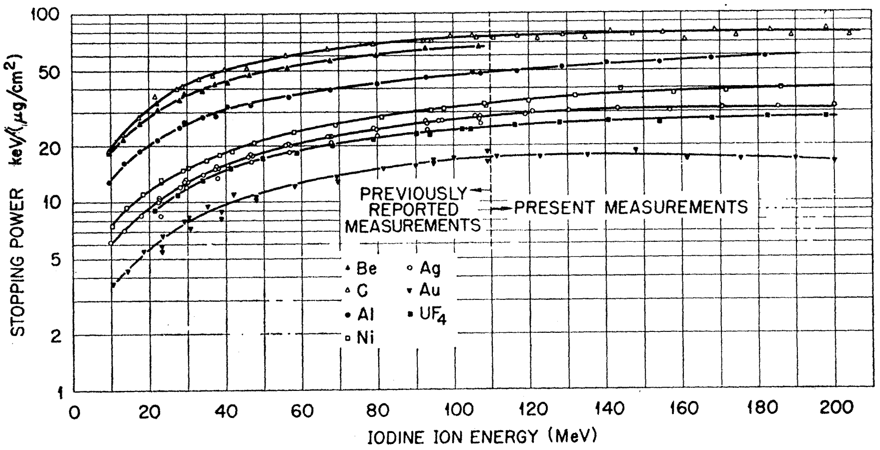

FIG. 1. Stopping power of several solid materials for iodine ions.

the stopping power is expected to decrease with velocity. It is expected that dE/dx should reach a maximum value at or below $v_0Z^{2/3}$ ($0.1c$ for ^{127}I). From the results in the figure it can be seen that this maximum has been reached in the case of Au at about 125 MeV corresponding to a velocity of $0.046c$. For the other materials measured the maxima appear to occur at somewhat higher velocities but still well below the value $v_0Z^{2/3}$.

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Paramagnetic Resonance and Relaxation of Some Rare-Earth Ions in $YCl_3 \cdot 6H_2O$*

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The paramagnetic resonance at $\nu = 9.3$ Gc/sec has been observed at helium temperatures for Ce^{3+}, Nd^{3+}, Dy^{3+}, Er^{3+}, and Yb^{3+} diluted in single crystals of $YCl_3 \cdot 6H_2O$. The principal values g_x, g_y, and g_z of the g tensor were measured and showed marked anisotropy. The spin bath relaxation rate T_b^{-1} was measured for Nd^{3+} and Er^{3+} over the temperature range $0.2 \leqq T \leqq 5$°K and for Ce^{3+} and Dy^{3+} over the range $1.3 \leqq T \leqq 5$°K, by observing the transient recovery of the microwave resonance following a saturating pulse. The temperature dependence of the Orbach process, $T_b^{-1} \propto \exp(-\Delta/T)$, is displayed for all four ions, with values of Δ in agreement with optical measurements in concentrated crystals. There is some evidence of phonon bottlenecking of the Orbach process for Dy^{3+}. The Raman process $T_b^{-1} \propto T^9$ was observed for Ce^{3+} and Dy^{3+}. The direct process $T_b^{-1} \propto \coth(h\nu/2kT)$ was observed for all four ions, and displayed a very large anisotropy, of order 10^3 to 10^4, for Nd^{3+} and Er^{3+}, which can be approximately understood in terms of the matrix elements of the Zeeman perturbation between ground and excited states. For Nd^{3+} there was some evidence for a phonon bottleneck of the direct process, $T_b^{-1} \propto T^2$.

I. INTRODUCTION

IN a previous paper,[1] referred to as I, we reported an experimental study of spin-lattice relaxation of some rare-earth ions in the host crystal LaF$_3$, by observing the transient recovery of the microwave paramagnetic resonance absorption following a saturating pulse. In this paper we present very similar studies for Ce^{3+}, Nd^{3+}, Er^{3+}, and Dy^{3+} in the host crystal $YCl_3 \cdot 6H_2O$, in the temperature range 0.2–5°K in fields of a few thousand Oersteds, corresponding to a microwave frequency of $\nu = 9.3$ Gc/sec. We refer to I for notation, theory, description of the apparatus, and experimental procedures. Our interest in studying rare-earth ions in the hydrated chlorides arose in connection with nuclear-spin refrigerators,[2] in which the magnetization of a system of paramagnetic ions is cyclically transferred by crystal rotation to a nuclear-spin system, by virtue of extreme anisotropies in the paramagnetic relaxation

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TABLE I. Paramagnetic resonance results for rare-earth ions in $YCl_3 \cdot 6H_2O$.

Ion	g_x	g_y	g_z	χ_0	Hyperfine constants
1.0% Ce^{3+}	2.67 ± 0.01	2.305 ± 0.010	0.782 ± 0.005	$69 \pm 2°$	
0.1% Nd^{3+}	0.26 ± 0.01	0.33 ± 0.02	3.50 ± 0.02	$63 \pm 2°$	$A_z^{143} = 0.0356 \pm 3$ cm^{-1}
					$A_z^{145} = 0.0222 \pm 2$ cm^{-1}
0.1% Dy^{3+}	2.00 ± 0.02	1.52 ± 0.01	16.52 ± 0.10	$-23 \pm 2°$	$A_z^{161} = 0.0471 \pm 2$ cm^{-1}
					$A_z^{163} = 0.0657 \pm 2$ cm^{-1}
0.1% Er^{3+}	see text	see text	13.74 ± 0.10	$77 \pm 2°$	$A_z^{167} = 0.0475 \pm 3$ cm^{-1}
1.0% Yb^{3+}	<0.5	<0.5	5.57 ± 0.05	$71 \pm 2°$	

rate and the g factor. The only substance yet reported which has such extreme anisotropies is $(Yb, Y) \times (C_2H_5SO_4)_3 \cdot 9H_2O$; sizeable proton polarizations have been obtained in this crystal.[3,4] As part of a program to find other suitable substances we selected the hydrated chlorides; although little was known about them, it appeared that they may be quite anisotropic. It has turned out that the direct relaxation process is exceedingly anisotropic, by three orders of magnitude, as discussed in Sec. III, but that the g factor is only moderately anisotropic. The anisotropy in the relaxation is the largest yet reported for paramagnetic crystals.

II. CRYSTAL STRUCTURE AND SAMPLE PREPARATION

The hydrated trichlorides of yttrium as well as the rare earths above praesodymium crystallize in a monoclinic structure with six waters of hydration, $YCl_3 \cdot 6H_2O$, whereas La, Ce, and Nd trichlorides crystallize with seven waters in a triclinic structure. We are concerned only with small fractions of rare-earth ions in the monoclinic structure, shown in Fig. 1, for $GdCl_3 \cdot 6H_2O$ from x-ray data.[5] There are two Gd atoms per unit cell, each on a twofold symmetry axis parallel to the b axis. The two sites are electrically and magnetically equivalent. The closest distance between Gd atoms is 6.525 Å in the b direction.

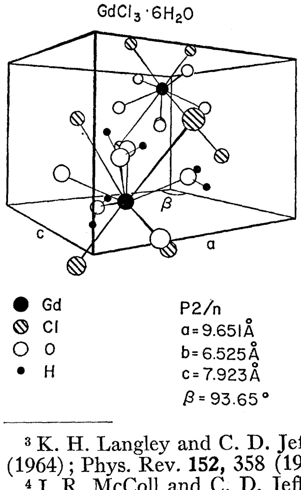

FIG. 1. The crustal structure of $GdCl_3 \cdot 6H_2O$ suggested by Marezio *et al.* (Ref. 5). The Gd atoms are on twofold axes parallel to the b axis. The closest Gd-Gd distance is 6.525 Å, along the b axis. Only a few of the hydrogen atoms are shown.

Although no paramagnetic resonance has been previously reported on rare-earth ions in these monoclinic crystals, extensive optical work, including Zeeman studies, has been done.[6–20] Crystal-field parameters have been calculated for $ErCl_3 \cdot 6H_2O$.[21] The optical work shows that the maximum Zeeman splitting for the ground state occurs with the magnetic field perpendicular to b; the principal axes (x, y, z) of the g tensor are shown in Fig. 2, in relation to the crystal axes (a, b, c) and the macroscopic form of a typical crystal. The angle χ_0 depends on the rare-earth ion; for a given ion, it may further vary from one Kramers doublet to the next. The optical data suggest that $g_x \approx g_y \neq g_z$; it may turn out that the waters of hydration are so arranged about the ion that the z axis is approximately an axis of sixfold symmetry.[19] It has also been suggested that the crystals may be ferroelectric or antiferroelectric and that the internal field created by the ferroelectric alignment causes the axis of quantization to shift from the crystallographic b axis to a plane perpendicular to this axis.[22] Harrop[21] used C_2 site symmetry for Er in finding the crystal-field parameters; however we will use in this paper the approximation that the rare-earth site symmetry in $YCl_3 \cdot 6H_2O$ is hexagonal, as suggested by the EPR data.

We have made microwave paramagnetic resonance measurements on the lowest Kramers doublet for several

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ions in dilute concentrations (0.1–5 at. %) in $YCl_3 \cdot 6H_2O$; the resonance data were fitted by the spin Hamiltonian

$$\mathcal{H} = \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z), \qquad (1)$$

for even-even isotopes. For odd isotopes with nuclear spin, it is necessary to add the hyperfine term

$$\mathcal{H}_{hfs} = A_x I_x S_x + A_y I_y S_y + A_z I_z S_z. \qquad (2)$$

These equations, together with Fig. 2, seem to describe the data for all ions except Er^+, as described below. The observed resonance parameters are summarized in Table I, and display large anisotropies. The resonance lines had linewidths of typically 10–30 Oe in low magnetic fields; at high fields, they broadened to several hundred Oe.

The crystals used in the resonance and relaxation experiments were prepared from 99.999% purity Y_2O_3 and 99.9% purity rare-earth oxides obtained from Lindsay Chemical Co. The oxides were slowly dissolved in a slight excess of reagent grade HCl. A saturated aqueous solution was put into small dishes in a desiccator at room temperature to grow seeds; from these, larger crystals were grown in a few days in the form of plates, approximately 5×5×1 mm as in Fig. 2, the best developed edge being the *a* axis. The crystals are quite hygroscopic.

III. RESONANCE AND RELAXATION MEASUREMENTS AND INTERPRETATION

A. $Nd{:}YCl_3 \cdot 6H_2O$

Optical studies[6,7] on $NdCl_3 \cdot 6H_2O$ have established two of the excited states in the $^4I_{9/2}$ ground multiplet at 62 and 250 cm^{-1} above the ground state. Pfeffer[23] suggested that the other two states are in the neighborhood of 135 cm^{-1}. We have made resonance and relaxation measurements at $\nu = 9.36$ Gc/sec on two $Nd{:}YCl_3 \cdot 6H_2O$ crystals grown from 0.1 and 1 atomic percent solutions. The resonance results are given in Table I. In Fig. 3 are shown some of the relaxation data over the range $0.2 \leqq T \leqq 5$°K with $z \parallel H = 1910$ Oe. In all cases the recovery of the saturated signal appeared to be exponential, with a well-defined rate. The data are well fit by the expression for the spin bath relaxation rate

$$T_b^{-1} = 7\times10^{-3}\coth(0.23/T) + 4\times10^{11} \times \exp(-89/T) + 4.8\times10^{-4}T^9 \text{ sec}^{-1}. \qquad (3)$$

The longest relaxation times, between 10 and 100 sec, were measured by modulation of the magnetic field at 80 cps and displaying the derivative of the resonance signal on a chart recorder, which traced out the recovery of the signal. We interpret the terms in Eq. (3) as representing the direct Van Vleck–Kronig process, the Orbach process, and the Raman process, respectively. The direct process is unusually weak; the Orbach rate determines $\Delta = 89$° for the level of the first crystal-field excited state, in good agreement with the value $\Delta = 62$ $cm^{-1} = 89$°K, determined for $NdCl_3 \cdot 6H_2O$ from optical spectroscopy.[6,7] Spin-lattice relaxation in polycrystalline $NdCl_3 \cdot 6H_2O$ has been measured by Weber,[24] whose data agree with ours for $T > 1.5$°; the lower-temperature data would not be expected to agree because the polycrystalline measurement conceals the large anisotropy in the direct process.

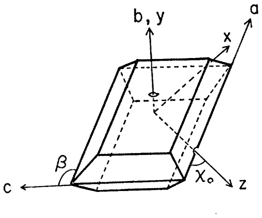

FIG. 2. The orientation of the principal directions, *x*, *y*, *z*, of the *g* tensor for rare-earth ions in $YCl_3 \cdot 6H_2O$ for which $\beta = 92$°; see Ref. 19.

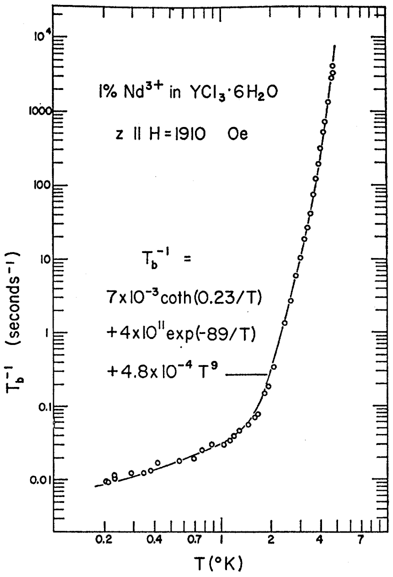

FIG. 3. Observed relaxation rate T_b^{-1} versus T for 1% Nd^{3+} in $YCl_3 \cdot 6H_2O$ with $z \parallel H$, in the range $0.2 < T < 5$°K.

This anisotropy, more than three orders of magnitude, is shown in Fig. 4 for 1% $Nd{:}YCl_3 \cdot 6H_2O$ at $T = 1.45$°K for various orientations θ between H and the z axis, with H in the *ac* plane. The microwave frequency was held fixed at $\nu = 9.37$ Gc and the external magnetic field rotated with respect to the crystal and cavity. The small angular range $86° < \theta < 94°$ could not be measured because the maximum field obtainable was only 19 kOe. The data shown with open circles indicate the region over which T_b^{-1} was also measured with a 0.1% Nd sample; no dependence on concentration was observed. The signal recovery traces were not quite exponential for $T_b^{-1} > 40$ sec^{-1}, possibly because of the onset of a phonon bottleneck.

We can roughly explain the *g*-factor data as well as the angular dependence of the direct process in the following way. Assuming that $J = \frac{9}{2}$ is a good quantum

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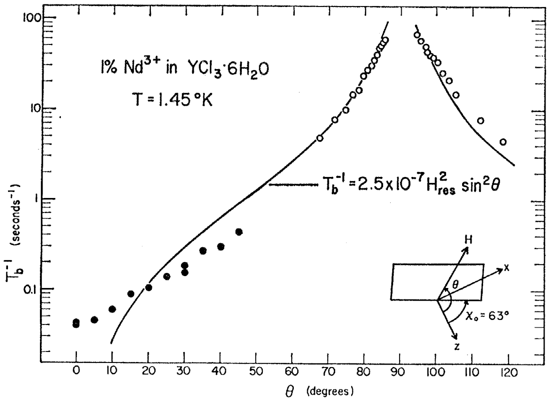

FIG. 4. Observed relaxation rate T_b^{-1} versus angle between H and z axis for 1% Nd^{3+} in YCl$_3$·6H$_2$O at $T=1.45$°K. The magnetic-field direction was rotated about the normal to the crystal plane. The data shown with open circles indicate the region over which data were also taken on a 0.1% sample. No dependence on concentration was found.

number for the ground manifold, the five Kramers doublets must be composed of linear combinations of $|J_z=\pm\frac{9}{2}\rangle$, $|\pm\frac{7}{2}\rangle$, $|\pm\frac{5}{2}\rangle$, $|\pm\frac{3}{2}\rangle$, and $|\pm\frac{1}{2}\rangle$. However, because the Nd^{3+} site symmetry is nearly hexagonal, (e.g., C_6 or C_{3h}) only functions differing by $\Delta J_z=\pm6$ are admixed, leading to these combinations: $\cos\alpha|\pm\frac{9}{2}\rangle+\sin\alpha|\mp\frac{3}{2}\rangle$; $\cos\beta|\pm\frac{7}{2}\rangle+\sin\beta|\mp\frac{5}{2}\rangle$; $|\pm\frac{1}{2}\rangle$. The Zeeman interaction $\mathcal{H}_z=\Lambda\beta\mathbf{H}\cdot\mathbf{J}$ when applied to the ground Kramers doublet $|a\rangle$, $|b\rangle$ leads to the usual expressions for the spectroscopic splitting factors:

$$g_z=2\Lambda|\langle a|J_z|a\rangle|, \tag{4a}$$

$$g_x=\Lambda|\langle a|J_++J_-|b\rangle|, \tag{4b}$$

$$g_y=\Lambda|\langle a|J_+-J_-|b\rangle|, \tag{4c}$$

where $\Lambda=8/11$ is the Landé g-factor for Nd^{3+}. From Eq. (4) and the observed values $g_z=3.5$, $g_x\approx g_y\approx0.25$, it follows that the ground doublet cannot be $|\pm\frac{1}{2}\rangle$. Although either of the other two combinations is possible, as a first approximation it is tempting to take the ground doublet as a pure $|\mp\frac{5}{2}\rangle$ state, which yields $g_z=40/11=3.63$, $g_x=g_y=0$, roughly in agreement with measurements. Clearly there must be admixed in a small amount of $|\pm\frac{7}{2}\rangle$ to prevent g_x and g_y from vanishing. The angular dependence of the direct process at constant frequency is seen to come mostly from the factor $\langle a|\mathbf{H}\cdot\mathbf{J}|i\rangle=H\langle a|J_x\sin\theta+J_z\cos\theta|i\rangle$ in Eq. (8) of I, where $|i\rangle$ is an excited state. In the rough approximation above, we see that the matrix element of J_x will dominate over that of J_z, and thus we expect

$$T_{1d}^{-1}(\theta)\propto H^2(\theta)\sin^2\theta. \tag{5}$$

In Fig. 4 the solid line is the curve

$$T_b^{-1}=2.5\times10^{-7}H^2(\theta)\sin^2\theta\ \text{sec}^{-1}, \tag{6}$$

which does fit the data except at small angles, where the additional admixtures into $|\mp\frac{5}{2}\rangle$ become more important. Further relaxation data at $\theta=84.5°$ where the direct process is strong, showed a low-temperature dependence $T_b^{-1}=25T^2$ sec^{-1} for both 0.1% and 1% crystals. This temperature dependence suggests a phonon bottleneck; its apparent independence of concentration is not consistent with this interpretation, however, unless the linewidths $\Delta H\approx250$ Oe for 0.1% and $\Delta H\approx1$ kOe for 1% somehow compensate for the spin-phonon heat-capacity ratio. The higher-temperature data at this orientation again displayed an Orbach process $T_{1O}^{-1}=7\times10^{11}\exp(-89/T)$ sec^{-1}, which is nearly twice as strong as observed for $H\parallel z$, Eq. (3). This apparent angular variation of the Orbach process has been observed before, e.g., for Nd^{3+} in lanthanum magnesium nitrate,[25] and may be caused by a large anisotropy of the excited state through which the relaxation is proceeding.

B. Dy:YCl$_3$·6H$_2$O

The levels of the ground multiplet $^6H_{15/2}$ of DyCl$_3$·6H$_2$O have been fairly well determined from optical experiments, the first and second excited states being at 34 cm^{-1} and at 63 cm^{-1}.[14,15] Gramberg[14] also reports Zeeman studies which indicate these parameters for the ground doublet: $g_x=1.8\pm0.1$, $g_y=1.66\pm0.2$, $g_z=18.06\pm0.2$, $\chi_0=-23.8\pm1°$. He also found that the principal axes of the g tensors of the excited states did not coincide with one another nor with that of the ground state.

We have observed resonance and relaxation on crystals of Dy:YCl$_3$·6H$_2$O grown from solutions of 5%, 1%, and 0.1% Dy^{3+}, respectively. The resonance parameters found, Table I, are close to those of Gramberg for the concentrated salt. Figure 5 shows some relaxation data taken on a 1% crystal at two different orientations and measured at $\nu=9.36$ Gc. The solid lines are the expressions

$$\mathbf{H}\parallel z,\quad T_b^{-1}=2.25T+5\times10^{-3}T^9+8\times10^9\times\exp(-49/T)\ \text{sec}^{-1}, \tag{7}$$

$$\mathbf{H}\parallel x,\quad T_b^{-1}=\frac{225\times250T^2}{225T+250}+5\times10^{-3}T^9+8\times10^9\exp\left(-\frac{49}{T}\right)\ \text{sec}^{-1}. \tag{8}$$

The Orbach process determines $\Delta=49$°K$=34$ cm^{-1}, in good agreement with the optical data. Weber[24] has found $T_{1O}^{-1}=1.7\times10^{10}\exp(-48/T)$ sec^{-1} in concentrated DyCl$_3$·6H$_2$O for $\mathbf{H}\parallel z$. The first term in Eq. (7) we interpret as the direct process; measurements on a 0.1% crystal at $H\parallel z$ yielded the same results as Eq. (7).

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[25] G. H. Larson and C. D. Jeffries, Phys. Rev. **141**, 461 (1966); **145**, 311 (1966).

In Eq. (8) the form required to fit the data for $H \parallel x$, $T_b^{-1}=ADT^2/(DT+A)$ is that expected[26] for a partial phonon bottleneck. The value of $D=225$, the observed linewidth $\Delta H=56$ Oe, and an estimated sound velocity $v=2\times10^5$ cm/sec lead to a phonon mean free path $\bar{l}=0.2$ mm. In order to investigate this further we took the additional data of Fig. 6 for 0.1% and 5% concentrations. The 0.1% crystal data are fit by

$$T_b^{-1}=250T+5\times10^{-3}T^9+2.7\times10^{10}\exp(-49/T)\ \text{sec}^{-1}. \tag{9}$$

The first term being linear in T suggests the not surprising result that the bottleneck is broken for this lower concentration. However the exponential term in Eq. (9) is also larger than in Eq. (8). This is very unusual and suggests that the Orbach process is also bottlenecked in Eq. (8); this possibility has been briefly considered earlier.[26] The data for a 5% crystal are also shown on Fig. 6 and seem anomalous. Why should the 5% crystal not be *more* bottlenecked than the 1%, rather than less? This is possibly because of the resonance linewidth $\Delta H=350$ Oe for the 5% crystal, compared to $\Delta H=56$ Oe for the 1% crystal, allowing the spins to relax to a larger bandwidth of phonons in the 5% crystal. This may more than compensate for the increased spin concentration in the 5% sample.

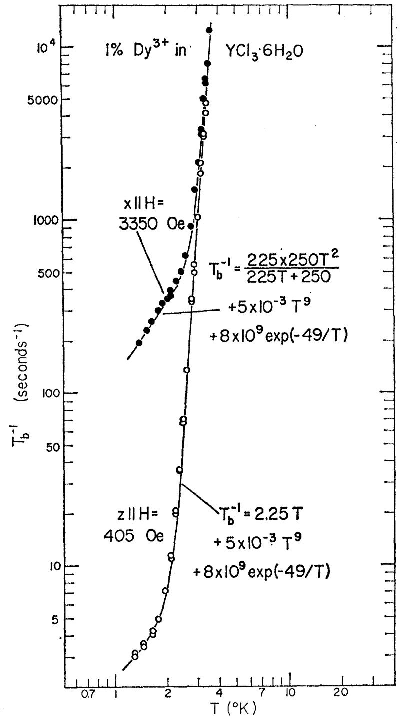

FIG. 5. Observed relaxation rate T_b^{-1} versus temperature for 1% Dy^{3+} in $YCl_3\cdot6H_2O$ for $H \parallel z$ and for $H \parallel x$.

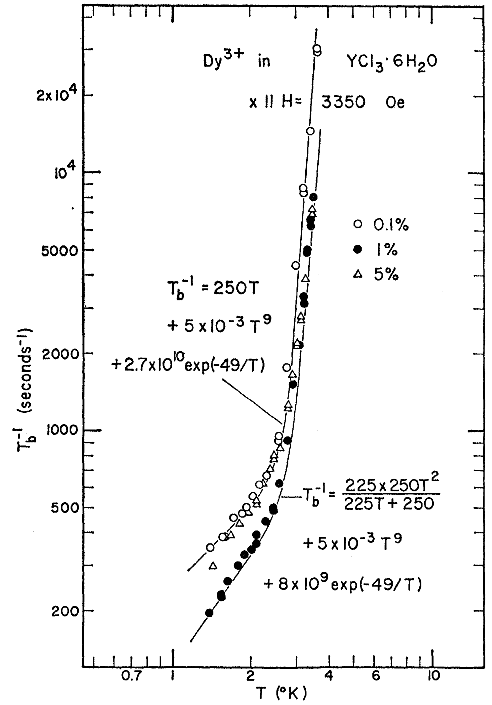

FIG. 6. Observed relaxation rate T_b^{-1} versus temperature for three concentrations of Dy^{3+} in $YCl_3\cdot6H_2O$ for H $\parallel x$.

Further relaxation data for the 1% crystal at $T=1.4$°K are shown in Fig. 7, as a function of the angle θ between H and z. The data display the surprising result that the rate is not symmetric with respect to the principal axes of the g tensor. However from Eq. (8) of I we recall that the direct process comes about through admixture with the excited states. But since the g tensors of the excited doublets will generally not be in the same orientation, this will make the direct

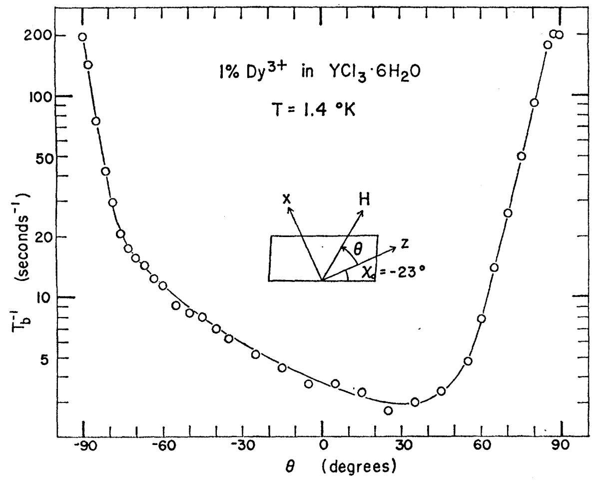

FIG. 7. Observed relaxation rate T_b^{-1} at resonance as a function of orientation for 1% Dy^{3+} in $YCl_3\cdot6H_2O$ at constant temperature $T=1.4$°K and frequency $\nu=9.36$ GHz. The magnetic field was rotated about the crystal b axis (y axis).

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[26] P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962).

process a complicated function of orientation. In Eq. (8) of I, the term $\langle a \,|\, \mathbf{H}\cdot\mathbf{J} \,|\, i \rangle$ will become

$$H \langle a(\theta) |\, J_x \sin\theta + J_z \cos\theta \,|\, i(\theta) \rangle,$$

where $a(\theta)$ and $i(\theta)$ will not necessarily be the same function of θ nor have the same symmetry. This is undoubtedly the reason for the skewed behavior of $T_b^{-1}(\theta)$ in Fig. 7.

C. Ce:YCl$_3$·6H$_2$O

Our resonance and relaxation measurements were made on crystals grown from 0.1% and 1% Ce^{3+} solutions. The measured parameters are given in Table I. The g factors are explained by assuming a nearly axial field, with the axis in the crystal plane parallel to z. For hexagonal site symmetry the $^2F_{5/2}$ ground multiplet of Ce^{3+} would split into pure J_z states $|\pm\frac{1}{2}\rangle$, $|\pm\frac{3}{2}\rangle$, and $|\pm\frac{5}{2}\rangle$. The $|\pm\frac{1}{2}\rangle$ state has $g_z = \Lambda = 0.86$, $g_x = g_y = 3\Lambda = 2.57$, reasonably close to the observed values for the ground doublet.

Relaxation data are shown in Fig. 8. For the 1% crystal the data are fit by

$$H \,\|\, x, \quad T_b^{-1} = 0.27T + 2.5\times10^{-5}T^9 + 2\times10^7 \times \exp(-60/T)\ \text{sec}^{-1}, \tag{10}$$

$$H \,\|\, z, \quad T_b^{-1} = 0.14T + 2.5\times10^{-5}T^9 + 2\times10^7 \times \exp(-60/T)\ \text{sec}^{-1}. \tag{11}$$

There seems to be a slight concentration dependence of the first term; however, the recovery was not strictly exponential, especially at low microwave powers, indicating some spectral diffusion. Measurements of $T_b^{-1}(\theta)$ at 1.4°K for the 0.1% crystal showed an anisotropy of 10:1, with a sharp skewed dip at $\theta = 10°$. The Orbach terms in Eqs. (10) and (11) indicate an excited state at $\Delta = 60\pm10°\text{K} \approx 42\ \text{cm}^{-1}$; there are no optical data to confirm this

D. Er:YCl$_3$·6H$_2$O

The splittings of the $^4\text{I}_{15/2}$ ground multiplet of Er^{3+} in YCl$_3$·6H$_2$O have been partially determined,[17] the first two excited states being at 16.91 and 37.07 cm^{-1}, respectively. Optical Zeeman studies[18] on the ground state yield the following parameters: $g_x = 0$, $g_y = 1.26$, $g_z = 13.26$, $\chi_0 = 76°$.

Our resonance and relaxation measurements were made on crystals grown from solutions containing 1% and 0.1% Er^{3+}, respectively. The resonance results indicated that one of the principal directions of the ground-state g tensor is in the crystal plane but that neither of the other two were, and that the orientation of these other two axes seemed to vary from sample to sample. This may have been caused by an imperceptible twinning of our samples; or possibly the Er^{3+} ion somehow reduces the site symmetry of the YCl$_3$·6H$_2$O host crystal. The resonance results on a 0.1% sample were: $g_z = 13.74\pm0.10$, $g_{\perp\,\text{min}} = 0.58\pm0.02$, $g_{\perp\,\text{max}} = 0.92\pm0.02$, $\chi_0 = 77\pm2°$. The $g_\perp$ factors were determined in the plane perpendicular to the z axis. For this 0.1% sample the direction corresponding to $g_{\perp\,\text{min}}$ seemed to be approximately 9° out of the crystal plane, but was as much as 20° for another sample.

Figure 9 shows some relaxation measurements as a function of temperature for two concentrations of Er^{3+} in YCl$_3$·6H$_2$O. The results are fit by the expressions

$$1\%,\ z \,\|\, H, \quad T_b^{-1} = 0.016 \coth(0.23/T) + 3.22\times10^6 \times \exp(-24.5/T)\ \text{sec}^{-1}, \tag{12}$$

1%, $z \perp H$ in crystal plane,

$$T_b^{-1} = 125T + 7.31\times10^6 \exp(-24.5/T)\ \text{sec}^{-1}, \tag{13}$$

0.1% $z \perp H$ in crystal plane,

$$T_b^{-1} = 165T + 8.8\times10^6 \exp(-24.5/T)\ \text{sec}^{-1}. \tag{14}$$

It is seen that in all three cases an Orbach process is demonstrated with the first excited energy level at $\Delta = 24.5°\text{K} = 17\ \text{cm}^{-1}$, in excellent agreement with the optically determined value. However, the strength of

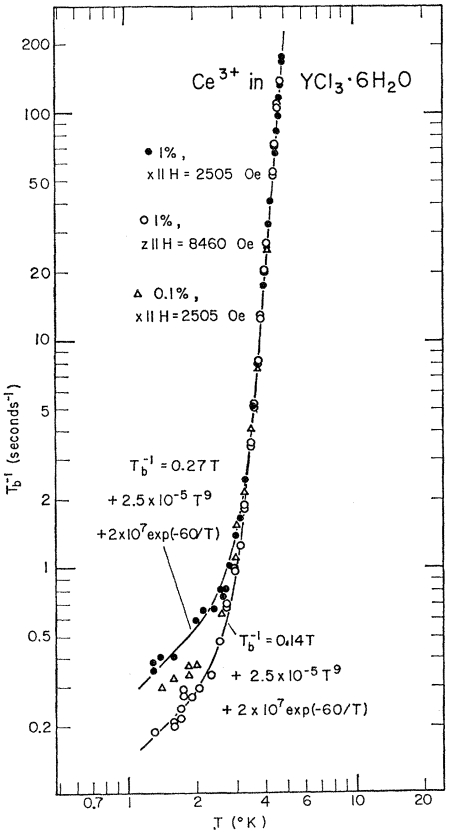

FIG. 8. Observed relaxation rate T_b^{-1} versus temperature for two concentrations of Ce^{3+} in YCl$_3$·6H$_2$O.

the Orbach process seems to depend rather strongly on sample orientation. This is probably for the same reason as in Nd^{3+} in $YCl_3 \cdot 6H_2O$, and suggests that the excited Zeeman splitting is very anisotropic. Relaxation measurements on concentrated $ErCl_3 \cdot 6H_2O$ have been reported by Weber,[24] who finds for $\mathbf{H} \parallel z$ an Orbach process $T_{10}^{-1} = 3.64 \times 10^6 \exp(-24.6/T)$ sec^{-1} in good agreement with our results.

The data in Fig. 9 indicate that the Raman process is very weak since no term in T^9 is needed to fit the data. From the observed relaxation data we may estimate that the Raman process is $CT^9 < 10^{-3} T^9$ sec^{-1}. The term $0.016 \coth(0.23/T)$ in Eq. (12) indicates a relatively weak direct process for $z \parallel H$. For $kT \gg h\nu$, this term may be replaced by $0.07T$. The concentration dependence was not checked for this orientation, but the observed fit to the coth form indicates that the true direct process is probably being observed here. The terms linear in T for the orientation $z \perp H$ are probably also manifesting a direct process. Since the observed rate is so fast for this orientation, a bottleneck of the direct process might be expected. However, the observed linewidths for the two samples for this orientation were 100 Oe for the 0.1% crystal, and 800 Oe for the 1% crystal. The effective bandwidth of phonons involved in the direct process relaxation is therefore large enough that the specific heat of the phonons remains large compared to the specific heat of the spin system. The slight apparent concentration dependence of T_b^{-1} for $z \perp H$ is probably due to a slight misorientation of the crystal, and it will be seen in Fig. 10 that the relaxation rate is very sensitive to angle for this orientation. Figure 10 shows some relaxation rate measurements for a sample of 0.1% $Er:YCl_3 \cdot 6H_2O$ at constant temperature $T = 1.39$°K as a function of the angle θ between H and z. The results are not quite symmetric with respect to the z axis; the maximum relaxation rate seems to occur at $\theta \approx 89°$, thus indicating that the excited-state g tensor is only slightly misaligned with respect to that of the ground state. The data can be nearly fitted with

$$T_b^{-1} = 10^{-6} H^2(\theta) \sin^2\theta \text{ sec}^{-1}, \qquad (15)$$

indicating that the ground state is only weakly connected to the excited states by the operator J_z.

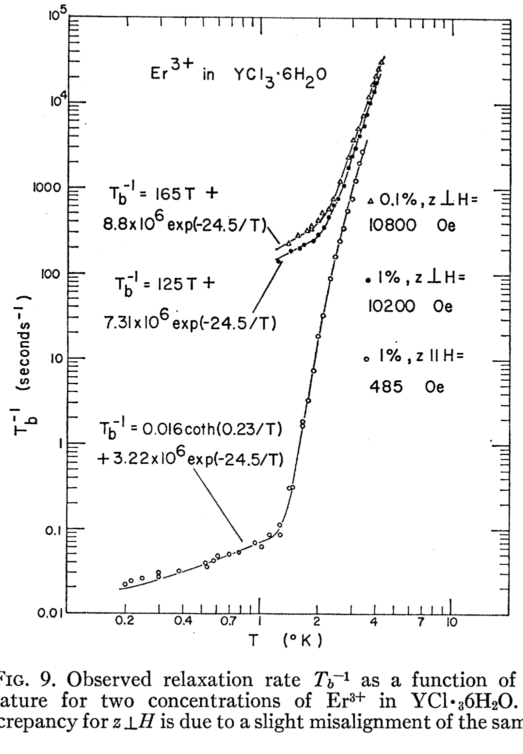

FIG. 9. Observed relaxation rate T_b^{-1} as a function of temperature for two concentrations of Er^{3+} in $YCl\cdot{}_36H_2O$. The discrepancy for $z \perp H$ is due to a slight misalignment of the samples.

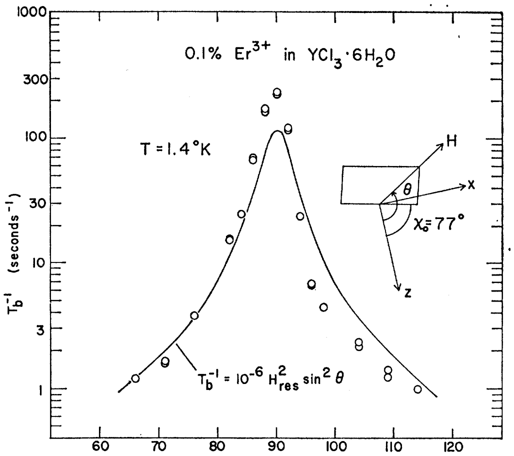

FIG. 10. Observed relaxation rate T_b^{-1} as a function of orientation between the magnetic field and the z axis at the constant temperature $T = 1.39$°K for 0.1% Er^{3+} in $YCl_3 \cdot 6H_2O$. The magnetic field was rotated about the normal to the crystal plane.

E. $Yb:YCl \cdot 6H_2O$

Magnetic resonance was observed for a 1% $Yb:YCl_3 \cdot 6H_2O$ crystal with the results of Table I. The g_x and g_y values are not well determined because the resonance signal was quite weak and the linewidth broadened from 17 Oe with $H \parallel z$ to more than 100 Oe with $\theta = 50°$. The signals were too weak to determine the hyperfine constants. Attempts to measure the relaxation rate also failed, probably because of inability to saturate the resonance. The $^2F_{7/2}$ ground multiplet of Yb^{3+} would split in a hexagonal field into these combinations of basis functions: $|\pm\frac{1}{2}\rangle$, $|\pm\frac{3}{2}\rangle$, and $\cos\phi\,|\pm\frac{5}{2}\rangle$ $\sin\phi\,|\mp\frac{7}{2}\rangle$. If the lowest doublet were predominantly $|\pm\frac{5}{2}\rangle$, this would predict $g_x = g_y = 0$, $g_z = 40/7 = 5.71$, not too far from those observed. The first excited state[19] is at 132 cm^{-1} so that the third-order Zeeman splitting will be quite small. Optical Zeeman studies[19] in $Yb:YCl_3 \cdot 6H_2O$ yield $g_x = g_y = 0$, $g_z = 5.65$, $\chi_0 = 71°$. Although our data indicates only that $g_x < 0.5$,

$g_y < 0.5$, it was thought that this crystal might actually have $g_\perp$ as small as a nuclear g factor, and thus would be suitable for use as a spin refrigerator.[4] However, McColl[27] did not observe any proton polarization enhancement upon rotation of a large field (~10 kOe) in the *ac* plane.

No paramagnetic resonance was found for $Sm:YCl_3 \cdot 6H_2O$ and for $Pr:YCl_3 \cdot 6H_2O$ in fields up to 19 kOe at $\nu = 9.3$ Gc.

IV. SUMMARY AND CONCLUSIONS

Magnetic resonance and spin bath relaxation has been measured for the Kramers ions Ce^{3+}, Nd^{3+}, Dy^{3+}, and Er^{3+} diluted into $YCl_3 \cdot 6H_2O$. Resonance was also observed for Yb^{3+} in $YCl_3 \cdot 6H_2O$ but the relaxation rate could not be measured, probably because of an inability to saturate the resonance line. The resonance results indicate the general feature that the rare-earth ions experience an effective crystalline field which is nearly C_6 or C_{3h} in character and that this pseudoaxis is perpendicular to the crystal twofold axis. Angular dependence of the relaxation rate and published optical Zeeman studies indicate, however, that the axis is not quite in the same direction for the excited states, even within a multiplet, as it is for the ground state. The direction of the pseudoaxis also depends on the ion under consideration. This latter result is in agreement with the x-ray structure since a C_2 site symmetry requires only that one principal direction of the g tensor be along the C_2 crystal axis. The other two principal directions of the g tensor will be determined by the crystal-field eigenfunctions. However, neither of these other two directions should display a C_6 or C_{3h} axial symmetry. The reason for the observed pseudohexagonal axis is not really understood.

The relaxation measurements show the same general features as similar measurements in hydrated crystals[25,26] and do not give evidence for cross relaxation as observed for anhydrous crystals such as LaF_3 in I. Usually a Raman process was found, of order $T_{1R}^{-1} \sim 10^{-4} T^9$ sec^{-1}. An exponential Orbach process was observed for all four ions. Except for Ce^{3+}, for which no optical data has been reported, the observed values of Δ are in excellent agreement with the optically determined values in the concentrated salts. The Orbach process displayed some angular dependence for Nd^{3+} and Er^{3+}, varying by nearly a factor of two for Nd^{3+} and approximately a factor of three for Er^{3+}. This is probably due to a large anisotropy in the excited state g factor. There was also evidence of a possible bottlenecked Orbach process with Dy^{3+}, which showed an increase by approximately a factor of three in the Orbach relaxation rate T_{1O}^{-1} when the concentration of Dy^{3+} was decreased from 1% to 0.1%. The direct process was displayed for all cases and was observed to be unusually anisotropic for Nd^{3+} and Er^{3+}, varying by 10^3 to 10^4. This is the largest anisotropy yet reported for paramagnetic relaxation. For orientations for which the direct process became most rapid, there was evidence of a phonon bottleneck for Nd^{3+} and Dy^{3+}, displayed by a T^2 temperature dependence. Attempts to check the concentration dependence of the bottleneck were somewhat thwarted by the fact that the magnetic resonance linewidth increased drastically with increasing concentration, probably due to crystal strains. The increased linewidth increases the effective bandwidth of phonons involved in the direct process and therefore increases their specific heat. Calculations of the mean free path for phonon scattering from the observed values of D yielded inconclusive results since it appeared that for Nd^{3+}, the hot phonons were being reflected once or twice before reaching the helium bath whereas for Dy^{3+}, they seemed to be scattered internally. The relaxation traces were usually exponential except for Nd^{3+} for the orientation at which a phonon bottleneck was observed. The angular dependence of the direct process relaxation rate for Ce^{3+} and Dy^{3+} displayed the unusual result that the rate was not symmetric with respect to the principal directions of the ground-state g tensor. However, this is probably because the principal directions of the g tensor of the excited state, which must be admixed into the ground state for Kramers ion relaxation, do not coincide with those of the ground state.

Since accurate wave functions and crystal-field parameters are not known, no attempts to estimate the relaxation rate were made using the phenomenological theory discussed in I. However, the experimental resonance and relaxation data should nevertheless be useful for further work with these crystals.

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[27] J. R. McColl (private communication).