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Cluster or Framework Considerations for the Structures of Tl_7Sb_2 , α -Mn, Cu_5Zn_8 and Their Variants $Li_{22}Si_{31}$, $Cu_{41}Sn_{11}$, $Sm_{11}Cd_{45}$, Mg_6Pd and Na_6Ti with Octuple Unit Cells*†

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Abstract

Eight intermetallic compounds described so far by clusters are compared. It is shown that a common framework exists for all these crystal structures. The voids within this common part are filled in different ways. Moreover, for each of these crystal structures all atoms together form a three-dimensional connected framework. Therefore, the framework description seems to be more adequate than the cluster description.

Several intermetallic compounds with complicated crystal structures have the common feature that they may be derived from a cubic body-centered lattice if one replaces the points of this lattice by 'clusters' of metal atoms.

Such a cluster is built up from different nested polyhedra with a common center which may be occupied or not. The atoms of these clusters are in contact with each other and with atoms of the neighboring clusters. Therefore, these crystal structures do not consist of isolated clusters but all metal atoms together form a three-dimensional framework.

This cluster concept was first used by Bradley & Jones (1933) for the description of the γ -brass structure. More recently many other authors have taken up this concept in connection with intermetallic compounds, because it is suitable for a simple description of the distribution of the different metal atoms over the positions occupied in a particular structure type.

We would prefer, however, to restrict the use of the term 'metal cluster' to compounds containing groups of three or more metal atoms, arranged in a polygonal or polyhedral array and bonded to each other by

metal-to-metal bonds. Such bonds should not exist between atoms of different clusters (compare with Cotton & Wilkinson, 1972). Typical examples are polynuclear metal carbonyls [e.g. $Rh_6(CO)_{16}$] and subhalides containing, for example, $[M_6X_8]^{4+}$ groups. Another type, Ag_6Ge_4 clusters, can be found, for example, in $Ag_6Ge_{10}P_{12}$ (von Schnering & Häusler, 1976). In the following discussion the term 'set of nested polyhedra' instead of 'cluster' will be applied to those intermetallic compounds, all the atoms of which are integrated in a three-dimensional network and do not form separated groups.

Different sets of nested polyhedra, the centers of which are arranged in a cubic body-centered lattice, result in different 'basic structures', e.g. the crystal structures of α -Mn (Oberteuffer & Ibers, 1970), Cu_5Zn_8 (γ -brass) (Brandon, Brizard, Chieh, McMillan & Pearson, 1974) and Tl_7Sb_2 (Stockhuyzen, Chieh & Pearson, 1977). Each such type of basic structure allows different stoichiometric compositions with different distributions of the various kinds of atoms. For example, γ - $Al_{12}Mg_{17}$ (Schobinger-Papamantellos & Fischer, 1970) is isotypic with α -Mn. Furthermore, the sets of nested polyhedra within a basic structure may become symmetrically inequivalent. In this case all sets of polyhedra within the crystal structure belong to the same type but they may differ in the distribution of metal atoms over the polyhedra (see Booth, Brandon, Brizard, Chieh & Pearson, 1977). Such crystal structures are superstructures of the corresponding basic structures, e.g. $Cu_{41}Sn_{11}$ (Booth *et al.*, 1977) and $Li_{22}Si_5$ (Axel, Schäfer & Weiss, 1966) of Cu_5Zn_8 and Tl_7Sb_2 , respectively.

Fornasini, Chabot & Parthé (1978) have shown an additional, more complicated, relationship between intermetallic compounds for the case of $Sm_{11}Cd_{45}$. They have compared the atomic parameters of $Sm_{11}Cd_{45}$ with those of $Li_{22}Si_5$, $Cu_{41}Sn_{11}$ and α -Mn. Half the structure of $Sm_{11}Cd_{45}$ is analogous to Tl_7Sb_2 , the other half is analogous to α -Mn. The centers of all polyhedra together, however, form a cubic body-centered lattice again.

In the following this possibility for relating crystal structures to each other is extended to such structures

* Part IX of the series *Verwandtschaftskriterien von Kristallstrukturtypen* [Part VIII: Koch & Hellner (1980)].

† *Editorial note*: The similarity between this paper and the two following papers, by Chabot, Cenzual & Parthé [*Acta Cryst.* (1981), **A37**, 6–11] and by Nyman & Hyde [*Acta Cryst.* (1981), **A37**, 11–17], has been recognized and they have been published together to give an indication of the activity in the field with which they are concerned.

coordination polyhedra (Donnay, Hellner & Niggli, 1964, 1966; Hellner, 1965, 1979). In the second column the corresponding cluster description is listed (Fornasini *et al.*, 1978). All point configurations are either face-centered lattices or they form polyhedra around these lattices. The following symbols are used:

.	CC	cluster center
(12 <i>tt</i>)	TT	truncated tetrahedron
(4 <i>t</i> ⁺)	IT	positive (inner) tetrahedron
(4 <i>t</i> ⁻)	OT	negative (outer) tetrahedron
(6 <i>o</i>)	OH	octahedron
(12 <i>co</i>)	CO	cubo-octahedron.

The structures of Tl_7Sb_2 , $\alpha\text{-Mn}$ and Cu_5Zn_8 are listed in the right part of Table 1, the corresponding description with symbols of lattice complexes and coordination polyhedra is added in the last column. $I(8c)$ symbolizes isolated cubes around an I configuration and $W^*[4t_c]$ means corner-connected tetrahedra around a configuration of the cubic invariant lattice complex W^* .

The different intermetallic phases included in Table 1 differ from each other by the occupation or non-occupation of some of the kinds of point configurations listed. Configurations $W^*[4t_c]$ or, with respect to the crystal structures with enlarged unit cells, the corresponding configurations $F(12co) + F''(12co) + F'''(12co) = W^*_{222}[4t_c]$, however, are occupied in every case. Therefore, a more careful discussion of these configurations seems reasonable.

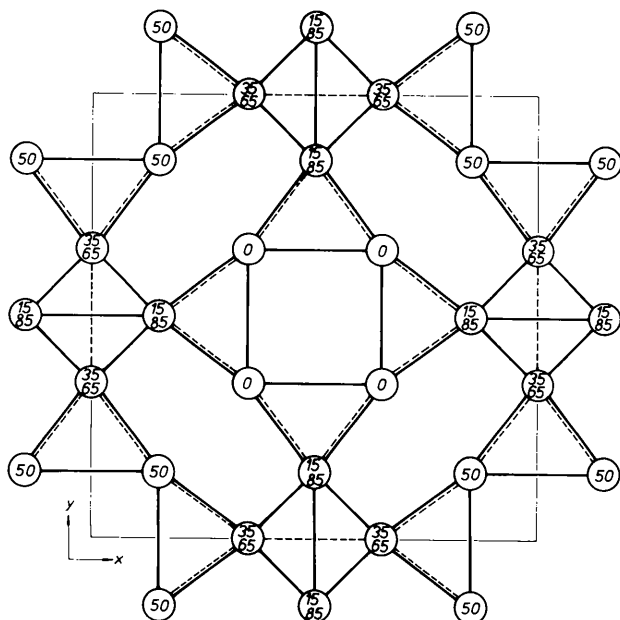


Fig. 1. Framework $W^*[4t_c]$ as part of the crystal structure of Tl_7Sb_2 : symmetry $I\bar{m}3m\ 24(h)\ xx0$, $x = 0.3497$, z coordinates in $n/100$.

Koch & Hellner (1980) have shown in detail how some properties of $W^*[4t_c]$ configurations with symmetry $I\bar{4}3m\ 24(g)\ xxz$, change depending on the coordinate parameters x and z . Figs. 1–3 illustrate these configurations for the three basic structures. In Tl_7Sb_2 , nearly ideal tetrahedra with common vertices

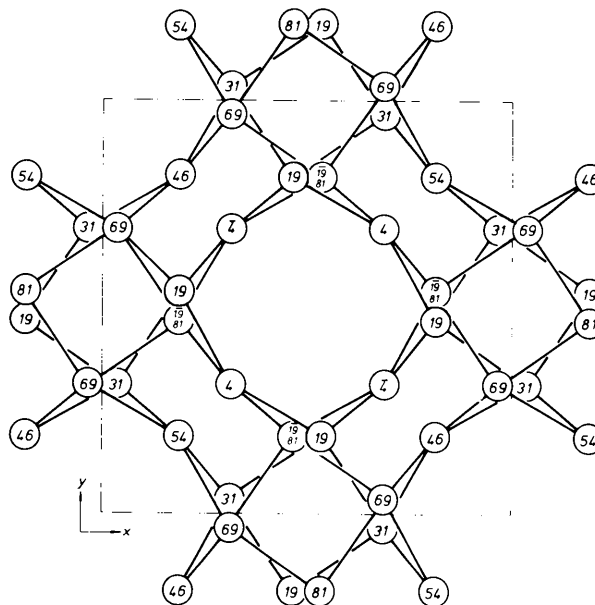


Fig. 2. Framework $W^*[4t_c]$ as part of the crystal structure of Cu_5Zn_8 : symmetry $I\bar{4}3m\ 24(g)\ xxz$, $x = 0.3128$, $z = 0.0366$, z coordinates in $n/100$.

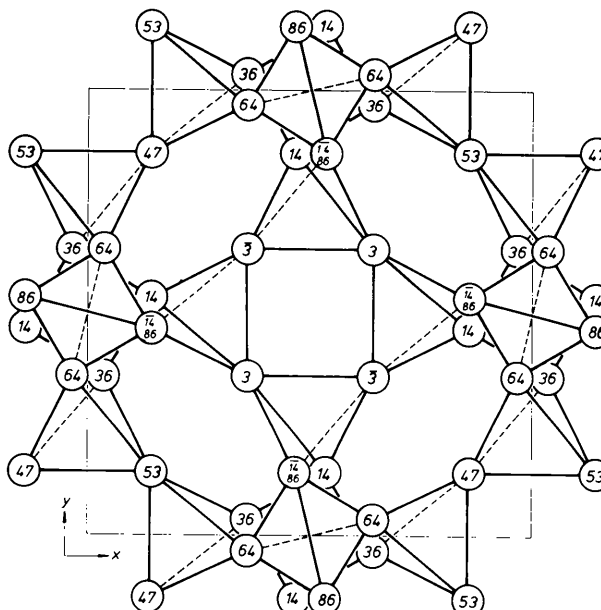


Fig. 3. Framework $W^*[4t_c]$ as part of the crystal structure of $\alpha\text{-Mn}$: symmetry $I\bar{4}3m\ 24(g)\ xxz$, $x = 0.3571$, $z = 0.0346$, z coordinates in $n/100$.

exist. Each $W^*[4t_c]$ atom belongs to two tetrahedra and, therefore, has six neighboring $W^*[4t_c]$ atoms with shortest distances. Because of the symmetry $Im\bar{3}m$, $24(h)xx0$, the vertices of the tetrahedra point exactly in the directions of the body diagonals of the unit cell. For α -Mn the corresponding configuration seems to be very similar. The difference becomes apparent in the twisting of the nearly ideal tetrahedra from their higher symmetrical position. In Cu_5Zn_8 , however, within $W^*[4t_c]$ only four shortest distances per atom exist forming four-sided meshes instead of tetrahedra. The two missing edges are about 28% longer, and there exist two further distances of nearly the same length.

Common to all three basic structures is the fact that a three-dimensional connected net or framework (Hellner, 1979) is built up by the atoms of the $W^*[4t_c]$ configurations. In addition this is true for the five other crystal structures under consideration. In each case the atoms at $W^*_{222}[4t_c] = F(12co) + F''(12co) + F'(12co) + F'''(12co)$ together form a three-dimensional connected framework. The corresponding coordination numbers within an appropriate range of distances vary between six and eight.

As shown by Koch & Hellner (1980) the voids around I within a $W^*[4t_c]$ framework change depending on the x and z parameters. For Tl_7Sb_2 cubo-octahedra are formed (Fig. 4) according to the symbols $(12co)$ and CO . The edges of these cubo-octahedra, however, are about 70% longer than the edges of the W^* tetrahedra. For Cu_5Zn_8 cubo-octahedra exist, too, but their triangular faces have different size (Fig. 5) and, in consequence, the quadrangular faces become rectangles. For α -Mn the corresponding polyhedron shows 24 vertices with almost equal distances to the polyhedron center (Fig. 6). It may be constructed from the vertices of a cubo-octahedron combined with those of a truncated tetrahedron.

These large voids around the points of an I lattice are filled up by sets of metal polyhedra with common centers in each of the eight crystal structures under consideration. The following combinations of

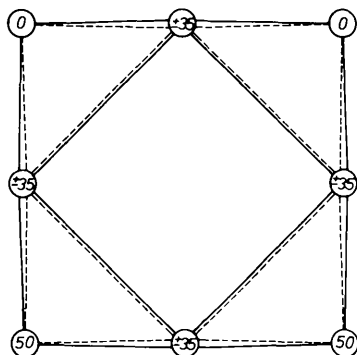


Fig. 4. Cubo-octahedral void around 000 in the $W^*[4t_c]$ framework of Tl_7Sb_2 , z coordinates in $n/100$.

polyhedra exist within the basic structures: $(\cdot 8c, 6o)$ in Tl_7Sb_2 , $(\cdot 12tt, 4t^-)$ in α -Mn, and $(4t^+, 4t^-, 6o)$ in Cu_5Zn_8 . The dot in these symbols means that the common center of the polyhedra is occupied by an atom. In addition, $(12tt, 4t^-)$ is contained in Na_6Tl and $(4t^-, 6o)$ in Na_6Tl and Mg_6Pd . The numbers of connections between the atoms in these arrangements of polyhedra are tabulated in the following coordination schemes.

		to	
		(8c)	(6o)
($\cdot 8c, 6o$):	from		
	\cdot	-	8 6
	(8c)	1	3 3
	(6o)	1	4 -

		to	
		(12tt)	(4t ⁻)
($\cdot 12tt, 4t^-$):	from		
	\cdot	-	12 4
	(12tt)	1	3 2
	(4t ⁻)	1	6 -

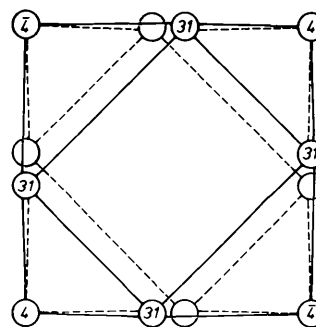


Fig. 5. Cubo-octahedral void around 000 in the $W^*[4t_c]$ framework of Cu_5Zn_8 , z coordinates in $n/100$.

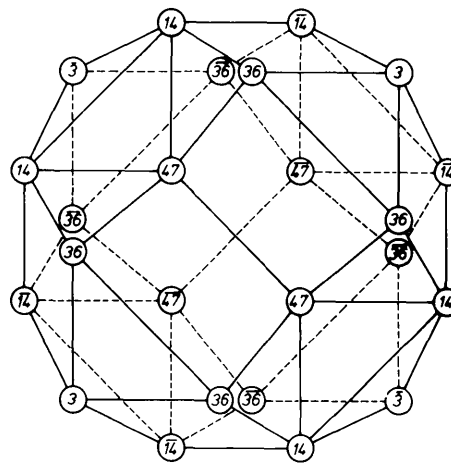


Fig. 6. Void around 000 in the $W^*[4t_c]$ framework of α -Mn, z coordinates in $n/100$.

$(4t^+, 4t^-, 6o)$:	from	to	$(4t^+)$	$(4t^-)$	$(6o)$
		$(4t^+)$	3	3	3
		$(4t^-)$	3	—	3
		$(6o)$	3	2	—
$(4t^-, 6o)$:	from	to	$(4t^-)$	$(6o)$	
		$(4t^-)$	—	3	
		$(6o)$	2	4	
$(12tt, 4t^-)$:	from	to	$(12tt)$	$(4t^-)$	
		$(12tt)$	3	2	
		$(4t^-)$	6	—	

It is remarkable that only these connection schemes occur within the eight crystal structures under consideration. In $\text{Sm}_{11}\text{Cd}_{45}$ and $\text{Li}_{22}\text{Si}_5$ two tetrahedra ($4t^+$) and ($4t^-$) with almost equal edge length replace the cube in the Tl_7Sb_2 arrangement with preservation of the corresponding connections.

$(\cdot 4t^+, 4t^-, 6o)$:	from	to	$(4t^+)$	$(4t^-)$	$(6o)$	
		$(4t^+)$	—	4	4	6
		$(4t^-)$	1	—	3	3
		$(4t^-)$	1	3	—	3
		$(6o)$	1	2	2	—

In addition to the short distances tabulated above, similar distances occur between atoms from polyhedra with different centers, *i.e.* atoms from different 'clusters'. Furthermore, some distances between atoms of the framework $W^*[4t_c]$ or $W_{222}^*[4t_c]$, respectively, and atoms of the polyhedra within the voids of these frameworks are of similar length. The occurrence of these additional short distances depends not only on the type of nested polyhedra under consideration but also on the type of the neighboring nested polyhedra.

With respect to the above connection schemes all three basic structures are different. If one relates the two tetrahedra ($4t^+$) and ($4t^-$) of Cu_5Zn_8 to the cube ($8c$) of Tl_7Sb_2 it becomes apparent that the structures differ in their connections (see Hellner & Koch, 1980). This seems to be important with respect to the problem of the distribution of the larger metal atoms (see Booth *et al.*, 1977; Fornasini *et al.*, 1978). On the other hand, the combination of a truncated tetrahedron and a tetrahedron ($12tt, 4t^-$) occurring in Na_6Tl differs from the $\alpha\text{-Mn}$ arrangement ($\cdot 12tt, 4t^-$) only with respect to the centering atom.

Table 2 shows the distribution of sets of nested polyhedra within the five intermetallic compounds with enlarged unit cells. Arrangements corresponding to one of the basic structures are designated by the respective

Table 2. The distribution of different sets of nested polyhedra within the five intermetallic compounds with enlarged unit cells

	$\text{Sm}_{11}\text{Cd}_{45}$	Mg_6Pd	Na_6Tl	$\text{Li}_{22}\text{Si}_5$	$\text{Cu}_{41}\text{Sn}_{11}$
F	Tl_7Sb_2	$(4t^-, 6o)$	$(4t^-, 6o)$	Tl_7Sb_2	Cu_5Zn_8
F''	$\alpha\text{-Mn}$	Cu_5Zn_8	Cu_5Zn_8	Tl_7Sb_2	Cu_5Zn_8
F'	$\alpha\text{-Mn}$	$(4t^-, 6o)$	Cu_5Zn_8	Tl_7Sb_2	Cu_5Zn_8
F'''	Tl_7Sb_2	$\alpha\text{-Mn}$	$(12tt, 4t^-)$	Tl_7Sb_2	Cu_5Zn_8

chemical formula. The other arrangements are described by the polyhedron symbol.

$\text{Cu}_{41}\text{Sn}_{11}$ is a superstructure of Cu_5Zn_8 as already stated by Booth *et al.* (1977). $\text{Li}_{22}\text{Si}_5$ should be regarded as a superstructure of Tl_7Sb_2 . Parts of $\text{Sm}_{11}\text{Cd}_{45}$ are analogous to Tl_7Sb_2 , other parts are analogous to $\alpha\text{-Mn}$. The polyhedra centers for both parts form configurations of the cubic invariant lattice complex D with the following relations:† $F + F''' = D'''$ and $F' + F'' = D''$. Mg_6Pd contains arrangements around F'' similar to Cu_5Zn_8 and arrangements around F''' similar to $\alpha\text{-Mn}$. Around $P_{222} = F + F'$ only tetrahedra and octahedra ($4t^-, 6o$) exist. The octahedra are considerably smaller than those in Cu_5Zn_8 . This fact reveals additional contacts between the atoms of the same octahedron. Na_6Tl , too, shows three different types of nested polyhedra within its $W_{222}^*[4t_c]$ framework. The voids around $D'' = F' + F''$ are filled up with Cu_5Zn_8 arrangements, those around F''' with truncated tetrahedra and negative tetrahedra, forming together Laves–Friauf polyhedra, not centered by additional atoms as in $\alpha\text{-Mn}$. Around F the combination of a tetrahedron and an octahedron as in Mg_6Pd occurs.

In summary it may be said that within these eight crystal structures the large voids around I or I_{222} are filled in several different ways. With the aid of the symbols given above the crystal structures may be described in the following way:

Tl_7Sb_2	$W^*[4t_c] + I(\cdot 8c, 6o)$;
$\alpha\text{-Mn}$	$W^*[4t_c] + I(\cdot 12tt, 4t^-)$;
Cu_5Zn_8	$W^*[4t_c] + I(4t^+, 4t^-, 6o)$;
$\text{Cu}_{41}\text{Sn}_{11}$	$W_{222}^*[4t_c] + I_{222}(4t^+, 3t^-, 6o)$;
$\text{Li}_{22}\text{Si}_5$	$W_{222}^*[4t_c] + I_{222}(\cdot 8c, 6o)$;
$\text{Sm}_{11}\text{Cd}_{45}$	$W_{222}^*[4t_c] + D'''(\cdot 8c, 6o) + D''(\cdot 12tt, 4t^-)$;
Mg_6Pd	$W_{222}^*[4t_c] + P_{222}(4t^-, 6o)$ $+ F''(4t^-, 4t^+, 6o) + F'''(\cdot 12tt, 4t^-)$;
Na_6Tl	$W_{222}^*[4t_c] + D''(4t^-, 4t^+, 6o)$ $+ F(4t^-, 6o) + F'''(12tt, 4t^-)$.

These symbols show very clearly the common feature of all these crystal structures, namely the three-dimensional connected frameworks $W^*[4t_c]$. For a description of the geometrical and physical properties this symbolism seems more adequate and useful than the cluster description.

† The superscript ' symbolizes a shift of $\frac{1}{4}$ of the configuration with respect to the standard description, '' refers to $\frac{1}{4}$ and ''' to $\frac{3}{4}$.

A further reason to consider the $W^*[4t_c]$ configuration as an important building unit within the intermetallic phases discussed above is the following: there exists an interesting relation to many inorganic crystal structures (Koch & Hellner, 1980), for which the anions form a framework $W^*[4t_c]$ with nearly ideal tetrahedra centered by Si, Al, Be, etc.

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References

- AXEL, H., SCHÄFER, H. & WEISS, A. (1966). *Z. Naturforsch. Teil B*, **21**, 115–117.
- BOOTH, M. H., BRANDON, J. K., BRIZARD, R. Y., CHIEH, C. & PEARSON, W. B. (1977). *Acta Cryst.* **B33**, 30–36.
- BRADLEY, A. J. & JONES, P. (1933). *J. Inst. Met.* **51**, 131–162.
- BRANDON, J. K., BRIZARD, R. Y., CHIEH, P. C., MCMILLAN, R. K. & PEARSON, W. B. (1974). *Acta Cryst.* **B30**, 1412–1417.
- COTTON, F. A. & WILKINSON, G. (1972). *Advanced Inorganic Chemistry*, p. 547 ff. New York: Interscience.
- DONNAY, J. D. H., HELLNER, E. & NIGGLI, A. (1964). *Z. Kristallogr.* **120**, 364–374.
- DONNAY, J. D. H., HELLNER, E. & NIGGLI, A. (1966). *Z. Kristallogr.* **123**, 255–262.
- FORNASINI, M. L., CHABOT, B. & PARTHÉ, E. (1978). *Acta Cryst.* **B34**, 2093–2099.
- HELLNER, E. (1965). *Acta Cryst.* **19**, 703–712.
- HELLNER, E. (1979). *Struct. Bonding (Berlin)*, **37**, 61–140.
- HELLNER, E. & KOCH, E. (1980). *Can. J. Chem.* **58**, 708–713.
- KOCH, E. & HELLNER, E. (1980). *Z. Kristallogr.* In the press.
- OBERTEUFER, J. A. & IBERS, J. A. (1970). *Acta Cryst.* **B26**, 1499–1504.
- SAMSON, S. (1972). *Acta Cryst.* **B28**, 936–945.
- SAMSON, S. & HANSEN, D. A. (1972). *Acta Cryst.* **B28**, 930–935.
- SCHNERING, H. G. VON & HÄUSLER, K.-G. (1976). *Rev. Chim. Minér.* **13**, 71–82.
- SCHOBINGER-PAPAMANTELLOS, P. & FISCHER, P. (1970). *Naturwissenschaften*, **57**, 128–129.
- STOCKHUYZEN, R., CHIEH, C. & PEARSON, W. B. (1977). *Can. J. Chem.* **55**, 1120–1122.

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Nested Polyhedra Units: A Geometrical Concept for Describing Complicated Cubic Structures*

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Abstract

A method for describing cubic giant cells is proposed. The structures may be regarded as arrangements of nested polyhedra units, isolated or linked, centred at sites of high point symmetry. Five basic types of nested polyhedra units, taken from well known cubic structures are defined: α -Mn (29 atoms), BCC (27), γ -brass (26), Ca_3Ag_8 (26) and Ti_2Ni (22) as well as variants of two of them, the non-centred α -Mn unit (28 atoms) and the centred Ca_3Ag_8 unit (27 atoms). All seven units have a cubo-octahedron as the outermost polyhedron.

* *Editorial note:* The similarity between this paper, the preceding paper by Hellner & Koch [*Acta Cryst.* (1981), **A37**, 1–6] and the following paper by Nyman & Hyde [*Acta Cryst.* (1981), **A37**, 11–17] has been recognized and they have been published together to give an indication of the activity in the field with which they are concerned.

Sixteen structures are described in this paper, among which some have more than 400 atoms in the unit cell. This purely geometric description has the advantage that it can be easily obtained from the atom coordinates. It further makes structural similarities evident and simplifies the task of visualizing and memorizing complicated cubic structures.

Introduction

In the course of our structural studies of rare-earth (or Y, Sc) alloys we have recently solved three crystal structures with large cubic unit cells: $Sm_{11}Cd_{45}$, $a = 21.699$ (3) Å (Fornasini, Chabot & Parthé, 1978), $Sc_{11}Ir_4$, $a = 13.350$ (4) Å (Chabot, Cenzual & Parthé, 1980a), and $Sc_{44}Os_7$, $a = 20.771$ (5) Å with $Mg_{44}Rh_7$ type (Chabot, Cenzual & Parthé, 1980b). The diffi-