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Nuclear Spin-Lattice Relaxation via Paramagnetic Centers*†

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The theory of nuclear spin-lattice relaxation via paramagnetic centers in diamagnetic crystals is investigated in terms of both the single-relaxation-center and the multirelaxation-center models. In this theory, the distances between centers are allowed to be finite. A new case is found for which the theory predicts a new dependence of the spin-lattice relaxation time upon the applied magnetic field, the concentration of the paramagnetic centers, and the magnitude of the diffusion constant. An adaptation of the theory to the rotating reference frame shows that under certain conditions the spin-lattice relaxation time in the rotating frame can be larger than in the laboratory frame.

I. INTRODUCTION

THE dominant role played by paramagnetic impurities in nuclear spin-lattice relaxation in certain diamagnetic crystals was recognized as early as 1947.[1] In 1949, Bloembergen proposed and investigated the idea of spin diffusion[2] as a means of transporting nuclear energy to the paramagnetic impurity centers. In this paper Bloembergen derived the transport equation for the nuclear magnetization and solved the time-independent case numerically to obtain an expression for T_1 in the diffusion-limited case. Later, Khutsishvili found an analytical solution to the equation.[3,4] de Gennes also solved the problem and showed that to a first-order approximation, the same T_1 expression could be obtained from either the steady state or the transient solution.[5] Blumberg investigated nuclear spin-lattice relaxation due to paramagnetic centers for the case where the effect of spin diffusion was negligible.[6] He derived the $t^{1/2}$ law for the growth of the nuclear magnetization a short time after the nuclear spin system was saturated. Blumberg also worked out a theory to cover the case in which spin diffusion is so fast that the relaxation rate depends completely on the rate at which paramagnetic centers can absorb energy (rapid-diffusion case). Khutsishvili subsequently solved this problem also[7] by taking the proper limits for his solution to the steady-state transport equation. In 1964, Rorschach derived a general expression for T_1 that linked the two limiting cases in one expression.[8] This solution shows a rather abrupt transition for the behavior of T_1 when going from one limiting case to the other (the rapid-diffusion case and the diffusion-limited case).

Most of the developments of the theory are based on the assumption that the paramagnetic-center concentration in the crystal is so dilute that the average impurity separation is essentially infinite in comparison to the range of direct interaction between the paramagnetic center and the surrounding nuclei. For some experiments, this assumption is violated. These theories also assume that the direct relaxation due to the paramagnetic centers is spherically symmetric.

In Sec. IIA of this paper the general spin-lattice relaxation-time equation in the laboratory reference frame is set up. In Sec. IIB, a spin-lattice relaxation time T_1 is computed from this equation for a spherically symmetric single-paramagnetic-center model for a *finite* average separation between centers. Various limiting cases are considered. In Sec. IIC, the general spin-lattice relaxation-time equation in the laboratory reference frame is solved for a multi-paramagnetic-center model, and its solutions are connected on to the single-center model.

A nonequilibrium value of magnetization may be generated along a magnetic field rotating in a plane that is perpendicular to the large applied static magnetic field. The time constant with which this magnetization decays, called the rotating reference frame spin-lattice relaxation time and denoted by T_1^r, may be different from T_1. The calculations of Sec. II are repeated in Sec. III for T_1^r.

II. SPIN-LATTICE RELAXATION TIME IN THE LABORATORY REFERENCE FRAME

A. Differential Equation for $M(\mathbf{r}, t)$

In a solid containing paramagnetic centers, the nuclear spins are acted upon by the time-varying local magnetic fields produced by these centers. If an initially saturated spin system is put in a static magnetic field $\mathbf{B}_0$, nuclear magnetization will be built up most rapidly near the paramagnetic centers due to the strong interactions of the nuclear spin system with the time-varying

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local fields at these sites. This gives rise to a spin-temperature gradient which causes spatial diffusion of nuclear spin energy. It will be assumed that the nuclear spins and the paramagnetic centers occupy fixed positions in space.

Let $M(\mathbf{r}, t)$ denote the nuclear spin magnetization at position $\mathbf{r}$ and time t. Then,

$$[\partial M(\mathbf{r}, t)/\partial t]_{\text{total}} = [\partial M(\mathbf{r}, t)/\partial t]_p + [\partial M(\mathbf{r}, t)/\partial t]_d. \tag{1}$$

The term $[\partial M(\mathbf{r}, t)/\partial t]_p$ represents the rate of change of $M(\mathbf{r}, t)$ due to the direct interaction of the nuclear spins with the paramagnetic centers, and is given by[2]

$$[\partial M(\mathbf{r}, t)/\partial t]_p = [M_0 - M(\mathbf{r}, t)]/T_{1p}(\mathbf{r}), \tag{2a}$$

where

$$[T_{1p}(\mathbf{r})]^{-1} = \sum_j [C_j/|\mathbf{r} - \mathbf{R}_j|^6]. \tag{2b}$$

M_0 is the equilibrium value of the nuclear spin magnetization at the lattice temperature T in the applied magnetic field $B_0\hat{z}$. $\mathbf{R}_j$ is the position of the jth paramagnetic center, and the sum is over all the paramagnetic centers of the lattice. As shown in Eq. (A27) of Appendix A, for $\omega_0\tau_c \ll \omega_p\tau_c'$, the term C_j has the value

$$C_j = 3\sin^2\theta_j \cos^2\theta_j \gamma_n^2\gamma_p^2\hbar^2 S(S+1)[\tau_c/(1+\omega_0^2\tau_c^2)], \tag{3}$$

where θ_j is the angle between the vector $(\mathbf{r} - \mathbf{R}_j)$ and the applied magnetic field $B_0\hat{z}$; γ_p and γ_n are the magnetogyric ratios of the paramagnetic center and nucleus, respectively; S is the spin of the paramagnetic center, τ_c is the correlation time of the z component of the paramagnetic center spin, τ_c' is the correlation time of the x or y component of the paramagnetic center spin, $\omega_0 = \gamma_n B_0$, and $\omega_p = \gamma_p B_0$.

The term $[\partial M(\mathbf{r}, t)/\partial t]_d$ represents the rate of change of $M(\mathbf{r}, t)$ due to the spatial transport of magnetization. When there is a spatially inhomogeneous distribution of magnetization, it has been shown[9] that due to spin-spin interaction

$$[\partial M(\mathbf{r}, t)/\partial t]_d = \sum_{\alpha,\beta=1}^{3} D^{\alpha\beta}(\partial^2/\partial x^\alpha \partial x^\beta) M(\mathbf{r}, t), \tag{4}$$

where $D^{\alpha\beta}$ is the $\alpha\beta$ component of a spin-diffusion tensor. Near the various paramagnetic centers, the value of $D^{\alpha\beta}$ goes to zero. The local field due to the paramagnetic center is different at different nuclear spin sites, and this tends to prevent the $\uparrow\downarrow \rightleftarrows \downarrow\uparrow$ transition from taking place. This process is necessary for spin diffusion, and when this process is quenched, the spin-diffusion rate goes to zero. This spin-diffusion quenching is normally introduced into a calculation by defining a radius b about each paramagnetic center, called the spin-diffusion barrier radius, inside of which $D^{\alpha\beta} = 0$ and outside of which $D^{\alpha\beta}$ has a constant value.

[9] I. J. Lowe and S. Gade, Phys. Rev. **156**, 817 (1967).

This radius b is defined as the distance from the paramagnetic center at which the change of B_p, the magnetic field of the paramagnetic center, is of the order of the local field B_l produced by nuclei at the sites of other nuclei. Its value is given by[8]

$$b = (3a\langle\mu_p\rangle_z/B_l)^{1/4}, \tag{5}$$

where $\langle\mu_p\rangle_z$ is the average effective value of the magnetic moment of the paramagnetic center in quenching spin diffusion and a is the distance between neighboring nuclear spins.

The magnetic field of the paramagnetic centers also broadens the resonance lines of the nuclei near the centers so that these nuclei normally do not contribute to the signal produced by the nuclei in a measurement. We can define a radius b_0 about each paramagnetic center, inside of which the nuclei have such broadened resonance lines that their contributions to a measured signal are unobserved. A reasonable criterion for the value of b_0 is that distance from the paramagnetic center, where B_p is of the order of B_l. Assuming $B_p \approx \langle\mu_p\rangle_z/r^3$, one has

$$b_0 = (\langle\mu_p\rangle_z/B_l)^{1/3}. \tag{6}$$

It is obvious that $b_0 > b$.

Substitution of Eqs. (2) and (4) into Eq. (1) yields

$$\partial m(\mathbf{r}, t)/\partial t = \sum_{\alpha,\beta=1}^{3} D^{\alpha\beta}(\partial^2/\partial x^\alpha \partial x^\beta) m(\mathbf{r}, t) - m(\mathbf{r}, t) \sum_j (C_j/|\mathbf{r} - \mathbf{R}_j|^6), \tag{7}$$

where $m(\mathbf{r}, t) = M_0 - M(\mathbf{r}, t)$. If one could find the general time-dependent solution to Eq. (7), one could then find the behavior of the total magnetization of the nuclear spin system as a function of time for a reasonable set of initial conditions (such as $m = M_0$ at $t = 0$). From this behavior, one could then deduce a nuclear spin-lattice relaxation time for this model. Unfortunately, this differential equation is difficult to manipulate, and a number of simplifying assumptions or approximations have to be made.

B. Single-Paramagnetic-Center Model

One type of assumption that can be made to solve Eq. (7) is that in each region of the sample, only *one* of the paramagnetic centers is important in determining the total nuclear spin-lattice relaxation rate in that region. The sample is thus divided up into "regions of influence." These regions are assumed to be spheres centered on the various paramagnetic centers and have radii R equal to the average separation of the paramagnetic centers:

$$R = (3/4\pi N_p)^{1/3}, \tag{8}$$

where N_p is the number of paramagnetic centers per unit volume in the sample. The second approximation is that $D^{\alpha\beta} = 0$ for $\alpha \neq \beta$, and that $D^{11} = D^{22} = D^{33} = D$.

The third approximation is that C_j, which is angularly dependent, can be replaced by the constant $\bar{C}$ equal to the value of C_j averaged over all angles:

$$\bar{C}=\tfrac{2}{5}S(S+1)\gamma_p^2\gamma_n^2\hbar^2[\tau_c/(1+\omega_0^2\tau_c^2)]. \tag{9}$$

With these approximations, Eq. (7) reduces to

$$\partial m(r,t)/\partial t=D\nabla^2 m(r,t)-(\bar{C}/r^6)m(r,t). \tag{10}$$

The paramagnetic center is located at the center of the coordinate system, and the region of interest for the solutions to the above equation is $r\leq R$. Even these simplifications are not enough to yield a nuclear spin-lattice relaxation time T_1, and one must resort to further round-about methods.

Let $\mathfrak{M}(t)$ denote the total observed magnetization in the sphere about the paramagnetic center.

$$\mathfrak{M}(t)=4\pi\int_{b_0}^{R} M(r,t)r^2dr. \tag{11}$$

In this model of noninteracting spheres of influence, the only way that $\mathfrak{M}(t)$ can change is by the direct relaxation of the nuclei in the sphere with the paramagnetic center in the sphere. Diffusion only moves magnetization around from one part of the sphere to another. Thus, since the nuclei for which $r<b_0$ are not observed, and since the nuclei for which $r<b$ have $D=0$ and thus do not make contact with the nuclei that have $r>b$, we can write

$$\frac{\partial\mathfrak{M}(t)}{\partial t}=4\pi\int_{b}^{R}[M_0-M(r,t)]\frac{\bar{C}}{r^6}r^2dr. \tag{12}$$

Let us now assume the distribution of magnetization in the sphere is such that $\partial\mathfrak{M}(t)/\partial t$ is exponential with a time constant T_1. Then

$$\begin{aligned}\partial\mathfrak{M}(t)/\partial t&=[\mathfrak{M}(\infty)-\mathfrak{M}(t)]/T_1\\&=\frac{4\pi}{T_1}\int_{b_0}^{R}[M_0-M(r,t)]r^2dr.\end{aligned} \tag{13}$$

Combining Equations (12) and (13) yields

$$T_1^{-1}=\int_b^R\frac{m(r,t)\bar{C}}{r^4}dr\bigg/\int_{b_0}^{R}m(r,t)r^2dr. \tag{14}$$

If one knew $m(r,t)$ for any particular time during the exponential relaxation process, one could compute T_1 from the above equation. This equation shows that T_1 is not extremely sensitive to the *detailed* shape of $m(r,t)$. We cannot solve Eq. (10) rigorously for $m(r,t)$, but we can find the time-independent solution rigorously[8] for $m(r)$ and use it to compute T_1 from Eq. (14). While $m(r)$ might not look like $m(r,t)$ in *detail*, these differences should not produce *major* errors in the computation of T_1.

Setting $\partial m(r,t)/\partial t=0$ in Eq. (10) yields

$$(r^2)^{-1}(\partial/\partial r)\{r^2[\partial m(r)/\partial r]\}-(\beta^4/r^6)m(r)=0, \tag{15}$$

where

$$\beta=(\bar{C}/D)^{1/4}. \tag{16}$$

The quantity β has the dimensions of length and is a measure of the competing contributions between direct relaxation and spin diffusion. Equation (15) for $m(r)$ is a second-order differential equation and yields a solution with two arbitrary constants whose values can be determined from boundary conditions. Since $D=0$ for $r<b$, no magnetization can flow across the sphere about the paramagnetic center with radius b. Thus

$$4\pi r^2D\left(\frac{\partial m(r)}{\partial r}\right)_r=4\pi\int_b^r\frac{\bar{C}}{r^6}m(r)r^2dr. \tag{17}$$

The integral in the above equation vanishes for $r=b$, so that $[\partial m(r)/\partial r]_b=0$, and we have our first boundary condition. Combining Eq. (17) with Eq. (14) yields

$$T_1^{-1}=R^2D\left(\frac{\partial m(r)}{\partial r}\right)_R\bigg/\int_{b_0}^{R}m(r)r^2dr. \tag{18}$$

The second boundary condition is set artificially by placing a magnetization sink at $r=R$, so that $m(R)$ has the fixed value of m_1. The value of m_1 will eventually cancel out of the expression for T_1; so its actual value is unimportant. The use of a magnetization sink is an artificial device to yield a nontrivial solution to Eq. (15). This artificial device, as well as the single-paramagnetic-center model, *should* work reasonably well for $\beta\ll R$, since for this case the direct interaction near the boundaries of the spheres of influence make a negligible contribution to T_1, and only this case has been studied in the past.[8] This restriction on R will be relaxed here to cover a wider range of experimental conditions. The solutions for the case $\beta\gg R$ are expected to have the least validity because:

(1) T_1 depends strongly on the behavior of the magnetization near the boundaries.

(2) The nuclei near the boundaries of the spheres of influence are acted on by several paramagnetic centers, so that the single-paramagnetic-center model should no longer be valid. That the solution to this problem for $\beta\approx R$ gives physically meaningful results will be shown by a comparison of this solution with an exact solution to the multicenter model carried out in Sec. II.

By making the substitution

$$m(r)=r^{-1/2}\chi(z), \tag{19}$$

$$z=\tfrac{1}{2}(\beta/r)^2, \tag{20}$$

Eq. (15) is transformed into the modified Bessel equation

$$z^2d^2\chi(z)/dz^2+zd\chi(z)/dz-[z^2+(1/4)^2]\chi(z)=0. \tag{21}$$

Equation (21) has the linearly independent solutions

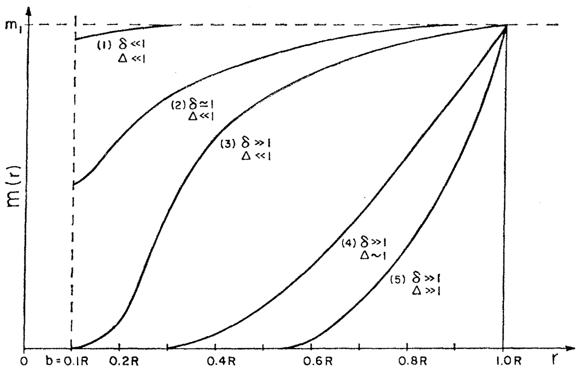

FIG. 1. $m(r)$ versus r for different values of δ and Δ. The value of R is arbitrarily picked as $10b$. The value of β is allowed to range from $0.5b$ to $100b$, thus making the range of δ from 0.125 to 5000.

$I_{1/4}(z)$ and $I_{-1/4}(z)$, where[10]

$$I_{\pm\nu}(z)=\sum_{m=0}^{\infty}\frac{(z/2)^{\pm\nu+2m}}{m!\Gamma(\pm\nu+m+1)} \tag{22}$$

for fractional values of ν. Letting

$$\begin{aligned}K_\nu(z)&=K_{-\nu}(z)\\&=\{\pi[I_{-\nu}(z)-I_\nu(z)]\}/2\sin\nu\pi,\end{aligned} \tag{23}$$

the solution to Eq. (15) can be written as

$$m(r)=r^{-1/2}[AI_{1/4}(\beta^2/2r^2)+BK_{1/4}(\beta^2/2r^2)], \tag{24}$$

where the constants A and B are to be determined from the previously discussed boundary conditions. The first boundary condition yields

$$A/B=K_{-3/4}(\delta)/I_{-3/4}(\delta), \tag{25}$$

where

$$\delta=\tfrac{1}{2}(\beta/b)^2. \tag{26}$$

The second boundary condition yields

$$m_1=R^{-1/2}[AI_{1/4}(\Delta)+BK_{1/4}(\Delta)], \tag{27}$$

where

$$\Delta=\tfrac{1}{2}(\beta/R)^2. \tag{28}$$

Solving for A and B and substituting the results into Eq. (24) yields

$$m(r)=m_1(R/r)^{1/2}\times\left(\frac{K_{3/4}(\delta)I_{1/4}(\beta^2/2r^2)+I_{-3/4}(\delta)K_{1/4}(\beta^2/2r^2)}{K_{3/4}(\delta)I_{1/4}(\Delta)+I_{-3/4}(\delta)K_{1/4}(\Delta)}\right). \tag{29}$$

Substituting Eq. (29) into Eq. (18) yields the general T_1 expression

$$T_1^{-1}=(4\pi\lambda N_pD\beta^2/R)\times\left(\frac{I_{-3/4}(\delta)K_{-3/4}(\Delta)-I_{-3/4}(\Delta)K_{-3/4}(\delta)}{I_{-3/4}(\delta)K_{1/4}(\Delta)+I_{1/4}(\Delta)K_{-3/4}(\delta)}\right), \tag{30}$$

where

$$\lambda^{-1}=\frac{3}{m_1R^3}\int_{b_0}^{R}m(r)r^2dr. \tag{31}$$

The term λ is a measure of the average value of $m(r)$ relative to its value at $r=R$, and it is independent of m_1. The expression for T_1 is also independent of m_1, as was predicted earlier.

The above expressions for $m(r)$, λ, and T_1 are complicated functions of Δ and δ. For several limiting cases, these expressions can be simplified and some physical insights about these results can be obtained.

Case 1: $R>b\gg\beta$

For the case where the direct relaxation rate is small enough, one has that $R>b\gg\beta$, and thus $1\gg\delta>\Delta$. The arguments of the modified Bessel functions in Eqs. (29) and (30) are all much less than one, so that these functions can be expanded in a power series and only the first few terms kept. This simplification yields

$$m(r)\cong m_1[1-(\beta^4/3b^3)(r^{-1}-R^{-1})+\tfrac{1}{12}\beta^4(1/r^4-1/R^4)], \tag{32}$$

$$\lambda\cong1+(b_0/R)^3, \tag{33}$$

$$T_1^{-1}\cong\tfrac{4}{3}\pi(N_p\bar{C}/b^3)[1+(b_0^3-b^3)/R^3-\tfrac{1}{4}(\beta/b)^4]. \tag{34}$$

This case is called the rapid-diffusion case by Rorschach.[8] Equation (32) shows $m(r)$ to be *almost* equal to m_1 for all r except near the diffusion barrier. This is reasonable, since for this case, the direct relaxation term is small and not able to establish a large spin-temperature gradient. Curve (1) of Fig. 1 shows a plot of $m(r)$ versus r for this case. The dependence of the dominant term of T_1 in Eq. (34) on various parameters is listed in Table I.

Case 2: $R\gg\beta\gg b$

For this case, the direct relaxation rate is large enough that $R\gg\beta\gg b$ and $\delta\gg1\gg\Delta$. Equations (29) and (30) can again be simplified by expanding those modified Bessel functions with arguments much less than one in a power series and keeping only the first few terms, and expanding those modified Bessel functions with arguments greater than 1 asymptotically. This simplification yields

$$m(r)\cong\frac{0.70m_1}{1-0.68(\beta/R)}(r/\beta)^{1/2}\exp(-\beta^2/2r^2),\quad r\ll\beta \tag{35a}$$

$$m(r)\cong m_1[1+0.68(\beta/R-\beta/r)],\quad r\gg\beta \tag{35b}$$

$$\lambda=1+0.34(\beta/R), \tag{36}$$

$$T_1^{-1}=\tfrac{8}{3}\pi N_p(\bar{C})^{1/4}(D)^{3/4}[1+1.02(\beta/R)]. \tag{37}$$

This case is called the diffusion-limited case by Rorschach.[8] Equations (35a) and (35b) show $m(r)$

[10] For the properties of modified Bessel functions and their recursion formulas, see G. N. Watson, *A Treatise on the Theory of Bessel Functions* (The University Press, Cambridge, England, 1944).

to be nearly equal to m_1 for $r>\beta$ and to decrease rapidly to a small value for $r<\beta$. Curve (3) of Fig. 1 shows a plot of $m(r)$ versus r for this case. As for case 1, λ is well approximated by the value 1. For $\beta/R\ll 1$, the dependence of the dominant term of T_1 in Eq. (37) on various parameters is listed in Table I.

Case 3: $\beta\gg R>b$

For this case, the direct relaxation rate is large enough that $\beta\gg R>b$ and $\delta>\Delta\gg 1$. The arguments of the modified Bessel functions in Eqs. (29) and (30) are all greater than one so that they can all be expanded asymptotically. This simplification yields

$$m(r)=m_1\left(\frac{r}{R}\right)^{1/2}\left[1+\exp\left(\frac{\beta^2}{r^2}-\frac{\beta^2}{b^2}\right)-\exp\left(\frac{\beta^2}{R^2}-\frac{\beta^2}{b^2}\right)\right]\times\left[1+\frac{3}{16}\left(\frac{R^2}{\beta^2}-\frac{r^2}{\beta^2}\right)\right]\exp\left(\frac{\beta^2}{2R^2}-\frac{\beta^2}{2r^2}\right),\quad(38)$$

$$\lambda=\beta^2/3R^2+11/6,\quad(39)$$

$$T_1^{-1}=[\tfrac{4}{3}(\pi N_p)]^2\bar{C}(1+6R^2/\beta^2),$$
$$=17.5\bar{C}N_p^2+40.4(\bar{C}D)^{1/2}N_p^{4/3}.\quad(40)$$

Equation (38) shows that $m(r)$ has the proper limiting value of m_1, but it falls very quickly to zero for r somewhat smaller than R. This is what one would expect, since for $\bar{C}$ large enough, diffusion is relatively unimportant in determining the magnetization value except for very near the boundary of the sphere. Curve (5) of Fig. 1 shows a plot of $m(r)$ versus r for this case. λ is much greater than 1, which follows from the average magnetization being much less than m_1. As long as $\beta/R\gg 1$, the spin-lattice relaxation time does not depend upon the diffusion constant D. This is physically reasonable since the direct relaxation rate is now so fast that spin diffusion does not have a chance to transport magnetization from one part of the sphere to another.

While this calculation is correct, the model on which it is based has no validity for actual experimental situations. As mentioned above $m(r)$ is different from zero only near the surface of the sphere. Since direct relaxation dominates in this case, those nuclei near the surface of the sphere are acted on by several paramagnetic centers and a multi-paramagnetic-center model, in which the angular dependence of C_j is kept, should be used to compute T_1.

Case 4: $R\approx\beta\gg b$

For this case, the direct relaxation rate is large enough that $R\approx\beta\gg b$ and $\delta\gg\Delta\approx 1$. For this case, neither the power-series expansions nor asymptotic expansions used for the previous cases will work. The behavior of $m(r)$ as a function of r will lie somewhere between that of $m(r)$ for cases 2 and 3. Curve (4) of Fig. 1 shows a plot of $m(r)$ versus r for such a case. Also, the behavior of λ and T_1^{-1} for case 4 should lie somewhere between that of cases 2 and 3. In both cases 2 and 3, as β/R approaches 1, the correction term to T_1^{-1} in β/R becomes of the same order of magnitude as the leading term and the limiting forms for T_1^{-1} are no longer valid. For case 2, the first-order correction term to T_1^{-1} is

$$\tfrac{8}{3}\pi N_p(\bar{C})^{1/4}(D)^{3/4}[1.02(\beta/R)]=10.4N_p^{4/3}(\bar{C})^{1/2}(D)^{1/2},\quad(41)$$

while for case 3, the first-order correction term to T_1^{-1} is

$$[\tfrac{4}{3}(\pi N_p)]^2(\bar{C})(6R^2/\beta^2)=40.4N_p^{4/3}(\bar{C})^{1/2}(D)^{1/2}.\quad(42)$$

Both these correction terms have the same dependence upon N_p, $\bar{C}$, and D, but they have different multiplying coefficients. In a crude fashion, this suggests that the behavior of T_1^{-1} should be of the form listed in Eqs. (41) and (42), but with a different multiplying coefficient. This argument should not be pressed too hard, however, because the model on which it is based is not very sound in this region. Sounder arguments that lead to the same behavior for T_1^{-1} listed in Eqs. (41) and (42) will be given in the next section.

To keep pace with the existing names for cases 1 and 2, this relaxation region is loosely designated as the diffusion-vanishing case, suggesting that the large value of β can be produced by the small value of the diffusion constant. The new features that distinguish the diffusion-vanishing case from the others are (a) T_1 is linearly dependent upon the applied magnetic field, and (b) T_1 is dependent upon the concentration of paramagnetic centers to the $-\frac{4}{3}$ power. Table I summarizes the dependence of the leading terms of T_1 upon various parameters for cases 1, 2, and 4.

TABLE I. The dependence of the leading terms in the relaxation time T_1 upon $\bar{C}$, B_0, τ_c, N_p, b, and D for the condition of $\omega_0\tau_c\gg 1$.

Case	Condition	Exponent dependence of T_1: $\bar{C}$	B_0	τ_c	N_p	b	D
Rapid diffusion	$\delta\ll 1$, $\Delta\ll 1$	-1	2	1	-1	3	0
Diffusion limited	$\delta\gg 1$, $\Delta\ll 1$	$-\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	-1	0	$-\frac{3}{4}$
Diffusion vanishing	$\delta\gg 1$, $\Delta\sim 1$	$-\frac{1}{2}$	1	$\frac{1}{2}$	$-\frac{4}{3}$	0	$-\frac{1}{2}$

C. Multi-paramagnetic-Center Model for the Diffusion-Vanishing Case

The direct spin-lattice relaxation term T_{1p}, listed in Eq. (2b), is strongly spatially dependent. For a sample containing many paramagnetic centers, $T_{1p}^{-1}(\mathbf{r})$ should have positions where it is a minimum, these positions being far away from the paramagnetic centers. A second type of approximation that can be used to solve Eq. (7)

is to expand $T_{1p}^{-1}(\mathbf{r})$ in a power series about a position $\mathbf{\Sigma}$, where it is a minimum, and keep only terms through second order in $\mathbf{r}$, where the origin for $\mathbf{r}$ is now taken at $\mathbf{\Sigma}$. Since this terminated power-series expansion accurately represents the direct relaxation term only for small r, when this approximation is used, solutions to Eq. (7) for $m(\mathbf{r},t)$, are acceptable if they are large only in the region for which $r<R$.

In the power-series expansion of $T_{1p}^{-1}(\mathbf{r})$ about $\mathbf{\Sigma}$, terms linear in x, y, z will be absent since position $\mathbf{\Sigma}$ is chosen to lie at a minimum for $T_{1p}^{-1}(\mathbf{r})$. By choosing the coordinate system so that terms in xy, xz, and yz do not appear in the second-order term the power-series expansion for $T_{1p}^{-1}(\mathbf{r})$ may be written as

$$[T_{1p}(\mathbf{r})]^{-1}=u_0+u_{xx}x^2+u_{yy}y^2+u_{zz}z^2, \qquad (43)$$

where the u's are constants that are evaluated in Appendix C. Inserting Eq. (43) into Eq. (7) and assuming that $D^{\alpha\beta}=0$ for $\alpha\neq\beta$ yields

$$\partial m(\mathbf{r},t)/\partial t=\left(D^{xx}\frac{\partial^2}{\partial x^2}+D^{yy}\frac{\partial^2}{\partial y^2}+D^{zz}\frac{\partial^2}{\partial z^2}\right)m(\mathbf{r},t)$$
$$=(u_0+u_{xx}x^2+u_{yy}y^2+u_{zz}z^2)m(\mathbf{r},t). \qquad (44)$$

The variables in Eq. (44) can be separated by making the substitution

$$m(x,y,z,t)=f_x(x)f_y(y)f_z(z)f_t(t). \qquad (45)$$

This yields the equations

$$D^{\alpha\alpha}[d^2f_\alpha(x_\alpha)/dx_\alpha^2]-u_{\alpha\alpha}x_\alpha^2f_\alpha(x_\alpha)=-k_\alpha f_\alpha(x_\alpha),$$
$$\alpha=x,y,z \qquad (46)$$

$$df_t(t)/dt=-f_t(t)/T_1(k_x,k_y,k_z), \qquad (47)$$

$$T_1^{-1}(k_x,k_y,k_z)=k_x+k_y+k_z+u_0, \qquad (48)$$

where k_x, k_y, and k_z are constants. Equation (46) is similar to that for the one-dimensional quantum-mechanical harmonic oscillator, whose solution is given in a number of standard texts.[11] This solution is

$$f_{\alpha,n(\alpha)}(x_\alpha)=\exp[-\tfrac{1}{2}(u_{\alpha\alpha}/D^{\alpha\alpha})^{1/2}x_\alpha^2]$$
$$\times H_{n(\alpha)}[(u_{\alpha\alpha}/D^{\alpha\alpha})^{1/4}x_\alpha], \qquad (49)$$

$$k_{\alpha,n(\alpha)}=[2n(\alpha)+1](D^{\alpha\alpha}u_{\alpha\alpha})^{1/2},$$
$$n(\alpha)=0,1,2,3,\cdots, \qquad (50)$$

where $H_{n(\alpha)}(\xi)$ are Hermite polynomials of order $n(\alpha)$. The Hermite polynomials form a complete set, so that we have found all the solutions. The general solution may now be written as

$$m(x,y,z,t)=\sum_{n(x),n(y),n(z)}(\text{constant})_{n(x),n(y),n(z)}$$
$$\times m(x,y,z,t)_{n(x),n(y),n(z)}, \qquad (51)$$

$$m(x,y,z,t)_{n(x),n(y),n(z)}=[\prod_\alpha f_{\alpha,n(\alpha)}(x_\alpha)]$$
$$\times\exp\{-t/T_1[n(x),n(y),n(z)]\}, \qquad (52)$$

$$T_1^{-1}[n(x),n(y),n(z)]=u_0+\sum_\alpha[2n(\alpha)+1](D^{\alpha\alpha}u_{\alpha\alpha})^{1/2}, \qquad (53)$$

where the constants in Eq. (51) are to be determined from some initial set of conditions. Equation (53) shows $T_1^{-1}[n(x),n(y),n(z)]$ to be a rapidly increasing function of $n(x)$, $n(y)$, and $n(z)$. If one is willing to wait long enough after some initial excitation of the nuclear spin system to make a measurement of the magnetization, only the (0, 0, 0) mode should make an appreciable contribution to $m(x,y,z,t)$, assuming that it has been initially excited. Since $H_0(\xi)=1$, the *long time solution* for $m(x,y,z,t)$ is

$$m(x,y,z,t)=(\text{constant})$$
$$\times\exp\left\{-\tfrac{1}{2}\left[\left(\frac{u_{xx}}{D^{xx}}\right)^{1/2}x^2+\left(\frac{u_{yy}}{D^{yy}}\right)^{1/2}y^2+\left(\frac{u_{zz}}{D^{zz}}\right)^{1/2}z^2\right]-\frac{t}{T_1}\right\}, \qquad (54)$$

$$T_1^{-1}\equiv T_1^{-1}(0,0,0)$$
$$=u_0+(D^{xx}u_{xx})^{1/2}+(D^{yy}u_{yy})^{1/2}+(D^{zz}u_{zz})^{1/2}. \qquad (55)$$

As mentioned at the beginning of this section, the expansions used in this model should only lead to valid results if $m(x,y,z,t)$ is small near the paramagnetic centers. From Eq. (54), we can conclude that a necessary and sufficient condition for our solution to satisfy this criterion is

$$(u_{\alpha\alpha}/D^{\alpha\alpha})^{1/2}R^2>1 \qquad (56)$$

for $\alpha=x$, y and z. Replacing $u_{\alpha\alpha}$ and $D_{\alpha\alpha}$ by their spherical averages, and using the results of Appendix B, the above condition can be crudely approximated by

$$\left(\frac{\frac{15}{2}(\bar{C}/R^8)}{D}\right)^{1/2}R^2\sim\frac{\beta^2}{R^2}>1, \qquad (57)$$

which is approximately the condition for the diffusion-vanishing case that was discussed for cases 3 and 4 of Sec. IIB.

For the purpose of making a quantitative estimate of T_1, using Eq. (55), it will be assumed that the paramagnetic centers form either a simple cubic lattice, a face-centered cubic lattice or a body-centered cubic lattice. It will be further assumed that $D^{xx}=D^{yy}=D^{zz}=D$. Using

$$u_0=\eta_0\bar{C}/L^6,$$
$$u_{\alpha\alpha}=\eta_{\alpha\alpha}\bar{C}/L^8,$$
$$\eta=\eta_{xx}^{1/2}+\eta_{yy}^{1/2}+\eta_{zz}^{1/2}, \qquad (58)$$

Eq. (55) can be rewritten as

$$T_1^{-1}=(\eta_0\bar{C}/L^6)+\eta[(\bar{C}D)^{1/2}/L^4], \qquad (59)$$

[11] See for example, Leonard I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955).

TABLE II. Constants used to evaluate T_1^{-1} for the diffusion-vanishing case. Only one of the positions of the $(T_{1p})^{-1}$ minima is given. The others within the unit cell can be found from the symmetry properties of the cube.

Paramagnetic center lattice	Position of $(T_{1p})^{-1}$ minimum in cubic unit cell	L^{-1}	η_0	η_{xx}	η_{yy}	η_{zz}	η	λ_0	λ
Simple cubic	$[\frac{1}{2}, 0, 0]$	$2N_p^{1/3}$	0.048	0.0135	0.0135	15	3.86	3.1	61
Face-centered cubic	$[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$	$2^{1/3}N_p^{1/3}$	0.5	15	15	30	13.3	1.95	33.2
Body-centered cubic	$[\frac{1}{2}, \frac{1}{2}, 0]$	$2^{2/3}N_p^{1/3}$	0.075	15	15	1.9	9.1	1.2	58.5

where $2L$ is the edge dimension of the cubic unit cell. The values of the η's are given in Table II for the applied magnetic field pointing along a cubic axis. Equation (59) can be rewritten in terms of the number of paramagnetic centers per unit volume, N_p, as

$$T_1^{-1}=\lambda_0\bar{C}N_p^2+\lambda(\bar{C}D)^{1/2}(N_p)^{4/3}. \tag{60}$$

The values of λ_0 and λ for the three cubic lattices are also given in Table II.

The form of T_1^{-1} in Eq. (60) is identical to T_1^{-1} given in Eq. (40) for case 3 of the single-center model. The coefficient of N_p^2 in Eq. (40) is much greater than that in Eq. (60), however. Those regions where the direct relaxation is a minimum are weighted most heavily in both models, but the value for the direct relaxation is made artificially high in the single-center model by neglecting the angular variation of the direct relaxation term in the process of replacing C_j by $\bar{C}$. This leads to the much larger coefficient of N_p^2 in Eq. (40). In contrast to this large difference of coefficients for N_p^2, the coefficient of $N_p^{4/3}$ in Eq. (40) agrees very well with the several computed coefficients of $N_p^{4/3}$ in Eq. (60). This could be attributed to the averaging effects on the relaxation rate due to diffusion, but the good agreement is more likely fortuitous and we ascribe no significance to it.

In Eq. (59), the ratio of the direct relaxation term to the one involving spin diffusion can be written in the form $(\eta_0/\eta)(\beta/L)^2$. All three lattices for the paramagnetic centers yield values for $\eta_0/\eta\ll 1$, as shown in Table II. Therefore, as long as β/L is less than 4 or 5, the direct relaxation term makes a negligible contribution to T_1 and may be dropped from Eqs. (59) and (60). The range of N_p for $1<\beta/L<5$ is 125.

One normally expects the paramagnetic centers to have a random spatial arrangement. The positioning of the paramagnetic centers in an ordered arrangement was assumed in order to compute the values of the u's in Eq. (43). This procedure does not seem unreasonable, since the form of T_1^{-1} in Eq. (60) should not depend upon the detailed arrangement of the paramagnetic centers, and the values of λ_0 and λ in Table II do not vary greatly for the three lattices for which they are evaluated. Averaging T_1^{-1} over a random distribution of paramagnetic centers yields

$$T_1^{-1}\cong\bar{\lambda}_0\bar{C}N_p^2+\bar{\lambda}(\bar{C}D)^{1/2}N_p^{4/3}, \tag{61}$$

where the expected order of magnitudes for the λ's are

$$\bar{\lambda}_0\approx 2, \qquad \bar{\lambda}\approx 50.$$

III. SPIN-LATTICE RELAXATION TIME IN THE ROTATING REFERENCE FRAME

A. Differential Equation for $M^r(\mathbf{r}, t)$

Besides the static magnetic field $B_0\hat{z}$ that was applied to the sample in Sec. II, let there now also be applied a magnetic field $\mathbf{B}_1(t)$ that rotates in the xy plane at the Larmor frequency $\omega_0/2\pi$. In the presence of this strong resonantly rotating magnetic field, the nuclear spin magnetization along the rotating field, denoted by $M^r(\mathbf{r}, t)$, behaves as if it were proceeding toward thermal equilibrium in the coordinate frame rotating with the field. The same arguments used in Sec. IIA to derive an equation for the time rate of change for $M(\mathbf{r}, t)$ can also be used to derive an equivalent one for $M^r(\mathbf{r}, t)$.

As in Sec. IIA, one may write that

$$[\partial M^r(\mathbf{r}, t)/\partial t]_{\text{total}}=[\partial M^r(\mathbf{r}, t)/\partial t]_p+[\partial M^r(\mathbf{r}, t)/\partial t]_d, \tag{62}$$

with

$$[\partial M^r(\mathbf{r}, t)/\partial t]_p=[M_0^r-M^r(\mathbf{r}, t)]/T_{1p}^r(\mathbf{r}). \tag{63}$$

M_0^r is the equilibrium magnetization along the rotating magnetic field. Equation (A26) of Appendix A demonstrates that one may write

$$[T_{1p}^r(\mathbf{r})]^{-1}=\sum_j(C_j^r/|\mathbf{r}-\mathbf{R}_j|^6), \tag{64}$$

and that for $\omega_p\tau_c'\gg 1$, and $\omega_0\gg\omega_1$,

$$C_j^r=\gamma_p^2\gamma_n^2\hbar^2S(S+1)\{\tfrac{1}{3}(1-3\cos^2\theta_j)^2[\tau_c/(1+\omega_1^2\tau_c^2)] + \tfrac{3}{2}\sin^2\theta_j\cos^2\theta_j[\tau_c/(1+\omega_0^2\tau_c^2)]\}. \tag{65}$$

$[\partial M^r(\mathbf{r}, t)/\partial t]_d$ in Eq. (62) represents the rate of change of $M^r(\mathbf{r}, t)$ due to the spatial transport of magnetization. It is shown in Appendix C that the diffusion tensor for magnetization in the Larmor rotating reference frame is exactly 1/2 that in the laboratory reference frame. Thus

$$[\partial M^r(\mathbf{r}, t)/\partial t]_d=\sum_{\alpha,\beta=1} D^{\alpha\beta r}(\partial^2/\partial x^\alpha\partial x^\beta)M^r(\mathbf{r}, t), \tag{66}$$

where $D^{\alpha\beta r}=\frac{1}{2}D^{\alpha\beta}$.

As in the case of spin diffusion in the laboratory reference frame, spin diffusion in the rotating reference frame is quenched near paramagnetic centers due to the local magnetic field of these paramagnetic centers. If B_1 is much larger than the nuclear spin-spin interaction, then the component of the magnetic field of the paramagnetic centers that lies along $\mathbf{B}_1(t)$ is the most effective component of this field in quenching spin diffusion. The value of this field, denoted by $B_{ix}{}^r$, is found from Eqs. (A23), (A4), and (A5) to be

$$B_{ix}{}^r = -(\gamma_n)^{-1}\exp(-i\omega_0 t)\sum_\nu [A_{i\nu}S_{\nu-}(t) \times\exp(i\omega_p t)+C_{i\nu}S_{\nu z}(t)+E_{i\nu}S_{\nu+}(t)\exp(-i\omega_p t)] + \text{complex conjugate}. \quad (67)$$

The same formalism as Rorschach's[8] may now be used to compute that part of the magnetic moment that is effective in quenching spin diffusion in the rotating reference frame. This analysis leads to the conclusion that only that part of $U_{ix}{}^r$ [denoted by $(U_{ix}{}^r)_{\text{eff}}$] whose Fourier spectrum lies between $-\frac{1}{2}(2\pi/T_2)$ and $+\frac{1}{2}(2\pi/T_2)$ is effective in quenching spin diffusion. T_2 is the "linewidth" of the nuclear resonance line. If $\omega_p\tau_c'\gg 1$, then $S_{\nu+}(t)$ and $S_{\nu-}(t)$ listed in Eq. (67) make a negligible contribution to $(U_{ix}{}^r)_{\text{eff}}$ because of the $\exp[i(\pm\omega_p-\omega_0)t]$ factor multiplying them. This leaves $S_{\nu z}(t)\exp(-i\omega_0 t)$ in Eq. (67) as the dominant contributor to $B_{ix}{}^r$. Only that part of $S_{\nu z}(t)$ whose Fourier spectrum lies near ω_0 is effective in quenching spin diffusion because of the $\exp(-i\omega_0 t)$ factor. Let us denote the spin diffusion barrier radius in the rotating reference frame by b^r, and use the same criteria in evaluating it (an admittedly crude one since it ignores angular variations in various coefficients) as is used in the laboratory reference frame. From the above arguments, it follows that for $\omega_0\tau_c\gg 1$, $b^r\ll b$; while for $\omega_0\tau_c\ll 1$, $b^r\approx b$.

It should be added at this point that the region about each paramagnetic center, inside of which the nuclei have broadened resonance lines and are unobservable, depends upon the method of observation. Assuming the magnetization to be observed by the same technique as the laboratory reference frame experiments, the radius of this region may also be taken to be b_0, the same radius as used in Sec. IIA.

Substitution of Eqs. (64) and (66) into Eq. (62) yields

$$\partial m^r(\mathbf{r},t)/\partial t=\sum_{\alpha,\beta} D^{\alpha\beta r}(\partial^2/\partial x^\alpha\partial x^\beta)m^r(\mathbf{r},t) - m^r(\mathbf{r},t)\sum_j (C_j{}^r/|\mathbf{r}-\mathbf{R}_j|^6), \quad (68)$$

where $m^r(\mathbf{r},t)=M_0{}^r-M^r(\mathbf{r},t)$. Equation (68) is identical in form to Eq. (7), and the same sets of approximations and formalism that were used to solve Eq. (7) may be used to solve it, too.

B. Single-Paramagnetic-Center Model—Rotating Reference Frame

To apply the single-paramagnetic-center-model solution of Sec. IIB to relaxation in the rotating reference frame, a set of approximations, identical to those of Sec. IIB, must be made. $D^{\alpha\beta r}$ must be set equal to zero for $\alpha\neq\beta$, and equal to D^r for $\alpha=\beta$. $C_j{}^r$ must be replaced by $\bar{C}^r$, its value averaged over all angles:

$$\bar{C}^r=\gamma_p{}^2\gamma_n{}^2\hbar^2 S(S+1)\left(\frac{4}{15}\frac{\tau_c}{1+\omega_1{}^2\tau_c{}^2}+\frac{1}{5}\frac{\tau_c}{1+\omega_0{}^2\tau_c{}^2}\right). \quad (69)$$

These approximations yield the equation

$$\frac{\partial m^r(r,t)}{\partial t}=D^r\nabla^2 m^r(r,t)-\frac{\bar{C}^r}{r^6}m(r,t). \quad (70)$$

Defining the parameters β^r, δ^r and Δ^r as

$$\beta^r=(\bar{C}^r D^r)^{1/4},$$
$$\delta^r=\tfrac{1}{2}(\beta^r/b^r)^2,$$
$$\Delta^r=\tfrac{1}{2}(\beta^r/R)^2, \quad (71)$$

and applying the procedures of Sec. IIB to Eq. (70), yields the following results for $T_1{}^r$, the spin-lattice relaxation time in the rotating reference frame:

Rapid-diffusion case: $R>b^r\gg\beta^r$

$$(T_1{}^r)^{-1}=\tfrac{4}{3}\pi\frac{N_p\bar{C}^r}{(b^r)^3}\left[1+\left(\frac{b_0}{R}\right)^3-\left(\frac{b^r}{R}\right)^3-\frac{1}{4}\left(\frac{\beta}{b}\right)^4\right]. \quad (72)$$

Diffusion-limited case: $R\gg\beta^r\gg b^r$

$$(T_1{}^r)^{-1}=\tfrac{8}{3}\pi N_p(\bar{C}^r)^{1/4}(D^r)^{3/4}(1+1.02\beta^r/R). \quad (73)$$

For the condition: $\beta^r\gg R>b$

$$(T_1{}^r)^{-1}=17.5\bar{C}^r N_p{}^2+40.4(\bar{C}^r D^r)^{1/2}N_p{}^{4/3}. \quad (74)$$

The discussion in Sec. IIB about the properties of the solutions of T_1 and properties of T_1 also holds for the above listed solutions for $T_1{}^r$.

Let us now compare T_1 and $T_1{}^r$ for a given sample (so that R is fixed) at a given temperature (so that τ_c is fixed). Let us assume that τ_c is long enough that $\omega_0\tau_c\gg\omega_1\tau_c\gg 1$, and therefore $\beta^r\gg\beta$. The forms of the solutions for T_1 and $T_1{}^r$ may be of the same type, but not necessarily. While T_1 might be in the rapid-diffusion region, $T_1{}^r$ might be in the diffusion-limited or diffusion-vanishing region. While T_1 might be in the diffusion-limited region, $T_1{}^r$ might be in the diffusion-vanishing region. Without knowing the precise values for the various constants that control the types of solutions for T_1 and $T_1{}^r$, little can be gained by a mere comparison of T_1 and $T_1{}^r$. This is not the case when τ_c is short enough that $1\gg\omega_0\tau_c\gg\omega_1\tau_c$ (it is assumed that τ_c' is still long enough that $\omega_p\tau_c'\gg 1$ so that our approximations are valid). This condition can be recognized by T_1 and $T_1{}^r$ being independent of ω_0 and ω_1, respectively. For this short τ_c condition

$$\bar{C}^r/\bar{C}=7/6, \tag{75}$$

$$b^r \approx b, \tag{76}$$

and

$$\beta^r/\beta=(7/3)^{1/4}=1.24. \tag{77}$$

Since β^r and β are now small and almost equal (because of the shortness of τ_c), and since b^r and b are also about equal, T_1 and T_1^r will both be given by either the diffusion-limited solution or the rapid-diffusion solution. Which solution holds depends upon the values of β and β^r. The ratio between T_1^r and T_1 may be calculated separately for each of these cases from Eqs. (34), (72), (37), and (73), or calculated for both these cases together from Eq. (30). Carrying out the second procedure yields to lowest order in b, b^r, β, and β^r,

$$T_1^r/T_1=1.62[I_{3/4}(\delta)I_{-3/4}(\delta^r)/I_{-3/4}(\delta)I_{3/4}(\delta^r)], \tag{78}$$

where $\delta^r=1.53\delta$. The ratio T_1^r/T_1 listed above is plotted as a function of δ in Fig. 2. In the rapid-diffusion region ($\delta \leq 0.1$), T_1^r/T_1 has the value 0.86. For this range of δ, T_1 varies as b^3 and T_1^r varies as $(b^r)^3$. Thus a small difference between b and b^r would strongly affect the ratio T_1^r/T_1 and the result should only be treated as approximate. In the diffusion-limited region ($\delta>2$), T_1^r/T_1 has the value 1.62. Since b and b^r do not enter into the values of T_1 and T_1^r in this region, this ratio should be more reliable than the one for the rapid-diffusion region. It is interesting that this theory predicts that under suitable conditions T_1^r can be larger than T_1.

C. Multi-paramagnetic-Center Model for the Diffusion-Vanishing Case—Rotating Reference Frame

Using arguments similar to those of Sec. IIC one can show that a multi-paramagnetic-center model is valid for the diffusion-vanishing case in the rotating reference frame. $T_{1p}^r(\mathbf{r})$ has a different spatial dependence than $T_{1p}(\mathbf{r})$, so the spatial positions where $T_{1p}^r(\mathbf{r})$ has minima will not necessarily coincide with those for $T_{1p}(\mathbf{r})$, and expansion coefficients may be different. Expanding $1/T_{1p}^r(\mathbf{r})$ about points where it is a minimum, keeping only terms through second order, and choosing a coordinate system so that terms in xy, xz, and yz do not appear in the second-order term yields

$$1/T_{1p}^r(\mathbf{r})=u_0^r+u_{xx}^r x^2+u_{yy}^r y^2+u_{zz}^r z^2, \tag{79}$$

where the u^r's are constants and are evaluated in Appendix B. Inserting Eq. (79) into Eq. (68) and assuming that $D^{\alpha\beta r}=0$ for $\alpha\neq\beta$ yields

$$\begin{aligned}\partial m^r(\mathbf{r},t)/\partial t &= [D^{xxr}(\partial^2/\partial x^2)+D^{yyr}(\partial/\partial y^2)+D^{zzr}(\partial^2/\partial z^2)]m^r(\mathbf{r},t)\\ &\quad -(u_0^r+u_{xx}^r x^2+u_{yy}^r y^2+u_{zz}^r z^2)m^r(\mathbf{r},t).\end{aligned} \tag{80}$$

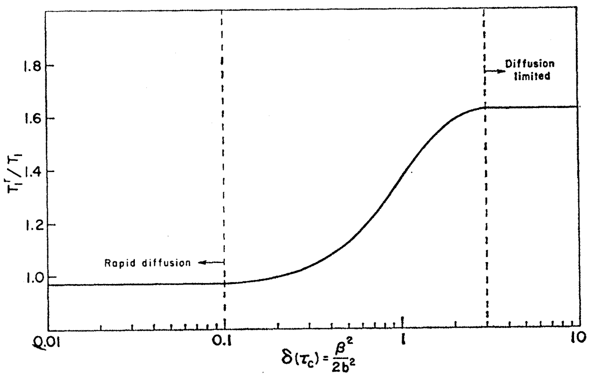

FIG. 2. The ratio of T_1^r/T_1 versus δ for the condition $\omega_p\tau'_c\gg1\gg\omega_0\tau_c\gg\omega_1\tau_c$.

Equation (80) is identical in form to Eq. (44), and the solutions of Eq. (44) may be used to yield a value of the spin-lattice relaxation in the rotating reference frame of

$$(T_1^r)^{-1}=u_0^r+(D^{xxr}u_{xx}^r)^{1/2}+(D^{yyr}u_{yy}^r)^{1/2}+(D^{zzr}u_{zz}^r)^{1/2}. \tag{81}$$

For the purpose of making a quantitative estimate of T_1^r using Eq. (81), it will be assumed that:

(1) $\omega_0\tau_c\gg1$, so that the second term in Eq. (65) is small in comparison to the first term and may be dropped.

(2) $D^{xxr}=D^{yyr}=D^{zzr}=D^r$.

(3) Paramagnetic centers form either a simple cubic lattice or a face-centered cubic lattice. Using

$$\begin{aligned}u_0^r&=\eta_0^r\bar{C}_1^r/L^6,\\ u_{\alpha\alpha}^r&=\eta_{\alpha\alpha}^r\bar{C}_1^r/L^4,\\ \eta^r&=(\eta_{xx}^r)^{1/2}+(\eta_{yy}^r)^{1/2}+(\eta_{zz}^r)^{1/2},\end{aligned} \tag{82}$$

Eq. (81) can be rewritten as

$$(T_1^r)^{-1}=\eta_0\bar{C}_1^r/L^6+\eta^r(\bar{C}_1^rD^r)^{1/2}L^4. \tag{83}$$

The quantity of $\bar{C}_1^r$ is defined in Appendix B. The values of the η's are given in Table III for the applied magnetic field pointing along a cubic axis. Equation (83) can be rewritten in terms of the number of paramagnetic centers per unit volume, N_p, as

$$(T_1^r)^{-1}=\lambda_0^r\bar{C}_1^rN_p^2+\lambda^r(\bar{C}_1^rD^r)^{1/2}N_p^{4/3}. \tag{84}$$

The values of λ_0^r and λ_1^r for two cubic lattices are also given in Table III. All of the remarks made about Eqs. (59) and (60) also hold for Eqs. (83) and (84) and need not be repeated. As in the multi-paramagnetic-center-model calculation in the laboratory reference frame, averaging $(T_1^r)^{-1}$ over a random distribution of paramagnetic centers yields

$$(T_1^r)^{-1}\cong\bar{\lambda}_0^r\bar{C}_1^rN_p^2+\bar{\lambda}^r(\bar{C}_1^rD)^{1/2}N_p^{4/3},$$

TABLE III. Constants used to evaluate $(T_1^r)^{-1}$ for the diffusion-vanishing case. Only one of the positions of the $(T_{1p}^r)^{-1}$ minima is given. The others within the unit cell can be found from the symmetry properties of the cube.

Paramagnetic center lattice	Position of $(T_{1p}^r)^{-1}$ minimum in cubic unit cell	L^{-1}	η_0^r	η_{xx}^r	η_{yy}^r	η_{zz}^r	η^r	λ_0^r	λ^r
Simple cubic	$[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$	$2N_p^{1/3}$	0.0080	0.165	0.165	0.66	1.62	0.51	25.9
Face-centered cubic	$[\frac{1}{4},\frac{1}{4},\frac{1}{4}]$	$2^{1/3}N_p^{1/3}$	0.255	25.5	25.5	87.4	19.4	1.02	48.9

where the expected orders of magnitude for the λ's are $\bar{\lambda}_0^r \approx 0.75$, $\bar{\lambda}^r \approx 37$.

IV. DISCUSSION

These calculations show that the introduction of a finite separation distance between paramagnetic centers does not greatly alter the calculated values of the spin-lattice relaxation time T_1 for the rapid-diffusion and diffusion-limited cases. It, however, has the advantage that the T_1 expression is extracted from the steady-state solution of the transport equation using the physically reasonable *assumption* that the shape of the magnetization distribution remains unchanged throughout the *observed* relaxation process, and is not very different from the steady-state distribution.

The use of a finite separation distance between paramagnetic centers permits the investigation of a new relaxation case, the diffusion-vanishing case. The single-center model is not particularly valid for this case but nevertheless seem to join on very nicely to the new model that is introduced, the multicenter model. The multicenter model is only valid for the diffusion-vanishing case, but appears to be a rigorous solution for this case. It has the advantages of introducing the spin-lattice relaxation time T_1 in a very natural way and takes into account the angular dependence of the direct spin-lattice relaxation rate, and the spin-diffusion constant.

Measurements of spin-lattice relaxation rates in the rotating reference frame are becoming common in current literature. The results of the calculations of Sec. III shows that it will probably be a useful tool for providing a quantitative test of spin diffusion. In the following paper are measurements we have made that test the spin-diffusion theory, using analyses based upon Secs. II and III of this paper.

APPENDIX A: DERIVATION OF T_{1pi} AND T_{1pi}^r

We give here a brief sketch of the derivation of the nuclear spin-lattice relaxation time due to the coupling of a nuclear spin I_i with a number of paramagnetic centers. The nucleus has spin I, magnetogyric ratio γ_n, and its interactions with other nuclear spins will be ignored. Each of the paramagnetic centers will be assumed to have a spin S, a magnetogyric ratio γ_p, and generate a fluctuating dipolar magnetic field at the site of the nucleus. The effects of the nuclear spin on the motion of the paramagnetic center will be ignored, and angular momentum of the paramagnetic center will be treated classically. Denoting the applied static magnetic field by $B_0\hat{z}$, the Hamiltonian for the ith nuclear spin is

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1(t), \tag{A1}$$

$$\mathcal{H}_0=-\hbar\omega_0 I_{iz}, \tag{A2}$$

$$\mathcal{H}_1(t)=\hbar[U_{i+}(t)I_{i+}+U_{i-}(t)I_{i-}+U_{iz}I_{iz}], \tag{A3}$$

$$U_{i+}(t)=\sum_\nu[A_{i\nu}S_{\nu-}(t)\exp(i\omega_p t)+C_{i\nu}S_{\nu z}(t)+E_{i\nu}S_{\nu+}(t)\exp(-i\omega_p t)], \tag{A4}$$

$$U_{i-}(t)=[U_{i+}(t)]^*, \tag{A5}$$

$$U_{iz}(t)=\sum_\nu[B_{i\nu}S_{\alpha z}(t)+C_{i\nu}S_{\nu+}(t)\exp(-i\omega_p t)+D_{i\nu}S_{\nu-}\exp(i\omega_p t)], \tag{A6}$$

where

$$\begin{aligned}
B_{i\nu}&=\gamma_p\gamma_n\hbar r_{i\nu}^{-3}(1-3\cos^2\theta_{i\nu}),\\
A_{i\nu}&=-\tfrac{1}{4}B_{i\nu},\\
C_{i\nu}&=-\tfrac{3}{2}\gamma_p\gamma_n\hbar r_{i\nu}^{-3}\sin\theta_{i\nu}\cos\theta_{i\nu}\exp(-i\phi_{i\nu}),\\
D_{i\nu}&=C_{i\nu}^*,\\
E_{i\nu}&=-\tfrac{3}{4}\gamma_p\gamma_n\hbar r_{i\nu}^{-3}\sin^2\theta_{i\nu}\exp(-2i\phi_{i\nu}),\\
F_{i\nu}&=E_{i\nu}^*,\\
\omega_p&=\gamma_p B_0,\ \omega_0=\gamma_n B_0.
\end{aligned} \tag{A7}$$

The summations over ν in Eqs. (A4) and (A6) are to be taken over all the paramagnetic centers in the sample. $r_{i\nu}$, $\theta_{i\nu}$, and $\phi_{i\nu}$ are the spherical coordinates of the vector connecting the ith nucleus and the νth paramagnetic center. The z axis of the coordinate system lies along the applied static magnetic field.

Assuming that the time dependence of $U_{i\alpha}(t)$ has a random component, we can calculate W_{nm}, the transition probability per unit time of the ith nuclear spin going from the unperturbed state n to the unperturbed state m using first-order perturbation theory[12]:

$$W_{nm}=(\hbar^2)^{-1}\int_{-\infty}^{\infty}\exp\left(-\frac{i}{\hbar}(E_n-E_m)\tau\right)\times[\langle n\mid\mathcal{H}_1(t+\tau)\mid m\rangle\langle m\mid\mathcal{H}_1(t)\mid n\rangle]_{\text{Av}}d\tau; \tag{A8}$$

[12] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), p. 273.

E_n is the energy of the nth eigenstate. The matrix elements in the large brackets above are averaged over an ensemble. Since $U_{i\alpha}(t)$, $(\alpha=+,-,z)$, are independent of the nuclear spin states, Eq. (A8) can be rewritten as

$$W_{nm}=(\hbar^2)^{-1}\sum_{\alpha,\beta}\langle n\mid I_\alpha\mid m\rangle\langle m\mid I_\beta\mid n\rangle$$
$$\times\int_{-\infty}^{\infty}\exp\left(-\frac{i}{\hbar}(E_n-E_m)\tau\right)[U_{i\alpha}(t+\tau)U_{i\beta}(t)]_{\mathrm{Av}}d\tau. \quad \text{(A9)}$$

The direct spin-lattice relaxation time for the ith spin, denoted by T_{1pi} is given by the formula[13]

$$1/T_{1pi}=\tfrac{1}{2}\sum_{n,m}(E_n-E_m)^2W_{nm}/\sum_n E_n^2. \quad \text{(A10)}$$

Substituting Eq. (A9) in Eq. (A10) and rearranging terms yields

$$1/T_{1pi}=-\sum_{\alpha,\beta}J_i^{\alpha\beta}(\omega^\alpha)\ \mathrm{Tr}\{[\mathcal{H}_0,I_\alpha][\mathcal{H}_0,I_\beta]\}/2\hbar^2\ \mathrm{Tr}\{\mathcal{H}_0^2\}, \quad \text{(A11)}$$

where

$$J_i^{\alpha\beta}(\omega^\alpha)=\int_{-\infty}^{\infty}\exp(i\omega^\alpha\tau)[U_{i\alpha}(t+\tau)U_{i\beta}(t)]_{\mathrm{Av}}d\tau \quad \text{(A12)}$$

and $\hbar\omega^\alpha$ is the energy difference between states coupled by the operator I_α.

$$\frac{\mathrm{Tr}\{[\mathcal{H}_0,I_\alpha][\mathcal{H}_0,I_\beta]\}}{\mathrm{Tr}\{\mathcal{H}_0^2\}}=-2, \quad \alpha=+,\beta=-,$$
$$=-2, \quad \alpha=-,\beta=+,$$
$$=0, \quad \text{otherwise.} \quad \text{(A13)}$$

Thus, Eq. (A11) reduces to

$$1/T_{1pi}=J_i^{+-}(\omega_0)+J_i^{-+}(-\omega_0). \quad \text{(A14)}$$

If we assume that the fluctuations of the direction of angular momentum of the paramagnetic centers is described by an exponential correlation time, then

$$[S_{\nu z}(t+\tau)S_{\nu z}(t)]_{\mathrm{Av}}=\tfrac{1}{3}S(S+1)\exp(-|\tau|/\tau_c), \quad \text{(A15)}$$

$$[S_{\nu+}(t+\tau)S_{\nu-}(t)]_{\mathrm{Av}}=[S_{\nu-}(t+\tau)S_{\nu+}(t)],$$
$$=\tfrac{2}{3}(S)(S+1)\exp(-|\tau|/\tau_c'), \quad \text{(A16)}$$

where τ_c is the correlation time of $S_{\nu z}$ and τ_c' is the correlation time of $S_{\nu x}$ and $S_{\nu y}$. Combining Eqs. (A15) and (A16) with (A14) and (A12) yields

$$(T_{1pi})^{-1}=\tfrac{2}{3}(S)(S+1)\sum_\nu\left[4A_{i\nu}^2\left(\frac{\tau_c'}{1+(\omega_p+\omega_0)^2(\tau_c')^2}\right)\right.$$
$$+4E_{i\nu}E_{i\nu}^*\left(\frac{\tau_c'}{1+(\omega_p-\omega_0)^2(\tau_c')^2}\right)$$
$$\left.+2C_{i\nu}C_{i\nu}^*\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2}\right)\right]. \quad \text{(A17)}$$

The computation of the spin-lattice relaxation time T_{1pi}^r for magnetization lying along a rotating magnetic field that rotates at the Larmor frequency in the x-y plane is similar to the one just carried out. The Hamiltonian for the ith nuclear spin is now given by

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_{\mathrm{rf}}+\mathcal{H}_1, \quad \text{(A18)}$$

where

$$\mathcal{H}_{\mathrm{rf}}=\hbar\omega_1(I_{ix}\cos\omega_0t-I_{iy}\sin\omega_0t),$$
$$\omega_1=\gamma_nB_1. \quad \text{(A19)}$$

B_1 is the magnitude of the rotating magnetic field. Since we now wish to compute the time rate of change of the transverse magnetization as viewed from the rotating Larmor reference frame, we shall transform $\mathcal{H}$ into the rotating Larmor reference frame, and denote it by $\mathcal{H}^r$.

$$\mathcal{H}^r=\mathcal{H}_0^r+\mathcal{H}_1^r(t), \quad \text{(A20)}$$
$$\mathcal{H}_0^r=-\omega_1\hbar I_{ix},$$
$$\mathcal{H}_1^r(t)=\hbar[U_{ix}^r(t)I_{ix}+U_{i+}^r(t)I_{i+}^r+U_{i-}^r(t)I_{i-}^r], \quad \text{(A21)}$$

where the operators I_{i+}^r and I_{i-}^r are defined as

$$I_{i+}^r=I_{iy}+iI_{iz},$$
$$I_{i-}^r=I_{iy}-iI_{iz}. \quad \text{(A22)}$$

The $U_{i\alpha}^r(t)$ are related to the $U_{i\alpha}(t)$ in the following way:

$$U_{ix}^r(t)=U_{i-}(t)\exp(i\omega_0t)+U_{i+}(t)\exp(-i\omega_0t), \quad \text{(A23)}$$
$$U_{i+}^r(t)=-\tfrac{1}{2}i[U_{i-}(t)\exp(i\omega_0t)-U_{i+}(t)$$
$$\times\exp(-i\omega_0t)+U_{iz}(t)], \quad \text{(A24)}$$
$$U_{i-}^r(t)=[U_{i+}^r(t)]^*. \quad \text{(A25)}$$

$\mathcal{H}^r$ in Eqs. (A20) through (A25) has the same form as in Eqs. (A1) through (A5) and the formalism for calculating T_{1pi}^r is identical to the one just used to calculate T_{1pi}. In carrying out this calculation, the effects of nuclear spin-spin interaction on the equation of motion of the transverse magnetization are ignored. This is permissible, provided that B_1 is large in comparison to the nuclear spin-spin interaction. Carrying out the formalism listed in Eqs. (A8) through (A17),

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

with $\mathcal{H}^r$ instead of $\mathcal{H}$, yields

$$T_{1pi}{}^r=\tfrac{1}{3}S(S+1)\sum_\nu\bigg[2A_{i\nu}{}^2\bigg(\frac{\tau_c'}{1+(\omega_p-\omega_0-\omega_1)^2(\tau_c')^2}+\frac{\tau_c'}{1+(\omega_p-\omega_0+\omega_1)^2(\tau_c')^2}\bigg)+2E_{i\nu}E_{i\nu}{}^*\times\bigg(\frac{\tau_c'}{1+(\omega_p+\omega_0+\omega_1)^2(\tau_c')^2}+\frac{\tau_c'}{1+(\omega_p+\omega_0-\omega_1)^2(\tau_c')^2}\bigg)+C_{i\nu}C_{i\nu}{}^*\bigg(\frac{\tau_c}{1+(\omega_0+\omega_1)^2(\tau_c)^2}+\frac{\tau_c}{1+(\omega_0-\omega_1)^2(\tau_c)^2}+\frac{2\tau_c'}{1+(\omega_p+\omega_1)^2(\tau_c')^2}+\frac{2\tau_c'}{1+(\omega_p-\omega_1)^2(\tau_c')^2}\bigg)+B_{i\nu}{}^2\bigg(\frac{\tau_c}{1+\omega_1{}^2\tau_c{}^2}\bigg)\bigg]. \quad \text{(A26)}$$

Under normal experimental conditions, $\omega_p\gg\omega_0\gg\omega_1$. This condition permits considerable simplification of Eqs. (A17) and (A26). For the calculations carried out in this paper, it is further assumed that $\omega_0\tau_c\ll\omega_p\tau_c'$ so that Eqs. (A17) and (A26) can be further simplified to the following results:

$$(T_{1pi})^{-1}=\tfrac{4}{3}S(S+1)\sum_\nu C_{i\nu}C_{i\nu}{}^*[\tau_c/(1+\omega_0{}^2\tau_c{}^2)],$$
$$=3\gamma_p{}^2\gamma_n{}^2\hbar^2S(S+1)[\tau_c/(1+\omega_0{}^2\tau_c{}^2)]\times\sum_\nu r_{i\nu}{}^{-6}\sin^2\theta_{i\nu}\cos^2\theta_{i\nu}, \quad \text{(A27)}$$

$$(T_{1pi}{}^r)^{-1}=\tfrac{1}{3}S(S+1)\sum_\nu\{B_{i\nu}{}^2[\tau_c/(1+\omega_1{}^2\tau_c{}^2)]+2C_{i\nu}C_{i\nu}{}^*[\tau_c/(1+\omega_0{}^2\tau_c{}^2)]\},$$
$$=\tfrac{1}{3}\gamma_p{}^2\gamma_n{}^2\hbar^2S(S+1)\sum_\nu\{(1-3\cos^2\theta_{i\nu})^2\times r_{i\nu}{}^{-6}[\tau_c/(1+\omega_1{}^2\tau_c{}^2)]+\tfrac{9}{2}\sin^2\theta_{i\nu}\cos^2\theta_{i\nu}\times r_{i\nu}{}^{-6}[\tau_c/(1+\omega_0{}^2\tau_c{}^2)]\}. \quad \text{(A28)}$$

APPENDIX B: EXPANSION OF THE INVERSE SPIN-LATTICE RELAXATION TIMES $T_{lp}{}^{-1}$ AND $(T_{lp}{}^r)^{-1}$ ABOUT MINIMUM POINTS

Using Eqs. (2b), (3), and (9), the formula for $T_{1p}{}^{-1}$ can be written as

$$[T_{1p}(\mathbf{r})]^{-1}=\tfrac{15}{2}\bar{C}\sum_j\frac{|\mathbf{R}_j-\mathbf{r}|^2\sin^2\theta_j\cos^2\theta_j}{|\mathbf{R}_j-\mathbf{r}|^{10}},$$
$$=\tfrac{15}{2}\bar{C}\sum_j\frac{(Z_j-z)^2[(X_j-x)^2+(Y_j-y)^2]}{[(X_j-x)^2+(Y_j-y)^2+(Z_j-z)^2]^5}, \quad \text{(B1)}$$

where

$$\mathbf{R}_j=X_j\hat{x}+Y_j\hat{y}+Z_j\hat{z}. \quad \text{(B2)}$$

A power-series expansion of $T_{1p}{}^{-1}$ about a point where it is a minimum will not have any terms linear in x, y, and z. It will be assumed that it doesn't have any terms in xy, xz, and yz, which is true for many symmetries. Keeping terms only through x^2, y^2, and z^2, the power-series expansion of $T_{1p}{}^{-1}$ is

$$[T_{1p}(\mathbf{r})]^{-1}=u_0+u_{xx}x^2+u_{yy}y^2+u_{zz}z^2, \quad \text{(B3)}$$

where

$$u_0=\tfrac{15}{2}\bar{C}\sum_j[Z_j{}^2(X_j{}^2+Y_j{}^2)/R_j{}^{10}], \quad \text{(B4)}$$

$$u_{xx}=\tfrac{15}{2}\bar{C}\sum_j\frac{Z_j{}^2}{R_j{}^{10}}\bigg(1-\frac{25X_j{}^2+5Y_j{}^2}{R_j{}^2}+\frac{60Y_j{}^2(X_j{}^2+Y_j{}^2)}{R_j{}^4}\bigg), \quad \text{(B5)}$$

$$u_{yy}=\tfrac{15}{2}\bar{C}\sum_j\frac{Z_j{}^2}{R_j{}^{10}}\bigg(1-\frac{25Y_j{}^2+5X_j{}^2}{R_j{}^2}+\frac{60Y_j{}^2(X_j{}^2+Y_j{}^2)}{R_j{}^4}\bigg), \quad \text{(B6)}$$

$$u_{zz}=\tfrac{15}{2}\bar{C}\sum_j\frac{(X_j{}^2+Y_j{}^2)}{R_j{}^{10}}\bigg(1-\frac{25Z_j{}^2}{R_j{}^2}+\frac{60Z_j{}^4}{R_j{}^4}\bigg). \quad \text{(B7)}$$

The parameters u_0, u_{xx}, u_{yy}, and u_{zz} are evaluated for the cases of paramagnetic centers arranged in a simple cubic lattice, a face-centered cubic lattice, and a body-centered cubic lattice. The edge dimension of the cubic unit cell is $2L$. The summations are carried out over the paramagnetic centers nearest and next nearest to the points where $T_{1p}{}^{-1}$ are minima. This is considered adequate since the sums converge very rapidly. The results are listed in Table II in terms of η's, which are defined as

$$u_0=\eta_0\bar{C}/L^6, \quad \text{(B8)}$$
$$u_{\alpha\alpha}=\eta_{\alpha\alpha}\bar{C}/L^8, \quad \text{(B9)}$$
$$\eta=\eta_{xx}{}^{1/2}+\eta_{yy}{}^{1/2}+\eta_{zz}{}^{1/2}. \quad \text{(B10)}$$

A similar expansion will now be carried out for $(T_{1p}{}^r)^{-1}$ listed in Eqs. (64) and (65). It will be assumed that $\omega_0\tau_c\gg1$, so that the second term in Eq. (65) may be dropped. Then

$$[T_{1p}{}^r(\mathbf{r})]^{-1}=\tfrac{5}{4}\bar{C}_1{}^r\sum_j[(1-3\cos^2\theta_j)^2/|\mathbf{r}-\mathbf{R}_j|^6], \quad \text{(B11)}$$

where

$$\bar{C}_1{}^r=\tfrac{4}{15}\gamma_p{}^2\gamma_n{}^2\hbar^2S(S+1)[\tau_c/(1+\omega_1{}^2\tau_c{}^2)]. \quad \text{(B12)}$$

Carrying out the power-series expansion and dropping terms higher order than the second yields

$$1/T_{1p}{}^r(\mathbf{r})=u_0{}^r+u_{xx}{}^rx^2+u_{yy}{}^ry^2+u_{zz}{}^rz^2, \quad \text{(B13)}$$

where

$$u_0{}^r=\tfrac{4}{5}\bar{C}_1{}^r\sum_j(Q_j{}^2/R_j{}^{10}), \quad \text{(B14)}$$

$$u_{xx}{}^r=\tfrac{4}{5}\bar{C}_1{}^r\sum_j\frac{1}{R_j{}^{10}}\bigg[(6X_j{}^2+6Y_j{}^2-4Z_j{}^2)-40\frac{X_j{}^2Q_j{}^2}{R_j{}^2}-5\frac{Q_j{}^2}{R_j{}^2}+60\frac{X_j{}^2Q_j{}^4}{R_j{}^4}\bigg], \quad \text{(B15)}$$

$$u_{yy}^r = \tfrac{4}{5}\bar{C}_1^r \sum_j \frac{1}{R_j^{10}} \left[(2X_j^2 + 6Y_j^2 - 4Z_j^2) - 40\frac{Y_j^2 Q_j^2}{R_j^2} - 5\frac{Q_j^4}{R_j^2} + 60\frac{Y_j^2 Q_j^4}{R_j^4} \right], \quad \text{(B16)}$$

$$u_{zz}^r = \tfrac{4}{5}\bar{C}_1^r \sum_j \frac{1}{R_j^{10}} \left[4(-X_j^2 - Y_j^2 + 6Z_j^2) + 80\frac{Z_j^2 Q_j^2}{R_j^2} - 5\frac{Q_j^4}{R_j^2} + 60\frac{Z_j^2 Q_j^4}{R_j^4} \right], \quad \text{(B17)}$$

and where

$$Q_j^2 = X_j^2 + Y_j^2 - 2Z_j^2. \quad \text{(B18)}$$

The parameters u_0^r, u_{xx}^r, u_{yy}^r, and u_{zz}^r are evaluated under the same conditions as for u_0, u_{xx}, u_{yy}, and u_{zz}, except that the body-centered cubic lattice was left out because we could not locate the $T_{1p}^r(\mathbf{r})$ minimum. The results are listed in Table II in terms of η^r's, which are defined as

$$u_0^r = \eta_0^r \bar{C}_1^r / L^6, \quad \text{(B19)}$$

$$u_{\alpha\alpha}^r = \eta_{\alpha\alpha}^r \bar{C}_1^r / L^8, \quad \text{(B20)}$$

$$\eta^r = (\eta_{xx}^r)^{1/2} + (\eta_{yy}^r)^{1/2} + (\eta_{zz}^r)^{1/2}. \quad \text{(B21)}$$

APPENDIX C: EVALUATION OF THE SPIN-DIFFUSION CONSTANT IN THE ROTATING REFERENCE FRAME

It has been shown[9] that for spin diffusion in the laboratory reference frame the secular terms of the dipole-dipole interaction Hamiltonian make the dominant contribution to the spin-diffusion process. The listed secular terms were

$$\mathcal{H}_{ds} = \hbar \sum_{i \neq j} \left[\tfrac{1}{2} A_{ij} (I_{i+} I_{j-} + I_{i-} I_{j+}) + B_{ij} I_{iz} I_{jz} \right], \quad \text{(C1)}$$

where

$$B_{ij} = -2A_{ij} = \tfrac{1}{2}\gamma_n^2 \hbar r_{ij}^{-3} (1 - 3\cos^2\theta_{ij}). \quad \text{(C2)}$$

$\mathbf{r}_{ij}$ is the vector connecting nuclei i and j, and θ_{ij} is the angle between the vector $\mathbf{r}_{ij}$ and the applied magnetic field $B_0\hat{z}$. The spin-diffusion constant, computed to first order from $\mathcal{H}_{ds}$, was

$$D_2^{\alpha\beta} = \tfrac{1}{2}\pi^{1/2} \sum_{i(i \neq k)} A_{ik}^2 X_{ki}^\alpha X_{ki}^\beta \Big(\sum_{j(j \neq i,k)} B_{kj}^2 \Big)^{-1/2}. \quad \text{(C3)}$$

The same argument used in Ref. 9 to derive the spin-diffusion equation in the laboratory reference frame, may also be used to derive a spin-diffusion equation for magnetization lying along the rotating magnetic field listed in Appendix A, except that only those terms that commute with $\mathcal{H}_0^r$ of Eq. (A20) will make a significant contribution to $D^{\alpha\beta r}$. These terms may be found by making a transformation to the coordinate system that rotates with angular speed ω_1 about $\hat{x}$ of the Larmor rotating coordinate system, and then choosing only those terms that are time-independent. These terms, denoted by $\mathcal{H}_{ds}^r$ are

$$\mathcal{H}_{ds}^r = -\tfrac{1}{2}\hbar \sum_{i \neq j} \left[\tfrac{1}{2} A_{ij} (I_{i+}^r I_{j-}^r + I_{i-}^r I_{j+}^r) + B_{ij} I_{ix} I_{jx} \right]. \quad \text{(C4)}$$

The relationship between operators I_{i+}^r, I_{i-}^r, and I_{ix} is the same as I_{i+}, I_{i-}, and I_{iz}. $\mathcal{H}_{ds}^r$ is thus identical in form to $\mathcal{H}_{ds}$, with each coefficient multiplied by $-\frac{1}{2}$. Thus to find $D^{\alpha\beta r}$, we need only take the formula for $D_2^{\alpha\beta}$ in Eq. (C3) and multiply each A_{ik} and B_{ik} by $-\frac{1}{2}$. This leads to the result that

$$D_2^{\alpha\beta r} = \tfrac{1}{2} D_2^{\alpha\beta}. \quad \text{(C5)}$$

The second-order correction to the diffusion tensor calculated in Ref. 9 also must be multiplied by a factor of $\frac{1}{2}$ when transformed into the rotating reference frame.