

into a single sum:

$$\Delta\Phi_{ij} = \sum_p \sum_{k=1}^3 p S_{ijk} \Delta x_k.$$

These lattice sums are the first-order terms of a Taylor expansion around the orthorhombic nuclear coordinates^{4,5} representing the average between the final and initial positions of the nuclei. Thus the accuracy of the calculation is much better than in the case of an expansion

about the monoclinic initial positions, since now the second-order terms of the Taylor expansion are zero and moreover the orthorhombic coordinates are better known than the monoclinic ones. The initial position is $\mathbf{r}_0 + \frac{1}{2}\Delta\mathbf{r}$ and the final $\mathbf{r}_0 - \frac{1}{2}\Delta\mathbf{r}$, where \mathbf{r}_0 stands for the orthorhombic coordinates and $\Delta\mathbf{r}_0$ for the displacements of the nuclei in question at the ferroelectric transition.¹²

¹² J. Hablützel, *Helv. Phys. Acta* **12**, 489 (1939).

Dependence of Spin-Lattice Relaxation Time Upon Magnetic Field for Two Salts of Neodymium*

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Measurements made below 1.5°K of the spin-lattice relaxation rate T_1^{-1} of Nd^{3+} in lanthanum fluoride and lanthanum magnesium nitrate as a function of the separation δ of the levels of the ground doublet give clear evidence for a dependence $T_1^{-1} \propto \delta^3 \coth(\delta/2kT)$, as expected for the direct process. There is also a second contribution at lower fields in LaF_3 , $T_1^{-1} \propto \delta^3 \coth(\delta/2kT)$, which we believe arises from "forbidden" relaxation transitions in the neodymium ions which have a hyperfine structure. The relaxation rate for the forbidden transition has been calculated, and it has been shown that under certain circumstances it can be more rapid than the relaxation rate for allowed transitions. There is a third contribution which depends upon the concentration of Nd^{3+} and may be due to cross relaxation to coupled pairs of Nd^{3+} ions. In lanthanum magnesium nitrate there is a phonon bottleneck as well as the direct process. Both salts show an Orbach process above 2°K. A modification of the usual pulse saturation technique has been used to obtain these measurements which gives some advantages over the standard method.

I. INTRODUCTION

THERE has recently been considerable interest in spin-lattice relaxation processes in both iron group and rare-earth salts. A comprehensive review of the theory for the rare-earth ions has been given by Orbach.¹ Considerable experimental data on the dependence on the temperature T has been given for ions diluted in lanthanum ethyl sulphate (LaES) and lanthanum magnesium nitrate (LaMN) by Scott and Jeffries,² and in CaF_2 by Beirig, Weber, and Warshaw.³ The temperature dependence in specimens which are sufficiently dilute to show no concentration dependence of the relaxation rate T_1^{-1} may usually be expressed for ions with Kramers' degeneracy as

$$T_1^{-1} = AT + Be^{-\Delta/kT} + CT^9 \text{ sec}^{-1}. \quad (1)$$

Let $\delta = h\nu$ be the energy splitting of the ground doublet,

which is usually proportional to the applied magnetic field H , although hyperfine splitting becomes important in low fields. The first term, the "direct" process, is due to simultaneous electron-spin reversal and emission or absorption of a phonon of frequency ν ; for large values of $\delta/2kT$ it is more exactly given by

$$A(\delta/2k) \coth(\delta/2kT).$$

The second term arises from the Orbach process in which a phonon is absorbed to excite the ion out of the ground doublet into an excited state at Δ , and the subsequent emission of a second phonon of slightly different energy which leaves the ion in the other component of the ground doublet. The third term is due to the Raman process, which is similar to the Orbach process except that the intermediate state may be virtual so that, unlike the first two processes, the whole phonon spectrum is used. Under certain circumstances, usually only at such low temperatures that the direct process is dominant, the relaxation may become bottlenecked by the creation of too many phonons in a narrow band at ν , in which case the first term must be replaced by

$$D(\delta^2/4k^2) \coth^2(\delta/2kT),$$

which at small values of $\delta/2kT$ approaches DT^2 .

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¹ R. Orbach, *Proc. Roy. Soc. (London)* **A264**, 456 (1961).

² P. L. Scott and C. D. Jeffries, *Phys. Rev.* **127**, 32 (1962).

³ R. W. Bierig, M. J. Weber, and S. I. Warshaw, *Phys. Rev.* **134**, A1504 (1964).

Although the temperature dependence of Eq. (1) has been verified in a number of rare-earth salts, little work has been done on the dependence of T_1^{-1} on δ , i.e., on the frequency ν and the field H .⁴ The parameter A is expected to depend strongly upon δ ; B and C are expected to be independent of δ , as long as it is small compared to crystal-field splittings. Here we will be concerned primarily with the dependence of A on δ .

Two different direct relaxation mechanisms have been considered. Waller⁵ first discussed a process in which the dipolar fields from neighboring paramagnetic ions fluctuate because of the lattice vibrations, and the fluctuating fields induce relaxation transitions. This process is generally very weak in dilute salts and should vary with the concentration, because a reduction in the concentration reduces the dipolar field from neighboring ions. A Waller process would show a dependence

$$T_1^{-1} \propto \delta^3 \coth(\delta/2kT),$$

where one power of δ comes from the probability of creating or destroying a phonon of energy δ , and the other two from the density of states at δ . For this process $A \propto \delta^2$.

A second direct process has been considered by Kronig⁶ and by Van Vleck,⁷ in which the relaxation transitions of the electron spin are induced by fluctuations in the electrostatic crystal potential due to the surrounding ions, not necessarily paramagnetic. For a Kramers' salt there are no matrix elements of the crystal potential between the components of a doublet, and Kronig and Van Vleck considered admixtures of excited doublets, due to the Zeeman interaction, in order to obtain finite transition probabilities. This admixture introduces an additional factor proportional to H^2 , and therefore to δ^2 , so that for this process

$$T_1^{-1} \propto \delta^5 \coth(\delta/2kT).$$

Calculations of T_1^{-1} for this process are found to give magnitudes which correspond to the experimentally measured values, so that it is usually assumed to be the mechanism of the direct relaxation. For this process $A \propto \delta^4$.

In order to test this prediction we have measured the field dependence of T_1^{-1} for the neodymium ion Nd^{3+} in both LaMN and in LaF_3 ; the results of these measurements are presented in Secs. IV and V. The low-temperature results in LaMN are explicable in terms of a direct process with $A \propto \delta^4$, which becomes bottlenecked at the larger values of δ . The low-temperature results in LaF_3 show two concentration-independent

processes. The first, in which $A \propto \delta^4$, is interpreted as the usual Kronig-Van Vleck process. The second, in which $A \propto \delta^2$, is shown to be due not to the Waller process but rather to a process in which the admixture of excited states, which is needed to give a finite transition probability, is due to hyperfine interaction (hfs) $\mathcal{Q}\mathbf{I} \cdot \mathbf{J}$ rather than the Zeeman interaction $\Delta\beta\mathbf{H} \cdot \mathbf{J}$. As the hyperfine interaction has no dependence upon δ we expect such a process to have

$$T_1^{-1} \propto \delta^3 \coth(\delta/2kT),$$

i.e., $A \propto \delta^2$. In fact the ratio of this new hfs process to the Kronig-Van Vleck process is given roughly by

$$(\mathcal{Q}I/\Delta\beta H)^2,$$

as discussed in detail in Sec. II. The hfs in some rare-earth salts is quite large so that at fields not too much below those normally used for EPR the new process may become important. The fact that this ratio is found experimentally to be an order of magnitude larger in LaF_3 is explained by a more complete theory which we discuss in Sec. V.

The experimental techniques are discussed in Sec. III.

II. INFLUENCE OF HYPERFINE STRUCTURE ON SPIN-LATTICE RELAXATION RATES

Culvahouse, Unruh, and Brice⁸ have pointed out the importance of hyperfine interactions in the estimation of spin-lattice relaxation rates for Co^{2+} ions in lanthanum zinc nitrate. They use a model in which the direct relaxation process in the absence of hyperfine structure is described in terms of a fluctuating g value. The introduction of a hyperfine interaction then influences the relaxation rate in two ways: There is an admixture of wave functions due to the static hyperfine interaction, and also relaxation transitions can be caused by a fluctuating part of the hyperfine interaction.

In the rare-earth ions it is simpler to follow the approach of Orbach¹ and Scott and Jeffries² where both of these effects of the hyperfine interaction can be taken into account together. Both the Zeeman interaction and the hyperfine interaction are considered as static and part of the unperturbed Hamiltonian; relaxation is induced by fluctuations of the crystalline electric potential caused by fluctuations in the positions of neighboring ions due to lattice waves. The rare earths are simpler to discuss than the iron group as the spin-orbit coupling is large, and hence J is a good quantum number. The static crystalline potential separates and admixes the different $|J_z\rangle$ states. Fluctuations of the crystalline potential cause these separations, and, more important, these admixtures, to fluctuate with time. The matrix elements of the Zeeman interaction $\Delta\beta\mathbf{H} \cdot \mathbf{J}$ and of the hyperfine interaction $\mathcal{Q}\mathbf{I} \cdot \mathbf{J}$ are affected in

⁴ D. A. Davids and P. E. Wagner, Phys. Rev. Letters **12**, 141 (1964), have measured T_1^{-1} for Fe^{3+} in $\text{K}_2\text{Co}(\text{CN})_6$ where they find $A \propto H^4$. H. Honig and E. Stupp, Phys. Rev. Letters **1**, 275 (1958), have worked on silicon doped with phosphorus also finding a term proportional to H^4 .

⁵ I. Waller, Z. Physik **79**, 370 (1932).

⁶ R. de L. Kronig, Physica **6**, 33 (1939).

⁷ J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

⁸ J. W. Culvahouse, W. P. Unruh, and D. K. Brice, Phys. Rev. **129**, 2430 (1963); W. P. Unruh and J. W. Culvahouse, *ibid.* **129**, 2441 (1963).

the same way by the fluctuations in J_z , so that in terms of the model used by Culvahouse, Unruh, and Brice, the dynamic fluctuation of the g tensor and of the hyperfine interaction are closely related. Note that we have used \mathcal{Q} rather than the more usual notation \mathcal{A} for the free ion hyperfine interaction to avoid confusion later on in this section with the state $|a\rangle$; \mathcal{Q} is related to the hyperfine-structure parameters A and B in the spin Hamiltonian as the interaction $\mathcal{Q}\mathbf{I}\cdot\mathbf{J}$ becomes

$$AS_zI_z + B(S_xI_x + S_yI_y)$$

in the spin Hamiltonian describing only the ground doublet. The diagonal elements of these two expressions must be the same, so for one of the states $|a\rangle$ of the ground doublet

$$\mathcal{Q}M\langle a|J_z|a\rangle = AM\langle a|S_z|a\rangle.$$

But

$$\Lambda\langle a|J_z|a\rangle = g_{II}\langle a|S_z|a\rangle,$$

where Λ is the Landé g factor, so that

$$\mathcal{Q} = A\Lambda/g_{II}.$$

We have used M for the expectation values of $\langle I_z \rangle$ rather than the more usual m to avoid confusion with the m in the crystalline potential V_n^m .

We shall extend the calculation of the direct process relaxation rate to include the effects of hyperfine interaction. We shall assume familiarity with the Scott and Jeffries paper, and we shall largely use their notation, but it is necessary to review briefly some parts of their analysis.

The fluctuating crystal potential is expanded in components which transform like spherical harmonics:

$$\mathfrak{H}_c' = \epsilon \sum_{nm} V_n^m, \quad (2)$$

where ϵ is the strain produced by lattice vibrations, and the operators V_n^m phenomenologically describe the spin-phonon coupling. We have preferred to work in terms of operators V_n^m rather than v_n^m used by Scott and Jeffries, where

$$\begin{aligned} V_n^m &= \frac{1}{2}(v_n^m + v_n^{-m}), \\ V_n^{-m} &= \frac{1}{2}(v_n^m - v_n^{-m}), \end{aligned} \quad (3)$$

as the V_n^m are Hermitian, and therefore correspond more closely to the oscillation modes of the complex surrounding the rare-earth ion. The usual expression for the rate of the direct relaxation process given, e.g., by Scott and Jeffries, is

$$T_{1d}^{-1} = (3/2\pi\rho v^3\hbar)(\delta/\hbar)^3 \coth(\delta/2kT) \times \sum_{nm} |\langle a|V_n^m|b\rangle|^2. \quad (4)$$

For a Kramers' doublet there are no matrix elements of V_n^m between the two components, so that it is necessary to consider admixtures from excited Kramers' doublets due to the Zeeman interaction. We also propose to consider admixtures due to the hyperfine interaction.

We shall label the components of the ground doublet $|a\rangle$ and $|b\rangle$, and those of the excited doublet $|c\rangle$ and $|d\rangle$, but in addition we shall specify the expectation value of $\langle I_z \rangle = M$.

Before proceeding with the body of the calculation we wish to consider some general relationships between matrix elements. For all of the materials in which rare-earth ions have been studied the static crystal potential has rhombic or higher symmetry. This implies that the crystal potential comprises a series of terms:

$$\mathfrak{H}_{\text{crystal}} = \sum_{nm} \mathcal{U}_n^m$$

such that the values of m which occur never have adjacent values. For hexagonal symmetry in the ethyl sulphates, m has values 6 and 0, in the double nitrates 6, 3, 0, and in LaF₃ with rhombic symmetry the values are 6, 4, 2, 0. A consequence of this is that the states of the system do not contain all values of J_z , and in particular never adjacent values. Hence if there are finite matrix elements of J_z

$$\langle a|J_z|c\rangle = -\langle b|J_z|d\rangle, \quad (5a)$$

the matrix elements

$$\langle a|J_z|d\rangle = \langle b|J_z|c\rangle = 0. \quad (5b)$$

A further consequence is that the only finite matrix elements of J_+ and J_- are

$$\begin{aligned} \langle a|J_+|d\rangle &= \langle d|J_-|a\rangle = \langle c|J_+|b\rangle = \langle b|J_-|c\rangle, \\ \langle a|J_-|d\rangle &= \langle d|J_+|a\rangle = \langle c|J_-|b\rangle = \langle b|J_+|c\rangle, \end{aligned} \quad (6a)$$

and

$$\langle a|J_{\pm}|c\rangle = \langle d|J_{\pm}|b\rangle = 0. \quad (6b)$$

The matrix elements of V_n^m are generally related as follows:

$$\langle c|V_n^m|b\rangle = -(-1)^n \langle a|V_n^m|d\rangle, \quad (7a)$$

$$\langle c|V_n^m|a\rangle = (-1)^n \langle b|V_n^m|d\rangle. \quad (8a)$$

For materials where the static crystal potential does not contain consecutive values of m , the matrix elements (7a) vanish for even m and those of (8a) vanish for odd m , so that

$$\langle c|V_n^m|b\rangle = -\langle a|V_n^m|d\rangle \quad \text{odd } m, \quad (7b)$$

$$\langle c|V_n^m|a\rangle = \langle b|V_n^m|d\rangle \quad \text{even } m. \quad (8b)$$

If the symmetry of the crystal potential were lower than rhombic it would be possible to have static crystal-field components \mathcal{U}_n^m with adjacent values of m . Under these circumstances the matrix elements (5b) and (6b) are not zero, and the restrictions which reduce (7a) and (8a) to (7b) and (8b) are not valid. The calculation which follows would then be a good deal more complicated.

With these relationships in mind we now consider the Hamiltonian for the combined Zeeman and hyperfine interactions when the external magnetic field H is

applied parallel to the crystal axis:

$$\mathcal{H} = (\Delta\beta H + \mathcal{Q}M)J_z + \frac{1}{2}\mathcal{Q}(J_+I_- + J_-I_+). \quad (9)$$

The finite matrix elements of the second term can be factorized, for example

$$\langle a, M | \frac{1}{2}\mathcal{Q}J_+I_- | d, M+1 \rangle = \frac{1}{2}\mathcal{Q}\langle a | J_+ | d \rangle \langle M | I_- | M+1 \rangle. \quad (10)$$

The first term in (9) causes admixture into the ground doublet of excited states with the same value of M which produces relaxation of the "allowed" EPR transitions in which

$$\Delta J_z = \pm 1, \quad \Delta I_z = 0,$$

with

$$T_{1d}^{-1} = K(\Delta\beta H + \mathcal{Q}M)^2 \times \sum_{cd} \frac{\sum_{nm} |\langle a | J_z | c \rangle \langle c | V_n^m | b \rangle + \langle a | V_n^m | d \rangle \langle d | J_z | b \rangle|^2}{\Delta_{cd}^2}, \quad (11)$$

where

$$K = (3/2\pi\rho v^5\hbar)(\delta/\hbar)^3 \coth(\delta/2kT) \quad (12)$$

$$T_{1d}^{-1} = K\mathcal{Q}^2 \sum_{cd} \frac{\sum_{nm} |\langle a, M | J_+I_- | d, M+1 \rangle \langle d, M+1 | V_n^m | b, M+1 \rangle|^2}{\Delta_{cd}^2} = K\mathcal{Q}^2 |\langle M | I_- | M+1 \rangle|^2 \sum_{cd} \frac{\sum_{nm} |\langle a | J_+ | d \rangle \langle d | V_n^m | b \rangle|^2}{\Delta_{cd}^2}. \quad (14)$$

The expression for the transition

$$\Delta J_z = -1, \quad \Delta I_z = +1$$

will be similar.

Suppose now that the external field is applied in the x direction. Keeping the z axis as the crystal axis the Hamiltonian for the combined Zeeman and hyperfine interactions is

$$\mathcal{H} = \frac{1}{2}\Delta\beta H(J_+ + J_-) + \mathcal{Q}J_zI_z + \frac{1}{2}\mathcal{Q}(J_+I_- + J_-I_+). \quad (15)$$

In first-order perturbation theory the eigenstates of the Kramers' doublets become

$$(1/\sqrt{2})\{|a\rangle \pm |b\rangle\}$$

and

$$(1/\sqrt{2})\{|c\rangle \pm |d\rangle\}.$$

To avoid the confusion caused by such long notation, and to emphasize the essential similarity between expressions for T_{1d}^{-1} for the two directions of the external field, the new states will be labeled

$$(1/\sqrt{2})\{|a\rangle + |b\rangle\} = |a^*\rangle,$$

$$(1/\sqrt{2})\{|a\rangle - |b\rangle\} = |b^*\rangle,$$

$$(1/\sqrt{2})\{|c\rangle + |d\rangle\} = |c^*\rangle,$$

and

$$(1/\sqrt{2})\{|c\rangle - |d\rangle\} = |d^*\rangle.$$

and Δ_{cd} is the energy of the excited doublet $|c\rangle$ and $|d\rangle$. The sum \sum_{cd} is to be taken over all excited doublets. Using the relationships (5) to (8) expression (11) reduces to

$$T_{1d}^{-1} = 4K(\Delta\beta H + \mathcal{Q}M)^2 \times \sum_{cd} \frac{\sum_{nm} |\langle a | J_z | c \rangle \langle c | V_n^m | b \rangle|^2}{\Delta_{cd}^2}. \quad (13)$$

All of the expressions for T_{1d}^{-1} we shall derive comprise two terms like expression (11), one due to admixture of each of the excited states $|c\rangle$ and $|d\rangle$. These are always equal so that the expression for T_{1d}^{-1} always simplifies to an expression like (13). In what follows we shall give only the simpler expression.

The second term in (9) produces admixtures of excited states with different M and causes relaxation of the "forbidden" EPR transitions where

$$\Delta J_z = \pm 1, \quad \Delta I_z = \mp 1.$$

For example, for $\Delta J_z = +1, \Delta I_z = -1$ the relaxation rate is

We are interested in the matrix elements of J_z, J_+, J_- and V_n^m between these states. The finite matrix elements are

$$\langle a^* | J_z | d^* \rangle = \langle a | J_z | c \rangle,$$

$$\langle b^* | J_z | c^* \rangle = -\langle b | J_z | d \rangle,$$

$$\langle a^* | J_+ + J_- | c^* \rangle = \langle b^* | J_+ + J_- | d^* \rangle = \langle a | J_+ + J_- | d \rangle, \quad (16)$$

$$\langle a^* | V_n^m | d^* \rangle = \langle b^* | V_n^m | c^* \rangle = -\langle a | V_n^m | d \rangle,$$

$$\langle a^* | V_n^m | c^* \rangle = \langle b^* | V_n^m | d^* \rangle = \langle a | V_n^m | c \rangle.$$

The first two terms in (15) cause admixtures which relax the "allowed" EPR transitions, but each term admixes a different component of the excited doublet. As the various V_n^m are assumed to be uncorrelated the two terms contribute separately giving

$$T_{1d}^{-1} = K(\Delta\beta H)^2 \sum_{cd} \frac{\sum_{nm} |\langle a^* | J_+ + J_- | c^* \rangle \langle c^* | V_n^m | b^* \rangle|^2}{\Delta_{cd}^2} + 4K\mathcal{Q}^2 M^2 \sum_{cd} \frac{\sum_{nm} |\langle a^* | J_z | d^* \rangle \langle d^* | V_n^m | b^* \rangle|^2}{\Delta_{cd}^2} = K(\Delta\beta H)^2 \sum_{cd} \frac{\sum_{nm} |\langle a | J_+ + J_- | d \rangle \langle d | V_n^m | b \rangle|^2}{\Delta_{cd}^2} + 4K\mathcal{Q}^2 M^2 \sum_{cd} \frac{\sum_{nm} |\langle a | J_z | c \rangle \langle c | V_n^m | b \rangle|^2}{\Delta_{cd}^2}. \quad (17)$$

The third term in (15) provides relaxation of the "forbidden" EPR transitions with

$$T_{1d}^{-1} = K \alpha^2 \sum_{cd} \frac{\sum_{nm} |\langle a^*, M | J_+ I_- | c^*, M+1 \rangle \langle c^*, M+1 | V_n^m | b^*, M+1 \rangle|^2}{\Delta_{cd}^2}$$

$$= K \alpha^2 |\langle M | I_- | M+1 \rangle|^2 \sum_{cd} \frac{\sum_{nm} |\langle a | J_+ | d \rangle \langle d | V_n^m | b \rangle|^2}{\Delta_{cd}^2}. \quad (18)$$

As one would expect, (18) and (14) are always identical, and at low fields (17) and (13) are also identical.

Our primary concern in this paper is with the dependence of the relaxation rate upon the applied field H . In addition to the explicit field dependence of expressions (17) and (13) all of the rates have an implicit field dependence because K contains the separation δ of the energy levels which is a function of field. The relationship between δ and H can be written explicitly only when $\Delta\beta H \gg \alpha M$ or $\Delta\beta H \ll \alpha M$; we shall limit ourselves to the former as our experimental results are for this approximation. The value of δ to be used in evaluating K in each of the relaxation rates is then, from first-order perturbation theory,

$$\text{for (13)} \quad \delta = (\Delta\beta H + \alpha M) \langle a | J_z | b \rangle, \quad (19)$$

$$\text{for (14)} \quad \delta = (\Delta\beta H + \alpha(M + \frac{1}{2})) \langle a | J_z | b \rangle, \quad (20)$$

$(M + \frac{1}{2})$ becomes $(M - \frac{1}{2})$ for the other forbidden transition.

$$\text{For (17)} \quad \delta = (\Delta\beta H + \alpha M) \langle a^* | J_+ + J_- | b^* \rangle, \quad (21)$$

$$\text{for (18)} \quad \delta = (\Delta\beta H + \alpha(M + \frac{1}{2})) \langle a^* | J_+ + J_- | b^* \rangle. \quad (22)$$

Again $(M + \frac{1}{2})$ becomes $(M - \frac{1}{2})$ for the other forbidden transition. In these expressions the second-order corrections to δ of order α^2/δ have been neglected.

III. EXPERIMENTAL TECHNIQUES

We have made measurements of the relaxation time of Nd^{3+} contained as an impurity in LaF_3 for a magnetic field range of 100 to 13 000 Oe and in LaMN over the range of 2240 to 4580 Oe. The method used is essentially the observation of the transient behavior of the microwave paramagnetic resonance signal, which is just proportional to the spin polarization. We always examined only the single resonance line of the even-even Nd isotopes, for which $\delta = g\beta H$. Although a number of different spectrometers were required to cover the frequency range, the basic technique, which we shall describe in some detail, was the same throughout.

The pulse-recovery method of relaxation time measurement used by Scott and Jeffries² requires a large pulse of microwave power to saturate partially the spin system, and then a low-level monitoring power to observe the recovery to thermal equilibrium. This method suffers from the disadvantage of giving weak signals because the monitor power level must be very low to prevent any enhancement of the recovery rate by the

microwave field. The problem is particularly severe when long relaxation times are involved and the power level must be maintained below 10^{-8} to 10^{-9} W.

The method we have used to overcome this difficulty works as follows: At time $t=0$ the microwave field has been on at a high enough level and for a long enough time to have saturated the spins; it is then turned off for a measured period of time τ_1 after which time the spins have reached a polarization

$$P(\tau_1) = P_0(1 - \exp[-\tau_1/T_1]),$$

where P_0 is the thermal equilibrium value of P and is a function of both the magnetic field and temperature of the lattice

$$P_0 = \tanh(g\beta H/2kT).$$

The power is then turned on again and the signal observed on an oscilloscope as the spins resaturate [Fig. 1(a)]. The difference between the height of the signal when the power is first turned on again and the height after the spins have reached their maximum saturation is proportional to $P(\tau_1)$. Next the experiment is repeated with a longer τ_2 [Fig. 1(b)], and so on for various values of τ , including an experiment at $\tau \gg T_1$ designed to give a reference signal proportional to P_0 . T_1 is then determined from the slope of a plot of $\ln[P_0 - P(\tau)]$ versus τ . The measurements of $P(\tau)$ are made directly on the oscilloscope face. The advantage of our method over the pulse recovery method is that the power level during the relaxation process can be reduced to an arbitrarily low point while the power level when signals are observed may be as high as desired.

In practice the microwave power can be switched off

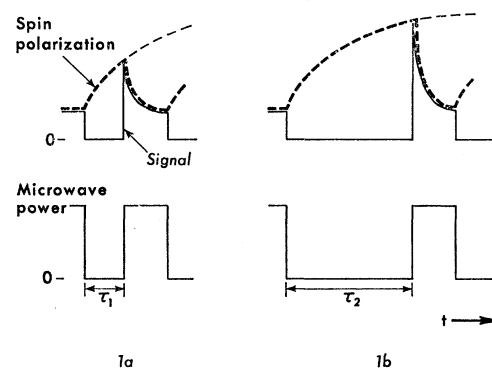


FIG. 1. Spin polarization, signals, and microwave power as a function of time during relaxation time measurements.

either with a diode switch, which prevents the microwaves reaching the cavity, or by switching the magnetic field off resonance. The latter method has the advantage that relaxation times may be measured at fields other than the resonance field, but it can be used only for specimens with long relaxation times as it is difficult to switch the field appreciably in less than 5 sec.⁹ For LaF₃ containing 0.1% Nd, T_1 is 23 sec at 0.2°K, so that we were able to use this technique to measure relaxation times from 100 to 2100 Oe using a single microwave frequency of 9.7 kMc/sec in a low-temperature spectrometer operating at 0.2°K, described by Ruby, Benoit, and Jeffries.¹⁰ The spin polarization P was measured after the spins had relaxed at a lower field for a period of τ sec by rapidly returning the field to the resonance value and observing the signal strength before the spins had time to return to thermal equilibrium. Since it was not easy to return the field to the exact resonance value quickly, the field was in practice swept through the resonance value and the signal height was measured on an oscilloscope as the field passed the resonance value. This experiment can be done with two different starting conditions. Firstly, one can allow the spin system to come to thermal equilibrium at a field a little below the resonance field. Then after pulsing to the lower field the initial polarization P is greater than the equilibrium value P_0 at the lower field. Secondly, one can allow the system to come to equilibrium on resonance under conditions of saturation, so that $P=0$. Then after pulsing to lower fields, P is less than P_0 . The results obtained using these two methods are in excellent agreement. The field was always switched in a time fast compared with the spin-lattice relaxation time so that a correction for the relaxation processes during switching was unnecessary.

Measurements in LaF₃ at fields above 2100 Oe and in LaMN were made by switching the microwave power rather than the field. They were made at a temperature of about 1.4°K in a conventional paramagnetic resonance spectrometer whose frequency was tunable. The high-power levels permissible during signal measurements made it possible to use a simple video detector. However, the shorter relaxation times encountered, both because of the higher temperatures and higher fields, prevented the use of a field switching technique; consequently diode switches were used to control the microwave power. Two switches were needed to cover the frequency range from 8.8 to 60 kMc/sec, one built into X-band wave guide using two Sylvania 1N419 diodes (these are no longer available) that covered the range from 8.8 to 18 kMc/sec, and a second in 6-mm wave guide using one type 1N270 diode and covering the range from 26 to 60 kMc/sec. Since the switches did not always give an adequate on-off

⁹ Honig and Stupp⁴ earlier used a field switching technique in measuring the long T_1 in phosphorus doped Si.

¹⁰ R. H. Ruby, H. Benoit, and C. D. Jeffries, Phys. Rev. 126, 51 (1962).

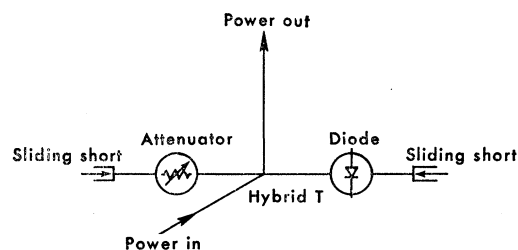


FIG. 2. Microwave switch with high on-off ratio.

ratio when inserted directly into the microwave system, the scheme of Fig. 2 was employed.¹¹ The system is essentially a bridge which may be balanced to give zero power output with the switch in one position. (The "positions" of the switch are determined by the polarity of the voltage across the diode.) When the switch is in the other position, the bridge is no longer balanced and output power is obtained. On-off ratios of 30 dB are easily obtained at all frequencies, but the insertion loss may be as high as 25 dB. In principle, our technique could be operated to advantage by turning the klystron off during the relaxation periods, eliminating the need for diode switches; but we found that, because of the design of our klystron power supplies, this simpler method was not feasible.

IV. RESULTS FOR Nd³⁺ IN LANTHANUM MAGNESIUM NITRATE

The relaxation measurements were made on a crystal of LaMN containing 1% neodymium isotopically enriched to 98.5% even-even isotopes. The crystal came from the same batch as the one used by Scott and Jeffries. The relaxation was measured with the external field in the direction perpendicular to the crystal axis for which $g_1=2.70$. For the parallel orientation the small value $g_{11}=0.36$ precluded observation of resonance for fields available to us. Measurements were made from 8.42 to 17.23 kMc/sec using the diode switching technique described in Sec. III and a tunable microwave cavity with video detection, except below 10 kMc/sec where a superheterodyne receiver was used.

The results of Scott and Jeffries² show that the direct process is seriously bottlenecked at 35 kMc/sec but not at 9.4 kMc/sec. In order to determine how serious the bottleneck was in our crystal, two measurements of the temperature dependence of T_1 were made at the high-frequency end of our range. The results of these measurements are shown in Fig. 3. The solid curves are plots of the equation

$$T_1^{-1} = B e^{-47.6/T} + T_1^{*-1}, \quad (23a)$$

where

$$T_1^{*-1} = [A(\delta/2k) \coth(\delta/2kT)]^{-1} + [D(\delta/2k)^2 \coth^2(\delta/2kT)]^{-1}. \quad (23b)$$

¹¹ This method of obtaining high on-off ratios with relatively poor diodes was suggested to us by Dr. P. L. Scott.

Equation (23b) gives the expected behavior² of a bottlenecked direct process. The Raman term in Eq. (1) has been omitted as this was found to be insignificant by Scott and Jeffries,² and the value of Δ in the Orbach term has been taken from Scott and Jeffries results. We have used

$$B = 9.3 \times 10^9 \text{ sec}^{-1}$$

to fit the value of $T_1 = 8.6$ msec at 2.61°K , which was found to be independent of frequency between 9 and 12.3 kMc/sec; this compares with $6.3 \times 10^9 \text{ sec}^{-1}$ found by Scott and Jeffries. We have also used

$$A = 1.66\nu^4 \times 10^{-40} \text{ sec}^{-1} (\text{°K})^{-1},$$

where ν is in c/sec, and $D = 16$, although D can be varied between 13 and 23 without making the fit with the experimental points very much worse.

At 9.37 kMc/sec the value of A is 1.3 compared with 1.7 found by Scott and Jeffries; and our value of D may be compared with that of 35 found by Scott and Jeffries in their crystal at 35 kMc/sec. We have previously assumed that D is a constant, but it is expected to be proportional to the width of the EPR line,² and the lines do generally become wider at high frequencies. This may account for the difference between our value of D and that of Scott and Jeffries, as otherwise the two crystals are almost identical.

The measurements of relaxation time as a function of frequency were made at around 1.4°K so as to make the contribution from the Orbach process negligible. As data were taken at different temperatures the quantity $\ln(A^{-1})$, where

$$A^{-1} = T_1(\delta/2k) \coth(\delta/2kT) - [D(\delta/2k) \coth(\delta/2kT)]^{-1} \quad (24)$$

has been plotted as a function of $\ln \nu$ in Fig. 4. The size of the bottleneck correction varies between 45% at the

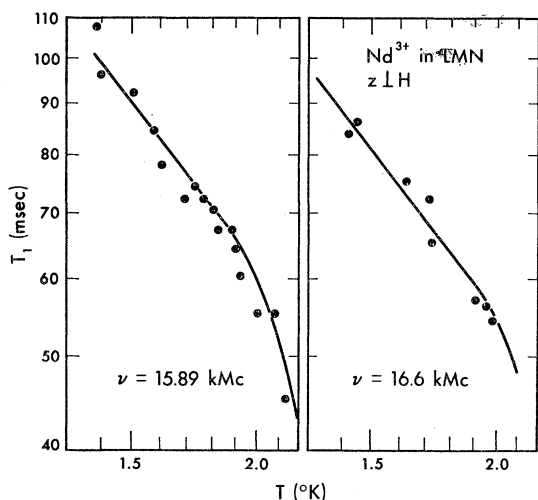


FIG. 3. A plot of $\ln T_1$ versus $\ln T$ at two microwave frequencies ν .

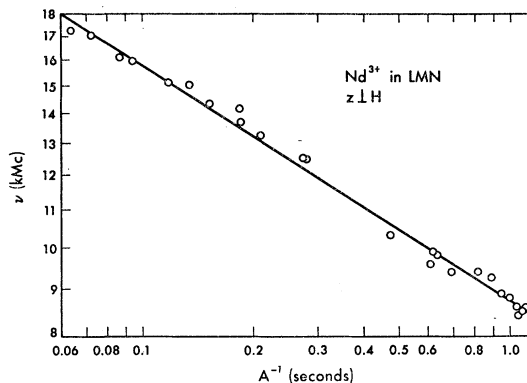


FIG. 4. A plot of $\ln \nu$ versus $\ln A^{-1}$, where A^{-1} is defined by Eq. (24).

highest frequency and 4% at the lowest frequency. As $A \propto \delta^4$ this graph is expected to be a straight line of slope 4. The slope of the best straight line through the points is 3.8 ± 0.3 where a large part of the error arises from the uncertainty in the size of D . Any possible variation of the size of D with frequency will lie within the uncertainty in the value of D , so it has been neglected. These results confirm the expected δ^4 dependence of the parameter A .

V. RESULTS FOR Nd^{3+} IN LaF_3

Two crystals of LaF_3 , containing 0.1% and 1.0% Nd^{3+} of natural isotopic abundance as an impurity, were obtained from Varian Associates who stated that the doping level is accurate to within a few percent. The EPR has been studied in detail by Baker and Rubins.¹² The crystals are complicated; there are six inequivalent sites in the unit cell with

$$g_x = 1.356 \pm 0.006,$$

$$g_y = 1.092 \pm 0.005,$$

and

$$g_z = 3.11 \pm 0.03.$$

The c axis of the g tensors are inclined at an angle of $45 \pm 2^\circ$ with respect to the crystalline z axis. Largely because of these complications, no wave functions are known for this salt, with the result that our interpretations of the data must be made on the basis of the field and temperature dependence of T_1 and cannot be put on a firm quantitative footing. Schulz¹³ has studied the temperature dependence of the spin-lattice relaxation time and finds a direct, an Orbach, and a Raman process. The direct process is unusually weak: at 1.5°K and in a field $H = 2100$ Oe, $T_1 = 3$ sec; at $T = 0.2^\circ\text{K}$, $T_1 = 23$ sec. It is the long relaxation time which led us to investigate the field dependence.

Below $\sim 1.5^\circ\text{K}$ the relaxation proceeds only by the

¹² J. M. Baker and R. S. Rubins, Proc. Phys. Soc. (London) 78, 1353 (1961).

¹³ M. Schulz (to be published).

“direct process” for which the temperature dependence is

$$T_{1d}^{-1} \propto \coth(\delta/2kT).$$

The results of many measurements of the total relaxation rate T_1^{-1} over the range $0.18 < T < 3^\circ\text{K}$ and at various values of H (for $H \parallel z$) are shown in Fig. 5 (which includes the data of Schulz at 2100 Oe). The relaxation rate does vary as $\coth(\delta/2kT)$ below 1.5°K , although at most fields it was possible to show only that $T_1^{-1} \propto T$ because $\coth(\delta/2kT)$ was not appreciably saturated. At 2100 Oe the saturation of $\coth(\delta/2kT)$ is clearly observed, and it would seem reasonable to assume that the temperature dependence is the same at all fields. Above 2°K , T_1 becomes independent of magnetic field and varies as $\exp(-60/T)$, corresponding to the Orbach process. The data for the field dependence of T_{1d}^{-1} for H parallel to z have been reduced to $T=0$ by plotting $\tanh(\delta/2kT)T_{1d}^{-1}$ as a function of H in Fig. 6. The solid curve is the reduced relaxation rate

$$T_{1d}^{-1} \tanh(\delta/2kT) = 0.86 \times 10^{-4} C^2 H + 2.1 \times 10^{-12} H^3 + 4.5 \times 10^{-19} H^5 \text{ sec}^{-1}, \quad (25)$$

where C is the percent concentration of the neodymium ions, and H is the field in Oe.

There can be little doubt that the term in H^5 is the Kronig-Van Vleck process, as that is the only process which is expected to have such a field dependence. The H^3 term could be due to a Waller process, but it is too large by several orders of magnitude and does not have the concentration dependence one would expect for the Waller process. We propose to show that it is probable that the H^3 term arises from the hfs relaxation process discussed in Sec. II. We shall also briefly discuss the possibility that the contribution which varies as $C^2 H$ is due to cross relaxation to pairs of closely coupled neodymium ions.

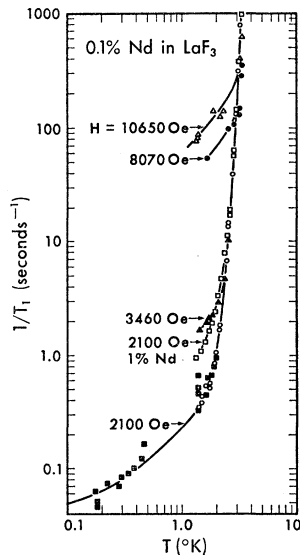


FIG. 5. Observed relaxation rate versus absolute temperature at several H fields for $0.1\% \text{ Nd}^{3+}$ in LaF_3 . The data shown as (\square) are for $1\% \text{ Nd}^{3+}$ in LaF_3 .

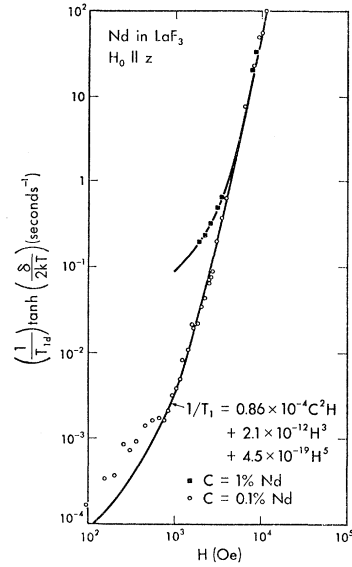


FIG. 6. Reduced relaxation rate $T_{1d}^{-1} \tanh(\delta/2kT)$ versus magnetic field H for 1% and 0.1% Nd in LaF_3 .

The relaxation rate for the Kronig-Van Vleck process in LaF_3 is an order of magnitude smaller than it is in LaES for H parallel to z . The value of $\Delta_{cd} = 60^\circ\text{K}$ for the first excited doublet, from the temperature dependence of the Orbach process, is considerably smaller than the value for Nd in LaES . Hence it appears that

$$\langle a | J_z | c \rangle \langle c | V_n^m | b \rangle$$

must be considerably smaller in LaF_3 .

To explain the H^3 term we suggest that the relaxation rate of the “forbidden” transitions for neodymium ions with hfs (20% of Nd isotopes have $I \neq 0$) given by expression (14), is greater than that of the ions without hfs for which the rate is given by expression (13) with \mathcal{Q} equal to zero. These ions then relax by cross relaxation to those with hyperfine structure, since the paramagnetic resonance lines overlap. The mechanism we envisage is illustrated by Fig. 7. When an ion without hfs makes a transition from its upper to lower state one of the “allowed” transitions a occurs for an ion with hyperfine structure [transitions b and c occur also but

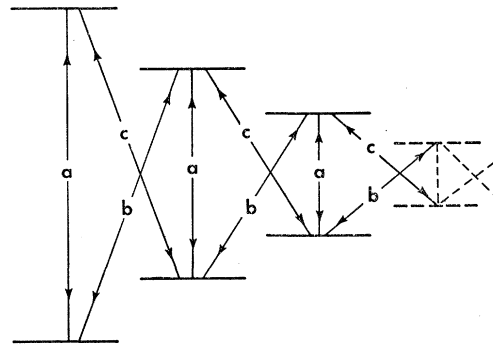


FIG. 7. Schematic energy level diagram showing the allowed transitions “ a ” and the forbidden transitions “ b ” and “ c .”

with a considerably lower probability by a factor of $(\mathcal{A}/h\nu)^2$. The ion with hyperfine structure then relaxes by a rapid transition b or c .

In the relaxation measurements we observe the recovery of the signal from one of the six ions in the unit cell which has no hyperfine structure. Hence 13% of all of the Nd ions contribute to this signal. The relaxation times observed are so long that it is probable that all of the forbidden EPR lines of all of the isotopes with hyperfine structure contribute to the cross-relaxation process. As the relaxation rate is proportional to \mathcal{A}^2 , Nd¹⁴³ ions relax about three times as rapidly as Nd¹⁴⁵ ions, so we assume that the 12% Nd¹⁴³ ions are mainly

responsible for the cross relaxation. Hence, there are about as many rapidly relaxing ions as there are ions contributing to the EPR line, so the relaxation rate of the latter becomes nearly equal to that of the fast relaxers. If the cross-relaxation rate is much faster than either the rate $T_{1d}(e)^{-1}$ for ions without hfs or the rate $T_{1d}(o)^{-1}$ for the forbidden transitions for those with hfs, the observed relaxation rate is given by

$$T_1^{-1} = T_{1d}(o)^{-1} + T_{1d}(e)^{-1} = C_1 H^3 \coth(\delta/2kT) + C_2 H^5 \coth(\delta/2kT), \quad (26)$$

where from (14) and (20), and neglecting $\mathcal{A}M$ in comparison with $\Lambda\beta H$:

$$C_1 = \frac{3(\Lambda\beta)^3 |\langle a|J_z|b\rangle|^3}{2\pi\rho\nu^5\hbar^4} \mathcal{A}^2 \left\{ [|\langle M|I_-|M+1\rangle|^2]_{\text{av}} \sum_{cd} \frac{\sum_{nm} |\langle a|J_+|d\rangle \langle d|V_n^m|b\rangle|^2}{\Delta_{cd}^2} + [|\langle M|I_+|M-1\rangle|^2]_{\text{av}} \sum_{cd} \frac{\sum_{nm} |\langle a|J_-|d\rangle \langle d|V_n^m|b\rangle|^2}{\Delta_{cd}^2} \right\}, \quad (27)$$

and from (14) and (20) with $\mathcal{A}=0$;

$$C_2 = \frac{3(\Lambda\beta)^3 |\langle a|J_z|b\rangle|^3}{2\pi\rho\nu^5\hbar^4} 4(\Lambda\beta)^2 \times \sum_{cd} \frac{\sum_{nm} |\langle a|J_z|c\rangle \langle c|V_n^m|b\rangle|^2}{\Delta_{cd}^2}. \quad (28)$$

$[|\langle M|I_-|M+1\rangle|^2]_{\text{av}}$ is the average value of

$$|\langle M|I_-|M+1\rangle|^2$$

over all values of M , and is $21/2$ for $I=7/2$;

$$[|\langle M|I_+|M-1\rangle|^2]_{\text{av}}$$

has the same value. One may roughly estimate the ratio of the two contributions in (26) to be of order $(\mathcal{A}I/\Lambda\beta H)^2$. Using the spin-Hamiltonian parameters for any of the Nd salts listed by Bowers and Owen¹⁴ one obtains for

$$\mathcal{A} = A\Lambda/g_{11} = 235 \text{ Mc/sec}$$

for Nd¹⁴³. Using this value we obtain

$$(\mathcal{A}I/\Lambda\beta H)^2 = 6.6 \times 10^5 H^{-2},$$

predicting a ratio

$$C_1/C_2 = 6.6 \times 10^5.$$

The experimental values of C_1 and C_2 from Eq. (25) give a ratio of 4.7×10^6 . This difference may be accounted for by the values of the matrix elements in (27) and (28). To get the experimental value of C_1/C_2

one requires that

$$\sum_{cd} \frac{\sum_{nm} |\langle a|J_+|d\rangle \langle d|V_n^m|b\rangle|^2 + |\langle a|J_-|d\rangle \langle d|V_n^m|b\rangle|^2}{\Delta_{cd}^2} = 34 \sum_{cd} \frac{\sum_{nm} |\langle a|J_z|c\rangle \langle c|V_n^m|b\rangle|^2}{\Delta_{cd}^2}. \quad (29)$$

The long relaxation time indicates that the matrix elements on the right-hand side of this expression are smaller than usual for neodymium so that the relationship is not unreasonable. Although one cannot evaluate the matrix elements one can from experimental measurements obtain some further information. The value of T_1^{-1} in the region where the H^5 term dominates was measured with H perpendicular to the z axis. The values of T_1^{-1} for H parallel and perpendicular to the z axis were roughly in the ratio of the squares of the values of H needed for resonance. The measurements were done at the same frequency so that δ and K remained constant. Comparison of Eqs. (13) and (17), when $\mathcal{A}=0$, shows that the experimental ratio leads to

$$\sum_{cd} \frac{\sum_{nm} |\langle a|J_+ + J_-|d\rangle \langle d|V_n^m|b\rangle|^2}{\Delta_{cd}^2} = 4 \sum_{cd} \frac{\sum_{nm} |\langle a|J_z|c\rangle \langle c|V_n^m|b\rangle|^2}{\Delta_{cd}^2}. \quad (30)$$

Hence from (29) and (30),

$$\sum_{cd} \frac{\sum_{nm} |\langle a|J_+|d\rangle \langle d|V_n^m|b\rangle|^2 + |\langle a|J_-|d\rangle \langle d|V_n^m|b\rangle|^2}{\Delta_{cd}^2} = 8.5 \sum_{cd} \frac{\sum_{nm} |\langle a|J_+ + J_-|d\rangle \langle d|V_n^m|b\rangle|^2}{\Delta_{cd}^2}. \quad (31)$$

¹⁴ K. D. Bowers and J. Owen, Rept. Progr. Phys. 63, 304 (1955).

If one assumes as an approximation that only the lowest excited state contributes appreciably to the sums in Eq. (31) one requires that

$$|\langle a|J_+|d\rangle|^2 + |\langle a|J_-|d\rangle|^2 = 8.5|\langle a|J_+ + J_-|d\rangle|^2$$

or

$$\begin{aligned} \langle a|J_+|d\rangle &= -\zeta\langle a|J_-|d\rangle, \\ \zeta &= 0.6 \text{ or } 1.6. \end{aligned} \quad (32)$$

The crystal field in LaF_3 has rhombic symmetry so that the states all comprise admixtures of the form

$$\alpha|\pm\frac{9}{2}\rangle + \beta|\pm\frac{5}{2}\rangle + \gamma|\pm\frac{1}{2}\rangle + \delta|\mp\frac{3}{2}\rangle + \epsilon|\mp\frac{7}{2}\rangle. \quad (33)$$

It is possible to choose coefficients in expression (33) to satisfy either condition (32). We conclude therefore that it is possible for cross relaxation to the forbidden hyperfine lines to be responsible for the H^3 term, but this could be proved only by an experiment on a sample enriched in even-even isotopes.

It is interesting to note that the mechanism we envisage for relaxation can only occur if

$$|\langle a|J_+|d\rangle| \approx |\langle a|J_-|d\rangle|.$$

If one of these matrix elements is much bigger than the other, only one of the diagonal relaxation processes in Fig. 7 is rapid, say b . The saturation of transitions a which occurs when even isotopes cross relax then produces a dynamic nuclear polarization similar to that described by Abragam.¹⁵ Throughout this polarization process each relaxation transition b maintains the Boltzmann distribution between the two states it connects; so when the saturating pulse is turned off and the system is left to relax, it does so at rate T_{1a}^{-1} . This is no faster than the relaxation rates of the even isotopes so that cross relaxation will not appreciably shorten the relaxation time. If both transition probabilities b and c are comparable no nuclear polarization is set up and the system relaxes with a rate

$$T_{1b}^{-1} + T_{1c}^{-1}.$$

¹⁵ A. Abragam, Phys. Rev. 98, 1729 (1955).

The fact that the term in $H \coth(\delta/2kT)$ depends upon the concentration C suggests that it is due either to pairs (or larger clusters) of neodymium ions to which isolated ions rapidly cross relax, or to a process in which the cross relaxation itself is the bottleneck in the relaxation of isolated ions. The $\coth(\delta/2kT)$ dependence eliminates the latter possibility because cross-relaxation processes are temperature-independent. However, the relaxation rate of isolated ions (of which there are C per unit volume) by cross relaxation to pairs (of which there are C^2 per unit volume) ought to vary as C and not as C^2 . The reason for this discrepancy is not understood.

VI. CONCLUSIONS

The theory of relaxation by the direct process developed by Van Vleck, and later by Orbach, is based on a model which assumes that the paramagnetic ion is situated in a simple electrostatic potential due to the surrounding ionic charges. Such a simple model appears to describe the situation in the rare-earth group rather well. The two crystals which we have measured are probably as close to ionic crystals as it will be possible to find among hosts for paramagnetic impurity ions, so they are well suited to test the theory. Both crystals give very clear confirmation of the relaxation rate $\propto \delta^5 \coth(\delta/2kT)$ predicted by the theory.

In addition, the results for LaF_3 show the important role that can be played by ions with hyperfine structure. At sufficiently low values of the external field (which for LaF_3 turns out to be about 2.2 kOe) ions with hyperfine structure may relax at a rate $\propto \delta^3 \coth(\delta/2kT)$. Ions without hyperfine structure can relax by cross relaxation to those with hyperfine structure.

ACKNOWLEDGMENTS

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