

## Far Infrared Spectra of Rare-Earth Iron Garnets\*

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Transmission measurements on a number of ferrimagnetic rare-earth iron garnets at low temperatures indicate that both collective and single-ion excitations are observable. Kaplan-Kittel exchange resonances, wherein a mutual precession of the iron and rare-earth sublattices occurs, have been observed at 2°K in YbIG (14.0 cm<sup>-1</sup>), ErIG (10.0 cm<sup>-1</sup>), SmIG (33.5 cm<sup>-1</sup>), and HoIG (38.5 cm<sup>-1</sup>). The exchange resonances are usually easily identified by their characteristic temperature dependence, which stems from the marked temperature dependence of the rare-earth sublattice magnetization. On the other hand, the single-ion transitions, resulting from transitions between rare-earth ion energy levels split by the crystalline electric field and the iron exchange field, are relatively independent of temperature below 70°K, because the iron sublattice producing the exchange field remains nearly completely ordered. The observation of single-ion transitions has permitted a rather detailed study of the fields acting on an individual rare-earth ion in the garnet structure. For example, measurement of the angular dependence and Zeeman shift of the exchange-split Kramers doublet of Yb<sup>3+</sup> in YbIG indicates that both the spectroscopic *g* values of the ground doublet and the exchange field acting on the doublet are anisotropic. Also, a slight temperature dependence of the single-ion splittings in both ErIG and SmIG suggests that a weak ferromagnetic rare-earth-rare-earth coupling exists. Further, single-ion transitions from the ground state of the rare-earth ion to higher crystal-field states as modified by the iron exchange field have been identified in ErIG and HoIG, but a detailed level assignment has not been possible. Finally, the absence of observable single-ion transitions in GdIG confirms the predicted dependence of these on crystal field-induced inequivalence of rare-earth ions, which is negligible for an *S*-state ion such as Gd<sup>3+</sup>.

### I. INTRODUCTION

BY means of far infrared spectroscopy it is possible to make direct measurements of transitions between the lowest lying rare-earth ion energy levels in rare-earth iron garnets (general formula 3R<sub>2</sub>O<sub>3</sub>·5 Fe<sub>2</sub>O<sub>3</sub>). The first far infrared investigation of a rare-earth iron garnet, namely, that of ytterbium, indicated that the splitting of the Yb<sup>3+</sup> ground-state doublet caused by the iron exchange field could be measured directly by far infrared techniques.<sup>1</sup> Such single-ion transitions are thought to be allowed in the rare-earth iron garnets because, due to anisotropy, the rare-earth ions are not equivalent.<sup>2</sup> A situation is possible in the garnets where a number of rare-earth ions may have the same longitudinal *g* value and thus may be equivalent in the sense that their magnetic moments all precess at the same frequency in a magnetic field, while, because of the low symmetry of the rare-earth sites, the transverse *g* values which govern the selection rules are not necessarily equal. Thus the ions are actually inequivalent and the single-ion transitions can be excited in this case.<sup>2</sup> The spectroscopic absence of any such transitions in the case of gadolinium illustrates the usual selection rule for exchange coupled spins, valid in the absence of anisotropy.

The manifest importance of the observation of strong single-ion transitions in magnetic crystals tends to overshadow the also important observation in ytterbium iron garnet (YbIG) of the collective exchange resonance

mode.<sup>1</sup> This exchange resonance, first discussed by Kaplan and Kittel,<sup>3</sup> brings into play both the rare earth and the iron sublattice magnetizations. Since all the rare-earth ions precess in phase with about the same amplitudes, only the net moment of the rare-earth sublattice enters in this mode.<sup>2</sup> The study of this exchange resonance thus yields information on the macroscopic magnetic properties of the crystal rather than single-ion properties.

The possibility of spectroscopically studying single-ion magnetic interactions has led to a continued investigation of YbIG and an introductory research into the spectra of other rare-earth iron garnets, namely, the garnets of gadolinium, erbium, samarium, and holmium. Although each of the free ions in the rare-earth series has different magnetic properties from its neighbors, it is advantageous first to consider the low-temperature far infrared absorption data for all iron garnets investigated as a whole. An account of these general results is given in the following section. The differences among the various rare-earth iron garnets are described in the remainder of this paper, where experimental results and interpretation for each of the garnets are presented in turn.

### II. GENERAL LOW-TEMPERATURE SPECTROSCOPIC RESULTS

Both the far infrared monochromator used in our transmission experiments and the cryostat for low-temperature and intermediate-temperature measurements have been described elsewhere.<sup>1,4</sup>

A composite diagram of the low-temperature (2°K) absorption frequencies for all of the rare-earth iron

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<sup>1</sup> A. J. Sievers, III, and M. Tinkham, *Phys. Rev.* **124**, 321 (1961).

<sup>2</sup> M. Tinkham, *Phys. Rev.* **124**, 311 (1961).

<sup>3</sup> J. Kaplan and C. Kittel, *J. Chem. Phys.* **21**, 760 (1953).

<sup>4</sup> R. C. Ohlmann and M. Tinkham, *Phys. Rev.* **123**, 425 (1961).

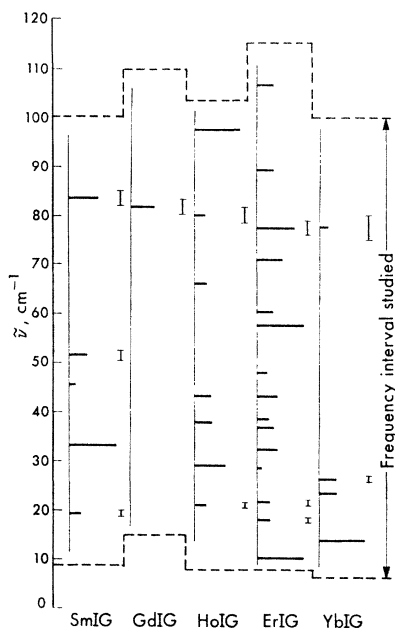


FIG. 1. Frequencies and relative intensities in the absorption spectra of the rare-earth iron garnets at 2°K. The relative intensity scales for both SmIG and GdIG are expanded tenfold relative to the scales used for ErIG, HoIG, and YbIG. The atomic number of the rare-earth ion increases from left to right.

garnets investigated is shown in Fig. 1. The estimated relative intensities or integrated absorptions ( $\chi_{\max}''\Delta\nu$ ) are shown, as well as the frequencies at which the absorptions occur for each ion. The intensities in adjacent columns can be compared on the same scale, provided the length of the intensity markers for SmIG and GdIG first is reduced by a factor of ten. The columns are arranged in order of increasing atomic number of the rare-earth ion.

A study of the experimental results in Fig. 1 indicates that, with the exception of GdIG, the absorption spectra of the rare earth iron garnets in the far infrared region are complex. With present techniques, it is not possible to extend the far infrared measurements to frequencies much lower than 10  $\text{cm}^{-1}$ ; however, the presence of any single-ion transitions corresponding to such low frequencies would produce dominant Schottky anomalies in the low-temperature specific-heat capacity.<sup>2</sup> Harris and Meyer<sup>5</sup> have measured the specific heat as a function of temperature for the rare-earth iron garnet series, and they find no anomalies corresponding to frequencies below 10  $\text{cm}^{-1}$ . Thus, for each ion, the ground-state splitting is in the far infrared region. In general, we have found quite good agreement between specific heat and spectroscopic measurements. In YbIG, for example, specific heat measurements predict the average ground-state doublet splitting to be 25.0  $\text{cm}^{-1}$ . For comparison, the average of the measured splittings from spectroscopic measurements<sup>1</sup> for the two inequivalent sites is 24.9  $\text{cm}^{-1}$ .

<sup>5</sup> A. B. Harris and H. Meyer, Phys. Rev. **127**, 101 (1962).

The apparent discrepancy between spectroscopic and specific heat measurements on GdIG, one of the simplest magnetic garnets, substantiates the mechanism which we feel accounts for the experimental observation of single-ion transitions. The specific heat measurements<sup>5</sup> show that the ground-state splitting of the gadolinium ion in the iron exchange field is 27.8  $\text{cm}^{-1}$ , yet no resonance is observed there. To interpret this fact, we note that in contrast with the other rare-earth iron garnets, the free  $\text{Gd}^{3+}$  ion, with a half-filled 4*f* shell, has  $L=0$ , and the crystal field interaction is then much smaller than the exchange interaction or the energy separation to excited states. Thus the crystal field has little effect, and the  $\text{Gd}^{3+}$  ions are in fact essentially equivalent. The absence of any observable magnetic absorption in the far infrared at 27.8  $\text{cm}^{-1}$  thus strongly supports our interpretation,<sup>2</sup> which attributes the observability of these spectroscopic transitions to the inequivalence of ions, produced by the local crystal fields. Within the limits of the sensitivity of our spectrometer, the  $\text{Gd}^{3+}$  ions appear equivalent. The exchange resonance in GdIG is also not observed, because its absorption strength depends on  $[g(\text{Gd})-g(\text{Fe})]^2$ , and both  $\text{Gd}^{3+}$  and  $\text{Fe}^{3+}$  have about the same  $g$  value, namely, 2.00.

The one absorption observed in GdIG (near 80  $\text{cm}^{-1}$ ) does not appear to be part of the magnetic spectrum but is probably related to a phonon transition. For, in each of the garnets in Fig. 1, an absorption occurs at roughly 80  $\text{cm}^{-1}$ . The regular decrease in frequency with increase in ionic mass across the series, visible in Fig. 1, supports such an assignment.

### III. ANGULAR DEPENDENCE OF SINGLE-ION TRANSITIONS IN YbIG

The principal values of the ground-state splitting for YbIG ( $\text{Yb}^{3+}; {}^2F_{7/2}$ ) were previously obtained indirectly by Wickersheim<sup>6</sup> from near infrared measurements. Using electron paramagnetic resonance (EPR)  $g$  values found for ytterbium in the isomorphous ytterbium gallium garnet, he found that the iron exchange field acting on the rare-earth ion appeared to be anisotropic.

We have attempted to measure directly the principal values of the ground-state doublet splittings in YbIG, and also to measure the corresponding  $g$  values from the superimposed Zeeman shift of the lines in a magnetic field.

A mosaic YbIG sample with a 12-mm diameter was used for these experiments. This sample was formed from four single crystals of YbIG which had first been oriented and then glued to a tapered crystal-quartz disk about 1 mm thick. A [110] axis was oriented along the direction of infrared energy propagation. Wickersheim<sup>6</sup> has found that at 77°K, 700 Oe is sufficient to rotate the net magnetization in YbIG to any crystallographic direction. Because the anisotropy field increases rapidly with decreasing temperature, we

<sup>6</sup> K. A. Wickersheim, Phys. Rev. **122**, 1376 (1961).

TABLE I. Anisotropic exchange field for YbIG.

	This work			(Wickersheim-White)			
	$\Delta E$ ( $\text{cm}^{-1}$ )	$g$	$H_{\text{eff}}$ (G)	$H_{\text{ex}} = \frac{gJ}{2(gJ-1)} H_{\text{eff}}$ (G)	$\Delta E$ ( $\text{cm}^{-1}$ )	$g$	$H_{\text{ex}}$ (G)
$x$	$11.0 \pm 1.2$	$3.9 \pm 1.8$	$0.62 \times 10^6$	$2.3 \times 10^6$	$11.8 \pm 0.2$	$2.8 \pm 0.1$	$3.6 \times 10^6$
$y$	$27.4 \pm 0.4$	$3.2 \pm 0.6$	$1.8 \times 10^6$	$7.3 \times 10^6$	$26.1 \pm 0.1$	$3.6 \pm 0.15$	$6.2 \times 10^6$
$z$	$31.8 \pm 0.4$	$4.1 \pm 0.6$	$1.7 \times 10^6$	$6.6 \times 10^6$	$30.6 \pm 0.2$	$3.7 \pm 0.15$	$7.1 \times 10^6$

estimated the applied external field necessary for the same task at 48°K to be about 12 kOe. Because our magnet was only capable of reaching fields of 26 kOe, the anisotropy fields then set a lower bound of roughly 48°K on the sample temperature usable in this experiment. Since the splitting of the ground doublet is only 25  $\text{cm}^{-1}$ , the absorption is greatly reduced at this elevated temperature due to the partial equalization of population between the two levels. In the absence of an applied field, the doublet absorption at 48°K was experimentally found to be only about 5%.

The magnetic shift of the absorption lines has been measured with the static magnetic field in the crystal [111], [110], and [100] directions. The number of inequivalent ions is different for the various crystal directions. Because of our limited sensitivity, only those absorptions which correspond to a large number of equivalent ions, and hence to large intensity, could be observed. For all crystal orientations, a linear Zeeman shift was recorded from 11 to 25.6 kOe. The extrapolated values of the two inequivalent single-ion splittings at zero field for the [111] direction are 23.1 and 26.7  $\text{cm}^{-1}$ , in reasonable agreement with our previously published zero-field values, 23.4 and 26.4  $\text{cm}^{-1}$ . The one observable splitting for the [110] direction extrapolated to 22.3  $\text{cm}^{-1}$ . The results of measurements in the [100] direction are more difficult to interpret. The extrapolation to zero field yielded two absorptions of about equal intensity at 28.8 and 27.1  $\text{cm}^{-1}$ . However, only one absorption is expected<sup>6</sup> at roughly this frequency when the net magnetization is along the [100] axis, the other site frequency being expected to be below 12  $\text{cm}^{-1}$ . Perhaps, because the [100] direction is the magnetically hardest crystal axis,<sup>7</sup> the sublattice magnetizations are not actually pointing exactly in this direction. For angles near the [100] direction, two single-ion absorptions are expected to replace the one absorption occurring at the exact [100] direction. In any case, since the geometry of the principal axes is known,<sup>6</sup> we can still calculate the principal values of the splittings referred to their local  $x$ ,  $y$ , and  $z$  axes by using only our measurements for the [111] and [110] directions. The experimental splittings at the principal directions, the experimental  $g$  values, and the corresponding values of the exchange field, as deduced from our measurements are given in

<sup>7</sup> R. F. Pearson, J. Appl. Phys. **33**, 1236S (1962).

Table I. These results are compared in the table with the corresponding values obtained by Wickersheim, and later refined by Wickersheim and White,<sup>8</sup> from near infrared measurements. The axis-labeling convention is that of reference 6.

The large errors in our measurement of the principal splittings and corresponding  $g$  values arise from a combination of the reduced absorption intensity at elevated temperatures and the small external field available to rotate the magnetization to a magnetically hard crystal axis. Thus our experimental results, although independently supporting the interpretation of an anisotropic rare-earth-iron exchange interaction reached by Wickersheim, are in fact less precise than the recent work by Wickersheim and White<sup>8</sup> on the same problem.

#### IV. ERBIUM IRON GARNET

Since the free  $\text{Er}^{3+}$  ion ground state ( $^4I_{15/2}$ ) has half-integral angular momentum, the crystal field interaction at the rare-earth ion sites, which can partially remove the  $(2J+1) = 16$ -fold degeneracy of the free-ion ground state, must at least leave Kramers degenerate states. Because  $\text{Yb}^{3+}$  also has half-integral angular momentum, the far infrared spectra of the two rare-earth iron garnets might be expected to be very similar. However, susceptibility measurements<sup>9</sup> previously had indicated that the crystal field splitting in ErIG is much smaller than in YbIG, and Fig. 1 indeed shows that the two spectra are strikingly different.

To construct the ErIG column in Fig. 1, the transmission through ErIG pressed powder samples was measured<sup>10</sup> from 8.3 to 115  $\text{cm}^{-1}$ . The samples were 12 mm in diameter and ranged in thickness from 0.14 to 1 mm. Fifteen absorption lines have been observed in this frequency interval at 2°K. The frequencies in  $\text{cm}^{-1}$  are:

10.0±0.2	36.9±0.5	60.5±0.8
18.2±0.4	38.6±0.5	71.0±1.0
21.6±0.4	43.3±0.5	77.5±1.5
28.4±0.4	48.1±0.6	89.3±2.0
32.2±0.4	57.5±0.8	107.0±4.0

<sup>8</sup> K. A. Wickersheim and R. L. White, Phys. Rev. Letters **8**, 483 (1962).

<sup>9</sup> M. Ball, G. Garton, M. J. M. Leask, D. Ryan, and W. P. Wolf, J. Appl. Phys. **32**, 267S (1961).

<sup>10</sup> A preliminary announcement of these measurements has been made. A. J. Sievers, III, and M. Tinkham, Bull. Am. Phys. Soc. **6**, 160 (1961).

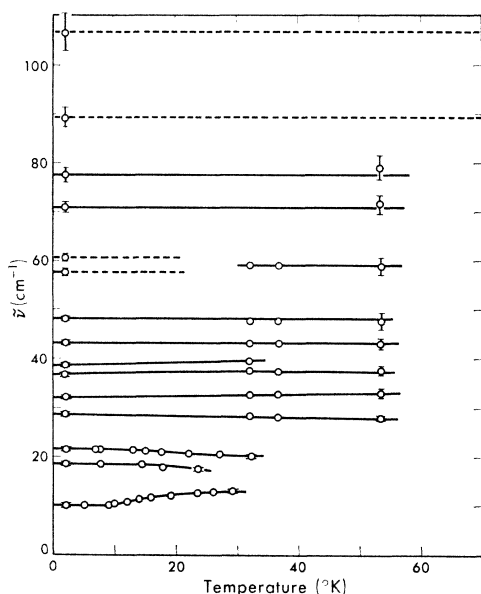


FIG. 2. Temperature dependence of the absorption spectrum in ErIG. The solid lines connect experimental points. The dashed lines denote the probable extrapolated curves.

The corresponding estimated relative absorption strengths ( $\chi_{\max}''\Delta\bar{\nu}$ ) shown in Fig. 1 were calculated assuming  $n = \sqrt{\epsilon} = 2.2$ , a value obtained from previously reported measurements<sup>1</sup> on YbIG. A change between ions in the rare-earth series in the garnet is not expected to appreciably alter the lattice dynamics for the structure or the index of refraction.

The lowest frequency absorption, at  $10.0 \pm 0.2 \text{ cm}^{-1}$ , has been identified as the Kaplan-Kittel exchange resonance from studies of the temperature dependence of the absorption frequency, the results being shown in Figs. 2 and 3. From measurements at 5°K with our thinnest sample (0.14 mm), the relative absorption maximum was found to be 65% with a full linewidth at half maximum absorption of  $1.6 \text{ cm}^{-1}$ . Because the effective bandwidth of the monochromator was relatively small ( $0.7 \text{ cm}^{-1}$ ) during this measurement, it was not expected to modify seriously the true linewidth. Estimates of approximate upper and lower bounds for the true linewidth have been obtained by assuming that the profiles of both the absorption line and the resolution function from the spectrometer could be described by Gaussian profiles in one limit and Lorentzian profiles in the other. The estimated bounds for the true linewidth are

$$0.9 \text{ cm}^{-1} \leq \Delta\bar{\nu} \leq 1.5 \text{ cm}^{-1}.$$

Hence the undistorted linewidth of the exchange resonance at 5°K is about  $1 \text{ cm}^{-1}$ . This result is to be compared with the estimates of the bounds for the exchange resonance linewidth for YbIG, which in the same approximation are

$$0.8 \text{ cm}^{-1} \leq \Delta\bar{\nu} \leq 1.5 \text{ cm}^{-1}.$$

The possibility that sample inhomogeneity or strain may be contributing to linewidth cannot be excluded, however.

Our assignment of the exchange resonance to the lowest frequency absorption has been confirmed by varying the sample temperature. Neglecting anisotropy, the exchange frequency is<sup>2,3</sup>

$$\omega_e = \lambda[\gamma_2 M_1 - \gamma_1 M_2(T)], \quad (1)$$

where  $\lambda$  is the molecular field constant,  $\gamma_1$ ,  $\gamma_2$  the spectroscopic splitting factors and  $M_1$ ,  $M_2$  the antiparallel sublattice magnetizations for the iron and rare earth sublattices, respectively. The lowest frequency absorption is seen in Figs. 2 and 3 to have the characteristic temperature dependence previously found<sup>1</sup> for YbIG, i.e., frequency increasing as the temperature is raised with accompanying decrease of  $M_2(T)$  in Eq. (1). When the lowest magnetic states are in the form of a Kramers doublet, it is possible to write the isotropic exchange frequency in terms of the doublet frequency, as has been shown elsewhere.<sup>11</sup> The exchange resonance for the garnets in the absence of magnetocrystalline anisotropy is then given by the simple expression

$$\omega_e = \bar{\omega}_2 \left[ 1 - \frac{3 M_2(T)}{5 M_2(0)} \right], \quad (2)$$

where  $\bar{\omega}_2$  is the frequency corresponding to the average doublet splitting. At absolute zero this expression reduces to

$$\omega_e = \frac{2}{5} \bar{\omega}_2. \quad (3)$$

Taking the next two higher frequency absorptions in Fig. 2 as transitions within the ground doublet for the two inequivalent sites, and averaging, the exchange frequency in the isotropic approximation is

$$\omega_e = \frac{2}{5} (19.9) = 8 \text{ cm}^{-1}. \quad (3a)$$

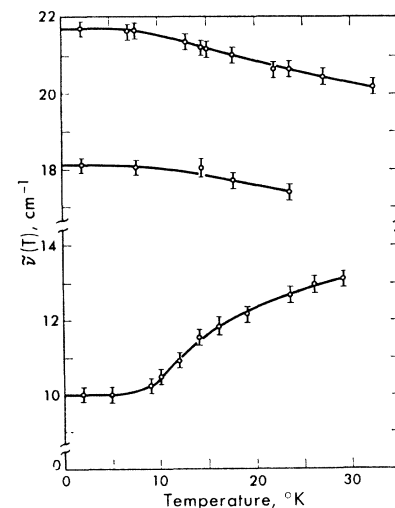


FIG. 3. Temperature dependence of the three lowest frequency absorptions in ErIG. The lowest frequency absorption is the Kaplan-Kittel exchange resonance. The next two higher frequency absorptions, which are slightly temperature dependent, are single-ion transitions.

<sup>11</sup> M. Tinkham, J. Appl. Phys. 33, 1248S (1962).

Unfortunately, sufficient information is not available to estimate the anisotropy correction, as was possible in the case of YbIG. However, the  $2\text{ cm}^{-1}$  correction necessary to agree with the experimental result of  $10\text{ cm}^{-1}$  is of the same order as the  $4\text{ cm}^{-1}$  correction which was previously found for YbIG.<sup>1,2</sup>

Another interesting result disclosed through variation of sample temperature is the slight temperature dependence of the ground-state single-ion transition frequencies as shown in Fig. 3. Although the higher frequency absorptions do not appear temperature dependent (Fig. 2), a variation could be hidden in the larger experimental errors for these higher frequencies. The experimental shift in frequency of the ground doublet with temperature at low temperature has been fitted by introducing a ferromagnetic rare-earth-rare-earth coupling. In the molecular field approximation, the single ion frequency then becomes

$$\omega_2(T) = \gamma_2[\lambda M_1 + \lambda' M_2(T)]$$

or

$$\omega_2(T) = \bar{\omega}_2 \left[ 1 + \frac{\lambda' M_2(T)}{\lambda M_1} \right], \quad (4)$$

where  $\bar{\omega}_2 = \gamma_2 \lambda M_1$  is the frequency of the ground doublet if  $M_2$  were zero,  $\lambda'$  is the ferromagnetic rare-earth coupling parameter,  $M_2(T)$  is the temperature-dependent rare-earth sublattice magnetization, and  $M_1$  is the iron sublattice magnetization, which is essentially temperature independent at low temperatures.

Using a simplified expression for the rare-earth sublattice magnetization  $M_2(T)$ , the temperature dependence of the observed single-ion splitting has been fitted by (4). The approximate expression which was used for  $M_2(T)$  is based on one ground doublet and one excited doublet, each split by different amounts in the iron exchange field. The details of this approximation are given elsewhere.<sup>12</sup> The fit gave  $\lambda'/\lambda = 0.05$ , and a separation between the two doublets of  $57^\circ\text{K}$  ( $40\text{ cm}^{-1}$ ). It is encouraging that this separation is roughly the strength of the crystal field splitting necessary to account for some of the remaining 12 absorptions in Fig. 2. The ratio of  $\lambda'/\lambda$  suggests that in ErIG the strength of the ferromagnetic rare-earth-rare-earth coupling is about 5% of that of the rare-earth-iron coupling.

This ferromagnetic coupling between rare-earth ions will not directly affect the exchange resonance because a sublattice cannot exert a torque on itself. However, this ferromagnetic coupling will change our estimate of the exchange resonance frequency because we have used the uncorrected  $\omega_2(T)$  in estimating the isotropic exchange frequency in Eq. (3a). The corrected contribution of the rare-earth-iron interaction to the single-ion splitting is  $\bar{\omega}_2 = 18.1\text{ cm}^{-1}$ . The predicted exchange resonance at absolute zero with neglect of anisotropy is then

$$\omega_e = 7.25\text{ cm}^{-1}.$$

<sup>12</sup> A. J. Sievers, III, Ph.D. thesis, University of California, 1962 (unpublished).

This result is still such that a reasonable, but slightly different, anisotropy correction ( $2.75\text{ cm}^{-1}$ ) will give agreement with the experimentally determined exchange resonance frequency.

We have re-examined the YbIG spectrum more closely in the light of this discovery and find a small downward shift in the upper absorption frequency ( $26.4\text{ cm}^{-1}$ ) of about  $0.4 \pm 0.2\text{ cm}^{-1}$  at  $21^\circ\text{K}$ , but no shift is observed for the lower frequency doublet absorption occurring at  $23.4\text{ cm}^{-1}$ . The shift is expected to be smaller for YbIG because the  $\text{Yb}^{3+}$  sublattice magnetization is only one-third as large as the  $\text{Er}^{3+}$  sublattice magnetization. From our data, the strength of the rare-earth-rare-earth coupling parameter  $\lambda'$  is estimated to be  $\sim 0.02\lambda$  for YbIG.

Because the rare-earth-rare-earth coupling has been shown<sup>9</sup> to be much weaker in the rare-earth gallium garnets than the coupling strengths we observe in the isomorphic rare-earth iron garnets, a question arises with respect to the origin of the latter. A mechanism which only acts between rare-earth ions in the ferromagnetic iron garnet has been proposed by Suhl.<sup>13</sup> It is suggested that the interactions between rare earth ions arise via the low-lying iron spin wave states as intermediate states. This mechanism was originally proposed<sup>14</sup> as a source of linewidth in nuclear magnetic resonance in ferromagnets, but given the highly anisotropic exchange interactions in the garnets, one might also expect a frequency shift. This shift would be expected to have the same order of magnitude as the calculated broadening near  $T=0$ , where the rare-earth ions are polarized, but the shift would disappear (except for the self-energy effect) as the rare-earth moments disordered. The linewidth predicted<sup>14</sup> for such an interaction (when transcribed to our case) is

$$\Delta\omega = -\left(\frac{1}{8}\right) \left(\frac{H_{\text{ex}}}{2\pi}\right)^{1/2} \left(\frac{H_{\text{anis}}}{H_{\text{anis}}}\right)^{1/4} \left(\frac{\hbar\omega_2}{g\mu_B H_{\text{ex}}}\right) \omega_2 \quad (5)$$

for an effective spin  $\frac{1}{2}$ . In (5),  $H_{\text{ex}}$  is the exchange field between iron moments;  $H_{\text{anis}}$ , the anisotropy field.  $H_{\text{anis}}$  causes the iron spin wave spectrum to have an energy gap at  $k=0$ . Since anisotropy fields, in general, fall rapidly with increasing temperature, the gap in the spin wave spectrum is temperature dependent. Both the coupling parameter  $\lambda'$  and the linewidth are expected to increase with temperature. We can estimate the linewidths near  $T=0$  for both YbIG and ErIG, since for each we have roughly  $H_{\text{ex}} \approx 6 \times 10^6\text{ Oe}$ ,  $H_{\text{anis}} \approx 3 \times 10^4\text{ Oe}$  and  $\omega_2 \approx 25\text{ cm}^{-1}$ . The linewidth is then estimated to be  $\Delta\bar{\nu} \approx 1\text{ cm}^{-1}$  at  $0^\circ\text{K}$ . This interaction not only predicts the order of magnitude of the observed line widths for single ion transitions in YbIG and ErIG at absolute zero but also accounts for the

<sup>13</sup> H. Suhl, unpublished comment at Osaka Magnetic Resonance Symposium, October 1961.

<sup>14</sup> H. Suhl, Phys. Rev. **109**, 606 (1958); J. Phys. Radium **20**, 333 (1959).

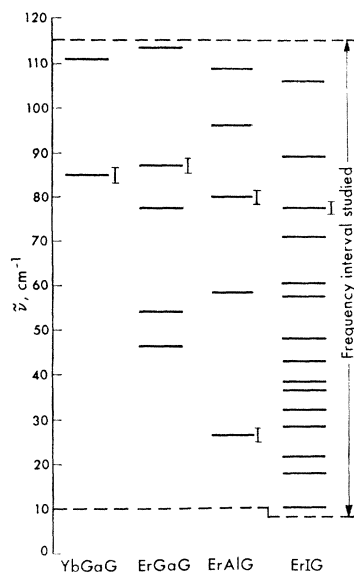


FIG. 4. Low-temperature absorption spectra of paramagnetic YbGaG, ErGaG, and ErAlG, compared with ferrimagnetic ErIG.

temperature dependence of the linewidths. In YbIG, for example, the theoretical expression predicts that the width increases by a factor of 2 when the sample temperature reaches 40°K. In the light of our previous measurements<sup>1</sup> of the linewidth in YbIG, such a change in width is in reasonable agreement with experiment. It is also suggestive that the observed shift in frequency due to this apparent coupling is of the same order of magnitude as this calculated width near  $T=0$ , where the rare-earth spins are almost completely ordered. Lacking any detailed theory, however, these observations must be considered to be somewhat speculative.

#### Absorption by Erbium in Paramagnetic Garnets

In order to understand better the remaining twelve absorption lines observed in ErIG, supplementary transmission measurements have been carried out with paramagnetic erbium gallium and erbium aluminum garnets. The garnets of iron and gallium are known to have very similar structures. However, the lattice constant of ytterbium aluminum garnet is appreciably smaller than that of ytterbium gallium garnet. A measure of the sensitivity of the rare-earth ion to its exact environment can be obtained from a comparison of measurements on these two compounds.

The results of our far infrared transmission measurements on ErGaG and ErAlG are compared with the spectrum obtained from YbGaG and ErIG in Fig. 4. The two absorptions observed in YbGaG at  $85 \pm 1$   $\text{cm}^{-1}$  and  $111 \pm 3$   $\text{cm}^{-1}$  have been tentatively identified as phonon transitions. As mentioned in Sec. II, the 85- $\text{cm}^{-1}$  line is characteristic of all the garnets, allowing for mass-dependent shifts. The  $\sim 110$ - $\text{cm}^{-1}$  line also appears in all cases in which the spectrum was followed to that high a frequency. The identification of the 85- $\text{cm}^{-1}$  absorption as a phonon transition was supported

through application of a 10.7 kOe magnetic field to the YbGaG sample at 2°K. No shift in the frequency of the absorption line at 85  $\text{cm}^{-1}$  was observed, although a shift of 0.8  $\text{cm}^{-1}$  could have been detected. If the transition were between crystal field levels, both the ground doublet, which has an average spectroscopic  $g=24/7$ , and the excited doublet of unknown  $g$  would split in an applied field. The ground state splitting itself is large enough to produce an observable shift of 0.8  $\text{cm}^{-1}$  in the transition frequency. No broadening or shift was detected.

Because only the well-shielded 4*f* shell loses electrons in going from Yb<sup>3+</sup> to Er<sup>3+</sup>, the phonon transitions for both garnets are expected to be very similar. The data on ErGaG in Fig. 4 indicate that two high-frequency absorptions occur at  $86 \pm 1$  and  $114 \pm 3$   $\text{cm}^{-1}$ . If they are identified as phonon transitions, the slight increase in the frequency of these transitions compared to those with Yb<sup>3+</sup> is in reasonable accord with the 3% smaller ionic mass of Er<sup>3+</sup>.

Three more absorptions have been observed in ErGaG at lower frequencies, namely, at

$$46.5 \pm 0.5, \quad 54.0 \pm 1, \quad \text{and} \quad 77 \pm 3 \text{ cm}^{-1}.$$

Application of a 10.7 kOe field *does* change the frequency of these absorptions. At high temperatures (40°K) two more absorptions appear at

$$24.0 \pm 0.4 \quad \text{and} \quad 32.0 \pm 0.5 \text{ cm}^{-1}.$$

These high-temperature absorptions probably arise from transitions between the two excited states at 46.5 and 54  $\text{cm}^{-1}$  and the third state at 77  $\text{cm}^{-1}$ , since the observed frequencies are within the experimental error in the appropriate differences, and since the temperature dependence of the observed intensity is at least qualitatively correct.

Five absorptions have been observed in ErAlG (see Fig. 4) at the following frequencies:

$$26.7 \pm 0.4, \quad 58.2 \pm 0.6, \quad 80 \pm 1, \quad 96 \pm 2, \quad \text{and} \quad 109 \pm 3 \text{ cm}^{-1}.$$

Again the lowest three frequencies have been seen to move in a 10.7 kOe field. Also, high-temperature measurements have revealed two absorptions at  $31.5 \pm 0.3$  and  $20.7 \pm 0.3$   $\text{cm}^{-1}$ . These frequencies correspond very closely to the difference from the lowest excited level to the second and from the second to the third. The two high-frequency absorptions at 96 and 109  $\text{cm}^{-1}$  cannot be definitely assigned to phonon transitions because the structure of ErAlG is slightly different from ErGaG. However, such an assignment is not inconsistent with the experimental results on ErGaG. A direct comparison of the absorption spectra in ErGa and ErAl garnets in Fig. 4 unfortunately indicates that the crystal-field levels are very sensitive to the exact crystal structure.

Even with this spectroscopic information available, it has not been possible to unscramble the ErIG spectrum, shown in Fig. 4, column 4. Qualitatively, it is

clear that the spectrum arises from transitions within the ground doublet and transitions between the ground state and the split Kramers doublets of the higher crystal-field levels plus a phonon transition or two. The problems in making any definite level assignment are on the surface threefold: (1) turning on the perturbation from an external field along the [111] axis of an ErGaG crystal (Fig. 4, column 2) to simulate the iron garnet problem changes each absorption into four absorptions because there are two inequivalent rare-earth sites for fields in the [111] direction; (2) the crystal field levels are close enough together that magnetic sublevels from different crystal field levels intermingle; and (3) simple perturbation theory probably cannot be used to describe the effect of the field, because the exchange field splittings are comparable to the separation between crystal field split levels, leading to important higher order effects of off-diagonal matrix elements of the exchange energy.

#### V. SAMARIUM IRON GARNET

The far infrared spectrum of samarium iron garnet (SmIG) in pressed powder samples and in one single crystal has been investigated from 9 to 100  $\text{cm}^{-1}$ . At 2°K, five absorptions are observed at

$19.4 \pm 0.5$ ,  $33.5 \pm 0.3$ ,  $46 \pm 1$ ,  $51.8 \pm 0.8$ , and  $83 \pm 2$   $\text{cm}^{-1}$ .

The strongest absorption is the one occurring at 33.5  $\text{cm}^{-1}$ , as is shown in Fig. 1.

The temperature dependences of the absorption frequencies are given in Fig. 5. The high-frequency absorption at 83  $\text{cm}^{-1}$  is temperature independent and has been tentatively identified with a phonon transition. Three of the lower frequency absorptions are seen to be definitely temperature dependent. Since more than one of the absorption frequencies is temperature dependent, an unambiguous experimental separation between the exchange resonance and single-ion transitions is no longer possible. However, it has been possible to make a somewhat plausible assignment, which we now consider.

$\text{Sm}^{3+}$ , although having a half integral angular momentum  $J=5/2$  in the free-ion ground state ( ${}^6H_{5/2}$ ), is different from the two previously considered rare-earth ions  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  in two respects. First, since  $\text{Sm}^{3+}$  has a less than half-filled  $4f$  shell, by Hund's rule  $\mathbf{L}$  and  $\mathbf{S}$  are oppositely directed; second,  $J$  is a less good quantum number in the crystal because the first excited level ( $J=7/2$ ) of the free ion is only 1100  $\text{cm}^{-1}$  above the ground state.

If, on the one hand, the Stark effects in the garnet are small compared to free-ion splittings, the antiferromagnetic coupling between  $\text{Fe}^{3+}$  and  $\text{Sm}^{3+}$  spins aligns the rare-earth magnetic moments parallel to the iron moments. The isotropic exchange resonance at 0°K then becomes

$$\omega_e = \bar{\omega}_2 [1 + (3/5)] = (8/5)\bar{\omega}_2.$$

On the other hand, large Stark splittings might be expected to alter this picture. The magnitude of the crystal field splitting in  $\text{YbGaG}$  for the  $J=7/2$  ground level is about 900  $\text{cm}^{-1}$ . Because the Stark splitting is an inverse function of the number of  $4f$  electrons, the splitting for  $\text{Sm}^{3+}$  ( $4f^5$ ) is expected to be considerably larger than the splitting for  $\text{Yb}^{3+}$  ( $4f^{13}$ ). With the first excited free ion state of  $\text{Sm}^{3+}$  only 1100  $\text{cm}^{-1}$  above the ground state, the crystal field splitting actually does not have to be much larger than observed in  $\text{YbIG}$  in order to thoroughly mix levels from different  $J$  states. In view of this fact, we wish to suggest that the rare-earth and iron moments may not be parallel, but because of this mixing may have the usual antiparallel sense found in the other garnets.

In view of the unusual temperature dependences observed in SmIG, it has been necessary to rely on the torque measurements of Pearson<sup>7</sup> and the specific heat measurements of Harris and Meyer,<sup>5</sup> to advance the interpretation of our data. Pearson has found that 100% samarium iron garnet crystals have the largest regular magnetocrystalline anisotropy energy of the entire rare earth series. Also, the easy axis appears to be along the [110] instead of the [111] axis found for many other garnets. This large anisotropy has led us to tentatively propose that the extremely temperature dependent absorption at 19.4  $\text{cm}^{-1}$  is the low-frequency "ferrimagnetic" mode, raised to infrared frequencies by the large anisotropy field, and falling rapidly in frequency as the anisotropy falls with increasing temperature.

Since the specific heat measurements have predicted accurately the average frequency of the ground doublet splittings for both  $\text{YbIG}$  and  $\text{ErIG}$ , we might take the average of the values,  $26.1 \pm 3$   $\text{cm}^{-1}$  and  $70 \pm 10$   $\text{cm}^{-1}$ , inferred for the two sites by Harris and Meyer. This leads to  $53 \pm 6$   $\text{cm}^{-1}$  for  $\bar{\omega}_2$ . This value should be taken with caution, however, since in fitting the SmIG specific heat data Harris and Meyer have noted an unexplained anomaly at low temperatures, and also the lattice specific heat is comparable to the magnetic contribution above 15°K, making the determination of the 70  $\text{cm}^{-1}$  level particularly uncertain. Moreover, if in fact the [110] axis is the easy axis, as indicated by the torque measurements, one would expect *three* inequivalent splittings with statistical weights 4:1:1, rather than two with equal weights. This casts further doubt on the precise value for  $\bar{\omega}_2$ , but not on the order of magnitude. If we then estimate  $\bar{\omega}_2 \approx 50 \pm 10$   $\text{cm}^{-1}$ , and use Eq. (3), we find  $\omega_e \approx 20$   $\text{cm}^{-1}$ . Knowing the frequency of the ferrimagnetic mode at  $T \approx 0$  to be 19  $\text{cm}^{-1}$ , we can correct the estimated  $\omega_e$  for the effect of anisotropy energy, obtaining finally  $\omega_e \sim 39$   $\text{cm}^{-1}$ . Considering the crudeness of the estimate, this is in reasonable agreement with the observed frequency of 33.5  $\text{cm}^{-1}$ . We should emphasize at this point that in obtaining this estimate we have used the assumption that Eq. (3), based on antiparallel moments as in

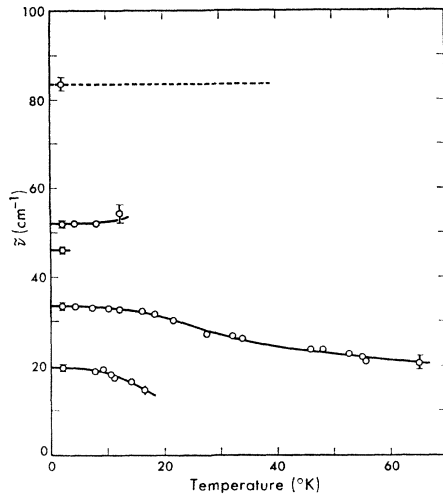


FIG. 5. Temperature dependence of the absorption spectrum in SmIG. The two lowest frequency absorptions,  $19.4 \text{ cm}^{-1}$  and  $33.5 \text{ cm}^{-1}$  at  $0^\circ\text{K}$ , appear to be the ferrimagnetic and exchange resonance modes, respectively.

YbIG and ErIG, is valid. If one now considers higher temperatures, we can explain the observed temperature dependence of the resonant frequency shown in Fig. 5 as resulting because the extremely rapid drop of the anisotropy correction (as monitored by the "ferrimagnetic resonance" mode) overpowers the relatively slow rise of  $\omega_e(T)$  that would be expected apart from anisotropy. Thus, the observed frequency decreases with increased temperature, rather than increasing as in YbIG or ErIG.

As the integrated absorptions for the SmIG spectrum are smaller by a factor of 10 than those of the other garnets in Fig. 1, the possibility of rare-earth impurities producing spurious spectral lines cannot be ignored. The extremely weak absorption at  $46 \text{ cm}^{-1}$  might possibly arise from such an impurity, or else from a single-ion transition with low statistical weight or small matrix element.

The pronounced temperature dependence of the absorption at  $51.8 \text{ cm}^{-1}$  shown in Fig. 5 directs attention to the Suhl mechanism for rare-earth-rare-earth coupling as an important interaction in SmIG. Since the coupling coefficient should increase with increasing temperature (because of the decrease in the anisotropy-induced gap in the spin-wave spectrum), the single-ion frequency should also increase with increasing temperature, if this effect overpowers the decrease in  $M_2(T)$ , as it does in our interpretation of the exchange resonance. If this is true, it appears that the absorption at  $51.8 \text{ cm}^{-1}$  probably is a single-ion transition. (Incidentally, the rather strong temperature dependence for this line suggests that the Suhl shift in frequency is probably  $5\text{--}10 \text{ cm}^{-1}$ . Correcting for this would improve the agreement found in the estimate of the exchange frequency in an earlier paragraph.) If the  $[110]$  direction is the easy direction, two other inequivalent

single-ion transitions also should exist, but they have not been observed with any confidence. A more sensitive spectrometer is apparently needed to complete the study of the SmIG spectrum, and the interpretation given here must be viewed as speculative.

## VI. HOLMIUM IRON GARNET

The one rare-earth iron garnet which we have studied having integral free rare-earth ion angular momentum ( $^3I_8$ ,  $J=8$ ) is holmium iron garnet (HoIG). The far infrared absorption spectrum has been measured in pressed powder samples from  $8$  to  $104 \text{ cm}^{-1}$ . The absorption frequencies in  $\text{cm}^{-1}$  observed in the powder samples at  $2^\circ\text{K}$  (see Figs. 1 and 6) are:

$21.5 \pm 0.4$	$66.6 \pm 0.6$
$29.4 \pm 0.4$	$80.6 \pm 0.9$
$38.5 \pm 0.5$	$98 \pm 2$
$43.5 \pm 0.5$	

As shown in Fig. 6, only the absorption at  $38.5 \text{ cm}^{-1}$  appears to be very temperature dependent. Measurements on 5% Ho-YIG single crystals (see Fig. 7) at frequencies to  $90 \text{ cm}^{-1}$  revealed lines at  $22.1 \pm 0.3$ ,  $29.4 \pm 0.4$ ,  $43.5 \pm 0.5$ ,  $66.5 \pm 0.6$ , and  $83.5 \pm 0.9 \text{ cm}^{-1}$ ; but they did not show the temperature dependent absorption line at  $38.5 \text{ cm}^{-1}$ . Since the exchange resonance is expected to vary with rare-earth concentration as well as with sample temperature, the  $38.5 \text{ cm}^{-1}$  line has been tentatively identified as the Kaplan-Kittel exchange resonance. As HoIG is expected to have a large magnetocrystalline anisotropy energy, according to Pearson's torque measurements,<sup>7</sup> the temperature dependence of the exchange resonance is not expected

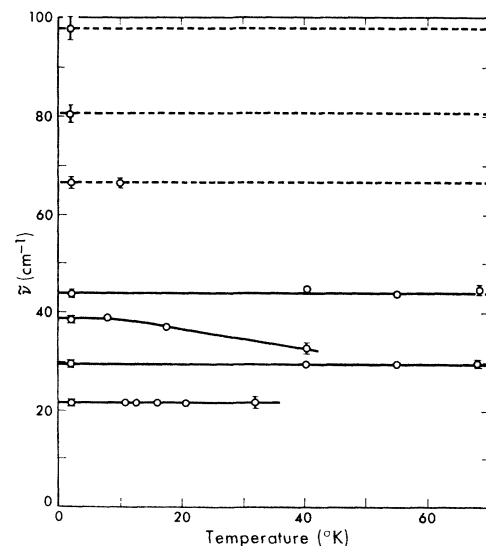


FIG. 6. Temperature dependence of the absorption spectrum in HoIG. The temperature-dependent absorption at  $38.5 \text{ cm}^{-1}$  has been identified with the exchange resonance mode.



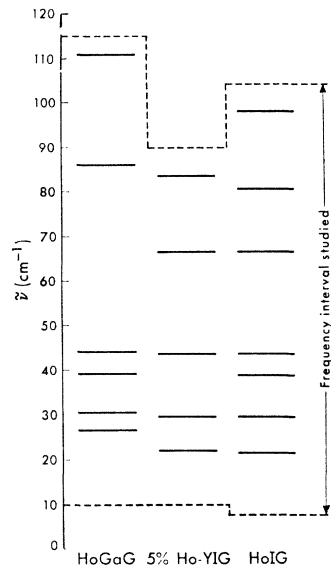


FIG. 7. Comparison of the low-temperature absorption spectrum of paramagnetic HoGaG with the spectra of ferrimagnetic Ho-YIG and HoIG.

or observed to follow the characteristic temperature dependence observed in YbIG and ErIG. Rather, it behaves more like that in SmIG.

Finally, it should be pointed out that in contrast to the temperature-dependent single-ion transitions previously observed in ErIG and SmIG, the lowest lying frequencies in HoIG are temperature independent up to 30°K, (see Fig. 6). For a rare-earth ion with integral  $J$ , it is expected that the local orthorhombic crystalline electric field splits the free ion ground state into non-degenerate levels. A magnetic field perturbation then shifts the crystal field levels only in second order, whereas the Kramers degenerate doublets for half-integral  $J$  are split in first order. Although the intrinsic rare-earth-rare-earth coupling might be nearly the same in ErIG and HoIG, measurement of the second-order shift in a HoIG transition frequency arising from a change of rare earth magnetization with temperature would be beyond the accuracy of our far infrared monochromator.

Supplementary transmission measurements with a holmium gallium garnet (HoGaG) single crystal gave six absorptions at

$26.5 \pm 0.4$	$44.2 \pm 0.6$
$30.3 \pm 0.4$	$86.0 \pm 1$
$39.0 \pm 0.4$	$111 \pm 2 \text{ cm}^{-1}$ ,

as depicted in Fig. 7. For an easy [111] direction each of the single-ion absorptions in HoGaG should split into two absorptions on passing to HoIG in Fig. 7 because of the two inequivalent sites in the iron garnets, which could have appreciably different second-order shifts due to the exchange interaction with the iron. The data of Fig. 7 indicate that the number of absorptions actually observed in the iron garnet only permits a one-to-one correspondence with the HoGaG data if one neglects the effects of nonequivalent sites. (The

specific heat data also do not distinguish two sites.) If one does this, the observed shifts in level position on going from HoGaG to HoIG are not unreasonable effects for an exchange interaction of reasonable size. However, it is also entirely possible that much more drastic rearrangements are occurring because of the large number of closely spaced levels in this system. Thus, a detailed interpretation of these results is not possible at present.

## VII. CONCLUSIONS

The far infrared spectroscopic investigation of the rare-earth iron garnets has provided a wealth of detailed information on magnetic interactions.

Ytterbium iron garnet has the simplest spectrum of the rare-earth ions with  $L \neq 0$ . From measurements with strong static fields along the easy [111] direction and also the [110] direction, the angular dependence of the rare-earth ion ground-state splitting in the iron exchange field has been found. The spectroscopic  $g$  values have been obtained from the superposed Zeeman shifts. Together, the principal values of the splittings and the corresponding  $g$  values confirm that the rare-earth-iron exchange interaction is anisotropic, as found by Wickersheim and White.

The spectrum of erbium iron garnet is exceedingly intricate. Although  $\text{Er}^{3+}$  has a half-integral  $J$  value as does  $\text{Yb}^{3+}$ , the crystal field splitting is of the same order as the exchange splitting of the Kramers doublets. Of the fifteen absorptions which have been found, only three magnetic absorptions have been identified. The lowest frequency absorption has the characteristic temperature dependence of the exchange resonance. The next two higher frequency absorptions, which are slightly temperature dependent, have been identified with the exchange split erbium ground state in the two inequivalent sites. The slight temperature dependence of the absorption frequencies can be accounted for by introducing a small rare-earth-rare-earth coupling. Supplementary transmission measurements with an erbium gallium garnet single crystal indicate that many of the remaining lines in the iron garnet are probably due to transitions to higher crystal field levels as split by the iron exchange field.

Two of the five absorptions observed in samarium iron garnet have been tentatively identified as arising from collective excitation modes, i.e., the customary "low-frequency ferrimagnetic resonance" and the exchange resonance. The ferrimagnetic resonance mode is raised to far infrared frequencies by the large magnetocrystalline anisotropy energy. Two other higher frequency absorptions are thought to be single-ion transitions, while the highest frequency absorption has been tentatively assigned to a phonon transition.

The rare-earth-iron exchange coupling in HoIG appears to be the same order of magnitude as the  $\text{Ho}^{3+}$  ion crystal field interaction. The anomalous tempera-

ture dependence of the exchange resonance is presumed to arise from a large magnetocrystalline anisotropy energy as in SmIG. Supplementary transmission measurements with samples of HoGaG and 5% Ho-YIG indicate that most of the remaining absorptions in the iron garnet are probably transitions to higher crystal field levels as modified by the iron exchange field.

The absence of any observable magnetic absorption spectrum in GdIG ( $L=0$ ) validates our conclusion that the strength of single rare-earth ion transitions is determined by the anisotropy and corresponding inequiv-

alence of the rare-earth ions produced by local crystalline electric fields at the various types of sites.

#### ACKNOWLEDGMENTS

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## Elastic Properties of $\beta$ -CuZn

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The elastic moduli of a single crystal of stoichiometric  $\beta$ -CuZn have been measured as a function of temperature in the range 4.2 to 800°K. The temperature variation was found to be normal for all elastic constants. In particular,  $c_{11}$  is unchanged on passing through the critical temperature  $T_c$ , while the shear constants  $C$  and  $C'$  exhibit a substantial change at  $T_c$ . This change is consistent with the configurational change due to disordering.

Measurements were also made on the composition dependence of the room-temperature elastic constants in the  $\beta$  field. A large variation with composition was found, amounting to almost 100% for the shear constant  $C'$ . This behavior is in qualitative agreement with theory, and suggests substantial contributions to the elastic moduli from second-neighbor interactions and the Fermi surface overlap.

### I. INTRODUCTION

THE temperature and composition dependence of the elastic moduli of  $\beta$ -CuZn have attracted considerable experimental and theoretical interest. In previous work the shear constant  $C'$  showed an anomalous increase with increasing temperature,<sup>1</sup> and for off-stoichiometric alloys the ratio  $C/C'$  was found to be abnormally large.<sup>2</sup> These observations were basically involved with the question of the stability of  $\beta$ -phase alloys, and this was investigated by Jones<sup>3</sup> and by Zener.<sup>4</sup> Jones found the  $\beta$  phase in CuZn to be rendered stable by a large contribution to the shear constants from the overlap of the Fermi surface with the Brillouin zone. Such an effect is not unexpected, since a bcc lattice of hard spheres will offer no resistance to a (110)  $[\bar{1}10]$  shear. Thus, the system will be unstable, so that in the real lattice the electrostatic interaction, second-neighbor terms, and the Fermi overlap must combine to offset the nearest-neighbor repulsive con-

tribution to  $C'$ . In the absence of second-neighbor interactions, a substantial electronic contribution to the shear constants is not unreasonable. With second-neighbor interactions, however, the electronic contribution becomes less clearly defined. Because these effects should depend sensitively on composition, in the present work we have studied the composition dependence of the room-temperature elastic constants in the  $\beta$  phase. To assist our understanding of second-neighbor effects, we have also examined the temperature dependence of the elastic constants of an alloy of equiatomic composition.

### II. EXPERIMENTAL RESULTS

The single crystals used in this experiment were grown by the Bridgman method, using graphite crucibles sealed under a partial pressure of argon in vycor tubes. After suitable orientation by Laue photographs, specimens were cut from the crystals and machined to have exposed faces perpendicular to both the  $[100]$  and  $[110]$  directions. These faces were lapped optically flat and finished to parallelism to within 0.0001 in. The material used for the alloys was 99.99% pure copper and 99.99% pure zinc. Several alloys made from high purity copper and zinc (99.999%) gave room-temperature elastic constants in agreement with corresponding

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