

The Crystal Structure of $\text{Al}_x\text{Cu}_2\text{Mg}_{12-x}\text{Si}_7$, (*h*-AlCuMgSi)

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The crystal structure of $\text{Al}_x\text{Cu}_2\text{Mg}_{12-x}\text{Si}_7$, (*h*-AlCuMgSi) has been solved from 302 independent reflections, registered by a four-circle diffractometer. The final *R* value is 0.109. The unit cell is hexagonal with $a=10.3932(9)$ and $c=4.0173(6)$ Å for $x \approx 4$. $Z=1$. The structure is probably disordered, the ideal space group being $P6_3/m$ but the data are best explained by space group $P\bar{6}$. The crystal structure is closely related to that of Th_7S_{12} , Si replacing Th and (Al+Mg), S. The Cu atoms of the present compound are situated at the voids on the lines $\frac{2}{3}, \frac{1}{3}, z$ and $\frac{1}{3}, \frac{2}{3}, z$ in the Th_7S_{12} structure.

The study of the alloy *h*-AlCuMgSi was a small part of a comprehensive work made by Phragmén¹ on the phases occurring in alloys of aluminium with copper, magnesium, manganese, iron and silicon. In several cases the phases isolated were studied by X-ray diffraction by Phragmén in collaboration with Professors Perlitz and Westgren at Stockholm University. The first single crystal photographs of *h*-AlCuMgSi were taken by Perlitz and some calculations were made by Westgren and one of the present authors when the work was discontinued in 1964. The present paper reports the crystal structure of *h*-AlCuMgSi.

EXPERIMENTAL

Following Phragmén's experiment, single crystals were prepared on making an alloy of composition (by weight) 13.8% Cu, 24.8% Mg, 22.2% Si and 39.2% Al. The metals were reacted in argon in graphite crucibles at about 1000 °C and the melt was slowly cooled. Powder photographs taken

from parts of the melts could be indexed with a hexagonal unit cell with $a=10.39$ and $c=4.02$ Å, in fair agreement with the values $a=10.30$ and $c=4.04$ kX given by Phragmén. For 6 samples prepared as above the maximum deviations in the cell edges found were about 10σ and the cell volumes ranged between 375.6 and 377.3 Å³ which may indicate that the phase has a small solid solubility range. The single crystals form needles extending along the crystallographic *c*-axis and these needles are often joined to form bundles.

The determination of the crystal structure showed, *vide infra*, that the unit cell contains 2 Cu, 7 Si and 12 (Mg+Al). No analysis of the present single crystals was made. Phragmén has given the following relative values for his preparation: 19.9% Al, 20.6% Cu, 31.8% Mg and 31.4% Si, from which he proposed the formula $\text{Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$. Fixing the sum (Al+Mg) to 12, the number of Cu atoms to 2 and those of Si to 7, a broad range of Mg/Al ratios will give copper percentages around 20.3 and silicon percentages around 31.3, in good agreement with the figures given above. The ratio Mg/Al found from Phragmén's analyses corresponds to an *x* value of 4.3 in the formula $\text{Al}_x\text{Cu}_2\text{Mg}_{12-x}\text{Si}_7$. We prefer, however, the value $x=4$ which gives slightly better overall agreement between observed and calculated percentages. Calculated values for $x=4$ are: 17.2% Al, 20.3% Cu, 31.1% Mg and 31.4% Si.

Powder photographs were taken in a Guinier-Hägg focusing camera. Strictly monochromatized $\text{CuK}\alpha_1$ radiation was used and KCl ($a=6.2909$ Å) was added as an internal standard. The following cell dimensions apply to the sample from which the single crystal was picked and were obtained from least-squares refinements: $a=10.3932(9)$ and $c=4.0173(6)$ Å. The calculated density for the composition $\text{Al}_4\text{Cu}_2\text{Mg}_8\text{Si}_7$ and $Z=1$ is 2.77 g cm⁻³. The linear absorption coefficient for $\text{CuK}\alpha$ radiation, is then 139 cm⁻¹. Preliminary Weissenberg photographs around [001] and precession

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photographs using [100] as projection axis indicated the Laue symmetry $6/m$. The only systematic absences found were those for $00l$, $l=2n+1$. It may be mentioned here that some spots in the $hk0$ Weissenberg photograph of the single crystal finally used were traversed by weak horizontal streaks. In the hkl photographs the streaks formed a small angle with the horizontal line, but were all parallel.

A small needle of length 0.075 mm and of diameter 0.013 mm was mounted on a PW 1100 four circle diffractometer so that the needle axis did not coincide with the ϕ -axis of the diffractometer. Graphite-monochromatized $\text{CuK}\alpha$ radiation ($\lambda=1.5418$ Å) and $\theta-2\theta$ scan technique were used. Data were collected up to $\sin \theta/\lambda=0.5932$ for positive h, k and for positive and negative l values. Out of the 524 reflections 47 had zero intensity, among those two of the expected $00l$ reflections, *viz.* [00-1] and [00-3]. Lorentz, polarization but not absorption corrections were applied and mean values of symmetry-related reflections were taken. In this way 302 independent reflections were obtained. 199 of these had $|F|$ values $\leq 3\sigma(|F|)$ and were used for the initial calculations.

A three-dimensional Patterson function showed maxima only at $w=0$ and $w=1/2$, which made fixed z values in the structure probable. Space group $P6/m$ could be ruled out from geometrical considerations. Thus space groups $P6_3/m$ and $P\bar{6}$ were first tried, though the second alternative would imply that the absence of odd $00l$ reflections in the amply exposed films is incidental rather than systematic. With $P6_3/m$ the Cu atoms were first located from the Patterson function and the positions of all other atoms were found from difference Fourier maps. The peak at $00\frac{1}{2}$ was weak and the occupation number for

Table 1. Positional and thermal parameters with estimated standard deviations in parentheses. The space group is $P\bar{6}$. The Al and Mg atoms were regarded as one species in the refinement. Finally assumed distribution of Al and Mg is indicated by italics.

Atom	x	y	z	$B(\text{Å}^2)$
Cu(1)	1/3	2/3	0	1.5(2)
Cu(2)	2/3	1/3	1/2	0.8(2)
Si(1)	0	0	0	0.9(2)
Si(2)	0.5822(12)	0.8621(11)	0	1.2(2)
Si(3)	0.4156(9)	0.1325(10)	1/2	1.0(2)
(Al, Mg)(4)	0.2425(9)	0.0020(10)	0	0.8(2)
(Al, Mg)(5)	0.7878(17)	-0.0080(20)	1/2	2.9(3)
(Al, Mg)(6)	0.6332(21)	0.1405(19)	0	2.3(3)
(Al, Mg)(7)	0.3790(14)	0.8587(14)	1/2	1.4(2)

this position was assumed to be $\frac{1}{2}$. In this way 19 extra atoms beside the 2 Cu atoms were found in the unit cell. The 7 Si atoms were identified by their coordination and the (Al+Mg) atoms were first considered as one species. In the trial structure so obtained the Si atoms at $\pm(00\frac{1}{4})$ had a somewhat queer coordination. After least-squares refinement of the atomic positions a Fourier map using F_o with the sign of F_c showed that the peak of (Al, Mg) at $y \approx 0$ and $x \approx 0.24$ (compare Table 1), being at close distance to Si at $00\frac{1}{4}$, was elongated in the x direction. This fact, in combination with the coordination of Si at $00\frac{1}{4}$ just mentioned, indicated either a disorder or a lower symmetry. As the deviation from circular form was small, a possible formal treatment is to assume anisotropic thermal movements of the atoms and a least-squares refinement this way led to $R=0.078$ as compared to $R=0.118$ for the isotropic case. Another possibility, still retaining space group $P6_3/m$, is to split the position $[0.24, 0, \frac{1}{4}]$ into two half-occupied sites, neglecting the disturbance on other atoms thereby introduced. The same procedure has earlier been used by Olofsson and Ganglberger² in their treatment of the related compound V_{12}P_7 . An isotropic refinement based on this assumption led to $R=0.085$.

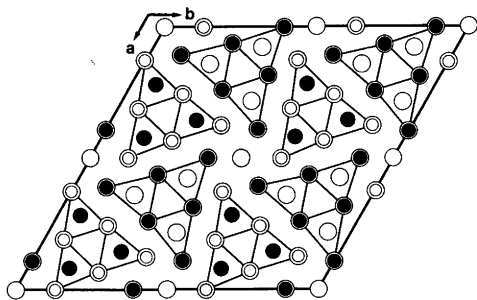
Finally, we may assume that the disturbance produced by the Si atoms $\pm(00\frac{1}{4})$ extends all over the unit cell, which leads to an ordered position of one of the above-mentioned Si atoms and to space group $P\bar{6}$. An isotropic least-squares refinement in space group $P\bar{6}$ led to $R=0.078$. In the final refinement runs the 103 weakest reflections were also included according to Arnberg, Hövmöller and Westman.³ This increased the value of R to 0.109, but the standard deviations of both positional and thermal parameters (Table 1) decreased about 15 %.

The F_c values of the reflections (001) and (003) as calculated by means of space group $P\bar{6}$ are quite small and they exceed the "observed" values for (00+1) and (00+3) (see above) only by about 40 %. Considering that the refinement in $P\bar{6}$ is used only as an approximation for a disordered structure, correction was only made for the real part of the anomalous dispersion. Lists of F_o and F_c are obtainable on request to Lars Arnberg. The goodness of S for the final refinement in space group $P\bar{6}$ was 3.06.

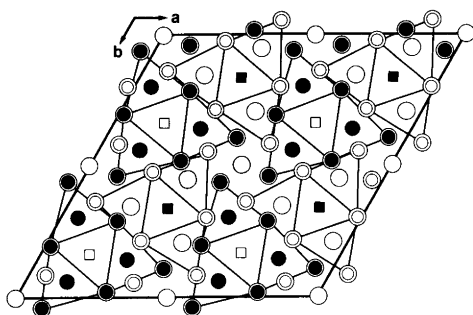
DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of $\text{Al}_x\text{Cu}_2\text{Mg}_{12-x}\text{Si}_7$ is closely related to that of Th_7S_{12} .⁴ It is seen from Fig. 1 that the positions of the Si atoms of the

1a



1c



1b

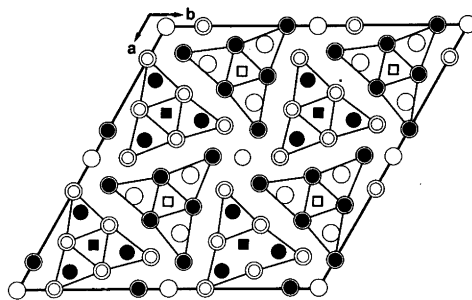


Fig. 1a–c. Projection down the *c* axis of the crystal structures of (a) Th_7S_{12} ,⁴ (b) $\text{Al}_x\text{Cu}_2\text{Mg}_{12-x}\text{Si}_7$, (c) $6\text{PbF}_2 \cdot \text{PbBr}_2$.⁵ Empty and filled circles or squares indicate atoms at $z=0$ and $1/2$, respectively. Squares in (b) and (c) denote in turn Cu and Cl^- . Single circles in (a), (b) and (c) indicate Th, Si and Pb and double ones S, (Al,Mg) and F.

alloy are nearly the same as those of the Th atoms in the sulfide. Likewise, the positions of the (Al,Mg) atoms correspond to those of the S atoms. The only difference between the structures is that the positions $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$ and $\frac{1}{3}, \frac{2}{3}, 0$ are occupied by Cu atoms in the alloy but are empty in the sulfide. There also occurs a slight disorder in Th_7S_{12} ; one Th atom being statistically distributed over $\pm(00\frac{1}{4})$ and 6 S atoms (S2) occupying two sets of half-filled 6-fold positions. The disorder is compatible with space group $P6_3/m$ but when describing the detailed coordination around Th ($00\frac{1}{4}$) one must assume a local ordering (see Ref. 4) which may be described by space group $P\bar{6}$. It seems probable that a similar disorder occurs in $\text{Al}_x\text{Cu}_2\text{Mg}_{12-x}\text{Si}_7$. As seen, this structure may be described either with space group $P6_3/m$ or space group $P\bar{6}$, the latter one being preferred by the present authors.

It may also be mentioned here that the present structure has some resemblances to that of $6\text{PbF}_2 \cdot \text{PbBr}_2$,⁵ at least with respect to the coordination of the Pb atoms, which correspond to the Si atoms of the alloy, see Fig. 1. The structure of the lead compound is, however, ordered in $P\bar{6}$; the

odd $00l$ reflections having measurable intensities. Structural similarities between lead halides and silicides are known, for instance for $\text{Pb}_7\text{S}_2\text{Br}_{10}$ related to Th_7S_{12} ,⁶ Ca_2Si ⁷ and Rh_2Si ,⁸ both of PbCl_2 type.

The crystal structure of $\text{Al}_x\text{Cu}_2\text{Mg}_{12-x}\text{Si}_7$ may be described in much the same way as the structures of V_{12}P_7 ² and $\text{Rh}_{20}\text{Si}_{13}$.⁹ Thus, we may depict blocks of joined trigonal prisms which are either empty or have P(Si) atoms at their centres, see Fig. 1. The prisms extend along the *c*-axis and the blocks are joined by P(Si) atoms situated on the lines $00z$.

Distribution of the Al and Mg atoms and their coordination. Contact distances up to 4.0 Å are summarized in Table 2 for all atoms. The maximum contact distances (Al,Mg,Si)–Si and (Al,Mg,Si)–(Al,Mg) were assumed to be 3.0 and 4.0 Å, respectively. It is seen from Table 2 that the (Al,Mg) atoms at position 4 are 12-coordinated, whereas those at positions 5–7 are 15-coordinated. It seems, therefore, natural to assume that 3 Al atoms occupy the 12-coordinated point position. With the formula $\text{Al}_4\text{Cu}_2\text{Mg}_8\text{Si}_7$ or possibly $\text{Al}_5\text{Cu}_2\text{Mg}_7\text{Si}_7$ one or

Table 2. Selected interatomic distances less than 4.0 Å. The final assignments of Al and Mg atoms are indicated as in Table 1.

Cu(1)–3 Si(2)	2.358(11)	(Al,Mg)(5)–Si(3)	2.708(20)
–6 (Al,2 Mg)(7)	2.702(8)	–2Si(2)	2.746(13)
		–2Si(1)	2.953(11)
Cu(2)–3 Si(3)	2.391(8)	–2(Al,Mg)(4)	3.057(15)
–6 (Al,Mg)(6)	2.734(12)	–2(Al,Mg)(4)	3.136(15)
		–2(Al,Mg)(6)	3.388(20)
Si(1)–3(Al,Mg)(4)	2.510(8)	–(Al,2 Mg)(7)	3.574(21)
–6(Al,Mg)(5)	2.953(11)	–2(Al,Mg)(5)	3.750(27)
–3 Si(2)	3.832(11)	–(Al,2 Mg)(7)	3.753(20)
		–Si(3)	3.920(20)
Si(2)–Cu(1)	2.358(11)		
–(Al,Mg)(4)	2.565(14)	(Al,Mg)(6)–Si(2)	2.668(20)
–(Al,Mg)(6)	2.668(20)	–2Cu(2)	2.734(12)
–2 (Al,Mg)(5)	2.746(13)	–2Si(3)	2.924(15)
–2(Al,2 Mg)(7)	2.902(12)	–2Si(3)	2.995(15)
–2 (Al,2 Mg)(7)	2.963(12)	–2(Al,Mg)(6)	3.213(29)
–2Si(1)	3.832(11)	–2(Al,Mg)(5)	3.388(20)
		–(Al,Mg)(4)	3.393(21)
Si(3)–Cu(2)	2.391(8)	–2(Al,2 Mg)(7)	3.443(18)
–2(Al,Mg)(4)	2.583(7)	–(Al,Mg)(4)	3.566(21)
–(Al,2 Mg)(7)	2.675(16)		
–(Al,Mg)(5)	2.708(20)	(Al,2 Mg)(7)–Si(3)	2.675(16)
–2(Al,Mg)(6)	2.924(15)	–2Cu(1)	2.702(8)
–2(Al,Mg)(6)	2.995(15)	–2Si(2)	2.902(12)
–(Al,Mg)(5)	3.920(20)	–2Si(2)	2.963(12)
		–2(Al,2 Mg)(7)	3.130(22)
(Al,Mg)(4)–Si(1)	2.510(8)	–2(Al,Mg)(4)	3.221(12)
–Si(2)	2.565(14)	–2(Al,Mg)(6)	3.443(18)
–2Si(3)	2.583(7)	–(Al,Mg)(5)	3.574(21)
–2(Al,Mg)(5)	3.057(15)	–(Al,Mg)(5)	3.753(20)
–2(Al,Mg)(5)	3.136(15)		
–2(Al,2 Mg)(7)	3.221(12)		
–(Al,Mg)(6)	3.393(21)		
–(Al,Mg)(6)	3.566(21)		

two additional Al atoms must be situated at one or more of the three remaining 3-fold positions. Considering the mean (Al,Mg)–Si distances and also the number of possible Al–Mg contacts, the present authors prefer position 7 for the remaining Al atoms, thereby assuming that only Mg atoms occupy positions 5 and 6.

With these assumptions the Al atoms at position 4 are coordinated by 4 Si, 6 Mg and 2 Al. The coordination polyhedron is an irregular, four-capped, tetragonal prism. The (Al+2Mg) or (2Al+Mg) atoms at position 7 are surrounded by 5 Si, 2 Cu, 4 Mg, 2 Al and 2 (Al+2Mg) or (2Al+Mg) positions in the form of a distorted five-capped pentagonal prism. The Mg atoms at position 5 coordinate 5 Si, 4 Mg, 4 Al and two positions

with mixed Al and Mg atoms in the form of a fairly regular five-capped pentagonal prism. Finally, the Mg atoms at position 6 have about the same coordination; the ligands are 5 Si, 2 Cu, 4 Mg, 2 Al and two positions with mixed Al and Mg atoms.

Coordination of the Si and Cu atoms. The Si(1), Si(2), Si(3), Cu(1) and Cu(2) atoms are all coordinated by three-capped trigonal prisms. With the assumptions made above the ligands are in turn: 3 Al, 6 Mg; 1 Cu, 3 Mg, 1 Al, 4(Al+2Mg); 2 Al, 5 Mg, 1 (Al+2Mg), 1 Cu; 3 Si, 6 (Al+2Mg); 3 Si, 6 Mg.

Acknowledgements. The authors are indebted to Mr. Torbjörn Palm who collected the single crystal data.

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Received May 21, 1979.