Lamb-Mössbauer factor and second-order Doppler shift of hematite

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Introduction

The recoilless fraction or Lamb−Mössbauer factor and the second-order Doppler shift (SOD) are of general interest in Mössbauer spectroscopy. Both quantities strongly depend on the binding of the resonant nucleus in the lattice and vary with material composition, lattice structure, and environmental conditions, like temperature or pressure. Also the Lamb−Mössbauer factor is closely related to the Debye−Waller factor, which is obtained from x-ray diffraction. In fact the Lamb−Mössbauer factor and the Debye−Waller factor originate from the same expression under the conditions of "slow" and "fast" scattering, respectively. Nuclear resonant scattering is "slow" because the stages of absorption and emission are well separated on a time scale given by lattice dynamics. In the case of electronic charge scattering, absorption and emission occur almost instantaneously on this time scale, and the scattering process is "fast." For this reason, the Lamb−Mössbauer factor depends only on the momentum of the incident photon, $\mathbf{k}$, whereas the Debye−Waller factor shows the same functional dependence on the momentum transfer, $\mathbf{q}$. For harmonic lattice vibrations, we obtain the relationship

$$\ln F_{DW} = \frac{q^2}{k^2} \ln F_{LM} \quad , \tag{1}$$

where we assumed that $\mathbf{k}$ and $\mathbf{q}$ point in the same direction. In the past, Lamb−Mössbauer factors have been determined mostly by conventional Mössbauer transmission spectroscopy. In this approach, the accuracy depends on precise knowledge of the area density of the resonant nuclei. Determination of this area density turns out to be the dominant source for systematic errors due to, e.g., uncertainties in the sample geometry, isotopic abundance, or mass density of the sample. Moreover, knowledge of the Lamb−Mössbauer factor of the radioactive source is required. The use of synchrotron radiation essentially eliminates errors related to source characteristics.

A nucleus that is bound in a lattice undergoes vibrational motion. Although the average velocity vanishes, the mean square velocity leads to a relativistic correction to the energy levels of the nucleus [1,2]. This energy shift is called SOD

$$\delta = -E_0 \frac{\langle \mathbf{v}^2 \rangle}{2c^2} \quad , \tag{2}$$

where E_0 is the nuclear transition energy. Conventional Mössbauer spectroscopy does not distinguish chemical isomer shift and SOD. Here we use nuclear resonant inelastic x-ray scattering (NRIXS) to measure the SOD independent of the chemical isomer shift.

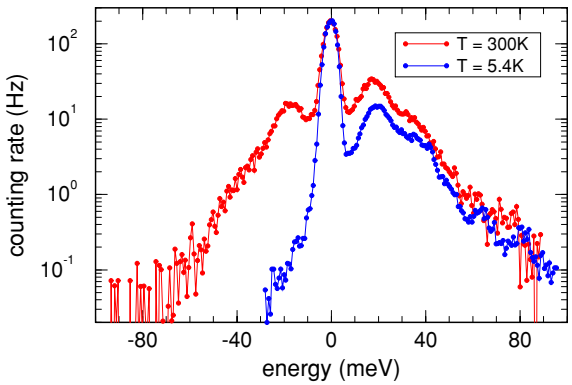

FIG. 1. NRIXS data of hematite at two different temperatures. The central peak indicates the position of the 14.4125 keV nuclear transition energy of ^{57}Fe. If the energy of the incident x-rays is below the nuclear resonance (negative energies), phonons have to be annihilated to achieve resonant excitation. At low temperatures this contribution, which is analogous to anti-Stokes lines, disappears.

Methods and Materials

In this report, we present the Lamb−Mössbauer factor and SOD from hematite (Fe_2O_3) powder for temperatures between 5.4 K and 300 K. The sample was 95 % enriched in ^{57}Fe. The data were obtained with NRIXS, where details on the scattering mechanism and evaluation procedures are given elsewhere [3,4]. The method of NRIXS including proper normalization of measured data was introduced earlier [5]. The experiments were performed in 1996 at beamline 3-ID of SRI-CAT. The high-heat-load monochromator consisted of two asymmetric silicon (111) reflections in a nondispersive setting. The first crystal was cooled by liquid gallium. A high-resolution, nested monochromator, as described earlier [6], provided an energy resolution of 5.5 meV at the 14.4125 keV nuclear transition energy of ^{57}Fe. The photon flux was approximately 5 GHz. An avalanche photodiode (APD) with an active area of 2 cm^2 was used to detect the emitted K-fluorescence radiation from the iron atoms in sample. The time delay between the output pulses of the APD detector and the bunch arrival signal that was derived from the RF of the storage ring was measured. The nonresonantly scattered radiation that appears promptly with respect to the bunch arrival signal was eliminated by counting in a time window of 30 ns to 100 ns after the arrival of the synchrotron radiation flash. The detector noise in this time window was less than 0.03 Hz. The energy of the incident radiation was tuned in steps of 0.75 meV. The samples were mounted inside a cryostat at a distance of ≈5 mm from the APD. An inclination angle of ≈10° between sam-

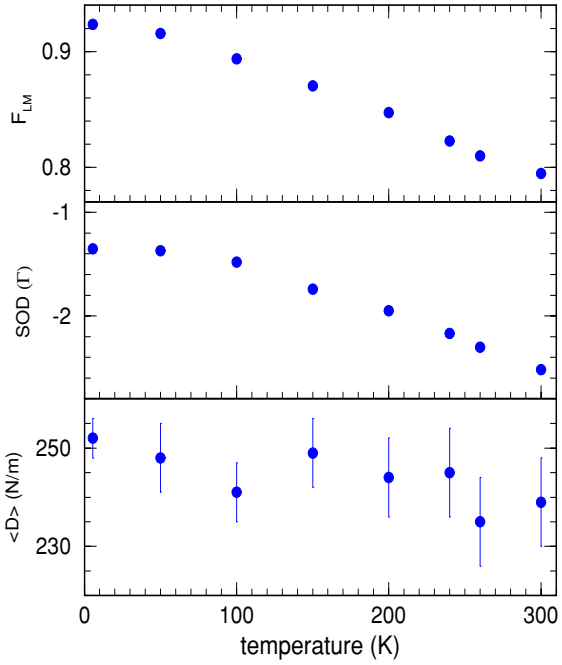

FIG. 2. Lamb–Mössbauer factor, F_{LM}, SOD, and average force constant, $\langle D \rangle$, of Fe in hematite for various temperatures. The SOD is given in natural linewidth of the excited nuclear level, $\Gamma = 4.66 \cdot 10^{-9}$ eV. If the lattice vibrations are harmonic, the average force constant is expected to be independent of temperature.

ple and incident beam increased the illuminated sample volume.

Results and Discussion

In Fig. 1, NRIXS data of the hematite sample is shown for 5.4 K and 300 K. The central peak indicates elastic scattering at the nuclear resonance energy. Side bands at lower and higher energy are explained by phonon assisted excitation of the nuclear resonance. These features are analogous to anti-Stokes and Stokes lines. The low-energy side band disappears at low temperature because phonon annihilation is no longer possible. The ratio of counting rates in low-energy and high-energy side bands is determined by the Boltzmann factor.

The moments of NRIXS spectra provide the Lamb–Mössbauer factor and SOD. In addition, average force constants and the partial phonon density of states (DOS) can be obtained. We evaluated our data using the program package PHOENIX [7]. The moments are shown in Fig. 2. The average force constant is almost independent of temperature, as one would expect for harmonic oscillations. The slight decrease with temperature is probably caused by anharmonicities that soften the lattice. The SOD decreases with increasing temperature, and the value of $-1.35(1)\,\Gamma$ for $T \to 0$ is caused by zero-point motion of the atoms. Classical theories of vibration predict proportionality of SOD and temperature. In Fig. 3, the partial phonon DOS of the iron atoms is shown. Lattice vibrations up to about 50 meV are strongly coupled to the iron sites. Vibrational modes at higher energies (65 meV and 80 meV) show small amplitudes. These are optical phonon modes that are characterized by large oscillations of the light oxygen atoms. The change of the partial phonon DOS with temperature was imperceptible. The measured response to temperature is much weaker than that of iron metal [8].

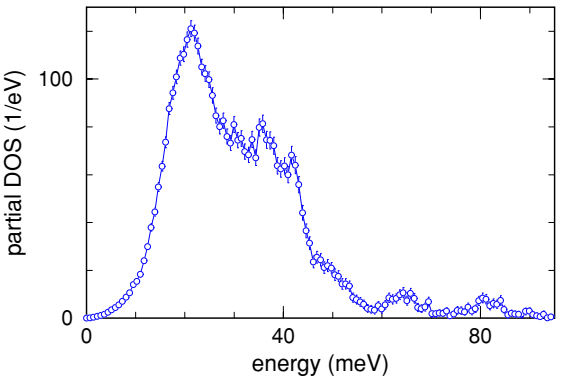

FIG. 3. Partial phonon density of states of the Fe atoms in hematite at 5.4 K. The phonon DOS was obtained from the data shown in Fig. 1.

Hematite undergoes a Morin transition around 250 K. The transition is characterized by a 90° rotation of magnetic moments. The present data does not indicate any influence of the Morin transition on the vibrational properties.

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