which leads to the "integral equation for scattering." Using this formalism it is shown that the resultant energy distribution differs from that of the one-dimensional treatment because of the appearance of additional energy- and angle-dependent pre-exponential factors.

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Numerical Solution of the Equation Governing Nuclear Magnetic Spin-Lattice Relaxation in a Paramagnetic-Spin-Doped Insulator*

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A numerical solution of the equation

$$\frac{\partial M^z}{\partial t} = D\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}(rM^z)\right) - \frac{(M^z - M_0^z)\overline{C}}{r^6}$$

governing nuclear relaxation in a paramagnetic-spin-doped insulator has been obtained. The results are expressed in terms of

$$\overline{m}(t) = \int_b^R [M_0^z - M^z(t)] r^2 \, dr \Big/ \int_b^R M_0^z r^2 dr \quad ,$$

where $M^z(0) = 0$, b is the so-called "diffusion barrier" and $(4\pi R^3/3)^{-1}$ equals the paramagnetic-spin concentration. Simple analytic forms for the long-time exponential decay of $\overline{m}(t)$ are obtained for either D or $\overline{C}$ dominating the relaxation process. Graphical solutions for the intermediate regions are also obtained. The short-time nonexponential solution of $\overline{m}(t)$ is discussed.

INTRODUCTION

Bloembergen[1] and others[2] have argued that the differential equation governing nuclear spin-lattice relaxation in an insulator with a low concentration of paramagnetic spins is

$$\frac{\partial M^z}{\partial t} = D\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}(rM^z)\right) - \frac{M^z - M_0^z}{T_1(r)} \quad , \tag{1}$$

where M_0^z is the equilibrium nuclear magnetization and

$$T_1(r)^{-1} = \langle 3(\gamma_e\gamma_n\hbar)^2 S(S+1)r^{-6} \sin^2\theta \cos^2\theta [\tau(1+\omega_0^2\tau^2)^{-1}] \rangle$$

$$= \overline{C}\tau(1+\omega_0^2\tau^2)^{-1} \quad , \tag{2}$$

where $\langle \rangle$ means angular average, D is the spin-diffusion constant, ω_0 is the nuclear Larmor frequency, and $\vec{r} = 0$ defines the location of a paramagnetic impurity. The boundary conditions defining the solution of Eq. (1) are

$$M^z(r, o) = 0, \tag{3}$$

which indicates saturation of the nuclear spin

system at $t = 0$ and

$$\frac{\partial M^z}{\partial r}(b, t) = \frac{\partial M^z}{\partial r}(R, t) = 0,$$

where b is called the "diffusion-barrier" radius[1] and R is defined as

$$N^{-1} = \tfrac{4}{3}\pi R^3 ,\qquad (4)$$

where N is the concentration of paramagnetic impurities.

There have been a number of approximate analytical solutions[2] of Eq. (1) and it is the purpose of this paper to check their range of validity by obtaining a numerical solution of Eq. (1).

In the usual solution of Eq. (1) an additional parameter b_0 is introduced which is defined as the radius which separates those nuclear spins contained in twice the NMR half-width and those outside this width, thus roughly[2(t)]

$$\mu/b_0^3 = \Delta M ,\qquad (5)$$

where μ/r^3 defines the local-field shift of nuclei arising from the angularly averaged dipole field of a paramagnetic impurity, and ΔM is the full width. The sphere defined by b_0 is generally considered to include those nuclei which are shifted out of the normal NMR signal. b, the diffusion-barrier radius, will be similarly defined as

$$\Delta M = \frac{\mu}{(b-a)^3} - \frac{\mu}{b^3} ,\qquad (6)$$

where a is approximately a lattice constant for the nuclear spin lattice. Equation (6) is equivalent to assuming no spin diffusion for spins whose resonance frequencies are more than a full width apart.

Contrary to what has been previously suggested,[2(t)] b can be larger or smaller than b_0. The crossover radius is determined by equating Eq. (5) to Eq. (6) to determine the conditions under which $b = b_0$; thus

$$\frac{\mu}{(b-a)^3} - \frac{\mu}{b^3} = \frac{\mu}{b^3} ,\qquad (7)$$

$$b_0 = \frac{2^{1/3} a}{2^{1/3} - 1} \approx 5a .\qquad (8)$$

For $b < 5a$, $b_0 < b$ and for $b > 5a$, $b_0 > b$. We will show that for a large b the nuclear spin-lattice relaxation time will be insensitive to our choice of b_0 and for b_0's less than b the spins between b_0 and b will relax very rapidly and will not contribute to the experimentally observed relaxation time. Thus, to avoid the added complication of defining both b and b_0 separately, we will always assume an effective $b_0 = b$.

To simplify the numerical evaluation of Eq. (1) we made the following changes of variable:

$$m = M_0^z - M^z, \quad r = \beta x,$$

$$v = rm, \quad \gamma = (\overline{C}^{1/2} D^{-3/2}), \qquad (9)$$

$$t = \gamma \tau, \quad \beta = (\overline{C}/D)^{1/4} .$$

Substituting Eq. (9) into Eqs. (1) and (3) we obtain

$$\frac{dv}{d\tau} = \frac{\partial^2 v}{\partial x^2} - \frac{v}{x^6} ,$$

$$v(x, 0) = \beta x M_0^z , \qquad (10)$$

$$\frac{\partial v}{\partial x} = \frac{1}{x} v \begin{cases} x = b/\beta \\ x = R/\beta \end{cases}.$$

The physical quantity that is "observed" and whose dependence we will calculate is

$$\overline{m}(t) = 4\pi \int_b^R [M_0^z - M^z(t)] r^2 \, dr / 4\pi \int_b^R M_0^z r^2 \, dr$$

$$= \int_b^R m(t) r^2 \, dr / \int_b^R m(t=0) r^2 \, dr$$

$$= \int_{b/\beta}^{R/\beta} v(x, \tau) x \, dx / \int_{b/\beta}^{R/\beta} v(x, 0) x \, dx . \qquad (11)$$

The amplitude of an experimentally observed free-induction decay signal at a time t after saturation should be proportional to $\overline{m}(t)$.

The ratio β/b, as can be seen from Eqs. (9) and (10), measures the relative importance of direct relaxation and spin diffusion. In Sec. I we will discuss the time dependence of Eq. (11) for $\beta/b \ll 1$ (rapid diffusion); in Sec. II, we will discuss, and obtain graphically, the exponential (long-time) solution of Eq. (11) for $\beta/b \gg 1$ (diffusion limited); and in Sec. III we will discuss for $\beta/b \gg 1$ the short-time (nonexponential) solution.

I. TIME DEPENDENCE FOR $\beta/b \ll 1$

For the diffusion constant D large enough such that

$$\beta/b \ll 1 , \qquad (12)$$

the diffusion effectively proscribes any spatial variation of $M^z(r, t)$ for $r > b$. As Blumberg[2(a)] has suggested, one then can solve Eq. (1) with the boundary condition given in Eq. (3) to obtain

$$\overline{m} = 1 - e^{-t/T_{1n}^0} ,$$

where

$$T_{1n}^0 = \frac{T_{1n}^0}{\gamma} = \frac{R^3 b^3/\overline{C}}{\gamma} = \left(\frac{R}{\beta}\right)^3 \left(\frac{b}{\beta}\right)^3 . \qquad (13)$$

In Fig. 1 the ratio ϵ is plotted

$$\epsilon = \frac{T_{1n}^0}{T_{1n}^{comp}}$$

$$= \frac{R^3 b^3/\overline{C}}{T_{1n}^{comp}} = \frac{(R/\beta)^3 (b/\beta)^3}{T_{1n}^{comp}} , \qquad (14)$$

as a function of β/b. Two points should be made: It can be seen from Fig. 1 that Eq. (12) can be realistically defined as
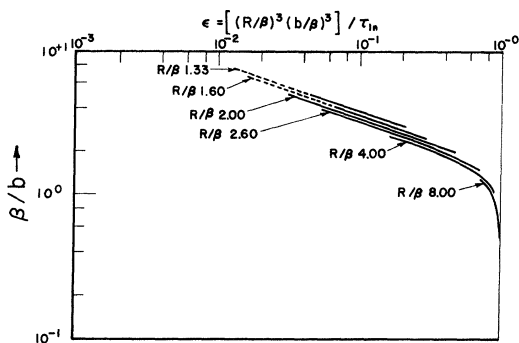
FIG. 1. Ratio $\epsilon = (R/\beta)^3(b/\beta)^3/\tau_{1n}$ is plotted as a function of β/b for $R/\beta = 1.33$, 1.60, 2.00, 2.60, 4.00, and 8.00.

$$\beta/b < \tfrac{1}{2} , \tag{15}$$

and that the spatial nonvariation of M^z for $\beta/b < \tfrac{1}{2}$ implies that the relaxation time T_{1n} will be independent of b_0.

II. EXPONENTIAL SOLUTION FOR $\beta/b \gg 1$

The computer solutions of the exponential (long-time) behavior of Eq. (11) are exhibited in Fig. 1. The range of R/β and b/β is taken to cover most practical experimental situations. As discussed in Ref. 2(f), the one-center approximation implicit in Eq. (1) breaks down for $R/\beta \to 1$, and a continuum theory [implicit in Eq. (1)] breaks down for $b/a \to 1$.

From the solutions given in Fig. 1 one obtains the useful heuristic result that for $\beta/b > 2.5$

$$T_{1n}^{\text{comp}} = T_{1n}^{\text{comp}}/\gamma \simeq \tfrac{1}{4}(R/\beta)^3 (R/\beta - 1)^{1/3} . \tag{16}$$

This is to be compared with the result obtained previously by approximate analytical arguments[2] that for $\beta \gg b$

$$T_{1n}^{aa}/\gamma \simeq \tfrac{1}{2}(R/\beta)^3 . \tag{17}$$

We believe Eq. (16) to be the most useful result obtained from our computer solutions. With the restriction that $\beta/b > 2.5$, Eq. (15) fits all points in Fig. 1 within a few percent.

III. NONEXPONENTIAL SOLUTION FOR $\beta/b \gg 1$

The short-time behavior for $\overline{m}(\tau)$ can be seen in Fig. 2 for two values of β/b. We note that for $\beta/b \gg 1$, the initial time dependence is not exponential. We can understand this result if we solve for $\overline{m}(\tau)$ assuming that for a large value of β/b the diffusion contribution to Eq. (1) can be ignored for short times. The reasonableness of this assumption stems from the initial constancy of M^z $(r, 0)$, implying that

$$D\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}(rM^z)\right) = 0, \quad t = 0. \tag{18}$$

Thus the diffusion contribution for weak diffusion will only contribute after a sizable gradient in $M^z(r, \tau)$ has been established. One then finds that for short times[2(g)]

$$\overline{m}(\tau) = 1 - \tau^{1/2} \int_{(\beta/R)^3 \tau^{1/2}}^{(\beta/b)^3 \tau^{1/2}} (1 - e^{-g^2}) g^{-2}\, dg$$

$$\times [(R/\beta)^3 - (b/\beta)^3]^{-1} . \tag{19}$$

If we additionally assume

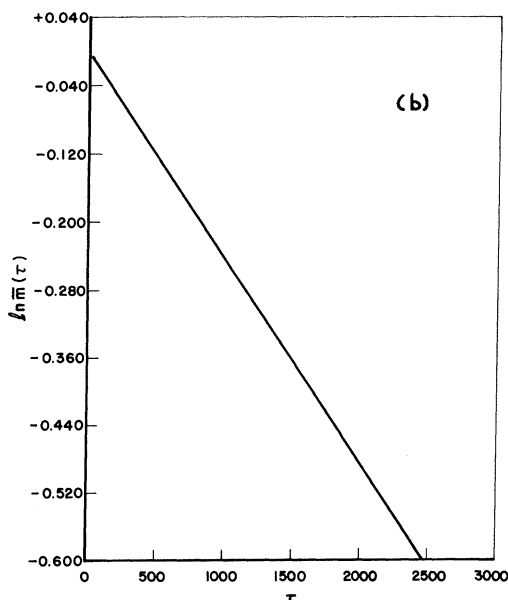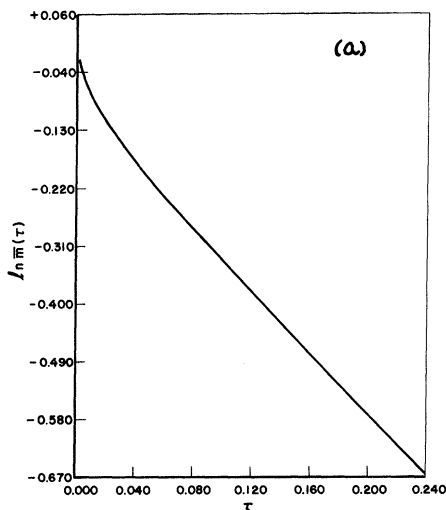FIG. 2. $\ln \overline{m}(\tau)$ as a function of τ is plotted for (a) $\beta/b = 5$, $R/\beta = 1.33$ and (b) $\beta/b = 0.5$, $R/\beta = 8.00$.
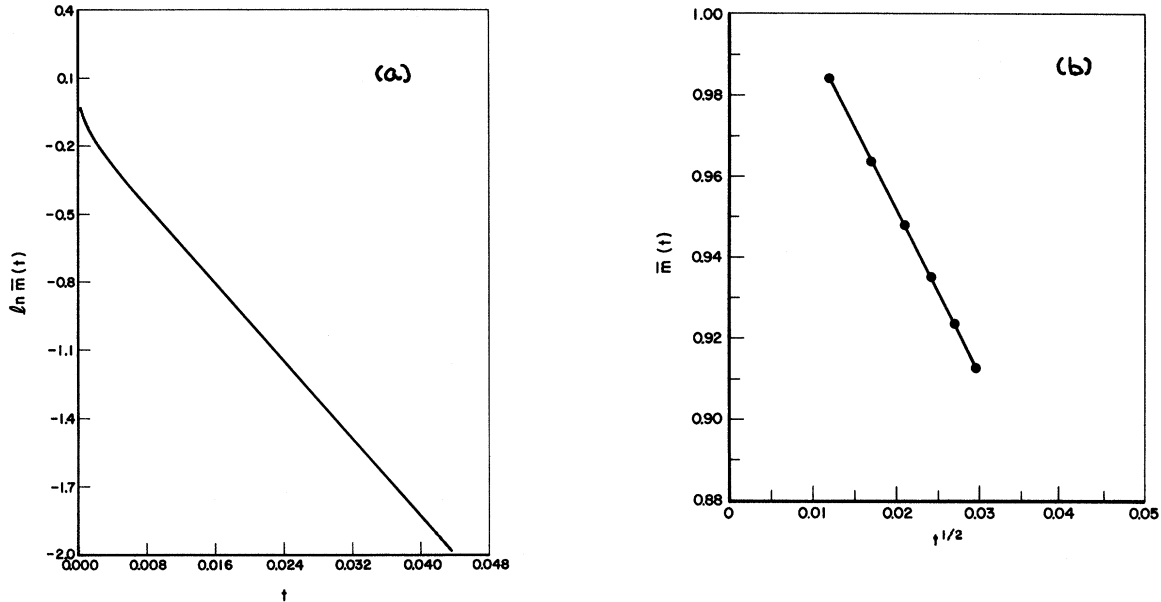
FIG. 3. (a) $\ln\overline{m}(t)$ is plotted as a function of t for $\beta/b = 3.8$ and $R/\beta = 1.05$. (b) $\overline{m}(t)$ is plotted as a function of $t^{1/2}$ for $\beta/b = 3.8$ and $R/\beta = 1.05$.

$$R/b \gg 1, \quad (\beta/R)^3\tau^{1/2} \to 0, \quad (\beta/b)^3\tau^{1/2} \gg 1, \qquad (20)$$

then $\overline{m}(\tau)$ simplifies as[2(a)]

$$\overline{m} \simeq 1 + (b/\beta)^3 + (b/R)^3 - \tau^{1/2}\pi^{1/2}$$

$$\times [1 + (b/R)^3 + \cdots] + \cdots, \qquad (21a)$$

$$\overline{m} \simeq 1 + (b/\beta)^3 + (b/R)^3 - \tfrac{4}{3}\pi^{3/2} N(\overline{C}t)^{1/2},$$

$$\times [1 + (b/R)^3 + \cdots] + \cdots. \qquad (21b)$$

From an experimental point of view, Eq. (21b) in real time is apparently extremely useful as its slope to lowest order is independent of D and b. Actually an experimenter must, after obtaining the coefficient $\tfrac{4}{3}\pi^{3/2} N\overline{C}^{1/2}$ from a section of his curve which is "visually" linear in $t^{1/2}$, check to see if the conditions given in Eq. (20) are satisfied. Thus, in effect, no conclusion can be drawn from the $t^{1/2}$ portion of the $\overline{m}(\tau)$ curve without knowing all the defining parameters.

In Fig. 3(a) is plotted $\ln m(t)$ for a particular set of parameters $R = 4 \times 10^{-7}$, $\overline{C} = 2.1 \times 10^{-38}$, $b = 10^{-7}$, $D = 10^{-12}$, $\beta/b = 3.8$. In Fig. 3(b) $\overline{m}(t)$ for the same set of parameters is plotted against t for t small, i.e., the nonexponential region in $\ln m(t)$. Writing

$$\overline{m}(t) = 1 - \alpha t^{1/2}, \qquad (22)$$

where

$$\alpha = \tfrac{4}{3}\pi^{3/2} N\overline{C}^{1/2}, \qquad (23)$$

one finds $\alpha \simeq 4$ from both graph and equation. We also find using the criteria of Eq. (20) that

$$(\overline{C}t)^{1/2}/b^3 > 2, \qquad (24)$$

$$(\overline{C}t)^{1/2}/R^3 < 0.1, \qquad (25)$$

which implies that $t^{1/2}$ behavior should exist between $1.4 \times 10^{-2} < t^{1/2} < 4.4 \times 10^{-2}$. Thus our result is consistent with the graphical solution in Fig. 3(b).

IV. CONCLUSION

From Fig. 1, one can conclude that there are two limiting equations describing the exponential time behavior of Eq. (11):

$$T_{1n}/\gamma = (R/b)^3(b/\beta)^3, \qquad \beta/b < \tfrac{1}{2} \qquad (26)$$

$$T_{1n}/\gamma = \tfrac{1}{4}(R/\beta)^3(R/\beta - 1)^{1/3}, \quad \beta/b > 2.5. \qquad (27)$$

For β/b between these limits numerical solutions can be obtained from Fig. 1. The $t^{1/2}$ behavior of Eq. (21b) for $\beta/b \gg 1$ is useful, for it determines the parameter $\alpha = \tfrac{4}{3}\pi^{3/2} N\overline{C}^{1/2}$, but an apparent $t^{1/2}$ dependence must be checked by the requirement that

$$2b^3/\overline{C}^{1/2} < t^{1/2} < (0.1)R^3/\overline{C}^{1/2}. \qquad (28)$$

ACKNOWLEDGMENT

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Temperature-Dependent Spin-Hamiltonian Parameters of Mn²⁺ in Trigonal Sites of CaCO₃ †

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The spin-Hamiltonian parameters of divalent manganese in $CaCO_3$ have been measured over the temperature range 4.2–850 °K using electron-spin-resonance-absorption techniques. Eigenvalues to the spin-Hamiltonian and best-fit parameters were obtained using perturbation calculations, where the off-diagonal component in the hyperfine interaction is treated as the major perturbation. The crystalline-field parameters and the hyperfine-coupling constant A were found to decrease in magnitude with increasing temperature, although there was no measurable variation of the g value over this temperature range. Variation in the parameters with temperature is discussed in terms of implicit (thermal-expansion) and explicit (lattice-vibration) effects. Contributions from implicit effects were evaluated using previously reported isothermal pressure-dependent data. After correcting the experimental data for the implicit effect, a large residual-temperature variation is found for the crystalline-field parameters D and a_0. This residual-temperature variation is attributed to lattice vibrations which couple into the crystalline-field splitting energy. Temperature variations in the axial crystalline-field-splitting energy can be explained, in part, by resonant vibrations which couple to the impurity ion via a relativistic second-order correction proposed by Wybourne. Temperature variations in the hyperfine-coupling constant A are also due primarily to explicit effects. A detailed theoretical analysis of the temperature dependence of A for Mn²⁺ in a noncubic environment has not been carried out. However, it is possible to qualitatively interpret this temperature variation if it assumed that a large-amplitude local-mode vibration couples strongly to the hyperfine-coupling parameter.

I. INTRODUCTION

In the past there has been a great deal of interest in the origin of crystal-field-splitting energies of S-state ions in various crystalline environments. Several mechanisms have been proposed to explain the manner in which the spin degeneracy of an S-state ion is lifted by the presence of a crystalline electric field.[1-11] In general, the crystal-field-splitting energy arises from mechanisms involving second- or higher-order perturbation terms in the spin-orbit, spin-spin, and crystal-field interactions. There has been some success in determining the most important contributions to the crystal-field-splitting energies for Mn²⁺ in ZnF_2 and MnF_2; however, it is not clear that the same mechanisms are predominant in other environments.[9-11] Recently, Wybourne showed that if relativistic radial wave functions are used in the crystal-field calculations, there would be an important second-order contribution to the ground-state splitting of rare-earth S-state ions.[12] Van Heuvelen extended these calculations to the Mn²⁺ ion and concluded that the relativistic contribution to the axial crystalline-field splitting D predicts the correct sign but about one-half the magnitude of D in a number of salts.[13] The relativistic contribution to the crystal-field-splitting parameters was shown to be important in the case of Mn²⁺ in NaCl.[14]

Another property of S-state ions which has been given a great deal of attention is the origin of the hyperfine interaction and the observed decrease of the hyperfine-coupling constant with increasing temperature in cubic environments.[15-29] Walsh, Jeener, and Bloembergen first recognized that the hyperfine-coupling temperature dependence $A(T)$ for Mn²⁺ in cubic environments is largely due to explicit effects, e.g., lattice vibrations.[15] However, as these investigators have pointed out, the implicit (thermal-expansion) effect also contributes to the variation of the hyperfine-coupling constant with temperature. In the case of Mn²⁺ in MgO, the implicit effect is small compared to the explicit effect. Simanek and Orbach proposed that the explicit temperature dependence of A for S-state ions in cubic environments is due to the mixing of the Mn²⁺ $3d$ orbitals with higher-lying ns orbitals through the orbit-lattice