Ferrimagnetic Resonance in Rare-Earth-Doped Yttrium Iron Garnet. III. Linewidth*

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Measurements of ferrimagnetic resonance linewidth have been made for single crystals of yttrium iron garnet (YIG) doped with each of the $4f$ rare earths (except Ce, Gd, Pm, and Lu). Starting from the lowest temperatures, the linewidth increases to a maximum in the range 30 to 150°K, and then decreases. Some structure is apparent in these curves; they are anisotropic; and they are frequency dependent [at least in the case of YIG(Tb)]. The linewidths are discussed in terms of transitions within the ground multiplet of the rare-earth ions in the magnetic crystal.

It seems possible to account for the general features of the data, in particular for the Tb case, by assuming that the rare-earth magnetization relaxes with a number of different relaxation times, some of which are comparable with the reciprocal of the microwave frequency.

IN many cases the low-temperature resonance properties of the rare-earth iron garnets cannot be measured because of the linewidths and huge anisotropies encountered. Thus the single-ion properties at least of the rare-earth ions in a magnetic lattice are best studied in yttrium iron garnet (YIG) in which a small fraction of the yttrium ions have been replaced by rare-earth ions. Previously[1] reported experimental studies of the low-temperature field for resonance surface of YIG doped with each of the $4f$ rare-earth elements have shown a distinctive new kind of anisotropy. In the case of YIG(Tb), Walker's analysis[2] shows that the combined crystal-field and exchange-field splittings of the Tb^{3+} ground state, $^7F_6$, can account for the very complicated field for resonance surface observed at a liquid helium temperature. Here we present the results of a study of the linewidth of YIG doped with each of the rare earths, with particular emphasis on the case of terbium. Finally the origin of the linewidth is discussed in terms of the energy levels of the rare-earth ions.

The crystals were grown under the direction of J. W. Nielsen. Their chemical and mechanical preparation were discussed in I. That paper also included a description of the microwave apparatus. Its output drives the Y axis of an $X-Y$ recorder. The X axis is driven by a Hall-effect probe mounted near the sample, thus giving a displacement proportional to magnetic field. On every trace at least two lithium or proton nuclear magnetic resonance (NMR) markers are introduced to calibrate the field. Our plot is of absorption vs field, and the field interval between points of half the maximum absorption can be readily measured on it. The linewidth values measured in these experiments were obtained in this way from semiautomatic traces.

In the range from about 4 to about 40°K we used a carbon resistance thermometer calibrated at three points. Above this range a copper constantan thermocouple was used. Both the resistor and the thermocouple were attached to the microwave cavity. Measurements were made by allowing the apparatus to warm from liquid helium temperatures or to cool from room temperature. In all cases the rate of change of temperature was sufficiently slow so as to make it unlikely that a significant differential existed between the sample and the cavity around it. The microwave power level was kept well below the point at which any power or heating effects could be observed.

Paper I also included a discussion of the composition of the specimens. We will continue in this paper to designate our samples as YIG ($X\%$ Z) where $X\%$ (except for Nd and Pm) indicates the fraction of yttrium ions replaced by ions of the rare earth Z in the starting mixture. That is to say, this is the intended dilution. Such analyses as have been made seem to indicate that this approximates the actual dilution except in the case of Pr and Nd where the actual dilution is somewhat lower. In those cases we use the value obtained from analysis for X.

SURVEY OF RESULTS

The linewidth as a function of temperature was measured for YIG doped with Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, and Yb. The exclusion of Ce, Pm, Gd, and Lu is discussed in I. The temperature range covered was from 1.5°K to room temperature or a bit above. Typically the linewidth increased from its low-temperature value to a maximum in the range from 30 to 150°K, and from this decreased till well above room temperature. The position of the peak for anyone of the rare-earth dopings varies with crystal direction. Figure 1 is a presentation of the data for YIG (0.15% Nd) which will serve as an example for the others. The corresponding curves for YIG doped with the other rare earths will be given in the Appendix. There is a considerable anisotropy in the shape of these plots for YIG(Nd), and this is typical. In some cases the peak is more clearly the sum of several peaks, and this accounts for the slight shoulders to be seen on the low-temperature side of the ΔH_{max}. Table I summarizes

* A short report of this work was presented at the Conference on Magnetism and Crystallography in Kyoto, Japan, September 29, 1961.

[1] J. F. Dillon, Jr., and J. W. Nielsen, Phys. Rev. **120**, 105–113 (1960), which will be referred to as I.

[2] L. R. Walker, Bull. Am. Phys. Soc. **5**, 418 (1960); J. F. Dillon, Jr., and L. R. Walker, Phys. Rev. **124**, 1401 (1961), hereafter referred to as II.

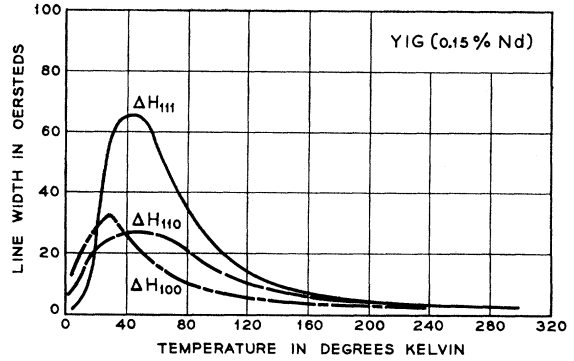

FIG. 1. Ferrimagnetic resonance linewidth plotted against temperature for YIG(0.15% Nd). Note the anisotropy of the linewidth in the region of the maximum. The frequency was 9.25 kMc/sec.

our data as far as the positions of the peaks and their heights are concerned. In an attempt to compare the various dopings, we have divided the maximum linewidth by the rare-earth concentration for each of these materials. Judging from the case of Tb doping discussed in detail later, it seems likely that this ratio is relatively independent of frequency. It will be seen that the effectiveness of the various rare earths differs over a wide range. Terbium impurity appears to make the greatest contribution to the linewidth, over a hundred times that of ytterbrium. In the Yb case, nevertheless, the rare earth has a very specific effect on the linewidth as well as on the low-temperature field for resonance. This contrasts with Tm where the increased linewidth is very small, but seems to be less specific, and there is no anomalous contribution to the field for resonance at liquid helium temperatures.

In the cases of Yb and Eu there is a very different behavior in the $\Delta H(T)$ curves at low temperature for certain crystal directions. This has been mentioned before,[3] and will be described more fully in another paper[4]; however, for completeness, a little must be included here. For YIG (2% Eu) at 1.5°K it is found that the measured linewidth varies spectacularly with the crystallographic orientation of the steady field. If we examine the (110) plane it is found that in a very narrow angular range near the [100] direction, the linewidth peaks sharply, increasing to several times its value well away from this direction. In the case of YIG(Yb) a similar effect is observed, but rather than being associated with a single direction, it takes place over arcs. The anomalous linewidth decreases rapidly with increasing temperatures, essentially disappearing by about 10 or 12°K. In the case of Yb the linewidth shows a peak vs temperature as is the case with other rare earths. The peaks observed for YIG(Yb) with H parallel to [110] and [111] occur at about 145°K, the highest temperature encountered. In the case of YIG(Eu) the linewidth temperature plot is essentially flat above a very mild peak at about 50°K.

TABLE I. Summary of linewidth peak positions.

Rare earth	Atomic No.	$T\|\Delta H_{\max}$ [100]	[110]	[111]	$\Delta H_{\max}$/fraction rare earth [100]	[110]	[111]	f (kMc/sec)
Pr	59	37	40	42	71 000	65 000	60 000	9.2
Nd	60	28	50	43	21 000	20 000	43 000	9.2
Pm	61	...	...	...	...	...	...	...
Sm	62	42	...	...	75 000	...	...	23
Eu	63	No peak, see text			...	...	...	...
Gd	64	Not measured			...	...	...	...
Tb	65	90	90	90	370 000	400 000	450 000	20.8
Dy	66	50	55	52	125 000	200 000	200 000	20.8
Ho	67	...	...	65	...	...	90 000	9.2
Er	68	60	...	...	20 000	...	...	23.8
Tm	69	61	...	...	750	...	...	9.2
Yb	70	90	145	145	1500	3000	3000	20.8

[3] J. F. Dillon, Jr., J. Appl. Phys. 32, 159S (1961).
[4] J. F. Dillon, Jr. (to be published).

LINEWIDTH OF YIG(Tb)

Special experimental effort has been devoted to the case of terbium-doped YIG, reflecting the availability of Walker's solution[2] for the splitting of this ion in a magnetic garnet lattice. Great care has been taken to acquire linewidth temperature data at three frequencies on a single sphere with the steady field along each of the principal crystallographic directions. The nine curves obtained are given in Fig. 2. The shoulders in the curves for [100] suggest that there are at least two maxima in each case, one at about 25°K, the other ranging from 65 to about 80°K. In the neighborhood of room temperature the linewidth is proportional to frequency, however, in the neighborhood of the linewidth maximum, the general tendency is for the linewidth to decrease slightly with increasing frequency. The curves for [111] are slightly different from the other in that they seem to be the sum of three single-peaked curves.

DISCUSSION

We may consider that we are dealing here with a three-component system. These are: first, the almost lossless ferric spin lattice; second, the lossy rare-earth ion lattice; and third, the crystal lattice which is presumably in good thermal contact with the outside world. In a resonance experiment, energy is injected into the ferric spin lattice. For highly pure YIG this energy finds its way to the lattice by way of various spin-phonon interactions, but in our case the energy reaches the lattice through the rare-earth ions. For this transfer the characteristics of the eigenstates of the rare-earth ions are obviously of great importance. In these magnetic crystals the splitting of the sublevels of the rare-earth ground multiplet by a crystal field and an exchange field are both significant. In II the problem is considered at length for the case of Tb^{3+} in YIG. A feature which emerges from the analysis and agrees with the experimental evidence available is that for an individual ion, the energy level scheme varies greatly with the orientation of the exchange field relative to the symmetry axes of the particular site. As an example, Fig. 3 gives the theoretical energy

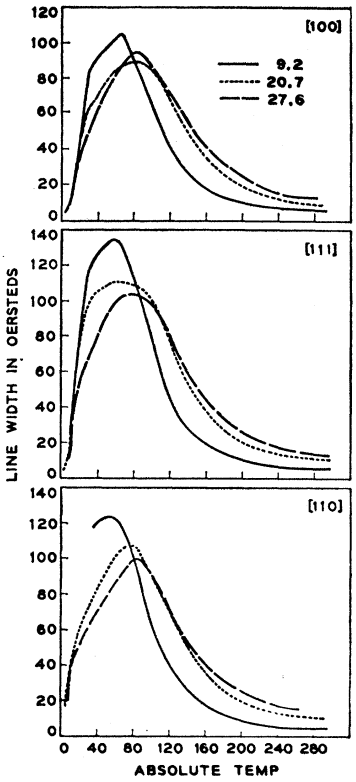

FIG. 2. Ferrimagnetic resonance linewidth for YIG(0.02% Tb) as a function of temperature. Data are shown for the field along the principal crystallographic directions for three frequencies, 9.2, 20.7, 27.6 kMc/sec.

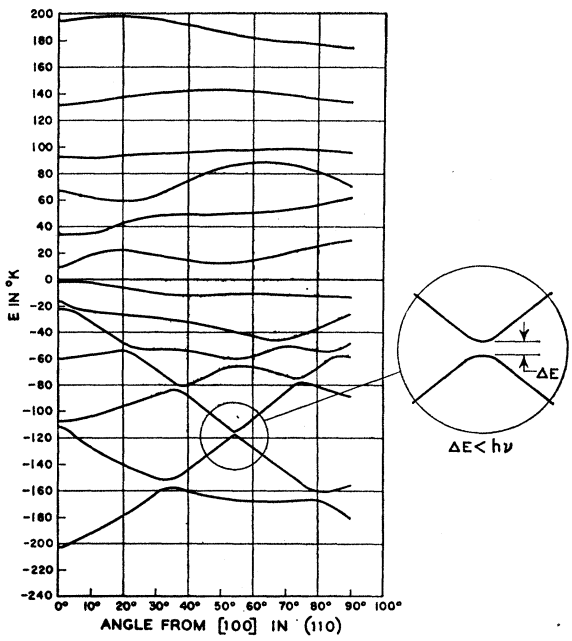

FIG. 3. Energy levels for Tb^{3+} in one of the inequivalent dodecahedrals sites in YIG. Levels are plotted as a function of the angle in the (110) plane between the [100] axis and the direction of the magnetization. This is a theoretical plot corresponding to a certain set of assumed parameters. These curves agree reasonably well with the low-temperature field for resonance data. This is taken from reference 2. The inset is intended to call attention to a region in which two excited levels approach to within less than a microwave photon energy of each other.

levels (for a certain set of parameters) for Tb^{3+} on one of the sites in YIG as the magnetization is moved around the (110) plane.[5]

In the case of terbium the ground state is $^7F_6$. The over-all splitting of the thirteen sublevels is about 400°K. We can expect several things to happen as the temperature is raised from absolute zero.

(a) The equilibrium population of the levels will change in accordance with the Boltzmann distribution.

(b) Thermal excitation of the lower frequency lattice vibrational modes will produce a spread in crystal fields, thus broadening the pure electronic levels, and spreading in angle the orientations of close approach.

(c) The local magnetization may diffuse away from the applied field, and therefore any effect sharp in angle will become increasingly blurred.

(d) The addition of higher frequency lattice modes to electronic states must spread the available levels upwards. Also this must affect the transition probabilities since Raman processes become available between higher states in the acoustic spectrum.

An examination of the garnet lattice shows that there are a number of inequivalent dodecahedral sites insofar as the site axes are disposed in six different ways relative to the crystal axes. Thus for any orientation of the exchange fields there are rare-earth ions with two to six (highest symmetry directions and a general direction) different level schemes to be considered.

In terms of these energy levels one may somewhat arbitrarily distinguish two different schemes for energy loss: (a) relaxation of the eigenstate populations as the magnetization precesses, and (b) the excitation of direct transitions between levels which approach within a microwave photon energy of each other. Let us consider these two processes in a little more detail.

(*a*) *Relaxation of Eigenstate Populations.* The general features of the data given in Fig. 2 can be accounted for by merely assuming a relaxation of the rare-earth magnetization involving a number of different relaxation times. The background for such an assumption lies in the characteristics of the rare-earth energy level schemes. Since the energy level diagrams vary strongly with orientation, any change in the direction of the exchange field will result in a change in the equilibrium population of states. Ferromagnetic resonance implies a precession of the magnetization, and thus of the exchange field. If the reciprocal of the relaxation time for the redistribution is at all comparable to the microwave frequency, relaxation-type losses will contribute to the linewidth.

The problem here is very similar to that considered

[5] This is Fig. 12(c) of II.

by Galt[6] and by Clogston[7] with regard to losses observed in ferrites containing divalent iron. Clogston considered the redistribution of the transient electrons in a ferrite containing Fe^{++} among the energy levels accessible to them. The whole formalism seems equally appropriate to the present case where we are concerned with the redistribution among states of the rare-earth ions. Clogston's assumption of a single relaxation time only gives a first approximation to the complicated situation of the rare-earth ions in YIG, however. Different directions of the magnetic field correspond to completely different energy level schemes, and there is no reason to expect them to behave in the same way. Thus, we expect inequivalent sites to behave differently. Furthermore, the rare-earth ion has a considerable number of levels, irregularly spaced; and it seems exceedingly unlikely that a single relaxation time could describe the approach to equilibrium. For Tb^{3+} ions in one site we might expect a half a dozen relaxation times to be important. The two to six inequivalent sites might increase the total number of distinct relaxation processes which are significant up to ten or twenty.

The relaxation times mentioned here express the transition probabilities between various states in the rare-earth ground multiplet. The probabilities depend on details of the eigenstates as well as on the modes of the acoustic spectrum excited at any temperature. An attempt to fit the $\Delta H(T,f)$ data would constitute a formidable statistical mechanical problem containing many more parameters than could be experimentally determined. Clearly the temperature dependences of the relaxation processes would be involved as would the temperature dependences of their relative contributions.

We believe that such a multiplicity of interrelated relaxation processes accounts for the over-all appearance of the $\Delta H(T)$ curves for Tb shown in Fig. 2. In particular it would account for the upward temperature shift of the maxima with increasing temperature, and for the near constancy of the maximum value of linewidth with temperature. The obvious shoulders in some $\Delta H(T)$ curves are to be ascribed to situations in which several distinctly different relaxation times are pertinent.

Parenthetically it might be pointed out that the addition of a frequency dependence to the τ's would enable us to include the "direct transition" mechanism (b) in the present discussion.

It is to be noted that the over-all appearance of the $\Delta H(T)$ curves for YIG(Tb) cannot be accounted for by simple application of the theory of linewidths in rare-earth garnets given by DeGennes, Kittel, and Portis.[8] That theory is based on the assumption that the exchange frequency between the ferric spin lattice and the rare-earth system is comparable to the reciprocal of the rare-earth lattice relaxation time in the region of the $\Delta H(T)$ peak, and that both of these quantities are much larger than the experimental frequency. It leads to the prediction that the maximum ΔH is directly proportional to the experimental frequency and occurs at a temperature which is independent of that frequency. Our data on the other hand indicate that in the YIG(Tb) case $\Delta H_{\max}$ is nearly independent of frequency and its temperature moves with the experimental frequency. The burden of the preceding discussion is that the application of a Galt[6] or a Clogston[7] type theory apparently can readily account for the experimental facts. These theories assume that the ferric-rare-earth exchange frequency is much greater than the reciprocal of the rare-earth-lattice relaxation time, and that the reciprocal is comparable to the experimental frequency.[9]

(*b*) *Excitation of Direction Transitions.* Let us turn now to the second of the loss mechanisms listed above, the excitation of transitions within the rare-earth multiplet. Among the interesting results given in II was the behavior of the absorption line with frequency for the steady field along one of the directions which gave an anomalous peak. The frequencies used ranged from 10 to 75 kMc/sec. In one case the height of the anomalous peak did not change with frequency, in two cases the height of the peak increased somewhat faster than linearly. Finally, in one case the height of the peak increased with increasing slope as the frequency was raised, till quite suddenly at about 65 kMc/sec the line became so broad that it could not be detected.

The anomalous peaks in the low-temperature field for resonance are associated with close approaches of the lowest two levels of the ground multiplet.[10] The interpretation given in II is that the sudden broadening of the line with frequency represents the approach of the microwave photon energy to the energy gap between those lowest two levels. In a sense the losses arise from a "paramagnetic resonance" with a zero-field splitting of about 65 kMc/sec. There is an enhancement of the resonance by the high resonant susceptibility of the iron lattice. Though no measurements have been made of linewidth vs temperature for this special direction at the high frequency, it seems clear that it must decrease rather rapidly as T increases.

An examination of energy level diagrams such as given in Fig. 3 discloses that there are many instances of close approaches between levels above the ground state. The point to be made here is that transitions

[6] J. K. Galt, W. A. Yager, and F. R. Merritt, Phys. Rev. **93**, 1119 (1954). J. K. Galt, Bell System Tech. J. **33**, 1023 (1954). J. K. Galt, Proc. Inst. Elec. Eng. **104**, Part B Suppl. 5, 189–197 (1956).

[7] A. M. Clogston, Bell System Tech. J. **34**, 739 (1955).

[8] P. G. DeGennes, C. Kittel, and A. M. Portis, Phys. Rev. **116**, 323 (1960).

[9] J. K. Galt and E. G. Spencer, this issue [Phys. Rev. **127**, 1572 (1962)], present a comparison of the assumptions and results of the "fast" and "slow" relaxation theories.

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

across these gaps can be excited directly by suitable microwave photons, and contribute importantly to the losses. The controlling factor here will be the absolute population difference between the two close levels. Neglecting some of the temperature effects mentioned above, we can determine this by applying the Boltzmann distribution to energy level diagrams such as in II. The population difference between two levels ΔE apart, whose average is E above the ground level, varies as

$$\frac{\Delta E}{kT}[e^{-E/kT}/\textstyle\sum_i e^{-E_i/kT}].$$

In this, the summation is over the sublevels of the multiplet, and all energies are measured above the ground state.

Figure 4 contains plots of the energy difference function given above for the close approaches between excited levels in the Tb^{3+} energy diagram given in Fig. 3. It will be seen that there is a maximum in the population difference, in fact, that the whole curve resembles strongly the $\Delta H(T)$ plots.

Our consideration of losses by direct transitions between close approaches of excited levels carries with it the suggestion that plots of linewidth vs orientation should contain sharp angular variations in the temperature region in which significant population differences exist. The theoretical energy level diagrams given in II, of which Fig. 3 is an example, were examined with this in mind. The theory in II contains nine parameters, only four of which have been optimized, therefore the levels shown are only approximations to the best possible set. Changes in parameters are likely to shift close approaches in angle, as well as change the gap. However in the case of a symmetry direction, moderate changes in parameters could only change the gap. With these points in mind, we have directed our attention to the close approaches between the second and third levels in the diagram of Fig. 3. These occur

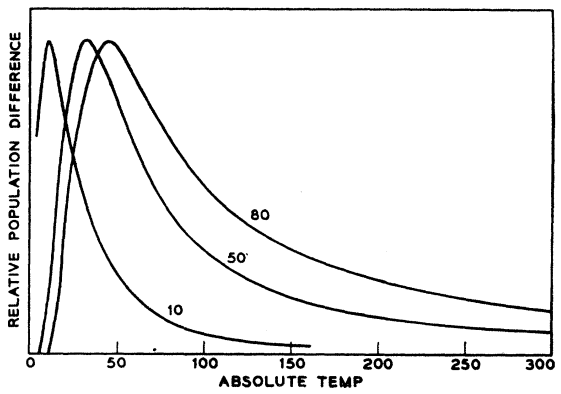

FIG. 4. Plots of the relative population difference between two levels 10, 50, or 80° above the lowest levels. These are from the Boltzmann function given in the text. All three have been normalized to the same maximum height.

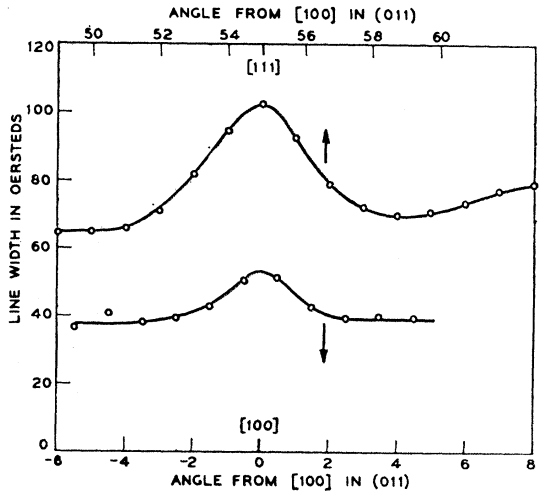

FIG. 5. Linewidth as a function of crystal direction in the (011) plane near [100] and [111] for YIG(0.02% Tb) as measured at 23°K. The frequency was 20.8 kMc/sec. [100] and [111] are directions or close approach between members of the rare-earth ground multiplet, and these peaks in ΔH appear to represent the excitation of transitions between these excited sublevels.

for the steady field along the [100] and [111] axes, and are thus tied to these directions insofar as small adjustments or thermal modulation of the parameters is concerned. For the [100] direction the other site has an even closer approach between the third and fourth levels only 35°K above the ground state, as can be seen in Fig. 12(b) of II.

Figure 5 shows plots of linewidth against angle near [100] and [111] made at about 23°K for YIG. The temperature was chosen out of convenience, rather than being exactly the temperature at which the largest population difference might be expected. It will be seen that near [111] the linewidth increases by about 50%, and the width of the maximum is only about 3°. Near [100] the percentage increase is perhaps 30%, and the width of the maximum only 2°. Similar measurements of linewidth at 1.5°K and at 295°K show no such anomaly. The data show a clear correlation between linewidth and the population difference of excited levels which are within approximately a microwave quantum of each other.

CONCLUSIONS

In general, ferrimagnetic resonance linewidths of rare-earth-doped yttrium iron garnet are anisotropic. Plots of $\Delta H(T)$ contain a maximum. The position of that maximum, ~30 to ~150°K varies with the rare earth, the crystal orientation of the applied field, and the microwave frequency.

For certain crystal directions YIG doped with Yb or Eu shows broad lines at the lowest temperatures available to us.

In the case of YIG(Tb) the temperature of the maximum value of $\Delta H(T)$ for the principal crystal

directions moves up with increasing frequency, though the maximum ΔH itself decreases slightly. There is some structure in $\Delta H(T)$.

Though previous theories assuming a mechanism with a single relaxation time constitute a first approximation, it seems possible to account for the salient features of these data by assuming the rare-earth magnetization relaxes with a number of relaxation times, some of which are comparable to the microwave frequencies. This assumption seems justifiable in view of the characteristics of the rare-earth energy levels.

In addition we believe that part of the losses at intermediate temperatures can be ascribed to transitions between excited sublevels of the rare-earth ground multiplet which approach within nearly a microwave photon of each other.

ACKNOWLEDGMENTS

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APPENDIX

We give in Figs. 6 to 13 plots of the experimental measurements of linewidth against temperature for the other rare earths which we have measured.

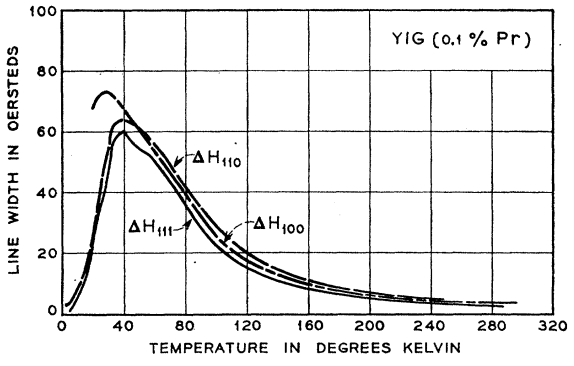

FIG. 6. Plots of linewidth against temperature for the principal crystallographic directions in YIG(0.1% Pr). Frequency, 9.2 kMc/sec.

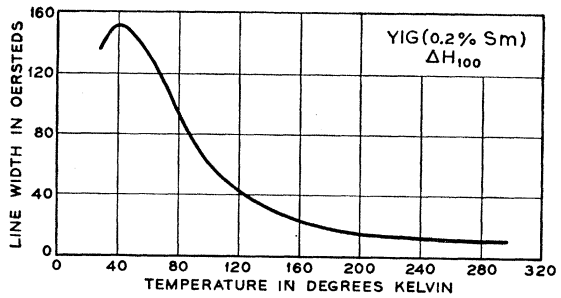

FIG. 7. Linewidth vs temperature for the steady field parallel to [100] in YIG(0.2% Sm). Frequency, 23 kMc/sec.

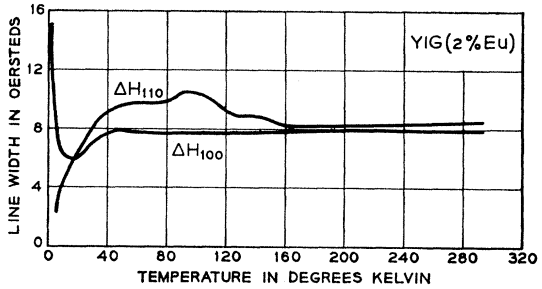

FIG. 8. Linewidth against temperature for the steady field parallel to [100] and [110] in YIG(2.0% Eu). Frequency, 23.25 kMc/sec.

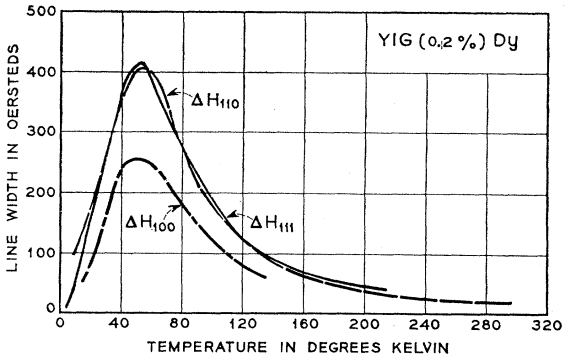

FIG. 9. Linewidth against temperature for the steady field along the principal crystallographic directions for YIG (0.2% Dy). Frequency, 20.8 kMc/sec.

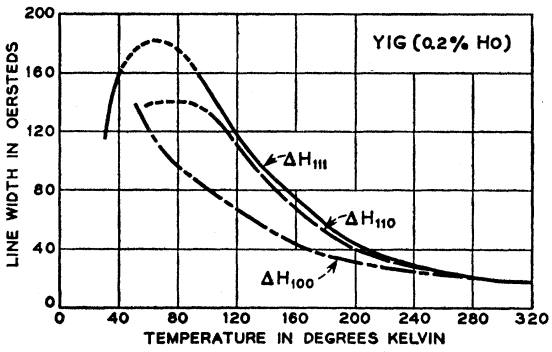

FIG. 10. Linewidth against temperature for H_{res} along the three principal directions in YIG(0.2% Ho). Frequency, 9.2 kMc/sec.

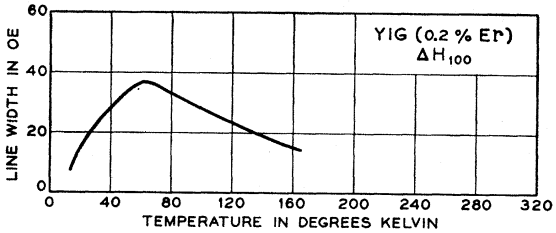

FIG. 11. Linewidth for the field along [100] plotted against temperature for YIG(0.2% Er). Frequency, 23.8 kMc/sec.

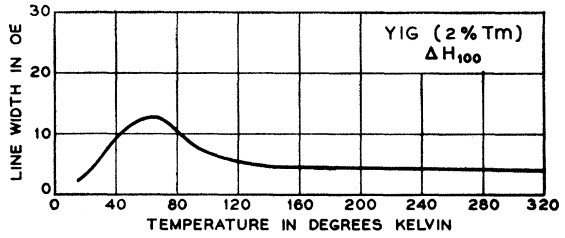

FIG. 12. Linewidth against temperature for YIG(2% Tm) with the field along [100]. Sparse data on the other principal directions indicate that the curves are very much the same. Frequency, 9.2 kMc/sec.

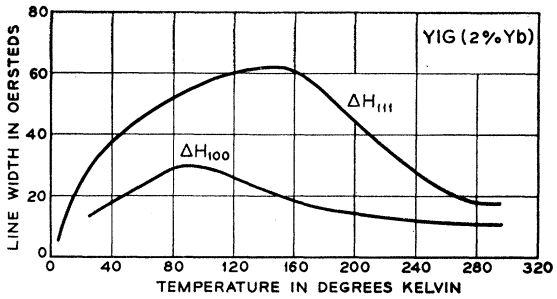

FIG. 13. Linewidth against temperature for the steady field along [111] and [100] directions in YIG(2% Yb). Frequency, 20.8 kMc/sec.

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Superconducting and Normal Specific Heats of Niobium*

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The measurements reported in this paper were undertaken to resolve differences in the published values of the low-temperature heat capacity of niobium and to determine the effect of high-temperature annealing (2340°C) and degassing on the same sample for which data had previously been published by Brown, Zemansky and Boorse. The new measurements cover the temperature interval 1.1 to 11.5°K and are significantly different from those obtained prior to the thermal treatment. The normal-phase heat capacity may be expressed by the usual relation, $C_n=\gamma T+\text{const}(T/\Theta_D)^3$, with $\gamma=(7.53\pm2\%)$ mJ/mole deg^2 and $\Theta_D=238°\text{K}\pm1.5\%$. The zero-field transition temperature, determined from the midpoint of the transition interval, was found to be 9.09°K. In the superconducting phase below 1.7°K, the total heat capacity C_s was found to be less than the lattice specific heat alone in the normal phase. This anomalous result, previously reported by the present authors, is comparable to that found in indium by Bryant and Keesom. This anomaly complicates the determination of the superconducting electronic specific heat C_{es} but by using a theory by Ferrell, it may be evaluated in the usual form, $a\gamma T_c\exp(-bT_c/T)$, with $a=12.6$ and $b=1.71$.

I. INTRODUCTION

SHORTLY after publication of the Bardeen-Cooper-Schrieffer theory (BCS) of superconductivity,[1] it appeared that a useful check on the theory could be made by comparing its predictions with experimental measurements of the superconducting electronic specific heat, C_{es}, as a function of the temperature. Although a number of C_{es} measurements had been made on pure metals at reduced temperatures t between 1 and 0.25, relatively few had been reported for smaller values of t and of these, only vanadium showed the dependence required by the theory.[2] Niobium, being identical in crystal structure and similar in chemical properties to vanadium, appeared suitable for a further test of the theory, especially since values of t approaching 0.1 could be obtained with liquid He[4] and the temperatures measured with good accuracy. The disadvantage of this choice lay principally in the difficulty of securing a specimen of the requisite purity and in carrying out a heat treatment which would eliminate internal stresses, particularly those arising from interstitial oxygen and nitrogen. In this connection, Wexler and Corak[3] had shown that in vanadium an increase in the amount of these gaseous inclusions decreased the transition temperature, increased the mechanical hardness, and produced in the material the irreversible characteristics of hard superconductors. Chou, White, and Johnston[4] observed changes of the same kind in niobium; annealing at successively higher temperatures, which presumably decreased the gas in their specimen, raised the transition temperature and improved the agreement between magnetic and calorimetric measurements. How large these effects may be has been demonstrated by the

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[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[2] H. A. Boorse, Phys. Rev. Letters **2**, 391 (1959).

[3] A. Wexler and W. S. Corak, Phys. Rev. **85**, 85 (1952).

[4] C. Chou, D. White, and H. L. Johnston, Phys. Rev. **109**, 788 (1958).