PHYSICAL REVIEW VOLUME 180, NUMBER 2 10 APRIL 1969

Magnetic Behavior of Cobalt in Garnets. I. Spin Resonance in Cobalt-Doped Yttrium Gallium Garnet

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(Received 17 September 1968)

We have studied the spin resonance at 24 and 56 kMc/sec of cobalt in single crystals of yttrium gallium garnet (YGaG). We find resonances associated with four different combinations of site and charge state. Tetrahedral Co^{2+} has the $^4A_2$ ground term with the tetragonal splitting parameter $2D=-36$ cm^{-1}. Octahedral Co^{2+} has the $^4T_1$ ground term with the trigonal splitting $\Delta_t=+650$ cm^{-1}. It is seen in otherwise pure YGaG, as well as in crystals counterdoped with Si^{4+}. Tetrahedral Co^{3+} has the ^5E ground term, with $D\sim 14$ cm^{-1}, $|a|=0.66$ cm^{-1}. This value of a, the fourth-order cubic field-splitting parameter, is exceptionally large and makes possible strong magnetic-dipole transitions between states with $S_z=\pm 2$. Electric-dipole transitions are also observed between these states. Octahedral Co^{4+} has the strong-field $^2T_2$ ground term, with $\Delta_t=+1000$ cm^{-1}; its spectrum is very weak relative to Co^{3+}, even in crystals counterdoped with Ca^{2+}. The absence of a resonance from octahedral Co^{3+} implies that this ion has the strong-field $^1A_1$ ground term. Cobalt does not appear to enter the dodecahedral site in our crystals. Our results are complementary to, and on the whole consistent with, the optical data of Wood and Remeika. We review the information available on crystal fields at the octahedral and tetrahedral sites in garnet, and on the hyperfine structure of cobalt.

I. INTRODUCTION

It has long been known that cobalt can enter the garnet lattice in three different sites and two or three different charge states.[1–8] In the ferrimagnet yttrium iron garnet (YIG) each combination of site and ionic charge ("species") has its own characteristic effect on the magnetic behavior,[2,4] particularly on the magnetocrystalline anisotropy. The anisotropy is discussed in the following paper,[9] hereinafter referred to as II. In order to understand the energy levels of each species in YIG, we have studied the spin resonance of cobalt-doped single crystals of yttrium gallium garnet (YGaG), which is close to YIG crystallographically.[10,11] Cobalt replaces gallium and in an otherwise pure crystal is predominantly trivalent. By counterdoping with silicon[2,4,6,12–17] (quadrivalent) or calcium[6,14–17] (divalent) one can produce other charge states of cobalt. We have identified the spin-resonance spectra of octahedral Co^{2+} and Co^{4+}, and tetrahedral Co^{2+} and Co^{3+}, and confirmed that octahedral Co^{3+} has the strong-field (low-spin) diamagnetic ground term. The results on octahedral Co^{2+} have been briefly reported before by ourselves and other workers.[18,19] We are unable to identify any spectra of dodechedral cobalt. We find that, whereas it is easy to drive the cobalt divalent, and to eliminate Co^{3+}, by addition of silicon,[1–8] only a very small fraction of the cobalt goes quadrivalent on the addition of calcium.

The optical spectra of cobalt-doped single-crystal garnets have been studied by Wood and Remeika.[8] By combining the microwave and optical data we are able to build up a consistent picture of the crystal fields at the octahedral and tetrahedral sites. In II we will apply our knowledge of crystal fields and energy levels in YGaG to the problem of understanding the magnetocrystalline anisotropy of cobalt-doped YIG.

II. EXPERIMENTAL

The spin-resonance measurements were made at 24 kMc/sec and 56 kMc/sec in superheterodyne spectrometers similar to those previously described.[20,21] Except in some measurements intended to identify electric-dipole transitions, the crystal was on the axis of a cylindrical cavity operating in the TE_{011} or TE_{012}

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[1] S. Geller, C. E. Miller, and R. G. Treuting, Acta Cryst. **13**, 179 (1960).

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[9] M. D. Sturge, E. M. Gyorgy, R. C. LeCraw, and J. P. Remeika, following paper, Phys. Rev. **180**, 413 (1969) (referred to as II).

[10] S. Geller and M. A. Gilleo, J. Phys. Chem. Solids **3**, 30 (1957); **9**, 235 (1959).

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[14] J. Verweel and B. J. M. Roovers, in *Solid State Physics in Electronics and Telecommunications, Brussels, 1958*, edited by M. Désirant and J. L. Michiels (Academic Press Inc., New York, 1960), Vol. III, p. 475.

[15] J. Verweel, Proc. Inst. Elec. Engrs. (London) **109B**, Suppl. 21, 95 (1962).

[16] D. I. Tchernev, J. Appl. Phys. **37**, 1318 (1967).

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[18] J. R. Chamberlain and R. W. Cooper, Proc. Phys. Soc. (London) **87**, 967 (1966).

[19] M. D. Sturge, F. R. Merritt, and J. P. Remeika, Appl. Phys. Letters **9**, 63 (1966).

[20] G. Feher, Bell System Tech. J. **36**, 449 (1957).

[21] S. Geschwind, Phys. Rev. **121**, 363 (1961).

mode. The rf **H** field in this arrangement is vertical, perpendicular to the static magnetic field. The **E** field is small and toroidal. The power in the cavity was monitored by a piece of phosphorus-doped silicon, which also provides a g marker.

The crystals were grown from a flux of PbO and B_2O_3 and had well-developed growth faces. Impurity concentrations were found spectrographically. Unintentional impurities were less than 10 ppm.

III. OCTAHEDRAL Co^{2+}

In uncompensated YGaG:Co there is a weak eight-line spectrum, quite sharp at 4°K, with principal axes along $\langle 111\rangle$ type directions. In a crystal counterdoped with silicon this is the dominant spectrum. It can be fitted with the usual spin Hamiltonian for effective spin $S=\frac{1}{2}$, nuclear spin $I=\frac{7}{2}$:

$$\mathcal{H}=g_{\parallel}\beta H_zS_z+g_{\perp}\beta(H_xS_x+H_yS_y)+AS_zI_z+B(S_xI_x+S_yI_y). \quad (1)$$

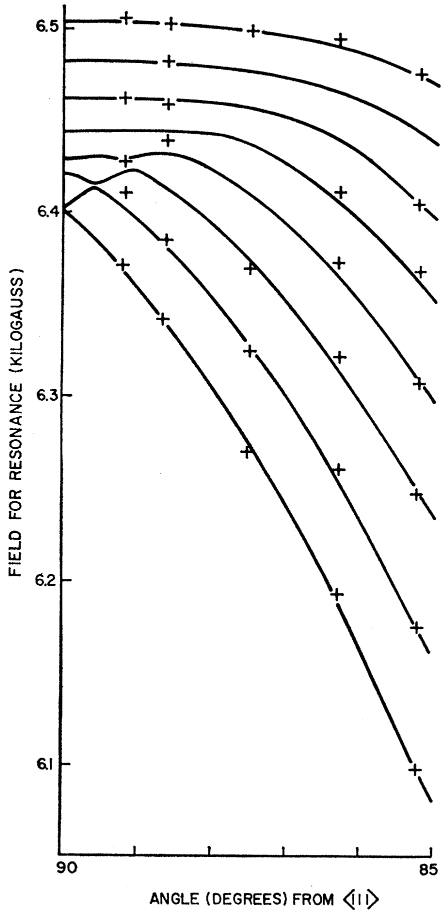

FIG. 1. Computer fit to the spin-resonance spectrum of Co^{2+} near $\theta=90°$. The parameters are given in the text. The crosses show the positions of points of inflection in the derivative spectra and indicate the estimated error.

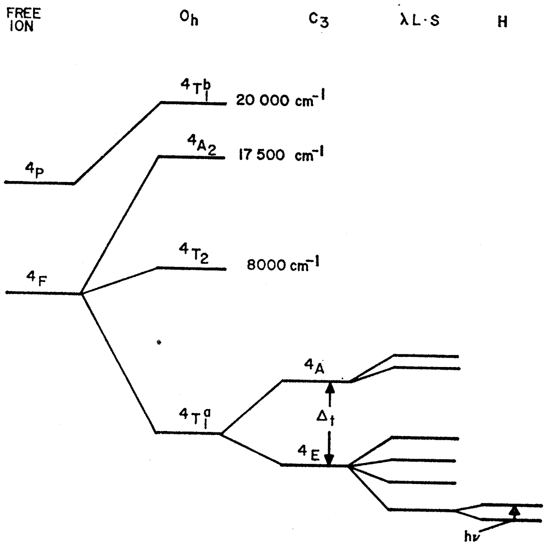

FIG. 2. Energy levels of the Co^{2+} ion in the octahedral site of garnet under successive deviations from spherical symmetry (not to scale). Only the quartet levels are shown. The positions of the cubic terms are taken from the data on Co^{2+} in MgO [R. Pappalardo, D. L. Wood, and R. C. Linares, J. Chem. Phys. **35**, 2041 (1961)] and are only approximate. The trigonal splitting Δ_t is found to be about 700 cm^{-1}; the spin-orbit splitting of ^4E is of order $\alpha\lambda\sim 200$ cm^{-1} (see text).

The parameters are

$$g_{\parallel}=7.027\pm0.002, \quad 10^4|A|=307.5\pm2\ \text{cm}^{-1},$$
$$g_{\perp}=2.665\pm0.002, \quad 10^4|B|=15\pm3\ \text{cm}^{-1}.$$

(These parameters differ slightly from those previously reported.[19]) Accurate determination of B from the data is difficult because it is so small that the second-order effects of A dominate the first-order effects of B. The complicated perpendicular spectrum which arises under this circumstance has been remarked on before,[22] but only qualitatively analyzed. The results of a computer fit to the spectrum near the $\langle 110\rangle$ direction are shown in Fig. 1.

The theory of Abragam and Pryce[23] enables us to interpret the empirical parameters of the spin Hamiltonian in terms of the spin-orbit and axial-field splittings of the $^4T_1$ ground term of Co^{2+}. The general arrangement of the quartet terms of Co^{2+} in a trigonally distorted octahedral site is shown in Fig. 2. The ground term $^4T_1{}^a$ is derived from both ^{4}F and ^{4}P parents [or, to put it in the strong-field formalism, from both $^4T_1(t_2e^2)$ and $^4T_1(t_2{}^2e)$ parents]. Matrix elements of orbital momentum and spin-orbit coupling, and hence the g factors, depend on the extent of this mixing.

The behavior of the ground term in zero magnetic field can be described by the following effective

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[23] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A206**, 173 (1951).

Hamiltonian[23]:

$$\mathcal{H}=\Delta_t(1-L_z'^2)-\alpha\lambda L_z'S_z-\alpha'\lambda(S_xL_x'+S_yL_y'). \quad (2)$$

Here L' is the effective orbital-momentum operator within ${}^4T_1$, which behaves formally like a ^{4}P term, and $S=\frac{3}{2}$. Δ_t is the trigonal splitting, and $\lambda=-\frac{1}{3}\zeta$, where ζ is the (positive) one-electron spin-orbit coupling parameter.

The parameters α and α' depend on the amount of P-F mixing: they are 1.5 for a pure F state and 1.0 in the strong-field limit (pure t_2e^2 configuration). While α and α' can in principle differ in an axial site, we find that for reasonable values of the trigonal field the difference is only 0.2%, which we will neglect.

Abragam and Pryce find that for negative $\alpha\lambda$, the lowest eigenstate of (2) has the following first-order spin and orbital contributions to the g factors (we put $\alpha=\alpha'$):

$$\begin{aligned} g_{S\parallel}&=2N^{-2}[1+18x^{-2}-4(x+2)^{-2}],\\ g_{S\perp}&=4N^{-2}[1+3x^{-1}(x+2)^{-1}],\\ g_{L\parallel}&=2\alpha N^{-2}[6x^{-2}-8(x+2)^{-2}],\\ g_{L\perp}&=8\alpha N^{-2}(x+2)^{-1}, \end{aligned} \quad (3)$$

where $N^2=1+6x^{-2}+8(x+2)^{-2}$ and x is the real positive root of

$$\tfrac{1}{2}(x+3)-[3x^{-1}+4(x+2)^{-1}]=\Delta_t/\alpha\lambda. \quad (4)$$

There are small second-order contributions to the g factors, which we call $g_\parallel^{(2)}$ and $g_\perp^{(2)}$. These arise from spin-orbit and trigonal field mixing of the ${}^4T_2$ and ${}^4A_2$ terms into the ground term; formulas for them are given by Abragam and Pryce. It is sufficiently accurate to calculate them on the assumption that the crystal-field splittings of Co^{2+} in garnet are the same as in MgO.[24,25] We find $g_\parallel^{(2)}=+0.075$, $g_\perp^{(2)}=+0.034$.

Substituting the experimental g factors into

$$\begin{aligned} g_\parallel&=g_{S\parallel}+g_{L\parallel}+g_\parallel^{(2)},\\ g_\perp&=g_{S\perp}+g_{L\parallel}+g_\perp^{(2)}, \end{aligned} \quad (5)$$

we find that we get the best fit with $x=0.82\pm0.01$, $\alpha=1.41\pm0.01$.

This value of α agrees almost exactly with that calculated on the assumption that the crystal-field splittings are the same as in MgO.[25] This agreement is somewhat surprising, since, as pointed out by Ray,[26] the calculation neglects covalency (except insofar as λ is treated as an adjustable parameter). One would expect covalency to reduce α below its theoretical value. It may be that there are cancelling errors; it is not certain that third-order corrections to the g factors are really negligible.

Substituting our value of x into (4), we find that $\Delta_t/\alpha\lambda=-3.17$. While we have no independent measure of λ in the solid, we know that typically in transition-metal ions it is between 70 and 90% of its free-ion value (178 cm^{-1} [27]). Taking $\alpha=1.41$, $\lambda=-145\pm15$ cm^{-1}, we find that $\Delta_t=650\pm80$ cm^{-1}.

This is the splitting of the ${}^4T_1{}^a$ ground term; the positive sign implies that the orbital doublet is lowest. This fact is of great importance in understanding the magnetic behavior of Co^{2+} in YIG, as we shall see in II. In this paper we would like to interpret this splitting in terms of the single-electron matrix elements of the trigonal field, v and v'.[28] The relative contributions of these depend on the mixing. According to Pappalardo, Wood, and Linares,[24] the ground term in MgO is

$$|{}^4T_1{}^a\rangle=-0.267|{}^4T_1t_2{}^4e^3\rangle+0.964|{}^4T_1t_2{}^5e^2\rangle. \quad (6)$$

If we assume this is the correct wave function in garnet, we have for the reduced matrix element

$$\begin{aligned} \langle{}^4T_1{}^a\|V_{\text{trig}}\|{}^4T_1{}^a\rangle=0.07&\langle{}^4T_1t_2{}^4e^3\|V_{\text{trig}}\|{}^4T_1t_2{}^4e^3\rangle\\ &+0.93\langle{}^4T_1t_2{}^5e^2\|V_{\text{trig}}\|{}^4T_1t_2{}^5e^2\rangle\\ &-0.515\langle{}^4T_1t_2{}^4e^3\|V_{\text{trig}}\|{}^4T_1t_2{}^5e^2\rangle, \end{aligned} \quad (7)$$

whence the splitting is[28]

$$\Delta_t=-0.97v-1.1v'. \quad (8)$$

Without more optical data we cannot determine v and v' independently. However, we can make a guess at them as follows: It has been found in other systems[29] that v' for an impurity ion is not particularly sensitive to which particular ion is involved, but depends primarily on the host lattice. It is known[30] that v' is about -1300 cm^{-1} for Cr^{3+} in the octahedral site of YGaG. This figure agrees with the result of a point-charge calculation,[31] using free-ion wave functions.[32] If we assume that v' for Co^{2+} lies between -1000 cm^{-1} and -2000 cm^{-1}, we find that

$$v\approx-1.1v'-\Delta_t=+1000\pm600\ \text{cm}^{-1}.$$

This is of the same order of magnitude as v for Cr^{3+} (Ref. 30) Ru^{3+} (Ref. 33) and (as we shall see) Co^{4+} in this site, but of the opposite sign. The positive sign is

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

[25] B. Bleaney and W. Hayes, Proc. Phys. Soc. (London) **B70**, 626 (1957); W. Low, Phys. Rev. **109**, 256 (1958).

[26] D. K. Ray, Fiz. Tverd. Tela 3, 2223 (1961) [English transl.: Soviet Phys.—Solid State 3, 1613 (1962)].

[27] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, 1961), p. 437.

[28] These one-electron trigonal field parameters are defined by M. H. L. Pryce and W. A. Runciman [Discussions Faraday Soc. **26**, 34 (1958)] as $v=-3\langle t_2\pm|V_{\text{trig}}|t_2\pm\rangle$, $v'=\langle t_2\pm|V_{\text{trig}}|e\pm\rangle$. See the original reference for the definitions of the trigonal basis functions $|t_2\pm\rangle$ and $|e\pm\rangle$. Reduced matrix elements [such as those in Eq. (7)] of V_{trig} among many-electron states can be expressed in terms of v and v' by standard methods [see, for instance, J. S. Griffith, *The Irreducible Tensor Method for Molecular Symmetry Groups* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962)].

[29] E. Feher and M. D. Sturge, Phys. Rev. **172**, 244 (1968).

[30] R. M. Macfarlane, Bull. Am. Phys. Soc. **11**, 243 (1966); (private communication).

[31] R. Pappalardo, Nuovo Cimento **26**, 748 (1962).

[32] R. E. Watson, MIT Solid State and Mol. Theory Group Tech. Rept. No. 12, 1959 (unpublished).

[33] I. A. Miller and E. L. Offenbacher, Phys. Rev. **166**, 269 (1968).

predicted by the point-charge model.[31] Large variations in v from ion to ion in the same site are common,[29] perhaps because of local ionic rearrangements to accommodate the impurity; but a change in sign is unusual.

We turn now to the hyperfine structure (hfs). Abragam and Pryce[23] give for the hyperfine constants

$$\begin{aligned} A &= Pg_{L\parallel} - \tfrac{1}{2}P_K g_{S\parallel} + A_{\mathrm{sd}}, \\ B &= Pg_{L\perp} - \tfrac{1}{2}P_K g_{S\perp} + B_{\mathrm{sd}}, \end{aligned} \tag{9}$$

where $P = 2\gamma\beta\beta_N\langle r^{-3}\rangle$, P_K is the core polarization term, and the g factors are defined in Eq. (3). A_{sd} and B_{sd} represent the small contribution of the d-electron spin moment: Using Abragam and Pryce's formulas we find $A_{\mathrm{sd}} = -0.07P$, $B_{\mathrm{sd}} = +0.03P$. Equation (9) cannot be solved uniquely since we do not know the signs of A and B. According to the choice of sign, we find $P = \pm 0.025$ cm^{-1}, $P_K = \pm 0.008$ cm^{-1}, or $P = \pm 0.031$ cm^{-1}, $P_K = \pm 0.013$ cm^{-1}. Either positive set would be reasonable, but the former set agree best with the data on Co^{2+} in Al_2O_3 (Ref. 34), MgO (Ref. 25) and other crystals.[23] As in the case of the trigonal field, the exact numbers obtained are not to be taken too seriously, since we have neglected covalency in the calculation.[26]

IV. TETRAGONAL Co^{2+}

At 77°K and 56 kMc/sec we observe an axial spectrum having tetragonal ⟨001⟩-type symmetry, with $g_\parallel^{\mathrm{eff}} = 2.42 \pm 0.01$, $g_\perp^{\mathrm{eff}} = 4.38 \pm 0.02$. The spectrum disappears on cooling to 20°K (decreasing in intensity by at least a factor of 5), showing that it arises from a state more than 30 cm^{-1} above the ground state. This is just what we would expect from tetrahedral Co^{2+}, which has a $^4A_2$ ground term split by a strong tetragonal crystal field. From the optical data,[8] this splitting is 36 cm^{-1}, but the sign is not determined. Our spectrum is consistent with the following spin Hamiltonian ($S = \frac{3}{2}$):

$$\begin{aligned} \mathcal{H} = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) \\ + D[S_z^2 - \tfrac{1}{3}S(S+1)], \end{aligned} \tag{10}$$

with $g_\parallel = 2.42 \pm 0.01$, $g_\perp = 2.19 \pm 0.01$, $-2D \gtrsim 30$ cm^{-1}. Resonance is observed between the $S_z = \pm\frac{1}{2}$ states, which are highest for negative D. The ground states have $S_z = \pm\frac{3}{2}$, and transitions between them are forbidden.

While there is no doubt, from the agreement with the optical data, that the line is due to Co^{2+}, we could observe no hyperfine structure. The line is 200–300 G wide at 77°K. Tetrahedrally coordinated Co^{2+} typically has $|A| \sim |B| \sim 0.003$ cm^{-1} (Ref. 35) (30 G) so it is not surprising that the hfs is not resolved. A similar phenomenon occurs in tetrahedral Co^{3+}, and we will discuss this "accidental" cancellation of the hfs in more detail when we discuss that case.

If we neglect the small spin-spin term in the Abragam and Pryce spin Hamiltonian,[36] we have

$$g_\parallel - g_\perp = 2Dk/\lambda, \tag{11}$$

where we have included the orbital reduction factor k to take account of covalency. Substituting our g values and $2D = -36$ cm^{-1}, we find that $\lambda/k = -157$ cm^{-1}. The free-ion value would be -178 cm^{-1}, so this is a reasonable value. Thus the anisotropy of our g values is consistent with the optical value of $|2D|$, and confirms that $2D$ is negative. As remarked by Wood and Remeika,[8] the ground-state splitting $2D$ is remarkably large. To a good approximation it should be given by[37,38]

$$2D = -8\lambda^2[1/E(^4B) - 1/E(^4E)], \tag{12}$$

where $E(^4B)$ and $E(^4E)$ are the energies of the tetragonal components of $^4T_2$ (see Fig. 3). Wood and Remeika found a group of absorption lines (the "S lines") at 4600 cm^{-1}, which they assigned to the $^4A_2 \rightarrow {}^4T_2$ transition of tetrahedral Co^{2+}. The major splitting of this group is 220 cm^{-1}, and this was tentatively assigned to the tetragonal splitting $|E(^4B) - E(^4E)|$. Substituting in (12) we find that $|2D| < 2.5$ cm^{-1}, since $|\lambda| < 178$ cm^{-1}. Subsequent work by Wood[39] has shown that this assignment is incorrect. He extended the room-temperature absorption measurements of Ref. 8 to the lattice cutoff of garnet at about 1500 cm^{-1}. He finds two weak absorption lines at 1795 and 1850 cm^{-1}. The integrated intensity of these is about 1/30 of the S lines. Now in S_4 symmetry $B \rightarrow B$ is electric-dipole forbidden except insofar as spin-orbit

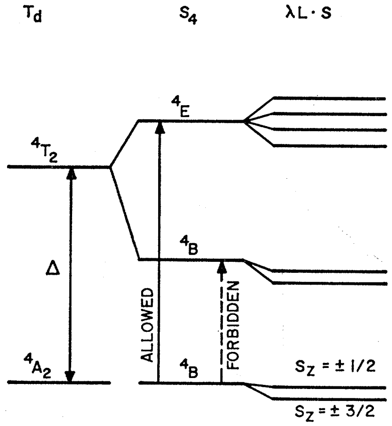

FIG. 3. Lowest-energy levels of Co^{2+} in the tetrahedral site of garnet. The allowed $^4B \rightarrow {}^4E$ transition is at about 4600 cm^{-1}, the "forbidden" $^4B \rightarrow {}^4B$ transition at 1800 cm^{-1}. Resonance is observed between the $S_z = \pm\frac{1}{2}$ states, 36 cm^{-1} above the ground state. Transitions between the $S_z = \pm\frac{3}{2}$ ground states are forbidden.

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[34] G. M. Zverev and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. **39**, 57 (1960) [English transl.: Soviet Phys.—JETP **12**, 41 (1961)].

[35] T. Estle and M. DeWit, Bull. Am. Phys. Soc. **6**, 445 (1961).

[36] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

[37] R. M. Macfarlane, J. Chem. Phys. **47**, 2066 (1967).

[38] J. P. Jesson, J. Chem. Phys. **48**, 161 (1968).

[39] D. L. Wood (private communication). These measurements were made on Co^{2+} in YAG (yttrium aluminum garnet); but the spectrum in YGaG should be almost identical (see Ref. 8).

coupling mixes ^4B and ^4E. It is therefore reasonable to assign the weak 1800-cm^{-1} transitions to $^4B\rightarrow{}^4B$, and the 4600-cm^{-1} transitions to $^4B\rightarrow{}^4E$. The 220-cm^{-1} splitting of ^4E could be the first-order spin-orbit splitting, or it could be vibronic.

The ground-state g factors are given to a good approximation by[36]

$$\begin{aligned} g_{\parallel}&=2-8\lambda k/E(^4B)\,,\\ g_{\perp}&=2-8\lambda k/E(^4E)\,. \end{aligned} \tag{13}$$

We can get good agreement with the observed g values by taking $\lambda k=-100$ cm^{-1} in (13), which gives $g_{\parallel}=2.44$, $g_{\perp}=2.17$. Combining with our previously obtained $\lambda/k=-157$ cm^{-1}, we find that $\lambda=125$ cm^{-1}, $k=0.8$, and $2D=-42$ cm^{-1} [from Eq. (12)], which is in good agreement with the optical value of -36 cm^{-1}.

Thus we are able to account for the ground-state splitting and g factors purely in terms of the tetragonal splitting of the $^4T_2$ term. This splitting, 2800 cm^{-1}, is remarkably large. It is given to first order by[40]

$$E(^4B)-E(^4E)=-(\tfrac{3}{4}\mu+\delta)\,, \tag{14}$$

where μ and δ are the tetragonal splittings of the one-electron e and t_2 orbitals, respectively (see Fig. 4). Second-order corrections to (14) are small. According to the point-charge model,[31] $\delta\approx-\mu=2500$ cm^{-1}, so the $^4T_2$ splitting should be roughly -600 cm^{-1}. However, Cu^{2+} on this site has $|\mu|=1200$ cm^{-1}.[41] If we take $\mu\sim-1200$ cm^{-1} (this figure is also consistent with the data for Co^{3+}, as we shall see), and substitute the experimental splitting in (14), we obtain $\delta\sim+3700$ cm^{-1}. The sign of δ is consistent with the point-charge model, and with the selection rules observed in the Cu^{2+} spectrum.[42]

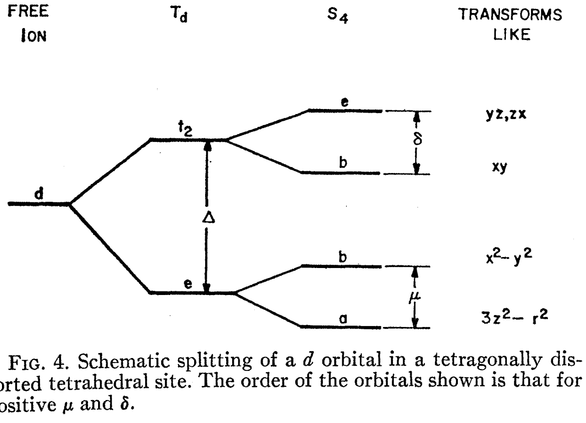

FIG. 4. Schematic splitting of a d orbital in a tetragonally distorted tetrahedral site. The order of the orbitals shown is that for positive μ and δ.

Besides the two Co^{2+} spin-resonance spectra which we have discussed, there are several other eight-line spectra in silicon-compensated crystals. These spectra have less than axial symmetry and we have not analyzed them in detail. They probably arise from octahedral Co^{2+} locally compensated by Si^{4+}. The total integrated intensity of these spectra is somewhat less than that of the regular octahedral Co^{2+} spectrum.

We looked carefully for a resonance from dodecahedral Co^{2+}. This should be like the tetrahedral-Co^{2+} spectrum, except that the $S_z=\pm\frac{1}{2}$ states should be lowest and the resonance should therefore persist to low temperatures. No sign of it was found, so we conclude that Co^{2+} does not occupy the dodecahedral site to any appreciable extent in our crystals.[43]

V. TETRAHEDRAL Co^{3+}

A typical spin-resonance spectrum of a crystal of YGaG:Co (without counterdoping) is shown in Fig. 5. The nominal Co/Ga ratio in this crystal is 0.13%. The angular dependence of the field for resonance of the strongest lines is shown in Fig. 6. For a general direction of magnetic field, there are three strong lines, but one is weak or vanishes when the microwave magnetic field H_{rf} lies in the (001) plane, and all three vanish when static field H is in the (001) plane, so that $H_{\mathrm{rf}}\parallel\langle 001\rangle$. The field for resonance can be described phenomenologically by the effective spin Hamiltonian[44]

$$\mathcal{H}_s^{\mathrm{eff}}=g_{\parallel}^{\mathrm{eff}}\beta H_z S_z^{\mathrm{eff}}+aS_x^{\mathrm{eff}} \tag{15}$$

with the z axis along a $\langle 100\rangle$-type direction. $S^{\mathrm{eff}}=\frac{1}{2}$, $g_{\parallel}^{\mathrm{eff}}=8.672\pm0.01$, $|a|=0.660\pm0.003$ cm^{-1} at 1.4°K. Any perpendicular g factor $g_{\perp}^{\mathrm{eff}}$ is less than 0.05, while the width $A(2I+1)$ of any unresolved hyperfine structure is less than 0.003 cm^{-1}. At 1.2°K and 56 kMc/sec the spin-lattice relaxation time (estimated from the power required for saturation) is about 10^{-4} sec.[45] No other strong resonance is observed up to 77°K, at which temperature the main resonance is broad but still visible.

The lowest energy levels of Co^{3+} in the tetragonally distorted tetrahedral site of garnet are shown in Fig. 7. The $^5T_2$ term is known from the optical data to be 8000 cm^{-1} above the ground state.[8] The magnitude of the tetragonal splitting μ of the ^5E ground term is not known for Co^{3+}, but we have seen that for other ions μ is in the range -1000 to -2000 cm^{-1}.

The negative sign of μ (^5B lowest) is predicted by the

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[40] C. J. Ballhausen, *Ligand Field Theory* (McGraw-Hill Book Co., New York, 1962), p. 101.

[41] R. Pappalardo, J. Mol. Spectry. **6**, 554 (1961).

[42] Positive δ means that the lowest state of Cu^{2+} in the tetrahedral site is ^2E rather than ^2B. Transitions to both ^2A and ^2B excited states are then allowed, as is observed in Ref. 41, whereas $^2B\rightarrow{}^2B$ would be forbidden. This argument neglects spin-orbit coupling, and assumes the excited-state assignments to be correct. It is therefore not conclusive.

[43] This result casts some doubt on the tentative assignment (Ref. 8) of the 14225-cm^{-1} "L_1" line to dodecahedral Co^{2+}. It could, perhaps, be a spin-forbidden transition of tetrahedral Co^{2+}.

[44] M. Tinkham, Proc. Phys. Soc. (London) **A68**, 258 (1955); Proc. Roy. Soc. (London) **A236**, 535 (1956).

[45] Under the present conditions of low concentration and strong inhomogeneous broadening, the homogeneous linewidth is determined by T_1 rather than by T_2. Consequently, the saturation parameter is proportional to T_1, rather than to $(T_1T_2)^{1/2}$. However, as pointed out in Ref. 34, cross relaxation can make the saturation method of measuring T_1 rather unreliable.

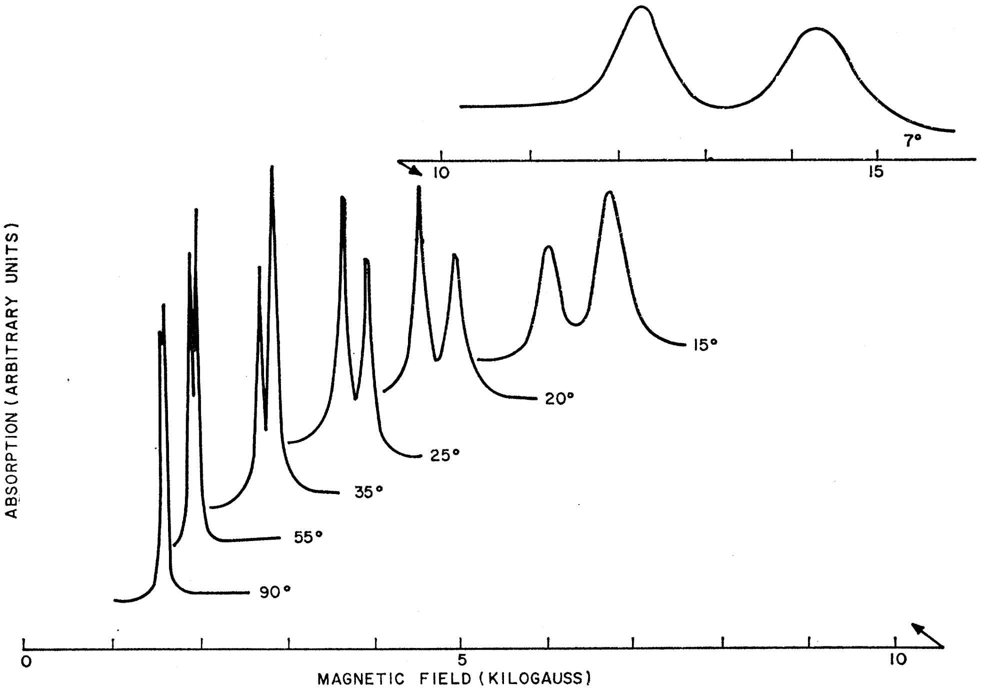

FIG. 5. Spin-resonance spectrum of Co^{3+} in YGaG at 4.2°K for various directions of magnetic field nominally in the $(1\bar{1}0)$ plane. Angles are measured from ⟨001⟩. The two lines come from sites oriented along ⟨100⟩ and ⟨010⟩ directions, and are distinct because of a 1° crystal misorientation. The resonance from ⟨001⟩ sites is forbidden, since $\mathbf{H}_{rf}$ is in the $\langle 1\bar{1}0\rangle$ direction.

point-charge model,[31] and is the only sign consistent with the persistence of the spin resonance to very low temperature (since the ${}^5A$ level would have $S_z=0$ lowest). In Ref. 8 μ was given as positive, on the grounds that strong optical transitions to both the ${}^5B$ and the ${}^5E$ components of the ${}^5T_2$ term are seen, whereas ${}^5B \rightarrow {}^5B$ would be forbidden. However, as in the case of tetrahedral Co^{2+}, the assignments in Ref. 8 could be mistaken. An alternative scheme, consistent with the spin-resonance data, would be to assign the 8300-cm^{-1}

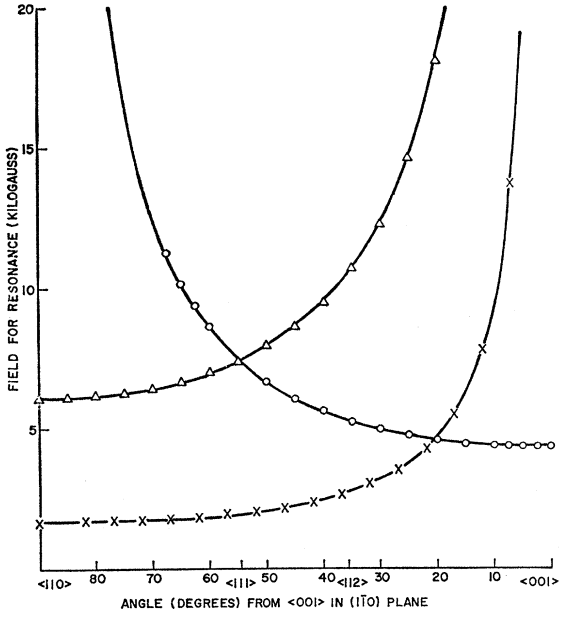

FIG 6. Field for resonance as a function of field direction in the $(1\bar{1}0)$ plane. Allowed transitions: ✕24 kMc/sec, ▲56 kMc/sec. ○, forbidden transitions (measured at 56 kMc/sec). These transitions, from ⟨001⟩ sites, are weakly allowed because, particularly at the higher frequency, the crystal extends into the region of the cavity where $\mathbf{H}_{rf}$ has a horizontal component.

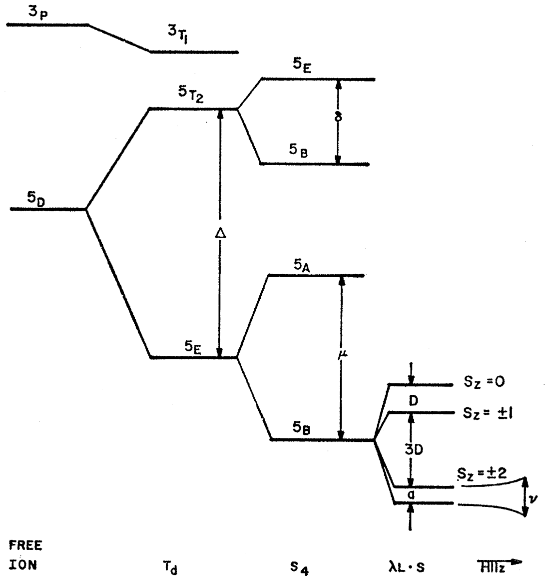

FIG. 7. Lowest-energy levels of Co^{3+} in the tetrahedral site of garnet, for $\mu<0$ and $\delta>0$ (not to scale).

band to the allowed $^5B\rightarrow{}^5E$ transition. The observed 1400-cm^{-1} splitting of this band, which is too large to be due to spin-orbit coupling, could be evidence for a Jahn-Teller effect in the degenerate excited state.[46] Alternatively, the upper component of this band, at 9200 cm^{-1}, could be assigned to the $^5B\rightarrow{}^3T_1$ transition (see Fig. 7), borrowing intensity from $^5B\rightarrow{}^5T_2$ transition by spin-orbit coupling. From the Tanabe-Sugano diagram[47] we estimate $^3T_1$ to be 9000–15 000 cm^{-1} above the ground state. It is possible that the weak "N" lines near 5200 cm^{-1}, which were unassigned in Ref. 8 but appear to be associated with Co^{3+}, arise from the forbidden $^5B\rightarrow{}^5B$ transition. This transition is made allowed by spin-orbit coupling and also be strain, which might account for some random variation in intensity relative to the 8300-cm^{-1} band. If this (very tentative) assignment is correct, $\delta=+3100$ cm^{-1}, consistent with the estimate for Co^{2+} (see Sec. IV). We will find additional evidence for a large positive value of δ in the g values (see below).

The ground level of the system ^5B is split by spin-orbit coupling into a doublet and three singlets, of which the lowest two (corresponding to $S_z=\pm2$) are nearly degenerate. The spin Hamiltonian for ^5B is[48]

$$\begin{aligned}\mathcal{H}=g_{\parallel}\beta H_zS_z+g_{\perp}\beta(H_xS_x+H_yS_y)+D[S_z^2-\tfrac{1}{3}S(S+1)]\\ +\tfrac{1}{6}a[S_x^4+S_y^4+S_z^4-\tfrac{1}{5}S(S+1)(3S^2+3S-1)]\\ +AS_zI_z+B(S_xI_x+S_yI_y)\,,\end{aligned}\tag{16}$$

where S now has its true value of 2. [We have neglected the small fourth-order axial term in (16).] Second-order perturbation expressions for the parameters are[36,49]

$$\left.\begin{aligned}&g_{\parallel}=2-8\lambda/E(^5B)\,,\quad g_{\perp}=2-2\lambda/E(^5E)\,,\\ &D=-\lambda^2[4/E(^5B)-1/E(^5E)]-4\lambda^2/E(^3T_1)\,,\\ &A=P(1/7+g_{\parallel}-2)-P\kappa\,,\\ &B=P(-1/14+g_{\perp}-2)-P\kappa\,.\end{aligned}\right.\tag{17a}$$

Here $E(\Gamma)$ is the energy of the excited state Γ above the ^5B ground state. We have neglected the tetragonal splitting of $^3T_1$. The fourth-order expression for the cubic field parameter is

$$a=-4D^2/\mu+\text{terms of order }\lambda^4/\Delta^3\,.\tag{17b}$$

P and κ are defined in Sec. III.

For this (negative) sign of D the $S_z=\pm2$ states are lowest. When $D\gg g\beta H$ they are isolated and can be described by the effective Hamiltonian (15) with $g_{\parallel}^{\text{eff}}=4g_{\parallel}$, $g_{\perp}^{\text{eff}}=0$, a unchanged. If the tetragonal splitting μ had the other sign (^5A lowest in Fig. 7), D would be positive, the $S_z=0$ state would be lowest, and no spin resonance would be seen at low temperature. This is the situation expected for Co^{3+} in the dodecahedral site. Thus the absence of a resonance does not imply that there is no dodecahedral Co^{3+} present. However, it is unlikely that so small an ion as Co^{3+} should substitute for Y^{3+}.[6,7]

If we substitute $g_{\parallel}=\frac{1}{4}(8.67)=2.168$ and $E(^5B)=8000$ cm^{-1} (from Ref. 8) into (17a), we find that $\lambda=-168$ cm^{-1}. This is too high; in the free Co^{3+} ion $\lambda\approx-150$ cm^{-1}.[50] On the other hand, if we accept the value of 5200 cm^{-1} for $E(^5B)$, we find that $\lambda=-110$ cm^{-1}. This is a very reasonable value, 73% of the free-ion value, as compared with 70% for tetrahedral Co^{2+}.

Taking this value of λ, we can get a rough idea of the other parameters. Substituting $E(^5E)=8300$, $E(^5B)=5200$, $E(^3T_1)=9200$ cm^{-1} in (17a), we find that $D=-14$ cm^{-1}. $|D|$ is rather less than we might have expected from the fact that the resonance is still visible at 77°K, since Orbach relaxation[51] should broaden the resonance beyond detection when $kT\sim|4D|$ (the separation of the $S_z=0$ state from the ground state).

If the terms of order λ^4/Δ^3 and higher in the expression for a [Eq. (17b)] can be neglected, we have $\mu=-4D^2/|a|\approx-1200$ cm^{-1}. This is consistent with the estimates for Cu^{2+} and Co^{2+} (see Sec. III), but only the sign and order of magnitude can be relied on.

The spin-resonance transition is very strong, as can be seen from Fig. 5, and shows a remarkable angular dependence of intensity. This can be accounted for in terms of a combination of magnetic-dipole transitions (made allowed by the cubic field mixing) and electric-dipole transitions, allowed because the site is not centrosymmetric (see Sec. VI).

Hyperfine structure is not observed because of an accidental cancellation between the (spin and orbital) dipolar contribution to A, $P(1/7+g_{\parallel}-2)$, and the core-polarization contribution $-P\kappa$. We can estimate $P\kappa$ from the data[35] on ZnO:Co^{2+}; Geschwind[52] has found empirically that for a given complex (in this case CoO$_4$) $P\kappa$ is independent of the charge state of the central ion to within a few percent. Substituting $|P\kappa|=0.010$ cm^{-1} in the formula for A, and using the experimental fact that $|A|<4\times10^{-4}$ cm^{-1}, we find that $|P|=0.034$

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[46] H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce, and H. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1958). For a discussion of the conditions under which the Jahn-Teller effect will split an optical absorption band, see M. D. Sturge, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York, 1967), Vol. XX, p. 91 (especially Sec. 23).

[47] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 753 (1954); **9**, 766 (1954).

[48] B. Bleaney and R. S. Trenam, Proc. Roy. Soc. (London) **A223**, 1 (1954).

[49] H. J. Gerritsen and E. B. Sabisky, Phys. Rev. **132**, 1507 (1963).

[50] The spin-orbit coupling parameters for the free Co^{3+} and Co^{4+} ions have not been determined experimentally. We arrived at the figure given in the text by interpolating between the known values for Co^{2+} and Co^{5+} [C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (U. S.) Circ. No. 467 (Government Printing Office, Washington, D. C., 1949), Vol. II, p. 89] with the aid of the calculations of J. Thorhallson, C. Fisk, and S. Fraga [J. Chem. Phys. **48**, 2925 (1968)].

[51] C. P. B. Finn, R. Orbach, and W. P. Wolf, Proc. Phys. Soc. (London) **77**, 261 (1961); R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

[52] S. Geschwind, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967), p. 265.

± 0.002 cm^{-1}, a thoroughly reasonable value (in ZnO:Co^{2+}, $|P|=0.036$ cm^{-1}) (Ref. 35).

We conclude that in the tetrahedral S_4 site of YGaG, Co^{3+} has the ^5B ground level described by the spin Hamiltonian (16). Since octahedral Co^{3+} is certainly present[6–8] the absence of any spin resonance attributable to it probably implies that its ground term is the strong-field $^1A_1(t_2{}^6)$ term, which is diamagnetic. This last conclusion is consistent with what is known about Co^{3+} in octahedral oxygen coordination. In Al$_2$O$_3$ [53] and Co$_3$O$_4$, in the octahedral site of spinels and in simple perovskites,[54,55] the ground term of Co^{3+} is the "strong-field" diamagnetic $^1A_1$ term. Only in exceptional cases, such as complex perovskites containing Sb^{5+} or Nb^{5+}, is the "weak-field" $^5T_2$ term lowest.[54]

VI. INTENSITIES IN THE Co^{3+} SPIN-RESONANCE SPECTRUM

The transition observed in the spin-resonance spectrum of Co^{3+} has $\Delta S_z=4$, and the mechanisms by which such a transition is observed are of some interest.

A. Magnetic-Dipole Transitions

Magnetic-dipole (MD) transitions are allowed because the cubic term involving $\frac{1}{6}a[S_x{}^4+\cdots]$ in (16) mixes the $S_z=\pm 2$ states. In a field H, at an angle θ on the z axis, the wave functions are

$$\begin{aligned}|+\rangle&=\cos\varphi\,|+2\rangle+\sin\varphi\,|-2\rangle\,,\\ |-\rangle&=-\sin\varphi\,|+2\rangle+\cos\varphi\,|-2\rangle\,,\end{aligned}\qquad(18)$$

where

$$\tan 2\varphi=a/4g_{\parallel}\beta H\cos\theta\,.$$

While S_+ and S_- have no matrix elements connecting these states, S_z has the matrix element

$$\langle +|S_z|-\rangle=2\sin 2\varphi=2a[a^2+(4g_{\parallel}\beta H\cos\theta)^2]^{-1/2}.\qquad(19)$$

Thus, contrary to the usual situation in spin resonance, it is the component of H_{rf} (the microwave-frequency magnetic field) parallel to the z axis which induces transitions. This selection rule is accurately obeyed in the Co^{3+} spectrum; when H_{rf} is in the (001) plane, no transitions are observed from the site whose z axis is along $\langle 001\rangle$. At 56 kMc/sec the specimen extends into the region where H_{rf} deviates from its nominal direction; this is why weak transitions are observed from the $\langle 001\rangle$ site at this frequency (see Fig. 6).

The condition for resonance is

$$(h\nu)^2=a^2+(4g_{\parallel}\beta H\cos\theta)^2\,,$$

whence

$$|\langle +|S_z|-\rangle|^2=(2a/h\nu)^2\,.\qquad(20)$$

Thus the transition probability should decrease with increasing microwave frequency and should be independent of field direction. The former is found to be true experimentally (near $\theta=0°$), but the latter is not, as can be seen immediately from Fig. 5.

We have considered the possibility that the Co^{3+} ion is at the dodecahedral site, where the rhombic field would mix the $S_z=0$ state into the $S_z=\pm 2$ states and permit $S_\pm$ to have matrix elements in second order. We could find no choice of rhombic- and axial-field parameters which would at the same time account for the angular dependence of intensity and give the observed zero-field splitting and the vanishingly small $g_\perp$.[56] So far as we can see, there is no MD mechanism consistent with the observed field for resonance which can give an appreciable variation of intensity with angle.

B. Electric-Dipole Transition—Theory

Since the tetrahedral site occupied by the Co^{3+} ion is not centrosymmetric, electric-dipole (ED) transitions within the d^n configuration are possible.[57] ED transitions have been observed in the spin resonance of tetrahedrally coordinated transition metal ions by Ludwig and Ham,[58] and in rare-earth ions by Williams[59] and Culvahouse *et al.*[60] Here we will discuss the selection rules and estimate the expected intensity of $\Delta S_z=4$ ED transitions.

The $|^5B,S_z=\pm 2\rangle$ states of Co^{3+} both transform as Γ_1 of S_4.[61] The ED operator $e\mathbf{r}$ transforms as $\Gamma_2(z)$, $\Gamma_3(x-iy)$, $\Gamma_4(x+iy)$, so that no ED transitions are possible when the dc magnetic field **H** is parallel to the z axis. When **H** has a perpendicular component, it mixes the $|+2\rangle$ state with the $|+1\rangle$ state (which transforms as Γ_4) and transitions become possible. We will find that the transition matrix element is proportional to the mixing, which varies as $H\sin\theta$; since at resonance H varies as $\sec\theta$, the ED intensity should vary as $\tan^2\theta$.

The predominant odd-parity component of the crystal field at the tetrahedral site is the third-order term which transforms as $Y_3{}^2-Y_3{}^{-2}$ (i.e., as xyz). This term is present in T_d symmetry (of which S_4 is a subgroup).[62] As far as the ED matrix elements are concerned, the symmetry can be regarded as being T_d. The ED transition probability is proportional to

$$|\langle +|e\mathbf{r}|-\rangle|^2=\sin^2 2\varphi\;|\langle\alpha|e\mathbf{r}|\beta\rangle|^2,\qquad(21)$$

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[53] D. S. McClure, J. Chem. Phys. 36, 2757 (1961).

[54] G. Blasse, J. Inorg. Nucl. Chem. 27, 748 (1965); J. Appl. Phys. 36, 879 (1965).

[55] C. S. Naiman, R. Gilmore, B. DiBartolo, A. Linz, and R. Santoro, J. Appl. Phys. 36, 1044 (1965).

[56] We are grateful to R. A. Faulkner for the use of his very fast computer subroutine for diagonalizing complex matrices, which materially reduced the time required for this search.

[57] N. Bloembergen, Science 133, 1363 (1961).

[58] G. W. Ludwig and F. S. Ham, Phys. Rev. Letters 8, 210 (1962).

[59] F. I. B. Williams, Proc. Phys. Soc. (London) 91, 111 (1967).

[60] J. W. Culvahouse, D. P. Schinke, and D. L. Foster, Phys. Rev. Letters 18, 117 (1967).

[61] We use Bethe notation to distinguish combined spin-orbital states from orbital states, which are in Mulliken notation.

[62] Distortion to S_4 only introduces fifth-order terms of the form $Y_5{}^2\pm Y_5{}^{-2}$ [J. L. Prather, Natl. Bur. Std. (U. S.) Monograph 19 (1961), Table 5].

where $|\pm\rangle$ are defined in (18) and $|\alpha\rangle$ and $|\beta\rangle$ are the zero-field wave functions:

$$|\alpha\rangle=2^{-1/2}\{|{}^5B,+2\rangle+|{}^5B,-2\rangle\},$$
$$|\beta\rangle=2^{-1/2}\{|{}^5B,+2\rangle-|{}^5B,-2\rangle\}.$$

In $T_d|\alpha\rangle$ transforms as $|\Gamma_3 v\rangle$ (i.e., as x^2-y^2), while $|\beta\rangle$ transforms as $|\Gamma_5\zeta\rangle$ (i.e., as xy). Thus

$$\langle\alpha|e\mathbf{r}|\beta\rangle=2g_\perp\beta/3D$$
$$\times\sum_\theta\{\langle\Gamma_3 v|e\mathbf{r}|\Gamma_5\theta\rangle\langle\Gamma_5\theta|\mathbf{H}\cdot\mathbf{S}|\Gamma_5\zeta\rangle$$
$$+\langle\Gamma_3 v|\mathbf{H}\cdot\mathbf{S}|\Gamma_5\theta\rangle\langle\Gamma_5\theta|e\mathbf{r}|\Gamma_5\zeta\rangle\}. \quad (22)$$

Here $\theta=\xi,\eta$ and $|\Gamma_5\theta\rangle$ is a linear combination of the $S_z=\pm1$ states, separated from the $S_z=\pm2$ states by 3D. Mixing of odd-parity orbitals into the d orbitals by the odd-parity component of the T_d crystal field makes the matrix element in (22) nonzero. We will estimate the extent of this mixing later.

It is easily seen, by writing out the matrix elements in terms of the coupling coefficients, that (22) is only nonzero when the microwave electric field $\mathbf{E}_{\mathrm{rf}}$ has a component perpendicular both to $\mathbf{H}$ and to the tetragonal z axis.

Substituting (22) in (21), we have

$$|\langle+|e\mathbf{r}|-\rangle|^2\propto[ag_\perp(\tan\theta)/g_{\parallel}]^2. \quad (23)$$

Thus, while the MD transition probability goes down with increasing microwave frequency as $(h\nu)^{-2}$, the ED probability (at given θ) remains constant.

We can make an order of magnitude estimate of the electric-dipole matrix element as follows. Since $e\mathbf{r}$ transforms as T_2 in T_d, the only matrix elements of $e\mathbf{r}$ within the ${}^5E$ term arise from spin-orbit mixing of ${}^5E$ with ${}^5T_2$. Hence

$$\langle{}^5E\Gamma_3 v|e\mathbf{r}|{}^5E\Gamma_5\theta\rangle\sim(\lambda/\Delta)\langle{}^5E|e\mathbf{r}|{}^5T_2\rangle \quad (24)$$

and

$$\langle+|e\mathbf{r}|-\rangle\sim(g_\perp\beta H\sin\theta/D)(\lambda/\Delta)\langle{}^5E|e\mathbf{r}|{}^5T_2\rangle. \quad (25)$$

We shall see that the oscillator strength for the ${}^5E\rightarrow{}^5T_2$ transition at 8000 cm^{-1} is 3×10^{-3}, so the oscillator strength for the ED transition at 24 kMc/sec (0.8 cm^{-1}) is (neglecting effective field corrections)

$$f_{ed}\sim3\times10^{-3}\times\frac{0.8}{8000}\times\left(\frac{g_\perp\beta H\sin\theta}{D}\right)^2\left(\frac{\lambda}{\Delta}\right)^2$$
$$\sim10^{-12}, \quad (26)$$

when $H\sin\theta\sim15$ kG. This is to be compared with the oscillator strength for MD transitions, which is[63]

$$f_{\mathrm{MD}}=(h\nu/6\pi mc^2)|\langle+|S_z|-\rangle|^2\sim10^{-11}. \quad (27)$$

While the ED oscillator strength appears from (26) to be an order of magnitude less than the MD, at microwave frequencies the effective electric field in a polarizable crystal can be very much larger than the external electric field, as has been discussed by Williams.[59] ED transitions may be two orders of magnitude stronger than calculated because of this effect; but the selection rules, which depend only on symmetry, will be the same.

To sum up, we might expect in tetrahedral Co^{3+} to see ED transitions, subject to the selection rule $\mathbf{E}_{\mathrm{rf}}\perp\mathbf{H}\perp\mathbf{z}$, whose strength varies as $\tan^2\theta$. At 24 kMc/sec their intensity should be within an order of magnitude (either way) of the MD intensity, and they should become relatively more important as the microwave frequency increases.

C. Electric-Dipole Transitions—Experimental

To determine the dipole nature of the transitions, we put a specimen at the electrical center[64] of a rectangular cavity resonant in the 101 mode at 24 kMc/sec. Because of the finite size of the specimen, there was still a substantial H_{rf} within it. We monitored H_{rf} by measuring the strength of the octahedral Fe^{3+} resonance near the ⟨111⟩ direction (iron is present as an unavoidable impurity). Since the octahedral site is centrosymmetric, the Fe^{3+} transition must be pure MD. The ratio of the area under the Co^{3+} resonance curve to that under the Fe^{3+} curve is a measure of the transition probability for Co^{3+} at fixed H_{rf}. Its angular dependence is shown in Fig. 8, both for the rectangular cavity (maximum E_{rf}, minimum H_{rf}) and for the cylindrical cavity (maximum H_{rf}, minimum E_{rf}). The ratio at $\theta=0°$ is practically the same in both cavities, proving

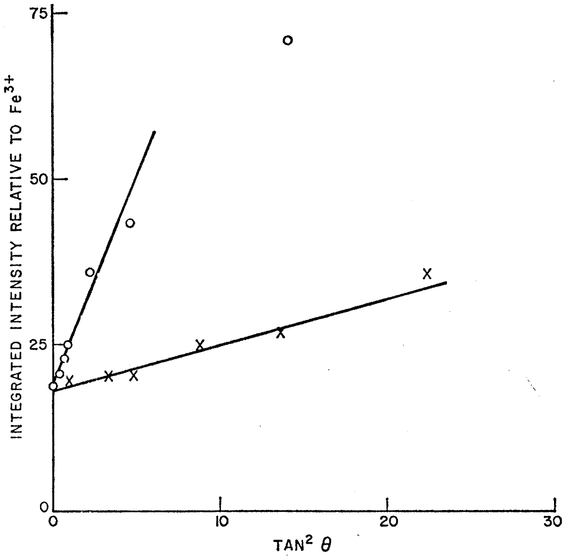

FIG. 8. Variation with θ (the angle between the magnetic field and the local z axis) of the integrated intensity at 24 kMc/sec of the $\Delta S_z=4$ transition of tetrahedral Co^{3+} normalized to the $-\frac{1}{2}\rightarrow-\frac{3}{2}$ transition of octahedral Fe^{3+}. ×, specimen at the center of a cylindrical cavity (maximum H_{rf}, minimum E_{rf}). ○, specimen at the electrical center of a rectangular cavity (maximum E_{rf}, minimum H_{rf}).

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[63] Reference 27, p. 57.

[64] This is not the same as the geometric center because of the asymmetry introduced by the sample support. We found the electrical center by looking for the point at which the specimen (after allowance for the effect of its support) produced the maximum shift in the resonant frequency of the cavity.

that Co^{3+} transition here is pure MD. However, the ratio varies roughly ten times more rapidly with angle in the rectangular than in the cylindrical cavity. This shows that at least 90% of the angular-dependent part is ED. The predicted $\tan^2\theta$ dependence of the ED contribution is well obeyed, except at large θ in the rectangular cavity, where the transition is probably beginning to saturate.

The predicted frequency dependence is followed qualitatively; at 56 kMc/sec the angular variation of intensity is much more pronounced than 24 kMc/sec. However, this could be partly due to the fact that the specimen extends further into the **E** field of the smaller cavity.

The predicted selection rule $\mathbf{E}_{\mathrm{rf}}\perp\mathbf{H}\perp\mathbf{z}$ is apparently not very well obeyed. This is probably because $\mathbf{E}_{\mathrm{rf}}$ in the specimen (which is rather irregular in shape) is not parallel to the face of the cavity. For the same reason, there is a random variation from specimen to specimen of the ratio of ED to MD intensity.

We conclude that the intensity of the $\Delta S_z=4$ resonance in tetrahedral Co^{3+} can be well accounted for by a combination of MD and ED transitions. This being so, we can use the strength of the MD component, relative to that of the g marker (silicon of known phosphorus concentration, placed close to the specimen) and (27) to determine the concentration of tetrahedral Co^{3+} in the specimen. Comparison with the optical spectrum then gives us the oscillator strength $f=3\times10^{-3}$ for the 8000-cm^{-1} $^5E\rightarrow{}^5T_2$ absorption band.[65] We will need this number in II.

VII. OCTAHEDRAL Co^{4+}

In a crystal counterdoped with calcium the spin-resonance spectrum is still dominated by the tetrahedral Co^{3+}. However, when the field is within 20° of the $\langle111\rangle$ direction we find (at 4.2°K and below) an eight-line spectrum with an integrated intensity less than 10^{-3} of the Co^{3+} spectrum. The linewidth at 1.4°K is 9 G (measured with a 7.5-G peak to peak field sweep). The angular variation of this spectrum is symmetric about $\langle111\rangle$, and is consistent with the usual $S=\frac{1}{2}$ spin Hamiltonian (1) with the following values of the parameters:

$$\begin{aligned} g_{\parallel}&=3.3385\pm0.001\,, & 10^4|A|&=367\pm1\ \mathrm{cm}^{-1},\\ g_{\perp}&=0.84\pm0.03\,, & 10^4|B|&=170\pm5\ \mathrm{cm}^{-1}. \end{aligned} \tag{28}$$

B was found by fitting the hfs at $\theta=0°$ to the formula[66]

$$H(I_z)=\frac{1}{g_{\parallel}\beta}\left\{h\nu-AI_z-\frac{B^2}{2h\nu}[I(I+1)-I_z^2]\right\}\,, \tag{29}$$

which is accurate to order $B^2/h\nu$, and fits the data within the precision of measurement.

At 1.4°K and 24 kMc/sec the lines are 50% saturated by an H_{rf} of 0.1 G, indicating a spin-lattice relaxation time of about 10^{-5} sec.[45]

We attribute this spectrum to octahedral Co^{4+}. This ion has the d^5 configuration, and can have either the weak-field (high-spin) $^6A_1$ ground term, or the strong-field (low-spin) $^2T_2(t_2{}^5)$ term. In Al_2O_3 it is the latter,[67,68] and we would expect the same in garnet.

The first-order theory of resonance in a $^2T_2$ term has been given by Stevens[69] and by Bleaney and O'Brien.[70] The effective Hamiltonian is (2) with $S=\frac{1}{2}$, and $\alpha=\alpha'=1$ (since configuration mixing is neglected in this treatment). For λ negative (since we have a hole in the t_2 shell) the lowest state has the g factors

$$\begin{aligned} g_{\parallel}&=2[(2+k)\cos^2\varphi-1]\,,\\ g_{\perp}&=\sqrt{2}k\sin2\varphi+2\sin^2\varphi\,, \end{aligned} \tag{30}$$

where $\tan2\varphi=\sqrt{2}\lambda/(\frac{1}{2}\lambda-\Delta_t)$. Here k is the orbital reduction factor (which may include some of the effects of configuration mixing as well as of covalency).

We can fit our values of $g_{\parallel}$ and $g_{\perp}$ with $\varphi=15.0\pm0.25°$, $k=0.87\pm0.01$. Since second-order contributions to the g factors have been neglected, the exact values of φ and k are not to be taken too seriously. The value of φ implies $\Delta_t/\lambda\approx-2$. For this term (neglecting configuration mixing) $\lambda=-\zeta$, and $\zeta\approx500$ cm^{-1} (75% of the free-ion value of approximately 670 cm^{-1}).[50] Hence $\Delta_t\approx+1000$ cm^{-1} and $v\approx-1000$ cm^{-1}.

Corrections from configuration mixing, both to λ and to Δ_t, are likely to be quite substantial, and the value of v is only approximate. The negative sign is opposite to that tentatively found for Co^{2+}, but the same as found for Cr^{3+} and Ru^{3+} in this site.[30,33]

That the first-order analysis is not completely adequate can be seen by applying it to the hfs. The empirical hfs constants are given in terms of P and $P\kappa$ (defined in Sec. III) by[70]

$$\begin{aligned} A&=(2P/7)[8\sin^2\varphi-6-2^{-1/2}\sin2\varphi]+P\kappa\cos2\varphi\,,\\ B&=(2P/7)[1-15(\sin2\varphi)/2\sqrt{2}]+P\kappa\sin^2\varphi\,. \end{aligned} \tag{31}$$

Substituting our values of $|A|$, $|B|$, and ϕ, we find (according to the choice of signs) that $P=\pm0.032$ cm^{-1}, $P\kappa=\pm0.018$ cm^{-1} or $P=\pm0.048$ cm^{-1}, $P\kappa=\pm0.137$ cm^{-1}. Only the first set is at all reasonable, but even here, the doubling in the core-polarization term $P\kappa$ on going from Co^{2+} to Co^{4+} is quite inconsistent with Geschwind's empirical generalization[52] than in a given environment $P\kappa$ is practically independent of ionic charge.[71] If we substitute $P\kappa=0.0080$ cm^{-1} in (31), the only reasonable values of P and φ consistent with the data are $P=0.033$ cm^{-1}, $\varphi=12°\,30'$, whence $\Delta_t/\lambda=2.5$.

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[65] We neglect the effective field correction (which is small at optical frequencies) in arriving at this figure.

[66] W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960), Eq. (8.23).

[67] M. G. Townsend and O. F. Hill, Trans. Faraday Soc. **61**, 2597 (1965).

[68] S. Geschwind (unpublished).

[69] K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 542 (1953).

[70] B. Bleaney and M. C. M. O'Brien, Proc. Phys. Soc. (London) **B69**, 1216 (1956).

[71] A similar discrepancy is found if one tries to fit the data of Ref. 67 on Co^{4+} in Al_2O_3 to Eq. (21).

TABLE I. Parameters in the spin Hamiltonian for four species of cobalt in YGaG.

Ion	Site	Ground term	T (°K)	S_{eff}	$g_{\parallel}$	$g_{\perp}$	D (cm^{-1})	$\lvert a \rvert$ (cm^{-1})	$10^4 \lvert A \rvert$ (cm^{-1})	$10^4 \lvert B \rvert$ (cm^{-1})
Co^{2+}	Oct.	$^4T_1$	4.2	$\frac{1}{2}$	7.027 ± 0.002	2.665 ± 0.002			307.5 ± 2	15 ± 3
Co^{2+}	Tet.	$^4A_2$	77	$\frac{3}{2}$	2.42 ± 0.01	2.19 ± 0.01	-18		<40	<30
Co^{3+}	Tet.	^5E	4.2, 1.2	2	2.168 ± 0.003	$\cdots$	~ -14	0.660 ± 0.003	<4	$\cdots$
Co^{4+}	Oct.	$^2T_2$	1.5	$\frac{1}{2}$	3.3385 ± 0.001	0.84 ± 0.03			367 ± 1	170 ± 5

This figure is probably as accurate as that derived directly from the g values. The g values derived from (30) with this value of φ deviate from those observed by less than ± 0.2. The second-order contributions are expected to be of order $8\lambda/\Delta$, which is about 0.2 in Co^{4+}.

Besides the sharp group of eight lines which we have analyzed there are several others, with much the same $g_{\parallel}$ but different $g_{\perp}$. These lines are broader than the main group, and some show rhombic splittings. The total integrated intensity in these lines is about the same as that in the sharp lines. Some of them probably arise from Co^{4+} locally charge compensated by Ca^{2+} in a nearest-neighbor dodecahedral site.

We searched for, but were unable to find, resonances associated with Co^{4+} in a tetrahedral or dodecahedral site. We would expect Co^{4+} to have the weak-field $^6A_1$ ground term in the former site, and probably in the latter as well. While strong absorption from Fe^{3+} impurity may have masked these lines, it is unlikely that there was much more Co^{4+} in these sites than in the octahedral sites. We conclude that 1% or less of the cobalt was forced quadrivalent by the calcium counterdoping.

VIII. CONCLUSIONS

The spin-resonance data on cobalt in garnets are summarized in Table I. What we have been able to deduce about crystal fields at the tetrahedral and octahedral sites, from these and other data, are summarized in Tables II and III. The figures given as "calculated" for Co^{2+} were obtained by substituting $\langle r^2 \rangle = 1.25$ a.u., $\langle r^4 \rangle = 3.65$ a.u.,[32] in the calculations of Pappalardo.[31] These are based on the point-charge model, including nearest neighbors only. The point-charge results for other ions do not differ greatly from those for Co^{2+}. We note that the point-charge model predicts the sign of the parameters correctly in every case, except for v in trivalent and quadrivalent ions at the octahedral site. A similar discrepancy has been noted in Al_2O_3.[29,53] Its origin is not understood.

TABLE II. Tetragonal crystal field parameters in the tetrahedral site of YGaG.

Ion	Term	Splitting (cm^{-1})	μ (Tentative values)	δ (Tentative values)	Notes
Co^{2+}	$^4T_2$	-2800	-1200	$+3700$	see Sec. IV
Co^{3+}	^5E	<0	-1200	$+3100$	see Sec. V
Cu^{2+}	^2E	± 1200	-1200	>0	Ref. 41
Co^{2+}	Calc.		-3200	$+2900$	Ref. 31

TABLE III. Trigonal crystal field parameters in the octahedral site of YGaG.

Ion	Term	Splitting (cm^{-1})	v (Tentative values)	v' (Tentative values)	Notes
Co^{2+}	$^4T_1$	$+650$	$+650$	-1300	see Sec. III
Co^{4+}	$^2T_2$	$+1000$	-1000		see Sec. VII
Cr^{3+}	^2E $^4A_2$	-26 $+0.7$	-800	-1300	Ref. 30
Ru^{3+}	$^2T_2$	$+1000$	-1000		Ref. 33
Co^{2+}	Calc.		$+500$	-1900	Ref. 31

As far as site preferences and charge states in single crystal YGaG are concerned, we come to the following conclusions. Co^{2+} exists in uncompensated crystals as well as in silicon-compensated ones. Its site preference is (in decreasing order): octahedral, tetrahedral, dodecahedral; indeed, there is no evidence that the latter site is occupied at all by Co^{2+}.

The preference of Co^{2+} for the octahedral over the tetrahedral site in our crystals is in accord with the results on polycrystals[1,2,4–7]; for instance, the octahedral: tetrahedral ratio for Co^{2+} in YIG is 5:1 over a range of concentrations from 2 to 50 at.%.[4] On the other hand, the refusal of Co^{2+} to enter the dodecahedral site in our crystals, while large concentrations have been obtained in this site in polycrystals,[1,3] shows that the crystal chemistry of heavily doped sintered polycrystals is not necessarily a reliable guide to the behavior of dilute impurities in single crystals.

Co^{3+} can occupy the tetrahedral site in uncompensated and in calcium compensated crystals, but is driven divalent by the addition of silicon. No definite conclusions can be drawn as to site preference, since neither octahedral nor dodecahedral Co^{3+} should be detectable by spin resonance. In sintered polycrystals Co^{3+} prefers the octahedral site, and does not enter the dodecahedral site.[7]

Co^{4+} exists in calcium-compensated crystals, but only in very small quantity. Only octahedral Co^{4+} has been identified.

ACKNOWLEDGMENTS

We are grateful to E. M. Gyorgy and R. C. Le Craw for drawing our attention to the problem of cobalt in garnet; to S. Geschwind, R. M. Macfarlane, and D. L. Wood for communicating their unpublished work, and for helpful discussions; to C. G. B. Garrett for helpful comments on the manuscript; and to K. A. Ingersoll and E. M. Kelly for technical assistance.