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Observation of second-order quadrupole shift in Mössbauer spectrum of amorphous YIG (yttrium iron garnet)

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A previously unsuspected quadrupole shift of the nuclear Zeeman lines in amorphous magnets has been observed by ^{57}Fe Mössbauer spectroscopy in speromagnetic amorphous yttrium iron garnet at 4.2 K. The distinctive shift pattern is shown to arise theoretically as a second-order perturbation of the Zeeman levels by the distribution of electric field gradients in the amorphous state. It is observed to have a form which agrees quantitatively with theoretical expectation if the relative orientation of the electric-field-gradient axes and the hyperfine-field direction at each iron site is random.

In iron-containing amorphous materials the ^{57}Fe Mössbauer spectrum at high temperatures consists of a broad-line doublet.[1–6] The shape and separation of the two lines are measures of the electric-field-gradient (EFG) distribution at the iron-nuclear sites via the quadrupole splitting (QS) of the excited nuclear state involved in the Mössbauer resonance. For temperatures below the spin-ordering or spin-freezing temperature this doublet evolves gradually into the familiar low-temperature six-line Zeeman pattern for iron which results from the hyperfine-field splitting of both the ground and excited nuclear levels. At very low temperatures for which the electronic magnetic moments approach their saturation values, it is a common dictum of the amorphous Mössbauer literature that the effects of the quadrupole energy are now contained only in the linewidths and line shapes of the six Mössbauer lines (where they combine with additional broadening contributions from the distribution of isomer shifts and of hyperfine fields to determine the precise details of Mössbauer line shape) and not in their positions.[2,7–11] In fact, a confirmation of the absence of quadrupole contributions to line position is usually interpreted as evidence that the material under observation is truly amorphous rather than microcrystalline. In fact, the vanishing of the first-order shift is only dictated by the amorphous state in ferromagnets where it implies a random orientation of EFG axes with respect to a unique spin direction. In speromagnets, for which the spin directions are random, it is quite possible for local EFG to influence local spin orientation (as it does in powders) and produce a nonzero first-order shift.

In this paper we wish to establish that the low-temperature quadrupole contributions to line position vanish in amorphous materials, if at all, only in a first-order perturbational approximation and that an interesting shift pattern for the six Mössbauer lines, with the symmetry $-a,+b,-b,+b,-b,+a$, is predicted to be present in second order. We also report the first measurement and observation of such a shift, which has been obtained at 4.2 K in amorphous speromagnetic $Y_3Fe_5O_{12}$, yttrium iron garnet (a-YIG). A vanishing first-order shift combined with an experimentally determined ratio $a/b \approx 3$ confirms that local EFG has negligible influence on local spin direction in speromagnetic a-YIG.

Theoretically, we calculate the eigenvalues of both iron-nuclear Mössbauer levels in the combined presence of an EFG and a spontaneous magnetic field at a probe site in an amorphous environment. In ^{57}Fe the ground nuclear level G has nuclear spin quantum number $I=\frac{1}{2}$ and is therefore perturbed only by the hyperfine field H. Defining a coordinate system XYZ, with H parallel to Z, enables us to write the ground-state Hamiltonian

$$H_G=-g_G\mu_N H I_Z \ , \tag{1}$$

where $g_G=+0.1805$ is the ground-state nuclear g factor[12] and $\mu_N=5.0508\times10^{-24}$ erg/G is the nuclear magneton. It can be immediately diagonalized to provide ground-state eigenvalues

$$\begin{aligned} E_2^G&=+(\tfrac{1}{2})g_G\mu_N H \ , \\ E_1^G&=-(\tfrac{1}{2})g_G\mu_N H \ . \end{aligned} \tag{2}$$

The excited nuclear level E has $I=\frac{3}{2}$ and possesses a nuclear quadrupole moment Q which is perturbed by the local EFG. We define this EFG by its components V_{xz}, V_{yy}, V_{zz} along its principal axes x,y,z which are related to XYZ via polar angles θ and ϕ in the form

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \\ -\sin\theta & \cos\phi & 0 \\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} . \tag{3}$$

The quadrupole Hamiltonian in system x,y,z has the familiar form

$$H_Q = \frac{e^2Qq}{4I(2I-1)} \times [3I_z^2 - I(I+1) \mp \eta(I_x^2 - I_y^2)] , \tag{4}$$

in which $I=\frac{3}{2}$, $q=V_{zz}/e$ where V_{zz} is the EFG component of largest magnitude, $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$, and $\eta=(V_{xx}-V_{yy})/V_{zz}$. In the absence of a magnetic field the Hamiltonian H_Q is readily diagonalized to give QS eigenvalues

$$E_Q = \pm 3q'(1+\eta^2/3)^{1/2} , \tag{5}$$

in which $q'=e^2Qq/12$. If we now introduce the field energy $-g_E\mu_N H_Z$, where[13] $g_E=-0.1030$, then the total Hamiltonian for level E becomes

$$H_E = H_Q - g_E\mu_N H I_Z , \tag{6}$$

and in general requires numerical diagonalization. If, however, H_Q can be treated as a perturbation of $H_0=-g_E\mu_N H I_Z$, then we can proceed as follows, working in the coordinate system XYZ for which the zeroth-order field energy is already diagonal.

Transforming (4) to the system XYZ via the transformation (3) we obtain

$$H_Q = \begin{bmatrix} u & e & f & 0 \\ e^* & -u & 0 & f \\ f^* & 0 & -u & -e \\ 0 & f^* & -e^* & u \end{bmatrix} , \tag{7}$$

where

$$u = (\tfrac{3}{2})(3c^2 - 1 + \eta s^2 \cos2\phi)q' , \tag{8}$$

$$e = \sqrt{3}(-3sc + \eta sc\cos2\phi + i\eta s\sin2\phi)q' , \tag{9}$$

$$f = (\sqrt{3/2})[3s^2 + \eta(1+c^2)\cos2\phi + 2i\eta c\sin2\phi]q' , \tag{10}$$

in which $c=\cos\theta$, $s=\sin\theta$, and * indicates a complex conjugate. Perturbing H_0 with H_Q of (7) we find, to second order, the energy levels

$$\begin{aligned} E_1 &= -(\tfrac{3}{2})h_E + u - (e^*e + f^*f/2)/h_E , \\ E_2 &= -(\tfrac{1}{2})h_E - u + (e^*e - f^*f/2)/h_E , \\ E_3 &= +(\tfrac{1}{2})h_E - u - (e^*e - f^*f/2)/h_E , \\ E_4 &= +(\tfrac{3}{2})h_E + u + (e^*e + f^*f/2)/h_E , \end{aligned} \tag{11}$$

where $h_E = g_E\mu_N H$.[14]

The allowed Mössbauer transitions are, in order of increasing energy, those between E_2^G of Eq. (2) and E_4, E_3, E_2, and those between E_1^G and E_3, E_2, E_1. It follows that the six Mössbauer lines L_1-L_6 have, to second order in quadrupole interactions, the mean energies

$$\begin{aligned} L_1 &= \delta - g_1\mu_N H + \langle u \rangle - a , \\ L_2 &= \delta - g_2\mu_N H - \langle u \rangle + b , \\ L_3 &= \delta - g_3\mu_N H - \langle u \rangle - b , \\ L_4 &= \delta + g_3\mu_N H - \langle u \rangle + b , \\ L_5 &= \delta + g_2\mu_N H - \langle u \rangle - b , \\ L_6 &= \delta + g_1\mu_N H + \langle u \rangle + a , \end{aligned} \tag{12}$$

in which δ is the isomer shift,

$$g_1 = (\tfrac{3}{2})|g_E| + (\tfrac{1}{2})g_G ,$$

$$g_2 = (\tfrac{1}{2})(|g_E| + g_G) ,$$

$$g_3 = (\tfrac{1}{2})(|g_E| - g_G) ,$$

and

$$a = \langle (e^*e + f^*f/2)/|g_E|\mu_N H \rangle , \tag{13}$$

$$b = \langle (e^*e - f^*f/2)/|g_E|\mu_N H \rangle . \tag{14}$$

If (θ,ϕ) are random we find from (8)−(10) that $\langle u \rangle = 0$ and

$$\langle e^*e \rangle = \langle f^*f \rangle = 2\langle E_Q^2/5 \rangle , \tag{15}$$

leading, from (13) and (14), to the expectation that $a=3\epsilon$, $b=\epsilon$ where

$$\epsilon = \langle E_Q^2 \rangle / 5|g_E|\mu_N H . \tag{16}$$

The ^{57}Fe Mössbauer absorption spectra were obtained in a standard transmission geometry with a conventional constant acceleration spectrometer using a ^{57}Co in Pd source. The absorber was a mosaic of small platelets. The room temperature Mössbauer spectrum[6] of vitreous YIG has established the existence of a broad quadrupole distribution with peak-to-peak splitting of 1.12 mm/s (which corresponds to $E_Q = 0.56$ mm/s) and an isomer shift of 0.31 mm/s (with respect to Fe metal). The spectrum of vitreous YIG at 4.2 K displays a well-resolved six-line pattern with good statistics and many channels per peak (Fig. 1). The average hyperfine field is 450 kOe and the isomer shift is 0.446 mm/s, indicating that iron is in the Fe^{3+} valence state.[15]

The 4.2 K a-YIG spectrum of Fig. 1 consists of well-separated lines, each of which is close to symmetric about its peak. This line shape symmetry is expected for a dense random packed structure like a-YIG[4] because of the approximately equal[16] distributions of positive and negative EFG. It is therefore not difficult to determine the line positions L_i ($i = 1-6$) with considerable accuracy by least-squares fitting the data with symmetric line functions. Even a fit with pure Lorentzians [Fig. 1(a)], although poor as regards line shape, is quite sufficient to establish the predicted QS shifts. However, we also give a *quantitative* fit to the data [Fig. 1(b)] which is obtained by using six independent lines, each a symmetric Gaussian distribution of natural width (FWHM=0.2 mm/s) Lorentzian lines. Line positions L_i in mm/s for the pure Lorentzian and Lorentz-broadened Gaussian least-squares fit to the data are given in Table I.

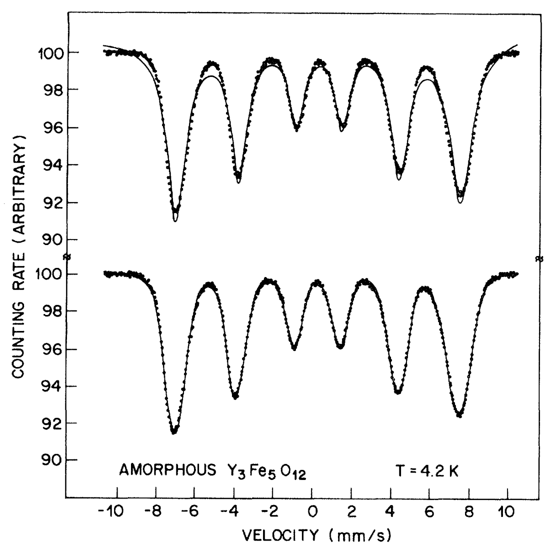

FIG. 1. Experimental ^{57}Fe Mössbauer spectrum of a-YIG taken at 4.2 K. In the upper curve the data have been fitted theoretically by a computer least-squares procedure to a model using six independent Lorentzians. In the lower curve the same experimental data are least-squares fitted to a model of six independent Lorentz-broadened symmetric Gaussian lines.

Using Eqs. (12) the isomer shift δ can be unambiguously determined from $(\frac{1}{4})(L_1+L_2+L_5+L_6)$ and is 0.261 (0.261) mm/s, corresponding to a shift of 0.446 (0.446) mm/s with respect to iron metal at room temperature (where the pure-Lorentz-determined values are in parentheses). From (L_1+L_6), (L_2+L_5), and (L_3+L_4) we can now verify that $\langle u \rangle = 0$ to within a rms accuracy of 0.004 mm/s. Even if (θ,ϕ) and q' are uncorrelated, this cancellation does not necessarily imply that (θ,ϕ) are random variables. From (8) it could equally well imply that $\langle q' \rangle = 0$. The former option is confirmed only by pursuing the second-order shifts. The field energy $\mu_N H$ follows from $(L_4+L_5-L_2-L_3)/2(g_2+g_3)$ and is 29.579 (29.530) mm/s corresponding to a mean hyperfine field of 450.4 (449.7) kOe. With these data we can now compute directly the line positions in the absence of a quadrupole shift (i.e., as $L_1 = \delta - g_1\mu_N H, \ldots, L_6 = \delta + g_1 \mu_N H$). These are shown in Table I in the columns marked $L_i(c)$. The difference ΔL_i between the observed $L_i(0)$ and the calculated QS=0 line positions $L_i(c)$ now give the *experimental determination* of the QS shifts; these are also given in Table I. From these we compute the mean observed second-order shift parameter $\epsilon = (\frac{1}{10})\sum_i |\Delta L_i|$ and find a value $\epsilon = 0.024$ (0.031) mm/s. Normalizing with respect to this value of ϵ we find a measured second-order shift pattern

$$-2.8, +1.1, -0.8, +1.3, -1.0, +2.7$$
$$(-3.3, +0.8, -0.6, +1.0. -0.9, +3.3),$$

which is to be compared with the expected theoretical prediction for random (θ,ϕ) of $-3, +1, -1, +1, -1, +3$. The anticipated pattern is unmistakably present even in the crude Lorentz fit (in parentheses). Final confirmation of the effect is obtained from its amplitude ϵ since the latter is directly related to the hyperfine field H and the quadrupole energy $\langle E_Q^2 \rangle$ via Eq. (16), and $\langle E_Q^2 \rangle$ can be determined directly from the measured E_Q spectrum obtained in the room temperature QS data of Ref. 6; it is 0.383 (mm/s)^2. The difference between $\langle E_Q^2 \rangle$ and $\langle E_Q \rangle^2$ is simply a measure of the width of the EFG distribution. Substitution into Eq. (16) now predicts the amplitude of the expected second-order shift to be 0.025 mm/s and is to be compared with the experimental amplitude of 0.024 (0.031) mm/s.

In conclusion, we have predicted and measured the quadrupole energy line shifts in the six-line Mössbauer spectrum of ^{57}Fe in a magnetically or-

TABLE I. Observed Zeeman line positions $L_i(0)$ for YIG at 4.2 K are compared with those calculated $L_i(c)$ in the absence of a quadrupole. The difference $\Delta L_i = L_i(0) - L_i(c)$ is a measure of the Zeeman quadrupole shift. All measurements are in mm/s.

	Pure Lorentz			Lorentz-broadened Gaussian		
	$L_i(0)$	$L_i(c)$	ΔL_i	$L_i(0)$	$L_i(c)$	ΔL_i
L_i	-7.069	-6.968	-0.101	-7.047	-6.980	-0.067
L_2	-3.901	-3.926	$+0.025$	-3.907	-3.934	$+0.027$
L_3	-0.904	-0.885	-0.019	-0.907	-0.887	-0.020
L_4	1.439	1.407	$+0.032$	1.440	1.408	$+0.032$
L_5	4.422	4.449	-0.027	4.430	4.455	-0.025
L_6	7.593	7.490	$+0.103$	7.567	7.502	$+0.066$

dered amorphous material. They arise in the second order of perturbation theory and should be present quite generally in amorphous iron-containing ferromagnets or speromagnets. They contain important information concerning the influence of local EFG on local hyperfine-field direction and specifically for speromagnetic amorphous YIG establish that local crystal-field anisotropy has a negligible influence on spin orientation in this material.

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