Polyhedral Packing in Giant Cells

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The structure of alloys can be described in terms of packing of polyhedra. The present paper is a study of the packing of polyhedra in giant cells: Ca_3Ag_8 (cI44); Tl_7Sb_2 (cI54); Ti_2Ni (cF96); Th_6Mn_{23} (cF116); $Cu_{41}Sn_{11}$ (cF416); $Sm_{11}Cd_{45}$ (cF448). Ca_3Ag_8, Ti_2Ni, and Th_6Mn_{23} can be described in terms of packing of *one* polyhedron; Tl_7Sb_2 in terms of packing of *two* polyhedra; $Cu_{41}Sn_{11}$ and $Sm_{11}Cd_{45}$ in terms of packing of *four* polyhedra. The polyhedra model proved successful for about 50 structure types treated up to now. The coordination numbers of the individual atoms in the treated structure types determined by the "maximum gap" method range from 8 to 16. © 1986 Academic Press, Inc.

1. Introduction

Consideration of coordination spheres of particular atoms has proved to be a useful approach to understanding the crystal chemistry of alloy structures. The search for a model to describe these structures led us to the polyhedral packing principle, which enables us to construct even complicated structures with few different polyhedra. The aim of this approach is to present a simple description of the complex alloy structures and to systematize the different known structure types.

Description of structures in terms of packing of single polyhedra is easy in the case of small cells. One can understand the structure of giant cells if one describes them in terms of packing of "polyhedra units." A "polyhedra unit" is constructed from two to five polyhedra.

2. Coordination Polyhedra

To define a coordination polyhedron, we first limit the coordination sphere. For this purpose Girgis (1) introduced the $\Sigma(r_A + r_B)/d_{AB}$ method. $\Sigma(r_A + r_B)$ is the sum of the radii of the atoms concerned (2) and d_{AB} is the interatomic distance between the central atom A and its neighbor B. The $\Sigma(r_A + r_B)/d_{AB}$ values versus the corresponding numbers of atoms are represented in a histogram. The widest range in which no atoms are present is called the "maximum gap" (3). 95% of the cases studied show such a "maximum gap" (4, 5). The number of nearest neighbors before this "maximum gap" is taken to be the conventional coordination number (CCN). The corresponding atoms (neighbors) constitute the coordination polyhedron around the atom considered (1). An example is shown in Fig. 1.
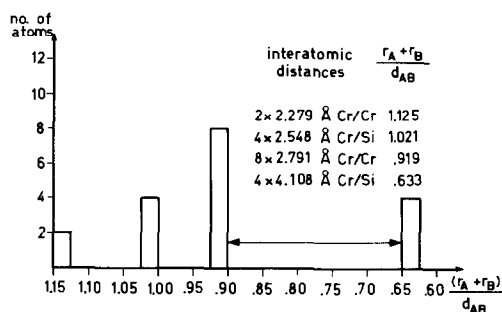
FIG. 1. Distribution of near neighbors as a function of their $(r_A + r_B)/d_{AB}$ values for Cr in the Cr_3Si structure type.

Table I shows the coordination numbers of the individual atoms in the treated structure types determined by the "maximum gap" method.

3. The Principle of Describing Structures with Coordination Polyhedra as Building Units

3.1. Procedure

To describe a structure using coordination polyhedra as building units one must first determine the coordination polyhedra of all the atomic positions of the structure by the "maximum gap" method mentioned above. The structure is described by packing the least number of polyhedra types (one or two are sufficient in most cases). If there is more than one possibility to describe the structure, certain priorities, which we mentioned in Girgis and Villars (8) are considered.

All the atoms in the unit cell *must be included* in the structure building polyhedra. The polyhedra should not interpenetrate.

3.2. Validity of This Model

The polyhedral packing principle has proven its validity for all structure types treated. More details are found in references (1, 5–8). Therefore it can be expected that this principle is valid for all in-

TABLE I

COORDINATION NUMBERS OF THE INDIVIDUAL ATOMS IN THE TREATED STRUCTURE TYPES

Compound	Atom		Eq. pts.	CN	
Ag_8Ca_3	Ag	1	8c	12	
	Ag	2	24h	12	
	Ca	1	12e	16	
$Cd_{45}Sm_{11}$	Cd	1	4b	16	
	Cd	2	4d	14	
	Cd	3	16e	8	
	Cd	4	16e	14	
	Cd	5	16e	14	
	Cd	6	16e	14	
	Cd	7	24f	13	
	Cd	8	24g	13	
	Cd	9	48h	12	
	Cd	10	48h	15	
	Cd	11	48h	12	
	Cd	12	48h	12	
	Cd	13	48h	13	
	Sm	1	4a	14	
	Sm	2	4c	16	
	Sm	3	16e	16	
	Sm	4	16e	16	
	Sm	5	48h	12	
$Cu_{41}Sn_{11}$	Cu	1	16e	12	
	Cu	2	16e	12	
	Cu	3	16e	12	
	Cu	4	16e	12	
	Cu	5	16e	12	
	Cu	6	16e	13	
	Cu	7	16e	12	
	Cu	8	24f	13	
	Cu	9	24g	13	
	Cu	10	24f	13	
	Cu	11	48h	11	
	Cu	12	48h	13	
	Cu	13	48h	11	
	Sn	1	16e	12	
	Sn	2	24g	13	
	Sn	3	48h	11	
$Mn_{23}Th_6$	Mn	1	4b	14	
	Mn	2	24d	12	
	Mn	3	32d	13	
	Mn	4	32f	12	
	Th	1	24e	16	
$NiTi_2$	Ni	1	32e	12	
	Ti	1	16c	12	
	Ti	2	48f	14	(center $3m$)
Sb_2Tl_7	Sb	1	12e	14	
	Tl	1	2a	14	
	Tl	2	16f	14	
	Tl	3	24h	14	

termetallic structures. We studied more than 50 structure types out of 106 with more than 5 representatives (*11*). In the future, such models will be even more important because of the enormous amount of data available. In the new Pearson's Handbook (*12*) there are more than 2200 structure types.

4. Structure Description

Table II summarizes the general remarks and abbreviations used in this paper.

4.1. Ca_3Ag_8 Structure Type

Ca_3Ag_8 crystallizes in the cubic space group $Im3m$ with 44 atoms per cell. The structure can be constructed from AgI icosahedra (Fig. 2a), symmetry $\overline{3}m$-D_{3d}.

Four icosahedra at the same height, whose central atoms at $z = 0.25$, constitute the lower polyhedral layer of the unit cell, sharing perpendicular triangular faces as shown in Fig. 2b. A mirror image polyhedra layer, whose central atoms at $z = 0.75$, which lies over it, shares horizontal trian-
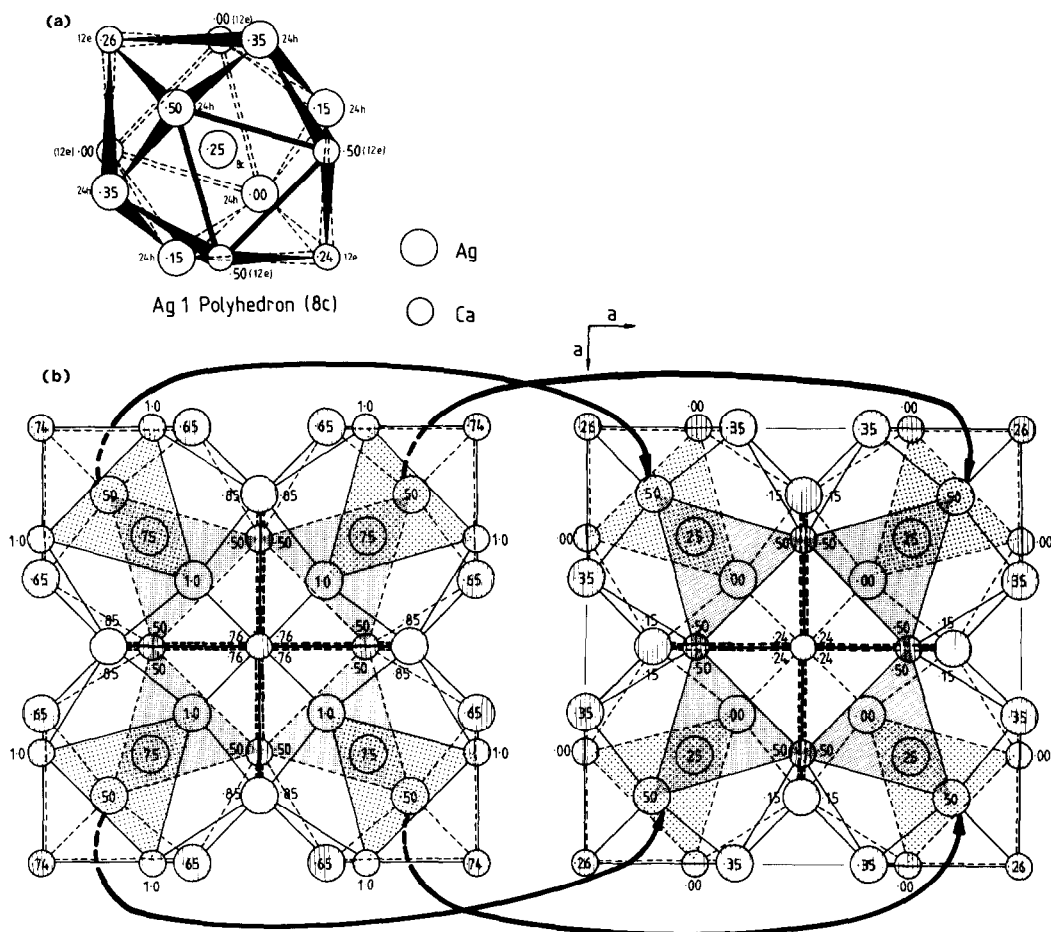
Fig. 2. Description of the Ca_3Ag_8 structure as a three-dimensional network of icosahedra connected by triangular faces. (a) Structure building polyhedron AgI. (b) The lower and the higher layer in the unit cell.

⦀	Linkage (contact) of the polyhedra of the same layer.
●	Linkage (contact) between polyhedra of the first and second or the third and fourth layers, respectively.
⋮	Linkage of the polyhedra between "double layers," i.e., between the second and the third layers (Ti$_2$Ni, Th$_6$Mn$_{23}$, Cu$_{41}$Sn$_{11}$, Sm$_{11}$Cd$_{45}$) or connection to neighboring unit cells at different heights (Ca$_3$Ag$_8$, Tl$_7$Sb$_2$).
⧄	The central polyhedron in a schematic representation.
CN	Coordination number.
△	Triangular face.
□	Quadrangular face.

gular faces. The connection to the neighboring unit cells is the same as mentioned above. Each icosahedron shares a triangular face with 6 neighboring icosahedra, namely two in the x, y, and z directions, respectively.

4.2. Tl$_7$Sb$_2$ Structure Type

The Tl$_7$Sb$_2$ structure crystallizes in the cubic space group $Im3m$ with 54 atoms per cell. The structure can be constructed from Tl1 and Tl2 polyhedra. Tl1 is a tetrakishexahedron (24 △; symmetry $m3m–O_h$) and Tl2 is a distorted rhombic dodecahedron (symmetry $3m–C_{3v}$) Fig. 3a. A Tl1 polyhedron at the center of the unit cell shares an atom with four Tl2 polyhedra; namely the two Tl2 polyhedra along [110] share an atom at $z = 0.33$ with the central Tl1 polyhedron while the two along [1Ī0] (mirror images of those along [110]), share an atom at $z = 0.67$ with it (Fig. 3c, schematic representation Fig. 3b).

The connections to the neighboring cells are perpendicular quadrangular faces between Tl2 polyhedra shared along the cell

diagonals, constituting "double polyhedra." The connection in the z direction occurs between Tl2 double polyhedra of the [110] and [1Ī0] direction belonging to unit cells at different heights, sharing quadrangular faces (Fig. 3d). Thus each Tl2 polyhedron shares a quadrangular face with three other Tl2 polyhedra and with one Tl1 polyhedron an atom.

4.3. Ti$_2$Ni Structure Type

Ti$_2$Ni crystallizes in the cubic space group $Fd3m$ (origin at $3m$) with 96 atoms per cell. The structure can be constructed from Ti1 polyhedra (icosahedra); symmetry $3m–D_{3d}$ (Fig. 4a).

There are four layers of chains in the unit cell, the heights of the central atoms are 0.0, 0.25, 0.5, 0.75. Each chain consists of icosahedra sharing perpendicular triangular faces. Chains of the same layer have no contact. The chains of the four different layers are superimposed in the [110] and the [1Ī0] direction alternatively and share a triangular face with two icosahedra of the layer above as well as below (Fig. 4c).

The contact to neighboring cells is the same as described above (Fig. 4b). Thus each icosahedron shares a triangular face with six further icosahedra.

4.4. Th$_6$Mn$_{23}$ Structure Type

Th$_6$Mn$_{23}$ crystallizes in the cubic space group $Fm3m$ with 116 atoms per cell. The structure can be constructed from Mn3 polyhedra consisting of three quadrangular and 16 triangular faces; symmetry $3m–C_{3v}$ (Fig. 5a).

Mn$_3$ polyhedra at the same height (central atom: $z = 0.12$) are interconnected by perpendicular triangular and quadrangular faces alternatively, forming chains along the [110] direction, which have no contact among themselves. A second layer of identical chains (central atom: $z = 0.38$) which is a mirror image of the first one, lies between the chains of the first layer sharing
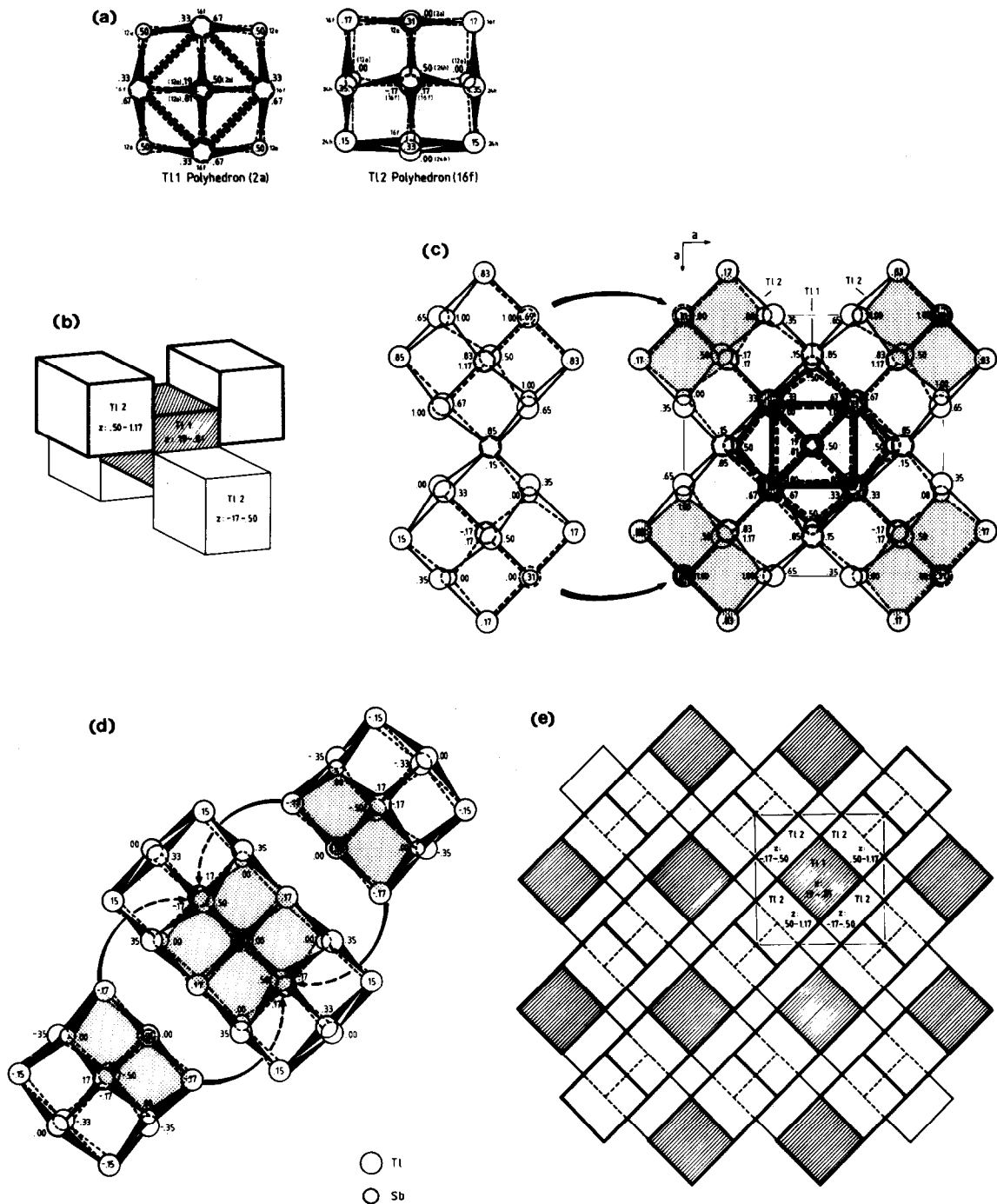
FIG. 3. Description of the Tl_7Sb_2 structure as a three-dimensional network of Tl2 "double polyhedra" connected by Tl1 polyhedra. (a) Structure building polyhedra Tl1 and Tl2. (b) Schematic representation of the five-polyhedron unit which corresponds to the unit cell. (c) The unit cell contents and two Tl2 polyhedra of the neighboring cell at the same height. (d) Linkage of a Tl2 "double polyhedron" with Tl2 polyhedra of the lower cells. (e) Schematic representation of the polyhedra packing. The borders of the unit cell are shown as well as the height range of the coordination atoms in the polyhedra.
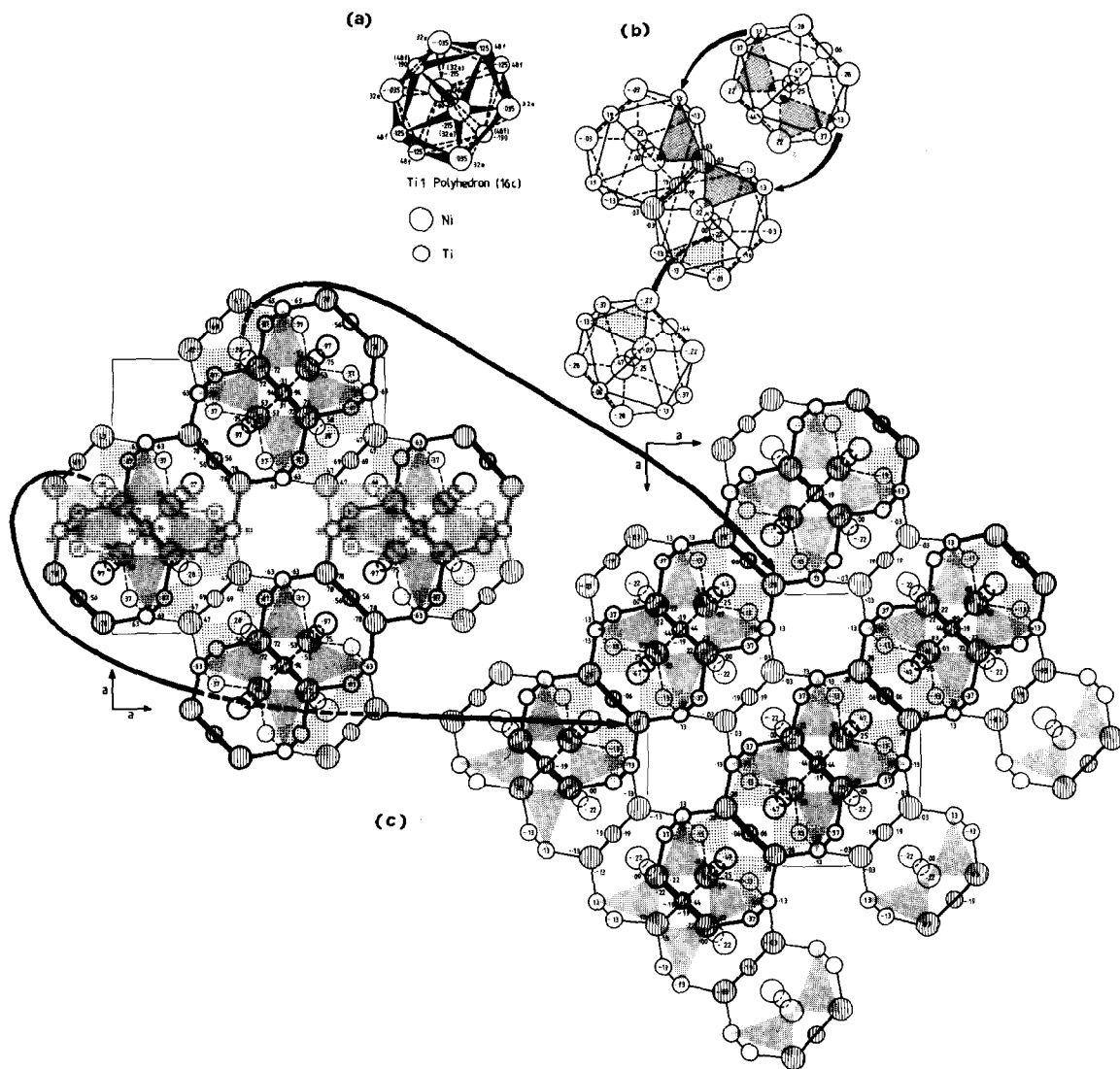
FIG. 4. Description of the Ti$_2$Ni structure as a three-dimensional network of horizontal chains of Ti1 icosahedra (sequences of layers alternatively [110], [1$\bar{1}$0], [110], [1$\bar{1}$0]). (a) Structure building polyhedron Ti1. (b) Linkage of a polyhedra chain with the upper and lower one. (c) First and second; third and fourth layer in the unit cell.

atoms at $z = 0.25$ (Fig. 5c). An identical "double layer" of chains, but running along [1$\bar{1}$0] and elevated by $z = 0.5$, shares quadrangular faces with the lower one; (Figs. 5b and c).

The connections to the neighboring cells correspond to those within the cell. Thus each polyhedron shares an atom, a triangular or a quadrangular face with six other polyhedra.
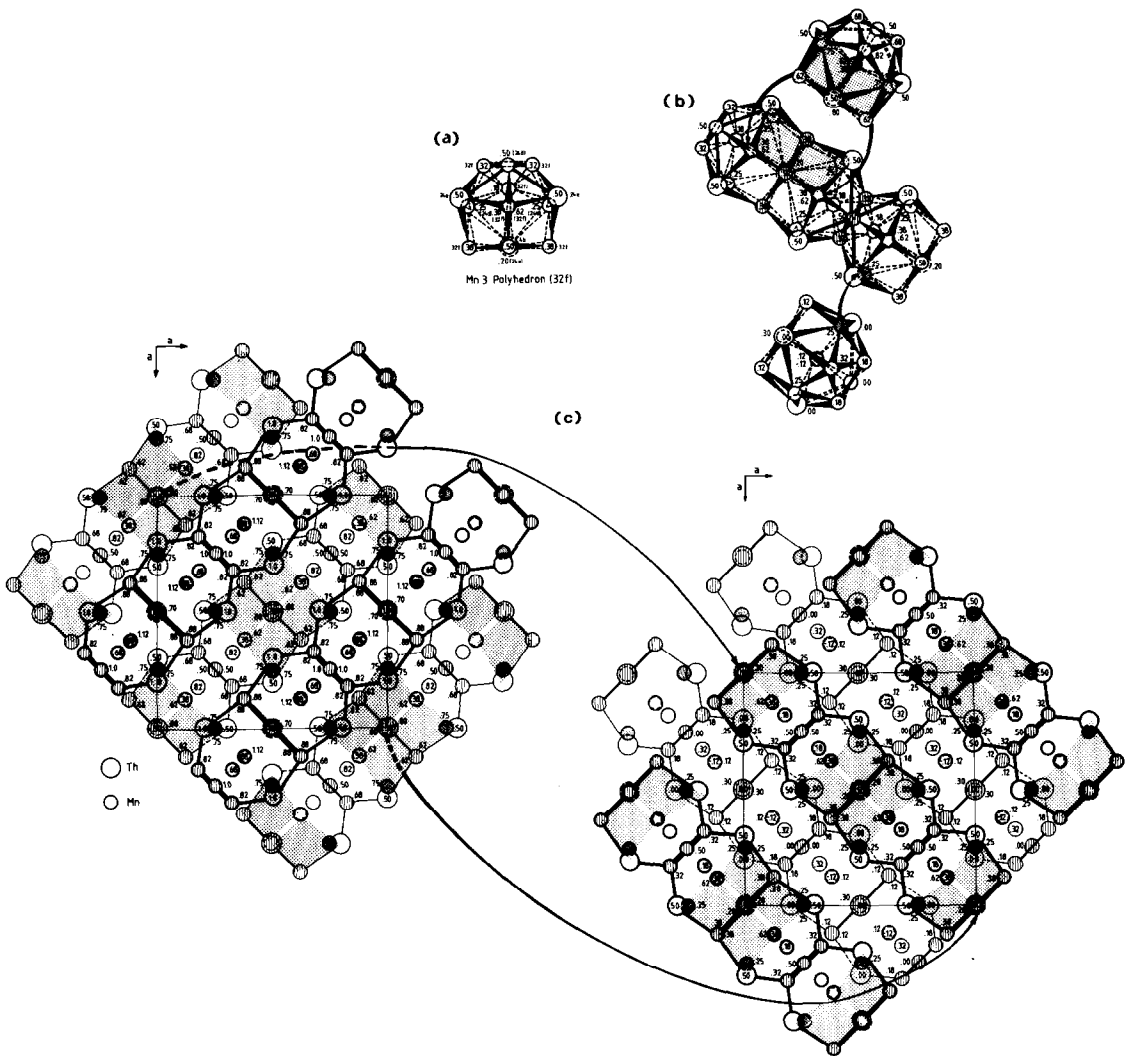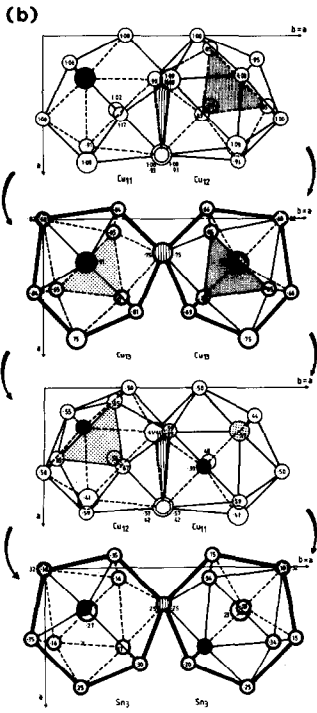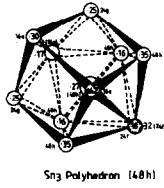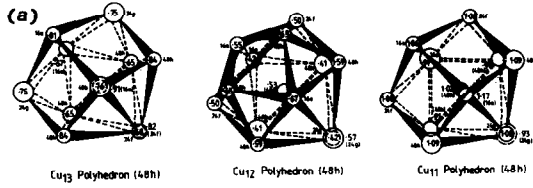
FIG. 5. Description of the Th_6Mn_{23} structure as a three-dimensional network of horizontal chains of Mn3 polyhedra (sequence of layers: [110], [110], [1$\bar{1}$0], [1$\bar{1}$0]. (a) Structure building polyhedron Mn3. (b) Linkage of a chain with the upper and lower one. (c) Upper and lower "double layer" in the unit cell.

4.5. $Cu_{41}Sn_{11}$ Structure Type

$Cu_{41}Sn_{11}$ crystallizes in the cubic space group $F\bar{4}3m$ with 416 atoms per cell. The structure can be constructed from Cu11, Cu12, Cu13, and Sn3 polyhedra. Cu11, Cu13, and Sn3 polyhedra are similar and consist of four quadrangular and 10 triangu-

lar faces; symmetry $m-C_s$; the Cu12 polyhedron consists of two quadrangular and 18 triangular faces; symmetry $m-C_s$ (Fig. 6a).

We first consider the lowest layer (Fig. 6c below, bold lines) and distinguish four quadrants consisting of four polyhedra (four-polyhedra unit) each. Within the units the polyhedra share atoms; the two polyhe-

(a)

Cu₁₃ Polyhedron (48h)   Cu₁₂ Polyhedron (48h)   Cu₁₁ Polyhedron (48h)

Sn₃ Polyhedron (48h)

Sn
Cu

(b)

Cu₁₁   Cu₁₂

Cu₁₃   Cu₁₃

Cu₁₂   Cu₁₁

Sn₃   Sn₃

(c)

(d)

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dra along [1$\bar{1}$0] are mirror images of those along [110]. The first and the fourth quadrant are occupied by Sn3, the second and the third by Cu13 polyhedra. The different units of four polyhedra share quadrangular faces while the units of the same kind share edges along [110] and [1$\bar{1}$0] directions. The second layer (Fig. 6c below, thin lines) consists of Cu11 and Cu12 polyhedra units, arranged as the first layer, but shifted by about a quarter of the cell diagonal. Thus each quadrant contains Cu11 as well as Cu12 polyhedra (Fig. 6b shows half a quadrant of each layer).

There are four layers in the cell, consisting alternatively of Sn3–Cu13 and Cu11–Cu12 units; each layer is displaced by about a quarter of the cell diagonal. In the z direction the polyhedra share corners and triangular faces (Fig. 6b). The schematic arrangement of the polyhedra in the unit cell is represented in Fig. 6d.

As connections to the neighboring cells correspond to those within the unit cell, each polyhedron is connected to eight other polyhedra sharing corners, edges, triangular (only between Cu12 and Cu13 polyhedra) and quadrangular faces.

4.6. Sm$_{11}$Cd$_{45}$ Structure Type

Sm$_{11}$Cd$_{45}$ crystallizes in the cubic space group $F\bar{4}3m$ with 448 atoms per cell. The structure can be described by packing Cd2 (24$\triangle$ faces; symmetry $\bar{4}3m$–T_d), Cd4 (18$\triangle$ and 3$\square$ faces; symmetry $3m$–C_{3v}), Sm2 (28$\triangle$ faces; symmetry $\bar{4}3m$–T_d) and Sm3 (28$\triangle$ faces; symmetry $3m$–C_{3v}) polyhedra. Both Cd polyhedra are highly distorted tetrakishexahedra while Sm polyhedra are distorted Kasper-16 polyhedra (Fig. 7a).

The packing principle corresponds to that of the Tl$_7$Sb$_2$ type (Figs. 3b and 7b).

Each Cd2 and Sm2 polyhedron is surrounded by four Cd4 or four Sm3 polyhedra, respectively (Fig. 7c). In the lower Cd unit (Fig. 7d left, thin lines) the Cd4 polyhedra along [110] share an atom at $z = 0.33$ with the central Cd2 polyhedron while those along [1$\bar{1}$0], mirror images of those along [110], share an atom at $z = 0.17$ with it. In the Sm unit, the polyhedra share triangular faces instead of atoms (Fig. 7d, right).

Four units at the same height (central atoms Cd2 and Sm2 at $z = 0.25$) constitute the lower layer (Fig. 7e, right) whereas the first and the fourth quadrant are occupied by Sm units sharing a triangular face; the second and the third are occupied by Cd units sharing a quadrangular face. Sm and Cd units have no contact.

The unit cell has two layers; the upper layer is shifted by $0\ \frac{1}{2}\ \frac{1}{2}$ so that Cd units lie above Sm units and vice versa (Fig. 7e), but without any connection between them. Cd4 or Sm3 "double polyhedra" along [110] of the upper layer overlap with similar ones along [1$\bar{1}$0] of the lower layer sharing triangular faces for the Sm and quadrangular faces for the Cd units (Figs. 7d, e).

As the connections to the neighboring cells correspond to those within the cell, each polyhedron shares atoms and quadrangular faces (Cd units) or triangular faces only (Sm units) with four other polyhedra.

5. Conclusions and Discussion

1. The polyhedral packing principle has proved valid for describing all structures treated (Table I). We studied earlier more than 50 structure types. It can therefore be expected that this principle is *valid for all intermetallic structure types*.

Other structure describing models are

FIG. 6. Description of the Cu$_{41}$Sn$_{11}$ structure as a network of two alternating layers consisting of two different polyhedra units each. (a) Structure building polyhedra Cu11, Cu12, Cu13 and Sn3. (b) Linkage of the layers in the z direction. (c) First and second; third and fourth polyhedra layer in the unit cell. (d) Schematic representation of the polyhedra packing in the unit cell.
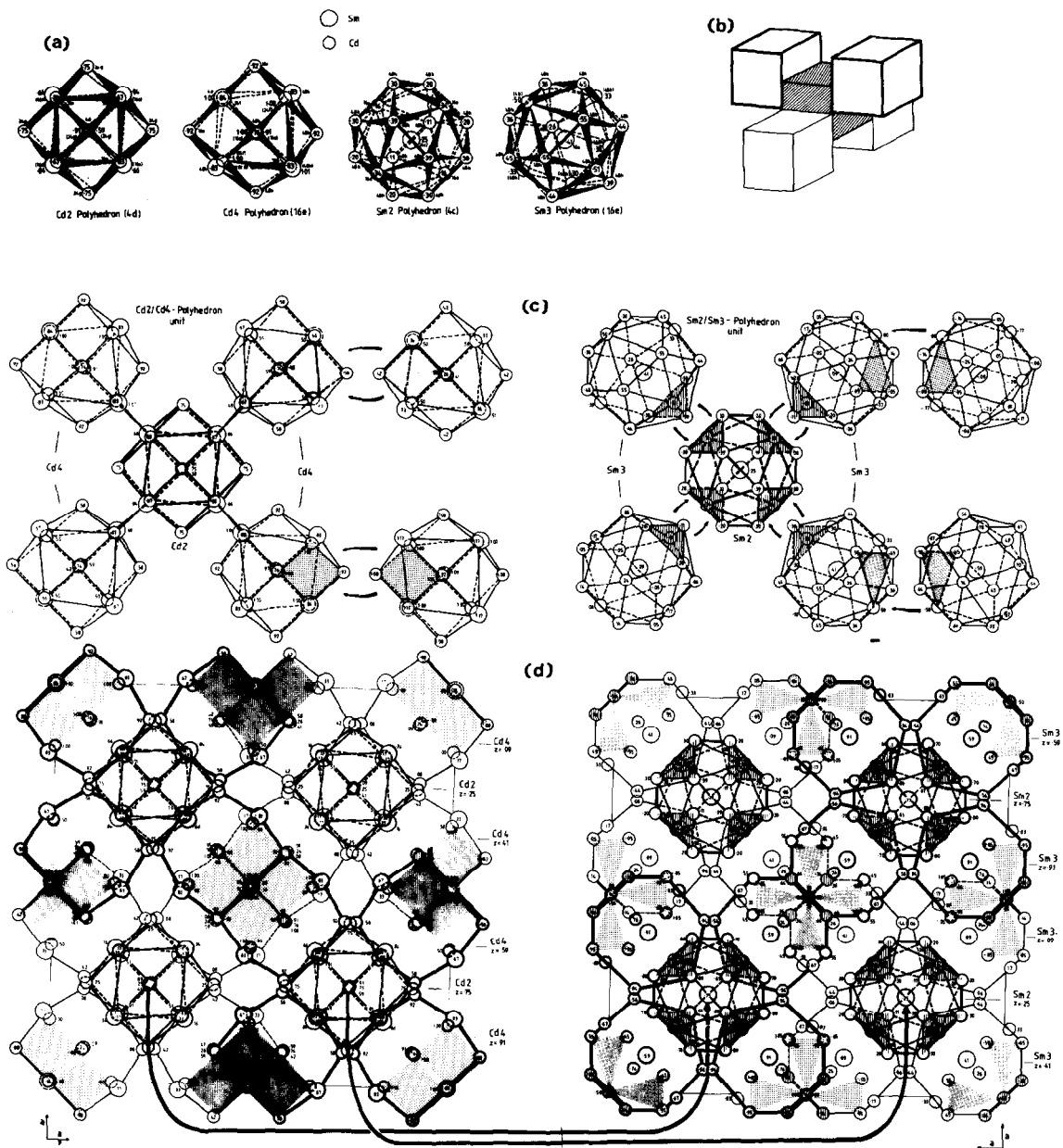
FIG. 7. Description of the $Sm_{11}Cd_{45}$ structure as a three-dimensional network of Cd2 and Cd4 polyhedra interpenetrating another three-dimensional network of Sm2 and Sm3 polyhedra without any contact. (a) Structure building polyhedra Cd2, Cd4, Sm2, and Sm3. (b) Schematic representation of a five-polyhedra-unit, the "building unit" of the structure. (c) Cd and Sm five-polyhedra building unit. (d) Linkages in the Cd and Sm network, respectively. (e) Schematic representation of the polyhedra-packing in the unit cell; Sm polyhedra as circles, Cd polyhedra as squares; Cd2 and Sm2 polyhedra are hatched.
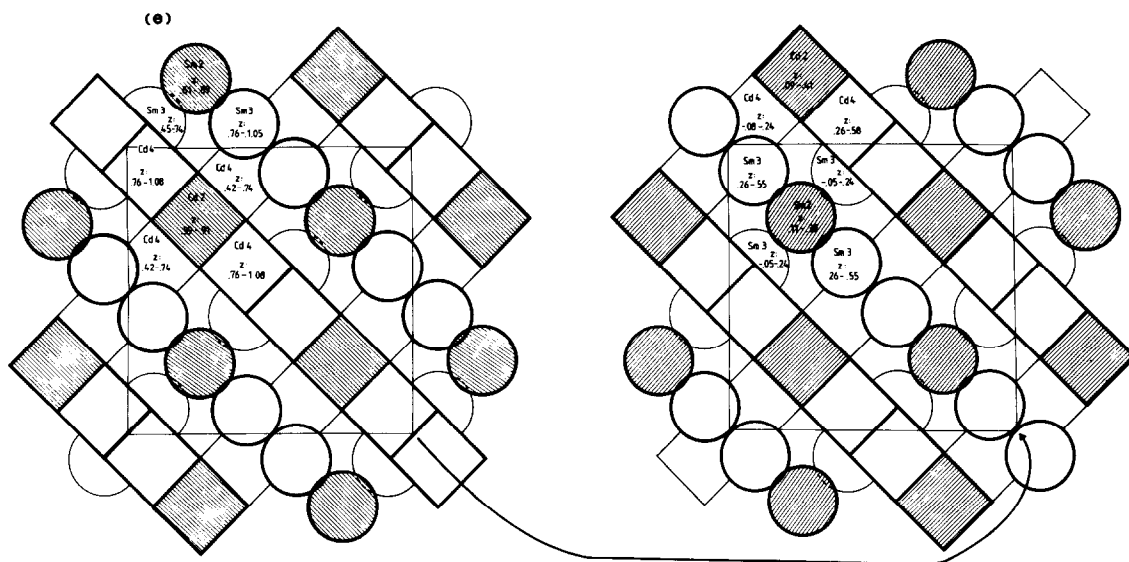
FIG. 7—*Continued.*

valid only for certain structures. But the validity for all structures has not been studied in general. Samson's (9) fascinating model for giant molecules, for example, describes the structure by packing Friauf polyhedra. This model is therefore limited to structures the atoms of which are surrounded by Friauf polyhedra. Another model is describing structures by stacking "Kagomé nets." This is again limited to structures which exhibit layers of atoms constituting Kagomé nets.

2. The polyhedral packing principle delivers a simple representation of the structures; e.g., Ca_3Ag_8 (cI44) can be described by packing icosahedra. The representation of structures with hundreds of atoms per cell proved more complicated. Even then the packing can be understood if one knows the packing unit and its contacts to the surrounding units, e.g., four-polyhedra-units for the $Cu_{41}Sn_{11}$ and five-polyhedra-units for the $Sm_{11}Cd_{45}$ structure type.

3. Icosahedra, 14 and 16 Kasper polyhedra, tetrakishexahedra, and rhombic dodecahedra play an important part in the description of these structures, although they belong to different structure types. In general cubes, cubo-octahedra, bicapped square antiprism beside those mentioned above are important in the description of intermetallic structures. This demonstrates their tendency to have high symmetry and coordination numbers.

4. The mean coordination number of the treated structures is equal to 13.2 which reinforces Laves' (10) statement that the metals and intermetallic phases tend to have high coordination numbers.

5. The small number of cubic structures described in this paper shows that certain "building blocks" repeatedly occur; namely chains along the cell diagonals in Th_6Mn_{23} and Ti_2Ni structures; the same five-polyhedra units in Tl_7Sb_2 and $Sm_{11}Cd_{45}$ whereas in Tl_7Sb_2 the unit consists of the whole unit cell content, in $Sm_{11}Cd_{45}$ just a part of it.

Acknowledgment

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