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Refinement of the Crystal Structure of Tetragonal Al_2Cu

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New single-crystal X-ray diffraction data have been obtained for the θ-phase of aluminum–copper (Al_2Cu). Results of the refinement are presented. The structure is found to be in accordance with the one determined by J. B. Friauf (*J. Amer. Chem. Soc.* **49**, 3107–3114 (1927)). The compound crystallizes in the tetragonal space group $I4/mcm$ (No. 140) with a unit cell of dimensions $a = 6.067(1)$ and $c = 4.877(1)$ Å. There are four formula-units per unit cell. A full-matrix least-squares refinement with 237 observed reflections and 8 parameters converged to $R_F = 0.032$ ($wR = 0.037$). In addition to more accurate values for the lattice parameters and the atomic coordinates, anisotropic temperature factors are obtained.

Introduction

The θ-phase is one of the many phases in the aluminum–copper phase diagram (*1*). Its structure was determined by Friauf (*2*) and confirmed by Bradley and Jones (*3*) and by Havinga *et al.* (*4*).

With the discovery of quasicrystals new interest grew in aluminum-containing alloys (*5*). In a search for icosahedral Al–Cu–Li quasicrystals, we obtained single crystals of θ-Al_2Cu. In this paper we report the results of new single-crystal X-ray diffraction experiments on this compound.

Experimental

Aluminum–copper–lithium alloy was prepared by melting together the elements and subsequent cooling of the crucible at 500°C (*6*). The material was broken and several submillimeter size single crystals with metallic luster were selected and tested on the diffractometer. Among these there were two specimens belonging to the θ-Al_2Cu phase. A bar-shaped crystal of dimensions 0.025 mm × 0.025 mm × 0.05 mm (longest direction parallel to the tetragonal axis) was selected for the experiment. All measurements were performed on an ENRAF-NONIUS CAD-4F diffractometer, equipped with a graphite monochromator, using Mo$K\bar{\alpha}$ radiation ($\lambda = 0.71073$ Å). The temperature of the measurement was 295 K.

Unit cell dimensions and their standard deviations were determined from the setting angles of 20 reflections in the range $23.01° < \theta < 26.86°$ in four alternate settings (*7*). The result is given in Table I, to-

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TABLE I

LATTICE PARAMETERS OF Al_2Cu FROM VARIOUS SOURCES

Source	a	c
Friauf (*2*)	6.052	4.870
Bradley and Jones (*3*)	6.066(1)	4.874(1)
Havinga *et al.* (*4*)	6.063(3)	4.872(3)
Present work	6.067(1)	4.877(1)

Note. The c-axis is the tetragonal unique axis. All values are in Å, with standard deviations in parentheses. Note that the values reported in Refs. (*2, 3*) are probably in x-units. The values for Refs. (*2, 3*) given here are obtained by multiplication of the values reported in Refs. (*2, 3*) by a correction factor of 1.002059 (*1, 17*).

gether with values from other investigations.

The intensities of all reflections in one hemisphere and up to $\theta = 50°$ were measured using the $\omega/2\theta$ scan-technique. The systematic extinctions pointed to the space group $I4/mcm$ (*8*), in accordance with the one determined by Friauf (*2*). Three reference reflections were measured in an interval of 2 hr. Their intensity variation (average 0.7%) was used to correct the measured intensities for drift in the intensity of the principal X-ray beam. Furthermore, the intensities were corrected for the Lorentz and polarization effects and for absorption (*9*) ($\mu = 126.1$ cm^{-1}). Standard deviations $\sigma(I)$ in the intensities were increased according to an analysis of the excess variance of the reference reflection: Variance was calculated based on counting statistics and the term (P^2I^2), where P (= 0.0047) is the instability constant (*10*). The 2026 measured reflections were combined into a unique set (Laue symmetry $4/mmm$) of 279 reflections with a consistency index $(\Sigma I - \bar{I})/\Sigma I)$ of 0.077. The 237 unique reflections satisfying the $I \geq 2.5\sigma(I)$ criterion of observability were used in the refinement.

The Patterson synthesis of the measured intensities was found to be in accordance with the structure obtained by Friauf (*2*). Using the single atomic coordinate parameter as a starting value, a full-matrix least-square refinement was carried out by minimizing $Q = \Sigma w(|F_o| - |F_c|)^2$. Unit weights were employed. With variation of the positional parameter, aniosotropic thermal parameters, and a single parameter correcting for secondary extinction ($g = 0.014(3) \times 10^4$) (*11*), an agreement was obtained with $wR = (\Sigma w(|F_o| - |F_c|)^2/(\Sigma w|F_o|^2))^{1/2} = 0.037$ and $R_F = \Sigma(|\,|F_o| - |F_c|\,|)/(\Sigma|F_o|) = 0.032$. A difference Fourier map of the final result did not show residual peaks outside ± 1.46 e/Å^3. A comprehensive list of crystallographic data including bond distances and a list of F_o, F_c, and $\sigma(F)$ are available as supplementary material.[2] Scattering factors were taken from Cromer and Mann (*12*). Anomalous dispersion factors were those given by Cromer and Liberman (*13*). All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages XTAL (*14*) and EUCLID (*15*) (calculation of geometric data).

Results and Discussion

Positional and thermal parameters of the final model are given in Table II. The positional parameter is in good agreement with the value obtained by Friauf (*2*), but is one order of magnitude more accurate. It differs slightly from the values given by Bradley and Jones (*3*) and by Havinga *et al.* (*4*).

[2] See NAPS document No. 04732 for 6 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 II

FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS FOR THE FINAL MODEL

	Cu	Al
x	0	0.1581(1)
y	0	$0.5 + x$
z	$\frac{1}{4}$	0
U_{11}	0.0087(2)	0.0104(3)
U_{22}	U_{11}	U_{11}
U_{33}	0.0062(2)	0.0109(5)
U_{12}	0	−0.0021(4)

Note. Standard deviations are in parentheses. The temperature factor for F is defined as $F(\mathbf{h}) = F_o(\mathbf{h}) \exp(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} h_i h_j a_i^* a_j^* U_{ij})$. U_{23} and U_{13} are zero by symmetry.

The closest distance found is between a copper and an aluminum atom of 2.59 Å, which is less than the Cu–Cu and the Al–Al distance in the respective pure elements (*1*). This bonding character might explain the relative low values found for the temperature factors, about one-quarter of the value they have in the elemental crystals (*16*).

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