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The Crystal Structure of the Intermetallic Compound $Mg_6Si_7Cu_{16}$*

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The earlier reported atomic positions in the structure of the intermetallic compound $Mg_6Si_7Cu_{16}$ (Bergman & Waugh) have been refined on the basis of single-crystal intensity data by application of a least-squares procedure. The atomic positions are essentially the same as those obtained by Nagorsen & Witte in an independent investigation, with the exception of the magnesium positions, which differ significantly. As Nagorsen & Witte used a semiquantitative procedure with successive adjustments of the positional parameters it may perhaps be concluded that the results presented here are more reliable. This conclusion is supported by the fact that the new positions correspond to better packing of the atoms.

The derivation of the trial structure demonstrates that no other atomic arrangement is possible even when intensity data are completely disregarded, provided that normal packing conditions exist.

Introduction

In an earlier paper (Bergman & Waugh, 1953) the determination of the crystal structure of the compound $Mg_6Si_7Cu_{16}$ was described briefly. Atomic positions in an early stage of refinement were given and it was intended to publish a detailed report on this structure determination with refined positional parameters at a later time. However, shortly after this paper had been published a paper (Nagorsen & Witte, 1953) describing an independent structure determination of the same compound appeared. The present paper will therefore consist largely of comparisons of the methods and results in the two investigations.

Experimental work

Preparation of the compound and isolation of single crystals

In order to avoid difficulties associated with the relatively high volatility of magnesium, a copper–silicon alloy was first prepared by melting the elements† in a sealed evacuated quartz tube in the atomic proportions 16:7. The relatively low-melting copper–silicon alloy was then melted with magnesium metal† in a sealed evacuated quartz tube to form an alloy of the composition $Mg_6Si_7Cu_{16}$. Good mixing was secured by vigorous shaking of the tube. The alloy was next allowed to cool to room temperature at a cooling rate of about 20° C. per hour. When the alloy pellet was broken up a large number of well developed crystals of octahedral habit and blue-grey color could be isolated.

Laue symmetry and unit-cell dimensions

The octahedral crystals showed Laue symmetry O_h–$m3m$. On the basis of rotation and Weissenberg photographs (rotation about [100]) it was established that the crystals have a face-centered cubic lattice with a cell constant approximately equal to 11·65 Å. These results agreed with those reported by Witte (1938) for the phase $Mg_6Si_7Cu_{16}$ in his preliminary investigation of this phase (a_0 = 11·67 Å). A refinement of the lattice parameter was not carried out as Witte's result was considered sufficiently accurate. Nagorsen & Witte (1953) report the parameter value 11·65 ±0·02 Å in their joint paper.

Diffraction intensity data

As the structure has cubic symmetry diffraction intensity data for the ($hk0$) reflections were sufficient for the refinement of the structure. These data were obtained by Weissenberg photography (Cu $K\alpha$ radiation) with application of the multiple-film technique of de Lange, Robertson & Woodward (1939) and Robertson (1943).

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* Contribution No. 2078 from the Gates and Crellin Laboratories.

† The materials used in this preparation were all of at least 99·9 % purity.

Derivation of the trial structure

Probable space groups

As the crystals show octahedral habit they must belong to one of the crystal classes O_h, O, and T_h. As, furthermore, the Laue symmetry was found to be O_h the only possible crystal classes are O_h and O. This was also pointed out by Nagorsen & Witte. As no systematic extinction could be recorded in addition to those corresponding to face-centering, the probable space groups are only two, namely O_h^5 and O^3. Up to this point this is the same argument as that of Nagorsen & Witte. In the following assignment of atomic positions there are, however, differences in the arguments. The results are, however, the same in spite of the fact that there is in one place an incorrect statement in Nagorsen & Witte's paper, as will be pointed out below.

In the two space groups O_h^5 and O^3 the special positions, including the 48-fold positions, are the same. As the next higher multiplicity is 96, and there are not more than 64 atoms of any one kind (64 copper atoms) in the unit cell it is clearly immaterial which of these two space groups is assigned. The structure has, however, the full O_h^5 symmetry. Nagorsen & Witte make in this connection the incorrect statement that the special positions of a multiplicity not greater than 32 are the same in the two space groups ('... bis einschliesslich zur 32 zähligen Punktlage ...').

The trial structure

The derivation of the trial structure was carried out on the assumption that the composition of the alloy corresponds exactly to the formula $Mg_6Si_7Cu_{16}$ and that consequently there are 24 magnesium atoms, 28 silicon atoms, and 64 copper atoms per unit cell. The point positions in space group O_h^5, excluding higher than 48-fold positions, are, in the notation of the *Internationale Tabellen* (1935):

$$\begin{array}{rll} & \multicolumn{2}{l}{(0, 0, 0;\ 0, \tfrac{1}{2}, \tfrac{1}{2};\ \tfrac{1}{2}, 0, \tfrac{1}{2};\ \tfrac{1}{2}, \tfrac{1}{2}, 0)+} \\ 4: & (a) & 0, 0, 0 \\ & (b) & \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2} \\ 8: & (c) & \tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4};\ \tfrac{3}{4}, \tfrac{3}{4}, \tfrac{3}{4} \\ 24: & (d) & 0, \tfrac{1}{4}, \tfrac{1}{4};\ \tfrac{1}{4}, 0, \tfrac{1}{4};\ \text{etc.} \\ & (e) & x, 0, 0;\ 0, x, 0;\ \text{etc.} \\ 32: & (f) & x, x, x;\ x, \bar{x}, \bar{x};\ \text{etc.} \\ 48: & (g) & x, \tfrac{1}{4}, \tfrac{1}{4};\ \tfrac{1}{4}, x, \tfrac{1}{4};\ \text{etc.} \\ & (h) & 0, x, x;\ x, 0, x;\ \text{etc.} \end{array}$$

It is immediately clear that 4 of the silicon atoms are in either the 4:(*a*) or the 4:(*b*) positions; they can arbitrarily be placed in the 4:(*b*) positions. It is also immediately clear that both the 24 magnesium atoms and the remaining 24 silicon atoms must be in two different sets of 24-fold positions. There is, however, no possibility of taking two sets of 24:(*e*) positions if the atomic radii are considered. It can consequently be concluded that the magnesium atoms are in the 24:(*d*) positions and the remaining 24 silicon atoms in a set of 24:(*e*) positions, or vice versa. The x parameter of the 24:(*e*) positions can be predicted to be in the range 0·15–0·25 on the basis of the atomic radii.

The 64 copper atoms are next to be placed. The choice of a 48-fold position is not acceptable as the remaining 16 copper atoms could not then be accommodated. Positions of type 24:(*e*) are impossible for the reason already given above. The only remaining possibility is to use two sets of 32:(*f*) positions. The positions in each of these two sets are at the vertices of tetrahedra with their centers at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $(\bar{\frac{1}{4}}, \bar{\frac{1}{4}}, \bar{\frac{1}{4}})$ etc. There is, however, in the arrangement described just enough room at these points to accommodate two tetrahedra of copper atoms, one positive and one negative, the latter outside the former as in γ-brass. The two possibilities of making the two tetrahedra both positive or both negative are easily ruled out on the basis of atomic-size considerations. The arrangement of the atoms is therefore completely derived with the exception of the differentiation between the magnesium and silicon atoms in the 24-fold positions. However, a simple inspection of the structure shows that placing the magnesium atoms in the 24:(*d*) positions would necessarily make the magnesium–copper distances far too short to be plausible. Even with silicon atoms in these positions a few rather short silicon–copper distances cannot be avoided. The structure is therefore completely derived and, as has been demonstrated, there is no other possible structure, provided of course that the structure is ordered and that the phase has the assumed composition.

Using Pauling's system of metallic radii (Pauling, 1947) and assuming coordination number twelve as a first approximation, and furthermore assuming that the magnesium atoms are in contact within each octahedral group (which is reasonable from the standpoint of packing), the approximate positional parameters shown in Table 1 were assigned.

Table 1. *Positional parameters*

Point positions	Atom	Parameter x		
		Approximate	Refined	N & W*
4: (*b*)	Si_I	—	—	—
24: (*d*)	Si_{II}	—	—	—
24: (*e*)	Mg	0·19	0·1824 ± 0·0003	0·212
32: (*f*)	Cu_I	0·17	0·1684 ± 0·0001	0·166
32: (*f*)	Cu_{II}	0·38	0·3770 ± 0·0001	0·379

* Nagorsen & Witte, 1953

Intensities calculated for this trial structure were, as expected, in excellent agreement with observed intensities.

Refinement of the trial structure

Projections

Three successive projections on the xy plane were calculated, the first one based on 20 of the observed reflections and the last one on all the 28 observed distinct reflections (there were no non-systematic absences). The successive adjustments of the positional parameters were all very small. The projections confirmed the assumption that the structure is completely ordered. The degree of disorder, if any, must at least be very small. The third projection is shown in Fig. 1.

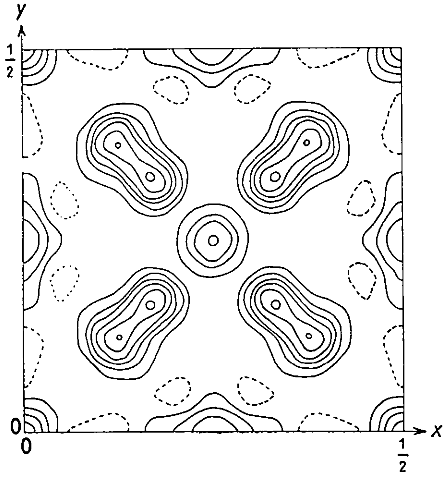

Fig. 1. The final Fourier projection. Contours at intervals of arbitrary magnitude.

Least-squares refinement

The final step in the refinement was carried out by application of the method of least squares (Hughes, 1941). The combined scale, temperature and absorption factor was determined separately by a graphical method. The quantity log $(\Sigma I_o/\Sigma F_c^2)$ with the summation taken over intervals of $\sin^2\theta$ of the magnitude 0·1 was plotted against $\sin^2\theta$ and a straight line was fitted through the points in the plot. From this curve was then obtained the combined scale, temperature and absorption factor. The weights of the observations were for simplicity taken proportional to $1/F_o^2$. The normal equations in the least-squares refinement were solved by the method described by Crout (1941). The refined parameters are given in Table 1.

Structure factors calculated on the basis of these parameters, as well as observed structure factors, are given in Table 2. The agreement is satisfactory. The reliability factor R was 11·2%.

Discussion

The arrangement of the magnesium atoms in octahedral groups is an interesting feature in this structure, but perhaps not very remarkable as good overall packing is achieved in this way. The magnesium atoms are surrounded by sixteen atoms in the first coordination polyhedron. They consist of four silicon atoms, four magnesium atoms and eight copper atoms. Quite unusual in intermetallic compounds is the coordination of the silicon atoms in the 4:(*b*) positions. These silicon atoms have only eight atoms, all copper atoms, in the first coordination polyhedron, which is a cube. These copper atoms are, however, relatively near the silicon atoms, as is to be expected in such a case. The silicon atoms in the 24:(*d*) positions have coordination number twelve, with four magnesium atoms and eight copper atoms at the vertices of a slightly distorted regular icosahedron. The copper atoms in one of the sets of 32:(*f*) positions have likewise a slightly distorted icosahedron for a first coordination polyhedron. Six copper atoms, three magnesium atoms, and three silicon atoms are at the vertices of this polyhedron.

Table 2. *Observed and calculated structure factors*

hkl	F_c	F_o	*hkl*	F_c	F_o
000	2395	—	10,2,0	91	82
200	−344	350	10,4,0	52	46
220	125	120	880	612	530
400	−537	530	10,6,0	− 80	80
420	111	120	12,0,0	257	250
440	986	1100	12,2,0	− 84	170
600	646	550	12,4,0	375	330
620	−236	260	10,8,0	108	110
640	−115	100	12,6,0	397	360
800	465	500	14,0,0	−227	230
820	81	85	10,10,0	89	100
660	544	550	14,2,0	56	73
840	−105	56	12,8,0	−291	220
10,0,0	− 26	48	14,4,0	109	140
860	−242	260			

Table 3. *Interatomic distances, bond numbers and calculated valences*

Type	Number	Interatomic distance*	Bond number, n	Calculated valence
Mg–Mg	4	2·99 Å	0·369	4·376
Mg–Si_{II}	4	3·01	0·165	
Mg–Cu_I	4	2·77	0·413	
Mg–Cu_{II}	4	3·04	0·147	
	16			
Si_{II}–Mg	4	3·01	0·165	6·096
Si_{II}–Cu_I	4	2·38	0·877	
Si_{II}–Cu_{II}	4	2·54	0·482	
	12			
Si_I–Cu_{II}	8	2·48	0·606	4·848
	8			
Cu_I–Mg	3	2·77	0·413	6·096
Cu_I–Si_{II}	3	2·38	0·877	
Cu_I–Cu_I	3	2·70	0·261	
Cu_I–Cu_{II}	3	2·54	0·481	
	12			
Cu_{II}–Si_{II}	3	2·54	0·482	4·344
Cu_{II}–Si_I	1	2·48	0·606	
Cu_{II}–Mg	3	3·04	0·147	
Cu_{II}–Cu_I	3	2·54	0·481	
Cu_{II}–Cu_{II}	3	2·87	0·136	
	13			

* Based on a_0 = 11·65 Å.

The copper atoms in the second set of 32:(*f*) positions have thirteen atoms in the first coordination polyhedron. Three magnesium atoms, four silicon atoms, and six copper atoms are at the vertices of this polyhedron, which is related to the icosahedron.

The interatomic distances are given in Table 3. In this table bond numbers as well as calculated valences of the various atoms are also given, as calculated using the relation

$$R(1)-R(n) = 0{\cdot}300 \log n\ ,$$

when R is the metallic radius and n the bond number (Pauling, 1947).

The positional parameters given by Nagorsen & Witte (1953), after change of origin, are included in Table 1. Only the magnesium atoms are given substantially different positions in the two investigations. The incomplete table of interatomic distances given by Nagorsen & Witte does not show to what extent the packing is unsatisfactory if their parameter is assumed correct. The Mg–Mg distances turn out to be 3·50 Å, as compared to 2·99 Å in this investigation. Also the rather large holes at (0, 0, 0) etc. appear difficult to explain. The long Mg–Mg distances are also unlikely in view of the results obtained by Florio, Rundle & Snow (1952) for the binary phase $\mathrm{Th_6Mn_{23}}$. This phase has the same general arrangement of the atoms in the unit cell. The Th atoms take the place of the Mg atoms and the Mn atoms take the place of the Cu and Si atoms. The $\mathrm{Th_6Mn_{23}}$ structure may therefore be considered as a special case of the more general $A_6B_7C_{16}$ type structure described here.† The Th–Th distance is 3·59 Å and the metallic radius of the thorium atom for coordination twelve is 1·795 Å (Pauling, 1947).

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† The paper by Florio *et al.* appeared in print after the work described here had been finished, with the exception of the last refinement. The atomic arrangement described has consequently been discovered by three independent groups of investigators.

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Growth Features on Crystals of Long-Chain Compounds. III

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Interlaced patterns have been observed on a monoclinic form of the paraffin $\mathrm{C_{34}H_{70}}$, on behenic acid and on the α-form of the n-alcohols $\mathrm{C_{34}H_{47}OH}$. The patterns are analysed using the method outlined in Part I, and deductions are made concerning the stacking sequences of the crystals on which they are observed. It is found that in crystals of tetratriacontane and behenic acid successive growth layers can be turned through 180°, and that this kind of stacking fault is responsible for the growth of polytypic crystals. It is further shown that growth round *imperfect* dislocations in behenic acid *does not produce polytypes*, but that, on the contrary, the normal structure is continued.

An interlaced pattern, observed on a crystal of the α-form of the n-alcohols, is also interpreted in terms of the stacking of successive layers. This pattern is the first example of a 'doubly interlaced pattern', i.e. an interlacing of two patterns which are themselves interlaced.

1. General introduction

In Part I of this series of papers we have discussed a method of obtaining information concerning the stacking of polytypic crystals from the interlaced patterns observed on them. The method was illustrated by means of patterns observed on crystals of the β-form of the n-alcohols. In this third paper we will