

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  $\text{Ni}_4\text{Mn}_{11}\text{Al}_{60}$  and  $\text{Cu}_2\text{Mn}_3\text{Al}_{20}$ , 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  $\text{Ni}_4\text{Mn}_{11}\text{Al}_{60}$  and  $\text{Cu}_2\text{Mn}_3\text{Al}_{20}$ , 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.

*Acta Cryst.* (1961). **14**, 987

## The Structure Analysis of the $T_4(\text{AlMnSiZn})$ Compound

BY A. DAMJANOVIC\* AND P. J. BLACK†

*Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

(Received 27 May 1959 and in revised form 9 December 1960)

The  $\beta(\text{AlMnSi})$  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  $\beta(\text{AlMnSi})$ , or replace manganese atoms. It is found that zinc replaces up to about 23% of manganese by occupying the manganese sites; the  $2(d)$  positions are again left vacant. The replacement of manganese by zinc in  $\beta(\text{AlMnSi})$  and in similar compounds is discussed. It is suggested that there is no real basis for classifying  $\beta(\text{AlMnSi})$ , and the structurally similar  $\text{Co}_2\text{Al}_5$  and  $\pi(\text{AlFeNi})$  phases as electron compounds.

### 1. Introduction

The surface of primary separation of the aluminium-

\* Now at the Faculty of Technology, University of Belgrade.

† Now at the Physics Department, University of Birmingham, England.

I wish to thank Prof. N. F. Mott and Dr W. H. Taylor for provision of facilities and for their interest and encouragement. I am indebted to Dr P. J. Black for his advice and criticism, and I am grateful to several colleagues for many valuable discussions. The mechanical computations were made in the Cambridge University Mathematical Laboratory and I am grateful to Dr M. V. Wilkes for allowing time on the EDSAC Digital Computer and to Mrs M. McGibbon for the calculations. The Admiralty Materials Laboratory kindly carried out the chemical analysis of the crystals.

I wish to thank Prof. P. Savić from the University of Belgrade for his constant encouragement, and Institute 'Boris Kidrič' in Belgrade for a grant.

### References

- BLACK, P. J. (1956). *Acta Met.* **4**, 172.  
 BLAND, J. A. (1958). *Acta Cryst.* **11**, 236.  
 BOOTH, A. D. (1946). *Proc. Roy. Soc. A*, **188**, 77.  
 BOOTH, A. D. & BRITTEN, K. H. V. (1948). *Proc. Roy. Soc. A*, **193**, 305.  
 DAMJANOVIC, A. (1957). Dissertation for the degree of Ph.D., Cambridge.  
 DAMJANOVIC, A. & BLACK, P. J. (1961). *Acta Cryst.* **14**, 987.  
 LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures*. London: Bell.  
 RAYNOR, G. V. (1944). *J. Inst. Met.* **70**, 531.  
 RAYNOR, G. V. & WAKEMAN, D. (1947). *Proc. Roy. Soc. A*, **190**, 82.  
 ROBINSON, K. (1952a). *Phil. Mag.* (7), **43**, 775.  
 ROBINSON, K. (1952b). *Acta Cryst.* **5**, 397.  
 ROBINSON, K. (1954). *Acta Cryst.* **7**, 494.  
 TAYLOR, W. H. (1954). *Acta Met.* **2**, 684.

rich corner of the Al-Mn-Si system has been investigated by Phillips (1943). Two distinct ternary phases are recognized and marked as  $\alpha(\text{AlMnSi})$  and  $\beta(\text{AlMnSi})$ . Pratt & Raynor (1951) have separated these two phases and found that they are of variable composition. The structure of  $\beta(\text{AlMnSi})$  has been

determined by Robinson (1952); it is similar to that of  $\text{Co}_2\text{Al}_5$  which had been previously solved by Bradley & Seager (1939) using the powder method. The major difference between these two structures is that one quarter of the cobalt sites in  $\text{Co}_2\text{Al}_5$  are vacant in  $\beta(\text{AlMnSi})$ . Also, the structure of another compound,  $\pi(\text{AlFeNi})$ , has been reported to be similar to that of  $\text{Co}_2\text{Al}_5$  (Bradley & Taylor, 1940). The occurrence of three different compounds with similar structures as well as the presence of 'vacant sites' in the structure of  $\beta(\text{AlMnSi})$ , but not in  $\text{Co}_2\text{Al}_5$ , nor in  $\pi(\text{AlFeNi})$ , was explained in terms of electron concentrations. These compounds were classified as electron compounds having similar electron-to-atom ratios.

In the present work it is found that the  $\beta(\text{AlMnSi})$  compound can take up some zinc and also iron. The distribution of zinc atoms in this quaternary compound, which is denoted by the symbol  $T_4$ , is investigated in order to see whether zinc atoms occupy the 'vacant sites' or some other positions in the structure and so to obtain more information about the factors stabilizing these compounds.

## 2. Preparation of crystals

Axon & Hume-Rothery (1948) have examined the Al-Mn-Si-Zn system in the range from 0 to 8 wt.% of zinc, 0 to 2 wt.% of manganese and 1% of silicon. In this range no  $\beta(\text{AlMnSi})$  crystals are reported.

For the preparation of alloys, pure zinc, pure aluminium and aluminium-manganese master alloy were used.\* Alloys were prepared in quantities of 50 g. in a small electric resistance furnace. Aluminium and aluminium-manganese master alloys were first melted in an alumina crucible and stirred with a silica rod while at a temperature of about 950 °C. A few minutes of stirring with the silica rod was enough to introduce silicon into the melt. Zinc was added subsequently. From the ingots containing approximately 90, 9 and 1% of zinc, aluminium and manganese, respectively, hexagonal crystals were extracted by the electrolytic method described by Raynor & Wakeman (1947). These crystals, denoted by  $T_4$ , were obtained only when ingots were rapidly quenched from above 460 °C.

30 mg. of  $T_4$  crystals were analyzed by Messrs. Johnson, Matthey & Co. Ltd. with the following result in weight percentage:

Zinc	10.83%
Manganese	22.22%
Silicon	3.65%
Aluminium	63.3 % (by difference),

\* Data for materials:

- (i) Pure zinc, presented by the Imperial Smelting Corporation Ltd., of Avonmouth. The major impurities were lead and cadmium, but both in quantity less than 0.0007%.
- (ii) Pure aluminium, presented to the Laboratory by the British Aluminium Co. Ltd.
- (iii) Aluminium-manganese master alloy containing 13.65 wt.% of manganese. The alloy was prepared from super-pure elements by the British Aluminium Co. Ltd.

or, in atomic percentage, 5.47, 13.26, 4.27 and 77% of zinc, manganese, silicon and aluminium, respectively. To check the chemical analysis the spectra of a few milligrammes of the  $T_4$  crystals were kindly photographed by Dr Nockolds, of the Department of Mineralogy and Petrology, Cambridge, and then compared with the spectra of a specimen containing high purity elements in the above proportion. No difference could be observed.

In a preliminary X-ray examination of the crystals, the Laue symmetry ( $6/m\bar{m}$ ) was found to be the same as for  $\beta(\text{AlMnSi})$  or  $\text{Co}_2\text{Al}_5$ , and the approximate unit-cell dimensions were close to those of  $\beta(\text{AlMnSi})$ . Systematic absences were consistent with the space group  $P6_3/mmc$ ; structures of  $\beta(\text{AlMnSi})$  and  $\text{Co}_2\text{Al}_5$  also belong to the same space group.

## 3. Accurate cell dimensions and content of the cell

The accurate cell dimensions were determined by the extrapolation method using Taylor & Sinclair's (1945) function of  $\theta$ . The dimensions of the hexagonal cell are:

$$a = 7.527 \pm 0.002 \text{ \AA} \quad (7.513 \text{ \AA}),$$

$$c = 7.818 \pm 0.003 \text{ \AA} \quad (7.745 \text{ \AA}).$$

The errors were estimated from the uncertainty in drawing extrapolation lines. For comparison, the dimensions of the (6/2) specimen of  $\beta(\text{AlMnSi})$  (Robinson, 1952) are given in brackets.

The density determined by the displacement method is  $3.9 \pm 0.1 \text{ g.cm.}^{-3}$ , and the calculated content of the unit cell is  $26.7 \pm 0.7$  atoms. It is not possible to accommodate 27 atoms in the unit cell if possible equivalent positions are to be fully occupied. If it is assumed that  $T_4$  is isostructural with  $\beta(\text{AlMnSi})$ , the ideal cell content would be 26 atoms which occupy the  $2(a)$ ,  $12(k)$  and two sets of  $6(h)$  positions. If, however,  $T_4$  is isostructural with  $\text{Co}_2\text{Al}_5$ , its content would be 28 atoms, and the  $2(d)$  positions would be also occupied. From the density measurement it was not possible to decide whether the  $2(d)$  positions are occupied or not and the detailed structure analysis was undertaken.

## 4. Structure determination

### (i) Collection of intensity data

Intensity data were collected from Weissenberg photographs using filtered  $\text{Mo } K\alpha$  radiation and multiple-film technique. Errors arising from absorption were considerably reduced by the use of very small ( $< 0.05 \text{ mm.}$ ), almost cylindrical crystals. Intensities were estimated by comparison with a standard scale prepared from the same crystal, and Lorentz and polarization corrections were applied.

### (ii) Electron-density projections

Electron-density projections were prepared using

40  $hk\cdot 0$  and 228  $h0\cdot l$  structure amplitudes with the corresponding signs from  $\beta(\text{AlMnSi})$  as a trial structure. In the final stage of the refinement, observed structure factors were scaled to the calculated values for various regions of  $\sin \theta/\lambda$  in the usual way. With this scaling all errors depending on  $\theta$  should be accounted for.

During the refinement on the projections both along the hexad and along the  $a$ -axis, large discrepancies were noticed between the observed structure factors,  $F_o$ , and calculated structure factors,  $F_c$ , for the strongest reflections; absolute values of the observed structure factors were always smaller.

If the  $h0\cdot l$  structure factors are divided according to the  $|F_c|$  values into groups of 0–10, 11–20 and so on, and the mean value of the  $|F_o|$  for each of these groups is plotted against the mean value of the corresponding  $|F_c|$ , all points lie on a smooth curve (Fig. 1). There are not enough  $hk\cdot 0$  structure factors to construct a similar curve. Structure factors of the strongest  $hk\cdot 0$  reflections will, however, fall on the curve for  $h0\cdot l$  reflections. The deviation of the curve from the straight line is taken to mean that intensities are affected by extinction.

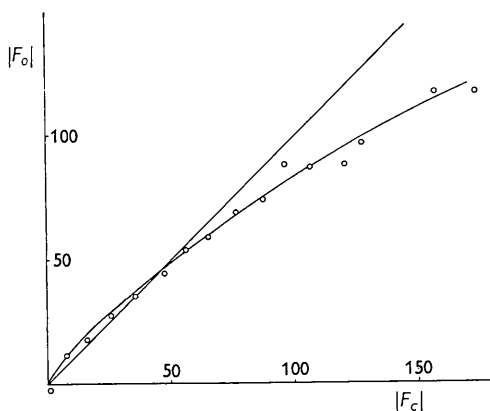


Fig. 1. The plot of the mean value of  $|F_o|$  against the mean value of  $|F_c|$ . The deviation from the straight line is interpreted as due to extinction.

For the smallest structure factors, the empirical curve is above the straight line. This is interpreted as

being due to their overscaling in various regions of  $\sin \theta/\lambda$ , since the medium-strong reflections used in this scaling are also influenced by extinction. In the final stage of the refinement, the strongest reflections were corrected according to this curve.

Even after the first synthesis it became evident that the  $2(d)$  positions are not occupied. For the final refinement both  $F_o$  and  $(F_o - F_c)$  projections were used. The following atomic parameters were obtained:

Atom	Position	$x$	$z$
Al	$2(a)$	0.0000	0.0000
Al	$6(h)_2$	0.4570	0.2500
Al	$12(k)$	0.2015	-0.0635
Mn (and Zn)	$(6(h)_1)$	0.1200	0.2500

Atomic parameters in  $T_4$  do not significantly differ from those in  $\beta(\text{AlMnSi})$ , except for the  $z$  parameter of aluminium atoms in the  $12(k)$  positions. For the  $(6/2)$  specimen of  $\beta(\text{AlMnSi})$  the corresponding param-

Table 1. Interatomic distances in  $T_4$  and  $\beta(\text{AlMnSi})^*$  in Å

Atom	Neighbour	Number of neighbours	$T_4$	$\beta(\text{AlMnSi})$
$2(a)$	$6(h)_1$	6	2.50 <sub>8</sub>	2.48 <sub>8</sub>
	$12(k)$	6	2.66 <sub>8</sub>	2.66 <sub>5</sub>
$6(h)_2$	$6(h)_1$	2	2.41 <sub>8</sub>	2.40 <sub>2</sub>
	$2(d)$	1	(2.73 <sub>3</sub> )	(2.72 <sub>0</sub> )
	$6(h)_2$	2	2.79 <sub>1</sub>	2.80 <sub>5</sub>
	$12(k)$	4	2.80 <sub>2</sub>	2.77
$12(k)$	$12(k)$	4	2.96 <sub>4</sub>	2.97
	$6(h)_1$	2	2.71 <sub>4</sub>	2.68
	$6(h)_1$	1	2.67 <sub>1</sub>	2.67
	$2(d)$	1	(2.23 <sub>3</sub> )	(2.23 <sub>5</sub> )
	$2(a)$	1	2.66 <sub>8</sub>	2.66 <sub>5</sub>
	$6(h)_2$	2	2.80 <sub>2</sub>	2.77
	$6(h)_2$	2	2.96 <sub>4</sub>	2.97
	$12(k)$	1	2.91 <sub>6</sub>	2.83 <sub>5</sub>
	$12(k)$	2	2.80 <sub>8</sub>	2.81 <sub>5</sub>
	$12(k)$	2	2.97 <sub>6</sub>	2.99
$6(h)_1$	$6(h)_1$	2	2.71 <sub>0</sub>	2.88 <sub>5</sub>
	$2(a)$	2	2.50 <sub>8</sub>	2.48 <sub>8</sub>
	$6(h)_2$	2	2.41 <sub>8</sub>	2.42
	$12(k)$	2	2.67 <sub>1</sub>	2.67
$2(d)$	$12(k)$	4	2.71 <sub>4</sub>	2.68
	$6(h)_2$	3	(2.25 <sub>3</sub> )	(2.23 <sub>5</sub> )

\* Interatomic distances for  $\beta(\text{AlMnSi})$  are taken from Robinson (1952) except those in brackets. Distances in brackets are those to an imaginary atom in the  $2(d)$  position.

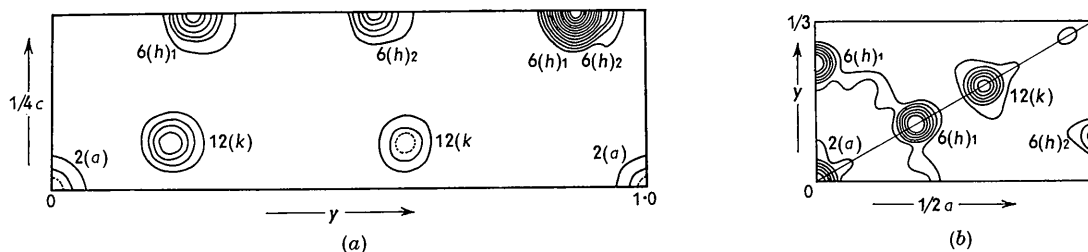


Fig. 2. (a)  $F_o$  projection down the  $a$  axis. The first contour is at 100 and the remainder at intervals of 400 arbitrary units. The dotted contours are at height 700. (b) Projection down the hexad. The first contour is at 0 and the remainder at intervals of 150 arbitrary units.

eter is  $-0.067$  (Robinson, 1952). Projections down the  $a$  and  $c$  axes are given in Fig. 2.

(iii) *Accuracy of atomic coordinates and interatomic distances*

Since systematic errors in intensity data were removed as described in (i) above, and since termination errors are eliminated in  $(F_o - F_c)$  syntheses, the accuracy of the atomic coordinates derived should be limited only by random errors in the measured intensities. For the estimation of the errors in atomic coordinates Booth & Britten's (1948) equation was used and the following standard deviations were obtained:

for atoms in  $6(h)_1$  positions  $\sigma(r) = 0.0015 \text{ \AA}$   
 for atoms in  $6(h)_2$  and  $12(k)$  positions  $\sigma(r) = 0.002 \text{ \AA}$

These give standard deviations in interatomic distances not greater than about  $0.005 \text{ \AA}$ , and only differences in interatomic distances greater than  $0.02 \text{ \AA}$  can be considered significant. Interatomic distances are given in Table 1 together with those of  $\beta(\text{AlMnSi})$ .

(iv) *Electron density*

Since the intensities were not measured on an absolute scale, electron-density maps could not provide evidence about the possibility of electron transfer to the transition-metal atoms (Black, 1955).

## 5. Distribution of atoms in the structure

With the structure analysis the ideal content of  $T_4$  is fixed at 26 atoms per unit cell and the measured density of the crystals indicates that all positions should be fully occupied. If so, there are, on the average, 1.4, 3.5, 1.1 and 20 atoms of zinc, manganese, silicon and aluminium per unit cell, respectively. From the content of the unit cell, as well as from the  $F_o$  and  $(F_o - F_c)$  projections, it is evident that both manganese and zinc atoms occupy sites of the same set of  $6(h)_1$  positions.

From the structure analysis no conclusion has been reached about the distribution of silicon atoms. It was previously suggested that silicon atoms in the  $\beta(\text{AlMnSi})$  structure occupy the  $2(a)$  positions (Robinson, 1952). One piece of evidence for this was that the distances of an atom in the  $2(a)$  position from the six neighbouring aluminium atoms are appreciably less than those between any other pair of aluminium atoms in the structure. In the  $\text{Co}_2\text{Al}_5$  structure, however, an aluminium atom in the  $2(a)$  position is surrounded in much the same way by its neighbouring cobalt and aluminium atoms and it is also at an abnormally short distance from all its six aluminium neighbours. Therefore these short contact distances should not be taken as evidence that the  $2(a)$  positions are occupied by silicon atoms. The chemical analysis of the  $T_4$  crystals, on the other hand, may suggest that silicon occupy

the  $6(h)_1$  positions together with manganese and zinc atoms.\*

## 6. Discussion of the results

Both the  $\beta(\text{AlMnSi})$  and  $\text{Co}_2\text{Al}_5$  structures have been regarded as electron compounds having compositions at the electron-rich boundary of the phase which corresponds, according to Brillouin zone considerations, to an average of 1.68 free electrons per atom. The 'effective valencies' thus derived, or the absorption of electrons into the  $3d$  orbitals of manganese and cobalt atoms, are close to those suggested by Raynor & Wakeman (1947) for transition metal atoms in electron rich surroundings. A third compound— $\pi(\text{AlFeNi})$ —which has been reported by Bradley & Taylor (1940) as having the  $\text{Co}_2\text{Al}_5$  type of structure, fitted the above scheme (Robinson, 1952).

The presence of such well-defined vacant sites in the  $\beta(\text{AlMnSi})$  structure, which are occupied by transition metal atoms in the  $\text{Co}_2\text{Al}_5$  and  $\pi(\text{AlFeNi})$  structures, was also explained in terms of electron concentration. This explanation, however, cannot account for the 'ordering' of the vacant sites, as has already been pointed out by Black (1956).

Extensive replacement of manganese by zinc atoms in the  $\beta(\text{AlMnSi})$  compound does not fit the above explanation. The Brillouin zone is practically unchanged by this replacement and yet the electron-to-atom ratio, as calculated with the same valency scheme, is  $2.1e/a$ ; this is much larger than the first Brillouin zone would require. If electronic factors were predominant, then zinc atoms in the quaternary  $T_4$  compound might be expected to occupy the vacant sites in the  $2(d)$  positions as in this way neither Brillouin zone nor calculated electron concentration would be appreciably changed. It seems, therefore, that there is no real basis for classifying these hexagonal structures as electron compounds.

Some features common to structures of Al-rich compounds of the transition metals† can be observed in the structure of  $T_4$ , but these will not be discussed here. Two points, however, need further comment: (i) the presence of vacant sites large enough to accommodate atoms of transition metals, and (ii) the atom for atom replacement of manganese by zinc.

(i) A possible explanation for the existence of vacant sites in  $\beta(\text{AlMnSi})$  and  $T_4$ , but not in  $\text{Co}_2\text{Al}_5$  nor in  $\pi(\text{AlFeNi})$ , could be provided by considering the empirical rule of Black (1956). He has pointed out that in this group of intermetallic compounds the number of close neighbours of a transition element atom decreases from 10 to 8 as the atomic number of the transition element increases. Thus, manganese atoms prefer to have ten and nickel eight (or nine) neighbours. According to this rule, manganese atoms do not

\* Reference may also be made to the structure of  $\text{Mn}_3\text{Al}_{10}$  (Taylor, 1959).

† See for instance Taylor (1954) and Black (1956).

occupy the  $2(d)$  positions in  $\beta(\text{AlMnSi})$  and  $T_4$ , since these positions are 9-coordinated. Cobalt atoms may have either ten or nine neighbours, and the  $\text{Co}_2\text{Al}_5$  structure occurs with six cobalt atoms in the 10-coordinated  $6(h)_1$  and with two cobalt atoms in the 9-coordinated  $2(d)$  positions. Similarly, iron atoms prefer to have ten neighbours, but may have nine, and nickel atoms are usually 8-coordinated, but may be fitted into 9-coordinated positions. For the  $\pi(\text{AlFeNi})$  structure with approximate formula  $\text{Fe}_3\text{NiAl}_{10}$ , the ratio of 3 Fe:1 Ni may suggest that iron and nickel atoms obey this rule and occupy the  $6(h)_1$  and  $2(d)$  positions, respectively.

(ii) As to the replacement of manganese by zinc atoms, it may be noted that Raynor & Wakeman (1947) have already pointed out that some aluminium-rich manganese compounds ( $\text{MnAl}_4$ ,  $\text{MnAl}_6$ ) can take up a small quantity of zinc, and that zinc probably replaces manganese atom for atom. More recently it has been shown that in the ternary  $T_3$  ( $\text{AlMnZn}$ ) compound some equivalent positions are partly occupied by zinc and partly by manganese atoms (Damjanovic, 1957, 1961). The  $T_4$  compound presents more direct evidence that zinc can replace manganese atoms in Al-rich compounds of the transition metals. Hume-Rothery & Coles (1954) have explained the substitution of manganese by zinc in  $\text{MnAl}_4$  and  $\text{MnAl}_6$  in terms of the divalency of manganese. This behaviour of manganese is related to the known stability of divalent manganese in many compounds which involves the exactly half-filled  $3d^5$  sub-grouping.\* The same explanation could hold for the replacement of manganese by divalent zinc in the  $T_4$  structure.

### 7. Solubility of iron and nickel in $T_4$

In the quaternary Al-Mn-Si-Fe system, which was investigated by Phillips & Varley (1943), and Phragmen (1950), only those phases belonging to the subsidiary ternary systems were found within the range of investigation. Phillips & Varley have reported that  $\beta(\text{AlMnSi})$ † crystals occur only as cores in  $\text{MnAl}_6$  and  $\alpha(\text{AlMnSi})$  crystals. No  $\beta(\text{AlMnSi})$  crystals have been separated and analyzed.

In order to obtain more information concerning these hexagonal compounds it was decided to examine the way in which iron atoms might be accommodated in the  $\beta(\text{AlMnSi})$  structure. Since attempts to prepare enough crystals of  $\beta(\text{AlMnSi})$  containing iron and suitable for X-ray work have failed, an attempt was made to prepare them from the zinc solution. The corresponding system has not been investigated. An ingot of approximately 1.4, 0.4 and 18 wt.% of manganese, iron and aluminium, respectively,‡ contained a large

\* It must be emphasized that this treatment, in terms of divalent manganese  $\text{Mn}^{++}$ , is quite distinct from discussion based on a concept of electron absorption by transition metals.

† Their notation is  $\beta(\text{MnSi})$ .

‡ The other constituent, zinc, is up to 100 wt.%. Silicon was introduced by the method described in Section 2.

proportion of crystals of the required intermetallic compound when quenched from about 550 °C. Melts allowed to cool slowly in the furnace did not contain them.

Extracted crystals were spectrographically analyzed by the Royal Naval Scientific Service, Department of Aeronautical and Engineering Research, Admiralty. The result of the analysis is as follows:

Manganese	28.4 wt. %
Zinc	7.3
Iron	6.5
Silicon	2.5
Aluminium	55.3

or in atomic percentages 17.9, 3.9, 4.1, 3.1 and 71.0% of manganese, zinc, iron, silicon and aluminium, respectively.

With the density  $\delta = 3.87 \pm 0.1$  g.cm.<sup>-3</sup>, measured by the flotation method, and with the unit-cell dimensions  $a = 7.47 \pm 0.05$  and  $c = 7.72 \pm 0.05$  Å, obtained from the layer-line separations on the corresponding oscillation photographs, the content of the unit cell is calculated to be  $25.4 \pm 0.8$  atoms. This indicates that the  $2(d)$  positions are left unoccupied. Assuming the other positions to be fully occupied, the content of the unit cell is:

Manganese	4.6 atoms
Zinc	1.0
Iron	1.1
Silicon	0.8
Aluminium	18.5

Fourier projections were prepared with the  $hk \cdot 0$  intensity data, collected from zero-layer Weissenberg photographs and corrected in the usual way. The plot of the  $F_o$  synthesis is essentially the same as that for the  $T_4$  structure and so it is not presented here. From this it may be concluded that the  $T_4$  compound can dissolve an appreciable amount of iron. In so doing the structure itself is not changed and the  $2(d)$  positions are again left unoccupied.

Frequently iron and manganese in this group of intermetallic compounds can replace each other to quite a considerable extent. Of the elements iron, cobalt, nickel and copper, iron is the only one which dissolves appreciably in  $\text{MnAl}_6$ , the replacement proceeding atom for atom (Raynor, 1944). In the aluminium-manganese-iron system no true ternary compound is found in equilibrium with the Al  $\alpha$ -solid solution; the miscibility of iron and manganese is not restricted by formation of stable ternary compounds. There is extensive replacement of iron by manganese atoms also; thus  $\text{FeAl}_3$  is the only one of the compounds of aluminium with iron, cobalt, nickel and copper, in which manganese dissolves appreciably, the replacement proceeding atom for atom (Raynor, 1944). Iron and manganese atoms in these structures are 10-coordinated and this might be an explanation for the ease with which these two elements replace each

other in the above compounds as well as in the  $T_4$  compound.

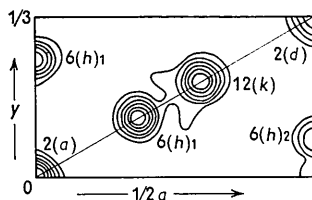


Fig. 3.  $F_0$  projection down the hexad of the  $T_4$  compound containing nickel. In the presence of nickel the  $2(d)$  positions are occupied. The first contour is at 0 and the remainder at intervals of 150 arbitrary units.

It is of interest to note that in a preliminary experiment it was found that the  $T_4$  compound can also dissolve nickel. The first electron-density projection has, however, shown clearly that in the presence of nickel the  $2(d)$  positions are (at least partially) occupied (Fig. 3), i.e. the structure is now of the  $\text{Co}_2\text{Al}_5$  type. It cannot be decided, however, whether nickel atoms occupy  $2(d)$  or  $6(h)_1$  positions, though it may be expected that the nickel atoms will occupy the  $2(d)$  positions since these are 9-coordinated and the preferred number of neighbours for nickel is either 8 or 9.

### 8. Conclusion

The  $\beta(\text{AlMnSi})$  compound can take up some zinc. This quaternary compound is denoted by the symbol  $T_4$ . The characteristic feature of the  $\beta(\text{AlMnSi})$  structure is the set of vacant sites corresponding to the  $2(d)$  positions. Detailed structure analysis has shown that these positions are left vacant in the  $T_4$  structure also, and that zinc replaces manganese atom for atom up to about 23%. This replacement is not consistent with the previous suggestion that  $\beta(\text{AlMnSi})$  is an electron compound. It is suggested that there is no real basis for classifying the  $T_4$  and  $\beta(\text{AlMnSi})$  structures, as well as the structurally similar  $\text{Co}_2\text{Al}_5$  and  $\pi(\text{AlFeNi})$  compounds as electron compounds.

Iron and nickel can be dissolved in the  $T_4$  compound. While iron replaces manganese, in the presence of nickel the  $2(d)$  positions are occupied. This difference in behaviour is in accordance with the preferential number rule of Black. It serves to show that structural analysis of compounds and a study of the possible replacement of one kind of atom by another, may

contribute to the discussion and better understanding of intermetallic compounds of this class.

We wish to thank Prof. N. F. Mott and Dr W. H. Taylor for provision of facilities and for their interest and encouragement. We are grateful to several colleagues, particularly Dr J. A. Bland and Dr P. J. Brown, for many valuable discussions. The computations were made in the Cambridge University Mathematical Laboratory and we are thankful to Dr M. V. Wilkes for allowing time on the EDSAC Digital Computer, and to Mrs M. McGibbon for assistance with the calculations. The Admiralty Materials Laboratory kindly carried out the chemical analysis of the crystals.

One of us (A. D.) wishes to thank Prof. P. Savić from the University of Belgrade for encouragement and the Institute 'Boris Kidrič', Belgrade for a grant. P. J. B. wishes to thank the Council of the Royal Society for a Mr and Mrs John Jaffé Donation Studentship.

### References

- AXON, H. J. & HUME-ROTHERY, W. (1948). *J. Inst. Met.* **74**, 315.  
 BLACK, P. J. (1955). *Phil. Mag.* **46**, 155.  
 BLACK, P. J. (1956). *Acta Met.* **4**, 172.  
 BOOTH, A. D. & BRITTEN, K. H. V. (1948). *Proc. Roy. Soc. A*, **193**, 305.  
 BRADLEY, A. J. & SEAGER, G. C. (1939). *J. Inst. Met.* **64**, 81.  
 BRADLEY, A. J. & TAYLOR, A. (1940). *J. Inst. Met.* **66**, 53.  
 DAMJANOVIC, A. (1957). Dissertation for Ph.D. degree, Cambridge.  
 DAMJANOVIC, A. (1961). *Acta Cryst.* **14**, 982.  
 HUME-ROTHERY, W. & COLES, B. R. (1954). *Advances in Physics*, **3**, 149.  
 PHILLIPS, H. W. L. (1943). *J. Inst. Met.* **69**, 291.  
 PHILLIPS, H. W. L. & VARLEY, P. C. (1943). *J. Inst. Met.* **69**, 317.  
 PHRÁGMEN, G. (1950). *J. Inst. Met.* **77**, 489.  
 PRATT, J. N. & RAYNOR, G. V. (1951). *Proc. Roy. Soc. A*, **205**, 103.  
 RAYNOR, G. V. (1944). *J. Inst. Met.* **70**, 531.  
 RAYNOR, G. V. & WAKEMAN, D. W. (1947). *Proc. Roy. Soc. A*, **190**, 83.  
 ROBINSON, K. (1952). *Acta Cryst.* **5**, 397.  
 TAYLOR, M. A. (1959). *Acta Cryst.* **12**, 393.  
 TAYLOR, W. H. (1954). *Acta Met.* **2**, 684.  
 TAYLOR, A. & SINCLAIR, H. B. (1945). *Proc. Phys. Soc.* **57**, 126.