Rare-Earth Ion Relaxation Time and G Tensor in Rare-Earth-Doped Yttrium Iron Garnet. II. Neodymium

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We present ferrimagnetic-resonance linewidth measurements at 9.3 Gc/sec and 16.9 Gc/sec between 1.5 and 250°K in the principal crystallographic directions for a single crystal of yttrium iron garnet (YIG) doped with 0.82% Nd. These results are compared with the linewidth predicted by the longitudinal (so-called "slow relaxing ion") mechanism of relaxation for a single Kramers doublet. We find that the temperature and frequency dependences of the linewidths are in good agreement with the predictions, but that the anisotropic exchange splitting of the ground-state Kramers doublet is not accurately described by a tensor G, according to $(G_1^2\mathbf{i}^2+G_2^2\mathbf{j}^2+G_3^2\mathbf{k}^2)^{1/2}$, probably through the admixture of higher states into the ground doublet. However, the tensor $G_1\sim40$ cm^{-1}; $G_2\sim20$ cm^{-1}; $G_3\sim80$ cm^{-1} describes the basic topology of the splitting. We also deduce τ, the relaxation time of the Nd^{3+} ion in the YIG environment. The results are somewhat limited except in the [111] direction, where they suggest that for $T<40$°K a direct process dominates, and is given by $(1/\tau)_D=(1/\tau^0)_D\coth(\delta_{111}/2kT)$ with $(1/\tau^0)_D\sim4\times10^{10}$ sec^{-1} for the average splitting in the [111] direction δ_{111} equal to 61.3 cm^{-1}. We cannot say whether this observed direct process is predominantly spin-magnon or spin-lattice, for a rough estimate shows that both processes could conceivably be of the observed order of magnitude. At higher temperatures, the temperature dependence of the observed relaxation time follows that expected for the Orbach or resonance process, as described by $(1/\tau)_O=B/[\exp(\Delta/kT)-1]$ with $B=9\times10^{11}$ sec^{-1} for a value of Δ of 85 cm^{-1}, as is indicated by the Orbach-process relaxation-time results reported for Nd^{3+} in yttrium gallium garnet, for which the value of B is about an order of magnitude smaller than the value reported here.

1. INTRODUCTION

IN a previous paper,[1] hereafter referred to as I, the longitudinal mechanism of relaxation was used to interpret ferrimagnetic resonance measurements on a sample of yttrium iron garnet (YIG) containing 5.1% Yb. In this paper, we should like to present measurements of linewidth for YIG containing 0.82% Nd, and to show that for this ion also, the results can be explained quantitatively in terms of the longitudinal mechanism. We shall deduce some values of the anisotropic splitting of the ground-state Kramers doublet of the Nd^{3+} ion. We shall also derive the relaxation time of the Nd^{3+} ion, and compare this with current theories.

We shall not describe here the details of the longitudinal mechanism, for which the reader is referred to I and the references contained therein. We shall make extensive use of the equations presented in I.

Before presenting the experimental results, we shall consider with reference to the Nd ion the approximations implicit in some of the equations in I with which we shall be comparing the observed linewidths.

The energy-level structure of Nd^{3+} in YIG is much more complicated than that of Yb^{3+}. The free-ion coupling is intermediate between Russell-Saunders and j-j.[2] Spin-orbit coupling separates the low-lying multiplets by only 2000 cm^{-1}.[3] This is not much greater than the crystal-field splittings, which cannot therefore be considered as a small perturbation on the free ion. The crystal-field splittings of Nd^{3+} in yttrium aluminum garnet (YAlG) have been measured by Koningstein and Geusic[4] and are shown diagrammatically in Fig. 1. Although the crystal-field parameters for YAlG are not exactly the same as those for YIG,[5] they are nevertheless sufficiently close for the YAlG results to act as a rough guide for the YIG case. As we shall show below the exchange interaction covers the range 10–90 cm^{-1}, so that the exchange interaction cannot be considered as a small perturbation on the crystal field. The outcome is

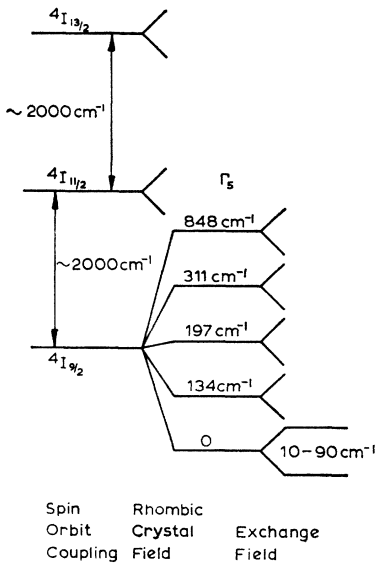

FIG. 1. Low-lying energy levels of Nd^{3+} in YAlG, (diagrammatic), after Koningstein and Geusic (Ref. 4).

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[1] B. H. Clarke, K. Tweedale, and R. W. Teale, Phys. Rev. **139**, A1930 (1965) (preceding paper).
[2] B. G. Wybourne, J. Chem. Phys. **32**, 639 (1960).
[3] For example see G. H. Dieke, *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1963), p. 237.
[4] J. A. Koningstein and J. E. Geusic, Phys. Rev. **136**, A711 (1964).
[5] M. T. Hutchings and W. P. Wolf, J. Chem. Phys. **41**, 617 (1964).

that the ground doublet will contain an appreciable admixture of higher states, and it is therefore unlikely that the splitting of the ground doublet by the exchange field can be described in terms of a tensor G according to the simple form:

$$\hbar\omega_n = (G_1^2\mathbf{i}^2 + G_2^2\mathbf{j}^2 + G_3^2\mathbf{k}^2)^{1/2}. \quad (1)$$

We shall show below that while the general topology of the ground doublet can be described by such a simple relation, the detailed description is poor.

As for the case of Yb,[1] we shall neglect the effect on the doublet splitting of the actual field applied in the resonance experiment, since such fields are very small compared to the exchange fields. We will also neglect cross-relaxation between the Nd ions, and scattering to spin-waves through the Nd ions upsetting the perfection of the YIG lattice.

Under these conditions, the linewidth is described by Eq. (1) of I, and in the principal crystallographic directions, the same simplifications as described in Sec. 4 of I will occur in the summation over the $n=6$ different orientations of the rare-earth (RE) site (see Fig. 2 of I). This is because the simplifications are a property of the symmetry of the site relative to the crystallographic axes, rather than of the ion occupying the site. Thus the linewidths in the principal crystallographic directions will be of the same form as given by Eqs. (4), (6), and (8) of I, though we must bear in mind that because of the likely admixture of higher states into the ground doublet in the Nd case, it might not be possible to express the values of $\hbar\omega_n$ and A_n in terms of a G tensor according to Eq. (1) above, as has been done in Eqs. (4), (6), and (8) of I.

Because of the small separation between the ground and first excited doublets, we cannot strictly apply the equations for a single Kramers doublet (such as the above mentioned equations) at temperatures above about 50°K, since at higher temperatures the excited doublet will be appreciably populated, and could therefore contribute to the redistribution of populations required during a precession cycle. However, the relaxation time associated with this higher doublet may be such that the ensuing contribution to the linewidth is negligible, and we shall show below that up to 150°K the relaxation times deduced by ascribing the experimental linewidth to the ground doublet alone are in reasonable agreement with theory.

2. EXPERIMENTAL RESULTS

Measurements of linewidth and field for resonance were made near 9.3 Gc/sec and 16.9 Gc/sec over the temperature range 1.5–250°K on a single crystal of Nd doped YIG for which chemical analysis gave the composition $(Nd_{0.0082}Y_{0.9918})_3\,Fe_5O_{12}$. The crystal was grown from the melt, using a PbO/PbF_2 flux. A spherical specimen (0.44 mm diam, with a variation in diameter less than ± 4 parts in 10 000) was prepared by the same techniques as given in I.

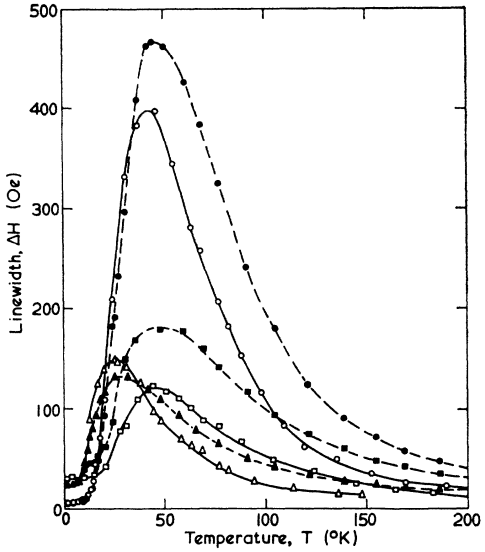

FIG. 2. Linewidth versus temperature for 0.82% Nd in YIG in the [111] direction (circles), the [100] direction (triangles) and the [110] direction (squares) at 9.3 Gc/sec (open symbols) and 16.9 Gc/sec (closed symbols).

In Fig. 2, we show the variation of linewidth with temperature for the [111], [100], and [110] directions at the two measurement frequencies. A qualitative examination shows that the results exhibit features in accordance with the predictions of the longitudinal mechanism as discussed at the end of Sec. 4 of I.

Comparison of the fields for resonance with those derived from static torque measurements[6] indicate that the dynamic shifts in the resonance fields are relatively small over the whole temperature range. This effect is in qualitative agreement with the shifts predicted by the longitudinal mechanism (Sec. 4 of I) for the values of δ and τ deduced below from the linewidths. In view of the smallness of the shifts, and the difficulties in estimating accurately the g factor, γ, in the absence of the dynamic shift, we have not made quantitative use of the observed shifts in this paper.

3. THE SPLITTING OF THE GROUND-STATE KRAMERS DOUBLET

As indicated by Eq. (10) of I, we can determine the active splitting of the Kramers doublet ground state in the principal crystallographic directions from a plot of log $(T\Delta H)$ versus $1/T$ at low temperatures. In the [100] and [110] directions, however, we find residual linewidths in the liquid-helium temperature range of the order of 30 Oe, which is a rather larger value than is to be expected from the host YIG.[7] As explained in Sec. 6 of I, this residual linewidth is probably a measurement

[6] R. F. Pearson (private communication).
[7] B. H. Clarke, J. Appl. Phys. **36**, 1211 (1965).

effect associated with slight misalignment of the sample and with [100] and [110] being very hard directions of magnetization at these low temperatures. (The anisotropy field is ~3000 Oe at 4.2°K.) This measurement effect prevents quantitative interpretation of the low temperature results for these two directions. However, the results for the [100] direction suggest that δ_{100} is not less than about 23 cm^{-1}. But since the maximum linewidth for this direction at 9.3 Gc/sec (147 Oe at 26°K) is greater than the maximum at 16.9 Gc/sec (132 Oe at 29°K), then the term $(1/kT)$ sech$^2(\delta_{100}/2kT)$ must diminish between the temperatures 26 and 29°K. This indicates that δ_{100} cannot be greater than ~30 cm^{-1}. We shall find in deriving the relaxation times for this direction that the most consistent results are given by the value $\delta_{100}=24$ cm^{-1}.

In the [110] direction, the linewidths at 9.3 Gc/sec are smaller than those at 16.9 Gc/sec over the whole temperature range, so that $(1/\tau_{110})>(\omega_1\omega_2)^{1/2}$ at all temperatures. Since the linewidth maximum occurs at the same temperature (50°K) for both measurement frequencies, then this maximum must be associated with the term $(1/kT)$sech$^2(\delta_{110}/2kT)$. However the linewidth maximum will occur at a lower temperature than the maximum value of this expression because of the $\omega\tau$ term, by an amount depending on the temperature dependence of τ. We can only infer that $\delta_{110}>55$ cm^{-1}.

We have already published a detailed analysis of the low temperature linewidths in the [111] direction.[7] The result 61.3 cm^{-1} is obtained for δ_{111}, which is a weighted average of the two actual values of the doublet splitting, δ_1 and δ_2, in this direction.

More information on the splitting of the doublet can be obtained from the magnitudes of the linewidths in the principal directions. In the following section, we shall determine relaxation times by multiplying the experimental linewidths by $(kT)/\text{sech}^2(\delta/2kT)$, and normalizing the maximum value to $\frac{1}{2}$. Reference to Eq. (4) of I shows that in the [100] direction, where the contributing sites have the same value of δ (and hence of τ), the above expression is proportional to $\omega\tau/[1+(\omega\tau)^2]$ and that the constant of proportionality is $(C/6M)(\sum_n A_n)_{100}$. We can therefore determine the magnitude of $(\sum_n A_n)_{100}$ and obtain the value 480(cm^{-1})^2.

In the [111] direction, the situation is more complicated. Here the linewidth is given by

$$\Delta H_{111}=\frac{C}{6MkT}\sum_{n,p}\left\{A_{n,p}\frac{\omega\tau_p}{1+(\omega\tau_p)^2}\,\text{sech}^2\left(\frac{\delta_p}{2kT}\right)\right\},$$

with $p=1$ and 2 (see Sec. 4 of I). If we make the approximation that the terms sech$^2(\delta_p/2kT)$ and $\omega\tau_p/[1+(\omega\tau_p)^2]$ can be replaced by sech$^2(\delta_{111}/2kT)$ and $\omega\tau_{111}/[1+(\omega\tau_{111})^2]$, respectively, where τ_{111} is a weighted average of τ_1 and τ_2, then we have

$$\Delta H_{111}=\frac{C}{6MkT}\frac{\omega\tau_{111}}{1+(\omega\tau_{111})^2}\,\text{sech}^2\left(\frac{\delta_{111}}{2kT}\right)(\sum_{n,p}A_{n,p})_{111},$$

and $(\sum_{n,p}A_{n,p})_{111}$ can be determined by the same method as was used for the [100] direction. We shall show below that it is unlikely that the two values of the doublet splitting in the [111] direction, δ_1 and δ_2, differ by more than 5 cm^{-1}, so that the approximation with regard to the sech^2 term will be good to within 15% at 25°K, and will improve rapidly with rising temperature. Because of the closeness of δ_1 and δ_2, it is also unlikely that the relaxation times associated with these two values of the doublet splitting are very different. Moreover, we normalize the term $(kT\Delta H_{111})/\text{sech}^2(\delta_{111}/2kT)$ at $\omega\tau_{111}=1$, where the term is not a rapid function of the relaxation time. With these approximations we obtain a value 3960(cm^{-1})^2 for $(\sum_{n,p}A_{n,p})_{111}$.

We cannot determine $\sum_n A_n$ for the [110] direction by the same method, since over the whole temperature range, $\omega\tau<1$ and we are therefore unable to normalize the term $(kT\Delta H_{110})/\text{sech}^2(\delta_{110}/2kT)$. Moreover, we have only determined a lower limit for δ_{110}.

Suppose we now assume that the ground doublet can be described by a G tensor according to Eq. (1). Then the four quantities determined above (δ_{100},δ_{111}, $(\sum_n A_n)_{100}$ and $(\sum_{n,p}A_{n,p})_{111}$) can be expressed in terms of this G tensor, as can be the weighting between the two sets of contributing sites in the [111] direction. The detailed equations will be found in I.

Any three of the four quantities can then be used to solve for G_1, G_2, and G_3. Where the [111] direction splitting is used, we determine δ_1 from δ_{111} by estimating the weighting term, use the G-tensor solution to re-estimate the weighting term, and iterate the whole process until the best fit is found. The results of the possible analyses are given in Table I.

In each case, calculation of the fourth quantity from the G tensor obtained from the other three gives poor agreement with the experimental value. The differences are too great to be attributed to the approximations made in the [111] direction. A solution like G_1~40 cm^{-1}, G_2~20 cm^{-1}, and G_3~80 cm^{-1} will describe the basic topology of the ground doublet, but the detailed

TABLE I. Best-fit G tensors.

Quantities used				G_1	G_2	G_3
				(cm^{-1})		
δ_{100}	δ_{111}	$(\sum_n A_n)_{100}$		32	10	103
δ_{100}	δ_{111}		$(\sum_{n,p}A_{n,p})_{111}$	No real solution obtained		
δ_{100}		$(\sum_n A_n)_{100}$	$(\sum_{n,p}A_{n,p})_{111}$	32	10	55
	δ_{111}	$(\sum_n A_n)_{100}$	$(\sum_{n,p}A_{n,p})_{111}$	61	33	94

description is poor. Thus we conclude that the ground doublet cannot be described accurately by a G tensor according to Eq. (1). This is not to say that the experimental results cannot be explained by the longitudinal mechanism, which adequately describes the observed temperature and frequency dependences of ΔH in a particular direction; rather that a more complicated expression than Eq. (1) is required to describe the ground doublet, probably due to the admixture of higher states into the ground doublet, as discussed above. We make no attempt here to deduce such an expression.

The weighting term between the two sets of sites in the [111] direction depends not only on the G tensor but also on the ratio of $\omega\tau/[1+(\omega\tau)^2]$ for the two sites. In the next section we shall show that, in the low-temperature range $kT<\delta/2$ over which we require the weighting, $\omega\tau$ is close to unity, so that the term $\omega\tau/[1+(\omega\tau)^2]$ is not a rapid function of the relaxation time. Moreover, the relaxation times are likely to be much the same for the two sets of sites, for the difference between δ_1 and δ_2 is not greater than about 5 cm^{-1}, at least on the above approximate G-tensor description. In determining the weighting term in the above analyses, we have therefore set the ratio of the $\omega\tau$ terms for the two sites equal to unity. Variation of this ratio within reasonable limits, while changing slightly the resulting solution, still cannot give a G tensor which fits all four measured quantities.

4. RELAXATION TIMES: EXPERIMENTAL RESULTS

As explained in Sec. 3, we can determine the term $\omega\tau/[1+(\omega\tau)^2]$ in the [100] and [111] directions by normalizing the maximum value of $(kT\Delta H)/\mathrm{sech}^2(\delta/2kT)$ to $\frac{1}{2}$. We can then solve for $\omega\tau$. In Fig. 3, the resulting inverse relaxation times are plotted as a function of temperature. Note that the [100] results are plotted on a displaced scale. For the [100] direction we have used the value 24 cm^{-1} for δ in the above expression. For the [111] direction, we have used the value 61.3 cm^{-1}, and the relaxation time for this direction is thus a weighted average of the two actual relaxation times associated with the two values of the ground doublet splitting.

The relaxation times deduced at the two different microwave frequencies are in good agreement, illustrating the ability of the longitudinal mechanism to account for the observed frequency dependence of the measured linewidths.

As stated previously, we cannot normalize the term $(kT\Delta H)/\mathrm{sech}\,(\delta/2kT)$ as above for the [110] direction since $\omega\tau<1$ over the whole temperature range. Neither can we estimate the normalizing term with sufficient accuracy from the G tensor because of its inexact description of the Kramers doublet ground state. We can therefore make no observation on the relaxation time in the [110] direction other than that it is somewhat shorter than τ for the [100] and [111] directions, at least at temperatures below 40°K.

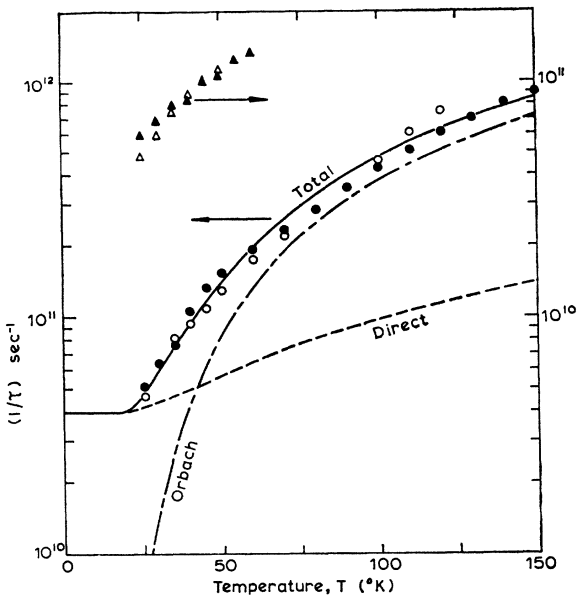

FIG. 3. Inverse relaxation times versus temperature for 0.82% Nd in YIG, legend as Fig. 2. Note the displaced scale for the [100] direction results. The solid line is the sum of direct and Orbach processes given by $(1/\tau^0)_D \coth(\delta/2kT)+B/[\exp(\Delta/kT)-1]$ with $(1/\tau^0)_D=4\times10^{10}$ sec^{-1}, $\delta=61.3$ cm^{-1}, $B=9\times10^{11}$ sec^{-1}, and $\Delta=85$ cm^{-1}.

5. RELAXATION TIMES: DISCUSSION

Because of the close proximity of higher crystal field levels, we expect that the Orbach process[8] might be the dominant two phonon relaxation mechanism. Svare and Seidel[9] have observed an Orbach process for Nd in yttrium gallium garnet (YGaG), which, of the diamagnetic garnets, has crystal-field parameters closest to those of YIG.[5] Their fit of the Orbach term

$$(1/\tau)_O=B/[\exp(\Delta/kT)-1]$$

gives values of 9×10^{10} sec^{-1} for B, and 85 cm^{-1} for Δ, where Δ is the separation between the ground and first excited doublets. Such a value of Δ gives reasonable agreement with the temperature dependence of our relaxation-time results for the [111] direction in the higher temperature range, but at lower temperatures a direct or one phonon process[8] is apparently dominant.

In Fig. 3, we show the fit obtained to the [111] direction inverse relaxation times by the sum (solid line) of a direct process (dashed line) and an Orbach process (linked line) using $\Delta=85$ cm^{-1} in the Orbach term, and using $\delta=61.3$ cm^{-1} in the direct-process term, $(1/\tau)_D$

[8] R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).
[9] I. Svare and G. Seidel, *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1963), p. 430.

$=(1/\tau^0)_D \coth(\delta/2kT)$. The fit shown corresponds to $(1/\tau^0)_D=4\times10^{10}$ sec^{-1} and $B=9\times10^{11}$ sec^{-1}, which latter value is only an order of magnitude different to that found by Svare and Seidel[9] for Nd in YGaG.

With the data available, we cannot say whether the observed direct process arises predominantly from spin-lattice or spin-magnon relaxation. Svare and Seidel[9] have also observed a direct process for Nd in YGaG, and crude extrapolation of their coefficient according to $(1/\tau^0)_D \propto \delta^5$ (see I) indicates a spin-lattice direct process coefficient for Nd in YIG of the order of 1.5×10^{12} sec^{-1}. As we found for the Yb case,[1] this extrapolation is apparently too strong. A more gentle extrapolation, as indicated by the Yb case, would here give a value of the order of 10^{10} sec^{-1} for $(1/\tau^0)_D$. We can also make a crude estimate of the spin-magnon direct process coefficient from the formula given by Huber.[10] Taking a G tensor $G_1\sim40$, $G_2\sim20$, $G_3\sim80$ cm^{-1} as approximately describing the ground doublet, and using the same values as given by Huber for the other terms, we obtain a value of the order of 5×10^{10} sec^{-1}, taking into account that for Nd the coupling to the iron sublattice is effectively ferromagnetic.[11] Thus, both spin-lattice and spin-magnon relaxation could conceivably contribute to the direct process observed in the [111] direction. More detailed calculations would be required to determine which process is dominant.

In the [111] direction, we have applied the longitudinal mechanism linewidth formula for a single Kramers doublet to a rather higher temperature than is justified in view of the close proximity of the first excited doublet. However, the relaxation-time results obtained apparently fit the expected form quite well, which suggests that though appreciably populated at these higher temperatures, this excited state does not contribute significantly to the measured linewidth.

In the [100] direction, the relaxation time results available are too limited to allow any quantitative deductions to be made regarding the dominant processes. In the [110] direction, the relaxation time for $T<40$°K is apparently somewhat shorter than for the other directions. Rough calculation shows that this favors a dominant spin-lattice direct process at least in this direction.

[10] D. L. Huber, Phys. Rev. **136**, A500 (1964).
[11] J. H. Van Vleck, J. Phys. Soc. Japan **17**, Suppl. B-1, 352 (1962).

6. CONCLUSIONS

We have compared measurements of the microwave resonance linewidth in the principal crystallographic directions of a single crystal specimen of YIG doped with 0.82% Nd with that predicted for a single Kramers doublet by the longitudinal (so-called "slow-relaxing ion") mechanism of relaxation. We have found that the temperature and frequency dependences are in accordance with the predictions, but that the anisotropic exchange splitting of the ground-state Kramers doublet is not accurately described by a G tensor according to $(G_1^2\mathbf{i}^2+G_2^2\mathbf{j}^2+G_3^2\mathbf{k}^2)^{1/2}$ probably through the admixture of higher states into the ground doublet, though we have not attempted here to calculate the effect of such admixture. A tensor $G_1\sim40$ cm^{-1}; $G_2\sim20$ cm^{-1}; $G_3\sim80$ cm^{-1} describes the basic topology of the splitting.

We have also deduced the relaxation time of the Nd^{3+} ion in the YIG environment. The results are somewhat limited except in the [111] direction, where they suggest that a direct process dominates for $T<40$°K. We have roughly estimated the spin-magnon and spin-lattice direct-process relaxation times, and find that both could conceivably contribute significantly to the observed direct process. More detailed calculations would be required to determine which is dominant.

At higher temperatures, the temperature dependence of the observed relaxation time follows that expected for the Orbach process using $\Delta=85$ cm^{-1} (as indicated by the Orbach-process relaxation time reported by Svare and Seidel for Nd in YGaG). We have deduced the value of the Orbach-process coefficient B, and find it to be an order of magnitude larger than reported for Nd in YGaG.

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