Nuclear Resonance Energy Analysis of Inelastic X-Ray Scattering

A. I. Chumakov,[1] A. Q. R. Baron,[1] R. Rüffer,[1] H. Grünsteudel,[1,2] H. F. Grünsteudel,[1] and A. Meyer[1,3]
[1]*European Synchrotron Radiation Facility, BP 220 F-38043 Grenoble Cedex, France*
[2]*Institut für Physik, Medizinische Universität zu Lübeck, D-23538 Lübeck, Germany*
[3]*Physik Department, Technische Universität München, D-85747 Garching, Germany*
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Inelastic scattering of x rays by gaseous, liquid, and solid samples was measured using a nuclear transition as a reference for the energy analysis of the scattered radiation. The samples were irradiated by a beam of synchrotron radiation with a bandwidth of 6.4 meV. The scattered radiation was analyzed using a resonance detector with a bandpass of 0.5 μeV. These studies introduce a new technique to measure the energy distribution of inelastic x-ray scattering. [S0031-9007(96)00311-0]

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Inelastic x-ray scattering [1] is becoming a well established technique, providing valuable information on phonon dynamics in solids and collective excitations in liquids [2,3]. In this paper we develop a new method of energy analysis of inelastic scattering, based on the use of a nuclear transition as an energy reference.

The properties of nuclear transitions make them an excellent instrument for energy analysis. The accuracy of the energy reference is determined by the width of the nuclear level and thus offers the potential of neV energy resolution. Time discrimination can be applied to separate the resonant nuclear scattering from the nonresonant electronic scattering due to the long lifetime of nuclear levels. These properties constitute a basis for using nuclear transitions for the energy analysis of inelastic x-ray scattering. To exploit this potential one needs an x-ray source which is tunable over a sufficient energy range, has a narrow bandwidth, and provides high enough spectral density to excite narrow nuclear levels. The first two conditions determine the accessible energy scale and therefore the field of application. The last requirement determines the general feasibility of the experiment.

Until recently, the only sources which provided the required spectral density were the radioactive sources of nuclear γ radiation. The energy tunability of these sources is obtained via Doppler shift and is limited to several μeV. Accordingly, radioactive sources are used in the studies of quasielastic Rayleigh scattering of Mössbauer radiation [4] or nuclear scattering with a spin flip in selective excitation double Mössbauer experiments [5]. The analysis of phonon excitations ($\sim$10 meV) is outside the range of this technique.

The development of synchrotron storage rings made it possible to excite nuclear levels with synchrotron radiation [6]. The superior spectral density of radiation at third generation sources provides a flux up to 10^4–10^5 photons per second within the natural width of nuclear levels [7]. The continuous spectrum of synchrotron radiation allows one to scan the energy of x rays over the range of phonon excitations, and modern high resolution monochromators [7,8] provide bandpasses of few meV. Thus synchrotron radiation sources have the requisite characteristics to use nuclear transitions for the energy analysis of inelastic x-ray scattering. The scope of this work is to study the feasibility of this method and to compare it to the energy analysis performed with crystal optics.

This work was performed at the Nuclear Resonance Beamline [9] at the European Synchrotron Radiation Facility. The storage ring was run in timing mode with 16 electron bunches equally spaced in the ring, providing pulses of radiation ($\sim$100 ps duration) every 176 ns. The average storage ring current was about 60 mA. The experimental setup is shown in Fig. 1. The 22.8 mm period undulator produced a beam of 14.4 keV x rays. The radiation was monochromatized by the water-cooled double-crystal Si(111) monochromator to the bandwidth of about 2.8 eV. This bandwidth was reduced to 6.4 meV by a compact high resolution monochromator, composed of channel-cut Si(422) and Si(12 2 2) crystals in a "nested" geometry [7,8]. The energy of radiation was varied in the range of about $\pm$100 meV around the energy of ^{57}Fe transition (14 413 eV). The flux on the sample was about 0.7×10^9 photon/s and the size of the beam was 1.5×0.4 mm^2.

The energy of the radiation scattered by the sample was analyzed using a resonance detector with a bandpass of 0.5 μeV. The detector consisted of a large area (200 mm^2) fast avalanche photodiode (APD) [10] covered by a 10 μm foil of α-iron, 95% enriched in the resonant

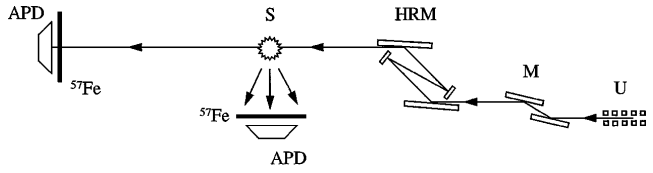

FIG. 1. The experimental setup. U, 22.8 mm period undulator; M, water-cooled double crystal Si(111) monochromator; HRM, compact high resolution monochromator using Si(422) and Si(12 2 2) channel-cut crystals in a nested geometry; S, sample; APD, avalanche photo diode; ^{57}Fe, 10 μm foil of ^{57}Fe.

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^{57}Fe isotope. It was located 1.5 mm below the sample, covering nearly a 2π solid angle. The detector accepted the scattered radiation between 8° and 172°, which corresponded to momentum transfers 1–15 Å^{-1}, with a typical value of 10 Å^{-1} at 90° scattering. Gaseous Xe (ambient pressure) was stored in a cell made of 80 μm kapton foil; a cell for water was made of 5 μm Mylar foil. Scattering by empty cells was about 7% in the case of Xe and below 1% in the case of water; no corrections for this contribution were made. The measurements were performed at room temperature.

The energy bandpass of the detector was determined by the process of resonant nuclear *scattering.* If the energy of the radiation coincided with the energy of the nuclear level, it excited the ^{57}Fe nuclei and was reemitted with a time delay determined by the lifetime of the nuclear excited state ($\tau_0 = 141$ ns). However, if radiation arrived at the detector with an energy far from the nuclear resonance, it passed through the resonant foil instantaneously and produced a "prompt" signal in the APD. The fast timing electronics counted only the delayed events in the time interval of about 15–150 ns after the pulse of synchrotron radiation. Precautions were taken against counting 6.4 keV fluorescence resulting from nuclear *absorption* (which may proceed inelastically [11] and hence spoil the energy resolution). A 0.3 mm Al absorber was placed between the ^{57}Fe foil and the APD. It attenuated the 6.4 keV radiation by a factor of 2×10^3, while only attenuating the 14.4 keV radiation by a factor of 2. Thus the detector measured the delayed 14.4 keV photons resulting from nuclear forward scattering [12], which proceeds only in the vicinity of the nuclear resonance. The bandwidth of the resonant detector was determined by the hyperfine splitting of ^{57}Fe nuclear transition, which is about 0.5 μeV in the case of α-iron. The efficiency over this energy range was calculated to be about 3%.

The intensity of the scattered radiation within the detector bandpass was measured as a function of the difference between the energy of the incident beam and the energy of nuclear level. This measurement directly provided the probability of inelastic scattering as a function of energy transfer. For the precise determination of the zero point of the energy transfer axis, a second resonance detector was placed approximately 300 mm downstream of the sample. The inelastic scattering into this detector was negligible, so it collected only the radiation of the incident beam transmitted through the sample. The peak of the delayed events counted by the "forward" detector determined the zero point on the axis of the energy transfer.

The instrumental function of the spectrometer is shown in Fig. 2(c). For this measurement the detector was exposed to the direct x-ray beam from the high resolution monochromator. Because of the high energy resolution of the detector, the instrumental function is just the energy bandpass of the monochromator. The data were approximated by a Gaussian distribution [solid line in Fig. 2(c)]. The energy resolution, obtained from the fit, was found to be 6.4 meV (FWHM).

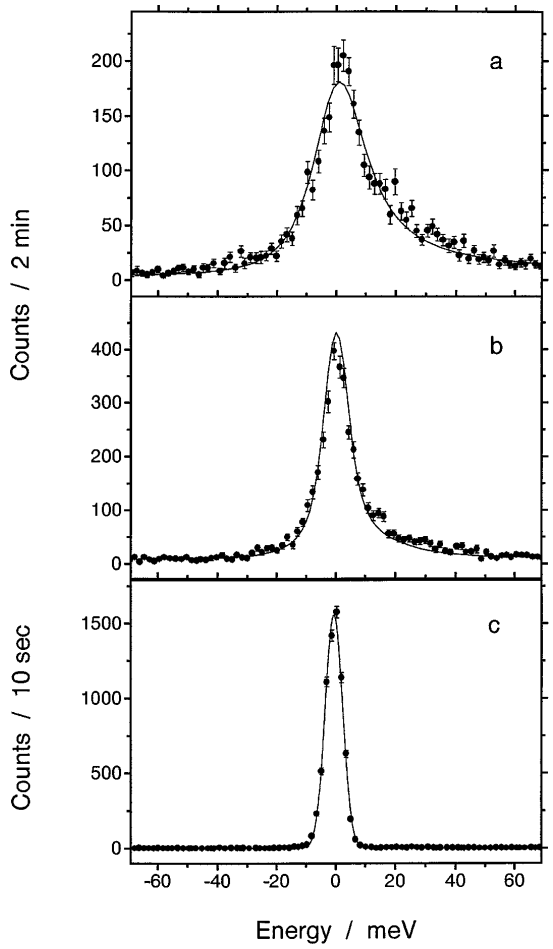

FIG. 2. Energy spectra of inelastic x-ray scattering by water (a) and by PMMA (b), compared with the instrumental function of the spectrometer (c). The solid line is a fit according to (a) Eq. (1), (b) Eq. (2), and (c) with a Gaussian distribution.

The energy spectra of x-ray scattering by polymethyl methacrylate (PMMA) and water samples are shown in Figs. 2(a) and 2(b), respectively, in comparison with the instrumental function [Fig. 2(c)]. The presence of inelastic scattering is clearly seen, both in the considerable broadening and in the long tails of the spectra. The left-hand sides of the spectra correspond to the scattering with the energy gain from the existing excitations in the sample. The right-hand sides correspond to the scattering with the energy loss to the existing excitations and to the creation of new excitations. In accordance with the small occupation of states at room temperature, both spectra show asymmetry, resulting from the higher probability to create the excitation as compared with the probability to find this excitation in the sample. The peak count rate was about 3.3 counts per second (cps) with PMMA and about 1.7 cps with water (the background count rate was about 0.05 cps).

Inelastic scattering by water [Fig. 2(a)] is determined by the dynamics of density fluctuations [2,3]. Theoretical analysis of this dynamics is beyond the scope of this paper and can be found elsewhere [13]. Here we check the detailed energy balance of scattering and estimate the characteristic energy transfer. For this purpose the spectra were approximated by a symmetric function $|\omega|/(\omega^2 + \Gamma^2)$, multiplied by the Bose occupation factor:

$$S_{\mathrm{H_2O}}(\omega) \propto \frac{\omega}{\omega^2 + \Gamma^2} \frac{1}{1 - \exp(-\omega\beta)}, \qquad (1)$$

where $S(\omega)$ is the energy spectrum of inelastic scattering, ω is the energy transfer, Γ is the half-width of the characteristic energy transfer, and $\beta = (k_B T)^{-1}$. Experimental data were fit by the convolution of Eq. (1) with the Gaussian approximation of the instrumental function. Comparison of the experimental data and the fit shows that the asymmetry of the energy spectra is well described by the energy dependence of the Bose factor. The best fit was obtained with $\Gamma = 10$ meV. It qualitatively agrees with the observed values of energy transfer in water [2,3].

Inelastic scattering by PMMA is determined by the density of vibrational states $g(\omega)$ according to the relation [14]

$$S_{\mathrm{PMMA}}(\omega) \propto q^2 \frac{g(\omega)}{\omega} \frac{1}{1 - \exp(-\omega\beta)}, \qquad (2)$$

where q is the momentum transfer. The experimental data were fit by Eq. (2), convoluted with the instrumental function. The density of vibrational states, $g(\omega)$, was taken from the results of neutron scattering [14]. The fit agrees well with the experiment.

Inelastic x-ray scattering by gaseous Xe is shown in Fig. 3. The peak count rate was 1.7 cps [15]. In contrast to scattering by PMMA and water samples, the energy spectrum is almost symmetric. A slight shift of the peak to the positive energy may be noted. According to the theory of inelastic neutron scattering by gas [16], the energy spectrum of energy transfer at ambient pressure is described by Doppler broadening. The recoil of Xe atom ($\sim$0.85 meV) is small compared with the energy of the thermal motion ($\sim$25 meV). Therefore one can consider the velocity distribution of the atoms to be Maxwell's distribution, not influenced by the scattering process, and obtain the energy spectrum of the scattered radiation as

$$S_{\mathrm{Xe}}(\omega) \propto \int P(\varphi) F(\theta) \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left(-\frac{(\omega - \omega_0)^2}{2\sigma^2}\right) d\Omega, \qquad (3)$$

$$\sigma^2 = \frac{\hbar^2}{\beta M} q^2, \qquad q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right), \qquad \omega_0 = \frac{\hbar^2}{2M} q^2,$$

where $P(\varphi) = \cos^2(\varphi)$ is the polarization factor, φ is the angle between the wave vector of the scattered radiation and the vertical plane, $F(\theta)$ is the atomic scattering factor, θ is the scattering angle, $\lambda = 0.86$ Å is the radiation wavelength, M is the mass of the Xe atom, and the integral is taken over the experimental solid angle. Equation (3) represents a superposition of normalized Gaussian distributions, which correspond to various values of the momentum transfer. The momentum transfer determines both the width, $\sigma(q)$, and the center position, $\omega_0(q)$, of each distribution. The superposition of all Gaussians provides the energy spectrum with long tails, slightly shifted to the positive energy. Calculations according to Eq. (3), convoluted with the instrumental function, show good agreement with the experimental data.

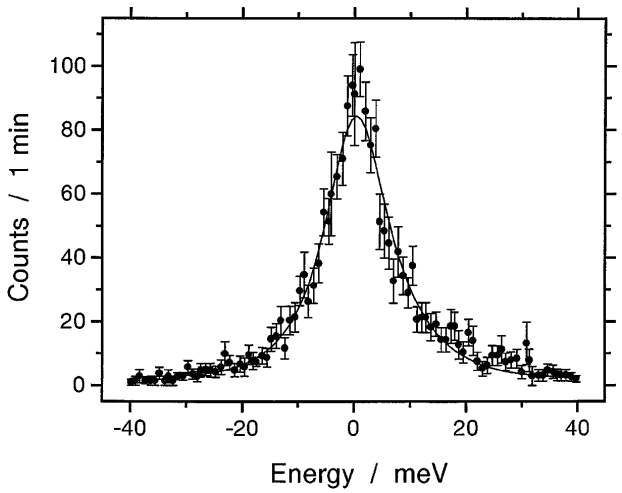

FIG. 3. Energy spectrum of inelastic x-ray scattering by gaseous Xe. The solid line is a fit according to Eq. (3).

We have demonstrated the feasibility of inelastic x-ray scattering studies with the nuclear resonant analysis of the scattered radiation. It offers a means to measure the energy distribution of the inelastic scattering, integrated over the momentum transfer. This new technique can be applied to measure a density of phonon states under the condition that q dependence of the dynamic scattering function $S(q, \omega)$ is a common factor before the energy dependence of scattering [see, e.g., Eq. (2)]. This, for instance, is the case for many types of polymers [14] and proteins [17], thus a wide field of application is anticipated. The notable merits of the technique are the precise determination of the zero point of the energy transfer axis and a small level of background, achieved using the timing gate.

The feasibility and energy resolution of the new technique are competitive with the established method of energy analysis using crystal optics. The count rates are similar: a few photons per second [2,3]. Presently, the best energy resolution reported in work with crystal optics (3.2 meV [3]) is better than the 6.4 meV reported here. However, the energy resolution of the present technique is dictated only by the monochromator element, not by the analyzer, therefore it may be easier to develop it further [18]. From the experimental point of view, the attractive feature of the new method is the simple

experimental setup, which does not require any special equipment (besides the nested high resolution monochromator, which, however, is nearly standard equipment). Therefore these studies may be performed at nearly any general purpose beam line of a third generation source of synchrotron radiation.

The present work has an important implication for recent measurements of nuclear inelastic absorption [11,19–21]. Comparing these two techniques, one can consider the nuclear inelastic absorption experiment as combining the inelastic scatterer and the resonant analyzer inside the sample. Therefore the analysis of measurements of nuclear inelastic absorption should take into account that the resonant nuclei in the sample can be excited not only by the primary x-ray beam but also by the radiation inelastically scattered by the surrounding atoms. Therefore the energy dependence of nuclear recoil is not the property of the Mössbauer atoms only, but, in general, may be influenced by the dynamics of the other atoms. The relatively high intensity of nonresonant inelastic scattering observed here suggests that this process has to be considered in the studies of nuclear inelastic absorption as well.

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[1] E. Burkel, *Inelastic Scattering of X-Rays with Very High Energy Resolution* (Springer-Verlag, New York, 1991), and references therein.
[2] F. Sette, G. Ruocco, M. Krisch, U. Bergmann, C. Masciovecchio, V. Mazzacurati, G. Signorelli, and R. Verbeni, Phys. Rev. Lett. **75**, 850 (1995).
[3] G. Ruocco, F. Sette, U. Bergmann, M. Krisch, C. Masciovecchio, V. Mazzacurati, G. Signorelli, and R. Verbeni, Nature (London) **379**, 521 (1996).
[4] J. A. Elliot, H. E. Hall, and D. St. P. Bunbury, Proc. Phys. Soc. **89**, 595 (1966).
[5] A. N. Artem'ev, G. V. Smirnov, and E. P. Stepanov, Sov. Phys. JETP **27**, 547 (1968) [Zh. Eksp. Teor. Fiz. **54**, 1028 (1968)].
[6] E. Gerdau, R. Rüffer, H. Winkler, W. Tolksdorf, C. P. Klages, and J. P. Hannon, Phys. Rev. Lett. **54**, 835 (1985).
[7] R. Rüffer, ESRF Annual Report, 1993, p. 84.
[8] T. Ishikawa, Y. Yoda, K. Izumi, C. K. Suzuki, X. W. Zhang, M. Ando, and S. Kikuta, Rev. Sci. Instrum. **63**, 1015 (1992); T. S. Toellner, T. Mooney, S. Shastri, and E. E. Alp, SPIE Proc. **1740**, 218 (1992).
[9] R. Rüffer and A. I. Chumakov, Hyperfine Interact. **97–98**, 589 (1996).
[10] A. Q. R. Baron and S. L. Ruby, Nucl. Instrum. Methods A **343**, 517 (1994).
[11] M. Seto, Y. Yoda, S. Kikuta, X. W. Zhang, and M. Ando, Phys. Rev. Lett. **74**, 3828 (1995).
[12] J. B. Hastings, D. P. Siddons, U. van Bürck, R. Hollatz, and U. Bergmann, Phys. Rev. Lett. **66**, 770 (1991).
[13] See, e.g., K. S. Singwi and A. Sjölander, Phys. Rev. **119**, 863 (1960).
[14] B. Gabryś, J. S. Higgins, K. T. Ma, and J. E. Roots, Macromolecules **17**, 560 (1984).
[15] To increase the count rate, these measurements were performed without the aluminum absorber. A compromise between the count rate and the quality of the instrumental function was achieved by adjusting the threshold of the detected signal.
[16] See, e.g., S. H. Chen, Y. Lefevre, and S. Yip, Phys. Rev. A **8**, 3163 (1973).
[17] See, e.g., S. Cusak and W. Doster, Biophys. J. **58**, 243 (1990).
[18] A high resolution monochromator providing 0.4×10^9 photons per second within 4.4 meV bandwidth was successfully tested by the authors during the preparation of the present publication. A 3 meV bandwidth monochromator is under study at the Advanced Photon Source [E. E. Alp (private communication)].
[19] X. W. Zhang, Y. Yoda, M. Seto, Yu. Maeda, M. Ando, and S. Kikuta, Jpn. J. Appl. Phys. **34**, L330 (1995).
[20] A. I. Chumakov, R. Rüffer, H. Grünsteudel, H. F. Grünsteudel, G. Grübel, J. Metge, O. Leupold, and H. A. Goodwin, Europhys. Lett. **30**, 427 (1995).
[21] W. Sturhahn, T. S. Toellner, E. E. Alp, X. W. Zhang, M. Ando, Y. Yoda, S. Kikuta, M. Seto, C. W. Kimball, and B. Dabrowski, Phys. Rev. Lett. **74**, 3832 (1995).