Observation of linewidth asymmetry in the Mössbauer Zeeman spectrum of amorphous yttrium iron garnet

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A measurement of the six-line Mössbauer Zeeman spectrum of ^{57}Fe in amorphous yttrium iron garnet at 4.2 K reveals a linewidth asymmetry involving the three line pairs L_i and L_{7-i}, $i = 1, 2, 3$. The major source of this asymmetry is found to be a positive correlation between isomer shift and hyperfine field with a degree of linearity of 18%. A complete linewidth analysis is given which also leads to separate estimates of the widths of the hyperfine field, isomer shift, and electric-field-gradient distributions in the glass.

Amorphous materials containing sufficiently large concentrations of iron in general exhibit long-range magnetic order below a transition temperature T_c. In amorphous metals, such as the iron-metalloid alloys $Fe_{1-x}M_x$ (where M is one or a combination of metalloids like B, P, C, Si, etc., and $0.15 \lesssim x \lesssim 0.3$), this order is ferromagnetic, while in amorphous insulators it is generally of speromagnetic, or spin-glass, character.[1-7] In such materials the ^{57}Fe Mössbauer spectrum can normally be studied in both the nonmagnetic ($T > T_c$) and magnetic ($T < T_c$) phases and provides a powerful probe of short-range compositional order in the amorphous environment.

In the paramagnetic phase a broad Mössbauer doublet spectrum is a direct measure of the distribution of electric field gradients (EFG) at the iron sites.[8,9] Below T_c this doublet is transformed by the spontaneous magnetic hyperfine field H into a six-line pattern. Many such magnetic, or Zeeman, iron Mössbauer spectra have been published in the literature, particularly for the amorphous iron-metalloid alloys, and recently an increasing attention has focused on the fact that these spectra also contain information concerning EFG and isomer shift distributions.[10,11] In particular, the six-line patterns generally contain a linewidth asymmetry involving the three line pairs i and $(7-i)$, where the lines are numbered from 1 to 6 in order of increasing energy.

In this Communication we report the first measure of such an asymmetry for an amorphous magnetic insulator, namely, one with the same chemical composition $Y_3Fe_5O_{12}$ as yttrium iron garnet (which we abbreviated as a-YIG), and establish that it is primarily a measure of correlations between hyperfine field and isomer shift, although other smaller correlation effects can also be estimated. Linewidth asymmetry has been observed previously in ferromagnetic amorphous alloys of the kind $Fe_{1-x}B_x$ and is thought to be due in the most part to correlations between hyperfine field, electric field gradient, and their relative orientation.[12-14]

The material was prepared using the roller quenched technique.[15] The experimental Zeeman Mössbauer spectrum for a-YIG at 4.2 K is shown in Fig. 1. It has been least mean-square fitted to six independent symmetric Gaussian distributions of natural-width Lorentzian lines, the optimum fit being shown by the full curve in Fig. 1. The mean hyperfine field is 450 kOe and the mean isomer shift 0.446 mm/sec, indicating that iron is in the Fe^{3+} valence state.[8]

If we consider a specific iron nuclear site in a-YIG below its transition temperature $T_c \sim 30$ K, we may define the direction of the local hyperfine field H in a polar representation (θ, ϕ) with respect to the local principal axes of EFG tensor at that site. Defining the EFG by its principal component q and axial asymmetry η (conventional notation), the six Mössbauer

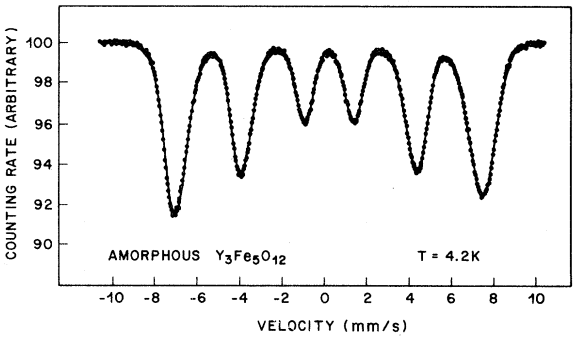

FIG. 1. Experimental ^{57}Fe Mössbauer Zeeman spectrum of amorphous yttrium iron garnet at 4.2 K. The fit to the data (continuous curve) is the best nonlinear least-squares fit using six independent Gaussian distributions of natural width Lorentzian lines. The Gaussian parameters corresponding to this fit are given in Table I.

Zeeman lines are given, to second order in EFG perturbation of hyperfine field energy, by[16,17]

$$\begin{aligned} L_1&=\delta-g_1\mu_N H+u-\alpha_+ \ , \\ L_2&=\delta-g_2\mu_N H-u+\alpha_- \ , \\ L_3&=\delta-g_3\mu_N H-u-\alpha_- \ , \\ L_4&=\delta+g_3\mu_N H-u+\alpha_- \ , \\ L_5&=\delta+g_2\mu_N H-u-\alpha_- \ , \\ L_6&=\delta+g_1\mu_N H+u+\alpha_+ \ , \end{aligned} \tag{1}$$

in which δ is the isomer shift, and $g_1=(g_G-3g_E)/2=0.2448$, $g_2=(g_G-g_E)/2=0.1418$, $g_3=(g_G+g_E)/2=0.0388$, where $g_E=-0.1030$ and $g_G=+0.1805$ are the excited and ground nuclear g factors for the Mössbauer levels.[17] The first- and second-order EFG perturbation energies are, respectively [where we define $c=\cos\theta$, $s=\sin\theta$, $c'=\cos(2\phi)$, and $s'=\sin(2\phi)$],

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

$$\alpha_\pm=(e^*e\pm\tfrac{1}{2}f^*f)/|g_E|\mu_N H \ , \tag{3}$$

in which

$$\begin{aligned} e&=\sqrt{3}(-3sc+\eta scc'+i\eta ss')q' \ , \\ f&=(\sqrt{3/2})[3s^2+\eta(1+c^2)c'+2i\eta cs']q' \ , \end{aligned} \tag{4}$$

where $q'=e_0^2Qq/12$ is an energy measure of the principal EFG component q (with e_0 being the electronic charge and Q the nuclear quadrupole moment), and * indicates a complex conjugate.

Mean line positions $\langle L_i\rangle$ (see Table I) therefore provide measures of $\langle\delta\rangle$, $\langle H\rangle$, $\langle u\rangle$, and $\langle\alpha_\pm\rangle$, where the brackets imply averages over all iron sites in the glass. In this respect we note from Eqs. (2) to (4) that if the angles θ,ϕ are random variables in the amorphous environment, then

$$\langle u\rangle=0 \ , \tag{5}$$

$$\langle\alpha_+\rangle=3\langle\alpha_-\rangle=\tfrac{3}{5}\langle E_Q^2/|g_E|\mu_N H\rangle \ , \tag{6}$$

where $E_Q=6|q'|(1+\eta^2/3)^{1/2}$ is the pure quadrupole doublet splitting when the hyperfine field H is zero. We have previously reported[17] that the relationships (5) and (6) are found to hold (to good approximation) in a-YIG, implying that the polar angles θ,ϕ are closely random variables within the glass. From $\langle L_i\rangle$ we determine the mean values $\langle\delta\rangle=0.446$ mm/sec with respect to iron metal at room temperature, $\langle H\rangle=450.4$ kOe ($\mu_N H=29.58$ mm/sec) and, from Eq. (6),

$$\langle E_Q^2\rangle=0.385\ (\text{mm/sec})^2 \ . \tag{7}$$

From Eq. (2) it now follows that

$$\langle u^2\rangle=\tfrac{1}{5}\langle E_Q^2\rangle=0.077\ (\text{mm/sec})^2 \ . \tag{8}$$

In addition to mean line positions, the best computer fit (Fig. 1) to the six-line Zeeman spectrum provides us with measures of the full width $2w_i$ at half height of each Gaussian component, as shown in Table I. It is clear that a linewidth asymmetry exists with $w_{7-i}>w_i\,(i=1,2,3)$, the disparity being greatest ($\approx$17%) for the outside lines L_1 and L_6. These linewidth asymmetries can be interpreted directly from the Eqs. (1) by deriving the mean-square linewidth fluctuations $W_i^2=\langle(L_i-\langle L_i\rangle)^2\rangle$. For Gaussian distributions these fluctuations are related to the half widths w_i by the equations $W_i^2=w_i^2/(2\ln 2)$. Defining deviations Δx of x ($x=H,\delta,u,\alpha_\pm$) from their mean values $\langle x\rangle$, they are most conveniently cast (to second order in q') in the form of three "symmetrized" widths:

$$\begin{aligned} \tfrac{1}{2}(W_1^2+W_6^2)&=a^2+g_1^2b^2+2\langle\Delta u\Delta\delta\rangle \\ &\quad+2g_1\mu_N\langle\Delta H\Delta\alpha_+\rangle \ , \\ \tfrac{1}{2}(W_2^2+W_5^2)&=a^2+g_2^2b^2-2\langle\Delta u\Delta\delta\rangle \\ &\quad-2g_2\mu_N\langle\Delta H\Delta\alpha_-\rangle \ , \\ \tfrac{1}{2}(W_3^2+W_4^2)&=a^2+g_3^2b^2-2\langle\Delta u\Delta\delta\rangle \\ &\quad+2g_3\mu_N\langle\Delta H\Delta\alpha_-\rangle \ , \end{aligned} \tag{9}$$

TABLE I. Mean positions $\langle L_i\rangle$, half widths at half height w_i, and mean-square widths $W_i^2=\langle(L_i-\langle L_i\rangle)^2\rangle$, of the six Gaussian distributions of natural width Lorentzian lines which make up the Zeeman spectrum ($i=1$–6) of Fig. 1 for amorphous YIG at 4.2 K. The origin of the spectrum corresponds to an isomer shift of +0.446 mm/sec with respect to iron metal at room temperature, and $W_i^2=w_i^2/(2\ln 2)$.

i	1	2	3	4	5	6
$\langle L_i\rangle$ (mm/sec)	−7.308	−4.168	−1.168	1.180	4.169	7.307
w_i (mm/sec)	0.601	0.541	0.458	0.468	0.572	0.703
W_i^2 (mm/sec)^2	0.261	0.211	0.151	0.158	0.236	0.357

where

$$a^2=\langle(\Delta u)^2\rangle+\langle(\Delta\delta)^2\rangle \ , \tag{10}$$

$$b^2=\mu_N^2\langle(\Delta H)^2\rangle \ , \tag{11}$$

and three asymmetries:

$$\begin{aligned}\tfrac{1}{4}(W_6^2-W_1^2)&=g_1\mu_N\langle\Delta H(\Delta\delta+\Delta u)\rangle\\&\quad+\langle\Delta\alpha_+(\Delta\delta+\Delta u)\rangle \ ,\\ \tfrac{1}{4}(W_5^2-W_2^2)&=g_2\mu_N\langle\Delta H(\Delta\delta-\Delta u)\rangle\\&\quad-\langle\Delta\alpha_-(\Delta\delta-\Delta u)\rangle \ ,\\ \tfrac{1}{4}(W_4^2-W_3^2)&=g_3\mu_N\langle\Delta H(\Delta\delta-\Delta u)\rangle\\&\quad+\langle\Delta\alpha_-(\Delta\delta-\Delta u)\rangle \ .\end{aligned} \tag{12}$$

In amorphous magnetic materials, the normal sequence of magnitudes for the root-mean-square (RMS) fluctuations $\sigma(x)\equiv\langle(\Delta x)^2\rangle^{1/2}$ are $\sigma(H)>>\sigma(\delta)\sim\sigma(u)>>\sigma(\alpha_\pm)$, so that the averages $\langle\alpha_\pm(\Delta\delta\pm\Delta u)\rangle$ in Eqs. (12) are expected to be small. If they are negligible within the context of Eqs. (12) then we should expect to find

$$(W_4^2-W_3^2)/(W_5^2-W_2^2)\approx g_3/g_2=0.27 \ .$$

A ratio of 0.28 is obtained for a-YIG using the W_i^2 values from Table I confirming this hypothesis. In fact, the correlations $\langle\Delta\alpha_\pm\Delta u\rangle$ can be directly calculated from Eqs. (2) to (4) for random θ,ϕ with the results $\langle\Delta\alpha_+\Delta u\rangle=0$, and $\langle\Delta\alpha_-\Delta u\rangle\approx+0.0003$ $(\text{mm/sec})^2$. Neglecting $\langle\Delta\alpha_\pm(\Delta\delta\pm\Delta u)\rangle$, the Eqs. (12) become overdetermined and consistently lead to the correlation values

$$\mu_N\langle\Delta H\Delta\delta\rangle=+0.071\ (\text{mm/sec})^2 \ , \tag{13}$$

$$\mu_N\langle\Delta H\Delta u\rangle=+0.028\ (\text{mm/sec})^2 \ . \tag{14}$$

The linewidth asymmetry is therefore primarily the result of a positive correlation between hyperfine field and isomer shifts. This effect is perhaps not unexpected in ferric materials since both H (for saturated spins) and isomer shift have long been used in this context as a qualitative measure of covalency. Thus, for example, the smaller H and smaller δ at the tetrahedrally coordinated iron site in crystalline YIG (compared to the octahedral site) is generally understood in terms of the larger covalency of Fe^{3+} in tetrahedral coordination. But how direct is this correlation? It is possibly a linear[10,11] one? This is a question we can now answer since a linear correlation $\Delta x\propto\Delta y$ between any two variables x and y leads to the result

$$\langle\Delta x\Delta y\rangle=\sigma(x)\sigma(y) \ , \tag{15}$$

and we are now in a position to estimate the RMS fluctuations $\sigma(H)$ and $\sigma(\delta)$.

Since $\sigma(u)=0.28$ mm/sec is already known from Eq. (8), since $\Delta u=u-\langle u\rangle=u$, $\sigma(H)$, and $\sigma(\delta)$ follow [via Eqs. (1) and (11)] from the parameters a and b in the symmetrized width Eqs. (9). As they stand, the three Eqs. (9) are underdetermined (five unknowns), but progress can be made as follows. We first attempt a zeroth-order fit by neglecting the correlation terms. The equations are then overdetermined (two unknowns) in the form

$$\begin{aligned}&\text{(i)}\ \ a^2+g_1^2b^2=0.309 \ ,\\ &\text{(ii)}\ \ a^2+g_2^2b^2=0.224 \ ,\\ &\text{(iii)}\ \ a^2+g_3^2b^2=0.155 \ .\end{aligned} \tag{16}$$

The solution with the smallest RMS deviation is $b^2\approx2.56$, $a^2\approx0.160$, leading to errors of $+0.004$, -0.013, and $+0.009$ in (i), (ii), and (iii), respectively, all units being $(\text{mm/sec})^2$. This gives zeroth-order estimates for $\sigma(H)$ and $\sigma(\delta)$ of 1.6 mm/sec and 0.29 mm/sec, respectively, implying from Eqs. (13) and (15) a linear degree of correlation $\langle\Delta H\Delta\delta\rangle/\sigma(H)\sigma(\delta)$ of only about $+15\%$.

Using Eqs. (3) and (4), and averaging over the random variables θ,ϕ, we can also compute

$$\begin{aligned}\sigma(\alpha_-)&\approx1.8\sigma(\alpha_+)\approx0.36\langle E_Q^2/|g_E|\mu_NH\rangle\\&\approx0.045\ \text{mm/sec} \ .\end{aligned} \tag{17}$$

Using Eq. (15) we find that the maximum possible values for the correlations involved in the symmetrized width Eqs. (9) as follows: [units $(\text{mm/sec})^2$] $2g_1\mu_N\sigma(H)\sigma(\alpha_+)\approx\pm0.020$, $2g_2\mu_N\sigma(H)\sigma(\alpha_-)\approx\pm0.020$, $2g_3\mu_N\sigma(H)\sigma(\alpha_-)\approx\pm0.005$, $2\sigma(u)\sigma(\delta)\approx\pm0.16$. Given these numbers, the probability is that the dominant correlations in this context are almost certainly $\langle\Delta u\Delta\delta\rangle$. Assuming this to be true and retaining only this correlation, the Eqs. (9) can be resolved to give

$$\begin{aligned}&\sigma(\mu_NH)=1.9\ \text{mm/sec (29 kOe)} \ ,\\ &\sigma(\delta)=0.21\ \text{mm/sec} \ ,\\ &\langle\Delta\delta\Delta u\rangle=-0.015\ (\text{mm/sec})^2 \ .\end{aligned} \tag{18}$$

Our final estimates for all pertinent fluctuations and correlations are gathered together in Table II. The degrees of linear correlation for $\langle\Delta H\Delta\delta\rangle$, $\langle\Delta H\Delta u\rangle$, and $\langle\Delta\delta\Delta u\rangle$ are found to be $\approx+18\%$, $\approx+5\%$, and $\approx-25\%$, respectively. By virtue of our neglect of some small correlations in the symmetrized linewidth equations, the last number is perhaps less accurate than the other two. In any event, it is quite evident that any theory which postulates a simple linear coupling between any of these variables is at variance with our findings. It is interesting to note that the distribution $\sigma(\delta)$ in a-YIG is about 80% larger than in crystalline YIG, while $\sigma(H)$ is about 40% smaller than its crystalline equivalent.[18,19] This provides additional evidence that δ and H cannot be linearly related.

With regard to the correlations involving Δu we

TABLE II. Summary of the findings of this Communication for mean values $\langle x \rangle$, root-mean-square fluctuations $\sigma(x) = \langle (\Delta x)^2 \rangle^{1/2}$, and correlations $\langle \Delta x \Delta x \rangle$ for $x = H$ (hyperfine field), δ (isomer shift), u [first-order Zeeman line shift in Eqs. (1)], and $\alpha_{\pm}$ [second-order Zeeman line shifts in Eqs. (1)] at the iron sites in a-YIG at 4.2 K. Units in mm/sec except where stated.

1. Mean values:	$\langle u \rangle = 0 (\pm 0.004)$
	$\langle \alpha_- \rangle \approx \langle \alpha_+ \rangle / 3 = 0.025$
	$\langle \delta \rangle = 0.446$ (with respect to iron metal)
	$\langle H \rangle = 450.4$ kOe
2. RMS fluctuations:	$\sigma(u) = 0.28$
	$\sigma(\alpha_-) \approx 1.8 \sigma(\alpha_+) = 0.045$
	$\sigma(\delta) = 0.21$
	$\sigma(H) = 29$ kOe
3. Correlations:	$\mu_N \langle \Delta H \Delta \delta \rangle = +0.071$ (mm/sec)^2
	$\mu_N \langle \Delta H \Delta u \rangle = +0.028$ (mm/sec)^2
	$\langle \Delta \delta \Delta u \rangle = -0.015$ (mm/sec)^2
	$\langle \Delta \alpha_{\pm} \Delta u \rangle < 0.001$ (mm/sec)^2
	$\langle \Delta \alpha_{\pm} \Delta \delta \rangle < 0.001$ (mm/sec)^2

note that these imply a coupling to both (θ, ϕ) and q', since $\Delta u = u - \langle u \rangle = u$ of Eq. (2). Since $\langle u \rangle = 0$, and $\langle q \rangle \neq 0$,[20] the electric field gradient is known to be essentially independent of θ, ϕ. It follows that *any* fluctuation variable Δx which is also independent of θ, ϕ would have a correlation

$$\langle \Delta x \Delta u \rangle = \langle (\Delta x) q \rangle \langle 3c^2 - 1 + \eta s^2 c \rangle = 0 \quad . \tag{19}$$

The significantly nonzero values for correlations $\langle \Delta H \Delta u \rangle$ and $\langle \Delta \delta \Delta u \rangle$ found in this paper, therefore signifiy a dependence of hyperfine field and isomer shift fluctuations directly upon the angular variables θ, ϕ.

In summary, we have measured the Mössbauer Zeeman spectrum of a-YIG at 4.2 K and observed a linewidth asymmetry between each of the line pairs L_i and L_{7-i}, $i = 1, 2, 3$. Since these line pairs are closely equal in area, the asymmetry is also evident in amplitudes. This asymmetry is dominantly the consequence of two correlation functions; one between the fluctuations of hyperfine field ΔH and isomer shift $\Delta \delta$, the other between hyperfine field and first-order Zeeman shift Δu, where the latter is a measure of electric-field-gradient perturbation. The outside linewidth inequality is closely a measure of the sum of these correlations and the middle and inner inequalities a measure of their difference according to the equations

$$\begin{aligned} W_6^2 - W_1^2 &\approx 0.979 \langle \Delta H (\Delta \delta + \Delta u) \rangle \quad , \\ W_5^2 - W_2^2 &\approx 0.567 \langle \Delta H (\Delta \delta - \Delta u) \rangle \quad , \\ W_4^2 - W_3^2 &\approx 0.155 \langle \Delta H (\Delta \delta - \Delta u) \rangle \quad , \end{aligned} \tag{20}$$

where W_i^2 is the mean-square linewidth $\langle (L_i - \langle L_i \rangle)^2 \rangle$ of the ith line. We find that the linewidth inequalities in a-YIG are primarily the result of the correlations between ΔH and $\Delta \delta$. We are also able to estimate the mean- and root-mean-square (σ) values of the hyperfine field, isomer shift, and Zeeman shift parameters, and to conclude that none of these variables is close to fully correlated with any other. The degree of linear correlation $\langle \Delta H \Delta \delta \rangle / \sigma(H) \sigma(\delta)$ of the most important correlation effect, for example, is only about 18%.

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