Al-Cu-Ru: An Icosahedral Alloy without Phason Disorder

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We present high-resolution x-ray diffraction measurements of the recently discovered face-centered icosahedral phase of $Al_{65}Cu_{20}Ru_{15}$. Analysis of the diffraction-peak profiles shows that this alloy is better ordered than the simple-icosahedral alloys previously studied. In particular, the peak broadening is well accounted for by simple lattice strain, with no measurable dependence of the peak widths on phason momentum. This implies a significantly diminished role for phason disorder in this system relative to the simple-icosahedral alloys.

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The original discovery of an icosahedral phase in rapidly quenched alloys of Al-Mn [1] has been followed by reports of icosahedral phases in many other intermetallic alloys. All of these systems share two characteristics: The diffraction patterns can be indexed using the set of basis vectors appropriate to a simple-icosahedral (SI) quasilattice, and all exhibit a significant degree of disorder signaled by broadened diffraction peaks. Indeed, it is quite surprising that the peak widths obtained from single-grain diffraction measurements on the stable Al-Li-Cu alloy[2] are only marginally narrower than those obtained from rapidly quenched ribbons of Al-Mn.[3] This point argued for the "universality" of disorder in the icosahedral alloys. Furthermore, the peak broadening in these systems offers no systematic dependence on the measured momentum transfer ($G_\parallel$) as is observed, for instance, in inhomogeneously strained crystals (in the literature this is often termed "phonon" strain). Instead, the peak widths are monotonically increasing functions of the phason momentum ($G_\perp$), a variable that appears due to the fundamental incommensurability of the icosahedral lattice.[4]

Several structural models that account for the gross features of the diffraction pattern from icosahedral alloys have been proposed. Quasicrystalline descriptions, such as the three-dimensional Penrose tiling (3DPT),[5] and the icosahedral glass (IG) model[6,7] both yield scattering functions consisting of an icosahedrally symmetric set of spots. While the large degree of disorder intrinsic to the IG model itself produces broadened diffraction peaks, the 3DPT, if modified by the inclusion of random linear phason strain, also produces diffraction peaks in qualitative agreement with experiment. In their ideal states, the IG and 3DPT models represent the extreme limits of disorder and order, respectively, and it was generally believed that the real icosahedral alloys lay somewhere in between these two limits.

The most recently discovered icosahedral alloys, Al-Cu-Fe[8,9] and Al-Cu-Ru, differ from the other alloys in several important ways. First, the diffraction patterns from these materials can be indexed to a body-centered icosahedral reciprocal lattice (BCI),[10–12] so that the direct-space 6D lattice is face-centered icosahedral (FCI). Even more startling, however, was the suggestion, from electron diffraction experiments, that these materials lacked the phason disorder present in all icosahedral alloys to date. For instance, the high-resolution electron micrographs of Al-Fe-Cu by Hiraga *et al.*[9] saw no evidence of shifts in the lattice planes (one of the signatures of phason strain), and bright-field images of grains larger than several microns show uniform illumination. However, the most direct test of the presence and degree of phason disorder in these materials is an analysis of the diffraction-peak widths from high-resolution x-ray measurements.

Here we present the first quantitative measure of phason disorder in samples of $Al_{65}Cu_{20}Ru_{15}$. These measurements provide direct evidence for the lack of phason disorder in this material. In striking contrast to such measurements on the simple-icosahedral structures such as Al-Mn and Al-Li-Cu, the peak broadening exhibits no systematic dependence on the phason momentum ($G_\perp$), but rather a linear dependence on the physical momentum transfer ($G_\parallel$). Even so, the peak widths are still several times narrower than those found in Al-Li-Cu. This observation indicates that quasicrystalline models, as opposed to the IG structure, are a more appropriate description of these new FCI alloys.

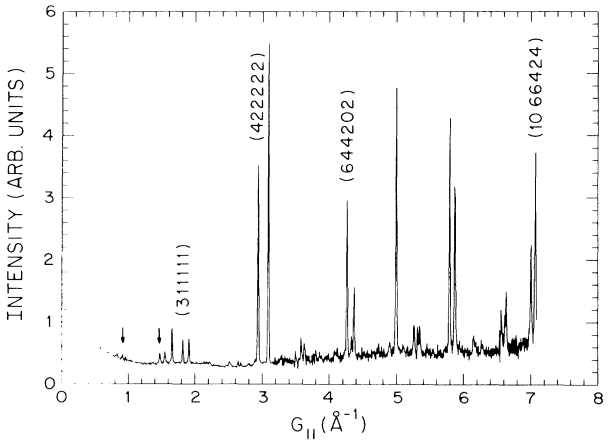

FIG. 1. Powder diffraction pattern from icosahedral $Al_{65}Cu_{20}Ru_{15}$. The difference in background scatter at higher Q reflects shorter counting times in this region. Arrows correspond to impurity peaks observed in this particular sample.

Samples of $Al_{65}Cu_{20}Ru_{15}$ were prepared by arc melting the appropriate quantities of Al, Ru, and Cu, and then annealed at 850°C for 48 h. The selected-area electron diffraction patterns of thinned samples were similar in appearance to those of Ref. 9, showing that Al-Cu-Ru is an icosahedral phase based on a BCI reciprocal lattice. The sample was then gently ground to a powder and loaded into a 1-mm glass capillary for the x-ray measurements. Figure 1 shows the powder diffraction pattern from the sample taken using Cu $K\alpha$ radiation, from a rotating-anode x-ray generator, monochromatized with a bent graphite (002) crystal. The spectrometer resolution was approximately 0.005 Å^{-1} (HWHM). With the exception of a couple of weak unidentified impurity peaks, denoted by arrows in Fig. 1, all peaks can be indexed using a BCI reciprocal lattice as discussed below.

In order to obtain reliable values for the intrinsic peak widths, high-Q-resolution scans were taken at the powder diffraction beam line (X7A) at the National Synchrotron Light Source using 1.4883-Å radiation and a Si(111) analyzer. The resolution measured with a Si poweder sample at 1.9 Å^{-1} was approximately 0.0005 Å^{-1} (HWHM). The diffraction peaks from the $Al_{65}Cu_{20}Ru_{15}$ specimen were fitted using both Gaussian and pseudo-Voigt line shapes; values for the HWHM and position of the peaks were relatively insensitive to the choice of line shape. The eighteen diffraction peaks that were measured here are found along the twofold, threefold, and fivefold high-symmetry directions as well as more general directions in reciprocal space.

In Fig. 2(a) we show the difference (Δ) between measured powder peak positions and those calculated for an ideal BCI reciprocal lattice. The observed peak positions were all found to be within 0.0012 Å^{-1} of the expected values. The small random peak displacements often seen

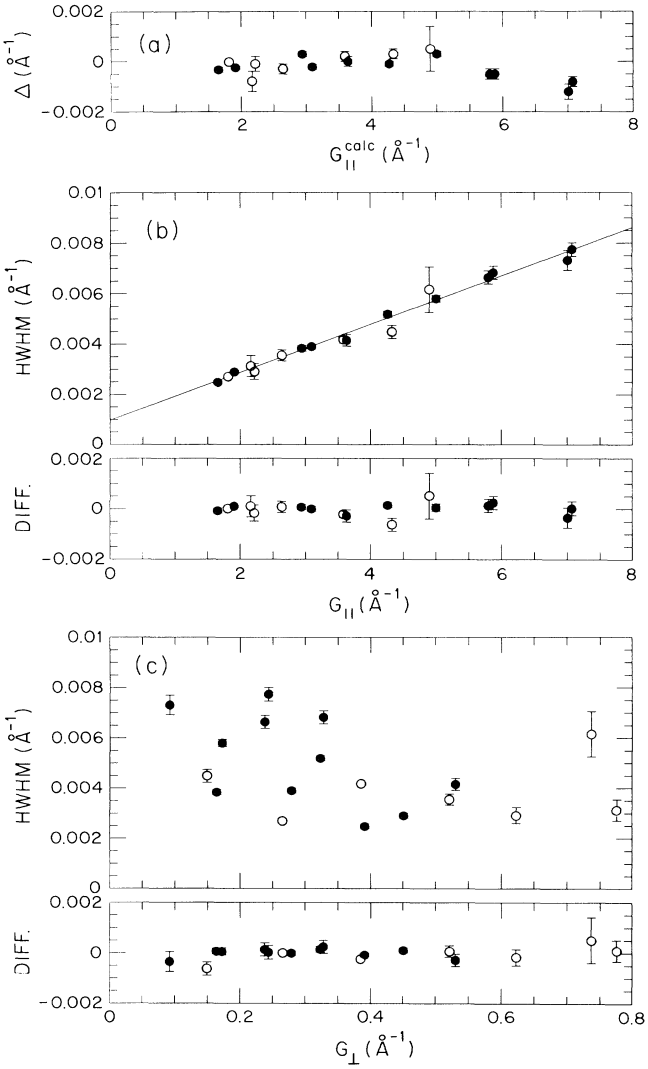

FIG. 2. Results of the high-resolution x-ray study of peak widths and positions in $Al_{65}Cu_{20}Ru_{15}$. Filled (open) circles denote diffraction peaks of even (odd) parity. Panel (a) shows the difference between the observed and calculated peak positions using the strong, fivefold axis peak at $Q=2.939$ Å (422222) as a reference point. Panel (b) displays the peak HWHM as a function of $G_{\parallel}$ along with the least-squares fit (solid line) as described in the text; the lower subpanel shows the fit residuals plotted against $G_{\parallel}$. Panel (c) shows the same data plotted as a function of $G_{\perp}$.

in the diffraction patterns of the SI alloys were absent.

In Figs. 2(b) and 2(c) we show the dependence of the peak widths (after a small correction for the instrumental resolution) on $G_{\parallel}$ and $G_{\perp}$, respectively. The subpanels show the residuals of a linear fit to the data in Fig. 2(b) as described below. These figures clearly show that the peak broadening is insensitive to the magnitude of the phason momentum (no systematic trends are evident), but increases linearly with increasing momentum

transfer. This behavior should be compared to the corresponding measurements of diffraction-peak broadening in the SI structures Al-Mn-Si by Horn *et al.*[3] and Al-Li-Cu by Heiney *et al.*,[2] which show no systematic trend in peak widths with increasing $G_{\parallel}$, but a roughly linear increase in the peak broadening with increasing $G_{\perp}$. However, in order to compare directly the magnitude of the broadening in the present measurement with those of Refs. 2 and 3, the relative scales of $G_{\perp}$ should be defined.

The BCI reciprocal lattice may be indexed using six unit vectors in the directions of the vertices of an icosahedron, with the restriction that all indices must be of the same parity. The BCI reciprocal lattice is invariant under inflations or deflations by a factor of $\tau = (1+\sqrt{5})/2$. Therefore, there are many possible choices for the fundamental reciprocal-lattice vector along a fivefold axis. One plausible choice would be to select the strongest observed peak along a fivefold axis at $Q = 2.939$ Å^{-1} as the (200000). A similar choice for the (100000) reciprocal-lattice vector was made in the x-ray measurements on SI alloys.[2,13] However, the criticism has been raised that this leads to a quasilattice constant $a_0 = \pi/Q_{100000} = 1.085$ Å which is unreasonably small for atomic separations.[14] A single inflation by τ^3 (the smallest allowed for a SI quasilattice) addresses this problem, leading to a quasilattice constant of 4.6 Å.[15] The (100000) reciprocal-lattice vector then corresponds to the diffraction peak along the fivefold axis which is a τ^3 deflation from the (100000) in Refs. 2 and 13. Accordingly, we have chosen to index our diffraction patterns with the fundamental Q_{200000} a factor of τ^3 lower than the strong reflection labeled (422222) in Fig. 1. This corresponds to the same scale factor chosen in Ref. 12. Although this reflection is extremely weak in the powder data, it is clearly observed in the electron diffraction patterns.

With this choice of "fundamental" reflection, the direct and dual reciprocal-lattice vectors for Al-Cu-Ru are given by

$$\mathbf{G}_{\parallel} = G_0 \sum_j n_j \mathbf{e}_j^{\parallel}, \quad \mathbf{G}_{\perp} = G_0 \sum_j n_j \mathbf{e}_j^{\perp},$$

where $G_0 = 0.347$ Å^{-1}, all n_j are of the same parity, and the unit vectors $\mathbf{e}_j^{\parallel}$ and $\mathbf{e}_j^{\perp}$ are defined by the "umbrella" convention of Ref. 14. Note that the assignment of a particular peak as the (200000) determines the scale of $G_{\perp}$. Consequently, the numerical scale of the $G_{\perp}$ axes in Fig. 2 can be inflated or deflated by powers of τ. In order to compare the magnitude of the peak widths in Fig. 2(c) with the corresponding data for the SI alloys, the $G_{\perp}$ scales in Refs. 2 and 3 should be deflated by τ^6.

Despite the ambiguity of the numerical scale for $G_{\perp}$, we can make a quantitative assessment of the relative role of phonon and phason disorder by fitting the data in Fig. 2(b) with simple functional dependences on $G_{\perp}$ and $G_{\parallel}$. One plausible guess is that the phonon and phason contributions to the peak widths add in quadrature, so that the diffraction-peak widths are given by[3]

$$\Delta G = [(\alpha G_{\parallel})^2 + (\beta G_{\perp})^2]^{1/2} + \gamma.$$

On the other hand, given the scatter that is evident in Fig. 2(c), we may choose to fit the $G_{\parallel}$ dependence of the data in Fig. 2(b) with the function

$$\Delta G = \alpha G_{\parallel} + \gamma,$$

and plot the residuals as a function of $G_{\parallel}$ and $G_{\perp}$, as is done in the subpanels of Figs. 2(b) and 2(c), in order to isolate any linewidth contribution not accounted for by linear phonon strain. This least-squares fit yields $\alpha = 0.00095(1)$ and $\gamma = 0.00099(3)$ with a χ^2 of 1.28, and clearly is an excellent description of the systematics of line broadening in Al-Cu-Ru. As is evident from the plot of the residuals as a function of $G_{\perp}$, there is essentially no contribution to the broadening that is dependent on $G_{\perp}$. Note that because of the different symmetries of the measured diffraction peaks, it is unlikely that a more complicated dependence of diffraction-peak width on $G_{\parallel}$ and $G_{\perp}$ could accidentally give such a good fit. The small, but finite, value for γ indicates that there may be some residual peak broadening which may be due to finite domain size (≈ 3000 Å), or some very small component of phason (phonon) disorder which is not described by a linear dependence on $G_{\perp}$ ($G_{\parallel}$).

The debate over the structure of icosahedral alloys has largely focused on the role and importance of disorder. Various quasicrystalline models have emphasized an underlying perfectly ordered quasilattice, which may be disordered by the presence of linear phason strain to account qualitatively for the observed linear $G_{\perp}$ dependence of the diffraction-peak widths in the SI alloys. On the other hand, the IG model is based upon an intrinsically disordered structure that yields peak broadening which is solely dependent upon the magnitude of $G_{\perp}$. Although the IG model has been criticized as being too disordered,[16] it successfully accounts for many of the important features observed in the diffraction patterns from the SI alloys.[7,17] For the FCI alloy Al-Cu-Ru our results indicate that the quasicrystalline description seems most appropriate. Diffraction measurements on Al-Cu-Fe find the same trends as described here.[18] Therefore, phason strain is not a "universal" feature of aperiodic crystals.

One can consider the BCI reciprocal lattice of Al-Cu-Ru as being produced by a FCI direct lattice, such as would occur for primitive translations along icosahedral twofold directions (as opposed to the threefold or fivefold directions which produce a simple-icosahedral quasilattice). Alternatively, as pointed out by Ebalard and Spaepen[11] and Devaud-Rzepski *et al.*,[12] a BCI reciprocal lattice can also arise from some form of superlattice ordering on a SI lattice. Indeed, in samples of Al-Cu-Fe, those authors have found evidence for antiphase

domains—regions where the FCI superlattice ordering changes phase on a fixed array of SI lattice positions. In such a case, the odd-parity diffraction peaks arise from the difference in scattering amplitude between the two structural units. In this measurement, the odd-parity peaks are generally weaker than those of even parity, as was also noted in Ref. 12. This may be taken as evidence that the odd-parity peaks arise from a rather weak difference in scattering power between the two structural units comprising the building blocks of the FCI quasilattice. However, it is interesting to note that there is no systematic dependence of peak width on the parity of the indices, plotted as filled (even parity) and open (odd parity) circles in Fig. 2. This result holds for any inflation by τ, even though the parity of some of the peaks changes with inflation. Therefore, in the present annealed sample, the antiphase-domain coherence length is as large as the overall lattice coherence length.

These results raise several important issues for further research. First, of course, is the question of how the BCI alloys differ so significantly from the SI alloys that phason disorder is suppressed. An important step in answering this question would be the identification of crystalline analogs to the FCI structures, much the same as the identification of icosahedral clusters in α(Al-Mn-Si) and R(Al-LI-Cu) led to a clearer notion of how such icosahedral clusters could be packed together. These alloys may also provide some indication as to the mechanism of phason-strain suppression. Our preliminary work seems to show that phason strain can be annealed away, contrary to the belief that these defects are "frozen in." In addition, further annealing experiments should be done to determine whether or not the phonon strain evident in these alloys can be reduced, and how the phonon and phason strain are interrelated; does the absence of one require the presence of the other? Finally, it will be interesting to see whether the electronic and vibrational properties of the FCI alloys are significantly different from those of the SI alloys, where disorder is claimed to obscure the subtle features introduced by aperiodicity.

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