

## Spin-Magnon Relaxation in Rare-Earth Iron Garnets\*

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The relaxation of paramagnetic ions coupled to a magnetic lattice is investigated. The exchange interaction is separated into static and dynamic parts. The dynamic part is responsible for the relaxation process. The relaxation occurs via the absorption and emission of magnons in a manner analogous to spin-lattice relaxation. The spin-magnon relaxation time is calculated for  $\text{Yb}^{3+}$  and  $\text{Eu}^{3+}$  ions in the iron garnets. Comparisons are made with the corresponding spin-lattice relaxation times. In each case the two relaxation mechanisms make nearly comparable contributions to the ferrimagnetic resonance linewidth and shift. The possibility of a contribution to the resonance linewidth and shift of the iron garnet from the presence of  $\text{Gd}^{3+}$  ions is also examined. It is found that probably neither relaxation mechanism makes an appreciable contribution to either the width or the shift. Finally, a discussion is given of the conditions under which the effects of the spin-magnon relaxation process might be uniquely observed.

### I. INTRODUCTION

AMONG those mechanisms by which a system of paramagnetic ions reaches a state of thermal equilibrium with the host crystal spin-lattice relaxation usually has the most prominent role. In this paper we will investigate another mechanism, spin-magnon relaxation, and compare its effects with those of spin-lattice relaxation. Although quantitative comparisons will be made only in the case of certain rare-earth ions in the iron garnets the general features of the theory will be applicable to any paramagnetic ion coupled to a magnetic lattice.

In spin-lattice relaxation, as formulated in the theories of Van Vleck<sup>1</sup> and Orbach,<sup>2</sup> the paramagnetic ion is coupled to the crystal lattice by an orbit-lattice interaction. The orbit-lattice interaction arises from the modulation of the crystal field caused by the thermal vibrations of the ionic complex in which the paramagnetic ion is imbedded. Schematically, we can expand the paramagnetic ion-crystal field interaction  $V_{\text{cryst}}$  as a power series in the strain tensor  $\epsilon$

$$V_{\text{cryst}} = V_0 + \mathbf{V}_1 \epsilon. \quad (1)$$

The symbol  $V_0$  denotes the static crystal field. The term  $\mathbf{V}_1 \epsilon$  is responsible for spin-lattice relaxation. The relaxation comes about through the absorption and emission of phonons by the paramagnetic ion.

In the case of spin-magnon relaxation the situation is completely analogous.<sup>3</sup> The paramagnetic ion is coupled to the magnetic lattice by an exchange interaction,  $-\Lambda \mathbf{S} \cdot \mathbf{J}$ , where  $S$  is the spin of the iron ion and

$J$  is the angular momentum of the paramagnetic ion.<sup>4</sup> If we take the direction of equilibrium magnetization to be the  $z$  axis, then  $-\Lambda \mathbf{S} \cdot \mathbf{J}$  can be expanded in a form similar to (1),<sup>5</sup>

$$-\Lambda \mathbf{S} \cdot \mathbf{J} = -\Lambda S J_z - \Lambda (S_z - S) J_z - \frac{1}{2} \Lambda (S_+ J_- + S_- J_+). \quad (2)$$

The term  $-\Lambda S J_z$  symbolizes the interaction of the paramagnetic ion with the static exchange field. It is the analog of the static crystal-field term in (1). The term  $-\Lambda (S_z - S) J_z$ , which can be written as the sum of products that are bilinear in the magnon annihilation and creation operators, characterizes the first-order scattering of magnons. It will not enter into our calculations and hence we will ignore it. It is the term  $-\frac{1}{2} \Lambda (S_+ J_- + S_- J_+)$  that is responsible for the direct relaxation process. Just as the strain tensor can be expanded as a linear combination of phonon annihilation and creation operators so can the operators  $S_+$  and  $S_-$  be written as linear combinations of operators which create and destroy magnons. In its action  $-\frac{1}{2} \Lambda (S_+ J_- + S_- J_+)$  is entirely similar to  $\mathbf{V}_1 \epsilon$  in that it induces transitions between the various levels of the paramagnetic ion while at the same time creating or destroying magnons.

The calculation of the spin-magnon relaxation time is almost identical to the calculation of the spin-lattice relaxation time. The inverse of the spin-magnon relaxation time between levels  $b$  and  $a$  for the direct process is written as the sum of the transition rate for the process in which a magnon is emitted and the paramagnetic ion makes a transition from  $b$  to  $a$  and the transition rate for the inverse process in which a magnon is absorbed and the transition of the paramagnetic ion is from  $a$  to  $b$ .

Since the magnons and phonons are both bosons the spin-magnon and spin-lattice relaxation times have the

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<sup>1</sup> J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

<sup>2</sup> R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

<sup>3</sup> The contribution of magnon absorption and emission to the relaxation of the  $\text{Fe}^{57}$  nucleus in the rare-earth iron garnets has been considered by Mme. Hartmann [F. Hartmann-Boutron, thesis, University of Paris, 1963 (unpublished)]. She found the effect to be negligible in comparison with the relaxation induced by the indirect coupling of the nuclear spins to the rare-earth ions.

<sup>4</sup> We ignore at this point the complications introduced by an anisotropic antiferromagnetic exchange interaction between the paramagnetic ion and the iron lattice.

<sup>5</sup> We follow in this respect P. G. de Gennes, F. Hartmann-Boutron, P. A. Pincus, and D. Saint-James, Phys. Letters **1**, 273 (1962).

same dependence on temperature. The principal difference in the analytic forms of the expressions for the relaxation times comes about because the magnon energy is to a first approximation quadratic in its dependence on the magnon wave vector whereas the phonon energy is proportional to the phonon wave vector.

In the case of the rare-earth ions in the iron garnets typical values of the parameter  $\Lambda$  appearing in (2) are on the order of 1–15  $\text{cm}^{-1}$ . A rough estimate of the relative magnitudes of the spin-magnon and spin-lattice relaxation times indicates that in most instances, spin-lattice relaxation is by far the dominant process. There are, however, important exceptions to this rule.

(A) If the levels  $a$  and  $b$  between which the relaxation takes place form a Kramers doublet, then spin-lattice relaxation can take place only when the excited states of the rare-earth ion are coupled in via the static exchange field. For large separations between the ground doublet and the excited states the admixture of the excited states into the ground doublet may be sufficiently small so as to make the spin-lattice relaxation time comparable with the spin-magnon relaxation time. As an example we have  $\text{Yb}^{3+}$  in the iron garnet, where the ground state of the ytterbium ion is a Kramers doublet and the excited states lie 550  $\text{cm}^{-1}$  away.

(B) The matrix elements of the orbit-lattice interaction between the levels  $a$  and  $b$  vanish because of the selection rules for angular momentum. This is the case when the relaxation is between any of the  $J=1$  levels and the  $J=0$  level of  $\text{Eu}^{3+}$ .

(C) The paramagnetic ion in question is an  $S$ -state ion, as, for example,  $\text{Gd}^{3+}$ .

We will investigate each of these examples in turn, comparing, wherever possible, the spin-magnon relaxation time with the corresponding spin-lattice relaxation time.

## II. $\text{Yb}^{3+}$ IN THE IRON GARNET—THEORY

In the investigation of the relaxation of ytterbium ions it is necessary to take into account the fact that the coupling of the ytterbium ion to the iron lattice is through an anisotropic antiferromagnetic exchange interaction. We write the interaction as

$$\mathcal{H} = \mathbf{S} \mathbf{A} \mathbf{J}^n, \quad (3)$$

where  $S$  ( $=\frac{5}{2}$ ) is the spin of the iron ion and  $J^n$  is the fictitious spin of the  $n$ th ytterbium ion. Equation (3) being linear in the rare-earth spin is the most general form of the exchange interaction appropriate to a Kramers doublet. We have made the approximation of replacing the exchange interaction of the ytterbium ion with the various iron ions by an average exchange interaction in which the ytterbium ion is taken to be coupled to a single iron spin. This approximation is expected to be particularly valid when the magnons

involved in the relaxation process have a long wavelength. It is equivalent to assuming that the two iron spins which are the nearest neighbors of the ytterbium ion move in unison. By making this approximation we can use experimental values for the components of the exchange tensor  $\mathbf{\Lambda}$ . We note that the anisotropy of the exchange tensor need not coincide with the anisotropy of the  $g$  tensor.<sup>6</sup>

The ground doublet of the ytterbium ion is split apart by the static term in (3). The relaxation time of the  $n$ th ion,  $T_1^n$ , for the direct process between the doublet levels is given by the expression

$$\begin{aligned} \frac{1}{T_1^n} = & \frac{\Omega(\hbar\omega_{0n} - g\beta H)^{1/2} |\xi_d^{ac}|^2}{16\pi\hbar Y^{3/2} S(\hbar\omega_{0n})^2} \left[ S^4 \Lambda_1^2 \Lambda_2^2 ((\gamma_1^n)^2 \right. \\ & + (\gamma_2^n)^2) + S^4 \Lambda_2^2 \Lambda_3^2 ((\gamma_2^n)^2 + (\gamma_3^n)^2) \\ & \left. + S^4 \Lambda_1^2 \Lambda_3^2 ((\gamma_1^n)^2 + (\gamma_3^n)^2) - 2S^3 \Lambda_1 \Lambda_2 \Lambda_3 \hbar\omega_{0n} \right] \\ & \times \coth \frac{\hbar\omega_{0n}}{2KT}. \quad (4) \end{aligned}$$

Here  $\Omega$  is the volume per unit cell of the iron lattice and  $g$  denotes the  $g$  factor appropriate to the iron spin. The constant  $Y$  is defined in terms of the energy of the acoustic magnon mode  $E_m^{ac}(k)$ ,

$$E_m^{ac}(k) = g\beta H + Yk^2. \quad (5)$$

The doublet splitting of the  $n$ th ytterbium ion is denoted by  $\hbar\omega_{0n}$ . The direction cosines of the static iron spin in the coordinate system whose axes are parallel to the  $n$ th rare-earth site are specified by  $\gamma_1^n$ ,  $\gamma_2^n$ , and  $\gamma_3^n$ . The symbols  $\Lambda_1$ ,  $\Lambda_2$ , and  $\Lambda_3$  denote the principal values of the exchange tensor. The factor  $\xi_d^{ac}$ , where  $d$  denotes the  $d$  sites, is a coefficient occurring in the expansion of the magnon creation operator for the acoustic mode  $A_k^{act}$  in terms of the operators  $S_+^j$  of the various iron spins.

$$A_k^{act} = (1/2SN)^{1/2} \sum_j e^{ik \cdot r_j} \xi_j^{ac} S_+^j. \quad (6)$$

Here the sum is over all the iron spins in a crystal having  $N$  unit cells.

Implicit in our calculation of the relaxation time is the assumption that the interaction of a ytterbium ion with the iron lattice is unaffected by the presence of the neighboring ytterbium ions. Such would be the case in very dilute garnets where there is a large separation between the ytterbium ions. We would expect that for higher concentrations of ytterbium ions coherence effects resulting from the coupling between the ytterbium ions would become important. The effect of coherence would be to lengthen the relaxation time. In the limit of extreme concentration the ytterbium

<sup>6</sup> This point has been discussed by Van Vleck [J. H. Van Vleck, J. Phys. Soc. Japan 17, Suppl. B-I, 352 (1962)]. In the same article attention is also drawn to the fact that in the first half of the trivalent rare-earth series,  $\text{Ce}^{3+}$ – $\text{Sm}^{3+}$ , the coupling between the rare-earth ion and the iron lattice is effectively ferromagnetic.

ions are all coupled to one another and to the iron lattice. A proper characterization of the behavior of the garnet in this limit would require treating the iron and rare-earth lattices each as a single system. The effects of this coherence on the relaxation time can be taken into account in a semiphenomenological manner by making the magnon dispersion constant  $Y$  depend on the concentration of ytterbium ions. Since the relaxation time is proportional to  $Y^{3/2}$  it would be expected that the effective value of  $Y$  for high concentrations of ytterbium ions would be greater than

the value of  $Y$  associated with a negligible concentration of ytterbium ions.

There is also the possibility that in high concentration the effects of cross relaxation between the ytterbium ions might be appreciable. Were this the case it would be more accurate to assign a common relaxation time to all the ytterbium ions. In a crude approximation the common relaxation time would be the one associated with the ytterbium ion which relaxes most rapidly.

The angular dependence of the expression

$$J(\gamma_1, \gamma_2, \gamma_3) = \frac{[S^4\Lambda_1^2\Lambda_2^2(\gamma_1^2 + \gamma_2^2) + S^4\Lambda_2^2\Lambda_3^2(\gamma_2^2 + \gamma_3^2) + S^4\Lambda_1^2\Lambda_3^2(\gamma_1^2 + \gamma_3^2) - 2S^3\Lambda_1\Lambda_2\Lambda_3\hbar\omega_0]}{S^2\hbar^2\omega_0^2} \quad (7)$$

is particularly interesting. We note that if the exchange interaction were isotropic,  $\Lambda_1 = \Lambda_2 = \Lambda_3 = \Lambda$ , then

$$J(\gamma_1, \gamma_2, \gamma_3) \equiv 0. \quad (8)$$

The explanation for this is in the structure of the isotropic interaction,  $\mathcal{H}_{\text{iso}}$

$$\mathcal{H}_{\text{iso}} = \Lambda S J_z + \Lambda (S_z - S) J_z + \frac{1}{2} \Lambda (S_+ J_- + S_- J_+). \quad (9)$$

In the presence of an isotropic antiferromagnetic exchange interaction the ytterbium spin is antiparallel to the average iron spin. If we choose a coordinate system such that the equilibrium direction of the average iron spin is along the  $-z$  axis then the state  $J_z = \frac{1}{2}$  is the state of lowest energy for the ytterbium spin. A transition from the upper state to the lower state of the ytterbium spin is therefore induced by the operator  $J_+$ . As can be seen from (9),  $J_+$  only occurs in the combination  $J_+ S_-$  so that a transition from the upper to the lower doublet level must be accompanied by a decrease of one unit in the total spin of the iron lattice. But from (6) it is evident that a decrease in the spin of the iron lattice corresponds to the destruction of an acoustic magnon and an equivalent lowering of the energy of the iron lattice. Hence energy is not conserved in transitions induced by the operator combinations  $J_+ S_-$  and  $J_- S_+$ .

An alternative way of stating this argument is as follows. The scalar interaction  $\Lambda \mathbf{S} \cdot \mathbf{J}$  can not change the total spin of the combined system of iron and ytterbium ions. But the only energy-conserving transitions contributing to the relaxation of the ytterbium ion are those in which the total spin of the iron and ytterbium systems changes by two units. Hence the isotropic exchange interaction can not give rise to a finite spin-magnon relaxation time for the direct process. Were the doublet separation of the ytterbium ion large enough to allow the excitation of the optical magnon modes, then energy conserving transitions in which the total angular momentum of the combined systems remained the same would be possible. The explanation is that the

excitation of certain of the optical modes is accompanied by a decrease in the total spin of the iron lattice and hence could be induced by the operator combination  $S_- J_+$ .

Had the coupling between the ytterbium ion and the iron lattice been through an anisotropic ferromagnetic exchange interaction the relaxation time would have been given by an equation similar to (4). The only difference between the two expressions would be in the sign of the fourth term in the bracketed factor. For a ferromagnetic coupling  $-2S^3\Lambda_1\Lambda_2\Lambda_3\hbar\omega_0$  is replaced by  $+2S^3\Lambda_1\Lambda_2\Lambda_3\hbar\omega_0$ . As a result of the sign change the cancellation for the isotropic interaction indicated by Eq. (8) does not take place. An isotropic ferromagnetic coupling does yield a finite spin-magnon relaxation time.

If the magnetization is in a (110) plane of the iron lattice the number of inequivalent rare-earth sites is reduced from six to four. The direction cosines for these sites are given by

$$\text{I } \gamma_1^2 = 0, \quad \gamma_2^2 = \sin^2\theta, \quad \gamma_3^2 = \cos^2\theta, \quad (10)$$

$$\text{II } \gamma_1^2 = \sin^2\theta, \quad \gamma_2^2 = 0, \quad \gamma_3^2 = \cos^2\theta, \quad (11)$$

$$\text{III } \gamma_1^2 = \left(\frac{1}{2} \cos^2\theta + \frac{1}{4} \sin^2\theta - (\sin\theta/\sqrt{2}) \cos\theta\right), \\ \gamma_2^2 = \left(\frac{1}{2} \cos^2\theta + \frac{1}{4} \sin^2\theta + (\sin\theta/\sqrt{2}) \cos\theta\right), \quad (12) \\ \gamma_3^2 = \frac{1}{2} \sin^2\theta,$$

$$\text{IV } \gamma_1^2 = \left(\frac{1}{2} \cos^2\theta + \frac{1}{4} \sin^2\theta + (\sin\theta/\sqrt{2}) \cos\theta\right), \\ \gamma_2^2 = \left(\frac{1}{2} \cos^2\theta + \frac{1}{4} \sin^2\theta - (\sin\theta/\sqrt{2}) \cos\theta\right), \quad (13) \\ \gamma_3^2 = \frac{1}{2} \sin^2\theta,$$

where  $\theta$  measures the angle between the magnetization and the [001] direction.

In Fig. 1 we have plotted the spin-magnon relaxation times at zero temperature for these four inequivalent sites as a function of  $\theta$ . The values shown were obtained from Eq. (4). In the calculation we used LeCraw and Spencer's<sup>7</sup> value for  $Y$

$$Y = 0.92 \times 10^{-28} \text{ erg cm}^2. \quad (14)$$

<sup>7</sup> R. C. LeCraw and E. G. Spencer, J. Phys. Soc. Japan 17, Suppl. B-I 401 (1962)

This value was determined for the yttrium iron garnet. In view of the preceding discussion we would expect, strictly speaking, that our value of  $Y$  would characterize the ytterbium-doped garnet only in the limit of infinite dilution. We have also taken Wickersheim's<sup>8</sup> values for the exchange constants

$$\begin{aligned} SA_1 &= 29.9 \text{ cm}^{-1}, & SA_2 &= 25.7 \text{ cm}^{-1}, \\ SA_3 &= 11.6 \text{ cm}^{-1}, \end{aligned} \quad (15)$$

and have set  $\Omega = 1.9 \times 10^{-21} \text{ cm}^3$ . The value of  $|\xi_{d^{ac}}|^2$  for the acoustic mode at  $\mathbf{k} = 0$  has been calculated by Douglass<sup>9</sup> who found  $|\xi_{d^{ac}}|^2 = \frac{1}{8}$ . Since the dependence of  $\xi_{d^{ac}}$  on  $\mathbf{k}$  is not known we made the approximation of using the value of  $\xi_{d^{ac}}$  appropriate to  $\mathbf{k} = 0$ . In plotting the graph we have also neglected the dependence of the relaxation time on the external field since for moderate fields the doublet splitting is much greater than  $g\beta H$ .

Two features of the graph are immediately evident. The relaxation times for the most part are on the order of  $10^{-8}$  to  $10^{-10}$  sec. Also, the relaxation times are highly anisotropic. In fact, for  $\theta = 14^\circ$  the relaxation time of site II is infinite. In the  $[001]$  and  $[111]$  directions we find

$$[001] \quad T_1^I = T_1^{II} = 12.9 \times 10^{-9} \text{ sec}, \quad (16)$$

$$T_1^{III} = T_1^{IV} = 0.69 \times 10^{-9} \text{ sec}, \quad (17)$$

$$[111] \quad T_1^I = T_1^{III} = 0.74 \times 10^{-9} \text{ sec}, \quad (18)$$

$$T_1^{II} = T_1^{IV} = 1.28 \times 10^{-9} \text{ sec}. \quad (19)$$

Since the  $\Gamma_8$  levels of the ytterbium ion are some  $550 \text{ cm}^{-1}$  away it is to be expected that the higher order relaxation processes will become important only at high temperatures. A rough calculation indicates that the Raman process becomes comparable with the direct process for a temperature on the order of  $150^\circ\text{K}$ . We mention in passing that the term  $(S_z - S)(\Lambda_{zx}J_x + \Lambda_{zy}J_y + \Lambda_{zz}J_z)$  while characterizing the first-order scattering of magnons does not contribute to the Raman relaxation time. The explanation is that the ytterbium spin combination  $(\Lambda_{zx}J_x + \Lambda_{zy}J_y + \Lambda_{zz}J_z)$  is the same as that found in the static field term in the Hamiltonian and hence can not induce transitions between the doublet levels split by the static exchange field.

### III. $\text{Yb}^{3+}$ IN THE IRON GARNET—COMPARISON WITH EXPERIMENT

Because of the presence of the iron lattice it is not possible to measure directly the relaxation times of the ytterbium ions. We can, however, obtain an indirect comparison of experiment with theory by utilizing the fact that the finite relaxation times of the ytterbium ions affect the ferrimagnetic resonance spectrum in ytterbium-doped yttrium iron garnets. In the slow

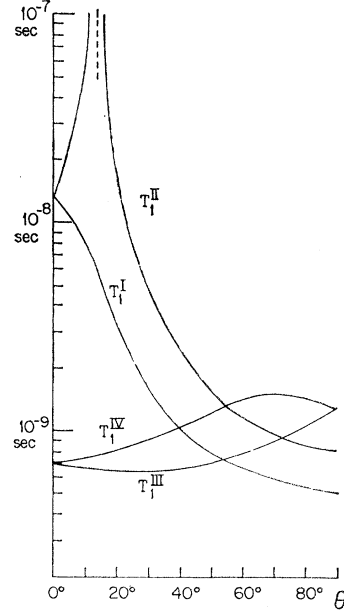


FIG. 1. Spin-magnon relaxation time of  $\text{Yb}^{3+}$  at zero temperature. The magnetization is in the  $(110)$  plane making an angle  $\theta$  with the  $[001]$  direction. The relaxation times of the four inequivalent sites are denoted by  $T_1^I$ ,  $T_1^{II}$ ,  $T_1^{III}$ , and  $T_1^{IV}$ . The curves were calculated from Eq. (4) using the magnon dispersion constant of LeCraw and Spencer (Ref. 7) and the exchange constants of Wickersheim (Ref. 8).

relaxing model of Van Vleck and Orbach,<sup>10</sup> Hartmann-Boutron,<sup>11</sup> and Teale and Tweedale<sup>12</sup> the dynamic shift  $S_d$ , and width  $\hbar\Delta\omega$  of the resonance line are given by the expressions

$$S_d = -\frac{Nc}{12} |S_z| \sum_{n=1}^6 Q_n \text{sech}^2 \frac{\hbar\omega_{0n}}{2KT} \frac{\omega^2 (T_1^n)^2}{1 + \omega^2 (T_1^n)^2}, \quad (20)$$

$$\hbar\Delta\omega = \frac{Nc}{12} |S_z| \sum_{n=1}^6 Q_n \text{sech}^2 \frac{\hbar\omega_{0n}}{2KT} \frac{\omega T_1^n}{1 + \omega^2 (T_1^n)^2}, \quad (21)$$

where  $N$  is the number of iron ions,  $c$  is the concentration of ytterbium ions, and  $\omega$  is the resonance frequency. The sum is taken over the six inequivalent rare-earth sites. The symbol  $Q_n$  denotes the expression<sup>10</sup>

$$\begin{aligned} Q_n &= -S_z^2 (1/2\hbar\omega_{0n})^2 \\ &\times \{ [(\Lambda_2^2 - \Lambda_1^2)(\gamma_2^n)^2 + (\Lambda_3^2 - \Lambda_1^2)(\gamma_3^n)^2]^2 \\ &\quad - (\Lambda_3^2 - \Lambda_1^2)^2 (\gamma_3^n)^2 - (\Lambda_2^2 - \Lambda_1^2)^2 (\gamma_2^n)^2 \}. \end{aligned} \quad (22)$$

Following Teale and Tweedale we can define an average relaxation time  $\bar{\tau}_{av}$  by the equation

$$\bar{\tau}_{av} = -S_d / \omega \hbar\Delta\omega, \quad (23)$$

where  $S_d$  and  $\hbar\Delta\omega$  are given by (20) and (21). In the

<sup>10</sup> J. H. Van Vleck and R. Orbach, Phys. Rev. Letters 11, 65, 303 (E) (1963).

<sup>11</sup> F. Hartmann-Boutron, Compt. Rend. 256, 4412 (1963).

<sup>12</sup> R. W. Teale and K. Tweedale, Phys. Letters 1, 298 (1962).

<sup>8</sup> K. A. Wickersheim, Phys. Rev. 122, 1376 (1961).

<sup>9</sup> R. L. Douglass, Phys. Rev. 120, 1612 (1960).

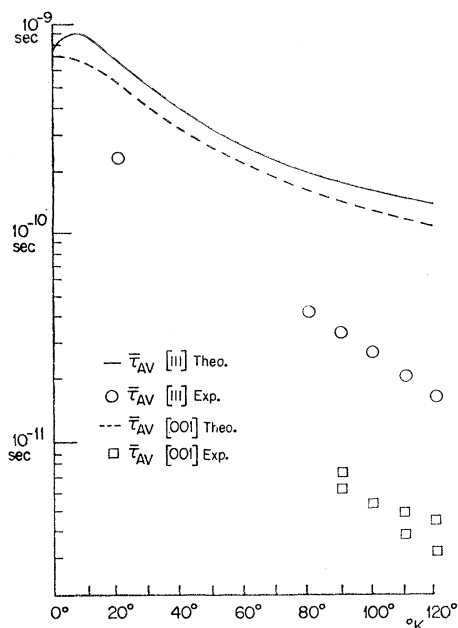


FIG. 2. Average spin-magnon relaxation time for  $\text{Yb}^{3+}$  in the [001] and [111] directions. The theoretical values of  $\bar{\tau}_{\text{av}}$  were calculated from Eqs. (4), (20), (21), and (23). Using the magnon dispersion constant of LeCraw and Spencer (Ref. 7) and the exchange constants of Wickersheim (Ref. 8). The experimental values are those of Teale and Tweedale (Ref. 12). Frequency 9600 Mc/sec.

slow relaxing model  $\bar{\tau}_{\text{av}}$  would equal  $T_1$  if the relaxation times for the six inequivalent sites were the same. In general, however,  $\bar{\tau}_{\text{av}}$  represents a weighted average relaxation time.

In Figs. 2 and 3 we have compared Teale and Tweedale's experimental results with our predictions for  $\bar{\tau}_{\text{av}}$  as a function of temperature in the cases in which the magnetization is along the [111] and [001] directions. The theoretical values of  $\bar{\tau}_{\text{av}}$  in Fig. 2 were calculated under the assumption that the relaxation of the ytterbium ion takes place via the spin-magnon interaction as characterized by Eq. (4). As is evident from the graph the spin-magnon relaxation theory yields relaxation times that are somewhat greater than the observed relaxation times. This fact may not be of great importance. Had we used the magnon dispersion constant of Meyer and Harris<sup>13</sup> rather than that of LeCraw and Spencer we would have obtained theoretical values for  $\bar{\tau}_{\text{av}}$  that would have been smaller than those depicted by a factor of  $\frac{1}{3}$ .

Of particular significance is the anisotropy in  $\bar{\tau}_{\text{av}}$ . We find in agreement with experiment that  $\bar{\tau}_{\text{av}}[111]$  is greater than  $\bar{\tau}_{\text{av}}[001]$ . However, the spin-magnon relaxation theory leads to the result  $\bar{\tau}_{\text{av}}[111]/\bar{\tau}_{\text{av}}[001] \simeq 1.3$  whereas experimentally  $\bar{\tau}_{\text{av}}[111]/\bar{\tau}_{\text{av}}[001] \simeq 5.5$ . Although  $\bar{\tau}_{\text{av}}$  is sensitive to the relative magnitudes of the exchange splitting constants, reasonable changes in these constants do not appreciably affect the ratio

<sup>13</sup> H. Meyer and A. B. Harris, J. Appl. Phys. 31, 49S (1960).

$\bar{\tau}_{\text{av}}[111]/\bar{\tau}_{\text{av}}[001]$ . Even so, the discrepancy may not be as serious as indicated for the following reasons.

(A) With one exception the experimental points shown lie between 80 and 120°K. It is in this temperature range that the higher order relaxation processes which we have not taken into account begin to become important. The presence of the higher order processes would lead to a shorter relaxation time than that calculated from Eq. (4).

(B) Teale and Tweedale's measurements of  $\bar{\tau}_{\text{av}}[001]$  were made on the pure ytterbium garnet. The assumption that the "back reaction" of the rare-earth lattice on the iron lattice can be neglected may not be valid for the undiluted ytterbium garnet. If this were the case for the applicability of the slow relaxing model would be open to question. Unfortunately, mitigating this argument is the fact that we would expect if coherence among the ytterbium ions were significant that the relaxation time in the pure garnet would be longer than the corresponding relaxation time in the doped garnet. The Teale-Tweedale experimental ratio  $\bar{\tau}_{\text{av}}[111]/\bar{\tau}_{\text{av}}[001]$ , where  $\bar{\tau}_{\text{av}}[111]$  is measured for the doped garnet and  $\bar{\tau}_{\text{av}}[001]$  is measured for the pure garnet, ought to be somewhat less than the calculated ratio were this analysis to apply.

(C) As was pointed out by Teale and Tweedale the shift for the [001] direction is small and difficult to measure. The large uncertainty in the measured value of the shift gives rise to a correspondingly large uncertainty in  $\bar{\tau}_{\text{av}}[001]$ .

Here we would like to comment on whether further refinements in the calculation of the spin-magnon relaxation time would lead to a significant improvement in the agreement between experiment and theory. Unfortunately this does not seem to be the case. The magnons involved in the relaxation process lie very close to the bottom of the acoustic band. For this reason modifications in our formulas that take into account the anisotropy in the magnon energy surface and the  $\mathbf{k}$  dependence of  $\xi_a^{ae}$  do not affect our results to any great extent.

In Fig. 3 we have made a similar comparison of experimental and theoretical values for  $\bar{\tau}_{\text{av}}$  but have assumed that the relaxation of the ytterbium ion takes place via the spin-lattice interaction. The general magnitude of the spin-lattice relaxation time is a point open to discussion. For reasonable values of the constants involved Orbach<sup>14</sup> obtained a relaxation time of  $10^{-7}$  sec. Measurements of the spin-lattice relaxation time in the diamagnetic ytterbium gallium garnet by Svare and Seidel<sup>14,15</sup> suggest, however, that a spin-lattice relaxation time for the iron garnet on the order of  $10^{-9} \tanh \hbar\omega_0/2KT$  sec would be more appropriate.

<sup>14</sup> R. Orbach, *Proceedings of the First International Conference on Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), p. 456.

<sup>15</sup> I. Svare and G. Seidel, *Proceedings of the First International Conference on Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), p. 430.

In making our comparison we have been somewhat generous to the spin-lattice relaxation theory. We have arbitrarily taken the relaxation time at zero temperature in the [001] direction for sites III and IV to be  $10^{-10}$  sec. The other relaxation times were calculated by appropriately scaling the [001] relaxation time using Wickersheim's<sup>8</sup> exchange splitting constants.<sup>16</sup> For this reason the absolute magnitudes of the spin-lattice relaxation times may not be as significant as the difference in the values for the [001] and [111] directions. We note that in agreement with experiment  $\bar{\tau}_{av}[111]$  is greater than  $\bar{\tau}_{av}[001]$  but the ratio  $\bar{\tau}_{av}[111]/\bar{\tau}_{av}[001]$ , while greater than the corresponding ratio for the spin-magnon relaxation process, is still less than the observed ratio.

In view of the comments on the effects of possible refinements in the spin-magnon theory it would appear that further advances would lie in the direction of an improved calculation of the spin-lattice relaxation time. In such a calculation the effects of the tetragonal and rhombic components of the crystal field would have to be taken into account. On the basis of our present calculations we can only conclude that while the anisotropy in  $\bar{\tau}_{av}$  tends to favor the spin-lattice relaxation theory it is not possible to rule out contributions from either of the relaxation processes. However, neither theory in their present state can account in a satisfactory way for the magnitude of the anisotropy in  $\bar{\tau}_{av}$ .

#### IV. $\text{Eu}^{3+}$ IN THE IRON GARNET

As was pointed out by LeCraw, Nilsen, Remeika, and Van Vleck,<sup>17</sup> hereafter referred to as LNRVV, matrix elements of the orbit-lattice interaction vanish between the  $J=1$  and  $J=0$  levels of  $\text{Eu}^{3+}$ . Thus, the relaxation between these levels must be due entirely to the spin-magnon process. In calculating the spin-magnon relaxation time we will neglect crystal-field effects entirely, taking the splitting between the  $J=1$  and  $J=0$  levels to be that of the free ion and assuming an isotropic antiferromagnetic exchange interaction. Since the crystal field is of predominantly cubic symmetry, which does not split  $J=1$  or affect the isotropy of the exchange interaction, these are probably not very important restrictions.

We write the interaction between the europium ion

<sup>16</sup> The anisotropy in the spin-lattice relaxation time has its origin in both the doublet splitting and the matrix element of the spin-phonon coupling between the doublet states. In the latter it arises from the interplay of the exchange interaction and the orbit-lattice interaction. In the absence of detailed information about the components of the orbit-lattice interaction we have assumed that the dependence of the matrix element on the direction of magnetization is the same as that of the doublet splitting. This approximation is admittedly crude. However, it enhances the effect of the anisotropy of the doublet splitting and so may lead to a relaxation time that is more anisotropic than that calculated with the exact value of the matrix element.

<sup>17</sup> R. C. LeCraw, W. G. Nilsen, J. P. Remeika, and J. H. Van Vleck, Phys. Rev. Letters **11**, 490 (1963).

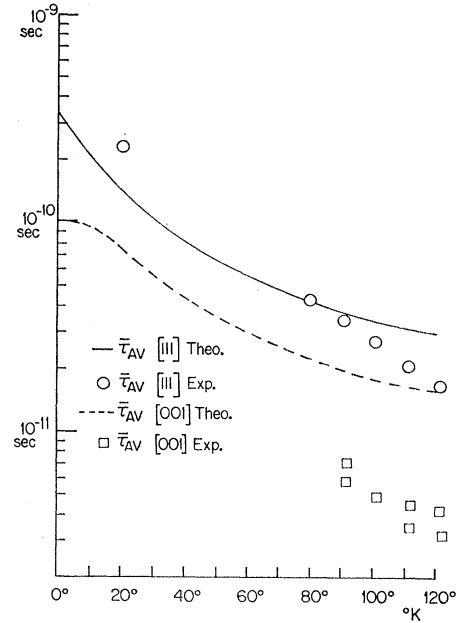


FIG. 3. Average spin-lattice relaxation time for  $\text{Yb}^{3+}$  in the [001] and [111] directions. The theoretical values of  $\bar{\tau}_{av}$  were calculated from Eqs. (20), (21), and (23) under the assumption that  $T_1^{\text{III}}[001] = T_1^{\text{IV}}[001] = 10^{-10}$  sec at zero degrees. The other relaxation times were obtained by an appropriate scaling (Ref. 16) using Wickersheim's exchange constants (Ref. 8). The experimental values are those of Teale and Tweedale (Ref. 12). Frequency 9600 Mc/sec.

and the iron lattice in the form

$$\mathcal{H} = \Lambda S^{\text{Fe}} \cdot S^{\text{RE}}, \quad (24)$$

where  $S^{\text{Fe}}$  is the spin of the iron ion and  $S^{\text{RE}}$  is the (true) spin of the Europium ion. The symbol  $\Lambda$  denotes an average exchange integral in the sense implied in the discussion following Eq. (3). As a result we find the following expression for the spin-magnon relaxation time for the direct process between the  $J=1$  and  $J=0$  levels.

$$\frac{1}{T_1} = \frac{8\pi S^{\text{Fe}} \Lambda^2}{N\hbar} \coth \frac{\hbar\bar{\omega}}{2KT} \sum_{\beta} \sum_{\mathbf{k}} \delta(E_m^{\beta}(\mathbf{k}) - \hbar\bar{\omega}) |\xi_d^{\beta}|^2. \quad (25)$$

Here  $N$  is the number of unit cells in the crystal,  $\hbar\bar{\omega}$  is the splitting between the  $J=1$  and  $J=0$  levels, and  $E_m^{\beta}(\mathbf{k})$  denotes the magnon energy appropriate to the  $\beta$ th mode. The symbol  $\xi_d^{\beta}$  is the coefficient for spins on the  $d$  sites in an expansion, similar to Eq. (6), in which the magnon creation operator for the  $\beta$ th mode is written as the sum of operators for the individual spins. The summation is over the allowed wave vectors  $\mathbf{k}$  and modes  $\beta$ .

In evaluating (25) we will use Wolf and Van Vleck's<sup>18</sup> value of  $\Lambda S^{\text{Fe}}$ ,  $35 \text{ cm}^{-1}$ , and the free ion value of  $\hbar\bar{\omega}$ ,  $352 \text{ cm}^{-1}$ . The major uncertainty in our results comes

<sup>18</sup> W. P. Wolf and J. H. Van Vleck, Phys. Rev. **118**, 1490 (1960).

from the integration over the magnon modes. The spin-wave spectrum of the yttrium iron garnet has been calculated numerically by Harris.<sup>19</sup> As is indicated in Fig. 12 of his paper, for  $\mathbf{k}$  lying along a  $[111]$  direction there are spin-wave modes whose energies lie above and below  $352 \text{ cm}^{-1}$ . For the purpose of obtaining a numerical estimate we will assume that the major contribution to the integration over the magnon modes comes from the mode whose energy at  $\mathbf{k}=0$  is  $10J_{ad}$ , where  $J_{ad}$  is the exchange integral between the  $a$  and  $d$  sites of the iron lattice. We write the energy of this mode as

$$E_m^1(k) = 10J_{ad} + Xk^2. \quad (26)$$

We use Harris' value of  $J_{ad}$ ,  $31.8 \text{ cm}^{-1}$ . From Fig. 12 of his paper we estimate  $X$  to be  $0.7 \times 10^{-23} \text{ erg cm}^2$ . The value of  $|\xi_{ad}^\beta|^2$  for the mode in question has been obtained by Douglass.<sup>9</sup> He finds that at  $\mathbf{k}=0$ ,  $|\xi_{ad}^\beta|^2 = \frac{1}{12}$ . With these values of the constants we obtain the result

$$1/T_1 = 2 \times 10^{11} \coth(240/T) \text{ sec}^{-1}. \quad (27)$$

Strictly speaking, the relaxation between the  $J=1$  manifold and the  $J=0$  level is characterized by three relaxation times. Our value for  $T_1$  must be viewed qualitatively as an "average" relaxation time. As such it does not differ greatly from the experimental relaxation time inferred by LNRVV

$$1/T_1 = 10^{11} - 10^{12} \text{ sec}^{-1} \quad (T=0). \quad (28)$$

Their value of  $T_1$  was obtained from measurements of the ferrimagnetic resonance linewidth in the europium iron garnet. As they indicated the relaxation times entering into their equations could either characterize the relaxation between the  $J=1$  and  $J=0$  levels (spin-magnon relaxation) or within the  $J=1$  manifold (spin-lattice relaxation). In order to determine the relative efficiencies of the two relaxation processes, we must also calculate the spin-lattice relaxation time.

Using the average strain model of Orbach<sup>2</sup> we obtain the following expression for the spin-lattice relaxation time for the direct process,  $T_1^{\text{SL}}$

$$\frac{1}{T_1^{\text{SL}}} = \frac{|\langle a|O_{\text{OL}}|b \rangle|^2 \omega_0^3}{2\pi\rho\hbar} \coth \frac{\hbar\omega_0}{2KT} \sum_p \frac{1}{v_p^5}. \quad (29)$$

Here  $\hbar\omega_0$  is a typical splitting between the  $J=1$  sublevels,  $\langle a|O_{\text{OL}}|b \rangle$  is the corresponding matrix element of the orbit-lattice interaction,  $\rho$  is the density of the crystal, and  $v_p$  is the velocity of sound of the  $p$ th mode.

In evaluating (29) we take  $\rho = 5.2 \text{ gm/cm}^3$ ,  $v_l = 3.87 \times 10^5 \text{ cm/sec}$ , and  $v_t = 7.17 \times 10^5 \text{ cm/sec}$ .<sup>13</sup> The splitting of the  $J=1$  manifold has been measured by Konigstein. He finds these levels to be at 309, 348, and  $390 \text{ cm}^{-1}$  above the ground state.<sup>20</sup> Therefore, we set  $\hbar\omega_0$  equal to  $80 \text{ cm}^{-1}$ .

<sup>19</sup> A. B. Harris, Phys. Rev. **132**, 2398 (1963).

<sup>20</sup> J. A. Konigstein (private communication).

The determination of  $\langle a|O_{\text{OL}}|b \rangle$  poses somewhat of a problem. We will take  $\langle a|O_{\text{OL}}|b \rangle = 500 \text{ cm}^{-1}$  which is perhaps a generous estimate. We then obtain the result

$$1/T_1^{\text{SL}} = 2 \times 10^{11} \coth(55/T) \text{ sec}^{-1}. \quad (30)$$

The spin-lattice relaxation time within the  $J=1$  manifold is thus estimated to be of the same order of magnitude as the spin-magnon relaxation time between the  $J=1$  and  $J=0$  levels. As is the case with ytterbium it is not possible to rule out contributions to the line width from either of the two relaxation processes.

## V. Gd<sup>3+</sup> IN THE IRON GARNET

Since Gd<sup>3+</sup> is an  $S$ -state ion we can neglect crystal field effects entirely in computing the spin-magnon relaxation time. The coupling between the gadolinium ion and the iron lattice is an isotropic antiferromagnetic exchange interaction. The ground state of the gadolinium ion is split apart into eight equally spaced levels by the static exchange field. At low temperatures,  $< 50^\circ\text{K}$ , only the lowest two of these levels are appreciably populated so that for our purposes the gadolinium ion can be viewed as a two-level system.

Because the exchange interaction is isotropic and the spin of the gadolinium ion is antiparallel to the average iron spin, the spin-magnon interaction induced by the exchange coupling can not give rise to a finite relaxation time for the direct process. There are, however, additional processes which could contribute to a finite spin-magnon relaxation time.

Foremost among these are the Raman processes. These are of two kinds, the Raman scattering of magnons induced by the term  $\Lambda(S_z^{\text{Fe}} - S_z^{\text{RE}})S_z^{\text{RE}}$ , and the Raman scattering induced by the term  $\frac{1}{2}\Lambda(S_+^{\text{Fe}}S_-^{\text{RE}} + S_-^{\text{Fe}}S_+^{\text{RE}})$ , which involves the excitation of the gadolinium ion to an intermediate state other than the two lowest levels. Since the two lowest levels are eigenstates of  $S_z^{\text{RE}}$  having eigenvalues  $M_S = +\frac{7}{2}$  and  $M_S = +\frac{5}{2}$ , they can not be connected by the operator  $S_z^{\text{RE}}$  associated with the first of the Raman processes. The second Raman process can not contribute to the relaxation time either since the intermediate states would have the eigenvalues  $M_S = \pm\frac{3}{2}, \pm\frac{1}{2}$ , etc. The relaxation process would then involve transitions for which  $\Delta M_S = \pm 2, \pm 3$ , etc. Such transitions can not be induced by the operators  $S_+^{\text{RE}}$  and  $S_-^{\text{RE}}$ . The third-order process involving transitions between states for which  $\Delta M_S = \pm 1$  can give rise to a finite relaxation time, but it is too long to have an observable effect on the ferrimagnetic resonance spectrum at low temperatures.

The dipolar coupling between the gadolinium ion and the iron ions has in it terms of the form  $S_+^{\text{Fe}}S_+^{\text{RE}}$  and  $S_-^{\text{Fe}}S_-^{\text{RE}}$  which raise or lower the spin of the iron lattice and the gadolinium ion simultaneously. As is evident from the discussion following Eq. (9), such terms do make possible a finite relaxation time for the

direct process. A rough calculation indicates that at zero degrees the relaxation time resulting from the dipolar coupling is on the order of  $10^{-7}$  sec.<sup>21</sup> In the absence of crystal-field effects the contribution of the rare-earth ion to the ferrimagnetic resonance linewidth is through the transverse relaxation effect. It is shown by Van Vleck<sup>22</sup> that the increase in line width caused by the transverse process can be written

$$\Delta\omega = \frac{c\omega}{6} \sum_n \frac{\omega_n/T_1^n}{\omega_n^2 + (1/T_1^n)^2} \tanh \frac{\hbar\omega_n}{2KT}, \quad (31)$$

where  $\omega$  is the resonance frequency,  $T_1^n$  is the longitudinal relaxation time, and  $\hbar\omega_n$  is the energy separation between the two lowest rare-earth levels. The symbol  $c$  denotes the ratio of rare-earth ions to iron ions, and the sum is over the six inequivalent rare-earth sites. In the case of gadolinium (31) reduces to

$$\Delta\omega = (c\omega/\omega_n)(1/T_1)\tanh(\hbar\omega_n/2KT). \quad (32)$$

Taking  $c = \frac{3}{5}$ ,  $\hbar\omega_n = 37$  cm<sup>-1</sup>,<sup>16</sup> and  $T_1 = 10^{-7}$  sec, we find for the contribution of the gadolinium ion to the fractional linewidth at zero degrees

$$\Delta\omega/\omega \simeq 10^{-6}, \quad (33)$$

which is probably too small to be observed.

We are therefore led to the conclusion that the spin-magnon relaxation process probably does not have an observable effect on the resonance spectrum in the gadolinium-doped iron garnet. This result is disappointing since an  $S$ -state ion, being virtually unaffected by the crystal field, makes possible a direct test of the spin-magnon relaxation theory.

## VI. SUMMARY AND CONCLUSIONS

It is evident from our calculations that in the case of Yb<sup>3+</sup> and Eu<sup>3+</sup> the spin-magnon and spin-lattice

<sup>21</sup> It is possible that the spin-lattice relaxation time may be of this order of magnitude at zero degrees and considerably shorter at liquid-nitrogen temperatures. We have not investigated this point in detail, however.

<sup>22</sup> J. H. Van Vleck, J. Appl. Phys. **35**, 882 (1964).

relaxation processes make nearly comparable contributions to the ferrimagnetic resonance linewidth and shift in the iron garnet. In the case of Gd<sup>3+</sup> probably neither relaxation process has any observable effect on the resonance spectrum.

On the basis of the discussion given above we can draw some general conclusions about the circumstances under which the effects of the spin-magnon relaxation process might be uniquely observed. The nearly complete absence of crystal-field effects on the  $S$ -state ions make them especially suitable for testing the theory. In order to have energy-conserving transitions leading to a finite relaxation time for the direct process the spin of the  $S$ -state impurity ion must be parallel to the average spin of the magnetic lattice. If the magnetic lattice were ferromagnetic this would require a ferromagnetic exchange interaction between the iron spin and the impurity ion. If the magnetic lattice were ferrimagnetic then the impurity ion could be coupled by a ferromagnetic exchange interaction to the majority lattice or by an antiferromagnetic exchange interaction to the minority lattice. In either case the contribution of the impurity ion to the resonance linewidth would be through the transverse relaxation mechanism and would be characterized by an equation similar to (32).

*Note added in proof.* Recent experimental evidence [T. Orbach (private communication)] suggests that neither the spin-magnon nor the spin-lattice relaxation process is important for Eu<sup>3+</sup>. The dominant relaxation mechanism may be the phonon modulation of the rare earth-iron exchange integral, as suggested by Orbach. This mechanism is under study and the results will be published at a later date.

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