

## Substitution of Divalent Cobalt in Yttrium Iron Garnet

S. GELLER,\* H. J. WILLIAMS, G. P. ESPINOSA\*, AND R. C. SHERWOOD

Bell Telephone Laboratories, Murray Hill, New Jersey

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Magnetic and crystallographic data are reported on the systems  $\{Y_3\}Co_xFe_{5-2x}M_xO_{12}$ ,  $M=Si$  or  $Ge$ . When  $M=Si$ , the maximum value of  $x$  appears to be between 1.00 and 1.25, while when  $M=Ge$ , the maximum value of  $x$  is 2.50. A distribution of the ions in these garnets is proposed that is compatible with the results and conclusions obtained on all other substituted yttrium-iron-garnet systems. In particular, it appears that a constant 20% of the  $Co^{2+}$  ions enter tetrahedral sites. When  $x \geq 1.00$ , some  $Ge^{4+}$  ions enter octahedral sites. The garnet  $\{Y_{2.7}Ca_{0.3}\}CoFe_{2.7}Ge_{1.3}O_{12}$  has a compensation point at 236°K; it is the first garnet reported which has a compensation point resulting from a difference in the temperature behavior of only the  $a$  and  $d$  sublattice magnetizations. The other garnets having compensation points all contain magnetic rare-earth ions in the  $c$  sites. The garnet  $\{Y_{2.5}Ca_{0.5}\}CoFe_3V_{0.5}Ge_{0.5}O_{12}$  has a higher Curie temperature, 410°K, than that, 350°K, of  $\{Y_3\}CoFe_3GeO_{12}$ . This is in accord with the expected effect of pentavalent vanadium substitution.

### INTRODUCTION

THE results of our investigations of the substitutions of divalent manganese, iron and nickel in yttrium iron garnet have already been reported.<sup>1,2</sup> Some preliminary results on substitution of divalent cobalt with electrostatic compensation by tetravalent silicon ions have been given.<sup>2</sup> In this paper, we report magnetic and crystallographic results on the systems  $\{Y_3\}Co_xFe_{5-2x}Si_xO_{12}$  and  $\{Y_3\}Co_xFe_{5-2x}Ge_xO_{12}$  and on some related garnets.

Unlike the other divalent ions, it appears that the  $Co^{2+}$  ion does enter the tetrahedral sites and thus an *exact* understanding of the magnetic behavior of these garnets cannot be obtained from the magnetization measurements alone. Nor can the x-ray diffraction technique resolve the problem. However, considerations of the results obtained on a substantial number of other systems have led to at least a tentative solu-

tion which is consistent with the behavior of these other systems.

As far as we have been able to ascertain at this time, the  $Co^{2+}$  ion is the only divalent ion which enters the tetrahedral sites in the garnet structure in substantial amount. Also, it is the only magnetic ion other than the  $Fe^{3+}$  ion which goes into tetrahedral sites in the garnets. Further it is thus far the only ion which if substituted in proper amount [and apparently because of its different (from  $Fe^{3+}$  ion) temperature dependence of magnetization] yields garnets with compensation points when there are no magnetic ions in the  $c$  sites.

### EXPERIMENTAL

The techniques employed for preparation of the polycrystalline specimens of the cobalt substituted garnets are the same as those described in the paper<sup>1</sup> on the other divalent ion substitutions. The firing conditions are given in Tables I-III. X-ray powder photographs were taken with Straumanis-type Norelco cameras of 114.59 mm diam; CrK radiation was used.

Magnetic measurements were made with applied fields  $H_a$  to 15.3 kOe with a pendulum magnetometer described elsewhere.<sup>3</sup> Measurements to fields of 80 kOe at 4.2°K were made with a Bitter-type magnet and an extraction method was used to determine the moments.

TABLE I. Data for garnets in the  $\{Y_3\}Co_xFe_{5-2x}Si_xO_{12}$  system.

$x$	$a$ , Å	$n_B^a$	Firing conditions, °C (hr)
0.10	12.371	4.50	1430 (19), 1430 (63)
0.20	12.362	3.98	1290 (1), 1405 (2), 1430 (5½)
0.40	12.349	3.17	1460 (15), 1390 (16)
0.60	12.333	2.26	1300 (½), 1340 (2), 1400 (3)
0.80	12.315	1.34	1290 (1), 1405 (2), 1430 (5½)
1.00	12.296	0.67	1400 (19), 1450 (68)

<sup>a</sup> Considered to be the 0°K, zero-field moments.

<sup>3</sup> R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. **103**, 572 (1956).

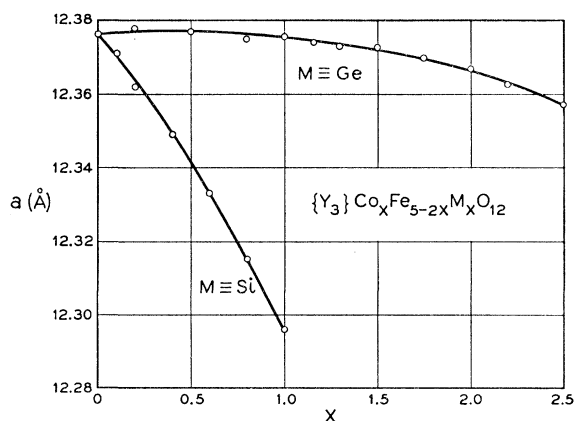


FIG. 1. Lattice constant ( $a$ ) versus  $x$ .

\* Present address: North American Aviation Science Center, 1049 Camino dos Rios, Thousand Oaks, California.

<sup>1</sup> S. Geller, H. J. Williams, R. C. Sherwood, and G. P. Espinosa, Phys. Chem. Solids **23**, 1525 (1962).

<sup>2</sup> S. Geller, H. J. Williams, R. C. Sherwood, and G. P. Espinosa, J. Appl. Phys. **33**, 1195 (1962).

TABLE II. Data for garnets in the  $\{Y_3\}Co_xFe_{5-2x}Ge_xO_{12}$  system.

$x$	$a, \text{\AA}$	$n_B^a$	$T_c, \text{ }^\circ\text{K}$	Firing conditions, $^\circ\text{C}$ (hr)
0.20	12.378	4.01		1250(1), 1300(2), 1400(2), 1425(2), 1430(2), 1440(2)
0.50	12.377	2.58		1440(1½), 1440(2), 1425(2½), 1410(16)
0.80	12.375	1.46	420	1300(2), 1370(16), 1375(16), 1390(48)
1.00	12.376	0.74	350	1300(66), 1435(17), 1435(16)
1.16	12.374	0.25	305	1250(1), 1380(2), 1370(16)
1.30	12.373	-0.06		1250(½), 1330(5), 1360(6), 1365(24)
1.50	12.373	-0.75	210	1435(17), (16)
1.75	12.370	-1.50	150	1225(1), 1300(2), 1350(2½), 1400(3½), 1420(1½), 1385(1), 1400(1½)
2.00	12.366	-2.15	85	1120(½), 1300(3), 1330(1), 1340(2)
2.20	12.363	-2.50	50	1100(1), 1350(2), 1375(1½), 1400(1), 1390(2), 1400(1)
2.50	12.357			1125(2), 1300(3), 1330(1), 1340(2)

<sup>a</sup> See footnote a, Table I.

CRYSTAL CHEMICAL DATA

Lattice constants ( $\pm 0.003 \text{\AA}$ ) of the various specimens  $\{Y_3\}Co_xFe_{5-2x}M_xO_{12}$ ,  $M = \text{Si}$  or  $\text{Ge}$ , are given in Tables I and II and plotted versus composition in Fig. 1. In the  $\{Y_3\}Co_xFe_{5-2x}Si_xO_{12}$  system, single phase specimens with  $0 \leq x \leq 1.00$  were obtainable, but one with  $x = 1.25$  was not precisely single phase. Thus the maximum value of  $x$  in this system probably lies between 1.00 and 1.25. In the  $\{Y_3\}Co_xFe_{5-2x}Ge_xO_{12}$  system, specimens with the maximum range  $0 \leq x \leq 2.50$  could be prepared.

The single-phase specimen  $\{Y_{2.9}Co_{0.1}\}[Fe_2](Fe_{2.9}Si_{0.1})O_{12}$  could not be obtained. However, one with formula  $\{Y_{2.8}Co_{0.2}\}Co_{2.0}Fe_{0.8}Ge_{2.2}O_{12}$  and lattice constant  $12.343 \text{\AA}$  was obtained.<sup>4-6</sup> The large difference,  $0.017 \text{\AA}$ , between this value and that,  $12.360 \text{\AA}$ , of the garnet  $\{Y_3\}Co_{2.2}Fe_{0.6}Ge_{2.2}O_{12}$  is additional evidence that, in the former, the  $0.2 \text{ Co}^{2+}$  ions are in dodecahedral sites.

Trivalent cobalt could not be put into the garnet (under our experimental conditions); a single-phase specimen with formula  $\{Y_3\}Co_{0.1}Fe_{4.9}O_{12}$  could not be prepared.

As in the case of  $Ni^{2+}$  ion substituted garnets,<sup>1</sup> firing in  $N_2$  produced garnets with slightly larger lattice constants than did firing in air.

The lattice constant of  $\{Y_{2.5}Ca_{0.5}\}CoFe_3Ge_{0.5}V_{0.5}O_{12}$  is  $12.400 \text{\AA}$ . Lattice constants for garnets in the system  $\{Y_{3-y}Ca_y\}CoFe_{3-y}Ge_{1+y}O_{12}$  are given in Table III.

TABLE III. Data for garnets in the system  $\{Y_{3-y}Ca_y\}CoFe_{3-y}Ge_{1+y}O_{12}$ .

$y$	$a$	$n_B^a$	Firing conditions, $^\circ\text{C}$ (hr)
0.10	12.375	0.43	1125(1½), 1380(22)
0.30	12.374	-0.22	1170(½), 1370(18)
0.40	12.373	-0.52	1170(½), 1360(2)
0.50	12.373	-0.79	1130(½), 1300-1350(2)

<sup>a</sup> See footnote a, Table I.

<sup>4</sup> Other garnets containing  $Co^{2+}$  ions in the dodecahedral sites have been reported (see Refs. 5 and 6).

<sup>5</sup> S. Geller, C. E. Miller and R. G. Treuting, *Acta Cryst.* **13**, 179 (1960).

<sup>6</sup> J. A. Kohn and D. W. Eckart, *Am. Mineralogist* **47**, 1422 (1962).

MAGNETIC DATA

The  $\{Y_3\}Co_xFe_{5-2x}Si_xO_{12}$  System

In this system magnetic saturation at  $1.4^\circ\text{K}$  was attained for specimens with  $x = 0.10, 0.60, 0.80,$  and  $1.00$ , the first three at about  $12.6 \text{ kOe}$ , the last at  $\leq 4.8 \text{ kOe}$ . The specimen with  $x = 1.00$  was magnetically saturated at  $4.8 \text{ kOe}$  (the lowest field at which measurements were made) over the entire temperature range  $1.4-300^\circ\text{K}$ . Curves of magnetization versus temperature for specimens with  $x = 0.60$  and  $1.00$  are given in Fig. 2. The specimen with  $x = 0.40$  was saturated at about  $40 \text{ kOe}$  at  $4.2^\circ\text{K}$ .  $0^\circ\text{K}$  moments are plotted versus  $x$  in Fig. 3 (curve 2).

The  $\{Y_3\}Co_xFe_{5-2x}Ge_xO_{12}$  System

In this system, specimens with  $x = 0.2, 0.5,$  and  $0.8$  were not magnetically saturated at  $1.4^\circ\text{K}$  at fields to  $14.24 \text{ kOe}$ . High-field measurements at  $4.2^\circ\text{K}$  indicated saturation at about  $70 \text{ kOe}$ . The specimen  $\{Y_3\}CoFe_3GeO_{12}$  was magnetically saturated at  $4.8 \text{ kOe}$  over the

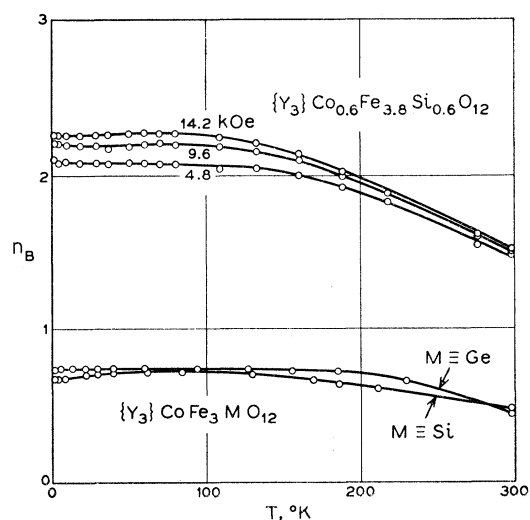


FIG. 2.  $n_B$  versus  $T$  for  $Y_3Co_{0.6}Fe_{3.8}Ge_{0.6}O_{12}$ ,  $Y_3CoFe_3GeO_{12}$ , and  $Y_3CoFe_3SiO_{12}$ . The curves for the specimens containing one  $Co^{2+}$  ion/formula unit give spontaneous magnetizations.

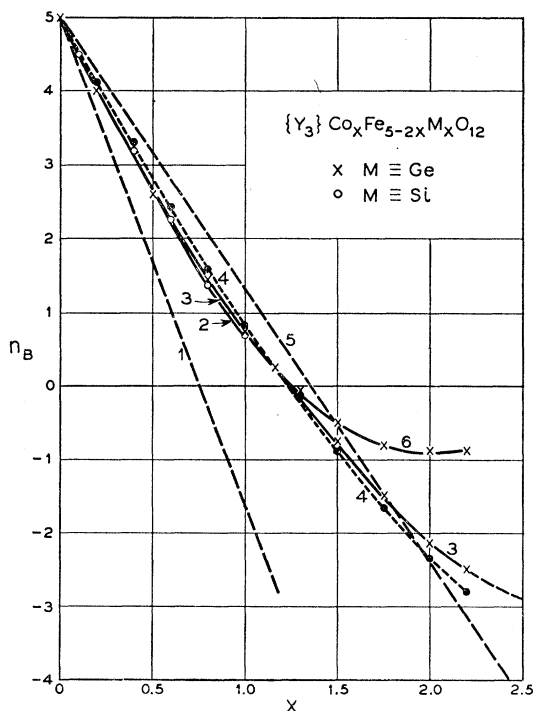


FIG. 3.  $n_B$  versus  $x$ : (1) calculated assuming all  $\text{Co}^{2+}$  ions in  $d$  sites with moment  $3.4 \mu_B$ , all  $\text{Ge}^{4+}$  ions in  $d$  sites, Néel model; (2) observed for system  $\{\text{Y}_3\}\text{Co}_x\text{Fe}_{5-2x}\text{Si}_x\text{O}_{12}$ ; (3) observed for system  $\{\text{Y}_3\}\text{Co}_x\text{Fe}_{5-2x}\text{Ge}_x\text{O}_{12}$ ; (4) from calculated values given in Table IV; (5) calculated assuming all  $\text{Co}^{2+}$  ions in  $a$  sites with moment  $3.7 \mu_B$ , all  $\text{Ge}^{4+}$  ions in  $d$  sites, Néel model; (6) for high values of  $x$  in system  $\{\text{Y}_3\}\text{Co}_x\text{Fe}_{5-2x}\text{Ge}_x\text{O}_{12}$  when extrapolation is made to  $H_a=0$  (see text).

entire range of temperature 1.4–300°K. The spontaneous magnetization at 0°K is  $0.74 \mu_B$ , is constant (see Fig. 2) to 150°K, and drops only  $0.02 \mu_B$  between 150 and 208°K.

Curves of  $n_B(H_a, T)$  versus  $T$  for  $\{\text{Y}_3\}\text{Co}_{1.16}\text{Fe}_{2.68}\text{Ge}_{1.16}\text{O}_{12}$  are shown in Fig. 4. The curve for  $n_B(9.6, T)$  differs by no more than  $0.02 \mu_B$  from that of  $n_B(14.24, T)$ . However, this may be taken to be an indication of “unsaturation,” because when the specimen was cooled in a field of 14.24 kOe, it appeared to be

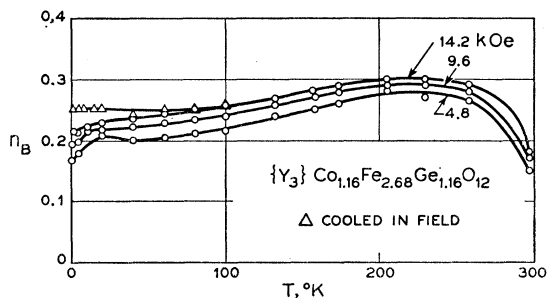


FIG. 4.  $n_B$  versus  $T$  at three different fields. When specimen was cooled in field of 14.2 kOe, saturation was attained at  $\leq 4.8$  kOe.

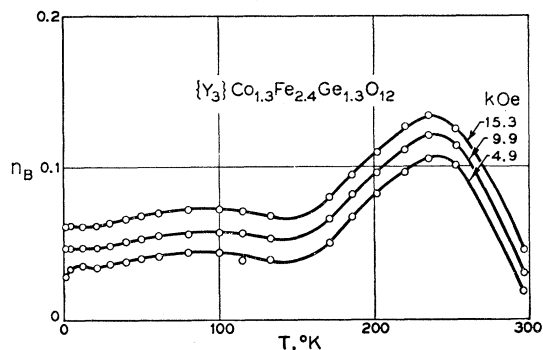


FIG. 5.  $n_B$  versus  $T$  at three different fields.

saturated at 4.8 kOe, and over the temperature range 0 to 80°K, the moment  $0.25 \mu_B$  was essentially constant (see Fig. 4).

Curves of  $n_B(H_a, T)$  versus  $T$  for the specimen with  $x=1.30$  are shown in Fig. 5. In this case again saturation was not attained at fields below 15.3 kOe. The curves appear to indicate a compensation point at about 150°K. However, this could not be ascertained by suspending a sintered piece of the specimen on a fine thread, cooling it to liquid  $\text{N}_2$  temperature in the presence of a small field from a permanent magnet and allowing it to warm in the presence of this field (but see following section).

Specimens with  $1.50 \leq x \leq 2.50$  were not saturated at fields to 14.24 kOe. Curves of  $n_B(H_a, T)$  versus  $T$  for the specimen with  $x=1.50$  are shown in Fig. 6. Also shown are the results on the same specimen cooled in a field of 14.24 kOe. The effect of cooling in the field is the “straightening” of the curves in the low-temperature region, but, unlike the case for the specimen with  $x=1.16$ , saturation was not attained. The drop in moment at temperatures below 40°K becomes progressively more marked as the value of  $x$  increases. However, cooling in a field of 14.24 kOe tends in all

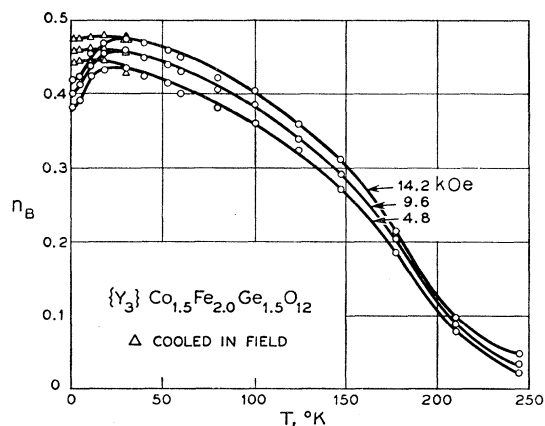


FIG. 6.  $n_B$  versus  $T$  at three different fields. Shown also are points obtained when the specimen was cooled in a field of 14.2 kOe.

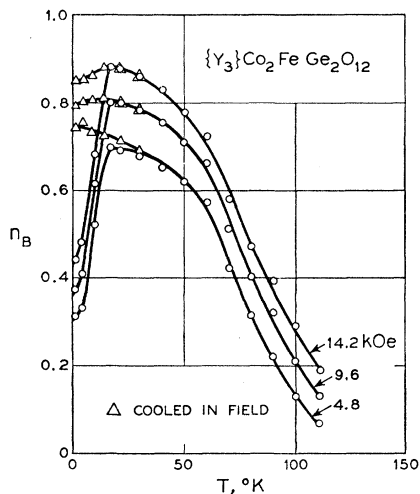


FIG. 7.  $n_B$  versus  $T$  at three different fields. Shown also are points obtained when the specimen was cooled in a field of 14.2 kOe.

cases to prevent the abrupt decrease in moment. Another example, for  $x=2.00$ , is shown in Fig. 7.

Specimens with  $1.50 \leq x \leq 2.50$  were also not magnetically saturated at fields to 80 kOe (Fig. 8) and for these, moments at "infinite" field were taken from extrapolations of  $n_B$  versus  $1/H_a$  to  $1/H_a=0$ . These magnetizations are considered to be the zero-field spontaneous magnetizations. (Reasons for this conclusion will be given later.) 0°K spontaneous magnetizations for this system are plotted versus  $x$  (curve 3) in Fig. 3.

Curie temperatures were determined, when possible, from extrapolation of  $n_B^2(0, T)$  versus  $T$  to  $n_B^2=0$  and/or from  $1/\chi_n$  versus  $T$  to  $1/\chi_n=0$ . These are listed in Table II and plotted versus  $x$  in Fig. 9. For comparison, the curves for the systems  $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$  and  $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$  are also shown.

A single-phase specimen containing no  $Fe^{3+}$  ions,  $Y_3Co_{2.5}Ge_{2.5}O_{12}$ , was prepared. Curves of  $\chi_n$  and  $1/\chi_n$  versus  $T$  are shown in Fig. 10. There appears to be an antiferromagnetic transition at about 8°K; the  $1/\chi_n$  versus  $T$  curve is concave downward between 20 and 40°K. Thus there may still be ferrimagnetism present. Above 40°K,  $1/\chi_n$  versus  $T$  follows a Curie-Weiss law

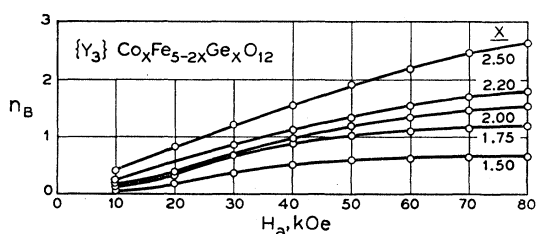


FIG. 8.  $n_B$  versus applied field  $H_a$  at 4.2°K.

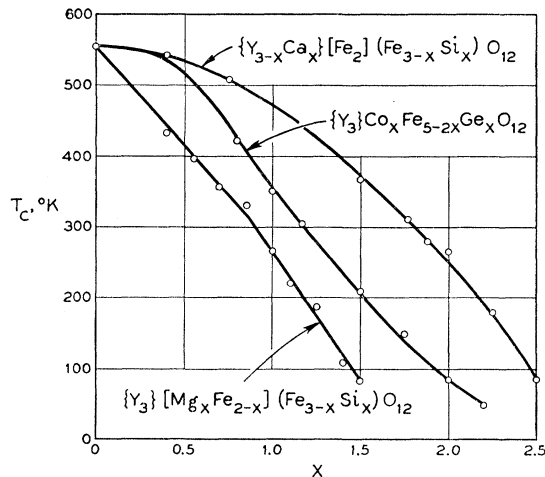


FIG. 9. Curie temperature versus  $x$  for the system  $\{Y_3\}Co_xFe_{5-2x}Ge_xO_{12}$  and  $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$ .

with  $c = \Delta T / \Delta(1/\chi_n) = 1.1 \times 10^{-3} \mu_B \text{ deg/Oe/formula unit}$ , which gives for the  $Co^{2+}$  ions an average effective paramagnetic moment of  $4.54 \mu_B$ .

### Other Garnets with $Co^{2+}$ Ion Substitutions

Garnets with general formula  $\{Y_{3-y}Ca_y\}CoFe_{3-y}Ge_{1+y}O_{12}$  were prepared with  $y=0.1, 0.3, 0.4,$  and  $0.5$ . The garnet with  $y=0.3$  has a compensation point at 236°K as shown in Fig. 11. This has also been confirmed by an experiment of the type described in the previous section. As the temperature went through the compensation point, the sintered piece turned 180° in the field and remained in the new direction. (The Curie temperature of this garnet is above room temperature.) This is the first garnet reported which has a compensation point and does not contain magnetic rare earth ions in the  $c$  sites. This must result from a

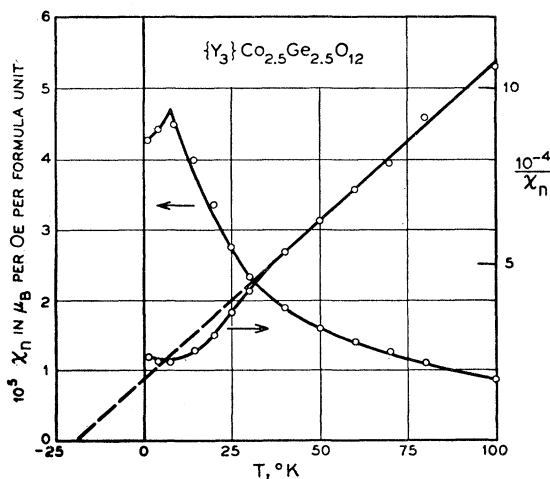


FIG. 10.  $\chi_n$  and  $1/\chi_n$  versus  $T$ .

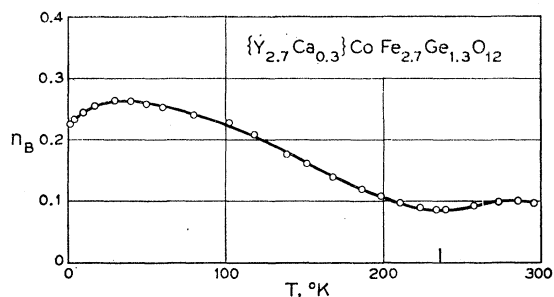


FIG. 11.  $n_B$  versus  $T$ . A compensation point is indicated at  $236^\circ\text{K}$ .

difference in the temperature dependence of the  $a$  and  $d$  sublattice magnetizations.

Magnetization versus temperature data are shown for the specimen with  $y=0.1$  in Fig. 12 and moments obtained at  $1.4^\circ\text{K}$  for specimens with  $y=0.4$  and  $0.5$  are given in Table III. Also shown in Fig. 12 are magnetization versus temperature data for the garnet  $\{Y_{2.5}Ca_{0.5}\}CoFe_3Ge_{0.5}V_{0.5}O_{12}$ . The Curie temperature  $410^\circ\text{K}$  of this garnet is higher than that  $350^\circ\text{K}$  of the garnet  $\{Y_3\}CoFe_3GeO_{12}$ , as would be expected on the basis of our work on  $V^{5+}$  ion substituted garnets.<sup>7</sup>

#### DISCUSSION

We shall assume that the  $0^\circ\text{K}$  moment of an octahedral  $Co^{2+}$  ion is  $3.7 \mu_B$  as it appears to be<sup>8</sup> in a pure normal cobalt ferrite  $(Fe)[CoFe]O_4$ . There does not appear to be an example of a ferrimagnetic compound from which a tetrahedral  $Co^{2+}$  ion moment can be readily derived. Electron-spin-resonance measurements<sup>9</sup> on cobalt-doped tetrahedral compounds give an average  $g$  value of 2.28. The largest deviation from this value is 0.03. Assuming that a tetrahedral  $Co^{2+}$  ion in a ferrimagnetic garnet has this average  $g$  value, the  $0^\circ\text{K}$  moment would be  $3.4 \mu_B$ . This value should be correct to within 5% and this suffices for the present discussion.<sup>10</sup>

It has been shown<sup>5</sup> that in garnets  $CoGd_2Co_2-Ge_3O_{12}$  and  $CoY_2Co_2Ge_3O_{12}$ , the likely distributions are  $\{CoGd_2\}[Co_2](Ge_3)O_{12}$  and  $\{CoY_2\}[Co_2](Ge_3)O_{12}$ . Also it was felt to be unlikely that in the garnets of type  $\{Ca_3\}M^{4+}CoGe_3O_{12}$   $M=Zr, Sn, Ti$ , there were

<sup>7</sup> S. Geller, G. P. Espinosa, H. J. Williams, R. C. Sherwood, and E. A. Nesbitt, *J. Appl. Phys.* **35**, 570 (1964); *Appl. Phys. Letters* **3**, 60 (1963).

<sup>8</sup> H. J. Williams and R. C. Sherwood (unpublished work).

<sup>9</sup> F. S. Ham, G. W. Ludwig, G. D. Watkins, and H. H. Woodbury, *Phys. Rev. Letters* **4**, 468 (1960); H. H. Woodbury and G. W. Ludwig, *Bull. Am. Phys. Soc.* **6**, 118 (1961).

<sup>10</sup> Following the completion of this manuscript, we became aware of the paper published by W. L. Roth [*Phys. Chem. Solids* **25**, 1 (1964)] on the magnetic structure of  $(Co^{2+})[Co_2^{3+}]O_4$ . This spinel-type compound is antiferromagnetic below  $40^\circ\text{K}$ . The  $Co^{2+}$  ions in octahedral sites have zero moment. The  $Co^{2+}$  ions in tetrahedral sites have, at  $4.2^\circ\text{K}$ , a moment of  $3.26 \mu_B$ , with which the value assumed by us for a tetrahedral  $Co^{2+}$  ion is in good agreement. As indicated, the difference does not affect any of our conclusions or proposals.

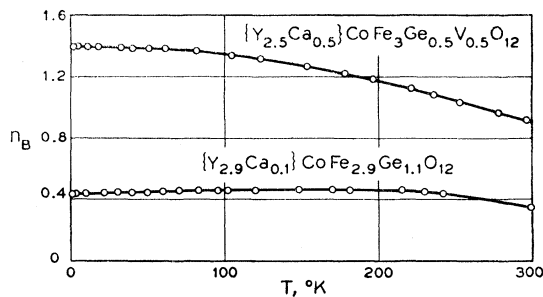


FIG. 12.  $n_B$  ( $14.2 \text{ kOe}, T$ ) versus  $T$ .

many  $Co^{2+}$  ions in tetrahedral sites; that is, the proposed<sup>5</sup> distributions were  $\{Ca_3\}[M^{4+}Co](Ge_3)O_{12}$ . These conclusions are still felt to be essentially correct; it is nevertheless possible (as pointed out in the earlier paper) that some  $Co^{2+}$  ions do occupy tetrahedral sites in these garnets. The ions  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Mn^{2+}$ , and  $Mg^{2+}$  all appear to prefer octahedral sites exclusively when substituted for  $Fe^{3+}$  ions (with appropriate electrostatic balance by tetravalent ions) in YIG.<sup>1,11</sup>

In Fig. 3 the straight line (1), obtained by assuming a simple Néel model with all  $Co^{2+}$  and  $Ge^{4+}$  ions in tetrahedral ( $d$ ) sites deviates considerably from the curve drawn through the observed points ( $n_B, x$ ); the deviation increases rapidly with increasing  $x$ . If all  $Co^{2+}$  ions are assumed to be in octahedral ( $a$ ) sites and all  $Ge^{4+}$  ions in  $d$  sites, the straight line (5) obtained by assuming a simple Néel model does not deviate considerably from the observed curve (3) except for  $x$  greater than about 2.2. It appears reasonable to conclude that the  $Co^{2+}$  ions prefer the  $a$  sites in the substituted YIG's, but that some of the  $Co^{2+}$  ions undoubtedly enter tetrahedral sites. The successful preparation of the garnets with  $x=2.2$  and  $2.5$  is itself ample proof of the latter part of the conclusion.

In attempting to determine the distributions of ions in these garnets one must consider the following parameters:

- (1) Amount of moment canting<sup>1,11</sup> (and in which site it occurs).
- (2) Fraction of  $Co^{2+}$  ions in tetrahedral sites.
- (3) Fraction of  $Ge^{4+}$  ions in octahedral sites.

Needless to say, because only the magnetization data for each specimen are known, a unique solution cannot be obtained. However, by drawing on the results and conclusions obtained on other garnet systems, some plausible conclusions may also be obtained on the  $Co^{2+}$  ion substituted YIG's.

In the system  $\{Y_3\}[Ni_xFe_{2-x}](M_x^{4+}Fe_{3-x})O_{12}$ , very little canting occurred in the tetrahedral sites.<sup>1</sup> As  $x$  increased from 0, the "effective" moment<sup>11</sup> of the tetrahedral  $Fe^{3+}$  ion appeared to go through a minimum

<sup>11</sup> S. Geller, H. J. Williams, G. P. Espinosa, and R. C. Sherwood, *Bell System Tech. J.* **43**, 565 (1964).

of  $4.90 \mu_B$  at  $x \cong 1.2$ , then increased to 5.0 again at  $x \cong 1.8$ , beyond which some canting occurred in the octahedral sites. This canting is also small; for  $\{Y_3\}-[Ni_2](FeGe_2)O_{12}$ , the reduction of the effective  $Ni^{2+}$  ion moment is about 4%. These results have been fully discussed in the paper<sup>1</sup> treating the  $Ni^{2+}$  ion substitutions; the explanation is compatible with that for the nonmagnetic ion substituted YIG's.<sup>11</sup>

Substitution of any ion for  $Fe^{3+}$  ions in the octahedral sites, weakens the  $a-d$  interactions whereupon the  $d-d$  interactions manifest themselves. Some canting occurs but not nearly as much in the case of a magnetic ion substitution as in that of a nonmagnetic ion substitution. Continued simultaneous substitution of a tetravalent ion in the  $d$  sites weakens the  $d-d$  interactions; thus tending to prevent canting of the  $d$ -site  $Fe^{3+}$  ion moments. Beyond  $x=1.8$ , the  $a$ -site ion canting is relatively smaller than in the system<sup>11</sup>  $\{Y_{3-x}Ca_x\}[Fe_2](Si_xFe_{3-x})O_{12}$  because the  $Ni^{2+}-O^{2-}-Ni^{2+}$  interaction is much weaker than the  $Fe^{3+}-O^{2-}-Fe^{3+}$  interaction.<sup>1</sup>

The same kind of reasoning should be applicable to the  $Co^{2+}$  ion substituted YIG's. Thus the deviation (see Fig. 3) in the region  $0 < x < 1.5$  of the observed  $n_B$  ( $0^\circ K$ ) versus  $x$  curve (3) from the Néel line (1) for all  $Co^{2+}$  ions in octahedral sites is too large to imply that it is caused by canting alone. It must imply that some  $Co^{2+}$  ions enter tetrahedral sites throughout the entire range of substitution.

As pointed out earlier, it was possible to prepare the garnets  $\{Y_3\}[Co_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$  for  $0 < x \leq 1.00$ . In this range the  $0^\circ K$  moments of these garnets (curve 2, Fig. 3) are essentially the same as those (curve 3, Fig. 3) of the analogous garnets containing Ge instead of Si. For  $x=1.00$ , the  $0^\circ K$  moments for the Si and Ge specimens are respectively 0.67 and 0.74. Thus because  $Si^{4+}$  ions have exclusive preference for  $d$  sites, the Ge substituted specimen with  $x=1.00$  has at most 0.01 Ge in  $a$  sites.

In the system  $Y_3Co_xFe_{5-2x}Ge_xO_{12}$ , there should not be much canting in either of the sites over the whole range of composition. It is difficult to say whether even for the end-member  $Y_3Co_{2.5}Ge_{2.5}O_{12}$  much canting in the octahedral sites should be expected, but it is probable that somewhere near this composition the intrasublattice interactions become dominant<sup>11</sup> because the garnet  $Gd_3Co_2GaGe_2O_{12}$  showed at most some tendency toward antiferromagnetism.<sup>12</sup>

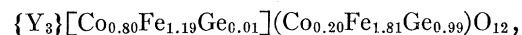
Inasmuch as the zero of canting in the  $Y_3[Ni_xFe_{2-x}](Ge_xFe_{3-x})O_{12}$  system occurs at  $x \cong 1.8$ , it should be expected to occur at a substantially lower value of  $x$  for the  $Y_3Co_xFe_{5-2x}Ge_xO_{12}$  system if substantial amounts of  $Co^{2+}$  ion enter tetrahedral sites. Consideration of all the points made above and the previous results and conclusions from the substituted yttrium iron garnet

TABLE IV. Distribution of ions,  $0^\circ K$  moments and average percent canting for moments in the system  $Y_3Co_xFe_{5-2x}Ge_xO_{12}$ .

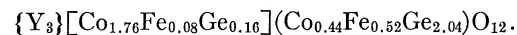
$x$	oct. $Co^{2+}$	oct. $Ge^{4+}$	$n_B$ ( $0^\circ K$ )		Average canting %
			obs	calc	
0.00	0.00	0.00	5.01	5.00	0.0
0.20	0.16	0.00	4.00	4.11	1.0
0.40	0.32	0.00	3.15	3.30	1.2
0.60	0.48	0.00	2.26	2.43	1.5
0.80	0.64	0.00	1.40	1.57	1.6
1.00	0.80	0.01	0.74	0.82	0.8
1.16	0.93	0.02	0.25	0.24	0.0
1.30	1.04	0.04	-0.06	-0.15	1.2
1.50	1.20	0.05	-0.75	-0.92	2.2
1.75	1.40	0.08	-1.50	-1.69	2.4
2.00	1.60	0.12	-2.15	-2.36	2.9
2.20	1.76	0.16	-2.50	-2.82	4.6

systems we have studied to date leads to an apparently acceptable (though, as stated above, not unique) solution to the problem of accounting for the  $0^\circ K$  moments of the  $Co^{2+}$  ion substituted garnets. A tedious trial and error technique was used to arrive at this conclusion. We shall not give its details, but rather proceed to the results.

It appears that a constant 20% of the  $Co^{2+}$  ions enter the tetrahedral sites. To about  $x=1.00$ , the general formula of the  $Co^{2+}$  substituted garnets may be written  $\{Y_3\}[Co_{0.8x}Fe_{2-0.8x}](Co_{0.2x}Fe_{3-1.2x}Ge_x)O_{12}$ . For  $x \geq 1.00$ , some  $Ge^{4+}$  ions enter octahedral sites, the amount increasing with increasing  $x$ . Thus for  $x=1.00$ , we arrive at a distribution formula



while for  $x=2.2$ , the formula which we propose is



In Table IV, we give the deduced distributions, a comparison of observed  $0^\circ K$  moments with those calculated on the basis of a simple Néel model and the average percent canting of magnetic moments in the sites in which canting occurs. It is necessary only to give the values of  $x$  and the amounts of  $Co^{2+}$  and  $Ge^{4+}$  ions in the octahedral sites for definition of the distribution formula. The zero of canting occurs at or near  $x=1.16$ . For  $x < 1.16$ , canting occurs in tetrahedral sites, while for  $x > 1.16$  canting occurs in octahedral sites. The calculated values of  $n_B$  from Table IV are plotted versus  $x$  in Fig. 3 (curve 4).

Some further discussion in connection with our proposed solution may be of interest. Although one might expect some variation in the fraction of  $Co^{2+}$  ions entering tetrahedral sites with variation of  $x$ , there is at least one precedent for this constancy: it is the case of  $Ti^{4+}$  ion substitution.<sup>13</sup> Further, if we were to suggest that more  $Co^{2+}$  ion entered tetrahedral sites at least

<sup>12</sup> R. M. Bozorth and S. Geller, Phys. Chem. Solids **11**, 263 (1959).

<sup>13</sup> S. Geller, R. C. Sherwood, H. J. Williams, and G. P. Espinosa J. Appl. Phys. (to be published).

for higher  $x$ , either the calculated moments would be higher or more  $\text{Ge}^{4+}$  ions would be required in the octahedral sites. It is also hardly likely that the amount of  $\text{Co}^{2+}$  ions entering tetrahedral sites would decrease with increasing  $x$ . If we concluded that less than 20% of the cobalt were in tetrahedral sites, the canting in tetrahedral sites for specimens with  $x < 1.00$  would be higher than for the  $\text{Ni}^{2+}$  ion substituted garnets. This could not be correct. (In fact for  $x \leq 1.0$  our proposed solution looks especially good.) For  $x = 2.5$  (to be discussed further later), at least 20% of the cobalt *must* be in tetrahedral sites unless this garnet has some subtle character, like a defect structure.

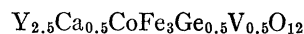
It was pointed out earlier that for  $x \geq 1.50$ , specimens were not magnetically saturated at fields to 80 kOe at 4.2°K. If we obtained the zero field moments by extrapolation of  $n_B$  versus  $H_a$  to  $H_a = 0$ , the moments obtained would have been *much* lower (see Figs. 3 and 8). These would have implied far greater canting in the octahedral sites, even greater than obtained in the system  $\{\text{Y}_{3-x}\text{Ca}_x\}[\text{Fe}_2](\text{Fe}_{3-x}\text{Ge}_x)\text{O}_{12}$ . Of course, it could have implied much greater amounts of tetrahedral  $\text{Co}^{2+}$  and octahedral  $\text{Ge}^{4+}$  contents, but these also looked improbable. Apparently the  $\text{Co}^{2+}$  ion introduces huge anisotropy which prevents saturation even at the high fields. The extrapolation to infinite field in the case of these garnets, definitely gives results which are more compatible with the results in other systems. In fact, the latter results showed us that the extrapolation to zero field could not be correct.

In the case of the specimen  $\text{Y}_3\text{Co}_{2.5}\text{Ge}_{2.5}\text{O}_{12}$ , it is possible that more than 20% of the  $\text{Co}^{2+}$  ions are in tetrahedral sites and that some  $\text{Ge}^{4+}$  ions are in octahedral sites. The plot of  $1/\chi_n$  versus  $T$  (Fig. 10) indicates that the specimen could still be ferrimagnetic and Fig. 3 also indicates that this may be so. Of course the Curie temperature would be very low. The indication of an antiferromagnetic transition could again be a result of anisotropy as for the other garnets with high  $x$ . However cooling in a field in this case does not produce any change. The extrapolation to infinite field gives  $3.75 \mu_B$ , while that of Fig. 3 gives  $2.9 \mu_B$ . The nature of the magnetic behavior of this garnet is not now clear.

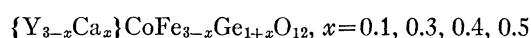
An interesting feature of the  $\text{Co}^{2+}$  ion substituted garnets is the way saturation is not attained at fields to 14.2 kOe for some specimens with  $x < 1.0$ , although it is attained at much higher fields. Yet for  $x = 1.0$ , saturation is attained at 4.8 kOe when either  $\text{Si}^{4+}$  or  $\text{Ge}^{4+}$  ions are used for electrostatic balance. For  $x = 1.16$ , saturation is attained at 4.8 kOe when the specimen is

cooled in a field of 14.2 kOe. For  $x \geq 1.50$ , saturation was not attained even at fields to 80 kOe. This would seem to indicate that somewhere near  $x = 1.00$ , the anisotropy goes through a zero, and then increases again. There is little point in speculating on how this happens; a solution to this problem may eventually be obtained from measurements on single crystals not now available. But if our proposed distributions of ions are correct, this result must be related to the *absolute* rather than *relative* amounts of  $\text{Co}^{2+}$  ion in the two sites.

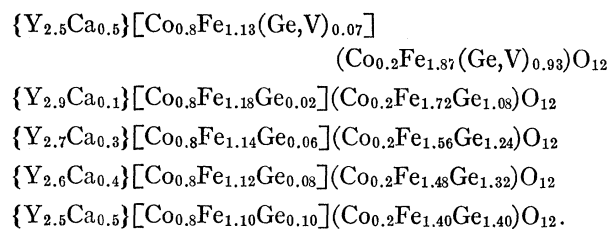
The specimens



and



were also essentially saturated at moderate fields. The 0°K moments of these are 1.39, 0.43,  $-0.22$ ,  $-0.52$ , and  $-0.79 \mu_B$ , respectively, (see also Table III). If it is assumed in each case that the same 20% of the  $\text{Co}^{2+}$  ions will enter tetrahedral sites and any canting is neglected, the distributions would be



In the first of these, it is not known whether the  $\text{Ge}^{4+}$ ,  $\text{V}^{5+}$  or a combination of both ions would enter octahedral sites.

Of course, again the solution to the distribution problem in these garnets is not unique. It may be that the amount of  $\text{Co}^{2+}$  ion in  $d$  sites decreases with increasing  $\text{Ge}^{4+}$  ion content. Whatever the change is, however, it must produce 0°K moments which are linear with the total  $\text{Ge}^{4+}$  ion per formula unit as observed (see Table III) and garnets which saturate at moderate fields. It seems unlikely that in any of these specimens all the  $\text{Co}^{2+}$  ion will be in octahedral sites, although such a formal solution can be found.

#### ACKNOWLEDGMENTS

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