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Nuclear Resonance Study of Gallium-Substituted Yttrium Iron Garnet

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Nuclear-magnetic-resonance (NMR) studies have been made of ^{57}Fe and of ^{69}Ga and ^{71}Ga in gallium-substituted yttrium iron garnet (YIG) as a function of gallium substitution at several temperatures. At 4°K the ^{57}Fe studies were made up to 43% gallium substitution, while the gallium nmr studies were made up to 55% substitution. Net-magnetization studies have also been made at 77°K up to gallium substitutions of 53%. From the ^{57}Fe nmr studies, as well as the net-magnetization studies, we have obtained approximately the site distribution of the iron ions and the magnetizations for the two sublattices. From the experimental concentration dependence of the ^{71}Ga hyperfine field we find that in pure YIG in the low-temperature limit the contribution to the Ga hyperfine field at the *d* site from iron ions on neighboring *d* sites is 0.57 of the contribution from neighboring *a* sites and oppositely directed.

I. INTRODUCTION

MANY studies have been made of the magnetic and crystallographic properties of the magnetic iron garnets. Studies have been made of the crystal structure of pure yttrium iron garnet (YIG) and also the magnetic- and crystallographic-properties of YIG with various nonmagnetic ions substituted for the iron.[1–5] The iron ions occupy both *a* (octahedral) and *d* (tetrahedral) sites in the garnet lattice. The ^{57}Fe hyperfine field in pure YIG at both the *a* and *d* sites was first determined by Mössbauer measurements.[6] The ^{57}Fe nuclear magnetic resonance (NMR) was then studied in the pure YIG[7] and the temperature dependence of the resonance frequencies at the two sites was determined.

We have studied the ^{57}Fe nuclear magnetic resonance as a function of gallium concentration in gallium-substituted yttrium iron garnet. Preliminary results have been reported previously.[8] Studies of the ^{69}Ga and ^{71}Ga nuclear magnetic resonances, which were the subject of a previous paper,[9] have been completed and are discussed in this paper, along with the ^{57}Fe results. We have also measured the net magnetization of gallium-substituted YIG as a function of gallium concentration up to higher concentrations than previously reported.[2,4,5]

Solid solutions of YIG with yttrium gallium garnet can be formed over the entire concentration range. The formula for these mixed garnets can be written

$$3\mathrm{Y_2O_3}\cdot(5-x)\mathrm{Fe_2O_3}\cdot x\mathrm{Ga_2O_3}. \tag{1}$$

Here $x/5$ is the fractional number of substituted gallium ions. In the garnet structure both *a* and *d* sites are available for the iron or gallium ions. The ratio of *d* to *a* sites is 3 to 2. The iron ions on these sites are antiferromagnetically aligned. Thus, in pure YIG a net magnetization results along the direction of the *d* sublattice. Equation (1) can be written:

$$\mathrm{Y_3[Fe_{2-y}Ga_y](Fe_{3-z}Ga_z)O_{12}}, \tag{2}$$

where $x=y+z$. Here $y/2$ and $z/3$ are the fractional number of gallium ions which substitute onto *a* and *d* sites, respectively. The ions on *a* sites are enclosed by square brackets and those on *d* sites by curved brackets.

A gallium substitution can in general occur on either the *a* or *d* sites. However, the net-magnetization studies at low temperatures show that the net magnetization decreases approximately linearly with gallium substitution, approaching zero at about $x=1.25$. In order to explain this result, one must assume that the nonmagnetic gallium ions substitute preferentially onto the *d* sites.

In disordered materials, such as these, the resonance lines are inhomogeneously broadened by a distribution of hyperfine fields. For these wide lines we have obtained the NMR spectra by plotting the amplitude of the spin-echo signal as a function of frequency across the inhomogeneously broadened lines. The main contribution to the hyperfine field at ^{57}Fe nuclei in these materials is proportional to the component of electronic spin of its parent ion along the quantization direction. If we let $\langle S_i \rangle$ be the expectation value of the electronic spin along the quantization direction for an ion on the *i*th sublattice, then the nuclear-resonance spectra provide information concerning $\langle S_i \rangle$ for iron ions with various neighbor environments.

The net magnetization depends not only on the values of $\langle S_i \rangle$ on individual iron ions, but on the distribution of iron ions on the two sublattices, so that the net-magnetization studies, together with the NMR results, allow us to determine the approximate distribution of of iron ions on the two sublattices. The hyperfine field at the gallium site is dependent on the number of iron ions on neighboring *a* and *d* sites so that the information obtained from the ^{57}Fe NMR studies and the net-

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[1] S. Geller and M. A. Gilleo, J. Phys. Chem. Solids **3**, 30 (1957).
[2] M. A. Gilleo and S. Geller, Phys. Rev. **110**, 73 (1958).
[3] M. A. Gilleo, J. Phys. Chem. Solids **13**, 33 (1960).
[4] E. E. Anderson *et al.*, J. Phys. Soc. Japan Suppl. **17**, 365 (1962).
[5] G. Villers *et al.*, J. Phys. Radium **20**, 382 (1959).
[6] G. K. Wertheim, J. Appl. Phys. Suppl. **32**, 110S (1961).
[7] C. Robert, Compt. Rend. **251**, 2684 (1960).
[8] R. L. Streever and G. A. Uriano, Bull. Am. Phys. Soc. **9**, 464 (1964).
[9] R. L. Streever and G. A. Uriano, Phys. Rev. Letters **12**, 516 (1964).

magnetization studies can be used to interpret the gallium results.

In Sec. II we discuss the experimental procedures and equipment used. In Sec. III the experimental results are given. A discussion and analysis of the data are given in Sec. IV.

II. EXPERIMENTAL METHODS

A. Samples

The samples used in this work were prepared by the Airtron Corporation. They were prepared by the usual ceramic method and consisted of polycrystalline powders of particle size 10 μ or less. In order to ensure good homogeneity, the sintering and grinding process was repeated several times. Sixteen samples were prepared corresponding to $x=0$, 0.25, 0.5, 0.65, 0.8, 1.0, 1.25, 1.5, 1.75, 2.0, 2.15, 2.3, 2.45, 2.6, 2.75, and 2.95. An x-ray analysis of the samples showed that although there were small changes in the lattice parameters at the higher concentrations, there was little, if any, deviation from the garnet structure.

B. Nuclear-Resonance Equipment

The ^{57}Fe, ^{69}Ga, and ^{71}Ga nuclear resonances were studied with conventional spin-echo equipment. An Arenberg Ultrasonics Laboratory (AUL) pulsed oscillator (AUL 650-C) was used to supply the rf pulses. The receiving coil was wound coaxially around the transmitting coil. For the resonance signals below 50 MHz, a preamplifier (AUL 620) was connected through a 50-Ω cable to the receiving coil. The preamplifier was followed by a wide band amplifier and detector (AUL 600-C). The spin-echo signal was observed on an oscilloscope. For frequencies above 50 MHz, a TV tuner was used to convert the rf signals down to about 20 MHz before passing the signals through the amplifier-detector combination.

The ^{57}Fe resonance studies were made at room temperature, 77°K (liquid nitrogen), and 4°K (liquid helium). The ^{69}Ga and ^{71}Ga resonance studies were made at 4 and 77°K. The 4° studies were made using a liquid-helium Dewar with an exposed helium finger. The finger of the Dewar fitted inside the transmitting coil of the pulsed oscillator. The powdered samples were sealed off in a glass tube under a helium atmosphere and placed inside the inner finger of the Dewar.

The nuclear resonance signal was calibrated by means of an auxiliariy VHF signal generator which was inductively coupled, by means of a one-turn coil, to the receiving coil.

C. Nuclear-Resonance Measurements

The nuclear-resonance line shapes were obtained by plotting the spin-echo amplitude as a function of frequency. Most of the measurements were made in zero applied magnetic fields with low rf levels (i.e., around 10 V peak to peak). For this case the signals were due mainly to nuclei in the domain walls. At each point across the line the rf pulse level was adjusted so that the echo signal was a maximum. This adjustment should compensate for any change in the domain wall-signal enhancement as one goes across the line. Several measurements were also made in applied magnetic fields. The signals were then due mainly to nuclei in the domains. For this case the rf level could not be adjusted to give a distinct signal maximum and the rf level was held at a high constant level of around 200 V peak to peak during these measurements.

In making the measurements, the two exciting rf pulse widths were kept constant and equal. For the broader lines (greater than 2 MHz) the pulse widths were left at their minimum value of around 1 μsec, while for the narrower lines broader pulses were used. (For best reproduction of the line shape the criterion is that the distribution in frequencies within the pulse should be less than the line width so that only a portion of the inhomogeneously broadened line is excited at each point across the line.) The separation in time between the pulses was kept fixed during the measurements. The separation was kept small enough so that the echo decay due to the transverse relaxation time T_2 was negligible.

After adjusting the pulsed oscillator to a particular frequency and adjusting the rf level to an echo maximum (for the case of zero applied field), the preamplifier (or TV tuner) was tuned to a maximum echo signal. The calibrator signal was then turned on and heterodyned with the nuclear signal and the frequency was measured by switching the calibrator signal into a counter. A 1000-Hz modulation was then put on the calibrator signal and the amplitude of the calibrator signal was then made equal to the amplitude of the echo, both being observed on the oscilloscope. The calibrator signal voltage was then taken to be the amplitude of the nuclear signal at that frequency.

The ^{57}Fe spin-echo signal intensity observed on the scope is proportional to the macroscopic nuclear moment. This is in turn proportional to the microscopic moment times the nuclear polarization. Thus, in order to correct the experimental line shapes for the additional nuclear polarization at the higher frequencies, we have divided the experimental zero field ^{57}Fe echo intensities at each point by the frequency corresponding to that point. The line shapes obtained when a magnetic field was applied were divided by an additional factor of ν to compensate for the change in enhancement which could not be compensated for by an rf level adjustment. Similar corrections must be applied to the gallium nuclear resonances. However, since there are two isotopes present with differing abundances and moments, the two gallium resonance lines were separated before the corrections were applied. This has been discussed previously.[9]

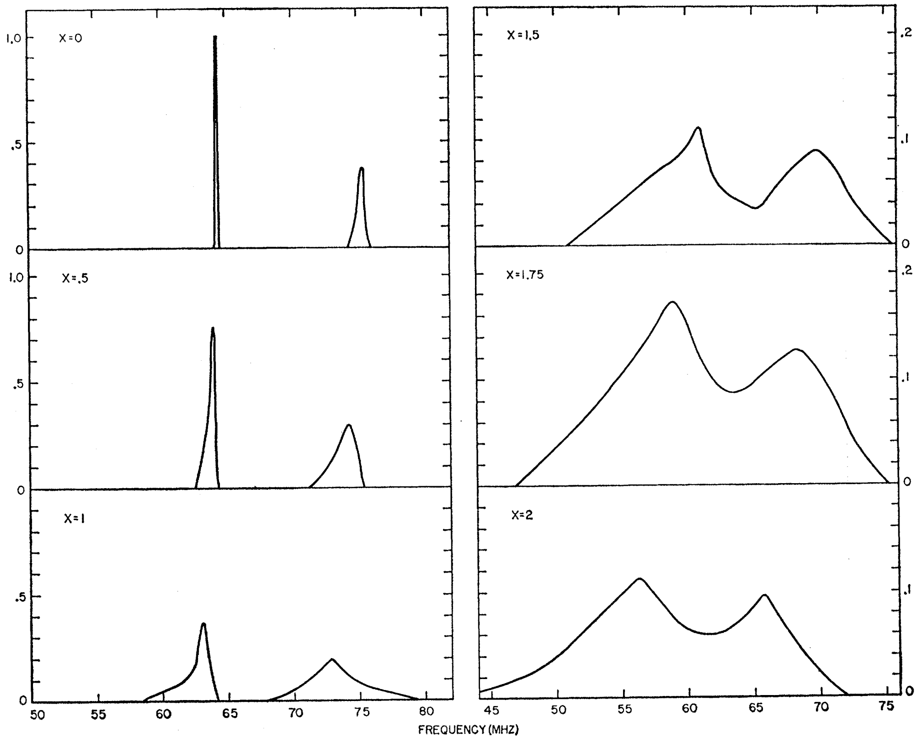

FIG. 1. The ^{57}Fe nuclear-resonance line shapes at 77°K for various gallium concentrations. These line shapes have been corrected for the increased nuclear polarization at the higher frequencies (see text). The high-frequency peak corresponds to nuclei on the a site and the low-frequency peak to nuclei on the d site.

D. Net Magnetization Measurements

The net magnetization measurements were made by means of a vibrating sample magnetometer. This was done by measuring the emf induced in the pickup coil of the magnetometer. If one holds the amplitude and frequency of vibration of the sample constant, the emf induced in the coil is then directly proportional to the macroscopic magnetic moment of the sample. The net magnetic moment was plotted as a function of applied field until saturation was obtained. An extrapolation of the high-field limit back to zero field was then done in order to obtain the net or spontaneous magnetization. These extrapolations were somewhat difficult to make at some of the concentrations owing to the fact that curves were somewhat nonlinear, some even going through a maximum, in the high-field limit. These measurements were made at 77°K over the concentration range from $x=0$ to $x=2.6$.

III. EXPERIMENTAL RESULTS

A. ^{57}Fe Results

The experimental ^{57}Fe resonance line shapes in zero applied fields at 77°K for various concentrations up to $x=2$ are shown in Fig. 1. The high-frequency peak is due to ^{57}Fe nuclei on a sites and the low-frequency peak is due to ^{57}Fe nuclei on d sites. The line shapes have been corrected for the increased nuclear polarization at the higher frequencies. In Fig. 2 are shown the corrected ^{57}Fe line shapes at 4°K in zero applied field.

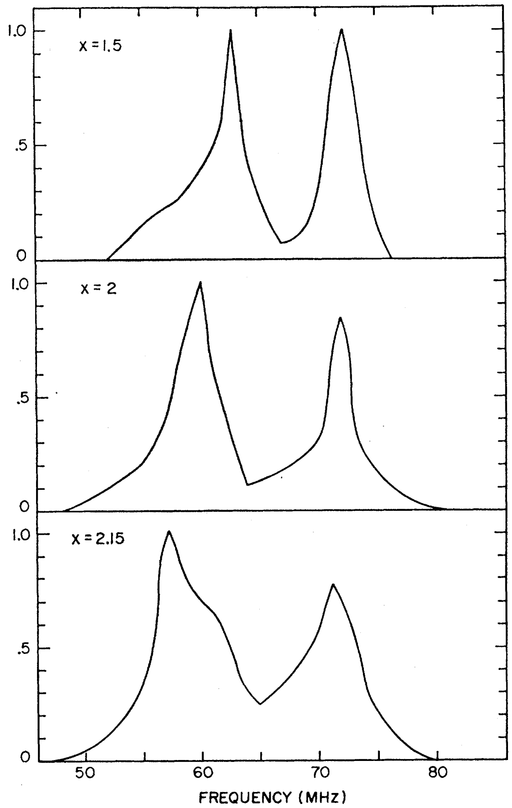

FIG. 2. The corrected ^{57}Fe nuclear-resonance line shapes at 4°K for various gallium concentrations.

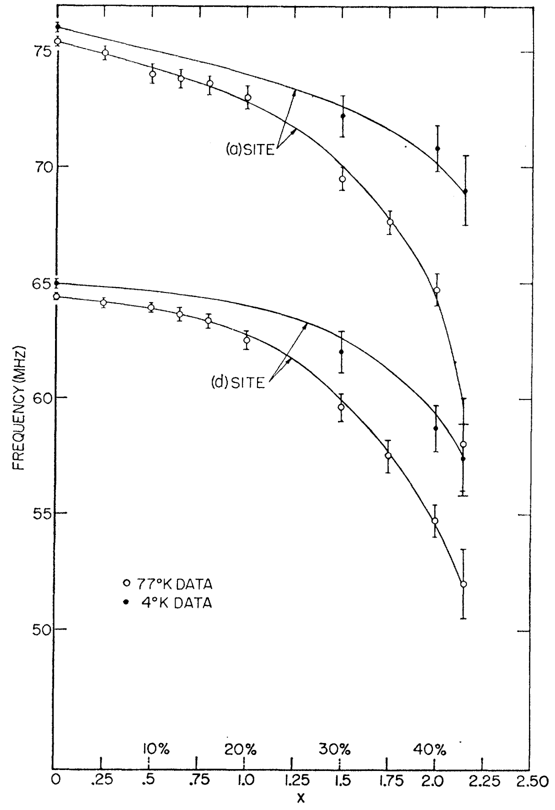

FIG. 3. The centers of gravity of ^{57}Fe resonance lines on the a and d sites are plotted as a function of x at both 77°K and 4°K.

Only a part of the lines could be traced above $x=2.15$ because of very weak signals.

In Fig. 3 we have plotted the centers of gravity of the ^{57}Fe resonance lines at 4°K and 77°K. The 4°K points for pure YIG have been taken from Boyd *et al.*[10] ^{57}Fe resonance line shapes were also traced out at room temperature for concentrations up to $x=1$. Figure 4 shows a plot of the centers of gravity of the ^{57}Fe resonance line for both sites at room temperature.

B. ^{69}Ga and ^{71}Ga Results

Some preliminary results of the ^{71}Ga and ^{69}Ga resonance studies were reported in an earlier paper.[9] The resonance line shape shown in that paper is typical. For a given value of x the spectrum consists of two inhomogeneously broadened resonance lines which overlap somewhat in frequency. The higher frequency line is due to ^{71}Ga nuclei and the lower frequency line is due to ^{69}Ga nuclei. The frequencies of the centers of gravity of the two lines are in the ratio of 1.3 to 1, which is in agreement with the ratios of the nuclear moments of ^{71}Ga to ^{69}Ga. As was discussed in the previous paper, if one considers the values of the nuclear moments and relative abundances of the two isotopes, the intensity of the ^{69}Ga resonance line is expected to be 0.95 times that of the ^{71}Ga line. This is in approximate agreement with observations.

In Fig. 5 we have plotted the corrected centers of gravity of the ^{71}Ga resonance lines as a function of x at various temperatures. The dashed lines represent calculations using a theory explained in Sec. IVD. The gallium ions substitute preferentially onto d sites, and we believe the ^{69}Ga and ^{71}Ga resonances to be due to nuclei on these sites.

We have also applied an external magnetic field to several of the samples at low temperatures. A sufficiently high rf level was used so that nuclei in the domains were being observed. The intensities of the two gallium lines were in the proper ratio after corrections for the loss in domain enhancement were made. The applied field is expected to add vectorially to the nuclear hyperfine field, thereby shifting the nuclear resonance frequency. The frequency shift of the center of gravity of the ^{71}Ga resonance in several samples was measured as a function of the applied magnetic field. The frequency of the center of gravity of the ^{71}Ga resonance in the $x=1.5$ sample was found to increase with a slope corresponding to about 13 MHz per T, (1 T equals 10^4 G). This is what one would expect if there were no shielding. As

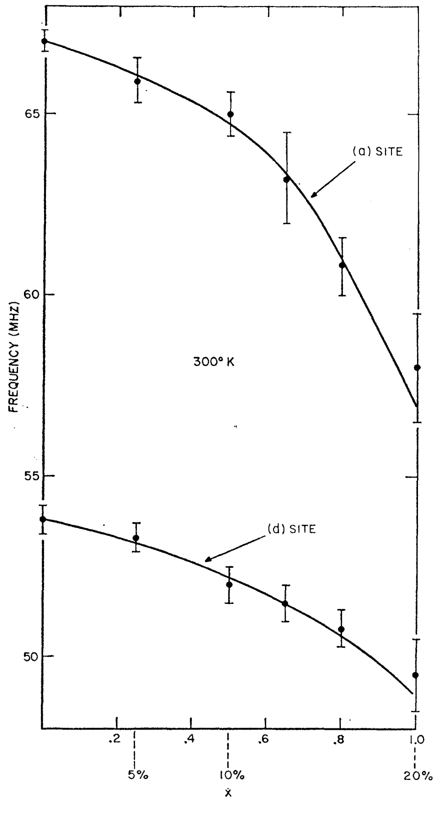

FIG. 4. The centers of gravity of ^{57}Fe resonance lines on the a and d sites are plotted as a function of x at 300°K.

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[10] E. L. Boyd, V. L. Moruzzi, and J. S. Smart, J. Appl. Phys. 34, 3049 (1963).

will be discussed in Sec. IVD, the net magnetization is along the a sublattice direction above $x=1.25$ at low temperatures. Thus, the nuclear hyperfine field must also be in the direction of the a sublattice magnetization. In several concentrations below $x=1.25$ the frequency decreased with approximately the same slope of 13 MHz per T. This was as expected since for these concentrations the net magnetization is along the d sublattice magnetization.

C. Relaxation Effects

Some relaxation time studies were made, although not in great detail. In both the iron and gallium one expects shorter relaxation times in the domain walls where the additional relaxation mechanisms due to domain wall motions are operative. This was found to be the case. The ^{57}Fe relaxation times in pure YIG have been previously studied by other workers.[11] In the case of ^{71}Ga, the longitudinal relaxation time T_1 in the domains in the presence of an applied field of 0.2 T at 4°K is of the order of 1 sec in a 5% sample and decreases with increasing gallium substitution. For the gallium resonance the T_2's were of the order of microseconds.

D. Net Magnetization Measurements

The spontaneous or net magnetization at 77°K is plotted as a function of gallium concentration in Fig. 6. In this figure the net magnetization of the pure YIG at 77°K has been set equal to unity. Anderson[4] has measured the magnetic moments in gallium-substituted YIG up to $x=1.0$ at room temperature and in the low-temperature limit. Our 77°K measurements as a function of concentration up to $x=1$ were close to Anderson's concentration dependence at 0°K. This was as expected since the net magnetization does not change much in this low-temperature region.

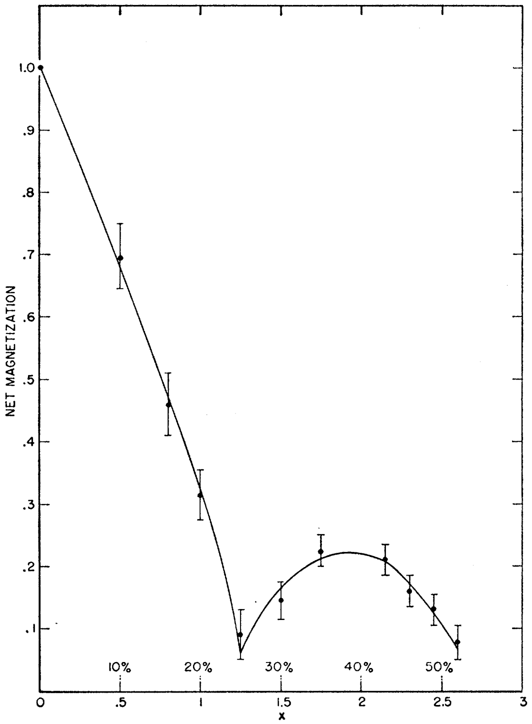

FIG. 6. The net magnetization at 77°K is plotted as a function of x. The net magnetization in pure YIG has been set equal to unity. The minimum at around $x=1.25$ corresponds to the fact that $n_a \approx n_d$ at this point, and this corresponds to the reversal of the sign of the net magnetization.

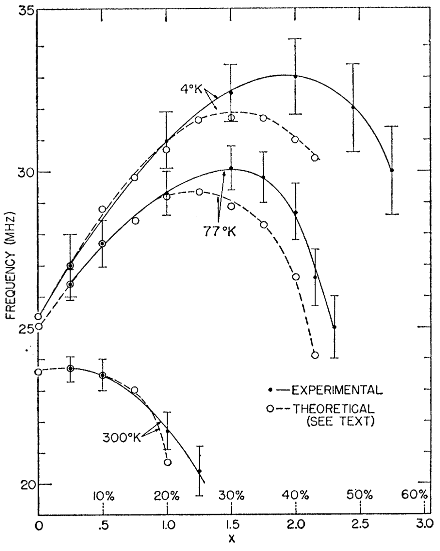

FIG. 5. The experimental centers of gravity of the ^{71}Ga resonance lines are plotted as a function of x at 4, 77, and 300°K (solid lines). The dashed lines represent calculations based on a theory explained in the text, using the parameters of Table III.

As mentioned in the introduction, gallium substitutes preferentially onto the d site in gallium-substituted garnets At low temperatures and low concentrations, the majority of the iron ions are fully aligned so that the net magnetization goes essentially as the difference in the number of iron ions on the two sites. In pure YIG, then, the net magnetization is along the direction of the iron spins on the d sites. Owing to preferential substitution on d sites, the d sublattice magnetization decreases and at about $x=1.25$ the two sublattice magnetizations are equal. At higher concentrations the magnetization increases, now lying along the direction of spins on the a sites. Finally, the net magnetization peaks and begins to decrease, this final decrease being associated with the decrease in ferromagnetism of the system.

IV. DISCUSSION OF RESULTS

A. Site Distribution of Ions

We would like to obtain a relationship between the net magnetization, the average value of ionic spin

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[11] C. Robert, Compt. Rend. 252, 1442 (1961).

$\langle S_i \rangle$ (where the subscript refers to a particular sublattice), and the number of iron spins on each sublattice. For the a sublattice we define σ_a to be the value of $\langle S_a \rangle$ relative to its maximum value in the fully aligned state and similarly for σ_d.

$$\sigma_a = [\langle S_a \rangle / \langle S_a \rangle_{\max}]_{\text{av}}. \tag{3}$$

The average will be over all spins on the sublattices. σ_a is then the average spin per iron ion (taken to be 1 in the fully aligned state) for iron ions on the a sublattice and similarly for σ_d. We define n_a and n_d by the relations $n_d = (3-z)/5$, $n_a = (2-y)/5$, so that n_a and n_d will be proportional to the actual number of iron spins on the two sublattices at any given concentration of gallium. (In pure YIG $n_d = 0.6$, $n_a = 0.4$). Letting n_g be the fractional gallium substitution we have

$$n_g + n_d + n_a = 1. \tag{4}$$

We define σ_m to be the value of the net magnetization relative to its maximum value (in pure YIG at 0°K). Then the following relation holds:

$$0.2\sigma_m = n_d \sigma_d - n_a \sigma_a. \tag{5}$$

σ_a and σ_d will be taken to be inherently positive quantities so that σ_m will be positive when the net magnetization lies along the direction of the d sublattice. At sufficiently low temperatures and low gallium substitutions $\sigma_a = \sigma_d = 1$, so that one can obtain n_a and n_d from the experimental values of σ_m and the auxiliary relation (4). At any finite temperature σ_a and σ_d will be less than unity so that we might obtain a better value for the n's by taking this into account. From (4) and (5) we have

$$n_a = [\sigma_d(1-n_g) - 0.2\sigma_m] / (\sigma_d + \sigma_a) \tag{6}$$

$$n_d = 1 - n_g - n_a. \tag{7}$$

For the purpose of calculating n_d and n_a and for our use later we would like to obtain an approximate relation between σ_d and σ_a and the nuclear resonance frequencies. As will be discussed in more detail in the next section, the major contribution to the hyperfine field at the ^{57}Fe nuclei will be proportional to the ionic spin on its parent ion $\langle S_i \rangle$.[12] We can write

$$\nu_i = A_i \langle S_i \rangle. \tag{8}$$

Here A_i is the hyperfine coupling constant for ions on the ith sublattice. We will assume A_i to be constant for a particular sublattice. Then, from Eqs. (3) and (8) we have, after averaging (8) over all ions on the sublattice

$$\sigma_a = \nu_a / \nu_{a0}, \quad \sigma_d = \nu_d / \nu_{d0}, \tag{9}$$

where ν_a and ν_d are the centers of gravity of the resonance lines for the two sites at a given temperature and gallium concentration and ν_{a0} and ν_{d0} are resonance frequencies for the two sites at 0°K in pure YIG.

TABLE I. Values of the sublattice magnetizations at 4, 77, and 300°K and the net magnetization at 77°K for various concentrations up to 43% gallium.

	σ_a			σ_d			σ_m
x	4°K	77°K	300°K	4°K	77°K	300°K	77°K
0	1.000	0.990	0.880	1.000	0.991	0.828	0.990
0.25	0.992	0.983	0.868	0.998	0.988	0.820	0.831
0.5	0.986	0.976	0.851	0.995	0.983	0.805	0.673
0.75	0.979	0.967	0.830	0.991	0.976	0.784	0.500
1.0	0.972	0.956	0.760	0.985	0.966	0.753	0.322
1.25	0.963	0.941		0.977	0.949		0.069
1.5	0.954	0.920		0.964	0.923		−0.163
1.75	0.940	0.890		0.945	0.888		−0.211
2.0	0.921	0.845		0.913	0.840		−0.218
2.15	0.903	0.783		0.885	0.798		−0.205

In Table I we list values of σ_a and σ_d calculated, using Eq. (9) and the center of gravity of the resonance lines at 300, 77, and 4°K, as shown in Figs. 3 and 4. We have taken $\nu_{a0} = 76.14$ MHz and $\nu_{d0} = 64.95$ MHz.[10] We also list σ_m at 77° obtained from the experimental results (Fig. 6) by taking σ_m in pure YIG at 77°K to be 0.99.[13] We have also used the values of σ_m, σ_a, and σ_d at 77°K in Eqs. (6) and (7) to obtain values of n_a and n_d at each concentration of gallium. These values were then smoothed graphically and are shown in Table II. From Table II, we see that at about $x = 1.25$, the quantity n_a becomes equal to n_d. It is at that point that the net magnetization curve (Fig. 6) goes through a minimum.

Of course, the center of gravity of the resonance lines will only be proportional to σ_a (or σ_d) if all the nuclei in different environments are contributing to the nuclear resonance. We will consider ions on a and d sublattices only. Then the iron ions on a sites have six nearest iron neighbors on d sites. If all the d neighbors to these iron ions are gallium ions then, assuming only nearest-neighbor a-d interactions, we expect no contribution to either the nuclear resonance or the net magnetization from these iron ions, even in the low-

TABLE II. The numbers of iron ions on the a and d sites for various gallium concentrations, calculated in the manner explained in Sec. IVA.

x	n_g	n_a	n_d
0	0	0.40	0.60
0.25	0.05	0.40	0.55
0.5	0.10	0.39	0.51
0.75	0.15	0.39	0.46
1.0	0.20	0.38	0.42
1.25	0.25	0.37	0.38
1.5	0.30	0.36	0.34
1.75	0.35	0.35	0.30
2.0	0.40	0.33	0.27
2.15	0.43	0.32	0.25

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[12] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

[13] E. E. Anderson, Phys. Rev. **134**, A1581 (1964).

temperature limit. Similarly, for the d site which has four nearest iron neighbors on a sites and four on d sites, we expect no contribution from those iron ions where all a site neighbors are gallium. In order to explain the Curie point and magnetization in substituted iron garnets in the low-temperature limit, Gilleo[3] assumed that he should exclude from participation in the ferromagnetism all iron ions linked (by a-d interactions) with less than two other iron ions, the argument being that these could not complete a ferromagnetic chain. This assumption is necessary to explain the decrease in magnetism at the higher gallium concentrations. The values from Table II can be used to calculate statistically, assuming random distribution within a sublattice, the number of a and d site iron ions linked to less than 2 iron neighbors by a-d interactions. At 40% gallium substitution, this is 19% of the iron ions on a sites and 1% of the d site ions. Restricting ourselves to concentrations less than about 40% gallium, one finds that the number of iron ions linked to less than 2 other iron ions is small. We believe, however, that at sufficiently low gallium concentrations at low temperatures even iron ions linked to only one other iron ion may be contributing to the nuclear resonance. Therefore, Eq. (9) should be a good approximation and the values of n_a and n_d obtained from Eqs. (6) and (7) should be reasonably good.

B. ^{57}Fe Data at 4 and 77°K

Contributions to the hyperfine field in these materials at the iron nuclei have been discussed by Watson and Freeman.[12] Since the major contribution to the ^{57}Fe hyperfine field will be from the core polarization of the parent atom, Eq. (8) of the preceding section should be a good approximation. As discussed in Ref. 12, the fact that the tetrahedral site is more covalently bonded than the octahedral site is probably the major cause of the smaller ^{57}Fe hyperfine field at that site. For a given site, however, A_i will depend primarily on the wave functions of the iron ion, as modified by the covalent effects of the neighboring oxygen ions, and thus should be essentially independent of gallium substitution.

In addition to the hyperfine field contribution from the spin of the parent atom, we can in general expect a contribution from neighboring iron spins. The gallium NMR studies give us information about the additional contribution to the nuclear hyperfine field on the d sublattice. These studies indicate that neighboring spins on both a and d sublattices contribute to the d site hyperfine field. Assuming that this additional contribution is the same for the iron ion as the gallium, we expect a net contribution in pure YIG at low temperatures of about 4% of the iron hyperfine field. The field will be antiparallel to the direction of the iron spin on the d site and so will increase the hyperfine field at that site (the major contribution to the hyperfine field from the core polarization being negative with respect to the spin of the parent atom). This contribution increases with gallium substitution, as seen from Fig. 5, but the total change in going from $x=0$ to $x=2$ is only about 0.5 T (at low temperatures) or 0.7 MHz of ^{57}Fe frequency. The field at the a site from spins on neighboring d sites may be smaller due to a smaller degree of covalency on that site.

In conclusion, we can say that the decrease in resonance frequency with increasing x, even at the low temperatures, is mainly due to a decrease in $\langle S_i\rangle$. However, in view of the effects discussed above, σ_a and σ_d will not be strictly proportional to the resonance frequency.

C. ^{57}Fe Room-Temperature Data

The experimental results of the frequency shift of the centers of gravity of the ^{57}Fe resonance lines at room temperature (Fig. 4) may be explained in terms of molecular-field theory, since we expect molecular-field theory to apply at high temperatures and low gallium concentrations. Using the two-sublattice model, the molecular fields acting on the a and d sites are given by

$$H_a=H_0+\gamma_{aa}M_a-\gamma_{ad}M_d\,, \tag{10}$$

$$H_d=H_0-\gamma_{ad}M_a+\gamma_{dd}M_d\,. \tag{11}$$

Here H_0 is the applied field which is zero for our case, M_a and M_d are the magnetic moments on the sublattices, and γ_{aa}, γ_{dd}, γ_{ad} are the molecular field coefficients. The value of the intrasublattice molecular-field coefficients are in doubt at this time. Estimates of γ_{aa} and γ_{dd} have varied from $\gamma_{aa}=\gamma_{dd}=0$ to $\gamma_{aa}=0.67\gamma_{ad}$, $\gamma_{dd}=0.21\gamma_{ad}$ (Ref. 13). The study of the gallium resonances, which is discussed in the next section, lends some support to γ_{dd} being of significant value. It is difficult, however, to relate the hyperfine-field contributions at the d site to the molecular-field coefficients, as will be discussed later. For the purposes of this calculation, we have assumed γ_{aa} and γ_{dd} are both zero.

We then follow the analysis of Boyd *et al.*[10] They obtain [Eqs. (12a) and (12b) of their paper]

$$\sigma_a=B_S\{-(3S/S+1)(\mu/\lambda)^{1/2}(\sigma_d/\tau)\} \tag{12}$$

$$\sigma_d=B_S\{-(3S/S+1)(\lambda/\mu)^{1/2}(\sigma_a/\tau)\}\,, \tag{13}$$

where B_S denotes a Brillouin function for spin S; $\tau=T/T_N$ where T_N is the Néel temperature (which equals the Curie temperature when a-a and d-d interactions are neglected). Their μ and λ corresponds to our n_d and n_a, respectively. In their case, n_d and n_a were constants but for our case they are variable.

Using the fact that the iron-ionic spin equals $\frac{5}{2}$ we obtain:

$$\sigma_a=B_{5/2}\{-(15/7)(n_d/n_a)^{1/2}(\sigma_d/\tau)\}\,, \tag{14}$$

$$\sigma_d=B_{5/2}\{-(15/7)(n_a/n_d)^{1/2}(\sigma_a/\tau)\}\,. \tag{15}$$

Also, from Eq. (13) in Ref. 10 we have

$$T_N(n_a,n_d)=(n_an_d)^{1/2}C\gamma_{ad}\,, \qquad (16)$$

where C is the Curie constant in pure YIG for N atoms. Experimental measurements[5] of the concentration dependence in gallium-substituted YIG agree with Eq. (16) within the experimental errors. Using the fact that $T_N(0.4,0.6)=553°\text{K}$, we can evaluate $C\gamma_{ad}$. Thus

$$T_N(n_a,n_d)=(553/(0.24)^{1/2})(n_an_d)^{1/2}. \qquad (17)$$

Equations (14) and (15) can then be put in the form

$$\sigma_a=B_{5/2}\{-(15/7)(n_d\sigma_d/(0.24)^{1/2})(553/T)\}\,, \qquad (18)$$

$$\sigma_d=B_{5/2}\{-(15/7)(n_a\sigma_a/(0.24)^{1/2})(553/T)\}\,. \qquad (19)$$

These two equations have been solved graphically for σ_a and σ_d, using the values of n_a and n_d from Table II. This was done for various values between $x=0$ and $x=1$. The values obtained for σ_a and σ_d from the graphical solution of Eqs. (18) and (19) are plotted in Fig. 7, along with the experimental values from Table II. The agreement with the experimental values seems to be fairly good in spite of the fact that we neglected *a-a* and *d-d* interactions. The over-all agreement could probably be improved by taking these interactions into account.

D. Discussion of the Gallium NMR Results

As seen in Sec. IIIB, we have found a hyperfine field at the gallium *d* site, which is in the same direction as the *a* sublattice magnetization. We have tried to fit the hyperfine field to a sum of contributions from iron spins on *a* and *d* sublattices.

$$H_n=A_af_a\sigma_a+A_df_d\sigma_d\,. \qquad (20)$$

H_n is defined to be positive when along the direction of the *a* sublattice magnetization. Here $f_a=n_a/0.4$ is the fractional number of iron ions on *a* sites relative to pure YIG and similarly for $f_d=n_d/0.6$. Thus, A_a and A_d are parameters which are a measure of the relative contribution to H_n in pure YIG from ions on the two sublattices. We may rewrite (20) as follows:

$$H_n=A_a(f_a\sigma_a+\beta f_d\sigma_d)\,, \qquad (21)$$

where $\beta=A_d/A_a$. This equation corresponds to Eq. (2) of our previous paper[9] where the notation has been changed. Using the values of n_a and from Table II and σ_a and σ_d at various temperatures from Table I, we have found values of A_a and β which give a best fit to the experimental hyperfine fields at low concentrations (up to $x=1$).

We have listed the value of A_a, β, and A_d necessary to fit the experimental curves of Fig. 5 at various temperatures in Table III. The theoretical curves using these values of A_a and β (converted to frequency units) are shown in Fig. 5. We see that the absolute values of A_a and β needed to fit the experimental curves decrease with increasing temperature. Also, the agreement becomes bad at high concentrations.

TABLE III. The values of the hyperfine-field parameters for various temperatures.

Temperature (°K)	A_a (T)	β	A_d (T)
4	4.58	−0.57	−2.61
77	4.13	−0.53	−2.17
300	3.16	−0.30	−0.95

In order to see why this should be, we should consider the mechanism responsible for the hyperfine field at the gallium ion in more detail. Consider first the contribution from neighboring iron spins on *a* sites. An iron and gallium ion will be separated by an intervening oxygen ion, as shown in Fig. 8. The Ga^{3+}-O^{--}-Fe^{3+} angle is somewhat less than 180° but is shown as 180° in the figure for simplicity. Following the usual superexchange picture,[14,15] the bonding between oxygen and gallium ions can be represented by a mixture of the ground and excited states shown in Fig. 8. In the ground state we consider two *p* electrons in the same oxygen orbital with the spin configurations shown by the arrows. We assume that in the excited state a *p* electron on the oxygen transfers to a 4*s* orbital on the gallium. The remaining *p* electron on the oxygen is now free to couple through a *p-d* exchange interaction

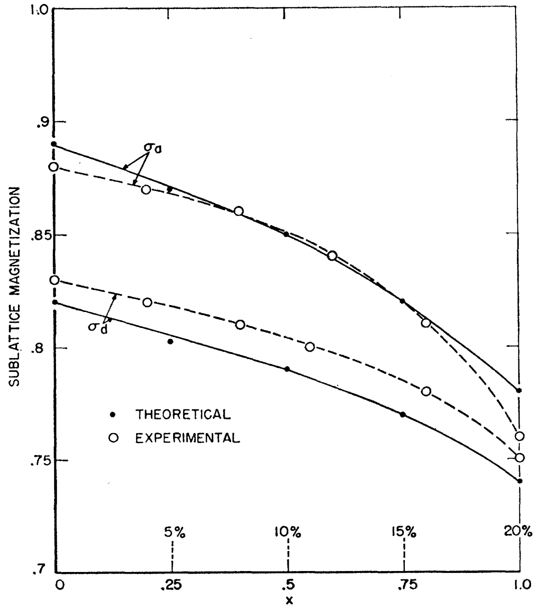

FIG. 7. The sublattice magnetizations on the *a* and *d* sites are plotted as a function of x. Dashed lines represent experimental points and solid lines represent calculations made using a molecular-field theory, assuming only *a-d* interactions.

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[14] P. W. Anderson, Phys. Rev. **79**, 350 (1950).

[15] J. H. Van Vleck, J. Phys. Radium **12**, 262 (1951).

with the *d* electrons on the iron ion. This coupling will be necessarily antiferromagnetic since the iron *d* shell is already half filled with $S=\frac{5}{2}$. Consequently, the *p* electron transferred into the gallium *s* orbtial will tend to be polarized with its spin along the direction of the iron spins on the *a* site. Considering only the direct Fermi contact interaction between the *s* electron and the nuclear spin, this will give a hyperfine field along the direction of the iron spins on *a* sites in agreement with experiment. It might be expected that only in the limit of low temperatures and low gallium substitutions will the 4*s* polarization reach its maximum value. At higher temperatures the component of *p* electron spin along the *a* magnetization direction will decrease, resulting in a decrease in A_a. For the *p*-*d* exchange we might expect $J\approx 10^3$ cm^{-1} or $J/k\approx 10^3$ °K (Ref. 15) so that the observed decrease of A_a with temperature seems quite reasonable.

Consider now the *d* sublattice contribution to the hyperfine field. For this case we find experimentally a hyperfine field at the gallium along the direction of the iron spins on the *d* sites. If, again, we consider the field as due to an electron partially transferred to a 4*s* orbital on the gallium, this electron must be coupled ferromagnetically to the neighboring iron spins on the *d* sites, as in the case of the *a* spins. The sign of the coupling for this case, however, does not appear to be as readily predicted theoretically as in the case of the *a* sublattice contribution, since the ordinary superexchange mechanism discussed above is not dominant. A_d is expected to decrease with temperature for the same reasons as A_a decreases, the more rapid decrease probably being due to the weaker interactions involved.

We can estimate the polarization of the 4*s* electron at the gallium site needed to provide the observed hyperfine field. One unpaired 4*s* electron spin will provide a hyperfine field of about 200 T via the Fermi contact interaction.[16] Walker *et al.*[17] have determined from Mössbauer-isomer-shift data that there is about 0.1 of a 4*s* electron associated with iron *d* site ions in YIG. Assuming the same 4*s* charge density for the gallium ion, we need a net 4*s* polariztaion of about 0.1 to provide the observed hyperfine field of 2 T. A polarization of this magnitude seems quite reasonable.

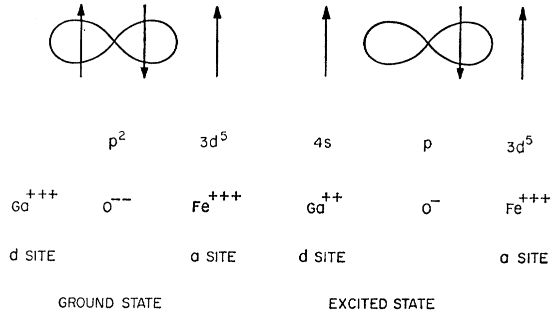

FIG. 8. A schematic diagram representing the single-electron-transfer superexchange process believed to result in a field at the site of the gallium ion. The Ga-O-Fe angle is shown as 180° for convenience.

V. CONCLUSION

We have been able to obtain the approximate site distribution of the iron ions from net magnetization and ^{57}Fe-NMR studies. The general features of the concentration dependence of the iron sublattice magnetizations and net magnetization appear to be fairly well understood. The gallium *d* site hyperfine field has been explained by assuming contributions to the field from iron spins on neighboring *a* and *d* sites. However, more theoretical work appears necessary before the gallium hyperfine-field contributions and the temperature dependence of the gallium hyperfine field can be fully understood. More detailed studies of the gallium NMR signal particularly at low concentrations and perhaps in single crystals might also be useful in order to better characterize the hyperfine interactions.

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[16] W. Marshall, Phys. Rev. **110**, 1280 (1958).

[17] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).