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RELAXATION PHENOMENA IN MÖSSBAUER SPECTRA OF MAGNETICALLY ORDERED ERBIUM IONS IN $\mathrm{ErFeO_3}$

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(Received 26 September 1966)

Recent low-temperature Er^{166} Mössbauer data, reported by Wiedemann and Zinn in a study of $\mathrm{ErFeO_3}$, are interpreted in terms of spin-relaxation effects. This appears to be the first time relaxation effects have been observed in the Mössbauer spectra from a magnetically ordered system.

Wiedemann and Zinn[1] have recently reported unusual Mössbauer spectra for Er^{3+} in $\mathrm{ErFeO_3}$, at sample temperatures below the Néel temperature (4.3°K)[2] of the erbium sublattice (the ferromagnetic iron-lattice Curie temperature is[3] 640°K). The Mössbauer transition employed was the $2^+ \rightarrow 0^+$, 80.6-keV gamma transition of Er^{166}. We show below that these spectra may be readily interpreted in terms of spin-relaxation effects. The $\mathrm{ErFeO_3}$ system, therefore, appears to be the first reported example of such behavior in the Mössbauer-effect (ME) spectra from a magnetically ordered system.

The spin-relaxation interpretation differs from that of Wiedemann and Zinn, who suggested that there are several magnetically inequivalent Er^{3+} sites in $\mathrm{ErFeO_3}$ and that the effective magnetic fields acting on the erbium nuclei in the various sites have different temperature dependences, thus leading to the observed spectra.[1] However, crystal structure,[4] magnetic structure,[2] and recent ME spectra[5] of Dy^{3+} in isomorphous $\mathrm{DyFeO_3}$ argue for at most two magnetically inequivalent Er^{3+} sites. The magnetic and Mössbauer data are, in fact, well represented by a single magnetic rare-earth site. With this assumption relaxation spectra were computed and excellent agreement between experiment and theory was obtained.

In order to discuss the rare-earth hyperfine fields, it is first necessary to decide on a model for the pertinent electronic properties of the magnetic erbium ions. In the temperature range of interest, the erbium ions are exposed to an exchange field made up of two contributions: (1) an effectively constant exchange field from the iron atoms, and (2) at $T \leq T_C(\mathrm{Er}^{3+})$, an induced molecular field in the erbium sublattice arising from exchange between the rare-earth ions. Near the transition temperature, the constant iron field dominates the erbium exchange field. The induced field in the erbium sublattice which gives rise to collective effects is consequently of less importance here than in the usual molecular field case. Therefore, within 20% of the erbium Curie temperature, i.e., within the temperature range of the observed relaxation effects in $\mathrm{ErFeO_3}$, a modified Weiss molecular-field model is expected to give a good description of the magnetic properties and hfs of the erbium ions. (It should also be noted that it is well known that sharp levels exist in rare-earth ions in ferromagnetic insulators, so that the assignment of "electronic transitions" between, say, exchange-field-separated levels of a Kramers doublet can be made in an unambiguous fashion.) At lower temperatures, where the erbium exchange field dominates the iron field, collective effects may be expected and the spin-wave approximation would be more appropriate for the discussion of ferromagnetic relaxation effects in Mössbauer hfs.[6,7]

A suitable approximation to relaxation effects within the molecular-field model may be obtained by assuming a simple dominant electronic relaxation, characterized by the selection rules $\Delta S_z = \pm 1$, $\Delta l_z = 0$. Thus a Mössbauer transition ω_A (see Fig. 1) will "change its energy" and become ω_B as a result of an electronic spin flip. The effect of spin relaxation on Mössbauer spectra in paramagnetic as well as ferromagnetic systems has been discussed in many recent publications.[6-13] Experimentally, however, relaxation effects have been reported only in paramagnetic systems[13-15] which in some cases were exposed to an external magnetic field.[13,15]

The influence of the relaxation process $\omega_A \rightleftarrows \omega_B$ on the Mössbauer spectra can be calculated, using the modified Bloch-equations method, in a very simple manner with closed-form formulas.[13] Thus, the part of the Mössbauer spectrum describing the behavior of the transitions ω_A and ω_B is given by

$$I_{AB}(\omega) = K\frac{(1+\tau\Gamma)P+QR}{P^2+R^2} \tag{1}$$

with

$$P = \tau[\Gamma^2-(\omega_0-\omega)^2+\delta^2]+\Gamma,$$

$$R = (\omega_0-\omega)(1+2\tau\Gamma)+(p_A-p_B)\delta,$$

$$Q = \tau[\omega_0-\omega-(p_A-p_B)\delta],$$

and

$$\omega_0 = \tfrac{1}{2}(\omega_A+\omega_B), \quad \delta = \tfrac{1}{2}(\omega_A-\omega_B).$$

K is an intensity normalization factor (proportional to the nuclear transition probability of the transitions ω_A and ω_B), τ is the spin relaxation time, and Γ is half the natural Mössbauer linewidth. p_A and p_B are the relative probabilities of ω_A and ω_B. From Fig. 1 it is clear that $p_A/p_B = \exp(\Delta/kT)$ and $p_A + p_B = 1$. We used these formulas to calculate relaxation spectra of $\mathrm{Er^{166}}$ in $\mathrm{ErFeO_3}$ at 1.5, 3.4, and 4.2°K. It was assumed that the relaxation time τ is about the same at all these temperatures. However, relative populations will change. It was found that $\tau = (2.0 \pm 0.5) \times 10^{-11}$ sec is the region where the calculated spectra resemble the experimental spectra. Then for each spectrum (corresponding to a different temperature) the ionic Zeeman splitting Δ was adjusted for the best fit to experiment (Fig. 2). The values obtained were $\Delta = 6.8 \pm 0.8$, 4.4 ± 0.5, and 2.8 ± 0.5°K for the spectra at 1.5, 3.4, and 4.2°K, respectively.

The agreement between theory and experiment, as shown in Fig. 2, is quite satisfactory and illustrates well the usefulness of the molecular-field approach to relaxation in $\mathrm{ErFeO_3}$.

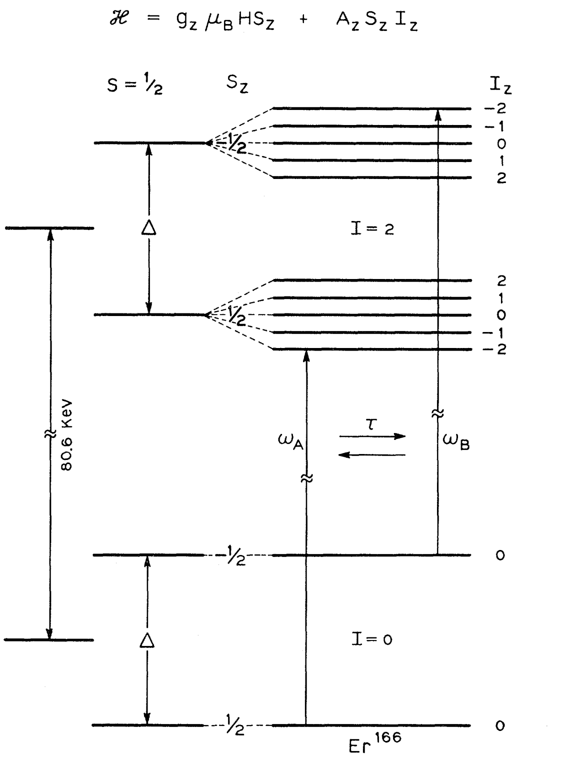

FIG. 1. Energy-level diagram of the hyperfine interaction of the ground Kramers doublet of trivalent $\mathrm{Er^{166}}$ in $\mathrm{ErFeO_3}$.

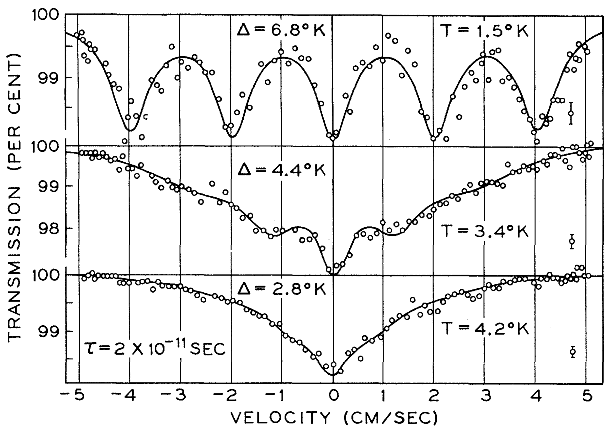

FIG. 2. Experimental Mössbauer data on Ref. 1 which are fit by solid curves computed from relaxation theory. A single relaxation time, $\tau = 2\times10^{-11}$ sec, and temperature-dependent molecular field splittings, Δ, were assumed.

It should be noted that at 1.5°K, or more generally as $T \rightarrow 0°K$, where a spin-wave formalism is more appropriate, the effects of spin fluctuations often turn out to be small[6,7] and the normal five-line effective field pattern will result. Thus the molecular-field model, though lacking rigorous justification, leads to the expected pattern in the low-temperature limit.

From the values of $\Delta(T)$ one may estimate the strengths of the molecular fields acting on Er^{3+} in $ErFeO_3$ at temperatures below T_N. In the molecular-field approximation, $\Delta(T)$ is given by

$$\Delta(T) = g_z \mu_B \{H_m^{Fe} + H_m^{Er} \tanh[\Delta(T)/2kT]\}, \quad (2)$$

where H_m^{Fe} is the molecular field from the iron sublattice and H_m^{Er} is the molecular field at 0°K due to the Er sublattice. Since the Mössbauer results yield $g_z = 12.6$ ($A_z = 2680$ Mc/sec), the values of H_m^{Fe} and H_m^{Er} were estimated to be $H_m^{Fe} = 1.3 \pm 0.4$ kOe and $H_m^{Er} = 7.0 \pm 1.0$ kOe. This value of H_m^{Fe} is in good agreement with that given in Ref. 3 (1 kOe).

In conclusion, we may say that although this is the first case in which relaxation effects on Mössbauer spectra were observed in a magnetically ordered system, the present case is by no means unique. We note that as approximate criteria for this effect it is sufficient that τ be of the order of ω_L^{-1} and that the exchange splitting of the doublet levels be of the order of kT. Under these conditions population changes or changes in τ will have their greatest effect on the Mössbauer spectra.

It should finally be noted that the ME in such systems offers a direct and extremely simple determination of the effective electronic relaxation time in a magnetically ordered environment.

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