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Magnetic Behavior of Cobalt in Garnets. II. Magnetocrystalline Anisotropy and Ferrimagnetic Resonance of Cobalt-Doped Yttrium Iron Garnet

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Measurements on single crystals of yttrium iron garnet (YIG) doped with cobalt, some counterdoped with silicon or calcium, show that the magnetocrystalline anisotropy is dominated by octahedral Co^{2+} and tetrahedral Co^{3+}. Both are present in uncompensated material. We calculate the single-ion anisotropy of ions of the $(3d)^n$ series ($n=4$–9), incorporated into the various sites of YIG. We find qualitative agreement with experiment in the case of cobalt. A preliminary study of ferrimagnetic resonance in uncompensated cobalt-doped crystals shows that octahedral Co^{2+} does not make the large contribution to the linewidth at 0°K predicted by Haas and Callen, and indicates that either octahedral Co^{2+} or tetrahedral Co^{3+} relaxes through an excited state 130 cm^{-1} above the ground state.

I. INTRODUCTION

The single-ion model[1,2] has been widely used in the interpretation of the magnetocrystalline anisotropy of ferrites and garnets.[3–6] It is particularly appropriate when the anisotropy is dominated by a dilute impurity, as it is, for instance, in cobalt-doped yttrium iron garnet (YIG). It is, however, only rarely that we have sufficient knowledge of the energy levels of the impurity ion to make accurate predictions of its contribution to the anisotropy. In the case of YIG we are fortunate in having an isomorphous diamagnet, yttrium gallium garnet (YGaG), which crystallographically is virtually identical to YIG.[7] By using the available spectroscopic and spin-resonance data on a number of 3*d* transition-metal impurity ions in YGaG, supplemented where necessary by theoretical estimates of crystal field parameters,[8] we are able to make reasonable predictions concerning their contributions to the anisotropy when incorporated in YIG.

Our experiments concern cobalt, for which a large number of optical[9] and spin-resonance[10] data are available. The crystal chemistry of the garnets has been extensively studied.[11] It has been shown that in sintered polycrystals Co^{2+} can enter all three sites,[12–14] while Co^{3+} can enter the octahedral and tetrahedral sites.[15] Such data, obtained at high concentrations on polycrystals formed at a high temperature, must be applied with caution to flux-grown single crystals containing small concentrations of impurity. In the preceding paper,[10] hereinafter called I, we confirmed that cobalt enters both the octahedral and tetrahedral sites of YGaG, and may have the charge states Co^{2+}, Co^{3+}, and Co^{4+}, of which the last is very rare. We did not find any dodecahedral cobalt.

It is reasonable to assume that the crystal field parameters in YIG are close to those in YGaG, but this is not necessarily true of site preference and charge states. It is known[3,16] that in the YIG-YGaG system gallium tends to prefer the tetrahedral site, and iron the octahedral. Furthermore, iron can change its charge state,[17] while gallium supposedly can not. However, we do not in fact find any qualitative difference between the crystal chemistry of cobalt in YIG and in YGaG.

Previous work[13,18] on the magnetic properties of cobalt-doped YIG has been on crystals compensated with germanium, so that all the cobalt was divalent. Now that very pure YIG is available,[19] it is possible to study the behavior of uncompensated material, which contains (as we shall see) both Co^{2+} and Co^{3+}. We can also obtain calcium-compensated YIG[17] from which Co^{2+} has been eliminated. By extending our measurements to 4.2°K we can make a more critical comparison with theory than was possible at higher temperatures.

Previous measurements[18] of the ferrimagnetic resonance linewidth of cobalt-doped YIG, like the anisotropy measurements, were confused by the presence of

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the compensating impurity. Since Fe^{2+}, which is present in large quantities in crystals compensated with quadrivalent impurity,[17,19] has pronounced effects on the relaxation behavior,[20–24] it is not possible to identify the effects of cobalt unambiguously under these circumstances. We have made preliminary measurements of linewidth in uncompensated material. These indicate that a species of cobalt (either octahedral Co^{2+} or tetrahedral Co^{3+}) behaves like a rare-earth ion[25–32] and that the Haas-Callen[33] mechanism of line broadening is unimportant.

II. SINGLE-ION THEORY OF THE MAGNETIC ANISOTROPY

We will apply the single-ion theory[1,2] to the problem of calculating the contribution of a substitutional impurity ion to the anisotropy of YIG. The free energy of a magnetic ion varies as the molecular field of fixed magnitude rotates relative to the crystallographic axes, because spin-orbit coupling makes some directions of the spin preferred to others. We make the following assumptions:

(a) The energy levels in the ground cubic term of an impurity ion in YIG are the same, except for the effects of exchange, as those in YGaG, as determined in I.

(b) The exchange energy can be written in the form $g\beta \mathbf{H}\cdot\mathbf{S}$, where $\mathbf{H}$ is the exchange field. $\mathbf{H}$ is assumed to lie parallel to the direction of magnetization and its magnitude to be independent of direction. $\mathbf{S}$ operates on the true spin of the impurity ion, and g has its spin-only value of 2. This "isotropic" assumption will be discussed later.

(c) We neglect any zero-point spin deviation.[34]

(d) We assume that we can neglect interaction with states outside the lower cubic term of the impurity ion. Some calculations not making this assumption have been made by Baltzer.[35] His results agree essentially with ours.

(e) We neglect the deviations from the molecular field model which are caused by spin canting. These are discussed by one of us elsewhere[36]; it is shown that in a pure ferromagnet large corrections sometimes have to be made to the single-ion anisotropy, because spin canting causes the local molecular field to deviate from the direction of the average magnetization. In the case of an isolated impurity, the correction should be small, since the impurity is only one of the four or six neighbors of its neighboring host ions; the other neighbors, being S-state Fe^{3+} ions, show negligible spin canting.

If, when the magnetization lies along $\langle hkl\rangle$, it makes an angle θ_n with the local axis at the nth site, the total free energy per unit volume is

$$F(hkl)=r^{-1}\sum_n F(\theta_n,T), \tag{1}$$

where

$$F(\theta_n,T)=-kT\ln Z(\theta_n),$$
$$Z(\theta_n)=\sum_i e^{-E_i(\theta_n)/kT}. \tag{2}$$

Here $E_i(\theta_n)$ is the ith eigenvalue of the ion on the nth site, and r is the number of magnetically inequivalent sites. The anisotropy constants K_1 and K_2 for a cubic crystal[37] can be written[38,39]

$$K_1=4\{F(110)-F(100)\},$$
$$K_2=27\{F(111)-F(100)\}-9K_1. \tag{3}$$

The tetrahedral sites in garnet have tetragonal symmetry axes oriented along $\langle 001\rangle$-type directions, and by symmetry Eq. (1) becomes

$$F(100)=\{\tfrac{1}{3}F(0)+\tfrac{2}{3}F(90)\},$$
$$F(110)=\{\tfrac{1}{3}F(90)+\tfrac{2}{3}F(45)\}, \tag{4}$$
$$F(111)=F(54.7).$$

The octahedral sites have trigonal axes oriented along

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[39] These relations only hold strictly if the higher-order terms in Eq. (2) can be neglected. By confining our attention to symmetry directions, we avoid the problem raised by J. Kanamori and H. Minatono [J. Phys. Soc. Japan **17**, 1759 (1962)], namely, that when the magnetization is not along a symmetry direction, an external field is required to keep it there, and if this field is neglected, self-contradictory results are obtained. Along a symmetry direction, the free energy is at a turning point, and no problem arises.

$\langle 111\rangle$-type directions, and for these sites

$$\begin{aligned} F(100)&=F(54.7),\\ F(110)&=\{\tfrac{1}{2}F(35.3)+\tfrac{1}{2}F(90)\},\\ F(111)&=\{\tfrac{1}{4}F(0)+\tfrac{3}{4}F(70.6)\}. \end{aligned} \tag{5}$$

The major axis of distortion at a dodecahedral site is along $\langle 110\rangle$-type directions, and

$$\begin{aligned} F(100)&=\{\tfrac{2}{3}F(45)+\tfrac{1}{3}F(90)\},\\ F(110)&=\{\tfrac{1}{6}F(0)+\tfrac{2}{3}F(60)+\tfrac{1}{6}F(90)\},\\ F(111)&=\{\tfrac{1}{2}F(35.3)+\tfrac{1}{2}F(90)\}, \end{aligned} \tag{6}$$

when rhombic distortion is neglected.[40]

The choice of effective Hamiltonian, from which to calculate the E_i in (2), depends on the orbital degeneracy. If the ground term is nondegenerate, we can use the conventional spin Hamiltonian[41]

$$\begin{aligned} \mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}+D\{S_z^2-\tfrac{1}{3}S(S+1)\}\\ +\tfrac{1}{6}a\{S_\xi^4+S_\eta^4+S_\zeta^4-\tfrac{1}{5}S(S+1)(3S^2+3S-1)\}, \end{aligned} \tag{7}$$

where we put $g_{\parallel}=g_{\perp}=2$, and neglect the fourth-order axial term. S is the true spin in the ground term, (ξ,η,ζ) refer to local cubic axes, and the z axis lies along the local trigonal or tetragonal axis.

If the ground cubic term is orbitally degenerate, we have to use the more general effective Hamiltonian[42]

$$\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}-\Delta_t\{L_z'^2-\tfrac{1}{3}L'(L'+1)\}-\alpha\lambda\mathbf{L}'\cdot\mathbf{S}. \tag{8}$$

Here $\mathbf{L}'$ is the effective angular momentum of the cubic term ($L'=1$ in all cases of interest). The second term in (8) represents the effect of the axial crystal field, which splits the cubic term by an amount Δ_t. The third term represents the spin-orbit interaction, which we treat as isotropic.

Tetrahedral Co^{3+} is a special case, since its ground term is ^5E, which is orbitally degenerate but has $L=0$. While the full Hamiltonian is the 10×10 ^5E matrix, we find that, because of the large tetragonal splitting in the tetrahedral site, we can with sufficient accuracy use the conventional spin Hamiltonian (7) acting on an orbitally nondegenerate state with $S=2$.

The exchange energy $g\beta H$ is of order 100–500 cm^{-1} for a transition-metal impurity in YIG. Typical crystal field splittings of orbitally nondegenerate terms are of order 1–10 cm^{-1}. As a first approximation, we treat the crystal field terms in D and a as perturbations. Only the a term contributes to the anisotropy of a cubic crystal in first order, since $\sum_n(3\cos^2\theta_n-1)=0$. The contribution of a to K_1/N, where N is the number of ions per unit volume, lies between $\frac{1}{6}a$ and a for the tetrahedral site, and between $-\frac{1}{2}a$ and a for the octahedral site, depending on the orientation of the local cubic axes (ξ,η,ζ). (For YIG, the contributions are approximately $0.8a$ and $0.33a$, respectively.[3])

To obtain the contribution of D to K_1 and K_2, we must go to second- and third-order perturbation theory. The spin Hamiltonian in a coordinate system with $z\|H$ is[43]

$$\begin{aligned} \mathcal{H}'=g\beta HS_z+\tfrac{1}{2}D(3\cos^2\theta-1)\{S_z^2-\tfrac{1}{3}S(S+1)\}\\ +\tfrac{1}{4}D\sin 2\theta\,\{S_zS_++S_+S_z+S_zS_-+S_-S_z\}\\ +\tfrac{1}{4}D\sin^2\theta\,\{S_+^2+S_-^2\}, \end{aligned} \tag{9}$$

where $S_\pm=S_x\pm iS_y$. Since $D\ll g\beta H$, the off-diagonal elements of $\mathbf{H}'$ are small.

Let us consider the particular case of tetrahedral Co^{3+}, for which $S=2$, at 0°K. The energy (to third order) is

$$\begin{aligned} E(\theta)=-2g\beta H+D(3\cos^2\theta-1)-\tfrac{3}{4}(D^2/g\beta H)\\ \times(3\sin^2 2\theta+\sin^4\theta)+\tfrac{1}{8}[D^3/(g\beta H)^2]\\ \times[9\sin^2 2\theta\sin^2\theta-(3\cos^2\theta-1)\\ \times(27\sin^2 2\theta+6\sin^4\theta)]. \end{aligned} \tag{10}$$

At 0°K, $F(\theta)=NE(\theta)$, and the anisotropy constants are [from Eqs. (4) and (10)]

$$\frac{K_1}{N}=\frac{11}{2}\frac{D^2}{g\beta H}-\frac{17}{4}\frac{D^3}{(g\beta H)^2}+\text{terms of order}\left\{\frac{D^4}{(g\beta H)^3}\right\}, \tag{11}$$

$$\frac{K_2}{N}=\frac{171}{4}\frac{D^3}{(g\beta H)^2}+\text{terms of order}\left\{\frac{D^4}{(g\beta H)^3}\right\}.$$

For general site and spin, we have to lowest order

$$\begin{aligned} K_1/N&=\gamma_1S(2S-1)(8S-5)D^2/g\beta H,\\ K_2/N&=\gamma_2S(2S-1)[3(2S-1)^2+(2S-1)(2S-3)\\ &\quad-\tfrac{3}{2}(S-1)]D^3/(g\beta H)^2. \end{aligned} \tag{12}$$

For tetrahedral sites oriented along $\langle 100\rangle$-type directions, $\gamma_1=-\frac{1}{12}$ and $\gamma_2=\frac{1}{4}$; for octahedral sites oriented along $\langle 111\rangle$-type directions, $\gamma_1=1/18$ and $\gamma_2=4/9$; and for dodecahedral sites oriented along $\langle 110\rangle$-type directions, $\gamma_1=1/48$ and $\gamma_2=-13/32$ (rhombic terms being neglected).

We could, if we wished, extend this treatment to finite temperatures, as was done for the $S=\frac{5}{2}$ case by Wolf[2] and for the uniaxial case by Kanamori.[37] However, the formulas obtained are very complicated, and it is more convenient to use our perturbation formulas only to extract values of D and $g\beta H$ from the data near 0°K. We then use the computer to calculate $F(\theta,T)$ exactly. By this means we can easily include such effects as the contribution of the fourth-order term in a, and of the spin-orbit mixing of the ^5A low-lying

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[40] A rough estimate of the rhombic terms shows their effect to be negligible when the ground term is nondegenerate.

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excited state of tetrahedral Co^{3+}, and satisfy ourselves that their contributions are negligible.

In the case of an orbitally degenerate term, such as the $^4T_1$ ground term of octahedral Co^{2+}, the crystal field splittings are likely to be large compared with the exchange splitting. Slonczewski[6] showed that the anisotropy can be very large in such a case. In his calculation he assumes that $\Delta_t \gg g\beta H \gg |\alpha\lambda|$, so that he can use first-order perturbation theory. This assumption is quite unjustified, as has been pointed out by Baltzer.[35] For instance, in YGaG:Co^{2+}, $\Delta_t = 650$ cm^{-1} and $\alpha\lambda = -200$ cm^{-1}, and we expect that in YIG, $g\beta H \sim 150$ cm^{-1}. Slonczewski's theory predicts much too large an anisotropy at 0°K, as we shall see when we come to discuss the experimental data.

We have calculated the single-ion anisotropy for ions of the $(3d)^n$ configuration, $n=4$-9, at the octahedral and tetrahedral sites and for cobalt ions at the dodecahedral site of YIG. We use (8) for degenerate ground terms and (12) for nondegenerate ones. The choice of crystal field parameters is discussed in the Appendix.

The exchange parameter was arbitrarily taken as 150 cm^{-1}, which is close to the figure we find appropriate for octahedral Co^{2+} (see Sec. IV). Varying this parameter could change K_1 and K_2 by a factor of up to 2 at 0°K. The effect of varying temperature is shown for two typical cases (octahedral Co^{2+} and tetrahedral Co^3) in Figs. 2 and 3 (see Sec. IV).

The results of these calculations (for 0°K) are given in Table I. The actual numbers are not to be taken very seriously, since the parameters used are often uncertain (particularly the exchange field), as is the effect of spin canting, anisotropic exchange, and other effects neglected in the calculation. However, the signs and orders of magnitude should be correct, for ions of the d^n configuration. We note that except for S-state and Jahn-Teller ions, whose anisotropy is very small, all octahedrally coordinated ions give positive K_1, and all tetrahedral ions negative K_1. The sign of K_2/K_1 gives the sign of the axial field parameter ($-\Delta_t$ or $+D$). These relations are predicted by the perturbation expressions (12), but they hold even when the perturbation expansion is not valid. We also note that although it requires orbital degeneracy in the ground level (positive Δ_t) to give a really large anisotropy (of order 100 cm^{-1}/ion),[6] it can be quite substantial even when an orbital singlet is lowest. For instance, 10^{19} tetrahedral Co^{3+} per cc (one Co^{2+} per 2×10^3 Fe^{+}) should double the intrinsic K_1 of YIG.

We have included Fe^{2+} and Fe^{4+} in Table I, to show what anisotropy would be expected if these ions had the $(3d)^n$ configuration ($n=4$ or 6). In fact, this picture of an isolated ion with a definite configuration probably does not hold for Fe^{2+} and Fe^{4+}. The anisotropy due to these ions in YIG is very much less than indicated in the table.[44] As has been pointed out by Kanamori,[45]

TABLE I. Estimated single-ion contributions to the magnetic anisotropy of YIG at 0°K.

Configuration	Site	Cubic field[a]	Ground term	Typical ion	Anisotropy (cm^{-1}/ion) K_1	K_2	Parameters[b] (cm^{-1}) Δ_t	$\alpha\lambda$	D	a	Notes and Refs.
$(3d)^4$	Oct.	W	^5E	Mn^{3+}	−0.4	−0.1			−3.4		c
	Oct.	S	$^3T_1$	Fe^{4+}	+3	+9	−1000	−200			d
	Tet.	W	$^5T_2$	Fe^{4+}	−85	−250	+3500	+100			d
$(3d)^5$	Oct.	W	$^6A_1$	Fe^{3+}	−0.01	0				+0.019	e
	Oct.	S	$^2T_2$	Co^{4+}	+33	−125	+1000	−500			
	Tet.	W	$^6A_1$	Fe^{3+}	−0.01	0				+0.006	e
				Co^{4+}	−0.03	0				+0.015	
	Dodec.	W	$^6A_1$	Co^{4+}	−0.2	0				+0.06	
$(3d)^6$	Oct.	W	$^5T_2$	Fe^{2+}	+65	−300	+1000	−100			d
					+3	+6	−1000	−100			d
	Oct.	S	$^1A_1$	Co^{3+}	0	0					
	Tet.	W	^5E	Co^{3+}	−7	−5			−14		
	Dodec.	W	^5E	Co^{3+}	+1	−4			+11		
$(3d)^7$	Oct.	W	$^4T_1$	Co^{2+}	+27	−82	+650	−200			f
	Oct.	S	^2E	Ni^{3+}	0	0					c
	Tet.		$^4A_2$	Co^{2+}	−4	−2			−18		
	Dodec.		$^4A_2$	Co^{2+}	+0.02	−0.02			+3		
$(3d)^8$	Oct.		$^3A_2$	Ni^{2+}	+0.04	+0.01			+6		
	Tet.		$^3T_1$	Ni^{2+}	−15	+17	−2500	−400			f
$(3d)^9$	Oct.		^2E	Cu^{2+}	0	0					c
	Tet.		$^2T_2$	Cu^{2+}	−35	−110	+3500	−700			

[a] W means "weak field" (Hund's rule, maximum spin, ground term); S means "strong field" (low-spin ground term).

[b] Exchange energy $g\beta H$ is arbitrarily taken as 150 cm^{-1}, which appears to be about right for Co^{2+} and Co^{3+} (see Sec. IV). The choice of the other parameters, and their definition, is discussed in the Appendix.

[c] Small or zero anisotropy for a Jahn-Teller ion such as Mn^{3+} only applies to static conditions. The dynamic Jahn-Teller effect has pronounced effects on acoustic and microwave measurements. [See E. M. Gyorgy, R. C. LeCraw, and M. D. Sturge, J. Appl. Phys. **37**, 1303 (1966), and references therein.]

[d] It is not suggested that Fe^{2+} and Fe^{4+} actually have these configurations (see text).

[e] Reference 3.

[f] These results agree qualitatively with those of P. K. Baltzer (Ref. 35).

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[44] R. P. Hunt (unpublished) (quoted in Ref. 21). We refer here to the cubic anisotropy: Induced (uniaxial) anisotropy can be quite large (see Ref. 23).

[45] J. Kanamori, in oral discussion following Ref. 38.

in a crystal (such as YIG) containing predominantly Fe^{3+} ions in nearest-metal-neighbor positions, electron transfer to and from the Fe^{2+} ion will tend to reduce the anisotropy. (The same is true of Fe^{4+}.) Furthermore, the presence of Fe^{2+} or Fe^{4+} leads to electrical conductivity,[17,46] indicating that the extra electron is in a weakly bound semiconductorlike state whose d character might well be small.

For impurity ions, the most vulnerable of our assumptions is the second, that the exchange field is isotropic. The most general anisotropic exchange interaction between two spins can be written[47,48]

$$\mathcal{H}_{\mathrm{ex}}=\mathbf{S}_1\cdot\mathbf{J}\cdot\mathbf{S}_2+\mathbf{S}_1\mathbf{S}_1:\mathbf{j}:\mathbf{S}_2\mathbf{S}_2+\mathbf{d}\cdot\mathbf{S}_1\times\mathbf{S}_2+\text{higher terms},\quad(13)$$

where $\mathbf{J}$ and $\mathbf{j}$ are tensors of second and fourth rank, respectively, and $\mathbf{d}$ is a vector. Only the first term can be written in the molecular field from $g\beta\mathbf{H}\cdot\mathbf{S}$; all the others constitute deviations from the molecular field model. However, $\mathbf{J}$ is a second-rank tensor varying as $3\cos^2\theta-1$, and cannot contribute in first order to the anisotropy in a cubic crystal. (It is the anisotropy in $\mathbf{J}$ which is observed in YbIG by Wickersheim and White,[49] and discussed by Moriya[48] and by Levy.[50]) It follows that if we accept the molecular field model, we must also accept isotropic exchange, as far as the magnetic anisotropy of a cubic crystal is concerned.

If the ground term is nondegenerate, the contributions of the higher terms to the anisotropy are likely to be small. The $\mathbf{j}$ term in cubic symmetry is

$$j_1(\mathbf{S}_1\cdot\mathbf{S}_2)^2+j_2(S_{1x}S_{2x}S_{1y}S_{2y}+\text{cyclic permutations}),$$

which does not contribute to K_2, but makes a contribution $4j_2S_1^2S_2^2$ to K_1. While we have no means of calculating j_2, we know that in all cases where it has been measured or calculated $j_1<0.05J$,[51] which in our case is about 1 cm^{-1}. Here J is a typical value of the (nearly equal) diagonal elements of $\mathbf{J}$; in the isotropic case the $\mathbf{J}$ term in (13) reduces to $J\mathbf{S}_1\cdot\mathbf{S}_2$. The anisotropic part of $\mathbf{J}$ is of order $(\delta g/g)^2J$, where $\delta g/g$ is a measure of the orbital momentum in the ground term.[48] For a nondegenerate ground term, $\delta g/g$ is small (of order 0.1 in Co^{3+}). We might expect j_2 to be of order $(\delta g/g)^4j_1\sim10^{-4}$ cm^{-1}, contributing 10^{-2} cm^{-1}/ion to K_1/N. Second-order contributions of the axial anisotropy in $\mathbf{J}$ are of the same order.[1] Similarly, the vector[52,53] term in $\mathbf{d}$ should contribute $(\delta g/g)^3J\sim10^{-2}$ cm^{-1} to K_1/N. The contributions to K_2/N are of higher order yet. The dipole-dipole interaction only has a very small effect.[37]

If we apply the above argument to the degenerate case, for which $\delta g/g\sim1$, we find a contribution to K_1 of order $4jS_1^2S_2^2\sim10$ cm^{-1}. This is less than, but of the same order as, the single-ion contribution of Co^{2+}. The vector term is of the same order. It is clear that we cannot completely rely on the molecular field model in such a case as Co^{2+}.

In conclusion, we have gone as far as we can within the framework of the molecular field model. While the choice of parameters is sometimes doubtful, none of the assumptions we have made should seriously affect our predictions, if the basic molecular field model is correct.

III. EXPERIMENT

A. Specimens

All measurements were made on flux-grown crystals of YIG, doped with cobalt, some counter-doped with silicon or calcium. Two control specimens contained no cobalt. The crystals were prepared from materials containing less than 10 ppm of unwanted impurity.

Total concentrations of cobalt and calcium were determined by atomic absorption analysis on samples from the same batch as the experimental specimens.[54] The concentrations of silicon, and of unwanted impurity, was determined spectrographically. The concentration in the experimental specimens may differ from the batch average by as much as a factor of 2.

We have estimated the number of Co^{2+} and Co^{3+} ions in tetrahedral sites from the infrared absorption spectra of the doped crystals. Tetrahedral Co^{3+} has a characteristic absorption band centered at 8300 cm^{-1}, where pure YIG is transparent.[9] The shape and position of this band is essentially the same in YIG as it is in YGaG (although at low temperatures there is additional structure in YIG, presumably because of exchange splittings). It is reasonable to assume that the oscillator strength is also the same. In I we found the oscillator strength in YGaG to be $f=(3\pm1)\times10^{-3}$. From the strength of the absorption in YIG, we obtain the tetrahedral Co^{3+} concentrations given in Table II, accurate to about a factor of 2.

Contrary to a previous report,[9] infrared absorption due to tetrahedral Co^{2+} can be detected in cobalt-doped YIG. The absorption spectrum of a crystal containing only cobalt is shown in Fig. 1(a). The spectrum is

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[46] This is not true if Fe^{2+} ions are formed by annealing in nitrogen rather than by silicon compensation [R. C. LeCraw (unpublished)]. It would be interesting to study the anisotropy of such crystals.

[47] P. W. Anderson, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. XIV, p. 99.

[48] T. Moriya, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. I, p. 90.

[49] K. A. Wickersheim and R. L. White, Phys. Rev. Letters **8**, 483 (1961).

[50] P. M. Levy, Phys. Rev. **135**, A155 (1964); Phys. Letters **19**, 8 (1965).

[51] D. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, Phys. Rev. Letters **11**, 10 (1963); E. A. Harris and J. Owen, *ibid.* **11**, 9 (1963); N. L. Huang and R. L. Orbach, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 3.

[52] T. Moriya, Phys. Rev. **120**, 91 (1960).

[53] I. Dzyaloshinsky, J. Phys. Chem. Solids **4**, 241 (1958).

[54] We are grateful to T. Kometani for carrying out these analyses.

TABLE II. Specimen analysis (in units of 10^{19} ions per cc).

Specimen No.	Atomic absorption analysis[a] Co	Si	Ca	Optical absorption (cm^{-1}) Tetrahedral Co^{3+} $\alpha_{1.3}$[b]	N	Tetrahedral Co^{2+} $\alpha_{1.6}$[c]	N
4006	3			27	4.5	1.2	0.3
4986	20			67	11	1.7	0.5
5112	2		12	9[d]	1.5	<0.2	<0.05
7955	8		33	20[d]	3	<0.3	<0.1
6624	3	20		<1[e]	<0.2	2.2	0.7
5084		12					
4977			16				

[a] Atomic absorption analysis was carried out on a randomly chosen sample from the same batch of crystals as the specimen. The concentration may vary from sample to sample in the same batch by a factor of up to 2.

[b] Peak absorption (in cm^{-1}) at 77°K in the $^5E \rightarrow {}^5T_2$ band of tetrahedral Co^{3+}. The bandwidth at this temperature is 2000 cm^{-1}. To obtain the number of Co^{3+} ions, we assume the oscillator strength $f = 3\times10^{-3}$, as it is in YGaG (see I).

[c] Peak absorption at 77°K in the 1.6-μ sharp-line precursor of the $^3A_2 \rightarrow {}^3T_1$ band of tetrahedral Co^{2+}. The linewidth is 80 cm^{-1}; background absorption from Co^{3+} is subtracted out. We assume the oscillator strength for this line is 3×10^{-5}, as it is in YGaG. The number of tetrahedral Co^{2+} ions per cc thus obtained is only expected to be accurate within a factor of 2.

[d] These figures are subject to ±50% errors because of the difficulty of subtracting out the Fe^{4+} background.

[e] After allowing for Co^{2+} absorption in this region.

similar to that of Co^{2+} in YGaG, although most of the $^4A_2 \rightarrow {}^4T_1$ band is obscured by the strong Co^{3+} absorption. The principal differences are a general shift to longer wavelength, and some extra structure (probably exchange splitting).

The infrared absorption of a crystal counterdoped with silicon is shown in Fig. 1(b). As might be expected, the Co^{2+} absorption is stronger. It is also somewhat different; in fact, we find small but consistent differences between the spectra of compensated and uncompensated YIG. This is presumably evidence that local charge compensation by Si^{4+} occurs in YIG to a greater extent than in YGaG,[9,10] where both the optical- and spin-resonance spectra indicate that most of the Co^{2+} ions are at axial sites with no sign of local charge compensation.

A rough estimate of the oscillator strength of these transitions from the data[55] on various crystals containing tetrahedral Co^{2+} gives $f = 3\times10^{-5}$ (within a factor of 2) for the $^4A_2 \rightarrow {}^4T_1$ line at 1.6 μ, which is allowed in T_d symmetry.

Our conclusions concerning the concentrations of cobalt, and of tetrahedral Co^{2+} and Co^{3+}, are summarized in Table II. While the infrared data and atomic-absorption-analysis data refer to different samples from the same batch, and cannot be precisely compared, it does look as if the concentrations determined by infrared absorption are somewhat high. It may be that oscillator strengths are consistently higher in YIG than in YGaG.

We have no means of determining directly the concentration of cobalt in the octahedral site. However, it is known[11–13] that in YIG, as in most garnets, Co^{2+} prefers the octahedral to the tetrahedral site. In polycrystalline YIG, doped with 2% or more cobalt and compensated with Si or Ge, 20% of the Co^{2+} is tetrahedral (the rest is octahedral).[13] In I we confirmed

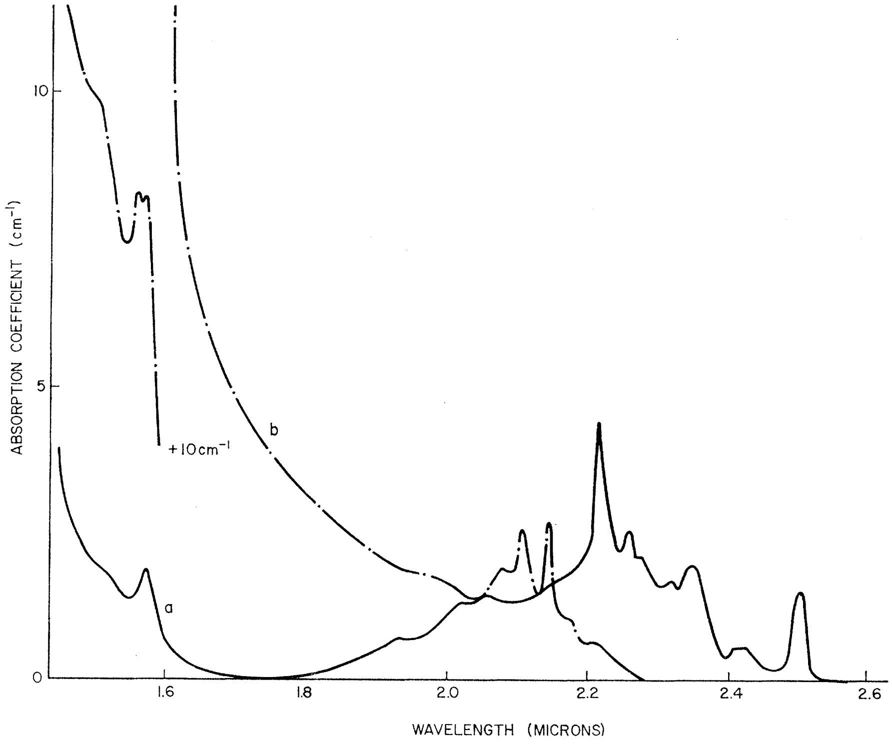

FIG. 1. Absorption spectrum of tetrahedral Co^{2+} in YIG (a) in an uncompensated crystal (No. 4986), (b) in a crystal counterdoped with Si^{4+} (No. 6624). The steep rise to shorter wavelengths is due to Fe^{2+}.

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[55] R. Pappalardo, D. L. Wood, and R. C. Linares, Jr., J. Chem. Phys. 35, 2041 (1961).

this result qualitatively for lower Co concentrations in single-crystal YGaG. Thus our uncompensated crystals presumably contain 10^{18}–10^{19} octahedral Co^{2+} per cc. This is borne out by the anisotropy data, as we shall see.

We see from the data in Table II that adding Ca^{2+} eliminates tetrahedral Co^{2+}, while adding Si^{4+} eliminates tetrahedral Co^{3+}, as might be expected; it is reasonable to suppose that the octahedral ions behave similarly.

B. Static Anisotropy Measurements

We measured the magnetocrystalline anisotropy of oriented spheres, roughly 1 mm in diam, with a recording torque magnetometer.[56] We made measurements at room temperature, 77, and 4.2°K. The torque curves in the (001) and (111) planes were accurately sinusoidal. The results for K_1 and K_2 are given in Table III. Measurements of the fields for resonance of freely suspended samples at 15 kMc/sec agree with the static data.

The anisotropy of pure YIG has been accurately measured[57] and we subtract it from all our data to obtain the figures for the effect of impurity given on the right of Table III. The figures for K_1 are accurate to ±500 erg/cc, and for K_2 to $\pm 10^4$ erg/cc.

IV. DISCUSSION OF ANISOTROPY DATA

A. Magnetic Anisotropy Due to Co^{2+}

There is more silicon than cobalt in crystal 6624 (see Table II), and we can safely assume that all the cobalt is divalent. Besides Co^{2+}, Fe^{2+} will be present because of the excess silicon.[17] The Fe^{2+} only affects the anisotropy slightly, as can be seen from the data on crystal 5084, which contains silicon but no cobalt.[58] The probable reasons why the contribution of Fe^{2+} is so small have already been discussed. Some of the cobalt ions will be in tetrahedral sites and a few may be in dodecahedral sites,[11,12] but their contribution per ion is small (see Table II) and we neglect it. We will assume that the concentration of octahedral Co^{2+} is the chemically determined cobalt concentration less the optically determined tetrahedral Co^{2+} concentration. Because the former could not be measured on the same crystal, there may be an error of a factor of up to 2. We obtain the anisotropy constants, reduced to cm^{-1}/ion, shown in Fig. 2. Also shown are the data of Okada *et al.*,[18] obtained by ferrimagnetic resonance, which agree well with ours, considering the uncertainty in relative concentration.

TABLE III. Magnetocrystalline anisotropy constants of cobalt-doped YIG.

Specimen No.	Dopants	T (°K)	K_1 (meas.) (10^4 erg/cc)	K_1 (corr.)[a] (10^4 erg/cc)	K_2 (10^4 erg/cc)
4006	Co	4	−2.80	−0.35	−15
		77	−2.80	−0.55	−10
		300	−1.08	−0.5	−0
4986	Co	4	−4.00	−1.55	−27
		77	−4.30	−2.05	−20
		300	−1.70	−1.1	
5112	Co, Ca	4	−3.20	−0.75	−0
		77	−2.70	−0.45	−0
		300	−0.75	−0.17	
7955	Co, Ca	4	−3.77	−1.32	−2
		77	−3.50	−1.25	−2
		300	−0.78	−0.2	
6624	Co, Si	4	+11.0	+13.5	−46
		77	+7.2	+9.4	−29
		300	−0.13	+0.44	
5084	Si	4	−1.86	+0.6	
		77	−3.4	−1.15	
		300	−0.57	<0.05	
4977	Ca	4	−2.45	<0.05	
		77	−2.32	−0.07	

[a] $K_1(\text{corr.}) = K_1(\text{meas.}) - K_1(\text{pure})$, where $K_1(\text{pure})$ is the anisotropy constant of pure YIG (see Ref. 57).

Slonczewski's[6] formulas reduce at 0°K to

$$K_1/N = \sqrt{3}(2-\sqrt{2})|\alpha\lambda| \approx +|\alpha\lambda|\,,$$

$$K_2/N = (6\sqrt{6}-3\sqrt{3}-27/2)\alpha\lambda \approx -4|\alpha\lambda|\,.$$

Substituting $\alpha\lambda$ from I, we find from these formulas that $K_1/N \approx 200\ cm^{-1}$ and $K_2/N \approx -800\ cm^{-1}$. These have the correct sign but are an order of magnitude too big. While his theory fails completely at 0°K, it can (as pointed out by Okada *et al.*[18]) give a reasonable account of the temperature variation of anisotropy between 100 and 300°K, if $\alpha\lambda$ is treated as an adjustable parameter. Such a fit (for $|\alpha\lambda| = 100\ cm^{-1}$) is shown (dotted line) in Figs. 2 and 3. Previous work has mostly been in this temperature range, which probably accounts for the success of Slonczewski's formulas.

With the more accurate treatment of Sec. II we can obtain good agreement with K_1/N and K_2/N at 0°K. We treat the exchange energy $g\beta H$ as an adjustable parameter. We get the best fit for $g\beta H$ in the range 150–200 cm^{-1}. If we assume nearest-neighbor interactions only, the fitted value of $g\beta H$, 175 cm^{-1}, implies a Co^{2+}-Fe^{3+} exchange parameter J of 12 cm^{-1}. This is to be compared with 27 cm^{-1} for the Fe^{3+}-Fe^{3+} exchange.[59] Such a reduction is quite reasonable; for instance, the nearest-neighbor Co^{2+}-Co^{2+} exchange in CoO is only 5 cm^{-1}.[60]

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[56] G. T. Craft, F. J. Donahoe, and W. F. Love, Rev. Sci. Instr. **26**, 360 (1955).

[57] E. M. Gyorgy (unpublished). These data agree essentially with those of Ref. 4.

[58] Our data on this crystal do not agree, even as to sign, with the microwave results of Judy (Ref. 22). The discrepancy is due to relaxation effects (Refs. 21 and 24). Even if the contribution per silicon atom were as large as Judy finds, the error involved in neglecting it would only be about 20%.

[59] E. E. Anderson, Phys. Rev. **134**, A1581 (1964).

[60] J. Kanamori, Progr. Theoret. Phys. (Kyoto) **17**, 177 (1957); **17**, 197 (1957).

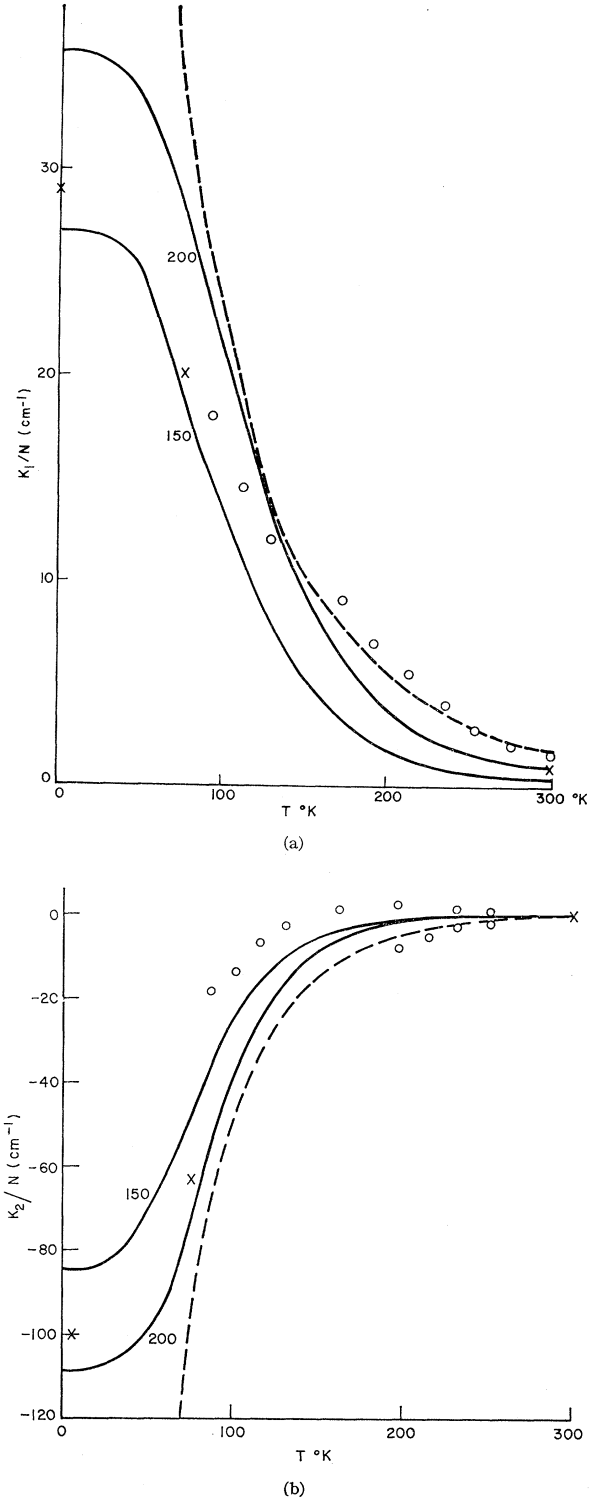

FIG. 2. Anisotropy constants per ion of YIG doped with octahedral Co^{2+}: (a) K_1/N; (b) K_2/N. ○, Okada *et al.* (Ref. 18). Results for two different dopings are shown in (b). ✕, present work. ———, theory of Sec. II; the parameter is the exchange splitting $g\beta H$. - - -, Slonczewski's theory (Ref. 6), with $|\alpha\lambda| = 100$ cm^{-1}.

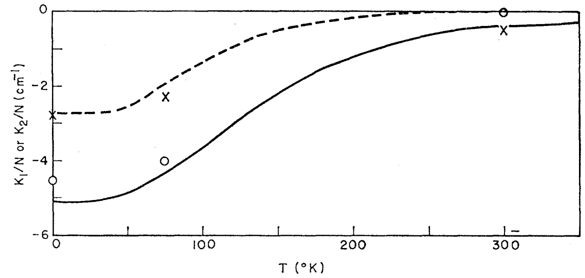

FIG. 3. Anisotropy constants of YIG doped with tetrahedral Co^{3+}. ✕, K_1; ○, K_2; ———, K_1(calc); - - -, K_2(calc). $D = -14$ cm^{-1}, $g\beta H = 200$ cm^{-1}.

At temperatures above 77°K, the calculated anisotropy constants fall below the observed ones. This may indicate that the molecular field model, which seems to work well at low temperatures, is failing as we approach the Curie point.

B. Magnetic Anisotropy Due to Tetrahedral Co^{3+}

We measured the anisotropy of two crystals doped with cobalt and calcium and of a control sample containing 1.6×10^{20} Ca^{2+} ions per cc and no cobalt. According to Nassau,[61] the control crystal should contain 5×10^{19} Fe^{4+} ions per cc. K_1 for this crystal differs from that of pure YIG by less than 500 erg/cc at 4.2°K, implying $K_1/N < 0.05$ cm^{-1}/Fe^{4+} ion. This result confirms that of Hunt,[44] shows that the Fe^{4+} contribution can be neglected. Octahedral Co^{3+} does not contribute to the anisotropy. In YGaG, Co^{4+} is only present in small amounts, and we will see that the same must be true in YIG. One would not expect much dodecahedral Co^{3+}, since Co^{3+} is much smaller than Y^{3+}.[15] Then all the anisotropy of YIG:Co, Ca must be attributed to tetrahedral Co^{3+}, and we obtain the anisotropy constants per ion given in the first two rows of Table IV.

TABLE IV. Contribution of tetrahedral Co^{3+} to the anisotropy of YIG.

Specimen No.	Concentration (10^{19} cm^{-3}) Oct. Co^{2+a}	Tet. Co^{3+b}	K_1/N^c [cm^{-1}/(Co^{3+} ion)] 4°K	77°K	300°K	K_2/N^c [cm^{-1}/(Co^{3+} ion)] 4°K	77°K
5112	d	1.5	−2.5	−1.5	−0.6		
7955	d	3	−2.2	−2.1	−0.3	−3	−3
4006	0.5	4.5	−3.5	−3.1	−0.55	−5.5	−4.5
4986	0.8	11	−2.9	−2.7	−0.57	−4.5	−4
Mean			−2.8	−2.3	−0.50	−4.5	−4
Estimated standard error^e			±0.2	±0.3	±0.05	±0.6	±0.4

[a] Determined from the anisotropy data (see text).
[b] See Table II.
[c] After correction for octahedral Co^{2+}.
[d] Assumed to be zero in calcium-compensated crystal.
[e] Excluding systematic errors in Co^{3+} concentration.

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[61] K. Nassau, Intern. J. Crystal Growth **2**, 215 (1968).

We now turn to the uncompensated samples, which contain both octahedral Co^{2+} and tetrahedral Co^{3+}. These ions have opposite signs for K_1 but the same signs for K_2 (see Table I), so that the apparent value of K_2/K_1 can be anomalously large when both ions are present and make roughly equal contributions. (While Co^{4+} could account for the data on the uncompensated samples, it would not account for the increase of K_1/K_2 with calcium compensation.)

In a particular crystal, let the concentration of Co^{3+}, relative to that in the calcium-compensated crystal 7955, be α, and the concentration of Co^{2+}, relative to that in the silicon-compensated 6624, be β. Then, assuming that only octahedral Co^{2+} and tetrahedral Co^{3+} contribute, we have, for the anisotropy constants at 4.2°K,

$$K_1 = 13.5\beta - 1.32\alpha,$$
$$K_2 = -46\beta - 2.0\alpha. \tag{14}$$

Solving for α and β, we can deduce the separate contributions of Co^{2+} and Co^{3+} at any temperature. We obtain the Co^{2+} concentrations, and Co^{3+} anisotropy constants, given in Table IV. Consistent Co^{2+} concentrations are obtained from the anisotropy at 4 and 77°K and from the optical data (see Sec. III). The anisotropy constants per Co^{3+} ion agree within experimental accuracy: The limit on the accuracy of the data in calcium-compensated crystals is the difficulty of measuring the Co^{3+} absorption in the presence of the intense Fe^{4+} background.[19] The consistency of these data shows that our assumptions are correct. It is, of course, no proof that the absolute values are correct, since there could be a systematic error in the determination of the Co^{3+} concentration.

While the signs of K_1 and K_2 agree with the predictions of the single-ion theory, it is not possible to fit their absolute magnitudes. We have seen that in YGaG, $D \sim -14$ cm^{-1}, and the temperature variation of Co^{3+} anisotropy in YIG suggests that $g\beta H \sim 200$ cm^{-1}. The experimental anisotropy constants are compared with those calculated from these parameters in Fig. 3. While $|K_1|$ is overestimated at low temperatures, $|K_2|$ is underestimated. Clearly this discrepancy is not due to an error in the tetrahedral Co^{3+} concentration, since this would affect K_1 and K_2 equally. Increasing D will improve the agreement with experiment (if we assume the concentration to have been overestimated) but the ratio K_2/K_1 is too large to be accounted for by any reasonable combination of parameters.

V. FERRIMAGNETIC RESONANCE LINEWIDTH IN COBALT-DOPED YIG

We studied the ferrimagnetic resonance of some of our uncompensated samples as a function of temperature at 13 and 17.5 kMc/sec. The spheres were free to orient themselves along the easy axis for magnetization, which is ⟨111⟩ in the present case. The variation with temperature of ferrimagnetic resonance linewidth in uncompensated YIG:Co is shown in Fig. 4. Below 77°K it can be fitted accurately by the empirical formula

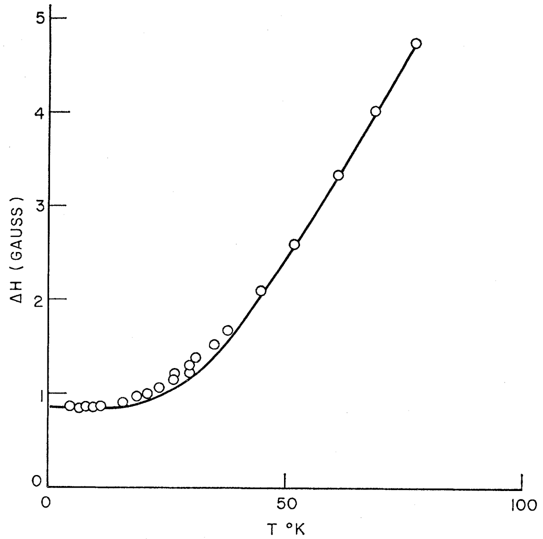

FIG. 4. Ferrimagnetic resonance linewidth of uncompensated YIG: Co (batch No. 4986) at 15 kMc/sec. The full line is Eq. (15). Above 150°K the linewidth is roughly constant, at 9–10 G in this sample.

$$\Delta H = A + BT^{-1}e^{-\theta/T}, \tag{15}$$

where $k\theta = 130 \pm 7$ cm^{-1}, and A and B depend on the sample. The constant term A is 0.85 G in the best-polished crystal, and is present in pure YIG. We attribute it to surface scattering,[62] the contribution of the cobalt at 0°K being (at the very most) 0.1 G. B is proportional to frequency and increases with cobalt concentration.

The exponential dependence of linewidth on $1/T$ and the proportionality to frequency is reminiscent of the effect of rare earths,[25–32] particularly Eu.[28] However, the linewidth reaches a plateau, rather than a peak, in the region 150–300°K. The linewidths in rare-earth garnets have generally been interpreted in terms of the longitudinal ("slow") relaxation theory. This theory has a long history[63] and has been applied to the rare-earth problem by a number of authors.[26–31] Other mechanisms giving the same general dependence on temperature and frequency exist.[32,64] However, the simplest interpretation of our data is that our crystals contain a species of cobalt with a number of excited states, the lowest 130 cm^{-1} above the ground state, through which longitudinal relaxation occurs.

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[62] R. C. LeCraw, E. G. Spencer, and C. S. Porter, Phys. Rev. **110**, 1311 (1958).

[63] J. K. Galt, Bell System Tech. J. **33**, 1023 (1954); A. M. Clogston, *ibid.* **34**, 739 (1955); J. K. Galt and E. G. Spencer, Phys. Rev. **127**, 1572 (1962).

[64] N. Kumar and K. P. Sinha, J. Appl. Phys. **39**, 1073 (1968).

The first excited state of octahedral Co^{2+} is at 160 cm^{-1} when the magnetization is along $\langle 111 \rangle$ and $g\beta H = 150$ cm^{-1}. While agreement with the observed activation energy is not very good, it is not out of range, considering the uncertainty in the parameters.

For Co^{3+}, if our estimate of $g\beta H$ is correct, the first excited state should be near 200 cm^{-1}, but since the fit of the theory to the anisotropy data is so poor, we can not rely on this figure. From the calculated angular dependence of the excited-state energy, we can estimate the pre-exponential factor from the formula of Van Vleck and Orbach[31]; one finds that the contribution of an octahedral Co^{2+} ion is about 10 times that of a tetrahedral Co^{3+} ion. Either species, in the concentration present (see Table IV), could give a linewidth of the observed order of magnitude. More work, on many different crystals, is needed to determine which species is responsible.

We have measured the linewidth of crystal 6624, which contains cobalt and excess silicon (see Table II). We find that the linewidth is roughly 15 G from 300 to 77°K. This is consistent with the results of Odaka *et al.*,[18] and with our own on uncompensated crystals when the contribution of Fe^{2+} is taken into account.[20] At 4°K reproducible resonance results cannot be obtained because of induced anisotropy effects.[21–24] We have therefore been unable to check our low-temperature data on a compensated crystal, and to confirm that the behavior shown in Fig. 4 is characteristic of Co^{2+} rather than Co^{3+}.

Since the optical and anisotropy data show that octahedral Co^{2+} is present in uncompensated crystals, the fact that the intrinsic linewidth of these crystals vanishes at 4.2°K shows that octahedral Co^{2+} does not make a temperature-independent contribution to the linewidth. This result is contrary to the prediction of Haas and Callen,[33] that scattering of magnons by the Co^{2+} ion should contribute strongly to the linewidth. They give, for the linewidth per Co^{2+} ion,

$$\frac{\Delta H}{N} \approx 1.5\times10^{-24}\left(\frac{\alpha\lambda}{g\beta}\right)^2\left(\frac{4\pi M}{H_{\rm ex}}\right)^3, \tag{16}$$

independent of temperature. Taking the value for $\alpha\lambda$ found in I, $4\pi M = 2500$ G, $H_{\rm ex} = 1.5\times10^6$ G, one finds that for $N = 10^{19}$ Co^{2+}/cc, $\Delta H \approx 7$ G. However, this estimate may be much too high. Haas and Callen use Slonczewski's model[6] for the ground term of Co^{2+}. This model gives much too large an anisotropy in the present case (see Sec. IV A). It is reasonable to suppose that it will also give too large a linewidth. A plausible way to estimate the contribution of the Haas-Callen mechanism is to substitute into (16) an effective value of $\alpha\lambda$ obtained by fitting Slonczewski's theory to the observed anisotropy at 4°K. Fitting to K_1/N gives $(\alpha\lambda)_{\rm eff} = 28$ cm^{-1}; fitting to K_2/N would give a still lower figure. Substituting into (16) now gives 0.07 G, consistent with the observed linewidth at 4°K, after correction for surface scattering, of less than 0.1 G. We conclude that our data are not necessarily inconsistent with the Haas-Callen's mechanism, though they do not, of course, offer it any support.

VI. CONCLUSIONS

We have found that tetrahedral Co^{3+}, which is an ion without orbital momentum in the ground state, can contribute quite substantially to the magnetic anisotropy of cobalt-doped YIG. We have shown that the single-ion theory can account qualitatively for the anisotropy of YIG containing tetrahedral Co^{3+} and octahedral Co^{2+}, but that quantitatively there are some discrepancies.

We have found that Co^{2+} is present in uncompensated cobalt-doped single-crystal YIG. Octahedral Co^{2+} does not, as has been predicted, produce a large temperature-independent linewidth in ferromagnetic resonance. There is a species of cobalt which looks like a rare earth in its effect on the linewidth.

ACKNOWLEDGMENTS

We wish to thank Professor J. H. Van Vleck and Dr. D. L. Wood for helpful discussions, Dr. P. K. Baltzer and Dr. Wood for communicating their unpublished work, and R. Blair, K. A. Ingersoll, and E. M. Kelly for technical assistance.

APPENDIX: CHOICE OF CRYSTAL FIELD PARAMETERS IN TABLE I

We have tried to use all the available spectroscopic, magnetic, and theoretical information available to arrive at reasonable values for the crystal field splittings. Discussion of each configuration follows. Except where otherwise stated, we take $v = -1000$ cm^{-1}, $\mu = 1200$ cm^{-1}, $\delta = -3500$ cm^{-1} (see I) and ζ to be 80% of its free-ion value. (The parameters are defined at the end of this Appendix.)

$(3d)^4$: (*a*) *Octahedral* Mn^{3+} (*weak-field* ^5E *ground term*). The orbital degeneracy of ^5E is not removed by the trigonal field, and in consequence this ion is subject to the Jahn-Teller effect. We assume (in accord with experimental evidence[65]) that there is a tetragonal distortion (elongation[66]) along $\langle 100 \rangle$-type directions, quenching the trigonal splitting. The energy level scheme is like that of tetrahedral Co^{3+}, and D is given by Eq. (17) of I. Since D is independent of the magnitude of the Jahn-Teller splitting, we can reasonably

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[65] D. B. Fraser, E. M. Gyorgy, R. C. LeCraw, J. P. Remeika, F. J. Schnettler, and L. G. Van Uitert, J. Appl. Phys. **36**, 1016 (1965); E. M. Gyorgy, R. C. LeCraw, and M. D. Sturge, *ibid.* **37**, 1303 (1966).

[66] See, for instance, the discussion of M. D. Sturge, in *Advances in Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York, 1967), Vol. XX, p. 120.

use the value of D for Mn^{3+} in rutile.[67] The small anisotropy calculated (and observed) is not inconsistent with the very pronounced dynamic effects of Mn^{3+} in YIG.[65]

$(3d)^4$: (*b*) *Octahedral* Fe^{4+} (*strong-field* $^3T_1$ *ground term*). If Fe^{4+} had the $(3d)^4$ configuration, which it probably does not (see text), it would presumably be in the strong-crystal-field, low-spin state, just as Co^{4+} is (see I). If the ground term has the pure $t_2{}^4$ configuration, then $\Delta_t = v$ and $\alpha\lambda = -\frac{1}{2}\zeta$.[68] (Coulomb mixing with the $t_2{}^3e$ configuration only has a 20% effect.) In the free ion $\zeta \approx 500$ cm^{-1}.[69]

$(3d)^4$: (*c*) *Tetrahedral* Fe^{4+} (*weak-field* $^5T_2$ *ground term*). There is no Coulomb mixing, and $\Delta_t = \delta$ and $\alpha\lambda = -\frac{1}{4}\zeta$.[68]

$(3d)^5$: (*a*) *Tetrahedral and dodecahedral* Co^{4+} ($^6A_1$ *ground term*). The cubic parameter a is calculated from Geschwind's[3] value for Fe^{3+} with the aid of Watanabe's[70] formula $a \propto \zeta^4\Delta^2$, for constant interelectronic repulsion. We take Δ the same for tetrahedral Co^{4+} as for tetrahedral Fe^{3+}, and doubled for dodecahedral Co^{4+}; $\zeta = 500$ cm^{-1} for Co^{4+} and 400 cm^{-1} for Fe^{3+}. We assume that the local cubic axes for dodecahedral Co^{4+} are the same as for Gd^{3+}.[71] We neglect the fourth-order axial term, which only contributes 25% in Fe^{3+}.[3]

$(3d)^6$: (*a*) *Octahedral* Fe^{2+} (*weak-field* $^5T_2$ *ground term*). There is no configuration mixing and $\Delta_t = v$. The sign of v in the octahedral site is uncertain, and we give the results for both signs of v. Neither is consistent with experiment,[44] which is not surprising (see text).

$(3d)^6$: (*b*) *Octahedral* Co^{3+}. We expect Co^{3+} to have the strong-field $^1A_1$ ground term in YIG (see I). It could, in principle, have the weak-field $^5T_2$ ground term, and would then behave in the way predicted for Fe^{2+}. There is no sign of this in the data.

$(3d)^6$: (*c*) *Dodecahedral* Co^{3+} (*weak-field* ^5E *ground term*). We use Eq. (17) of I (with the sign reversed, since ^5A rather than ^5B is now the ground level), and put $\lambda = -110$ cm^{-1}, $E(^5B) = E(^5E) = \Delta = 14\,000$ cm^{-1}, and $E(^3T_1) = 6000$ cm^{-1}.

$(3d)^7$: (*a*) *Octahedral* Ni^{3+} (*strong-field* ^2E *ground term*). We expect Jahn-Teller distortion to quench the trigonal splitting. The ground level is then a Kramer's doublet and cannot contribute to the anisotropy.

$(3d)^7$: (*b*) *Dodecahedral* Co^{2+} ($^4A_2$ *ground term*). We use Eq. (12) of I, with the tetragonal splitting of $^4T_2$ calculated from Eq. (14) of I, using Pappalardo's[8] point-charge values for the single-electron tetragonal splitting parameters μ and δ.

$(3d)^8$: (*a*) *Octahedral* Ni^{2+} ($^3A_2$ *ground term*). We assume Δ and ζ to be the same as for Ni^{2+} in MgO, and use Macfarlane's formula[72] $D = 10^{-3}(1.5v - 4.2v')$. We take the values of v and v' estimated for Co^{2+} (see I).

$(3d)^8$: (*b*) *Tetrahedral* Ni^{2+} ($^3T_1$ *ground term*). The cubic field is extremely weak and the ground term is derived almost entirely from the ^3F term of the free ion. Neglecting ^3P mixing, we have

$$\Delta_t(^3T_1) = -3\delta/5 + 3\mu/20$$

and

$$\alpha\lambda = -\tfrac{3}{4}\zeta.$$

Our results agree qualitatively with those of Baltzer.[35]

$(3d)^9$: (*a*) *Octahedral* Cu^{2+} (^2E *ground term*). Cu^{2+} should behave just like Ni^{3+}.

$(3d)^9$: (*b*) *Tetrahedral* Cu^{2+} ($^2T_2$ *ground term*). $\Delta_t = \delta$, if there is no Jahn-Teller distortion.

Definitions of Parameters

D: Axial field parameter in an orbitally nondegenerate term [see Eq. (7)].

v, v': One-electron trigonal field parameters[73]:

$$v = -3\langle t_2+ | V_{\text{trig}} | t_2+ \rangle, \quad v' = \langle t_2+ | V_{\text{trig}} | e+ \rangle.$$

$\alpha\lambda$: Spin-orbit coupling parameter in an orbitally degenerate term [see Eq. (8)].

Δ: Cubic field splitting.

Δ_t: Axial field splitting of an orbital triplet [see Eq. (8)].

δ, μ: One-electron tetragonal field parameters:

$$\delta = 3\langle t_2(yz) | V_{\text{tetrag}} | t_2(yz) \rangle,$$
$$\mu = -2\langle e(3z^2 - r^2) | V_{\text{tetrag}} | e(3z^2 - r^2) \rangle.$$

ζ: One-electron spin-orbit coupling parameter:

$$\zeta = -3\langle t_2+, +\tfrac{1}{2} | V_{\text{so}} | t_2+, +\tfrac{1}{2} \rangle.$$

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