

## Gallium-Substituted Yttrium Iron Garnet

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Spontaneous moments, near 0°K, of specimens with  $x$  to 3.00 in the system  $Y_3Fe_{5-x}Ga_xO_{12}$  have been measured and the ionic distribution determined by means of the model given previously by Geller, Williams, Espinosa, and Sherwood. It is shown that although for  $x$  to about 2.75, the preference of  $Ga^{3+}$  ions for tetrahedral sites is greater than that of  $Al^{3+}$  ions in the analogous system  $Y_3Fe_{5-x}Al_xO_{12}$ , for greater  $x$ , the preference of  $Ga^{3+}$  ions for tetrahedral sites may be the same as or less than that of  $Al^{3+}$  ions. The  $Ga^{3+}$  ion distribution in this system is such that to  $x \approx 2.50$ , the garnets act like ideal Néel ferrimagnets. Comparisons are made with the results of other investigations on this system.

## INTRODUCTION

WHILE it was indicated in the first study<sup>1</sup> of gallium-substituted yttrium iron garnets that a complete solid-solution range existed between yttrium iron and yttrium gallium garnets, spontaneous-magnetization measurements were made only on compositions  $Y_3Fe_{5-x}Ga_xO_{12}$ ,  $x=0.25$  and  $x=0.75$ . (Other studies<sup>2,3</sup> have also been made in this range of substitution). Since then, two investigations<sup>4,5</sup> have extended the study of the static magnetic behavior of this system to larger values of  $x$ . There is some measure of disagreement among the results, and the methods of determination of the distribution of the  $Ga^{3+}$  ions over the octahedral and tetrahedral sites have differed. Our study extends the earlier range to  $x=3.00$  and makes use of the model proposed by Geller, Williams, Espinosa, and Sherwood<sup>6</sup> to determine the  $Ga^{3+}$  ion distribution. An important feature of this work is the conclusion that although the preference of  $Ga^{3+}$  ions for tetrahedral sites is greater than that of  $Al^{3+}$  ions in the region to  $x \approx 2.75$ , it appears that beyond this point the preference of  $Ga^{3+}$  ions for tetrahedral sites may be the same as, or possibly less than, that of  $Al^{3+}$  ions.

## EXPERIMENTAL

Details of our techniques of specimen preparation have been given previously.<sup>7</sup> Firing data are given in Table I. Powder photographs were taken with 114.6-mm-diam-Norelco cameras and CrK radiation. Magnetic measurements were made on all specimens in the temperature range 1.2–2.2°K (which for purpose of discussion may be assumed to be 0°K) with a vibrating-sample magnetometer<sup>8</sup> and a superconducting solenoid.

<sup>1</sup> M. A. Gilleo and S. Geller, *J. Appl. Phys.* **20**, 389 (1958); *Phys. Rev.* **110**, 73 (1958).

<sup>2</sup> G. Villers and J. Loriers, *Compt. Rend.* **245**, 2033 (1957).

<sup>3</sup> E. E. Anderson, J. R. Cunningham, Jr., G. E. McDuffie, Jr., and R. F. Stauder, *J. Phys. Soc. Japan* **17**, Suppl. B-1, 365 (1962).

<sup>4</sup> B. Lüthi and T. Henningsen, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (Institute of Physics and the Physical Society, London, 1965), p. 668.

<sup>5</sup> R. L. Streever and G. A. Uriano, *Phys. Rev.* **139**, A305 (1965).

<sup>6</sup> S. Geller, H. J. Williams, G. P. Espinosa, and R. C. Sherwood, *Bell System Tech. J.* **43**, 565 (1964).

<sup>7</sup> S. Geller, H. J. Williams, R. C. Sherwood, and G. P. Espinosa, *J. Phys. Chem. Solids* **23**, 1525 (1962).

<sup>8</sup> S. Foner, *Rev. Sci. Instr.* **30**, 548 (1959).

Calibration was carried out with spectroscopically pure nickel. The sample dimensions were typically  $\approx 0.05 \times 0.05 \times 0.5$  cm.

## MAGNETIC AND CRYSTALLOGRAPHIC DATA

In the range of composition  $0 \leq x \leq 2.40$ , all specimens were saturated magnetically at fields  $\leq 25$  kOe. For  $x=2.60, 2.75$ , and  $3.00$ , saturation was not attained and spontaneous moments were obtained by extrapolation of the straight-line portions of  $n_B$  versus  $H_a$  to  $H_a=0$ . The spontaneous moments are listed in Table II and

TABLE I. Lattice constants and firing data for  $Y_3Fe_{5-x}Ga_xO_{12}$  specimens.

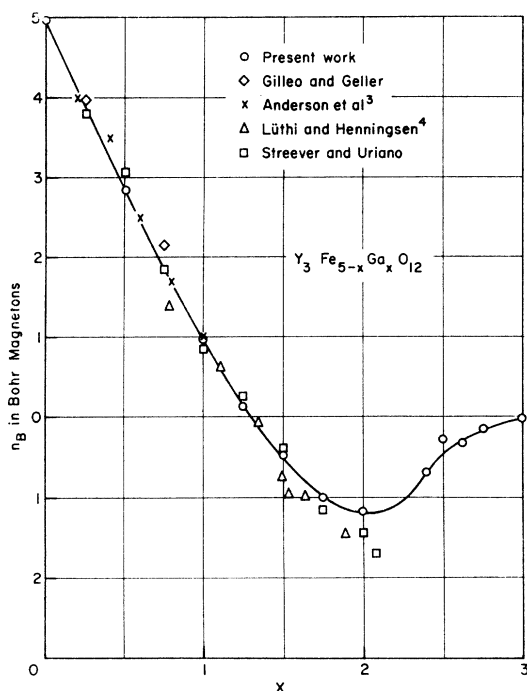
$x$	$a$ (Å)	Firing conditions, <sup>b</sup> °C (h)
0.50	12.368	1200( $\frac{3}{2}$ ), 1410(15)
1.00	12.361	1175( $\frac{1}{2}$ ), 1350(3)
1.25	12.356	1210( $\frac{1}{2}$ ), 1375( $5\frac{1}{2}$ )
1.50	12.352	1175( $\frac{1}{2}$ ), 1350(3)
1.75	12.346	1210( $\frac{1}{2}$ ), 1375( $5\frac{1}{2}$ )
2.00	12.341	1150(1), 1375( $5\frac{1}{2}$ )
2.40	12.333	1125( $\frac{1}{2}$ ), 1410(5), 1410(16)
2.50	12.332	1250( $\frac{1}{2}$ ), 1405(20)
2.60	12.329	1170( $\frac{1}{2}$ ), 1405(18)
2.75	12.327	1270( $\frac{1}{2}$ ), 1405(17)
3.00	12.321	1200( $\frac{1}{2}$ ), 1400(5)
5.00	12.274 <sup>a</sup>	

<sup>a</sup> From G. P. Espinosa, *Inorg. Chem.* **3**, 848 (1964).

<sup>b</sup> Numbers not in parentheses are firing temperatures, numbers in parentheses are firing periods; commas mean that the specimen was re-ground and recompact before the following firing.

TABLE II. Spontaneous moments  $n_B$ , in Bohr magnetons, of garnets in the  $Y_3Fe_{5-x}Ga_xO_{12}$  system.

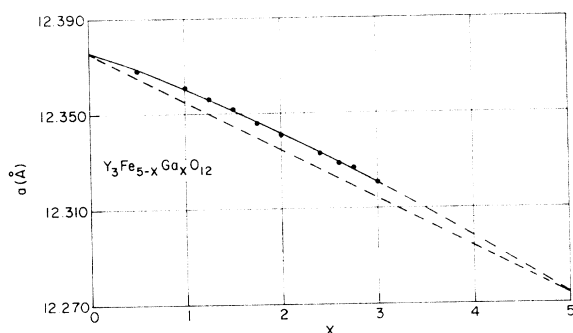
$x$	$n_B$ based on distribution of Table III and ideal Néel model	
	$n_B$	$n_B$
0.50	2.85	2.85
1.00	0.98	1.00
1.25	0.11	0.15
1.50	-0.45	-0.50
1.75	-0.98	-0.95
2.00	-1.17	-1.10
2.40	-0.67	-0.65
2.50	-0.27	-0.27
2.60	-0.33	-0.20
2.75	-0.13(?)	0.05
3.00	0(?)	0.50

FIG. 1. Spontaneous moment versus  $x$ .

plotted versus  $x$  in Fig. 1. Lattice constants are plotted versus  $x$  in Fig. 2.

### IONIC DISTRIBUTION

As in the case of the  $Y_3Fe_{5-x}Al_xO_{12}$  system,<sup>6</sup> we make use of Fig. 27 of Ref. 6 to determine the distribution of  $Ga^{3+}$  ions in the  $Y_3Fe_{5-x}Ga_xO_{12}$  system. In accordance with this figure<sup>9</sup> we rewrite the formula as  $\{Y_3\}[Fe_{2-x}Ga_x](Fe_{3-y}Ga_y)O_{12}$ , where now  $x+y$  replaces the  $x$  of the previously written formula. We look at a curve for the particular  $x+y$ , find the moment corresponding to that observed, and read off the value of  $f_t$ , the fraction of  $Ga^{3+}$  ions in tetrahedral sites, i.e.,  $y/(x+y)$ . The results are given in Table III and in

FIG. 2. Lattice constant versus  $x$ .

<sup>9</sup> It is necessary to use a more accurate plot than that of Fig. 27 of Ref. 6 to obtain accurate values of  $f_t$ . We have used the original plot, obtained from the data given in Ref. 6, from which Fig. 27 was taken.

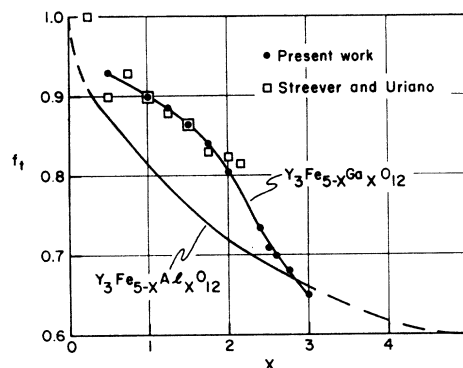
TABLE III. Fraction of  $Ga^{3+}$  ions  $f_t$  in tetrahedral sites in the  $Y_3Fe_{5-x}Ga_xO_{12}$  system.

$x$	$f_t$	$f_t$ (Streever and Uriano)
0.50	0.93	0.90
1.00	0.90	0.90
1.25	0.885	0.88
1.50	0.865	0.865
1.75	0.84	0.86
2.00	0.805	0.825
2.40	0.735	
2.50	0.71	
2.60	0.70	
2.75	0.68(?)	
3.00	0.65(?)	
5.00	0.60(required)	

Fig. 3 are plotted versus  $x$  as in  $Y_3Fe_{5-x}Ga_xO_{12}$ . (Values for  $x=2.75$  and  $3.00$  were estimated by extrapolation and the plausibility of the results confirmed by comparisons with results given in Ref. 6.)

Using the distributions found by the above means, a comparison has been made between the measured moments and those calculated on the basis of the Néel model.<sup>10</sup> Results are shown in Table II. Within the error of the determination of  $f_t$ , there appears to be no canting<sup>4</sup> of  $Fe^{3+}$  ions for  $x \leq 2.50$ . Essentially, this is as would be expected on the basis of the model given in Ref. 6. For decreasing  $f_t$  as  $x$  (i.e., total substitution) increases, one should expect increasing canting of  $d$ -site  $Fe^{3+}$  ions.

Shown also in Fig. 3 is the  $f_t$ -versus- $x$  curve for the  $Y_3Fe_{5-x}Al_xO_{12}$  system. For most of the range investigated, the  $Ga^{3+}$  ions have a substantially greater preference for tetrahedral sites than do the  $Al^{3+}$  ions. While it has been shown<sup>11</sup> why one might expect the  $Ga^{3+}$  ion to have a greater preference than the  $Fe^{3+}$  ion for tetrahedral sites, it would appear<sup>11</sup> that this preference would be about equal to but not greater than that of the  $Al^{3+}$  ion. We can offer no hypothesis as to why this

FIG. 3. Fraction  $f_t$  of  $Ga^{3+}$  and  $Al^{3+}$  ions in tetrahedral sites in  $Y_3Fe_{5-x}Ga_xO_{12}$  and  $Y_3Fe_{5-x}Al_xO_{12}$  (see Ref. 6), respectively.

<sup>10</sup> L. Néel, Ann. Phys. (Paris) 3, 137 (1948).

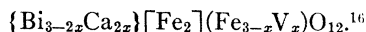
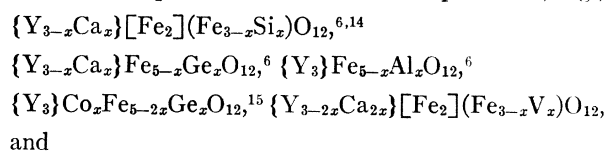
<sup>11</sup> S. Geller, J. Chem. Phys. 33, 676 (1960).

does not hold.<sup>12</sup> Figure 3, however, does indicate that at  $x \approx 2.75$  the  $f_t$ -versus- $x$  curves may cross or may be coincident beyond this point. Unfortunately, we cannot learn from static magnetic measurements anything about ionic distributions in specimens with  $x$  greater than 3.00. Furthermore, the accuracy desired is not attainable by means of x-ray diffraction analysis. It would seem to us to be worthwhile to know what the nature of the distribution of  $\text{Ga}^{3+}$  ions is in the range  $3.0 < x < 5.0$ . It appears from Fig. 3 that the  $f_t$ -versus- $x$  curve could actually cross the line  $f_t = 0.60$ , below which the  $\text{Ga}^{3+}$  ions would then actually be preferring octahedral sites. For the system  $\text{Y}_3\text{Fe}_{5-x}\text{Al}_x\text{O}_{12}$ , however, the curvature of the  $f_t$ -versus- $x$  curve indicates that  $f_t > 0.60$  over the whole range  $0 < x < 5.00$ .

### COMPOSITIONAL COMPENSATION POINT

Figure 1 shows that the value of  $x$  at which a zero spontaneous moment is attained in this system is 1.30. This is the point at which arithmetic equality of octahedral and tetrahedral sublattice magnetization occurs. Streever and Uriano<sup>5</sup> report compensation at  $x \approx 1.25$ ; however, if they had plotted their curve similarly to that of our Fig. 2, they would also have obtained the value of 1.30 for  $x$  at compensation. Lüthi and Henningsen<sup>4</sup> report compensation at  $x = 1.3$ ; Matthews, Singh, and LeCraw<sup>13</sup> report compensation at  $x \approx 1.25$ .

Matthews *et al.*<sup>13</sup> indicate that the  $\text{Y}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$  system is unusual in the respect that it has such a compositional compensation point. On the contrary, this phenomenon is not unique; in fact, several systems have been reported which exhibit compensation, e.g.,



Furthermore, there is no doubt that many more could be constructed: see Fig. 27 of Ref. 6.

### ADDITIONAL DISCUSSION

It has been shown<sup>17</sup> recently that spontaneous moments in this system appear to be sensitive to thermal treatment of the specimen. We have not attempted to investigate this. Except for the point at  $x = 2.50$ , the smoothness of the  $n_B$ -versus- $x$  curve for our data attest to its consistency. For comparison, we have plotted in Fig. 2 the data obtained by several other investigators.<sup>18</sup> To a value of  $x = 1.5$ , all these data

<sup>12</sup> The  $\text{Ga}^{3+}$  ion behaves strangely in another respect which is not understood. Perovskite-like compounds with  $\text{Y}^{3+}$ ,  $\text{Sm}^{3+}$ , and  $\text{Gd}^{3+}$  (and probably of smaller rare-earth) ions do not exist, while those of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  do [S. Geller and M. A. Gilleo, *Acta Cryst.* **10**, 239 (1957)]. Still another anomaly exists. Although the ionic radii of  $\text{Fe}^{3+}$ ,  $\text{Ga}^{3+}$  and  $\text{Al}^{3+}$  decrease in the order written, the  $\{\text{R}_3\}[\text{M}_2](\text{M}_3)\text{O}_{12}$  garnets exist as follows: for  $\text{Fe}^{3+}$ , the largest  $R$  is  $\text{Sm}^{3+}$  (that is,  $\{\text{Nd}_3\}[\text{Fe}_2](\text{Fe}_3)\text{O}_{12}$  does not exist); for  $\text{Ga}^{3+}$ ,

fall near our curve in such a manner that it would probably be the best curve for them.

Most of the other investigators give very little information regarding preparation. The probability, however, is small that the firing conditions of any two sets of data were the same. It will be noticed that four out of five points obtained by Anderson *et al.*<sup>3</sup> fall almost precisely on our curve; the one which does not is that for  $x = 0.4$ . In the region  $x \leq 1.5$ , two points from the Streever and Uriano work fall precisely on our curve; their values for  $x = 1.00$ , 1.25 and 1.50 differ by  $0.1\mu_B$  from ours, while that for  $x = 0.50$  differs by  $0.22\mu_B$  from ours. Noting these observations, we feel that at least for the region  $x \leq 1.00$ , the moment differences are caused less by a difference in thermal treatment than by imprecision in the compositions.

For  $x > 1.50$ , on the other hand, the differences in results may be caused by differences in heat treatment. Such sensitivity of ionic distribution to thermal treatment might account for the deviation of our point for  $x = 2.50$  of  $+0.18\mu_B$  from the curve for the system. This difference implies a difference of only 0.01 in  $f_t$  or of a shift of 0.02  $\text{Ga}^{3+}$  ion per formula unit from octahedral to tetrahedral sites.

For comparison, the  $f_t$  values obtained by Streever and Uriano are listed in Table III and plotted versus  $x$  in Fig. 3. Considering the differences in observed moments, one should expect some differences in  $f_t$ , but there should be none for  $x = 0.75$ . For their specimen with  $x = 0.50$  for a moment of  $3.07\mu_B$ , we would have  $f_t = 0.89$  compared with 0.90 found by them; for  $x = 2.00$ , we would have exactly the same  $f_t$  found by Streever and Uriano, and for  $x = 2.15$ , we would have  $f_t = 0.82$  compared with 0.815. Thus according to the moments obtained for *their* specimens, our values of  $f_t$  would be in excellent agreement with theirs.

The moments versus  $x$  obtained by Lüthi and Henningsen<sup>4</sup> are also plotted in Fig. 2. In general, again our method would in this case give very nearly the same  $f_t$ 's found by these authors using the first statistical treatment of Gilleo and Geller<sup>1</sup> (since modified further by Gilleo<sup>19</sup>). The reason that this method appears to work so well is the favorable distribution of  $\text{Ga}^{3+}$  ions, that is, in such manner that for the range of substitution to  $x \approx 2.50$ , these garnets behave essentially like ideal Néel ferrimagnets.

the largest  $R$  is  $\text{Pr}^{3+}$  (that is, both  $\text{Nd}_3\text{Ga}_2\text{Ga}_3\text{O}_{12}$  and  $\text{Pr}_3\text{Ga}_2\text{Ga}_3\text{O}_{12}$  do exist); for  $\text{Al}^{3+}$ , the largest  $R$  is  $\text{Gd}^{3+}$ .

<sup>13</sup> H. Matthews, S. Singh and R. C. LeCraw, *Appl. Phys. Letters* **7**, 165 (1965).

<sup>14</sup> G. A. Smolenskii, V. P. Polyakov and V. M. Iodin, *Izv. Akad. Nauk. SSSR, Ser. Fiz.* **25**, 1396 (1961).

<sup>15</sup> S. Geller, H. J. Williams, G. P. Espinosa, and R. C. Sherwood, *Phys. Rev.* **136**, A1650 (1964).

<sup>16</sup> S. Geller, G. P. Espinosa, H. J. Williams, R. C. Sherwood, and E. A. Nesbitt, *J. Appl. Phys.* **35**, 570 (1964).

<sup>17</sup> D. C. Leo, D. A. Lepores and J. W. Nielsen, *J. Appl. Phys.* **37**, 1083 (1966).

<sup>18</sup> Streever and Uriano (Ref. 5) do not give actual spontaneous moments. We have calculated these from their 4-4K sublattice moments and the  $\text{Ga}^{3+}$  ion distributions they obtained from NMR and magnetization measurements.

<sup>19</sup> M. A. Gilleo, *J. Phys. Chem. Solids* **13**, 33 (1960).