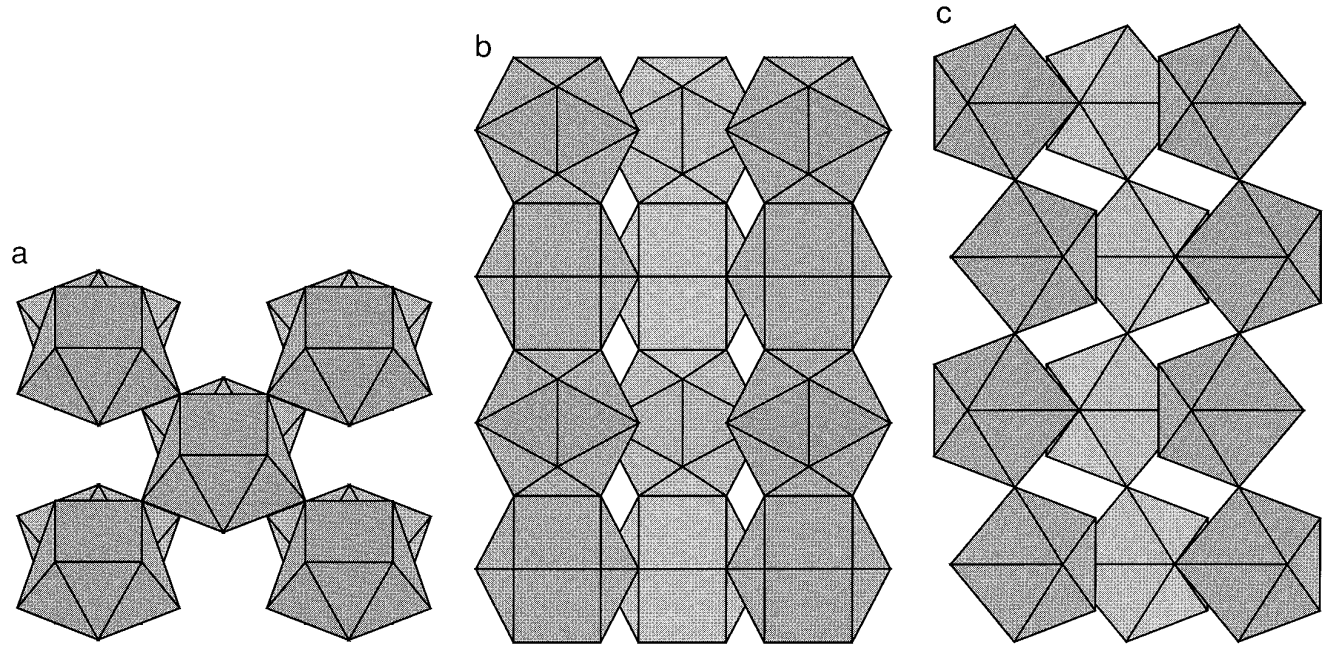

FIG. 2. $MnAl_6$, (a) view along a, (b) view along b, (c) view along c.

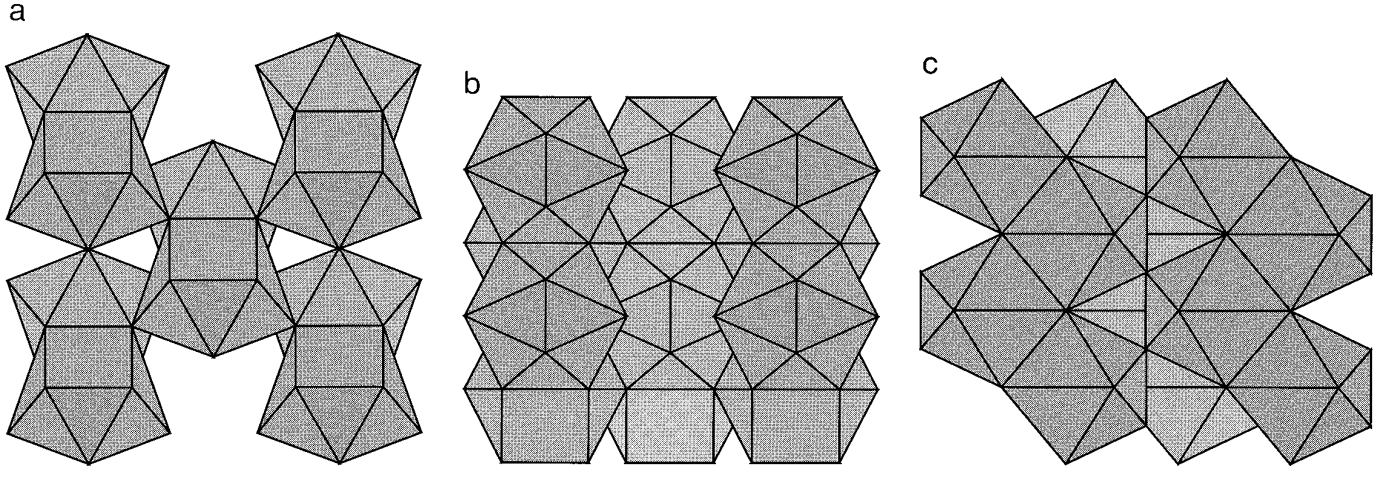

FIG. 3. Fe_2Al_5, (a) view along a, (b) view along b, (c) view along c.

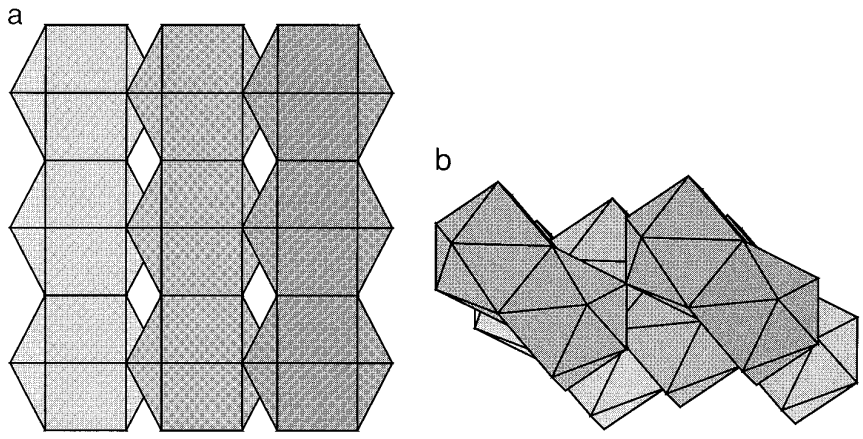

FIG. 4. The Fe_2Al_5 slabs that make up $CsCdI_3 \cdot H_2O$ and Mn_4Al_{11}. (a) $CsCdI_3 \cdot H_2O$ partial structure. (b) Mn_4Al_{11} partial structure.

ful, since it does yield a sensible picture of the packing in the compound. The polyhedra share faces, edges, and vertices in a complex pattern, but some simple features are discernable. The structure of Fe_2Al_5 contains infinite slabs of polyhedra extending along the *c* axis and the 110 direction (Fig. 4a). The same sheets are present in $CsCdI_3 \cdot H_2O$. The structure of Mn_4Al_{11} (10, 11) consists of Fe_2Al_5 slabs extending perpendicular to the *c* axis, while in WAl_4 (12) the pattern is more complex. The Fe_2Al_5 slabs that make up $CsCdI_3 \cdot H_2O$ and Mn_4Al_{11} are shown in Fig. 4.

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