where $(Q_{11}+2Q_{12})_0$ is the value of the striction constants at zero temperature and α is the temperature coefficient.

Equation (6) has the form of a Curie-Weiss law, i.e.,

$$\epsilon = C/(T-T_\theta),$$

with

$$C=\frac{4\pi C_0}{4\pi+2\sigma\alpha(Q_{11}+2Q_{12})_0 C_0} \tag{7}$$

and

$$T_\theta=\frac{4\pi T_0-2\sigma(Q_{11}+2Q_{12})_0 C_0}{4\pi+2\sigma\alpha(Q_{11}+2Q_{12})_0 C_0}. \tag{8}$$

From Eq. (7),

$$(1/C^2)(\delta C/\delta\sigma) = -(1/4\pi)2\alpha(Q_{11}+2Q_{12})_0$$

or

$$\alpha = -2\pi(Q_{11}+2Q_{12})_0^{-1}(1/C^2)\delta C/\delta\sigma.$$

Using Samara's tabulated data for $1/C^2$ and $\delta C/\delta\sigma$ for single crystals (Table I of Ref. 6), we may deduce a value of $\alpha\simeq+1.2\times10^{-3}$ °K^{-1}.

This temperature dependence is much too weak to detect from direct measurements of the striction constants, which are at best accurate to $\pm10\%$, but provides a very simple explanation for the observed change in Curie constant with hydrostatic stress.

PHYSICAL REVIEW VOLUME 171, NUMBER 2 10 JULY 1968

Molecular-Field Theory for Randomly Substituted Ferrimagnetic Garnet Systems*

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(Received 27 December 1967)

The proposed model is capable of reproducing, with no adjustable parameters, the substitution dependence of the magnetic moment at 0°K of various substituted rare-earth iron garnets. Maxima in the temperature dependence of the moments are predicted and agree with experimental observations. The model also predicts that the hyperfine field in these systems has a different temperature and substitution dependence from that of the corresponding sublattice magnetization.

INTRODUCTION

SUBSTITUTED rare-earth iron garnets (IG) show a wide variety of interesting magnetic properties.[1–5] Theoretical models for these systems, one based on Néel's[6] model, another suggested by de Gennes[7] based on Yafet and Kittel's model,[8] and one suggested by Gilleo,[9] show little agreement with experimental observations.[3] In this paper, an extremely simple statistical local-molecular-field model is suggested, which is capable of reproducing the substitution dependence of the magnetic moment at 0°K of many substituted rare-earth IG systems. At 0°K, the theory has no adjustable parameters, although certain inequalities have to be fulfilled among the various exchange parameters. The theory predicts maxima in the temperature dependence of the moments of certain systems, in complete agreement with experimental observations. The model also predicts that the hyperfine field in these systems has a different temperature and substitution dependence from that of the corresponding sublattice magnetization.

MODEL

The formula unit for the system in which we are interested is customarily written as

$$\{Cc_zR_{3-z}\}[A_y\mathrm{Fe}_{2-y}](D_x\mathrm{Fe}_{3-x})\mathrm{O}_{12}. \tag{1}$$

Cc is a diamagnetic substitute for the magnetic rare earth R, located in the dodecahedral "c" site. A is a diamagnetic substitute for the iron in the octahedral "a" site. D is a diamagnetic substitute for the iron in the tetrahedral "d" site. In Table I, the number of equivalent nearest neighbors and exchange parameters for the various sites are given.

* Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U.S. Air Force, under AFOSR Grant No. AF-AFOSR-1258-67.

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TABLE I. Number of equivalent neighbors and strength of exchange in °K.

Site				
a	$6d$ $J_{ad}=-35^{a}$ -36.6^{c} -32.5^{e}	$8a$ $J_{aa}=-8.2^{a}$ -11.2^{c} -0.7		$6c$ $J_{ac}=-0.015^{b}$ -0.3^{d}
d	$4a$ $J_{da}=J_{ad}$	$4d$ $J_{dd}=-15.0^{a}$ -15.8^{c} -2.8^{e}	$2c$ $J_{dc1}=-4.0^{f}$	$4c$ $J_{dc2}=-0.3^{f}$
c	$2d$ $J_{cd1}=J_{dc1}$	$4d$ $J_{cd2}=J_{dc2}$	$4a$ $J_{ca}=J_{ac}$	$4c$ $J_{cc}=+0.05^{b}$ -0.19^{d}

[a] Reference 12.
[b] Reference 16.
[c] Reference 18.
[d] Reference 17.
[e] Reference 13.
[f] References 11 and 15.

Our molecular-field equations for the system expressed by formula 1, taking into account interactions up to fourth-nearest neighbor, are the following:

$$\sigma_i(T)=\frac{\langle S_i^z\rangle}{S_i}=\sum_{m_1m_2m_3m_4=0}^{N_{1i}N_{2i}N_{3i}N_{4i}} P(N_{1i},m_1)P(N_{2i},m_2)P(N_{3i},m_3)P(N_{4i},m_4)B_{S_i}(z_i), \qquad i=a,d,c, \quad (2)$$

where

$$kTz_i=2\sum_{j=1}^{4} m_jJ_{ij}S_iS_j\sigma_j(T)+g\beta S_iH. \quad (3)$$

J_{ij} are exchange parameters (Table I), H is an external magnetic field, and $B_S(z)$ is a simple Brillouin function for spin S. N_{ji} is the number of equivalent jth nearest neighbors to the ith site. $P(N_{ji}, m_j)$ is the probability that out of the N_{ji} equivalent neighboring sites, m_j are filled with magnetic ions. $P(N_{ji}, m_j)$ is a simple binomial expression in $n_c=(3-z)/3$, $n_d=(3-x)/3$ or $n_a=(2-y)/2$.

Equations (2) have an especially simple form at 0°K. At 0°K, the function $B_S(z)$ is 1 for $z>0$ and -1 for $z<0$. Thus $\sigma_i(0°K)$ is almost independent of the exact values of J_{ij}; only their relative values will decide, for a certain combination $(m_1, m_2, m_3, m_4,)$ the sign of z_i.[10] The total magnetic moment, per formula unit of a substituted rare-earth IG will be given in the present model by

$$M/N\beta=15n_d\sigma_d-10n_a\sigma_a-3\mu_Rn_c\sigma_c, \quad (4)$$

where μ_R is the expectation value of the rare-earth ionic moment at 0°K.

SUBSTITUTED YTTRIUM IG

For substituted yttrium IG, only two inequalities have to be fulfilled in order to get the theoretical curves shown in Figs. 1 and 2. These inequalities are (J_{ij} are negative)

$$-8J_{aa}<-J_{ad},$$
$$-4J_{dd}<-J_{ad}. \quad (5)$$

The physical meaning of these inequalities is that the intersublattice exchange with a single neighbor is larger than the intrasublattice exchange with all the nearest neighbors. Thus, if an ion at the site "a" has a single "d"

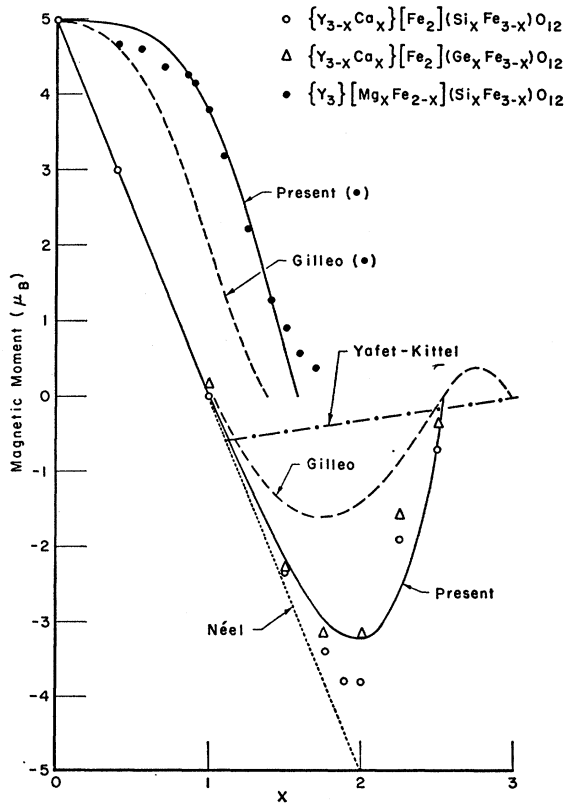

FIG. 1. Theoretical and experimental behavior of the magnetic moment at 0°K of the systems $\{Y_3\}[Fe_2](D_xFe_{3-x})O_{12}$ and $\{Y_3\}[A_xFe_{2-x}](D_xFe_{3-x})O_{12}$.

[10] The word "almost" was used because at high substitutions, the solution of Eqs. (2) will depend on the exact values of J_{ij}.

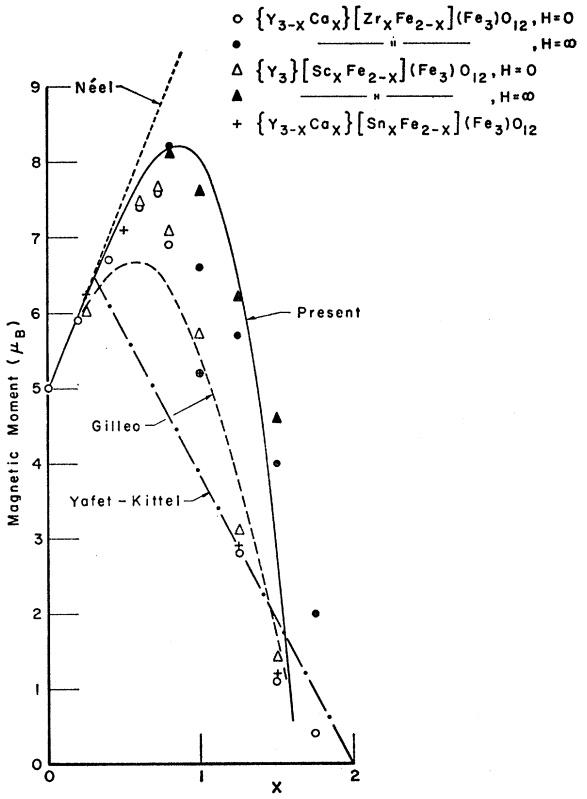

FIG. 2. Theoretical and experimental behavior of the magnetic moment at 0°K of the system $\{Y_3\}[A_xFe_{2-x}](Fe_3)O_{12}$.

neighbor, it will point opposite to the "d" sublattice magnetization, but if no "d" first-nearest neighbors are present, it will point opposite to the "a" sublattice magnetization (parallel to the "d" sublattice magnetization) because of the intrasublattice exchange. In the present model, an ion at the "a" (or "d") site can have either direction, depending on how the nearest-neighbor sites are occupied. Thus, the average sublattice magnetization σ_a (or σ_d) (Eq. 2) can be smaller than 1, even at 0°K.

SUBSTITUTED EuIG AND GdIG

In the case when the "c" site is occupied by a magnetic ion (Gd or Eu in Figs. 3 and 4), fair agreement with experimental results is obtained if the following additional inequalities are fulfilled:

$$\begin{aligned} -4J_{dd} &< -J_{dc1}, \\ -4J_{cc} &< -J_{dc1}, \\ -4J_{ac} &< -J_{dc2}, \\ -6J_{ac} &< -J_{aa}. \end{aligned} \qquad (6)$$

The physical meaning of these inequalities is similar to that of the inequalities (5). These are sufficient but by no means necessary conditions to obtain agreement with the experimental observations. It is possible that some of the inequalities could be changed or restricted, to improve the agreement with the experimental results.

The experimental results for the concentration dependence of the sample $\{Gd_3\}[Fe_{2-x}Sc_x](Fe_3)O_{12}$ led Geller[3] to the conclusion that the Gd magnetic moments are canted. He came to this conclusion because the behavior of the magnetic moment of the above sample was not that of three times the Gd moment minus the moment of $\{Y_3\}[Fe_{2-x}Sc_x](Fe_3)O_{12}$. Our model rules out such an expectation. GdIG is not just YIG plus Gd in a passive role. The presence of the Gd changes the direction of the moments in the "d" site. For example, an ion in the "d" site with no first-nearest neighbors on the "a" site will point opposite to the average "d" sublattice magnetization in the case of YIG; but in GdIG, owing to the antiferromagnetic exchange with the Gd, it will point parallel to the average "d" sublattice magnetization. Thus, in the present model, no canting has to be invoked to explain the results of $Gd_3[Sc_xFe_{2-x}]Fe_3O_{12}$.

COMPARISON BETWEEN PRESENT AND PREVIOUS MODELS

The failure of Gilleo's model[9] at 0°K is not surprising. He assumes the existence of paramagnetic centers whenever the center has less than two magnetic

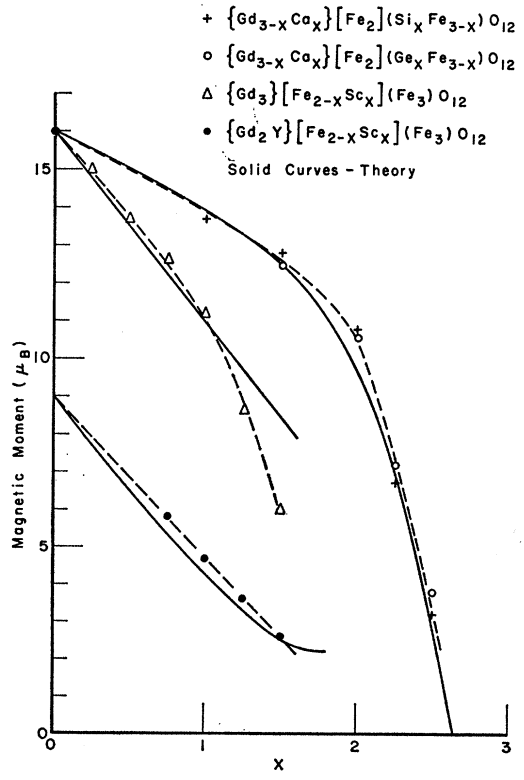

FIG. 3. Theoretical and experimental behavior of the magnetic moment at 0°K of the systems $\{Cc_xGd_{3-x}\}[Fe_2](D_xFe_{3-x})O_{12}$, $\{Gd_3\}[A_xFe_{2-x}](Fe_3)O_{12}$, and $\{YGd_2\}[A_xFe_{2-x}](Fe_3)O_{12}$.

first-nearest neighbors. This is obviously wrong. There is experimental evidence that such paramagnetic centers do not exist even at 4.2°K. In the Mössbauer spectra of $Eu_3Ga_{3.03}Fe_{1.97}O_{12}$,[11] there is no indication of the existence of paramagnetic centers (according to Gilleo more than 20% of the iron had to be paramagnetic). Theoretically, at 0°K all moments have to be ordered because of exchange with farther neighbors. It is worthwhile to point out that use of Gilleo's model to obtain the relative amounts of substitutes in the "a" and "d" sites will certainly yield wrong results.[4,5] The best way to establish the relative amounts of substitutes in the "a" and "d" sites of a rare-earth IG is by the Mössbauer effect method.[11]

The model given by Yafet and Kittel for ferrites has limited success in the case of the substituted garnet systems.[3] The reason for this is that the random substitution destroys the translational symmetry of the crystal; there are no well-defined magnetic or chemical unit cells. Because of the short-range exchange interactions, intrasublattice coherence and long-range correlations are destroyed, and a macroscopic molecular-field model is not applicable. However, in metals, long-range correlations are preserved by the conduction electrons, and thus Yafet and Kittel's model might be applicable in alloys.[7]

Although Yafet and Kittel's model, as applied by de Gennes,[7] seems simpler than the present model, it is not parameter-independent even at 0°K. The concentration dependence of the magnetic moment at 0°K is a function of the exact ratio of the exchange parameters (in Figs. 1 and 2, the ratios from Ref. 12 were used; the ratios from Ref. 13 give slightly better agreement in Fig. 1 but much worse in Fig. 2).

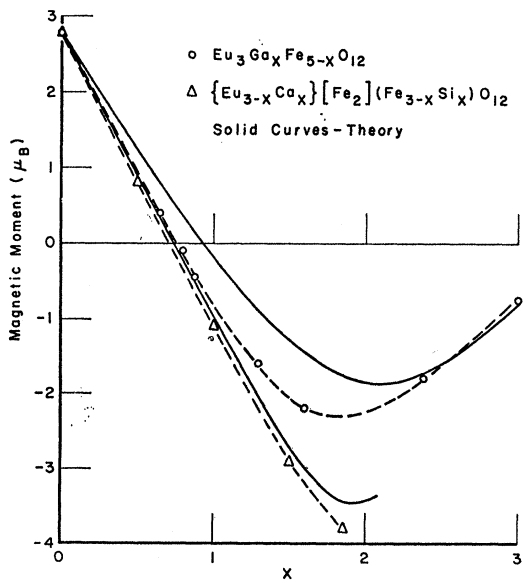

FIG. 4. Theoretical and experimental behavior of the magnetic moment at 0°K of the systems $\{Ca_xEu_{3-x}\}[Fe_2](D_xFe_{3-x})O_{12}$ and $\{Eu_3\}[A_yFe_{2-y}](D_zFe_{3-z})O_{12}$.

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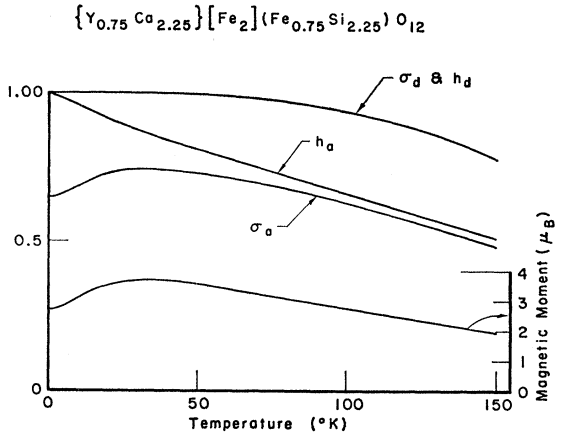

FIG. 5. Theoretical temperature dependence of σ_a, σ_d, h_a, h_d and the total magnetic moment of the system $\{Y_3\}[Fe_2](D_{2.25}Fe_{0.75})O_{12}$.

Our model requires certain inequalities among the various exchange interactions. The exchange parameters given in Refs. 11, 13–17 fulfill most of these inequalities. Exchange parameters deduced from high-temperature measurements using a molecular-field model do not fulfill these inequalities.[12,18] Since we are interested mainly in the behavior close to 0°K, the parameters from Refs. 11 and 13–17 are the most reliable.

TEMPERATURE AND SUBSTITUTION DEPENDENCE OF HYPERFINE FIELDS AND SUBLATTICE MAGNETIZATION

In randomly substituted ferrimagnets, the measured hyperfine fields (by Mössbauer effect or spin echo techniques) acting on the nuclei of the magnetic ions have no simple correlation with the corresponding sublattice magnetization. Since the measured hyperfine fields are signless quantities (both signs give the same Mössbauer spectrum), the measured average hyperfine field $h_i(T)$ corresponding to $\sigma_i(T)$ is given by

$$h_i(T) = \sum_{m_1m_2m_3m_4} P(N_{1i}, m_1)\,P(N_{2i}, m_2)\,P(N_{3i}, m_3) \times P(N_{4i}, m_4)\,|\,B_{S_i}(z_i)\,| \qquad (7)$$

and thus $h_i(T)$ has a completely different dependence on substitution and temperature. The interpretation of hyperfine field measurements in such systems is not

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simple.[4] The hyperfine field is obviously not proportional to the sublattice magnetization (Fig. 5).

In Fig. 5 we also show the temperature dependence of the magnetic moment of the substituted garnet system $\{Y_3\}[Fe_2](D_{2.75}Fe_{0.75})O_{12}$, calculated by the persent model, using the exchange coupling constants of Ref. 13. The magnetic moment rises with temperature, reaches a maximum at 37°K, and then decreases. Such phenomena were observed in many garnet systems and never explained.[1–3] In fact, the sample $\{Y_{0.75}Ga_{2.25}\}$-$[Fe_2]$ $(Fe_{0.75}Si_{2.25})O_{12}$ has exactly the behavior predicted by our model in Fig. 5. The explanation of these maxima in the temperature dependence of the magnetic moments is very simple. Those ions in the "a" site, whose magnetic moments are opposite to the average "a" site sublattice magnetization, are coupled oppositely only by weak intrasublattice exchange. When the temperature is raised from 0°K, the magnetic moments of these ions decrease rapidly and thus the average "a" sublattice moment increases. This increase competes with the general decrease of the magnetic moments, and thus a maximum is obtained in the temperature dependence.

In the present model we assumed perfect parallel or antiparallel ordering of single-ion spins at 0°K. This might be an oversimplification. Canting like that in the YK model[8] might exist. The existence or nonexistence of canted local spins can be easily checked experimentally by performing Mössbauer studies on single crystals of substituted garnets. If no local canting exists, then, when the γ ray is parallel to the easy magnetization direction, all $\Delta m=0$ absorption lines will disappear in the Mössbauer spectrum.

TRANSITION TEMPERATURES

Solving Eqs. (2) at the limit of high temperatures, one gets formulas for the critical transition temperatures. For the yttrium-substituted IG system, the transition temperature is given by

$$T_N(n_a, n_d) = (35/12)\{-4J_{dd}n_d-8J_{aa}n_a\pm[96J_{ad}n_an_d + (4J_{dd}n_d-8J_{aa}n_a)^2]^{1/2}\}. \quad (8)$$

This result is in agreement with previous formulas in which J_{aa} and J_{dd} were assumed to be zero.[4,19] There it was assumed that

$$T_N(n_a, n_d) = CJ_{ad}(n_an_d)^{1/2}, \quad (9)$$

where C is the experimental Curie constant for pure YIG. Transition points, predicted by Eqs. 8 or 9, are not in agreement with experimental Néel points over the entire range of substitution.

The failure of the model in predicting Néel points in contrast to its success in predicting the magnetic moment at 0°K is not surprising. To predict the Néel points, one needs a more exact model and also good knowledge of the substitution dependence of the exchange parameters. On the other hand, at 0°K, the calculation of the magnetic moment in our model is reduced to a simple count of the number of localized magnetic moments pointing either up or down. Thus, one expects good agreement with experimental results.

To summarize, one can say that the suggested model is able to explain many properties and previously unexplained phenomena of randomly substituted ferrimagnetic garnet systems. It is also shown that in such systems, hyperfine fields and sublattice magnetizations are not proportional quantities.

ACKNOWLEDGMENTS

I am grateful to Dr. P. M. Levy for useful discussions, for critical reading of the manuscript, and for supporting this research through his contract.

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