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Magnetic Anisotropy of Europium in Iron Garnet at Low Temperatures*

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Trivalent europium (Eu^{3+}) has an anomalous magnetic behavior at low temperatures because its first magnetic state is removed by approximately 500°K from the nonmagnetic ground state. The effect of a crystal field or a europium-iron (Eu-Fe) exchange interaction on the energy of the ground state is the result of the partial breakdown of the *LS* coupling caused by these perturbations. We calculate the first-order cubic anisotropy constant K_1 for the ground state of Eu^{3+} in europium iron garnet (EuIG) due to the combined action of the Eu-Fe exchange and crystalline field. The use of the single-ion (molecular-field) approximation permits us to replace the Eu-Fe exchange interaction by an effective exchange field acting on the Eu^{3+} ions; the assumption is made that the anisotropy in the Eu-Fe exchange does not make a major contribution to the anisotropy of the ground state. We find that the isotropic exchange field and fourth-rank crystalline field first contribute to the cubic anisotropy of the ground state of Eu^{3+} in the fifth order of the energy; likewise the second-rank crystalline field first contributes in the sixth order. The fifth- and sixth-order perturbation formulas for a Hermitian operator have been derived and are given in an Appendix. We calculate the anisotropy energy for a single Eu^{3+} ion in EuIG and average the results over the six magnetically inequivalent sites of the garnet structure. The order of magnitude of the calculated anisotropy constant K_1 is in agreement with the experimental data that are available at low temperatures, but detailed comparison is not possible at present because of a relatively large number of poorly known parameters.

I. INTRODUCTION

THE magnetic anisotropy of rare-earths in the iron garnets has been the subject of recent experimental and theoretical investigations.[1] Barring the anomalous resonance peaks, the theory of the magnetocrystalline anisotropy of the RE ions is reasonably well understood. As europium iron garnet (EuIG) presents mathematical difficulties not encountered for other rare-earths (high-order perturbation energies) its anisotropy energy has not been calculated. For Eu^{3+} the ground state is nonmagnetic; any effect on this state by a crystal or exchange field comes from the partial breakdown of the *LS* coupling caused by these perturbations. Fortunately for Eu^{3+} in EuIG, the ratio of the crystal or exchange field splittings to the spin-orbit interaction energy ($\lambda\mathbf{L}\cdot\mathbf{S}$) is large enough to permit us to expand the ground-state energy in a perturbation series in the parameters $\beta H_{\mathrm{ex}}/\lambda$ and $V_{\mathrm{crys}}/\lambda$. The recent experimental results on the crystal field[2] and exchange field[3] in EuIG have supplied the necessary data for us to make a simplified calculation (neglecting anisotropic exchange) of the cubic anisotropy constant K_1.

The garnets belong to the cubic crystallographic group, for which the energy can be expanded in terms of the angle that the magnetic field (for this problem the spin of the iron sublattice) makes with the crystallographic axes, in the following form

$$E=K_0+K_1(\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2)+K_2\alpha_1^2\alpha_2^2\alpha_3^2+\cdots,$$

where K_0 is the isotropic energy, and the constants K_1, K_2, $\cdots$ represent the anisotropy energy; K_1 is the first-order cubic anisotropy constant and K_2 is the second-order cubic anisotropy constant. The α's are the direction cosines of the field with respect to the crystallographic axes. For Eu^{3+} the contributions to K_2 enter in higher order perturbations than those for K_1; therefore it is reasonable to assume that K_2 is less than K_1. To study the anisotropy of Eu^{3+} in EuIG at low temperatures it will suffice to calculate the variation of the ground-state energy as a function of the direction of the exchange field. Because of the spin-orbit interaction, only the ground state is appreciably populated at low temperatures, i.e., for T much less than $E(J=1)/k=480°\mathrm{K}$.

The magnetic properties of EuIG have been discussed by Wolf and Van Vleck.[3] They were able to explain the magnetization data on EuIG by assuming that:

(1) the coupling between the Eu^{3+} ions is small, and may be neglected in comparison to the europium-iron (Eu-Fe) and iron-iron (Fe-Fe) interactions,

(2) the Eu-Fe exchange interaction does not affect the spin of the iron sublattice and therefore this interaction may be treated by using the molecular-field (single-ion) approximation. It is then possible to talk about an "exchange field" due to the resultant spin of the ferrimagnetically coupled iron atoms,

(3) the crystalline field from the neighboring oxygens may be neglected.

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[1] G. P. Rodrique, J. H. Meyer, W. P. Wolf, and R. V. Jones, Cruft Laboratory Technical Report No. 322, Harvard University, 1960 (unpublished). R. L. White and J. P. Andelin, Phys. Rev. **115**, 1435 (1959); Y. Ayant and J. Thomas, Compt. Rend. **248**, 387, 1955 (1959); J. F. Dillon, Jr. and J. W. Nielsen, Phys. Rev. Letters **3**, 30 (1959); *ibid.* **120**, 105 (1960); J. F. Dillon, Jr. and L. R. Walker, *ibid.* **124**, 1401 (1961); *ibid.* **126**, 2261E (1962); J. W. Henderson and R. L. White, *ibid.* **123**, 1627 (1961); W. P. Wolf, M. Ball, M. T. Hutchings, M. J. M. Leask, and A. F. G. Wyatt, J. Phys. Soc. Japan **17**, Suppl. B-I, 443 (1962).

[2] J. A. Konigstein, J. Chem. Phys. **42**, 1423 (1965).

[3] W. P. Wolf and J. H. Van Vleck, Phys. Rev. **118**, 1490 (1960).

In an anisotropy calculation, crystalline field effects cannot be neglected, but assumptions (1) and (2) can and will be maintained. With the assumptions (1) and (2), the calculation of the anisotropy constant K_1 reduces to evaluating a single-ion Hamiltonian and averaging the result over magnetically inequivalent complexes.

The single-ion Hamiltonian for Eu^{3+} in EuIG is

$$\mathcal{H}_{\mathrm{Eu}^{3+}}=\lambda\mathbf{L}\cdot\mathbf{S}+\mathcal{H}_{\mathrm{Eu-Fe}}+V_{\mathrm{crystal}}+\beta\mathbf{H}_{\mathrm{mag}}\cdot(\mathbf{L}+2\mathbf{S}).$$

The first term, the spin-orbit interaction, is much greater than the remaining terms[4] which shall be treated as perturbations on the degenerate states $|JM_J\rangle$. The Eu-Fe exchange interaction Hamiltonian[5] is just Eq. (3.2) or Eq. (3.3) of I with the *molecular-field* approximation. This Hamiltonian may be divided into two parts:

$$\mathcal{H}_{\mathrm{Eu-Fe}}=2\beta\mathbf{H}_{\mathrm{ex}}\cdot\mathbf{S}+\mathcal{H}_{\mathrm{aniso}}.$$

The isotropic component of the Eu-Fe exchange interaction is written in the notation of Wolf and Van Vleck.[3] As no accurate data exist on the anisotropy of the Eu-Fe exchange interaction, we simplify the calculation of the anisotropy energy by considering only the isotropic component of the Eu-Fe exchange. In the discussion of the results we indicate why the anisotropic exchange does not make a major contribution to the anisotropy of EuIG.

The third term of the Hamiltonian is the crystalline potential for the $4f$ electrons of Eu^{3+} in the electric field of the neighboring oxygen ions. The last term represents a small magnetic field used to align (saturate) the iron sublattice in a specific direction. It is of sufficient strength to overcome the magnetic anisotropy of the iron sublattice (S-state ions), but can be neglected when calculating the anisotropy of the ground state of Eu^{3+} as it is much smaller than the exchange interaction or crystal-field energies.

The anisotropic energy of the ground state of Eu^{3+} will be found by evaluating the effect of the perturbation

$$\mathcal{H}_{\mathrm{perturbation}}=2\beta\mathbf{H}_{\mathrm{ex}}\cdot\mathbf{S}+V_{\mathrm{crystal}}$$

on the state $J=0$. As the perturbation energy is much smaller than the energy intervals between the multiplet levels, it is possible to expand the energy in terms of $1/h\nu_J$ where $h\nu_J$ is the energy interval between the ground and Jth multiplet level.

The contributions of the isotropic exchange interaction and the crystalline field to the fourth-degree anisotropy[6] first enters in the fifth- and sixth-order energies. These contributions are evaluated (Sec. II) using the perturbation formulas derived in Appendix A, and the perturbation Hamiltonian shown above. The fifth- and sixth-order energies contain terms that depend on the direction of the exchange field with respect to the axes of the local g tensor (local D_2 symmetry axes). As the anisotropy constant K_n represents the energy that depends on the direction of the field with respect to the crystal axes, the first-order cubic anisotropy constant K_1 is found by averaging the single-ion energies (the fourth-degree anisotropies) over the six magnetically inequivalent complexes in the garnet structure. These averages over the inequivalent sites are performed in Appendix B. The resulting expression for K_1 is written in terms of constants that may be empirically determined. In the concluding section the first-order cubic anisotropy constant of Eu^{3+} found from this calculation is compared with the K_1 extrapolated from the experimental results of Miyadai,[7] and the results are discussed.

II. THE CONTRIBUTION OF THE ISOTROPIC EXCHANGE INTERACTION AND CRYSTAL FIELD TO THE FOURTH-DEGREE ANISOTROPY OF THE GROUND STATE

In this section the lowest order contributions of the crystal field and isotropic exchange interaction to the fourth-degree anisotropy of the ground state will be determined. For the exchange and crystal-field energies *much less* than the energy interval between the ground and first-excited state, it is found that the fourth- or sixth-rank harmonics of the crystalline potential first enter the cubic anisotropy in the fifth-order energy, and that the second-rank harmonics enter in the sixth-order energy. The formulas for the fifth- and sixth-order energies have been derived in Appendix A. After the matrix elements of the exchange interaction and crystal field are evaluated between states in the different levels of the ground LS multiplet of Eu^{3+}, the fifth- and sixth-order energy contributions to the fourth-degree anisotropy are determined.

A. The Lowest Order of the Energy to Give Cubic Anisotropy (for Isotropic Exchange)

The fourth-degree anisotropy energy is found by using the perturbation formulas in Appendix A. Whether one refers the unperturbed wave functions and the perturbation Hamiltonian to the z axis of the crystal field (crystal-field quantization) or alternatively to the direction of the exchange field (exchange-field quantization) is irrevelant; the final eigenvalues must be the same in either case.

In the crystal-field quantization the exchange interaction must be referred to the local D_2 symmetry axes of

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[4] The spin-orbit constant λ is about 325 cm^{-1}, the crystalline field splitting of the first-excited state is about 70 cm^{-1} (see Ref. 2) and the exchange field βH_{ex} is 16.7 cm^{-1} (see Ref. 3).

[5] P. M. Levy, Phys. Rev. **135**, A155 (1964), hereafter referred to as I.

[6] The phrase fourth-degree anisotropy should not infer cubic anisotropy. The latter is obtained after the fourth-degree anisotropy for each ion has been averaged over the inequivalent magnetic complexes of the garnet structure.

[7] T. Miyadai, J. Phys. Soc. Japan **15**, 2205 (1960).

a garnet (c) site; these are also the axes for the g tensor.[8] The exchange field transforms as a vector, thus:

$$2\beta\mathbf{H}_{\text{ex}}\cdot\mathbf{S}=\beta(H_-S_++H_+S_-+2H_zS_z)\,, \qquad (2.1)$$

where

$$H_\pm=H_{\text{ex}}\sin\theta e^{\pm i\phi}\,,$$
$$H_z=H_{\text{ex}}\cos\theta\,.$$

θ, ϕ = angles the exchange field makes with respect to the g-tensor axes and $S_\pm$ and S_z are quantized along the z axis of the crystal field. In this quantization the nth order energy with V orders of the exchange interaction ($V<n$) and $n-V$ orders of the crystal field yields an expression that transforms as a pth rank tensor, where $p\leq V$. For the energy to be independent of the sense of the exchange field, the order V must be even. To obtain a fourth-degree anisotropy from the nth order energy, it is necessary that[9] $V=4$ and $n\geq 5$. A sixth-degree angular variation requires $V=6$ and $n\geq 7$.

In the exchange field quantization the crystalline potential must be rotated so that its z axis coincides with the direction of the exchange field. The crystalline potential is expressed as a series of spherical harmonics (2.2); each harmonic transforms under spatial rotations as an nth-rank tensor into other harmonics of the same rank. In this quantization the nth-order energy transforms as a fourth-rank tensor if one includes (in the energy) the harmonics Y_2^m of the crystalline potential twice, or the harmonic Y_4^m once.

We conclude that in order to obtain contributions to the first-order cubic anisotropy constant K_1 of the ground state, it is necessary to evaluate fifth- and sixth-order energies.[10] Either one fourth-rank harmonic or two second-rank harmonics and four exchange terms lead to fourth-degree anisotropy.

High order energies are extremely tedious to evaluate because of the many terms that enter. For this reason only the first-order cubic anisotropy constant of the ground state will be evaluated. This requires a calculation of fifth- and sixth-order energies. Only the terms which transform as fourth-rank tensors need to be retained, lower ranks contribute only to the isotropic energy K_0 upon averaging over the inequivalent complexes.

B. The Exchange-Field and Crystal-Field Quantizations of the Hamiltonian

It is simpler to evaluate the energy in an exchange-field quantization, as there are at most two orders of the crystalline field entering a calculation of K_1, whereas four orders of the exchange interaction enter. The crystalline potential may be written as[11]

$$V_{\text{crystalline}}=\sum_{n=0}^{2l}\sum_{m=-n}^{n}B_n^m r^n Y_n^m$$
$$\doteq\sum_{n=0}^{2l}\sum_{m=0}^{n}\beta_n A_n^m\langle r^n\rangle O_n^m\,, \qquad (2.2)$$

where β_n is the reduced matrix element that relates the operator equivalent[12] O_n^m to the spherical harmonic Y_n^m, and $A_n^m\langle r^n\rangle$ is a crystal-field parameter.

To quantize the Hamiltonian (2.2) along the direction of the exchange field it is necessary to know how the operator equivalents transform under rotations. Standard operator equivalents[13] are related to the spherical harmonics by

$$O_n^m\doteq\beta_n C_n^m[Y_n^m+(-1)^m Y_n^{-m}]\,. \qquad (2.3)$$

The proportionality constant (a reduced matrix element) relating the two depends not only on the rank (n) of the harmonics but also on the component (m).

As the two components Y_n^m and Y_n^{-m} transform differently under rotations, we represent the rotation of an operator equivalent as

$$P_{\{\alpha\beta\gamma\}}O_n^m=\beta_n^{-1}\sum_{m'=-n}^{n}C_n^m$$
$$\times[\mathfrak{D}_{m'm}^{(n)}+(-1)^m\mathfrak{D}_{m',-m}^{(n)}]Y_n^{m'}\,,$$

where $\mathfrak{D}_{m'm}^{(n)}$ is a matrix element of the rotation operator for the spherical harmonic $Y_n^{m'}$.[14]

For the spatial quantization parallel to the direction of the exchange field we find that the perturbation

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[8] The g tensor describes the magnetic behavior of an ion in a crystalline field.

[9] It should be emphasized that the following conclusions are only true if the exchange and crystal-field energies are much smaller than the energy intervals between the ground and excited states. Otherwise the perturbation series with the energy intervals as denominator is inapplicable. Also the following conclusions hold for an isotropic exchange interaction; with an anisotropic exchange interaction the fourth-order energy contributes to the cubic (fourth-degree) anisotropy.

[10] Averaging higher order energies over cubic symmetry can give additional contributions to lower order anisotropies. As it is an implicit assumption that the energy perturbation series converges, higher order corrections, compared to the contributions from lower orders, will be small. That higher orders contribute to the lower order anisotropies may be rationalized as follows. The energy of order n transforms as a Vth-rank tensor (V is the number of exchange terms in the energy) but not necessarily as an irreducible Vth-rank tensor. A reducible tensor can be expressed in terms of irreducible tensors of equal or lower rank. Averaging over cubic symmetry reduces a tensor to a set of irreducible tensors of equal or lower rank which are invariant under the cubic symmetry group. In this manner higher order energies contribute to the first-order cubic anisotropy constant.

[11] The dot over the equal sign stresses that the equality holds only for a restricted set of states.

[12] See K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952) for an explanation of these operator equivalents.

[13] D. A. Jones, J. M. Baker, and D. F. Pope, Proc. Phys. Soc. (London) 74, 249 (1959).

[14] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), Chap. 4.

Hamiltonian, Eqs. (2.1) and (2.2), is written as

$$\mathcal{H}_{\text{perturbation}} \doteq \sum_{n=0}^{2l} \sum_{m=-n}^{n} D_m{}^{(n)} \beta_n \langle r^n \rangle O_n{}^{|m|} + 2\beta H_{\text{ex}} S_z, \quad (2.4)$$

where

$$D_m{}^{(n)} \equiv A_n{}^0 \mathfrak{D}_{m0}{}^{(n)} \gamma_n{}^m,$$

$$\gamma_n{}^m \equiv \sum_{m'=0}^{n} N_n{}^{m'} (A_n{}^{m'}/A_n{}^0) \times [\mathfrak{D}_{mm'}{}^{(n)} + (-1)^{m'} \mathfrak{D}_{m,-m'}{}^{(n)}]/\mathfrak{D}_{m0}{}^{(n)}, \quad (2.5)$$

and $\gamma_n{}^{-m} = (-)^m (\gamma_n{}^m)^*$. The $N_n{}^m$ is a ratio of the *normalization*[15] of the spherical harmonic to that of the operator equivalent, i.e.,

$$B_n{}^m / B_n{}^0 \equiv N_n{}^m A_n{}^m / A_n{}^0, \quad (2.6)$$

where

$$N_n{}^m = N \left\{ \frac{Y_n{}^0}{Y_n{}^m + (-1)^m Y_n{}^{-m}} \times \frac{O_n{}^{|m|}}{O_n{}^0} \right\}.$$

From the difinition of the spherical harmonics[16] and the standard operator equivalents,[13] the $N_n{}^m$ (2.6) are

$$N_n{}^0 = 1, \quad N_2{}^2 = 1/\sqrt{6}, \quad N_4{}^2 = 1/2\sqrt{(10)},$$
$$N_4{}^4 = 1/\sqrt{(70)}, \quad N_6{}^2 = 1/2\sqrt{(105)}, \quad (2.7)$$
$$N_6{}^4 = 1/6\sqrt{(14)}, \quad N_6{}^6 = 1/\sqrt{(231)}.$$

From the form (2.4) of the perturbation Hamiltonian we have the following useful result: if the matrix elements of the axial Hamiltonian ($A_n{}^{m'} = 0$, $m' \neq 0$) are known in the exchange-field quantization, the corresponding matrix elements for the Hamiltonian (2.2) are found by multiplying the matrix elements for $m' = 0$ by $\gamma_n{}^m$.

With the z axis of the crystalline field as the quantization axis, we find:

$$\mathcal{H}_{\text{perturbation}} = \sum_{n=0}^{2l} \sum_{m=0}^{n} \beta_n A_n{}^m \langle r^n \rangle O_n{}^m + \beta H_{\text{ex}} (\sin\theta e^{-i\phi} S_+ + \sin\theta e^{i\phi} S_- + 2 \cos\theta S_z). \quad (2.8)$$

The above Hamiltonians, the fifth- and sixth-order corrections to the energy of the ground state, and an average of the single-ion energies over the inequivalent complexes will give the first-order cubic anisotropy constant of the ground state that arises from the combined effects of the crystalline field and the isotropic europium-iron exchange interaction.

C. The Fifth- and Sixth-Order Energies of the Ground State

The highest order energy that has been evaluated explicitly is that of the fourth order.[17] The fifth- and sixth-order corrections to the energy have been derived and are presented in Appendix A. For the special case of a nonmagnetic ground state, i.e.,

$$\langle n | \mathcal{H} | n \rangle = 0,$$

the fifth-order energy (A4) is[18]

$$W_0{}^{(5)} = \sum_{n' \cdots n^{\text{IV}}}{}' \frac{\mathcal{H}_{0n'} \mathcal{H}_{n'n''} \mathcal{H}_{n''n'''} \mathcal{H}_{n'''n^{\text{IV}}} \mathcal{H}_{n^{\text{IV}}0}}{h^4 \nu_{0n'} \nu_{0n''} \nu_{0n'''} \nu_{0n^{\text{IV}}}} - \sum_{n'n''n'''}{}' \frac{\mathcal{H}_{0n'} \mathcal{H}_{n'0} \mathcal{H}_{0n''} \mathcal{H}_{n''n'''} \mathcal{H}_{n'''0}}{h^4 \nu_{0n'}{}^2 \nu_{0n''}{}^2 \nu_{0n'''}{}^2} \times (\nu_{0n'} \nu_{0n''} + \nu_{0n'} \nu_{0n'''} + \nu_{0n''} \nu_{0n'''}), \quad (2.9)$$

where

$$\mathcal{H}_{n'n''} \equiv \langle n' | \mathcal{H} | n'' \rangle, \quad h\nu_{0n'} \equiv E_0 - E_{n'},$$

and the sixth-order energy (A5) is[18]

$$W_0{}^{(6)} = \sum_{n' \cdots n^{\text{V}}}{}' \frac{\mathcal{H}_{0n'} \mathcal{H}_{n'n''} \mathcal{H}_{n''n'''} \mathcal{H}_{n'''n^{\text{IV}}} \mathcal{H}_{n^{\text{IV}}n^{\text{V}}} \mathcal{H}_{n^{\text{V}}0}}{h^5 \nu_{0n'} \nu_{0n''} \nu_{0n'''} \nu_{0n^{\text{IV}}} \nu_{0n^{\text{V}}}} - \sum_{n' \cdots n^{\text{IV}}}{}' \frac{\mathcal{H}_{0n'} \mathcal{H}_{n'0} \mathcal{H}_{0n''} \mathcal{H}_{n''n'''} \mathcal{H}_{n'''n^{\text{IV}}} \mathcal{H}_{n^{\text{IV}}0}}{h^5 \nu_{0n'} \nu_{0n''} \nu_{0n'''} \nu_{0n^{\text{IV}}}}$$
$$\times \left(\frac{\nu_{0n'} + \nu_{0n''}}{\nu_{0n'} \nu_{0n''}} + \frac{\nu_{0n'''} + \nu_{0n^{\text{IV}}}}{\nu_{0n'''} \nu_{0n^{\text{IV}}}} \right) - \tfrac{1}{2} \sum_{n' \cdots n^{\text{IV}}}{}' \frac{\mathcal{H}_{0n'} \mathcal{H}_{n'n''} \mathcal{H}_{n''0} \mathcal{H}_{0n'''} \mathcal{H}_{n'''n^{\text{IV}}} \mathcal{H}_{n^{\text{IV}}0}}{h^5 \nu_{0n'} \nu_{0n''} \nu_{0n'''} \nu_{0n^{\text{IV}}}} \left(\frac{\nu_{0n'} + \nu_{0n''}}{\nu_{0n'} \nu_{0n''}} + \frac{\nu_{0n'''} + \nu_{0n^{\text{IV}}}}{\nu_{0n'''} \nu_{0n^{\text{IV}}}} \right)$$
$$+ \tfrac{1}{3} \sum_{n'n''n'''}{}' \frac{\mathcal{H}_{0n'} \mathcal{H}_{n'0} \mathcal{H}_{0n''} \mathcal{H}_{n''0} \mathcal{H}_{0n'''} \mathcal{H}_{n'''0}}{h^5 \nu_{0n'} \nu_{0n''} \nu_{0n'''}} \left(\frac{1}{\nu_{0n'}{}^2} + \frac{1}{\nu_{0n''}{}^2} + \frac{1}{\nu_{0n'''}{}^2} + \frac{1}{\nu_{0n'} \nu_{0n''}} + \frac{1}{\nu_{0n'} \nu_{0n'''}} + \frac{1}{\nu_{0n''} \nu_{0n'''}} \right). \quad (2.10)$$

The enumeration of the terms that enter the sixth-order energy (2.10) is greatly simplified, as Van Vleck noted,[19] by rearranging the sums that enter in the following way:

$$\sum_{n' \cdots n^{\text{V}}}{}' \frac{\mathcal{H}_{0n'} \mathcal{H}_{n'n''} \mathcal{H}_{n''n'''} \mathcal{H}_{n'''n^{\text{IV}}} \mathcal{H}_{n^{\text{IV}}n^{\text{V}}} \mathcal{H}_{n^{\text{V}}0}}{h^5 \nu_{0n'} \nu_{0n''} \nu_{0n'''} \nu_{0n^{\text{IV}}} \nu_{0n^{\text{V}}}} = \sum_{n'''}{}' \frac{1}{h^5 \nu_{0n'''}} \left| \sum_{n'n''}{}' \frac{\mathcal{H}_{0n'} \mathcal{H}_{n'n''} \mathcal{H}_{n''n'''}}{\nu_{0n'} \nu_{0n''}} \right|^2 \quad (2.11)$$

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[15] If the normalization was independent of the component of the operator equivalent, then $N_n{}^m \equiv 1$.

[16] A. R. Edmonds, Ref. 14, p. 21.

[17] K. F. Niessen, Phys. Rev. 34, 253 (1929).

[18] These formulas have been checked by expanding the energy denominator of the exact energy ot a two-level system. One level is the ground state, the other level is so chosen as to have the term or terms to be verified enter the energy expression for the system. The first terms of the fifth- and sixth-order energy do not require verification. The remaining terms have been checked and found to be correct.

[19] J. H. Van Vleck (private communication). For this rearrangement the property of the Hermitian Hamiltonian $H_{ab} = H_{ba}{}^*$ has been used.

and

$$\frac{1}{2}\sum_{n'\cdots n^{\text{IV}}}{}' \frac{\mathcal{H}_{0n'}\mathcal{H}_{n'n''}\mathcal{H}_{n''0}\mathcal{H}_{0n'''}\mathcal{H}_{n'''n^{\text{IV}}}\mathcal{H}_{n^{\text{IV}}0}}{h^5\nu_{0n'}\nu_{0n''}\nu_{0n'''}\nu_{0n^{\text{IV}}}} \times\left(\frac{\nu_{0n'}+\nu_{0n''}}{\nu_{0n'}\nu_{0n''}}+\frac{\nu_{0n'''}+\nu_{0n^{\text{IV}}}}{\nu_{0n'''}\nu_{0n^{\text{IV}}}}\right) =\Big(\sum_{n'n''}{}' A_{n'n'',0}\Big)\Big(\sum_{n'n''}{}' A_{n'n'',0}\chi_{n'n'',0}\Big), \quad (2.12)$$

where

$$A_{n'n'',0}\equiv\frac{\mathcal{H}_{0n'}\mathcal{H}_{n'n''}\mathcal{H}_{n''0}}{h^2\nu_{0n'}\nu_{0n''}}, \quad \chi_{n'n'',0}\equiv\frac{\nu_{0n'}+\nu_{0n''}}{\nu_{0n'}\nu_{0n''}}.$$

The number of terms entering the fifth-order energy is small when the Hamiltonian (2.4) is quantized along the exchange-field direction and a rearrangement of the energy (2.9) is not warranted.

The rearrangements (2.11) and (2.12) are most helpful in classifying the contributions to the sixth-order energy. The terms that enter the "third-order processes" (2.11) and (2.12) are of the form V^3, V^2H, VH^2, and H^3. Here V refers to the crystal field, H to the exchange field. Of these terms only V^2H, VH^2, and H^3 contribute to the fourth-degree anisotropy when we square the third-order processes, i.e.:

$$(V^2H+VH^2+H^3)^2=2V^2H\times H^3+(VH^2)^2 + \text{lower rank terms.}$$

For each value of the index n, the third-order processes may be subdivided into the terms V^2H, VH^2, and H^3. We make the final subdivision of the sixth-order energy (2.10) knowing that in an exchange-field quantization different components of the second-rank operator equivalents do not interact, i.e., the effect of each $O_2{}^m$ may be separately evaluated.[20]

It remains to ascertain which contributions from the fifth- and sixth-order energies lead to terms that transform as fourth-rank tensors, and which J levels (excited states) are involved in these corrections to the energy of the ground state. Consider the fifth-order energy; the first term of Eq. (2.9) may have terms that have fourth-rank transformation properties; the second term will definitely not enter as can be seen by the following reasoning. If the "second-order processes" of the second term contain only the exchange interaction, then

$$\sum_{n'}\frac{H_{0n'}H_{n'0}}{hV_{0n'}{}^k}, \quad k=1 \text{ or } 2$$

is invariant under spatial rotations. This leaves the fourth-degree dependence to the "third-order processes" (2.9)

$$H_{0n''}H_{n''n'''}H_{n'''0},$$

which must contain one order of the crystalline field ($O_4{}^m$) and two orders of the exchange interaction. The fourth-rank harmonics have nonvanishing matrix elements in multiplet level for $J\geq 2$, but the isotropic exchange interaction has only first-rank components for which $\Delta J\leq 1$. There are no values of the indices n'' and n''' which satisfy these conditions. When we consider the second-order process with one order of the exchange interaction and one crystalline field, we arrive at the same conclusion, that is, the second term of Eq. (2.9) does not contribute to the fourth-degree anisotropy of the fifth-order correction to the energy.

For the sixth-order energy, the first and third terms of Eq. (2.10) contribute to the fourth-degree anisotropy. The remaining two terms will not contribute to the fourth-degree anisotropy of the sixth-order energy; this can be reasoned by using arguments analogous to those used for the fifth-order energy.

The highest J level (manifold) that enters the fifth- and sixth-order corrections to the ground-state energy (for fourth-degree anisotropy) is the fourth, as the matrix elements of the exchange interaction vanish for $\Delta J>1$. The sixth-order contributions to the energy of the ground state from the level $J=3$ were found on evaluation to be about 3% of the total sixth-order energy correction arising from the levels $J=1$ and 2; therefore the contributions from the levels $J=3$, 4 will be neglected in the sixth-order energy calculations.

D. Evaluation of the Matrix Elements of the Crystalline Potential and the Isotropic Exchange Interaction

Prior to evaluating the fifth- and sixth-order energy corrections (2.9) and (2.10) it is necessary to know the matrix elements of the perturbation Hamiltonian (2.4), (2.8) between states in the same J level (manifold), and also between states in different J levels. The matrix elements of the isotropic exchange interaction (2.1) are proportional to the matrix elements

$$\langle JM_J|S_q|J'M_{J'}\rangle.$$

These can be found by using the Wigner-Eckart theorem. However, all these elements have been previously evaluated[21]; we give in Table I those matrix

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[20] According to this cataloging the sixth-order energy contribution to the anisotropy constant K_1 may be evaluated with the least possible chance of missing terms that contribute, as follows, (1) Evaluate the terms that contribute to a specific index n''': term V^pH^{3-p}, ($p=0, 1, 2$), and harmonic $O_2{}^m$. Sum these terms (2) Sum over the contributions of each harmonic $O_2{}^m$ for a specific index n''' and term V^pH^{3-p}. (3) Sum over the components m of $O_2{}^m$, to find the contribution of each term V^pH^{3-p} for a specific index n'''. (4) Multiply the contribution from V^2H by the one from H^3 and the product by two. Add to this the contribution from squaring the terms VH^2. This gives the total contribution from a specific index n'''. (5) Sum the contributions from each index n''' over all indices n''' that contribute to the sixth-order energy; this gives the sixth-order energy correction of the state $J=0$ due to the perturbation Hamiltonian (2.1) and (2.2).

[21] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, England, 1932); p. 167; E. M. Corson, *Perturbation Methods in the Quantum Mechanics of n-Electron Systems* (Blackie & Son Ltd., London, 1951), pp. 54, 55.

TABLE I. The matrix elements of the first-rank spin operator[a] between states of total angular momentum J and J'. Here $S_0=S_z$, $S_\pm=S_x\pm iS_y$, and $q=M_J-M_{J'}$.

$\langle JM_J|Sq|J'M_{J'}\rangle$

J	M_J \ J' / $M_{J'}$	0	1		2			3			
		0	0	±1	0	±1	±2	0	±1	±2	±3
0	0	0	2	$\mp2\sqrt{2}$							
1	0	2	0	$1/\sqrt{2}$	$\sqrt{3}$	$\mp3/\sqrt{2}$					
	±1	$\mp2\sqrt{2}$	$1/\sqrt{2}$	$\pm\frac{1}{2}$	$\pm\sqrt{6}$	$\frac{3}{2}$	∓3				
2	0		$\sqrt{3}$	$\pm\sqrt{6}$	0	$\sqrt{\frac{3}{2}}$	0	$3(2/7)^{1/2}$	$\mp2(6/7)^{1/2}$		
	±1		$\mp3/\sqrt{2}$	$\frac{3}{2}$	$\sqrt{\frac{3}{2}}$	$\pm\frac{1}{2}$	1	$\pm2(3/7)^{1/2}$	$4/\sqrt{7}$	$\mp2(10/7)^{1/2}$	
	±2			∓3	0	1	±1		$\pm2/\sqrt{7}$	$(10/7)^{1/2}$	$\mp2(15/7)^{1/2}$

J	M_J \ J' / $M_{J'}$	3				4		
		0	±1	±2	±3	0	±1	±2
3	0	0	$\sqrt{3}$			$2(11/21)^{1/2}$	$\cdots$	
	±1	$\sqrt{3}$	$\pm\frac{1}{2}$	$\sqrt{\frac{5}{2}}$		$\cdots$	$\frac{1}{2}(55/7)^{1/2}$	$\cdots$
	±2		$\sqrt{\frac{5}{2}}$	±1	$\sqrt{6}/2$		$\cdots$	$(11/7)^{1/2}$
	±3			$\sqrt{6}/2$	$\pm\frac{3}{2}$			$\cdots$

[a] See J. H. Van Vleck, Ref. 21.

elements of the spin S_q that are necessary to evaluate the fifth- and sixth-order energy corrections.

The matrix elements of the crystal field (2.2) are evaluated by using the tabulated values[22] of the matrix elements of the operator equivalents (2.3). The matrix elements of the second-rank component O_2^0 of the crystalline potential (2.2) are given in Table II for the manifolds $J=1$, 2, and 3.

$$V_2=(a/3)O_2^0, \tag{2.13}$$

where

$$a=3A_2^0\langle r^2\rangle\alpha(^7F_1) \tag{2.14}$$

and $\alpha(^7F_1)$ is the reduced matrix element β_2 for the $^7F_1$ level of Eu^{3+}. The matrix elements for $A_2^2\neq0$ are obtained by multiplying those for A_2^0 (Table II) with the γ_n^m Eq. (2.5) for $n=2$. The γ_2^m for $m=0$, 1, and 2 have been evaluated by using the matrix elements of the rotation operator for spherical harmonics[14] and the normalization constants $N_2^{m'}$ Eq. (2.7).

$$\begin{aligned}\gamma_2^0&=1+\frac{\sin^2\theta}{3\cos^2\theta-1}\cos2\phi\frac{A_2^2}{A_2^0},\\ \gamma_2^1&=1-\frac{1}{3}\frac{\cos^2(\theta/2)e^{i2\phi}-\sin^2(\theta/2)e^{-i2\phi}}{\cos\theta}\frac{A_2^2}{A_2^0},\\ \gamma_2^2&=1+\frac{2}{3}\frac{\cos^4(\theta/2)e^{i2\phi}+\sin^4(\theta/2)e^{-i2\phi}}{\sin^2\theta}\frac{A_2^2}{A_2^0}.\end{aligned} \tag{2.15}$$

The matrix elements of the fourth-rank component V_4 of the crystalline potential (2.2) between the states $|JM_J\rangle$ and $|J'M_{J'}\rangle$ required for the cubic anisotropy calculation are

$$\begin{aligned}\langle00|V_4|40\rangle&=(63/5)(2/11)^{1/2}bD_0^{(4)}(\theta,\phi),\\ \langle10|V_4|30\rangle&=(3/5)(42)^{1/2}bD_0^{(4)}(\theta,\phi),\\ \langle20|V_4|20\rangle&=(18/5)bD_0^{(4)}(\theta,\phi),\end{aligned} \tag{2.16}$$

TABLE II. The matrix elements of the second-rank crystalline potential $V_2=(a/3)O_2^0$ (quantized along the direction of the exchange field) between states of total angular momentum $|JM_J\rangle$ and $|J'M_{J'}\rangle$. For ΔM_J even, multiply the matrix elements by a $\sin^2\theta$; for ΔM_J odd, multiply by a $\sin2\theta$. The angle θ is between the exchange field and the z axis of the crystal field. Only the second-rank (degree) variations of the matrix elements are tabulated.

J	M_J \ J' / $M_{J'}$	0	1		2			3		
		0	0	±1	0	±1	±2	0	±1	±2
0	0	0	0	0	$2/\sqrt{3}$	$\pm\sqrt{2/3}$	$-\sqrt{2/3}$	0	0	0
1	0	0	1	$\pm1/2\sqrt{2}$	0	$-\sqrt{2}/12$	$\pm\sqrt{2}/6$	$5/(42)^{1/2}$	$\pm1/(14)^{1/2}$	$-\frac{1}{6}(5/7)^{1/2}$
	±1	0	$\pm1/2\sqrt{2}$	$\cdots$	$-\sqrt{6}/12$	$\cdots$	$\cdots$	$\mp\frac{1}{4}(3/7)^{1/2}$	$-1/(42)^{1/2}$	$\pm\frac{1}{3}(5/21)^{1/2}$
2	0	$2/\sqrt{3}$	0	$-\sqrt{6}/12$	$11/21$	$\pm11\sqrt{6}/252$	$11\sqrt{6}/126$	0	$\cdots$	$\cdots$
	±1	$\pm\sqrt{2/3}$	$-\sqrt{2}/12$	$\cdots$	$\pm11\sqrt{6}/252$	$\cdots$	$\cdots$	$-13/12(21)^{1/2}$	$\pm(11/9)(1/7)^{1/2}$	$\cdots$
	±2	$-\sqrt{2/3}$	$\pm\sqrt{2}/6$	$\cdots$	$11\sqrt{6}/126$	$\cdots$	$\cdots$	$\mp\frac{1}{2}(1/21)^{1/2}$	$\cdots$	$\pm(11/9)(5/14)^{1/2}$
3	0	0	$5/(42)^{1/2}$	$\mp\frac{1}{4}(3/7)^{1/2}$	0	$-13/12(21)^{1/2}$	$\mp\frac{1}{2}(1/21)^{1/2}$	$2/9$	$\pm\sqrt{3}/108$	$(30)^{1/2}/54$

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[22] See Ref. 12.

where

$$V_4=(b/20)\{O_4^0+(A_4^2/A_4^0)O_4^2+(A_4^4/A_4^0)O_4^4\},$$

$$D_0^{(4)}(\theta,\phi)\equiv\tfrac{1}{8}\{(35\cos^4\theta-30\cos^2\theta+3)+\sin^2\theta(7\cos^2\theta-1)\times\cos 2\phi(A_4^2/A_4^0)+\sin^4\theta\cos 4\phi(A_4^4/A_4^0)\},\quad(2.17)$$

$$b=20A_4^0\langle r^4\rangle\beta(^7F_2),$$

and $\beta(^7F_2)$ is the reduced matrix element β_4 for the $^7F_2$ level of Eu^{3+}.

E. Evaluation of Fifth- and Sixth-Order Energies

The matrix elements of the crystal field and isotropic exchange interaction, Tables I, II and Eqs. (2.16), and the formulas for the fifth- and sixth-order corrections to the ground-state energy, Eqs. (2.9), (2.11), and (2.12), are sufficient for us to evaluate the contribution of the isotropic exchange interaction and crystalline field to the first-order cubic anisotropy constant of the ground state of Eu^{3+} in EuIG. The fifth-order energy (2.9) is very easy to evaluate for the quantization axis along the direction of the exchange field. Considering the levels $J=1$ and 2 one finds that only one term contributes. Including the levels $J=3$ and 4, a total of three contribute to the fifth-order energy. If we chose the quantization axis along the z axis of the crystalline field, the levels $J=1$ and 2 alone would produce many more terms than the exchange-field quantization. For this reason we have not checked the fifth-order energy by evaluating it in the crystal-field quantization.

The above remarks are not true for the sixth-order corrections to the energy, Eqs. (2.10), (2.11), and (2.12). For this order, both directions of spatial quantization are tedious; the crystal field more so. It is necessary to counter-check the results found for this order and therefore we have used both quantizations to evaluate the sixth-order energy.

The fifth-order energy correction to the ground state for *one* magnetic ion is

$$\frac{1}{\hbar}W_0^{(5)}=\frac{432}{5}\left(\frac{1}{\omega_1^2\omega_2^2}+\frac{1}{\omega_1^2\omega_2\omega_3}+\frac{2}{\omega_1\omega_2\omega_3\omega_4}\right)\times D_0^{(4)}(\theta_i,\phi_i)b\beta^4H_{\text{ex}}^4,\quad(2.18)$$

where $\hbar\omega_J\equiv E_J^{(0)}-E_0^{(0)}$, the unperturbed energy of the level J with respect to the ground-state energy.

θ_i, ϕ_i = angles the exchange field $\mathbf{H}_{\text{ex}}$ makes with respect to the g-tensor axes (D_2 symmetry axes) of the ith magnetic complex; $A_n^m\langle r^n\rangle$ = the crystal field parameters referred to the g-tensor axes. The crystal field constant b, and $D_0^{(4)}(\theta_i,\phi_i)$ are defined by Eqs. (2.17).

The sixth-order energy correction for one magnetic ion, exclusive of the levels $J=3$ and 4 is

$$\frac{1}{\hbar}W_0^{(6)}=a^2\beta^4H_{\text{ex}}^4\sum_{n=0}^{5}\xi_n/\omega_1^{5-n}\omega_2^n,$$

where

$$\xi_0=4[-128(\gamma_0)^2+(\gamma_1)^2],$$

$$\xi_1=4[-240(\gamma_0)^2+29(\gamma_1)^2],$$

$$\xi_2=(1/21)[-3\times3968(\gamma_0)^2+4616(\gamma_1)^2+7\times128(\gamma_2)^2],\quad(2.19)$$

$$\xi_3=(8/3)49[-8\times1328(\gamma_0)^2+671(\gamma_1)^2+80(\gamma_2)^2],$$

$$\xi_4=(4/21)[73(\gamma_1)^2-192(\gamma_2)^2],$$

$$\xi_5=(4/9)[(\gamma_1)^2+16(\gamma_2)^2],$$

and

$$\gamma_0=(\cos^2\theta_i-1/3)\gamma_2^0(\theta_i,\phi_i),$$

$$\gamma_1=\sin(2\theta_i)\gamma_2^1(\theta_i,\phi_i),$$

$$\gamma_2=\sin^2\theta_i\gamma_2^2(\theta_i,\phi_i).$$

The γ_2^m are given by Eqs. (2.15) and the crystal-field constant a is defined by Eq. (2.14).

The first-order cubic anisotropy constant K_1 for the ground state of Eu^{3+} is obtained by averaging the fifth- and sixth-order energies (2.18) and (2.19) for the magnetic ions over the inequivalent sites in the garnet structure. This will be done in Sec. III.

III. COMPARISON OF THEORY WITH EXPERIMENT

In this section the contribution from the fifth- and sixth-order energies to the first-order cubic anisotropy constant of the ground state of Eu^{3+} in EuIG will be evaluated. The constant K_1 predicted from this calculation will be compared with the extrapolated experimental value of K_1. A discussion of the approximations used in deriving the results and the conclusions are presented in the concluding sections.

A. The Contribution from the Isotropic Exchange Interaction and Crystalline Field

The first-order cubic anisotropy for the ground state of Eu^{3+} arising from the combined effects of the crystalline field and isotropic exchange interaction, is found by averaging the fifth- and sixth-order energies (2.18) and

TABLE III. The averages of several functions of the direction cosines of the exchange field over the inequivalent (c) sites of the garnet structure. The angles θ, ϕ represent the field direction with with respect to the local D_2 symmetry axes (p,q,r). The rth axis (see Fig. 1) has been chosen as the axis of spatial quantization. The relation of the axes p, q, r to the crystallographic axes (x,y,z) is shown in Fig. 1. Only the cubic anisotropy term is retained. All coefficients in this table should be multiplied by $(\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2)$.

	p parallel to x	q parallel to y	r parallel to z
$\langle\sin^4\theta\rangle$	1/6	1/6	−2/3
$\langle\sin^4\theta\cos 4\phi\rangle$	−5/2	−5/2	10/3
$\langle\sin^4\theta\cos 2\phi\rangle$	−5/6	5/6	0
$\langle\sin^4\theta\cos^2 2\phi\rangle$	−7/6	−7/6	4/3

(2.19) for one magnetic ion over the six inequivalent sites in the garnet structure. As seen from Table III these averages depend on which g-tensor axis g_x, g_y, or g_z is parallel to a crystallographic axis (the local axis of quantization is z). (See Fig. 1.)

The only data available for the crystalline field around Eu^{3+} in EuIG are given by Koningstein.[2] Although this is not explicitly mentioned, we infer[23] that his data are referenced to an axis of quantization parallel to the local D_2 symmetry axis which coincides with a local pseudocubic fourfold axis. This axis is not parallel to any of the crystal axes (x,y,z).[24]

To coincide with the axes in which the experimental crystal parameters are given, the cubic averages (Table III) with the p or q axis, i.e., g_x or g_y of the g tensor parallel to a crystallographic axis, should be used for averaging the terms in the energies (2.18) and (2.19). The cubic average of the fifth-order energy is

$$(1/\hbar)\langle W_0{}^{(5)}\rangle = 504[1 \pm (A_4{}^2/A_4{}^0) - (3/7)(A_4{}^4/A_4{}^0)]b \times \beta^4 H_{\text{ex}}{}^4[(\omega_1{}^2\omega_2{}^2)^{-1} + (\omega_1{}^2\omega_2\omega_3)^{-1} + (\omega_1\omega_2\omega_3\omega_4)^{-1}] \times (\alpha_1{}^2\alpha_2{}^2 + \alpha_1{}^2\alpha_3{}^2 + \alpha_2{}^2\alpha_3{}^2), \quad (3.1)$$

where the α's are the direction cosines of the exchange field with respect to the crystal axes, and the upper sign is for the $p(g_x)$ axis parallel to a crystallographic axis. The cubic average of sixth-order energy is

$$(1/\hbar)\langle W_0{}^{(6)}\rangle = -(8/3)a^2\beta^4 H_{\text{ex}}{}^4[1 \pm (10/3)(A_2{}^2/A_2{}^0) - (7/9)(A_2{}^2/A_2{}^0)^2] \sum_{n=0}^{5} (\xi_n/\omega_1{}^{5-n}\omega_2{}^n) \times (\alpha_1{}^2\alpha_2{}^2 + \alpha_1{}^2\alpha_3{}^2 + \alpha_2{}^2\alpha_3{}^2), \quad (3.2)$$

where

$$\xi_0 = 33, \quad \xi_2 = 614/7, \quad \xi_4 = 121/21,$$
$$\xi_1 = 89, \quad \xi_3 = 6614/147, \quad \xi_5 = -1/3.$$

The crystal-field parameters for Eu^{3+} in EuIG as given by Koningstein[25] are

n	m	$A_n{}^m\langle r^n\rangle$ (cm^{-1})
2	0	105
	2	±95
4	0	−140
	4	700
6	0	30
	4	−630

The crystal-field constants a and b are given by Eqs. (2.14) and (2.17) in terms of the reduced matrix elements $\alpha(^7F_1)$ and $\beta(^7F_2)$ of the excited states of Eu^{3+}; these are given by Judd[26]:

$$\alpha(^7F_1) = -1/5, \quad \beta(^7F_2) = -2/189.$$

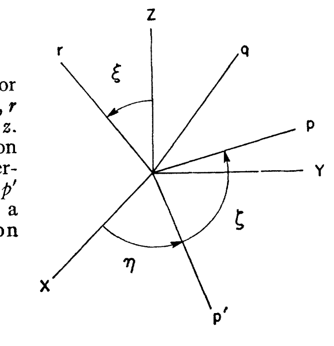

FIG. 1. Relation of g tensor (local D_2 symmetry) axes p, q, r to crystallographic axes x, y, z. η is a counterclockwise rotation about the z axis. ξ is a counterclockwise rotation about the p' axis, the line of nodes. ζ is a counterclockwise rotation about the r axis.

With the above parameters we find from Eqs. (2.14) and (2.17) that

$$a = -63 \text{ cm}^{-1}$$

and

$$b = 29.6 \text{ cm}^{-1}.$$

The exchange field constant H_{ex} is given by Wolf and Van Vleck[3] at absolute zero:

$$\beta H_{\text{ex}} = 16.7 \text{ cm}^{-1}.$$

The "centers of gravity" of the excited J levels (except for $J=2$) for Eu^{3+} in EuIG have been estimated from the data of Koningstein.[2] The energy of the level $J=2$ is that of the free Eu^{3+} ion.[3]

Level	Energy (cm^{-1})
$^7F_1$	352
$^7F_2$	924
$^7F_3$	~1960
$^7F_4$	3026

Evaluating the fifth- and sixth-order energies (3.1) and (3.2) by using the numerical values given above, and comparing the results with the definition of K_1 (see Introduction), we find[27]

		$(K_1)_{Eu^{3+}} \times 10^{-4}$ (ergs/cc)	
Contribution from (3.1)	=	15	
Contribution from (3.2):			
$\pm A_2{}^2/A_2{}^0 > 0$	=	−14	(3.3)
$\pm A_2{}^2/A_2{}^0 < 0$	=	12	

These results are the contributions of the crystalline field and isotropic Eu-Fe exchange interaction to the first-order cubic anisotropy constant of the ground state of Eu^{3+} in EuIG.

B. Experimental Value of the First-Order Cubic Anisotropy Constant

The first-order cubic anisotropy constant for EuIG has been determined experimentally by Miyadai[7] in

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[23] We can infer a particular choice of axes from (1) the pseudocubic potential used to fit the experimental data and (2) the fact that Koningstein (see Ref. 2) compared his $A_n{}^m$ with those obtained from the point-charge calculation of Hutchings and Wolf (see Ref. 24).

[24] See M. T. Hutchings and W. P. Wolf, J. Chem. Phys. **41**, 617 (1964), Fig. 1.

[25] J. A. Koningstein, see Ref. 2, Table III.

[26] B. R. Judd, Mol. Phys. **2**, 407 (1959).

[27] The result (3.3) was converted from (cm^{-1}/cc) to (ergs/cc) by using the relation 1 cm^{-1} = 1.985×10^{-16} ergs.

the temperature range 170°K–230°K. As the results are given in units of K_1/M_s (oersteds), they must be multiplied by the bulk magnetization of EuIG to obtain the constant K_1. This magnetization is found from a graph given by Wolf and Van Vleck.[28]

$$M=(M/N\beta)\beta/V=19.5(M/N\beta)\ \text{ergs/Oe-cc},$$

where $V=\frac{1}{4}$ volume of unit cell$=(1.9/4)\times10^{-21}$ cc, and $M/N\beta$ is given for EuIG by Wolf and Van Vleck.[28]

The anisotropy for Eu^{3+} alone is found by subtracting the anisotropy of the iron sublattice from the anisotropy of EuIG. The anisotropy of the iron sublattice is just that found for yttrium iron garnet (YIG).[29]

$$(K_1)_{Eu^{3+}}=(K_1)_{EuIG}-(K_1)_{YIG}. \tag{3.4}$$

With the first-order cubic anisotropy constants (K_1) for EuIG found by Miyadai[30] and the K_1 for YIG given by Rodrique *et al.*,[1] we find that the first-order anisotropy constant for Eu^{3+} is equal to (all K_1 in units of ergs/cc)

T (°K)	$(K_1)_{EuIG}\times10^{-4}$	$(K_1)_{YIG}\times10^{-4}$	$(K_1)_{Eu^{3+}}\times10^{-4}$
0	?	−2.48	?
170	−21.2	−1.58	−19.6
190	−16.3	−1.39	−14.9
210	−11.5	−1.23	−10.3
230	−8.5	−1.04	−7.5

To determine the anisotropy constant K_1 of the ground state, it is necessary to extrapolate the experimental values to $T=0$°K. This may be done using the approximation[31]

$$K_1(T)=\frac{(K_1)_{J=0}+(K_1)_{J=1}e^{-E_1/kT}+(K_1)_{J=2}e^{-E_2/kT}}{1+3e^{-E_1/kT}+5e^{-E_2/kT}}. \tag{3.5}$$

In postulating this we assume that the $(K_1)_J$'s remain constant within the temperature range $170°\text{K}\leqslant T\leqslant230°\text{K}$. This approximation is valid if the redistribution of the population of the magnetic states within a multiplet level is small, i.e.,

$$\Delta(E_J)_{\text{magnetic states}}\ll E_J$$

and

$$kT\ll E_J.$$

Another assumption implied by the constancy of the $(K_1)_J$'s is that the crystal and exchange fields are independent of temperature. This is a fair approximation to make for the temperature interval that is being considered.

With the approximation (3.5) we find that

$$(K_1)_{J=0}=-38\times10^4\ \text{ergs/cc} \tag{3.6}$$

fits to the experimental data fairly well.

C. Discussion of Results

On comparing the estimated anisotropy constant K_1 (between 1 and 27×10^4 ergs/cc) with the extrapolated experimental constant K_1 (-38×10^4 ergs/cc), we find that the orders of magnitude are in agreement, but not the signs. It is not possible to infer more about the validity of the formulas (3.1) and (3.2) from the above comparison.

Provided there are no erroneous assumptions made in the derivation of the formulas (3.1) and (3.2), some possible sources of the discrepancy between our results and the estimated anisotropy are:

(1) The extrapolation of the experimental value of the anisotropy constant K_1 for $T=0$°K may be inaccurate. Although the approximations used in the extrapolation seem justified we have no means of further testing its validity. It would be useful to have data at lower temperatures.

(2) The crystal-field parameters are poorly known. From data on ytterbium in yttrium gallium garnet[32] we know that the field is not cubic; there is no reason to expect the field in EuIG to be cubic. It is therefore questionable to fit the energy levels of Eu^{3+} in EuIG to a pseudocubic crystalline potential.[2]

As mentioned by Wolf,[33] the 318 cm^{-1} level, used by Koningstein in the determination of the parameters A_2^m, may not be of the europium ion as this level also exists for ytterbium in yttrium gallium garnet.[32] As the remaining parameters $A_{4,6}^m$ were determined by using the A_2^m, a re-examination of this level may lead to new crystal field parameters.

(3) The contribution of the anisotropic Eu-Fe exchange interaction has been neglected.

To estimate how justified we are in neglecting the anisotropy in the Eu-Fe exchange interaction, we calculated some of the major contributions to the anisotropy constant K_1 arising from the nearest excited J levels. We conclude that

(a) For Eu^{3+} ($L=S=3$) the reduced matrix elements (which largely determine the magnitude of the matrix elements) for the anisotropic components of the exchange are one-sixth as large as those for the isotropic component;

(b) The contribution from the first-excited level ($J=1$) is negligible even though it enters in the fourth-order of the ground-state energy;

(c) the upper excited levels ($J=2$, 3, 4) have contribution to K_1, from the fourth- and sixth-rank compo-

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[28] See Ref. 3, Fig. 1.

[29] G. P. Rodrique *et al.*, Ref. 1.

[30] In Miyadai's article, Ref. 7, K_1/M_s should be multiplied by 10^{-4} not 10^{-5}.

[31] The states with $J>2$ are hardly populated for $T\leq230$°K and may be neglected. E_3 corresponds to 2800°K.

[32] M. T. Hutchings and W. P. Wolf, Ref. 24.

[33] W. P. Wolf (private communication).

nent[34] of the anisotropic exchange, which enter in the fourth-order of the ground-state energy. As estimated from the Yb-Fe exchange interaction in the garnets,[35] the ratios α_{4q}/α_{00} may be particularly large. It is possible that these terms may by force of numbers, in spite of unfavorable reduced matrix elements and energy denominators, make a non-negligible contribution to the ground-state energy.

D. Conclusions

The experimental data on Eu^{3+} in the gallium and iron garnets[2] show that the effect of the crystalline field on the J levels is much larger than that of the exchange field. From this observation and the above remarks, we conclude that although they enter in higher orders of the energy, the crystalline field and isotropic exchange produce the major contributions to the anisotropy of the ground-state energy of Eu^{3+} in EuIG. It is not possible at present to make a detailed comparison between the calculated value and experimental value of the ground-state anisotropy constant K_1. Two reasons may be cited:

(1) Many of the empirical parameters entering the formulas for K_1 are poorly known, and

(2) the empirical value of K_1 has not been determined for temperatures low enough to give only the ground-state anisotropy.

ACKNOWLEDGMENT

We should like to thank Professor J. H. Van Vleck for suggesting this study and for his guidance throughout it.

APPENDIX A

The Fifth- and Sixth-Order Perturbation Formulas for a Hermitian Operator

Whereas general expressions for the pth-order perturbation formulas are given in the literature,[36] the fourth-order is the highest that has been explicitly evaluated.[17] In this Appendix we give the fifth- and sixth-order perturbation formulas for a Hermitian operator. We choose to take the Hamiltonian as a specific example of a Hermitian operator.

The pth-order energy of a Hamiltonian operator is found by expanding the energy W and the wave function Ψ in terms of a parameter λ, which is smaller than one. In matrix notation this is[37]

$$\begin{aligned} W_n &= W_n^{(0)}+\lambda W_n^{(1)}+\lambda^2 W_n^{(2)}+\cdots, \\ \psi_n &= \textstyle\sum_{n'} S(n',n)\psi_{n'}^{(0)}, \qquad\qquad (\text{A1}) \\ S(n',n) &= \delta(n',n)+\lambda S^{(1)}(n',n)+\lambda^2 S^{(2)}(n',n)+\cdots. \end{aligned}$$

The matrix formulation of the energy eigenvalue problem

$$(\mathcal{H}_0+\mathcal{H})\psi=W\psi$$

is written as

$$\textstyle\sum_{n'} \{W_{n''}^{(0)}\delta(n'',n')+\lambda\mathcal{H}(n'',n') -\delta(n'',n')W_n\}S(n',n)=0. \qquad (\text{A2})$$

We have evaluated the Hamiltonian in the representation $\{\psi^{(0)}\}$ that diagonalizes the unperturbed Hamiltonian

$$\mathcal{H}_0\psi_n^{(0)}=W_n^{(0)}\psi_n^{(0)}.$$

By substituting the expansions of the energy and the wave function (A1) in the infinite set of equations (A2), and equating the sum of all terms of the same order to zero, one obtains the following recursion relationships[38]:

$$\begin{aligned} W_n^{(p)} &= \sum_{n''}{}' \mathcal{H}_{nn''}C_{n''n}^{(p-1)}-\sum_{\mu=2}^{p-2} W_n^{(\mu)}C_{nn}^{(p-\mu)}, \\ C_{n'n}^{(p)} &= \frac{1}{h\nu_{nn'}}\Big\{\sum_{n''} \mathcal{H}_{n'n''}C_{n''n}^{(p-1)} \qquad\qquad (\text{A3}) \\ &\qquad -\sum_{\mu=1}^{p-1} W_n^{(\mu)}C_{n'n}^{(p-\mu)}\Big\}. \end{aligned}$$

The value of $C_{nn}^{(p)}$ is convention; as it does not affect the energy it may be left undetermined.

By successive applications of the formulas (A3) the corrections to the energy were obtained to sixth order in λ. We have checked the third- and fourth-order energies with those given by Niessen.[17] The general formulas for the pth-order energy, and the coefficients (A3) agree with those given by Corson.[21]

The fifth-order energy correction is

$$\begin{aligned} W_n^{(5)} = {} & \sum_{u'\cdots u^{\text{IV}}}{}' \frac{\mathcal{H}_{nn'}\cdots\mathcal{H}_{n^{\text{IV}}n}}{h^4\nu_{nn'}\cdots\nu_{nn^{\text{IV}}}} -\mathcal{H}_{nn}^3\sum_{n'}{}'\frac{\mathcal{H}_{nn'}\mathcal{H}_{n'n}}{h^4\nu_{nn'}^4} -\sum_{n'\cdots n'''}{}' (\mathcal{H}_{nn}\mathcal{H}_{nn'}\cdots\mathcal{H}_{n'''n}+\mathcal{H}_{nn'}\mathcal{H}_{n'n}\mathcal{H}_{nn''}\mathcal{H}_{n''n'''}\mathcal{H}_{n'''n}) \\ & \times\left(\frac{\nu_{nn'}\nu_{nn''}+\nu_{nn'}\nu_{nn'''}+\nu_{nn''}\nu_{nn'''}}{h^4\nu_{nn'}^2\nu_{nn''}^2\nu_{nn'''}^2}\right)+\sum_{n'n''}{}' (\mathcal{H}_{nn}^2\mathcal{H}_{nn'}\mathcal{H}_{n'n''}\mathcal{H}_{n''n}+\mathcal{H}_{nn}\mathcal{H}_{nn'}\mathcal{H}_{n'n}\mathcal{H}_{nn''}\mathcal{H}_{n''n}) \\ & \times\left(\frac{\nu_{nn'}^2+\nu_{nn''}^2+\nu_{nn'}\nu_{nn''}}{h^4\nu_{nn'}^3\nu_{nn''}^3}\right), \qquad (\text{A4}) \end{aligned}$$

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[34] If we represent an anisotropic exchange interaction as

$$\mathcal{H}_{\text{ex}}=-2\Sigma_{lm}\,[\alpha_{lm}Y_l^m(\text{Eu})]\mathbf{S}(\text{Eu})\cdot\mathbf{S}(\text{Fe}),$$

the spherical harmonics Y_4^m represent the fourth-rank component of the anisotropic exchange, and the Y_6^m the sixth-rank component.

[35] P. M. Levy, Phys. Letters **19**, 8 (1965).

[36] E. M. Corson, Ref. 21.

[37] J. H. Van Vleck, Ref. 21, Sec. **34**.

[38] A prime on the summation symbol restricts the sum to $n''\neq n$.

where

$$\mathcal{H}_{n'n''}\equiv\langle n'|\mathcal{H}|n''\rangle \quad \text{and} \quad h\nu_{nn'}\equiv E_n^{(0)}-E_{n'}^{(0)}.$$

The sixth-order energy correction is

$$\begin{aligned}
W_n^{(6)}={}&\sum_{n'\cdots n^{\mathrm{V}}}{}' \frac{\mathcal{H}_{nn'}\cdots\mathcal{H}_{n^{\mathrm{V}}n}}{h^5\nu_{nn'}\cdots\nu_{nn^{\mathrm{V}}}}-\mathcal{H}_{nn}\sum_{n'\cdots{}^{\mathrm{IV}}n}{}' \frac{\mathcal{H}_{nn'}\cdots\mathcal{H}_{n^{\mathrm{IV}}n}}{h^5\nu_{nn'}^2\cdots\nu_{nn^{\mathrm{IV}}}^2}(\nu_{nn'}\nu_{nn''}\nu_{nn'''}+\nu_{nn'}\nu_{nn''}\nu_{nn^{\mathrm{IV}}}+\nu_{nn'}\nu_{nn'''}\nu_{nn^{\mathrm{IV}}}\\
&+\nu_{nn''}\nu_{nn'''}\nu_{nn^{\mathrm{IV}}})-\sum_{n'\cdots n^{\mathrm{IV}}}{}' \frac{\mathcal{H}_{nn'}\mathcal{H}_{n'n}\mathcal{H}_{nn''}\cdots\mathcal{H}_{n^{\mathrm{IV}}n}}{h^5\nu_{nn'}^2\cdots\nu_{nn^{\mathrm{IV}}}^2}[(\nu_{nn'}+\nu_{nn''})\nu_{nn'''}\nu_{nn^{\mathrm{IV}}}+(\nu_{nn'''}+\nu_{nn^{\mathrm{IV}}})\nu_{nn'}\nu_{nn''}]\\
&-\tfrac{1}{2}\sum_{n'\cdots n^{\mathrm{IV}}}{}' \frac{\mathcal{H}_{nn'}\mathcal{H}_{n'n''}\mathcal{H}_{n''n}\mathcal{H}_{nn'''}\mathcal{H}_{n'''n^{\mathrm{IV}}}\mathcal{H}_{n^{\mathrm{IV}}n}}{h^5\nu_{nn'}\cdots\nu_{nn^{\mathrm{IV}}}}\left(\frac{\nu_{nn'}+\nu_{nn''}}{\nu_{nn'}\nu_{nn''}}+\frac{\nu_{nn'''}+\nu_{nn^{\mathrm{IV}}}}{\nu_{nn'''}\nu_{nn^{\mathrm{IV}}}}\right)\\
&+\mathcal{H}_{nn}\sum_{n'\cdots n'''}{}' \frac{\mathcal{H}_{nn'}\mathcal{H}_{n'n}\mathcal{H}_{nn''}\mathcal{H}_{n''n'''}\mathcal{H}_{n'''n}}{h^5\nu_{nn'}\nu_{nn''}\nu_{nn'''}}+2\left(\frac{1}{\nu_{nn'}^2}+\frac{1}{\nu_{nn''}^2}+\frac{1}{\nu_{nn'''}^2}+\frac{1}{\nu_{nn'}\nu_{nn''}}+\frac{1}{\nu_{nn'}\nu_{nn'''}}+\frac{1}{\nu_{nn''}\nu_{nn'''}}\right)\\
&+\mathcal{H}_{nn}^2\sum_{n'\cdots n'''}{}' \frac{\mathcal{H}_{nn'}\cdots\mathcal{H}_{n'''n}}{h^5\nu_{nn'}}\left(\frac{\nu_{nn'}\nu_{nn''}+\nu_{nn'}\nu_{nn'''}+\nu_{nn''}\nu_{nn'''}}{\nu_{nn'}^2\nu_{nn''}^2\nu_{nn'''}^2}+\frac{\nu_{nn''}^2+\nu_{nn'''}^2+\nu_{nn''}\nu_{nn'''}}{\nu_{nn''}^3\nu_{nn'''}^3}\right)\\
&+\tfrac{1}{3}\sum_{n'\cdots n'''}{}' \frac{\mathcal{H}_{nn'}\mathcal{H}_{n'n}\mathcal{H}_{nn''}\mathcal{H}_{n''n}\mathcal{H}_{nn'''}\mathcal{H}_{n'''n}}{h^5\nu_{nn'}^2\nu_{nn''}^2\nu_{nn'''}^2}\left(\nu_{nn'}+\nu_{nn''}+\nu_{nn'''}+\frac{\nu_{nn'}\nu_{nn''}}{\nu_{nn'''}}+\frac{\nu_{nn'}\nu_{nn'''}}{\nu_{nn''}}+\frac{\nu_{nn''}\nu_{nn'''}}{\nu_{nn'}}\right)\\
&-\mathcal{H}_{nn}^2\sum_{n'n''}{}' \frac{\mathcal{H}_{nn'}\mathcal{H}_{n'n}\mathcal{H}_{nn''}\mathcal{H}_{n''n}}{h^5\nu_{nn'}^3\nu_{nn''}^3}\tfrac{3}{2}\left(\nu_{nn'}\left(1+\frac{\nu_{nn'}}{\nu_{nn''}}\right)+\nu_{nn''}\left(1+\frac{\nu_{nn''}}{\nu_{nn'}}\right)\right)\\
&-\mathcal{H}_{nn}^3\sum_{n'n''}{}' \frac{\mathcal{H}_{nn'}\mathcal{H}_{n'n''}\mathcal{H}_{n''n}}{h^5\nu_{nn'}\nu_{nn''}}\left(\left(\frac{1}{\nu_{nn'}}+\frac{1}{\nu_{nn''}}\right)\left(\frac{1}{\nu_{nn'}^2}+\frac{1}{\nu_{nn''}^2}\right)\right)+\mathcal{H}_{nn}^4\sum_{n'}{}' \frac{\mathcal{H}_{nn'}\mathcal{H}_{n'n}}{h^5\nu_{nn'}^5}.
\end{aligned}\qquad\text{(A5)}$$

APPENDIX B

Cubic Averages of Functions of Direction Cosines Referred to *g*-Tensor Coordinates

The fifth- and sixth-order energies Eqs. (2.18) and (2.19) depend on the direction of the exchange field with respect to the local *g*-tensor axes (D_2 symmetry axes). If the magnetic complexes in a crystal are not equivalent, i.e., if the local *g*-tensor axes have inequivalent orientations with respect to the crystallographic axes, it is necessary to average the energies that depend on the field direction over all the inequivalent sites. In this way one obtains the dependence of the energies on the direction of the field referred to the crystallographic axes.

In crystals belonging to the cubic group, as the garnets, the magnetically inequivalent sites are related by cubic symmetry transformations about the crystallographic axes. In the garnet structure one axis of the local *g* tensor always coincides with a crystal axis, the remaining two axes are rotated 45° to the crystal axes.[39] To determine the averages of functions of the direction cosines of the exchange field entering the fifth- and sixth-order energies Eqs. (2.18) and (2.19), it is necessary to express the cubic symmetry transformations $\{Q_i\}$ in the *g*-tensor coordinates.

To do this we first rotate the *g*-tensor axes to coincide with the crystal axes, carry out the transformation Q_i and then rotate the *g*-tensor axes back to their original position. This is symbolically written as

$$RQ_iR^{-1}=Q_i', \qquad \text{(B1)}$$

where R represents the rotation that takes the crystal axes into the *g*-tensor axes, and Q_i' is an element of a cubic symmetry transformation expressed in the *g*-tensor coordinates. Multiplying Eq. (B1) from the right by R we find

$$RQ_i=Q_i'R. \qquad \text{(B2)}$$

Stated in words this says: first rotating the crystal axes to coincide with the *g*-tensor axes and then performing a cubic average expressed in terms of *g*-tensor coordinates, is equivalent to first performing a cubic average expressed in terms of the crystal axes, in which this average is simple, and then rotating the crystal axes to the *g*-tensor axes. For the full cubic group

$$R\{Q_i\}=\{Q_i\}R, \qquad \text{(B3)}$$

that is, a rotation commutes with the full group, but *not* with one element of the group, Nevertheless, each element commutes with a rotation in the sense implied by Eq. (B2).

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[39] The *g*-tensor axes are local D_2 symmetry axes.

To perform the averaging over the six inequivalent sites, it is necessary to relate the angles θ_i, ϕ_i the exchange field makes with the local g-tensor axes p, q, r (g_x, g_y, g_z) to the angles θ, ϕ the exchange field makes with respect to the crystal axes x, y, z (see Fig. 1). The operator R that rotates the coordinate axes x, y, z into the axes p, q, r is given by Goldstein.[40]

We represent the cubic symmetry transformations Q_i by 3×3 matrices with one element, ±1, in each row and column. The relation between the g-tensor coordinate axes and the crystallographic axes is

$$\begin{bmatrix} p_i \\ q_i \\ r_i \end{bmatrix} = RQ_i \begin{bmatrix} x \\ y \\ z \end{bmatrix}, \qquad \text{(B4)}$$

where

$$\begin{aligned} p_i &= \alpha_{1i} = \sin\theta_i \cos\phi_i, & x &= \sin\theta \cos\phi, \\ q_i &= \alpha_{2i} = \sin\theta_i \sin\phi_i, & y &= \sin\theta \sin\phi, \\ r_i &= \alpha_{3i} = \cos\theta_i, & z &= \cos\theta. \end{aligned}$$

Whereas there are only six magnetically inequivalent sites in the garnets, there are 24 elements to the cubic group. This full group must be used in the averaging process in order to obtain the cubic symmetry properties of the crystal. For the full cubic group the averages of the direction cosines α_{qi} are

$$\textstyle\sum_i \alpha_{ni}\alpha_{n'i} = (N/3)\delta_{nn'}, \quad n = 1, 2, 3$$

and

$$\begin{aligned} \textstyle\sum_i \alpha_{ni}^2\alpha_{n'i}\alpha_{n''i} = {} & (N/3)(\alpha_1^4+\alpha_2^4+\alpha_3^4)\delta_{nn'}\delta_{nn''} + (N/3) \\ & \times(\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2)\delta_{n'n''}(1-\delta_{nn'}\delta_{nn''}). \qquad \text{(B5)} \end{aligned}$$

These averages are based on the following property of the direction cosines:

$$\alpha_1^2+\alpha_2^2+\alpha_3^2 = 1. \qquad \text{(B6)}$$

As the transformation (B4) is linear, we have that

$$\begin{bmatrix} p_i^4 \\ q_i^4 \\ r_i^4 \end{bmatrix} = \begin{bmatrix} p_i \\ q_i \\ r_i \end{bmatrix}^4 = \left[RQ_i \begin{bmatrix} x \\ y \\ z \end{bmatrix} \right]^4. \qquad \text{(B7)}$$

The cubic average over the six inequivalent sites for any combination of the direction cosines is performed by using the rotation R and the full cubic group averages (B5). Let us consider the average

$$\tfrac{1}{6}\textstyle\sum_i \alpha_{ni}^4(\theta_i,\phi_i) = \tfrac{1}{6}\sum_i \left[\sum_{n'} R_{nn'}\alpha_{n'i}(\theta,\phi)\right]^4, \qquad \text{(B8)}$$

where $R_{nn'}$ is a matrix element of the rotation R given by Goldstein.[40] By using the averages (B5) and the unitarity of the rotation operator R, i.e.,

$$\textstyle\sum_{n'} R_{nn'}^2 = 1, \qquad \text{(B9)}$$

we find that the *anisotropic* part of the average (B8) is

$$\begin{aligned} \tfrac{1}{6}\textstyle\sum_i \alpha_{ni}^4(\theta_i,\phi_i) = {} & \left[1-(5/3)\textstyle\sum_j R_{nj}^4\right] \\ & \times(\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2). \qquad \text{(B10)} \end{aligned}$$

All the averages encountered in the fifth- and sixth-order energies, i.e., Eqs. (2.18) and (2.19) can be evaluated by using Eq. (B10) and some trigonometric identities. For example, we find the average of $\sin^4\theta \cos4\phi$ from the identity

$$\langle \sin^4\theta \cos4\phi \rangle = 4(\langle \sin^4\theta \sin^4\phi \rangle + \langle \sin^4\theta \cos^4\phi \rangle) - 3\langle \sin^4\theta \rangle.$$

By using the averages (B10) and retaining only fourth-degree terms, we find

$$\begin{aligned} \langle \sin^4\theta \cos4\phi \rangle = {} & \left[5-(20/3)\sum_{n=1}^{2}\sum_{j=1}^{3} R_{nj}^4 + 5\sum_{j=1}^{3} R_{3j}^4\right] \\ & \times(\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2). \end{aligned}$$

The necessary averages for the fifth- and sixth-order energies are given in Table III. For these averages one axis of the g-tensor axes is parallel to a crystal axis and the other two are at 45° with respect to the remaining crystal axes, e.g., for p parallel to x (see Fig. 1)

$$\eta = \zeta = 0°, \quad \text{and} \quad \xi = 45°.$$

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[40] H. Goldstein, *Classical Mechanics* (Addison-Wesley Publishing Company Inc., Cambridge, Massachusetts, 1950), p. 109, Eq. (4–46).