Observation of fluctuations in the magnetic moments of microscopic particles through the Raman scattering of Mössbauer radiation

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A frequency-shifted component has been detected in the Mössbauer spectrum of nuclei contained in magnetic FeOOH microscopic particles. This shifted component is evidence that the ^{57}Fe nuclei in an excited state undergo a transition to another hyperfine sublevel. This observation is a direct indication of fluctuation processes in the microscopic particles which were studied.

The method of Raman scattering of Mössbauer radiation, or the "selective excitation double Mössbauer (SEDM) method," as it has been called in the English-language physics literature, consists of a selective excitation of nuclear transitions and a frequency analysis of the γ rays emitted in the process. This method, which was first implemented in Ref. 1 and which was subsequently developed in more detail in Refs. 2 and 3, has not yet been adopted widely. This experimental arrangement provides a unique opportunity for directly observing a relaxation of hyperfine magnetic fields which occurs during the lifetime of the nucleus in an excited state, τ_0. Accordingly, the SEDM method is very pertinent for solving a typical problem of Mössbauer spectroscopy, where it is not possible to distinguish a relaxation from an inhomogeneous broadening of a line on the basis of the shape of the hyperfine-structure spectra. Magnetic microscopic particles and clusters, which combine a significant broadening of the hyperfine-splitting spectra with a high probability for magnetization fluctuations, are attractive as a subject of study and also for demonstrating the capabilities of the SEDM method.[4] In the present study we used microscopic crystals of goethite, FeOOH. In large volumes this is an antiferromagnet with $T_N = 393$ K, while in a microscopic-crystal form (with a crystallite size ~ 1000 Å) it exhibits anomalously broadened hyperfine-structure spectra which are strongly temperature-dependent.[5] The test sample was prepared from goethite particles grown by a technique similar to that of Ref. 5 and enriched to 95% in the isotope ^{57}Fe.

An SEDM spectrometer was assembled for determining the frequency spectrum of the Mössbauer γ radiation (Fig. 1). In this spectrometer, a single-line Mössbauer source (150 mCi of ^{57}Co:Cr), attached to a first (constant-velocity) vibrator is used to selectively excite a nuclear transition between certain hyperfine sublevels of the ^{57}Fe nuclei in the goethite. The Mössbauer γ rays emitted as a result of the decay of the nuclei excited in this fashion are energy-analyzed by a Mössbauer absorber (potassium ferrocyanide with an effective thickness $\mu t = 18$), which puts in motion a second (constant-acceleration) vibrator. The radiation which passes through the absorber is

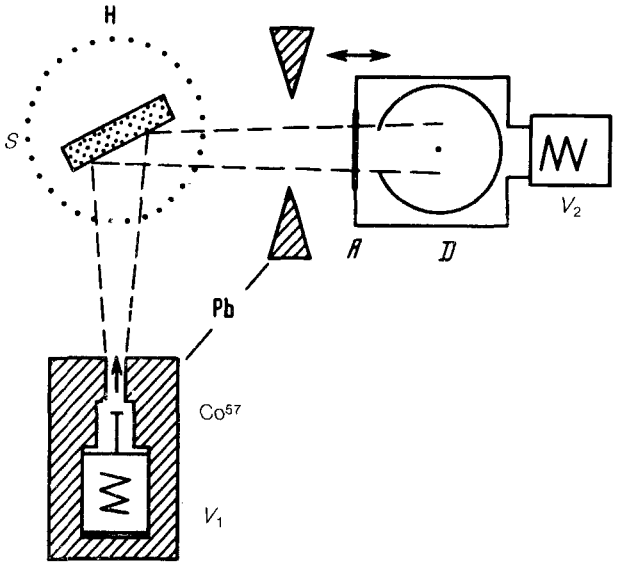

FIG. 1. Layout of the spectrometer of the selective excitation double Mössbauer method. *S*—Test sample; *H*—heater; *A*—analyzer; $V_{1,2}$—vibrators; D—detector.

detected by a gas-filled proportional counter filled with xenon. The test sample can be placed in an oven designed for this particular scattering geometry.

In the experiments the Doppler shift of the line of the source should be chosen in such a way that the transition $-1/2 \rightarrow -3/2$ is selectively excited in the resonant nuclei of the scatterer. If processes associated with the dynamics of the hyperfine fields do not occur in the sample, it constitutes a passive reflector of the primary γ radiation (the transition $-3/2 \rightarrow 1/2$ is forbidden by the selection rules), and the scattering should occur in a purely elastic fashion. If, on the other hand, the hyperfine fields in the sample participate in fluctuation processes, the scatterer should contribute certain changes to the γ spectra. The outward manifestations of these changes will be some set of frequency-shifted hyperfine components; their form will depend on the particular scattering mechanism.[6,7]

In our case we would expect that the system would have a broad distribution of relaxation times as a result of the scatter of the particles in volume. Accordingly, the observed SEDM spectrum should consist simultaneously of a purely elastic component, corresponding to the fraction of particles with a slow relaxation, $\omega_{\text{REL}} \ll \tau_0^{-1}$, and an inelastic component, corresponding to crystallites with frequencies exceeding $\sim 10^6$ s^{-1}. For particles with very fast relaxation processes (for which the hyperfine structure collapses, as we know), however, the selective excitation occurs along the edge of an isolated absorption line which becomes progressively narrower, away from a resonance. Accordingly, the contributions from the fast-relaxation particles in the SEDM spectrum should have a vanishing weight, and the sensitivity of the method will actually be limited to a frequency window $\sim 10^6$–10^9 s^{-1}. As the sample is heated, the distribution of relaxation frequencies will shift with respect to this observation window, so the observed SEDM spectra should be transformed in a substantial way.

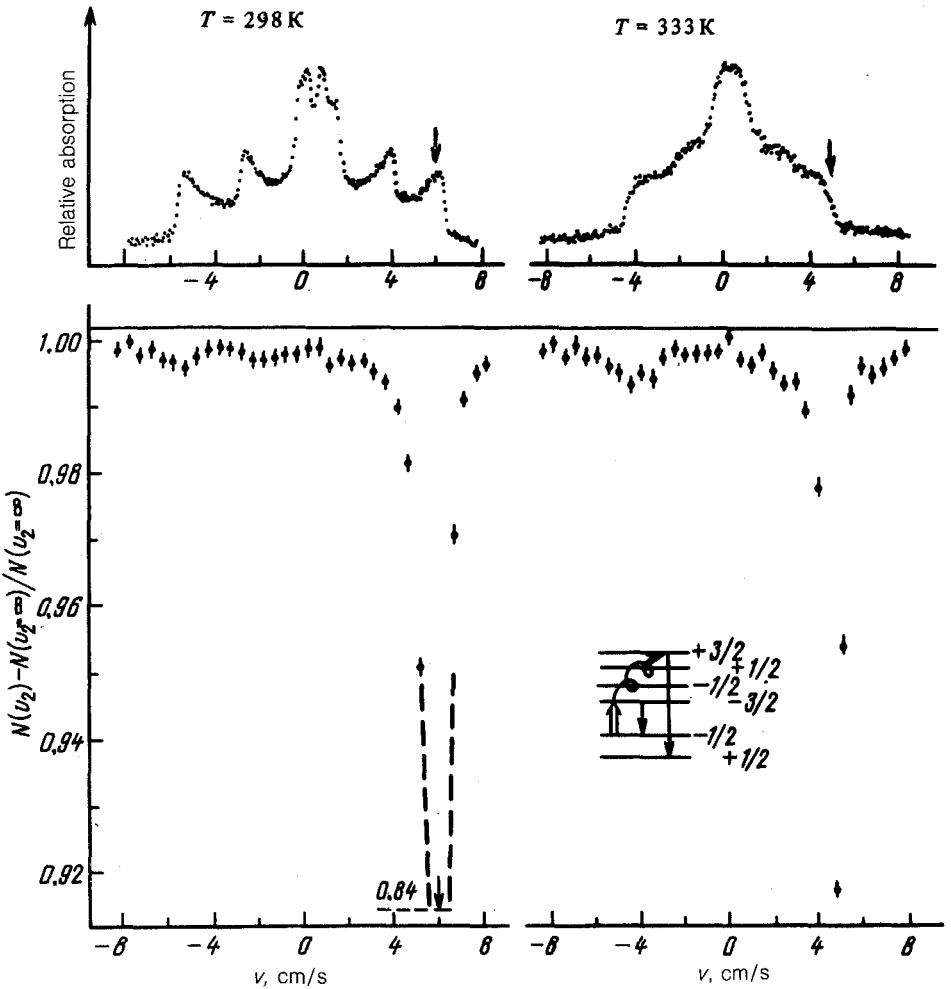

FIG. 2. (a) Absorption spectra and (b) SEDM spectra of goethite at various temperatures. The inset shows the scheme of transitions among the energy sublevels of the ^{57}Fe nuclei during the simplest type of relaxation: an abrupt flipping of the magnetic moment and of the hyperfine field at the Mossbauer nucleus, which follows the moment.

Figure 2 shows SEDM spectra of a goethite sample at $T = 298$ K and $T = 333$ K, along with the corresponding absorption spectra. The selective excitation was carried out at the energies marked by the arrows in this figure. A common feature of the absorption spectra is a pronounced broadening of the hyperfine lines; at 333 K, the spectrum is in fact tending toward a characteristic relaxation shape. With regard to the SEDM spectra, we note that the first of them is dominated by the elastic component, while the traces of relaxation are barely discernible. This result means that the situation with regard to the dynamics of the hyperfine fields at $T = 298$ K in the sample is basically static or quasistatic in comparison with the time τ_0. The broaden-

ing observed in the absorption spectrum should thus be linked primarily with the "instantaneous" nonuniform distribution of hyperfine fields. In this case the relative number of microscopic particles which have a high relaxation rate is still low, but it should increase with increasing temperature. Indeed, at $T = 333$ K the SEDM spectrum acquires a clearly expressed broad distribution of frequency-shifted spectral components. This result means that at this temperature the hyperfine fields have enough time, over the lifetime $\tau_0 = 140$ ns, to change markedly at what is now a substantial number of resonant nuclei. Judging from the shape of the spectrum, flippings of the hyperfine fields are the most probable processes. Note also that the elastic component is smaller by a factor of 2.5 than in the case $T = 298$ K; this decrease is an obvious consequence of the decrease in the relative number of "slow" particles with increasing temperature.

In summary, this SEDM experiment proves that the anomalous shape of the absorption spectra of goethite microscopic particles may be caused to a significant extent by a relaxation of magnetic moments, in addition to the static spread of hyperfine fields. This conclusion runs into serious contradictions with the present interpretation,[5] which is based on a mechanism of an interparticle interaction. It is also pertinent to note that, in contrast with the previous case, of the observation of shifted, comparatively narrow hyperfine components, corresponding to a purely abrupt flipping of the hyperfine magnetic field,[7] in our experiments the inelastic part of the SEDM spectrum has a very large width. The probable explanation here is that in this situation the Mössbauer nuclei are embedded in the magnetic microscopic crystal, and the hyperfine magnetic field is proportional to the projection of the collective magnetic moment of the sublattice onto the quantization axis; i.e., this field takes on a continuous series of values.[8] The SEDM method thus makes it possible not only to detect the very fact that the hyperfine fields are exhibiting a dynamic behavior but also to identify the actual mechanism for the relaxation of the magnetic moments. A detailed study of this topic is to be carried out.

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