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Partial phonon density of states of Fe in an icosahedral quasicrystal $Al_{62}Cu_{25.5}{}^{57}Fe_{12.5}$ by inelastic nuclear-resonant absorption of 14.41-keV synchrotron radiation

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We use a recently developed method based on inelastic nuclear-resonant absorption of x rays to measure the iron-partial vibrational density of states (VDOS) in a quasicrystal. The results differ from those obtained by inelastic neutron scattering in an astounding way: whereas the neutron results exhibit a very smooth and featureless behavior, the iron-partial VDOS is strongly peaked at one energy value. [S0163-1829(99)50522-5]

After the research on quasicrystals (QC's) by Shechtman *et al.*[1] a natural question that almost immediately emerged was: How will this type of long-range order in condensed matter affect the dynamical properties of these novel materials? Group theoretical methods predicted the existence of two types of lattice dynamics, viz., phonons and phasons.[2] The latter type of dynamics turned out to correspond to atomic jumps[3] rather than propagating modes as in incommensurably modulated crystals,[4] such that the terminology should be considered as a misnomer.

Many types of techniques have been applied to the study of phonon dynamics in QC's:[5] inelastic neutron scattering (INS), specific heat and thermal conductivity, ultrasound and light scattering. An excellent review of this whole subject matter is given by Quilichini and Janssen[5] and where most of the original references to the literature can be found. By far the most detailed information is obtained by INS from large single-grain samples. Studies of the latter type have been performed on $i-$Al-Cu-Fe,[6] $i-$Al-Cu-Li (and its $R-$Al-Cu-Li approximant),[7] $i-$Al-Pd-Mn,[8] and $d-$Al-Ni-Co.[9] In all these systems the acoustic modes are narrow and well defined in the long-wavelength limit. Beyond a characteristic wave vector, the phonon lineshapes broaden dramatically and finally merge into a broad band of optical modes. In Al-Pd-Mn some additional flat modes have been observed at lower frequencies.[8]

In a sense these results are somewhat disappointing in that the line broadening impedes one to observe richer details. Equally featureless are the ''generalized'' vibrational density of states (GVDOS) results obtained on powder samples by the INS time-of-flight method.[10] In general these results exhibit two or at most three maxima in the GVDOS. Nonapproximant periodic structures of similar composition exhibit a richer fine structure in the GVDOS. This prosaic lack of details is somewhat at variance with the rather glamorous theoretical results, which propose self-similar diagrams of dispersion curves, critical states, etc., leading to a predicted highly structured vibrational density of states.

In this paper, we adopt a method to study phonon dynamics to the realm of QC's, with as a spinoff a surprising result. This recently developed method is resonant inelastic scattering of synchrotron radiation by the atomic nuclei. In our case the nuclear resonance used was the 14.41 keV Mössbauer level of ^{57}Fe. The sample studied was a powder of $i-Al_{62}Cu_{25.5}Fe_{12.5}$ fully enriched in ^{57}Fe. The sample was prepared by melt spinning and subsequent annealing as has been thoroughly described in Ref. 11. The quality of the sample has been checked by x-ray diffraction. Several (thick) batches of finely ground powder were put into plexiglass containers with a thin Mylar window and scanned separately as a matter of checking the reproducibility.

The rigidity of the lattice leads to a finite probability for recoilless nuclear-resonant absorption, given by the Lamb-Mössbauer factor f_{LM}. Thus the recoil fraction $1-f_{LM}$ gives the inelastic fraction of nuclear absorption, which is accompanied by phonon creation or annihilation processes. The possibility to study the energy spectrum of this inelastic fraction using nuclear-resonant absorption of synchrotron radiation[12,13] opens a new pathway to study element-specific vibrational dynamics.

The experiments were performed at the Nuclear Resonance Beamline[14] of the European Synchrotron Radiation Facility. The area of inelastic nuclear-resonant scattering has recently been reviewed by Chumakov and Rüffer.[15] For our study, the experimental setup was as shown in Fig. 1. The pulsed broad-band radiation of the undulator (U) is reduced in bandwidth by the pre- and high-resolution monochromator (PM, HRM, respectively). The current HRM used in this study provided a resolution $\Delta E \approx 1$ meV, corresponding to a relative resolution $\Delta E/E \approx 10^{-7}$. This is, however, broad band with respect to the nuclear level width of ^{57}Fe, which is $\Delta E_n/E_n \approx 10^{-12}$. The time structure of the synchrotron radia-

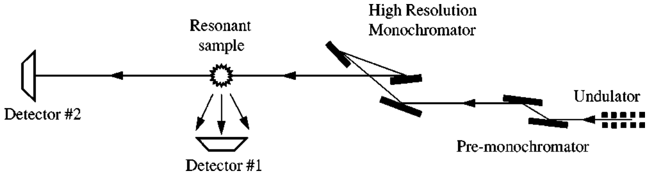

FIG. 1. Setup of the inelastic nuclear-resonant scattering experiment showing pre- and high-resolution monochromator (HRM), resonant sample, as well as avalanche photodiode detectors (APD's).

tion, as well as the very fast avalanche photodiode detectors (APD's) allows one to easily discriminate between electronic (prompt) scattering and the nuclear-resonant (delayed) deexcitation due to the lifetime of the nuclear level (ca. 0.14 μs for the ^{57}Fe first excited state).

The deexcitation of the nuclear system proceeds through two main channels: a coherent one (in forward and Bragg-diffracted directions) and an incoherent (spherical wave) one. The APD mounted close to the sample but out of the forward direction (lower APD in Fig. 1) probes the incoherent signal. Since this channel includes high branching ratio internal-conversion processes on nuclear deexcitation, it is advantageous to detect the 6.4 keV $K\alpha$ iron fluorescence that results from the ensuing electronic cascade. The coherent forward-scattering channel proceeds only elastically; thus it provides the possibility to measure the instrumental function of the high-resolution monochromator with detector No. 2. Incoherent scattering of the primary 14.4 keV radiation is negligible and does not influence the absorption measurements.[15]

The energy spectrum of nuclear absorption is measured as a function of energy shift between the nuclear level and the energy of the incident radiation delivered by the HMR (Fig. 1). This is shown for our sample in Fig. 2. The energy spectrum consists of three components: (1) There is an elastic component centered at zero energy shift. (2) There are two energy-shifted components, one due to phonon creation $(\Delta E>0)$, and one due to phonon annihilation $(\Delta E<0)$. The instrumental function (measured with the detector No. 2) is also shown in Fig. 2. This gives the form of the elastic component (1) (the two curves are normalized to equal intensities at zero energy shift).

The methodology for extracting the partial vibrational DOS from the energy spectrum has been presented by Sturhahn *et al.*[13] and recently generalized by Kohn *et al.*[16] These methods rest on two basic assumptions. The first is that the energy spectrum $S(E)$ shown in Fig. 2 can be normalized using the Lipkin sum rule[17] stating that the first moment of the energy spectrum is given by the recoil energy of the free nucleus: $\int_{-\infty}^{\infty} S(E)E\,dE = E_{\mathrm{R}}$ ($E_{\mathrm{R}} \approx 1.956$ meV for ^{57}Fe). The second is that $S(E)$ can be expanded into single $S_1(E)$ and multiphonon components $S_n(E)$ as in a harmonic lattice. $S(E)=f_{\mathrm{LM}}\Sigma_n S_n(E)$. The VDOS $\mathcal{D}(E)$ is then given by the single-phonon contribution: $S_1(E) = (E_{\mathrm{R}}/E)\mathcal{D}(E)/[1-\exp(-\beta E)]$ (where $1/[1-\exp(-\beta E)]$ is the Bose-Einstein occupation factor and $\beta = 1/k_{\mathrm{B}}T$). The multiphonon contribution $S_n(E)$ can be expressed as a convolution of $S_{n-1}(E)$ and $S_1(E)$, allowing one to extract $S_1(E)$ as described in Refs. 13,15,16 and 18.

The resulting Fe-partial VDOS $\mathcal{D}(E)$ for the $i-\mathrm{Al}_{62}\mathrm{Cu}_{25.5}\mathrm{Fe}_{12.5}$ sample is shown in Fig. 3. The most striking feature of this curve is the sharp maximum at about 27 meV. The neutron-weighted GVDOS of Klein *et al.*[10] is also shown. (Both curves have been arbitrarily normalized to unit area as the two data sets cannot be compared in a straightforward manner. The problem is the neutron data, which only represent a *generalized* VDOS as discussed below.) The

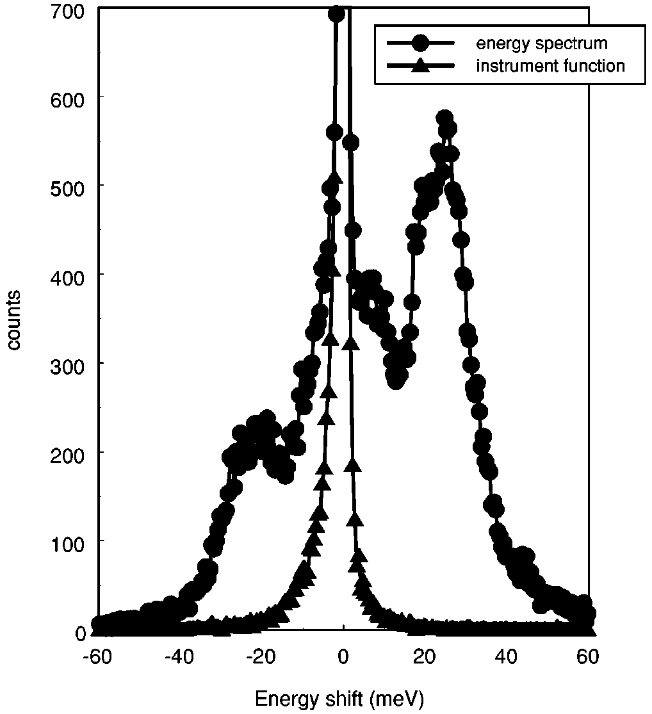

FIG. 2. Energy spectrum of the $i-\mathrm{Al}_{62}\mathrm{Cu}_{25.5}\mathrm{Fe}_{12.5}$ sample at room temperature and the instrument function showing resolution. Solid lines are to guide the eye.

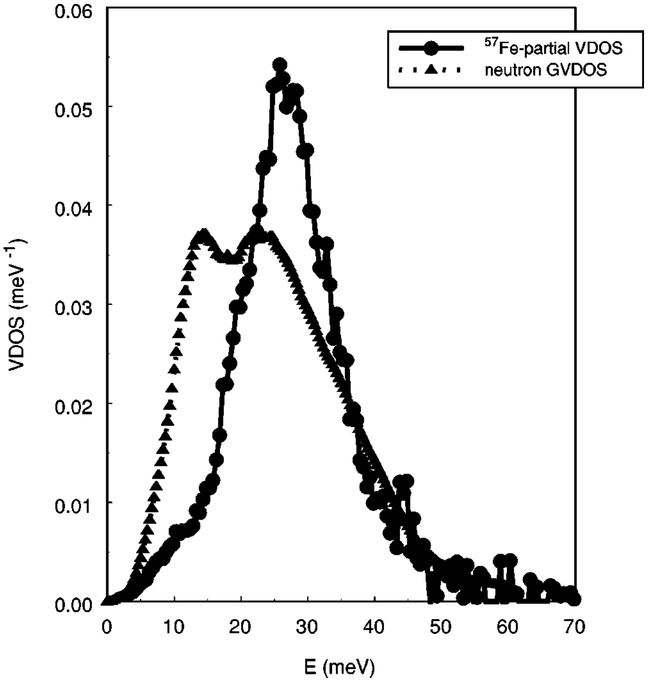

FIG. 3. Results for the iron-partial VDOS (our results) as compared to the neutron-weighted GVDOS from Klein *et al.* (Ref. 10). Solid lines are to guide the eye.

maximum of the Fe-partial VDOS lies near but *definitely above* the upper maximum of the neutron-weighted GVDOS curve. It is also much sharper. This is the first time to our knowledge that such sharp structures have been seen in the vibrational DOS of a QC.

The second striking feature is the low intensity of the iron-partial VDOS in the *low-energy* region up to (and actually above) the maximum observed in the neutron GVDOS as compared to the intensity at larger energies.

The result for the behavior of the iron-partial VDOS in the low-energy limit $E\rightarrow 0$, is affected by the deconvolution of the resolution function up to about 3 meV (and so lower-energy data are not shown). The function VDOS/E^2 is flat between 3 and 8 meV, but with deviations above this, so that there seems to be at least an indication of a VDOS$\propto E^2$ corresponding to a Debye model up to about 8 meV. The neutron-weighted GVDOS actually shows no region of quadratic behavior.

A number of significant differences between this technique and the inelastic neutron-scattering technique must be outlined.

(i) As the resonant process involves only one single nucleus, it is purely incoherent. This is in marked contrast with the INS technique, where as a rule we have both coherent (two-body) and incoherent (one-body) contributions. The formulas derived are obtained as the one-phonon term from a multiphonon expansion for a periodic lattice and harmonic vibrations.[19] Neutron-scattering theory provides in general only a link between the VDOS and the (1) *incoherent* scattering function for a (2) *monoatomic Bravais* lattice. Some theoretical efforts have been devoted to the extension of this scheme to coherent scattering, but the fact that in general we cannot meet these two simplifying basic assumptions proves an abiding source of difficulties in INS which eventually results in that we can only talk about a *generalized* density of states.[20] In the case of nuclear-resonant inelastic scattering, we really measure an unspoiled VDOS.

(ii) Moreover, the VDOS measured is element specific: in the case of ^{57}Fe only the iron-partial VDOS is measured. *Both these features imply that our data should be able to offer much more reliable and stringent tests of theoretical calculations.* [A variant of the method allows us to measure also an element-non-specific *generalized* VDOS for samples of arbitrary atomic composition.[21] The various partial densities of states are then weighted by the *electronic* (rather than nuclear) x-ray scattering cross sections of the corresponding elements, and we run into similar problems as with neutron scattering.]

(iii) Only small samples are required. Thus it becomes even possible to compare ^{nat}Fe- and ^{57}Fe-containing single crystals. This is important since in $i-$Al-Cu-Fe it is possible to grow small single-grain samples but not samples of the size that would be required for neutron-scattering studies.[22] The anisotropy of the density of states based on the coupling factor $\mathbf{s}\cdot\mathbf{e}$, where $\mathbf{s}=\mathbf{k}/k$, with $\mathbf{k}$ the wave vector of the photon and $\mathbf{e}$ the polarization vector of the phonon, can be studied.[18,16] (In neutron-scattering studies we have something similar with $\mathbf{k}$ replaced by the momentum transfer $\mathbf{Q}$).

(iv) The energy resolution (ΔE, currently ≈ 1 meV) is not as good as in neutron scattering. However ΔE is constant over the energy range instead of increasing as in the case of time-of-flight INS.

That the ^{57}Fe DOS can turn out to be so vastly different from the neutron GVDOS can be understood by noting that the coherent Fe-Fe and incoherent Fe dynamical structure factors amount only to 6.1% of the total neutron-scattering intensity in $i-\mathrm{Al}_{62}\mathrm{Cu}_{25.5}\mathrm{Fe}_{12.5}$. But it remains surprising that the spectral weight of the iron dynamics is situated towards the *high-energy* part of the spectrum, and that *Fe hardly contributes to the first maximum of the* DOS around 15 meV, which probably corresponds to the Van Hove singularity of the acoustic phonons. Our unexpected result was not anticipated by Klein *et al.*[10] which led them to a false paradigm, viz., that in contradistinction to crystalline nonapproximant phases, QC's would have no sharp features in their DOS. The iron-partial VDOS seems actually to have more the character of a damped harmonic oscillator (or an Einstein oscillator) than that resulting from the dispersion curve that one would expect, e.g., even in a first approximation by considering a diatomic linear chain (Cu and Fe having almost the same mass).[23] We would in general expect also in three dimensions that the acoustic branches have the same energy spectra for each atom type, but the optical modes may be essentially different for various atoms. This has been already shown in practice by F. Parak[24] with the example of myoglibine.

In conclusion we have discovered an unexpected result for the iron dynamics within an Al-Cu-Fe QC by adopting a recently developed innovating nuclear technique. These results constitute a strong motivation for a neutron-scattering study using isotopically enriched samples.

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