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Inelastic-neutron-scattering measurements of phonons in icosahedral Al-Li-Cu

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Inelastic-neutron-scattering measurements on a single grain of icosahedral Al-Li-Cu are presented. Within experimental error the acoustic-phonon dispersion at small, but finite, **q** is independent of direction, confirming the isotropic elasticity expected for icosahedral crystals. By following the longitudinal-phonon dispersion curve along a fivefold axis we can identify the location of a "quasi-Brillouin-zone boundary." The measurements also suggest the presence of an optical or localized mode along the twofold axis at approximately 10–11 meV. We compare these results to theoretical calculations for one- and two-dimensional quasiperiodic systems.

Since their discovery in 1984 the icosahedral alloys have been the subject of intense scrutiny, and significant advances have been made in our understanding of the structure of this new class of solids. Beyond their interesting diffraction patterns, however, what other properties of real quasiperiodic alloys distinguish them from "ordinary" crystals? Clearly, in light of the aperiodic order inherent to these materials, the elementary excitations of icosahedral alloys should exhibit features not found in crystalline solids.

Theoretical calculations of the dynamical properties of icosahedral alloys are hindered by the very same property that makes them so interesting; Bloch's theorem, as used in the calculation of electronic band structure and vibrational spectra of periodic crystals, is an inappropriate starting point for analogous calculations in quasicrystalline materials. Although there have been no calculations of the dynamical structure factor for three-dimensional icosahedral solids, some physical insight regarding the dynamical properties of three-dimensional quasicrystalline systems may be obtained from theoretical studies of lower-dimensional models.[1–5] The principal result of these calculations is that there are well-defined, long-wavelength ($\mathbf{q} \approx \mathbf{0}$) propagating modes which, at shorter wavelengths ($\mathbf{q} \gg \mathbf{0}$), exhibit a dense set of gaps arranged in a self-similar, hierarchal structure. Although these studies provide a valuable starting point for the investigation of dynamics in real alloys, it is not at all clear how applicable they are to the actual materials in question.

Here we report on inelastic neutron-scattering measurements of phonons in icosahedral Al-Li-Cu. These measurements were made at room temperature on a 0.4-g single grain of $Al_{60.3}Li_{29.2}Cu_{10.5}$ with a mosaic of approximately 1.2°, grown by methods described elsewhere.[6] No evidence of second-phase inclusions, such as the cubic *R* phase, were found in neutron- and x-ray-diffraction scans. As shown in Fig. 1, the sample was oriented with a twofold plane coincident with the scattering plane so that measurements could be made along the high-symmetry twofold, threefold, and fivefold axes. In principle, the reciprocal space of a quasiperiodic structure is densely filled with Bragg peaks although only a small number have significant intensity. Figure 1 displays only the subset of strongest Bragg points in the twofold plane calculated for an icosahedral quasilattice without atomic decoration. The relative intensities of diffraction peaks will, of course, be modified by atomic decoration. Here we are merely interested in a rough idea of which are the strongest candidate zone centers as described below. Preliminary measurements were made on the H-7 triple-axis spectrometer at the High Flux Beam Reactor at Brookhaven National

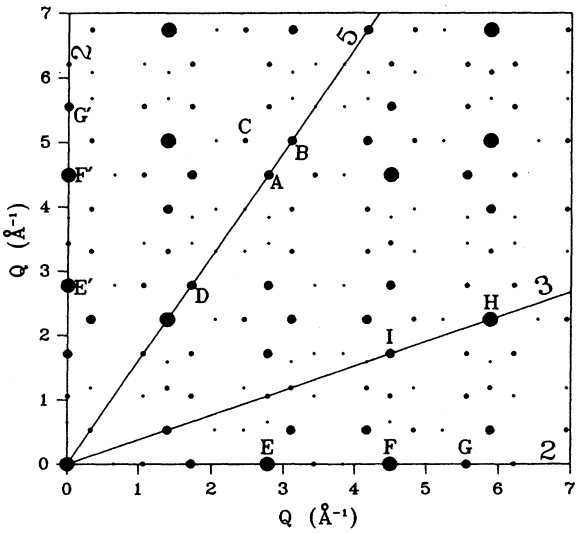

FIG. 1. A schematic of the twofold plane. Axes are labeled as the twofold, threefold, and fivefold directions. Letters denote the "zone-centers" from which inelastic scattering measurements were made.

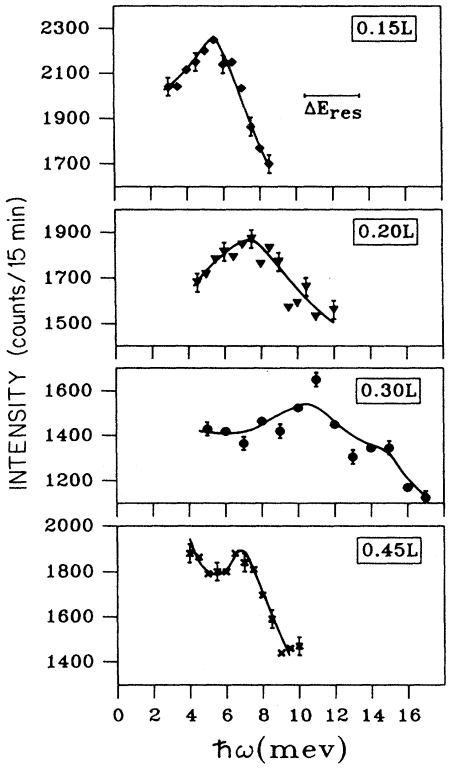

FIG. 2. Constant-**Q** scans of the longitudinal modes along a fivefold axis for a fixed final energy of 30.5 meV. Lines are intended as a guide to the eye. The horizontal bar denotes the energy resolution for this configuration.

Laboratory. Most of the data presented here, however, were taken on the 2T triple-axis spectrometer at the Orphée reactor at the Laboratoire Léon Brillouin in Saclay, France using double focusing Cu(111) and pyrolitic graphite (002) as monochromator and analyzer, respectively. Even though the sample is large in comparison to the grain size typically found for icosahedral alloys, it is indeed still quite small by neutron-inelastic-scattering standards. Therefore, long measuring times per point were necessary and relaxed collimation was required to take full advantage of the focussing optics.

The spectrometer was operated at fixed final energies of 14.7, 30.5, or 42 meV where the pyrolytic graphite filter, placed after the sample to reduce the higher harmonic content of the scattered beam, is most effective. Since there are several subtle processes which can produce spurious inelastic peaks, frequently the neutron groups were measured at two different values of fixed final energy or in both the energy gain and energy loss spectrometer configurations. Furthermore, measurements were made from several Bragg points along each high-symmetry direction.

For the measurement of phonons one usually has at least some estimate, based on a simple model of the interatomic forces, for the form of the inelastic structure factor. For the case at hand, such calculations are extremely difficult and so we have applied a few simple rules of thumb to determine where acoustic modes might best be observed. For instance, close to a zone center the inelastic structure factor for acoustic phonons generally scales in proportion to the static structure factor for that Bragg peak. One- and two-dimensional calculations of the inelastic structure factor for quasiperiodic tilings confirm this tendency.[4,5] Furthermore, the phonon cross section increases as Q^2. Here, $\mathbf{Q}=\mathbf{G}+\mathbf{q}$, with $\mathbf{q}$ defined as the wave vector of the excitation measured from a zone center (Bragg point) at $\mathbf{G}$. Therefore, the most obvious points in reciprocal space to begin a search for acoustic phonons are close to the most intense and highest $\mathbf{G}$ diffraction peaks. Accordingly, along the fivefold axis, data were taken near points A and D; for the twofold axes, near E, E', F, F', and G and G'; and along the threefold axis, measurements were made near H and I.

Figure 2 shows some constant-**Q** scans taken between points A and B along the fivefold axis in Fig. 1 using a fixed final energy of 30.5 meV. Since $\mathbf{Q}$ is parallel to $\mathbf{q}$, these neutron groups correspond to longitudinal modes. The corresponding phonon dispersion curve determined from these data is displayed in Fig. 3 along with the transverse and longitudinal branches measured for all three high-symmetry directions. In the indexing scheme of Bancel *et al.*[7] for icosahedral crystals, the strong diffraction peaks at points A and B are labeled as the (200000) and $(0\bar{1}111\bar{1})$, and their separation along the fivefold axis is 0.623 Å^{-1}. We clearly see that as $\mathbf{q}$ in-

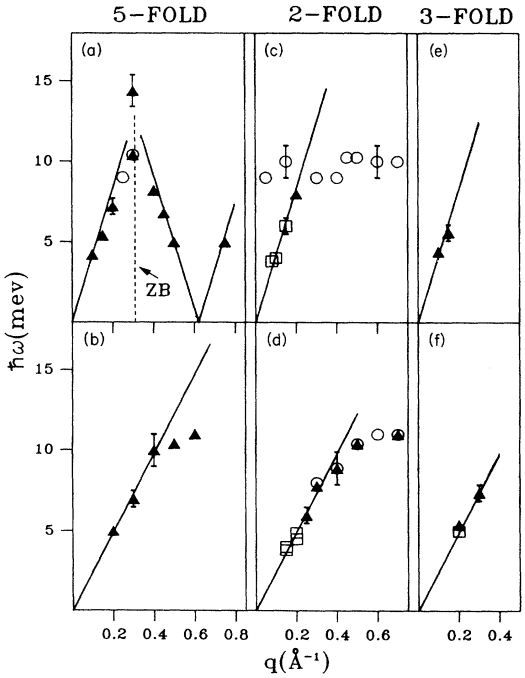

FIG. 3. The measured dispersion relations for fivefold (a) longitudinal and (b) transverse modes; twofold (c) longitudinal and (d) transverse modes; and threefold (e) longitudinal and (f) transverse modes. Circles, triangles, and squares denote measurements made at fixed final neutron energies of 42, 30.5, and 14.7 meV, respectively. The solid lines represent the initial slope of the dispersion curves calculated from measured sound velocities as described in the text.

creases, the energy of this mode first increases, falls below the extrapolated linear dispersion relation, reaches a maximum, and then decreases as the next strong diffraction peak is approached. This is precisely the behavior that one observes for propagating acoustic modes in a periodic crystal as **q** traverses a Brillouin zone and so, by analogy, we label the dashed vertical line in Fig. 3(a) as a "quasi-zone boundary." At $\mathbf{q} \approx 0.3$ Å^{-1} the energy position of the peak is a maximum and there are indications of a shoulder at higher energy (≈ 14.5 meV), pointing to the presence of a gap in the dispersion curve. The broadening of the phonon peaks as **q** increases makes it difficult to clearly resolve these two excitations. However, the higher-energy shoulder is also observed in constant-**Q** scans at a fixed final energy of 42 meV, and a clear peak at $\mathbf{q} \approx 0.3$ Å^{-1} is evident in constant-energy scans at 15 meV.

An important result of these measurements, illustrated by the dispersion curves in Fig. 3, is that well-defined propagating acoustic modes are observed along all three high-symmetry directions. The dispersion relations for both the longitudinal and transverse modes are, within experimental uncertainty, independent of direction out to at least $q \approx 0.2$ Å^{-1}. Furthermore, transverse scans along the twofold axes in this plane (say from points *F* and *F'*) probe transverse modes of different polarization, and these two modes were found to be indistinguishable to within experimental precision. Therefore, at least along the twofold axes, the slope of the dispersion curves is also independent of polarization. These conclusions agree, in the elastic limit, with the results of ultrasonic measurements on icosahedral Al-Li-Cu,[8] as well as neutron scattering measurements performed recently on Al-Cu-Fe.[9] We point out that the absence of elastic anisotropy in icosahedral alloys is consistent with the fact that the symmetry of the icosahedral point group ($m\bar{3}\bar{5}$) is higher than cubic. As a result, the elastic properties may be completely specified by only two elastic constants (shear and compression).[10]

The dispersion relations measured here can be related to the result of the ultrasonic measurements by considering the long-wavelength limit of ω vs **q**. As $\mathbf{q} \rightarrow 0$, the low-frequency vibrations in a solid are sound waves with a linear dispersion relation, $\omega = v_j q$, where v_j is the appropriate transverse or longitudinal sound velocity. From ultrasonic measurements of a single grain of icosahedral Al-Li-Cu, Reynolds *et al.*[8] report that $v_L = 6.4 \pm 0.1 \times 10^5$ cm/s and $v_T = 3.8 \pm 0.1 \times 10^5$ cm/s for the icosahedral twofold and fivefold axes. We have used these values to calculate the initial slope of the phonon dispersion relation for the longitudinal and transverse modes (represented by the solid lines in Fig. 3), and find excellent agreement with the ultrasonic measurements.

It is interesting to compare the behavior of the longitudinal mode in Fig. 3(a) with that of the transverse mode in Fig. 3(b). Another Bragg point, the $(3211\bar{1}1)$ (point *C* in Fig. 1), is located at the same distance (0.623 Å^{-1}) from the (200000) as point *B*, but there is no indication of an associated transverse branch originating from this center. Elastic scans of the $(3211\bar{1}1)$ show that its intensity is approximately 0.01 of the (200000). We conclude that the inelastic structure factor for the transverse-acoustic branch associated with point *C* is very small, rendering it unobservable. Although in principle the reciprocal space of an icosahedral structure is densely filled with zone centers and zone boundaries, only the acoustic modes associated with the strongest Bragg points are observed.

Another interesting feature is found along the twofold directions in Fig. 3(c). In addition to the longitudinal acoustic branch, there is evidence of a dispersionless mode at 10–11 meV. In the absence of specific knowledge of the inelastic structure factor for the icosahedral phase of Al-Li-Cu it is difficult to interpret this feature. However, the dispersionless nature of the excitations observed in the 10–11-meV range strongly suggests that they are associated with an optical or localized mode. Measurements of the phonon density of states (PDOS) from polycrystalline Al-Li-Cu have been reported by Suck *et al.*[11] They found that the PDOS of icosahedral Al-Li-Cu is very similar to that of the crystalline *R* phase; the essential difference was the relative intensities of the features. Interestingly, they report a split first peak in the PDOS with maxima at about 13 and 16.5 meV. A direct comparison, however, between the PDOS and single grain measurements requires full knowledge of the phonon dispersion curves so that one can calculate the relative weights of various features.

We also find that both the longitudinal and transverse phonon excitations broaden as **q** increases. This is clearly seen in Fig. 2 for the longitudinal-acoustic branch along the fivefold axis, where the energy width of the excitation initially increases, and then decreases as **q** approaches point *B*. Note that the $|\mathbf{q}| = 0.45$-Å^{-1} longitudinal mode can also be characterized as a 0.17-Å^{-1} longitudinal mode originating from point *B*. Broadening of the phonon excitations at finite **q** can arise from structural disorder. For instance, Benoit, Possigue, and Azougarh[5] found that the introduction of defects (interchanging long and short bonds) into the Fibonacci sequence resulted in broadened phonon peaks. In the case of Al-Li-Cu, by analogy, the broadening may be related to the presence of quenched-in phason strain—a universally observed phenomenon in simple icosahedral alloys that can be described in terms of mistakes in quasicrystalline tiling models.[12]

The general form of the phonon dispersion curves bear a strong similarity to those calculated by Ashraff, Luck, and Stinchcombe for a two-dimensional Fibonacci sequence,[3] and Benoit, Possigue, and Azougarh for a one-dimensional Fibonacci chain.[5] In particular, both report the absence of acoustic branches associated with weak Bragg peaks, the presence of quasi-zone boundaries associated with the strongest Bragg peaks, and a stripe of intensity just at the lower edge of the gap separating the acoustic modes from dispersionless bands. We caution the reader, however, that these similarities only suggest that some of the predictions of these calculations may be extended to three dimensions. The real alloy system studied here is not composed of a set of Fibonacci sequences of atoms, or an undecorated Penrose tiling.

Additional inelastic-neutron-scattering measurements of both the icosahedral phase and the related crystalline

phases of Al-Li-Cu, will be required to sort out the specific features which are unique to quasicrystallinity. Furthermore, the difficulties inherent to the calculation of the dynamic structure factor for a real three-dimensional quasicrystal precludes any direct comparison with a theoretical model at this point. We hope that these initial measurements will stimulate further theoretical efforts in this area.

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