PHYSICAL REVIEW B VOLUME 34, NUMBER 12 15 DECEMBER 1986

Rapid Communications

The Rapid Communications section is intended for the accelerated publication of important new results. Since manuscripts submitted to this section are given priority treatment both in the editorial office and in production, authors should explain in their submittal letter why the work justifies this special handling. A Rapid Communication should be no longer than 3½ printed pages and must be accompanied by an abstract. Page proofs are sent to authors, but, because of the accelerated schedule, publication is not delayed for receipt of corrections unless requested by the author or noted by the editor.

Neutron scattering study of the vibrational density of states in icosahedral and crystalline $Al_{0.80}Mn_{0.20}$

P. F. Miceli, S. E. Youngquist, D. A. Neumann, and H. Zabel
Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

J. J. Rush and J. M. Rowe
Institute for Materials Science and Engineering, National Bureau of Standards, Gaithersburg, Maryland 20899

(Received 18 September 1986)

We present an inelastic neutron scattering study of the vibrational density of states, $\bar{g}(E)$, for the icosahedral and crystalline phases of $Al_{0.80}Mn_{0.20}$. At low energy transfers we find nearly identical $\bar{g}(E) \propto E^2$ dependences indicating that the two materials are elastically similar. In the intermediate energy range, 20–35 meV, the crystalline $\bar{g}(E)$ shows weak structure while that of the icosahedral phase remains smooth. Above 40 meV there is an excess of the icosahedral $\bar{g}(E)$ compared with that of the crystalline material. These results provide a direct test for models of the interatomic forces and dynamics of the icosahedral phase.

The discovery of crystals with long-range bond orientational order displaying fivefold symmetry[1,2] has led to intense current research interest. While most of the present activity has concentrated on this striking icosahedral symmetry, the effects that this new type of order has on the physical properties are also of fundamental significance. Recent calculations of the electron and phonon density of states of "quasiperiodic" structures have shown characteristic differences from the density of states of crystalline systems.[3–5] The most prominent feature of these calculations is the existence of localized states and the self-similarity exhibited in any slice of reciprocal space. To address these ideas experimentally, we have performed the first measurement of the vibrational density of states in a sample with icosahedral symmetry.[6] In order to determine the role of structure, we have performed the same experiment on a sample of the same composition displaying long-range translational order.

In this inelastic neutron scattering study we have used a $Al_{1-x}Mn_x$ sample which was rapidly quenched from the melt into the icosahedral phase by the usual melt-spinning technique. We chose the composition $x=0.20$ because previous x-ray measurements have indicated that the largest fraction of icosahedral phase is present in the alloy, with a negligible amount of crystalline Al.[7] Because of the small neutron scattering lengths of both Al and Mn it was necessary to prepare a large sample in order to obtain an adequate signal. To ensure the homogeneity of our sample, the ribbons were pulverized and small samples taken from each quenching run were examined by x-ray diffraction, before the powder was mixed together. It was then split into two parts, one of which was annealed at 800 °C for 48 h in order to obtain the crystalline phase. The icosahedral and crystalline samples weighed 106 and 121 g, respectively. Neutron-diffraction patterns for both samples were measured at the National Bureau of Standards high-resolution powder diffractometer and are shown in Fig. 1.

Because of the powder nature of these samples, inelastic neutron scattering yields an orientational average of the vibrational modes rather than the detailed phonon dispersion. The latter could be accomplished only if sufficiently large single (quasi) crystals were available. We obtained the vibrational density of states from our inelastic scattering data through the incoherent approximation,[8] where the coherent dynamic scattering function is replaced by its incoherent counterpart. The validity of this approximation will be justified later in the paper. For the case of a binary AlMn system, the incoherent dynamic scattering function is[9]

$$\frac{d^2\sigma}{d\Omega dE} \propto \frac{k'}{k}\frac{n(E)+1}{E}[xI_{\mathrm{Mn}}(E)+(1-x)I_{\mathrm{Al}}(E)]\bar{g}(E)\ , \tag{1}$$

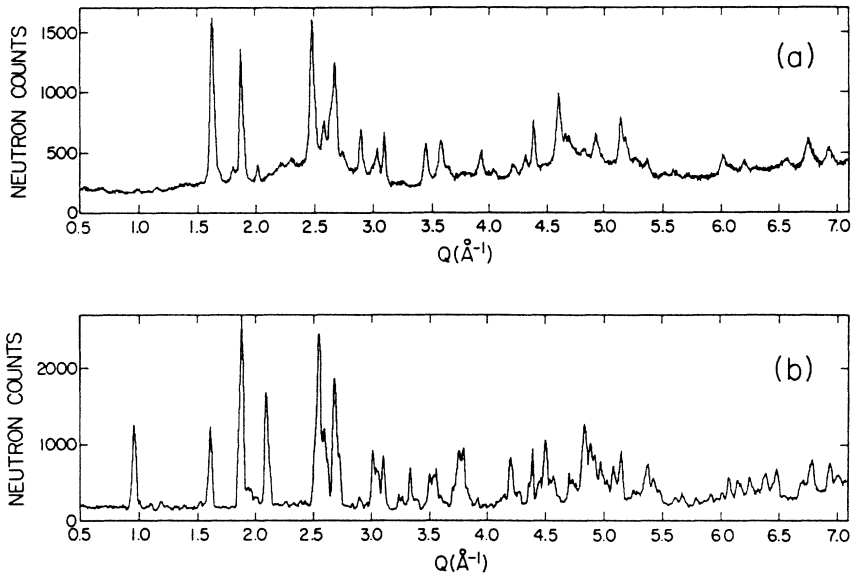

FIG. 1. Neutron powder diffraction pattern for (a) icosahedral and (b) crystalline $Al_{0.8}Mn_{0.2}$.

with

$$I_j(E) \equiv \frac{\sigma_j}{m_j} \langle (\mathbf{Q}\cdot\boldsymbol{\gamma}_j)^2 e^{-W_j} \rangle, \quad j = \text{Al,Mn} \ . \tag{2}$$

$\mathbf{k},\mathbf{k}'$ are the incident and final neutron wave vectors, $\hbar\mathbf{Q}$ is the momentum transfer, and $n(E)$ is the Bose occupation factor for a vibrational energy E. m, σ, and $\boldsymbol{\gamma}$ are the nuclear mass, coherent scattering cross section, and displacement vector, respectively. W is the Debye-Waller factor and is assumed to be small at the temperatures used in these measurements. The angle brackets indicate an average over all j sites and over all modes with energy E. Since the samples are powder, we also include in this an average over all orientations which is equivalent to an average over Q directions. The neutron-weighted vibrational density of states is then given by

$$\bar{g}(E) = \frac{x I_{\text{Mn}}(E) g_{\text{Mn}}(E) + (1-x) I_{\text{Al}}(E) g_{\text{Al}}(E)}{x I_{\text{Mn}}(E) + (1-x) I_{\text{Al}}(E)} \ , \tag{3}$$

where $g_{\text{Al}}(E)$ and $g_{\text{Mn}}(E)$ are the vibrational density of states for the Al and Mn sites, respectively.

The inelastic neutron scattering data were collected on two triple-axis spectrometers located at the National Bureau of Standards reactor. All of the triple-axis scans were performed with constant momentum transfer $\hbar\mathbf{Q}$ and fixed final energy using a graphite analyzer crystal. For the scans above a vibrational energy of 10 meV, the final neutron energy was fixed at 35 meV, a copper monochromator was used, and the collimation was 60′-40′-40′-40′. Data were collected at Q's of 4 and 6 Å^{-1}. Below 20 meV, scans were done with fixed final energies of both 13.8 and 14.8 meV, a graphite monochromator was used, and the collimation was either 40′-20′-40′-40′ or 40′-40′-40′-40′. In this case data were collected at Q's of 4.1 and 4.5 Å^{-1}. The overlap of the data in the energy range of 10–20 meV allowed the data to be appropriately scaled. In all triple-axis scans, a pyrolytic graphite filter was placed in the scattered beam to remove higher-order harmonic contaminations. The use of different monochromators in different energy regimes is necessitated by resolution considerations and by the physical constraints of the spectrometer. A combination of graphite and Cu monochromators at low- and high-incident neutron energies, respectively, allows the measurement of the density of states throughout the entire energy range with the resulting $\bar{g}(E)$ resolutions of $\sim$0.5 meV at the low-energy portion (0–15 meV) and $\sim$3 meV at higher energies.

One of the spectrometers was also equipped with a Be filter and later with a Be-graphite-Be filter placed in front of a well-shielded detector. This assembly essentially takes the place of the third axis in a triple-axis spectrometer providing analysis of the final neutron energy. However, instead of doing a constant-Q scan, the scattering angle was fixed at 90°, allowing Q to vary as a function of energy. The advantage of this arrangement is a somewhat higher count rate than for the triple-axis work, and for the case of the Be-graphite-Be filter, improved energy resolution ($\sim$5 meV for the Be and $\sim$2 meV for the Be-graphite-Be filters). Again, data were collected using both copper and graphite monochromators, this time with collimations of 60′-40′ and 40′-20′, respectively.

Contributions to the scattering from fast background and the sample can were measured and subtracted directly. Multiphonon and multiple scattering corrections were obtained by extrapolation from higher energies where the one-phonon scattering is absent. This was justified by a calculation of these contributions to the scattering; however, our results are essentially independent of the subtraction procedure used. Throughout this experiment the samples were kept at liquid-nitrogen or liquid-helium temperature, and the actual sample temperature was always used during the analysis of the data.

The measured, vibrational density of states $\bar{g}(E)$ (weighted by the neutron scattering lengths and vibrational amplitudes) of icosahedral and crystalline $Al_{0.80}Mn_{0.20}$ are shown in Figs. 2(a) and 2(b), respectively (see Table I

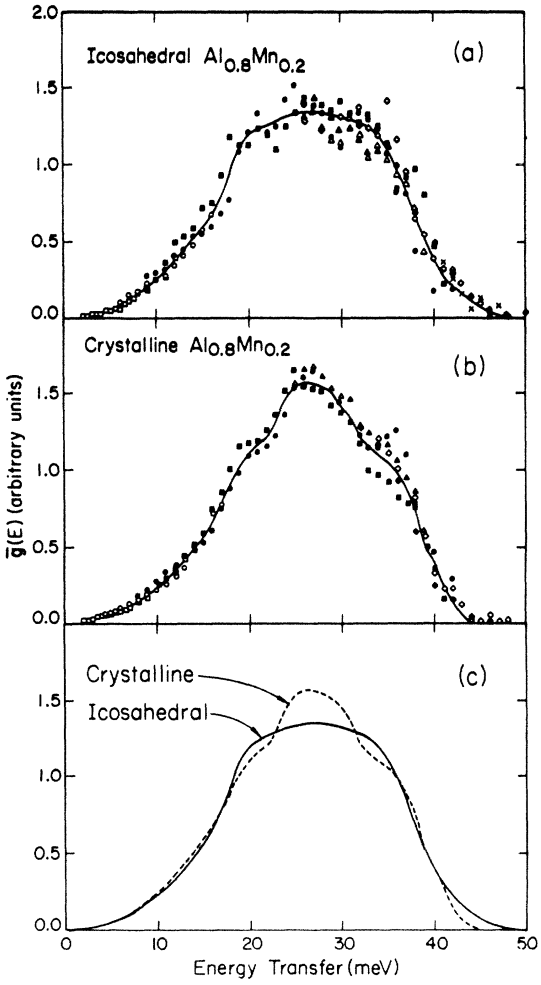

FIG. 2. Measured neutron weighted vibrational density of states for (a) icosahedral and (b) crystalline phases of $Al_{0.8}Mn_{0.2}$. The experimental conditions are shown in Table I. The solid lines are to guide the eye. The good overlap between scans with different Q demonstrates that the incoherent approximation provides good results. (c) compares the icosahedral (solid) and the crystalline (dashed) results which are normalized to have the same area.

TABLE I. Experimental conditions in Fig. 2.

Symbol	Mode[a]	Collimation[b]	E_F (meV)	Q (Å^{-1})
□	3-PG	40′-20′-40′-40′	13.8	4.1
○	3-PG	40′-40′-40′-40′	14.8	4.5
■	3-Cu	60′-40′-40′-40′	35.0	6.0
●	3-Cu	60′-40′-40′-40′	35.0	4.0
◆	1-Cu	60′-40′	3.0	· · ·
◇	2-Cu	60′-40′	1.0	· · ·
△	2-PG	c	1.0	· · ·
▲	2-PG	40′-40′	1.0	· · ·
×	2-Cu	60′-40′	1.0	· · ·

[a]PG: Pyrolytic graphite monochromator, Cu: copper monochromator, 1: Be filter, 2: Be-graphite-Be filter, 3: triple axis.
[b]Collimation from first to last collimator.
[c]40′-40′ for crystalline, 40′-20′ for icosahedral.

for experimental conditions), and are compared in Fig. 2(c). In both cases $\bar{g}(E)$ exhibits the usual E^2 dependence expected for a three-dimensional system out to an energy of 10–15 meV. Since $\bar{g}(E)$ is nearly identical for the two samples in this region, they must be elastically similar. Between 20 and 35 meV, $\bar{g}(E)$ of the crystalline sample shows some structure, including a pronounced maximum at 27 meV, while the spectra of the icosahedral sample is essentially featureless. The icosahedral density of states also displays a distinct high-energy tail compared to that of the crystalline material. This smoothing of the icosahedral $\bar{g}(E)$ over that of the crystalline phase may be attributable to the nonpropagating nature of the higher-energy vibrational states characteristic of systems lacking translational symmetry.

As can be seen in Fig. 2, there is little apparent Q dependence in any of our measurements, indicating that the incoherent approximation is indeed satisfied in spite of the fact that Al is a completely coherent scatterer and Mn has only a small incoherent scattering cross section. This lack of Q dependence is not surprising since the size of the Brillouin zone of the crystalline sample is less than 0.04 Å^{-1}, while for a material without translational symmetry it is essentially the inverse of the crystallite size. However, some Q dependence in the vibrational density of states of coherently scattering amorphous materials has been reported for a Q as high as 9 Å^{-1}.[9]

To demonstrate that the techniques we have used are capable of measuring the features of $\bar{g}(E)$ of a weak coherent scatterer, we have also performed a similar measurement on pure Al powder. This is a much more stringent test of the incoherent approximation than either of the two $Al_{0.80}Mn_{0.20}$ alloys, since the Brillouin zone is much larger and, therefore, coherent effects should persist to much higher Q's. In Fig. 3 the average of only two scans is compared to the density of states calculated from the phonon dispersion measured along the symmetry directions[10] and broadened by our instrumental resolution.

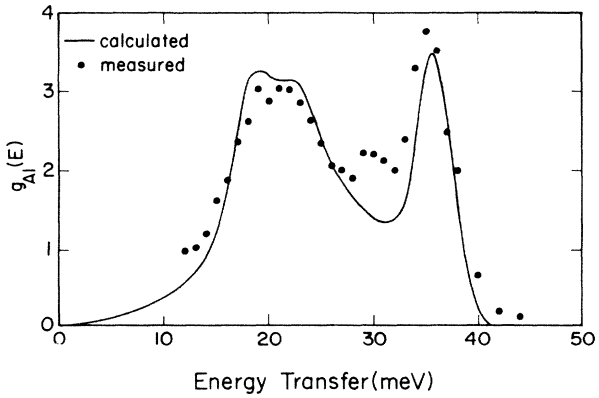

FIG. 3. Data points show our measured vibrational density of states for aluminum using triple-axis and Be-graphite-Be filter techniques. For comparison, the solid line is calculated from the known Al phonon dispersion (Ref. 9) and broadened for instrumental resolution. The good agreement demonstrates the ability of these techniques to reproduce the vibrational density of states for a coherent scatterer.

Note that all of the major features of the density of states are reproduced rather well, showing once again that we are justified in making the incoherent approximation. It is also clear that if there were an appreciable amount of pure Al phase in the icosahedral sample, it would have been seen as a peak in the measured density of states around the energy 35 meV.

As previously mentioned, the main difference between the crystalline and icosahedral $Al_{0.80}Mn_{0.20}$ $\bar{g}(E)$ occurs in the middle and upper regions of the energy range. We have not observed any features in $\bar{g}(E)$ which could clearly be identified as localized states, although one may speculate that the increased $\bar{g}(E)$ around 45 meV is an indication of localized excitations. The absence of sharp features due to these modes is not too surprising since in the present experiment we are taking an orientational average of all modes and convoluting that average with the instrumental resolution. The results presented here do, however, provide a direct test for models of the interatomic forces and dynamics of the quasicrystalline state.

We thank H. L. Fraser for providing us with the quenched $Al_{1-x}Mn_x$ ribbons. This work was supported in part by the National Science Foundation under Grant No. DMR83-04890 and by the U.S. Department of Energy, Division of Materials Science, under Contract No. DE-AC02-76ER01198. Two of us (S.E.Y.) and (D.A.N.) acknowledge financial support by AT&T Bell Laboratories.

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

[2]R. Field and H. L. Fraser, Mater. Sci. Eng. **68**, L1 (1984).

[3]F. Nori and J. P. Rodriguez, Phys. Rev. B **34**, 2207 (1986).

[4]T. Odagaki and D. Nguyen, Phys. Rev. B **33**, 2184 (1986).

[5]J. P. Lu, T. Odagaki, and J. L. Birman, Phys. Rev. B **33**, 4809 (1986).

[6]Preliminary results presented in conference proceeding: P.F. Miceli, S. E. Youngquist, D. A. Neumann, H. Zabel, J. J. Rush, and J. M. Rowe, in *Phonon Scattering in Condensed Matter V,* edited by A. C. Anderson and J. P. Wolfe, Solid State Sciences, Vol. 68 (Springer-Verlag, Berlin, 1986).

[7]S. E. Youngquist, P. F. Miceli, D. G. Wiesler, H. Zabel, and H. L. Fraser, Phys. Rev. B **34**, 2960 (1986).

[8]V. S. Oskotskii, Fiz. Tverd. Tela (Leningrad) **13**, 928 (1968) [Sov. Phys. Solid State **9**, 420 (1967)].

[9]N. Lustig, J. S. Lannin, J. M. Carpenter, and R. Hasegawa, Phys. Rev. B **32**, 2778 (1985).

[10]G. Gilat and R. M. Nicklow, Phys. Rev. **143**, 487 (1966).