Magnetic Properties of Diamagnetic-Substituted Ytterbium Iron Garnet Explained by the Statistical Model of the Molecular Field. I. The Spontaneous Magnetization of Si-Ca-Substituted Ytterbium Iron Garnet

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The magnetic moments of the single-crystal garnets $Yb_{2.9-x}Bi_{0.1}Ca_xFe_{5-x}Si_xO_{12}$, with $0<x\leq 1.4$, have been determined between 4.2 and 295 °K, in magnetic fields up to 15 kOe. Using the molecular-field model and assuming a random distribution of the substituted ions with a random distribution of canting angles, the temperature dependence of the spontaneous magnetization of the Si-Ca-substituted ytterbium iron garnet (YbIG) was explained. A theoretical fit to the experimental results was obtained using the exchange parameters of pure YbIG, assuming they are the same for the substituted crystals.

I. INTRODUCTION

The interesting magnetic properties of the three-sublattice ferrimagnetic garnets and their application to microwave devices or bubble memories have stimulated much research on the growth and magnetic characterization of multication rare-earth iron garnet (*R*IG) crystals. The magnetic properties of pure *R*IG's were first measured and interpreted by Pauthenet,[1] using a collinear Néel ferrimagnetic model extended to three sublattices. Such a model does not fit the diamagnetically substituted ferrimagnetic *R*IG. In order to explain the deviation from the collinear model, Geller[2,3] in a phenomenological explanation, assumed the existence of canting angles in the iron sublattices, but did not provide a mathematical model to calculate the spontaneous magnetization.

Statistical models by Gilleo[4] and Borghese[5] failed to explain completely the variation of the spontaneous magnetization with composition at 4.2 °K. From semiempirical analyses of experimental magnetization-temperature curves of substituted yttrium iron garnet (YIG) and GdIG, Dionne[6,7] showed that good agreement between theory and experiment could be obtained if the molecular field coefficients were reduced with diamagnetic substitution. His results indicated that a linear relationship existed between the coefficients and the levels of substitution and that the effect was probably the result of increased canting in one sublattice caused by substitutions in the opposing sublattice.

Nowik[8,9] and Rosencwaig[10] were able to fit the experimental results of the spontaneous magnetization of substituted garnets at 4.2 °K by means of a statistical model that assumes a random distribution of substituted ions. While Nowik assumed the existence of a canting angle for the ions with only one magnetic first neighbor, Rosencwaig assumed a random distribution of canting angles. The experimental results fitted were mostly those of substituted YIG with only two magnetic sublattices.

The aim of the present work was to investigate theoretically the magnetic properties of a three-magnetic-sublattice garnet as a function of both diamagnetic substitution and temperature and to compare the results with experimental data. For these purposes Si-Ca-substituted YbIG single crystals were grown. The magnetic properties of these systems were investigated and explained theoretically. The measurements were done on single crystals in order to include the magnetic anisotropy of these crystals as part of the investigation.

II. THEORETICAL CONSIDERATIONS

Nowik[8,9] assumed that the diamagnetic substituted *R*IG can be considered a solid solution between the diamagnetic rare-earth garnet and the ferrimagnetic rare-earth garnet. The diamagnetic ions are randomly distributed and the number of magnetic neighbors of each ion in the garnet is variable. According to the molecular field model the temperature dependence of the magnetization of each lattice is given by a Brillouin function and one has to consider all the possible interactions due to the random distribution of the magnetic ions. According to Rosencwaig[10] we must also consider the distribution of canting angles.

The Si-Ca-substituted YbIG, with the formula of $\{Yb_{2.9-x}Ca_xBi_{0.1}\}[Fe_2](Fe_{3-x}Si_x)O_{12}$, has diamagnetic substitutions in sites $\{c\}$ and (d). The composition and temperature dependence of the spontaneous magnetization of these garnets is given in μ_B units by

$$M_0(x, T) = 15n_d(x)\sigma_d(x, T) - 10n_a(x)\sigma_a(x, T) - 5.035n_c(x)\sigma_c(x, T), \quad (1)$$

where $n_i(x)$ is the concentration of magnetic ions in site i, $\sigma_i(x, T)$ is the mean magnetization per ion in site i, and the value of 5.035 μ_B is taken for the magnetization of $3Yb^{3+}$ ions.[11]

In our case, we have

$$n_d(x) = \tfrac{1}{3}(3-x), \quad n_c(x) = \tfrac{1}{3}(2.9-x), \quad \text{and } n_a(x) = 1. \tag{2}$$

Considering the interactions of each magnetic ion with only its nearest and next nearest neighbors, the temperature dependence of the mean magnetization of each site σ_1 is given by

$$\sigma_a(x, T) = \sum_{m=0}^{N_{ad}} P_{ad}(m, x) \cos\phi_a(m, x)\, B_{2.5}(z_a(m, x, T)),$$

$$\sigma_d(x, T) = \sum_{m=0}^{N_{dd}} P_{dd}(m, x) \cos\phi_d(m, x)\, B_{2.5}(z_d(m, x, T)),$$

$$\sigma_c(x, T) = \sum_{m=0}^{N_{cd}} \sum_{m_1=0}^{N_{cc}} P_{cd}(m, x)\, P_{cc}(m_1, x) \cos\phi_c(m, x) \times B_{0.5}(m, m_1, x, T), \tag{3}$$

where $B_s(z)$ is the Brillouin function of spin s and argument z and $P_{ij}(m)$ is the probability that of N_{ij} neighbors j of ion in site i, m are diamagnetic and is given by

$$P_{ij}(m) = \binom{N_{ij}}{m} n_j^{N_{ij}-m} (1-n_j)^m. \tag{4}$$

The number of neighbors in the garnet used in the calculations is

$$N_{ad} = 6, \quad N_{aa} = 8, \quad N_{da} = 4, \quad N_{dd} = 4, \quad N_{cd} = 2, \quad N_{cc} = 4. \tag{5}$$

The arguments of the Brillouin functions in (3) are

$$\begin{aligned} z_a(m, x, T) &= (2/kT)[(N_{ad}-m) J_{ad} s_a s_d \sigma_d(x, T) \cos\phi_a(m, x) + N_{aa} J_{aa} s_a s_a \sigma_a(x, T) \cos\phi_a(m, x)], \\ z_d(m, x, T) &= (2/kT)[(N_{da} J_{ad} s_a s_d \sigma_d(x, T) \cos\phi_d(m, x) + (N_{dd}-m) J_{dd} s_d s_d \sigma_d(x, T) \cos\phi_d(m, x)], \\ z_c(m, m_1, x, T) &= (2/kT)[(N_{cd}-m) J_{cd} s_c s_d \sigma_d(x, T) \cos\phi_c(m, x) + (N_{cc}-m_1) J_{cc} s_c s_c \sigma_c(x, T) \cos\Phi_c(m, x), \end{aligned} \tag{6}$$

where J_{ij} is the exchange parameter of the interaction between the spin of the ion in site i and the spin of the ion in site j. We took, in the calculation,

$$-s_a = s_d = 2.5, \quad s_c = -0.5. \tag{7}$$

In (3) and (6), following Dionne[6] and Rosencwaig,[10] we took into consideration that the spins in sites $\{c\}$ and $[a]$ deviate from the mean direction of magnetization by a canting angle $\phi_{c,a}(m)$, due to the diamagnetic substitution in site (d). No canting of the ions in the (d) site occurs because there is no diamagnetic substitution in the $[a]$ site. Therefore $\cos\phi_d(m, x) = 1$.

According to Rosencwaig[10] the canting angles of spins in site $[a]$ are given by

$$\cos\phi_a(m, x) = \frac{S_{da} - S_{aa}\delta_a \cos\theta_a(x)}{[S_{da}^2 + (S_{aa}\delta_a)^2 - 2S_{da}S_{aa}\delta_a \cos\theta_a(x)]^{0.5}}, \tag{8}$$

where

$$S_{da}(m) = 2.5\,(N_{ad}-m), \quad S_{aa} = 2.5\,N_{aa}, \quad \delta_a = J_{aa}/J_{ad}. \tag{9}$$

θ_a is the mean canting angle of the spins in site $[a]$ and it is defined by formula (12) in Ref. 10. The canting angles of the spins $\{c\}$ are given by

$$\cos\phi_c(m, x) = \frac{S_{dc} - S_{cc}\delta_c \cos\theta_c(x)}{[S_{dc}^2 + (S_{cc}\delta_c)^2 - 2S_{dc}S_{cc}\delta_c \cos\theta_c(x)]^{0.5}}, \tag{10}$$

where

$$\begin{aligned} S_{dc}(m) &= 2.5\,(N_{cd}-m), \\ S_{cc}(x) &= N_{cc}\, n_c(x)\, 0.833, \\ \delta_c &= J_{cc}/J_{cd}. \end{aligned} \tag{11}$$

The value of 0.833 represents the spin of the Yb^{3+} ion, as compared with 2.5 for Fe^{3+}. The mean canting angle θ_c is given by

$$\cos\theta_c(x) = \sum_{m=0}^{N_{cd}} P_{cd}(m, x) \frac{N_{cd}-m}{2N'_{cc}} \frac{J_{cd}}{J_{cc}}; \qquad N'_{cc}(x) = N_{cc}\, n_c(x). \tag{12}$$

We mentioned before that we considered interactions with nearest- and next-nearest neighbors. This is correct for sites $[a]$ and (d) but the nearest neighbor of the $\{c\}$ ions are also (d) ions, followed by $[a]$ and $\{c\}$ ions. The interactions J_{cd} and J_{ca} are about the same magnitude and approximately cancel one another.

For sites $[a]$ and (d) we considered both intersite and intrasite interactions and we also took into account the intrasite exchange J_{cc} for the $\{c\}$ site. We shall see later that this provides a good fit to the experimental results.

III. EXPERIMENTAL PROCEDURE

Single crystals of the garnets $Yb_{2.9-x}Ca_xBi_{0.1}Fe_{5-x}Si_xO_{12}$, with $0 < x \leq 1.4$, were grown by the flux method. Details of growth procedure and compositional analysis are described elsewhere.[12,13] It was found that some of the Bi^{3+} ions used in the

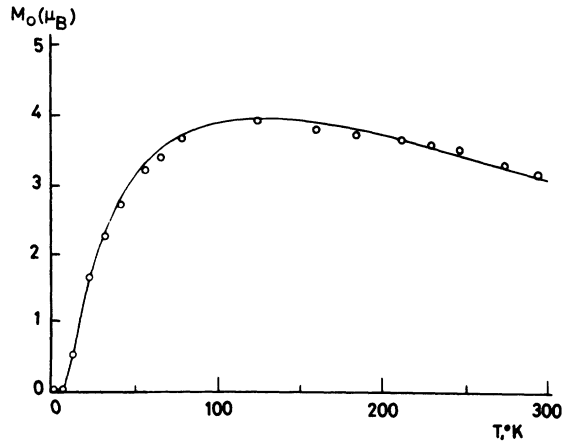

FIG. 1. Spontaneous magnetization of YbIG: line, calculated with parameters of Eq. (13); point, experimental results of Geller (Ref. 15).

flux entered into the crystals in concentrations of about 3 at.%. A similar result was reported earlier by Nielsen.[14] Due to the relatively large ionic radius of Bi^{3+} and Ca^{2+}, these ions go to the $\{c\}$ sites of the garnet. The Si^{4+} ion with a small radius goes into the (d) sites. Therefore, the formula of the garnet can be written as $\{Yb_{2.9-x}Bi_{0.1}\ Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$.

The magnetization of the grown crystals was measured with a null-coil-pendulum magnetometer, in magnetic fields between 2.5 and 15 KOe at temperatures between 4.2 and 295 °K. Due to the high anisotropy of the crystals the measurements were made along defined crystallographic directions. The easy direction is [111] in all measured crystals.

It was found that the magnetization M is linear with the field H over the ranges of fields and temperatures involved. The spontaneous magnetization was determined by extrapolation of the M-vs-H curve to zero field.

TABLE I. Canting angles of $Yb_{2.9-x}Bi_{0.1}Ca_xFe_{5-x}Si_xO_{12}$ as a function of the number of magnetic nearest neighbors. (Only angles with probability higher than 1%.)

x	No. of neighbors	ψ_a(deg.) 0	1	2	3	4	ψ_c(deg.) 0
0.54							−15
0.80				2			−22
0.94				4	22		−25
1.035				5	27		−28
1.4		4	6	10	43	−16	−38

IV. RESULTS AND DISCUSSION

A. Exchange Parameters

In order to calculate the temperature dependence of the spontaneous magnetization we have to know the values of the exchange parameters. These parameters were calculated by fitting Eqs. (1) and (3) to the experimental results of the spontaneous magnetization of pure YbIG, obtained by Geller *et al.*[15] The following parameters were obtained:

$$J_{ad}=34;\quad J_{dd}=13.6,\quad J_{aa}=3.4,$$
$$J_{cd}=2.2;\quad J_{cc}=0.29,\quad J_{ca}=0\,^\circ\mathrm{K}. \tag{13}$$

Figure 1 shows the experimental points of Geller[15] with the curve calculated with the above parameters. The calculated compensation point was $T_{cp}=6.4\,^\circ$K as compared with $T_{cp}=6\,^\circ$K of Geller[15] and $T_{cp}=7.6\,^\circ$K of Henderson.[16]

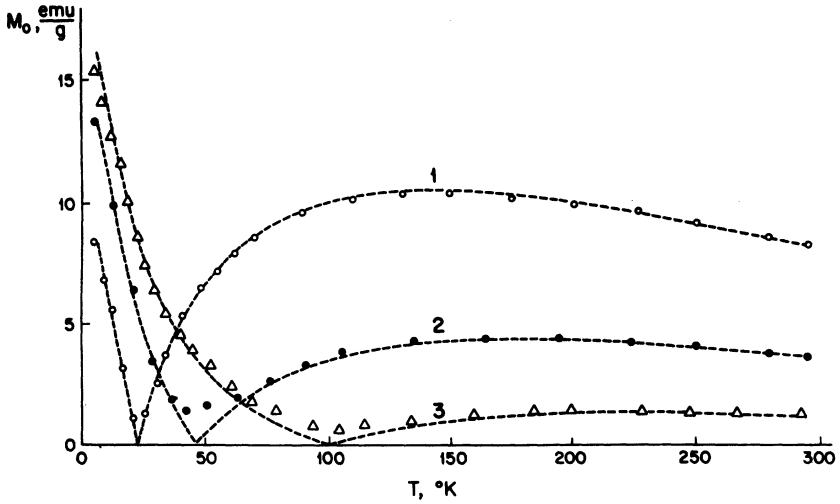

FIG. 2. Spontaneous magnetization of $Yb_{2.9-x}Bi_{0.1}Ca_xFe_{5-x}Si_xO_{12}$, in direction [111]: points, experimental results; lines, calculated curves. $1-x=0.54$; $2-x=0.80$; $3-x=0.94$.

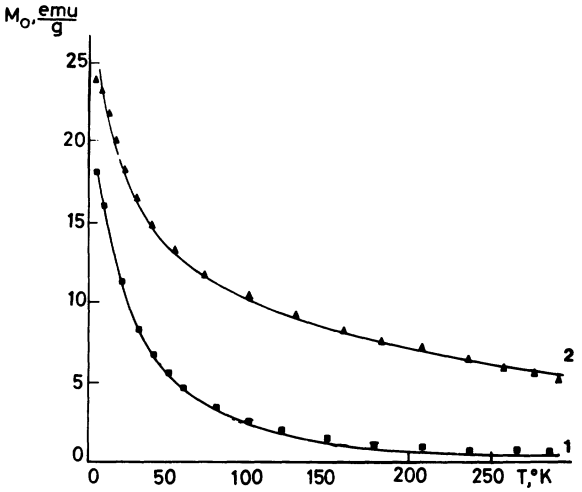

FIG. 3. Spontaneous magnetization of $Yb_{2.9-x}Bi_{0.1}Ca_xFe_{5-x}Si_xO_{12}$, in direction [111]: points, experimental results; lines, calculated curves. $1-x=1.035$, $2-x=1.4$.

B. Spontaneous Magnetization

The spontaneous magnetization of the Si-Ca-substituted YbIG crystals could be calculated using Eqs. (1) and (3), with the exchange parameters obtained above and the number of neighbors given by Eq. (5). The diamagnetic substitution could change the exchange parameters by changing the length of the bonds M-O, M'-O, and the angle between the two bonds M-O-M', M and M' being two magnetic cations. These quantities are changed very little in our case, as it results from the changes in the unit-cell dimensions of the garnets. We assumed, therefore, that the exchange parameters are the same for all substituted YbIG crystals and made the calculations with the parameters obtained from pure YbIG.

Equations (3) are implicit equations of the σ_i's at each temperature. The solution of the σ_i's was calculated between 0 and 300 °K, at each degree, using an iteration method. We started with $\sigma_a^0=\sigma_d^0=\sigma_c^0=1$ at 0 °K, and at each temperature T we started the iterations by taking $\sigma_i^0(T)=\sigma_i(T-1)$, where $\sigma_i(T-1)$ is the solution of Eqs. (3) at temperature $T-1$. The calculated curves of the spontaneous magnetization of the Si-Ca–substituted YbIG are shown together with the experimental results in Figs. 2 and 3. It may be seen from these figures that good agreement is obtained between the calculated curves and the experimental results for each crystal investigated, justifying our assumption that the J_{ij} remain unchanged with diamagnetic substitution.

Table I shows the canting angles of the spins in sites $[a]$ and $\{c\}$ which contribute to the spontaneous magnetization, i.e., which have a probability higher than 1%. The canting angles are shown as a function of the number of the nearest neighbors of the respective ions. Table II shows a comparison between the experimental values of the spontaneous magnetization at 4.2 °K and the values calculated according to the different models mentioned in Sec. I. It can be seen that the best fit to the experimental results is given by the statistical model of the molecular field with a distribution of canting angles. From columns 3 and 4 it can be seen that from x about 1, one gets significant differences between the canted spin model and the statistical collinear model. This results from the values of the canting angles as shown in Table I. It should also be mentioned that these differences increase with increasing temperatures and increasing values of x. From Figs. 2 and 3 one can conclude that the statistical model with canted spins provides a good explanation of the experimental results.

TABLE II. Spontaneous magnetization M_0 of $Yb_{2.9-x}Bi_{0.1}Ca_xFe_{5-x}Si_xO_{12}$, at 4.2 °K (in μ_B units).

	M_0, calculated				
x	Néel	Gilleo	Nowik[a]	Rosencwaig	M_0 expt.
0.54	1.65	0.35	1.38	1.38	1.38
0.80	2.55	0.85	2.09	2.08	2.08
0.95	2.90	1.07	2.47	2.46	2.38
1.035	3.00	1.27	2.72	2.69	2.68
1.40	0.45	1.92	3.62	3.38	3.31

[a]Without canting.

V. CONCLUSIONS

Using the statistical model of the molecular field with the assumption of a random distribution of canting angles, we explained the spontaneous magnetization of garnet crystals of the type $Yb_{2.9-x}Bi_{0.1}Ca_xFe_{5-x}Si_xO_{12}$ for temperatures between 4.2 and 295 °K and for $0<x\leq 1.4$. The spontaneous magnetization was calculated for all values of x, with the exchange parameters of pure YbIG.

Note added in proof. Preliminary Mössbauer results obtained by Professor I. Nowik, from the Hebrew University, show that substituted ions with different charges do not distribute at random but are distributed to maintain charge equilibrium. The statistics have to be revised accordingly, especially if one makes larger substitutions.

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Magnetic Properties of Diamagnetic-Substituted Ytterbium Iron Garnet Explained by the Statistical Model of the Molecular Field. II. Spontaneous Magnetization of Ga-Substituted Ytterbium Iron Garnet

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The magnetic moments of the single-crystal garnets $Yb_3Ga_xFe_{5-x}O_{12}$, with $0<x\leq 3.75$, have been determined between 4.2 and 295 °K, in magnetic fields up to 15 kOe. Using the statistical-molecular-field model, the temperature dependence of the spontaneous magnetization of Ga-substituted ytterbium iron garnet (YbIG) could be explained for all compositions for temperatures lower than $0.7T_C$, where T_C is the Curie temperature of the crystal. The theoretical fit to the experimental results was obtained using the exchange parameters of YbIG.

I. INTRODUCTION

In Paper I,[1] we explained the spontaneous magnetization of diamagnetic-substituted ytterbium iron garnet (YbIG) with diamagnetic substitution in only one site of the iron. We investigated the $Yb_{2.9-x}Bi_{0.1}Ca_xFe_{5-x}Si_xO_{12}$ system which was prepared with $0<x\leq 1.4$. The aim of this work was to investigate the spontaneous magnetization of diamagnetically substituted YbIG for higher concentrations of diamagnetic ions and for simultaneous diamagnetic substitutions into both iron sites.

For this purpose, Ga-substituted YbIG single crystals were grown. The Ga^{3+} ion, which has an ionic radius near that of Fe^{3+}, enters in both $[a]$ and (d) sites, with a strong preference for the (d) site. Since the $Yb_3Ga_xFe_{5-x}O_{12}$ crystals with $x>2$ have Curie points below room temperature, we could investigate the magnetization properties in the vicinity of the Curie temperature.

II. THEORETICAL CONSIDERATIONS

The formula of the garnet can be written as $\{Yb_3\}[Fe_{2-x_a}Ga_{x_a}](Fe_{3-x_d}Ga_{x_d})O_{12}$, with $x=x_a+x_d$, since the Ga^{3+} ions substitute for Fe^{3+} ions in both (d) and $[a]$ sites. The fraction $f=x_d/x$ of the tetrahedral Ga^{3+} ions varies with x from about 0.93 for small x to 0.60 for $x=5$.[2] The spontaneous magnetization of the garnet is given, in μ_B, by

$$M_0(x,T)=15n_d(x_d)\sigma_d(x,T)-10n_a(x_a)\sigma_a(x,T)-5n_c(x_c)\sigma_c(x,T), \quad (1)$$

with

$$n_a(x_a)=\tfrac{1}{2}(2-x_a),\quad n_d(x_d)=\tfrac{1}{3}(3-x_d),\quad \text{and } n_c(x_c)=1. \quad (2)$$

The temperature dependence of the mean magnetization of each site is given by

$$\sigma_a(x,T)=\sum_{m=0}^{N_{ad}}\sum_{m_1=0}^{N_{aa}}P_{ad}(m)P_{aa}(m_1)\cos\phi_a(m)\times B_{2.5}(z_a(m_i,x,T)),$$

$$\sigma_d(x,T)=\sum_{m=0}^{N_{da}}\sum_{m_1=0}^{N_{dd}}P_{da}(m)P_{dd}(m_1)\cos\phi_d(m)\times B_{2.5}(z_d(m_i,x,T)), \quad (3)$$

$$\sigma_c(x,T)=\sum_{m=0}^{N_{cd}}P_{cd}(m)\cos\phi_c(m)\,B_{0.5}(z_c(m,x,T)),$$

with the arguments of the Brillouin functions