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Ferrimagnetic Resonance in Rare-Earth Doped Yttrium Iron Garnet. I. Field for Resonance

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Resonance experiments have been performed on YIG crystals doped with each of the rare earth ions except Lu, Gd, and Pm. Except for Ce these are thought to replace Y as trivalent ions. This paper presents measurements of the field for resonance in the (110) plane at 1.5°K for each of these samples. In several cases there are also data up to about 25°K. Except for Ce, Eu, and Tm the curve H_{res} in (110) at 1.5°K shows characteristic structure. For Pr, Ho, and Tb this structure is dominated by very narrow peaks in H_{res}. For Nd, Sm, Dy, and Er it is relatively broad in angle. For Yb most of the structure is relatively broad in angle, but there is a very sharp but small spike in H_{res}. Only in the case of Tb and Yb do sharp spikes appear at other than symmetry directions. In some cases the height of the peaks falls off rapidly with increasing temperature starting at the lowest temperatures, but in other cases it does not change at first, then falls off.

THE first ferrimagnetic resonance results reported on single crystal yttrium iron garnet (YIG) aroused interest largely because of the narrow lines observed.[1] These results also showed a peak in the linewidth versus temperature plot somewhat below 50°K. Since that time the measured linewidths have dropped substantially as specimen preparation techniques have improved and higher purity crystals have been prepared.[2,3] Samples of YIG have become the preferred experimental material for studies of linewidth. However, even in the earliest work, some anomalies were observed at very low temperatures.[1,4] The variation of field for resonance with crystal direction, i.e., the surface $H_{\text{res}}(hkl)$, was highly convoluted in the case of one particular batch of crystals, and apparently quite normally behaved in the case of some other batches. In order to clarify experimentally these earlier data, a program of research was undertaken to study the effects of rare earth impurities in YIG. Interesting results also have been obtained with the addition of impurities other than members of the rare earth group. This paper will present an experimental survey of the field for resonance data for YIG crystals doped with each of the rare earth ions which we would expect to have an effect. Preliminary reports for several ions have already been given.[5,6] A more detailed study for the cases of certain ions will be given in later papers. We will also present later the results of the linewidth versus temperature measurements made on these samples with the steady field along various crystal directions.

Of the rare earth ions, we have attempted to introduce all except promethium, gadolinium, and lutetium. Promethium has no naturally occurring isotope, and the difficulties of preparing a macroscopic purified quantity of the 25 year Pm^{145} or the 1 year Pm^{146} remove it from the realm of the practical. An indication of the effect of the Gd^{+++} ion is found in the work of Geschwind and Walker,[7] and is probably so slight that other rare earths present as impurities in ordinary high-purity gadolinium would surely override the effect of the gadolinium itself. Similar considerations are thought to apply to Lu^{+++} whose electron configuration is $4f^{14}$ and thus has no net magnetic moment.

SAMPLE PREPARATION AND MOUNTING

The crystals used in these experiments were grown from the oxide-fluoride fluxes first described by Nielsen.[8] The starting mixture was modified by the inclusion of the appropriate rare earth oxide. For the most part the crucibles were cooled through the growth range at 5°/hour. From each batch the soundest crystals were chosen, and a slice sawn off near a sound face. This section was diced into 0.025 in. cubes, and these cubes were in turn ground into rough spheres on an improved version of the Bond sphere grinder.[9] These rough spheres were then ground further and polished using the two pipe technique also described by Bond.[10] In this case the grinding was done with a slurry of American Optical 303 ½ emery in water, and the polishing with Linde *A*, in water. The polishing procedure called for removing at least 0.0005 in. of material from the surface by polishing after the bottom of the grinding pits was reached. For the most part all of the spheres were brought down to a diameter of 0.016 in.

The orientation of the samples was performed by x-ray goniometer techniques using instruments developed in collaboration with Bond.[11] The spheres were affixed to the end of thin quartz fibers, perhaps 0.006 in.

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[1] J. F. Dillon, Jr., Phys. Rev. **105**, 759–760 (1957).

[2] R. C. LeCraw, E. G. Spencer, and C. S. Porter, Phys. Rev. **110**, 1311 (1958).

[3] E. G. Spencer, R. C. LeCraw, and A. M. Clogston, Phys. Rev. Letters **3**, 32 (1959).

[4] J. F. Dillon, Jr., Phys. Rev. **111**, 1476–1478 (1958).

[5] J. F. Dillon, Jr., and J. W. Nielsen, Phys. Rev. Letters **3**, 30–31 (1959).

[6] J. F. Dillon, Jr., and J. W. Nielsen, J. Appl. Phys. (to be published).

[7] S. Geschwind and L. R. Walker, J. Appl. Phys. **30**, 163*S*–170*S* (1959).

[8] J. W. Nielsen, J. Appl. Phys. (to be published).

[9] W. L. Bond, Rev. Sci. Instr. **22**, 344 (1951).

[10] W. L. Bond, Rev Sci. Instr. **25**, 401 (1954).

[11] W. L. Bond and J. F. Dillon, Jr. (unpublished).

in diameter, with Ambroid cement in such a way that the glue only wetted the sphere on the side near the fiber. Thus supported the sphere was oriented in the x-ray beam to within about 2′. It was then transferred to a single crystal sapphire specimen rod so that the oriented axis was parallel to the axis of the rod. This transfer is effected by bringing the sphere to within about 0.0005 in. of the end of the rod and then covering the whole end of the rod and the sphere with a thin quartz cement.[12] The use of a sapphire rod is considered important in that its high thermal conductivity serves to counteract any tendency of the sphere to assume a temperature different from that of the cavity.

EXPERIMENTAL APPARATUS

The experiments described in this paper consist of the determination of the field required for ferrimagnetic resonance as a function of crystal direction for single crystal spheres of doped YIG in the temperature range from 1.5 to 25°K. The low temperatures were achieved by insulating the cavity assembly in a metal Dewar located between the pole pieces of an electromagnet. To measure a moderately complicated $H_{\mathrm{res}}(\theta)$ curve requires temperature stability for periods of perhaps one half hour. For the most part this is accomplished by working with the cavity and sample immersed in the cryogenic liquid or solid with the appropriate pressure maintained by pumping.

The TE_{102} cavity is iris coupled to waveguide input and output arms. It is oriented so that the H plane is horizontal. The sample is in the center of this cavity. Barring distortion by the dielectric sample rods, h_{rf} has a fixed direction in the horizontal plane. The coupling between the spin system of the sample and the magnetic field of the cavity may be varied by changing the angle between H_{dc} and h_{rf}. It turns out that this freedom is very valuable because of the wide range of linewidths encountered even in the course of a single experiment.

It will be seen below that the angular dependence of H_{res} is often very steep. It has therefore been found worthwhile to elaborate on the usual simple method of rotating the crystal. A schematic representation of this is included in Fig. 1. The short single crystal sapphire specimen rod described above is attached to a long fused quartz rod which is brought through an "O" ring out of the top of the Dewar. There it is held in a collet type clamp at the center of a worm gear driven by a worm. A selsyn drives the shaft on which the worm is mounted. It is also connected to the shaft of a counter which displays the angular setting, and can be read to about 0.2°. The transmitter selsyn is located conveniently, and it is fitted with a dial indicator which can be read or set to 0.1°. The total backlash in the system is about 0.2°, and this can be effectively eliminated by always rotating the specimen rod in one sense. This feature of our equipment enables us to set the angle of the crystal axes in azimuth quickly and accurately.

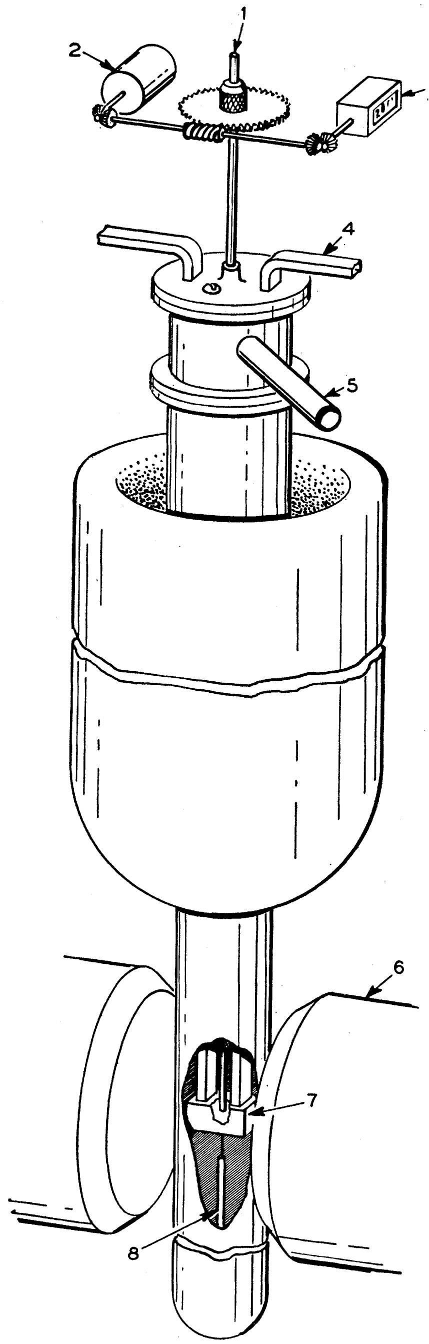

FIG. 1. The microwave cavity (7) is oriented between the pole pieces (6) of the magnet in such a way that angle between the rf magnetic field at the sample and the steady field may be varied from 0 to 90°. The copper rod (8) provides a heat conduction path between the cavity and any cryogenic liquid or solid lying below it in the Dewar. The thaft (1), at the lower end of which the specimen is mounted, is turned by a selsyn (2) driven by a remote transmitter. The counter (3) gives an indication of the sample orientation.

The microwave circuit used here is extremely simple.

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[12] Obtainable from Thermal American Fused Quartz Company, Dover, New Jersey.

A klystron is sawtooth modulated across a mode whose center frequency is that of the cavity. A detector on the output arm of the cavity enables us to see the transmission characteristic of the cavity displayed. Merely examining this on the face of an oscilloscope as the steady field is varied enables us to find the center of the resonance. The microwave circuit contains appropriate padding attenuators, and arrangements for sampling the mode pattern as well as for measuring the frequency. The output arm contains a properly padded rotating vane attenuator.

The stainless steel Dewar was fabricated to our specifications by the Hofman Laboratories, Incorporated.[13] The only unusual feature is the very long small diameter section which continues a full eighteen inches below the center of the pole pieces. By varying the heat leak to the cavity from a long heavy rod of copper extending down through this region, and also the power dissipated in small winding attached to the cavity, we can obtain data at various intermediate temperatures. The whole dewar assembly is held in a precision mount and thus can be moved along three perpendicular axes. It is centered so that the magnet can be freely rotated about a vertical axis. The Dewar has associated with it a pump, a safety valve, several manometers, a manostat, and a suitable valving arrangement.

The field measurements were made in every case by counting the frequency of the Li *NMR*.

The temperatures quoted are derived either from published temperature verus pressure curves or from a carbon resistance thermometer in good thermal contact with the silver cavity.

In cases where the linewidth was still very narrow, we would often observe a number of magnetostatic modes as well as the uniform precession. In every case it was possible to identify unequivocally the (1,1,0) mode by observing the strengths of the absorptions as the angle between the steady field and the rf field was varied near zero.

IMPURITY CONCENTRATIONS

In these experiments we would like to know accurately the impurity concentration in the doped crystals. This is rendered particularly difficult by the chemical similarity of all of the rare earths and yttrium as well as by the low level of the doping. In every case we know the weights of the oxides put into the crucible from which the crystals were grown, that is to say we know the intended percentage of the impurity. Since there might be concentration coefficients of unknown size operating in the kinetic system from which the crystals are grown, we cannot simply take this intended dilution as the actual dilution. As an example it might be pointed out that it has not been possible to make praseodymium iron garnet at all, presumably for reasons of ionic size.

TABLE I. Rare earth doping level in starting mixtures as compared with that found in crystals by analysis.

Element	Atomic No.	Intended dilution (atomic %)	Analysis (atomic %)	Ratio $\left(\frac{\text{measured}}{\text{intended}}\right)$
La	57	21.6	3.8	0.18
Ce	58	0.18	0.23	1.3
Pr	59	0.19	0.10	0.53
Nd	60	0.19	0.15	0.79
Pm	61			
Sm	62	0.19	0.21	1.1
Eu	63	1.13	1.25	1.11
		4.85	4.97	1.02
Gd	64			
Tb	65	1.13	1.7	1.5
Dy	66	0.19	0.15	0.79
Ho	67	0.19	0.24	1.3
Er	68	0.19	0.25	1.3
Tm	69	0.19	0.24	1.3
		1.93	2.4	1.2
Yb	70	0.19	0.18	0.95
		2.10	2.3	1.1
Lu	71			

From this it may seem unlikely that praseodymium impurity will appear in a crystal of YIG in the same proportion in which it appears in the melt. Miss Shirley Vincent of these laboratories has measured the impurity level in our crystals by x-ray fluorescence analysis. Table I gives a summary of the intended impurity levels as well as those determined by her analysis. In the case of terbium, results for lower levels of doping have not been given, since our microwave measurements clearly showed that those particular analyses were not significant in the range of 0.1 atomic % and below. The other results are given though there is really no good criterion for judging them. The most heartening feature about the bulk of these analyses is that they do not give results which differ greatly from the intended dilutions. The exceptions to this are La, Pr, and Nd where the analyses are believed to be good within 10% of the amount of impurity present. Apparently for these elements a concentration coefficient does operate in the growth process in such a way that less impurity appears in the crystal than is present in the melt. We conclude that the impurity level is essentially that given by the intended dilution except in these three cases.

PURE YIG

In a program devoted to the effect of impurities on the magnetic properties of YIG crystals it would be desirable to have as a reference the corresponding properties of pure YIG. In the case of the linewidth versus temperature data it is not at present possible to do this. Most of the linewidth observed in our present samples is almost certainly associated with the residual impurities—rare earth and other. In the case of the anisotropy it is probable that the impurity level is so low with regard to the magnetic ions that we are very close to observing the true anisotropy of pure YIG.

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[13] Hofman Laboratories, Incorporated, 5 Evans Terminal, Hillside, New Jersey.

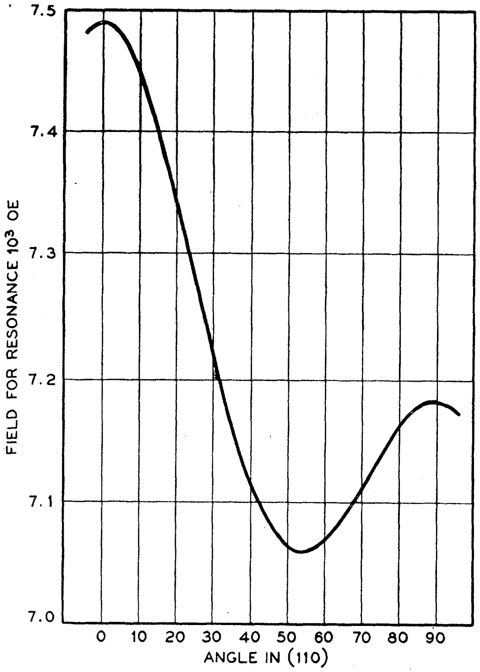

FIG. 2. Field for resonance in (110) plane of highest purity YIG measured to date. Frequency was 20 240 Mc/sec, and the temperature 1.5°K.

Practically all of the rare earth ions introduced into YIG in low concentrations produced characteristic field for resonance surfaces. Crystals grown from ordinary yttrium oxide invariably showed some structure in the low temperature $H_{\mathrm{res}}(hkl)$ surface that could be attributed to residual rare earth impurities. However crystals grown using specially purified yttrium oxide such as that mentioned by Spencer, LeCraw, and Clogston[3] showed no such structure at 1.5°K. The (110) section of the field for resonance surface is shown in Fig. 2 for 1.5°K. If the fields for the principal directions are used to determine a g value and first and second order anisotropy constants, one obtains $g=1.998$, $K_1/M_s=-126.4$ oe, and $K_2/M_s=-17.8$ oe. However an analysis of these particular crystals for silicon showed that about 0.16 atomic percent of the iron ions were replaced by silicon ions. From experiments in which crystals were intentionally doped with silicon we know that it has a considerable effect on the low-temperature field for resonance surface. The presumption is that Si^{++++} forces the presence of Fe^{++}, and that this has a large anisotropy associated with it. Thus we expect that due to the silicon present in our best sample of YIG, its low-temperature anisotropy differs slightly from that of "absolutely pure YIG." There may also be other low-level impurities affecting our measured properties. However at this stage it seems the best we can do is to take this sample as our reference.

CERIUM

Ground State for Ce^{+++}: $4f^1\ {}^2F_{\frac{5}{2}}$

The initial attempt to observe the effect of Ce^{+++} ion in YIG was made on crystals grown from a melt in which 0.18 at.% of the yttrium was replaced by cerium. The plot of H_{res} [in(110)] will not be given since it shows no clear effect. It does have a little structure near the [110] axis and a flattening of the curve near the [111] directions. Later it will be seen that these characteristics are associated with small impurities of Tb^{+++}. Thus it seems that the cerium doping in these crystals is not such as to cause significant effects in the low-temperature field for resonance. Cerium can exhibit a valence of four, and since these crystals are grown under strongly oxidizing conditions, it seems likely that Ce^{++++} ions would be available to enter the growing crystal. Presumably this would require the simultaneous incorporation of a divalent ion in order to maintain charge neutrality. The fact that our cerium doping has produced no effect may mean that there is no major effect, or that only Ce^{++++} with no magnetic moment is in the crystal. The analysis indicates that Ce is not rejected by the growing crystal as are Pr, Nd, and La. This tends to corroborate the Ce^{++++} supposition.

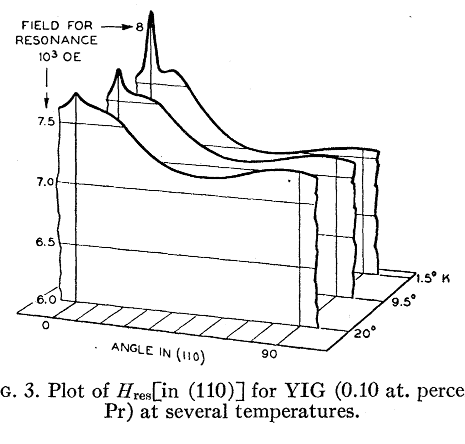

FIG. 3. Plot of H_{res}[in (110)] for YIG (0.10 at. percent Pr) at several temperatures.

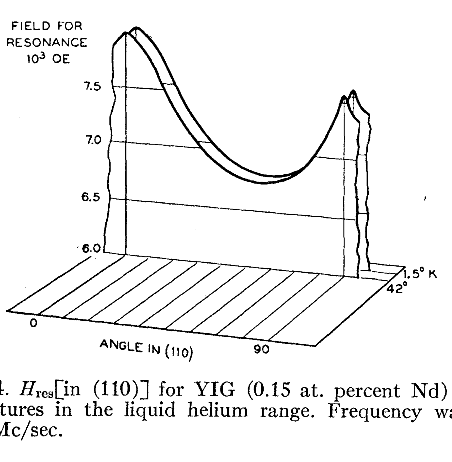

FIG. 4. H_{res}[in (110)] for YIG (0.15 at. percent Nd) at two temperatures in the liquid helium range. Frequency was near 20 280 Mc/sec.

PRASEODYMIUM

Ground State of Pr^{+++}: $4f^2\ {}^3H_4$

In this case 0.1% of the yttrium atoms in the melt were replaced by praseodymium. Analysis indicates that somewhat less appears in the crystals. Though praseodymium iron garnet has not been made, there is no trouble in substituting a small fraction of the element into YIG as an impurity. This also applies to the case of neodymium. Figure 3 shows H_{res} in (110) at three low temperatures where the anomaly is clearly evident. The anomaly consists of a single spike along [100]. In all of these experiments it has only been practical to look at H_{res} in principal crystallographic planes. In this case we have only looked in (110). It is entirely possible that there is other structure to be seen on examination of the other planes. It will be seen that the height of the anomalous peak is still rising steeply at the lowest temperature at which we took measurements.

NEODYMIUM

Ground State of Nd^{+++}: $4f^3\ {}^4I_{9/2}$

Neodymium was introduced into the starting mixture for these crystals at a level of 0.19 at.%. About 0.15 at. % appears in the crystals. While the plot of H_{res} in (110) at the lowest accessible temperatures is similar in form to that shown for pure YIG, (see Fig. 4) note that the total excursions of the field for resonance are approximately twice as large. In the pure YIG we know that the peak in (110) at [110] is actually a saddle, and if viewed in the (110) plane it would appear as a minimum. From the data presented here it is not clear whether there is a saddle or a true maximum in the field for resonance surface when the applied steady field lies along [110]. Note that H_{res} in (110) is essentially identical at 1.5 and 4.2°K. The introduction of perhaps $\frac{1}{5}$%Nd^{+++} has changed the total excursion of H_{res} from about 400 oe for pure YIG to roughly 1200 oe. Further data on the temperature dependence of the H_{res} surface and on the profile of that surface in other crystallographic planes seem desirable.

SAMARIUM

Ground State for Sm^{+++}: $4f^5\ {}^6H_{\frac{5}{2}}$

Again in the case of samarium we attempted to grow crystals with a doping of 0.19 at.%. The 1.5°K H_{res} in (110) is given in Fig. 5. The curve now has a shoulder about 18° from [100]. Its total excursion is about 1600 oe. Measurements on the temperature dependence of the peaks and the shoulder should show whether they still change rapidly with temperature as the anomalous spikes in the Pr^{+++} and Ho^{+++} or whether the shape of the curve is not changing with temperature in the lowest range as was the case in pure YIG and in the Nd^{+++} doped material.

EUROPIUM

Ground State for Eu^{+++}: $4f^6\ {}^7F_0$

A sample prepared from a crystal batch whose starting materials were doped with 1.13 at.% Eu gave the H_{res} in (110) at 1.5°K shown in Fig. 6. This shows some

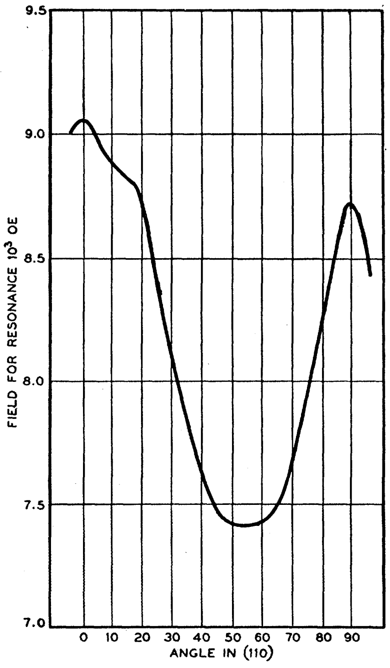

FIG. 5. H_{res}[in (110)] for YIG (0.19 at. percent Sm) as measured at 1.5°K. Frequency was 23 220 Mc/sec.

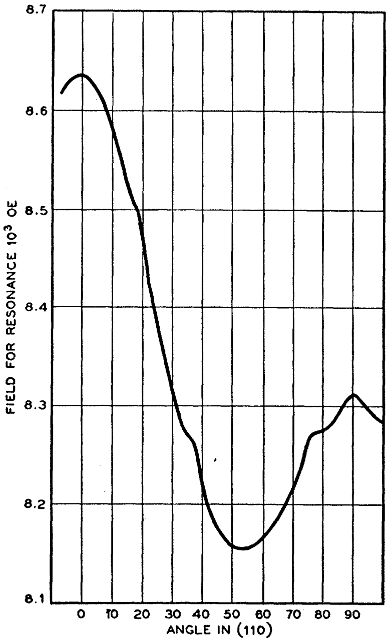

FIG. 6. H_{res} [in (110)] for YIG (1.13 at. percent Eu) at 1.5°K. The frequency was 23 228. The structure apparently corresponds to the presence of about five terbium ions per million yttrium atoms.

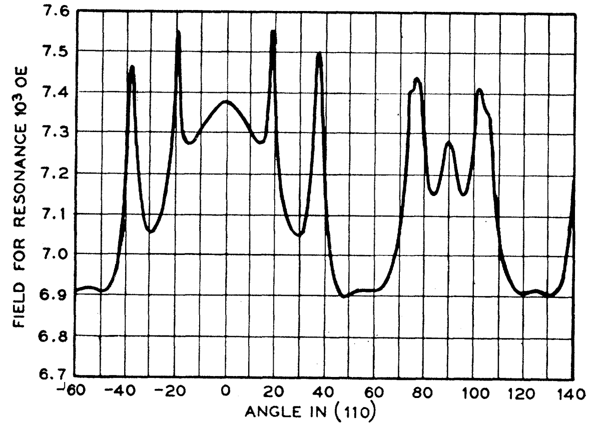

FIG. 7. H_{res} [in (110)] for YIG (0.019 at. percent Tb) at 1.5°K. The frequency was 20 470 Mc/sec.

structure identical to that seen in the case of the Ce sample. At that point it was remarked that this is at least mostly attributable to residual Tb^{+++} impurities presumably introduced in the yttrium oxide from which the crystal was grown. By comparing the height of the anomalies in this curve with those in samples intentionally doped with terbium, we estimate the terbium impurity level to be about 0.005 at.%. Thus there appears to be no effect on the field for resonance by the Eu^{+++} ion. This is in accord with what we should expect considering that the $J=0$ for the ground state of the ion. However in correlating the properties of the rare earth ions in crystals with their ground states, the cases of europium and to a lesser extent samarium are always more complicated than the others by the proximity of higher states. In the case of Eu^{+++} the state $4f^6\,{}^7F_1$ lies only about 300 cm^{-1} above the ground state, and other excited states are correspondingly low. That the proximity of these higher energy states is important is clear from the $M_s(T)$ curves given by Pauthenet[14] for polycrystalline EuIG. Compared with the YIG data, these show that at the lowest temperatures each Eu^{+++} ion contributes about 0.8 μ_B to the magnetization.

TERBIUM

Ground State of Tb^{+++}: $4f^8\,{}^7F_6$

Preliminary results on Tb doped YIG were reported in our earlier letter.[5] These data have led Walker to consider the problem of anisotropy of YIG doped with Tb^{+++} ions, and because of his interest we have studied the terbium case in far greater detail than any other. A full report of the measurements will be given elsewhere. A curve showing H_{res} in (110) at 1.5°K is given in Fig. 7. The intended doping here is 0.019 at.%, a great deal lower than that of the sample on which Tb data was reported before. Here the excursions are very sharp, but it can be seen how they are superimposed on the ordinary low order anisotropy field for resonance curve. Terbium shows more of these anomalous peaks than any other of the doped crystals we have examined. Only in this case have sharp peaks at other than symmetry directions been observed, though again we must emphasize the reservations implicit in our examination only of H_{res} in principal planes. There is a peak at [110]. There is one about thirteen degrees from it at 77° which appears to be double. The slight bump near [111] does not increase in size on increasing the concentration of Tb, and is thought to represent dysprosium present as an impurity. Finally there are sharp well defined peaks at about 37° and about 19°.

DYSPROSIUM

Ground State of Dy^{+++}: $4f^9\,{}^6H_{15/2}$

In the starting material from which these crystals were grown 0.19 at.% of the yttrium atoms were replaced by dysprosium atoms. The values of the field for resonance in (110) for a number of temperatures are shown in a three dimensional fashion in Fig. 8.[6] In the cases of praseodymium, holmium, and terbium doped YIG the sharp peaks which constitute the structure in the H_{res} curves decrease in height rapidly with increasing temperature, starting at the lowest temperatures available to us. In this case the peaks are not so sharp in angle, and they do not immediately begin to fall off on warming the crystal. The maximum at [100] stays approximately constant in height out to about 10°. That at [111] drops off soon after 4.2°, and that at [110] begins to drop off at the lowest temperatures. A comparison of this curve with those published for YIG with an unknown impurity[4] are remarkably similar. In fact, a comparison of those earlier curves with corres-

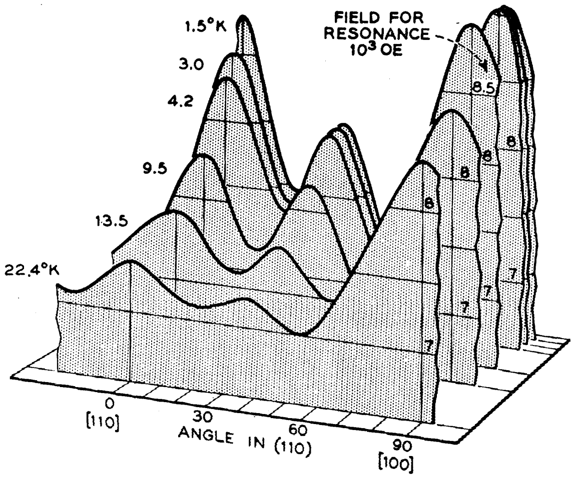

FIG. 8. H_{res} [in (110)] for YIG (0.19 at percent Dy) at several temperatures. The frequencies were near 20 000 Mc/sec. The curves have been adjusted vertically so that the lower minimum in each curve lies at the same apparent field.

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[14] R. Pauthenet, thesis, Universite de Grenoble, 1958 (unpublished).

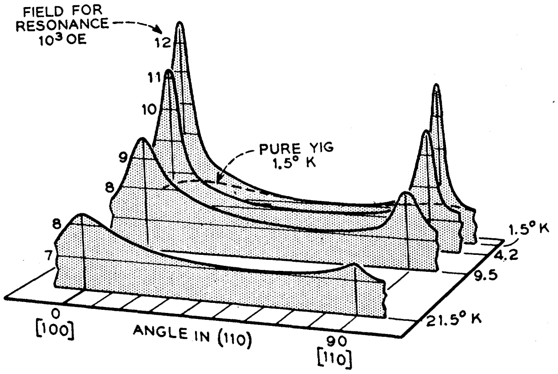

FIG. 9. H_{res} [in (110)] for YIG (0.19 at. percent Ho) at several temperatures. The measuring frequencies are near 20 000 Mc/sec, but to clarify the comparison, the curves have been adjusted vertically so the minima all appear to be at the same field. The dashed curve at 1.5° applies to pure YIG.

ponding H_{res} plots for YIG doped with each of the rare earths leads us to conclude that the most important impurity in the original crystals was dysprosium in a concentration of perhaps 0.3 or 0.4 at.%. We also know from earlier work the shape of the field for resonance in (100) and (111). The peak at [110] is a true maximum not merely a saddle point as in pure YIG, and it is considerable sharper when viewed in (100) than in (110).

HOLMIUM

Ground State of Ho^{+++}: $4f^{10}\ {}^5I_8$

The intended dilution of the Ho crystals was 0.19 at.%. The H_{res} plots at several temperatures below 25° are shown in Fig. 9. The data of Fig. 2, that is H_{res} [in (110)] for the purest YIG we have been able to measure is plotted as the dotted line at the appropriate temperature, 1.5°K. Here again it is seen that the height of the anomalies falls off starting from the lowest temperatures. Here the peaks in the (110) plane occur only in symmetry directions.

ERBIUM

Ground State for Er^{+++}: $4f^{11}\ {}^4I_{15/2}$

The intended dilution of these crystals was 0.19 at.%. The 1.5°K H_{res} surface is shown in Fig. 10. Though it contains no very sharp anomalies the doping has obviously strongly affected the anisotropy surface. The H_{res} maximum at [110] is higher than that at [100] and the minimum at [111] is markedly wide and flat. As in several other cases the slight structure in H_{res} between [111] and [100] supposedly represents the terbium impurity. In the case of YIG(Er) we have an example of direct data on the g value. Figure 10(a) and (b) represent the field for resonance curve as measured at two different frequencies, 23 220 and 20 234 Mc/sec. The field differences between the two are plotted and expressed in g value between the two. Almost the same value is measured in the various directions 1.961 ± 0.003. Whether the spread represents a slight shift in frequencies or a real variation of g with direction is not yet clear. Similar determinations in several other cases are planned.

THULIUM

Ground State of Tm^{++++}: $4f^{12}\ {}^3H_6$

The intended doping of our initial sample in this case was 0.19 at.%. The H_{res} in (110) plot for 1.5°K showed no structure other than that attributable to impurity terbium. A second sample with ten times as much thulium in it also showed no anomalous structure. However in this case the first order anisotropy field K_1M_s at 1.5°K was −162 oe. Comparing this with the −126.4 oe for pure YIG, it is clear that the thulium has made some contribution to the ordinary anisotropy. In terms of the discussion below it appears that in the trivalent

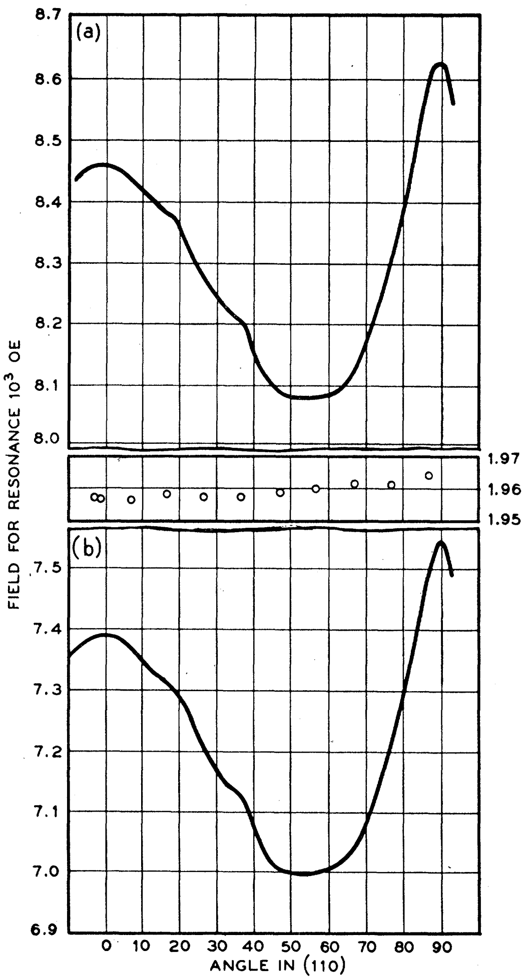

FIG. 10. H_{res} [in (110)] for YIG (0.19 at. percent Er) at 1.5°K. The measurements have been made at two frequencies: (a) 23 220 Mc/sec, and (b) 20 234 Mc/sec. The differences in field are plotted as g values between (a) and (b).

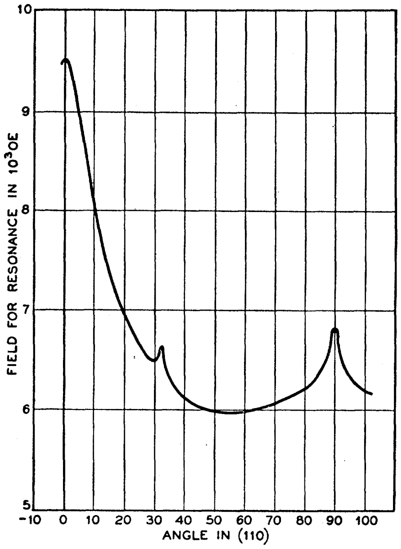

FIG. 11. H_{res} [in (110)] of YIG (2.10 at.%) at 1.5°K. The frequency was 20 729 Mc/sec.

thulium ground multiplet in these crystals the lowest and the next to lowest levels are well separated.

YTTERBIUM

Ground State of Yb^{+++}: $4f^{13}\,{}^2F_{7/2}$

Samples were made up with intended dilutions of 0.19 and 2.10 at.%. Even in the lower of these two dilutions there was a clear effect. In Fig. 11 the H_{res} in (110) curve is given for the 2.10 at.% Yb sample. The total excursion of the field is over 3000 oe. There is a sharp peak at about 32°, and another not quite so sharp one along [110]. Perhaps this curve is most different from the others in the small height of the spike at 32°. It is very sharp, but in the 0.19 at.% sample there is merely a slight bump in the curve. The case of Yb^{+++} is of particular interest in view of the paramagnetic resonance experiments on Yb^{+++} in yttrium gallium garnet recently reported by Boakes, Garton, Ryan, and Wolf[15] and by Carson and White.[16]

CONCLUSION

In this paper we have presented experimental data on the field for resonance in the (110) plane of YIG samples doped with each rare earth element which might be expected to produce an effect. 1.5°K data is given in all cases and there is higher temperature information for some. In a few instances the addition of the rare earth ions has had practically no effect. In several cases there are sharp high peaks in the field for resonance as the angle of the steady field is varied around the (110) plane. Other dopings are associated with structure in H_{res} [θ in (110)] which is broader in angle. Data has only been presented for H_{dc} in (110). Undoubtedly there is interesting structure to be measured in the other principal planes. Also it is conceivable that there is some structure in a general direction well away from any of the principal planes. A sharp spike in such a direction in a cubic crystal has a multiplicity of forty eight, and thus would be a dominant feature in the over-all character of the surface.

The complicated behavior of the field for resonance in these crystals arises in the splitting of the ground manifold by both the crystal and exchange fields. Kittel[17] suggested that the sharp peaks in the YIG (Tb)H_{res} surface arose from crossings or near crossings between the lowest and the next to lowest members of the rare earth ground multiplet as the angle of the magnetic field was varied relative to the crystal axes. Walker[18] has shown that in the case of the terbium ion such near crossings exist. He was able to account for the observed H_{res} surface almost quantitatively. Parallel analysis would probably account for the observed H_{res} surfaces and all of the cases we have presented here.

There is little reason to expect any similarity between the behavior of ions of neighboring atomic number since the multiplicities of the ground states are different.

At this stage we seem to be able to make one observation on the characteristics of the H_{res} surfaces arising from each of the rare earths. Some of the (110) sections of these surfaces show sharp peaks, namely Pr, Tb, and Ho. Others show broad peaks or perhaps it is better to say the structure in them is relatively broad in angle. These are Nd, Sm, Dy, Er, and Yb. Our observation is this: The sharp anomalies occur for elements whose trivalent ions have an even number of $4f$ electrons, and thus ground states whose J's are integral. The broad angle anomalous structure is associated with elements whose trivalent ions have an odd number of $4f$ electrons, and thus ground states whose J's are half integral. The only exceptions here are elements for which we have not seen any structure: Ce, Eu, Tm, and Yb which shows a very small, but sharp peak. Of course, it is yet known what is to be seen on exploration of the rest of the surfaces.

The quantity we measure in these experiments is field for resonance. This depends on the curvature of the energy surface about the direction of the magnetization. Only in the simplest cases is it possible to derive the anisotropy energy surface itself from the field for resonance surface. For all of the interesting structure here it is simply not practicable. Torque measurements on doped crystals would produce curves which could be integrated, to give the actual energy surfaces. Dr. R. F. Pearson of the Mullard Research Laboratories, with

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[15] Boakes, Garton, Ryan, and Wolf, Proc. Phys. Soc. (London) **74**, 663–5 (1959).

[16] J. W. Carson and R. L. White, J. Appl. Phys. (to be published).

[17] C. Kittel, Phys. Rev. Letters **3**, 169 (1959); C. Kittel, Phys. Rev. **117**, 681–687 (1960).

[18] L. R. Walker (to be published).

whom we are cooperating is now measuring torque curves on these same samples.

Discontinuities in the slope of the energy surface with angle produce very high anomalies in the field for resonance which may be very much higher than the total excursions of the anisotropy energy surface. However, we do expect that there will be very large anisotropies associated with rare earth ions in the garnet lattice. And if one attempts to extrapolate to the anisotropy surface of the rare earth garnets themselves, it seems certain that the total excursions will be very large. It is probably impossible to saturate many of the rare earth garnets in other than easy directions with the fields available in the laboratory. Williams and Sherwood[19] have measured the magnetization versus temperature for terbium iron garnet for a number of crystal directions. Along [111], which our data shows to be an easy direction, the curve is apparently well behaved. However, their plots of $M(T)$ show that they were unable to saturate the crystals in the available field in the other principal directions until the temperature had been raised considerably. An important consequence of this is to make suspect any measurements of the magnetization of the rare earth garnets in the low-temperature region which have been made on polycrystalline samples. Also measurements on g and line width made in resonance experiments at low temperatures are questionable.

Ferrimagnetic resonance linewidths in the rare earth iron garnets are for the most part so large that resonance experiments are difficult. Measurements of g value and the anistropy at low temperatures are simply not practicable. However, by studying the properties of YIG doped with rare earth ions one could obtain most of the desired information. In lightly doped samples such as ours, the probabliity of rare earth ions in neighboring dodecahedral sites is small. Thus the rare earth ions are subjected to exchange fields only from the iron sublattices. But in the rare earth iron garnets, there is a coupling between the rare earth ions. Though this is a good deal smaller than the iron-rare earth coupling, it is nevertheless important. Details such as the positions of anomalies in the energy surface would almost certainly be different because the net exchange field acting on the rare earth ion would be different. Also, of course, the slightly different lattice constant would manifest itself in a different crystal field.

It is our intention to publish shortly a more complete experimental study of the effects of terbium impurities in YIG. This will include the variations of field for resonance with concentration; temperature, frequency, and lattice constant; and will include data taken with the steady field in each of the principal planes. Measurements of linewidth versus temperature for various significant directions in YIG doped with each of the rare earths will be given in a later publication.

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[19] H. J. Williams and R. C. Sherwood (unpublished).