Diffuse Scattering from the Icosahedral Phase Alloys

A. I. Goldman,(1),(a) C. A. Guryan,(2) P. W. Stephens,(2) J. M. Parsey, Jr.,(3) G. Aeppli,(3) H. S. Chen,(3)
and F. W. Gayle(4)

(1)*Brookhaven National Laboratory, Upton, New York 11973*
(2)*State University of New York, Stony Brook, New York 11794*
(3)*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*
(4)*Reynolds Metals Company, Richmond, Virginia 23261*

(Received 13 May 1988)

We present neutron and x-ray measurements of the diffuse scattering from single-grain samples of the icosahedral phase of Al-Li-Cu. The x-ray measurements were analyzed to determine the integrated intensity of the diffuse scattering relative to the sharp diffraction peaks, as well as the length scale of the correlations which produce the diffuse scattering. The neutron data show that these correlations are static rather than dynamic in nature. In addition, we present a simple model based on the disordered packing of icosahedral clusters of atoms, which reproduces the unusual ringlike nature of this scattering. Quantitatively, this model overestimates the degree of disorder present in these alloys.

PACS numbers: 61.55.Hg, 61.10.Dp, 61.50.Em

Much of the work in the field of icosahedral-phase (IP) alloys has focused on the unusual diffraction properties of these materials. The observed icosahedrally symmetric pattern of diffraction spots can be understood from various viewpoints. However, the diffuse scattering observed in electron-diffraction patterns of rapidly quenched alloys such as Al-Mn,[1] $FeTi_2$,[2] and Ti-Mn,[3] as well as in single-grain x-ray precession photographs of Al-Li-Cu,[4] has not yet been fully characterized or satisfactorily explained. While many of the details of the diffuse scattering vary from system to system, and even among samples of the same alloy, there are features which are common to all of the alloys that have been studied. For instance, in the twofold planes, rings or arcs of diffuse scattering are observed along the fivefold axes. The centers of these rings are not an element of the *simple* icosahedral reciprocal lattice, but instead correspond to $\tau^{-1}\mathbf{G}_{100000}$ [here $\mathbf{G}_{100000}$ is the fundamental reciprocal-lattice vector in the notation of Bancel *et al.*[5] and $\tau=(\sqrt{5}+1)/2$].

Here we report on single-grain x-ray and neutron measurements of the diffuse scattering from Al-Li-Cu IP alloys. Our results confirm the existence of a diffuse ring (which is in fact a *three-dimensional shell* of scattering) centered at $\tau^{-1}\mathbf{G}_{100000}$ and we have determined both an integrated intensity and correlation length, parameters which are necessary for detailed comparison with models for the diffuse scattering. The neutron measurements show that this scattering results from static disorder rather than dynamic mechanisms. Furthermore, we show that this diffuse scattering can be obtained from a disordered packing of icosahedral clusters of atoms, such as that found in the icosahedral-glass model.[6]

The x-ray measurements were made on a single-grain sample (0.2×0.8 mm^2) studied previously by Heiney *et al.*[7] The diffraction data were taken at room temperature with use of Mo $K\alpha$ radiation with the sample oriented such that a twofold plane $(hk0)$ was nominally in the scattering plane of the apparatus [Fig. 3(a) shows a sketch of the diffraction plane]. Using the x-ray precession photographs of Denoyer *et al.*[4] as a guide, we have focused our attention on the region close to the diffuse ring. Figure 1 shows scans taken through the center of the diffuse ring along the directions of the three mutually perpendicular twofold axes, defined as $(h00)$, $(0k0)$, and $(00l)$. The data shown here have had a 2θ-dependent background (as a result of the glass capillary support and glue) subtracted from them; this background was determined from several scans taken outside of the diffuse ring. All three scans exhibit the same basic features: the maxima at $\zeta=\pm0.37$ Å^{-1} that define the shell of diffuse scattering, and a central diffuse peak at $\tau^{-1}\mathbf{G}_{100000}$. This central diffuse peak has not been seen in previous measurements on IP alloys. Both quasicrystalline and icosahedral-glass models based on a simple-icosahedral quasilattice predict that there should be no scattering at this position. Similarly, the existence of small regions of the R phase of Al-Li-Cu coherently oriented with the IP cannot explain the scattering here since this position corresponds to the (230) reflection, forbidden for a bcc lattice. It is possible that the central peak is a sample-dependent feature which is not intrinsic to the IP alloys in general. On the other hand, the model we describe below does show evidence for scattering at $\zeta=0$.

Both the position and size of the diffuse ring in the twofold plane agree with the x-ray precession photographs of Denoyer *et al.*, and as shown in Fig. 1(c), this ring is actually part of a three-dimensional shell of scattering. Additional scans along other directions through the diffuse scattering confirm that the shell is roughly spherical, but further work is required to deter-

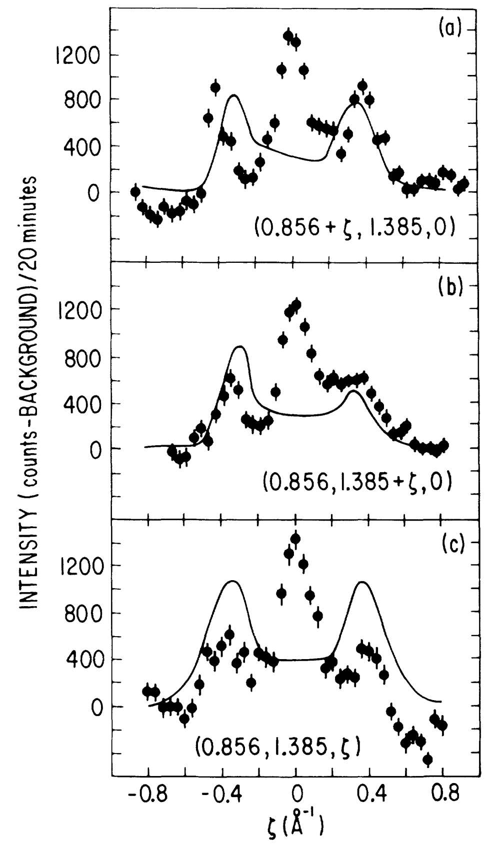

FIG. 1. X-ray diffraction scans (filled circles) through the center of the diffuse scattering $\mathbf{Q}=(0.856,1.385,0)$ parallel to (a) $(h00)$, (b) $(0k0)$, and (c) $(00l)$. The solid lines are calculated from simulations described in the text. For comparison, the peak intensity of the (110000) sharp diffraction maxima along a twofold axis was 2800 counts/s.

mine the precise intensity contours of the scattering.

The x-ray data yield two quantities required for any quantitative comparison with theoretical models for the diffuse scattering. First of all, the width of the diffuse shell, which is ≈ 0.1 Å^{-1} (HWHM), is a measure of the length scale [$\xi = 1/0.1$ Å$^{-1} \approx 10$ Å] of the correlations which produce this feature. Secondly, we can compare the integrated intensity of the diffuse scattering with that of the sharp diffraction maxima. If we assume that the diffuse shell is spherical, the integrated intensity of the scattering is

$$I_{\text{diffuse}} = I_{\text{peak}} 4\pi q_r^2 \delta q \ ,$$

where q_r is the radius of the shell and δq is its HWHM. Taking the sample mosaic and spectrometer resolution into account, we find that the ratio of the integrated intensity of the diffuse shell to that of the (110000) diffraction peak is 0.1 ± 0.05.

The neutron measurements were made on a 1-cm^3 crystal of Al-Li-Cu grown by one of us. Figure 2 shows a scan taken parallel to the $(0k0)$ axis through the center of the diffuse scattering with use of the Brookhaven National Laboratory H9A spectrometer operated in a triple-axis configuration with an energy resolution of 0.3 meV (FWHM). The open circles in Fig. 2 correspond to data taken with the spectrometer set for elastic scattering. In addition to the underlying diffuse scattering contribution, there are also two sharp peaks which result from tails of out-of-plane diffraction peaks brought in by the large mosaic of the sample ($\approx 11°$) and the relatively poor vertical resolution of the instrument. The large mosaic of the crystal and poor vertical resolution also obscures the separation of the distinct peaks shown in Fig. 1. The closed circles in Fig. 2 correspond to data taken at a neutron energy gain of 0.4 meV. No excess scattering in the region of the diffuse ring was observed. This sets a limit of less than 0.4 meV on the inelasticity of the diffuse scattering. We conclude that correlations which give rise to the diffuse scattering are static rather than dynamic in nature. Further details of these neutron-scattering measurements will be presented elsewhere.

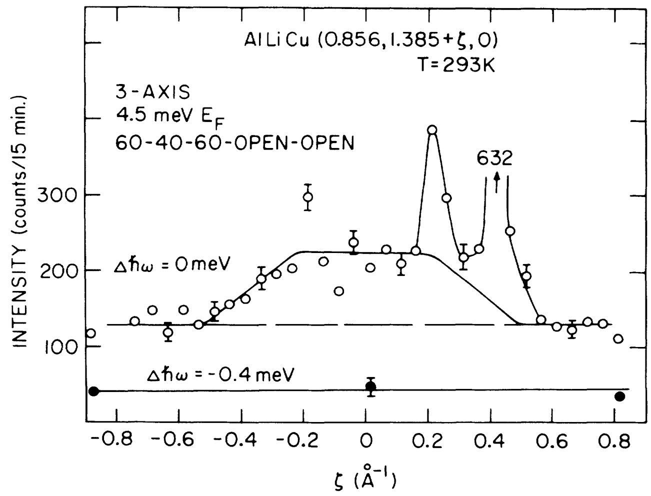

FIG. 2. Neutron measurements through the center of the diffuse scattering along the $(0k0)$ direction for $\Delta\hbar\omega = 0$ meV (elastic scattering) and $\Delta\hbar\omega = -0.4$ meV. The solid and dashed lines are guides to the eye.

Several descriptions of the IP alloys are based upon either quasiperiodic[8] or randomly packed[6] collections of icosahedral clusters of atoms which are also found in crystalline alloys close in composition to the IP alloys. For instance, the cubic R phase of Al-Li-Cu may be characterized as a bcc packing of icosahedral clusters of Al, Li, and Cu atoms.[9] The width of the shell of diffuse scattering in Fig. 1 suggests that only correlations between adjoining icosahedral clusters are necessary to explain the pattern of diffuse scattering. The frozen disorder that produces the scattering might then be due to randomness in the manner in which two icosahedral clusters are connected. For instance, in the R phase of Al-Li-Cu, the icosahedral clusters are packed along (111) directions, and therefore connect to only eight of the twenty faces (threefold directions) of an icosahedron. One can introduce disorder by allowing icosahedral clusters to join to *any* of the twenty faces with some probability P_j. The diffuse scattering can be calculated from an average over the scattering due to the possible two-cluster configurations:

$$S_{\text{diffuse}}(\mathbf{Q}) = f^2_{\text{cluster}}\langle | 1 + P_j e^{i\mathbf{Q}\cdot\mathbf{R}_j} |^2 \rangle . \qquad (1)$$

In Eq. (1) we only include correlations between nearest-neighbor icosahedral clusters. The $\mathbf{R}_j$ are the twenty intercluster vectors along threefold axes, and f^2_{cluster} is the cluster form factor describing the scattering pattern due to the arrangement of atoms within a single cluster. In Fig. 3(b), we show f^2_{cluster} calculated in one quadrant of a twofold plane using the atomic positions determined by Guryan *et al.*[10] for the *R* phase of Al-Li-Cu. Note that this form factor has a strong maximum in the region of the diffuse scattering observed in the IP alloy.

In Figs. 3(c) and 3(d) we show $S_{\text{diffuse}}(\mathbf{Q})/f^2_{\text{cluster}}$ and $S_{\text{diffuse}}(\mathbf{Q})$ for one quadrant of a twofold plane calculated from Eq. (1) (with $P_j = \frac{1}{20}$ for all j). Figure 3(c) corresponds to the intensity pattern obtained from the configurational average of the possible two-point correlations (centers of the icosahedra) and is independent of the specific decorations of the icosahedral clusters. This pattern will be compared below with the scattering from an undecorated face-packed icosahedral glass. Figure 3(d) is the product of Fig. 3(c) with f^2_{cluster} shown in Fig. 3(b). The important feature of Fig. 3(d) is that the maximum in f^2_{cluster} at $\tau^{-1}\mathbf{G}_{100000}$ now appears as a ring of scattering centered on that wave vector, in qualitative agreement with the present measurements and the precession photographs of Denoyer *et al.*

In order to explain the presence of diffuse scattering in the IP alloys, quasicrystalline models (i.e., models based on Penrose tilings) must incorporate some provision for topological or chemical disorder. For instance, Steinhardt has considered the effect of "constrained substitutional disorder" on the scattering pattern from IP alloys.[11] In contrast, the icosahedral-glass model describes an *intrinsically disordered* structure which produces sharp diffraction maxima. While a strictly random packing of icosahedral clusters is more disordered than the best experimental samples,[7] some degree of simulated annealing during the growth of a random network eliminated the most obvious discrepancy between the icosahedral glass and experimental diffraction patterns.[12] The dominant type of disorder found in the icosahedral glass structure is described by Eq. (1) since, in its simplest form, the structure is built by randomly packing icosahedral clusters. To illustrate this point, Fig. 3(e) shows an intensity map of the scattering from an undecorated simulation of face-packed icosahedra.[6] There is a significant "diffuse" background which is very similar to the intensity contours found in Fig. 3(c). If we decorate this network with the Al-Li-Cu clusters, we obtain the pattern shown in Fig. 3(f) [the product of Fig. 3(b) and 3(e)]. The most intense diffuse scattering found in this pattern (yellow and green regions), beyond that associated with the sharp diffraction maxima, appears as a ring of scattering about $\tau^{-1}\mathbf{G}_{100000}$, again quite similar to the experimental pattern of Denoyer *et al.* We have also compared our experimental scans in Fig. 1 with simulated scans through the diffuse ring in

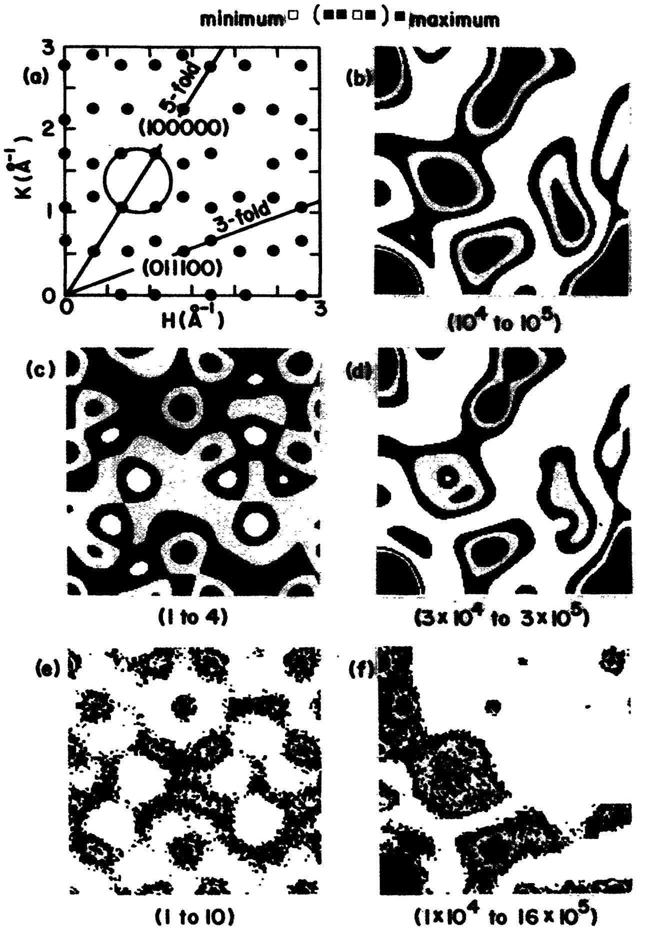

FIG. 3. (a) A schematic representation of one quadrant of a twofold plane which defines the ($hk0$) plane of the measurements. Filled circles correspond to the most intense reflections from an undecorated quasicrystal. Also shown is the position of the diffuse ring reported by Denoyer *et al.* in Ref. 4. (b)-(f), intensities plotted on a logarithmic scale over the ranges indicated in parentheses below each panel. (b) The icosahedral cluster form factor f^2_{cluster} in the twofold plane for Al-Li-Cu (Ref. 10). (c) The intensity pattern of the two-point structure factor, $S_{\text{diffuse}}/f^2_{\text{cluster}}$, from Eq. (1) as described in the text. (d) The two-cluster structure factor, S_{diffuse}. (e) The undecorated face-packed icosahedral glass structure factor in the twofold plane. (f) The decorated face-packed icosahedral glass structure factor. The yellow and green intensity about $\tau^{-1}\mathbf{G}_{100000}$ represents the diffuse ring shown schematically in (a).

Fig. 3(f) (solid lines in Fig. 1). These curves were calculated by averaging over the scattering patterns from several samples of face-packed icosahedra, and have been multiplied by a single scale factor for comparison with the experimental data. The x-ray spectrometer vertical resolution acts to broaden, and therefore weaken, the peaks in Fig. 1(c) as compared with the calculation. The position, size, and width of this diffuse shell agree fairly well with the experimental pattern of diffuse scattering. Furthermore, excess scattering above background at the center of the shell is predicted by the model, although a strong diffuse peak at this position is not calculated.

A quantitative measure of the disorder in the IP alloys can be made by comparing the integrated intensities of the diffuse scattering relative to the sharp diffraction maxima in our calculation, to the experimental value. For our simulations, we find that $I_{\text{diffuse}}/I_{110000} \approx 0.5-5$. The range of values for this ratio results from uncertainty in the calculation of the integrated intensity of the (110000) diffraction maximum relative to the forward scattering. This ratio is about an order of magnitude larger than that determined in the x-ray measurement described above. What seems clear is that while the character of the diffuse scattering from Al-Li-Cu can be described by the disorder intrinsic to the icosahedral-glass model, this model overestimates the degree of this disorder. This result provides strong evidence for the view that the IP alloys are best described by a degree of disorder which is bounded by the icosahedral-glass model (extreme disorder) at one end, and quasicrystals (no disorder) at the other end.

We wish to thank F. Denoyer, P. Heiney, P. Horn, H. Moudden, and P. Steinhardt for their assistance and useful discussions. We also thank the Brookhaven National Laboratory x-ray scattering group for the use of their rotating-anode facility and their assistance as well as D. Schneider for his help in producing the color graphics. Work at Brookhaven was supported by the U.S. Department of Energy under Contract No. DE-AC02-76-CH00016. Work at the State University of New York, Stony Brook, was supported by the National Science Foundation, Low Temperature Physics Grant No. DMR-8702042.

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[a] Present address: Department of Physics, Iowa State University, Ames, IA 50011.

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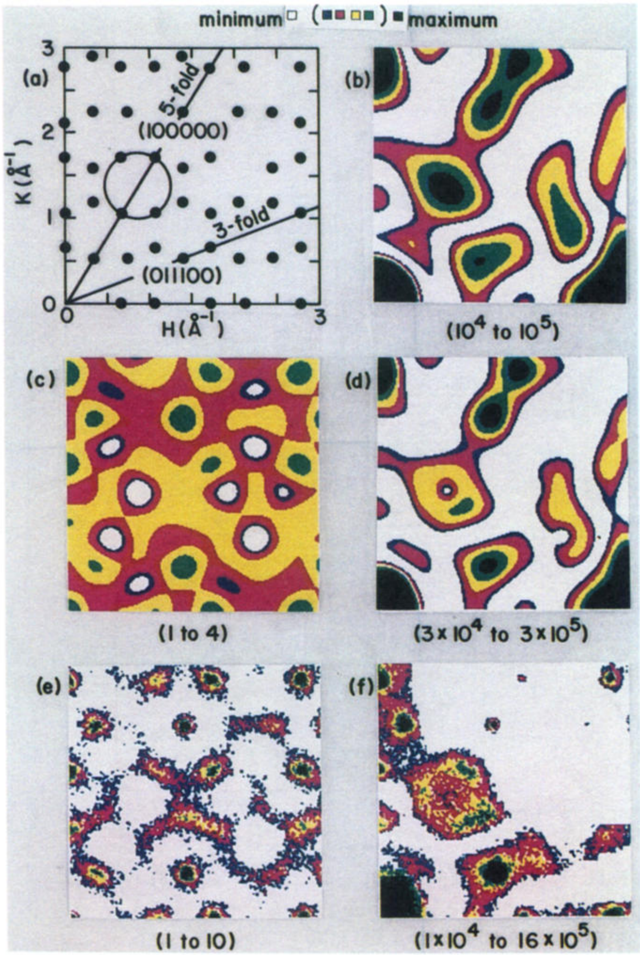

(10⁴ to 10⁵)

(1 to 4)

(3 × 10⁴ to 3 × 10⁵)

(1 to 10)

(1 × 10⁴ to 16 × 10⁵)

FIG. 3. (a) A schematic representation of one quadrant of a twofold plane which defines the $(hk0)$ plane of the measurements. Filled circles correspond to the most intense reflections from an undecorated quasicrystal. Also shown is the position of the diffuse ring reported by Denoyer *et al.* in Ref. 4. (b)–(f), intensities plotted on a logarithmic scale over the ranges indicated in parentheses below each panel. (b) The icosahedral cluster form factor f^2_{cluster} in the twofold plane for Al-Li-Cu (Ref. 10). (c) The intensity pattern of the two-point structure factor, $S_{\text{diffuse}}/f^2_{\text{cluster}}$, from Eq. (1) as described in the text. (d) The two-cluster structure factor, S_{diffuse}. (e) The undecorated face-packed icosahedral glass structure factor in the twofold plane. (f) The decorated face-packed icosahedral glass structure factor. The yellow and green intensity about $\tau^{-1}\mathbf{G}_{100000}$ represents the diffuse ring shown schematically in (a).