PHYSICAL REVIEW VOLUME 181, NUMBER 2 10 MAY 1969

Faraday Rotation in Rare-Earth Iron Garnets

W. A. Crossley,* R. W. Cooper, and J. L. Page
Mullard Research Laboratories, Redhill, Surrey, England

and

R. P. van Stapele
Philips Research Laboratories, Eindhoven, Netherlands

(Received 8 November 1968)

The Faraday rotation of yttrium, gadonlinium, and terbium iron garnets at 1.15 μ is presented as a function of temperature between 100 and 450°K. The rotation is analyzed in terms of electric and magnetic dipole contributions from the various magnetic sublattices (Fe^{3+} octahedral, Fe^{3+} tetrahedral, RE^{3+}), and the contributions are separated by a least-squares fit to magnetization data. The similarities and differences in the electric dipole contributions are discussed, and it is suggested that charge-transfer processes are important. The effect of a knowledge of the electric dipole contributions at 1.15 μ on published results at longer wavelengths is investigated, and deductions of g factors in this region are shown to be probably in error. In an Appendix, theoretical derivations are given for the form of the electric dipole rotation due to magnetic ions in various circumstances.

INTRODUCTION

Yttrium iron garnet (YIG) and the rare-earth iron garnets (RIG) are well known to have a transparent "window" in the region ~1.1–5 μ wavelength (9100–2000 cm^{-1}). Absorption beginning at the high-frequency end is due to both transitions in the near infrared and visible, between crystal-field-split levels of the magnetic ions, and what appear to be change-transfer processes, involving oxygen and ferric ions, in the uv.

These compounds also give a large Faraday rotation, and two contributions may be distinguished—a dispersive rotation from the electric dipole transitions mentioned above, and a nondispersive rotation from magnetic dipole transitions having resonance frequencies in the far-infrared and microwave regions.

From the work of Mathews *et al.*[1] on Ga-doped YIG it appears that the Fe^{3+} ions on different crystal sites (octahedral and tetrahedral) give different contributions of opposite sign to the dispersive rotation, the octahedral ions giving the greater, positive, part. In a previous paper,[2] we reported attempts to deduce the separate contributions at 1.15 μ by fitting the measured rotation of YIG and TbIG as a function of temperature to sublattice magnetization curves of Anderson.[3] In the present work we report further measurements on GdIG at 1.15 μ and the results of fitting the rotation of all three compounds to directly measured sublattice moments.

In Sec. I we summarize the theoretical situation for Faraday rotation, showing in an Appendix that one expects the rotation caused by an ion to be proportional to its magnetic moment in a wide range of circumstances, including the presence of an exchange field.

In Sec. II we describe the experimental methods used and the crystal preparation. The experimental results and the results of the computer fit are presented in Sec. III and interpreted in terms of possible transitions.

Finally, in Sec. IV, we discuss the implications of our results for the method of determining gyromagnetic ratio from long-wavelength Faraday rotation measurements.

I. ORIGIN OF THE ROTATION

Defining the Faraday rotation per unit length as positive for right-hand rotation of the field vector looking along the direction of the light beam, we can write

$$\theta=\frac{\omega}{2c}(n^{-}-n^{+})=\frac{\omega}{2c}\,\frac{(n^{-})^{2}-(n^{+})^{2}}{2\bar{n}} \tag{1}$$

for light of angular frequency ω. n^+ and n^- are the refractive indices for right- and left-hand circularly polarized light, and $\bar{n}$ is the mean refractive index.

Since $n^2=\epsilon\mu$ (dielectric constant × magnetic permeability), we rewrite Eq. (1) in regions away from absorption peaks and obtain $\theta=\theta_E+\theta_M$, where

$$\theta_E=\frac{\pi\omega}{c\bar{n}}[\chi_e^{-}-\chi_e^{+}]\tfrac{1}{9}(\bar{n}^2+2)^2 \tag{2a}$$

and

$$\theta_M=\frac{\pi\omega\bar{n}}{c}[\chi_m^{-}-\chi_m^{+}] \tag{2b}$$

are the contributions from electric and magnetic susceptibilities, respectively. The magnetic susceptibility is small at optical frequencies, and we have taken $\bar{\mu}=1$ and $\bar{\epsilon}=\bar{n}^2$. We have included the Lorentz-Lorenz correction in θ_E.

---

* Work performed while at Philips Research Laboratories, Eindhoven, Netherlands.

[1] H. Matthews, S. Singh, and R. C. LeCraw, Appl. Phys. Letters **7**, 165 (1965).

[2] R. W. Cooper, W. A. Crossley, J. L. Page, and R. F. Pearson, J. Appl. Phys. **39**, 565 (1968).

[3] E. E. Anderson, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 660.

Wangsness[4] has calculated $\chi_m^{\pm}$, using the classical equations of motion for a magnetic moment; for a ferrimagnetic material with all the sublattice moments aligned along the direction of the light beam, and light frequency much greater than the ferromagnetic and exchange resonance frequencies (~0.3 and ~30 cm^{-1}), one finds

$$\theta_M = \frac{2\pi\bar{n}}{c}\sum_i \gamma^i M^i. \tag{3}$$

The summation is over all the sublattices i having moments M^i and gyromagnetic ratios γ^i. The M^i take the appropriate algebraic sign (direction relative to light beam) and the γ^i will normally be positive, giving a positive rotation.

This formula has been used with some success to explain the Faraday rotation of ferrimagnets in the 5–8 μ region (2000–1250 cm^{-1}),[5] where it was assumed that the electric dipole contribution to the total rotation (θ_E) was zero, but some discrepancies remain. We show below that the assumption of zero θ_E in this frequency region is not necessarily valid, even though there may only be a small frequency dependence of the measured rotation. Here we take Eq. (3) to represent accurately the magnetic contribution to the rotation at all frequencies much greater than the exchange resonance frequency, with the γ^i gyromagnetic ratios characteristic of the various ions.

The electric dipole contribution is obtained by inserting the quantum-mechanical expressions for ac susceptibility into Eq. (2a), and is

$$\theta_E = \frac{N\pi(\bar{n}^2+2)^2}{9\bar{n}c\hbar}\sum_{g,n}\frac{\omega^2}{\omega_{ng}{}^2-\omega^2} \times\{|\langle n|V_-|g\rangle|^2 - |\langle n|V_+|g\rangle|^2\}\rho_g \tag{4}$$

for each type of ion present in the crystal.

g runs over ground states with occupation probability ρ_g, and n runs over excited states at energies $\hbar\omega_{ng}$ above the ground states. N is the number of ions per unit volume, and $V_{\pm}$ the electric dipole moment operators for right- and left-hand circularly polarized light.[6]

To simplify this expression we consider the states $|g\rangle$ and $|n\rangle$ to be in two reasonably closely spaced groups, the separation of the groups being ω_0, much greater than the spacings within the groups. If the frequency ω is such that E_n, $E_g \ll \hbar\omega \ll \hbar\omega_0$, where E_n and E_g are the energies of excited and ground states relative to their respective mean energies, then the frequency denominator in (4) may be expanded;

$$\frac{\omega^2}{\omega_{ng}{}^2-\omega^2} = \frac{\omega^2}{\omega_0{}^2-\omega^2}\left(1 - \frac{2\omega_0(E_n-E_g)}{\hbar(\omega_0{}^2-\omega^2)}+\cdots\right), \tag{5}$$

since $\hbar\omega_{ng} = \hbar\omega_0 + E_n - E_g$.

Then we recognize three contributions to θ_E:

$$\theta_E(1) = \sum_g \rho_g \sum_n \{|\langle n|V_+|g\rangle|^2 - |\langle n|V_-|g\rangle|^2\} \times\frac{\omega^2}{\omega_0{}^2-\omega^2}, \tag{6a}$$

$$\theta_E(2) = -\sum_g \rho_g \sum_n \{|n|V_+|g\rangle|^2 - |\langle n|V_-|g\rangle|^2\} \times\frac{2\omega_0\omega^2E_n}{\hbar(\omega_0{}^2-\omega^2)^2}, \tag{6b}$$

$$\theta_E(3) = \sum_g \rho_g \sum_n \{|\langle n|V_+|g\rangle|^2 - |\langle n|V_-|g\rangle|^2\} \times\frac{2\omega_0\omega^2E_g}{\hbar(\omega_0{}^2-\omega^2)^2}. \tag{6c}$$

For the case of paramagnetic ions in an applied field, $\theta_E(1)$ is well known as the "paramagnetic" rotation, since it is usually proportional to the magnetic moment of the ion, and $\theta_E(2)$ and $\theta_E(3)$ are known as the "diamagnetic" rotation, being proportional (through E_n and E_g) to the applied field, practically independent of temperature except at very low T, and (through the frequency denominator) much smaller than $\theta_E(1)$ in the frequency region we are considering.[7]

It is also well known that if the ground state of the ion is an orbital singlet, then the summation over the excited states in (6a) and (6c) goes to zero, and $\theta_E(2)$ is the only remaining term.[7]

The detailed situation at low temperatures, for ions acted upon by an exchange field, has been discussed by Clogston[8] and by Dillon *et al.*[9] The latter authors consider an S-state ion making an allowed electric dipole transition to an excited P state, in the limits of low temperature (only the lowest spin state occupied) and exchange energy much smaller than the spin-orbit coupling energy. Under these conditions the exchange field acting on the upper state does not enter into the expression for $\theta_E(2)$, only the spin-orbit coupling of this state being important.

In the RIG ($R_3Fe_5O_{12}$) the Fe^{3+} ions are in $3d^5{:}^6S$ ground states, and thus the first allowed ionic electric dipole transition is to a state such as $3d^44p{:}^6P$. Transitions to the crystal-field-split levels of $3d^5$ are also possible if odd crystal fields or phonon mixing lift the selection rule forbidding $3d^5 \to 3d^5$ transitions, but are normally of lower intensity.

---

[4] R. K. Wangsness, Phys. Rev. **95**, 339 (1954).

[5] G. S. Krinchik and M. V. Chetkin, Zh. Eksperim. i Teor. Fiz. **41**, 673 (1961) [English transl.: Soviet Phys.—JETP **14**, 485 (1962)]; B. Johnson and R. S. Tebble, Proc. Phys. Soc. (London) **87**, 935 (1966).

[6] Y. R. Shen, Phys. Rev. **133**, A511 (1964).

[7] M. J. Stephen, Mol. Phys. **1**, 301 (1958).

[8] A. M. Clogston, J. Appl. Phys. **31**, 198S (1960).

[9] J. F. Dillon, H. Kamimuna, and J. P. Remeika, J. Phys. Chem. Solids **27**, 1531 (1966).

The absorption spectrum of YIG shows very strong broad absorptions in the region 20 000–60 000 cm^{-1}, with weaker and somewhat narrower lines in the region 9000–20 000 cm^{-1}. The latter are ascribed to the "forbidden" $3d^5 \rightarrow 3d^5$ transition, but the strength and intensity of the broad bands strongly suggests that they derive from charge-transfer processes involving O^{2-} and Fe^{3+} ions.[8] The RIG's show additional sharp peaks of low intensity at frequencies down to 2000 cm^{-1}, depending on the actual rare-earth ion. These are $4f \rightarrow 4f$ transitions between spin-orbit and crystal-field-split levels.[10]

The Faraday rotation of YIG as a function of frequency[11] also suggests a strong contribution from transitions in the uv, with smaller, highly dispersive, contributions superimposed in the infrared and visible (due to the "forbidden" lines).

In the Appendix we evaluate the various contributions in Eq. (6), without specifying the excited state of the transition involved beyond its having such an orbital angular momentum character as to permit electric dipole transitions. We show there that the dominant contributions to Faraday rotation from ions in an exchange field are the following. For a ground state with orbital angular momentum,

$$\theta_E(1)=K_1\frac{\omega^2}{\omega_0{}^2-\omega^2}M. \tag{7}$$

For a ground state with zero orbital angular momentum (S state or orbital singlet resulting from crystal field),

$$\theta_E(1)=-K_2\frac{\Delta g}{g}\frac{\omega^2}{\omega_0{}^2-\omega^2}M, \tag{8a}$$

$$\theta_E(2)=K_3\lambda\frac{\omega^2\omega_0}{(\omega_0{}^2-\omega^2)^2}M. \tag{8b}$$

Here M is the magnetic moment of the ion, Δg is the deviation of g from 2.002, λ is the spin-orbit coupling constant for the upper state, and K_1, K_2, and K_3 are constants, proportional to the reduced matrix elements for the transitions, and slightly dependent on ω through $\bar{n}$.

Δg will be very small for true S-state ions like Fe^{3+} ($3d^5$:^6S) and Gd^{3+} ($4f^7$:^8S), but for ions such as Cr^{3+} in octahedral surroundings ($^4A_2$) $\Delta g \sim 0.02$ and the two contributions (8a) and (8b) can easily be of the same order.

Then, even though the exact nature of the transition giving the strong electric dipole absorption and Faraday rotation in the RIG may be unknown, we can say that the rotation is proportional to the magnetic moment of the ions (or groups of ions for a charge-transfer process) involved.

The total Faraday rotation for a RIG can then be written

$$\theta=\frac{2\pi\bar{n}}{c}[\gamma_{\mathrm{Fe}}(M_{\mathrm{Fe}^t}-M_{\mathrm{Fe}^0})-\gamma_R M_R] -A(\omega)M_{\mathrm{Fe}^0}+B(\omega)M_{\mathrm{Fe}^t}-C(\omega)M_R. \tag{9}$$

[In Eq. (9) we have set the gyromagnetic ratios for octahedral and tetrahedral Fe^{3+} ions equal, and have given signs to the magnetic moments correct for T greater than the compensation temperature. Below this temperature all the moments change sign.]

$A(\omega)$ and $B(\omega)$ will be expected to have frequency variation as in (8b); for GdIG, $C(\omega)$ will also have this variation, but for other rare earths $C(\omega)$ will be like (7) or (8a).

Equation (9) can be rewritten as

$$\theta(T)=A'M_{\mathrm{Fe}^0}(T)+B'M_{\mathrm{Fe}^t}(T)+C'M_R(T), \tag{10}$$

giving the temperature dependence of the Faraday rotation in terms of that of the sublattice moments. Since these moments are known from NMR, Mössbauer, and total magnetization data, a simple least-squares fit to Eq. (10) gives A', B', and C' and, through the calculated magnetic contribution, the coefficients for the electric dipole contributions A, B, and C.

II. EXPERIMENTAL

Measurements were made on single-crystal blocks of YIG, GdIG, and TbIG up to 7 mm thick, at the He-Ne laser wavelength of 1.15 μ. This wavelength lies on the edge of the YIG window at the short-wavelength cutoff, and is clear of intra-f transitions of Tb^{3+}.

The crystals were grown by standard techniques from lead-oxide–lead-fluoride fluxes, using starting materials (oxides) of 99.999% purity, except for Gd$_2$O$_3$, which was 99.9% pure.

Measurements were made over the temperature range 80–450°K in a saturating magnetic field up to 8.7 kOe. In all samples a variation of Faraday rotation with applied field was found above saturation. For YIG and GdIG the effect was small, but for TbIG a field dependence of $-3.8°$/cm Oe was observed at 300°K. For TbIG it was necessary to extrapolate the observed rotations to zero internal field, to remove the discontinuity in $|\theta|$ which otherwise appears at the compensation temperature 245°K because of this field dependence. (Below the compensation temperature the applied field acts parallel to the exchange field on the Tb^{3+} ions, which give the greatest contribution to the rotation, but above this temperature the field is antiparallel to the exchange field.)

---

[10] D. L. Wood and J. P. Remeika, J. Appl. Phys. 38, 1038 (1967).
[11] J. F. Dillon, J. Appl. Phys. 39, 922 (1968).

III. RESULTS AND DISCUSSION

A. Least-Squares Analysis

For YIG and GdIG the NMR data of Litster and Benedek[12] and of Gonano *et al.*[13] were used for the temperature dependence of the Fe^{3+} octahedral, Fe^{3+} tetrahedral, and Gd^{3+} sublattice moments.

For TbIG the Fe^{3+} sublattices were taken to behave as in YIG and GdIG (there being essentially little difference between these), and the Tb^{3+} sublattice moment was deduced from these data and the total magnetization data of Harrison *et al.*[14]

van Wieringen[15] has measured the 14.4-keV Fe^{57} Mössbauer spectrum of a TbIG sample (taken from the same crystal as the sample used in the Faraday-rotation measurements) as a function of temperature. The results, while not so accurate as the NMR results for YIG, again indicate no significant deviation from the Fe^{3+} sublattice moment behavior in YIG. Using the Mössbauer method, the Curie temperature of the sample was found to be 543°K, and this is not sufficiently different from YIG to invalidate our use of YIG magnetization curves directly (i.e., without normalizing to a new Curie temperature).

In both GdIG and TbIG a compensation temperature exists, below which the combined moments of the rare-earth and Fe^{3+} octahedral ions (which are always parallel) are greater than the Fe^{3+} tetrahedral moment. In an applied magnetic field all the moments swing through 180° at this temperature; exactly at the compensation temperature the net moment is zero. The effect gives a sharp change of sign of the Faraday rotation at T_{comp}, since all the signs in Eqs. (9) and (10) are changed.

This is taken account of in the analysis by always keeping the moments in (10) the same sign and using the negative of the measured rotation below T_{comp}.

Then a least-squares analysis of the experimental data in terms of Eq. (10) gives A', B', and C', and the estimated errors in these values.

The magnetic rotation in Eq. (9) has been calculated using the g factor 2.00 for Fe^{3+} and Gd^{3+}, and the free-ion g factor 1.50 for Tb^{3+}. In the absence of direct measurements on GdIG and TbIG, $\bar{n}$ in these compounds has been taken as that measured in pure YIG.[16] When the sublattice moments are measured in μ_B per two formula units, we find that the multipliers for the moments derived from $2\pi\bar{n}\gamma/c$ have the following values for the various sublattices:

$$\left.\begin{array}{l}\mathrm{Fe}^{3+}\text{ octahedral}\\ \mathrm{Fe}^{3+}\text{ tetrahedral}\\ \mathrm{Gd}^{3+}\end{array}\right\}\ 9.15$$

$$\mathrm{Tb}^{3+}\qquad 6.86.$$

Table I. Electric dipole parameters at 1.15 μ.

	A	B	C
YIG	−40.3± 1.7	−21.4± 1.2	
GdIG	−42.4± 1.8	−27.1± 1.3	−1 ±0.2
TbIG	−9 ±15	−10 ±11	−84.4±2.5

The results for the derived values of the electric dipole contributions A, B, and C at 1.15 μ are shown in Table I. Also, in Figs. 1–3 are plotted the experimental rotation (crosses) and theoretical fit (line) for YIG, GdIG, and TbIG. The sign of the rotation has been reversed below T_{comp} to make the intrinsic behavior of the rotation clearer.

We note that all the electric dipole parameters A, B, and C are negative, implying that each ion gives a positive contribution to the rotation when its magnetic

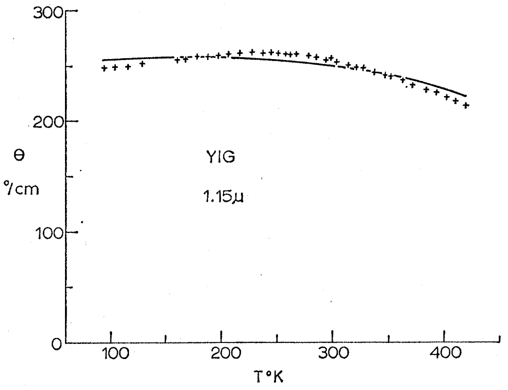

Fig. 1. Experimental and theoretical Faraday rotation of YIG at 1.15-μ wavelength as a function of temperature.

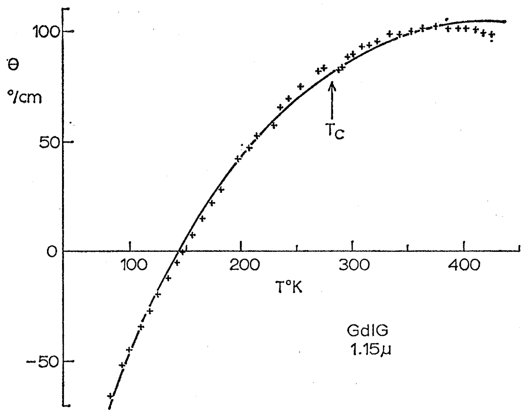

Fig. 2. Experimental and theoretical Faraday rotation of GdIG at 1.15-μ wavelength as a function of temperature. The negative of θ is plotted below the compensation temperature.

---

[12] J. D. Litster and G. B. Benedek, J. Appl. Phys. **37**, 1320 (1966).

[13] R. Gonano, E. Hunt, and H. Meyer, Phys. Rev. **156**, 521 (1967)

[14] F. W. Harrison, J. F. A. Thompson, and K. Tweedale, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 664.

[15] J. S. van Wieringen (unpublished).

[16] B. Johnson and A. K. Walton, Brit J. Appl. Phys. **16**, 475 (1965).

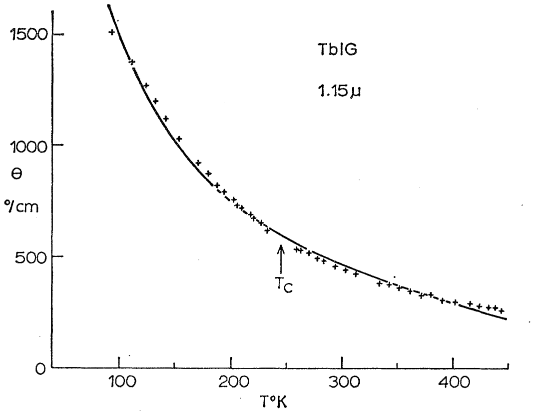

FIG. 3. Experimental and theoretical Faraday rotation of TbIG at 1.15-μ wavelength as a function of temperature. The negative of θ is plotted below the compensation temperature.

moment is antiparallel to the light-beam direction. This is what is normally observed for paramagnetic ions in applied fields.

B. YIG

For YIG it is obvious that the major part of the electric dipole rotation comes from the octahedral Fe^{3+}, and the minor part, of opposite sign, from the tetrahedral Fe^{3+}. This agrees with the measurements of Mathews *et al.*[1] on YIGaG, where the Ga^{3+} ions go preferentially (about 80%) into tetrahedral sites. Reducing the number of tetrahedral Fe^{3+} ions reduces the negative contribution and increases the total electric dipole rotation.

It is seen that the rotation due to an octahedral Fe^{3+} ion is about 1.9 times as strong as that from a tetrahedral Fe^{3+}. This could be explained in terms of a difference in the constant K_3 (difference in reduced matrix element) or in the resonance frequency in Eq. (8b). $\theta_E(2)$ depends on ω_0^{-3} at low frequencies, so that a difference of about 25% in ω_0 would explain the factor of 1.9 ($\sqrt[3]{1.9}=1.24$). In case ω is not negligible with respect to ω_0 then the denominator in (8b) can vary still more rapidly with ω_0. (But note that we have assumed ω to be so far from ω_0 that relaxation effects can be neglected.)

We can also calculate the electric dipole rotation at 0°K and obtain $806-639=167$°/cm. Considering that the errors in each contribution are emphasized by taking the difference, this agrees excellently with the value of 154°/cm measured at 10°K.[1]

C. GdIG

The parameters for the Fe^{3+} sublattices in GdIG are quite close to the values in pure YIG, again showing the dominant positive contribution from the octahedral sites. Within the accuracy of the fit, the octahedral parameter is the same as in YIG, but the tetrahedral parameters differ by more than the estimated accuracy.

The Gd^{3+} parameter is much smaller that the Fe^{3+} ones. If the rotation is due to transitions in the ions Fe^{3+} and Gd^{3+}, this may reflect the much higher excited states of Gd^{3+} compared to Fe^{3+} (the lowest Gd^{3+} level is at 32 000 cm^{-1}). But if the transitions involve charge-transfer processes, it is more difficult to decide what the relative frequencies might be. However, the weaker exchange field acting on the rare-earth site indicates smaller overlap of rare-earth wave functions with O^{2-} $2p$ functions and possibly a weaker charge-transfer intensity.

We must note that although the Gd^{3+} ion contributes relatively little to the electric dipole rotation, the modification of the Fe^{3+} tetrahedral parameter in GdIG by only 25% is quite sufficient to alter the total rotation by considerably more than this. Changes in the ionic surroundings between the compounds might be expected to affect the results only slightly because the lower and upper states involved are S and P, which are relatively insensitive to crystal fields. The variation in the Fe^{3+} parameters is more likely to result from a charge-transfer process involving an Fe-O-Gd combination, similar to the Fe-O-Ti charge transfer observed by Townsend.[17] Presumably the rotation depends on $M_{\text{Fe}}+M_{\text{Gd}}$ and gives an extra contribution to both the Fe^{3+} parameters compared with YIG. It is also possible that the extra absorption process would alter the parameters by affecting the intensity or resonance frequency of the other processes present.

D. TbIG

The rotation of TbIG is much larger than that of YIG or GdIG, and the rapid increase at low temperatures shows the strong effect of the Tb^{3+} moment increase. The dominant contribution from the Tb^{3+} makes it difficult to estimate the Fe^{3+} contributions with any accuracy, as is obvious from the variances given in Table I. There appears to be a considerable modification to the Fe^{3+} octahedral and tetrahedral parameters compared with YIG, but the exact extent is uncertain.[18]

In contrast, the accuracy of the Tb contribution is good; and, as expected for an ion obeying Eq. (7), the electric dipole parameter is large. As in Ref. 2, we may compare the magnitude of this parameter, 84.4, with those which we have measured for Tb^{3+} in diamagnetic hosts: 38.5 and 56.3 in TbGaG and TbAlG, respectively, at 300°K. Tb^{3+} is essentially paramagnetic in TbIG at the temperatures of our experiments ($g\beta H_{\text{ex}}/kT\ll 1$) and we can make direct comparison of these figures. It is clear that the Tb^{3+} contribution depends on the host material, and we may once more invoke charge-transfer processes of Tb-O groups to explain the differences. A

---

[17] M. G. Townsend, Solid State Commun. **6**, 81 (1968).

[18] We also note that the actual Fe^{3+} parameters depend on the magnetization curves used. In Ref. 2, where Anderson's estimates of $M_{\text{Fe}}{}^{o}$ and $M_{\text{Fe}}{}^{t}$ were used rather than direct measurements, very different parameters were obtained.

strong charge-transfer process involving Fe-O-Tb (Fe^{3+} on the same sites as Ga^{3+} and Al^{3+}) would also provide a large modification of the Fe^{3+} parameters, as is observed if we take the quantities in Table I at their face value.

At applied magnetic field strengths greater than necessary to cause magnetic saturation, the rotation of TbIG decreases linearly with field. Here the applied field is acting in opposition to the exchange field at the Tb site, and we may use the gradient of the curve to deduce an effective "Verdet constant" for Tb^{3+}. Correcting for the small field dependence in YIG and using measured susceptibilities, we can convert this to the equivalent of our parameter C in Eq. (9). The observed field dependence of $-3.8°/\text{cm kOe}$ at 300°K leads to a value for C of $87.5°/\text{cm}\ \mu_B$, in excellent agreement with the value in Table I.

IV. LONG-WAVELENGTH ROTATION

It is interesting to calculate the effect of our results on previous measurements of the rotation in garnets at long wavelengths ($>5\ \mu$). It is normally observed that the rotation is independent of wavelength in this region, and the assumption is made that the only contribution is from the nondispensive magnetic rotation, Eq. (3).

Consider, however, the Tb^{3+} electric dipole contribution in TbIG. Using Eq. (7),

$$\theta_E(\text{Tb}) = \frac{K\omega^2}{\omega_0^2 - \omega^2} M_{\text{Tb}} \tag{11}$$

[the negative sign for the Tb^{3+} moment is already in (11)], and we know from Table I that

$$\frac{K\omega^2}{\omega_0^2 - \omega^2} = 84.4, \quad \omega = 8690\ \text{cm}^{-1}\ (1.15\ \mu).$$

We have no exact knowledge of ω_0; but from general spectral data we may reasonably take it to be in the region $(20\text{–}40)\times10^3\ \text{cm}^{-1}$. Then at, say, 6.5 μ (1540 cm^{-1}), we find

$$2.16 M_{\text{Tb}} \leqslant \theta_E(\text{Tb}) \leqslant 2.38 M_{\text{Tb}} \tag{12}$$

as the extreme relations for the extreme ω_0 values. M is 36 μ_B at 0°K and the contribution to the rotation of the order 80°/cm.

Using the different frequency variation (8b) for the Fe^{3+} sublattices, we can also evaluate approximate values for the Fe^{3+} electric dipole parameters at 6.5 μ, here letting ω_0 range between 25 and $50\times10^3\ \text{cm}^{-1}$. θ_E/M then has the values in Table II.

The figures indicate that at 6.5 μ there should still be a detectable contribution from the dispersive rotation in YIG, but that if the ferric parameters for TbIG have any meaning, the contribution there will be much smaller. Actually, these parameters must all be further modified for dispersion of the refractive index. Using $\bar{n}$ for YIG as the only available figure, this gives a decrease of 5%.

TABLE II. Electric dipole parameters at 6.5 μ (θ_E/M).

	YIG	TbIG
Octahedral	1.0–1.2	(0.2 –0.3)±100%
Tetrahedral	−0.5–−0.6	(−0.25–−0.3)±100%

Chetkin and Shalygin[19] have measured the Faraday rotation of TbIG at 6.5 μ. Assuming the rotation to arise entirely from the magnetic contribution, they found it necessary to allow the g factor for Tb^{3+} to differ from 1.50 and to be rather strongly temperature-dependent. In view of our conclusions concerning the magnitude of the dispersive contributions at 6.5 μ, we have reanalyzed their data (as simply taken from the published graph) in terms of the relation

$$\theta = AM_{\text{Fe}} + BM_{\text{Tb}}, \tag{13}$$

where

$$M_{\text{Fe}} = M_{\text{Fe}}{}^t - M_{\text{Fe}}{}^0.$$

An attempt to separate the two Fe^{3+} contributions was unsuccessful, partly because of inaccuracies in taking data from a small graph and probably also because of the (apparent) smallness of the Fe^{3+} electric dipole contribution at 6.5 μ shown in Table II.

Again performing a computer least-squares analysis of Eq. (13), we found that

$$A = 8.19 \pm 0.13,$$
$$B = -4.31 \pm 0.10.$$

The experimental and theoretical curves are shown in Fig. 4.

Now the calculated magnetic rotation at 6.5 μ, taking $g_{\text{Fe}} = 2.00$, $g_{\text{Tb}} = 1.50$, and the value of $\bar{n}$ appropriate to

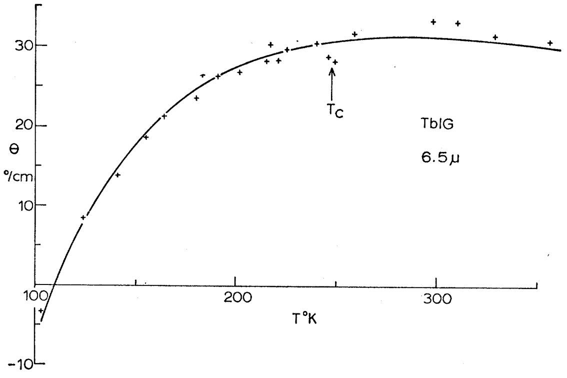

FIG. 4. Experimental and theoretical Faraday rotation of TbIG at 6.5-μ wavelength as a function of temperature. The crosses are the experimental points taken from Ref. 19. The negative of θ is plotted below the compensation temperature.

---

[19] M. V. Chetkin and A. N. Shalygin, Zh. Eksperim. i Teor. Fiz. **52**, 882 (1967) [English transl.: Soviet Phys.—JETP **25**, 580 (1967)]; J. Appl. Phys. **39**, 561 (1968).

YIG, is

$$\theta_M = 8.49M_{\mathrm{Fe}} - 6.37M_{\mathrm{Tb}}\,.$$

Our figure for $\theta_E(\mathrm{Tb}^{3+})$, corrected for $\bar{n}$ dispersion, is in the range $(2.1\text{–}2.3)M_{\mathrm{Tb}}$, and thus we can calculate

$$A = 8.49\,,$$
$$B = -(4.1\text{–}4.3)\,.$$

There is good agreement between the above values and those from the computer fit. Errors may have occurred through the use of $\bar{n}$ for YIG, and the deviation of the Fe^{3+} parameter may be an indication of some residual Fe^{3+} dispersive rotation.

The fact that we have already used $g_{\mathrm{Tb}} = 1.50$ to obtain the dispersive Tb^{3+} contribution at 1.15 μ does not influence the results significantly, since the magnetic rotation at 1.15 μ is only about 8% of the electric and a 12% change in the magnetic parameter would only affect the electric by 1%.

Because of the number of unknown quantities, these calculations are not accurate enough to prove that g_{Tb} is independent of temperature in the region 100–350°K, but the Faraday rotation of a RIG is so complex in origin that measurements at 6.5 μ alone are insufficient to provide accurate estimates of g_R.

Further, the effects of anisotropy on the rotation have not been considered; these can not only induce ellipticity in the transmitted beam, but can also make the rotation a nonlinear function of the crystal thickness.

V. CONCLUSIONS

By comparing the temperature variation of Faraday rotation and sublattice magnetic moments it is possible to distinguish the contributions to the rotation from the two Fe^{3+} and the rare-earth sublattices in YIG, GdIG, and TbIG at 1.15 μ. Using calculated values for magnetic dipole contributions, the electric dipole contribution can be deduced. These show that the octahedral and tetrahedral Fe^{3+} ions give contributions of opposite sign, the octahedral being about twice as large as the tetrahedral. The Fe^{3+} contributions in GdIG seem to be somewhat different from those in YIG, and those in TbIG may be considerably different. Charge-transfer processes may account for the differences.

The Gd^{3+} electric dipole contribution is much smaller than the Tb^{3+}, as would be expected for such an S-state ion, and the Tb^{3+} is of the same order as for Tb^{3+} in nonmagnetic garnets.

From the separate contributions it has been shown that at longer wavelengths ($\sim 7\ \mu$) the dispersive electric dipole contributions to the rotation are not necessarily negligible, and deductions of rare-earth g factors from rotation measurements at such wavelengths are invalid.

We have also shown theoretically that the electric dipole rotation for magnetic ions is usually proportional to the ground-state moment, even for orbital singlet ground states. If the orbital singlet derives from an S-state ion, the rotation is proportional to the spin-orbit parameter for the excited state and has frequency dependence $\omega^2\omega_0/[(\omega_0^2-\omega^2)^2]$; but if the orbital singlet is the result of a crystal field splitting, there is another term which can be of the same order. This term is proportional to the deviation of the g factor from the spin-only value and has frequency dependence $\omega^2/(\omega_0^2-\omega^2)$.

The exchange field acting on the upper state does not affect the rotation, whatever the relative sizes of the exchange and spin-orbit coupling energies. Thus the only effect of the exchange field detected in the Faraday rotation is on the population of the ground spin states.

ACKNOWLEDGMENTS

The authors would like to thank Dr. R. J. Elliott and Dr. R. F. Pearson for many helpful discussions.

APPENDIX: FARADAY ROTATION FROM ELECTRIC DIPOLE TRANSITIONS

We consider an ion or an ionic complex with ground states g and excited states n. Let the total Hamiltonian acting on the system be $H = H_0 + H_1$, where H_0 gives the unsplit ground states from which the g are split by H_1, and similarly for the excited states and the n. H_1 will contain the low-symmetry crystal fields, spin-orbit interaction, and applied and exchange magnetic fields. Then

$$\begin{aligned} H_0|g\rangle &= E_g{}^0|g\rangle\,, \\ H_0|n\rangle &= E_n{}^0|n\rangle\,, \end{aligned} \tag{A1}$$

$E_g{}^0$ and $E_n{}^0$ being the unperturbed energies of the ground and excited states.

Now assume that the $|g\rangle$ and $|n\rangle$ have been chosen so that the matrix of H_1 is diagonal.

$$\begin{aligned} \langle g|H_1|g'\rangle &= E_g\delta_{gg'} \quad \Big(\sum_g E_g = 0\Big)\,, \\ \langle n|H_1|n'\rangle &= E_n\delta_{nn'} \quad \Big(\sum_n E_n = 0\Big)\,, \end{aligned} \tag{A2}$$

and the perturbation is such that

$$|E_n|\,,|E_g| \ll E_n{}^0 - E_g{}^0 \equiv \hbar\omega_0\,. \tag{A3}$$

Here ω_0 is the mean resonance frequency for transitions between the groups $|g\rangle$ and $|n\rangle$.

Omitting constants, including the frequency-dependent refractive index, the formula for the electric dipole Faraday rotation is

$$\theta = \sum_g \rho_g \sum_n \{|\langle g|V_+|n\rangle|^2 - |\langle g|V_-|n\rangle|^2\} \times \frac{\omega^2}{\omega_{ng}{}^2 - \omega^2}\,. \tag{A4}$$

V_+ and V_- are the electric dipole operators for right- and left-hand circularly polarized light, ρ_g is the occupation probability of ground state $|g\rangle$, and $\hbar\omega_{ng}\equiv\hbar\omega_0+(E_n-E_g)$.

We are interested in the frequency region where

$$\omega<\omega_0,$$

$$\hbar\omega_0,\hbar\omega\gg|E_n|,|E_g|,$$

and

$$\omega_0^2-\omega^2\gg\omega_0|E_n-E_g|/\hbar,$$

so that Eq. (A4) can be expanded to first order in $\omega_0(E_n-E_g)/(\omega_0^2-\omega^2)$. We can then separate out three distinct terms:

$$\sum_g \rho_g\frac{\omega^2}{\omega_0^2-\omega^2}\sum_n\{|\langle g|V_+|n\rangle|^2-|\langle g|V_-|n\rangle|^2\}, \tag{A5a}$$

$$\sum_g \rho_g E_g\frac{2\omega^2\omega_0}{\hbar(\omega_0^2-\omega^2)^2}\sum_n\{|\langle g|V_+|n\rangle|^2-|\langle g|V_-|n\rangle|^2\}, \tag{A5b}$$

$$-\sum_g \rho_g\frac{2\omega^2\omega_0}{(\omega_0^2-\omega^2)^2}\sum_n\{|\langle g|V_+|n\rangle|^2-|\langle g|V_-|n\rangle|^2\}\frac{E_n}{\hbar}. \tag{A5c}$$

Equation (A5a) is normally called the "paramagnetic" term, and Eqs. (A5b) and (A5c) are the "diamagnetic" terms.

In each of the three terms we are dealing with sums like

$$\sum_n|\langle g|V|n\rangle|^2\langle n|A|n\rangle. \tag{A6}$$

In (A6), V is either V_+ or V_-, and A is the unit operator in Eqs. (A5a) and (A5b), but is H_1 in (A5c).

Equation (A6) can be rewritten, using a slightly different notation $\phi_g=|g\rangle$, etc., as

$$\sum_n\sum_{n'}(V^\dagger\phi_g,\phi_n)^*(V^\dagger\phi_g,\phi_{n'})(\phi_{n'},A\phi_n). \tag{A7}$$

If we define the projection operator P so that

$$P\psi\equiv\sum_n(\phi_n,\psi)\phi_n,$$

then (A7) is equivalent to

$$(P(V^\dagger\phi_g),AP(V^\dagger\phi_g)). \tag{A8}$$

Note that if the set $\{\phi_n\}$ is complete and orthonormal, the definition of P is independent of $\{\phi_n\}$.

Using (A8), the sums over n occurring in (A5) become

$$(\phi_g,[V_+PAPV_- - V_-PAPV_+]\phi_g), \tag{A9}$$

with A either the unit operator or H_1.

Provided that the set of ground states $|g\rangle$ is not an orbital singlet, we can show that the sums in (A5) do not go to zero; and because of the frequency factors (A5) is the dominant contribution.

We then need to evaluate (A9), taking A as the unit operator. Since $PP=P$, we obtain

$$(\phi_g,[V_+PV_- - V_-PV_+]\phi_g). \tag{A10}$$

Because we are not using the perturbed energies directly, we can absorb the spin-orbit energy into H_0, leaving H_1 only the applied and exchange fields. Then we have to deal with complete multiplets, the ground states being $|j,m\rangle$ and the excited states $|j',m'\rangle$ for $j'=j$, $j\pm1$ (in the usual angular-momentum notation).

The operators V_+ and V_- are essentially like the spherical harmonic operators $Y_{1,1}$ and $Y_{1,-1}$; thus we can write

$$[V_+V_- - V_-V_+]\sim[Y_{1,1}Y_{1,-1}-Y_{1,-1}Y_{1,1}], \tag{A11}$$

so that

$$[V_+V_- - V_-V_+]\sim Y_{1,0}. \tag{A12}$$

Since P is a scalar operator, $[V_+PV_- - V_-PV_+]$ is also equivalent to $Y_{1,0}$; and because $Y_{1,0}$ and $M_z=L_z+2S_z$ commute with J_z, (A10) becomes

$$\langle j,m|[V_+PV_- - V_-PV_+]|j,m\rangle=Cm$$
$$=C'\langle g|M_z|g\rangle.$$

Thus the contribution (A5a) is

$$\frac{\omega^2}{\omega_0^2-\omega^2}C'\sum_g\rho_g\langle g|M|g\rangle=C''\frac{\omega^2}{\omega_0^2-\omega^2}M, \tag{A13}$$

and we have the well-known result that the paramagnetic rotation is proportional to the ground-state magnetic moment.

If the ground state has zero orbital angular momentum (${}^{2S+1}S$), then the excited state for allowed electric dipole transitions must have angular momentum character ${}^{2S+1}P$, which will split into three multiplets under spin-orbit coupling. Assuming that the splittings are $\ll\omega_0$, $\omega_0-\omega$, then we can take the basis of the projection operator P as the product of spin and orbital functions; since the spin cannot change in electric dipole transitions, we can ignore the spin functions and write

$$P\psi=\sum_{m=-1}^{m=1}(\phi_{l,m},\psi)\phi_{l,m}. \tag{A14}$$

Here $\phi_{l,m}$ is an $l=1$, $m_l=m$ orbital angular momentum eigenfunction.

P so defined commutes with the time-reversal operator K, for, since the $\phi_{l,m}$ are a complete set,

$$KP\psi=(P\psi)^*=\sum_m(\phi_{l,m}{}^*,\psi^*)\phi_{l,m}{}^*$$
$$=\sum_{m'}(\phi_{l,m'},\psi^*)\phi_{l,m'}$$
$$=P\psi^*=PK\psi. \tag{A15}$$

Writing the ground-state function as $|g\rangle=|\phi,m_s\rangle$, where ϕ denotes the orbital part and m_s is the spin-projection quantum number, (A9) for contribution (A5a) becomes

$$\begin{aligned}(\phi,[V_+PV_- - V_-PV_+]\phi) &= (K[V_+PV_- - V_-PV_+]\phi,K\phi)\\ &= (\phi,[V_+PV_- - V_-PV_+]^\dagger K^\dagger K\phi)\\ &= -(\phi,[V_+PV_- - V_-PV_+]\phi). \qquad \text{(A16)}\end{aligned}$$

Thus, as a consequence of time-reversal invariance, $\langle g|[V_+PV_- - V_-PV_+]|g\rangle=0$, and the paramagnetic term in the rotation is zero. The same summation occurs in (A5b), so that the only term to consider is (A5c).

In the more general case in which the orbital singlet ground state may have originated from a cubic crystal field splitting, as an alternative to being an ionic S state, we write the ground- and excited-state functions as

$$\begin{aligned}|g\rangle &= |\phi_g,\chi_{S,m}\rangle,\\ |n\rangle &= |\phi_n,\chi_{S,m}\rangle.\end{aligned} \qquad \text{(A17)}$$

Here $\chi_{S,m}$ is a spin function for spin S and z component m.

Letting H_1 contain the low-symmetry crystal fields, the spin-orbit interaction, and the exchange field, we have

$$H_1=V_{\mathrm{cr}}+V_{LS}-g\beta H_{\mathrm{ex}}S_z. \qquad \text{(A18)}$$

The eigenfunctions of H_0+H_1 are combinations of the basic functions $|\phi_n\chi_{S,m}\rangle$, but we can take just these basic functions as basis for P, and let P operate only on the orbital part.

With $A=H_1$, (A9) becomes

$$\begin{aligned}&\langle g|[V_+PH_1PV_- - V_-PH_1PV_+]|g\rangle\\ &\quad=\langle\phi_g|[V_+PV_{\mathrm{cr}}PV_- - V_-PV_{\mathrm{cr}}PV_+]|\phi_g\rangle\\ &\qquad\qquad\qquad\times\langle S,m_s|S,m_s\rangle\\ &\quad\quad-g\beta H_{\mathrm{ex}}\langle\phi_g|[V_+PV_- - V_-PV_+]|\phi_g\rangle\\ &\qquad\qquad\qquad\times\langle S,m_s|S_z|S,m_s\rangle\\ &\quad\quad+\langle g|[V_+PV_{LS}PV_- - V_-PV_{LS}PV_+]|g\rangle. \qquad \text{(A19)}\end{aligned}$$

For the usual time-reversal reasons, the first two terms in (A19) are zero, and we see that the Faraday rotation does not depend on the effect of the exchange field on the excited states.

The third term can be evaluated using

$$V_{LS}=\sum_i(\nabla V\wedge\mathbf{p}_i)\cdot\mathbf{S}_i\left(\frac{-e}{2m^2c^2}\right)=\sum_i C_i\mathbf{L}_i\cdot\mathbf{S}, \qquad \text{(A20)}$$

where the summation is over the number of electrons and the symbols have the usual meanings. The term becomes

$$\langle\phi_g|[V_+P\sum_i C_iL_{iz}PV_- - V_-P\sum_i C_iL_{iz}PV_+]|\phi_g\rangle \times\langle S,m_s|S_z|S,m_s\rangle. \qquad \text{(A21)}$$

As L_i changes sign under time reversal, (A21) reduces to

$$2\langle\phi_g|V_+P\sum_i C_iL_iPV_-|\phi_g\rangle m_s,$$

and the rotation is proportional to the ground-state moment, but with frequency dependence $\omega_0\omega^2/(\omega_0^2-\omega^2)^2$.

However, if the orbital singlet ground state is derived from a crystal field (e.g., $^4A_2$ or $^3A_2$ for Cr^{3+} or Ni^{2+}, respectively, on octahedral sites, or $^3A_2$ and $^4A_2$ for V^{3+} and Co^{2+} on tetrahedral sites), then the contribution from (A9) with A the unit operator is not zero, for the ground state is not pure $|A_2,Sm_s\rangle$ but has some $|T_2,Sm_s\rangle$ mixed in, as is apparent when the g factor differs from 2.002.

If λ is the ground-state spin-orbit coupling parameter when this coupling is written λL_zS_z, the ground state is

$$|\phi_g,m_s\rangle=|A_2,m_s\rangle-\frac{2\lambda m_s}{\Delta}|T_2,m_s\rangle+\cdots, \qquad \text{(A22)}$$

Δ being the separation of T_2 from A_2. Then (A9) becomes (A is the unit operator)

$$\begin{aligned}&\langle A_2|[V_+PV_- - V_-PV_+]|A_2\rangle-(4\lambda m_s/\Delta)\\ &\qquad\times\langle A_2|[V_+PV_- - V_-PV_+]|T_2\rangle. \qquad \text{(A23)}\end{aligned}$$

The first term is zero, but the second is not zero. In terms of Δg, the deviation of the ground-state g factor from 2.002, (A23) is

$$-\frac{\Delta g}{2g}\frac{m}{\beta}\langle A_2|[V_+PV_- - V_-PV_+]|T_2\rangle. \qquad \text{(A24)}$$

Thus for an orbital singlet ground state there are two contributions proportional to the ground-state moment, one with frequency dependence $\omega^2/(\omega_0^2-\omega^2)$ and depending on the fraction of orbital moment mixed into the ground state, and the other going as $\omega^2\omega_0/(\omega_0^2-\omega^2)^2$ and depending only on the spin-orbit coupling in the excited state. The exchange field is only effective in so far as it determines the ground-state populations.

Since Δg can easily be 0.02, the two terms can be of more or less equal importance for ions with orbital singlet ground states derived from crystal fields (e.g., Cr^{3+} in $\mathrm{CrBr_3}$); but for true S-state ions such as Fe^{3+} and Gd^{3+}, the second term should be much larger.