Refinement of the Crystal Structure of Hexagonal Al$_2$CuLi

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The crystal structure of the T$_1$ phase of Al–Cu–Li has been determined by means of single crystal X-ray diffraction. The compound crystallizes in the hexagonal space group $P6/mmm$ (No. 191) with a unit cell of dimensions $a = b = 4.954(3)$ Å and $c = 9.327(4)$ Å. The least-squares refinement on F with isotropic temperature parameters for all atoms converged at $R_F = 0.087$ ($wR = 0.095$), for 371 observed reflections and eight parameters. Although a global agreement is observed with the structure proposed by J. C. Huang and A. J. Ardell (*Mater. Sci. Technol.* **3**, 176 (1987)), some significant differences are found. These differences are interpreted in terms of a more likely coordination of Li and Al atoms. © 1990 Academic Press, Inc.

Introduction

The T$_1$ phase in the aluminum–copper–lithium phase diagram was identified by Hardy and Silcock (*1*) as a hexagonal phase with lattice constants $a = 4.96$ Å and $c = 9.35$ Å (c-axis unique) of composition Al$_2$CuLi. The space group could not be determined unequivocally; it was found to be $P6/mmm$ or one of its maximal acentric subgroups. Convergent beam electron diffraction pointed to the space group $P6/mmm$ as the correct symmetry (*2, 3*). Recently, a model for the structure of this phase was proposed by Huang and Ardell (*4*), based on the diffraction data published by Hardy and Silcock (*1*). They also compared the intensities predicted for this model with new electron diffraction experiments.

In this paper we present results of the refinement of the structure of Al$_2$CuLi on newly measured single-crystal X-ray diffraction data. Some significant differences with the structures proposed by Huang and Ardell (*4*) are found, although the global appearance of their model is confirmed.

Experimental

The title compound was prepared in an inert environment by melting together the elements in the proper composition using a tungsten crucible and subsequent cooling of the melt to 500°C with a rate of 1.5 K/min. Single crystals of the hexagonal phase were

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obtained of sizes up to several millimeters. They have a light-gray color and metallic luster.

A platelet of thickness 0.012 mm and in the plane with a shape of one-quarter of an ellipse with edges of 0.05 and 0.10 mm was selected for the diffraction experiment. All diffraction experiments were performed on an ENRAF-NONIUS CAD-4F diffractometer, equipped with a graphite monochromator and using $Mo\,K\bar{\alpha}$ radiation (λ = 0.71073 Å). The temperature of the measurement was 295 K.

Unit cell dimensions and their standard deviations were determined from accurately measured positions of four alternate settings of 17 reflections in the θ-range from 16.3° to 19.9° (5). A hexagonal cell of dimensions a = 4.954(3) Å and c = 9.327(4) Å (c-axis unique) was found, which is in reasonable agreement with the values reported by Huang and Ardell (4).

Intensities of all reflections in one hemisphere and up to θ = 50° were measured using the $\omega/2\theta$ scan-technique. Three reference reflections were monitored at regular intervals and showed only a small change during data collection. A 360° ψ-scan for the close to axial reflection ($4\bar{2}0$) showed a variation in intensity up to 13% about the mean value. Intensities were corrected for variation in the intensities of the reference reflections, for Lorentz and polarization effects, and for absorption. The latter was done by using the measured crystal dimensions and a Gaussian integration method (6). Minimum and maximum corrections are 1.11 and 1.40, respectively. Variance was calculated based on counting statistics and the term (P^2I^2), where P (= 0.027) is the instability constant (7) as derived from the excess variance of the three reference reflections: $\sigma^2(I) = \sigma_{cs}^2(I) + (0.027I)^2$.

Averaging in Laue symmetry $6/mmm$ gave a consistency index $R_I = \Sigma(I - I_{av})/\Sigma I$ = 0.16, for reflections satisfying the $I >$

$2.5\sigma(I)$ criterion of observability. Because of this rather high value for R_I, averaging was performed in subgroups of $P6/mmm$.[1] The lowest value was obtained for Laue symmetry mmm, with respect to one of the three orientation variants of the C-centered orthohexagonal unit cell (R_I = 0.083). Other symmetries, ranging from 3 to 6 mm, gave R_I values in between 0.10 and 0.15. They should be compared with $R_\sigma = \Sigma\sigma(I)/\Sigma I$ = 0.17 for observables (R_σ = 0.21 for all reflections). These results could suggest that the structure have orthorhombic symmetry $Cmmm$, despite its hexagonal lattice. However, as discussed in the next section, refinements in this symmetry did not show a significant deviation from $P6/mmm$ symmetry. Therefore, within the limits of our data set, we have to conclude to $P6/mmm$.

The high value of R_I can be explained in part by the low accuracy of the measurement, expressed by R_σ = 0.17. Of influence may also be an inadequate absorption correction. Note that the variation in absorption correction is larger than 16%. A factor of unknown magnitude is a possible poor quality of the crystal. It was observed that over several weeks crystals became covered with a grayish "dust," supposedly lithium oxide, an indication that lithium was leaking from the sample. This loss of lithium itself will hardly have any effect on the diffraction. However, the accompanying internal strain may be an explanation for the orthorhombic appearance of the symmetry of the diffraction pattern.

The 4287 measured reflections were combined into a unique set (Laue symmetry $6/mmm$) of 490 reflections, with a consistency index for averaging observables of R_I = 0.16 (R_I = 0.17 for all reflections). The 374 reflections satisfying the $I \geq 2.5\sigma(I)$ were

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[1] We thank one of the referees for suggesting the possibility of orthorhombic symmetry.

used in the final refinements. No systematic extinctions were observed.

The density of the material was measured using a water-filled picnometer of approximate volume of 5×10^3 mm^3 and a batch of single crystals with a total weight of 134.68 mg. Due to the (slow) chemical reaction between water and alloy, the weight of the picnometer filled with both water and alloy decreased continuously in time. The first reading was used. However, it may still be lower than the true value, resulting in an underestimate of the density of the sample. The resulting value for the density is 3.2×10^{-3} g/mm^3, with an estimated standard deviation of 0.2×10^{-3} g/mm^3.

Refinement

A Patterson synthesis was made by calculating points of the Patterson function on a grid of resolution 0.25 Å. For both symmetries $6/m$ and $6/mmm$ strong peaks are at the positions (0, 0, 0.468), (0.5, 0, 0), and (0.5, 0, 0.466). They can be a result of atoms at the special position 6i in $P6/mmm$, generated by (0.5, 0, z) with z = 0.234. Because of the intensity of the peaks, this position should involve most of the Cu atoms. Weaker, but still significantly positive peaks are at ($\frac{1}{3}$, 0.171, 0.236), (0.5, 0, 0.405), (0.5, 0, 0.122), and (0.67, 0.33, 0.358). The first can be explained as a vector from (0.33, 0.67, 0) to a symmetry equivalent of (0.5, 0, 0.236), meaning the presence of Al on position 2c: ($\frac{1}{3}$, $\frac{2}{3}$, 0). The remaining three are explained by putting an aluminum atom on special position 2e: (0, 0, z), (0, 0, $-z$), with z = 0.358. Replacing this position by an aluminum at (0, 0, 0.5) as in the model proposed by Huang and Ardell (4) cannot explain all Patterson peaks and is thus incorrect. The remaining space can be filled with lithium at special position 2d: ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}$), ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{2}$) and at 1a: (0, 0, 0). The Patterson function in other, lower, symmetries

did not deviate significantly from the one calculated in $P6/mmm$.

The calculated density for Al$_2$CuLi is 3.1×10^{-3} g/mm^{-3} for 3 formula units per unit cell, and 4.1×10^{-3} g/mm^{-3} for Z = 4. The measured density shows the most probable value for Z to be 3, in accordance with Huang and Ardell (4) and the structure derived from the Patterson synthesis. For Z = 3, the structure model derived from the Patterson synthesis has 3Cu + 3Al occupying the 6i position, 2c fully occupied by Al, 2e half occupied by Al, and 2d and 1a occupied by Li.

Trial structures were refined starting in a symmetry $P3$ and going up to $P6/mmm$. At each stage, the best model found in a particular symmetry could be matched by an almost equivalent model in a higher symmetry. This led to a final structure model in space group $P6/mmm$, No. 191 (12). It turned out that the Al(3) position is fully occupied. Analysis of difference Fourier maps showed that the 1a position for Li(2) has to split into a twofold position (0, 0, $\pm z$), with z = 0.051. This results in Z = 3.3.

A possible lowering of the symmetry to orthorhombic was tested by refining the corresponding model in the orthohexagonal unit cell, with space group $Cmmm$. A differently averaged data set was used for this refinement. Only a small improvement of the consistency index wR_{F^2} was observed, from 0.095 for $P6/mmm$ to 0.091 for $Cmmm$. The deviation of the structural parameters from their $P6/mmm$ values was not significant. Apparently, the additional parameters, introduced by lowering the symmetry to $Cmmm$, are not the correct ones to account for the orthorhombic appearance of the diffraction symmetry. As discussed in the previous section, we do not have a conclusive explanation for this lower diffraction symmetry. However, within the limited accuracy of our data set, we have to describe the structure as hexag-

onal, space group $P6/mmm$. Note that in two independent CBED experiments, there was no reason to consider a symmetry lower than hexagonal (2, 3).

In the refinements a strong correlation was observed between the temperature factors and the site occupation factors (s.o.f.). Because of the necessity of refining the latter, it was not possible to use anisotropic temperature factors. Even then, the correlation between s.o.f.'s and isotropic temperature factors was too high to be able to vary all independent parameters. The s.o.f.'s of Cu(1) and Al(1) were fixed in the final refinements with s.o.f.'s satisfying the ratio Al/Cu of 2 in the unit cell. The temperature factors of Al(1) and Cu(1) were constrained to be equal and the isotropic temperature factors of Li(1) and Li(2) were set equal. The final full-matrix least-squares refinement converged at $wR_{F^2} = (\Sigma w(|F_o| - F_c|)^2/(\Sigma w|F_o|^2))^{1/2} = 0.095$ and $R_F = \Sigma| |F_o| - |F_c| |)/(\Sigma|F_o|) = 0.087$. Three reflections with $(w | |F_o| - |F_c| |) > 10)$ were excluded from the final refinement cycles. In the final difference Fourier map the highest peaks and the deepest troughs were located near the Cu(1) and Li positions and amounted to 5 and -3 e/$\mathring{A}^3$. Final fractional atomic coordinates, s.o.f.'s, and isotropic thermal parameters are given in Table I. A comprehensive list of crystallographic data including bond distances and a list of observed and calculated structure factors are available as supplementary material.[2] Scattering

[2] See NAPS document No. 04749 for 7 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.50 for postage of any microfiche orders.

TABLE I

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS FOR THE FINAL STRUCTURE MODEL

Atom	x	y	z	s.o.f.	U ($\mathring{A}^2$)
Cu(1) 6i	$\frac{1}{2}$	0	0.2363(1)	0.556	0.0039(2)
Al(1) 6i	$\frac{1}{2}$	0	0.2363(1)	0.444	0.0039(2)
Al(2) 2c	$\frac{1}{3}$	$\frac{2}{3}$	0	1.0	0.0061(8)
Al(3) 2e	0	0	0.3568(7)	1.0	0.0091(9)
Li(1) 2d	$\frac{1}{3}$	$\frac{2}{3}$	1/2	1.0	0.025(9)
Li(2) 2e	0	0	0.051(9)	0.666	0.025(9)

Note. Standard deviations are given in parentheses. The temperature factors in the structure factors are defined by $\exp(-8\pi^2 U(\sin(\theta)/\lambda)^2)$. Note that the unit cell used here is shifted over 0.5 c with respect to the unit cell used in Ref. (4).

factors were taken from Cromer and Mann (8). Anomalous dispersion factors are those given by Cromer and Liberman (9). All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages *XTAL* (10) and *EUCLID* (11) (calculation of geometric data).

Discussion

The structure as proposed by Huang and Ardell (4) consists of atoms in four layers. The special position 6i: ($\frac{1}{2}$, 0, z), defines two layers at z and $1 - z$, which are statistically occupied by aluminum and copper atoms. Layers at $z = 0$ have aluminum in the twofold special position ($\frac{1}{3}$, $\frac{2}{3}$, 0) and layers at $z = \frac{1}{2}$ accommodate lithium at ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}$). Together these layers form a more or less closed packed structure (Table II), however, with empty channels along c at $x = y = 0$. Huang and Ardell (4) fill these channels with a single aluminum atom at (0, 0, $\frac{1}{2}$) and a lithium atom at (0, 0, 0), leading to a unit cell content of $Z = 3$. Within the $z = 0$, $\frac{1}{2}$ layers, this gives a shortest distance of 2.860 $\mathring{A}$. However, it leaves empty space around the (0, 0, $\pm\frac{1}{4}$) positions.

TABLE II

INTERATOMIC DISTANCES FOR THE NEAREST NEIGHBORS OF EACH OF THE FIVE INDEPENDENT ATOMS

Central atom	Coordinating atom	Distance (Å)
Al/Cu(1)	2 × Al/Cu(1)	2.477(2)
	2 × Al(2)	2.627(2)
	2 × Al(3)	2.720(3)
	2 × Li(1)	2.845(2)
	2 × Li(2)	3.02(2)
Al(2)	6 × Al/Cu(1)	2.627(2)
	3 × Al(2)	2.860(2)
	3 × 1.3 × Li(2)	2.90(1)
Al(3)	1 × Al(3)	2.671(3)
	6 × Al/Cu(1)	2.720(3)
	1 × Li(2)	2.85(8)
	6 × Li(1)	3.157(2)
Li(1)	6 × Al/Cu(1)	2.845(2)
	3 × Li(1)	2.860(2)
	6 × Al(3)	3.157(2)
Li(2)	1 × Li(2)	0.95(12)
	1 × Al(3)	2.85(8)
	6 × Al(2)	2.90(1)
	6 × Al/Cu(1)	3.02(2)

Note. Standard deviations in the last digit are given in parentheses.

From the Patterson synthesis we determined that the single aluminum at $(0, 0, 0.5)$ has to be replaced by two aluminums at $(0, 0, \pm0.35)$. This was confirmed by the subsequent refinement. The single lithium position had to be replaced by a partially occupied twofold position. This leads to coordination distances around Al(3) and Li(2) more reasonable than those in the model by Huang and Ardell (4) (Table II). A drawback of our model is the Li(2) position, for which the partial occupation of 1.3 atoms per 2 positions occasionally leads to the improbable short distance of 1 Å. This may be attributed to the insensitivity of the calculated structure factors to the exact lithium positions and to a possible additional disorder not included in our model.

The consequence of putting more atoms in the channel on $x = y = 0$ is that the unit cell contents become higher than $Z = 3$; we obtain $Z = 3.3$. In the light of the large disorder observed in this structure it might not be impossible that a noninteger number of atoms is present in the unit cell. A second possible explanation is an additional ordering of the lithium atoms in some supercell, for which the additional reflections are too weak to be observed. The calculated density for the model proposed here is 3.48×10^{-3} g/mm^3, still within 2σ of the experimental value and compatible with an expected underestimate of the experimental value.

A second difference with the model by Huang and Ardell (4) is the value of the Z-parameter of Al/Cu(1), which they give as 1/4. Here, the Patterson synthesis definitely points to a value different from 1/4, which was confirmed in the refinement (Table I). The effect on the structure is that the nearest neighbor distances of Al(2) become shorter and those of Li(1) become longer than the distance of 2.735 Å obtained for both for $z = 1/4$. This is exactly as in the cubic R phase, Al$_5$CuLi$_3$, and the icosahedral T$_2$ phase, Al$_6$CuLi$_3$, in which the nearest neighbor distances of the lithium atoms are also longer than the nearest neighbor distances of the copper and aluminum atoms (13, 14).

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