

FIG. 2. A typical curve of gain as a function of discharge current taken at 450 Mc/sec.

It will be seen that the frequency for maximum gain is proportional to the square root of the discharge current. As the plasma frequency is also proportional to the square root of the discharge current, the results are in agreement with our theoretical expectations.

We did not include a probe in the system for measuring plasma density because of the possibility of interferences with the rf fields. We have made measurements of density with a dipole resonance technique. So far there is approximately a 50% error between the plasma-density measurements made by this technique and the frequency for maximum gain. This may be due to the relatively short length of the system and consequent errors in the diagnostic technique. We do not, as yet, fully understand the reason for this discrepancy. Further measurements are in progress to observe the same type of

Table I. The frequency for maximum gain as a function of discharge current.

Working frequency $f$ (100 Mc/sec)	Arc current at maximum gain $I$ (mA)	$f/I^{1/2}$
450	21	98.2
500	26	98.0
645	40	102.0
670	41	104.5

interaction in a magnetic field both at low and high frequencies. We also hope to clear up the discrepancy between our diagnostic measurements and our beam-plasma measurements.

However, we feel that the results obtained already conclusively demonstrate the presence of a new type of beam-plasma interaction.

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#### OBSERVATION OF PARAMAGNETIC $g$ -VALUE SHIFTS BY EXCHANGE INTERACTIONS\*

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In any ionic magnetic material in which the interactions between the neighboring magnetic ions are not negligible, the paramagnetic resonance condition for any one particular ion will depend explicitly on these interactions. In the simplest terms we may picture the neighbors polarized by the applied field producing an internal field which shifts the resonance from its "isolated" value. Unfortunately this effect is

generally unobservable, because in addition to setting up a time-average internal field, the interactions also produce fluctuating fields which in most cases are much larger and broaden the one-ion absorption. The purpose of this note is to draw attention to cases where the broadening is absent, and the  $g$ -value shift, though small, is readily observable. Experimental results for  $\text{Yb}^{+3}$  in  $\text{Tm}_3\text{Al}_5\text{O}_{12}$  and  $\text{Tm}_3\text{Ga}_5\text{O}_{12}$

qualitatively confirm our prediction and lead to an interaction energy of the expected order of magnitude. In other materials it may prove possible to use measurements of the shift to make quite accurate quantitative measurements of exchange and quadrupole-quadrupole interactions.

In certain cases our effect may also help to explain the discrepancies between Curie constants as deduced from susceptibility measurements and calculated from  $g$  values determined by paramagnetic resonance.

Let us consider a dilute assembly of ions (class  $A$ ) which in the absence of mutual interactions shows paramagnetic resonance that can be described by a conventional one-ion spin Hamiltonian,  $\mathcal{H}_S$ , with known parameters. Instead of these ions being dispersed in a diamagnetic matrix, as is usual, let us consider here a paramagnetic host crystal in which the magnetic ions (class  $B$ ) have an even number of electrons. The energy levels of the  $B$ -class ions resulting from the crystal field and spin-orbit coupling will generally be nondegenerate singlets, and we consider the common situation in which the energy separations are large compared with Zeeman and interaction energies. In the absence of an applied field the singlet states are nonmagnetic, and there is therefore no first-order interaction between the  $A$ - and  $B$ -class ions. There will, however, be interactions of higher orders, of which we consider here the second-order term proportional to an applied field. This arises from the polarization of the  $B$ -class ions by the second-order Zeeman effect and is closely related to Van Vleck temperature-independent paramagnetism. Such a term will shift the paramagnetic resonance spectrum of the  $A$ -class ions in the same way as an internal field, but being independent of time it will not broaden the lines, in contrast to the interaction between spins with more than one state populated. We may obtain an estimate

of the shift from the following simple example.

For the  $A$  class let us consider ions whose only low-lying states can be described by a Kramers doublet,  $S_A' = 1/2$ , which interacts with an applied field  $H_0$  as  $\mathcal{H}_A = \mu_B \vec{H}_0 \cdot g' \vec{S}_A'$ . Each  $A$ -class ion, in general, interacts with a number of  $B$ -class ions, but to second order there are no cross terms and we can therefore consider the effect of each neighbor independently and sum the perturbations at the end. Let us describe the states of one particular  $B$ -class neighbor by  $|n\rangle$  with energies  $E_n$ , of which  $E_0$  is the nondegenerate ground state. The splittings  $E_n - E_m$  by the crystal field and spin-orbit coupling are typically of the order of 10-100  $\text{cm}^{-1}$ , and we shall consider the situation for which  $kT \ll E_n - E_0$ . We shall also assume that the terms in the  $A$ - $B$  interaction potential are small compared with the  $B$ -ion splittings. This will generally be true for rare-earth-rare-earth interactions and it may also apply to some cases of transition group ions. If the interactions are too big we may again expect broadening of the lines.

For the interaction potential we shall for definiteness take the usual Heisenberg form  $V_{AB} = J \vec{S}_A \cdot \vec{S}_B$ , though it will become clear that more complicated anisotropic forms will give qualitatively similar effects. We shall denote the interaction of a  $B$ -class ion with an applied field by  $\mathcal{H}_B = -\vec{H}_0 \cdot \vec{M}_B$ , where  $\vec{M}_B$  is the magnetic-moment operator,  $\mu_B(\vec{L} + 2\vec{S})$ .

Considering now the combined perturbation of an applied field and the interaction for a particular  $A$ - $B$  pair in its ground state  $|\pm, 0\rangle$ , we see that the first-order effect of the interaction is indeed zero since  $\langle 0 | \vec{S}_B | 0 \rangle$  vanishes identically by time-reversal symmetry.<sup>1</sup> To find the second-order terms, it is convenient to follow the usual spin-Hamiltonian procedure<sup>1,2</sup> of evaluating the matrix elements of one system (here the  $B$ -class ion) while keeping the other in operator form. Thus the second-order perturbation of the ground state

$$\sum_n \frac{\langle \pm, 0 | J \vec{S}_A \cdot \vec{S}_B - \vec{H}_0 \cdot \vec{M}_B | \pm, n \rangle \langle \pm, n | J \vec{S}_A \cdot \vec{S}_B - \vec{H}_0 \cdot \vec{M}_B | \pm, 0 \rangle}{E_0 - E_n} = \sum_n \frac{[J \vec{S}_A \cdot \langle 0 | \vec{S}_B | n \rangle - \vec{H}_0 \cdot \langle 0 | \vec{M}_B | n \rangle]^2}{E_0 - E_n} \quad (1)$$

may be written in the form

$$\vec{H}_0 \cdot \alpha' \cdot \vec{H}_0 - \mu_B \vec{H}_0 \cdot g' \cdot \vec{S}_A + \vec{S}_A \cdot D' \cdot \vec{S}_A, \quad (2)$$

where  $\alpha'$ ,  $g'$ , and  $D'$  are second-rank tensors, the order of magnitude of whose components are  $\alpha_{jk}' \sim \mu_B^2/\Delta E$ ,  $g_{jk}' \sim 2J/\Delta E$ ,  $D_{jk}' \sim J^2/\Delta E$ . If we now express the components of the real spin  $S_A$  in Eq. (2) in terms of those of the effective spin  $S_A' = 1/2$  of our  $A$ -class ion, we find that the form of the first two terms is left unaltered, but the third term is reduced to a scalar constant, as it must be by Kramers' theorem. The values of the components of  $\alpha'$  and  $g'$  will be changed, but their order of magnitude remains the same.<sup>3</sup>

The first term in Eq. (2) is simply the usual second-order Zeeman effect which gives rise to the temperature-independent paramagnetic susceptibility of the  $B$ -class ions, and it makes no contribution to the observable microwave resonance spectrum.

The second term, however, which is proportional to both the applied field and the  $A$ - $B$  interaction, has the same form as the spin Hamiltonian of the isolated  $A$ -class ions, and it therefore contributes directly to the  $g$  tensor which is observed in paramagnetic resonance.

In general, the principal axes of the  $g'$  due to any one particular  $B$ -class neighbor will not coincide with those of the magnetic  $g$  tensor, but when we sum  $g'$  over all neighbors, the axes of  $\sum g' = G'$  will coincide with those of  $g$ , provided the point symmetry is orthorhombic or higher. The only effect of the interactions will then be to change the numerical value of the observed  $g$  tensor. We can therefore detect this effect only in cases for which we have accurate knowledge of what the  $g$  values ought to be in the absence of exchange interactions.

A good example of this situation is afforded by  $\text{Yb}^{+3}$  in rare-earth aluminum and rare-earth gallium garnets. Previous results for dilute concentrations of  $\text{Yb}^{+3}$  in diamagnetic yttrium gallium garnets (YGG),<sup>4</sup> yttrium aluminum garnet (YAG),<sup>5</sup> lutecium aluminum garnet (LAG), and lutecium gallium garnet (LGG)<sup>6</sup> have shown that the three principal  $g$  values vary only slightly with host lattice, with a mean value close to  $3g_j$ . The small variation which is observed is found to be a smooth function of the parameters  $x$  and  $y$ ,<sup>7</sup> which define the positions of the  $\text{O}^{-2}$  ions that provide the immediate environment of the rare-earth ions and dominate the crystal field (see Fig. 1).

We have recently observed the resonance of  $\text{Yb}^{+3}$  in thulium aluminum (TmAG) and thulium gallium garnets (TmGG),<sup>8</sup> which are examples

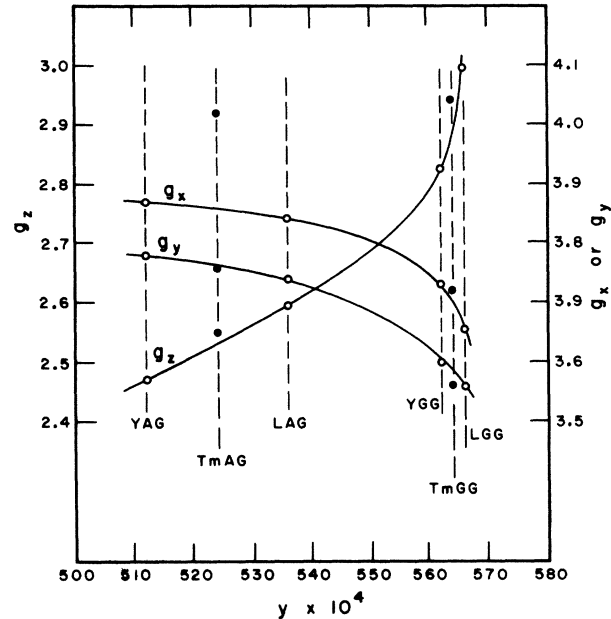


FIG. 1. Variation of principal  $g$  values with lattice parameter  $y$  for  $\text{Yb}^{+3}$  in four diamagnetic garnets YGG, YAG, LuGG, and LuAG (open circles) and the two paramagnetic garnets TmAG and TmGG (closed circles). A similar variation is found with the lattice parameter  $x$ .

of the  $B$ -class host lattices described above. Linewidths in all cases were the same as for the diamagnetic lattices ( $\sim 20$  gauss). Paramagnetic susceptibility measurements had previously shown<sup>6</sup> that the  $\text{Tm}^{+3}$  ions in both these materials have singlet ground states, with the energies of the first excited states of the order of  $100k$ . Neither the states nor their energies have been determined, but we may note a qualitative difference between the temperature-independent susceptibilities of TmGG and TmAG, from which we may expect  $G'$  to be larger for the latter, by perhaps a factor of two.

The experimental results are shown in Fig. 1. It may be seen that at least one of the points for TmAG lies well away from the smooth curves for the other garnets, while those for TmGG show smaller but still significant differences.

In the absence of detailed information of the  $\text{Tm}^{+3}$  wave function, we can here only hope to estimate an order of magnitude for the exchange constant  $J$ . Using  $G' \sim 0.02$  and  $\Delta E \sim 100k$ , we find  $J \sim 1k$  in very reasonable agreement with the magnitudes found in other garnets.<sup>9</sup> If the matrix elements and energy denominators in Eq. (1) were known accurately, this estimate

could, of course, be refined considerably and a study of the exchange shift should then lead to quite accurate estimates of the exchange-interaction potential. In such a case it may be necessary to consider an interaction more general than the scalar coupling between the spins, but this is readily carried through in the analysis outlined above. Specifically we should allow for the shift produced by magnetic-dipole interactions which are long range and depend on sample shape, but, in general, their effect will be quite small.

Our analysis may readily be extended to  $A$ -class ions with  $S' > 1/2$ . For these the term  $\vec{S}_A \cdot D' \cdot \vec{S}_A$  in Eq. (2) would not reduce to an unobservable constant and it would provide additional independent data. For  $S' \geq 2$  there may, in addition, be fourth-degree terms arising from higher order perturbations, as in the usual crystal-field spin Hamiltonian.

Another extension of our general effect may be observed in susceptibility measurements in concentrated paramagnetic (Kramers) salts, which have both exchange interactions between the ions and a temperature-independent term in the susceptibility arising from low-lying states. For such a case it is customary to fit  $\chi$  to an expression of the form

$$\chi = C/(T + \theta) + \alpha,$$

where  $C$  is generally taken to be equal to the Curie constant in the absence of interactions. That is, for  $S' = 1/2$ ,  $C = Ng^2 \mu_B^2 / 4k$ , where  $g$  is the value measured by paramagnetic resonance for the ion in a similar diamagnetic host lattice. Whenever discrepancies are found, these are ascribed to changes in the magnetic  $g$  value produced by the difference in the crystalline electric field between the concentrated and dilute structures. Our analysis now shows that an equally important effect can arise from the cross terms between the exchange and off-diagonal Zeeman interactions.

The order of magnitude of the change in Curie constant  $\Delta C$  can be approximately estimated from our order of magnitude expression for  $g'$ :

$$\Delta C/C \approx 2 \sum g' / g \sim 4 \sum J / g \Delta E \sim \theta \alpha / C,$$

since  $\theta \sim \sum J/k$  and  $\alpha/k \sim C/\Delta E$ . For a typical case of a paramagnetic rare-earth garnet (e.g., ErGG<sup>9</sup>), this leads to  $\Delta C/C \sim 0.03$ . This fraction may be increased significantly if the interactions are of electric quadrupole-quadrupole origin rather than simple exchange coupling. In this case the Weiss constant may be quite small, being itself a second-order effect,<sup>10</sup> but the cross term producing the  $g$ -value shift could be quite large.

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<sup>3</sup>If the  $A$ -class ion is a rare earth with total angular momentum  $J$  and Landé factor  $g_J$ , the relation between  $S_A$  and  $S_A'$  is given by

$$\vec{S}_A = (g_J - 1) \vec{J} = [(g_J - 1)/g_J] (g \vec{S}_A').$$

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