

The Crystal Structure of $\text{Sm}_{11}\text{Cd}_{45}$ with γ -Brass and α -Mn Clusters

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$\text{Sm}_{11}\text{Cd}_{45}$ crystallizes with a new cubic structure type in space group $F\bar{4}3m$, with $a = 21.699(3) \text{ \AA}$, 448 atoms in the unit cell, $Z = 8$, $D_x = 8.73$, $D_m = 8.72 \text{ g cm}^{-3}$, and $\mu(\text{Mo } K\alpha) = 306 \text{ cm}^{-1}$. Direct methods, absorption correction, and least-squares refinement led to $R = 0.050$ for 492 independent reflexions. $\text{Pr}_{11}\text{Cd}_{45}$, $\text{Nd}_{11}\text{Cd}_{45}$, $\text{Gd}_{11}\text{Cd}_{45}$, $\text{Tb}_{11}\text{Cd}_{45}$, $\text{Dy}_{11}\text{Cd}_{45}$, $\text{Ho}_{11}\text{Cd}_{45}$, $\text{Er}_{11}\text{Cd}_{45}$, $\text{Tm}_{11}\text{Cd}_{45}$, $\text{Lu}_{11}\text{Cd}_{45}$ and $\text{Y}_{11}\text{Cd}_{45}$ are isostructural with $\text{Sm}_{11}\text{Cd}_{45}$. A cluster concept is developed which helps in the description of this and related structures. Disregarding details concerning the occupation of the sites in a cluster, the structure of $\text{Sm}_{11}\text{Cd}_{45}$ can be described as an arrangement of 16 clusters or pseudo-atoms of two types which are distributed according to the face-centred-cubic NaTl structure, a $2 \times 2 \times 2$ superstructure of W. One of these clusters, which contains 27 atoms, is similar to the clusters found in γ -brass phases except that it has an extra atom at its centre (thus it corresponds more closely to the clusters in $\text{Li}_{22}\text{Pb}_3$ or $\text{Li}_{22}\text{Si}_3$). The second cluster which consists of 29 atoms is identical to the clusters found in α -Mn.

Introduction

In the course of a study of the intermediate phases formed in rare-earth–cadmium systems, cubic-face-centred phases with cell parameters between 21.4 and 21.8 Å and approximate composition RCd_4 were found with $R = \text{Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu}$ and Y (Bruzzone, Fornasini & Merlo, 1973). We describe in this report the determination of this unknown structure type. The particular compound on which single-crystal studies were performed was SmCd_4 which, according to a phase-diagram study (Bruzzone & Fornasini, 1974), melts congruently at 798 °C.

Experimental

SmCd_4 was prepared by melting stoichiometric amounts of the elements (Sm 99.0%, Cd 99.999%) in a Ta container closed by welding under an argon atmosphere. The homogeneity of the sample was checked by metallographic examination. Intensities were measured on a plate-like crystal ($0.16 \times 0.16 \times 0.08 \text{ mm}$) with graphite-monochromated $\text{Mo } K\alpha$ radiation on a Philips PW 1100 automatic four-circle diffractometer. The least-squares refinement of 2θ values of 30 reflexions with *PARAM* (XRAY system, 1976), yielded $a = 21.699(3) \text{ \AA}$. Possible space groups were $F432$, $F\bar{4}3m$, and $Fm\bar{3}m$ according to the systematic absences and the Laue symmetry. Scans in the θ – 2θ mode were used out to a limit of $\sin \theta/\lambda = 0.647 \text{ \AA}^{-1}$ to collect 510 non-equivalent intensities. An empirical absorption correction based on the comparison of several sets of equivalent reflexions was

applied with *CAMEL JOCKEY* (Flack, 1975, 1977). The structure was solved by direct methods in the space group $F\bar{4}3m$. The phases of the 123 largest normalized structure factors ($E > 1$) were determined with *SINGEN* and *TANGEN* (XRAY system, 1976). Evaluation of E maps and successive Fourier maps gave the whole structure. Positional and isotropic thermal parameters refined satisfactorily with *CRYLSQ* (XRAY system, 1976). Scattering factors were from Cromer & Mann (1968). $R = \sum |\Delta F| / \sum |F_o|$ with isotropic thermal parameters was 0.050 for 492 non-equivalent reflexions with $|F_o| > 3\sigma_F$. The strongest reflexion, 660, was excluded from the refinement because its very high intensity led to a saturation of the counter. The final positional and isotropic thermal parameters are listed in Table 1.*

Isotypic phases

Ten rare-earth (and Y)–cadmium compounds should be isotypic with $\text{Sm}_{11}\text{Cd}_{45}$ according to powder diagram studies (Bruzzone, Fornasini & Merlo, 1973). For NdCd_4 , for which the observed powder diagram was published, we have calculated a simulated powder pattern with *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977) assuming the $\text{Sm}_{11}\text{Cd}_{45}$ type of structure. A comparison of the published diagram with the

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33441 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. The point positions of $\text{Sm}_{11}\text{Cd}_{45}$, compared with those of other cluster structures

For cluster structures the sequential numbering of atoms of one kind, as is conventional in crystallographic literature, is less informative than the grouping of atoms in clusters. For the notation of the cluster sites see text.

Cluster	$\text{Sm}_{11}\text{Cd}_{45}$ ($F\bar{4}3m$, $a = 21.699 \text{ \AA}$; 27-atom and 29-atom clusters)			$\text{Li}_{12}\text{Si}_5$ ($F23$, $a = 18.75 \text{ \AA}$; only 27-atom clusters)			$\text{Cu}_4\text{Sn}_{11}$ (γ -brass) ($F\bar{4}3m$, $a = 17.98 \text{ \AA}$; only 26-atom clusters)			α -Mn ($I43m$, $a = 8.911 \text{ \AA}$; only 29-atom clusters)			
	x	y	z	$B (\text{\AA}^2)$	x	y	z	x	y	z	x	y	z
Cluster A													
A CC 4(a)	Sm	0	0	0.9 (2)	Li	0	0	—	—	—	Mn	0	0
A TT 48(h)	—	—	—	—	—	—	—	—	—	—	Mn	0.0448 × 2	0.0448 × 2
A IT 16(e)	Cd	0.0834 (2)	0.0834 (2)	0.0834 (2)	Li	0.080	0.080	0.080	0.080	0.0573	—	0.0448 × 2	0.1410 × 2
A OT 16(e)	Cd	0.9126 (2)	0.9126 (2)	0.9126 (2)	Si	0.911	0.911	0.911	0.911	0.9113	—	0.0448 × 2	0.1410 × 2
A OH 24(f)	Cd	0.1573 (3)	0	2.0 (2)	Li	0.167	0	0	0	0	—	0.9089 × 2	0.9089 × 2
A CO 48(h)	Sm	0.1735 (1)	0.1735 (1)	0.0142 (1)	Li	0.161	0.167	0.005	0.005	0.1562	—	0.1785 × 2	0.1785 × 2
Cluster B													
B CC 4(c)	Sm	$\frac{1}{2}$	$\frac{1}{2}$	1.1 (2)	Li	$\frac{1}{2}$	$\frac{1}{2}$	—	—	—	Mn	$\frac{1}{2}$	$\frac{1}{2}$
B TT 48(h)	Cd	0.2958 (2)	0.2958 (2)	0.3904 (2)	—	—	—	—	—	—	Mn	0.2948 × 2	0.2948 × 2
B IT 16(e)	—	—	—	—	Li	0.330	0.330	0.330	0.330	0.3005	—	0.2948 × 2	0.3910 × 2
B OT 16(e)	Cd	0.1636 (2)	0.1636 (2)	0.1636 (2)	Li	0.167	0.167	0.167	0.167	0.1657	—	0.1589 × 2	0.1589 × 2
B OH 24(g)	—	—	—	—	Si	0.428	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.4241	—	0.1589 × 2	0.1589 × 2
B CO 48(h)	Cd	0.4377 (1)	0.4377 (1)	0.2627 (2)	Li	0.413	0.413	0.250	0.250	0.4084	—	0.4285 × 2	0.4285 × 2
Cluster C													
C CC 4(b)	Cd	$\frac{1}{2}$	$\frac{1}{2}$	0.7 (2)	Li	$\frac{1}{2}$	$\frac{1}{2}$	—	—	—	Mn	$\frac{1}{2}$	$\frac{1}{2}$
C TT 48(h)	Cd	0.5455 (1)	0.5455 (1)	0.6403 (2)	—	—	—	—	—	—	Mn	0.2948 × 2	0.2948 × 2
C IT 16(e)	—	—	—	—	Li	0.583	0.583	0.583	0.583	0.5504	—	0.2948 × 2	0.2948 × 2
C OT 16(e)	Sm	0.4059 (2)	0.4059 (2)	0.4059 (2)	Li	0.420	0.420	0.420	0.420	0.4166	—	0.1589 × 2	0.1589 × 2
C OH 24(f)	—	—	—	—	Si	0.678	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.6765	—	0.1589 × 2	0.1589 × 2
C CO 48(h)	Cd	0.6728 (2)	0.6728 (2)	0.5123 (2)	Li	0.658	0.667	0.497	0.497	0.6465	—	0.4285 × 2	0.4285 × 2
Cluster D													
D CC 4(d)	Cd	$\frac{1}{2}$	$\frac{1}{2}$	1.9 (3)	Li	$\frac{1}{2}$	$\frac{1}{2}$	—	—	—	Mn	$\frac{1}{2}$	$\frac{1}{2}$
D TT 48(h)	—	—	—	—	—	—	—	—	—	—	—	0.0448 × 2	0.0448 × 2
D IT 16(e)	Cd	0.8297 (2)	0.8297 (2)	0.8297 (2)	Li	0.833	0.833	0.833	0.833	0.8062	—	0.0448 × 2	0.1410 × 2
D OT 16(e)	Sm	0.6618 (2)	0.6618 (2)	0.6618 (2)	Si	0.665	0.665	0.665	0.665	0.6664	—	0.0448 × 2	0.1410 × 2
D OH 24(g)	Cd	0.9105 (3)	$\frac{1}{2}$	1.4 (1)	Li	0.917	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.9309	—	0.9089 × 2	0.9089 × 2
D CO 48(h)	Cd	0.9161 (2)	0.9161 (2)	0.7637 (2)	Li	0.917	0.917	0.750	0.750	0.9087	—	0.1785 × 2	0.1785 × 2

Table 2. *Compounds with the Sm₁₁Cd₄₅ structure type*

Lattice constants (in Å) are after Bruzzone, Fornasini & Merlo (1973).

Pr ₁₁ Cd ₄₅	21.842	Dy ₁₁ Cd ₄₅	21.512
Nd ₁₁ Cd ₄₅	21.783	Ho ₁₁ Cd ₄₅	21.478
Sm ₁₁ Cd ₄₅	21.693	Er ₁₁ Cd ₄₅	21.450
Gd ₁₁ Cd ₄₅	21.603	Tm ₁₁ Cd ₄₅	21.427
Tb ₁₁ Cd ₄₅	21.550	Lu ₁₁ Cd ₄₅	21.402
		Y ₁₁ Cd ₄₅	21.492

calculated one showed excellent agreement between observed and calculated intensities and confirms that this compound is isotypic with Sm₁₁Cd₄₅. Assuming that all the remaining RC₄ compounds are isotypic with Nd₁₁Cd₄₅, we list their lattice constants in Table 2.

The cluster concept

For the discussion of the structure of Sm₁₁Cd₄₅, it is convenient to use the cluster concept originally adopted by Bradley & Jones (1933) for the description of the γ -brass phases. They recognized that all γ -brass phases are made up of clusters each with 26 atoms forming pseudo-atoms which are packed in a simple cubic-body-centred arrangement. The feature that distinguishes one γ -brass phase from another and which is responsible for their different symmetries is the manner in which the constituent atoms in the clusters are ordered. If there is only one type of cluster, two pseudo-atoms are arranged in a similar manner to the atoms in the structure of W (*A2* type). These are the γ -brass phases with body-centred-cubic cells where $a \sim 9$ Å and for which V₅Al₈ (Brandon, Pearson, Riley, Chieh & Stokhuyzen, 1977) is an example. The γ -brass phases with primitive cubic cells have about the same cell size as the body-centred-cubic phases but contain two closely related yet different types of clusters. The pseudo-atom arrangement in this case corresponds to the atomic arrangement in the CsCl structure (*B2* type). An example is Cu₉Al₄ (Arnberg & Westman, 1978). Later, γ -brass phases with face-centred-cubic cells, e.g. Cu₄₁Sn₁₁ (Booth, Brandon, Brizard, Chieh & Pearson, 1977; Arnberg, Jonsson & Westman, 1976), were found. Their characteristic unit-cell parameter of $a \sim 18$ Å is twice as large as those found in the primitive and body-centred phases. This type of structure contains 16 clusters, i.e. four clusters of four different, yet closely related, types of cluster, which are arranged in a $2 \times 2 \times 2$ superstructure of the body-centred-cubic W structure. This superstructure can be described as a quaternary version of the face-centred-cubic NaTl structure (*B32* type). A diagram of the NaTl structure is shown in Fig. 1. The letters inscribed in the circles correspond to the different positions that a cluster can

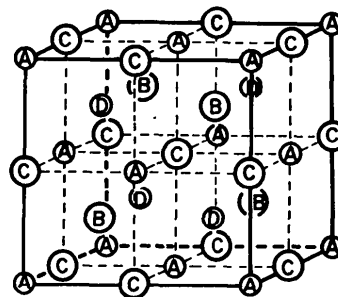


Fig. 1. The structure of NaTl ($2 \times 2 \times 2$ superstructure of the *A2* type). Small circles denote the Tl sites. The inscribed letters correspond to the designation of the clusters used in the description of γ -brass phases with face-centred cells, Li₂₂Pb₅ and Sm₁₁Cd₄₅.

take in the unit cell. Thus the centre of cluster *A* is at 0,0,0, *B* is at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, *C* is at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and *D* is at $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$. The remaining cluster centres are found by the translational vectors of the face-centred Bravais lattice. This cluster designation corresponds to the notation adopted by Pearson, Brandon & Brizard (1976) and is different from that used by Westman (1972).

It will now be shown that this cluster concept can be applied to other structures besides the γ -brass phases. The structures we propose to discuss here are Li₂₂Pb₅ (Zalkin & Ramsey, 1958), α -Mn (Oberteuffer & Ibers, 1970) and Sm₁₁Cd₄₅. In α -Mn, which is body-centred-cubic with $a \sim 9$ Å, there are only two identical clusters per unit cell arranged as in W. Li₂₂Pb₅ and Sm₁₁Cd₄₅ have the large face-centred-cubic cell with the 16 clusters arranged as in NaTl.

The difference amongst all the cited face-centred structures lies in the individual construction of the clusters and in the occupation of the cluster sites. Thus one has to distinguish between clusters which are (a) comprised of different types of polyhedra and (b) those which have different site occupations but the same types of polyhedra.

Considering only the polyhedral construction of the clusters, one finds three different types of clusters: 26-atom, 27-atom, and 29-atom clusters.

All clusters in the γ -brass phases are of the 26-atom type. The difference between structures having different cubic Bravais lattices is due to the different atomic distributions on the sites of the 26-atom clusters. This will be discussed later. In Li₂₂Pb₅ there are only 27-atom clusters, while in α -Mn there are only 29-atom clusters. The structure of Sm₁₁Cd₄₅ is a hybrid, as there are both 27-atom clusters as in Li₂₂Pb₅ and 29-atom clusters as in α -Mn which are arranged in a similar way to the atoms in the binary NaTl structure.

The three types of clusters are constructed of different polyhedra, as shown in Fig. 2 and described in detail below.

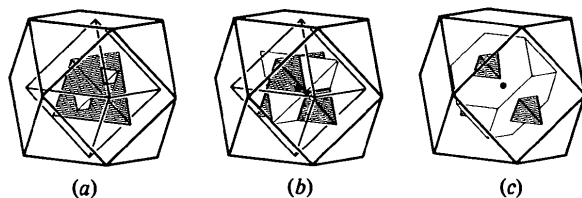


Fig. 2. The polyhedral construction of the (a) 26-atom, (b) 27-atom and (c) 29-atom clusters. The outermost cubo-octahedra (CO), common to all clusters, are drawn with bold lines. Either an octahedron (OH) (26-atom and 27-atom clusters) or a truncated tetrahedron (TT) (29-atom cluster) is inscribed in this polyhedron. The tetrahedra (IT and/or OT) are outlined with thin lines of which the negative one (OT) has been shaded. Only the 27-atom and 29-atom clusters have an atom at their centres (CC) which is indicated in the diagram by a black dot.

The 26-atom cluster is formed by an inner (positive) tetrahedron (IT) of four atoms which is surrounded by an outer (negative) tetrahedron (OT) of four more atoms. The latter is surrounded by an octahedron (OH) of six atoms and finally the whole is surrounded by a cubo-octahedron (CO) of 12 atoms (Fig. 2a).

The 27-atom is similar to the 26-atom cluster except that it has an extra atom at the centre of the cluster (CC). This additional atom dilates the inner tetrahedron to such an extent that the inner (positive) and outer (negative) tetrahedra merge together to form a cube (Fig. 2b).

The 29-atom cluster consists of a cluster centre (CC) surrounded by a truncated tetrahedron (TT) of 12 atoms. Above each of the centres of the four hexagonal faces of this truncated tetrahedron are the four atoms of the outer tetrahedron (OT). The whole arrangement is surrounded by a cubo-octahedron (CO) of 12 atoms (Fig. 2c). The polyhedron around the cluster centre consisting of TT and OT atoms is the Kasper triangulated polyhedron for coordination 16. The 17-atom aggregate of the centred Kasper polyhedron is referred to by Samson (1969) as a Friauf polyhedron. The complete 29-atom cluster (Friauf polyhedron and surrounding cubo-octahedron) is a segment of the cubic Laves phase from which it is possible, in principle, to derive idealized point positions of the cluster sites. Such point positions were used in the construction of Fig. 2.

In Table 1, the point positions for $\text{Sm}_{11}\text{Cd}_{45}$ are compared with those of $\text{Li}_{22}\text{Si}_5$, $\text{Cu}_{41}\text{Sn}_{11}$ and α -Mn. Since the best R obtained for the structure determination of $\text{Li}_{22}\text{Pb}_5$ was only 0.19 we prefer to use here the point positions of the isotypic $\text{Li}_{22}\text{Si}_5$ structure (Axel, Schäfer & Weiss, 1966). The types of polyhedra present in each cluster can be recognized directly from the x , y and z values of the point positions. For a cluster centre (CC) at δ, δ, δ one finds as idealized point positions for a surrounding truncated tetrahedron (TT): $x + \delta$, $x + \delta$, $z + \delta$, where $3(x + \delta) = (z + \delta) + 2\delta$

and $x \sim \frac{1}{24}$, $z \sim \frac{1}{8}$; for a tetrahedron (IT or OT): $x + \delta$, $x + \delta$, $x + \delta$, where $x_{\text{IT}} \sim \frac{1}{12}$ for a 27-atom but $x_{\text{IT}} < \frac{1}{12}$ for a 26-atom cluster, and $x_{\text{OT}} \sim \frac{1}{12}$; for an octahedron (OH): $x + \delta$, δ , δ , where $x \sim \frac{1}{6}$; and for a cubo-octahedron (CO): $x + \delta$, $x + \delta$, δ , where $x \sim \frac{1}{6}$. The idealized point positions for TT, OT and CO have been derived from the cubic Laves phase MgCu_2 (C15 type). For the idealized 27-atom cluster it was assumed that IT and OT form a cube and that the OH vertices centre the CO square faces. The good agreement between corresponding point positions serves as a proof for the applicability of the cluster concept to these compounds.

The ordering of the atoms on the cluster sites

In $\text{Sm}_{11}\text{Cd}_{45}$ the two 27-atom clusters A and D , and the two 29-atom clusters B and C , have different atom distributions on the cluster sites. In $\text{Li}_{22}\text{Si}_5$, consisting of only 27-atom clusters, one finds two different types of atom distributions at the cluster sites. In this case the clusters A and D , and B and C are identical. Thus, considering all details of the cluster site occupation, the cluster arrangement in $\text{Li}_{22}\text{Si}_5$ corresponds to the binary NaI structure type. In $\text{Cu}_{41}\text{Sn}_{11}$ all four 26-atom clusters have a different distribution of Cu and Sn atoms and in α -Mn the two 29-atom clusters are obviously identical.

Pearson, Brandon & Brizard (1976) have examined reasons for the ordering of the atoms on the sites of the 26-atom clusters in γ -brass phases. For binary alloys with one kind of atom at least 10% larger than the other, they found as an essential criterion for the ordering of the atoms that the larger atoms could not be nearest neighbours. That is to say, the observed bond distances must be larger than the sum of the radii of the component atoms (provided that the proportion of larger atoms is not so high that this becomes impossible). They were then able to construct models representing all the possible arrangements of the atoms at the cluster sites and neighbouring clusters on the application of this condition. For example, three possible solutions for γ -brass structures with F cells are obtained if the large atoms L occupy the following types of polyhedra in each of the four clusters: (1) A OT, B CO, C -, D OH which gives a composition of $L_{11}M_{41}$; (2) A OT, B OH, C OH, D OT which gives a composition of L_5M_{21} ; (3) A CO, B -, C OT, D OT which gives a composition of L_5M_{21} . The first solution corresponds to the structure of $\text{Cu}_{41}\text{Sn}_{11}$. The second solution corresponds to the structure of $\text{Li}_{22}\text{Pb}_5$ if the cluster centres are filled with Li atoms. Since the same structure type is also found with $\text{Li}_{22}\text{Si}_5$, where the Si atom is smaller than the Li atom, it appears reasonable to extend the ordering criterion to include the condition that no contacts between the minority atoms should exist. The third possibility, which, incidentally, was

Table 3. *Interatomic distances (Å) in Sm₁₁Cd₄₅ up to 3.9 Å*

E.s.d.'s are in parentheses. Asterisks indicate distances more than 10% larger than the sum of the metallic radii and these have not been considered in the calculations of the coordination polyhedra.

Cluster A	Cluster B	Cluster C	Cluster D
Sm A CC—4Cd A IT 3.134 (2) —4 Cd A OT 3.286 (2) —6 Cd A OH 3.413 (6)	Sm B CC—12 Cd B TT 3.356 (4) —4 Cd B OT 3.246 (2)	Cd C CC—12 Cd C TT 3.350 (4) —4 Sm C OT 3.538 (2)	Cd D CC—4 Cd D IT 2.995 (3) —4 Sm D OT 3.315 (1) —6 Cd D OH 3.484 (6)*
Cd A IT—1 Sm A CC 3.134 (2) —3 Cd A OT 3.709 (1)* —3 Cd A OH 3.020 (4) —3 Sm A CO 3.146 (3) —1 Cd B OT 3.015 (3)	Cd B TT—2 Sm A CO 3.429 (3) —1 Sm B CC 3.356 (4) —3 Cd B TT 2.905 (5) —2 Cd B OT 3.221 (5) —2 Cd B CO 3.325 (3) —1 Sm C OT 3.395 (3) —1 Cd C CO 2.814 (5)	Cd C TT—2 Cd B CO 3.167 (4) —1 Cd C CC 3.350 (3) —3 Cd C TT 2.793 (2) —2 Sm C OT 3.361 (3) —2 Cd C CO 2.940 (4) —1 Sm D OT 3.598 (3) —1 Cd D CO 2.924 (5)	Cd D IT—1 Cd A OT 3.114 (3) —1 Cd D CC 2.995 (2) —3 Sm D OT 3.653 (1) —3 Cd D OH 3.010 (4) —3 Cd D CO 3.013 (4)
Cd A OT—1 Sm A CC 3.286 (2) —3 Cd A IT 3.709 (5)* —3 Cd A OH 3.082 (3) —3 Sm A CO 3.442 (4) —1 Cd D IT 3.116 (4) —3 Cd D CO 3.233 (3)	Cd B OT—1 Cd A IT 3.015 (3) —3 Sm A CO 3.256 (3) —1 Sm B CC 3.246 (3) —6 Cd B TT 3.221 (3) —3 Cd B CO 3.781 (4)*	Sm C OT—3 Cd B TT 3.395 (3) —3 Cd B CO 3.257 (3) —1 Cd C CC 3.538 (2) —6 Cd C TT 3.361 (3) —3 Cd C CO 3.341 (3)	Sm D OT—3 Cd C TT 3.598 (2) —3 Cd C CO 3.261 (4) —1 Cd D CC 3.315 (1) —3 Cd D IT 3.653 (5) —3 Cd D OH 3.129 (3) —3 Cd D CO 3.255 (3)
Cd A OH—1 Sm A CC 3.413 (6) —2 Cd A IT 3.020 (4) —2 Cd A OT 3.082 (3) —4 Sm A CO 3.794 (3)* —2 Cd B CO 2.980 (5) —2 Cd D CO 3.094 (4)	Cd B CO—1 Cd A OH 2.980 (5) —2 Sm A CO 3.264 (3) —2 Cd B TT 3.325 (3) —1 Cd B OT 3.781 (3)* —1 Cd B CO 3.822 (3)* —2 Cd C TT 3.167 (4) —1 Sm C OT 3.257 (3) —2 Cd C CO 3.214 (3) —2 Cd D CO 3.257 (4)	Cd C CO—2 Sm A CO 3.384 (1) —1 Cd B TT 2.814 (5) —2 Cd B CO 3.214 (3) —2 Cd C TT 2.940 (3) —1 Sm C OT 3.341 (3) —1 Sm D OT 3.261 (4) —1 Cd D OH 2.901 (5) —2 Cd D CO 3.165 (4)	Cd D OH—2 Sm A CO 3.251 (5) —2 Cd C CO 2.901 (5) —1 Cd D CC 3.484 (6)* —2 Cd D IT 3.010 (4) —2 Sm D OT 3.129 (3) —4 Cd D CO 3.618 (3)*
Sm A CO—1 Cd A IT 3.146 (3) —1 Cd A OT 3.442 (3) —2 Cd A OH 3.794 (3)* —2 Cd B TT 3.429 (3) —1 Cd B OT 3.256 (3) —2 Cd B CO 3.264 (3) —2 Cd C CO 3.384 (4) —1 Cd D OH 3.251 (5) —2 Cd D CO 3.189 (3)			Cd D CO—1 Cd A OT 3.234 (4) —1 Cd A OH 3.094 (4) —2 Sm A CO 3.189 (3) —2 Cd B CO 3.257 (1) —1 Cd C TT 2.924 (5) —2 Cd C CO 3.165 (4) —1 Cd D IT 3.013 (4) —1 Sm D OT 3.255 (3) —2 Cd D OH 3.618 (3)*

missed by Pearson, also corresponds to a composition of L_5M_{21} . Neglecting the Sm atoms at the cluster centres, the remaining Sm atoms in $Sm_{11}Cd_{45}$ occupy the same sites as in the third solution. However, since other cluster types exist in $Sm_{11}Cd_{45}$, the above conclusions concerning possible atom ordering on the cluster sites drawn from the γ -brass phases are not necessarily valid.

In order to find the possible site occupations for the minority atoms in a structure built up of 27-atom and 29-atom clusters one has to consider the distances between the different sites. In Table 3 are listed the interatomic distances in $Sm_{11}Cd_{45}$ up to 3.9 Å. One can see that the contractions of certain Cd—Cd distances (2.793 instead of 3.08 Å) are similar to those observed in other rare-earth (and Y)—cadmium compounds, e.g. YCd_6 (Larson & Cromer, 1971). We need to record the close contacts of each site in each cluster. To do this, we shall use a table as shown in Fig. 3 where each of

the possible polyhedra in the four clusters is represented by a square. Black squares correspond to polyhedra which do not occur in a particular cluster. A polyhedral site which is occupied by a minority atom L is indicated by an inscribed square. The numbers inscribed in the different squares correspond to the number of atoms which are nearest neighbours to the L atom in the inscribed square. Sites for which the corresponding squares have an inscribed number cannot be occupied by other L atoms because the ordering criterion requires that there are no L — L contacts. Fig. 3 shows the close contacts of all sites of the A and C clusters. Since an atom on a TT site in a C (or B) cluster has three other TT neighbours, the TT sites can never be occupied by L atoms. To obtain models for possible ordering of the minority components on the 27-atom and 29-atom clusters one has to look for possible combinations of L atom sites using the close-contact data illustrated in Fig. 3.

The only possible combinations are those where no numerals appear in the inscribed squares. For the composition $L_{11}\text{M}_{45}$ several different combinations are possible; two of these are shown in Fig. 4 of which one with the minority atoms in *A* CC and CO, *B* CC, *C* OT and *D* OT corresponds to the actual structure of $\text{Sm}_{11}\text{Cd}_{45}$. Thus in $\text{Sm}_{11}\text{Cd}_{45}$ the ordering criterion is obeyed with respect to the Sm–Sm contacts.

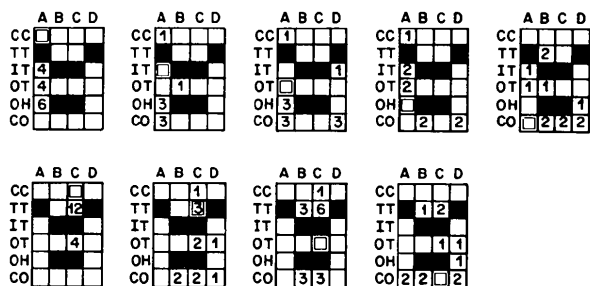


Fig. 3. Nearest-neighbour tables for the different sites in the *A* (27-atom) and *C* (29-atom) clusters.

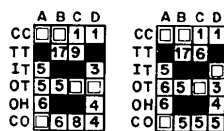


Fig. 4. Nearest-neighbour tables for two possible site occupations which correspond to the formula $L_{11}\text{M}_{45}$.

The individual coordination polyhedra

According to the cluster concept used above one might expect the same coordination polyhedra for corresponding atoms in clusters of the same type. However, there are variations in the distances which are due to small differences in bonding and consequently the coordination polyhedra are different. The coordination number (CN) for each atom was evaluated with the gap criterion for the distribution of the distances (Bruzzzone, Fornasini & Merlo, 1970). The atomic distribution around one atom was calculated and represented by plotting the number of surrounding atoms at a distance d against the ratio $d/\sum r$, where $\sum r$ = the radius of the central atom + the radius of the surrounding atom. The radii used for this calculation were 1.54 Å for the Cd and 1.81 Å for the Sm atom. In each case the lower gap limit occurs at $d/\sum r \leq 1.09$. According to this limit, the coordination polyhedra are given in Table 4.

The structure of $\text{Sm}_{11}\text{Cd}_{45}$ shows a variety of coordination polyhedra. Of the 448 atoms in the unit cell only 168, distributed on nine independent positions, maintain some features of the body-centred-cubic arrangement of the W substructure. Sm at *A* CC is surrounded by a distorted CN 14 polyhedron, formed by a cube plus an octahedron; Sm at *D* OT has the same polyhedron, except that a vertex is replaced by a triangular face, achieving CN 16. In Cd (*A* IT), Cd (*A* OT), Cd (*A* OH), Cd (*D* CC), Cd (*D* IT), Cd (*D* OH)

Table 4. Coordination data of $\text{Sm}_{11}\text{Cd}_{45}$

Position	Atom	Coordinated atoms	CN	Description of polyhedron	
Cluster A					
<i>A</i> CC	4(<i>a</i>)	Sm	14 Cd	14	Cube plus octahedron
<i>A</i> IT	16(<i>e</i>)	Cd	4 Sm + 4 Cd	8	Cube
<i>A</i> OT	16(<i>e</i>)	Cd	4 Sm + 7 Cd	11	Cube plus defect octahedron [CN 8 + (6–3)]
<i>A</i> OH	24(<i>f</i>)	Cd	1 Sm + 8 Cd	9	Cube plus defect octahedron [CN 8 + (6–5)]
<i>A</i> CO	48(<i>h</i>)	Sm	12 Cd	12	Deformed icosahedron
Cluster B					
<i>B</i> CC	4(<i>e</i>)	Sm	16 Cd	16	Kasper polyhedron
<i>B</i> TT	48(<i>h</i>)	Cd	4 Sm + 8 Cd	12	Icosahedron
<i>B</i> OT	16(<i>e</i>)	Cd	4 Sm + 7 Cd	11	New kind of polyhedron
<i>B</i> CO	48(<i>h</i>)	Cd	3 Sm + 9 Cd	12	Deformed icosahedron
Cluster C					
<i>C</i> CC	4(<i>b</i>)	Cd	4 Sm + 12 Cd	16	Kasper polyhedron
<i>C</i> TT	48(<i>h</i>)	Cd	3 Sm + 9 Cd	12	Icosahedron
<i>C</i> OT	16(<i>e</i>)	Sm	16 Cd	16	Kasper polyhedron
<i>C</i> CO	48(<i>h</i>)	Cd	4 Sm + 8 Cd	12	Icosahedron
Cluster D					
<i>D</i> CC	4(<i>d</i>)	Cd	4 Sm + 4 Cd	8	Cube
<i>D</i> IT	16(<i>e</i>)	Cd	3 Sm + 8 Cd	11	Cube plus defect octahedron [CN 8 + (6–3)]
<i>D</i> OT	16(<i>e</i>)	Sm	16 Cd	16	Similar to Sm at <i>A</i> CC, see text
<i>D</i> OH	24(<i>g</i>)	Cd	4 Sm + 4 Cd	8	Cube
<i>D</i> CO	48(<i>h</i>)	Cd	3 Sm + 8 Cd	11	Defect cube plus defect octahedron [CN (8–1) + (6–2)]

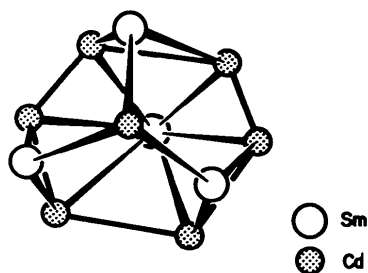


Fig. 5. Coordination polyhedron of Cd (*B OT*). The Cd atom in the centre is not shown.

and Cd (*D CO*) some atoms of the octahedron and/or of the cube are missing, the CN varying from 8 to 11.

Another group of 264 atoms, distributed on eight independent positions, contains CN 12 (icosahedron) and CN 16 Kasper polyhedra. These are usually found in the 29-atom clusters *B* and *C*. Cd (*B TT*), Cd (*C TT*) and Cd (*C CO*) are icosahedrally coordinated and the polyhedra around Sm (*A CO*) and Cd (*B CO*) can also be described as deformed icosahedra with one pentagonal face centred by a pair of Cd, the atom centring the other pentagonal face being lost. Sm (*B CC*) and Sm (*C OT*) both have a CN 16 Kasper polyhedron, which consists of a truncated tetrahedron of 12 Cd atoms plus a tetrahedral group of four Cd atoms lying above the centres of the hexagonal faces. A similar environment is found for Cd (*C CC*) except that the four Cd above the hexagonal faces are replaced by Sm.

Finally, 16 Cd atoms in position *B OT* have a CN 11 polyhedron of a new kind shown in Fig. 5. It can be derived from a truncated tetrahedron, if one triangular face is replaced by a vertex. This gives a figure with three triangular faces, three nearly planar pentagonal faces and one hexagonal face. The coordination is completed by another Sm atom emerging from the hexagonal face.

The same coordination polyhedra as in $\text{Sm}_{11}\text{Cd}_{45}$ are also found in other structures of the Cd-rich rare-earth-cadmium systems, where geometrical factors play an important role and where good space-filling is obtained. A cube plus an octahedron is the coordination figure around rare-earth atoms in $R\text{Cd}_3$ compounds with the orthorhombic ErCd_3 structure type (Fornasini & Merlo, 1972); icosahedra are present around some Cd atoms in the phases $\text{EuCd}_{3.6}$ and $\text{YbCd}_{3.6}$ with $\text{GdAg}_{3.6}$ type (Palenzona, 1971), also in $R_{13}\text{Cd}_{58}$ compounds with $\text{Pu}_{13}\text{Zn}_{58}$ type (Bruzzzone, Fornasini & Merlo, 1973) and $R\text{Cd}_6$ compounds with YCd_6 type (Larson

& Cromer, 1971); CN 16 Kasper polyhedra are present around the rare-earth atoms in $R\text{Cd}_6$ compounds with YCd_6 type and in YbCd_2 with MgZn_2 structure type (Iandelli & Palenzona, 1968).

References

- ARNBERG, L., JONSSON, A. & WESTMAN, S. (1976). *Acta Chem. Scand. Ser. A*, **30**, 187–192.
- ARNBERG, L. & WESTMAN, S. (1978). *Acta Cryst. A* **34**, 399–404.
- 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. B* **33**, 30–36.
- BRADLEY, A. J. & JONES, P. (1933). *J. Inst. Met.* **51**, 131–162.
- BRANDON, J. K., PEARSON, W. B., RILEY, P. W., CHIEH, C. & STOKHUYZEN, R. (1977). *Acta Cryst. B* **33**, 1088–1095.
- BRUZZONE, G. & FORNASINI, M. L. (1974). *J. Less-Common Met.* **37**, 289–292.
- BRUZZONE, G., FORNASINI, M. L. & MERLO, F. (1970). *J. Less-Common Met.* **22**, 253–264.
- BRUZZONE, G., FORNASINI, M. L. & MERLO, F. (1973). *J. Less-Common Met.* **30**, 361–375.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst. A* **24**, 321–324.
- FLACK, H. D. (1975). *J. Appl. Cryst.* **8**, 520–521.
- FLACK, H. D. (1977). *Acta Cryst. A* **33**, 890–898.
- FORNASINI, M. L. & MERLO, F. (1972). *Acta Cryst. B* **28**, 3094–3096.
- IANDELLI, A. & PALENZONA, A. (1968). *J. Less-Common Met.* **15**, 273–284.
- LARSON, A. C. & CROMER, D. T. (1971). *Acta Cryst. B* **27**, 1875–1879.
- OBERTEUFFER, J. A. & IBERS, J. A. (1970). *Acta Cryst. B* **26**, 1499–1504.
- PALENZONA, A. (1971). *J. Less-Common Met.* **25**, 367–372.
- PEARSON, W. B., BRANDON, J. K. & BRIZARD, R. Y. (1976). *Z. Kristallogr.* **143**, 387–416.
- SAMSON, S. (1969). *Developments in the Structural Chemistry of Alloy Phases*, edited by B. C. GIessen, pp. 65–106. New York: Plenum.
- WESTMAN, S. (1972). *Crystallographic Studies on Gamma-Brass-Like Phases in Binary Alloy Systems*. A special report of *Chem. Commun. Univ. Stockholm*, 37 pp.
- XRAY system (1976). Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1977). *J. Appl. Cryst.* **10**, 73–74.
- ZALKIN, A. & RAMSEY, W. J. (1958). *J. Phys. Chem.* **62**, 689–693.