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T-Phase $Al_{18}Mg_3Mn_2$

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Abstract

A complete structure determination of the ternary alloy *T*-phase $Al_{18}Mg_3Mn_2$ has been carried out and has confirmed that the *T* phase has a similar structure to that of *E*-phase $Al_{18}Cr_2Mg_3$ [Samson (1958). *Acta Cryst.* **11**, 851–857].

Comment

In phase-diagram studies of the Al-rich part of the Al–Mg–Mn system (Ohnishe Nakatani & Shimizu, 1973), the *T* phase was found to have a very similar powder diffraction pattern to that of the *E* phase. The crystal structure of the *E* phase has been determined successfully by Samson (1958) using a single-crystal multiple-film method. Since the computed powder diffraction intensities based on Samson's parameters for the *E* phase were in close agreement with the observed powder diffraction intensities, Ohnishe *et al.* (1973) concluded that the *T* phase was also *F*-centred cubic with a lattice constant $a = 14.529(1)$ Å, space group $Fd\bar{3}m$, and basic composition $Al_{18}Mg_3Mn_2$. This paper reports the single-crystal structure analysis of the *T* phase.

In the diamond space group, $Fd\bar{3}m$, there are two sets of eight equivalent positions [8(*a*) and 8(*b*)] which are related by a translation of $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ with respect to one another. The Mg atoms located at position 8(*b*) are surrounded by 16 nearest neighbours: 12 Al atoms [position 96(*g*)] at the vertices of a truncated tetrahedron and four Mg atoms [position 16(*d*)] at the vertices of a regular tetrahedron. The coordination polyhedron of each Mg 8(*b*) atom may be described by a Friauf polyhedron (Friauf, 1927) with 16 vertices and 28 triangular faces (Fig. 1). These 17-atom polyhedra (Friauf polyhedra) link tetrahedrally by sharing the Mg 16(*d*) atoms. From the atomic arrangement just described, it is clear that there are large interstices with their centroids at the position 8(*a*), the second set of eight equivalent positions. In the *T* phase all of these interstices are filled with cubic close-packed 10-atom clusters comprising six Al atoms [position 48(*f*)] and four Mn atoms [position 16(*c*)]. Each 10-atom cluster has six Al 48(*f*) atoms situated at the vertices of a regular octahedron which is in turn surrounded by four Mn 16(*c*) atoms at the vertices of a regular tetrahedron (Fig. 2). These 10-atom clusters with their centroids at position 8(*a*) are connected tetrahedrally through sharing the Mn 16(*c*) atoms.

In summary, the whole structure is composed of two different groups (Figs. 1 and 2), with each group bonded tetrahedrally to four groups of the same kind and surrounded by, but not bound to, four groups of the other kind. Thus, the whole structure consists of two intertwinning diamond lattices, one being formed by the Friauf polyhedra and the other by the 10-atom clusters. The coordination polyhedron of Mg 16(*d*) is an approximate hexagonal prism with two Mg 8(*b*) atoms on the pseudo-hexagonal axis. The coordination geometry of the Al 48(*f*) atoms may be described as a distorted pentagonal prism with ten atoms [six Al 96(*g*) and four Al 48(*f*) atoms] at the vertices and two Mn 16(*c*) atoms on the axis of this prism. Al atoms at position 96(*g*) adopt the same coordination as Al 48(*f*) but the prisms are more distorted. The coordination polyhedra around each Mn 16(*c*) atom are distorted icosahedra bound by 20

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equilateral triangular faces with six Al 48(*f*) atoms and six Al 96(*g*) atoms on the vertices.

All of the interatomic distances in the *T* phase are comparable with those in the *E* phase. The most significant difference in interatomic distances between these two alloys was observed for Al 48(*f*)—Al 48(*f*) [2.825 (2) Å in the *T* phase compared to 2.890 (13) Å in the *E* phase]. As for the *E* phase, the closest interatomic distance [Mn 16(*c*)—Al 48(*f*) 2.573 (1) Å] in the *T* phase was found in the icosahedra of Mn 16(*c*).

We conclude that the structure of the *T* phase is isomorphous with that of the *E* phase.

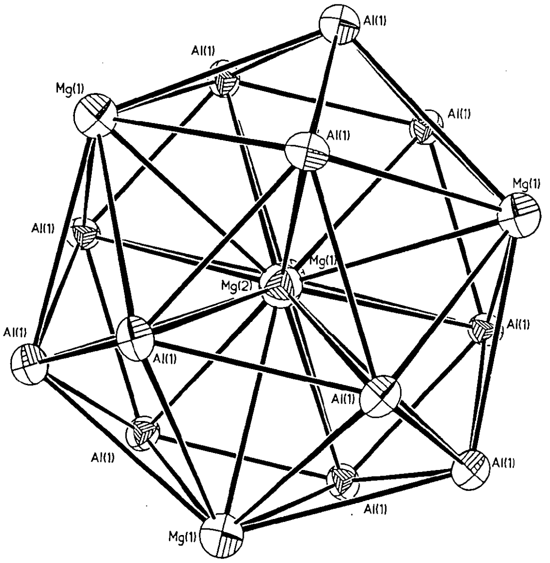

Fig. 1. *ORTEP* (Johnson, 1965) plot of the Friauf polyhedron showing the nearest neighbours of Mg 8(*b*). Displacement ellipsoids are shown at the 100% probability level.

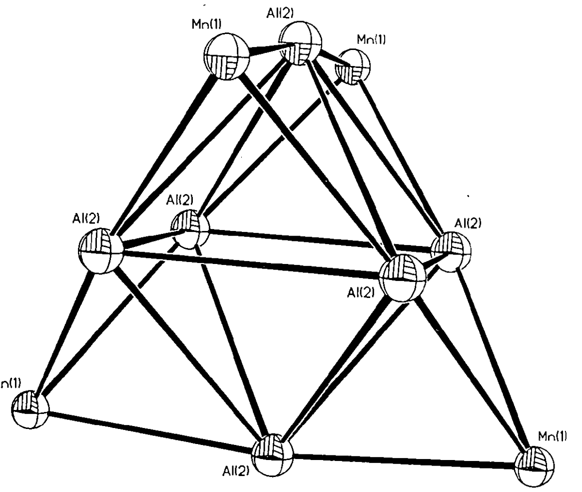

Fig. 2. *ORTEP* (Johnson, 1965) plot of the atomic arrangement of the 10-atom cluster, the centroid of which lies in position 8(*a*). Displacement ellipsoids are shown at the 100% probability level.

Experimental

The T phase is difficult to grow as the solubility of Mn in Al, Mg and Al-Mg alloys is low and a detailed phase diagram of the ternary Al-Mg-Mn system is not available. An Mn master alloy (Al-11 at. %, Mg-9 at. %) was prepared at about 1173 K using the available partial phase-diagram data for the ternary system Al-Mg-Mn. Be powder was added to prevent Mn and Mg from oxidation and Mg from volatilization. The Mn master alloy was grown in an alumina crucible (99.7% purity) under a protective argon atmosphere. The most stable *T* phase was found at 753.5 ± 6.5 K. *T*-phase crystals of optimum size for single-crystal X-ray analysis were grown successfully by the liquid-phase epitaxial method under oscillating heat treatment between 733 and 743 K over a minimum of 10 days. The crystals were then extracted from the ternary cast by electrolytic reaction in a dilute 1*N* HCl solution.

Crystal data

$Al_{18}Mg_3Mn_2$
$M_r = 668.5$
Cubic
$Fd\bar{3}m$
$a = 14.517$ (3) Å
$V = 3060$ (3) Å^3
$Z = 8$
$D_x = 2.902$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 31 reflections
$\theta = 7.5$-22.5°
$\mu = 2.786$ mm^{-1}
$T = 298$ K
Truncated octahedral shape
0.18 × 0.18 × 0.16 mm
Metallic grey

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans (2θ speed 5.33-29.30° min^{-1})
Absorption correction: empirical
$T_{min} = 0.272$, $T_{max} = 0.406$
1402 measured reflections
307 independent reflections
239 observed reflections [$F > 5\sigma(F)$]

$R_{int} = 0.0645$
$\theta_{max} = 32.5°$
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 21$
2 standard reflections monitored every 100 reflections intensity variation: 2.0%

Refinement

Refinement on *F*
$R = 0.0269$
$wR = 0.0267$
$S = 1.02$
239 reflections
17 parameters
$w = 1/[\sigma^2(F) + 0.00005F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}

Extinction correction: $F^* = F_c[1.0 + (0.002\chi \times F_c^2/\sin 2\theta)]^{-1/4}$
Extinction coefficient: $\chi = 0.00003$ (1)
Atomic scattering factors from *SHELXTL/PC* (Sheldrick, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

		x	y	z	U_{eq}
Mn(1)	16(*c*)	1/4	1/4	0	0.0105 (1)
Al(1)	96(*g*)	0.19195 (4)	*x*	0.82571 (6)	0.0139 (2)

Al(2)	48(*f*)	3/8	3/8	0.01258 (8)	0.0121 (3)
Mg(1)	16(*d*)	0	1/2	0	0.0170 (3)
Mg(2)	8(*b*)	1/8	5/8	1/8	0.0208 (5)

Table 2. *Selected geometric parameters* (Å)

Distorted icosahedron		
Mn 16(*c*)—	6 Al 96(*g*)	2.797 (1)
	6 Al 48(*f*)	2.573 (1)
	12	
Distorted pentagonal prism		
Al 96(*g*)—	2 Al 96(*g*)	2.746 (2)
	2 Al 96(*g*)	2.922 (1)
	1 Al 96(*g*)	2.749 (2)
	2 Al 48(*f*)	2.830 (1)
	1 Al 48(*f*)	2.720 (1)
	1 Mn 16(*c*)	2.797 (1)
	1 Mg 8(*b*)	3.222 (1)
	2 Mg 16(*d*)	3.112 (1)
	12	
Distorted pentagonal prism		
Al 48(*f*)—	2 Al 96(*g*)	2.720 (1)
	4 Al 96(*g*)	2.830 (1)
	4 Al 48(*f*)	2.825 (2)
	2 Mn 16(*c*)	2.573 (1)
	12	
Approximate hexagonal prism		
Mg 16(*d*)—	12 Al 96(*g*)	3.112 (1)
	2 Mg 8(*b*)	3.143 (1)
	14	
Friauf polyhedron (Fig. 1)		
Mg 8(*b*)—	12 Al 96(*g*)	3.222 (1)
	4 Mg 16(*d*)	3.143 (1)
	16	

Lorentz-polarization corrections were applied. Structure solution in space group $Fd\bar{3}m$ using direct methods located all the atomic positions and species correctly. The position with point symmetry $\bar{3}m$ was used as the origin of the atomic coordinate system in this structure solution instead of the position with point symmetry $\bar{4}3m$ used by Samson (1958). It was found that all the atomic positions obtained from this solution were equivalent to those derived in Samson's solution of the *E* phase with the position of Cr corresponding to Mn in our solution of the *T* phase. Final refinement of the structure was carried out using a full-matrix least-squares method. All calculations were performed using the *SHELXTL/PC* software system (Sheldrick, 1990).

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Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71742 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1077]

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$Nd_2(OH)_2(CrO_4)_2$ and $[Tb_2(CrO_4)_3(H_2O)_5].2H_2O$

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Abstract

The structures of neodymium hydroxide chromate and pentaaquaterbium(III) chromate dihydrate have been determined. Two kinds of Nd atoms, with different environments, are present in the structure of $Nd_2(OH)_2(CrO_4)_2$. The coordination polyhedron of the eight O atoms around the Nd atoms is a square antiprism. In $[Tb_2(CrO_4)_3(H_2O)_5].2H_2O$, the Tb atoms are nine-coordinated and are located in two types of site. The coordination polyhedra consist of both a tricapped trigonal prism and a monocapped square antiprism. In the two title compounds the CrO_4 groups are nearly regular tetrahedra, having mean Cr—O distances of 1.651 (7) and 1.650 (7) Å for $Nd_2(OH)_2(CrO_4)_2$ and $[Tb_2(CrO_4)_3(H_2O)_5].2H_2O$, respectively.

Comment

This work is part of a series of structural studies of lanthanoid chromates (Leppä-aho & Valkonen, 1991, 1992; Leppä-aho, 1993). At the moment six structures are known for rare-earth chromates: $[Ln_2(CrO_4)_3(H_2O)_5].2H_2O$ [Ln = Nd, Eu (Leppä-aho & Valkonen, 1991), La (Habekost, Christensen & Hazell, 1991) and Sm (Bueno, Parada, Monge & Ruiz-Valero, 1991*a*)]; $Ln_2(OH)_2(CrO_4)_2$ [Ln = Yb Leppä-aho & Valkonen, 1992), Er (Bueno, Parada, Monge & Ruiz-Valero, 1991*b*), Gd and Tb (Leppä-aho, 1993)]; $[Yb_2(OH)_2(CrO_4)_2(H_2O)_{2.5}].0.5H_2O$ (Leppä-aho & Valkonen, 1992); $La(OH)(CrO_4)$ (Bueno, Parada, Garcia, Puebla, Monge & Ruiz-Valero, 1989); $Ce(CrO_4)_2.2H_2O$ (Lindgren, 1977); $Ln_3(OH)(CrO_4)_4.3.5H_2O$ [Ln = La (Habekost, Christensen & Hazell, 1991), Pr and Nd (Leppä-aho, 1993)]. In the two title compounds, $[Tb_2(CrO_4)_3(H_2O)_5].2H_2O$ and $Nd_2(OH)_2(CrO_4)_2$, Tb has the highest and Nd the lowest atomic number known for this type of lanthanoid compound.

In the synthesis of $Nd_2(OH)_2(CrO_4)_2$, 264 mg of Nd_2O_3 was mixed with 4 cm^3 of 0.6 mol dm^{-3} H_2CrO_4; $[Tb_2(CrO_4)_3(H_2O)_5].2H_2O$ was synthesized by mixing 220 mg of Tb_4O_7 with 6 cm^3 of 0.3 mol dm^{-3} H_2CrO_4. The mixtures were put in a

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