Position of the Zeeman lines in the Mössbauer spectra of paramagnetic materials

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The energy positions of the mixed electron-nuclear transitions (Z-lines) are analyzed as a function of the external magnetic field strength ($H < 200$ Oe) for Mössbauer spectra of the paramagnetic hyperfine structure of $^{57}Fe^{3+}$ impurity ions in an $Al(NO_3)_3 \cdot 9H_2O$ single crystal. Analysis of the experimental data indicates that weak random magnetic fields inside the crystal are responsible for the characteristic asymmetry of the Z-lines and tend to keep the lines in the same position. The random fields are also responsible for the novel dependence $E = (E_0^2 + bH_2)^{1/2}$, which is reported here for the first time.

I. INTRODUCTION

New lines lying far beyond the range of Doppler velocities typical for Fe^{3+} were found in Refs. 1 and 2, where Mössbauer spectra of ^{57}Fe nuclei in an $Al(NO_3)_3 \cdot 9H_2O{:}Fe^{3+}$ aluminum nitrate single crystal were studied in weak external magnetic fields $H \sim 10^2$ Oe. The physical origin of these lines is as follows. In a weak magnetic field the Zeeman energy associated with the interaction of the electron and Fe ion moments is comparable to the energy of the magnetic hyperfine interaction, and in this case both the ground and the excited nuclear states have a mixed electron-nuclear structure. If the nuclear transition alters the state of the electron shell as well as the state of the nucleus, the Zeeman interaction may supply some of the energy needed for the transition. For this reason the new lines were called Z-lines in Ref. 3.

The presence of mixed electron-nuclear states is a necessary but not a sufficient condition for Z-lines to be observed. A detailed theoretical analysis reveals that Z-lines of appreciable intensity can be present only when the symmetry of the crystal field is such that the lowest term of the paramagnetic ion splits into Kramers doublets whose $\hat{g}$ and $\hat{A}$ tensors are markedly anisotropic. This is precisely the situation for aluminum nitrate.[4] In addition, the angle of the magnetic field **H** relative to the principal axes of $\hat{A}$ must also lie within a certain rather narrow range.

The problem of analyzing how the energy position E of the Z-lines depends on the orientation of **H** relative to the crystallographic axes was considered in Ref. 3. Rather surprisingly, E was found to be much less sensitive than the line intensities to the direction of **H**. On the other hand, E varied greatly when **H** was decreased along a constant direction. The experimental results for the three fields **H** = 50, 65, and 78 Oe are closely approximated by the formula

$$E = (E_0^2 + bH^2)^{1/2}, \tag{1}$$

where E_0 is the unshifted ($H = 0$) position of the outermost line in the spectrum and b is a numerical constant.

The physical mechanisms for this behavior of the Z-lines were elucidated in Ref. 3. Weak random magnetic fields $H_r \sim 1$–10 Oe were found to play a decisive role in forming the Z-lines; these fields are generated by the magnetic moments of nearest-neighbor paramagnetic ions and nuclei. Instead of causing line broadening of the type commonly found in EPR, NMR, and other resonance spectra, these fields stabilize the positions of the Z-lines when the direction of the external field is changed. In addition, they are responsible for the rather complicated dependence (1) of E on H—the position of the hyperfine structure (HFS) lines in Mössbauer spectra is generally assumed to be determined by the energy difference between the sublevels of the ground and excited nuclear states.

In the present work we carried out careful experimental tests of Eq. (1) for a wide range of fields. This project was undertaken jointly by the I. V. Kurchatov Institute of Atomic Energy (IAÉ) and the Center for Nuclear Studies (KFA, at Julich, West Germany). Two single-crystal aluminum nitrate samples were used. Figure 3 shows the results, which are seen to agree closely with the predictions of the theory, which we will briefly describe in Sec. 2.

2. THEORY

The FHS spectra for an isolated paramagnetic ion are determined by the familiar hyperfine interaction between the ion nucleus and the electron shell, described by the Hamiltonian $\mathscr{H}_{hf} = A\,\mathbf{IS}$, and the Zeeman interaction between the ion magnetic moment and the field **H**, described by $\mathscr{H}_z = \mu_B g\mathbf{HS}$. (The direct Zeeman interaction of the nucleus with **H** can be neglected for the fields $H \sim 100$ Oe of interest to us.)

The interaction of the electron shell with the electric fields inside a crystal splits the ground-state term of the ion into a series of sublevels. These sublevels are doubly degenerate (Kramers doublets) for ions with half-integer spin, and for each doublet the original hyperfine and Zeeman interactions are transformed and described by tensors, so that the effective spin Hamiltonian can be written in the form

$$\mathscr{H}^{(i)} = \mathscr{H}_{hf}^{(i)} + \mathscr{H}_z^{(i)} = \hat{A}^{(i)}\mathbf{IS'} + \mu_B \hat{g}^{(i)}\mathbf{HS'}. \tag{2}$$

The tensors $\hat{A}$ and $\hat{g}$ may be highly anisotropic for certain crystal field symmetries.

The Hamiltonian (2) completely determines the hyperfine structure of both the ground-state and excited nuclear levels. For sufficiently strong fields ($\sim 10^3$ Oe for $^{57}Fe^{3+}$) the Zeeman interaction is usually much stronger than the hyperfine interaction, and the latter can be treated by perturbation theory. The spectra can thus be described in terms of a suitable effective hyperfine magnetic field whose magnitude depends on the direction of $\mathbf{H}$ (Ref. 5). The state of the electron shell of course remains unchanged during the nuclear transition, and the effective hyperfine field formalism can accommodate the vast majority of the experimentally observed spectra for both paramagnetic and magnetically ordered materials.

The transformation of the spectral lines as the external field $\mathbf{H}$ decreases is generally accompanied by substantial broadening due to weak random fields present in the crystal.[6] A special situation arises when the tensors $\hat{A}$ and $\hat{g}$ are highly anisotropic (as they are for Fe^{3+} in aluminum nitrate). We analyze this situation by expressing the Hamiltonian (2) in a coordinate system for which $\hat{A}$ and $\hat{g}$ are diagonal:

$$\mathscr{H}^{(i)}=\mu_B(g_{xx}^{(i)}S_x'H_x+g_{yy}^{(i)}S_y'H_y+g_{zz}^{(i)}S_z'H_z)$$
$$+A_{xx}^{(i)}S_x'I_x+A_{yy}^{(i)}S_y'I_y+A_{zz}^{(i)}S_z'I_z. \quad (3)$$

Here $i = 1, 2, 3$ is the number of the Kramers doublet, and for definiteness we choose a doublet with

$$A_{yy}\gg A_{xx}, \ A_{zz}, \quad g_{yy}\gg g_{xx}, \ g_{zz}. \quad (4)$$

The assumption (4) allows us to neglect terms containing the small A-components in the Hamiltonian (3); however, these terms cannot be omitted from $\mathscr{H}_z$, because their relative contribution depends on the direction of $\mathbf{H}$. We will be interested in the case when $\mathbf{H}$ is almost parallel to the plane corresponding to the small g-components (the xz plane in our case). The Hamiltonian (3) then simplifies to

$$\mathscr{H}=\mu_B(g_{xx}S_x'H_x+g_{zz}S_z'H_z+g_{yy}S_y'H_y)+A_{yy}S_y'I_y. \quad (5)$$

It is easy to see that the nuclear spin operator I_y in (5) is a constant of the motion; we can therefore derive the simple expression

$$E_{M,\,\sigma}=\sigma[\mu_B^2(g_{xx}H_x+g_{zz}H_z)^2+(\mu_Bg_{yy}H_y+A_{yy}M)^2]^{1/2} \quad (6)$$

for the level energies, where M is the quantum number for the operator I_y, and σ is the projection of the electron spin on an axis $\mathbf{n}$ whose direction depends both on M and on $\mathbf{H}$. The observed position of the spectral lines is of course given by the energy difference between the excited and ground-state nuclear states:

$$E_{M,\,\sigma\to M_0,\,\sigma_0}=\pm(E_{M,\,\sigma}\mp E_{M_0,\,\sigma_0}). \quad (7)$$

We will now examine the effects of the random magnetic fields. Expression (6) shows that a small change in the projection H_y can substantially alter the position of each of

the energy levels of the mixed electron-nuclear system of the $^{57}Fe^{3+}$ ion. Indeed, estimates show that a change in H_y by 1 Oe suffices to shift the levels by $\sim 10\Gamma$, where Γ is the natural width of the Mössbauer line. However, it is possible for the shifts in the ground and excited states to cancel one another under certain conditions, so that the positions of the lines are "stabilized." We have the obvious condition

$$\partial E_{M,\,\sigma\to M_0,\,\sigma_0}/\partial H_y=0 \quad (8)$$

for this to occur; (8) is satisfied when

$$H_y=H_y^0=-(A_{yy}M+A_{yy}^0M_0)/2\mu_Bg_{yy}. \quad (9)$$

We then get an expression for E in (7) which is of the form (1) with

$$b=\mu_B^2(g_{xx}^2\cos^2\alpha+g_{zz}^2\cos^2\gamma), \quad (10)$$

where α and γ are the angles between $\mathbf{H}$ and the x and z axes.

The line positions given by (7) lie outside the usual velocity range for Mössbauer spectra, which is given by the simple expression

$$E_0=\tfrac{1}{2}(A_{yy}M-A_{yy}^0M_0),$$

and the excess energy is contributed by the Zeeman interaction of the electrons with the external field.

The effects of the random magnetic fields on the Z-lines are quite distinctive. The components H_{ry} produced by the random fields are distributed as shown in Fig. 1. The peak of the distribution corresponds of course to the y-component H_y of the external field. If H_y coincides with H_y^0 (curve a) then the conditions are optimal for observing the Z-lines. If H_y differs slightly from H_y^0, the situation can be described as follows. The Z-line for ions acted upon by the resultant field $\mathbf{H}_s = \mathbf{H} + \mathbf{H}_r$ is greatly broadened near the distribution peak and cannot be observed. On the other hand, the ions that experience a field H_s with $H_s \approx H_y^0$ (on the tail of curve b, Fig. 1) will give a distinct Z-line in the same position as for case a), but the intensity will be less. Rotation of $\mathbf{H}$ by a small angle will therefore alter only the line intensity and will leave the position unchanged. The weak random magnetic fields thus stabilize the position of the Z-line in a novel way which to our knowledge is unique. On the other hand, Eq. (1) implies that the position of the Z-line is sensitive to the magnitude $H = |\mathbf{H}|$.
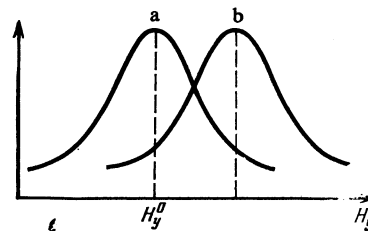

FIG. 1. Sketch showing distribution of the y-component of the random magnetic field $\mathbf{H}_r$ for two values of the y-component of the external field: a) $H_y = H_y^0$; b) $H_y \neq H_y^0$.
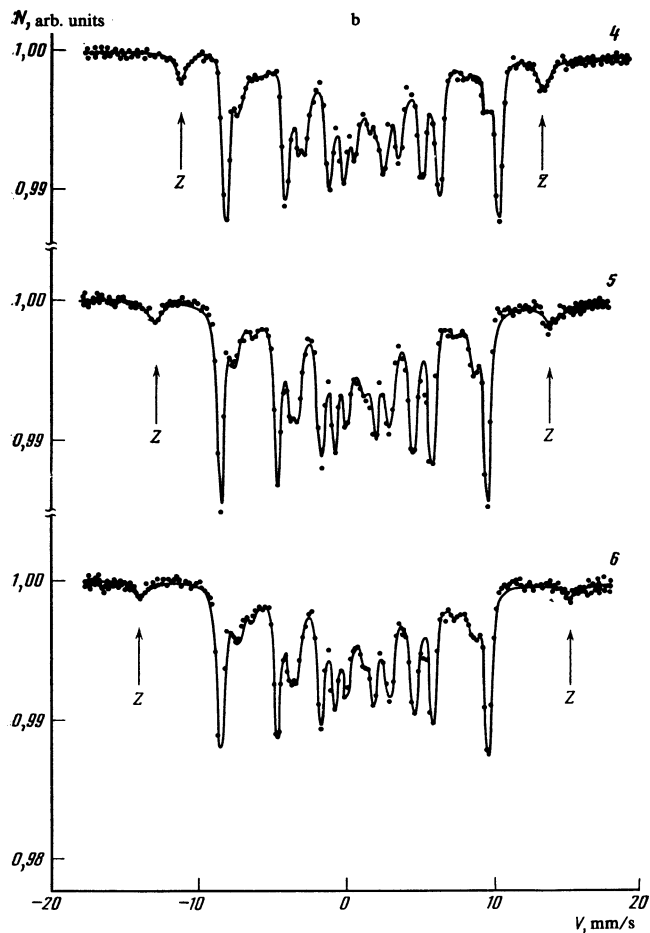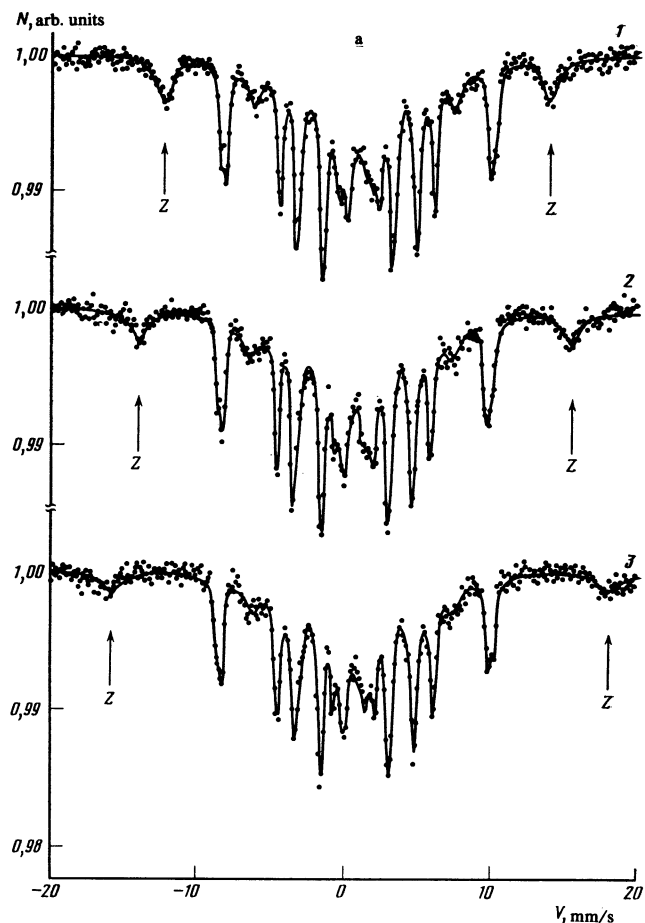
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FIG. 2. Mössbauer spectra for ^{57}Fe nuclei in an $Al(NO_3)_3 \cdot 9H_2O{:}Fe^{3+}$ aluminum nitrate single crystal at $T = 4.2$ K for several orientations (a, b) and magnitudes of the external magnetic field H. a) results recorded at IAÉ: 1) $H = 110$ Oe; 2) $H = 142$ Oe; 3) $H = 171$ Oe. b) results recorded at KFA: 4) $H = 114$ Oe; 5) $H = 150$ Oe; 6) $H = 175$ Oe. The solid traces give the best (least-square) fit to the experimental points.
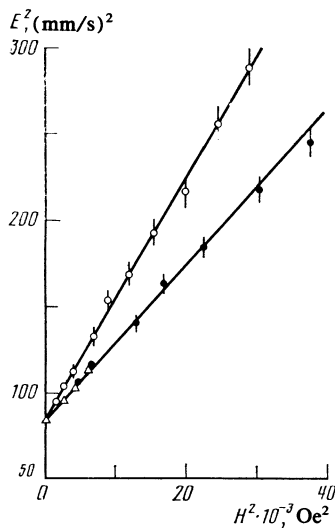

FIG. 3. Position of the Z-lines as a function of the magnitude of the external field H according to Eq. (1): the light and dark circles O and ● show results found at IAÉ and KFA, respectively; the open triangles △ give data from Ref. 3.

3. EXPERIMENT

Z-lines in the Mössbauer spectra of $Al(NO_3)_3$ $\cdot 9H_2O{:}Fe^{3+}$ single crystals were observed previously in Refs. 1–3. For the most part, Eq. (1) describes the positions of the Z-lines in the spectra in Ref. 3, which were recorded for several fields H. However, because those experimental results were too incomplete to establish the unusual dependence (1) unambiguously, we supplemented them by systematically recording spectra for a wide range of H. The experimental method and the technique used to fabricate the samples are described in Refs. 2 and 3.

Figure 2a, b shows some typical spectra recorded at IAÉ and KFA. Figure 3 shows the corresponding data for the position of the Z-lines as a function of the magnitude of the external field.[2] Both results are in excellent agreement with (1). The slopes of the lines $E^2(H^2)$ differ because H made different angles with the x, z axes of the hyperfine interaction tensor, so that according to Eq. (9) the values of b were different.

We thus have convincing experimental support for the

dependence (1), and thus also for the role played by the random magnetic fields. We note that the independence of the Z-line positions on the direction of H was already established experimentally in Ref. 3. The small changes in the line positions observed there as H changed direction were due solely to the angular dependence of the factor b and have no bearing on the basic dependence (1).

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²⁾We note that in terms of the hyperfine magnetic field acting on the ^{57}Fe nucleus, the maximum observed splitting (the distance between the outermost lines of the spectrum) is equal to $H_{hf} > 10^6$ Oe ($\Delta v \approx 34$ mm/s).

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