

Electric Field Gradients in Eu-Sc-Fe Garnets

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The electric quadrupole interactions at the octahedral, tetrahedral, and dodecahedral sites in the $\text{Eu}_{3-y}\text{Sc}_{2+y}\text{Fe}_3\text{O}_{12}$ ($0 \leq y \leq 0.5$) garnet system were studied with ^{57}Fe and ^{151}Eu Mössbauer spectroscopy. The electric field gradient tensor at the three sites was calculated using a monopole-point-dipole model. It is shown that the dipole contribution to the electric field gradient tensor is not negligible even for very small values of the oxygen dipole polarizability. The importance of the overlap and second-order $4f$ contributions is discussed.

Introduction

$\text{Eu}_{3-y}\text{Sc}_{2+y}\text{Fe}_3\text{O}_{12}$ ($0 \leq y \leq 0.5$) series belongs to the garnets which are cubic compounds with $Ia\bar{3}d$ (O_h^h) space group. The general chemical formula of the garnets is usually written as $\{X_3\}\{Y_2\}(Z_3)\text{O}_{12}$, where the cations X , Y , and Z occupy the dodecahedral (c), octahedral (a), and tetrahedral (d) sites, respectively. The special c , a , and d sites have no positional degrees of freedom. The oxygen atoms are in general h positions characterized by three positional parameters x , y , and z (I). The point symmetries of the c , a , d , and h sites are $222(D_2)$, $\bar{3}(S_6)$, $\bar{4}(S_4)$, and $1(C_1)$, respectively (2).

The Mössbauer effect is an excellent tool for studying the electric quadrupole interactions (3) in rare-earth iron garnets. Using

different Mössbauer nuclei it is in principle possible to determine in these compounds the properties of the electric field gradient (EFG) tensor at all three cation sites. In general the EFG tensor in an ionic compound embraces two contributions, one arising from the charge distribution of the surrounding ions in the crystal lattice (lattice/ligand contribution), and another arising from the electron distribution in incompletely filled electronic shells of the Mössbauer atom (valence contribution). Therefore, any component V_{ij} of the EFG tensor at a nuclear site may be written as

$$V_{ij} = (1 - \gamma_\infty)V_{ij}^{\text{latt}} + (1 - R)V_{ij}^{\text{val}} \quad (1)$$

where γ_∞ and R are the Sternheimer anti-shielding and shielding factors, respectively.

The iron ions in the investigated series are in the Fe^{3+} (high spin) oxidation state, with the $^6S_{5/2}$ ground state. Thus no contribution to the EFG is expected from the five $3d$ electrons due to their spherical symmetry. The europium ions are also in the trivalent oxidation state with $4f^6$ electronic con-

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figuration. For Eu^{3+} ions with the ground state 7F_0 there is no first-order $4f$ contribution to the EFG. However, the first two excited states 7F_1 and 7F_2 lie relatively low. Consequently, the 7F_2 state gives rise to a second-order $4f$ contribution to the EFG (4). It has a sign opposite to the lattice contribution and is weakly temperature dependent. The Eu^{3+} ions in the investigated garnets occupy the c sites, whereas the Fe^{3+} ions are at the a and d sites (5). Using ${}^{151}\text{Eu}$ and ${}^{57}\text{Fe}$ Mössbauer effect we measured the quadrupole coupling constants at all three sites. The main components of the EFG tensor V_{zz} were derived from these constants and compared with those calculated with monopole-point-dipole lattice sums. The importance of other contributions to the EFG tensor is discussed.

Experimental and Results

The polycrystalline samples of a series $\text{Eu}_{3-y}\text{Sc}_{2+y}\text{Fe}_3\text{O}_{12}$ used in this study had nominal compositions $y = 0.0, 0.2,$ and 0.5 . They are the same as those used by Mondegarian *et al.* (6). X-ray diffraction studies showed (6) that they are single phase. Mössbauer absorbers were prepared by mixing garnet powders with boron nitride and pressing the mixture into lucite containers which were covered with iron-free aluminium foils. The thickness of the garnet absorbers was in the range 20–30 mg/cm^2 .

The Mössbauer effect measurements were performed in the paramagnetic region between liquid nitrogen and room temperature using the 14.41-keV transition in ${}^{57}\text{Fe}$ and the 21.53-keV transition in ${}^{151}\text{Eu}$. The Mössbauer spectra were recorded with a standard spectrometer in which the source of gamma rays moved with a constant acceleration and the multichannel analyzer was operated in the time mode. The spectrometer was calibrated with a Michelson interferometer using a He/Ne laser. A sym-

metric sawtooth reference signal was used, producing two mirror Mössbauer spectra that were folded with a special computer program (7). The sources used were ${}^{57}\text{Co}(\text{Rh})$ and ${}^{151}\text{Sm}(\text{SmF}_3)$. They were kept at the temperature $T_s = 4.2$ or 300 K. The spectra were obtained in transmission geometry. The gamma rays were detected with a Xe- CO_2 filled proportional counter. The spectra below room temperature were obtained in a cryostat with the stability of the absorber temperature T_a of 0.1 K.

${}^{57}\text{Fe}$ Mössbauer spectra of all investigated samples can be fitted with two Lorentzian symmetric quadrupole doublets (Fig. 1) corresponding to Fe^{3+} ions at the a and d sites. The separation $\Delta(i)$ between the two lines of the i th doublet ($i = a, d$) is given by

$$\Delta(i) = \frac{1}{2}eQ_e|V_{zz}(i)|(1 + \eta^2/3)^{\frac{1}{2}} \quad (2)$$

where $-e$ is the charge of the electron, V_{zz} is the principal component of the EFG tensor, Q_e is the quadrupole moment of the Fe nucleus and η is the asymmetry parameter (3). The quadrupole splitting Δ for ${}^{57}\text{Fe}$ is defined as a positive quantity since the two lines of a doublet are indistinguishable for normal powder samples. The point symmetries of the a and d sites imply (8) that the EFG tensor is axially symmetric ($\eta = 0$) at these sites. V_{zz} lies along the $[111]$ and $[100]$ crystallographic directions at the a and d sites, respectively. Mössbauer parameters at the a and d sites derived from computer fits of the ${}^{57}\text{Fe}$ spectra are shown in Table I.

The point symmetry of the c site requires (8) that the EFG tensor is not axially symmetric ($\eta \neq 0$). V_{xx} , V_{yy} , and V_{zz} are directed along the local axes parallel to the face diagonals and the edge of a cubic unit cell. A typical ${}^{151}\text{Eu}$ Mössbauer spectrum is shown in Fig. 2. At first glance it appears that the spectrum is a single line. This, however, is not the case as can be seen from a single line fit (Fig. 2a) with a transmission integral method (9). In the literature many ${}^{151}\text{Eu}$

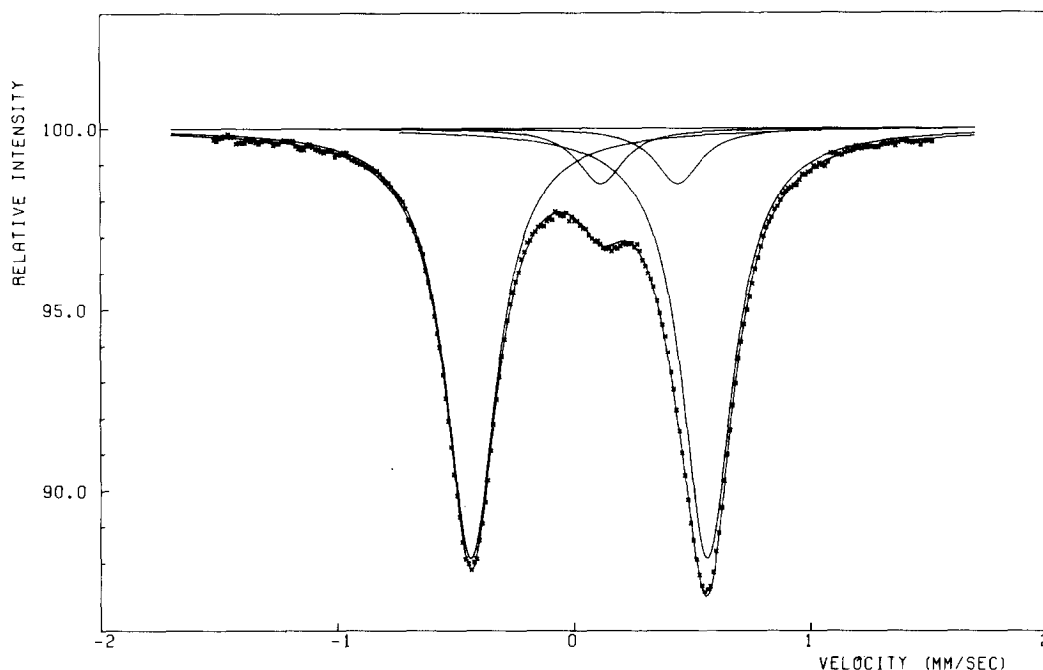


FIG. 1. ^{57}Fe Mössbauer spectrum of the $y = 0.2$ sample at 294.0 K, with the source at the same temperature. The full line is a least-squares computer fit with two symmetric quadrupole doublets, which are also shown.

spectra of compounds in the paramagnetic region with unresolved quadrupole splittings are fitted with single Lorentzian lines (10). This may lead to incorrect values of isomer shifts, as discussed by Goodman *et al.* (11), and later more correctly by Nichols *et al.* (12). We fitted the ^{151}Eu spectra with 12 lines which must be present when $\eta \neq 0$, using a method described by Shenoy and Dunlap (13). Because of the strong overlap of the 12 lines the spectra were fitted with the transmission integral method (9). The positions of the lines depend on the isomer shift δ , the quadrupole coupling constant $eV_{zz}Q_B$, the ratio $R_Q = Q_e/Q_g$ of the excited and ground state quadrupole moments and the asymmetry parameter η , whereas their intensities depend on η (13). The value of R_Q is 1.312 (14). It should be noticed that the sign of the quadrupole coupling constant can be unambiguously determined from the fits of the ^{151}Eu spectra.

Mössbauer parameters of the ^{151}Eu spectra are presented in Table II.

We have calculated the lattice contribution to the EFG tensor at the a , d , and c sites using a monopole-point-dipole model (15, 16). It is assumed in this model that the EFG tensor consists of the monopole V_{ij}^m and the dipole V_{ij}^d contribution. V_{ij}^m arises from the point charges of the ions, whereas V_{ij}^d is due to the induced electric dipole moments. In a garnet structure only oxygen ions contribute to V_{ij}^d because the electric field has nonzero values only at the h sites. Since the induced dipole moments contribute to the electric field themselves, they have to be calculated with a self-consistent iterative method (17). The calculation of the lattice contribution is hampered by the fact that the value of the dipole polarizability α of oxygen is not well known (15, 16, 18), and is usually estimated from the best fit of the theoretical EFG's to the measured

TABLE I
⁵⁷Fe MÖSSBAUER PARAMETERS OF THE Eu_{3-y}Sc_{2+y}Fe₃O₁₂ SERIES IN THE PARAMAGNETIC REGION

Nominal composition y	T _s [K]	T _a [K]	δ(a)[mm/s]	δ(d)[mm/s]	Δ(a)[mm/s]	Δ(d)[mm/s]
0.0	4.2	69.4	0.262(0.002)	0.039(0.001)	0.315(0.003)	1.003(0.001)
	4.2	174.2	0.234(0.002)	0.016(0.001)	0.315(0.004)	1.004(0.001)
0.2	294.0	294.0	0.280(0.002)	0.065(0.001)	0.313(0.004)	1.001(0.001)
	4.2	68.6	0.256(0.002)	0.039(0.001)	0.330(0.004)	1.001(0.001)
	4.2	147.0	0.240(0.003)	0.021(0.001)	0.327(0.004)	1.001(0.001)
	294.0	294.0	0.280(0.002)	0.066(0.001)	0.326(0.003)	1.000(0.001)
0.5	4.2	75.0	0.252(0.002)	0.041(0.001)	0.381(0.004)	1.005(0.001)
	4.2	146.9	0.231(0.002)	0.021(0.001)	0.369(0.004)	1.001(0.001)
	293.0	293.0	0.275(0.001)	0.068(0.001)	0.377(0.004)	0.997(0.001)

Notes: The isomer shifts δ are relative to ⁵⁷Co(Rh) source at temperature T_s. Quadrupole coupling constant Δ = $\frac{1}{2}eQ|V_{zz}|$. Numbers within parentheses are standard deviations as obtained from computer fits.

data. In our calculations we used values of α in the range 0.1–1.0 Å³. The lattice sums (15, 16) were calculated with a spherical boundary method in which the summation is performed by considering the contribution from all lattice sites inside a sphere of a given radius. The calculations of the monopole contribution were performed for a sphere radius of 50 Å, whereas the dipole contribution was calculated for a sphere radius of 100 Å since it converges slower than the monopole contribution. The EFG tensors thus obtained were diagonalized and the principal values of V_{ij} were designated according to the usual convention |V_{zz}| ≥ |V_{yy}| ≥ |V_{xx}|. We assumed in our calculations that the investigated compounds are completely ionic so that the ions have charges equal to their valencies. The crystal structure data necessary to calculate the lattice sums are the lattice constant a and the oxygen positional parameters x, y, and z. The coordinates of the ions in a unit cell were taken from (2). The values of a were measured in (6). Because the compounds were prepared in a polycrystalline form, the values of oxygen positional parameters cannot be determined straightforwardly by means of X-ray diffraction, as can the lat-

tice constants. To calculate the oxygen positional parameters we used the expressions derived by Hawthorne (19), which relate the oxygen positional parameters to the average ionic radii r{X}, r{Y}, and r{Z} at the c, a, and d sites, respectively. The average ionic radii were calculated with the known cation distribution (5) and with the Shannon radii of Eu³⁺, Fe³⁺, and Sc³⁺ ions at proper crystallographic sites (20).

It is apparent from Eqs. (1) and (2) that in comparing the experimental EFG's with the calculated ones the values of the nuclear quadrupole moments of the Mössbauer nuclei and the Sternheimer factors have to be known. Unfortunately, very often these quantities are not precisely determined. This is particularly true for the ⁵⁷Fe nucleus. It was believed until 1981 that Q_e = 0.21 b (14) for ⁵⁷Fe. From ab initio calculations of the EFG tensor in FeCl₂ and FeBr₂ molecules and experimental quadrupole splittings for these molecules trapped in rare-earth matrices, it has recently been shown by Duff *et al.* (21) that Q_e = 0.082 b. This has been confirmed by Vajda *et al.* (22) using shell-model calculations of the J^π = 10⁺ isomer state in ⁵⁴Fe, together with an experimental value of the relative quadru-

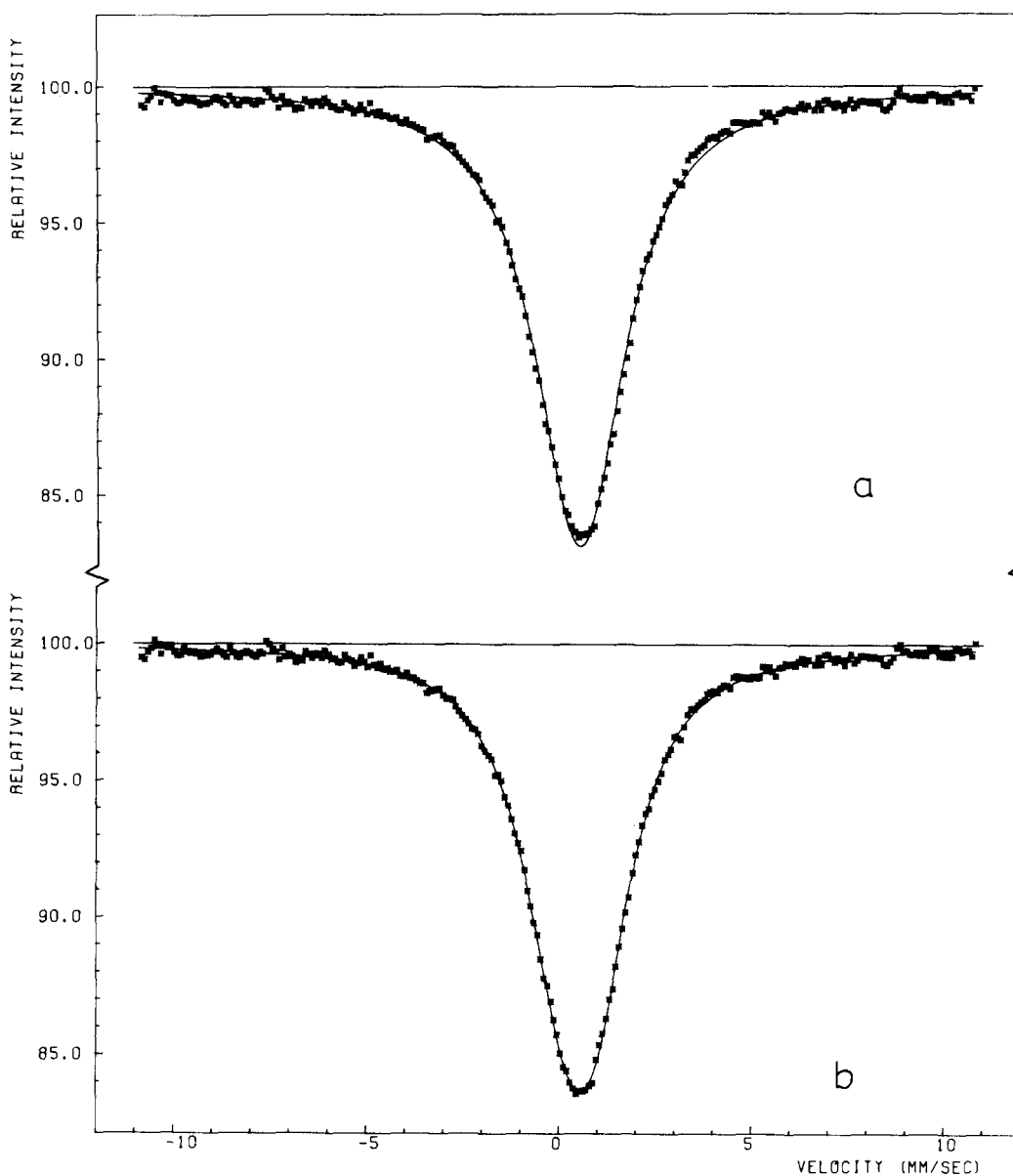


FIG. 2. ^{151}Eu Mössbauer spectrum of the $y = 0.2$ sample at 294.0 K, with the source at the same temperature. The full line is a least-squares computer fit with (a) a single line, and (b) 12 lines.

pole moments of the ^{54}Fe and ^{57}Fe isomers. The new value of Q_e for ^{57}Fe requires the reinterpretation of all hitherto performed calculations of the EFG tensor in Fe-containing materials.

The experimental values of V_{zz} at the a , d , and c sites together with the calculated

ones at these sites are presented in Table III. The experimental values V_{zz}^{exp} were calculated from the room temperature quadrupole splitting constants given in Tables I and II. The following numerical values were adopted: $Q_e = 0.082$ b (21), $\gamma_\infty = -9.14$ (23) for ^{57}Fe data, and $Q_g = 1.14$ b

TABLE II
¹⁵¹Eu MÖSSBAUER PARAMETERS OF THE
 Eu_{3-y}Sc_{2+y}Fe₃O₁₂ SERIES IN THE PARAMAGNETIC
 REGION (THE ISOMER SHIFT δ IS RELATIVE TO THE
¹⁵¹Sm(SmF₃) SOURCE KEPT AT ROOM
 TEMPERATURE)

Nominal composition <i>y</i>	<i>T_a</i> [K]	δ [mm/s]	$eV_{zz}Q_0$ [mm/s]	η
0.0	77.4	0.634(0.047)	3.89(0.69)	0.63(0.44)
	295.0	0.568(0.044)	4.24(1.84)	0.64(0.45)
0.2	77.4	0.628(0.048)	4.42(1.36)	0.52(0.42)
	294.0	0.563(0.045)	4.36(0.85)	0.51(0.43)
0.5	77.4	0.631(0.058)	4.45(0.98)	0.55(0.42)
	292.0	0.559(0.050)	4.73(0.93)	0.67(0.46)

(14), $\gamma_\infty = -61.38$ (24) for ¹⁵¹Eu data. For the *a* and *d* sites the values of V_{zz}^m and V_{zz}^d are given separately. The total contribution can be obtained by simply adding them. For the *c* site $V_{zz}^{m+d}(c)$ (and $\eta^{m+d}(c)$) is given. It is obtained after adding tensorially the monopole and dipole contributions.

Discussion

The values of the isomer shifts δ derived from the ⁵⁷Fe and ¹⁵¹Eu Mössbauer spectra (Tables I and II) confirm that the iron and europium ions are in the trivalent oxidation state (3, 10). For a given absorber temperature *T_a*, they are practically the same for all three compounds. This means that the electronic charge density at the centers of the nuclei does not change with the amount of Sc³⁺ substitution. The decrease of the isomer shifts with increasing temperature is caused by the second-order Doppler effect (3). The observed inequality $\delta(a) > \delta(d)$ is characteristic for garnets (25). It is a result of the covalency effects that are stronger at the *d* sites than at the *a* sites. This is partly due to the fact that the Fe–O distance is shorter at the former site than at the latter (26).

The values of $\Delta(a)$ and $\Delta(d)$ (Table I) do not change with temperature, as is expected for the Fe³⁺ ions. The inequality

TABLE III
 CRYSTAL STRUCTURE PARAMETERS FOR THE Eu_{3-y}Sc_{2+y}Fe₃O₁₂ SERIES TOGETHER WITH EXPERIMENTAL AND CALCULATED VALUES OF V_{zz} IN UNITS OF 10¹⁴ esu AT DIFFERENT SITES (THE CALCULATED VALUES WERE ALREADY MULTIPLIED BY $(1 - \gamma_\infty)$)

Nominal composition <i>y</i>	<i>a</i> (Å)	Oxygen positional parameters			$ V_{zz}^{3p}(a) $	$V_{zz}^m(a)$	$V_{zz}^d(a)$	$ V_{zz}^{3p}(d) $	$V_{zz}^m(d)$	$V_{zz}^d(d)$	$V_{zz}^{3p}(c)$	$\eta^{exp}(c)$	$V_{zz}^{m+d}(c)$	$\eta^{m+d}(c)$
		<i>x</i>	<i>y</i>	<i>z</i>										
0.0	12.637	-0.0289	0.0576	0.1526	12.242(0.156)	-9.603	8.176 ^a 1.075 ^b	39.153(0.039)	-6.074	-4.772 ^a -0.417 ^b	8.91(3.87)	0.64(0.45)	-26.40 ^a -17.67 ^b	0.32 ^a 0.85 ^b
0.2	12.652	-0.0287	0.0576	0.1525	12.751(0.117)	-9.897	8.182 ^a 1.075 ^b	39.114(0.039)	-6.155	-4.525 ^a -0.388 ^b	9.16(1.79)	0.51(0.43)	-25.78 ^a -19.19 ^b	0.38 ^a 0.85 ^b
0.5	12.619	-0.0283	0.0577	0.1522	14.746(0.156)	-10.535	8.497 ^a 1.118 ^b	38.996(0.039)	-6.185	-4.339 ^a -0.366 ^b	9.94(1.95)	0.67(0.46)	-23.46 ^a -21.81 ^b	0.43 ^a 0.83 ^b

^a Using $\alpha = 1.0 \text{ \AA}^3$.

^b Using $\alpha = 0.1 \text{ \AA}^3$.

$\Delta(a) < \Delta(d)$, characteristic for garnets (25), is also fulfilled (Table I). The values of $\Delta(d)$ do not change with the Sc^{3+} substitution y , whereas the $\Delta(a)$ values increase with y . The quadrupole coupling constant $eV_{zz}Q_g$ and the asymmetry parameter η at the c sites (Table II) are the same, within the experimental error, for all the samples. The large errors in the values of $eV_{zz}Q_g$ and η , caused by a very small quadrupole interaction at the c site as compared with the quadrupole interaction at the ^{151}Eu sites in other materials (27), hinder the detection of possible temperature changes of $V_{zz}^{\text{exp}}(c)$. Although only absolute values of $V_{zz}^{\text{exp}}(a)$ and $V_{zz}^{\text{exp}}(d)$ were determined (Table III), their signs are expected to both be negative, because it was shown experimentally for several iron garnets that the signs of V_{zz} at the a and d sites are negative (28, 29). Since the crystal structure parameters do not change dramatically from one iron garnet to the other, it is reasonable to assume that the signs of V_{zz} at the a and d sites are also negative in other iron garnets (30).

Inspection of Table III shows that the monopole contribution is negative at the a and d sites, whereas the dipole contribution is positive at the a , and negative at the d site. Thus, the monopole contribution alone predicts the right sign of V_{zz} at the a and d sites. It can also be noticed that the relative change of the $V_{zz}^m(a)$ value upon going from the $y = 0.0$ sample to the $y = 0.5$ sample is 9.7%, whereas the corresponding change of the $V_{zz}^m(d)$ value is 1.8%. This may explain, at least partially, the experimental result of the $\Delta(a)$ dependence on, and the $\Delta(d)$ independence from the Sc^{3+} substitution y . However, the monopole contribution alone cannot explain the observed inequality $|V_{zz}^{\text{exp}}(a)| < |V_{zz}^{\text{exp}}(d)|$. For $\alpha = 1.0$ and 0.1 \AA^3 , the $V_{zz}^d(a)$ values constitute in the investigated samples 80.7–85.1% and 10.6–11.2% of the $V_{zz}^m(a)$ values, respectively. For the d sites these percentages are 70.2–78.6 and 5.9–6.9. The smallest value of $\alpha = 0.1 \text{ \AA}^3$

used in our calculations is even smaller than the lower limit of the range $0.2\text{--}2.9 \text{ \AA}^3$ of α values used in the literature (for a review of α values used in the calculation of dipole contribution in oxides see, e.g., Refs. (16, 17)). Even for such a small value of α , the dipole contributions at the a and d sites cannot be neglected. The dipole contribution added to the monopole one improves the agreement between the experimental and calculated values of V_{zz} at the d sites and worsens the agreement at the a sites. It is clear from Table III that it is not possible to obtain agreement between V_{zz}^{exp} and $V_{zz}^m + V_{zz}^d$ at the a and d sites for any value of α . One may, therefore, expect that apart from the lattice contribution to the EFG, other contributions should play an important role. Indeed, it was realized at the beginning of the seventies that a significant contribution to the EFG tensor (overlap contribution V_{ij}^{ov}) arises from the overlap distortion of the filled metal orbitals by the ligands (31, 32). Thus, the total EFG at the iron sites is

$$V_{ij} = (1 - \gamma_{\infty})V_{ij}^{\text{latt}} + (1 - R)V_{ij}^{\text{ov}}. \quad (3)$$

The values of V_{zz}^{ov} at the a and d sites were calculated for the garnets YIG (33, 34) and SmIG, GdIG, DyIG, YbIG, LuIG (30, 34). For these sites the overlap contribution turned out to be negative and comparable in magnitude to the monopole contribution. As expected, the absolute value of the overlap contribution at the d site is larger than at the a site (30, 33, 34). Thus, the experimentally observed inequality $|V_{zz}^{\text{exp}}(a)| < |V_{zz}^{\text{exp}}(d)|$ is accounted for mainly by the overlap effects. We did not perform lengthy overlap calculations. We tried, however, to estimate the V_{zz}^{ov} values at the a and d sites in the following way. There is a general trend in REIG, as expected from metal–ligand distance considerations, that the absolute values of V_{zz}^{ov} decrease with the increase of the lattice constant (30, 34). It may, therefore, be assumed that V_{zz}^{ov} in the

investigated samples is roughly the same as in SmIG (q'_1 in Sharma's notation (30)), which has the closest lattice constant to the one of our samples. With this assumption it is possible to estimate the value of the dipole polarizability α , which is of crucial importance for the lattice contribution. Using Eq. (3) with $R = 0.32$ (35), and putting $V_{zz} = V_{zz}^{\text{exp}}$ and $V_{zz}^{\text{latt}} = V_{zz}^m + V_{zz}^d$, one finds a value of α of about 0.4 \AA^3 using a -site V_{zz} data, and of about 4 \AA^3 using d -site V_{zz} data. So estimated values of α will not change too much if one uses Sharma's V_{zz}^{ov} values for other REIG (30). This paradoxical result, also found in other rare-earth garnets (36), seems to indicate either that the V_{zz}^{ov} values in the investigated garnets are dramatically different from those in other REIG, or that the overlap calculations in garnets should be still refined. The latter is in accordance with papers (36, 37) in which it was shown that the present overlap calculations in REIG and YIG fail in explaining the experimental results. A possible reason of this failure was given by Housley and Grant (37). These authors pointed out that in ionic materials in which the electric fields, and therefore the induced dipole moments, are large, the direct application of the LCAO molecular theory is inappropriate. In the investigated garnet series the electric fields at oxygen sites are large because they are the source of the nonnegligible dipole contribution V_{zz}^d , even for very small values of α . Thus, it is not surprising that the overlap calculations cannot explain the experimental results. Housley and Grant (37) suggested that in overlap calculations the molecular orbitals should be formed using atomic orbitals for the valence electrons centered on the displaced (by the electric fields) shell positions rather than at the nuclear positions.

The monopole-point-dipole lattice sum calculations at the c site produce the order of magnitude of the observed $V_{zz}^{\text{exp}}(c)$ value. They cannot, however, account for the pos-

itive sign of $V_{zz}^{\text{exp}}(c)$, regardless of the value of dipole polarizability α . This indicates that the second-order $4f$ contribution is of significant importance at the c site. The overlap effects at the c site are negligible since the $4f$ electrons in the rare-earths are well localized and the RE-O distance is much larger than the Fe-O distances at the a and d sites, so that there is small overlap of the $4f$ wavefunctions with those of the ligands.

The experimental uncertainties of the lattice constants and the oxygen positional parameters are usually about 0.004 \AA and 0.0005 , respectively (38). To estimate how these uncertainties influence the values of the calculated EFG, we calculated monopole and dipole (with $\alpha = 1 \text{ \AA}^3$) contributions for the $y = 0.0$ sample at the three sites. It turned out that the change of 0.004 \AA in the lattice constant alters these contributions by about 1.5%. They are changed by about 10% when the oxygen parameters are changed by 0.0005 . It is thus seen that the uncertainties of the lattice constants influence the V_{zz} values to a much lesser extent than the uncertainties of the oxygen positional parameters.

Summarizing, this paper shows that the monopole contribution to the EFG tensor in the $\text{Eu}_{3-y}\text{Sc}_{2+y}\text{Fe}_3\text{O}_{12}$ garnets can explain the signs and the changes with the Sc^{3+} substitution y of the experimental quadrupole coupling constants at the a and d sites. The monopole and dipole contributions do not account for the experimental values at these sites for any value of the dipole polarizability α . The contribution from induced quadrupole moments at oxygen sites, which was neglected in our calculations, would probably improve the situation. But, as was pointed out by Artman (15), the quadrupole polarizability tensor is not well defined either experimentally or theoretically. Thus, it was of no use to include the quadrupole contribution in the calculations. The present calculations show that the di-

pole contribution is not negligible, even for very small values of the dipole polarizability of oxygens. Its neglect is one of the reasons of the failure of Sharma's model (30) in explaining the experimental results in REIG. The lattice together with the overlap contribution would probably explain the experimental data in the Eu-Sc-Fe garnet series. It seems, however, that overlap calculations in garnets should be still refined since they do not account for the experimental data even in relatively simple rare-earth garnets. The present paper also indicates the importance of the second-order 4f contribution at the *c* sites.

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