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$Al_{69}Ta_{39}$ – a new variant of a face-centred cubic giant cell structure

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Abstract

The structure of $Al_{69}Ta_{39}$, cF432, $a = 1915.3(10)$ pm, $F\bar{4}3m$, $Z = 4$, 38 variables, was determined from 523 X-ray intensities of a single crystal with $I > 3\sigma(I)$ and refined to $wR(I) = 0.050$. $Al_{69}Ta_{39}$ represents a new structure type composed of four compositionally and three topologically distinct metal atom clusters as present in α-Mn-, γ-brass- and $Cd_{45}Sm_{11}$-type structures. The compositions of the clusters range from $Al_{10}Ta_{16}$ to $Al_{23}Ta$. Deviations from the crystallographic composition $Al_{72}Ta_{39}$ are due to 50% occupation of one Al site. Eleven out of 17 primary coordination polyhedra are of the Frank–Kasper type. The remaining polyhedra can also be considered as being exclusively terminated by triangulated faces. They are either of b.c.c. type or they combine features of both Frank–Kasper and b.c.c. coordinations.

1. Introduction

Although the phases of the Al–Ta system have been the subject of several investigations [1–9], only two phases in the neighbourhood of the elemental constituents have been characterized structurally so far, namely Al_3Ta of Al_3Ti-type structure [1] and the Ta-rich phase $AlTa_2$ adopting a σ-CrFe-type structure [2]. The information about the lattice symmetries of further intermediate phases is conflicting [3, 4, 6]. Just recently we performed a combined X-ray and electron diffraction study which proved that the symmetry of the phase which has been termed $Al_{17}Ta_{12}$ [3], Al_3Ta_2 [4, 6] or Al_2Ta [8] is face-centred cubic [9].

In 1965 Raman already presumed that the large cubic cell of the phase which he named $Al_{17}Ta_{12}$ arises from an α-Mn- or γ-Cu_5Zn_8-type superstructure [3]. F.c.c. phases with comparable lattice constants of about 2 nm are *e.g.* $Cu_{41}Sn_{11}$, cF416, forming a γ-brass superstructure [10], $Mg_{44}Rh_7$, cF408 [11] and $Cd_{45}Sm_{11}$, cF448 [12]. The latter two materials contain atom clusters as present in α-Mn and γ-brass related structures. Since we were not able to interpret the powder X-ray diffractogram of the cubic phase on the basis of available structural data of giant cell structures, we made efforts to grow crystals of that phase in order to determine the structure from single-crystal X-ray intensities. Here we report the results of the single-crystal structure analysis of the phase, the composition of which turned out to be $Al_{69}Ta_{39}$.

2. Sample preparation and crystal growth

The title phase can be synthesized by arc melting of the elements (Al 99.93%, Ta 99.9%; cold-pressed pellets of about 300 mg). According to Guinier photographs, as-cast samples of compositions $0.35 \leqslant x_{Ta} \leqslant 0.45$ always contained traces of Al_3Ta and/or σ-$AlTa_2$. Although the samples showed good crystallinity, no single crystals could be found. Annealing experiments at 1720 K led to monoclinic AlTa [9] by evaporation of aluminium [7]. Coarser material was obtained from ingots of Al_3Ta. The samples were wrapped in tantalum foil (99.9% Ta) and transferred into a Ta ampoule which was closed by welding. Subsequently reactions were performed in an induction furnace using a cyclic temperature programme, running 5 cycles of 3 min each in the temperature interval between 1720 and 1820 K. A Guinier photograph of the ingot showed that the cubic phase was formed. The Ta foil was mainly transformed into σ-$AlTa_2$ by reaction with evaporated Al.

3. Single-crystal X-ray structure analysis

The quality of several crystals was checked with a precession camera. The photograph of a single crystal

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of approximate size $50\times70\times80$ μm^3 mounted along a face diagonal confirmed the cubic F-type lattice and pointed to Laue symmetry $m\bar{3}m$. Possible space groups are $F432$ (No. 209), $F\bar{4}3m$ (No. 216) and $Fm\bar{3}m$ (No. 225) [13]. 5169 intensities were collected in a 2Θ range from 2° to 46° by a CAD4 automatic four-circle diffractometer in an ω–2Θ scan mode using Ag Kα radiation (50 kV, 26 mA). The lattice parameter determined from 25 reflections is $a = 1915.3(10)$ pm. The orientation matrix was controlled every 600 reflections. ψ scans for four reflections were carried out for empirical absorption correction.

Data reduction and absorption correction with the ψ scan data were performed with the program package SDP Plus [14]. Data averaging in space groups $Fm3m$ (No. 225), $Fm3$ (No. 202) and $F\bar{4}3m$ (No. 216) led to internal $R_i(I)$ of 0.064, 0.063 and 0.061 for 524, 840 and 977 independent, observed and accepted reflections respectively. Therefore a structure of Laue symmetry $m\bar{3}m$ was assumed. For reasons given below, space group $F\bar{4}3m$ was finally chosen for the structure refinement. Including anomalous dispersion effects, 523 intensities ($I > 3\sigma(I)$) were used to refine 38 variables.

Since we could not derive a structural model using Patterson or direct methods of the program SHELX76 [15], we attempted to develop a model on the basis of known structural data assuming that Ta atoms occupy only sites with coordination numbers CN > 12. Following Raman's idea from 1965 of an α-Mn superstructure, the α-Mn structure [16] was analysed in terms of coordination numbers. It can also be described using the cluster concept developed by Bradley and Jones [17]. The term "cluster" used here should not be mistaken for the idea of isolated metal atom clusters because of the close packing in intermetallics. Thereafter α-Mn consists of one sort of cluster of point symmetry $\bar{4}3m$ built of nested units. It is composed of a central atom at a site labelled CC which has CN 16. Twelve atoms with CN 12 form a truncated tetrahedron (site TT) and four atoms with CN 16 which are located above the hexagonal faces of TT build an outer tetrahedron (site OT) about CC. Finally 12 additional atoms with CN 13 positioned at the vertices of a cubo-octahedron (site CO) complete the cluster (see Fig. 3(a)). This cluster of 29 atoms is located at 0 0 0 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ in a cI58 cell. The tendency of the distribution of Al and Ta atoms on sites of different CNs is known for σ-$AlTa_2$, with Al occupying sites of CN 12 and Ta with CN 14 and 15 positions [2]. If the sites in α-Mn with CNs 13 and 16 were occupied by Ta and those with CN 12 by Al, the composition would be $Al_{17}Ta_{12}$. A corresponding decoration is realized in the structure of the χ phase $Al_{12}Mg_{17}$ [18].

In order to generate a structural model, the atom positions of α-Mn were transformed according to the following group–subgroup relations: $I\bar{4}3m$ (cI58) $\xrightarrow{-k2} P\bar{4}3m$ (cP58) $\xrightarrow{-k2;\ 2a,\ 2a,\ 2a} F\bar{4}3m$ (cF464). Whereas in the body-centred cell the sequence of clusters along [111] is AA, it is AB in the primitive cell and $ABCD$ in the face-centred cell. Thus four distinct clusters, termed A, B, C and D with centres at 0 0 0, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ respectively, are generated (see Fig. 1). As a starting model the respective sites with CNs 16 and 13, *i.e.* CC, OT and CO for clusters A to D, were occupied by Ta atoms. The program SDP Plus refined this model to $R(F) = 0.14$. Strikingly, the displacement parameters of the Ta atoms at site CC in cluster C, site OT in cluster D and sites CO in clusters B and D increased drastically. The atoms at these sites were removed. Difference Fourier synthesis using the program SHELX76 [15] yields the Al atoms of another nine sites, among them again CO of clusters B and D and OT of cluster D, but no noticeable electron density at CC of cluster C was observed. During the refinement a non-Poisson weighting scheme $w' = 1/\sigma(F)^2$ was used. After applying an additional weighting scheme $w = w' \exp[r(\sin\Theta/\lambda)^2]$ with $r = 0.2$ nm^2 [19], the structure refinements converged at $R(F) = 0.039$, $wR(F) = 0.025$ and $R(I) = 0.059$, $wR(I) = 0.050$. Table 1 contains the crystallographic data. Table 2 lists the final positional and isotropic displacement parameters of the 17 crystallographically different atoms. In cluster D the displacement parameters of the two tetrahedra IT and OT forming a cube (Al6 and Al7) were constrained; OH (Al8) is occupied only by 50% Al. Other types of disorder are observed for *e.g.* Pt_3Zn_{10} [20] and (Fe, Ni)$Zn_{6.5}$ [21].

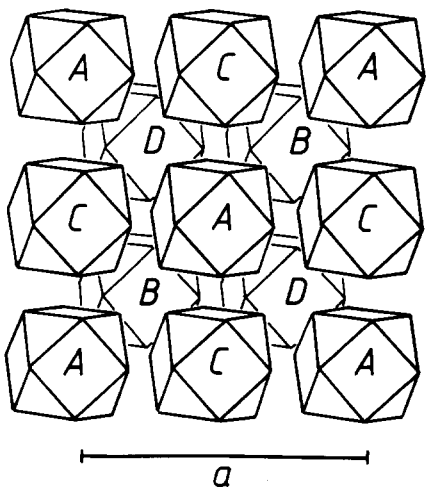


Fig. 1. Arrangement of cluster types A, B, C and D in the approximately 2 nm f.c.c. cell; the clusters are represented by cubo-octahedra.

TABLE 1. Crystallographic data for $Al_{69}Ta_{39}$

Chemical formula	$Al_{69}Ta_{39}$
Molar mass	8918.7 g mol^{-1}
Number of formula units, Z	4
Space group	$F\bar{4}3m$ (No. 216)
a	1915.3(10) pm
Volume V	$7026.0(6)\times10^6$ pm^3
Density ρ_x	8.43 g cm^{-3}
Radiation, λ	Ag Kα, 56.083 pm
Mass absorption coefficient μ	344.4 cm^{-1}
Crystal size	$0.05\times0.07\times0.08$ mm^3
2Θ range	2°–46°
Measured reflections	$+h, +k, +l; -h, -k, -l$
Number of observations	5169
of asymmetric unit	977
with $F_o^2>3\sigma(F_o^2)$	523
$R_i(F)$, $R_i(F^2)$	0.041, 0.061
Number of variables	38
Weighting schemes	$w'=1/\sigma(F^2)$
	$w=w'\exp[r(\sin\Theta/\lambda)^2]$ with $r=0.2$ nm^2
$R(F)$, $R(F^2)$	0.039, 0.059
$Rw(F)$; $Rw(F^2)$	0.025, 0.050
Difference electron density $\Delta\rho$	10.3×10^{-6} e pm^{-3}

Counting all sites, the number of atoms per unit cell is 444; the crystallographic composition is $Al_{72}Ta_{39}$. However, since site OH of cluster *D* (Al8) is only half occupied, the Pearson symbol is cF432. Thus the chemical formula is $Al_{69}Ta_{39}$ if we neglect a phase width due to possible mutual Al–Ta substitution at some sites with CN < 16.

As seen from Table 3, there is a conspicuously short interatomic distance of 240 pm between Al1 and Al3 compared with the shortest d(Al–Al) of 264 pm in σ-$AlTa_2$ and 286 pm in f.c.c. Al. Notice that comparable close contacts are also observed in the parent structure α-Mn [16] and the derived carbide $Yb_{10+x}Mn_{13-x}C_{18}$ [22]: Mn atoms at site TT are 226 or 223 pm apart respectively. This is about 17% shorter than the distance Mn–Mn in f.c.c. manganese [23]. Alternative refinements in space group $F23$ (No. 196) with uncoupled parameters for both Al1 and Al3 (48*h*, *xxz* in $F\bar{4}3m$—$t2\rightarrow 48h, xyz$ in $F23$) did not result in a significant change in that distance. Least-squares refinements in space group $F23$ assuming merohedral twinning with twinning elements $m\|e.g.$ [110] (SHELXL92 [24]) did not alter the distance either.

4. Powder X-ray diffraction

A powder diffractogram of an arc-melted sample containing the cubic phase ($a=1916.09(2)$ pm) and traces of Al_3Ta was recorded stepwise in increments of 0.02° in the 2Θ range 6°–115° with use of a PW 1050/25 (Philips, Eindhoven, Netherlands). The positional parameters of the derived structural model were used to start a Rietveld refinement [25]. The refinements converged at $R_I=0.043$ for $Al_{69}Ta_{39}$ and 0.078 for Al_3Ta. The agreement factors for the profile are $R_P=0.079$ and $R_{P,w}=0.112$ with $w=1/\sigma^2$. Shifts in the positional parameters gave rise to changes in the interatomic distances of less than 10 pm. Figure 2 shows the measured, calculated and difference diffractograms.

TABLE 2. Atomic coordinates and equivalent isotropic displacement parameters of $Al_{69}Ta_{39}$, space group $F\bar{4}3m$ (No. 216)

Cluster	Site	Atom	x	y	z	B (10^4 pm^2)
A	CC (4*a*)	Ta1	0	0	0	0.36(4)
	TT (48*h*)	Al1	0.0472(3)	0.0472(3)	0.1411(4)	0.2(1)
	OT (16*e*)	Ta2	0.9119(1)	0.9119(1)	0.9119(1)	0.81(2)
	CO (48*h*)	Ta3	0.18494(4)	0.18494(4)	0.0064(1)	0.63(1)
B	CC (4*c*)	Ta4	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0.34(4)
	TT (48*h*)	Al2	0.2963(4)	0.2963(4)	0.3974(6)	1.2(1)
	OT (16*e*)	Ta5	0.1564(1)	0.1564(1)	0.1564(1)	0.33(1)
	CO (48*h*)	Al3	0.4244(3)	0.4244(3)	0.2597(4)	0.3(1)
C	IT (16*e*)	Al4	0.555(1)	0.555(1)	0.555(1)	1.4(3)
	OT (16*e*)	Ta6	0.4066(1)	0.4066(1)	0.4066(1)	0.19(2)
	OH (24*f*)	Al5	0.6641(1)	$\frac{1}{2}$	$\frac{1}{2}$	1.0(1)
	CO (48*h*)	Ta7	0.65603(4)	0.65603(4)	0.5274(1)	0.49(1)
D	CC (4*d*)	Ta8	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	0.51(4)
	IT (16*e*)	Al6	0.825(1)	0.825(1)	0.825(1)	1.7(2)
	OT (16*e*)	Al7	0.667(1)	0.667(1)	0.667(1)	
	OH (24*g*)[a]	Al8	0.899(4)	$\frac{3}{4}$	$\frac{3}{4}$	1.7(5)
	CO (48*h*)	Al9	0.923(1)	0.923(1)	0.767(1)	1.6(1)

[a]Occupancy $f=50\%$.

TABLE 3. Interatomic distances (pm) of the first coordination sphere in $Al_{69}Ta_{39}$, including the first atom(s) of the second coordination sphere

Cluster *A*			Cluster *B*		
Ta1–Ta2	292.2(2)	4×	Ta4–Al2	309(1)	12×
Ta1–Al1	298.9(6)	12×	Ta4–Ta5	310.5(2)	4×
Ta1–Al9	492(2)	6×	Ta4–Al3	473.7(7)	12×
Al1–Al3	240(1)		Al2–Al2	251(1)	
Al1–Al1	254(1)	2×	Al2–Al3	260(1)	2×
Al1–Al1	256(1)		Al2–Al2	274(1)	2×
Al1–Ta3	288(1)	2×	Al2–Ta7	280(1)	
Al1–Ta2	289(1)	2×	Al2–Ta3	284(1)	2×
Al1–Ta1	289(1)		Al2–Ta6	299(1)	
Al1–Ta5	297(1)		Al2–Ta5	301(1)	2×
Al1–Al9	301(2)	2×	Al2–Ta4	309(1)	
Al1–Al5	394(1)		Al2–Al8	410(2)	
Ta2–Al9	279(2)	3×	Ta5–Al3	295.0(7)	3×
Ta2–Al6	288(2)		Ta5–Al1	297.2(7)	3×
Ta2–Al1	289(1)	6×	Ta5–Ta3	297.5(3)	3×
Ta2–Ta1	292.2(2)		Ta5–Al2	301.0(9)	6×
Ta2–Ta3	318.6(2)	3×	Ta5–Ta4	310.5(2)	
Ta2–Al8	439(5)	3×	Ta5–Al2	479(1)	3×
Ta3–Al8	271(4)		Al3–Al1	240(1)	
Ta3–Al9	277(2)	2×	Al3–Al5	251.4(7)	
Ta3–Al2	284(1)	2×	Al3–Al2	260(1)	2×
Ta3–Al3	286.2(6)	2×	Al3–Ta6	285.4(8)	
Ta3–Al1	287.6(6)	2×	Al3–Ta3	286.2(6)	2×
Ta3–Ta5	297.5(3)		Al3–Ta5	295.0(7)	
Ta3–Ta7	316.2(2)	2×	Al3–Al9	297(2)	2×
Ta3–Ta2	318.6(2)		Al3–Ta7	297.8(7)	2×
Ta3–Al6	348(2)				
Ta3–Ta3	352.4(2)		Al3–Al1	402.7(9)	
Ta3–Al7	438(2)	2×			

Cluster *C*			Cluster *D*		
Al4–Al5	257(2)	3×	Ta8–Al6	249(2)	4×
Al4–Ta7	279(2)	3×	Ta8–Al7	275(2)	4×
Al4–Al4	298(3)	3×	Ta8–Al8	285(1)	6×
Al4–Ta6	303(2)	3×			
Al4–Al7	372(3)		Ta8–Al9	470(2)	12×
Ta6–Al3	285(4)	3×	Al6–Al8	248(5)	3×
Ta6–Al5	286.9(2)	3×	Al6–Ta8	249(2)	
Ta6–Ta7	286.9(3)	3×	Al6–Al9	288(3)	3×
Ta6–Al2	299(1)	3×	Al6–Ta2	288(2)	
Ta6–Al4	303(2)	3×	Al6–Al7	303(3)	3×
			Al6–Ta3	348(2)	3×
Ta6–Al9	467(2)	6×			
			Al6–Al6	406(3)	3×

(*continued*)

TABLE 3. (*continued*)

Cluster *C*			*Cluster D*		
Al5–Al3	251.4(7)	2×	Al7–Al8	258(5)	3×
Al5–Al4	257(2)	2×	Al7–Ta7	269(2)	3×
Al5–Ta6	286.9(2)	2×	Al7–Ta8	275(2)	
Al5–Al9	287(2)	2×	Al7–Al6	303(3)	3×
Al5–Ta7	303.8(2)	4×	Al7–Al9	310(3)	3×
Al5–Al1	394.3(6)	2×	Al7–Al4	372(3)	
Ta7–Al7	269(2)		Al8–Al6	248(5)	2×
Ta7–Al9	278(2)	2×	Al8–Al7	258(2)	2×
Ta7–Al4	279(2)		Al8–Ta3	271(6)	2×
Ta7–Al2	280(1)		Al8–Ta8	285(8)	
Ta7–Ta6	286.9(3)		Al8–Ta7	291(4)	2×
Ta7–Al8	291(5)		Al8–Al9	336(2)	4×
Ta7–Al3	297.8(7)	2×			
Ta7–Al5	303.8(3)	2×	Al8–Al8	404(8)	
Ta7–Ta3	316.2(2)	2×			
Ta7–Ta7	348.4(2)	2×	Al9–Ta3	277(2)	2×
			Al9–Ta7	278(2)	2×
Ta7–Al6	431(2)	2×	Al9–Ta2	279(2)	
			Al9–Al5	287(2)	
			Al9–Al6	288(3)	
			Al9–Al3	297(2)	2×
			Al9–Al1	301(2)	2×
			Al9–Al7	310(3)	
			Al9–Al8	336(2)	2×
			Al9–Al4	410(3)	

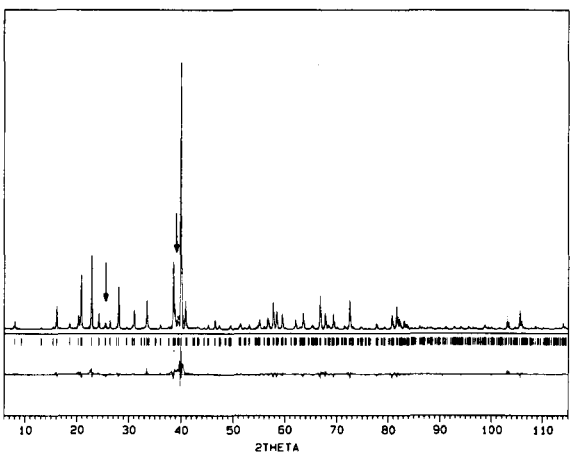
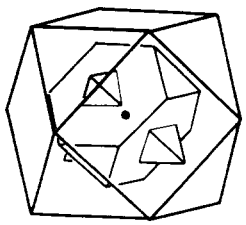


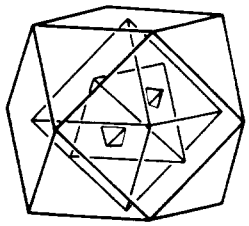
Fig. 2. Two-phase Rietveld analysis of $Al_{69}Ta_{39}$ and Al_3Ta (traces, strongest intensities indicated by arrows): powder diffractogram and difference plot.

5. Structure description by a cluster concept

It is a proven method [17] to elucidate the architecture of such a complex structure in terms of 24–29-atom clusters aligned along the threefold axes. As seen from Table 1, clusters *A* and *B* are of the point set combination CC, TT, OT, CO which is characteristic for α-Mn-type clusters, whereas cluster *C*, built up by IT, OT, OH



(a)



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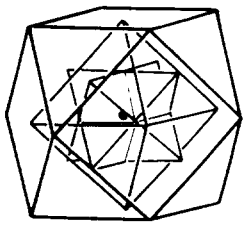

(c)

Fig. 3. Idealized cluster types *A*, *B*, *C* and *D* in $Al_{69}Ta_{39}$: (a) *A*, *B*, α-Mn, sequence of sites CC, IT, TT, CO; (b) *C*, γ-Cu_5Zn_8, sequence of sites IT, OT, OH, CO; (c) *D*, $Cd_{45}Sm_{11}(A)$, sequence of sites CC, IT, OT, OH, CO.

and CO sites, is of the γ-brass type. Cluster *D* (CC, IT, OT, OH, CO) shows features of one sort of clusters found in $Cd_{45}Sm_{11}$, namely *A* and *D*; Fornasini *et al.* [12] termed this cluster $Li_{22}Si_5$. Nesper and von Schnering, however, found that the centres (site CC) of all four clusters in the silicide are empty, resulting in the composition $Li_{21}Si_5$ [26]. Therefore we name the fully occupied cluster *D* of $Al_{69}Ta_{39}$ $Cd_{45}Sm_{11}(A)$. In contrast with *e.g.* $Li_{21}Si_5$ [26] or $Cu_{41}Sn_{11}$ [10] which are composed of clusters of a single type (γ-brass) but with different atomic distributions, $Al_{69}Ta_{39}$ contains, like Os_7Sc_{44} [27] or $Cd_{45}Sm_{11}$ [12], clusters of different types and compositions. The unique sequence of clusters along the threefold axis is (the local composition is given in parentheses): *A*, α-Mn ($Al_{17}Ta_{12}$); *B*, α-Mn′ ($Al_{24}Ta_5$); *C*, γ-Cu_5Zn_8 ($Al_{10}Ta_{16}$); *D*, $Cd_{45}Sm_{11}(A)$ ($Al_{23}Ta$) (see Fig. 3). Therefore $Al_{69}Ta_{39}$ represents a new structure type in the row of approximately 2 nm f.c.c. giant cell structures.

6. Structure description by an extended Frank–Kasper concept

A more detailed description of the structure is based on the coordination polyhedra of the 17 crystallographically distinct atoms. A fruitful concept to rationalize coordination configurations in several structurally complex intermetallic phases was developed by Frank and Kasper [28]. An important aspect of the concept is that a close packing of atoms represented by hard spheres of similar size is achieved in so-called tetrahedrally close-packed (t.c.p.) structures. Here all atoms are arranged to slightly distorted tetrahedra which fill space completely. As a consequence of such a packing, atoms of the first coordination shell of each atom form polyhedra which are exclusively terminated by triangulated faces. The analysis of possible coordination polyhedra was limited to configurations with coordinating atoms S_q having surface coordination numbers $q=5$ and 6. Applying Euler's theorem to such triangulated convex polyhedra leads to two restrictions concerning the number v_q of S_q atoms of the first coordination shell of coordination number *Z*:

$$v_5 = 12, \qquad Z - v_6 = 12 \tag{1}$$

The four well-known Frank–Kasper (FK) polyhedra ($Z=12$, 14, 15, 16) follow from these relations. Frank and Kasper did not rule out the possibility of S_4 atoms in t.c.p. structures, but they did not include this surface coordination in their analysis. Taking S_4 atoms additionally into account leads to the relations

$$2v_4 + v_5 = 12, \qquad 2Z - v_5 - 2v_6 = 12 \tag{2}$$

Equations (2) contain the relations of the more constrained case $v_4=0$. Interestingly, from this point of view the CN 14 polyhedron taken from the b.c.c. structure can be considered as t.c.p.: $v_4=6$, $v_5=0$, $v_6=8$, $Z=14$. Subsequently we shall show that relation (2) holds for all coordination configurations occurring in $Al_{69}Ta_{39}$ as long as defects at the Al8 position are disregarded.

The coordination polyhedra about the 17 distinct atoms are depicted in Figs. 4–7. Fragments of distorted cubes which are reminiscent of a b.c.c. coordination are emphasized by bold lines. Characteristic data of the coordination polyhedra are listed in Table 4. The frequencies of the various surface atoms S_q fulfil the relations of t.c.p. structures composed of S_4, S_5 and S_6 atoms. Eleven polyhedra are of the FK type, among them Ta1, Ta4 and Ta5 ($Z=16$), Ta6 and Ta7 ($Z=15$), Ta2 ($Z=14$) and Al1–Al5 ($Z=12$). The configurations of Ta8 and Al6 are of b.c.c. type with $Z=14$; the remaining four (Ta3 and Al7–Al9) exhibit hybrids of b.c.c. and FK polyhedra.

The topological distinction of regions of FK-type-coordinated atoms and of atoms showing b.c.c-type-affected coordination polyhedra is reflected in the unusually high Al content of cluster *D*. Ta8 at the centre of cluster *D*, which is exclusively surrounded by Al atoms, is the core of b.c.c.-related coordinations. The

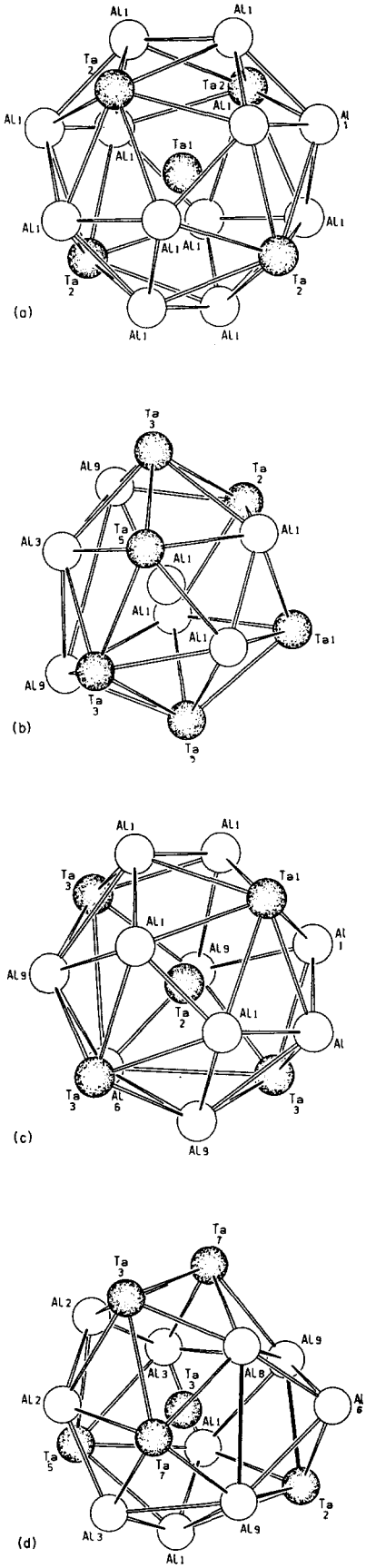

Fig. 4. Coordination polyhedra about atoms of cluster *A*.

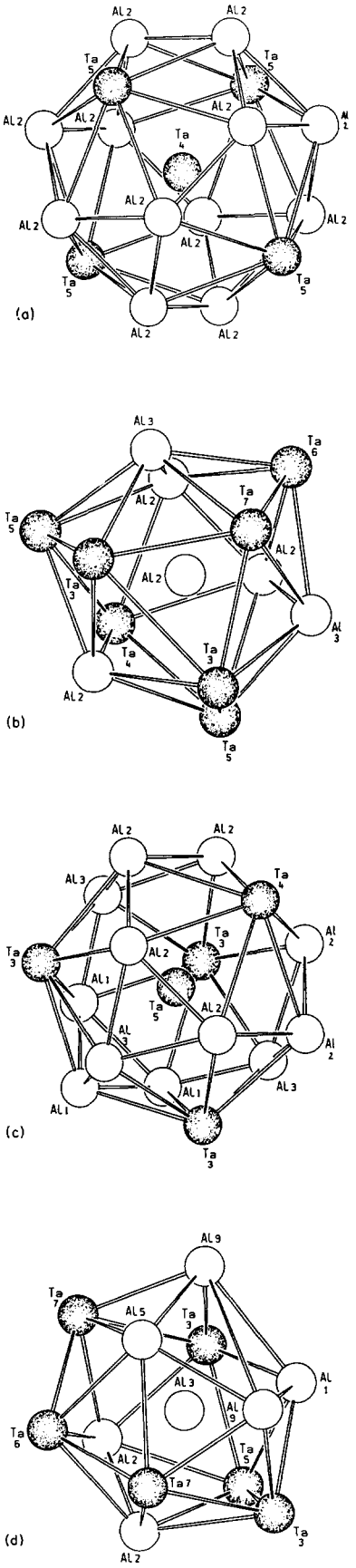

Fig. 5. Coordination polyhedra about atoms of cluster *B*.

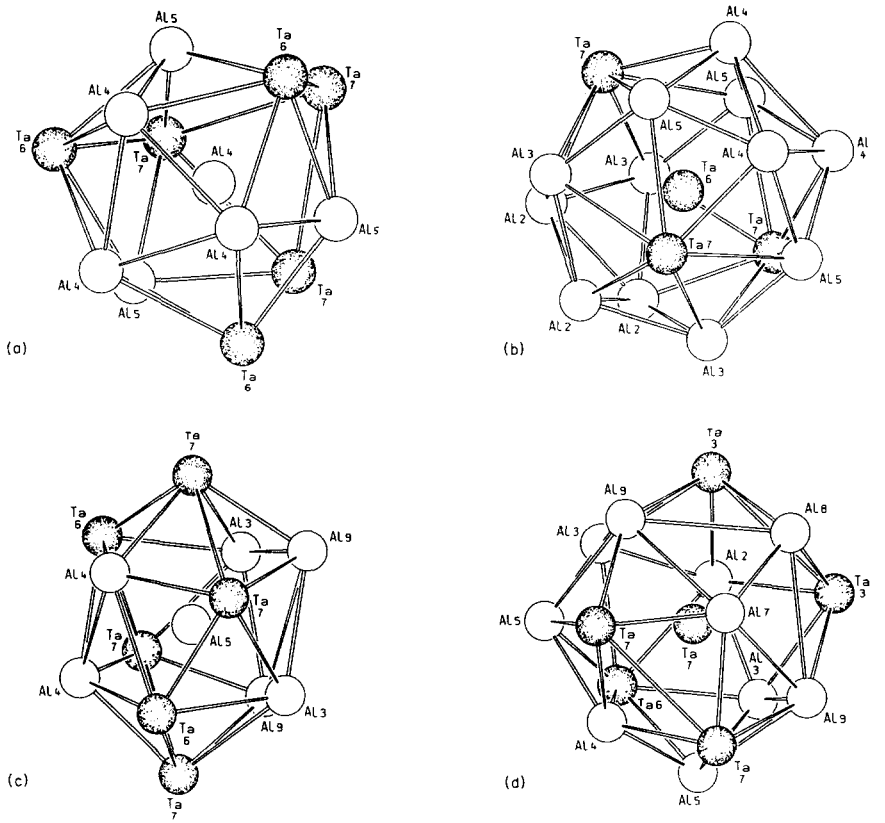

Fig. 6. Coordination polyhedra about atoms of cluster *C*.

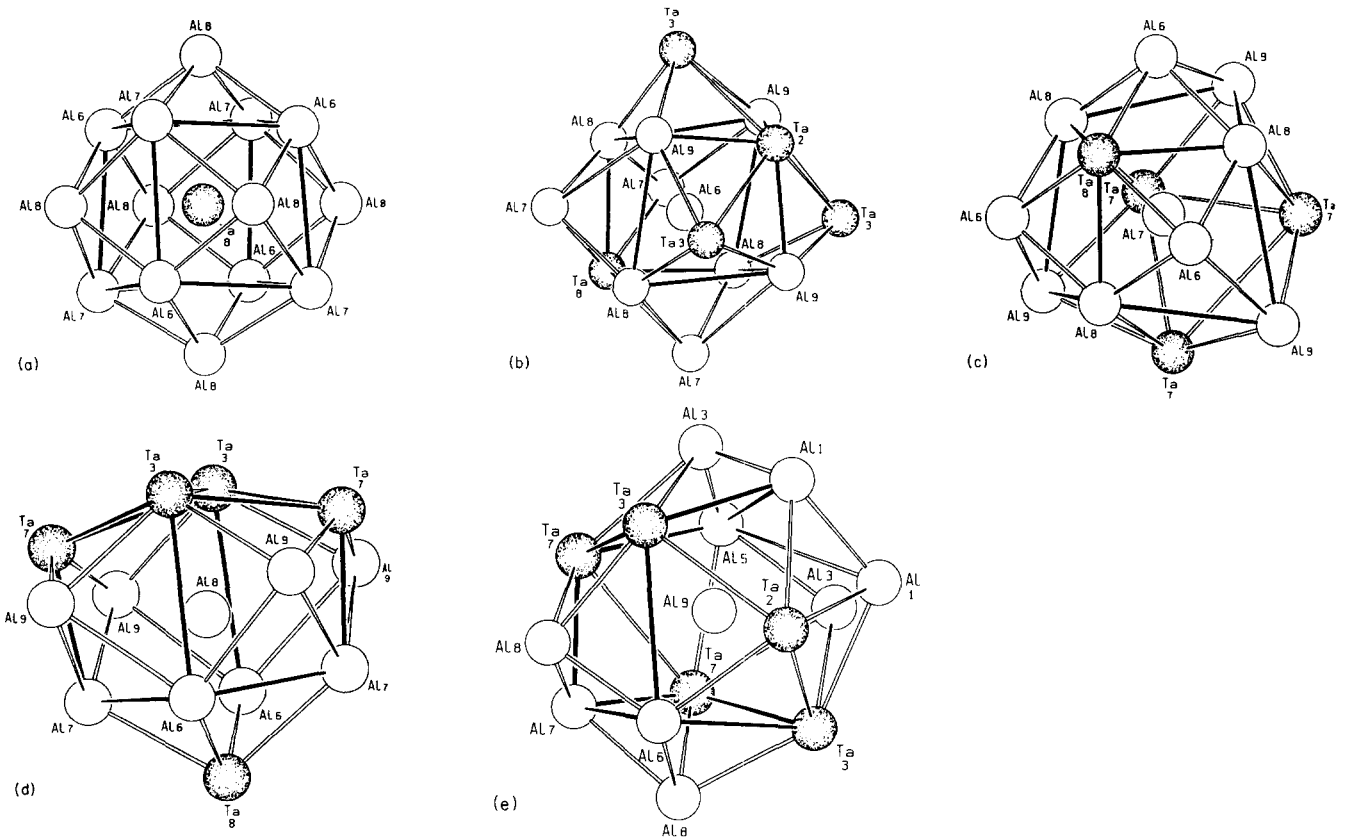

Fig. 7. Coordination polyhedra about atoms of cluster *D*.

TABLE 4. Coordination numbers, frequency of surface coordination numbers and mean distances central atom–coordination shell (pm) for $Al_{69}Ta_{39}$

Cluster	Atom	Z (=CN)	v_4	v_5	v_6	$\langle d \rangle$ (pm)
A	Ta1	16	0	12	4	297
	Al1	12	0	12	0	279
	Ta2	14	0	12	2	293
	Ta3	15	1	10	4	299
B	Ta4	16	0	12	4	309
	Al2	12	0	12	0	281
	Ta5	16	0	12	4	299
	Al3	12	0	12	0	279
C	Al4	12	0	12	0	284
	Ta6	15	0	12	3	292
	Al5	12	0	12	0	282
	Ta7	15	0	12	3	300
D	Ta8	14 (11)	6	0	8	272
	Al6	14	6	0	8	293
	Al7	13	3	6	4	284
	Al8	13	5	2	6	290
	Al9	14	4	4	6	296

mean distances between central and peripheral atoms show the expected dependence on the number of nearest neighbours. The value for Ta8 (272 pm) is too small but can be rationalized by the 50% occupancy of the site of Al8, leading to a reduction in the coordination number from 14 to 11.

It is interesting to notice the mutual influence of neighbouring clusters on the local coordination. Whereas the distinct sites (CC, TT, OT, CO) of the α-Mn clusters originally have CNs 16, 12, 16, 13, these are changed to 16, 12, 14, 15 and 16, 12, 16, 12 for clusters *A* and *B* in $Al_{69}Ta_{39}$ respectively. The sites IT, OT, OH and CO of γ-brass of original CNs 12, 12, 13, 13 are altered to 12, 15, 12, 15 for cluster *C* in $Al_{69}Ta_{39}$. The interaction between the clusters is "constructive" in the sense that all atoms of clusters *B* and *C* reach FK coordinations. This is not completely true for all atoms of cluster *A*, since Ta3 has one S_4 atom (Al6) in its coordination. Al6 provides the link to cluster *D*, which is built up of atoms which all have several S_4 atoms in their coordination shells.

7. Conclusions

According to an X-ray crystal structure analysis, the composition of the cubic phase in the Al–Ta system hitherto called Al_2Ta, $Al_{17}Ta_{12}$ or Al_3Ta_2 is $Al_{69}Ta_{39}$, Pearson symbol cF432. Small deviations from this composition due to marginal mutual substitution at some sites with coordination numbers less than 16 seem possible.

$Al_{69}Ta_{39}$ represents a new type of approximately 2 nm f.c.c. giant cell structure. It is composed of three topologically distinct clusters similar to those in α-Mn, γ-Cu_5Zn_8 and $Cd_{45}Sm_{11}$.

The structure of $Al_{69}Ta_{39}$ can be regarded as a modified Frank–Kasper phase which is disturbed by partly disordered regions of high Al content. In these regions some coordinating atoms have surface coordination number four. Since all atoms have triangulated coordination shells, the local requirement for a description of the structure in terms of completely space-filling tetrahedra is fulfilled.

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