dimensions reported by Pignataro & Post (1955) were used in the calculations. Hydrogen atoms, 1·08 Å from the carbon atoms and assumed rotating freely about the C–C axes, were included in the calculations. Structure factors were computed assuming tilts of 0, $2\frac{1}{2}$, 5 and $7\frac{1}{2}$ degrees with the results shown in Table 2 and in Fig. 6.

Table 2. *R factor as a function of molecular tilt*

R	0	$2\frac{1}{2}$	5	$7\frac{1}{2}$
All reflections	12·77	12·02	11·02	13·21
All reflections except (002) and (201)	12·39	11·78	10·44	13·53
Reflections of type $l^2/(h^2+k^2+l^2) \geq 0{\cdot}5$ only	10·81	9·42	6·45	12·45

The (002) and (201) reflections were very intense and appeared to suffer strongly from extinction effects. They have therefore been excluded from some of the above calculations. It is clear that there is a distinct minimum in *R* when the molecular tilt is 5°. As might be expected, the minimum is sharpest when it is computed for reflections whose *l* index is relatively large.

Although the evidence is scanty for the low temperature form, the 10° tilt indicated for the phase appears physically reasonable and consistent with the high temperature data. The onset of the transition appears to involve a diminution of the angle of tilt above the transition as well as molecular disorder of the type described.

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The Crystal Structure of Mn_3Al_{10}

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The crystal structure of a previously unknown intermetallic compound Mn_3Al_{10}, hereinafter referred to as φ(AlMn), has been determined by X-ray analysis. The cell dimensions and atomic parameters of the structure and the interatomic distances between neighbouring atoms are given. The structure is very similar to that of β(AlMnSi) (Robinson, 1952) and comparisons between the two structures are made.

Introduction

Work by the author has shown the published Al–Mn phase diagram (Hansen, 1958) to be incorrect in the region 33* to 45% Mn. Crystals of the intermetallic compound φ(AlMn) of approximate composition 37% Mn have been grown by suitable heat treatment of aluminium–manganese alloys in alumina crucibles under an argon atmosphere (the phase appeared in approximately single-phase ingots of composition 37% Mn). The manganese and aluminium used were of the highest available purity (both 99·99%), and care was taken to ensure that no contamination occurred during the thermal treatment. Chemical analysis of the ingot from which the crystals used in this work were extracted gave a silicon content of less than 0·05%.

The unit-cell

The hexagonal unit-cell dimensions were measured by the method of Farquhar & Lipson (1946), using Cu $K\alpha$ radiation, and found to be:

$$a = 7{\cdot}543 \pm 0{\cdot}001, \quad c = 7{\cdot}898 \pm 0{\cdot}001 \text{ Å} .$$

The Laue group was determined as $6/mmm$.

The density of φ(AlMn) was measured, by the displacement method, as $3{\cdot}65 \pm 0{\cdot}05$ g.cm.$^{-3}$. The calculated density for Mn_3Al_{10}, assuming two formula units per unit cell, (the number found in the subsequent structure determination) is 3·74 g.cm.$^{-3}$. The agreement between the two density values is satisfactory, the difference between them probably being due to porosity in the material.

Refinement of the structure

The unit-cell dimensions of φ(AlMn) and β(AlMnSi) are very similar, and the Laue groups of the two phases are identical; obviously, therefore, an intimate relationship exists between the two structures. The refinement proceeded on the assumption that the space

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* Weight compositions are used throughout this paper.

Table 1. *Interatomic distances in* φ(AlMn) *and* β(AlMnSi)

			φ(AlMn)		β(AlMnSi)		
Atom	Neighbour	No. of neighbours	Distance (Å)	Standard deviation (Å)	Distance (Å)	Standard deviation (Å)	Difference in bond lengths (Å)
X	Al_2	6	2·65	0·01	$2{\cdot}66_5$	0·01	$0{\cdot}01_5$
	Mn_1*	6	2·53	0·005	2·486	0·003	0·044
Al_1	Al_1	2	2·75	0·01	$2{\cdot}80_5$	0·03	$0{\cdot}05_5$
	Al_2†	4	2·84	0·01	2·77	0·03	0·07
	Al_2	4	2·99	0·01	2·97	0·03	0·02
	Mn	2	2·41	0·005	2·420	0·007	0·01
Al_2	*X*	1	2·65	0·005	$2{\cdot}66_5$	0·01	$0{\cdot}01_5$
	Al_1†	2	2·84	0·01	2·77	0·03	0·07
	Al_1	2	2·99	0·01	2·97	0·03	0·02
	Al_2	2	2·79	0·01	$2{\cdot}81_5$	0·03	$0{\cdot}02_5$
	Al_2	2	3·03	0·01	2·99	0·03	0·04
	Al_2*	1	2·95	0·01	$2{\cdot}83_5$	0·04	$0{\cdot}11_5$
	Mn_1	1	2·67	0·01	2·67	0·03	0
	Mn_1	2	2·71	0·01	2·68	0·02	0·03
Mn_1	*X**	2	2·53	0·005	2·486	0·003	0·044
	Al_1	2	2·41	0·005	2·420	0·007	0·01
	Al_2	4	2·71	0·01	2·68	0·02	0·03
	Al_2	2	2·67	0·01	2·67	0·03	0

* denotes bonds with lengths in φ(AlMn) and β(AlMnSi) which are significantly different, according to the criteria of Cruickshank (1949).

† denotes a bond with lengths in φ(AlMn) and β(AlMnSi) which are almost significantly different, according to the same criteria.

X denotes atoms Al_0 in φ(AlMn) and Si in β(AlMnSi).

group of φ(AlMn) is the same as that of β(AlMnSi) (i.e. D_{6h}^4–$C6/mmc$) and that the atomic arrangements in the two phases are similar, the silicon atoms in the latter being replaced by aluminium atoms in the former (this yields a formula of Mn_3Al_{10} for φ(AlMn)). The fact that the structure refined satisfactorily is taken as proof that the above assumptions are correct. For a diagram of the structure the reader is referred to Fig. 4 of the paper by Robinson.

The atoms were distributed as follows:

$$\begin{array}{lll} 6\,Mn_1 & \text{in } 6(h); & (x_1, 2x_1, \tfrac{1}{4}) \\ 2\,Al_0 & \text{in } 2(a); & (0, 0, 0) \\ 6\,Al_1 & \text{in } 6(h); & (x_2, 2x_2, \tfrac{1}{4}) \\ 12\,Al_2 & \text{in } 12(k); & (x_3, 2x_3, z_3)\,. \end{array}$$

All the above parameters could be determined from a two-dimensional projection perpendicular to the *a* axis: therefore only data for this setting were obtained.

A small approximately cubic single crystal of φ(AlMn) was selected and zero-layer normal-beam Weissenberg photographs taken with Mo $K\alpha$ radiation for rotation about the *a* axis. The multiple-film technique of Robertson (1943) was used, and the intensities of the reflexions on the exposed films were estimated visually by comparison with a standard intensity scale prepared from the same crystal.

The structure was refined by means of F_o-F_c syntheses (Lipson & Cochran, 1953). The atomic scattering factors of Viervoll & Øgrim (1949) were used. Two scaling operations were found to be necessary: the F_o's were first scaled with respect to the F_c's in regions of $\sin\theta$. Then it was noticed that the large F_o's were much smaller in magnitude than the large F_c's: this is due to extinction in the crystal. Accordingly, an empirical correction was applied (the *small* F_o's were scaled to the small F_c's in regions of $\sin\theta$. The scaling factors thus obtained were then applied to *all* the F_o's and from a curve of scaled F_o's versus F_c's the empirical scaling factor to be applied to the large F_o's was determined).

The atomic parameters were determined as:

$$\begin{aligned} x_1 &= 0{\cdot}1215 \pm 0{\cdot}0003 \\ x_2 &= 0{\cdot}4550 \pm 0{\cdot}0005 \\ x_3 &= 0{\cdot}1995 \pm 0{\cdot}0008 \\ z_3 &= -0{\cdot}0630 \pm 0{\cdot}0005\,. \end{aligned}$$

Some estimate of the accuracy of the structure determination* is given by the arbitrary factor $R = \Sigma|F_o-F_c|/\Sigma|F_o|$, in this case 9·0%. The standard deviation of the parameters has been estimated in accordance with the formula due to Cruickshank (1949) and quoted by Lipson & Cochran (1953) as $\sigma(x_n) = \overline{[\partial(\varrho_o-\varrho_c)/\partial x]^2}/C_n$.

Discussion

Table 1 above gives the interatomic distances in the structure φ(AlMn) smaller than 3·2 Å. For comparison

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* Tabulated values of F_o and F_c are available.

the values given by Robinson (1952) for β(AlMnSi) are quoted (X denotes Al_0 in φ(AlMn) and Si in β(AlMnSi)). The criteria suggested by Cruickshank (1949) for judging whether a difference between two interatomic distances is significant have been used. These show that two bonds have significant differences in length, and that a third has an almost significant difference (these bonds are indicated in Table 1). Robinson (1952) quotes 'probable errors' in interatomic distances: these have been multiplied by 1·5 to convert them into standard deviations.

The similarity between the structure of φ(AlMn) and that of β(AlMnSi) is very interesting. The occurrence of an aluminium atom in φ(AlMn) at the 2(a) site reputedly occupied by silicon in β(AlMnSi) does not appear to have greatly influenced the structure. This immediately prompts the suggestion that the silicon atom in β(AlMnSi) does not exclusively occupy the 2(a) site.

Robinson assumed the silicon atoms to occupy the 2(a) sites for, essentially, the following reasons:

(1) The silicon content was approximately two atoms per unit cell, and the site 2(a) was the only occupied two-fold position in the structure.

(2) In the ($hki0$) projection of the electron density, the origin peak was found greater, both in height and electron count, than peaks corresponding to other aluminium atoms.

(3) The distance of the atom at (0, 0, 0) from its six aluminium neighbours is appreciably less than that between any other pair of aluminium atoms in the structure.

Each of the above reasons is open to criticism. To consider each in order:

(1) The ideal silicon content of β(AlMnSi) is 7·7 atomic percent: Pratt & Raynor (1951) obtained a specimen containing 8·9 atomic percent silicon: this implies that silicon can be accommodated in positions other than the 2(a) site.

(2) The electron count associated with the origin peak in the present work is greater than that associated with the other aluminium peaks (this difference is not regarded as significant in view of the limitations of the experimental techniques, and also as the 2(a) site lies on a centre of symmetry). Table 2 gives data relevant to this point. For comparison, ratios of the electron counts associated with various atomic peaks in this work and in that of Robinson (1952) are given.

Table 2. *Electron counts in* φ(AlMn) *and* β(AlMnSi)

(a) Ratios of number of electrons associated with equal areas surrounding each peak in electron-density projections.

Material	Atomic peaks	Ratios of number of electrons associated with each peak
φ(AlMn)	$Al_0 : Al_2 : Al_2 : Al_1$	1·00 : 0·80 : 0·75 : 0·85
β(AlMnSi)	$Si : Al_2 : Al_1$	1·00 : 0·85 : 0·80

(b) Peak heights in electron-density projection of φ(AlMn).

Atomic peak	1 Al_0	1 Al_2	2 Al_2	2 Al_1
Height (arbitrary units)	255	200	362	389

(3) The distance of the atom at (0, 0, 0) from its six aluminium neighbours is the same in φ(AlMn) as in β(AlMnSi). Furthermore, the interatomic distance (2·67 Å) is not less than those occurring in other aluminium–manganese intermetallic compounds (e.g. aluminium–aluminium interatomic distances of 2·57, 2·62 and 2·64 Å occur in $MnAl_6$ (Nicol, 1953), and of 2·61, 2·62, 2·63 and 2·65 Å occur in δ(MnAl) (Bland, 1958). This, however, has become known only since the publication of the structure of β(AlMnSi).

The author suggests, in view of the great similarity of the two structures and of the fact that Robinson's three reasons for the unique occupation of the 2(a) site by silicon are not convincing, that the silicon atoms in β(AlMnSi) do not exclusively occupy the 2(a) site, but that some, at least, are otherwise distributed in the structure.

The similarity between the structures of φ(AlMn) and β(AlMnSi) has been considered in the above paragraphs. The differences between the two structures are now discussed.

The diameter of an aluminium atom is greater than that of a silicon atom, and the larger unit cell of φ(AlMn) relative to that of β(AlMnSi) is therefore readily understood. The c axis of φ(AlMn) is approximately 1·9% longer than that of β(AlMnSi) and the a axis approximately 0·4% longer. Robinson (1952) noted that an increase of silicon content in β(AlMnSi) caused a decrease in c, a and c/a.

It is desirable to explain the differences in bond lengths in terms of the replacement of silicon in β(AlMnSi) by aluminium *in* φ(AlMn). However, even if all the silicon occurs on one type of site (i.e. site 6(h) or 12(k)) only either one site in three (i.e. if site 6(h) be occupied) or one site in six (i.e. if site 12(k) be occupied) is occupied by a silicon atom. Therefore, the bond lengths (for bonds involving sites that may be occupied by silicon) given in Table 1 are the weighted means of bonds to silicon *and* aluminium atoms, and comparison of bond lengths in the two structures cannot provide direct evidence of the quantitative difference caused by the replacement of aluminium by silicon.

However, the bonds which have significantly different lengths in the two structures are the X–Mn_1 bonds and certain Al_1–Al_2 and Al_2–Al_2 bonds (the Al_1–Al_2 bond in question is, according to the Cruickshank criterion, only possibly significant but is sufficiently close to the fully significant level to warrant consideration here). All these bonds are longer in φ(AlMn) than in β(AlMnSi). The structures of these two materials are layered perpendicular to the z axis (with atoms X at height zero, Al_2 at approximately $6c/100$ and Mn_1 and Al_1 at $c/4$): the length of the Mn_1–X bond is determined primarily by the length of the z axis of the crystal, and this in turn is determined by the closeness with which the layers can be packed together, and therefore bears a direct relationship to the length of the X–Al_2 and Al_1–Al_2 bonds (as the latter two bonds link atoms in the different layers, their lengths are related to the length of the hexad axis). Thus all the significant differences in bond lengths are associated with bonds involving Al_2 atoms, and as all these bonds are longer in the φ(AlMn) structure than the β(AlMnSi) structure it seems possible (bearing in mind that the atomic radius of aluminium is greater than that of silicon) that the silicon atoms in β(AlMnSi) preferentially occupy some of the $12(k)$ sites in the structure (i.e. the sites occupied by Al_2 atoms in φ(AlMn)).

Conclusion

The structure of Mn_3Al_{10} has been accurately determined and its similarity with that of β(AlMnSi) suggests that the silicon atoms in β(AlMnSi) do not occupy the origin sites exclusively as had been previously assumed. The significant bond-length differences between the two structures indicate that the occupation of the $12(k)$ sites by silicon in β(AlMnSi) is probably greater than the occupation of the $2(a)$ and $6(h)$ sites.

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The Crystal Structure of Hexagonal L-Cystine

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The structure of hexagonal L-cystine, space group $P6_122$, has been solved by three-dimensional methods. The structure is essentially composed of glycine-like sheets lying perpendicular to the c-axis with the C–R bonds pointing alternately up and down in successive sheets and linked together in pairs by disulphide bridges. There is a very satisfactory three-dimensional network of hydrogen bonds linking the molecules together. Crystallographic data for the space group $P6_122$ are given.

Introduction

The work described here on the structure of hexagonal L-cystine $[S\text{–}CH_2\text{–}CH(NH_2)\text{–}COOH]_2$ is part of a programme of research on the structures of proteins and peptides which is in progress in this laboratory, and has a particular bearing on the structures of insulin and gramicidin S.

Insulin contains three cystinyl linkages per molecule of 6,000 mW., and a knowledge of the possible conformations of these linkages is of great interest. Gramicidin S, a decapeptide, forms a series of derivatives, N-iodoacetyl, N-chloroacetyl and N-acetyl, which crystallize in the same space group as hexagonal L-cystine, namely $P6_122$ (Schmidt, Hodgkin & Oughton, 1957), and the latter has been used as a model for gaining experience in the analysis of structures crystallizing in this highly symmetrical space group.

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