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The Structure Analysis of the T_3(AlMnZn) Compound

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Of the three aluminium-rich intermetallic compounds, T_1, T_2 and T_3, which separate as primary constituents in the Al–Mn–Zn system, T_3 is shown to be structurally similar to $Ni_4Mn_{11}Al_{60}$ and $Cu_2Mn_3Al_{20}$, although it is T_1 which corresponds in composition and in electron concentration (*e/a*) with the latter two. In the final stage of the structure analysis of the T_3 compound, interatomic distances and the atomic environments had to be used as the criteria for determining the distribution of different atoms amongst some of the available sites. A possible explanation is given for the fixed composition of $Ni_4Mn_{11}Al_{60}$ and the varying composition of T_3.

1. Introduction

In an examination of the Al–Mn–Zn system in the range from 0 to 95 wt.% of zinc and from 0 to 3 wt.% of manganese, Raynor & Wakeman (1947) found three aluminium-rich ternary phases, T_1, T_2 and T_3, which may crystallize as primary constituents from slowly cooled alloys. The structures of these phases were not known. The ideal formula of the T_1 phase is $ZnMn_5Al_{24}$. Its composition can be related to those of $Ni_4Mn_{11}Al_{60}$ and $Cu_2Mn_3Al_{20}$; it was suggested that the formation of all three phases is controlled to a considerable extent by two factors:

(i) a ratio of four aluminium atoms to one atom of heavy element, and
(ii) the attainment of a definite electron-to-atom ratio.

Robinson (1952*a*, 1954) has solved the structure of the $Ni_4Mn_{11}Al_{60}$ compound and has shown that the basic structure of $Cu_2Mn_3Al_{20}$ is essentially the same as that of $Ni_4Mn_{11}Al_{60}$, but that the structure of T_1 is appreciably different, its unit-cell dimensions being related to, but different from, those of $Ni_4Mn_{11}Al_{60}$ and $Cu_2Mn_3Al_{20}$. In this paper it is shown that the structure of the ternary T_3 compound is essentially similar to that of $Ni_4Mn_{11}Al_{60}$, though its composition does not satisfy the above requirements for the formation of the compounds $Ni_4Mn_{11}Al_{60}$ and $Cu_2Mn_3Al_{20}$.

2. Preparation of crystals

For the preparation of alloys the following materials were used.

(i) pure zinc presented by the Imperial Smelting Corporation, Ltd., of Avonmouth. The major impurities are lead and cadmium, but both in quantity less than 0·0007%,
(ii) super-purity aluminium kindly presented by the British Aluminium Co. Ltd., and
(iii) aluminium–manganese master alloy containing 13·65 wt.% of manganese. The alloy was prepared from the super-pure elements by the British Aluminium Co. Ltd.

Ingots of about 50 g. were prepared by melting together in a sintered alumina crucible weighed-out quantities of aluminium and aluminium–manganese

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master alloy. While the alloy was thoroughly stirred, zinc was added gradually; in this way burning of zinc was prevented. The alloys cooled in the furnace at the rate of about 4 °C. per minute. Crystals were extracted by the electrolytic method described by Raynor & Wakeman (1947). The extracts from the ingots containing 1 wt.% of manganese and 9, 14 and 19 wt.% of aluminium consisted mostly of twinned crystals which were identified as the T_3 crystals.

Hand-sorted and cleaned crystals from the melt containing 14 wt.% of aluminium were analyzed both by the Admiralty Materials Laboratory (I), and by Messrs. Johnson, Matthey and Co. Ltd. (II), with the following results (in at.%):

	I*	II	Average
Zinc	15·8	15·6	15·7
Manganese	16·9	16·9	16·9
Aluminium	67·3	67·5	67·4

The analysis of T_3 crystals can be represented by either of the formulae $(\mathrm{Mn, Zn})\mathrm{Al}_{2.06}$ and $\mathrm{Mn}(\mathrm{Al, Zn})_{4.92}$, which conform closely with $(\mathrm{Mn,Zn})\mathrm{Al}_2$ and $\mathrm{Mn}(\mathrm{Al,Zn})_5$. For crystals extracted by Raynor & Wakeman the formula would be $\mathrm{Mn}_{2.8}\mathrm{Zn}_{2.2}\mathrm{Al}_{11}$ or $(\mathrm{Mn, Zn})_5\mathrm{Al}_{11}$.

3. Unit cell and space group

From rotation photographs, orthorhombic unit-cell dimensions were found to be:

$$a = 7{\cdot}78,\ b = 23{\cdot}8,\ c = 12{\cdot}6\ \text{Å}\ (\pm 0{\cdot}5\%)\,.$$

These dimensions are comparable with those of $\mathrm{Ni_4Mn_{11}Al_{60}}$ and $\mathrm{Cu_2Mn_3Al_{20}}$, which are as follows:

	a	*b*	*c*
$\mathrm{Ni_4Mn_{11}Al_{60}}$	7·55 Å	23·8 Å	12·5 Å
$\mathrm{Cu_2Mn_3Al_{20}}$	7·72	24·2	12·5

The density was measured by the displacement method. To avoid inaccuracy due to residual air on the rough hollow surfaces of the crystals, they were covered by the measuring liquid while under vacuum. This was done with the apparatus shown in Fig. 1. The density was $3{\cdot}97 \pm 0{\cdot}10$ g.cm.$^{-3}$, and so the content of the unit cell is 147 ± 5 atoms.

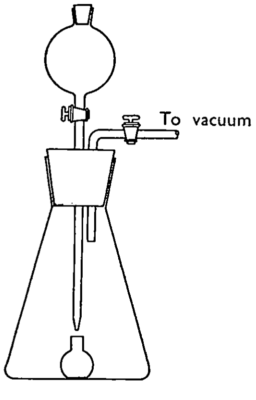

Fig. 1. The apparatus used for density measurements by the displacement method. Crystals are covered with the liquid while they are under vacuum.

Systematic absences are compatible with three space groups: D_{2h}^{17}-*Cmcm*, C_{2v}^{16}-*C2cm* and C_{2v}^{12}-*Cmc2*. To aid the choice of the space group, information from intensity statistics was sought. Of the three possible space groups, only D_{2h}^{17}-*Cmcm* is centrosymmetrical. For C_{2v}^{16}-*C2cm* and C_{2v}^{12}-*Cmc2* the $(0yz)$ and $(xy0)$ projections, respectively, have no centre of symmetry. All the evidence favoured the space group D_{2h}^{17}-*Cmcm*. It should be noted that $\mathrm{Ni_4Mn_{11}Al_{60}}$ belongs to the same space group.

4. Structure determination

For the structure determination only projections on (001) and (100) were considered. Using filtered Mo $K\alpha$ radiation and multiple-film technique, the $hk0$ and $0kl$ reflections from a single crystal of T_3, with approximately circular cross-section having a diameter of about 0·05 mm., were recorded on zero-layer Weissenberg photographs. Altogether 122 $hk0$ and 143 $0kl$ intensities were estimated by eye with an intensity scale and were corrected for polarization and Lorentz effects, but not for absorption.

The unit-cell dimensions and symmetry of T_3 and of $\mathrm{Ni_4Mn_{11}Al_{60}}$ suggested that these two structures may be similar. The $\mathrm{Ni_4Mn_{11}Al_{60}}$ structure was therefore taken as a basis for the trial structure. Numerous

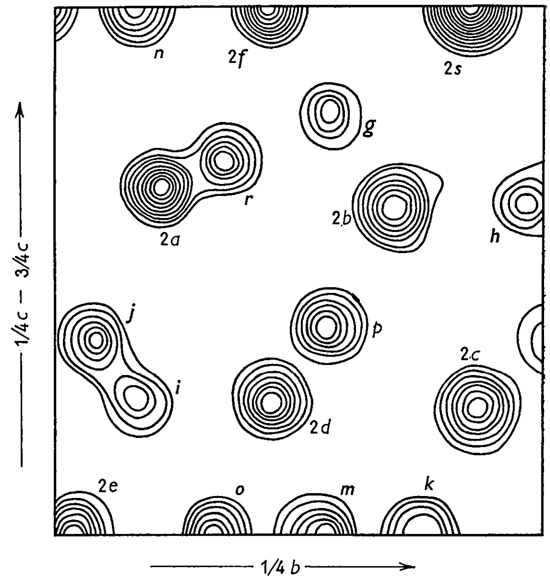

Fig. 2. The asymmetric unit of the final projection down the *a* axis. The first contour is at 50 and the remainder at intervals of 200 arbitrary units. Letters refer to Table 1. Figures mark number of atoms that are related by the mirror plane perpendicular to *a*.

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* Trace impurities are neglected. A separate check shows iron and silicon <0·01%, copper and magnesium <0·001%, and a still smaller amount of calcium.

Table 1. *Atomic parameters for the T_3 structure*

Atom	Number of equivalent positions		Co-ordinates		Occupied by
		x	*y*	*z*	
a	16(*h*)	0·1820	0·5535	0·9375	80% Al 20% Zn
b	16(*h*)	0·2025	0·8261	0·0600	Al
c	16(*h*)	0·1822	0·7187	0·1270	Al
d	16(*h*)	0·2055	0·8901	0·8750	Al
e	8(*g*)	0·2170	0·0094	0·2500	Al
f	8(*g*)	0·2055	0·8921	0·2500	80% Al 20% Zn
g	8(*f*)	0·0000	0·6387	0·8513	Al
h	8(*f*)	0·0000	0·7431	0·9414	Al
i	8(*f*)	0·0000	0·5393	0·1245	Al
j	8(*f*)	0·0000	0·9774	0·9126	Zn
k	4(*c*)	0·0000	0·8095	0·7500	Al
m	4(*c*)	0·0000	0·6396	0·2500	Zn
n	4(*c*)	0·0000	0·5428	0·7500	80% Mn 20% Zn
o	4(*c*)	0·0000	0·0811	0·2500	80% Mn 20% Zn
p	8(*f*)	0·0000	0·6388	0·0543	80% Mn 20% Zn
r	8(*f*)	0·0000	0·9150	0·0858	80% Mn 20% Zn
s	8(*g*)	0·1822	0·7135	0·7500	80% Mn 20% Zn

refinements were carried out using both F_o and $F_o - F_c$ projections, F_o's being scaled to F_c's in regions of $\sin\theta/\lambda$ in the usual way. Final parameters are given in Table 1 together with the most probable distribution of atoms among various equivalent positions, in accordance with the discussion which follows (§ 6). With this distribution of atoms, a reasonable agreement was obtained between observed and calculated structure factors, the agreement index R being 0·17 both for $0kl$ and for $hk0$ structure factors. Interatomic distances are listed in Table 2, and final projections of electron density are given in Figs. 2 and 3. Values of F_o and F_c are available in a thesis (Damjanovic, 1957).

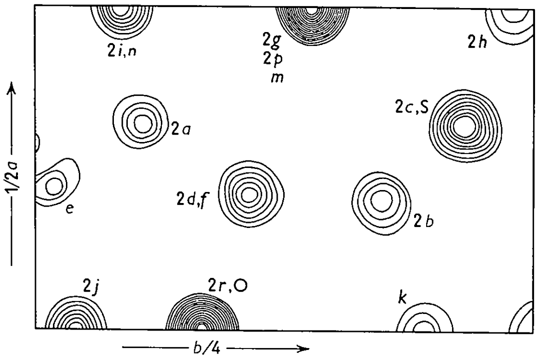

Fig. 3. The asymmetric unit of the final projection down the *c* axis. The first contour is at 50 and the remainder at intervals of 200 arbitrary units. Letters refer to Table 1. Figures mark number of atoms that are related by the mirror plane perpendicular to *c*.

5. Accuracy of the atomic coordinates

The principal advantage of the $F_o - F_c$ synthesis is the removal of the major part of errors arising from series termination. For the procedure used in this work, it may be expected that the random errors in the measured intensity data will set the limit to the accuracy of the derived atomic coordinates. Hence the standard deviations in atomic coordinates, according to Booth's equation (1946), are:

for aluminium atoms $\sigma(x) = 0·004$ Å
for heavy element atoms $\sigma(x) = 0·002$

and, according to Booth & Britten's equation (1948):

for aluminium atoms $\sigma(x) = 0·009$ Å
for heavy element atoms $\sigma(x) = 0·004$

If the values $\sigma(x) = 0·007$ and $\sigma(x) = 0·003$ Å are accepted for aluminium and heavy atoms, respectively, the standard deviation of interatomic distances should not be greater than $\sigma(d) = 0·014$ Å, and so only differences greater than $2·33\sqrt{2}\sigma(d) \simeq 0·04$ Å are significant (Lipson & Cochran, 1953).

In the (001) projection (Fig. 3) atoms (d) and (f), and atoms (c) and (s), are almost exactly superposed. The y-parameters for these pairs of atoms can be determined separately from the (100) projection, but refinement of the x-parameters is difficult when overlap is as close as in the c-projection; these parameters may therefore be somewhat less accurate than others.

6. Discussion of the structure

According to the chemical analyses, and assuming that all the seventeen equivalent positions in the structure, marked by letters, are fully occupied, the content of the unit cell (on an average) is:

aluminium atoms	102·5
manganese atoms	25·7
zinc atoms	23·8

Altogether, there are 152 atoms in the unit cell, in agreement with the density measurements. The (j), (m), (n), (o), (p), (r) and (s) positions, which are, according to the F_o and $F_o - F_c$ projections, occupied

Table 2. *Interatomic distances in the T_3 structure in Å units*

Al–*a*	2·99 (Al–*a*);	2·83 (Al–*a*);	3·00 (Al–*b*);
	2·85 (Al–*d*);	2·91 (Al–*e*);	2·83 (Al–*f*);
	2·70 (Al–*g*);	2·74 (Al–*i*);	2·77 (Al–*i*);
	3·08 (Zn–*j*);	3·20 (Zn–*j*);	2·60 (Mn–*r*);
	2·77 (Mn–*n*);	2·88 (Mn–*p*).	
Al–*b*	3·00 (Al–*a*);	2·70 (Al–*c*);	2·74 (Al–*c*);
	2·78 (Al–*d*);	2·86 (Al–*f*);	2·70 (Al–*g*);
	2·94 (Al–*h*);	2·84 (Al–*h*);	2·85 (Mn–*p*);
	2·66 (Mn–*r*);	2·72 (Mn–*s*).	
Al–*c*	2·74 (Al–*b*);	2·70 (Al–*b*);	3·10 (Al–*c*);
	2·83 (Al–*c*);	2·73 (Al–*d*);	2·80 (Al–*h*);
	2·77 (Al–*h*);	2·99 (Al–*k*);	2·82 (Zn–*m*);
	2·54 (Mn–*p*);	2·47 (Mn–*s*).	
Al–*d*	2·85 (Al–*a*);	2·78 (Al–*b*);	2·73 (Al–*c*);
	3·15 (Al–*d*);	2·87 (Al–*e*);	2·84 (Al–*i*);
	2·95 (Al–*k*);	2·66 (Zn–*j*);	2·87 (Zn–*m*);
	2·55 (Mn–*p*);	2·35 (Mn–*o*);	3·16 (Mn–*r*).
Al–*e*	2·91 (2 Al–*a*);*	2·87 (2 Al–*d*);	2·79 (Al–*f*);
	2·80 (2 Al–*i*);	2·67 (2 Zn–*j*);	2·53 (Mn–*n*);
	2·40 (Mn–*o*).		
Al–*f*	2·83 (2 Al–*a*);	2·86 (2 Al–*b*);	2·79 (Al–*e*);
	2·72 (2 Al–*g*);	2·77 (Mn–*n*);	2·67 (2 Mn–*r*);
	2·66 (Mn–*s*).		
Al–*g*	2·70 (2 Al–*a*);	2·70 (2 Al–*b*);	2·72 (2 Al–*f*);
	2·55 (Al–*g*);	2·73 (Al–*h*);	2·62 (Mn–*n*);
	2·56 (Mn–*p*);	2·61 (2 Mn–*s*).	
Al–*h*	2·94 (2 Al–*b*);	2·84 (2 Al–*b*);	2·77 (2 Al–*c*);
	2·80 (2 Al–*c*);	2·73 (Al–*g*);	2·88 (Al–*k*);
	2·86 (Mn–*p*);	2·88 (2 Mn–*s*).	
Al–*i*	2·77 (2 Al–*a*);	2·74 (2 Al–*a*);	2·84 (2 Al–*d*);
	2·80 (2 Al–*e*);	2·86 (Zn–*m*);	2·51 (Mn–*n*);
	2·53 (Mn–*p*).		
Al–*k*	2·99 (4 Al–*c*);	2·95 (4 Al–*d*);	2·88 (2 Al–*h*);
	2·60 (Mn–*o*);	2·69 (2 Mn–*s*).	
Zn–*j*	3·20 (2 Al–*a*);	3·08 (2 Al–*a*);	2·66 (2 Al–*d*);
	2·67 (2 Al–*e*);	2·45 (Zn–*j*);	2·48 (Mn–*o*);
	2·64 (Mn–*r*);	2·56 (Mn–*r*).	
Zn–*m*	2·82 (4 Al–*c*);	2·87 (4 Al–*d*);	2·86 (2 Al–*i*);
	2·47 (2 Mn–*p*).		
Mn–*n*	2·77 (4 Al–*a*);	2·53 (2 Al–*e*);	2·77 (2 Al–*f*);
	2·62 (2 Al–*g*);	2·51 (2 Al–*i*).	
Mn–*p*	2·88 (2 Al–*a*);	2·85 (2 Al–*b*);	2·54 (2 Al–*c*);
	2·55 (2 Al–*d*);	2·56 (Al–*g*);	2·86 (Al–*h*);
	2·53 (Al–*i*);	2·47 (Zn–*m*).	
Mn–*o*	2·35 (4 Al–*d*);	2·40 (2 Al–*e*);	2·60 (Al–*k*);
	2·48 (2 Zn–*j*).		
Mn–*r*	2·60 (2 Al–*a*);	2·66 (2 Al–*b*);	3·16 (2 Al–*d*);
	2·67 (2 Al–*f*);	2·56 (Zn–*j*);	2·64 (Zn–*j*).
Mn–*s*	2·72 (2 Al–*b*);	2·47 (2 Al–*c*);	2·66 (Al–*f*);
	2·61 (2 Al–*g*);	2·88 (2 Al–*h*);	2·69 (Al–*k*);
	2·83 (Mn–*s*).		

* Figure in bracket means the number of neighbours.

by heavy atoms, can accommodate a maximum of 44 atoms, which is less than the total number of manganese and zinc atoms (49·5) in the unit cell. Therefore, at least some groups of equivalent positions must be occupied partly by one kind of atom, partly by another. In the course of the refinement this possibility was taken into account, but from the F_o and $F_o - F_c$ projections alone no definite conclusion could be drawn about the detailed distribution of atoms among various equivalent positions.

If the values of the agreement index R were taken as the most important criterion for the correctness of the structure, then a number of different assumptions for the detailed distribution of atoms could be proposed without much change in the values of R. One such distribution scheme would be as follows:

The (*j*), (*m*), (*n*), (*o*), (*p*), (*r*) and (*s*) positions are all occupied by heavy element atoms, each on an average by 58% manganese and 42% zinc atoms. The (*a*) and (*f*) positions are occupied by aluminium and excess of zinc in the approximate ratio of 4:1. The (*b*), (*c*), (*d*), (*e*), (*g*), (*h*), (*i*) and (*k*) positions are occupied only by aluminium atoms. Such a distribution would also be in agreement with the F_o and $F_o - F_c$ projections. Though this distribution gives the lowest R index ($R = 0{\cdot}15$), a different distribution of heavy atoms in the (*j*), (*m*), (*n*), (*o*), (*p*), (*r*) and (*s*) positions is finally proposed for the reason given below.

For the final distribution of heavy element atoms, given in Table 1, not only data from the F_o and $F_o - F_c$ projections and values of the R index are used, but also interatomic distances are considered as well as the general knowledge of this group of intermetallic compounds of aluminium with transition metals. For instance, in such compounds it was observed that (Taylor, 1954; Black, 1956):

(i) some, but not all, of the contacts which a transition metal atom makes with its neighbours are abnormally short,
(ii) transition metal atoms are not normally in contact with one another,
(iii) there is a trend in the preferred coordination number of the transition metal atoms. For a manganese atom the preferred number is 10.

Among the heavy atoms, only those in the (*n*) positions have no contact with other heavy atoms. An atom in the (*n*) position has 12 neighbours, all at distances $d \leq 2{\cdot}77$ Å, but four of them are at short distances (2·51–2·53 Å). Atoms in the (*n*) positions thus comply with the observations under (i) and (ii), but not with (iii). The average contact distance which these atoms make with their neighbouring atoms is 2·66 Å, and so it is comparable with, for instance, 2·58 and 2·65 Å for the average Mn_1–Al and Mn_2–Al distances in the δ(MnAl) structure (Bland, 1958), respectively. Therefore, it seems reasonable to suppose that the (*n*) positions are occupied by manganese atoms.

Similarly, it is supposed that the (*o*), (*p*) and (*r*) positions are occupied by manganese, and the (*j*) and (*m*) positions by zinc atoms. Atoms in the (*o*), (*p*) and (*r*) positions are not in contact either with each other or with the manganese atoms in the (*n*) positions. However, they are in short contact with the (*j*) or with the (*m*) atoms (and also with some aluminium atoms). The mean contact distances which the (*o*), (*p*) and (*r*) atoms make with their neighbours are close to the mean Al–Mn contact distances in other structures of this class of compounds. An atom in the (*m*) position, on the other hand, is at the short distance

(2·47 Å) from two (*p*) atoms, but at 'normal' distances from its aluminium neighbours. The average contact distance which an atom in the (*m*) position makes with its aluminium neighbours (2·85 Å) does not resemble the average Mn–Al distance. An atom in the (*j*) position is in a short contact both with the (*o*) atom (2·48 Å), and with the (*r*) atom (2·56 Å), and also with another (*j*) atom (2·45 Å).* All this supports the above assumption that the (*j*) and (*m*) positions are occupied by zinc and the (*o*), (*p*) and (*r*) by manganese atoms.

The (*s*) positions should also be occupied by heavy atoms. Here, an (*s*) atom has 10 aluminium neighbours at the average distance (2·67 Å) which is nearer to the average Mn–Al distance than to the average Zn–Al distance for the (*j*) and (*m*) atoms (2·85 Å). The only objection to placing manganese atoms in these positions is mutual contact of two (*s*) atoms (2·83 Å). However, this cannot be taken as a serious objection to the assumption that the (*s*) positions are occupied by manganese atoms. In the β(AlMnSi) structure the distance between two manganese atoms is $2{\cdot}88_5$ Å (Robinson, 1952*b*), and it is even shorter ($2{\cdot}71_0$ Å) when zinc replaces manganese (up to about 23%) in these positions (Damjanovic, 1957).

The (*o*), (*p*), (*r*) and (*n*) positions can accommodate only 24 manganese atoms per unit cell. Even assuming that there are less than 152 atoms per unit cell, it would be rather difficult to accommodate all manganese atoms in these positions only (particularly if the composition of crystals extracted by Raynor & Wakeman is considered). The only possible positions where the excess of the manganese atoms can be placed are the (*s*) positions. With these, the total number of positions available for manganese atoms becomes larger than their number per unit cell. It is proposed that all these positions are occupied not only by manganese but also by the excess of zinc atoms; so, there would be on the average about 20% of zinc and 80% of manganese in these equivalent positions.

That zinc can replace manganese atoms in this group of intermetallic compounds has been suggested by Raynor & Wakeman (1947). They found that $MnAl_6$ can take up a small quantity of zinc, and that zinc probably replaces manganese in the compound atom for atom. The extent of the substitution is about 4 at.%. As they noticed, it is improbable that this amount of zinc corresponds with the maximum solubility of zinc in the $MnAl_6$ compound, since $MnAl_6$ crystals will separate from alloys richer in zinc than those used for the extraction of analyzed $MnAl_6$ crystals. In the same work it was shown that zinc dissolves in the $MnAl_4$ compound up to a limit of approximately 5·2%, the substitution of zinc for manganese atoms taking place atom for atom. More recently, it has been shown that the β(AlMnSi) compound can also take up some zinc, and that zinc replaces manganese atoms at least up to 23% (Damjanovic & Black, 1961).

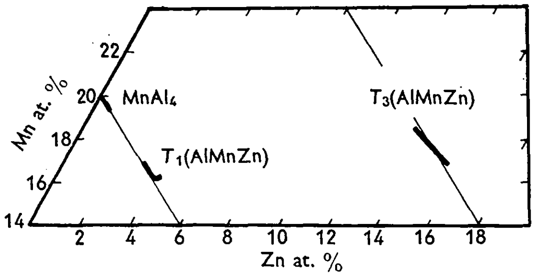

Fig. 4. Composition of the ternary T_1 and T_3 compounds of the Al–Mn–Zn system. The binary $MnAl_4$ compound is also included. Two lines of constant atomic percentage of aluminium are shown.

The compositions of the T_3 crystals extracted by Raynor & Wakeman and those extracted in this work, when plotted on a graph (Fig. 4), lie approximately on the line of constant atomic percentage of aluminium. This suggests that in this range of composition, a simple atom-for-atom substitution of manganese by zinc is possible, and that it occurs more readily than the substitution of aluminium by zinc. It seems that in the T_1 compound, up to a point, the replacement of manganese by zinc atoms also occurs more easily than the replacement of aluminium by zinc.

7. Relationship to other structures

The structure of T_3 can be related to that of $Ni_4Mn_{11}Al_{60}$. All positions which are occupied in the $Ni_4Mn_{11}Al_{60}$ structure are also occupied in the T_3 structure, except a set of 4(*c*) positions which in $Ni_4Mn_{11}Al_{60}$ are occupied by aluminium atoms (Al_{10}, Robinson, 1954). In the T_3 structure the (*j*) and (*m*) positions are occupied by zinc atoms, while aluminium atoms are placed in the corresponding positions of $Ni_4Mn_{11}Al_{60}$. It was assumed that in the $Ni_4Mn_{11}Al_{60}$ structure, nickel atoms occupy a particular set of equivalent positions and do not substitute for manganese atoms. The corresponding positions in T_3, marked by (*s*), are occupied mainly by manganese atoms. The relationship between the T_3 and $Cu_2Mn_3Al_{20}$ structures cannot be discussed since the $Cu_2Mn_3Al_{20}$ structure has not yet been solved in detail.

Both T_3 and the $Cu_2Mn_3Al_{20}$ compound are of varying compositions, while $Ni_4Mn_{11}Al_{60}$ is of fixed composition. This variation in the T_3 compound can be explained by the substitution of manganese with zinc atoms. The fixed composition of the $Ni_4Mn_{11}Al_{60}$ might be reconciled with the tendency of nickel atoms to occupy a particular set of equivalent positions by themselves, and not to share equivalent positions with manganese atoms. This assumption finds support in the fact that nickel does not replace manganese in $MnAl_6$ (Raynor, 1944). In the β(AlMnSi) structure

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* The distance between two (*j*) atoms, which are supposed to be zinc, indicates that short contacts between zinc atoms are possible in this class of compounds.

nickel probably enters 'holes' in the structure and does not substitute for the manganese atoms (Damjanovic & Black, 1961).

8. Conclusion

Of the three intermetallic compounds, T_1, T_2 and T_3, which separate as primary constituents in the Al–Mn–Zn system, T_3 is structurally similar to $Ni_4Mn_{11}Al_{60}$ and $Cu_2Mn_3Al_{20}$, though its composition is not based on the requirements for the latter two. It has been shown previously that T_1, the composition of which conforms to the same requirements as $Ni_4Mn_{11}Al_{60}$ and $Cu_2Mn_3Al_{20}$, has an appreciably different structure.

To find the detailed distribution of atoms in the T_3 structure, it was necessary to use, not only the data from F_o and F_o-F_c projections, but also the general knowledge of this group of intermetallic compounds. An important feature of the structure is that zinc, to some extent, replaces manganese atoms. Some abnormally short interatomic distances between manganese and aluminium atoms are also observed in this ternary compound and, in addition, some short interatomic distances between manganese and zinc atoms. Caution should, however, be exercised at present in discussion of these short interatomic distances, since possible complication may arise from the replacement of atoms occurring in this ternary compound. It is hoped that the atom-for-atom replacement of manganese by zinc atoms in this compound, as well as in some others, may help in the discussion of valencies of transition metal atoms in this class of intermetallic compounds.

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The Structure Analysis of the T_4(AlMnSiZn) Compound

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The β(AlMnSi) compound can take up some zinc. The resulting quaternary compound is denoted by the symbol T_4. There are at least two ways in which zinc atoms may be accommodated in the structure. They may either enter the 2(*d*) positions, which are vacant in the structure of β(AlMnSi), or replace manganese atoms. It is found that zinc replaces up to about 23% of maganese by occupying the manganese sites; the 2(*d*) positions are again left vacant. The replacement of manganese by zinc in β(AlMnSi) and in similar compounds is discussed. It is suggested that there is no real basis for classifying β(AlMnSi), and the structurally similar Co_2Al_5 and π(AlFeNi) phases as electron compounds.

1. Introduction

The surface of primary separation of the aluminium-rich corner of the Al–Mn–Si system has been investigated by Phillips (1943). Two distinct ternary phases are recognized and marked as α(AlMnSi) and β(AlMnSi). Pratt & Raynor (1951) have separated these two phases and found that they are of variable composition. The structure of β(AlMnSi) has been

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