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Nuclear Spin-Lattice Relaxation in Dilute Paramagnetic Sapphire

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The exchange of energy between nuclear spin system and lattice has been theoretically and experimentally studied for circumstances in which the nuclear Zeeman energy levels are not necessarily equally spaced. Starting from the master rate equations for the nuclear energy level populations, expressions are found for the population difference of an adjacent pair of energy levels as a function of time. For nuclear spin I, this population difference in general returns to thermal equilibrium with the lattice as a sum of $(2I)$ exponential terms. Under certain conditions, exact solutions of the rate equations may be obtained. As an example, detailed exact solutions are found for an artificial physical situation, in which the nuclear spins ($I=5/2$) are presumed to interact, independently of each other, with a rapidly fluctuating paramagnetic ion (the lattice). From the solutions to this model system, some conclusions are drawn which are consistent with more sophisticated statistical arguments. First, in the limiting case of equally spaced energy levels, these solutions reduce to a single exponential term; a unique spin-lattice relaxation time T_1 may then be defined. Second, it is found that even for unequally spaced levels, any pair of level populations recovers to thermal equilibrium *asymptotically* as an exponential with this same time constant T_1.

The methods illustrated in the foregoing example are extended to include the effects of nuclear dipole-dipole interactions. Approximate solutions to the rate equations are found, for $I=5/2$, in terms of a slight extension of previous descriptions of nuclear spin-lattice relaxation in dilute paramagnetic solids formulated by Bloembergen, de Gennes, and Khutsishvili. These solutions are applied to the particular example of the Al spins in Al_2O_3: 0.035% Cr^{3+}, in order to predict the results of experimental measurements of transient nuclear magnetization made during this research. For the limiting case of equally spaced energy levels, our solution predicts that the Al spins should relax exponentially, with estimated time constant $T_1 \approx 0.6$ sec at 80°K, for an external field of 9 kG. Experimentally, we observe the Al spin relaxation proceed asymptotically as an exponential with $(T_1)_{\mathrm{asymp}} \approx 0.78$ sec at 80°K. The slight discrepancy is accounted for by introducing, in a qualitative manner, the effect of second-order quadrupole splitting of the nuclear Zeeman levels. Further measurements of the transient magnetization associated with an adjacent pair of nuclear energy levels are performed when the energy levels are far from equal spacing; the results of all measurements convincingly demonstrate the validity of the normal modes description of nuclear spin-lattice relaxation employed here. All experimental observations agree quantitatively with the estimated spin temperature time constant $T_1=0.6$ sec. A slight anisotropy in T_1 as a function of crystal orientation in the field H_0 is reported. It is believed that this anisotropy reflects anisotropy of the spin diffusion process in the noncubic sapphire lattice.

I. INTRODUCTION

THE problem of the exchange of energy between a nuclear spin system and its surroundings has been of continuing interest for a number of years. Nuclear spin-lattice relaxation is, in general, described by solutions to a family of differential rate equations involving the populations of the various nuclear spin energy levels and the coupling between the nuclear spins and the "lattice". For nuclear spin I, the number of nondegenerate single-spin energy levels is $(2I+1)$; in this case, there are a total of $(2I)$ independent, linear, coupled rate equations to be solved.

To our knowledge, these rate equations have not been examined in detail. Indeed, for most physical systems studied heretofore, the rate equations are found to have a degenerate solution, which describes an exponential recovery of the nuclear spin system toward thermal equilibrium with the lattice with a single time constant T_1.

In the present work, we shall be concerned with physical systems for which the single exponential solution to the rate equations does not apply. In particular, we shall consider a nuclear spin system for which the $(2I+1)$ energy levels are unequally spaced. We shall restrict ourselves to nuclear relaxation in dilute paramagnetic crystals. The numerical results obtained will be compared with the results of experiments on a single ruby crystal performed during this research.

Bloembergen[1] first performed a series of experiments which outlined the main features of the paramagnetic relaxation mechanism. In brief, the dipolar interaction between the paramagnetic ion moment and the nuclear moment gives rise to a transition probability for the nuclear spin proportional to r^{-6}, where r represents the distance between paramagnetic ion and nucleus. Those nuclear spins lying close to the impurity are, therefore, rapidly relaxed. Nuclear spins far from the impurity ion do not "feel" this direct dipolar interaction; nevertheless, by an exchange of energy through mutual flips with neighboring nuclei via the nuclear dipole-dipole interaction, nuclear magnetization can travel by a random walk process through the crystal toward the impurity ion. The bulk nuclear magnetization thus relaxes toward its equilibrium value in accordance with the "spin diffusion" equation,

$$\partial M/\partial t = D\nabla^2 M - C(M-M_0)\textstyle\sum_n |\mathbf{r}-\mathbf{r}_n|^{-6}. \qquad (1)$$

In this equation, D represents the spin diffusion coefficient, C the strength of the dipole-dipole interaction between paramagnetic ion moment and nuclear moment, and M_0 the equilibrium value of the nuclear magnetization.

The diffusion equation has been solved independently by de Gennes[2] and by Khutsishvili,[3] making use of

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[1] N. Bloembergen, Physica 15, 386 (1949).

[2] P-G de Gennes, J. Phys. Chem. Solids 7, 345 (1958).

[3] G. R. Khutsishvili, Proc. Inst. Phys. Acad. Sci. Georgia (U.S.S.R.) 4, 3 (1956).

boundary conditions applicable to *dilute* paramagnetic impurities. Their solution predicts that the magnetization relaxes exponentially toward its equilibrium value M_0 with a time constant given by $1/T_1=8.5N_0C^{1/4}D^{3/4}$, where N_0 represents the number of paramagnetic ions per cubic centimeter. This conclusion has been confirmed experimentally for a number of substances.

It is the purpose of this work to examine the problem of nuclear spin-lattice relaxation from the point of view of the relaxation rate dependence on the nuclear spin I. When $I=1/2$, nuclear relaxation proceeds according to the solutions of de Gennes, Khutsishvili, and Bloembergen. For spin $I>1/2$, a description of the relaxation process can be obtained from solutions of the master rate equations for the populations of the $(2I+1)$ energy levels. These equations will be solved in considerable detail for various special circumstances. Explicit attention will be devoted to the case $I=5/2$, both because the equations admit solutions without undue labor, and because the results are subject to the experimental demonstration to be described. In particular, interest is centered on (1) the case of equally spaced energy levels, and (2) the case of unequally spaced energy levels. In the former case one would expect that the concept of a local spin temperature would be applicable; in this situation, the recovery of the total magnetization may be shown to follow a single exponential, characteristic of the constants C and D when suitably modified by their dependence on I. In the second case, the magnetization recovery of an *adjacent pair* of levels is described by a linear combination of $(2I)$ exponential functions, whose individual characteristic times are related to C and D.

An experiment has been performed on the aluminum nuclei ($I=5/2$) in dilute ruby ($0.035\%\,Cr^{3+}$ in Al_2O_3) which does indeed demonstrate the validity of the obtained solutions. The Al_2O_3 lattice produces an axially symmetric quadrupolar coupling between the Al nucleus and the crystalline electric field gradient. This interaction provides an additional splitting of the nuclear energy levels, over the Zeeman splitting due to the applied magnetic field H_0. First-order perturbation theory gives one the magnetic resonance frequencies[4]

$$\nu_{m+1\rightarrow m}=\nu_0+(3A/h)[(3/2)\cos^2\theta-\tfrac{1}{2}](2m+1), \quad (2)$$

where $\nu_0=-\gamma H_0/(2\pi)$ is the resonance frequency in the absence of the quadrupolar perturbation, $A=e^2qQ[4I(2I-1)]^{-1}$ is the quadrupolar coupling constant, and θ is the angle between the crystalline axis of symmetry and $\mathbf{H}_0$. The resonance spectrum of the Al nuclei thus consists of a central line $(1/2\rightarrow -1/2)$ and two symmetric satellite pairs. Temporarily neglecting second-order quadrupole effects, it is seen that for the angle $\theta=\theta_0=\cos^{-1}(1/\sqrt{3})$ all five frequencies overlap; this condition corresponds to the case (1) of equally spaced energy levels mentioned previously. For orientation angles far from θ_0, that is, for unequally spaced energy levels, the experimental situation corresponds to case (2).

By means of pulsed nuclear magnetic resonance techniques, the spin energy level populations are disturbed from their equilibrium values. Subsequently, the magnetization is examined after it has relaxed toward thermal equilibrium. Experimental details will be described more fully in Sec. III.

In order to make a true test of the theory of spin-lattice relaxation via dilute paramagnetic impurities, one usually performs experiments wherein the dependence of the relaxation upon temperature, magnetic field, and impurity concentration is examined. The experiments to be described here do not fall into this category. We shall be concerned principally with the dynamic properties of the spin system under the conditions specified. It is nevertheless interesting to notice the close agreement between our order-of-magnitude calculations and the experimental results obtained in ruby.

II. THEORY

1. Direct Interaction

Consider a nuclear spin $\mathbf{I}$ possessing a quadrupole moment (eQ), situated in a large magnetic field $\mathbf{H}_0$ and in an axially symmetric electric field gradient (eq) inclined at an angle θ with respect to $\mathbf{H}_0$. The energy eigenvalues obtained by straightforward perturbation theory, assuming the quadrupolar interaction to be much smaller than the Zeeman energy, are to first order,[4]

$$E_m=-\gamma\hbar H_0 m+\frac{e^2qQ}{4I(2I-1)}\,\frac{(3\cos^2\theta-1)}{2}\times[3m^2-I(I+1)]. \quad (3)$$

When, in addition, the nuclear spin is a distance $\mathbf{r}$ from a paramagnetic ion with magnetic moment $\gamma_e\hbar S$, there is a dipolar interaction of the form

$$H_{\mathrm{dip}}=\hbar^2\gamma_e\gamma r^{-3}[\mathbf{S}\cdot\mathbf{I}-3r^{-2}(\mathbf{S}\cdot\mathbf{r})(\mathbf{I}\cdot\mathbf{r})]. \quad (4)$$

In a crystal at a finite temperature, lattice vibrations produce a fluctuating crystalline electric field, which in turn perturbs the orbital motion of the outer paramagnetic ion electrons. Fluctuations in spin-orbit coupling then induce transitions of the paramagnetic spin among its Zeeman energy levels in the field $\mathbf{H}_0$. Bloembergen[1] has shown how, under these conditions, H_{dip} may be treated as a time dependent perturbation on the nuclear spin system. Assuming that the electron spin resonance is described by a Debye function with correlation time τ (representing the mean lifetime of the electron spin in one of its states), and that the nuclear resonance frequency is sufficiently low to allow one to neglect the effect of the nonsecular part of the electron spin Hamiltonian, the result of his calculation of the nuclear transi-

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[4] R. V. Pound, Phys. Rev. **79**, 685 (1950).

tion probability per unit time is

$$\begin{aligned} W_{m\pm1\rightarrow m} &= (9/4)r^{-6}\sin^2\phi\cos^2\phi(2\pi)^{-1} \\ &\quad\times\hbar^2\gamma_\epsilon^2\gamma^2\langle S_z^2\rangle_{\mathrm{av}}\tau(I\mp m)(I\pm m+1) \\ &= (3/4)\hbar^2\gamma_\epsilon^2\gamma^2S(S+1)r^{-6}\sin^2\phi \\ &\quad\times\cos^2\phi\,\tau[\pi(1+\tau^2\nu_0^2)]^{-1}(I\mp m)(I\pm m+1), \end{aligned} \tag{5}$$

where ν_0 is the nuclear resonance frequency and ϕ is the angle between $\mathbf{r}$ and $\mathbf{H}_0$.

We consider the rate equations and their solutions, when $I>1/2$, for an idealized model, in which all nuclei are at the same distance $\mathbf{r}$ from a single paramagnetic impurity, and when spin diffusion is neglected. For our purposes it is sufficient to average Eq. (5) over the angle ϕ and write

$$W_{m\pm1\rightarrow m} = W(I\mp m)(I\pm m+1), \tag{6}$$

where

$$W = (1/10)\hbar^2\gamma_\epsilon^2\gamma^2S(S+1)r^{-6}\tau[\pi(1+\tau^2\nu_0^2)]^{-1} = \mathrm{C}r^{-6}.$$

For those nuclear spins a distance $\mathbf{r}$ from a single impurity, the family of rate equations may be written

$$dN_m/dt = \textstyle\sum_n N_nW_{n\rightarrow m} - N_m\sum_n W_{m\rightarrow n}, \tag{7}$$

where N_m is the total number of spins in state m. Defining N_m^0 as the equilibrium number of spins in state m, and taking account of detailed balancing, Eq. (7) may be cast into the general form

$$dn_m/dt = \textstyle\sum_n W_{mn}(n_n - n_m), \tag{8}$$

where $n_m = (N_m - N_m^0)/\sum_m N_m$ is the departure of the fractional relative population of the mth state from its thermal equilibrium value.

The solution of this family of rate equations is formally equivalent to the solution of a normal modes problem with real coefficients, where, for this simple model, one has $2I$ degrees of freedom. Using Eq. (6) for the W_{mn}, and defining the quantity a_m by $a_m = (n_m - n_{m-1})$, one obtains the set of $(2I)$ coupled equations

$$(1/W)(da_m/dt) = \textstyle\sum_k A_{mk}a_k, \tag{9}$$

where

$$\begin{aligned} A_{mk} = {} & [I(I+1)-(m+1)m]\delta_{m+1,k} \\ & -2[I(I+1)-m(m-1)]\delta_{m,k} \\ & +[I(I+1)-(m-1)(m-2)]\delta_{m-1,k}, \end{aligned}$$

$m=I,\ I-1,\ \cdots,\ -(I-1)$. The additional constraint on the system is the conservation of the total number of spins:

$$(d/dt)\textstyle\sum_m n_m = 0.$$

The solution is of the form

$$a_m = \textstyle\sum_j a_{mj}\exp(-\lambda_j t), \tag{10}$$

where the $2I$ values of λ_j are obtained from the secular determinant

$$|A_{mk} - \lambda\delta_{mk}| = 0. \tag{11}$$

For our simple model, Eq. (11) is easily factored. One obtains the roots[5]

$$\lambda_j/W = 2,\ 6,\ \cdots,\ (2I+1)!/(2I-1)!. \tag{12}$$

In the special case $I=1/2$, Eq. (12) yields the single time constant $\lambda = 1/T_1 = 2W$. The spin-lattice relaxation toward equilibrium is in this case correctly described by a single exponential recovery time T_1.

In any transient magnetization experiment one might perform, the magnetization of an adjacent pair of levels is the physically measurable quantity. Since this magnetization is directly proportional to a_m, we propose to solve Eq. (10) in detail for our idealized situation. We restrict ourselves to the special case $I=5/2$. Orthogonalization of the a_{mj} gives the matrix relation

$$(a_m) = \begin{bmatrix} 1.0 & 1.0 & 1.0 & 1.0 & 1.0 \\ 1.0 & 0.5 & 0.25 & -1.25 & -2.5 \\ 1.0 & 0 & -0.67 & 0 & 3.33 \\ 1.0 & -0.5 & -0.25 & 1.25 & -2.5 \\ 1.0 & -1.0 & 1.0 & -1.0 & 1.0 \end{bmatrix} \begin{bmatrix} a_1\exp(-2Wt) \\ a_2\exp(-6Wt) \\ a_3\exp(-12Wt) \\ a_4\exp(-20Wt) \\ a_5\exp(-30Wt) \end{bmatrix}, \tag{13}$$

where the $a_1, \cdots, a_5$ are determined by the initial conditions of the spin system at time $t=0$.

We shall distinguish between two different physical situations, first considering the case of unequally spaced energy levels (for example, $\theta=0°$). Under these circumstances, one is able, by means of an intense burst of radiation at one resonance frequency, to invert the populations of an adjacent pair of energy levels without disturbing the others. When, for example, the central resonance line is inverted at $t=0$, the initial conditions are, approximately,

$$a_{5/2}(0) = a_{-3/2}(0) = 0;\quad a_{3/2}(0) = a_{-1/2}(0) = \beta;$$
$$a_{1/2}(0) = -2\beta;$$

where $\beta \approx \gamma\hbar H_0/kT$, and where it has been assumed that the quadrupolar interaction is much smaller than the Zeeman interaction $Ah^{-1} \ll \gamma H_0$. The numerical solutions for the various transitions are given below, and are

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[5] R. Sher and H. Primakoff [Phys. Rev. **119**, 178 (1960)] have obtained λ_j for a similar, but more general, physical situation for the special cases $I=1$ and $I=3/2$. Equations (136) and (141) of their work are equivalent to our Eq. (12). These authors have also demonstrated, under quite general conditions, the validity of using the master rate equations as a starting point for a description of the nuclear relaxation, as we have done here.

shown in Fig. 1.

$$\begin{aligned}
&(1/2\rightarrow -1/2 \text{ inverted});\\
&\quad a_{1/2}=-\beta/315[18\exp(-2Wt)\\
&\qquad\quad +112\exp(-12Wt)+500\exp(-30Wt)];\\
&(3/2\rightarrow 1/2 \text{ inverted});\\
&\quad a_{3/2}=-\beta/1260[396\exp(-2Wt)\\
&\qquad\quad +135\exp(-6Wt)+18\exp(-12Wt)\\
&\qquad\quad +1125\exp(-20Wt)+675\exp(-30Wt)];\\
&(5/2\rightarrow 3/2 \text{ inverted});\\
&\quad a_{5/2}=-\beta/35[2\exp(-2Wt)\\
&\qquad\quad +15\exp(-6Wt)+28\exp(-12Wt)\\
&\qquad\quad +20\exp(-20Wt)+5\exp(-30Wt)].
\end{aligned}\tag{14}$$

The qualitative resemblance of these recovery curves to those obtained experimentally is striking. Although the order of magnitude of the time scale is quite wrong, the apparent agreement in curvature is convincing enough to justify the extension of these methods to include spin diffusion.

Now consider what happens when the energy levels are equally spaced ($\theta=\theta_0$). It is no longer possible to invert just one pair of adjacent levels with an rf pulse, since only a single resonance frequency exists for *all* $\Delta m=1$ transitions. (Mathematically, the normal modes problem has become fivefold degenerate.) If one applies an rf pulse at ν_0 which inverts the populations of all levels (180° pulse), the initial conditions are then $a_m=-2\beta$ for all m. Inspection of Eq. (13) with these initial condtions tells us immediately that

$$a_m(t)\propto\exp(-2Wt)\text{ for all }m,\tag{15}$$

and hence, the total magnetization recovers to its thermal equilibrium value exponentially with time constant

$$1/T_1=2W.\tag{16}$$

This particular solution was obtained for liquids with a different method by Bloembergen,[6,7] who made the similar assumption that the difference in population between two adjacent energy levels is independent of m. Equation (15) can be very properly called the spin temperature solution, since it can be derived immediately from the spin temperature assumptions of (1) equally spaced energy levels, and (2) level populations described at all times by a single parameter, namely, the Boltzmann factor at temperature T_s. In fact, if one makes the assumption that the solution of the rate Eq. (8) is consistent with the existence of a spin temperature, then[8]

$$1/T_1=(1/2)\textstyle\sum_{n,m}W_{nm}(E_n-E_m)^2/\sum_n E_n{}^2,\tag{17}$$

and the relation (16) follows immediately.

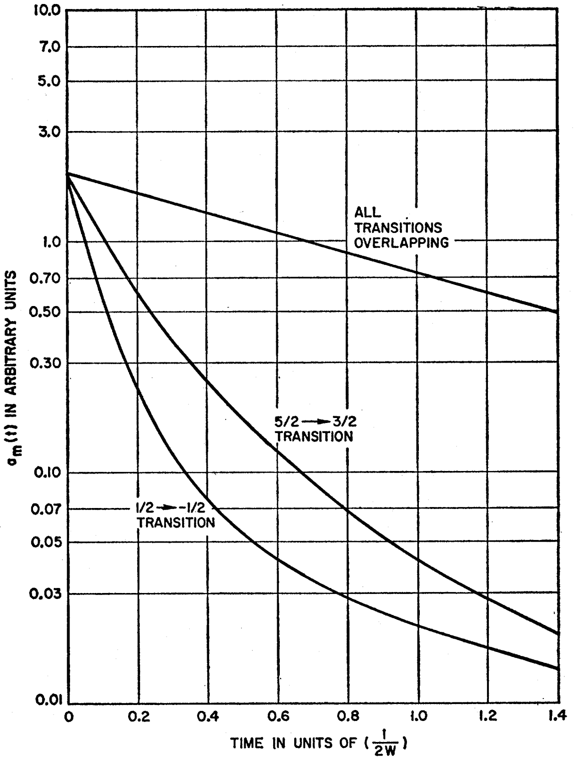

FIG. 1. Semilogarithmic plots of the theoretical population differences between adjacent spin-energy levels as a function of time following population inversion of the particular level pair. The curves shown are representative of solutions to the direct interaction problem, and are given by Eqs. (13) and (15) in the text.

The result (15) is plotted in Fig. 1; for comparison purposes, all amplitudes at $t=0$ are made identical. One notes two features peculiar to the spin temperature solution; its characteristic decay time is independent of I, and it is also the *slowest* mode of decay for the spin system. Therefore, any pair of level populations proceeds towards thermal equilibrium *asymptotically* as an exponential with $T_1=1/(2W)$, *regardless* of whether or not the energy levels are equally spaced. In other words, the spin system reaches a sort of internal Boltzmann equilibrium, *before* finally recovering to thermal equilibrium with the lattice. These latter statements are quite general, and might be expected on the basis of general statistical mechanics arguments. They will be used in Sec. III for a qualitative interpretation of certain observed relaxation rates.

This model is applicable to a real dilute paramagnetic crystal under the conditions investigated by Blumberg.[9] He postulates that, immediately following a burst of rf energy which saturates the nuclear spin system, the gradient of the local magnetization is everywhere zero, and hence spin diffusion will not occur. For times short compared with the time necessary to establish a finite magnetization gradient, the relaxation will be domi-

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[6] N. Bloembergen, *Nuclear Magnetic Relaxation* (M. Nijhoff, The Hague, 1948).

[7] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

[8] L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).

[9] W. E. Blumberg, Phys. Rev. **119**, 79 (1960).

nated by the direct interaction. Blumberg then performs an integral of the local magnetization over the volume of the crystal, with the result that the magnetization recovers toward thermal equilibrium proportionally with the square root of the time. It may be seen from the above model that his solution remains valid for any spin value I, provided the energy levels are equally spaced. If this is not the case, it may still be said that the population difference of an adjacent pair of levels recovers initially toward thermal equilibrium as the sum of $(2I)$ terms, each proportional to the square root of the time. We do not observe this square-root effect experimentally, and shall not consider it further here.

2. Spin Diffusion

In this section, we deal with the solution of Eq. (1) for dilute paramagnetic crystals when $I>1/2$. We shall first examine the situation of equally spaced energy levels. The local magnetization $M(\mathbf{r},t)$ at any point in the crystal is then obtainable from a single parameter, the local spin temperature $T_s(\mathbf{r},t)$. It will be convenient to idealize the model by restricting our calculations to an isotropic lattice. In addition, we shall assume Gaussian line shapes, and shall average over all angles that occur. These restrictions will not affect the order of magnitude to be obtained.

The probability per unit time P for a mutual spin flip of neighboring nuclei is determined by the strength of the dipole-dipole interaction. The term of interest in the dipolar Hamiltonian, which conserves the Zeeman energy of the pair of spins involved, is

$$H_{\mathbf{I}\cdot\mathbf{I}}=-1/4\gamma^2\hbar^2r_{ij}^{-3}(1-3\cos^2\theta_{ij})[I_{i+}I_{j-}+I_{i-}I_{j+}]. \quad (18)$$

For mutual flips of nearest neighbors only, application of first-order time dependent perturbation theory, with the above assumptions, gives

$$P(m\rightarrow m+1,\ n\rightarrow n-1)=(\pi/10)(2\pi\langle\Delta\omega^2\rangle)^{-1/2}\hbar^2\gamma^4a^{-6}\times[(I-m)(I+m+1)(I+n)(I-n+1)], \quad (19)$$

where a is the nearest-neighbor distance and $\langle\Delta\omega^2\rangle$ represents the second moment of the resonance line. For equally spaced energy levels, the Van Vleck dipolar second moment for a rigid lattice is[10]

$$\langle\Delta\omega^2\rangle=(3/5)g\gamma^4\hbar^2a^{-6}I(I+1), \quad (20)$$

where g is a geometrical factor defined by $\sum r_{ij}^{-6}=ga^{-6}$. Hence

$$P(m\rightarrow m+1,\ n\rightarrow n-1)=P_0(I-m)(I+m+1)(I+n)(I-n+1), \quad (21)$$

where

$$P_0=(1/6g)(\tfrac{1}{2}\pi\langle\Delta\omega^2\rangle)^{1/2}[I(I+1)]^{-1}.$$

Consider those nuclear spins within a volume v of the crystal far from an impurity ion, where v has position coordinates (x,y,z). At a particular time t, the number of spins within v, in state m, is $N_m(x,y,z,t)$. We *assume* the existence of a "local" spin temperature $T_s(x,y,z,t)$; then

$$N_m(x,y,z,t)=[N/(2I+1)][1-m\beta(x,y,z,t)], \quad (22)$$

where $\beta(x,y,z,t)=\gamma\hbar H_0/[kT_s(x,y,z,t)]$, and where N is the total number of spins in volume v. The number of spins in any state m will change with time, due to mutual spin flips with neighboring nuclei. Hence, for transport of the population of state m in the x direction,

$$\begin{aligned}N_m(x,t)&-N_m(x,0)\\&=-Nt\left[\frac{1-m\beta(x)}{2I+1}\right]\sum_n\left[\frac{1-n\beta(x+a)}{2I+1}\right][P(m\rightarrow m-1,\ n\rightarrow n+1)+P(m\rightarrow m+1,\ n\rightarrow n-1)]\\&\quad+Nt\sum_n\left[\frac{1-n\beta(x+a)}{2I+1}\right]\left[\left(\frac{1-(m-1)\beta(x)}{2I+1}\right)P(m-1\rightarrow m,\ n\rightarrow n-1)\right.\\&\quad\left.+\left(\frac{1-(m+1)\beta(x)}{2I+1}\right)P(m+1\rightarrow m,\ n\rightarrow n+1)\right]+\text{similar terms involving }\beta(x-a). \quad (23)\end{aligned}$$

Performing the sums over the states n, neglecting terms in β^2, and collecting, one obtains

$$\begin{aligned}N_m(x,t)&-N_m(x,0)\\&=\left[\frac{2NtP_0I(I+1)}{3(2I+1)}\right][\beta(x+a)+\beta(x-a)-2\beta(x)]\\&\quad\times[(I-m)(I+m+1)-(I+m)(I-m+1)]. \quad (24)\end{aligned}$$

This equation may be written

$$\beta(x,t)-\beta(x,0)=(4t/3)P_0I(I+1)\times[\beta(x+a)+\beta(x-a)-2\beta(x)]. \quad (25)$$

Expanding the left-hand side in powers of t, the right-hand side in powers of a, and neglecting higher-order terms, one has

$$\partial\beta(x,t)/\partial t=(4/3)P_0a^2I(I+1)[\partial^2\beta(x,t)/\partial x^2]. \quad (26)$$

Since the local magnetization $M(x,t)$ is proportional to $\beta(x,t)$, upon generalizing to three dimensions, one has the familiar (isotropic) diffusion equation

$$\partial M(\mathbf{r},t)/\partial t=D\nabla^2M(\mathbf{r},t), \quad (27)$$

where

$$D=(2a^2/9g)(\tfrac{1}{2}\pi\langle\Delta\omega^2\rangle)^{1/2}.$$

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[10] J. H. Van Vleck, Phys. Rev. 74, 1168 (1948)

The relation $D\propto I(I+1)$ has been given by Bloembergen.[1] If one includes the direct interaction of nuclei with paramagnetic ions, the result is, again, Eq. (1).

The diffusion equation (1) has been solved by de Gennes[2] and Khutsishvili.[3] An outline of the pertinent features of their solution appears here. One assumes the existence of a sphere of radius b surrounding an impurity ion. Within this sphere, the nuclear resonance is broadened beyond observability by the nearby paramagnetic ion moment. Negligible spin diffusion occurs across the surface of the sphere, due to the shift in Larmor frequency of spins within the sphere; hence, b is referred to as the diffusion barrier radius.

The exact value of b is not essential for the solution of the diffusion equation, so long as the condition $b\ll R$ is satisfied, where R is the average spacing between two neighboring paramagnetic impurities. With this assumption, a solution to Eq. (1) exists, of the form

$$M(\mathbf{r},t)=M_0[1+\phi(\mathbf{r})\exp(-\lambda_0 t)],$$

where $\phi(\mathbf{r})$ satisfies the equation

$$D\nabla^2\phi(\mathbf{r})-\textstyle\sum_n C\phi(\mathbf{r})|\mathbf{r}-\mathbf{r}_n|^{-6}+\lambda_0\phi(\mathbf{r})=0. \tag{28}$$

It is seen that the magnetization recovers exponentially with time constant $\lambda_0=1/T_1$. From the asymptotic properties of $\phi(\mathbf{r})$ at large r, and from the boundary condition $M(0,t)=0$, de Gennes obtains

$$\lambda_0=1/T_1=4\pi N_0A_0D, \tag{29}$$

where A_0 is a length parameter, $A_0=0.68(C/D)^{1/4}$, called by de Gennes the pseudopotential radius. The quantity A_0 may be regarded as the scattering amplitude of a single impurity.

We shall now turn to the situation where the energy levels are unequally spaced. Some of the mutual spin flips generated by the dipolar interaction are no longer possible, since they do not conserve Zeeman energy. One anticipates *a priori* that this reduction in the number of ways in which spin energy can be transported through the crystal will result in a decrease in the diffusion constant D. We intend to derive the appropriate diffusion equation for the population difference of an adjacent pair of energy levels. We shall again make use of the idealized model approximations, namely, Gaussian line shapes, an isotropic lattice, and averaged angular dependences.

The change in population of the mth state in a time t, for transport in the x direction, is

$$\begin{aligned}
&N_m(x,t)-N_m(x,0)\\
&=-tN_m(x)\left[\frac{N_{m+1}(x+a)}{N}P(m\rightarrow m+1,m+1\rightarrow m)\right.\\
&\qquad\left.+\frac{N_{m-1}(x+a)}{N}P(m\rightarrow m-1,m-1\rightarrow m)\right]\\
&\qquad+t\frac{N_m(x+a)}{N}[N_{m+1}(x)P(m+1\rightarrow m,m\rightarrow m+1)\\
&\qquad+N_{m-1}(x)P(m-1\rightarrow m,m\rightarrow m-1)]\\
&\qquad\qquad+\text{similar terms involving }(x-a),
\end{aligned} \tag{30}$$

where

$$\begin{aligned}
&P(m\rightarrow m-1,m-1\rightarrow m)\\
&\quad=(1/5)(2\pi\langle\Delta\omega_m{}^2\rangle)^{-1/2}\hbar^2\gamma^4a^{-6}(I+m)^2(I-m+1)^2,
\end{aligned}$$

and $\langle\Delta\omega_m{}^2\rangle$ is the second moment of the $m\rightarrow m-1$ transition. This quantity has been calculated for our conditions[11] for the central line, neglecting any quadrupolar broadening, with the result

$$\langle\Delta\omega_{1/2}{}^2\rangle=\left[\frac{4}{27}I(I+1)+\frac{2I^2(I+1)^2+3I(I+1)+13/8}{18(2I+1)}\right]\times(9/5)g\hbar^2\gamma^4a^{-6}. \tag{31}$$

For $I=5/2$, $\langle\Delta\omega_{1/2}{}^2\rangle=(107/105)\langle\Delta\omega^2\rangle\approx\langle\Delta\omega^2\rangle$. In keeping with the spirit of this calculation, we assume that the second moments of all transitions are approximately equal:

$$\langle\Delta\omega_{5/2}{}^2\rangle=\langle\Delta\omega_{3/2}{}^2\rangle=\langle\Delta\omega_{1/2}{}^2\rangle=\langle\Delta\omega^2\rangle. \tag{32}$$

This approximation is not strictly valid, even for our simple model, a fact that can be demonstrated by an explicit second-moment calculation for $\langle\Delta\omega_{5/2}{}^2\rangle$ and $\langle\Delta\omega_{3/2}{}^2\rangle$. However, the assumption will have little quantitative effect on the results to be obtained presently. In experimental practice, measured linewidths should be used.

Expansion of Eq. (30), by the same methods previously used, gives the family of coupled equations

$$\begin{aligned}
\frac{\partial n_m(\mathbf{r},t)}{\partial t}=\frac{P_0a^2}{2I+1}\{&(I-m)^2(I+m+1)^2\nabla^2[n_m(\mathbf{r})-n_{m+1}(\mathbf{r})]\\
&+(I+m)^2(I-m+1)^2\nabla^2[(n_m(\mathbf{r})-n_{m-1}(\mathbf{r})]\}.
\end{aligned} \tag{33}$$

Including the direct interaction, we obtain

$$\partial a_m(\mathbf{r},t)/\partial t=\textstyle\sum_k A_{mk}a_k(\mathbf{r}), \tag{34}$$

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[11] K. Kambe and J. F. Ollom, J. Phys. Soc. Japan **11**, 50 (1956).

where

$$\begin{aligned}A_{mk}=&\{W[I(I+1)-(m+1)m]\\&+[P_0a^2/(2I+1)][I(I+1)-(m+1)m]^2\nabla^2\}\delta_{m+1,k}\\&-2\{W[I(I+1)-m(m-1)]\\&+[P_0a^2/(2I+1)][I(I+1)-m(m-1)]^2\nabla^2\}\delta_{m,k}\\&+\{W[I(I+1)-(m-1)(m-2)]+[P_0a^2/(2I+1)]\\&\times[I(I+1)-(m-1)(m-2)]^2\nabla^2\}\delta_{m-1,k}.\end{aligned}$$

A solution to Eq. (34) exists, of the form

$$a_m(\mathbf{r},t)=\textstyle\sum_j \alpha_{m,j}\phi_m(\mathbf{r})\exp(-\lambda_j t),\tag{35}$$

where the $\phi_j(\mathbf{r})$ and λ_j are determined by the solution of the secular determinant. For $I=5/2$, this secular determinant can be approximated by the following (factored) equation:

$$\begin{aligned}(\lambda+145\xi(\mathbf{r})+20W)(\lambda+33\xi(\mathbf{r})+6W)\\\times(\lambda+13\xi(\mathbf{r})+12W)(\lambda+253\xi(\mathbf{r})+30W)\\\times(\lambda+75\xi(\mathbf{r})+12W)=0,\end{aligned}\tag{36}$$

where

$$\xi(\mathbf{r})=[P_0a^2/(2I+1)][\nabla^2\phi(\mathbf{r})/\phi(\mathbf{r})],$$

and where

$$W=-C\textstyle\sum_n|\mathbf{r}-\mathbf{r}_n|^{-6}.$$

It is evident that each of the factors in Eq. (36) is of the form

$$D_j\nabla^2\phi_j(\mathbf{r})-\textstyle\sum_n C_j|\mathbf{r}-\mathbf{r}_n|^{-6}\phi_j(\mathbf{r})+\lambda_j\phi_j(\mathbf{r})=0.\tag{37}$$

The solution of these equations for the λ_j may therefore be taken over from the previous work of de Gennes.[2] The results for the $(2I)=5$ values of λ_j are given below, to two significant figures, in terms of the previously obtained solution λ_0 for equally spaced energy levels [Eq. (29)]:

$$\begin{aligned}\lambda_1=0.33\lambda_0;\quad \lambda_2=0.88\lambda_0;\quad \lambda_3=2.0\lambda_0;\\ \lambda_4=3.6\lambda_0;\quad \lambda_5=6.1\lambda_0.\end{aligned}\tag{38}$$

The experimentally measurable quantity $a_m(t)$ is given by the integral over the crystal volume:

$$a_m(t)=\int a_m(\mathbf{r},t)d\mathbf{r}=\sum_j \alpha_{mj}\exp(-\lambda_j t)\int\phi_j(\mathbf{r})d\mathbf{r}.\tag{39}$$

The initial conditions of the experiment prescribe the values of the terms $\alpha_{mj}\int\phi_j(\mathbf{r})d\mathbf{r}=a_{mj}$; one therefore must solve the family of equations

$$a_m(t)=\textstyle\sum_j a_{mj}\exp(-\lambda_j t),\tag{40}$$

in order to predict the characteristic decay toward thermal equilibrium of any adjacent pair of energy level populations. This has been done for various initial conditions. The results of these calculations are shown in Figs. 3 through 7, where they may be compared quantitatively with the experiments described in the next section.

One notes that λ_0 no longer represents the slowest mode of decay of the system, due to the appearance of additional off-diagonal terms in the rate equation matrix as the lines begin to overlap. In practice, solution (40) goes smoothly into the single exponential rate given by solution (29). We shall see that, insofar as we are able to perform the experiments, this is indeed the case.

III. EXPERIMENT

1. Methods

Pulsed nuclear magnetic resonance methods have been used to disturb the nuclear spin system from thermal equilibrium and to measure the rate at which this system recovers, under conditions similar to those defined in previous sections. The nuclear spin system for these experiments is comprised of Al nuclei ($I=5/2$) in an Al_2O_3 single crystal containing approximately 0.035% Cr_2O_3.[12] This concentration of Cr^{3+} spins is sufficiently low to allow us to neglect the interactions of the Cr^{3+} spins upon each other (hence, we may use the term "dilute paramagnetism"), and yet sufficiently high to render relaxation of the nuclear spins by quadrupolar interactions negligible. The sapphire lattice provides an axial electric field gradient at the Al sites; the interaction of this static field gradient with the nuclear quadrupole moment yields the expression (2), correct to first order, for the observed frequencies of the nuclear resonance lines in a large field $\mathbf{H}_0$.

The ruby crystal was cut in the form of a cylinder, 0.25 in. in diameter and 1.5 in. in length, in a manner such that the crystalline axis of symmetry (c axis) was perpendicular to the cylinder axis. The radio frequency coil was close-wound about the cylindrical sample, and the assembly was mounted between the pole faces of a 12-in. Varian magnet, with the cylinder axis orthogonal to the field direction. The sample itself could be rotated about its cylinder axis, allowing adjustment of the angle between the c axis and $\mathbf{H}_0$ to approximately 1/4 degree.

The pulsed rf equipment operated at the fixed frequency $\nu_0=9.86$ Mc/sec, and utilized phase coherent detection of the nuclear signals. Details of the unit are very similar to those of a previously described system.[13] The transition of interest was selected by adjusting the field $\mathbf{H}_0$.

All relaxation recovery data were taken by means of a two-pulse sequence. The first pulse (180°) approximately inverted the populations of a pair of levels; after a time t, a (90°) pulse tipped the remanent magnetization into the plane of the rf coil; the amplitude of the ensuing Bloch decay was then measured as a function of time t. We define the amplitude of the nuclear Bloch decay signal immediately following the number 2 pulse applied to the $(m\rightarrow m-1)$ transition to be $S_m(t)$. We may then use the relation $[S_m(t)-S_m(\infty)]\propto a_m(t)$ as the

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[12] R. D. Olt, Appl. Optics **1**, 25 (1962).

[13] J. J. Spokas and C. P. Slichter, Phys. Rev. **113**, 1462 (1959).

basis for the comparisons to be made between theory and experiment in the following sections.

Adjustment of the pulse lengths was somewhat complicated by the rather complex resonance line shapes inherent in sapphire.[14,15] For these measurements, however, exact pulse lengths were not critical, so long as the lengths actually used did not change in the course of a relaxation measurement. Typical 180° inverting pulses used in these experiments were of the order of 10 μsec in length. The frequency spread of the rf inverting pulse is therefore of the order 100 kc/sec; satellite lines lying within roughly ± 50 kc/sec of the resonance under observation will find their relative populations somewhat perturbed from thermal equilibrium by this pulse. The technique of adiabatic fast passage would avoid this difficulty, but it is not easily applied for relaxation times shorter than a few seconds. Fortunately, the effect is negligible for the angles $\theta = 0°$ and $\theta = 90°$. It is ignored in interpretation of the results reported here.

Temperature was not a crucial parameter in these experiments. Data were taken at room temperature and at the temperature of liquid nitrogen, but no attempt was made to control T with precision. The liquid nitrogen Dewar used was standard in form. Unless stated otherwise, data reported here were taken at 80°K, in order to take full advantage of the available signal-to-noise ratio.

2. Relaxation at $\theta = \theta_0$

If one neglects the effects of second-order quadrupole splitting, all nuclear transitions occur at the same frequency. Hence, one expects to observe exponential relaxation of the spin system toward thermal equilibrium with the time constant given by Eq. (29); $\lambda_0 = 1/T_1 = 8.5 N_0 C^{1/4} D^{3/4}$. It is of interest to calculate T_1 for our ruby crystal at $\theta = \theta_0$. This value for T_1 represents the limiting case of fastest spin system recovery for an ideal crystal. We shall retain the simplifying approximations in Sec. II, i.e., an isotropic diffusion coefficient D derived on the basis of mutual spin flips between nearest neighbors only, and an isotropic direct interaction between Cr^{3+} spin and nuclear spin, even though we are applying the calculation to a single crystal.

We take the values[16] $\tau = 4.4 \times 10^{-5}$ sec at 80°K, $S = 3/2$ for the Cr^{3+} ion, $\nu_0 = 9.86$ Mc/sec; from Eq. (6), we obtain $C = 0.47 \times 10^{-42}$ cm^6/sec. From Eq. (27), for assumed Gaussian line shapes, $D = a^2/(18 g T_2)$, where T_2 is the spin-spin relaxation time. From the experimental Bloch decays observed during the course of this research, $T_2 \approx 40$ μsec. We take $a \approx 3$ Å, $g \approx 3$, and obtain $D = 4.2 \times 10^{-13}$ cm^2/sec. The impurity concentration of 0.035% Cr^{3+} indicates that $N_0 = 1.65 \times 10^{19}$ cm^{-3}. Hence

$$T_1 = 1/\lambda_0 = 0.6 \text{ sec.} \tag{41}$$

The pseudopotential radius is then $A_0 = 2.2$ Å, roughly equal to the lattice parameter a. We can estimate the diffusion barrier radius by using Bloembergen's criterion, $b = [\mu_\epsilon^2 H_0/(\mu_n k T)]^{1/3} a$, from which we get $b \approx 10$ Å. It is seen that the lengths a, b, and A_0 are all much less than the mean distance R between impurities, since $R \approx N_0^{-1/3} \approx 50$ Å. Therefore we expect de Gennes' type of solution to be valid. Accordingly, we take Eq. (41) to be the representative numerical value on which comparison is made between theory and experiment.[17]

In practice, second-order quadrupole splitting in ruby[4] is large enough to be important for angles very near to θ_0. The effect of this interaction is to introduce an additional splitting of the energy levels, so that complete overlapping of all five resonance lines can never be obtained. In view of our admittedly crude assumptions concerning line shapes and widths, there is no way to take this nonideal situation into account in a quantitative manner.

Nevertheless, a qualitative guess can be made about the recovery rate of the spin system at the angle of maximum overlap. Consider the following hypothetical situation: the five observable resonance lines are sufficiently close together in frequency so that the initial 180° rf burst inverts the populations of *all* the energy levels, and yet sufficiently far apart so that there is no appreciable overlapping of any of these resonance lines. Under these circumstances, one would expect from the discussion in Sec. II that spin-lattice relaxation would proceed according to a sum of five exponential terms, with time constants given by Eq. (38). Due to the initial conditions that prevail immediately following the inverting pulse, the four shortest relaxation modes ($\lambda_2, \lambda_3, \lambda_4, \lambda_5$) are largely suppressed, with the result that the spin system for the most part relaxes exponentially toward thermal equilibrium with a characteristic recovery time $1/\lambda_1 = T_1 = 1.8$ sec.

Our experimental conditions at $\theta = \theta_0$ fall somewhere between these two extremes, since second-order quadrupole splitting is just of the order of the characteristic width of the resonance lines. Hence, we should observe a relaxation process which is rapid at first, but which quickly beomes exponential with a time constant having a value intermediate between 0.6 and 1.8 sec. This discussion is summarized in Fig. 2, which shows a semi-

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[14] C. M. Verber, H. P. Mahon, and W. H. Tanttila, Phys. Rev. **125**, 1149 (1962).

[15] A. H. Silver, T. Kushida, and J. Lambe, Phys. Rev. **125**, 1147 (1962).

[16] J. H. Pace, D. F. Sampson, and J. S. Thorp, Phys. Rev. Letters **4**, 18 (1960).

[17] Blumberg (see reference 9) has given a different result for the spin-lattice relaxation rate when the experimental conditions are such that $A_0 < b$. He argues that, physically, this condition implies the spin diffusion mechanism carries nuclear Zeeman energy to the paramagnetic ion more rapidly than the paramagnetic ion can transmit it to the lattice. He then shows that, if this is true, nuclear spin-lattice relaxation should take place exponentially with a time constant given by $1/T_1 = (4\pi/3) N_0 C b^{-3}$. Using previously computed values for N_0, C, and b, we obtain $T_1 \approx 50$ sec for our ruby crystal. This result is incompatible with our experimental data,

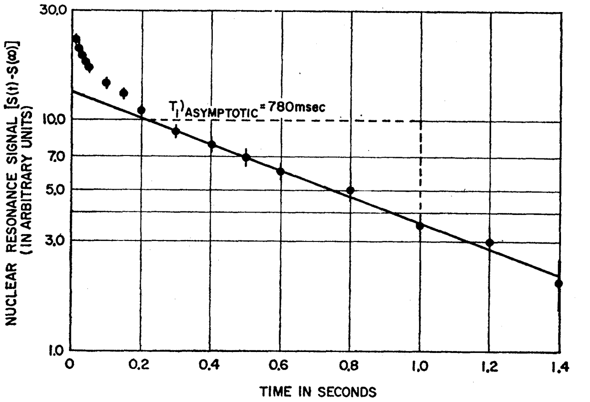

FIG. 2. Aluminum nuclear spin-lattice relaxation in 0.035% ruby at the orientation angle of maximum resonance overlap $\theta \approx \cos^{-1}(1/\sqrt{3})$. Temperature ≈ 80°K. $(T_1)_{\text{asymp}}$ as calculated in the text should lie between the limits 0.6 and 1.8 sec.

logarithmic plot of nuclear resonance signal height vs time. The heavy line represents the best straight line through the asymptotic part of the recovery curve. The slope of this line gives $T_1 = 0.78$ sec.

In view of the many approximations made in these calculations, this sort of agreement between theory and experiment must be regarded as somewhat fortuitous. In particular, the assumptions of Gaussian line shapes, and line widths independent of the angle θ, are incorrect from a detailed standpoint.[14,15] Nevertheless, the general principles underlying the calculations are apparently valid.

3. Relaxation for θ far from θ_0

We now consider the relaxation process for angles θ such that the five resonance frequencies are well separated. The data presented in Figs. 3 and 4 were taken at liquid nitrogen temperature. The experimental points shown are averages over several measurements for the particular angles $\theta = 0°$ and $\theta = 90°$; the scatter in the points has been omitted for the sake of clarity. Signal-to-noise ratios were approximately 50/1 for the $(1/2 \rightarrow -1/2)$ transition, and 30/1 for the $(5/2 \rightarrow 3/2)$ transition. The maximum signal $[S(0) - S(\infty)]$ has been normalized to the value 2 in each instance. It should be mentioned that agreement between theoretical curves and experiment is equally good for the $3/2 \rightarrow 1/2$ transition.

The theoretical curves shown in Figs. 3 and 4 have been calculated from Eqs. (38) and (40), using the appropriate initial conditions to determine the a_{mj}. They have been expressed in terms of the previously estimated spin temperature time constant $1/\lambda_0 = 0.6$ sec [Eq. (41)]. It is seen that quantitative agreement between theoretical description and experimental results is excellent.

One notes the systematic difference between the experimental relaxation curves for $\theta = 0°$ and $\theta = 90°$. It is believed that this difference is the result of the anisotropy inherent in the diffusion constant D. This anisotropy has been considered in the original work of Bloembergen.[1] He observed spin-lattice relaxation of the F^{19} nuclei in CaF_2 for various magnetic field directions with respect to the single crystal axes, and found that T_1, and hence D, were isotropic. However, the sapphire lattice possesses axial rather than cubic symmetry. Hence it is not difficult to argue that spin diffusion proceeds with a different rate parallel to the c axis than it does in a direction perpendicular to the c axis. It follows that T_1 will vary as one rotates the crystal in the field $\mathbf{H}_0$. When $D_{\parallel} \approx D_{\perp}$, this variation in T_1 will be slight. Evidently this condition holds for sapphire.

For the $(1/2 \rightarrow -1/2)$ transition, the population difference recovers as a sum of only three exponentials. Of these three, only the two fastest relaxation modes are observable with the signal-to-noise ratios presently available. It would be easy to misinterpret the magnitude of the nuclear relaxation mechanism by an observation of one transition alone. For instance, if one defines the relaxation time constant T_1 as the time involved for $[S(t) - S(\infty)]$ to decay to $(1/e)$ of its initial value $[S(0) - S(\infty)]$, one would obtain the answer $T_1 = 120$ msec for the $(1/2 \rightarrow -1/2)$ transition. It is clear that this is neither a complete nor an accurate description of the relaxation process.

Experiments somewhat similar to those we have described here have been performed by Tanttila and Jennings[18] on alkali halides. They have shown that for

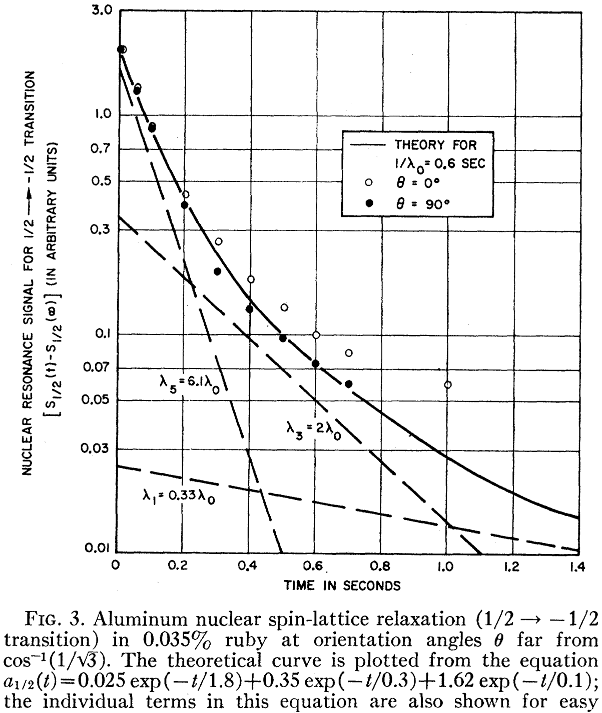

FIG. 3. Aluminum nuclear spin-lattice relaxation $(1/2 \rightarrow -1/2$ transition) in 0.035% ruby at orientation angles θ far from $\cos^{-1}(1/\sqrt{3})$. The theoretical curve is plotted from the equation $a_{1/2}(t) = 0.025 \exp(-t/1.8) + 0.35 \exp(-t/0.3) + 1.62 \exp(-t/0.1)$; the individual terms in this equation are also shown for easy visualization. Temperature ≈ 80°K.

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[18] W. H. Tanttila and D. A. Jennings, Bull. Am. Phys. Soc. **5** 598 (1960).

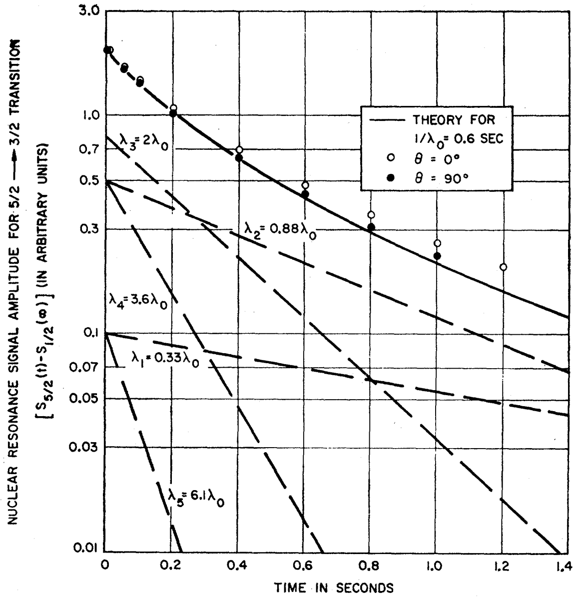

FIG. 4. Aluminum nuclear spin-lattice relaxation ($5/2 \to 3/2$ transition) in 0.035% ruby at orientation angles θ far from $\cos^{-1}(1/\sqrt{3})$. The theoretical curve is plotted from the equation $a_{5/2}(t)=0.1\exp(-t/1.8)+0.5\exp(-t/0.7)+0.8\exp(-t/0.3)+0.5 \times\exp(-t/0.17)+0.1\exp(-t/0.1)$; the individual terms in this equation are also shown. Temperature≈80°K.

spins I greater than 1/2, the relaxation time T_1 is increased when one strains the crystals sufficiently to broaden the satellite lines (via the quadrupolar interaction) beyond observability by grinding them into a powder. They attribute this increase in T_1 to a decrease in the diffusion constant D, which comes about due to the decrease in the number of ways in which energy-conserving nuclear spin flips can occur in pairs. One effectively accomplishes the same end in the present experiment in ruby, by rotation of the crystalline axis away from the angle θ_0. The difference in the two experiments lies in the fact that in the present experiment, the satellite lines are not wiped out, but merely removed from resonance; hence, the relaxation problem must be treated in a different manner.

4. Further Experiments

In addition to the foregoing experiments, a further test of the normal modes description of the relaxation process may be made. One inverts the populations of one adjacent pair of levels, and then observes the transient population difference corresponding to a different transition.

The rf power unit was modified to deliver the number 1 rf pulse at a frequency f_1, and the number 2 pulse at a frequency f_2. In the particular arrangement employed, the broad-band class C power amplifier was driven by a Tektronics type 190A variable frequency signal generator for f_1, and by a 9.8643-Mc/sec crystal-controlled oscillator, of the electron coupled variety, for f_2. The bandwidth of the power amplifier was sufficient to deliver pulses of either frequency without appreciable attenuation. By simultaneous tuning of f_1 and H_0, the desired initial configuration of the energy level populations could be obtained. As in previous experiments, the nuclear Bloch decay amplitude of the resonance at f_2 immediately following the number 2 pulse was measured as a function of time between the number 1 and number 2 pulses.

Two experiments of this nature have been performed. The first of these experiments consists of inverting the ($3/2 \to 1/2$) transition, and then observing the ($1/2 \to -1/2$) transition. The first pulse doubles the population difference between the 1/2 and $-1/2$ energy levels at time $t=0$. The result is a nuclear signal that is enhanced by a factor of two,[19] as shown in Fig. 5. Relaxation of the 1/2 and $-1/2$ level populations now proceeds initially in a more rapid manner than one might expect from the preceding data. This effect may be understood from the following rather loose argument, in which the concept of a spin temperature ascribed to a pair of levels is employed.

We arbitrarily associate a "temperature" T_m with each adjacent pair of energy levels ($m, m-1$). Before the initial (180°) pulse, $T_m = T_L$ for all m. The result of an inverting pulse applied to, say, the (3/2,1/2) pair of levels will be a "heating up" of the spins originally in the (3/2) and (1/2) states to a negative temperature $T_{3/2}=-T_L$, and simultaneously a "cooling" of the (5/2,3/2) and (1/2, $-1/2$) spins to a temperature $T_L/2$. It will be recalled from Sec. II that the spin system as a whole, if perturbed from thermal equilibrium with the lattice, will first recover to some sort of internal Boltz-

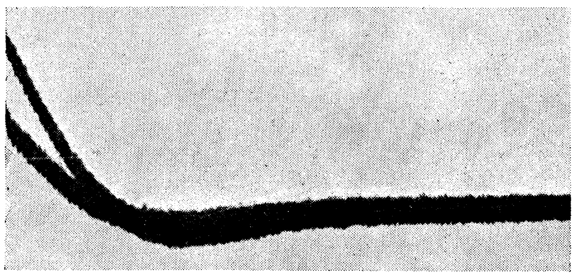

FIG. 5. Superimposed photographs of the Bloch decay of the ($1/2 \to 1/2$) transition. The lower trace is the normal Bloch decay $S(\infty)$ corresponding to Boltzmann equilibrium of the level populations; the upper trace is the (enhanced) Bloch decay of the ($1/2 \to -1/2$) transition 1 msec after inversion of the populations of the 3/2 and 1/2 energy levels [$S(t=1$ msec)]. Orientation $\theta=0°$, $T=80°$K. The 340-kc/sec beat note appearing on the trace is spurious pickup generated at the detector by the 9.86-Mc/sec and 10.20-Mc/sec cw oscillators. Total sweep from left to right is 300 μsec.

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[19] Enhancement of the nuclear Al signal in ruby has also been obtained by other methods, notably by microwave pumping of the Cr^{3+} electron spin resonance [R. D. Spence and J. A. Cowen, J. Chem. Phys. **32**, 624 (1960)]. In this case, polarization of the nuclear spins is accomplished by an electron spin flip-nuclear spin flip mechanism described by A. Abragam and W. G. Proctor [Compt. rend. **246**, 2253 (1958)].

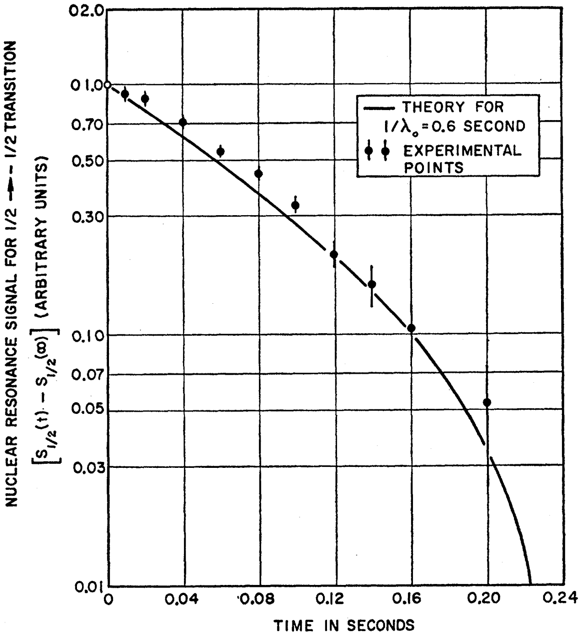

FIG. 6. Aluminum nuclear spin-lattice relaxation ($1/2 \rightarrow -1/2$ transition) in 0.035% ruby at $\theta=0°$, following inversion of the 3/2 and 1/2 populations. The theoretical curve is plotted from the equation $a_{1/2}(t)=1.2\exp(-t/0.1)-0.16\exp(-t/0.3)-0.04 \times\exp(-t/1.8)$. Temperature$\approx$80°K.

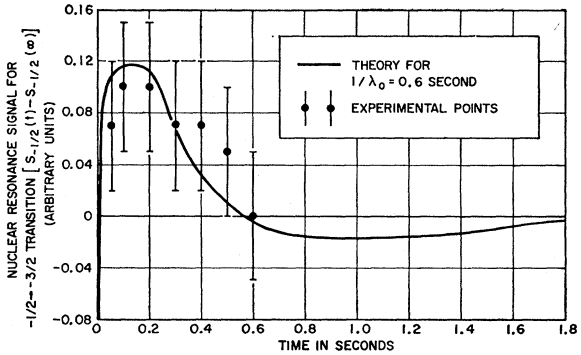

FIG. 7. Aluminum nuclear spin-lattice relaxation ($-1/2 \rightarrow -3/2$ transition) in 0.035% ruby, following inversion of the $+3/2$ and $+1/2$ populations. The theoretical curve is plotted from the equation $a_{-1/2}(t)=-0.05\exp(-t/1.8)+0.05\exp(-t/0.7)-0.1 \times\exp(-t/0.3)+0.95\exp(-t/0.17)-0.84\exp(-t/0.1)$. Temperature$\approx$80°K.

mann equilibrium (characterized by a temperature T_B), and then proceed exponentially toward thermal equilibrium with the lattice. Since the inverting pulse has supplied energy to the spin system as a whole, T_B must be larger than T_L. Therefore, the temperature $T_{1/2}$ associated with the population difference of the $(1/2, -1/2)$ states must rise from its initial value $T_L/2$, *through* the temperature T_L, to the temperature $T_B > T_L$, before finally returning to T_L.

This behavior is, in fact, what the normal modes solution describes. Unfortunately, experimental signal-to-noise limitations did not allow us to observe the $(1/2 \rightarrow -1/2)$ transition recovery all the way through the population difference corresponding to T_L. Nevertheless, the experimental points shown in Fig. 6 demonstrate most of the features described. The experiment has the additional feature that it agrees quantitatively with the normal modes solution for $1/\lambda_0=0.6$ sec. Note that the time scale is more rapid, by a factor of 5, than the time scales of Figs. 2, 3, and 4.

For the second experiment of this same nature, θ and H_0 were varied until f_1 and f_2 corresponded, respectively, to the $(3/2 \rightarrow 1/2)$ and $(-1/2 \rightarrow -3/2)$ transitions. After the inverting pulse at f_1, the departure and subsequent return of the $(-1/2, -3/2)$ populations to thermal equilibrium was observed at f_2. The results of this experiment are shown in Fig. 7. The limits on the experimental accuracy in this graph represent confidence estimates, rather than a scatter average of the experimental points. Nevertheless, reasonable agreement with the calculated curve for $1/\lambda_0=0.6$ sec is found. The behavior of the populations of this pair of levels is, again, consistent with the qualitative thermodynamic arguments given previously.

The relaxation of this pair of levels bears a striking resemblance to the relaxation process described by Solomon[20] in liquid hydrofluoric acid. In his experiment, he applied a 180° pulse to one kind of spin (protons), and observed the motion of the longitudinal component of magnetization of the other kind (fluorine nuclei). This is quite analogous to what we have done here. There is a difference in the two experiments, which arises from the extra degrees of freedom inherent in our problem; namely, our population difference departs from its thermal equilibrium value in the "wrong" sense, and must later go back through this difference value as the entire system recovers to internal Boltzmann equilibrium.

ACKNOWLEDGMENTS

We express our appreciation to the Linde Crystal Products Division of Union Carbide for the loan of a cobalt-doped sapphire crystal, on which preliminary measurements were made, and to R. T. McNamara, for his assistance with the experimental equipment and for performing and checking certain of the numerical computations.

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[20] I. Solomon, Phys. Rev. **99**, 559 (1955).

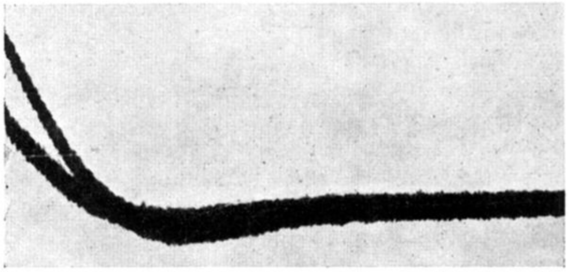

FIG. 5. Superimposed photographs of the Bloch decay of the $(1/2 \rightarrow 1/2)$ transition. The lower trace is the normal Bloch decay $S(\infty)$ corresponding to Boltzmann equilibrium of the level populations; the upper trace is the (enhanced) Bloch decay of the $(1/2 \rightarrow -1/2)$ transition 1 msec after inversion of the populations of the 3/2 and 1/2 energy levels $[S(t=1\text{ msec})]$. Orientation $\theta=0°$, $T=80°$K. The 340-kc/sec beat note appearing on the trace is spurious pickup generated at the detector by the 9.86-Mc/sec and 10.20-Mc/sec cw oscillators. Total sweep from left to right is 300 μsec.