Effects of a nontrigonal crystal field on spectroscopic properties of Fe^{2+} ions in yttrium iron garnet: Si(Ge)

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Spectroscopic properties of Fe^{2+} ion induced by tetravalent dopants in yttrium iron garnet (YIG) are reconsidered in view of the low-symmetry crystal-field (CF) effects on the ^5D term energy-level structure. Orbital wave functions and energies are found from diagonalization of the CF Hamiltonian consisting of cubic, trigonal, and nontrigonal components. The ground state of the Fe^{2+} ion appears to be an orbital singlet distinct from the $^5A_{1g}$ singlet assumed previously, and well separated from the higher-lying states. The spin-Hamiltonian formalism is adopted to describe the spectroscopic properties of the ground singlet. A numerical method is worked out to deal with the extremely complicated Fe^{2+} in the YIG:Me^{4+} case. The second-order $B_0^{(2)}$, $B_1^{(2)}$, $B_2^{(2)}$ and fourth-order $B_0^{(4)}$, $B_1^{(4)}$, $B_2^{(4)}$, $B_3^{(4)}$, $B_4^{(4)}$ spin-Hamiltonian parameters, and the g_x, g_y, g_z, g_{xz} components of the Zeeman g tensor are calculated for a wide range of the microscopic parameters. The very-low-symmetry parameters $B_1^{(2)}$, $B_1^{(4)}$, and $B_2^{(4)}$ have not been discussed in the literature as yet. The properties of the nearby (I) and far (II) Fe^{2+} centers can now be well explained by our results. The Fe^{2+} II centers can be regarded as more anisotropic than the I centers. The dominant parameter $B_0^{(2)}$ (the conventional D) is found to be positive and of the value of several cm^{-1}. Hence we expect the model considered to account well also for the single-ion magnetocrystalline anisotropy of Fe^{2+} ions in YIG:Me^{4+} which has not been satisfactorily explained by previous models.

I. INTRODUCTION

In recent years several studies have been reported of yttrium iron garnet (YIG) doped with tetravalent dopants.[1–14] A wide variety of interesting effects have been observed in YIG:Si and YIG:Ge, including a number of photomagnetic effects.[15–20] It has generally been assumed that Me^{4+} dopants substituting for Fe^{3+} induce Fe^{2+} ions at octahedral sites[21,22] and the Fe^{2+} centers are responsible for these effects. Ferrous ions are found also in nominally pure YIG[9,23–27] and rare-earth garnets with some impurities.[28–32] The presence of small amounts of Fe^{2+} ions strongly influences the spectroscopic and magnetic properties of these important materials for a number of technical applications. Hence the electronic structure of Fe^{2+} ion in garnets has been a matter of considerable interest; however, it is still not satisfactorily explained.

Of the two basically different models, viz. a purely electronic model[6,8,33,34] and small polaron model,[14,20,23] the former has attracted more interest.[1–5,7,9–12,15–20,22] The electronic model assumes the electrons of the Fe^{2+} centers are well localized, at least at low temperatures, where the thermally induced electron hopping[13] is very small. In the framework of the electronic model the following models of energy levels of an induced Fe^{2+} ion have been considered up to now:

(i) The model proposed by Hartwick and Smit[33] is based on the anisotropic ground doublet energy states arising from the lowest trigonal doublet $^5E_g(^5T_{2g})$ split by exchange-field, spin-orbit coupling and Coulomb field due to tetravalent dopant ions. Hence the simple model takes into account only the two lowest of the 15 states of the $^5T_{2g}$ submultiplet. This approach has met some difficulties in explaining ferromagnetic resonance,[4,33] effective concentration of Fe^{2+} ions,[1,3,8] the spin-orbit coupling constant for Fe^{2+} in the crystal,[8] and the temperature dependence of magnetostriction.[7]

(ii) The model[34] considered earlier by us neglected crystal-field (CF) components of symmetry lower than trigonal and assumed the ground orbital singlet $^5A_{1g}(^5T_{2g})$ well separated from the higher ^5E_g doublet. We have adopted a spin-Hamiltonian approach,[35] taking into account for the first time the fourth-order terms[36] for the spin $S=2$. This approach has yielded the cubic single-ion anisotropy constants[37] $K_1(Fe^{2+})$ and $K_2(Fe^{2+})$ of values close to experimental values[8]; however, the discrepancy in the sign of K_2 still remained.[34]

(iii) Alben *et al.*[6] have proposed for Fe^{2+} in YIG:Si a Hamiltonian consisting of a cubic, trigonal, and nontrigonal CF components, spin-orbit coupling, and isotropic exchange. Attempting a numerical calculation of the photodetachment cross section and related quantities, they have diagonalized this Hamiltonian

within the ${}^5T_{2g}$ submultiplet. However, neither ground energies nor ground-state wave functions have been explicitly given. Unlike Hartwick and Smit,[33] the authors[6] have considered the origin of all CF components in a unified way and provided some predictions of the CF parameters involved. The nontrigonal CF component has appeared to be essential in explaining the experiment.[6]

Seeking a better microscopic model for the magnetocrystalline anisotropy of Fe^{2+} ions induced in garnets, we have reconsidered the crystal-field Hamiltonian of Alben *et al.*[6] within the ${}^5D(d^6)$ free-ion term states. We have found that the model Hamiltonian[6] contains information which has not been exploited by these authors. Our caculations indicate the spectroscopic properties of Fe^{2+} in YIG:Si(Ge) can well be interpreted in terms of a spin Hamiltonian for a certain range of the trigonal and nontrigonal CF parameters. Due to the very low C_1 symmetry[6] of the Fe^{2+} environment in YIG:Si(Ge) the resulting spin Hamiltonian comprises three and five terms of second and fourth order, respectively.

The aim of this paper is to give a full theoretical account of the spin-Hamiltonian parameters for the orbital singlet ground state of Fe^{2+}, predicted within the model assumptions,[6] which is now quite different from the ${}^5A_{1g}$ singlet considered previously.[34] A brief outline of this paper has been presented previously.[38] The results of this paper will serve as a basis for consideration of the magnetocrystalline anisotropy of Fe^{2+} in YIG:Si(Ge) in a forthcoming publication.

II. LOW-SYMMETRY CRYSTAL FIELD

In the section we consider the crystal-field (CF) Hamiltonian proposed for Fe^{2+} in YIG:Si by Alben *et al.*[6] and consisting of the cubic, trigonal, and nontrigonal CF components, respectively,

$$\hat{\mathcal{H}}_{CF}=\hat{\mathcal{H}}_{cub}+\hat{\mathcal{H}}_{trig}+\hat{\mathcal{H}}_{ntrig} \quad . \tag{1}$$

In terms of spherical tensor operators $O_q^{(k)}(\hat{L}_x,\hat{L}_y,\hat{L}_z)$ with the quantization axis z coinciding with one of the four [111] trigonal axes, the cubic CF is[39]

$$\hat{\mathcal{H}}_{cub}=-\tfrac{3}{4}Dq[O_0^{(4)}+(\tfrac{10}{7})^{1/2}(O_{+3}^{(4)}-O_{-3}^{(4)})] \quad . \tag{2}$$

The free Fe^{2+} ion ground term ${}^5D(3d^6)$ is split by $\hat{\mathcal{H}}_{cub}$ Eq. (2) into ${}^5E_g$ and ${}^5T_{2g}$ states, where the latter is the lowest, and the wave functions have the form[39] for E_g:

$$\Psi_4=(\tfrac{1}{3})^{1/2}|-2\rangle-(\tfrac{2}{3})^{1/2}|1\rangle,$$

$$\Psi_5=(\tfrac{1}{3})^{1/2}|2\rangle+(\tfrac{2}{3})^{1/2}|-1\rangle \quad ,$$

and for ${}^5T_{2g}$:

$$\Psi_1=|0\rangle,\ \Psi_2=(\tfrac{2}{3})^{1/2}|-2\rangle+(\tfrac{1}{3})^{1/2}|1\rangle \quad ,$$
$$\Psi_3=(\tfrac{2}{3})^{1/2}|2\rangle-(\tfrac{1}{3})^{1/2}|-1\rangle \quad . \tag{3}$$

The trigonal CF operator[6] $(3\hat{L}_z^2-6)$ is equivalent to $2O_0^{(2)}(\hat{L}_x,\hat{L}_y,\hat{L}_z)$. The nontrigonal CF operator[6] $(3\hat{L}_x^2-6)$ is equivalent to $2O_0^{(2)\prime}(\hat{L}_{\bar{x}},\hat{L}_{\bar{y}},\hat{L}_{\bar{z}})$ with the $\bar{x}$, $\bar{y}$, and $\bar{z}$ axes along the y, z, and x axes, respectively. Hence, using the Euler angles[40] $\alpha=-90°$, $\beta=-90°$, and $\gamma=0$, we can express the operator $O_0^{(2)\prime}$ in the $\{xyz\}$ frame as $\{-O_0^{(2)}+\frac{1}{2}\sqrt{6}(O_{+2}^{(2)}+O_{-2}^{(2)})\}$. It leads finally to an equivalence

$$\hat{\mathcal{H}}_{trig}+\hat{\mathcal{H}}_{ntrig}\equiv-\Delta O_0^{(2)}+\Gamma(O_{+2}^{(2)}+O_{-2}^{(2)}) \quad , \tag{4}$$

where the parameters Δ and Γ are related to D_z and D_x of Alben *et al.*[6] as follows:

$$\Delta=2D_z+D_x,\quad \Gamma=(\tfrac{3}{2})^{1/2}D_x \quad . \tag{5}$$

The symmetry of the Hamiltonian equation (4) has actually no bearing with the orthorhombic symmetry[41,42] in spite of a similar form. The second term in Eq. (4) accounts partially for the reduction from C_{3i} to C_1 symmetry.[6]

Using Eqs. (2) and (4) we have diagonalized the Hamiltonian equation (1), taking into account both ${}^5T_{2g}$ and ${}^5E_g$ submultiplets in Eq. (3), for a wide range of Δ and Γ. The simpler ${}^5T_{2g}$ approximation based on the neglect of the ${}^5E_g$ submultiplet used by Alben *et al.*[6] has been found poor for Fe^{2+} in low-symmetry CF.[42] We take Dq in Eq. (2) as[39] 1000 cm^{-1}, which is well confirmed by recent experimental data.[9] We give below only some numerical results which reveal the important consequences of the model.

The Hamiltonian equation (4) completely removes the ${}^5T_{2g}$ and ${}^5E_g$ orbital degeneracy resulting in five distinct orbital singlet states with spin $S=2$. As may be seen in Table I, some Δ and Γ values indicate that the energy splitting E_1 between the ground orbital singlet and the next level is fairly large compared with the spin-orbit coupling constant $|\lambda|\approx 60$–110 cm^{-1} for Fe^{2+} in crystals.[43] Hence, there exists a region of Δ and Γ in which the subsequent effects of spin-orbit coupling on the energy-level structure of Fe^{2+} ion can be accounted for by perturbation theory and the spin-Hamiltonian approach.[35]

Alben *et al.*[6] have treated D_x and D_z in Eq. (5) as an adjustable positive parameter with values up to 100–300 and about 200 cm^{-1}, respectively. Their data on the photoinduced anisotropy coefficients and the thermally induced anisotropy (all at 4.2 K) could be fitted with somewhat different values of D_x and D_z, all lying, however, in the overall range 150–300 for D_x and 50–200 for D_z. This corresponds to Γ between 184 and 367 and Δ between 250 and 700

TABLE I. Calculated values for the energy splitting E_1 between the ground and the next orbital singlet for Fe^{2+} in YIG:Si(Ge) for various trigonal $\Delta(D_z)$ and nontrigonal $\Gamma(D_x)$ CF parameters. The cubic $Dq = 1000$ cm^{-1}. The values in parentheses at each entry refer to D_z for a given pair (Γ, Δ). All values are in cm^{-1}.

Γ, D_x \ Δ	100	300	400	500	600	700
50,41	169(30)	124(130)	. . .	. . .	96(280)	. . .
100,82	397(9)	285(109)	256(159)	235(209)	215(259)	199(309)
150,123	639(−11)	473(89)	424(139)	386(189)	354(239)	326(289)
200,163	889(−36)	678(68)	609(118)	554(168)	508(218)	467(268)
250,204	1142(−52)	895(48)	808(98)	737(148)	676(198)	625(248)
300,245	1395(−72)	1195(28)	1016(78)	930(128)	856(178)	792(228)

(cm^{-1}). The Γ and Δ from the latter range yield just the large energy splitting E_1 (see Table I). This fact promotes the application of the spin-Hamiltonian approach for Fe^{2+} in YIG:Si(Ge).

The nature of the ground orbital singlet is now quite different from the ${}^5A_{1g}(\Psi_1)$ singlet[34] which had failed to explain the magnetic anisotropy data. The wave functions of the Hamiltonian equation (1) are linear combinations of Ψ_i Eq. (3)

$$\Phi_j = \sum_{i=1}^{5} \alpha_{ji} \Psi_i \tag{6}$$

and the mixing coefficients α_{ij} are shown in Table II for representative values of $\Gamma = 250$ and $\Delta = 300$ cm^{-1}. It is seen that the ground singlet arises predominantly from the lower trigonal doublet[36] (Ψ_2, Ψ_3) with a strong admixture of the singlet Ψ_1. Thus we may expect different spectroscopic and magnetic properties for the Fe^{2+} ion in the framework of the present model[6] as compared with previous models.[8,33,34]

III. SPIN-HAMILTONIAN FORMALISM

The derivation method for the spin Hamiltonian by tensor algebra in perturbation theory[44] has recently been outlined.[35] Our method is based on adopting the recoupling procedure for tensor products to separate $\langle\langle$ orbital $\rangle\rangle$ and $\langle\langle$ spin $\rangle\rangle$ parts in perturbation theory. A brief summary of the salient steps of this derivation can be found in Ref. 35. The complete spin Hamiltonian for spin $S = 2$ can be written as

$$\tilde{\mathcal{H}}_{ZF} + \tilde{\mathcal{H}}_{Ze} = B^{(2)} \cdot \tilde{O}^{(2)}(\hat{\vec{S}}) + B^{(4)} \cdot \tilde{O}^{(4)}(\hat{\vec{S}}) + \mu_B \vec{H} \cdot g \cdot \hat{\vec{S}} \ , \tag{7}$$

where the generalized scalar product is defined as

$$B^{(k)} \cdot \tilde{O}^{(k)} \equiv \sum_{q=-k}^{+k} (-1)^{k-q} B_{+q}^{(k)} \tilde{O}_{-q}^{(k)}$$

and the operators $\tilde{O}_q^{(k)}(\hat{S}_x, \hat{S}_y, \hat{S}_z)$ denote the spherical tensor operators[35,44] with $S = 2$. We have derived previously[44] general expression for the spin-Hamiltonian parameters $B_q^{(k)}$ in Eq. (7) taking into account spin-orbit (λ) and spin-spin coupling (ρ). Then we have been able to relate explicitly the $B_q^{(k)}$ with the microscopic parameters λ, ρ, and the energies E_i for $3d^4$ and $3d^6$ ions in tetragonal (trigonal)[36] and orthorhombic[41,42] symmetry. However, this method[36,41,42] is not applicable for Fe^{2+} in

TABLE II. The mixing coefficients α_{ij} of the wave functions Φ_j [see Eq. (6)] for Fe^{2+} in YIG:Si(Ge) with $Dq = 1000$, $\Delta = 300$, and $\Gamma = 250$ cm^{-1}.

Energy level (cm^{-1})	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5
$E_0 = 0$	0.4002	0.6474	0.6474	0.0290	0.0290
$E_1 = 895$	0.0000	0.7037	−0.7037	0.0693	−0.0693
$E_2 = 2386$	−0.9137	−0.2843	−0.2843	0.0415	0.0415
$E_3 = 10\,578$	0.0702	−0.0099	−0.0099	0.7053	0.7053
$E_4 = 11\,862$	0.0000	0.0693	−0.0693	−0.7037	0.7037

YIG:Si(Ge) because of the extremely low C_1 symmetry. The basic wave functions[44] are now complicated linear combinations Eq. (6) varying with Δ and Γ.

Below we give an outline of the procedure adopted to calculate the $B_q^{(k)}$'s for Fe^{2+} in YIG:Si(Ge). As the present method can be applied to a spin Hamiltonian for arbitrary symmetry and the resulting formulas are rather lengthy, we give the details elsewhere.[45] Using the formulas[44] for various components of the tensor products involved in the theory, we have reformulated general expressions[44] for the $B_q^{(k)}$'s to a form of multidimensional matrices ("arrays"). For example, the second-order parameters[44] $B_0^{(2)}(\lambda^2)$ and $B_{\pm 2}^{(2)}(\lambda^2)$ are given by

$$B_0^{(2)}(\lambda^2) = \tfrac{1}{3}\lambda^2\{2W[2,2,1] + W[1,3,1] + W[3,1,1]\} \ , \tag{8}$$

$$B_{+2}^{(2)}(\lambda^2) = (\tfrac{2}{3})^{1/2}\lambda^2 W[3,3,1] \ ,$$
$$B_{-2}^{(2)}(\lambda^2) = (\tfrac{2}{3})^{1/2}\lambda^2 W[1,1,1] \ . \tag{9}$$

The Zeeman g tensor components have the form

$$g_{pr} = 2 - \lambda\{W[p,r,1] + W[r,p,1]\} \ . \tag{10}$$

The matrix W is defined as

$$W[p,r,b] \equiv \sum_a L[p,b,a]^* L[r,a,1]/E[a] \ , \tag{11}$$

where $E[a]$ denotes the energies[44] here found from diagonalization of the Hamiltonian equation (1) (see Table II). We exclude the ground energy level from summation in Eq. (11) putting $E[1]$ as infinity, whereas $E[2] \equiv E_1$, $E[3] \equiv E_2$, etc. The symbol $L[q,i,j]$ in Eq. (11) represents a matrix element of the orbital operator $\hat{L}_q$ arising from spin-orbit coupling,[44] within the basis $\{\Phi_j\}$ Eq. (6). For convenience we have renumerated in Eqs. (8)–(11) the $q = -1, 0, +1$ components[44] of $\hat{L}_q$ as $q = 1$, 2, and 3, respectively. Hence we have

$$L[q,i,j] \equiv \{\check{L}_q(\Phi)\}_{ij} \ ,$$
$$\check{L}_q(\Phi) \equiv A^T \check{L}_q(\Psi) A \ , \tag{12}$$

where the matrix $\check{L}_q(\Psi)$ refers to the initial basis $\{\Psi_i\}$ Eq. (3), and $\check{A} \equiv \{\alpha_{ij}\}$ is the matrix of the mixing coefficients α_{ij} Eq. (6). The orbital operators $\tilde{O}_q^{(2)}(\hat{\tilde{L}})$ arising from the spin-spin coupling[36,44] have been treated in a similar way as $\hat{L}_q$ in Eq. (12). An appropriate program has been written to calculate all necessary matrices and thence the parameters $B_q^{(k)}$ by computer. The results for various Δ and Γ are presented in Sec. IV.

IV. SPIN HAMILTONIAN FOR Fe^{2+} IN YIG:Si(Ge)

First we shall consider the symmetry of a spin Hamiltonian resulting from Eq. (7) for Fe^{2+} in YIG:Si(Ge). From group theory[46] the total number of real and imaginary invariants of second order is, for the C_1 symmetry, three and two, respectively. Corresponding numbers for the fourth-order invariants are five and four. The matrices of the orbital operators $\hat{L}_q$ and $\tilde{O}_q^{(2)}(\hat{L})$ within the basis $\{\Psi_i\}$ Eq. (3) are found imaginary and real, respectively. Hence, as the Hamiltonian equation (4) is truncated from the most general form for the C_1 symmetry[46] and contains no imaginary parts; the same holds within the basis $\{\Phi_j\}$ Eq. (6) due to the real matrix $\check{A}$ in Eq. (12). This ensures that the $B_q^{(k)}$'s calculated by the method outlined in Sec. III will contain no imaginary parts, which in general are admitted by theory[46,47] and can as well as be derived from the general expressions.[44] Hence the zero-field spin Hamiltonian for Fe^{2+} in YIG:Si(Ge) in the limits of the model assumptions (see Sec. II) should consist of only real invariants[46] of the form

$$\mathfrak{H}_{ZF} = B_0^{(2)}\tilde{O}_0^{(2)} + B_1^{(2)}(\tilde{O}_{+1}^{(2)} - \tilde{O}_{-1}^{(2)}) + B_2^{(2)}(\tilde{O}_{+2}^{(2)} + \tilde{O}_{-2}^{(2)}) + B_0^{(4)}\tilde{O}_0^{(4)} + B_1^{(4)}(\tilde{O}_{+1}^{(4)} - \tilde{O}_{-1}^{(4)})$$
$$+ B_2^{(4)}(\tilde{O}_{+2}^{(4)} + \tilde{O}_{-2}^{(4)}) + B_3^{(4)}(\tilde{O}_{+3}^{(4)} - \tilde{O}_{-3}^{(4)}) + B_4^{(4)}(\tilde{O}_{+4}^{(4)} + \tilde{O}_{-4}^{(4)}) \ . \tag{13}$$

The operators $\tilde{O}_q^{(k)}$ in Eq. (13) are expressed in the x, y, and z local axes of the Hamiltonian equation (4) which differ for each of the basic 12 orientationally nonequivalent Fe^{2+} sites.[6] So long as the CF Hamiltonian is assumed as Eq. (4) the form Eq. (13) holds for each Fe^{2+} site.

Below we present the calculated total spin-Hamiltonian parameters[44] the $B_q^{(2)} = B_q^{(2)}(\lambda^2) + B_q^{(2)}(\rho)$ and $B_q^{(4)} = B_q^{(4)}(\lambda^4) + B_q^{(4)}(\lambda^2\rho) + B_q^{(4)}(\rho^2)$, for a wide range of Γ and Δ fulfilling the perturbation condition $E_1 >> \lambda$ (see Sec. II). Each contribution to $B_{+q}^{(k)}$ and $B_{-q}^{(k)}$ has been calculated from an independent expression [cf. Eq. (9)]. The results show the relationships as required by symmetry between the $B_{+q}^{(k)}$'s and $B_{-q}^{(k)}$'s leading with the use of $B_{|q|}^{(k)} \equiv B_{+q}^{(k)}$ to the form Eq. (13). It proves the correctness of our numerical method.

The contributions to the $B_q^{(k)}$'s arising from spin-spin coupling depend in a different way on Γ and Δ than the pure spin-orbit-coupling contributions. The former contributions amount even up to 250 and 125% of the latter for $B_0^{(4)}$ and $B_3^{(4)}$, respectively, for

TABLE III. Calculated spin-Hamiltonian parameters for Fe^{2+} in YIG:Si(Ge) vs Δ with $\Gamma=200$, $\lambda=-80$, and $\rho=0.18$. All values except g_z(dimensionless) are in cm^{-1}.

Δ	100	300	400	500	600
$B_0^{(2)}(D)$	1.9(−2.9)	6.6(−9.9)	8.8(−13.2)	11.1(−16.6)	13.4(−20.1)
$B_1^{(2)}=-B_{-1}^{(2)}$	−3.0	−3.4	−3.4	−3.4	−3.4
$B_2^{(2)}=B_{-2}^{(2)}$	−2.0	−1.5	−1.2	−1.0	−0.9
g_z	2.175	2.311	2.383	2.459	2.538
$B_0^{(4)}$	0.013	0.015	0.048	0.095	0.160
$B_1^{(4)}=-B_{-1}^{(4)}$	−0.011	−0.039	−0.055	−0.073	−0.093
$B_2^{(4)}=B_{-2}^{(4)}$	0.0052	0.0040	0.0037	0.0036	0.0035
$B_3^{(4)}=-B_{-3}^{(4)}$	0.0016	0.0008	0.0004	0.0001	−0.0002
$B_4^{(4)}=B_{-4}^{(4)}$	0.0025	0.0012	0.0008	0.0005	0.0004

certain Δ and Γ. The second-order parameters are less influenced by spin-spin coupling, although in the whole range of Δ and Γ studied (see below) the $B_2^{(2)}(\rho)$ amounts to between 14 and 20% of the $B_2^{(2)}(\lambda^2)$. It confirms our earlier conclusion[36,41,42] on the significant role of the spin-spin coupling in spin Hamiltonian for $3d^4$ and $3d^6$ ions.

Tables III and V give a dependance of the $B_q^{(k)}$'s on Δ with $\Gamma=200$ and 300 cm^{-1}, respectively. We use here[36,48] $\rho=0.18$ and $\lambda=-80$ cm^{-1}. The results with $\lambda=-90$ cm^{-1} are available from the author on request. The value $\lambda=-80$ cm^{-1} refers to the lower limit of the covalency reduction factor[43] 0.65 for Fe^{2+} in crystals with the free-ion λ value taken as[48] -123 cm^{-1}. Although some authors[39,43] use $\lambda_{fi}=-100$ cm^{-1}, the $|\lambda|$ value 54 and 25 cm^{-1} found[8] for Fe^{2+} in YIG:Ge seems to suggest an inadequacy of the energy-level model adopted.[33]

Some explanation is needed for the first column in Table III. To cover a wide range of Δ and Γ we have also calculated the $B_q^{(k)}$'s with $\Delta=100$ and $\Gamma=150$, 200, 250, and 300. However, the results show $|B_1^{(2)}|>|B_2^{(2)}|\approx B_0^{(2)}$ and the corresponding D_z is negative (see Table I), which seems not to account for the actual situation of Fe^{2+} in YIG:Si(Ge).[6] Hence we refrain from presenting these results in full here.

Table IV shows the dependance of the $B_q^{(k)}$'s on λ. Besides the $\lambda=-80$ cm^{-1} columns of Table IV together with the $\Delta=300$ and 400 columns of Table III and V illustrate a detailed dependence of the $B_q^{(k)}$'s on Γ.

In Tables III–V we give also the conventional[39] axial $D=-\frac{3}{2}B_0^{(2)}$ (Refs. 35 and 44). The other conventional parameters[36,44] E, a, and F are less useful for the present case. It is worth noting that no equivalency to conventional terms exists for $B_1^{(4)}$ and $B_2^{(4)}$, while the second term in Eq. (13) equivalent to

$$B_1^{(2)}\left(\tfrac{3}{2}\right)^{1/2}(\hat{S}_x\hat{S}_z+\hat{S}_z\hat{S}_x) \tag{14}$$

has been considered up to now only by a few authors.[49]

TABLE IV. Calculated spin-Hamiltonian parameters for Fe^{2+} in YIG:Si(Ge) vs λ with $\Delta=300$, $\Gamma=250$, and $\rho=0.18$. The last column is with $\Delta=400$. All values except g_z (dimensionless) are in cm^{-1}.

$\lvert\lambda\rvert$	100	90	80	70	80
$B_0^{(2)}(D)$	7.1(−10.6)	5.8(−8.6)	4.6(−6.9)	3.5(−5.3)	6.3(−9.4)
$B_1^{(2)}=-B_{-1}^{(2)}$	−4.3	−3.5	−2.8	−2.2	−2.9
$B_2^{(2)}=B_{-2}^{(2)}$	−2.1	−1.8	−1.4	−1.2	−1.2
g_z	2.292	2.263	2.234	2.205	2.287
$B_0^{(4)}$	0.0053	0.0032	0.0017	0.0007	0.0138
$B_1^{(4)}=-B_{-1}^{(4)}$	−0.0429	−0.0283	−0.0179	−0.0106	−0.0260
$B_2^{(4)}=B_{-2}^{(4)}$	0.0057	0.0038	0.0024	0.0014	0.0023
$B_3^{(4)}=-B_{-3}^{(4)}$	0.0014	0.0008	0.0004	0.0002	0.0002
$B_4^{(4)}=B_{-4}^{(4)}$	0.0020	0.0013	0.0009	0.0005	0.0006

TABLE V. Calculated spin-Hamiltonian parameters for Fe^{2+} in YIG:Si(Ge) vs Δ with $\Gamma=300$, $\lambda=-80$, and $\rho=0.18$. All values except g_z(dimensionless) are in cm^{-1}.

Δ	300	400	500	600	700
$B_0^{(2)}$ (D)	3.4(−5.1)	4.7(−7.0)	6.0(−9.1)	7.4(−11.1)	8.9(−13.3)
$B_0^{(2)}=-B_{-1}^{(2)}$	−2.4	−2.5	−2.6	−2.6	−2.7
$B_2^{(2)}=B_{-2}^{(2)}$	−1.4	−1.3	−1.1	−1.0	−0.9
g_z	2.186	2.227	2.270	2.315	2.364
$B_0^{(4)}$	−0.0014	0.0039	0.0122	0.0244	0.0414
$B_1^{(4)}=-B_{-1}^{(4)}$	−0.0093	−0.0138	−0.0190	−0.0250	−0.0319
$B_2^{(4)}=B_{-2}^{(4)}$	0.0015	0.0015	0.0015	0.0016	0.0017
$B_3^{(4)}=-B_{-3}^{(4)}$	0.0003	0.0002	0.0000	−0.0000	−0.0001
$B_4^{(4)}=B_{-4}^{(4)}$	0.0007	0.0005	0.0003	0.0002	0.0002

The g tensor is found from Eq. (10) to be fully anisotropic in spherical coordinates.[44] However, its components are mutually related, and $\tilde{\mathcal{H}}_{Ze}$ in Eq. (7) resolves for Fe^{2+} in YIG:Si(Ge) into a conventional Hamiltonian

$$\tilde{\mathcal{H}}_{Ze}=\mu_B(g_xH_x\hat{S}_x+g_yH_y\hat{S}_y+g_zH_z\hat{S}_z)+\mu_Bg_{xz}(H_x\tilde{S}_z+\hat{S}_x)\ , \tag{15}$$

in accordance with symmetry requirements [cf. Eqs. (13) and (14)]. The g_z is given in Tables III–V while the other components in Eq. (15) are collected in Table VI for some extreme values of Δ and Γ with $\lambda=-80\ cm^{-1}$.

The above results reveal the significance of the very-low-symmetry effects for spectroscopic properties of Fe^{2+} in YIG:Si. The spin-Hamiltonian parameters $B_1^{(2)}$, $B_2^{(2)}$ and $B_1^{(4)}$, $B_2^{(4)}$ appear to attain considerable values comparing with the axial parameters $B_0^{(2)}$ and $B_0^{(4)}$, respectively.

Below we summarize the quantitative conclusions of Tables III–VI.

a. $B_q^{(k)}$ *versus* Δ *for constant* Γ. In the range $\Delta=300$–600 (700) $B_1^{(2)}$ is nearly insensitive to Δ for any Γ considered, whereas $B_0^{(2)}$ increases twice and $B_2^{(2)}$ decreases slightly with Δ. $B_0^{(4)}$ is the most sensitive to Δ. It increases about 10 times for $\Gamma=200$, while it changes sign between $\Delta=300$ and 400 for $\Gamma=300$ and then increases strongly with Δ. There exists a wide range of Δ where $B_1^{(4)}$ is dominant over the axial $B_0^{(4)}$. $B_2^{(4)}$ depends only slightly on Δ but attains for $\Delta=300$ with $\Gamma=250$, 300 values which are comparable with $|B_0^{(4)}|$. Among the fourth-order parameters only $B_3^{(4)}$ and $B_4^{(4)}$ appear to be less important in magnitude.

b. $B_q^{(k)}$ *versus* Γ *for constant* Δ. In the range $\Gamma=200$–300, $B_2^{(2)}$ is nearly insensitive to Γ for any Δ considered. $B_0^{(2)}$ and $B_1^{(2)}$ decreases with Γ and the ratio $B_q^{(2)}(\Gamma=200)/B_q^{(2)}(\Gamma=300)$ is almost the same for each Δ, being 1.9–1.8 for $B_0^{(2)}$ and 1.4 for $B_1^{(2)}$. The fourth-order parameters all decrease several times with Γ, and the most sensitive as regards magnitude and sign (for $\Delta=300$) is $B_0^{(4)}$.

c. $B_q^{(k)}$ *versus* λ. With the increasing degree of covalency[43] ($|\lambda|=100$–$70\ cm^{-1}$), the second-order parameters are reduced about 2 times, whereas the fourth-order $B_0^{(4)}$ and $B_3^{(4)}$ about 7 times while $B_1^{(4)}$, $B_2^{(4)}$, and $B_4^{(4)}$ about 4 times.

d. Zeeman term. The g tensor is strongly anisotropic consisting of four different components. The relation $g_z>g_y\approx g_{xz}>g_x\approx$ isotropic g value holds for the whole range (Γ,Δ) studied. The most sensitive to the CF parameters is g_z, which increases with Δ and decreases with Γ.

TABLE VI. Calculated components of Zeeman g tensor for Fe^{2+} in YIG:Si(Ge) for some values of Δ and Γ ($\lambda=-80\ cm^{-1}$). For g_z see Table III and V.

Γ	200	200	300	300
Δ	300	600	300	700
g_x	2.031	2.021	2.026	2.018
g_y	2.108	2.065	2.101	2.060
g_{xz}	2.099	2.100	2.069	2.078

The results of this section (Tables III–VI) can serve as a source of information on the lower and upper limit of spin-Hamiltonian parameters for an Fe^{2+} ion at distorted trigonal sites in other crystals, too, prediced in the framework of the model taking into account a nontrigonal CF component of the form as in Eq. (4).

V. CONCLUSIONS

The extensive study reported here of the model taking into account the nontrigonal crystal-field component proposed by Alben *et al.*[6] indicates the usefulness of the spin Hamiltonian for a description of the spectroscopic properties of Fe^{2+} in YIG:Me^{4+}. On symmetry grounds it is found that the spin-Hamiltonian parameters of second order, $B_0^{(2)}$, $B_1^{(2)}$, and $B_2^{(2)}$, and of fourth order, $B_0^{(4)}$, $B_1^{(4)}$, $B_2^{(4)}$, $B_3^{(4)}$, and $B_4^{(4)}$, are relevant for Fe^{2+} in the very low C_1 symmetry sites in YIG:Me^{4+}. The Zeeman g tensor involves four components: g_x, g_y, g_z, and g_{xz}. We have worked out a numerical method to calculate all necessary parameters. The results are presented for a wide range of the values of the microscopic parameters — the trigonal and nontrigonal CF parameters, and the spin-orbit coupling constant (see Tables III–VI).

It is of interest to consider the bearings of our results on the "two-center model" developed by Enz *et al.*[16] and by Lems *et al.*[17] The model assumes[16–19] two types of Fe^{2+} centers induced in YIG by Me^{4+} dopants, center I is an Fe^{2+} ion residing near its "parent" Me^{4+} ion, while center II is an Fe^{2+} ion far from Me^{4+} ions. The authors[16,17] have suggested that the magnetic effects of the two centers may be different which qualitatively explained many photoinduced effects.[3,6,18] The relative proportion of the two centers can be altered with Me^{4+} ions concentration and temperature. For high doping level there are no centers II, while for low doping level there exist both types of centers. Centers I have lower energy and are preferentially occupied at low temperatures. The number of the centers II in lightly doped samples increases with temperature due to thermal agitation. Irradiation of a lightly doped sample with light redistributes Fe^{2+} ions not only between orientationally inequivalent sites but also changes substantially the relative proportion of the centers I and II. This manifests itself in the so-called, "second-type" photoinduced changes of certain properties YIG:Me^{4+} as magnetocrystalline anisotropy, optical absorption, and dichroism, domain-wall mobility.[1–6,15–20] To explain the experiments[2,16,19,29] it is assumed that the Fe^{2+} ions have a much greater magnetocrystalline anisotropy when in distant (II) than in near (I) centers. Below we shall show that this assumption gains a clear quantitative confirmation in view of our numerical results.

The parameters involved in the previous model,[33] V_{12}, the matrix element of the Coulomb attraction of Me^{4+} ion and δ, the disorder potential, have no clear variation with the type of the center.[1,3,4,7,8] The present model CF Hamiltonian equation (4) reflects clearly the distinction between centers I and II. The nontrigonal CF parameter (D_x) should attain higher values for centers I, exhibiting stronger local low-symmetry distortions of the lattice. The distortions make the trigonal axes less dominant[2] and hence a slightly smaller trigonal parameter $\Delta(D_z)$ can be expected for centers I than centers II. The results in Sec. IV indicate that the present model predicts that the dominate parameter $B_0^{(2)}(D)$ attains higher values with higher Δ and smaller Γ, i.e., for centers II. Hence the Fe^{2+} centers II can be regarded as more anisotropic than the centers I.

Experiments[2] on lightly Si-doped YIG at 4.2 K show that the Fe^{2+} ion is at least 1.8 times more anisotropic when in distant (II) than in near (I) centers. If we prescribe the lower value $\Gamma \approx 200$ admissible by the experiment[6] to a center II and the upper value $\Gamma \approx 300$ to a center I, one obtains the ratio $B_0^{(2)}(\mathrm{II})/B_0^{(2)}(\mathrm{I})$ to be 1.9–1.8 for all Δ values considered. The other spin-Hamiltonian parameters may strongly contribute to single-ion anisotropy constants[37] K_1 and K_2 and thus to the anisotropy field.[2] However, now due to the positive value of $B_0^{(2)}$, one can expect[34] $K_1 > 0$ and $K_2 < 0$ and both the values close to the experimental ones.[8] An alternative single-ion model of magnetocrystalline anisotropy of Fe^{2+} ion in YIG:Me^{4+} is now in progress.

Experimental knowledge of the spin-Hamiltonian parameters for Fe^{2+} in YIG:Me^{4+} would enable us to test and verify the considered energy-level structure. Hence it seems worthwhile[50] to reconsider the interpretation of the experimental data,[1–4,7–8] previously based on the ground doublet model.[33] Besides, one can think of EPR techniques with the application of high magnetic fields[51] using isostructural diamagnetic garnet matrices.[50,52] The variation of the $B_q^{(4)}$ parameters with the CF parameters Δ and Γ seem to be attractive for experimental investigations with the use of high pressure.[27] The computational methods[53] will be helpful when studying low-symmetry CF effects, including the fourth-order spin-Hamiltonian terms.

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