

Determination of the crystal structure of icosahedral Al-Cu-Li

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The x-ray diffraction of a single crystal of the icosahedral phase of Al-Cu-Li has been measured on a diffractometer. Only 37 symmetrically inequivalent reflections were found with nonzero intensity. The structures considered, decorations of the Penrose packing with edge length 0.5039 nm, were refined to match the intensity data. An excellent agreement ($R_F = 7.0\%$) is obtained for Cu or Al occupying vertex and edge-center positions of both rhombohedra and Li or Al occupying two body-diagonal sites of the prolate rhombohedron. The icosahedral and cubic structure are compared.

INTRODUCTION

The discovery of alloys with a diffraction pattern exhibiting icosahedral point symmetry has created a great deal of interest.¹ Various structure models for these so-called quasicrystals have been put forward since,²⁻¹¹ all of which account for the icosahedral symmetry. Nevertheless, quantitative agreement with experimental diffraction data is rather poor for the rapidly quenched Al-Mn quasicrystal.¹² One of the most stable icosahedral phases has been found in the Al-Cu-Li system,¹³ and in this case Shen *et al.*⁹ have shown how a decoration of vertices and edges of the rhombohedral cells of the Penrose packing, with randomly distributed Cu and Al atoms, gives good agreement with powder-diffraction data. They arrived at a reliability factor of 0.11 considering 20 reflections. The stability of the Al-Cu-Li quasicrystal allows the production and isolation of single crystals large enough to be investigated by means of single-crystal x-ray diffraction, giving a solid experimental basis for further refinement of the atomic structure.

Single-crystal x-ray diffraction data have already been reported,^{14,15} and it was shown that both the diffraction geometry and the intensities obey the icosahedral symmetry in very good approximation, and that the reflections can be indexed on the basis of a six-dimensional primitive lattice. In this paper, we report on the measurement of single-crystal x-ray diffraction intensities, forming a complete set up to order 10. Using these intensities, the structure was refined by considering various decorations of the rhombohedra of the three-dimensional Penrose packing.^{16,17} A considerable improvement of the fit, as compared to a random atom decoration, is achieved by allowing a partial ordering of Al, Cu, and Li atoms over the vertices and edge centers, as well as over the two sites on the long body diagonal of the prolate rhombohedron.

EXPERIMENT

The diffraction experiment has been performed at room temperature on an Enraf Nonius CAD-4F four-circle diffractometer with monochromized Mo $K\alpha$ radiation, using the θ - 2θ scan technique. The irregular shape of the crystal did not allow absorption corrections to be calculated and therefore the geometry of the measurement was chosen as to minimize and equalize absorption as much as possible.¹⁴ A set of all symmetrically inequivalent reflections with order less than 11 was generated; the order of a reflection is defined in analogy with modulated structures as $m = \sum_j |m_j|$, where m_j are six integer coordinates of the diffraction positions with respect to the six vectors:¹⁸

$$\begin{aligned} \mathbf{q}_1 &= (\tau, 0, 1), & \mathbf{q}_2 &= (\tau, 0, -1), & \mathbf{q}_3 &= (1, \tau, 0), \\ \mathbf{q}_4 &= (0, 1, \tau), & \mathbf{q}_5 &= (0, -1, \tau), & \mathbf{q}_6 &= (1, -\tau, 0), \end{aligned} \quad (1)$$

where $\tau = (1 + \sqrt{5})/2$ is the golden mean. With $|\mathbf{q}| = 4.203 \text{ nm}^{-1}$, this procedure yields 1414 unique reflections of which 557 with $\theta < 40^\circ$ were measured. Thirty-seven reflections were found with intensities larger than twice the standard deviation in the counting statistics. Hereafter, these 37 strong reflections were measured three times for icosahedrally symmetric diffraction vectors and subsequently averaged. The Lorentz and polarization correction factors were applied to the intensities.

REFINEMENT

The models for the structure considered are several decorations of the three-dimensional Penrose packing (one of the decorations is depicted in Fig. 1). Structure factors were calculated numerically as

$$\begin{aligned} F(hkl) &= \sum_j f_j(\sin(\theta)/\lambda) \exp(-\frac{1}{4}B_j |\mathbf{S}|^2) \\ &\quad \times \exp(2\pi i \mathbf{S} \cdot \mathbf{r}_j), \end{aligned} \quad (2)$$

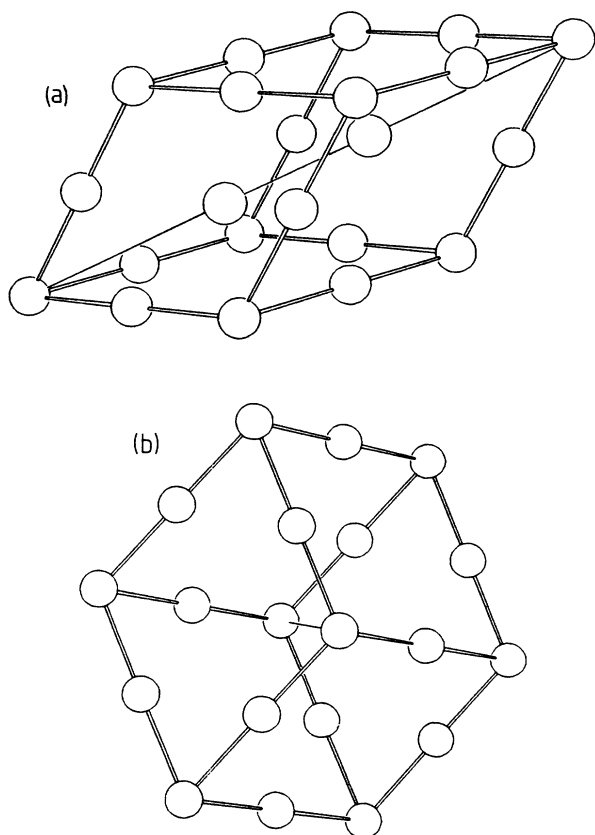


FIG. 1. The decorated rhombohedron (a) and the oblate rhombohedron (b), which form the 3D Penrose tiling.

where j runs over all atomic positions within a sphere of a radius of five edge lengths [$=5(0.5039 \text{ nm})$]. $\mathbf{S} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$, is the diffraction wave vector, with length $|\mathbf{S}| = 2 \sin(\theta)/\lambda$. The noninteger components are defined with respect to the same orthogonal coordinate system $\{\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*\}$ as the \mathbf{q} vectors [Eq. (1)]. In the case of a fractional occupancy of a site with different kinds of atoms, the product of the atomic form factor, $f_j(\sin(\theta)/\lambda)$, and the Debye-Waller factor is taken as a weighted average over the three atomic fractions. Only one independent parameter, B' , was used for the temperature factor. The individual temperature parameters of Cu, Al, and Li were then taken as B' divided by their respective masses. Values for f_j , including the anomalous scattering contribution, were taken from the International Tables.¹⁹ The atomic positions \mathbf{r}_j were determined with a computer program based on the dual-grid method.²⁰⁻²² The assumption that the integrated intensity is proportional to its maximum value for each reflection, is accurate for calculated structure factors, because the reflection width due to the size effect is independent of $|\mathbf{S}|$. Indeed, some of the calculated structure factors were compared with corresponding analytically determined ones reported by Ishihara²³ and were found to agree within 2%.

Two decorations have been investigated, for which the occupied sites are, respectively, (a) face centers, diagonal

sites, and vertices,⁷ (b) edge centers, diagonal sites, and vertices.⁹ (See Fig. 1.) In the prolate rhombohedron, the two internal sites divide the long body diagonal in three segments in the ratio $\tau:1:\tau$. These positions are the centers in the so-called Friauf polyhedron,²⁴ formed by the edge centers and vertices of the prolate rhombohedron. The best fit of the calculated structure factors to the measured ones has been determined by varying six independent variables. The fractional occupancies of the three sites (vertex, edge center, body diagonal) by each of the three kinds of atoms is described by nine parameters. Assuming no vacancies to occur, and assuming a definite stoichiometry, this reduces to only four independent parameters. One further independent parameter is supplied by B' in the Debye-Waller factor [Eq. (2)], and as the sixth parameter, the overall scale of the intensities has been varied. The reliability factor R_F is defined as

$$R_F = \frac{\sum ||F_0| - |F_c||}{\sum |F_0|}, \quad (3)$$

where $|F_0|$ is the square root of the observed intensity, and F_c is the calculated structure factor. The stoichiometry of the alloy is assumed to be Al_6CuLi_3 , corresponding to a density of 2.633 g/cm^3 for both decorations considered here. Positioning an "average" atom (0.6Al, 0.3Li, 0.1Cu) at all available positions results in a reliability factor of $R_F = 0.49$ for model (a) and $R_F = 0.29$ for model (b), after optimizing the Debye-Waller factor and the scale factor. After also optimizing the occupation fractions, the reliability factor of model (a) did not improve much: the optimum value is $R_F = 0.41$, while (b) improved to $R_F = 0.070$, indicating an excellent fit to the experiment.

In Table I we give the occupation fractions and temperature factors corresponding to the best fit. A model of type (b) with randomly distributed Al and Cu on the edge centers and vertices, as proposed by Shen *et al.*,⁹ resulted in $R_F = 0.10$ after optimizing the temperature and scale factor. The vertex-only model, used predominantly in the beginning of quasicrystal research, gives a poor fit, with a reliability factor of $R_F = 0.43$. The indexing method used here (Table II) corresponds to what Shen *et al.*⁹ inadvertently call icosahedral indices. (Reference 9 and this work use a different ordering of the \mathbf{q} -vector coordinates $0, 1, \tau$ [Eq. (1)].) We prefer this choice over the one with a \mathbf{q} vector shorter by a factor of τ^3 (called 6D indices in Ref. 9), because now all strong reflections are of low order.

TABLE I. Occupation fractions and temperature factors for the best fit to the diffraction data.

Atom	Temperature factor B'		Site	
	(10^3 pm^2)	Edge center	Body diagonal	Vertex
Al	0.20	0.75	0.17	0.69
Cu	0.083	0.10	0.00	0.22
Li	0.76	0.15	0.83	0.09

TABLE II. Calculated and measured structure factors of the 37 strongest reflections and the standard deviation in the measured values (in arbitrary units). The diffraction vector length is defined as $|\mathbf{S}| = 2 \sin(\theta)/\lambda$. The standard deviations are the maximum of the one based on counting statistics and the one obtained from averaging equivalent reflections.

6D indices	Length (nm ⁻¹)	$ F_c $	$ F_0 $	$\sigma(F_0)$	Order
(200000)	8.406	7.68	7.84	0.08	2
($\bar{1}$ 10000)	4.419	7.13	6.90	0.07	2
(110000)	7.150	6.66	6.85	0.08	2
(11 $\bar{1}$ $\bar{1}$ 0 $\bar{1}$)	5.013	5.17	5.15	0.13	5
(100000)	4.203	4.56	4.63	0.08	1
(1101 $\bar{1}$)	9.398	4.00	4.30	0.15	5
(1101 $\bar{1}$ 1)	9.398	3.78	3.96	0.08	5
(11 $\bar{1}$ $\bar{1}$ 01)	12.31	3.62	3.44	0.10	5
($\bar{2}$ $\bar{2}$ 0000)	8.838	3.11	3.22	0.14	4
(11 $\bar{1}$ 1 $\bar{1}$)	5.194	3.47	3.17	0.06	6
($\bar{1}$ 10100)	2.365	2.95	3.00	0.07	3
(220000)	14.30	2.84	2.86	0.16	4
($\bar{1}$ 11 $\bar{1}$ 1)	7.654	2.87	2.74	0.08	6
(2 $\bar{1}$ $\bar{1}$ 000)	7.654	2.68	2.63	0.09	4
(211000)	13.60	2.31	2.40	0.12	4
(110200)	11.03	2.47	2.40	0.11	4
(11 $\bar{1}$ 000)	6.098	2.16	2.38	0.07	3
(2 $\bar{1}$ 1000)	9.497	2.32	2.26	0.10	4
(2 $\bar{1}$ 0000)	5.479	2.02	2.11	0.09	3
(2 $\bar{1}$ 0 $\bar{1}$ 00)	5.195	2.35	2.02	0.07	4
(11 $\bar{1}$ 1 $\bar{2}$ 1)	8.012	1.63	1.90	0.14	7
(1 $\bar{1}$ 21 $\bar{1}$ 1)	11.29	1.68	1.88	0.14	7
(210000)	10.95	1.52	1.86	0.12	3
(210100)	12.39	2.38	1.82	0.15	4
(11112 $\bar{1}$)	13.81	1.48	1.70	0.16	7
($\bar{1}$ $\bar{1}$ 4111)	7.413	1.20	1.66	0.12	9
(1 $\bar{1}$ 111 $\bar{1}$)	13.60	1.54	1.65	0.21	6
(11111 $\bar{1}$)	12.39	1.78	1.60	0.16	6
(110 $\bar{1}$ 00)	8.294	1.88	1.58	0.13	3
(1111 $\bar{2}$ 1)	15.93	1.60	1.58	0.19	7
(111000)	10.02	1.81	1.53	0.14	3
(11211 $\bar{1}$)	15.93	1.67	1.51	0.20	7
($\bar{1}$ 02020)	5.708	1.21	1.30	0.10	5
(1 $\bar{1}$ 11 $\bar{2}$ 1)	8.011	1.32	1.16	0.15	7
(2 $\bar{1}$ 00 $\bar{1}$ 1)	6.682	1.06	1.13	0.17	5
(1 $\bar{2}$ 11 $\bar{2}$ 2)	5.289	0.54	1.05	0.12	9
(2 $\bar{1}$ $\bar{1}$ 0 $\bar{1}$ 0)	3.613	0.58	0.86	0.18	5

DISCUSSION AND CONCLUSIONS

The resulting atomic structure is most easily discussed by comparison with the $Im\bar{3}$ cubic phase, designated as the R phase by Hardy and Silcock.²⁵ The R phase has the slightly different stoichiometry Al_5CuLi_3 and is isostructural with the $(Al,Zn)_{49}Mg_{32}$ phase.^{26,27} As shown by Henley and Elser the unit cell of the cubic phase can be built from the same two rhombohedra as are found in the Penrose packing.³ One cubic unit cell consists of eight prolate rhombohedra (PR), and six rhombic dodecahedra (RD).³ The latter consists of two PR and two oblate rhombohedra (OR). Figure 2 shows two PR inscribed in the cubic unit cell. Comparison of the atomic sites ($A-H$, as defined in Ref. 26) with the rhombohedral dissection of the cubic structure unit cell then shows the following. Position A and C form the vertices of the PR,

B and F are on the edge centers, and the position D corresponds to the two positions on the body diagonal.³ The atomic assignment for the cubic structure of Al_5CuLi_3 by Cherkashin *et al.*²⁷ gives Cu or Al on positions A , B , C , and F , and Li on position D . This compares favorably with the structure determined here for the icosahedral phase (Table I). Analysis of the RD in terms of its inscribed PR and OR shows the same assignment for the A , B , C , and F positions. Position D is only contained in the isolated PR. The remaining positions are all in the interior of the RD. Position H is on the body diagonal of the PR, position G is on an edge center, and position E is equally distributed among edge centers and the body diagonal of the PR. It follows that the occupation of position E cannot be matched by a decoration of the rhombohedra with different occupancies of edge center and body diagonals. For the G and H positions Cherkashin *et*

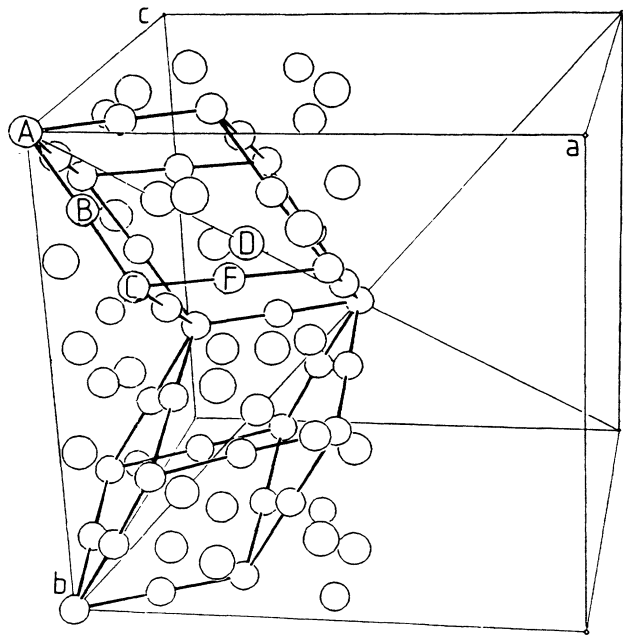


FIG. 2. The unit cell of the cubic phase Al_5CuLi_3 . Only atoms with $0 \leq x < \frac{1}{2}$, $0 \leq y \leq 1$, and $0 \leq z < \frac{1}{2}$ are drawn. The two isolated prolate rhombohedra are indicated, as they occur in the cubic structure. Special positions of the structure are indicated by capitals, as defined in Ref. 26.

*al.*²⁷ report the presence of a Li and an Al or Cu atom, respectively. However, according to the icosahedral phase, Li should be on *H* and Al or Cu on *G*. A redetermination of the structure of the cubic phase using new single-crystal data,²⁸ showed the *G, H* occupation to be interchanged as compared to the structure in Ref. 27. There is, therefore, a high degree of correspondence between the atomic structure of both phases, in agreement with EXAFS observations of Ma *et al.*⁸ who found the local surrounding of Cu atoms to be similar in the cubic and icosahedral phase.

The edge length of 0.504 nm is small considering the radii of the Al, Cu, and Li atoms. Assuming the Li atoms to be completely ionized at edge and vertex positions we find for the average of the atomic radii at edge and vertex positions, respectively, $r_e = 0.134$ nm and $r_v = 0.135$ nm, resulting in an approximate stress-free edge length of $2r_e + 2r_v = 0.538$ nm. Some charge transfer from Al to Cu atoms is likely to take place, but as only one out of eight vertex and edge positions is occu-

pied by a Cu atom, the bonds along rhombohedron edges are expected to be under considerable compressive stress. Introduction of vacancies as proposed by Bergman *et al.*,²⁶ may reduce the stress. Making use of the continuum theory of lattice defects²⁹ we estimate a fraction of 0.2 vacancies per position required to fully eliminate the compressive stress. Unfortunately, randomly distributed vacancies cannot be determined with a structure refinement because it only affects the overall scale of the diffraction intensities. The density of the icosahedral phase, however, is calculated to be 2.63 g/cm^3 without vacancies, and 2.26 g/cm^3 in the case of the large vacancy concentration estimated above, and an accurate measurement of the density of the phases can give an answer to this problem.

The large holes in the prolate rhombohedron are preferentially occupied with Li atoms, which seems to be a result of size differences, because the Li atom has a larger radius in the pure metal (0.155 nm) than Cu and Al have (0.129 and 0.143 nm, respectively). One would, however, expect charge transfer to occur from Li to Cu and Al due to the difference in electronegativity, reducing the radius of the Li atoms. The bond energy of a Li_2 molecule is 1.8×10^{-19} J/atom at a distance of 0.267 nm (in our structure 0.270 nm). This value may be compared to a bonding energy of 0.50×10^{-19} J/atom of an Al—Li bond in ordered Al_3Li . The energetically favorable Li_2 bond may therefore hinder charge transfer from the Li atoms and explain that Li and not Cu or Al occupies the large holes in the inner of the PR.

In summary, based on the 3D Penrose packing, and using newly measured single-crystal x-ray diffraction data, we have refined the structure of the icosahedral phase Al_6CuLi_3 . An excellent agreement between observed and calculated intensities is obtained. Furthermore, it is shown that the decoration of the rhombohedra compares favorably with the structure of the cubic phase. This is especially so if the recent redetermination of the cubic structure is considered,²⁸ which is slightly different from the structure reported in Ref. 27.

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