

## Ferrimagnetic Resonance Relaxation in Rare-Earth Iron Garnets

P. E. SEIDEN

*IBM Watson Research Center, Yorktown Heights, New York*

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A quantitative analysis has been made of the ferrimagnetic resonance relaxation in rare-earth iron garnets. The data considered consist of measurements of the ferrimagnetic resonance linewidth of yttrium-iron garnet substituted with neodymium, samarium, dysprosium, holmium, erbium, and ytterbium taken from 4.2°K to just below the Curie point as well as measurements of other investigators for terbium and thulium. The data are conveniently divided into the two groups of odd and even electron ions. The ions in each group behave in a similar manner, the only exceptions being thulium and ytterbium. It is assumed that all the relaxation occurs through the strongly relaxing rare-earth ions but we find that both the "fast-relaxation" theory of de Gennes, Kittel, and Portis and the "slow-relaxation" theory of Clogston and Van Vleck and Orbach fail to provide agreement with experiment. We have, however, formulated an empirical relation containing a relaxation term of the "slow-relaxation" type that provides an excellent fit to the data when one regards the relaxation of the rare earth as being the familiar one-ion spin-lattice relaxation due to the direct (one-phonon) and Orbach (two-phonon) processes. The observed temperature dependence of the linewidth is satisfactorily accounted for if one assumes the direct process for the odd electron ions and the Orbach process for the even electron ions. In the case of thulium one finds it necessary to assume the direct process and for ytterbium one finds evidence for both processes, the direct process being dominant at low temperatures and the Orbach process dominant at high temperatures. The analysis allows evaluation of the iron rare-earth exchange frequency and the rare-earth relaxation parameters. The exchange frequencies are found to be in good agreement with the values obtained by other investigators. In the one case where independent relaxation time measurements exist, that of samarium-iron garnet, the behavior we find from the linewidth measurements agrees with that found by Caspari *et al.* by  $\gamma$ - $\gamma$  correlation experiments. The frequency dependence predicted by the empirical relation is also in accord with experiment and a quantitative calculation of the frequency dependence of the peak value of the linewidth and the temperature of the linewidth peak yields excellent agreement with the data of Dillon for terbium.

### I. INTRODUCTION

MEASUREMENTS of the linewidth of the rare-earth iron garnets have shown that all the non- $S$ -state ions (except europium where  $J=0$ ) behave in a similar manner.<sup>1-3</sup> At low temperatures the linewidth increases as a function of temperature until a peak is reached between 40–150°K, at which point the linewidth decreases with temperature up to the immediate vicinity of the Curie point. Since the linewidth of pure yttrium-iron garnet is very small ( $\leq 0.5$  Oe) and even a small percentage substitution of a rare earth into yttrium iron garnet increases the linewidth by at least an order of magnitude, it seems clear that one can attribute the loss to the relaxation of the rare-earth ions.

Kittel<sup>4</sup> has proposed an explanation of the behavior of the linewidth in the rare-earth garnets along these lines by assuming a lossless iron lattice coupled by an exchange field to the rare-earth lattice consisting of strongly relaxing rare-earth ions. This model predicts a linewidth behavior of the type observed, with the linewidth peak occurring when the exchange coupling is of the same order of magnitude as the inverse relaxation

time, i.e.,  $\omega_{\text{ex}}\tau \sim 1$ . Because of the very short relaxation times involved the theory based on this model is usually called the "fast-relaxation" theory. Although the theory qualitatively accounts for the temperature dependence of the linewidth, a detailed quantitative comparison with experiment reveals a number of discrepancies.

Recently there has been an attempt<sup>2,5</sup> to account for the behavior of these materials by considering the details of the motion during a precession cycle. When the relaxation time is of the order of the precession frequency, the instantaneous field, about which the rare-earth ion precesses, changes during a precession cycle. The populations of the rare-earth levels then relax toward their new equilibrium distributions during the cycle. This relaxation engenders an additional component of loss. A loss process of this type has previously been discussed by Galt<sup>6</sup> and Clogston<sup>7</sup> for ferrites in the context of a different problem. Their theory also predicts a behavior similar to that observed experimentally but in this case the linewidth peak occurs at  $\omega\tau \sim 1$ . Recently, Van Vleck and Orbach<sup>8</sup> carried out a quantum-mechanical calculation of a model of this type and obtained results essentially in agreement with Clogston.

Since the precession frequency  $\omega \ll \omega_{\text{ex}}$ , the relaxation time at the peak is longer than it is in the case where

<sup>1</sup> G. P. Rodrigue, H. Meyer, and R. V. Jones, *J. Appl. Phys.* **31**, 376S (1960).

G. P. Rodrigue, J. E. Pippin, W. P. Wolf, and C. L. Hogan, *IRE Trans. Microwave Theory Tech.* **MTT-6**, 83 (1958).

<sup>2</sup> J. F. Dillon, Jr., *Phys. Rev.* **127**, 1495 (1962).

<sup>3</sup> P. E. Seiden, in *Magnetic and Electric Resonance and Relaxation, Proceedings of Colloque Ampère, Eindhoven July, 1962* (North-Holland Publishing Company, Amsterdam 1963), p. 488; and in *Paramagnetic Resonance, Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, July 1962* (Academic Press, Inc., New York, 1963), Vol. II, p. 443.

<sup>4</sup> C. Kittel, *Phys. Rev.* **115**, 1587 (1959).

<sup>5</sup> R. W. Teale and K. Tweedale, *Phys. Letters* **1**, 298 (1962); B. H. Clarke, R. F. Pearson, R. W. Teale, and K. Tweedale, *J. Appl. Phys.* **34**, 1269 (1963).

<sup>6</sup> J. K. Galt, *Bell System Tech. J.* **33**, 1023 (1954); W. A. Yager, J. K. Galt, and F. R. Merritt, *Phys. Rev.* **99**, 1203 (1955).

<sup>7</sup> A. M. Clogston, *Bell System Tech. J.* **34**, 739 (1955).

<sup>8</sup> J. H. Van Vleck and R. Orbach, *Phys. Rev. Letters* **11**, 65 (1963).

$\omega_{\text{ex}}\tau \sim 1$ . For this reason we call this theory the "slow-relaxation" theory.

Teale and Tweedale<sup>5</sup> have recently applied this model to explain the difference observed between static and resonance anisotropy measurements in the garnets and found that they could successfully explain the experimental observations as being due to having  $\omega\tau > 1$  at low temperatures so that the rare-earth ions cannot relax to their equilibrium configuration within the period of measurement (a precession cycle).

Up to the present time there has been no detailed comparison of theory with the experimental data for ferrimagnetic resonance linewidths and we here undertake an analysis of this kind. In this paper we present a quantitative comparison between the theoretical predictions and extensive measurements of the ferrimagnetic resonance linewidth in rare-earth-substituted yttrium iron garnet. In Sec. II we discuss the theories that have been proposed for this problem and present their results. After describing the experiments, the data obtained and the disagreement with theory in Sec. III, we formulate an empirical equation in Sec. IV and show that it provides an excellent fit to the data. We include an examination of the relaxation of the rare-earth ions by considering the one-ion relaxation processes which have successfully accounted for the behavior of rare-earth ions in paramagnetic salts. Finally in Sec. V we discuss the empirical equation in reference to the "slow-relaxation" theory in order to illustrate the main problems remaining in explaining the relaxation behavior of the rare-earth iron garnets.

## II. THEORIES OF RELAXATION IN THE RARE-EARTH GARNETS

We here consider the magnetic structure of the rare-earth garnets in the molecular field approximation in the usual manner.<sup>9</sup> This structure is made up of three sublattices. Two of them contain iron ions (the octahedral and tetrahedral sites) and are coupled together by a molecular field of the order of  $6 \times 10^6$  Oe. This is the largest effective field that will enter our discussions and in what follows we will assume that the iron sublattices are infinitely tightly coupled and consider then only one iron sublattice (the resultant). This sublattice is coupled to the rare-earth sublattice by a molecular field of an order of magnitude less than the iron-iron field and is the coupling that will be explicitly considered. The rare-earth-rare-earth molecular field is at least another order of magnitude smaller and is neglected. We then have a resulting two-sublattice system for which we must determine the resonance behavior.

Kittel<sup>4</sup> considered a lossless iron sublattice and expressed the loss in the rare-earth sublattice by means of an equation of the Landau-Lifshitz form. The equations of motion are,

$$\begin{aligned} \mathbf{M}_F &= -\gamma_F \mathbf{M}_F \times (\mathbf{H} + \lambda \mathbf{M}_R), \\ \mathbf{M}_R &= -\gamma_R \mathbf{M}_R \times (\mathbf{H} + \lambda \mathbf{M}_F) - (\tau \lambda M_F M_R)^{-1} \mathbf{M}_R \\ &\quad \times [\mathbf{M}_R \times (\mathbf{H} + \lambda \mathbf{M}_F)], \end{aligned} \quad (1)$$

where  $F$  denotes the iron sublattice,  $R$  the rare-earth sublattice, and  $\lambda$  is the Weiss molecular field constant. Assuming a solution of the form  $e^{i\omega t}$  we can obtain the secular equation for  $\omega$  and find the following solutions<sup>4,10</sup>:

$$\frac{\Delta\omega}{\omega} = \frac{N_R}{N_F} \frac{\hbar}{\omega_{\text{ex}}^2} \frac{1}{kT} \tau \quad \omega_{\text{ex}}\tau \ll 1, \quad (2a)$$

$$\frac{\Delta\omega}{\omega} = \frac{N_R}{N_F} \frac{1}{\omega_{\text{ex}}\tau} \quad \omega_{\text{ex}}\tau \ll 1, \quad (2b)$$

where  $N_R/N_F$  is the concentration of the rare-earth ions relative to the ferric ions. The ways in which these equations fail to describe the behavior of the rare-earth garnets will be pointed out.

It was later suggested<sup>11</sup> that the Landau-Lifshitz equations may not properly describe the relaxation of the rare-earth ions and that perhaps the Bloch-Bloembergen equations should be used for the rare-earth sublattice.

$$\begin{aligned} (m_R)_{x,y} &= -\lambda_R [\mathbf{M}_R \times (\mathbf{H} + \lambda \mathbf{M}_F)]_{x,y} - (m_R)_{x,y} / \tau \\ M_{Rz} &= -\gamma_R \mathbf{M}_R \times (\mathbf{H} + \lambda \mathbf{M}_F)_z - (M_{Rz} - M_{R0}) / \tau. \end{aligned} \quad (3)$$

Solving the secular equation in the same manner as above one finds the same high-temperature solution [Eq. (2a)] but the low-temperature solution becomes

$$\Delta\omega/\omega \sim 1/\omega\tau$$

which differs from Eq. (2b) by  $\omega_{\text{ex}}/\omega$ . However, this result is incorrect since Eqs. (3) relax the total component of  $\mathbf{M}_R$  transverse to  $\mathbf{H}$  while one should only relax the component of  $\mathbf{M}_R$  transverse to the instantaneous field  $\mathbf{H} + \lambda \mathbf{M}_F$ . Equations (3) are then correct in the system of coordinates where  $\mathbf{H} + \lambda \mathbf{M}_F$  is taken as the  $z$  axis. In this system the secular determinant is of the same form as that for Eqs. (1), and therefore must yield the same solution [Eqs. (2)]. Therefore, as far as the rare-earth garnets are concerned there appears to be no difference between the Landau-Lifshitz and Bloch-Bloembergen relaxation terms.

We now turn our attention to the "slow-relaxation" theory. Clogston<sup>7</sup> has derived equations of motion for the case where the relaxation time is of the same order of magnitude as the precessional frequency. Assuming a time dependence of  $e^{i\omega t}$ , these equations may be

<sup>10</sup> P.-G. de Gennes, C. Kittel, and A. M. Portis, Phys. Rev. **116**, 323 (1959).

<sup>11</sup> R. Orbach, *Paramagnetic Resonance, Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, July 1962* (Academic Press, Inc., New York, 1963), Vol. II, p. 456.

<sup>9</sup> R. Pauthenet, Ann. Phys. (Paris) **3**, 424 (1958).

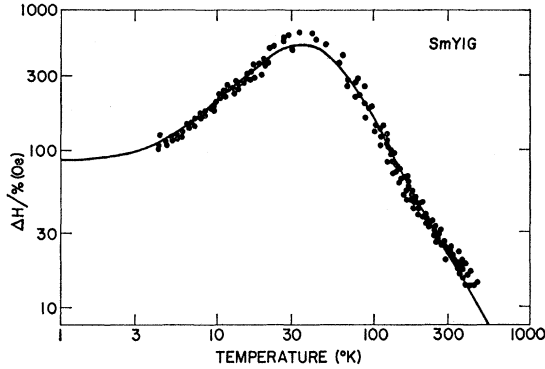


FIG. 1. Linewidth of samarium-substituted yttrium iron garnet as a function of temperature. The ordinate is the linewidth in Oe per percent rare-earth substitution.

written as,

$$\begin{aligned} \dot{m}_{Rz} &= -\gamma_R [\mathbf{M}_R \times (\mathbf{H} + \lambda \mathbf{M}_F)]_z \\ &\quad + \frac{\gamma_R}{M_R} \sum_i \left( \frac{\partial \epsilon_i}{\partial \phi} \right)_{\phi_0} \left( \frac{\partial N_{i\infty}}{\partial \phi} \right)_{\phi_0} \frac{i\omega\tau}{1+i\omega\tau m_{Rz}}, \\ \dot{m}_{Ry} &= -\gamma_R [\mathbf{M}_R \times (\mathbf{H} + \lambda \mathbf{M}_F)]_y \\ &\quad - \frac{\gamma_R}{M_R} \sum_i \left( \frac{\partial \epsilon_i}{\partial \theta} \right)_{\theta_0} \left( \frac{\partial N_{i\infty}}{\partial \theta} \right)_{\theta_0} \frac{i\omega\tau}{1+i\omega\tau} m_{Rz}, \end{aligned}$$

where  $\epsilon_i$  is the energy of the  $i$ th energy level and  $N_{i\infty}$  is the thermal-equilibrium population of the level. The derivatives are evaluated at the equilibrium angles  $\theta_0$  and  $\phi_0$ . These equations yield a solution of the form

$$\begin{aligned} \Delta H &= -\frac{1}{M_F} \sum_i \left[ \left( \frac{\partial \epsilon_i}{\partial \theta} \right)_{\theta_0} \left( \frac{\partial N_{i\infty}}{\partial \theta} \right)_{\theta_0} \right. \\ &\quad \left. + \left( \frac{\partial \epsilon_i}{\partial \phi} \right)_{\phi_0} \left( \frac{\partial N_{i\infty}}{\partial \phi} \right)_{\phi_0} \right] \frac{\omega\tau}{1+(\omega\tau)^2}. \end{aligned} \quad (4)$$

Assuming a two-level system, we have

$$\epsilon_{\pm} = \pm \hbar\omega_{\text{ex}}/2, \quad (N_{\pm})_{\infty} = \frac{N_R e^{(-\hbar\omega_{\text{ex}}/2kT)}}{2} \operatorname{sech} \frac{\hbar\omega_{\text{ex}}}{2kT},$$

so that

$$\begin{aligned} \sum_i \left( \frac{\partial \epsilon_i}{\partial \theta} \right) \left( \frac{\partial N_{i\infty}}{\partial \theta} \right) &= - \left| \frac{\partial \epsilon}{\partial \theta} \right| \frac{\partial}{\partial \theta} [(N_{-})_{\infty} - (N_{+})_{\infty}] \\ &= -N_R \frac{\hbar\omega_{\text{ex}}'}{2} \frac{\partial}{\partial \theta} \tanh \frac{\hbar\omega_{\text{ex}}}{2kT} \\ &= -N_R \frac{\hbar^2 \omega_{\text{ex}}'^2}{4kT} \operatorname{sech}^2 \frac{\hbar\omega_{\text{ex}}}{2kT}, \end{aligned} \quad (5)$$

where  $\omega_{\text{ex}}' = (\partial\omega_{\text{ex}}/\partial\theta)_{\theta_0}$ . A similar expression obtains for the  $\phi$  term. Since  $M_F = N_F \gamma_F \hbar$  (ignoring the weak

temperature dependence of  $M_F$ , we assume a saturated iron sublattice) Eq. (4) becomes

$$\frac{\Delta H}{H} = -\frac{1}{2} \frac{N_R}{N_F} \frac{\hbar\omega_{\text{ex}}'^2}{kT} \frac{\tau}{1+(\omega\tau)^2} \operatorname{sech}^2 \frac{\hbar\omega_{\text{ex}}}{2kT}, \quad (6)$$

which is of the same form as the results of Van Vleck and Orbach.<sup>8</sup> The exchange frequency may in general be written as

$$\omega_{\text{ex}} = (\omega_{\text{ex}})_I + (\omega_{\text{ex}})_A f(\theta, \phi),$$

where  $I$  and  $A$  stand for isotropic and anisotropic parts, respectively. Taking the angular derivative of  $f(\theta, \phi)$  evaluated at  $\theta_0$  on  $\phi_0$  gives us just a number of the order of one for any reasonable form of anisotropy. Therefore,  $\omega_{\text{ex}}' \simeq (\omega_{\text{ex}})_A$  but since the exchange anisotropy is very large for these materials being of the same order as  $\omega_{\text{ex}}$  [i.e.,  $(\omega_{\text{ex}})_I$  is small] we will assume for the rest of this paper that  $\omega_{\text{ex}}' \simeq \omega_{\text{ex}}$ .

At high temperatures, where  $\omega\tau \ll 1$  and  $\hbar\omega_{\text{ex}}/2kT \ll 1$ , the sech factor is just unity and we have, to within a factor of 2, just Eq. (2a) so that at high temperatures the "fast-" and "slow"-relaxation theories give the same result. At low temperatures, however, where  $\omega\tau \gg 1$ , we have

$$\frac{\Delta H}{H} = -\frac{1}{2} \frac{N_R}{N_F} \frac{\omega_{\text{ex}}^2}{\omega^2} \frac{\hbar}{kT} \frac{1}{T\tau} \operatorname{sech}^2 \frac{\hbar\omega_{\text{ex}}}{2kT}. \quad (7)$$

When  $\hbar\omega_{\text{ex}}/2kT > 1$  the sech becomes an exponential, and, at very low temperatures, the temperature dependence of the linewidth becomes very strong:

$$\Delta H \sim e^{-\hbar\omega_{\text{ex}}/kT} / T\tau.$$

### III. EXPERIMENTAL MEASUREMENTS AND COMPARISON WITH THEORY

The samples used for the linewidth experiments consisted of small, well-polished single crystal spheres of yttrium iron garnet substituted with from 0.1 to 10% of dysprosium, erbium, holmium, samarium, neody-

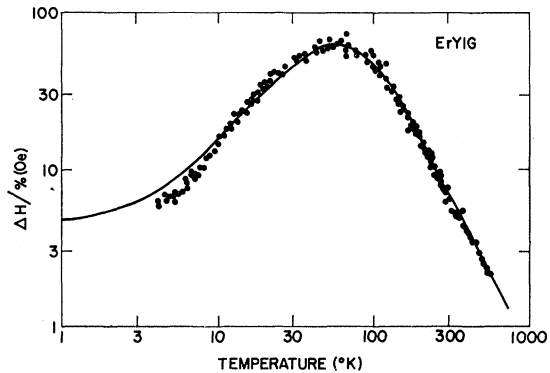


FIG. 2. Linewidth of erbium-substituted yttrium iron garnet as a function of temperature.

TABLE I. Composition of measured samples of rare-earth-substituted yttrium iron garnet.

	Rare earth						
	Pr	Nd	Sm	Dy	Ho	Er	Yb
Atomic %	0.2	0.3	0.5	0.7	0.1	0.7	0.7
Substitution	1.4	1.6	1.5	1.2	0.8	1.8	1.8
	4.6	6.2	3.2	2.1	1.9	4.0	4.0
				3.0	7.2	9.7	7.3
				7.7			10.7

mium, praeodymium, and ytterbium, at least three different concentrations being made for each rare earth. Substituted garnets were used since the linewidths of most of the concentrated materials are so large that one cannot measure them over the whole temperature range of interest. The rare-earth concentrations were measured by x-ray spectrographic analysis.<sup>12</sup> Table I lists the various samples used in obtaining the data to be presented here.

The ferromagnetic resonance linewidth along the [111] crystal direction was measured from 4.2 to 500°K at 9200 Mc/sec for all the samples and the data for each rare earth have been placed on the same curve by plotting linewidth per percent rare-earth substitution. The fact that a single, well-defined curve results, illustrates the linear dependence of the linewidth upon rare-earth concentration.

The data can be roughly divided into the two groups of odd and even electron ions with only two exceptions that will be noted below. Firstly, we consider the linewidth behavior of the odd electrons ions, samarium, erbium, dysprosium, and neodymium shown in Figs. 1-4. The general behavior indicates a more or less linear dependence on temperature below the peak and an inverse quadratic dependence above the peak. In the case of the even electron ions, holmium and praseodymium (Figs. 5-6), we see that the temperature dependences are stronger, being  $1/T^2$  above the peak and  $1/T^3$  (or

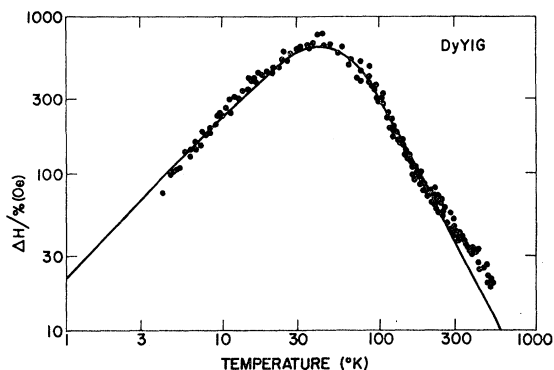


FIG. 3. Linewidth of dysprosium-substituted yttrium iron garnet as a function of temperature.

<sup>12</sup> J. C. Lloyd and J. D. Kuptsis, *Advances in X-Ray Analysis* (Plenum Press, Inc., New York), Vol. 6 (to be published).

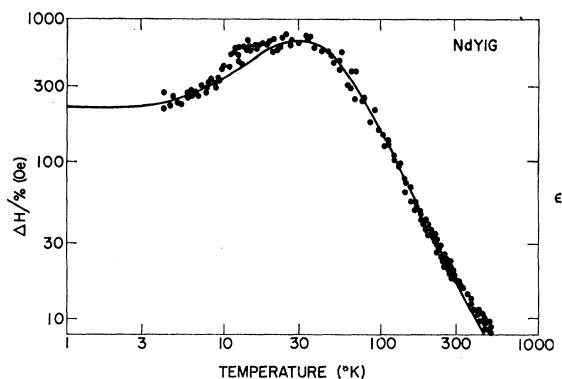


FIG. 4. Linewidth of neodymium-substituted yttrium iron garnet as a function of temperature.

more for holmium) at low temperatures. For the case of ytterbium (Fig. 7) we find a very strong temperature dependence above the peak and a very weak dependence below. In all these cases we see that the strong temperature dependence given by Eq. (7) is not observed (except perhaps in the case of holmium between 10 and 30°K). We however still have  $\tau$  as a parameter, and to fit the data for the odd electron ions for example, one would need to have

$$\tau \sim e^{-h\omega_{\text{ex}} kT/T^2};$$

that is,  $\tau$  would increase with temperature at low temperatures. This is not reasonable at least if one regards  $\tau$  as due to spin-lattice interactions. Alternatively one could suppress the exponential by arguing that the argument of the sech term actually involves the splitting between two low-lying states so that  $h\omega_{\text{ex}}/k < 8^\circ\text{K}$ . In this case for odd electron ions one requires  $\tau \sim \tau T^{-2}$  at low temperatures and  $T^{-1}$  at high temperatures, a behavior which is not at all expected although perhaps possible. However, for the case of ytterbium<sup>13</sup> where we know<sup>14</sup> that we have only a single ground-state doublet with a splitting of the order of 35°K with the next lowest level being 791°K away, it is difficult to find a reason for suppressing the factor.

#### IV. AN EMPIRICAL MODEL

The failure of the "slow-relaxation" theory to predict the proper behavior of the linewidth at low temperatures causes one to search further for the proper explanation of the experimental results. At present we have no theoretical explanation available but we have found an

<sup>13</sup> It should be pointed out here that there exist inconsistencies in the published data on the rare-earth garnets. For example, there are three published measurements on ytterbium-substituted yttrium iron garnet, Refs. (2) and (5) and the data presented here. All three are somewhat different. The reasons for this are not known but nevertheless in no case is an exponential behavior found at low temperatures.

<sup>14</sup> K. A. Wickersheim, *Phys. Rev.* **122**, 1376 (1961); A. J. Sievers, III, and M. Tinkham, *ibid.* **124**, 321 (1961); A. Brooks Harris and Horst Meyer, *ibid.* **127**, 101 (1962); and R. Pappalardo and D. L. Wood, *J. Chem. Phys.* **33**, 1374 (1960).

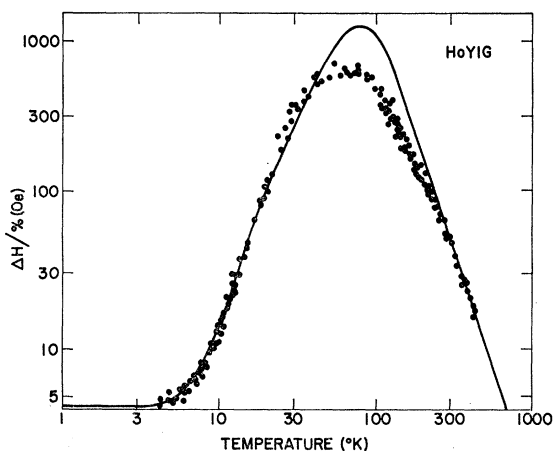


FIG. 5. Linewidth of holmium-substituted yttrium iron garnet as a function of temperature.

empirical relation that provides rather phenomenal agreement with experiment. The relaxation term is still of the "slow-relaxation" type but the coefficient is changed. We choose

$$\Delta H = \lambda M_R \{ \omega \tau / [1 + (\omega \tau)^2] \}. \quad (8)$$

A discussion of the possible theoretical significance of such a term will not be attempted here. At present we will just explore its consequences. This relation may be rewritten by letting

$$\begin{aligned} \lambda M_R &= \lambda M_{R0} \tanh(h\omega_{\text{ex}}/2kT) \\ &= \frac{N_R \omega_{\text{ex}}}{N_F \gamma_F} \tanh \frac{h\omega_{\text{ex}}}{2kT}, \end{aligned}$$

where again  $M_0 = N\gamma h$  and  $\gamma_R \lambda M_F = \omega_{\text{ex}}$ . We then have

$$\frac{\Delta H}{H} = \frac{N_R}{N_F} \frac{\omega_{\text{ex}} \tau}{1 + (\omega \tau)^2} \tanh \frac{h\omega_{\text{ex}}}{2kT}. \quad (9)$$

At high temperatures when  $\omega \tau \ll 1$  and  $h\omega \ll kT$  so that we may expand the tanh we obtain again just Eq. (2a) and the high-temperature limit of Eq. (5). Therefore, for high temperatures nothing is changed. For low temperatures, however, the tanh is unity and we have with  $\omega \tau \gg 1$

$$\frac{\Delta H}{H} = \frac{N_R \omega_{\text{ex}}}{N_F \omega^2 \tau},$$

which differs from Eq. (2b) by a factor  $\omega_{\text{ex}}^2/\omega^2$  (of the order of  $10^4$ ) and also differs considerably from Eq. (7), the most important feature being the absence of the exponential factor.

We now wish to obtain a relation giving the temperature at which one finds the peak in the linewidth. A simple polynomial expression is most easily obtained if we approximate Eq. (9) by using the high- and low-temperature forms and combining them to obtain the

relation

$$\frac{\Delta H}{H} = \frac{N_R}{N_F} \left[ \frac{2kT}{\omega_{\text{ex}}^2 \tau \hbar} + \tau \frac{\omega^2}{\omega_{\text{ex}}} \right]^{-1}. \quad (10)$$

Assuming a power law for  $\tau$ ,

$$\tau = K/T^n, \quad (11)$$

we can find the temperature at which the linewidth peak occurs ( $T_P$ ) by differentiating Eq. (7) with respect to  $T$  and setting the result equal to zero. We find,

$$T_P^{2n+1} = [n/(n+1)] \omega_{\text{ex}} \omega^2 K^2 \hbar / k, \quad (12)$$

or,

$$[n/(n+1)] (\omega \tau)^2 (\hbar \omega_{\text{ex}} / k T_P) = 1.$$

$\omega_{\text{ex}} \approx 10^{12}$  and corresponds to an effective temperature ( $T_{\text{ex}} = \hbar \omega / k$ ) of the order of  $10^3$  K, which is roughly the same order as  $T_P$ . Therefore the peak condition is that  $\omega \tau$  is of the order of unity although not necessarily exactly unity.

The linewidth at the peak is given by [from Eqs. (10-12)]

$$\left( \frac{\Delta H}{H} \right)_P = 2 \frac{N_R \omega_{\text{ex}}^2 K \hbar / k}{N_F T_P^{n+1}} \frac{n}{2n+1},$$

or since

$$T_P^{2n+1} \sim \omega^2$$

$$\left( \frac{\Delta H}{H} \right)_P \sim \omega^{[2(n+1)/(2n+1)]}. \quad (13)$$

Before one can compare in detail the experimental data to the relations given here we must say something about the details of the relaxation process. We assume that the relaxation in question is the one-ion relaxation usually considered for the case of paramagnetic resonance. This problem has been considered in detail by Orbach<sup>15</sup> and we shall here follow his treatment. The net relaxation rate is given as a sum of the relaxation

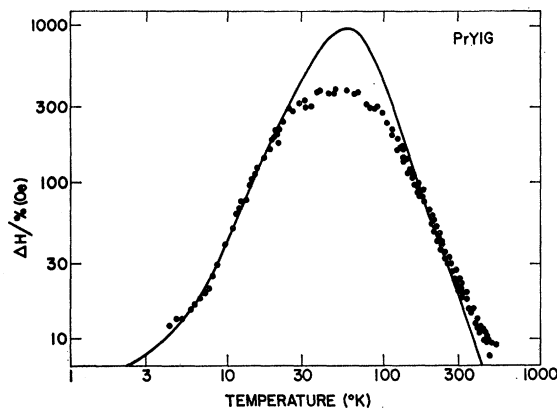


FIG. 6. Linewidth of praeosodium-substituted yttrium iron garnet as a function of temperature.

<sup>15</sup> R. Orbach, Proc. Roy. Soc. (London) A264, 458 (1961).

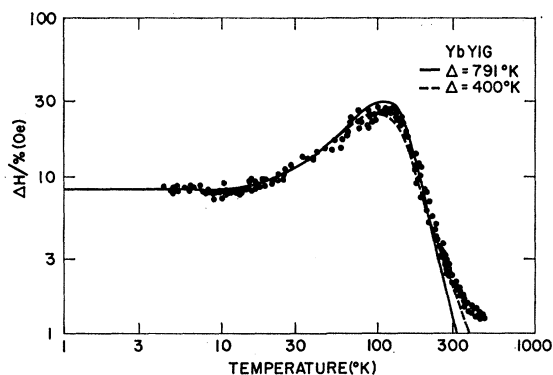


FIG. 7. Linewidth of ytterbium-substituted yttrium iron garnet as a function of temperature.

rates of three relaxation processes. The first to be considered is the direct process which involves the emission of a phonon with energy equal to the energy lost by the magnetization. The temperature dependence of the relaxation time for this process is given by

$$\tau_D = K_1 \tanh \delta/2T, \quad (14)$$

which gives the usual  $1/T$  dependence when  $\delta \ll T$ .  $\delta$  is the splitting, in degrees Kelvin, of the levels between which the relaxation is taking place, and  $K_1$  is a constant which depends on the details of the wave functions, crystal fields, spin-orbit coupling, exchange energy, etc., and its calculation is a problem of great complexity for a system like the rare-earth iron garnets. We will here simply regard  $K_1$  as a parameter.

Secondly, we consider relaxation by means of the Orbach process. In this case a phonon is absorbed, raising the system to a higher energy level, after which a phonon is emitted with an energy equal to the energy of the absorbed phonon plus the energy lost by the magnetization. For this process we have

$$\tau_O = K_2 \sinh^2(\Delta/2T), \quad (15)$$

where  $\Delta$  is the energy of the intermediate state relative to the ground state.<sup>16</sup>

The third relaxation process, the Raman process, will not be considered here since there is no indication of its appearance in the rare-earth iron garnets.

Before proceeding, one additional point must be mentioned.<sup>2</sup> Since there are a number of inequivalent sites for the rare-earth ions and many levels that may be excited, for some ions there will be a multiplicity of  $\tau$ 's. We will here, however, assume one single  $\tau$  for each process which is in some sense an average. We can then

<sup>16</sup> We choose this form for  $\tau_O$  instead of the more familiar exponential form since we assume that the linewidth of the excited state is relatively independent of temperature as has been experimentally observed. Also since the linewidths of the excited states are wide the associated relaxation times approach the Debye limit and as is discussed further on one would not expect a large temperature dependence. Eq. (15) is obtained directly from Orbach's Eq. (38) in Ref. 15 by assuming  $\Gamma_0 = \text{const}$ .

of course never expect to explain any behavior depending on the detailed ionic structure.

The fit of the data to Eq. (9) is made in a straightforward manner. For the odd electron ions we assume the direct process for  $\tau$  which successfully accounts for the observed temperature dependence. The solid curves in Figs. 1-4 are plots of Eq. (9) using Eq. (14) for  $\tau$ , and are in agreement with the data. In the case of the even electron ions holmium and praseodymium (Figs. 5-6) we see that the temperature dependences are much stronger, indicating that the Orbach process is of importance. We therefore now use Eq. (15) in conjunction with Eq. (9) and obtain the solid curves of Figs. 5-6. In this case the agreement is not quite as good in the peak region although the general fit over the whole temperature range is good. Figure 8 gives data for terbium kindly supplied by J. F. Dillon, Jr. The theoretical curve is obtained assuming the Orbach process and the results are similar to the other even electron ions.

The theoretical curves given in Figs. 1-9 were obtained by first fitting Eq. (9) at high and low temperatures sufficiently far from the peak so that the high- and low-temperature approximations for Eq. (9) are valid. Using this procedure for the odd electron ions, one obtains values for the constant factor  $\omega_{\text{ex}}^2 K_1 \delta$  from the high-temperature region and for the factor  $\omega_{\text{ex}}/K_1 \delta$  from the low-temperature region. From these two factors one can then separately obtain  $\omega_{\text{ex}}$  and  $K_1 \delta$ . In the cases where curvature is evident at low temperatures  $K_1$  and  $\delta$  are separated by fitting Eq. (9) to the data over the region of curvature. The values obtained for the constants are put into Eq. (9) and theoretical curves are then plotted. In the even electron case one obtains  $\omega_{\text{ex}}$ ,  $K_2$  and  $\Delta$  in a similar manner. Also for these ions we attribute the tailing off of the linewidth at very low temperatures to the influence of the direct process and we obtain  $K_1$  in this region by considering both relaxation processes and assuming  $\delta$  is sufficiently large such that  $\tanh \delta/2T \approx 1$ . Table II gives the values for these constants obtained for all the rare earths along with measured values of the exchange frequency obtained by other workers and the value of  $K_1 \delta$  obtained by Caspari, Frankel, and Wood<sup>17</sup> for samarium by  $\gamma$ - $\gamma$  correlation experiments where they also observed that  $\tau \approx 1/T$ . The agreement between our results and the other values is quite good. The differences found for  $\omega_{\text{ex}}$  are of the same order as the differences between these parameters as measured by the various other workers.

We now want to consider the two exceptions to the simple odd-even electron behavior given above. Figure 9 gives the data of Miyadai<sup>18</sup> for the case of thulium<sup>19</sup> and instead of the even electron behavior one finds a be-

<sup>17</sup> M. E. Caspari, S. Frankel, and G. T. Wood, Phys. Rev. **127**, 1519 (1962).

<sup>18</sup> T. Miyadai, J. Phys. Soc. Japan **17**, 1899 (1962).

<sup>19</sup> We previously reported (Ref. 3) that thulium behaved in the same manner as the other even electron ions. Analysis of these samples, however, showed them not to be thulium.

TABLE II. Exchange frequencies and relaxation parameters for rare-earth ions in yttrium iron garnet.

Rare earth	$\omega_{ex}$ ( $10^{12}$ cps) Sievers and Tinkham <sup>a</sup>	$\omega_{ex}$ ( $10^{12}$ cps) Pauthenet <sup>b</sup>	$\omega_{ex}$ ( $10^{12}$ cps) Aleonard <sup>c</sup>	$\omega_{ex}$ ( $10^{12}$ cps) Present work	$K_1$ ( $10^{-9}$ sec)	$\delta$ (°K)	$K_1 \frac{1}{2} \sigma$ ( $10^{-9}$ sec°K)	$\frac{K_1 \frac{1}{2} \delta}{(10^{-9} \text{ sec}^\circ\text{K})}$ Caspari <i>et al.</i> <sup>d</sup>	$K_2$ ( $10^{-9}$ sec)	$\Delta$ (°K)
Nd				1.97	0.17	16	1.33			
Sm	6.1			1.54	35	8.8	1.83	2.16		
Dy		1.44	2.96	2.03			1.7			
Er	1.8	0.84	2.29	0.49	1.95	6	5.86			
Pr				2.97	8.25				4.44	10
Ho	7	0.84	2.3	3.61	15.4			0.73		35
Tb		1.74	2.87	11 <sup>f</sup>					34 <sup>f,g</sup>	
Tm		0.37					1.56 <sup>o</sup>			
Yb	2.5		6.95		5.83	56	163		$3.9 \times 10^{-6}$	791

<sup>a</sup> A. J. Sievers, III, and M. Tinkham (see Ref. 14).

<sup>b</sup> See Ref. 9.

<sup>c</sup> Roland Aleonard, J. Phys. Chem. Solids 15, 167 (1960).

<sup>d</sup> (See Ref. 17).

<sup>e</sup> From data of Tomonao Miyadai (see Ref. 18).

<sup>f</sup> From data supplied by J. F. Dillon, Jr.

<sup>g</sup> This value is  $\frac{1}{2} K_2 \Delta^2$ .

havior similar to the odd electron ions indicative of the direct process as is shown by the theoretical curve based on this process.

The other exception is ytterbium. The data for ytterbium was shown in Fig. 7. There is a temperature independent linewidth up to about 15°K where the linewidth begins to increase slowly up to the peak at 120°K. Above the peak the linewidth decreases very rapidly. This behavior is indicative of a competition between the direct and Orbach processes. Using both processes we have fitted the data as shown in Fig. 7. For ytterbium one has a simple exchange split Kramers doublet with the next level 791°K away.<sup>14</sup> Using this value for  $\Delta$  we obtain the solid curve in Fig. 7. The dotted curve shows the results of using  $\Delta = 400^\circ\text{K}$ , showing that the linewidth is not too sensitive to this choice. Of course in these two cases  $K_2$  is changed to normalize the curve at 200°K. In the low-temperature region one obtains  $\delta = 56^\circ\text{K}$  in comparison with the value of 34–38°K obtained spectroscopically.<sup>14</sup> Orbach<sup>11,20</sup> has estimated the relaxation

rates for the case of ytterbium iron garnet and finds

$$\tau_D \simeq 10^{-7} \tanh(19/T),$$

$$\tau_O \simeq 10^{-11} \sinh^2(395/T).$$

The values obtained from Fig. 7 are<sup>21</sup>

$$\tau_D \simeq 6 \times 10^{-9} \tanh(28/T),$$

$$\tau_O \simeq 4 \times 10^{-14} \sinh^2(395/T).$$

If one looks again at the data with particular attention to the high-temperature region it is seen that for some rare earths (Figs. 3, 6–9) the temperature dependence of the linewidth seems to become less above 300°K. One may expect an effect like this if  $\tau$  approaches the inverse Debye frequency ( $\omega_D = k\theta_D/\hbar$ ).<sup>10</sup> This value is about 0.013  $\mu\text{sec}$  in the garnets. The relaxation time, at which one finds the onset of the decrease in temperature dependence, is for most of the rare earths of the order of a micro-micro second which is still long compared to  $1/\omega_D$  and for this reason the change in temperature dependence seems to be a bit premature. For the case of ytterbium the deviation is large and between 300–500°K the temperature dependence is  $1/T$ , indicating  $\tau \sim \text{constant}$ . In this case at 500°K,  $\tau \simeq 0.03 \mu\text{sec}$ , and for relaxation times this short deviation from the assumed temperature dependences for  $\tau$  would certainly be expected.

We now wish to consider the frequency dependence of the linewidth and for this purpose we have reproduced in Fig. 10 the data of terbium-substituted yttrium iron garnet obtained by Dillon<sup>2</sup> at 9.2, 20.7 and 27.6 kMc/sec. He finds a linear frequency dependence at high temperatures as is predicted by Eq. (9) and below the peak this temperature dependence inverts, again in

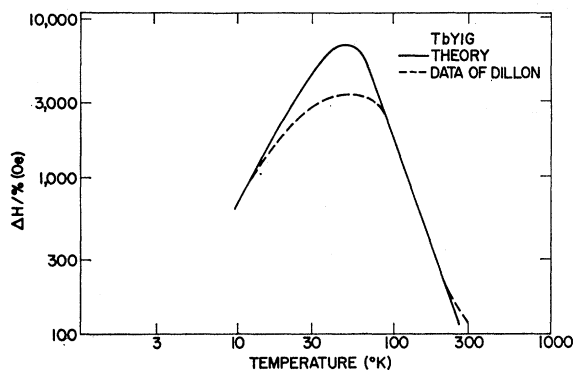


FIG. 8. Linewidth of terbium-substituted yttrium iron garnet as a function of temperature.

<sup>20</sup> R. Orbach, J. Appl. Phys. 33, 2144 (1962).

<sup>21</sup> In this case since we have a different relaxation process dominant in the high- and low-temperature regions it was necessary to assume an  $\omega_{ex}(2.5 \times 10^{12})$  and evaluate  $K_1$  from the low-temperature region and  $K_2$  from the region above the peak.

TABLE III. Frequency dependence of the linewidth peak for 0.02% terbium-substituted yttrium iron garnet.<sup>a</sup>

$\omega/2\pi$ (kM/sec)	$(\Delta H)_P$ (Oe) meas.	$(\Delta H)_P$ (Oe) cal.	$T_P$ (°K) meas.	$T_P$ (°K) cal.
9.2	124	...	54	...
20.7	106	105	78	75
27.6	100	99.6	85	84

<sup>a</sup> Data of J. F. Dillon, Jr., see Ref. 2. (The [110] direction results were chosen because the fine structure is absent making it easier to determine an unambiguous  $T_P$ .)

accord with Eq. (9). Equation (12) gives us a relation predicting the frequency dependence of the peak temperature. For the case of terbium (Fig. 8) we have the Orbach process where

$$\tau_0 \sim \sinh^2(\Delta/2T) \simeq \Delta/4T^2$$

for  $T \gg \Delta$  which is approximately valid at the peak temperature. Therefore, we use Eq. (12) with  $n=2$  and find

$$T_P \sim \omega^{2/5},$$

similarly from Eq. (13)

$$(\Delta H)_P \sim \omega^{-1/5}.$$

Assuming the measured values of  $T_P$  and  $\Delta H$  for 9.2 kMc/sec, Table III gives the measured values for 20.7 and 27.6 kMc/sec along with the values calculated from the above relations. The agreement is seen to be excellent.

## V. DISCUSSION

We have shown that the "slow-relaxation" theory of Clogston and Van Vleck and Orbach is not successful in predicting the behavior of the linewidth in the rare-earth iron garnets although it has apparently been successful in explaining the line shift.<sup>5</sup> We have however also shown an excellent fit to the empirical relation given in Eq. (9). At this point we should return to the "fast-relaxation" theory in order to point out where it fails to agree with experiment. Since the temperature dependence predicted by this theory is identical to that of the empirical equation we cannot use this as a criterion for contrasting them. There are, however, two points where the "fast-relaxation" theory and the empirical equation do give different results and can be easily compared. The first is the frequency dependence

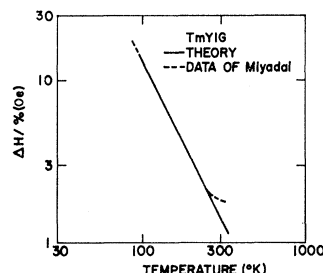


FIG. 9. Linewidth of thulium-substituted yttrium iron garnet as a function of temperature.

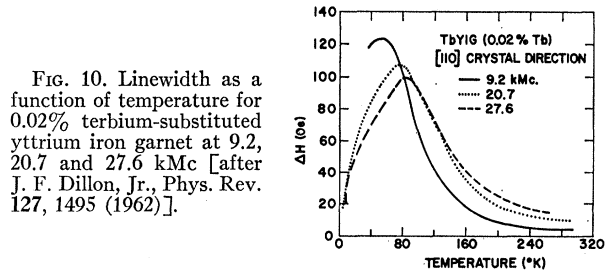


FIG. 10. Linewidth as a function of temperature for 0.02% terbium-substituted yttrium iron garnet at 9.2, 20.7 and 27.6 kMc [after J. F. Dillon, Jr., Phys. Rev. 127, 1495 (1962)].

of the linewidth in the low-temperature region. Equation (2b) predicts a linear frequency dependence while Eq. (9) predicts an inverse dependence. Figure 10 clearly shows that the inverse dependence is indeed observed. Furthermore Eqs. (2) give a peak temperature independent of frequency which is not observed and, moreover, the prediction of Eq. (12) is seen to be very well obeyed (Table III). The second point of comparison comes in evaluating  $\omega_{ex}$ . If one fits the data in the manner outlined in the last section by using Eqs. (2) instead of Eq. (9) one finds  $\omega_{ex} \simeq 10^{16}$  which is clearly much too large.

The difference between the "slow-relaxation" model of Clogston and the empirical relation can be seen quite readily by reexamining Eq. (4). From Eqs. (4) and (5) the linewidth may be written as

$$\Delta H = \frac{N_R}{M_F} \frac{h\omega_{ex}}{4} \frac{\omega\tau}{1+(\omega\tau)^2} \left( \frac{\partial}{\partial\theta} + \frac{\partial}{\partial\phi} \right) \left( \tanh \frac{h\omega_{ex}}{2kT} \right),$$

or, since  $\omega_{ex} = \gamma_R \lambda M_F$ ,  $M_{R0} = N_R \gamma_R h$  and  $M_R = M_{R0} \tanh h\omega_{ex}/2kT$ ,

$$\Delta H = \frac{\lambda \left[ \frac{\partial M_R}{\partial\theta} + \frac{\partial M_R}{\partial\phi} \right] \omega\tau}{4 \left[ 1 + (\omega\tau)^2 \right]}.$$

Thus, we see that the theory predicts that the linewidth is proportional to the angular derivative of the rare-earth magnetization as is indeed reasonable for the model from which this behavior is calculated. The experiment however seems to show that the linewidth is proportional to the rare-earth magnetization itself.

In addition to the measurements reported here, experiments have been performed on the switching time as a function of temperature of rare-earth-substituted yttrium iron garnet toroids.<sup>22</sup> In the low-temperature region these measurements also are not in accord with the results of Clogston's calculations. It therefore appears that although the Clogston model works well for the ferrite problem for which it was constructed and explains both resonance and switching, it is not, at least in its present form, suitable for explaining all the properties of the garnets. Although we cannot at present formulate theoretically a suitable model it is apparent that there is something missing from present calcula-

<sup>22</sup> W. Palmer, Conference on Magnetism and Magnetic Materials, Atlantic City, 1963, J. Appl. Phys. (to be published).



tions. One should here mention that the original calculation of Galt<sup>6</sup> which is supposed to be made on the basis of the same model used by Clogston<sup>7</sup> yields an equation of the desired type [Eq. (4)]. However, it is believed that this analysis is not correct because of Galt's handling of the relaxation term. Clogston uses a relaxation term that describes relaxation toward the instantaneous magnetic field while Galt's term relaxes toward a different field.<sup>23</sup> This is analogous to the problem discussed in Sec. II on the application of the Bloch-Bloembergen equation.

Although we cannot justify it theoretically the empirical equation [Eq. (9)] does provide an excellent fit to the data, and it is useful, in closing, to review the main features of this agreement. *Firstly*, we have assumed well-known relaxation processes which are believed to be appropriate for the rare-earth ions in the garnets. *Secondly*, using these processes the temperature dependence of the linewidth is accounted for. *Thirdly*, in fitting Eq. (9) to the data two parameters are evaluated, the exchange frequency ( $\omega_{ex}$ ) and the coefficient

<sup>23</sup> This was pointed out to the author by A. J. Heeger. In addition, it has previously been noted that the energy loss obtained from this theory is not positive definite (Ref. 7).

of the rare-earth relaxation term ( $K_1$  and  $K_2$ ). In the cases where comparison with independent measurements is possible good agreement is found. *Fourthly*, the frequency dependence of the temperature of the linewidth peak and the linewidth at the peak obtained from Eqs. (12) and (13) is in excellent agreement with experiment. *Finally*, there are no adjustable parameters remaining in the analysis. Of course there *still* remains the problem of justifying Eq. (9) on theoretical grounds but such an excellent fit to experiment makes it very plausible that a relation of this sort should be the correct one.

Lastly, it should be noted that even if this relation should prove to be correct so that one would be able to account for the linewidth behavior there would still remain the intriguing problem of why some ions relax by the direct process and others by the Orbach process.

#### ACKNOWLEDGMENTS

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## Reflectivity of HgSe and HgTe from 4 to 12 eV at 12 and 300°K

WILLIAM J. SCOULER AND GEORGE B. WRIGHT

Lincoln Laboratory,\* Massachusetts Institute of Technology, Lexington, Massachusetts

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The reflectivity of etched samples of HgSe and HgTe has been measured from 4–12 eV (3000–1050 Å) at room and He temperatures. Several peaks found in the reflectivity spectrum have been assigned to interband transitions at the  $L$  and  $X$  points in the Brillouin zone. Doublets, which are due to the effect of spin-orbit interaction, are resolved when the samples are cooled to He temperature. The values for  $L_3$  splitting (valence band) for both HgSe and HgTe are in agreement with other measurements of these materials in the visible region where a doublet due to  $L_{2V}$ – $L_{1C}$  transitions is found. Other transitions are also discussed.

### I. INTRODUCTION

IN recent years, the measurement of the optical reflectivity of semiconductors in the visible and ultraviolet has given much information concerning interband transitions and the over-all band structure of both diamond and zincblende structure materials.<sup>1</sup> The simi-

larities in the reflectivity spectra of semiconductors, and the known general appearance of the band structure for the diamond and zincblende materials have been helpful in interpreting the data. In addition, detailed band structure calculations on Ge and Si have supported the interpretations.<sup>2</sup> While the cumulative evidence makes the identifications very plausible, it should be noted that no experiments reported have demonstrated the symmetry of the states involved in the transitions.

In this paper, we report on reflectivity measurements

\* Operated with support from the U. S. Army, Navy, and Air Force.

<sup>1</sup> H. R. Philipp and E. A. Taft, Phys. Rev. **113**, 1002 (1959); **120**, 37 (1960); J. Tauc and A. Abraham, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Science, Prague, 1961); M. Cardona, J. Appl. Phys. Suppl. **32**, 2151 (1961); H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters **8**, 59 (1962); H. R. Philipp and H. Ehrenreich, *ibid.* **8**, 92 (1962); R. E. Morrison, Phys. Rev. **124**, 1314 (1961); M. Cardona and D. L. Greenaway, *ibid.* **125**, 1291 (1962); D. L. Greenaway, Phys. Rev. Letters **9**, 97 (1962); H. R. Philipp and H. Ehrenreich, Phys. Rev. **129**, 1550

(1963); M. Cardona and G. Harbeke, J. Appl. Phys. **34**, 813 (1963); M. Cardona and D. L. Greenaway, Phys. Rev. **131**, 98 (1963); J. C. Phillips, J. Phys. Chem. Solids **12**, 208 (1960).

<sup>2</sup> J. C. Phillips and L. Liu, Phys. Rev. Letters **8**, 94 (1962); J. C. Phillips, Phys. Rev. **125**, 1931 (1962); D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters **9**, 94 (1962).