RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 37, NUMBER 14 15 MAY 1988-I

Structure of icosahedral clusters in cubic $Al_{5.6}Li_{2.9}Cu$

Christopher A. Guryan and Peter W. Stephens
Department of Physics, State University of New York at Stony Brook, Stony Brook, New York 11794

Alan I. Goldman
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

Frank W. Gayle
Metallurgy Laboratory, Reynolds Metals Company, Richmond, Virginia 23261

(Received 29 September 1987; revised manuscript received 7 January 1988)

We present a structure refinement of crystalline $Al_{5.6}Li_{2.9}Cu$ based on x-ray and neutron-diffraction data. We find that clusters of atoms form nearly ideal icosahedra in a bcc lattice, with different positions and occupancies than those proposed in previous work. Since neutrons and x rays have very different scattering amplitudes for Al, Li, and Cu, and since their respective diffraction profiles therefore consist of different peak intensities, the close agreement of the structural parameters from the two fits is a strong argument for the correctness of our results. These should be useful in packing-model descriptions of the related icosahedral phase.

The structure of icosahedral phase alloys has been of interest since their initial discovery in rapidly quenched Al-Mn.[1] Both three-dimensional Penrose tiling[2] (3D PT) and icosahedral glass[3] (IG) descriptions successfully account for the observed icosahedral symmetry of diffraction patterns, yet these models cannot be considered complete until a description of the actual atomic positions is included. A natural starting point for the decoration of packing units in icosahedral alloys is the atomic structure found in related crystalline phases, which consist of a bcc lattice of nearly icosahedral clusters of atoms. Elser and Henley[4] have pointed out that both crystals and Penrose tilings can be built from the same rhombohedral building blocks, so that the known atomic placement of atoms in a crystalline phase can be used to model a related icosahedral phase; this has been done for Al-Mn-Si (Ref. 4) and Al-Zn-Mg (Ref. 5) alloys. Alternatively, the icosahedral clusters present in the crystalline phases provide a natural building block for either quasiperiodic[6] or random[3] packing. In either case, the quasilattice constant is correctly given by the separation between icosahedral clusters connected at faces.

Recently, alloys of Al-Li-Cu have attracted interest because of reports that an icosahedral phase[7] *i*(Al-Li-Cu) can be grown with large grain sizes.[8] As a prelude to the determination of an atomic model of *i*(Al-Li-Cu), it is important to have a clear picture of the actual atomic packing in a crystalline analogue. Such information would be useful for the determination of diffraction peak intensities,[9] as well as for probes of the local atomic environment, such as extended x-ray-absorption fine structure (EXAFS), NMR, and the Mössbauer effect. Marcus and Elser[10] have pointed out that a crystalline phase *R*(Al-Li-Cu) is related to the *i* phase; indeed, EXAFS results indicate that the Cu sites in the two materials are nearly identical.[11] An earlier crystallographic study[12] claimed *R*(Al-Li-Cu) to be isostructural to $(Al,Zn)_{49}Mg_{32}$ alloys. However, as we will discuss below, this study did not actually refine the structure, and so a more systematic examination of the atomic packing *R*(Al-Li-Cu) and its relation to the *i* phase is warranted.

The model arrived at by our fits, as described below, is a bcc lattice [lattice constant = 13.89(1) Å] of icosahedral atomic clusters attached at local threefold axes. Each cluster is constructed of four shells of nearly icosahedrally symmetric polyhedra, as described by Bergman, Waugh, and Pauling;[13] the final atomic positions and occupancies for our fits are shown in Table I. The center of the cluster, site *A*, is vacant. The first shell is constructed by placing mostly Al atoms around the center at the 12 vertices of a regular icosahedron on sites *B*. Sites *D* and *E* comprise a second shell, filled by placing mostly Li atoms at the 20 face positions of the first shell. Another layer of roughly equal amounts of Al and Cu atoms at vertex positions (site *C*) constitutes a third shell. Sites *F* and *G* are filled by stacking Al with a small percentage of Cu in the interstices of the *D*, *E*, and *C* atoms, forming the outermost shell. The *F* and *G* atoms are the vertices of the network shown in Fig. 1(b). Each *F* and *G* atom is shared between two adjacent truncated icosahedra (TI), with 48 *F* atoms shared between the TI at the origin and those at body centers, and 12 *G* atoms shared between the TI at the origin and those at cube corners. The structure is completed by 12 Li atoms per unit cell, outside of the TI, between some of the hexagonal and pentagonal faces at sites *H*. We find small distortions from an ideal icosahedral shape for the clusters brought about by the cubic crystal environment. The greatest distortion is that TI edges (sites *G*) are pulled together along the cubic ⟨100⟩ directions, as illustrated in Fig. 1. This is consistent with EXAFS results[11] which indicate that the icosahedral symmetry of atomic clusters is more perfect in *i*(Al-Li-Cu) than in the *R* phase.

The *R*(Al-Li-Cu) was cast as a 2 kg melt in a graphite crucible and allowed to cool slowly in the furnace. A region was selected which contained large blocky grains of

© 1988 The American Physical Society

TABLE I. List of positional parameters and occupancies. Labels are after Bergman *et al.*;[13] occupancies refer to atoms per unit cell, with each unit cell containing two icosahedra. Icosahedral values are for clusters with ideal icosahedral symmetry; experimental values are weighted averages of positional parameters and occupancies from fits in Fig. 2. Estimated errors (numbers in parentheses, of the same order of magnitude as the last significant digit) encompass both neutron and x-ray standard deviations.

	Icosahedral			Experimental			
Site	x	y	z	x	y	z	Occupancy
A 2:(a)	0	0	0	0	0	0	0.0(4) Al
B 24:(g)	0	0.0955	0.1545	0	0.095(6)	0.155(3)	22(1) Al, 2(1) Cu
C 24:(g)	0	0.1910	0.3090	0	0.181(1)	0.315(3)	13(1) Al, 11(1) Cu
D 16:(f)	0.1910	0.1910	0.1910	0.184(4)	0.184(4)	0.184(4)	2(1) Al, 14(1) Li
E 24:(g)	0	0.3090	0.1180	0	0.30(1)	0.12(1)	1(2) Al, 23(2) Li
F 48:(h)	0.1545	0.1910	0.4045	0.157(4)	0.191(3)	0.405(1)	44(2) Al, 4(2) Cu
G 12:(e)	0.0955	0.4635	0	0.096(3)	$\frac{1}{2}$	0	12(1) Al, 0(1) Cu
H 12:(e)	0.1910	0	$\frac{1}{2}$	0.20(1)	0	$\frac{1}{2}$	0.6(6) Al, 11.4(6) Li
							94.6 Al, 48.4 Li, 17 Cu

approximately 1 to 5 mm diameter. Wafers of thickness 0.5 mm were sliced in which the grains of R-phase material were visible with a minimum of intercellular eutectic phases. Single-crystal grains were manually extracted and eutectic regions removed; two samples, totaling 2 g, were separately ground to powder for the diffraction studies. The samples were subsequently analyzed using inductively coupled plasma emission spectroscopy to be 10.58 ±0.04 at.% Cu and 30.4%±0.4% Li, leading to a stoichiometric composition of $Al_{5.6}Li_{2.9}Cu$.

A portion of each sample was passed through a 75-μm mesh sieve and then loaded into a 1-mm glass capillary for x-ray study. To ensure the consistency of the samples, scans of each were made using Mo $K\alpha$ radiation from a rotating anode and a pyrolitic graphite (PG) (002) monochromator; these scans were summed for refinement. The samples were then combined and loaded into an Al holder for neutron-diffraction measurements, which were made on a triple-axis spectrometer at the Brookhaven National Laboratory High Flux Beam Reactor. The spectrometer configuration was 20′ (arc minute) collimator, PG filter, bent PG (002) monochromator, 40′, sample, 40′, bent PG (004) analyzer, 20′, detector, for $\lambda = 2.651$ Å neutrons. The absorption of the sample for both x-ray and neutron diffraction was determined to be sufficiently small that no corrections were made, and both x-ray and neutron scattering data were taken while the sample was twirled through 90° or 360° to minimize preferred orientation effects.

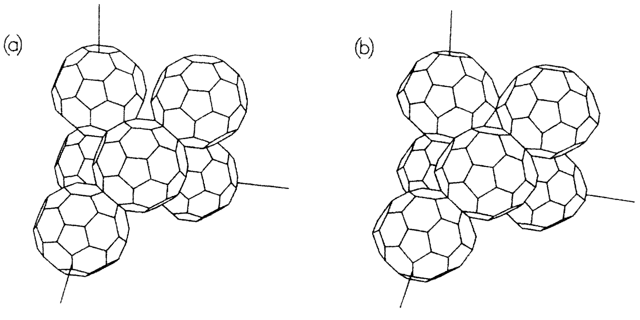

FIG. 1. (a) bcc lattice of spheres made of regular pentagons and hexagons. Clusters share hexagonal faces along ⟨111⟩ directions. (b) Diagram of model as discussed in text. Atoms in F and G sites occupy vertices; clusters are distorted to share edges in ⟨100⟩ directions.

The diffraction data and fits from the refinements are shown in Fig. 2. All major peaks could be indexed to a bcc lattice, but small shoulders in the x-ray data, presumably due to small amounts of impurity phases, were excluded from the fits. In the neutron data, Al peaks from the sample holder were excluded.

An earlier study by Cherkashin, Kripyakevich, and Oleksiv[12] found that R(Al-Li-Cu) was isostructural with $(Al,Zn)_{49}Mg_{32}$ (Ref. 13) and so was a 162-atom cubic unit cell with the symmetry of space group Im3 (T_h^5); however no systematic refinement was done. In particular, they set all of the atomic positions equal to those determined by Bergman, Waugh, and Pauling,[13] and substituted Li for Mg and Cu for Zn, except in site H in which Al was substituted for Mg in order to obtain the correct stoichiometry. While we find good qualitative agreement between their data and ours, the diffraction pattern calculated from their model shows strong differences from both data sets. This model has been improved by Dmowski *et al.*[14] by shifting some atomic positions and occupancies, but again no refinement was performed. Nonetheless, we were able to successfully refine our data starting from the $(Al,Zn)_{49}Mg_{32}$ structure.

To arrive at the results in Table I, we performed Rietveld refinement[15] of x-ray and neutron data independently, constraining the relative abundancies of Al and Cu in the fits to the measured value for our sample. The values listed in Table I and used in the models in Fig. 1 are the average of the neutron and x-ray numbers weighted by their respective standard deviations. Both fits converged to values that are substantially in agreement: of 20 quantities fit (with one constraint), eight have estimated error bars which overlap the weighted average value, 17 agree to within two standard deviations, and all agree to within three standard deviations. The overall thermal factor yielded a rms position fluctuation of 0.14(7) Å; inclusion of individual atomic thermal factors did not significantly alter the fit.

The R factors[15] given in Table II are a standard crys-

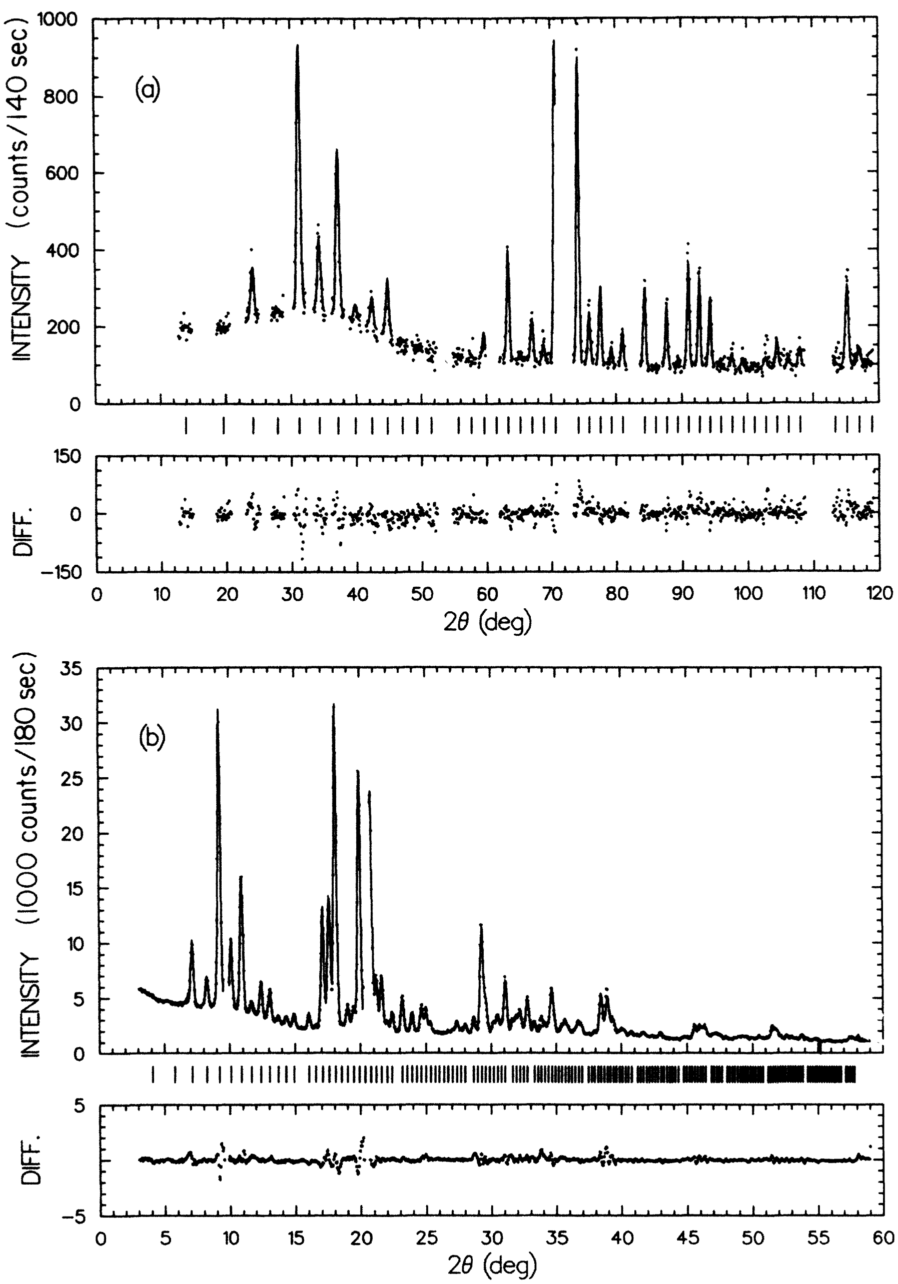

FIG. 2. Diffraction data and fits as discussed in text. Bars beneath horizontal axes mark allowed peak positions; lines are results of fits. (a) Neutron data. (b) X-ray data.

tallographic measure of the goodness of fit of the calculated profile to the data, defined as

$$R_i \equiv 100 \left(\sum \left| I_{\text{obs}} - \frac{1}{c} I_{\text{calc}} \right| \right) \Big/ \sum I_{\text{obs}} \,,$$

$$R_p \equiv 100 \left(\sum \left| y_{\text{obs}} - \frac{1}{c} y_{\text{calc}} \right| \right) \Big/ \sum | y_{\text{obs}} | \,,$$

$$R_{\text{wp}} \equiv 100 \left[\sum W \left(y_{\text{obs}} - \frac{1}{c} y_{\text{calc}} \right)^2 \Big/ \sum W (y_{\text{obs}})^2 \right]^{1/2} ,$$

$$R_e \equiv 100 \left[(N - P + C) \Big/ \sum W (y_{\text{obs}})^2 \right]^{1/2} ,$$

where I_{obs} and I_{calc} are the observed and calculated integrated intensities of each peak, c is an overall scale factor, y_{obs} and y_{calc} are the observed and calculated intensities as a function of scattering angle, $W(y_{\text{obs}})$ is the statistical weight of an observed point (i.e., $\sqrt{y_{\text{obs}}}$), and $N-P+C$, the number of data points minus the number of parameters plus the number of constraints, is the number of degrees of freedom of the fitting routine. R_{wp} and R_e are the weighted profile and the expected R factor for the fit, so that $(R_{\text{wp}}/R_e)^2$ is a measure of goodness of fit χ^2. A perfect fit to a data set would have only statistical errors, leading to a χ^2 of 1; in crystallographic refinements χ^2 customarily ranges between 2 and 4. The best fit to our

TABLE II. List of R factors (discussed in text) for fits in Fig. 2. Avg. refers to the weighted average parameters presented in Table I. Best refers to the best fit for each data set.

	Neutrons		X rays	
	Avg.	Best	Avg.	Best
R_i	12.55	9.64	5.72	5.13
R_p	28.95	24.69	11.37	10.66
R_{wp}	27.45	24.38	12.80	12.09
R_e	18.77	18.74	3.33	3.30

x-ray data has a χ^2 of 13.4. This high value of χ^2 for the x rays can be explained by the statistics of the x-ray data: systematic errors, such as the line shape of the diffraction peaks, become more significant as number of counts at each data point increases.

One important check on the validity of a structural model is the length of atomic bonds between sites. We have calculated that the lengths of all bonds in this model are greater than 2.52 Å; this is consistent with metallic radii of 1.225, 1.248, and 1.173 Å for Li, Al, and Cu.[16]

The importance of this measurement to the study of the i-phase alloys is twofold. First, with the correct atomic positions and occupancies in hand, modeling of the i-phase structure by either decomposing the clusters into Penrose bricks, or taking the clusters as a whole and packing them together noncrystallographically, can proceed. In addition, by comparing the local packing of atoms in the crystalline phases of α(Al-Mn-Si) and R(Al-Li-Cu) we find some indication as to why the lattice forms a more stable i-phase alloy than other systems: of the 160 atoms in R(Al-Li-Cu), only the 12 atoms in sites H are not contained in the nearly icosahedral clusters, whereas 30 of 138 atoms in the α(Al-Mn-Si) unit cell are not members of clusters, but rather form connections between clusters along ⟨100⟩ directions. α(Al-Mn-Si), then, is best thought of less as a periodic packing of nearly icosahedral clusters than a lattice of such clusters embedded in a matrix of atoms that are not related by icosahedral symmetry operations. In addition, the F and G sites comprising a single shell are of the same composition in R(Al-Li-Cu), while there is a distinct difference in composition between the corresponding sites in $(Al,Zn)_{49}Mg_{32}$.[13] The crystalline phase related to i(Al-Li-Cu) therefore exhibits significantly stronger local icosahedral symmetry than other known prototypes.

We thank D. E. Cox for his expert assistance with the Rietveld routines, W. E. Pilgrim for the chemical analysis, and H. M. Edwards for assistance in casting. The work was supported by the National Science Foundation, Low Temperature Physics Grant No. DMR-8702042 (C.A.G. and P.W.S.) and the U.S. Department of Energy under Contract No. DE-AC02-76-80016 (A.I.G.).

---

[1] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).

[2] D. Levine and P. J. Steinhardt, Phys. Rev. Lett. **53**, 2477 (1984).

[3] P. W. Stephens and A. I. Goldman, Phys. Rev. Lett. **56**, 1168 (1986).

[4] V. Elser and C. L. Henley, Phys. Rev. Lett. **55**, 2883 (1985).

[5] C. L. Henley and V. Elser, Philos. Mag. B **53**, L59 (1986).

[6] P. Guyot and M. Audier, Philos. Mag. B **52**, L15 (1985).

[7] M. D. Ball and D. J. Lloyd, Scr. Metall. **19**, 1065 (1985); P. Sainfort and B. Dubost, J. Phys. (Paris) Colloq. **47**, C3-321 (1986); C. Bartges, M. H. Tosten, P. R. Howell, and E. R. Ryba, J. Mater. Sci. **22**, 1663 (1987).

[8] B. Dubost, J. M. Lang, M. Tanaka, P. Sainfort, and M. Audier, Nature **324**, 48 (1986); F. W. Gayle, J. Mater. Res. **2**, 1 (1987).

[9] Y. Shen, S. J. Poon, W. Dmowski, T. Egami, and G. J. Shiflet, Phys. Rev. Lett. **58**, 1440 (1987).

[10] M. A. Marcus and V. Elser, Philos. Mag. B **54**, L101 (1986).

[11] Y. Ma, E. A. Stern, and F. W. Gayle, Phys. Rev. Lett. **58**, 1956 (1987).

[12] E. E. Cherkashin, P. I. Kripyakevich, and G. I. Oleksiv, Krystallografiya **8**, 846 (1963) [Sov. Phys. Crystallogr. **8**, 681 (1964)].

[13] G. Bergman, J. T. Waugh, and L. Pauling, Acta Crystallogr. **10**, 154 (1957). A description of this structure is also given in L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell Univ. Press, Ithaca, NY, 1960).

[14] W. Dmowski, T. Egami, Y. Shen, S. J. Poon, and G. J. Shiflet, Philos. Mag. **56**, L63 (1987).

[15] H. M. Rietveld, J. Appl. Crystallogr. **2**, 65 (1969); A. W. Hewat, United Kindgom Atomic Energy Authority Research Group Report No. RRL73-1897, 1973 (unpublished).

[16] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell Univ. Press, Ithaca, NY, 1960).