Anisotropic inelastic nuclear absorption

A. I. Chumakov, R. Rüffer, and A. Q. R. Baron
European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France

H. Grünsteudel
Institüt fur Physik, Medizinische Universität zu Lübeck, D-23538 Lübeck, Germany
and European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France

H. F. Grünsteudel
European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France

V. G. Kohn
Russian Research Center ''Kurchatov Institute,'' 123182 Moscow, Russia
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The dynamics of iron atoms in the $^{57}FeBO_3$ single crystal was studied using inelastic nuclear absorption. The energy spectra of nuclear recoil along several crystallographic directions were measured. The densities of phonon states, weighted by the projection of the phonon polarization vector in various directions were derived and the Lamb-Mössbauer factors along these directions were calculated. The projected density of states reveals a pronounced anisotropy, while the Lamb-Mössbauer factor shows no directional dependence. [S0163-1829(97)08441-5]

Inelastic nuclear absorption of synchrotron radiation is a relatively new method to study lattice dynamics. After the first observation,[1] several successful applications of the method were performed.[2–8] Up to now the energy spectra of inelastic nuclear absorption (in other words, the energy spectra of nuclear recoil) were measured with polycrystalline or amorphous samples. Hence the information on lattice dynamics was obtained in an integral form, where the modes of vibrations along various directions were averaged. In this work we show the possibility to measure separately the frequency distribution of lattice vibrations along different directions. The reason why the energy spectra of nuclear recoil are sensitive to the direction of vibrations is that the energy of a photon in the reference system of a vibrating nucleus is determined by the projection of the velocity of the nucleus to the wave vector of the photon. In order to reveal this sensitivity, one should use a single-crystal sample. We have measured the energy spectra of inelastic absorption of 14.4-keV synchrotron radiation by ^{57}Fe nuclei of an $^{57}FeBO_3$ single crystal. A pronounced dependence of the energy spectra of nuclear recoil on the orientation of the incident x-ray beam relative to the crystal was observed. The frequency distributions of lattice vibrations along several crystallographic directions were derived and the Lamb-Mössbauer factors along these directions were calculated.

The experiment was performed at the Nuclear Resonance Beamline (Ref. 6), ID 18, at the European Synchrotron Radiation Facility (ESRF). The storage ring was operated in ''$\frac{1}{3}$ fill'' mode. The nuclei in the crystal were excited by a beam of 14.413-keV radiation with a bandwidth of 4.4 meV. The energy of the beam was varied in the range of ± 200 meV around the energy of the nuclear resonance with a step size of ~ 0.8 meV. The intensity of nuclear absorption was measured by counting the yield of the delayed 6.4-keV K_α-fluorescence radiation from the iron atoms, which results from internal nuclear conversion. An avalanche photo diode detector[9] was used. The typical count rate was about 40 counts per second at the relative energy 20 meV. The details of the experimental setup may be found in Refs. 6 and 7.

The measurements were performed with a ferric borate $^{57}FeBO_3$ single crystal. The crystal has a calcite-type structure with $R\bar{3}c$ space group.[10] The sample had the shape close to a hexagonal platelet (Fig. 1) with a thickness of $\sim 110\ \mu$m and an area of ~ 1 cm^2. The surface of the platelet coincided with the (111) crystallographic plane. The enrichment in the ^{57}Fe isotope was $\sim 95\%$. The data were taken at room temperature.

Energy spectra of inelastic nuclear absorption were mea-

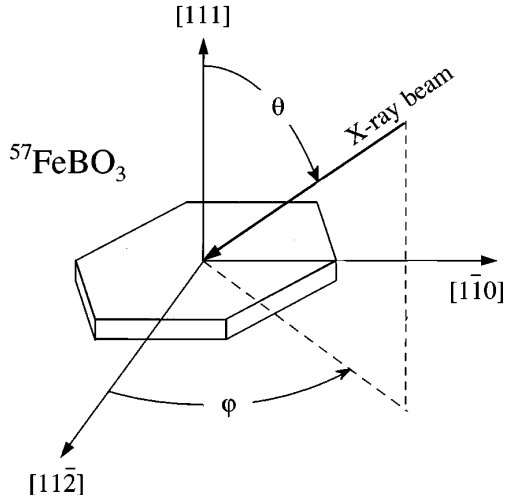

FIG. 1. Orientation of the incident x-ray beam relative to the crystal.

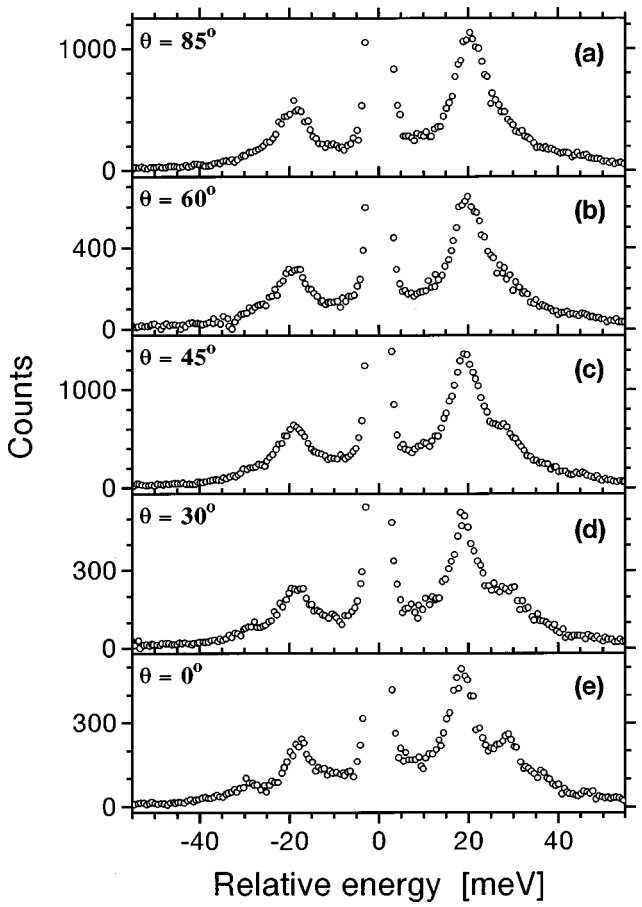

FIG. 2. Energy spectra of inelastic nuclear absorption of synchrotron radiation in the $^{57}FeBO_3$ single crystal for various polar angles θ between the direction of the incident x-ray beam and the [111] axis. The azimuthal angle was kept constant (φ=90°).

sured for several polar angles θ and azimuthal angles φ between the incident x-ray beam and the [111] axis (Fig. 1). In the first set of measurements the polar angle was varied from $\theta=0°$ to $\theta=85°$ while the azimuthal angle was kept constant $\varphi=90°$. Afterwards the polar angle was kept constant $\theta=85°$ [i.e., the incident beam was almost parallel to the (111) crystallographic plane] and the azimuthal angle was changed to $\varphi=0°$. These two azimuthal orientations are not equivalent, because the crystal has a three-fold rotation symmetry around the [111] axis.[10]

The energy spectra of nuclear recoil are shown in Figs. 2 and 3. The intense central peak in the spectra originates from the high probability of elastic (recoilless) absorption. The side parts of the spectra show the probability of inelastic absorption with a creation (right-hand side) or an annihilation (left-hand side) of the phonons. The spectra are asymmetric in accordance with the relatively low occupation of the phonon states at room temperature. The peaks of inelastic absorption (e.g., at ± 20 meV and ± 30 meV) show the most probable energies of the phonons, which likely are related to the low-dispersive parts of the dispersion relations, where the phonon energy does not depend much on the phonon momentum.

The spectra show a pronounced dependence on the polar angle and no dependence on an azimuthal angle. When the polar angle is high [Figs. 2(a) and 2(b)], the spectra consist

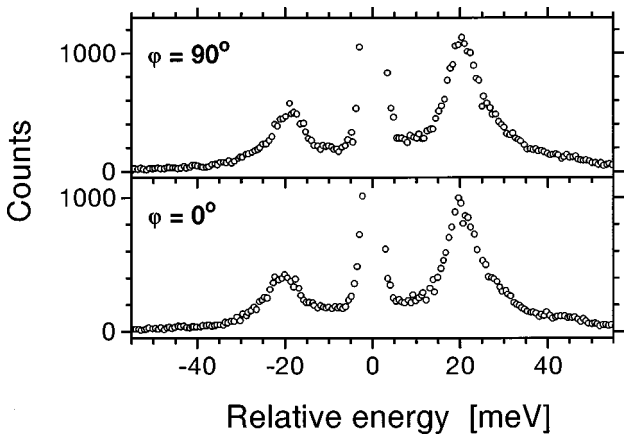

FIG. 3. Energy spectra of inelastic nuclear absorption of synchrotron radiation in the $^{57}FeBO_3$ single crystal for various azimuthal angles φ of the incident x-ray beam. The polar angle was kept constant (θ=85°).

of one peak at about ± 20 meV in the energy-loss and energy-gain sides of the spectrum, respectively. When the angle decreases [Figs. 2(c)–2(e)], this peak remains in the spectrum, but an additional peak appears at about ± 30 meV. In contrast to the sensitivity of the spectra to the polar angle, the spectra at two azimuthal angles (0° and 90°) coincide within the experimental accuracy (Fig. 3).

The Lamb-Mössbauer factors for various directions of the incident x-ray beam and the corresponding densities of states were calculated using the experimental data. The available theory of inelastic nuclear absorption[11] considers only the simplest case of a cubic Bravais lattice. However, it can be shown[12] that similar expressions are also valid in the general case of an anisotropic crystal. In particular, the probability density of inelastic nuclear absorption $S(E,\mathbf{k})$ as a function of the wave vector of the x-ray quantum $\mathbf{k}$ can be written as

$$S(E,\mathbf{k})=f_{\mathrm{LM}}(\mathbf{k})\sum_{n=1}^{\infty} S_n(E,\mathbf{k}); \quad S_1(E,\mathbf{k})=\frac{E_R\, g(|E|,\mathbf{s})}{E(1-e^{-\beta E})};$$

$$S_n(E,\mathbf{k})=\frac{1}{n}\int_{-\infty}^{+\infty} S_1(E',\mathbf{k})S_{n-1}(E-E',\mathbf{k})dE' \quad (n\geqslant 2). \tag{1}$$

Here $f_{\mathrm{LM}}(\mathbf{k})$ is the Lamb-Mössbauer factor; $S_n(E,\mathbf{k})$ is the n-phonon contribution to inelastic absorption; $\mathbf{s}=\mathbf{k}/k$; $E_R=\hbar^2k^2/2M=1.956$ meV is the recoil energy of a free ^{57}Fe nucleus; $\beta=(k_BT)^{-1}$; k_B is the Boltzmann constant; and T is the temperature. In contrast to the corresponding expression for an isotropic crystal,[11] Eq. (1) contains the ''projected'' density of phonon state $g(E,\mathbf{s})$ instead of the conventional density of phonon states. It includes the contributions of various modes of lattice vibrations, which are weighted by the projections of the phonon polarization vector to the wave vector of x-ray quantum:

$$g(E,\mathbf{s})=V_0\sum_j \int \frac{d\mathbf{q}}{(2\pi)^3}\,\delta(E-\hbar\omega_j(\mathbf{q}))|\mathbf{s}\mathbf{e}_j(\mathbf{q})|^2. \tag{2}$$

Here V_0 is the volume of the unit cell; ω_j and $\mathbf{e}_j$ are the frequency and the unit polarization vector of jth mode of

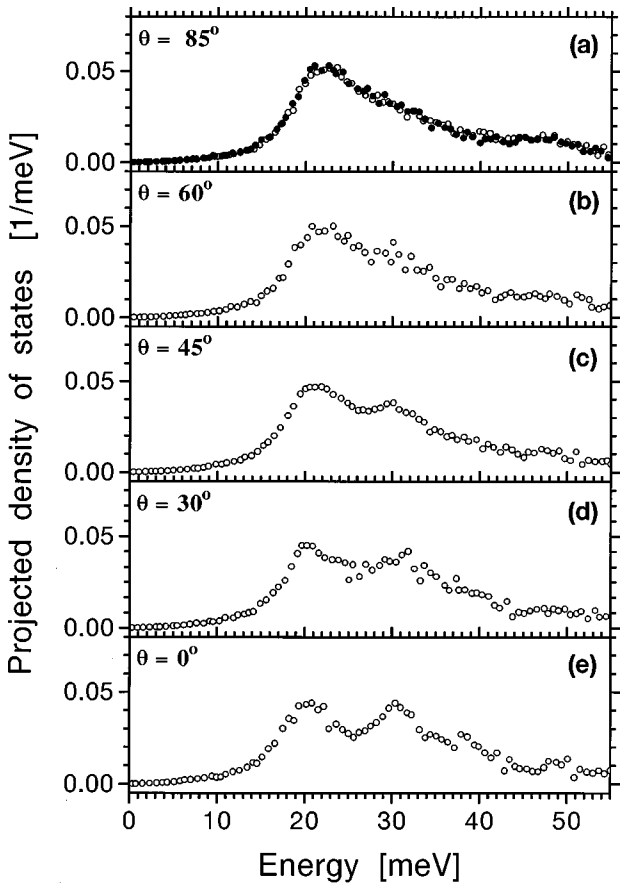

FIG. 4. The projected densities of phonon states [as defined by Eq. (2)] along several crystallographic directions. The polar angles θ for various directions is indicated in the figure. The data for the azimuthal angle $\varphi = 90°$ are shown with open circles and for $\varphi = 0°$ with solid circles.

lattice vibration; **q** is the wave vector of the phonon, and the integral is taken over these wave vectors in the first Brillouin zone. It can be shown[12] that the procedure to normalize the energy spectra of inelastic absorption, to calculate the Lamb-Mössbauer factors and to derive the density of states, which was initially applied to polycrystalline samples,[2,7] is valid for the anisotropic crystals as well. In this case it provides, however, the projected density of states [Eq. (2)].

Therefore the conventional method[2] to treat the data was used. Namely, the spectra were normalized using Lipkin's sum rule[13] (first momentum of the spectrum equals the recoil energy of a free nucleus). The recoil fraction of nuclear absorption ($l - f_{\mathrm{LM}}$) was calculated from the area of the inelastic part of the normalized spectrum. The multiphonon contributions were subtracted using an iterative procedure and the projected density of states was derived from the one-phonon term (the details can be found in Refs. 2 and 7).

The derived projected densities of states are shown in Fig. 4. They show the frequency distribution of lattice vibrations, weighted by the projection of the phonon polarization vector to the direction of x-ray beam.[14] Figure 4(a) shows the frequency distribution of vibrations along two nonequivalent axes, which lie in the (111) plane, namely along the [110] axis and the [112] axis.[15] Like the original energy spectra [Figs. 3(a) and 3(b)], they are identical within the experimental accuracy. This gives a strong indication that the vibrations of the iron atoms are mostly isotropic within the (111) plane. In contrast, the vibrations perpendicular to the (111) plane have considerably different frequency distribution [Fig. 4(e)]. In addition to the pronounced additional peak at 30 meV, which can be seen in the original experimental spectrum, Fig. 2 also contains indications of two other peaks at ~ 38 and ~ 49 meV. These might correspond to low-dispersive high-frequency optical modes, because the chains of alternating iron and boron atoms, which have very different masses, are located just along the [111] axis. The projected densities of states for intermediate directions [Figs. 4(b)–4(d)] show the gradual growth of the contribution of the perpendicular mode when the polar angle decreases.

The Lamb-Mössbauer factors were calculated with two different methods: from the area of the inelastic part of the normalized energy spectra, and from the derived projected densities of states. Similar to Ref. 7, this gave a good chance to check the reliability of the results. The factors given in Table I are the mean values from two methods, and the given uncertainties are taken from the maximum discrepancy between them. In most cases the discrepancy was much smaller, therefore the indicated error of 0.02 is an upper bound. It is worthwhile to emphasize, that the measurements of inelastic nuclear absorption give in general more reliable values of the Lamb-Mössbauer factors than conventional Mössbauer spectroscopy or nuclear forward scattering techniques. This is because neither the recoil fraction of the radioactive source nor the sample thickness are involved in the calculations.

In contrast to the pronounced anisotropy of the projected densities of states (Fig. 4), the Lamb-Mössbauer factors (Table I) do not depend on the crystal orientation within the experimental uncertainty. Although this is a surprise, it is not a contradiction. The Lamb-Mössbauer factor is not very sensitive to the details of the density of phonon states. It is determined mostly by the low-energy part of the density of states; and one can see from Fig. 4 that all densities of states look similar below 25 meV (Fig. 4). The constant value of the Lamb-Mössbauer factor along six nonequivalent crystallographic directions gives strong indication that the mean-square displacement of the iron atoms in the ferric borate crystal is mostly isotropic. The magnitude of the mean-square displacement can be obtained from the Lamb-Mössbauer factor as $\langle u^2 \rangle = -\ln(f_{\mathrm{LM}})/k^2 = 0.0042(5)$ Å^2. In this concern we note that our results do not confirm the large anisotropy of the mean-square displacement, which was reported earlier on the basis of crystal structure refinement[10] as

TABLE I. Lamb-Mössbauer factors, calculated for the various orientation of the incident x-ray beam relative to the crystal.

Polar angle θ	85°	85°	60°	45°	30°	0°
Azimuthal angle φ	0°	90°	90°	90°	90°	90°
f_{LM}	0.82(2)	0.81(2)	0.81(2)	0.80(2)	0.81(2)	0.81(2)

$\langle u^2\rangle_{\parallel}=0.0030(2)$ Å^2 and $\langle u^2\rangle_{\perp}=0.0008(12)$ Å^2, where $\langle u^2\rangle_{\parallel}$ and $\langle u^2\rangle_{\perp}$ stands for the mean-square displacement parallel and perpendicular to the (111) plane, respectively.

In summary, we have studied the lattice dynamics of the $^{57}FeBO_3$ single crystal using inelastic nuclear absorption. It is almost the only suitable technique to study the phonons in ferric borate: a neutron scattering experiment would be difficult due to the large content of boron and the absence of sufficiently large crystals while inelastic x-ray scattering would suffer from the strong absorption by iron atoms. The densities of phonon states, weighted by the projections of the phonon polarization vector to various crystallographic directions were derived and the corresponding Lamb-Mössbauer factors along these directions were calculated. The results show that the lattice vibrations along the different directions within the (111) plane have similar frequency distributions, whereas the vibrations perpendicular to the (111) plane are significantly different. In contrast to this anisotropy, the calculated values of the Lamb-Mössbauer factors do not show a pronounced angular dependence. From the methodological point of view, the observed combination of the pronounced anisotropy of the density of phonon state and the isotropic mean-square displacement of the iron atoms provide a striking example of the advantages of the inelastic absorption technique compared, e.g., to Mössbauer spectroscopy, where the Lamb-Mössbauer factor is the only parameter to study the lattice dynamics.

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[14] The instrumental function of the monochromator was not eliminated from the original spectra, therefore the derived density of states may be considered as the true ones, convoluted with the instrumental function.

[15] More precisely, they still contain a small $[\propto\cos(85°)=0.09]$ contribution of the density of states along the [111] axis.