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The Structure of β(AlMnSi)–Mn_3SiAl_9

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The structure of Mn_3SiAl_9 is similar to that of Co_2Al_5 with manganese and silicon atoms replacing cobalt and aluminium atoms, respectively. The major difference between the two structures is that two atomic sites per unit cell, occupied by cobalt atoms in Co_2Al_5, are vacant in Mn_3SiAl_9. The structural similarity of the two compounds (and of the π(AlFeNi) phase) is accounted for in terms of a prominent Brillouin zone with an inscribed Fermi distribution corresponding to 1·68 electron states per atom. It is suggested that the 'holes' in the structure of Mn_3SiAl_9 occur so as to preserve an electron/atom ratio in the neighbourhood of 1·68. The transitional metal atoms must effectively reduce the total number of electron states, the extent of this effect being estimated to be 4·1, $2{\cdot}6_5$, $1{\cdot}8_5$ and $0{\cdot}6_5$ states per atom for Mn, Fe, Co and Ni, respectively. Raynor's suggestion that the reduction in the total number of electron states is due to absorption of otherwise free electrons into vacancies in the 3*d* orbitals of the transitional metal atoms receives qualitative support.

1. Introduction

This X-ray examination of single crystals of ternary compounds occurring in the Al–Mn–Si system forms part of a programme of structural work on aluminium-rich intermetallic compounds. The research is being carried out in conjunction with the metallographic examination of the alloys by Raynor and his collaborators in the University of Birmingham, England (see, for example, Pratt & Raynor, 1951), and I am indebted to Dr Pratt and Prof. Raynor for all the specimens used in the present work.

The phase diagram of the aluminium-rich portion of the Al–Mn–Si system has been given by Bückle (1938) and by Phillips (1943). In addition to Al, Si, $MnAl_4$ and $MnAl_6$, Bückle recognised three ternary compounds, which were denoted by the symbols T, X and Y, whilst Phillips confirmed the existence of T and X, but called them α and β respectively. This latter nomenclature has been adopted by Pratt & Raynor (1951) and is used here. α(AlMnSi) has been shown by Phragmén (1950) to have a cubic structure with $a_0 = 12{\cdot}625$ kX., but the details of the atomic arrangement are as yet unknown. No crystallographic data have previously been reported for β(AlMnSi), to which the structural formula Mn_3SiAl_9 has been assigned as a result of the present investigation.

2. Specimens

Crystals of β(AlMnSi) up to 2 or 3 mm. in linear dimensions had been extracted electrolytically from a number of slowly cooled or quenched alloys. All the specimens are from melts containing 6% manganese and amounts of silicon up to 6%. In Table 1 are listed the chemical compositions of this range of samples, each one being denoted by a symbol (y/x), y and x being the manganese and silicon contents by weight of the original melts.

Table 1. *Compositions and electron/atom ratios* (E/A) *of* β(AlMnSi) *samples*

	Composition (atomic %)			
Sample	Mn	Si	Al†	E/A*
(6/1)	21·08	5·68	73·24	1·65
(6/1·5)	22·37	5·72	71·92	1·57
(6/2)	22·05	6·50	71·45	1·59
(6/2·5)	22·13	6·59	71·28	1·59
(6/3)	21·21	7·26	71·53	1·66
(6/4)	22·56	7·69	69·75	1·57
(6/5)	21·64	8·19	70·17	1·65
(6/6)	19·60	8·88	71·52	1·78
Mn_3SiAl_9	23·1	7·7	69·2	1·54

† By difference.
* Computed on the basis of +3, +4 and −3·66 electrons/atom for Al, Si and Mn, respectively (see § 5 (ii)).

It is to be noted that as x increases, so also does the silicon content in the extracted crystals. With this tendency there also seems to be a gradual change in the crystal habit. Crystals extracted from the melt (6/1) are very thin hexagonal plates with highly reflecting faces. As the silicon content increases, the habit remains the same, except that the thickness of the plates increases and, as a result, side faces develop. The sample from melt (6/6), however, shows no outward indication of a hexagonal structure and is also very much more brittle than the other samples.

3. Experimental data

Full details of the experimental procedure are not presented here, nor are tables comparing observed structure factors with those calculated from the final

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structure; these details are available elsewhere (Robinson, 1951).

(i) *Powder photographs*

Powder photographs of four of the samples taken with monochromatic Fe $K\alpha$ radiation in a 9 cm. diameter Debye–Scherrer camera have been indexed in terms of a hexagonal unit cell. It has not been possible to use extrapolation methods for determining the lattice parameters, because of the general weakness of the high-angle reflexions; a_0 has been determined as a mean of the values obtained from the spacings of the (30$\bar{3}$0), (33$\bar{6}$0), (43$\bar{7}$0) and (52$\bar{7}$0) reflexions, whilst c/a has been deduced from the spacings of the (30$\bar{3}$5), (30$\bar{3}$6), (20$\bar{2}$7) and (30$\bar{3}$7) lines, using the value of a_0 already found. The results are given in Table 2, from

Table 2. *Lattice parameters of* β(AlMnSi) *specimens*
(Fe $K\alpha$, λ = 1·9373 Å)

Specimen	a_0 (Å)	c_0 (Å)	c/a
(6/1)	7·519	7·768	1·0331
(6/2)	7·513	7·745	1·0308
(6/3)	7·509	7·736	1·0299
(6/6)	7·500	7·722	1·0297

which it can be noted that a_0 and c_0 decrease with increasing silicon content.

(ii) *Single-crystal photographs*

The Laue symmetry is $6/mmm$ and the systematic absences are consistent with space group D^4_{6h}–$C6/mmc$.

Intensity data have been taken from oscillation and equatorial Weissenberg photographs of a small, almost cube-shaped, fragment of the sample (6/2), having linear dimensions of approximately 0·15 mm. The use of Mo $K\alpha$ radiation reduces considerably the effect of absorption. Intensities have been estimated visually by comparison with a standard intensity scale prepared from the same crystal and have been corrected for the Lorentz and polarization factors. A further approximate correction has been made for the variation with $\sin\theta$ of the separation of the $K\alpha_1\alpha_2$ doublet.

In the final stages of refinement of the structure these corrected intensities, I'_{hkil}, have been reduced to an absolute scale of intensity by putting $F_{hkil}=G\sqrt{I'_{hkil}}$, F_{hkil} then being the observed structure factor and G being a factor whose variation with $\sin\theta/\lambda$ for the ($hki0$) reflexions is shown in Fig. 1. This curve has been obtained by plotting the mean value of $F_{hki0}(\text{calc.})/\sqrt{I'_{hki0}}$

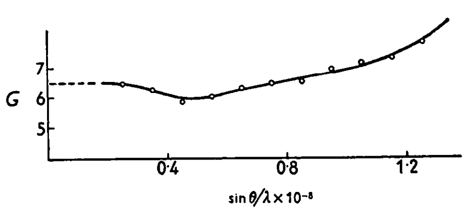

Fig. 1. Variation of the factor G with $\sin\theta/\lambda$. The broken part of the curve is an extrapolation.

taken over reflexions lying within the ranges of $\sin\theta/\lambda\times10^{-8}=0·2-0·3, 0·3-0·4, \ldots, 1·2-1·3$, F_{hki0} (calc.) being the structure factors calculated after the previous electron-density synthesis. Any error in the approximate correction for the separation of the $K\alpha_1\alpha_2$ doublets would then be automatically allowed for in this final scaling of the observed intensities.

(iii) *The number of atoms per unit cell*

Both the unit-cell dimensions and the space group of β(AlMnSi) are similar to those given by Bradley & Cheng (1938) for the compound Co_2Al_5, in which there are 28 atoms per hexagonal unit cell. It is also significant that the compositions of the samples shown in Table 1 approximate closely to $(Mn,Si)_2Al_5$. There are, however, large differences between the intensities of lines on powder photographs of β(AlMnSi) and Co_2Al_5. Moreover, the density of the β(AlMnSi) crystals is considerably less than that of Co_2Al_5, that of the sample (6/2) being 3·74 g.cm.$^{-3}$ against 4·14 g.cm.$^{-3}$ for the binary compound. With this density and the composition given in Table 1 the sample (6/2) would have only 25·6 atoms per unit cell instead of the 28 of Co_2Al_5.

4. Determination of the structure

(i) *Projection down the hexad axis*

A Patterson synthesis of the ($hki0$) intensities of β(AlMnSi) could be interpreted moderately well in terms of Bradley & Cheng's Co_2Al_5 structure assuming manganese to replace cobalt, viz:

6 Mn_1 in 6(h); $x, 2x, \frac{1}{4}$ with x=0·128 .
2 Mn_2 in 2(d); $\frac{2}{3}\frac{1}{3}\frac{1}{4}$.
2 Al_0 in 2(a); 000 .
6 Al_1 in 6(h); $x, 2x, \frac{1}{4}$ with x=0·467 .
12 Al_2 in 12(k); $x, 2x, z$ with x=0·196 and z=−0·061 .

Much better agreement could, however, be obtained merely by the omission of the two Mn_2 atoms. Calculation of the structure factors of a few low-order ($hki0$) reflexions confirmed that these atomic positions must be left vacant and should not even be filled by lighter atoms (Al or Si); this is in agreement with the much lower density of β(AlMnSi) compared with that of Co_2Al_5.

Successive stages of refinement of this projection of the structure produce shifts of all the atoms from the positions occupied in Co_2Al_5. In Fig. 2 is shown the final synthesis using all reflexions with $\sin\theta/\lambda < 1·3$ Å^{-1} without any artificial convergence factor. The position which would be occupied by the Mn_2 atoms is marked by the letter M; it is clear that there is no appreciable electron density in this region. Parameters estimated graphically from this synthesis are given in column 1 of Table 3; series-termination errors estimated by the F_c synthesis method of Booth

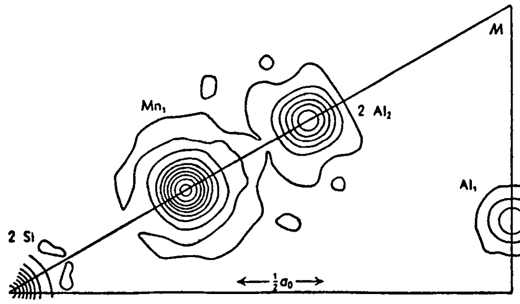

Fig. 2. The asymmetric unit of the projection of electron density down the hexad axis of β(AlMnSi). The first contour is at 50 and the remainder at intervals of 100 arbitrary units.

(1946) are shown in column 2 and the parameters after correction for this type of error in column 3.

Table 3. *The parameters of the* β(AlMnSi) *structure*

Parameter	Atom	1	2	3	4
x	Mn_1	0·1192	0·0007	0·1199	0·0010
x	Al_1	0·4579	−0·0001	0·4578	0·0030
x	Al_2	0·2006	0·0001	0·2007	0·0022
z	Al_2	$-0{\cdot}068_2$	$0{\cdot}001_3$	−0·067	0·003

1. Parameters from F_o synthesis.
2. Difference of 1 from parameters from F_c synthesis.
3. Parameters corrected for series-termination errors.
4. Standard deviation in the parameters.

It is desirable to have some estimate of the accuracy of these atomic parameters. Since allowance has already been made for the effect of series-termination and since there is no pronounced overlapping of peaks in this projection (see Fig. 2), the main source of error is likely to be in the experimental inaccuracies of the observed structure factors. An estimate of this effect has been made by the method recommended by Cruickshank (1949), which depends on the use of the quantities $\Delta F = |F_o - F_c|$. This is shown in column 4 of Table 3. A further approximate estimate of the accuracy of the structure is given by the arbitrary factor $R_1 = \Sigma|F_o - F_c| \div \Sigma|F_o|$, which in the final synthesis of this projection is reduced to 0·11.

(ii) *The z parameters*

All the z parameters except that of the Al_2 atoms are fixed by symmetry.* This one parameter has been estimated from a synthesis of the (000l) structure factors and the details of its determination are given in Table 3. The one-dimensional synthesis is shown in Fig. 3.

* It should be noted that this would not be the case if the symmetry were lower than C_{6h}^4–$C6/mmc$, i.e. if the space group were C_{6v}^4–$C6mc$ or D_{3h}^4–$C\bar{6}2c$. A thorough investigation has been made to see whether the results given in § 6 (iii), which are there attributed to electron absorption, might not be interpreted equally well merely by atomic shifts consistent with the requirements of these space groups of lower symmetry; in no case has this been possible.

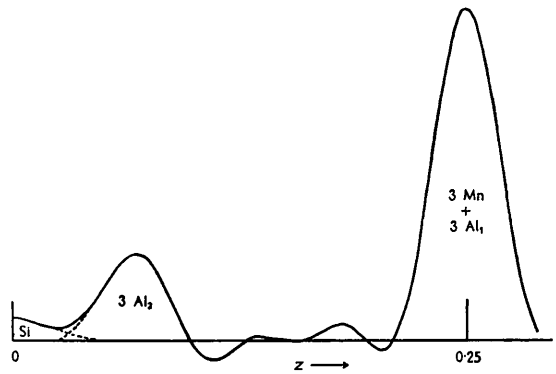

Fig. 3. One-dimensional electron-density synthesis along the c axis of β(AlMnSi).

Direct solution of the structure-factor equation for the one unknown z parameter using the observed structure factors of (000l) reflections gives a mean value for this parameter of $\pm 0{\cdot}067_4$ with a standard deviation of $0{\cdot}003_1$, in agreement with the value given in Table 3.

(iii) *Location of the silicon atoms*

During the process of refinement of the (hki0) projection of the electron density it became possible to distinguish between silicon and aluminium atoms. Three pieces of information suggested that the silicons occupy the 2(a) positions (at the origin of Figs. 2 and 3):

(1) The silicon content of the sample (6/2) corresponds to 1·7 atoms per unit cell and that of the other samples also approaches two atoms per cell. The position 2(a) is the only twofold position occupied in this structure.

(2) At all stages in the refinement of the (hki0) projection of the electron density the origin peak

Table 4. *Interatomic distances in* β(AlMnSi)

Atom	Neighbour	No. of neighbours	Distance (Å)	Probable error (Å)
Si	Al_2	6	$2{\cdot}66_5$	0·01
	Mn_1	6	2·486	0·002
Al_1	Al_1	2	$2{\cdot}80_5$	0·02
	Al_2	4	2·77	0·02
	Al_2	4	2·97	0·02
	Mn_1	2	2·420	0·005
Al_2	Si	1	$2{\cdot}66_5$	0·01
	Al_1	2	2·77	0·02
	Al_1	2	2·97	0·02
	Al_2	2	$2{\cdot}81_5$	0·02
	Al_2	2	2·99	0·02
	Al_2	1	$2{\cdot}83_5$	0·03
	Mn_1	1	2·67	0·02
	Mn_1	2	2·68	$0{\cdot}01_5$
Mn_1	Si	2	2·486	0·002
	Al_1	2	2·420	0·005
	Al_2	4	2·68	$0{\cdot}01_5$
	Al_2	2	2·67	0·02

remains greater than the peak corresponding to $2Al_2$ both in height and in total electron count.

(3) The distance of the atom at (000) from its six neighbouring aluminium atoms is appreciably less than that between any other pair of aluminium atoms in the structure (see Table 4).

The structural formula of β(AlMnSi) is therefore Mn_3SiAl_9 with two 'molecules' per unit cell. In atomic per cent this ideal composition is Mn = 23·1%, Si = 7·7% and Al = 69·2%; this should be compared with the range of compositions given in Table 1.

5. Discussion

(i) *Description of the structure*

An important feature of the structure is the layering of atoms parallel to the basal plane, there being puckered sheets at heights $z = 0$ and $\frac{1}{2}$, and flat sheets at heights $z = \frac{1}{4}$ and $\frac{3}{4}$. There are also well defined sheets of atoms parallel to $\{11\bar{2}0\}$ (see Fig. 4). This marked tendency to form layer structures seems likely to be a general feature of aluminium-rich intermetallic compounds, although the structures of only a few have as yet been determined in detail.

Details of the interatomic distances in the structure are shown in Table 4. The strangest feature concerns the ten atoms surrounding the manganese atoms. The closer proximity to Mn_1 of the two Al_1 atoms than of the two smaller Si atoms is remarkable, but all these four atoms are considerably closer to the manganese atom than would normally be expected in 10-co-ordination. The larger Mn_1–Al_2 distances are close to those which would be expected from the interatomic distances of manganese and aluminium atoms in the pure metals (*c.* 2·6 Å and 2·86 Å, respectively). A similar division into close and more distant neighbours surrounding chromium atoms has been noted in the compound $Cr_4Si_4Al_{13}$ (Robinson, 1951), and in Co_2Al_9 one aluminium atom approaches much closer to a cobalt atom than do the other aluminium neighbours (Douglas, 1950). It is suggested in § 6 (ii) below that the shortening of the bonds between transitional metal atoms and some aluminiums is connected in some way with electron transfer. The separations of pairs of aluminium atoms vary considerably from 2·77 Å upwards. Depending on whether an upper limit for atoms in contact is fixed at 2·9 Å or at 3·0 Å the mean Al–Al distance for the structure is $2{\cdot}79_5$ Å with a standard deviation of $0{\cdot}02_5$ Å or 2·87 Å with a standard deviation of 0·09 Å, in essential agreement with the distance of closest approach in pure aluminium (2·86 Å).

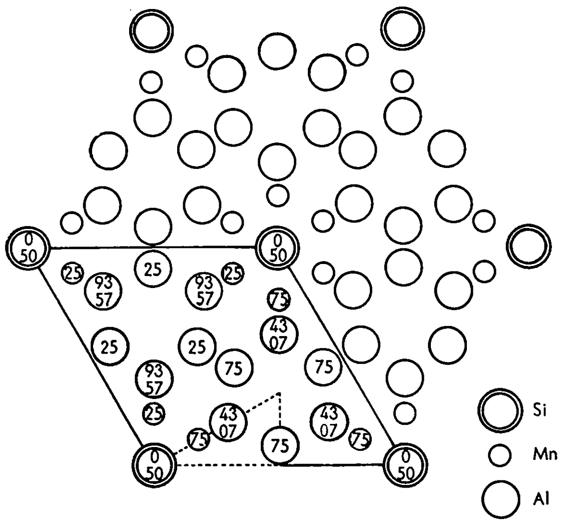

Fig. 4. Projection of the β(AlMnSi) structure down the hexad axis. Heights of atoms above the $z = 0$ plane are marked in hundredths of c_0.

The main interest in the structure, however, lies in its peculiar similarity to that of Co_2Al_5 and in the *regular* array of vacant atomic sites which it possesses. That these sites correspond to quite large holes in the structure may be gauged from Fig. 5. Surrounding

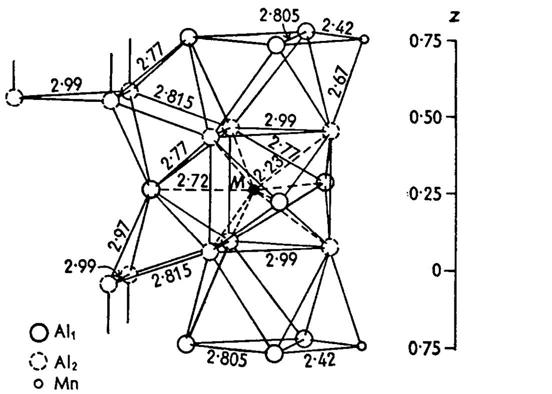

Fig. 5. Perspective view of the group of aluminium atoms surrounding the vacant site *M* together with some of their contacts with other groups of atoms. Distances in Ångström units.

the centre of each hole is a group of nine aluminium atoms—six Al_2 at a distance of $2{\cdot}23_5$ Å and another three Al_1 at a distance of 2·72 Å. Thus it would need only a small displacement of the surrounding aluminiums for this site to be capable of taking a manganese or silicon atom. The fact that in Co_2Al_5 the site is occupied by a cobalt atom is proof of this. Why, then, are the holes maintained in the structure of Mn_3SiAl_9 and what is the relationship between Mn_3SiAl_9 and Co_2Al_5 that they should have such similar structures? An answer to both these questions can be found by a consideration of the prominent Brillouin zones of the structures.

(ii) *The first prominent Brillouin zone of the structures*

Associated with this type of structure there is a very prominent Brillouin zone formed by planes which give very intense X-ray reflexions and all of which have interplanar spacings close to 2 Å. These strong

Table 5. *Values of p and of F^2 for planes contributing to the Brillouin zones of* Co_2Al_5*-type structures*

$p\ (= 1/2d_{hkil})$ is the distance of a plane from the origin of reciprocal space.
The first plane has too small an intensity to be effective in the case of Co_2Al_5.

		Mn_3SiAl_9		Co_2Al_5*		$Mn_3Si_2Al_9$
$(hkil)$	Multiplicity	p (Å^{-1})	$F^2 \times 10^{-2}$	p (Å^{-1})	$F^2 \times 10^{-2}$	$F^2 \times 10^{-2}$
$(30\bar{3}0)$	6	0·231	103	0·2262	28	71
$(30\bar{3}1)$	12	0·239	228	0·2356	161	228
$(21\bar{3}2)$	24	0·241	100	0·2390	108	117
$(20\bar{2}3)$	12	0·247	152	0·2485	216	190
(0004)	2	0·258	228	0·2633	299	282
$(22\bar{4}0)$	6	0·266	106	0·2612	253	143

* From the data given by Bradley & Cheng (1938).

Table 6. *Calculation of electron/atom ratios (E/A) associated with the inscribed prolate spheroids of the Brillouin zones*

Structural formula	No. of atoms per cell	Mean atomic volume (v)	p (min.) (Å^{-1})	p (0004) (Å^{-1})	Volume of spheroid (V) (Å^{-3})	$E/A = 2\,vV$.
Co_2Al_5	28	13·76	0·2356	0·2633	0·0611	1·68
Mn_3SiAl_9	26	14·56	0·231	0·2588	0·0578	1·68
$Mn_3Si_2Al_9$	28	13·76*	0·2262*	0·2633*	0·0564	1·55

* Assuming unit cell dimensions as in Co_2Al_5.

reflexions are listed in Table 5 and drawings of the zones of Mn_3SiAl_9 and Co_2Al_5 in reciprocal space are shown in Fig. 6, the only major difference between them being the omission of the $\{30\bar{3}0\}$ faces from the Co_2Al_5 zone.

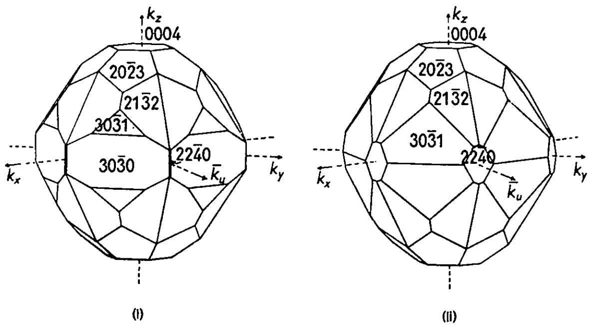

Fig. 6. The first prominent Brillouin zones of (i) the Mn_3SiAl_9 structure, and (ii) the Co_2Al_5 structure.

If V is the volume of the Fermi distribution of electrons plotted in reciprocal space and v is the mean atomic volume, then it can be shown than an electron compound would be expected to have an average of $2Vv$ free electrons per atom. If the theory of Jones (1934) is applicable to complicated structures of this type, then it might be inferred from the prominence and highly symmetrical nature of the Brillouin zones shown in Fig. 6 that the limit of the Fermi distribution corresponds closely to the inscribed prolate spheroid of the zones. Hence it can be shown that these structures might well be associated with *electron* compounds having compositions at the electron-rich boundary of the phase corresponding to an average of 1·68 free electrons per atom (see Table 6).

A third compound—π(AlFeNi)—has been reported by Bradley & Taylor (1940) to have a Co_2Al_5-type structure. From their published X-ray photographs it may be inferred that this compound resembles Co_2Al_5 in having 28 atoms per unit cell with Fe and Ni atoms replacing Co atoms.

Now if aluminium and silicon contribute their normal complement of 3 and 4 free electrons per atom, respectively, to the structure as a whole it is necessary to suppose that in these three compounds the transitional metal atoms *prevent* some of these electrons from behaving as if free. Only then could the average electron/atom ratio be as low as 1·68. From the characteristic electron/atom ratio of the structures (1·68) and the compositions at electron-rich boundaries of the phases we may estimate the magnitude of this effect as follows:

Mn	Fe	Co	Ni	
4·1	$2{\cdot}6_5$*	$1{\cdot}8_5$	$0{\cdot}6_5$*	electrons per atom.

* (Assuming the difference between Fe and Ni to be 2·0 electrons per atom.)

In estimating these values the following compositions have been used to represent the electron-rich state:

β(AlMnSi): Mn = 19·60 atomic %, Si = 8·88 atomic %; sample 6/6 (Table 1).
Co_2Al_5: Co = 27·2 atomic %; estimated from diagram given by Bradley & Seager (1939).
π(AlFeNi): Fe = 17·7 atomic %, Ni = 8·7 atomic %; estimated from Fe-poor corner of the π single phase field given by Bradley & Taylor (1940).

The values determined above are close to those suggested by Raynor (1944) for the electronic behaviour of these elements in electron-rich surroundings, namely:

Mn	Fe	Co	Ni	
3·66	2·66	1·71	0·61	electrons per atom.

The occurrence of the three different compounds with similar structures is therefore to be explained by the fact that they are electron compounds with similar electron/atom ratios. It should be emphasised that this could also be demonstrated by using other sets of 'effective valencies' for the transitional metal atoms, provided they *increase algebraically* by units of one electron per atom from Mn to Fe, Fe to Co, etc., as may be seen from the following examples:

'Effective valency' of				Electron/atom ratio of		
Mn	Fe	Co	Ni	β(AlMnSi)	Co_2Al_5	π(AlFeNi)
−5	−4	−3	−2	1·52	1·37	1·33
−2	−1	0	1	2·11	2·18	2·12
0	1	2	3	2·50	2·73	2·65

By fixing the magnitude of the average electron/atom ratio of the structure (1·68) from the size of the prominent Brillouin zone, however, the magnitudes of the 'effective valencies' are fixed, and these prove to be close to the scale suggested by Raynor (1944).

Next it is necessary to consider the holes in the structure of β(AlMnSi). If they were fully occupied by manganese atoms the composition would be Mn_4SiAl_9 and, using Raynor's 'effective valency' for Mn, the electron/atom ratio would be as low as 1·16, which would not correspond to that of the Brillouin zone. Occupation of the holes by silicon atoms ($Mn_3Si_2Al_9$) would, however, only slightly increase the electron/atom ratio to 1·71. On the other hand the number of electrons per atom associated with the Brillouin zone of such a structure would fall to 1·55 (see Tables 5 and 6), since the shape of the zone would be that of Mn_3SiAl_9 (because of the inclusion of the $\{30\bar{3}0\}$ faces), whilst the mean atomic volume would be that of Co_2Al_5. Thus, inclusion of silicon in the holes would also produce an electronically less stable state of affairs. It seems likely, therefore, that although these atomic sites might possibly be occupied on the grounds of packing considerations alone, yet the electronic factors tip the scales against it.

6. Evidence for electron absorption in the manganese atoms

(i) *Introduction*

A mechanism has been suggested by Raynor by which the transitional metal atoms may prevent some electrons, which would otherwise be free, from behaving as if they were free. Such electrons are considered to be absorbed into vacancies which exist in the atomic orbitals of the 3*d* shell in the transitional metal atoms, the extent of the absorption varying from 3·66 electrons per atom for manganese to 0·61 electrons per atom for nickel. Douglas (1950) has given some evidence for an excess of electrons in the cobalt atoms in Co_2Al_9, and it is interesting to see what conclusions can be drawn from the structure of Mn_3SiAl_9 in this respect.

(ii) *Electron counts*

Counts of total number of electrons associated with equal areas surrounding each peak of the (*hki*0) electron-density projection, which had been put on to an absolute scale by using the curve of Fig. 1, are as follows:

Peak	2 Si	Mn_1	2 Al_2	Al_1
No. of electrons	27·0	24·2	23·7	10·9

The total electron count from these areas is, however, only 380 per unit cell instead of the 412 expected from two 'molecules' of Mn_3SiAl_9. A further 24 electrons per cell can be found in the 30% of the total projection area not ascribed to any peak, the final deficiency of 8 electrons per cell being attributed to error in putting the F's on an absolute scale.

It is therefore impossible to make an *absolute* estimate of the total electron content of the individual atoms merely from a projection of the structure. However, the electron count of Mn_1 *relative* to those of the aluminium atoms is greater than the normal ratio of 25:13, particularly in the case of Al_1. This is particularly significant in that the chemical analysis of the sample (6/2) suggests a deficiency of manganese, giving the equivalent of only 5·74 manganese atoms per cell instead of six. It is also significant that the Al_1 atoms, which must be considered as the most likely donors in the proposed electron transfer, are those lying very close to Mn_1 (§ 5 (i), above), suggesting that such a transfer is associated with a shortening of the Mn–Al interatomic distances. Comparison of Mn_1 with 2 Si is only consistent with the suggested electron absorption if allowance is made for the chemical deficiency of manganese, the amount then being about one excess electron per manganese atom.

An attempt has also been made to detect excess electrons by using an $(F_o - F_c)$ synthesis of only those (*hki*0) reflections having $\sin\theta/\lambda < 0{\cdot}5$ Å^{-1}, since this would be the limit of any contribution to F of the 3*d* electrons in manganese atoms. Although indicating a slight excess, the method is considered to be unreliable because of the small number of terms available, and it is proposed to carry out a three-dimensional analysis on these lines as soon as data have been collected.

(iii) *Critical low-angle* (*hkil*) *reflexions*

As a further test of the proposed electron absorption low-angle reflexions, whose intensities have an appreciable contribution from the manganese atoms, have been compared with $(10\bar{1}3)$, to whose intensity the manganese atoms contribute little. Intensities have been estimated photometrically from photographs of a flat plate powder specimen taken in a 20 cm. diameter semi-focusing camera using Cu $K\beta$ radiation monochromatized by reflexion from a plane lithium fluoride crystal. They have been corrected for the Lorentz, polarization and absorption factors and also

Table 7. (i) *Structure factors, F, of critical low-angle reflexions relative to* $|F(10\bar{1}3)|=100$

	$\|F_c\|$					
$(hkil)$	A	B	C	D	E	$\|F_o\|$
$(10\bar{1}0)$	78·0	89·8	74·5	86·0	90·5	85
(0002)	112	131	106	125	118	113
$(10\bar{1}2)$	30·1	39·8	26·3	34·5	36·1	39·5
$(20\bar{2}1)$	46·2	55·3	42·2	51·2	51·2	54
$(10\bar{1}3)$	100	100	100	100	100	100

(ii) *Ratios of intensities of pairs of reflexions*

		Calc. ratio $I(hkil)/I(h'k'i'l')$					Observed ratio
$(hkil)$	$(h'k'i'l')$	A	B	C	D	E	
$(20\bar{2}1)$	$(20\bar{2}2)$	2·53	5·08	1·90	3·73	3·87	3·5
$(21\bar{3}0)$	$(21\bar{3}1)$	1·75	0·92	2·46	1·30	1·32	1·0

A. *F* calculated for 6 Mn atoms/cell without absorbed electrons.
B. *F* calculated for 6 Mn atoms/cell each with 3·66 absorbed electrons.
C. *F* calculated for 5·74 Mn atoms/cell without absorbed electrons.
D. *F* calculated for 5·74 Mn atoms/cell each with 3·66 absorbed electrons.
E. As *D*, but assuming trebly ionised Al_1 atoms.

for the thermal vibrations of the atoms using a factor of the form $\exp(-2B\sin^2\theta/\lambda^2)$ with $B(=0{\cdot}26\times10^{-16}$ cm.$^2)$ estimated from the high-angle portion of the curve in Fig. 1 ($\sin\theta/2 > 0{\cdot}7$ Å^{-1}). Since the reflexions are not strong, extinction has been neglected.

In Table 7(i) the observed structure factors are compared with those calculated on various assumptions ($A-E$) regarding the state of the manganese atoms. The atomic scattering factors used in these calculations are for the normal atoms those given by Viervoll & Ögrim (1949), whilst the contribution of the proposed 3·66 additional 3*d* electrons in the manganese atoms has also been estimated from the data given by these authors. The scattering factors for the proposed trebly ionised Al_1 atoms in *E* are taken from James & Brindley (1931).

In Table 7(ii) are shown observed and calculated intensity ratios of two pairs of neighbouring reflexions on oscillation photographs. Each pair consists of one reflexion whose manganese contribution is in phase with the resultant amplitude and one with the manganese atoms out of phase with the resultant, so that the intensity ratio is markedly dependent on the electronic state of the manganese atoms.

In both tables, *B* is an improvement on *A* with the exception of the (0002) reflexion. This suggests that the electron transfer may be taking place in the (000*l*) plane, in agreement with the very low electron count found for the Al_1 atoms. Similarly, *D* and *E* are improvements on *C* and also show some improvement on *B*, but it is difficult, except in the case of (0002), to assess whether *E* is better than *D*.

7. Conclusion

The results given in the two previous subsections support the suggestion that electrons may be absorbed into the 3*d* shells of the manganese atoms, but to what extent it is difficult to say. The electron counts indicate a smaller effect by about a half than is suggested by Raynor, whilst the examination of the intensities of the critical (*hkil*) reflexions suggests something closer to Raynor's value. Generalization of these tendencies must, however, await results from other structures which are now under examination. Caution should also be exercised at present in making generalizations about other features of these structures, such as the shortening of some interatomic distances between aluminium and transitional metal atoms mentioned in § 5 (i).

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