Hyperfine Interactions in Europium Iron Garnet

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The temperature dependence of the hyperfine fields at the Eu^{151} nuclei in europium iron garnet (EuIG) has been measured by the Mössbauer effect. The magnetic hyperfine fields at the two magnetically inequivalent Eu sites are 630±5 and 570±5 kOe, respectively, extrapolated to 0°K. The ratio of the g factor of the 22-keV excited state to that of the ground state is $g_{22}/g_g=0.5332(5)$, and that of the spectroscopic quadrupole moments is $Q_{22}/Q_g=1.28(4)$.

I. INTRODUCTION

THE hf interactions in EuIG have been previously measured by the Mössbauer effect[1,2] and by a specific-heat measurement.[3] The Mössbauer measurements[1,2] showed that the temperature dependence of the hf field follows within the experimental accuracy the temperature dependence of the Eu sublattice magnetization.[4,5] The quoted measurements[1,2] left yet some questions open. In no case did the analysis of the experimental data take into account the existence of the two magnetically inequivalent rare-earth sites.[6] Also, there is some disagreement with respect to the experimental results. Kienle[1] reports a hf field extrapolated to 0 °K of 600±6 kOe whereas Onn *et al.*,[3] get 565±15 kOe (the value from Ref. 2 is 670±100 kOe). In addition, Nowick and Ofer[2] report a quadrupole coupling constant of the ground state $eQ_gV_{zz}/h=-240\pm100$ Mc/sec, whereas Kienle[1] quotes $eQ_gV_{zz}/h=-17\pm15$ Mc/sec. These inconsistancies stimulated the interest for a new investigation. This was especially so because the magnetic properties,[7] and also the hf interactions, in EuIG can be calculated very accurately, as has been shown by Gilat and Nowick[8] and by Eicher.[9]

II. Eu^{151} AND EuIG PROPERTIES

The nucleus Eu^{151} stands roughly on the border line of the strongly deformed nuclei.[10] This makes the application of any of the current nuclear models to this nucleus very questionable. (The nuclear properties relevant to this work have been determined in a number of investigations,[1,11–14] and the reader is referred to these papers for this information.)

The magnetic properties of EuIG have been investigated in detail both theoretically and experimentally,[5,7–9] and we shall refer to this work in Sec. V of this paper.

There is only one point which should be mentioned here: Eicher[9] has shown that to a very good approximation one can assume that $\mathbf{H}_{\text{eff}}$ and the electric field gradient $\mathbf{V}''$ are parallel; we will therefore call the direction of $\mathbf{H}_{\text{eff}}$ and thus of $\mathbf{V}''$ the z direction, and thus denote the field gradient by V_{zz}.

III. EXPERIMENTAL

The experiments were performed in a conventional Mössbauer setup. The motion of the source was sinusoidal. The difference between the reference and the pickup signal was always smaller than 0.5%. The multichannel analyzer operated as a multiscaler. The channel stepping was performed by a crystal clock with the frequency stabilized to 2×10^{-5}. The reference signal was produced by a digital operating function generator with an accuracy of 5×10^{-5} using the stepping pulses. Therefore there was an exact correspondence between the cycles of the loudspeaker drive and the multichannel sweep. The temperatures were measured using carbon resistors, and they are accurate to about 1°K. The source material was Sm^{151} as Sm_2O_3. EuIG single crystals were grown from the flux.[15] The single crystals were ground to powders and then pressed to form absorbers which contained approximately 15 mg/cm² Eu^{151}; this assured that we were working essentially with "thin" absorbers.

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IV. EXPERIMENTAL RESULTS

Spectra obtained at 4.2 and 296°K are shown in Figs. 1 and 2. The almost complete symmetry of the spectra with respect to $v=0$ indicates a very small isomer shift between source and absorber and a small quadrupole splitting as compared to the magnetic splitting. Barret and Shirley[16] show that, for a purely magnetic splitting for a g-factor ratio of 0.53, many of the allowed 18 lines coincide and the observed typical pattern occurs for a $\frac{5}{2} \rightarrow \frac{7}{2}$ $M1$ transition. In our case, there are in principle 36 lines because of the two magnetically inequivalent sites. Since the general line pattern is similar to that observed in a compound with only one magnetic site,[16] we conclude that the difference of the hf interactions on the two sites is small. The two outer lines of the six most intense lines show at all temperatures a small but noticeable splitting. This indicates the difference of the hf fields on the two magnetically inequivalent sites. These splittings are seen to be unequal on both sides of the velocity scale, which is clearly an effect of a quadrupole splitting.

The insert in Fig. 1 shows the outermost lines, which are hardly visible even in spectra with very high statistical accuracy on an extended scale. Here the splitting from the two different magnetic sites is visible. The difference in the splitting of the two lines on the opposite parts of the velocity scale is again an effect of the quadrupole splitting. This figure also shows that only from the spectra with high statistical accuracy the quadrupole interaction constants can be deduced with reasonable accuracy (see Table I).

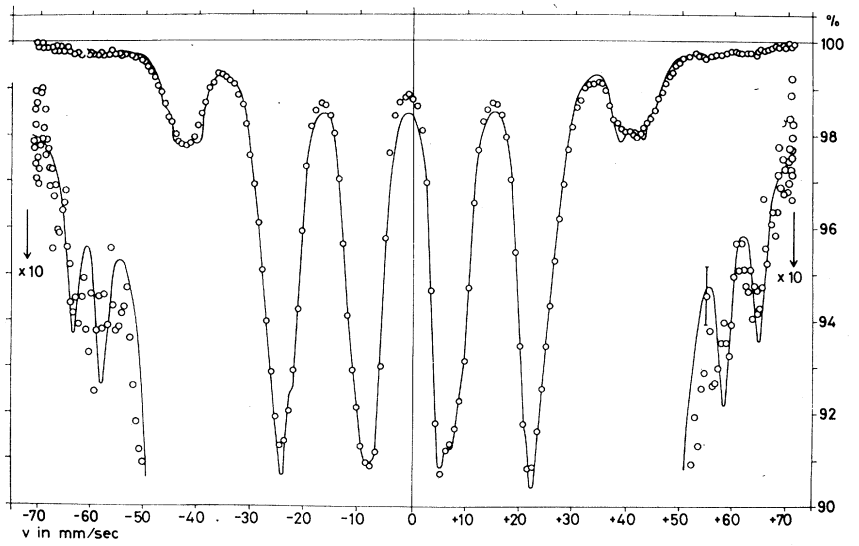

FIG. 1. Mössbauer absorption spectrum of EuIG at $T=4.2$ °K, source Sm_2O_3, absorber and source at 4.2 °K. Positive velocity refers to a motion of the source towards the absorber. The full line is the result of a least-squares fit with the parameters listed in Table I. The inserts show the outermost lines, which are usually not visible, on a tenfold extended scale.

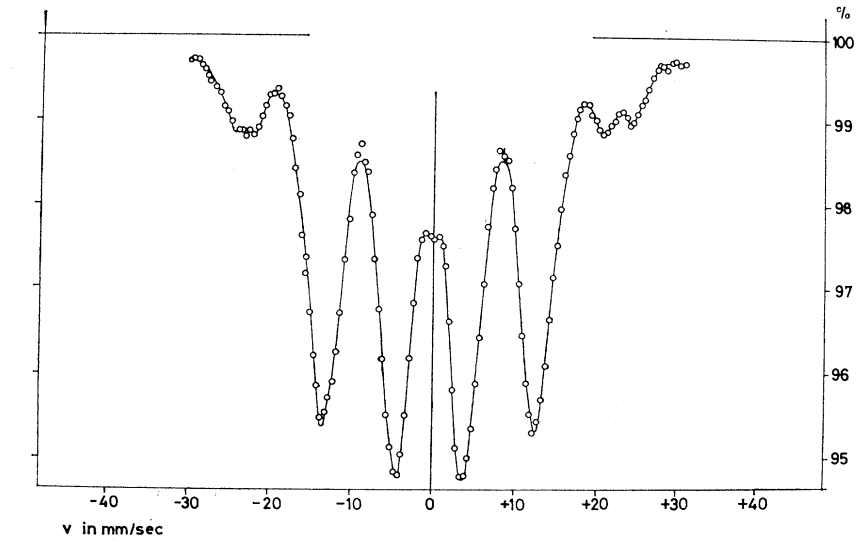

FIG. 2. The same as Fig. 1, but $T=296$ °K.

[16] P. H. Barret and D. A. Shirley, Phys. Rev. **131**, 123 (1963).

The energies of the various lines may be represented by the following formula:

$$E_{g\text{-}22,i}=E_0+\delta+g_g\mu_n H_{\text{eff}}(i)\left(m_g-\frac{g_{22}}{g_g}m_{22}\right)+\frac{eQ_gV_{zz}(i)}{4I_g(2I_g-1)}$$
$$\times\left(3m_g^2-I_g(I_g+1)-\frac{4I_g(2I_g-1)}{4I_{22}(2I_{22}-1)}\frac{Q_{22}}{Q_g}\right.$$
$$\left.\times[3m_{22}^2-I_{22}(I_{22}+1)]\right), \quad (1)$$

where E_0 is the γ-ray energy, δ is the isomer shift between source and absorber, which the fits show to be equal for the A and B sites, $H_{\text{eff}}(i)$ is the magnetic field at the nucleus, g_g is the ground-state g factor, m_g is the magnetic quantum number for the ground-state spin, $V_{zz}(i)$ is the electric field gradient at the nucleus, and Q_g is the ground-state spectroscopic quadrupole moment.

Values with index "22" refer to the 22-keV excited state; $i=A,B$ refers to the two magnetically inequivalent sites. Some of the spectra showed an additional line at $v=0$. This is attributed to Eu_2O_3 impurities, which occurred as inclusions in the EuIG single crystals and could not be completely washed out. Therefore a line at $v=0$ with arbitrary intensity was added to the above energies.

To evaluate the relevant parameters from the measured spectra, Lorentz lines with energies according to Eq. (1) were fitted to the spectra with a least-squares program.[17] The relative intensities of the lines were fixed by the appropriate Clebsch-Gordan coefficients neglecting any $E2$ contributions. The linewidth was assumed to be the same for all lines. The results of the least-squares fits are shown in Table I.

The occupation ratio of the sites A and B was also fitted and gave 1.0 ± 0.1, which is to be expected for the iron sublattice magnetization pointing in the [111] direction.

The curves calculated with the parameters in Table I are also shown in Figs. 1 and 2. It can be seen that generally the data points are very well represented by the calculated curves. There are still some discrepancies outside the statistical error of the data points. It can be seen that the χ^2 of the fits exceeds 1 in those cases in which the statistical accuracy of the spectra is very high.

We only can think of the following reasons as explanations for the discrepancies seen in Figs. 1 and 2:

(a) Drifts in the experimental setup. If they are purely statistical and the measuring times are long enough, they should result in a Gaussian contribution to the Lorentzian line shape. Yet, this folding would only result in a larger linewidth and since the pure Lorentzians are too broad already, this can hardly be a reason for the discrepancies.

(b) The formula for the energy (1) used for the fit is not exact[9]; it neglects an angle between the magnetic field and the field gradient and also neglects the asymmetric contribution to the field gradient. Inclusion of these two effects would, however, complicate the evaluation of the data enormously; we suggest that inclusions of these contributions might have improved the fits.

(c) Any velocity smearing would, again, result in an increase in the experimental linewidth and can therefore not be responsible for the observed effect.

We therefore are left with the conclusion that the reasons listed under (b) are most likely responsible for the imperfect fits.

V. DISCUSSION OF RESULTS

A. Eu^{151}, Nuclear Results

The ratio of the g factors, averaged over all measurements is

$$g_{22}/g_g=0.5332(5).$$

The error includes the statistical error and a contribution which comes from the calibration error via the correlation of the parameters used in the fit. This contribution was calculated from the correlation matrix. The g-factor ratio is, though more accurate, in good agreement with previous measurements.[1,2,16]

The ratio of the spectroscopic quadrupole moments averaged over the various measurements is

$$Q_{22}/Q_g=1.28(4),$$

where the error has been calculated in the same way as for the g-factor case. With $Q_g=1.16(8)$[12] b, we calculate $Q_{22}=1.49(10)$ b.

The quadrupole moment ratio is in agreement with the values due to Nowick and Ofer[2] $[Q_{22}/Q_g=1.3(5)]$ and to Suzuki *et al.*,[14] $[Q_{22}/Q_g=1.57(24)]$. The first value could be questioned because it was derived from coupling constants an order of magnitude larger than those determined in the present experiment, and also the two inequivalent sites in the garnet structure were neglected. Recently Kalvius[18] has obtained $Q_{22}/Q_g=1.30\pm0.03$ from the hf splitting of various divalent Eu compounds; this value is in very good agreement with the result of the present experiments. (We should perhaps emphasize that the determination of the quadrupole moment ratio by a Mössbauer experiment does *not* depend on any nuclear model.)

We may compare this ratio with the predictions of two nuclear models keeping in mind that the application of any nuclear model to Eu^{151} is questionable. Within the framework of the strong coupling model,[10] we can regard both the ground state and the 22-keV state as bandheads of rotational bands and calculate, assuming a constant intrinsic quadrupole moment,

$$Q_{22}/Q_g=1.31$$

[17] We are indebted to C. Reinsch, TH München, for making the general purpose least-squares program available to us.

[18] G. M. Kalvius (private communication).

TABLE I. Experimental results of the measurements in EuIG. Errors are statistical errors plus calibration errors.

	Unit											
Temperature	°K	1.5	4.2	4.2	11	29	47	77	175	220	296	456
χ^2/χ^2 (ideal)		1	1.8	10	1	1	1	1.7	1	1	1.2	1.5
Half width	mm/sec	1.6(1)	1.6(7)	1.6(1)	1.6(1)	1.6(1)	1.6(1)	1.6(1)	1.6(1)	1.6(1)	1.4(2)	1.3(2)
Isomer shift	mm/sec	−0.4(1)	−0.4(1)	−0.5(1)	−0.4(1)	−0.4(1)	−0.4(1)	−0.4(1)	−0.4(1)	−0.4(1)	−0.4(1)	−0.4(1)
$\frac{g_a\mu_K H(A)}{h}$	10^3 Mc/sec	26.5(4)	26.4(4)	26.5(4)	26.8(4)	26.8(4)	26.5(4)	26.0(3)	22.8(3)	18.7(2)	14.5(2)	7.0(2)
$H_{\text{eff}}(A)$	kOe	625(10)	623(10)	625(10)	632(10)	632(10)	629(10)	615(10)	514(8)	451(8)	343(6)	151(4)
$\frac{g_a\mu_K H(B)}{h}$	10^3 Mc/sec	24.0(4)	23.7(4)	23.7(2)	24.1(4)	24.2(4)	24.0(4)	23.4(3)	19.2(2)	17.3(2)	12.5(2)	4.9(2)
$H_{\text{eff}}(B)$	kOe	568(10)	561(10)	561(10)	570(10)	571(10)	566(10)	555(10)	454(8)	395(8)	297(6)	118(4)
$\frac{eQ_aV_{zz}(A)}{h}$	Mc/sec	−21(7)	−22(4)	−23(2)	−25(9)	−27(8)	−25(14)	−21(4)	−28(10)	−21(8)	−11(4)	
$\frac{eQ_gV_{zz}(B)}{h}$	Mc/sec	23(8)	12(5)	14(2)	13(10)	30(11)	5(12)	25(4)	41(12)	28(10)	27(4)	
g_a/g_g		0.5331(3)	0.5332(2)	0.5331(1)	0.5331(3)	0.5334(3)	0.5314(7)	0.5332(2)	0.5331(3)	0.5334(3)	0.5340(6)	0.5330(4)
Q_a/Q_g		1.32(10)	1.32(6)	1.28(5)	1.47(22)	1.38(12)	1.60(35)	1.38(7)	1.24(10)		1.24(5)	

in surprising agreement with the experiment. This agreement though seems to be fortuitous, because Eu^{151} lacks other properties of strongly deformed nuclei. Within the shell model, the ground-state quadrupole moment is calculated as 0.2 b assuming it to be a $^4d_{5/2}$ proton state,[19] showing that the shell-model description is not adequate.

B. EuIG Properties

The temperature dependence of the magnetic field and the electric field gradient at the nucleus have been calculated by Eicher[9] and by Gilat and Nowick[8]; because the first calculations are the more complete ones, we shall compare our measurements with them. The $^7F_0$ ground state of Eu^{3+} produces no hyperfine fields at the nucleus, because its total angular momentum is zero. The hyperfine fields at the nucleus are produced by the mixing of the $^7F_0$ ground state with the ^7F_J excited states via the exchange interaction and the crystal field. The magnitude of the exchange interaction is fairly accurately deduced by Geller *et al.*[5] The exact knowledge of the magnitude of the crystal field can only come from a careful analysis of the crystal-field splitting in EuIG, which has not been performed yet. Eicher[9] in his calculations obtained the crystal field parameters of EuIG by extrapolating those of YbGaG. He derived the latter by analyzing the experimental data known at that time. A succeeding exact analysis[20] showed that his parameters can only be regarded as order of magnitude estimates. Thus, this must also be true for all his calculations on EuIG.

Figure 3 shows the temperature dependence of the hf field at the nucleus for the A and B sites, respectively. The errors include the statistical error and the error of the velocity calibration. Also shown are the measurements of Kienle,[1] which fall always roughly between the values of the A and B sites. This is not surprising, because he fitted his spectra with only one magnetic site. This temperature dependence of the hf field is also in good agreement with that of the europium sublattice magnetization.[5] The calculated temperature dependence of the hf fields on the A and B sites for three different sets of crystal field parameters[9] is also contained in that figure. The comparison with the measurements shows that for the smallest set of crystal field parameters ($A_2^0\langle r^2\rangle = A_2^2\langle r^2\rangle = 83.5$ cm^{-1} for the curves $A3$ and $B3$) the difference between the measured and calculated hf field is still too large, indicating still smaller values for the parameters. The average value of the hf field calculated by Eicher[9] is 585 kOe, whereas the measured value is 600 kOe. This would indicate that the Fe-Eu interaction is 25.6°K rather than 25°K as assumed by Eicher[9] (in contrast Ref. 5 quotes 22°K and Ref. 7, 24°K).

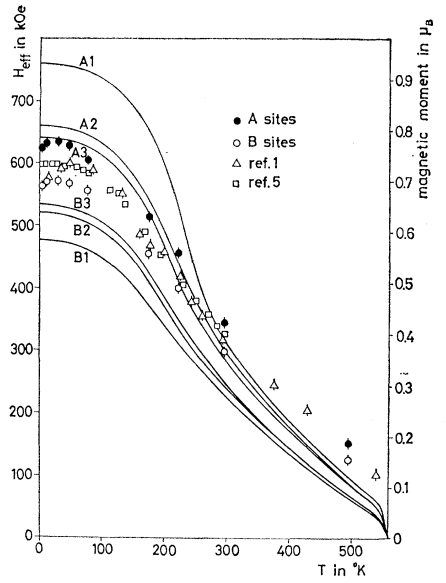

FIG. 3. Temperature dependence of the hf field at the nucleus for the A and B sites. The solid curves $A1$, $A2$, $A3$, $B1$, $B2$, $B3$ are the calculations from Ref. 9. The figure contains also the hf fields of Ref. 1, which are denoted by the triangles. The squares give the magnetic moment per Eu^{3+}-ion as determined in Ref. 5.

At high temperatures the measured hf fields are higher than the calculated ones because in all calculations the effect of the ^7F_J states for $J>2$ have been neglected. With increasing temperature these states are more populated and thus contribute to the hf field.

The values of the hf field extrapolated to 0°K are $H_{eff}(A)=630\pm5$ kOe and $H_{eff}(B)=570\pm5$ kOe, where the average value is in good agreement with Kienle's result ($H_{eff}=600\pm6$ kOe),[1] and also with the refined specific-heat measurements ($H_{eff}=597\pm4$ kOe).[3]

Figure 4 shows the temperature dependence of the quadrupole interaction at the A and B site eQ_gV_{zz}/h.

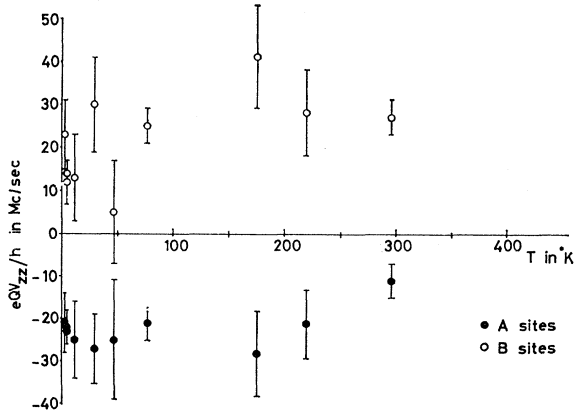

FIG. 4. Temperature dependence of the quadrupole coupling constant eQV_{zz}/h for the A and B sites.

[19] H. Kopfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958), p. 456.

[20] R. A. Buchanan, K. A. Wickersheim, J. J. Pearson, and G. F. Hermann, Phys. Rev. **159**, 245 (1967); **159**, 251 (1967).

Because of the smallness of these terms, the errors are large. The error in the ratio of the quadrupole moments is essentially determined by the error of the data taken with high statistical accuracy ($T=4.2$, 77, and 296°K) and therefore relatively small. The values of the quadrupole constants extrapolated to 0°K are $eQV_{zz}(A)/h = -25$ Mc/sec and $eQV_{zz}(B)/h=+15$ Mc/sec.

The field gradient at the nucleus has two contributions and is[21]:

$$V_{zz}=V_{zz,4f}(1-R)+V_{zz,\mathrm{lat}}(1-\gamma_\infty), \qquad (2)$$

where the first term comes from the $4f$ electrons, the second one from the lattice, and R and γ_∞ are Sternheimer correction factors. The first term has been calculated by Eicher.[9] Using again his case 3, which most closely reproduces the experimental magnetic hf fields we get:

$$eQV_{zz,4f}(A)(1-R)/h=-80 \text{ Mc/sec}$$

and

$$eQV_{zz,4f}(B)(1-R)/h=-8 \text{ Mc/sec}.$$

Here we have used $R=0.2$, which should be a good estimate.[21] An estimate of the lattice term is more difficult. The field gradient is given by the relation[21]:

$$V_{zz,\mathrm{lat}}=-4A_2^0/e = -4A_2^0\langle r^2\rangle/e\langle r^2\rangle_{4f}(1-\sigma_2). \qquad (3)$$

Here, $A_2^0\langle r^2\rangle$ is the crystal field parameter, $\langle r^2\rangle_{4f}$ is the squared radius of the $4f$ electrons, and σ_2 is another Sternheimer factor. The Sternheimer factors γ_∞ and σ_2 have been determined by Blok and Shirley[22] as $(1-\gamma_\infty)/(1-\sigma_2)=360$. Using $A_2^0\langle r^2\rangle=83.5$ cm^{-1} as done by Eicher[9] the whole lattice term gets negative, and it can be seen that the agreement between the calculated and measured coupling constant is very poor. On the other hand, a compilation of crystal field parameters in various rare-earth gallium garnets shows[23] that the sign of $A_2^0\langle r^2\rangle$ should be negative.[24] This change in sign does not change the sign of $V_{zz,4f}$. Using $A_2^0\langle r^2\rangle=-83.5$ cm^{-1} we get $V_{zz,\mathrm{lat}}(1-\gamma_\infty)=45$ Mc/sec and therefore finally $eQV_{zz}(A)/h=-35$ Mc/sec and $eQV_{zz}(B)/h=+37$ Mc/sec. These values are in qualitative agreement with the experimental results. In view of the mentioned difficulties a final theoretical interpretation of the experimental results needs a careful crystal field analysis in EuIG.

Note added in proof. Since the submission of this paper, another paper has appeared [E. R. Bauminger, I. Nowik, and S. Ofer, Phys. Letters **29A**, 199 (1969)] giving the hf constants in EuIG. These authors use the 103-keV γ line in ^{153}Eu and get the following results: $H_{\mathrm{eff}}(A)=636$ kOe, $H_{\mathrm{eff}}(B)=562$ kOe; $eQ_g{}^{151}V_{zz}(A)/h = -23$ Mc/sec, $eQ_g{}^{151}V_{zz}(B)/h=+15$ Mc/sec (the values for the quadrupole coupling constants have been converted by using $Q_g{}^{153}/Q_g{}^{151}=2.53$). These authors also arrive at the conclusion that $A_2^0\langle r^2\rangle$ must be negative. All these results are in good agreement with those of the present paper.

ACKNOWLEDGMENTS

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[21] R. G. Barnes, R. L. Mössbauer, E. Kankeleit, and J. M. Poindexter, Phys. Rev. **136**, A175 (1964).

[22] J. Blok and D. A. Shirley, Phys. Rev. **143**, 278 (1966).

[23] P. Grünberg, S. Hüfner, E. Orlich, and J. Schmitt, Phys. Rev. **184**, 285 (1969).

[24] The complete crystal field analysis for YbGaG of Ref. 20 shows indeed that $A_2^0\langle r^2\rangle=-70$ cm^{-1} rather than $A_2^0\langle r^2\rangle=+402$ cm^{-1} as assumed in Ref. 9.