where $A$, $B$, $C$, $D$ are operators $S_i^{\pm}$, $I_i^{\pm}$. Further, we write

$$S_j^z = S - S_j^- S_j^+, \tag{C2}$$

$$I_j^z = \tfrac{1}{2}(I_j^+ I_j^- - I_j^- I_j^+). \tag{C3}$$

Equations (C1)–(C3) correspond to treating the $S$ spins by the Callen[8] factorization with $\alpha=0$ (appropriate for low temperatures) and the $I$ spins by the Callen factorization with $\alpha=1$ (appropriate for high temperatures). We then have

$$\begin{aligned}
&\langle S_i^z S_j^+ I_i^- \rangle \simeq \langle S_i^z \rangle \langle S_j^+ I_i^- \rangle,\\
&\langle S_i^z I_i^- I_i^+ \rangle \simeq \langle S_i^z \rangle \langle I_i^- I_i^+ \rangle,\\
&\langle S_i^+ I_i^- I_i^z \rangle \simeq \langle S_i^+ I_i^- \rangle \langle I_i^z \rangle,\\
&\langle S_i^+ S_i^- I_i^z \rangle \simeq \langle S_i^+ S_i^- \rangle \langle I_i^z \rangle,\\
&\langle S_i^+ I_i^- S_i^z \rangle \simeq \langle S_i^z \rangle \langle S_i^+ I_i^- \rangle,\\
&\langle S_k^z S_j^+ I_i^- \rangle \simeq \langle S_k^z \rangle \langle S_i^+ I_i^- \rangle,\\
&\langle S_k^+ I_i^- S_j^z \rangle \simeq \langle S_k^+ I_i^- \rangle \langle S_j^z \rangle,\\
&\langle S_k^z I_k^- I_i^+ \rangle \simeq \langle S_k^z \rangle \langle I_k^- I_i^+ \rangle,\\
&\langle S_k^+ I_i^- I_k^z \rangle \simeq \langle S_k^+ I_i^- \rangle \langle I_k^z \rangle,\\
&\langle S_k^+ S_j^- I_i^z \rangle \simeq \langle S_k^+ S_j^- \rangle \langle I_i^z \rangle,\\
&\langle S_k^+ I_i^- S_i^z \rangle \simeq \langle S_i^z \rangle \langle S_k^+ I_i^- \rangle.
\end{aligned} \tag{C4}$$

Further, assuming that

$$\begin{aligned}
&\langle S_k^z \rangle = \langle S^z \rangle,\\
&\langle I_k^z \rangle = \langle I^z \rangle \simeq 0,\\
&\langle S_i^+ S_k^- \rangle \simeq 0,\\
&\langle I_i^+ I_k^- \rangle \simeq 2I(I+1)\delta_{ik},
\end{aligned} \tag{C5}$$

and Fourier-transforming gives the factorizations (14).

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# Ferromagnetic Resonance in the Highly Anisotropic Ferrimagnet Gallium Iron Oxide

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Resonance measurements at 70 Gc/sec have been made on single crystals of $Ga_{2-x}Fe_xO_3$ ($x\simeq 1.1$) in the temperature range from 1.2 to 360°K. The resonance spectra of this complex and highly anisotropic ferrimagnet can be fitted using three parameters. In the range above 200°K the $g$ value was found to be $1.94\pm 0.04$, with an asymptotic value of 1.96 at high temperatures. At 4.2°K the anisotropy fields are 31 and 58 kG along the intermediate and hard magnetic axes, respectively. The same parameters fit the low-field resonance modes where **M** and **H** are not parallel, and thus confirm the above values. The observed linewidths are large and anisotropic, varying from approximately 400 to 2400 G.

## INTRODUCTION

THERE has been much recent interest in the properties of gallium iron oxide ($Ga_{2-x}Fe_xO_3$ with $0.7\leq x\leq 1.4$). This highly unusual material was originally synthesized by Remeika,[1] who found it to be ferromagnetic and piezoelectric. Macroscopic magnetic measurements[2,3] showed it to be highly anisotropic, having three magnetically inequivalent axes, with a net moment of $\sim 1\mu_B$ per Fe ion. Moreover, it was observed to have a magnetoelectric effect that is nondiagonal and an order of magnitude larger than in any other material.[4] Crystallographic investigations[5] showed that there are four cation sites: two octahedral sites ($Fe_1$ and $Fe_2$) occupied by $Fe^{3+}$, one octahedral site ($Ga_1$) which may be occupied by either $Fe^{3+}$ or $Ga^{3+}$, and one tetrahedral site ($Ga_2$) occupied by $Ga^{3+}$. Mössbauer measurements[6] firmly established the suggested[7] ferrimagnetic structure of the material. This ferrimagnetism is due to spins of presumably equal magnitude unequally distributed on the sublattices.[6] Extensive measurements[8] on samples with $x=1.15$ have found the proportion of iron on the four sites to be $Fe_1$ (0.90), $Fe_2$ (0.87), $Ga_1$ (0.54), and $Ga_2$ ($\sim 0$).

Previous resonance work[9] yielded complex line shapes and multiple resonances. Because of the low magnetic fields used, the interpretation of these data was necessarily inconclusive. In the present work, the use of high magnetic fields (high microwave frequency) ensured that the magnetization was saturated in all

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directions at all temperatures. Consequently, ferromagnetic resonance theory could be applied in a straightforward manner, and meaningful values of the anisotropy fields, $g$ value, and linewidths obtained.

## THEORY

The ferromagnetic resonance mode of a ferrimagnet may be found from the familiar equation of motion for the magnetization $\mathbf{M}$ [10]:

$$(1/\gamma)(\partial\mathbf{M}/\partial t)=\mathbf{M}\times[\mathbf{H}-(1/M)\nabla_M E_A], \quad (1)$$

where $\nabla_M E_A$ is the gradient of the anisotropy energy $E_A$ with respect to the direction of $\mathbf{M}$ and $\mathbf{H}$ is the externally applied field. Static and dynamic demagnetizing fields have been neglected since the samples used were spherical in shape and small compared to the rf wavelength inside the material. The gyromagnetic ratio $\gamma$ is assumed isotropic. For orthorhombic symmetry the anisotropy energy may be expressed in the form

$$\begin{aligned}E_A&=k_a\alpha_a^2+k_b\alpha_b^2+k_c\alpha_c^2\\&=(k_a-k_c)\alpha_a^2+(k_b-k_c)\alpha_b^2+k_c,\end{aligned} \quad (2)$$

where the $\alpha$'s are the direction cosines of $\mathbf{M}$ with respect to the easy ($c$), intermediate ($a$), and hard ($b$) axes of magnetization. Omitting the constant term and relabeling we have

$$E_A=K_a\alpha_a^2+K_b\alpha_b^2, \quad (3)$$

with $K_a$, $K_b>0$, since $c$ is the easy axis. Thus we have

$$\nabla_M E_A=\mathbf{i}2K_a\alpha_a+\mathbf{j}2K_b\alpha_b, \quad (4)$$

where the $x$, $y$, and $z$ coordinates are chosen along the $a$, $b$, and $c$ axes, respectively.

Consider first the external field applied along the easy direction, i.e., $\mathbf{H}=H\mathbf{k}$. From Eqs. (1) and (4) we have

$$\begin{aligned}&(1/\gamma)(\partial\mathbf{M}/\partial t)\\&=\mathbf{M}\times[-\mathbf{i}(2K_a/M^2)M_x-\mathbf{j}(2K_b/M^2)M_y+\mathbf{k}H].\end{aligned} \quad (5)$$

For $H$ greater than the coercive force, $\mathbf{M}\simeq M_z\mathbf{k}$, and taking $M_x$ and $M_y$ each proportional to $\exp(i\omega t)$, we can solve Eq. (5) for the resonance frequencies. Using the equivalent anisotropy fields

$$H_a=2K_a/M, \qquad H_b=2K_b/M, \quad (6)$$

we find

$$\omega^2/\gamma^2=(H+H_a)(H+H_b) \quad (7)$$

or, alternatively,

$$H=\tfrac{1}{2}\{-(H_a+H_b)+[(H_a-H_b)^2+4\omega^2/\gamma^2]^{1/2}\}, \quad \mathbf{H}\text{ along the }c\text{ axis.} \quad (8)$$

Now consider the case for $\mathbf{H}$ along the intermediate ($a$) direction, $\mathbf{H}=H\mathbf{i}$. The situation is more complex here since for $H<H_a$, $\mathbf{M}$ will not be along $\mathbf{H}$ (but will lie in the $xz$ plane). The resonance frequencies are found to be

$$\begin{aligned}\omega^2/\gamma^2=&[H-(2K_a/M^2)M_x][H-(2/M^2)(K_a-K_b)M_x]\\&+(4K_aK_b/M^4)M_z^2.\end{aligned} \quad (9)$$

Using the fact that $\mathbf{M}$ will lie along the vector sum of the anisotropy and external fields, two resonance conditions[11,12] are obtained,

$$\omega^2/\gamma^2=H_aH_b-(H_b/H_a)H^2, \quad \text{for} \quad H<H_a \quad (10)$$

and

$$\omega^2/\gamma^2=(H-H_a)(H+H_b-H_a), \quad \text{for} \quad H>H_a. \quad (11)$$

For $H$ along the $b$ axis the analogous equations are

$$\omega^2/\gamma^2=H_aH_b-(H_a/H_b)H^2, \quad \text{for} \quad H<H_b \quad (12)$$

and

$$\omega^2/\gamma^2=(H-H_b)(H+H_a-H_b), \quad \text{for} \quad H>H_b. \quad (13)$$

By measuring the resonance field in each of the three principal directions at a given temperature, Eqs. (7), (11), and (13) may be solved for the three quantities $H_a$, $H_b$ and the $g$ value ($g=\hbar\gamma/\beta$). The validity of the assumptions made in the above derivations may then be confirmed by observing the low-field resonance modes in the $a$ and $b$ directions, whose resonance fields are given by Eq. (10) and (12) in terms of these quantities.

## EXPERIMENTAL TECHNIQUE AND RESULTS

In order for resonance to occur at the high magnetic fields required by the high anisotropy, a spectrometer operating at 70.1 Gc/sec was utilized. The high fields were obtained with one of the Naval Research Laboratory's Bitter-type solenoids, and the field measurements have an uncertainty of about 1%. Field modulation and lock-in detection were employed. The single-crystal samples of $Ga_{2-x}Fe_xO_3$ used had nominal values of $x\simeq 1.1$, and were ground into small spheres, polished, and x-ray oriented. It is known that the value of $x$ may vary between crystals in the same batch,[2,3] and that their Curie temperatures will therefore be different. Thus, while measurements at temperatures of 77°K and below gave results which were virtually sample-independent, the scale of the high-temperature behavior is determined by the Curie temperatures of the individual samples. For $x\simeq 1.1$, the Curie temperature is approximately 350°K.[2]

The measured resonance fields for a typical sample having a diameter of 0.010 in. are shown in Fig. 1 as a function of temperature. At 4.2°K and with $\mathbf{H}$ along $b$, resonance occurs at 72 kG, while with $H$ along $c$ the resonance has already gone through zero field at 210°K. This latter behavior may be understood from

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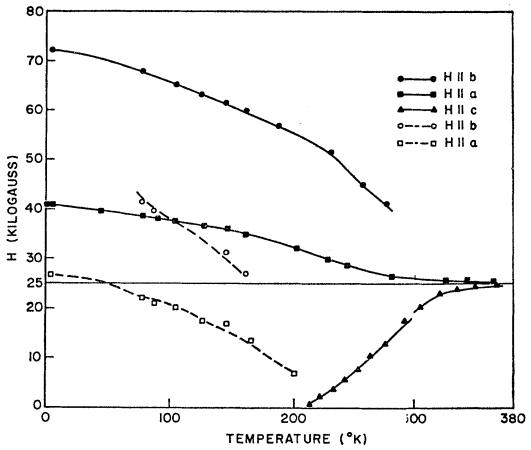


FIG. 1. Resonance field versus temperature. The full curves are the usual resonance modes for which **M** || **H**, and the dashed curves are the low-field modes for which **M** and **H** are not parallel. The horizontal line at 25 kG represents the resonance field at 70 Gc/sec for a free electron.

Eq. (8), since $H$ will become negative if $H_a$ and $H_b$ are very large. From the curves of the calculated anisotropy fields versus temperature presented in Fig. 2, it is seen that at 4.2°K the anisotropy is indeed quite large ($H_a=31$ kG and $H_b=58$ kG). Using these values the resonance field at 4.2°K for **H** || $c$ is calculated to be −16 kG. Thus the spread of resonance fields due to anisotropy in the bc plane is almost 90 kG. To observe the low-temperature resonance with **H** along $c$ would necessitate measurements at nearly twice the frequency employed.

In the region above 210°K in which all three principal axis resonances were observed, a computer solution of Eqs. (7), (11), and (13) yielded the anisotropy fields shown in Fig. 2, and the $g$ value. The $g$ value was found to be constant with temperature, having a value of 1.94±0.04, with an asymptotic value of 1.96 at high temperatures. For temperatures below 210°K the $g$ value was assumed to remain constant at 1.94, and Eqs. (11) and (13) were then solved for the anisotropy fields.

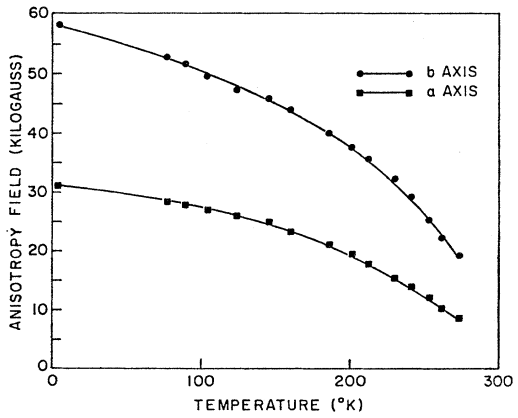


FIG. 2. Anisotropy field versus temperature. The anisotropy fields $H_i=2K_i/M$ are calculated from the resonance data of Fig. 1, as explained in the text.

The variation of linewidth with temperature for the three principal directions is shown in Fig. 3. Both the linewidths and their anisotropy are seen to be large. The linewidths are small and independent of temperature in the range from 77 to 230°K. There is a peaking of $\Delta H$ at about 270°K in the $b$ and $c$ directions. In the $a$ and $c$ directions, room-temperature measurements on one sample at 24 Gc/sec did not show any significant frequency dependence of $\Delta H$. The linewidths of the low-field modes at 77°K are essentially the same as those of the high-field modes, but the former increase more rapidly with increasing temperature than the latter.

## DISCUSSION

A comparison of Figs. 1 and 2 show that the resonance fields (solid curves) in the intermediate and hard directions are always at least 25% greater than the respective anisotropy fields. Thus **M** will be essentially along **H** as was assumed in Eqs. (11) and (13).

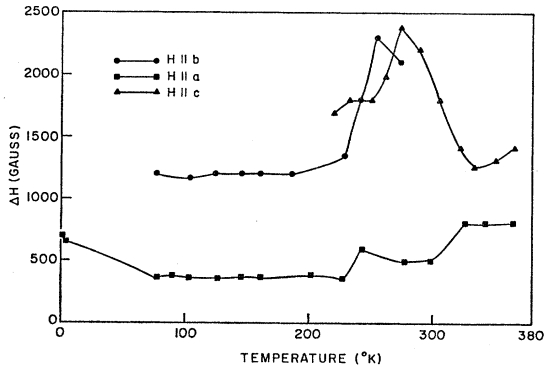


FIG. 3. Resonance linewidth versus temperature. $\Delta H$ is the field difference between peaks of the derivative of the absorption curve.

On the other hand, the low-field modes (dashed curves) occur at fields lower than the anisotropy fields at the same temperature. Equations (10) and (12) are then applicable to these modes and, using the data shown in Fig. 2, agreement between the measured and calculated resonance fields is found within the combined experimental uncertainties (~5%). This agreement is an independent check on the validity of the assumptions made in the calculations. The results are consistent with the assumption of a temperature-independent, isotropic $g$ tensor. The assumed isotropy of the $g$ tensor is also consistent with the approach of the resonance fields for **H** along both the $a$ and $c$ directions to the same asymptotic limit at high temperatures. Since the spins are thought to have equal magnitudes,[6] the effective $g$ value determined by resonance is also that of the individual ions.

The anisotropy fields as determined by resonance measurements are in fair agreement with the somewhat less accurate static magnetization[3] and torque[13] measurements. Preliminary calculations[13] show that the dipolar fields give a large contribution to the anisot-

[13] J. Schelleng (private communication).

ropy. The single-ion anisotropy due to the low symmetry of the crystalline fields at the $Fe^{3+}$ sites is also probably large.

In regard to the linewidth, the large anisotropy is not readily understood. The observed behavior is similar to that expected from a "polycrystalline" sample in which all the crystallographic axes of the individual crystallites are nearly parallel. In this case, the narrowest linewidths would be observed for an external field direction in which the internal fields contributed least to the resonance field, i.e., the $a$ direction for gallium iron oxide. The linewidth maxima in the $b$ and $c$ directions at 270°K are perhaps associated with spin fluctuations due to the nearness in temperature of the broad ferrimagnetic-paramagnetic transition. Here again, one would expect the smallest effect for the $a$ direction.

As to the various mechanisms which contribute to the magnitude of a ferrimagnetic resonance linewidth, many may be ruled out as being too small to explain the large observed linewidths. These include surface pit scattering and scattering due to random atomic disorder. The magnitude of $\Delta H$ is, however, not inconsistent with two-magnon scattering if there are long-wavelength fluctuations of the internal fields.[14] This is a result of the fact that fluctuations which correspond to the wavelengths of magnons degenerate with the $k=0$ magnons give rise to a greatly enhanced scattering. Such fields may arise from strains in the vicinity of dislocation lines and impurity atom clusters via magnetostriction. For $Ga_{2-x}Fe_xO_3$ in particular, it is conceivable that the value of $x$ itself varies over distances of the order of several hundred lattice spacings.

## ACKNOWLEDGMENTS

I would like to thank V. J. Folen and G. T. Rado for many valuable discussions. The single crystals employed were grown by R. A. Becker.

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# Itinerant-Electron Theory of Pressure Effects on Ferromagnetic Transition Temperatures: Ni and Ni-Cu Alloys*

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The rate of change of Curie temperature with pressure is calculated for Ni and Ni–Cu alloys by considering the pressure-induced shift of the pole in the uniform static spin susceptibility. The short-range Hamiltonian of Hubbard, Kanamori, and Gutzwiller is employed to describe the interactions among $d$ electrons and, following Kanamori, these interactions are treated in the $t$ approximation. The spin susceptibility is calculated using the Green's-function technique of Martin and Schwinger; the density-of-states curve for paramagnetic Ni computed by Hodges *et al.* is employed in making numerical evaluations. Account is taken of inter-$d$-band interactions, and of the effect on the number of $d$ holes of changes in the conduction band due to compression. Good agreement with experiment is obtained for Ni. For Ni–Cu alloys, calculations based on the rigid-band model yield poor results; but the use of an almost equally simple model in which a $d$ hole is assumed never to enter a Cu site leads to substantial improvement.

## I. PERSPECTIVE COMMENTS

THE effects of pressure on magnetic properties in the $3d$ transition metals have been studied experimentally for some years.[1–7] However, theoretical efforts directed at explaining these results using quantum-statistical rather than thermodynamic[8–13] approaches have lagged considerably behind. The basic physical ingredients necessary to a more fundamental theory have not in fact been available until recently, and are, even at the present time, reasonably well established only for metals such as Ni, which have nearly filled $3d$ bands.[14] The most important of these are a Hamiltonian which gives correctly the quasiparticle energy levels of the paramagnetic state and a procedure for describing approximately the interactions among the particles via the Coulomb forces in a way which is both tractable and justifiable, and which, because of the strength of these forces, transcends perturbation theory.

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