Temperature dependence of nuclear forward scattering of synchrotron radiation in α-^{57}Fe

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The resonant forward scattering of synchrotron radiation by ^{57}Fe nuclei was investigated over the temperature range from 9.7 to 1048 K. The temperature dependence of the Lamb-Mössbauer factor and the internal magnetic field were determined from the observed time spectra. The data presented here demonstrate the suitability of the synchrotron technique for precise measurements of these quantities. In addition these results demonstrate in a straightforward way the difference between the x-ray Debye-Waller factor and the Lamb-Mössbauer factor.

For more than 30 years Mössbauer spectroscopy has been a valuable tool for studying the local environments of resonant absorbing nuclei in a variety of condensed-matter systems. The measured absorption spectra are sensitive to small changes of the nuclear levels involved in the transition, in particular due to the monopole (local charge density), dipole (local magnetic field), and quadrupole (local electric field gradient) terms of the hyperfine interaction. Furthermore, the spectra are sensitive to the thermal motion of the nucleus about its equilibrium position through the Lamb-Mössbauer factor f. Twenty years ago it was suggested that synchrotron radiation (SR) could replace the source in Mössbauer spectroscopy.[1] The breakthrough towards this goal was achieved with the first observation of resonant nuclear Bragg scattering from ^{57}Fe in yttrium-iron-garnet.[2] Recently, nuclear forward scattering (NFS) of SR from ^{57}Fe was observed,[3] demonstrating that SR-based Mössbauer spectroscopy can be applied more generally, not being limited to specialized systems (such as single crystals that exhibit pure nuclear reflections).

In this paper we present a study of the temperature dependence of NFS from α-Fe, enriched in ^{57}Fe, in a range from 9.7 to 1048 K. The analysis of the measured time spectra leads to values for the temperature dependence of f of unprecedented precision. The sprectra also contain the temperature dependence of the magnetic field at the nucleus.

The f factor has a role in resonant nuclear scattering that is analogous to that of the Debye-Waller factor

$$e^{-2M} = \langle e^{i\mathbf{q}\cdot\mathbf{r}}\rangle^2 \approx e^{-\langle(\mathbf{q}\cdot\mathbf{r})^2\rangle} \quad (1)$$

in both nonresonant and resonant electronic x-ray scattering. Here, $\mathbf{r}$ is the instantaneous displacement vector of the atom from its mean position and $\langle\cdots\rangle$ represents a time average. Due to the explicit dependence on the momentum transfer $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$, the Debye-Waller factor reduces most strongly the intensities of high order (large $\mathbf{q}$) Bragg reflections and predicts no temperature dependence in forward scattering ($\mathbf{q} = 0$). The temperature dependence of scattering from Mössbauer nuclei is not described by the Debye-Waller factor since, unlike the electronic scattering case, which is fast on the time scale of thermal vibrations, resonant nuclear scattering is a slow process[4] and the average is taken separately for $\mathbf{k_i}$ and $\mathbf{k_f}$. This gives rise to the Lamb-Mössbauer factor

$$f = \langle e^{i\mathbf{k}_f\cdot\mathbf{r}}\rangle \langle e^{-i\mathbf{k}_i\cdot\mathbf{r}}\rangle \approx e^{-\frac{1}{2}[\langle(\mathbf{k}_f\cdot\mathbf{r})^2\rangle+\langle(-\mathbf{k}_i\cdot\mathbf{r})^2\rangle]}, \quad (2)$$

which even in forward scattering ($\mathbf{k}_i = \mathbf{k}_f$) becomes temperature dependent.

The Lamb-Mössbauer factor f contains lattice dynamics information through its dependence on $\mathbf{r}$. So apart from its importance in Mössbauer effect studies, an accurate determination of the temperature dependence of f can be valuable in the study of lattice dynamics and phase transitions. A precise measurement of f is difficult with conventional Mössbauer spectroscopy. These difficulties are discussed in numerous articles, e.g., Ref. 5, and involve background determination and source effects such

as source resonant self-absorption and imprecise knowledge of the source parameters such as its f factor.

The first study of f in Fe used conventional Mössbauer spectroscopy and was done in 1962 (Ref. 6) at two temperatures, but the internal conversion coefficient α, necessary for an absolute determination of f, was not well known at that time. Hence this measurement was used to obtain an upper limit for α through the restriction $f < 1$. In 1969, Kovats and Walker[7] studied the temperature dependence of f with particular attention to the vicinity of the α-γ transition. The uncertainties given are of order $\pm 10\%$ and no data were taken below room temperature. To our knowledge, the most recent measurement was done in the vicinity of the Curie temperature $T_C \approx 1043$ K in 1986 by Kolk *et al.*[8] The error bars shown in their Fig. 3 indicate an uncertainty of $\pm 4\%$. None of those measurements directly used the influence of f on the shape of the Mössbauer absorption spectrum,[9] but relied instead on intensity determination.

Recently, a method exploiting the line shape for the measurement of f has been developed for conventional Mössbauer spectroscopy.[10] The method described in the present work is conceptually similar in that it also uses a shape, rather than an intensity determination, to extract f. However, instead of using the line shape of an absorption spectrum, our method uses the time evolution of NFS following impulse excitation by SR. This evolution is dependent on both the local hyperfine fields and the number of coherently excited nuclei. The splitting resulting from the hyperfine fields leads to beating in the time spectra (quantum beats[11]). The number of coherently excited nuclei determines the envelope that modulates the quantum beats of the time spectrum. It is proportional to the effective thickness χ, which is given by

$$\chi = \frac{\lambda^2}{4\pi}\,\eta\, f\, L \left(\frac{1}{1+\alpha}\right)\left(\frac{2j_1+1}{2(2j_0+1)}\right), \tag{3}$$

where λ is the photon wavelength, η is the volume density of resonant nuclei, L is the sample thickness, and j_0, j_1 are the total spin quantum numbers of the ground and excited states, respectively.

Let us consider the case where the magnetic field at the nuclei in an α-Fe sample is aligned vertically. In this case the intensity $I(t)$ for the forward scattering of an incident horizontally polarized (**E**-field) SR pulse is simply given by[12]

$$I(t) \propto \left| \int_0^\infty e^{i\omega t + \frac{i}{2}\chi\left(\frac{1}{\tau(\omega-\omega_0+\delta\omega/2)-i/2} + \frac{1}{\tau(\omega-\omega_0-\delta\omega/2)-i/2}\right)} d\omega \right|^2, \tag{4}$$

where ω is the incident photon frequency, τ is the natural lifetime of the 14.4 keV resonance, and $\omega_0 \pm \delta\omega/2$ are the resonant frequencies of the two excited $\Delta m = 0$ transitions. The splitting $\delta\omega$ is proportional to the magnetic field at the nucleus. A previous measurement[12] shows the influence of χ on $I(t)$. In that experiment χ was changed by varying the sample thickness L. In the present study L was fixed and the temperature was varied, leading to changes in $I(t)$ dominated by two contributions. First, there is a change in χ resulting from the change in f. These changes are most pronounced in the time evolution when χ is considerably larger than 1. A sample thickness L resulting in a large $\chi \simeq 40$ at room temperature was chosen to enhance the influence of the changes in f on $I(t)$ both at low temperatures (where df/dT is small) and at high temperatures (where the resulting $\chi \simeq 15$ is still large). The other contribution is the change of $\delta\omega$ due to the changing magnetic field at the nucleus, resulting in quantum beats with changing beat frequency.

All our data presented here were collected using the X-25 wiggler beam line of the National Synchrotron Light Source (NSLS). In a preliminary experiment at the A-2 wiggler beam line at the Cornell High Energy Synchrotron Source (CHESS) it was found that an external magnetic field $B \geq 0.1$ T is required to guarantee sample saturation. The NSLS storage ring operated in single bunch mode with an interbunch time of 567 ns. A high-resolution polarizing monochromator[13] located downstream of a high heat load monochromator (part of the beam line) was used to define the incoming beam. Its two important output features are the energy width of approximately 10 meV resulting in an acceptable reduction of the nonresonant prompt signal, and the pure horizontal **E**-field polarization achieved by 45.1° Bragg-angle reflections. All measurements were made using the same sample, a $95 \pm 0.5\%$ enriched, polycrystalline ^{57}Fe foil. Its thickness $L = 10.57 \pm 0.13$ μm was measured by Cu $K\alpha$ x-ray absorption (using $\mu_{\rm abs} = 0.2363$ μm^{-1} for the absorption coefficient). An external magnetic field of 0.6 T was applied to align the internal magnetic field vertically. For the low temperature measurements (10–348 K) a Displex closed-cycle He cryostat was used. For the high temperature measurements (513–1048 K) a vacuum furnace was used. Thermometry was accomplished with a Si diode at low temperatures and Chromel-Alumel thermocouples at high temperatures. The detector system was the same as that used in several earlier experiments (e.g., Ref. 3).

Spectrum accumulation varied from 2 to 6 h depending on the sample temperature. With cryostat and furnace windows in place, the prompt count rate (with 30% detector efficiency) was between 0.9 and 1.8 MHz. The delayed rate was between 1 and 10 Hz (depending on the temperature) of resonant signal and 3 Hz of background in a time window from 25 to 190 ns. Background subtraction was accomplished by drawing a smooth curve under the minima of the quantum beats, since ideally they go to zero. This curve, when compared to background spectra taken with the monochromator tuned 140 meV below resonance, showed only slight differences which did not affect the values of the parameters extracted from the fit. The least-squares fits included three free parameters: f, $\delta\omega$, and an intensity scaling factor. In evaluating Eq. (4), we used an accurate analytic series expansion[14] of the

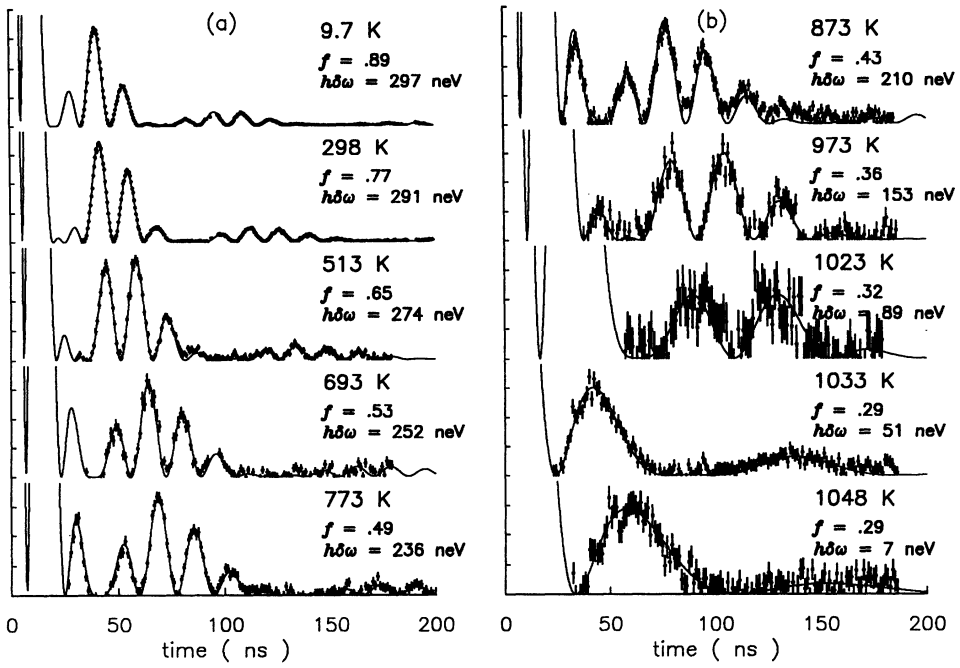

FIG. 1. Selected forward scattering time spectra from 9.7 K to 1048 K. The vertical intensity scale is different for each spectrum. Solid lines are theoretical fits whose parameters f and $\hbar\delta\omega$ are given. See Table I for uncertainties.

Fourier integral. In the analysis the literature values of $\alpha = 8.21 \pm 0.12$, $\tau = 141.11 \pm 0.20$ ns, and $\lambda = 0.860\,25$ Å wavelength[15] were used. The number density η and the thickness L at each temperature were corrected for thermal expansion using Fe lattice constants vs temperature given in Ref. 16.

To illustrate the effect of the changing f factor and splitting with temperature, some representative spectra along with their best-fit theoretical curves are shown in Fig. 1. The quantum beats resulting from the magnetic splitting are modulated by an envelope determined by χ. As the temperature increases, the envelope is shifted to later times due to the decrease in f. At the same time, the quantum beat frequency decreases reflecting the decreasing magnetic field at the nuclear site.[17] Small changes of f significantly affect the relative intensities of the quantum beat maxima, particularly in the low temperature regime, where the change of $\delta\omega$ is small compared to the change of f [see first two spectra in Fig. 1(a)]. As the temperature approaches $T_C \approx 1043$ K, the splitting decreases dramatically [see Fig. 1(b)], and a distinction between the envelope and the quantum beats can no longer be made. This can be seen in the spectrum for $T = 1033$ K. Above T_C, the energy spectrum approximates that of a single line with only an envelope modulation and no beating. Finally, it is interesting to

TABLE I. Summary of fitting results for the Lamb-Mössbauer factor f and the splitting $\hbar\delta\omega$. Also listed are the relative values of f normalized to the low temperature value.

Temperature [K]	f	$f/f_{9.7\,\mathrm{K}}$	$\hbar\delta\omega$ [neV]
9.7	0.890 ± 0.020	1	297.42 ± 0.31
50	0.886 ± 0.020	0.996 ± 0.003	297.24 ± 0.31
100	0.868 ± 0.019	0.976 ± 0.003	296.13 ± 0.31
150	0.850 ± 0.019	0.955 ± 0.003	295.44 ± 0.31
200	0.823 ± 0.018	0.925 ± 0.003	294.31 ± 0.31
250	0.796 ± 0.018	0.895 ± 0.003	292.71 ± 0.30
298	0.771 ± 0.017	0.866 ± 0.003	290.60 ± 0.30
348	0.739 ± 0.016	0.831 ± 0.003	287.40 ± 0.30
513	0.649 ± 0.015	0.730 ± 0.003	274.44 ± 0.32
693	0.526 ± 0.014	0.591 ± 0.004	252.33 ± 0.38
773	0.492 ± 0.012	0.553 ± 0.002	236.36 ± 0.31
873	0.430 ± 0.010	0.483 ± 0.002	209.67 ± 0.29
973	0.359 ± 0.010	0.403 ± 0.003	152.95 ± 0.34
1008	0.336 ± 0.012	0.377 ± 0.006	119.20 ± 0.46
1023	0.316 ± 0.012	0.355 ± 0.006	89.02 ± 0.67
1031	0.298 ± 0.009	0.335 ± 0.004	60.76 ± 0.50
1033	0.286 ± 0.008	0.322 ± 0.003	50.97 ± 0.57
1042	0.295 ± 0.010	0.332 ± 0.005	19.49 ± 1.4
1048	0.285 ± 0.008	0.321 ± 0.003	6.97 ± 0.60

compare the spectra at 693 K and 1048 K. The f factor has changed by approximately a factor of 2, but the envelope of the 1048 K measurement is nearly the same as that of the 693 K spectrum. The reason is simple. The reduction in χ by a factor of 2 has been roughly compensated by the collapse of the two $\Delta m = 0$ lines to a single line with twice the strength.

The results from the fitting of all our spectra are summarized in Table I. The uncertainties in the absolute values of f are dominated by the combined uncertainties in α, thickness L, and enrichment. They correspond to a $\sim 2\%$ effect for the relative uncertainty σ_f/f. In addition, we also have the statistical error resulting from the nonlinear least-squares fits which, when combined with the small uncertainties in the natural lifetime τ and the calibration of the electronic time-to-amplitude converter module, give a contribution to σ_f/f that varies from $\sim 0.3\%$ at low temperatures to $\sim 1.5\%$ at high temperatures where the resonant signal is weaker. It is important to note that the relative change of f defined as $f/f_{9.7\,\mathrm{K}}$ is determined to a higher precision than the absolute value of f since it does not depend on uncertainties in sample thickness, enrichment, and α. In Fig. 2, $f/f_{9.7\,\mathrm{K}}$ is plotted as a function of temperature, showing the typical flattening at low temperature due to the onset of zero point motion of the nucleus.

In Fig. 3 we plot our values of $\hbar\delta\omega$ in comparison with the early results of Nagle *et al.*[18] and Preston *et al.*[6] on a scale normalized to the room temperature value. In this plot, our values from Table I have been corrected for the external magnetic field (0.6 T) used. Below the immediate vicinity of T_C, based on superposition and the opposite directions of the internal and external fields,[19] the correction is simply the addition of the constant 5.37 neV (calculated with the knowledge of the ground and excited state gyromagnetic ratios[6]). Somewhere just below T_C, the internal magnetic field should have the same magnitude as the external field and hence they should add to zero. We did not observe such a zero crossing. To understand this, more investigation with better data close to the magnetic transition is necessary, both with and without an external field. It is also interesting to note that studies of f close to T_C done by Kolk *et al.*[8] suggest the existence of magnetoelastic effects as a consequence of the magnetic phase transition. In addition, neutron scattering measurements[20] show a strong softening of the elastic constant c_{11} at T_C, which should affect f. Detailed studies in the vicinity of T_C which could elucidate these issues are beyond the scope of the present work.

In summary, the temperature dependence of NFS of SR from the 14.4 keV Mössbauer resonance has been studied using the same α-Fe sample, enriched in ^{57}Fe, over the entire temperature range from 9.7 to 1048 K. The strength of the time domain approach of NFS with SR is well illustrated in the precision measurement of the temperature dependence of the Lamb-Mössbauer factor. This strength is a consequence of the simple and sensitive relation between the observed time evolution and the sample parameters. In addition to the method being free from making absolute intensity measurements, the broadband pulsed SR excitation removes difficulties associated with the nuclear source in conventional Mössbauer experiments. More intense SR sources and faster, low-noise detection systems will facilitate f-factor determinations and Mössbauer effect studies in general.

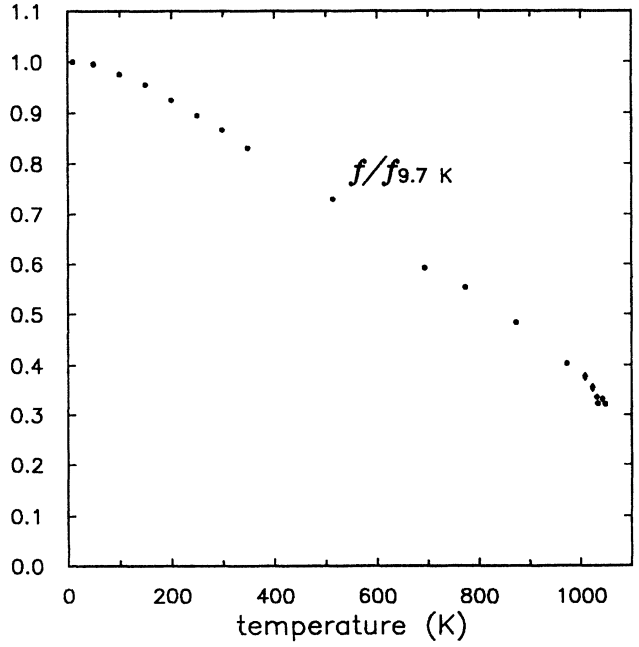

FIG. 2. Measured temperature dependence of the Lamb-Mössbauer factor f for α-^{57}Fe.

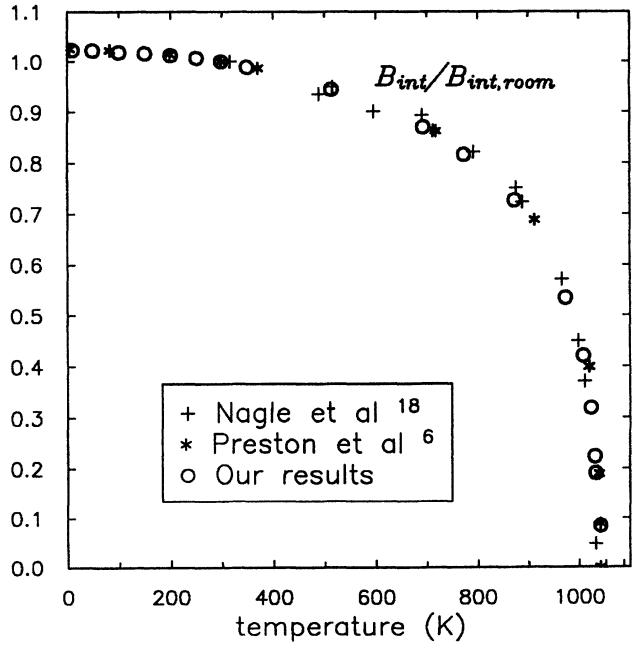

FIG. 3. The temperature dependence of the internal magnetic field B_{int} which is proportional to the hyperfine splitting. Our results from Table I, after being corrected for the applied magnetic field, are compared to the previous results of others. The vertical scale has been normalized to the room temperature value.

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