PHYSICAL REVIEW B VOLUME 18, NUMBER 11 1 DECEMBER 1978

Nuclear magnetic relaxation by paramagnetic impurities in superionic conductors

Peter M. Richards
Sandia Laboratories, Albuquerque, New Mexico 87185*
(Received 26 June 1978)

NMR relaxation by paramagnetic impurities in superionic conductors is treated in a manner which is valid over a wide range of temperatures, encompassing regions where $W\tau_c >> 1$ and $W\tau_c << 1$, as well as the intermediate case $W\tau_c \sim 1$. Here W and τ_c are the hopping rate and paramagnetic-impurity relaxation time, respectively. Recent experiments have shown the importance of paramagnetic impurities for relaxing rapidly diffusing nuclei even in nominally "pure" samples, and they have been carried out over the entire range of $W\tau_c$ values. Both nearest-neighbor-only and long-range dipolar interactions are treated. The former are handled by a discrete hopping model, the latter by a classical diffusion equation. This equation is similar to that solved by others, but is more general in that it is valid for arbitrary $W\tau_c$ and includes both particle and spin diffusion. Nuclear dipole-dipole interactions are accounted for by assuming they make an additive contribution to the transverse relaxation function. As examples of the two models, theory and experiment are compared for linewidth data in PbF_2:Mn and for T_1 and T_2 data in "pure" Li_5AlO_4. Good agreement is found for the linewidth peak in PbF_2, without any adjustable parameters. The anomalous frequency dependence at low temperature in α-Li_5AlO_4 can be explained, but only with a τ_c which is too short to describe higher-temperature behavior.

I. INTRODUCTION

Nuclear magnetic resonance (NMR) has proved to be a useful tool for investigating the motion of rapidly diffusing ions in superionic conductors.[1,2] It has recently been demonstrated[3–5] that paramagnetic impurities have a marked effect on the relaxation processes because a mobile ion can readily migrate to the vicinity of an impurity where it is relaxed. A feature of superionics is that one can go from the region of slow solidlike diffusion to rapid liquidlike behavior by varying the temperature typically between 300 and 700 K.

One set of conditions applies in the slow-diffusion range, characterized by $W\tau_c << 1$, where τ_c is the relaxation time (either longitudinal or transverse depending on the particular situation) of the paramagnetic ion and W is the diffusive hopping rate. In this case a nucleus stays in the vicinity of a paramagnetic ion long enough for its instantaneous relaxation rate to be described by the quasistatic value $1/T_i(r)$, where $T_i(r)$ [$i=1$ or 2 depending on whether one is calculating longitudinal (T_1) or transverse (T_2) relaxation] is the relaxation time a nuclear spin would have if its position were held fixed a distance r from the impurity. Extensive treatment of this situation exists in the literature. Abragam's text[6] summarizes the early work where the additional assumption $WT_1(a) < 1$ is also implicit (a is the nearest-neighbor distance). An important consideration for slow particle diffusion is that at sufficiently low temperature spin diffusion can be the more effective means of carrying the unrelaxed spin magnetization to the vicinity of a paramagnetic ion. Then not only should W be replaced by the spin-diffusion rate, roughly $1/T_2$, but one must account for a critical barrier distance b from the impurity. Spins cannot diffuse by energy-conserving spin flips to a distance closer than b because of detuning due to the static local field set up by the impurity. Rorschach[7] has treated this situation in detail for arbitrary values of $WT_1(a)$.

In the rapid-diffusion region where $W\tau_c >> 1$, the effective fluctuation rate of the paramagnetic spin as viewed by the nucleus becomes W, and another set of conditions applies.[8] The treatments have generally considered only one regime or the other, whereas data in superionics can range from $W\tau_c << 1$ to $W\tau_c >> 1$. This was demonstrated particularly well in the recent work[4] on ^{7}Li resonance in Li_5AlO_4. Previous studies have also concentrated on the case where $T_1(r) \propto r^6$, appropriate to classical dipole coupling, and assumed a continuum model. However, one of the systems of interest[3] is PbF_2:Mn, where the dominant F-Mn coupling is a nearest-neighbor transferred hyperfine interaction. Here a discrete-lattice hopping model with nearest-neighbor interactions would be more suitable. Another needed refinement is that a complete description of T_2 requires inclusion of broadening by nuclear dipole-dipole interaction since this mechanism dominates at low temperatures.

Comparison of existing data with theory therefore requires an expression which is valid over a broader range of variables than is currently available and which includes strong nearest-neighbor interactions. The purpose of this paper is to provide such a calculation. Section II gives the theory for nearest-neighbor interactions and a discrete-lattice hopping model, as applicable to the PbF_2:Mn experiments. Section III extends Rorschach's calculations for dipole interactions by assuming the presence of both particle and spin diffusion, with the latter being restricted to distances from the impurity greater than the barrier b. In an obvious extension of Sec. II, we incorporate an arbitrary value of $W\tau_c$ into the diffusion equation of Sec. III. The Sec. II results are applied to PbF_2 in Sec. V, while those of Sec. III are applied to Li_5AlO_4 in Sec. VI.

In both models it is assumed that the nuclear dipole-dipole contribution to $1/T_2$ can be accounted for in a simple semiadditive manner described in Sec. IV. The calculations are restricted to low paramagnetic-impurity concentration c so that the relaxation rates are linear in c. In this sense the results are less general than some refinements[9,10] of the work in Refs. 6 and 7.

II. DISCRETE HOPPING, NEAREST-NEIGHBOR INTERACTIONS

We assume that the mobile nucleus whose resonance is being studied performs a simple, uncorrelated random walk governed by standard rate equations. If it is on a site which is a nearest neighbor of a paramagnetic impurity, it experiences an interaction of the general form

$$H'(t) = \hbar \sum_{\alpha\beta} A_{\alpha\beta} S_\alpha(t) I_\beta \quad , \tag{1}$$

where $S_\alpha(t)$ and I_β are components of the electronic and nuclear spins, respectively. Apart from precession in the applied field at frequency ω_e, time dependence of $S_\alpha(t)$ comes primarily from interaction with lattice vibrations at the high temperatures of interest, and we assume it may be described by a characteristic relaxation time τ_c which is the same for longitudinal and transverse components ($T_1 = T_2$ for the electron spins) in the neglect of spin-spin interactions and for coupling to high-frequency phonons (Raman processes). For an isotropic transferred hyperfine interaction $A\vec{I}\cdot\vec{S}$, we have

$$A_{00} = 2A_{1,-1} = 2A_{-1,1} = A \tag{2}$$

with the other components $A_{\alpha\beta} = 0$. Here and henceforth we use a notation in which $\alpha = 0, \pm 1$ corresponds to the components $I_z, I_\pm = I_x \pm iI_y$ and $S_z, S_\pm = S_x \pm iS_y$. For the classical dipole interaction $A_{\alpha\beta}$ is given by the usual formulas.[11] The interaction is taken as zero if the nucleus is not on a nearest-neighbor-to-an-impurity site.

Let the nucleus remain on a site where H' is given by (1) for a time τ and then hop to a site where $H' = 0$. As derived in Appendix A, the Kubo-Tomita perturbation technique[12] and suitable averaging give

$$\tilde{I}_\alpha(t+\tau) = f_\alpha(\tau)\tilde{I}_\alpha(t) \tag{3}$$

with

$$f_\alpha(\tau) = \exp\left[-\int_0^\tau (\tau - u) G_\alpha(u)\, du\right] \quad , \tag{4}$$

and $G_\alpha(u)$ as given by Eqs. (A4) and (A5). The quantity $\tilde{I}_\alpha(t)$ is the "rotating frame" value $\tilde{I}_\alpha(t) = I_\alpha(t) e^{i\alpha\omega_0 t}$, where ω_0 is the NMR frequency for an applied field in the z direction. We further take the z component $\tilde{I}_0(t)$ to refer to the departure of I_z from its thermal equilibrium value in the presence of an applied field.

In the absence of nuclear dipole-dipole or other couplings—which will be included later—$\tilde{I}_\alpha$ is unchanged between time $t+\tau$ and the time it next comes onto a site which neighbors a paramagnetic impurity. If there are n "encounters" with an impurity between 0 and the observing time t, it follows that

$$\tilde{I}_\alpha(t) = \prod_{i=1}^{n} f_\alpha(\tau_i)\tilde{I}_\alpha(0) \quad , \tag{5}$$

where τ_i is the duration of the ith encounter. The reasonable assumption is made in Eq. (5) that for low concentration c the fraction of time spent in vicinity of an impurity is small so that the ion is not experiencing an encounter at the particular time t.

The relaxation function is given by the average of $\prod_{i=1}^{n} f_\alpha(\tau_i)$. Two averages are involved, first with respect to each τ_i and second with respect to the number of encounters n. We assume that the probability of making an encounter with the same impurity ion twice within an electronic relaxation time τ_c is vanishingly small. If τ_c is not much shorter than τ_i, this requires the additional stipulation that there is negligible probability of the nucleus returning to the same site after it has jumped away. This is reasonable for lattices with a large coordination number in the absence of correlations which make return jumps more probable. It clearly is totally inapplicable in situations such as one-dimensional hopping in a densely filled lattice. With the above restriction the f's are statistically independent so that

$$\left\langle\left\langle \prod_{i=1}^{n} f_\alpha(\tau_i) \right\rangle\right\rangle = \langle\langle f_\alpha\rangle^n\rangle \quad , \tag{6}$$

where the double angular brackets indicate averages both with respect to τ and with respect to n. The inner average is

$$\langle f_\alpha\rangle = W\int_0^\infty d\tau\, e^{-W\tau} f_\alpha(\tau) \quad , \tag{7}$$

where W is the hopping rate, since $e^{-W\tau}W\,d\tau$ is the probability of the nucleus remaining at a given site for a time between τ and $\tau+d\tau$ before jumping.

It is shown in Appendix B that the probability of there being n encounters in time t is

$$P(n\,|\,t)\approx[(Zc)^n/n!](Wt)^n e^{-ZcWt}\ , \tag{8}$$

where Z is the number of host sites which are nearest neighbors to a nuclear-spin site and c is the impurity concentration. Equation (8) is derived on the assumptions $Zc \ll 1$ and that the random walk is self-avoiding. The average required in Eq. (6) is thus

$$\begin{aligned}\langle\langle f_\alpha\rangle^n\rangle &= \sum_{n=0}^{\infty} P(n\,|\,t)\langle f_\alpha\rangle^n\\ &= e^{-ZcWt}\sum_{n=0}^{\infty}\frac{(Zc\langle f_\alpha\rangle Wt)^n}{n!}\\ &= e^{-(1-\langle f_\alpha\rangle)ZcWt}\ ,\end{aligned} \tag{9}$$

from which we obtain the relaxation rates by comparison of (9) with Eqs. (5) and (6),

$$1/T_{1,2}=(1-\langle f_{0,1}\rangle)ZcW\ . \tag{10}$$

The quantity $\langle f_\alpha\rangle$ is in general a complicated expression obtained by the use of Eqs. (A4) and (A5) in Eq. (4). It produces the expected results[3] in appropriate limits. If $W\tau_c \ll 1$ and $G_\alpha(0)\tau_c/W \gg 1$ or if $W\tau_c \gg 1$ and $G_\alpha(0)/W^2 \gg 1$, $\langle f_\alpha\rangle \ll 1$ which means that on the average the nuclear spin relaxes completely during one encounter. In this case the relaxation time is just the average time required to hop to the vicinity of a paramagnetic center, $T_{1,2}=1/ZcW$, as given by Eq. (10) for $\langle f_\alpha\rangle \ll 1$. If $W\tau_c \gg 1$ and $G_\alpha(0)/W^2 \ll 1$, then

$$\begin{aligned}\langle f_\alpha\rangle &\approx \int_0^\infty du\,e^{-u}\left[1-\frac{1}{2}\frac{G_\alpha(0)}{W^2}u^2\right]\\ &= 1-\frac{G_\alpha(0)}{W^2}\ ,\end{aligned} \tag{11}$$

[for this illustration only we are also assuming that $\omega_e, \omega_0 \ll W$ so that the secular and nonsecular parts of $G_\alpha(t)$ contribute equally; see Eqs. (A4) and (A5)] and Eq. (10) becomes

$$1/T_{1,2}=ZcG_{0,1}/W\ . \tag{12}$$

Here the hopping nucleus must undergo many encounters before being relaxed, and therefore the rate is given by an average square interaction ZcG_α narrowed by the hopping rate W, which is the effective inverse correlation time if $1/W \ll \tau_c$.

Another limit of interest is $W\tau_c \ll 1$, $G_\alpha(0)\tau_c/W \ll 1$. This is an intermediate region where the hopping rate is slow compared with electronic spin fluctuations but fast enough to prevent complete relaxation during the average time of an encounter. Equation (4) then reduces to

$$f_\alpha(\tau)\approx 1-\eta_\alpha\tau\ , \tag{13}$$

where

$$\eta_\alpha=\int_0^\infty G_\alpha(u)\,du \tag{14}$$

is the relaxation rate a nucleus would have if it were not allowed to hop away from the impurity site. Use of (14) in (7) and (10) then yields

$$1/T_{1,2}=Zc\,\eta_{0,1} \tag{15}$$

which can be regarded as the average relaxation rate for a nucleus which hops through the crystal, i.e., the rate is η_α for the fraction Zc of the time it is a neighbor of an impurity and zero otherwise.

Results of this section are compared with data on the linewidth in PbF_2:Mn in Sec. V.

III. CONTINUUM MODEL, DIPOLAR INTERACTIONS

Time dependence of the rotating-frame nuclear-spin vector considered as a function both of position $\vec{r}$ and time t is given by

$$\frac{\partial\tilde{I}_\alpha(\vec{r},t)}{\partial t}=\left(\frac{\partial\tilde{I}_\alpha}{\partial t}\right)_{\text{relaxation}}+\left(\frac{\partial\tilde{I}_\alpha}{\partial t}\right)_{\text{hopping}}\ . \tag{16}$$

The second term on the right-hand side of (16) is the change brought about by discrete hops of the nucleus and is approximated by $D\nabla^2\tilde{I}_\alpha$ in a continuum model where equilibrium spatial properties of the average $\tilde{I}_\alpha$ are slowly varying compared to a lattice constant. The diffusion coefficient is taken as $D=\frac{1}{6}a^2W$ for a jump rate W and a jump distance a. The first term on the right-hand side of (16) describes the interaction with the perturbation $H'(r,t)$ of Eq. (1), where now $A_{\alpha\beta}=A_{\alpha\beta}(\vec{r})$ varies as r^{-3} for dipolar electronic-nuclear coupling. To make the equations manageable we must reduce this term to the form

$$\left(\frac{\partial\tilde{I}_\alpha}{\partial t}\right)_{\text{relaxation}}=-\eta_\alpha(r)\tilde{I}_\alpha\ , \tag{17}$$

where $\eta_\alpha(r)$ is an effective relaxation rate which describes the average decay of the nuclear spin while it remains a distance r from the impurity. The following considerations are helpful in arriving at a suitable expression for $\eta_\alpha(r)$. The total decay which takes place during the time τ the spin is at rest at r is given by Eqs. (3) and (4). An obvious extension of these equations is

$$\tilde{I}_\alpha(t+\Delta t)=f_\alpha(\Delta t)\tilde{I}_\alpha(t)\quad , \tag{18a}$$

$$f_\alpha(\Delta t)=\exp\left[-\int_0^{\Delta t}(\Delta t-u)\,G_\alpha(r,u)\,du\right] \tag{18b}$$

for intermediate times $0<\Delta t<t$, where the interaction $G_\alpha(r,u)$ is now evaluated at the fixed position r. If the decay is exponential,

$$f_\alpha(\Delta t)\propto\exp[-\eta_\alpha(r)\,\Delta t]$$

for all Δt of interest, there is obviously no problem since Eqs. (17) and (18) would be perfectly compatible. However, as is well known,[12] $f_\alpha(\Delta t)$ is Gaussian,

$$f_\alpha(\Delta t)\propto\exp[-\tfrac{1}{2}G_\alpha(r,0)\,\Delta t^2]$$

for times Δt short compared with the correlation time τ_c of $G_\alpha(r,u)$ and becomes exponential only for $\Delta t\gg\tau_c$. We argue as a reasonable compromise that $\eta_\alpha(r)$ be defined in such a way that the average amount of decay during the dwell time τ be given correctly. That is,

$$\exp[-\eta_\alpha(r)\,W^{-1}]=\left\langle\exp\left[-\int_0^{\tau}(\tau-u)\,G_\alpha(r,u)\,du\right]\right\rangle\quad , \tag{19a}$$

where the average is with respect to the probability $We^{-W\tau}\,d\tau$ that the particle remains at r for a time between τ and $\tau+d\tau$. Equation (19a) is sensible as long as $\eta_\alpha(r)$ as so defined satisfies $\eta_\alpha(r)\,W^{-1}\lesssim 1$, i.e., it requires more than one encounter to relax the spin so that the full average dwell period W^{-1} is the pertinent time of interest. Suppose, however, that the right-hand side of (19a) is less than $1/e$ which occurs, for example, if

$$\tfrac{1}{2}G_\alpha(r,0)\,W^{-2}>1$$

for $W\tau_c\gg 1$ or

$$G_\alpha(r,0)\,W^{-1}\tau_c>1$$

for $W\tau_c\ll 1$. Then the relaxation is completed in less than the mean residence time W^{-1} and we must be concerned with what occurs on a shorter time scale. A physically acceptable choice is then to define $\eta_\alpha(r)$ as the time, less than W^{-1}, required for the spin to relax to $1/e$ of its initial value,

$$\exp\left[-\int_0^{1/\eta_\alpha}(\eta_\alpha^{-1}-u)\,G_\alpha(r,u)\,du\right]=\frac{1}{e}\quad .$$

Since (19a) is to be used only for $\eta_\alpha(r)\,W^{-1}\leq 1$, we will not make a serious error in keeping only the first two terms of an expansion of the exponents on both sides of the equation, whereby

$$\begin{aligned}\eta_\alpha(r)&=W\left\langle\int_0^{\tau}(\tau-u)\,G_\alpha(r,u)\,du\right\rangle\\&=W^2\int_0^{\infty}d\tau\,e^{-W\tau}\int_0^{\tau}(\tau-u)\,G_\alpha(r,u)\,du\\&=\int_0^{\infty}d\tau\,e^{-W\tau}G_\alpha(r,\tau)=\frac{\langle G_\alpha(r,\tau)\rangle}{W}\end{aligned} \tag{19b}$$

for $\langle G_\alpha(r,\tau)\rangle\leq W^2$, while if $\langle G_\alpha(r,\tau)\rangle>W^2$ we use

$$1=\int_0^{1/\eta_\alpha}(\eta_\alpha^{-1}-u)\,G_\alpha(r,u)\,du \tag{20}$$

as the definition of $\eta_\alpha(r)$. [The third equality in (19b) is the result of partial integration.] Note that if $W\tau_c\ll 1$, both Eqs. (19) and (20) reduce to

$$\eta_\alpha(r)\approx\int_0^{\infty}G_\alpha(r,u)\,du$$

which is the form used in previous treatments.[6,7,9,10] The conditions under which (20) is of practical importance are thus $W\tau_c\gtrsim 1$ and $G_\alpha(r,0)/W^2\gtrsim 1$. [It should be remarked that (19b) and (20) do not in general agree when $\langle G_\alpha(r,\tau)\rangle=W^2$. This could be corrected by replacing the left-hand side of Eq. (20) with a number of the order unity which is determined self-consistently to give agreement with (19b) when $\langle G_\alpha(r,\tau)\rangle=W^2$ and becomes unity for $\langle G_\alpha(r,\tau)\rangle\gg W^2$. For example if $W\tau_c\gg 1$ so that $G_\alpha(r,\tau)\approx G_\alpha(r,0)$ where the integrand is important, this number would be 2 when $G_\alpha(r,0)=W^2$. In the opposite extreme of $W\tau_c\ll 1$ there is no discrepancy, however, as noted above.]

As long as (19) is used or $W\tau_c\ll 1$, $\eta_\alpha(r)$ is proportional to $G_\alpha(r,0)$ and thus varies as r^{-6} for dipolar interactions. If however, $W\tau_c\gg 1$ and $G_\alpha(a_0,0)/W^2>1$, Eq. (20) gives

$$\eta_\alpha(a_0)=[\tfrac{1}{2}G_\alpha(a_0,0)]^{1/2}\propto a_0^{-3}\quad ,$$

where a_0 is the distance of closest approach to an impurity. This creates a complicated variation wherein $\eta_\alpha(r)$ varies as r^{-3} for $r\ll r_c$ and as r^{-6} for $r\gg r_c$ where r_c is a critical radius such that

$$\tfrac{1}{2}G_\alpha(r_c,0)\,\tau^2=1\quad .$$

In almost all cases of interest $r_c<a_0$ when $W\tau_c>1$ and this feature of there being a region where $\eta_\alpha(r)\propto r^{-3}$ is not likely to be important. It will henceforth be ignored in the main text, but Appendix C shows, for completeness, how the equations can be modified to account for it.

Equations (16) and (18) then yield the familiar

$$\frac{\partial\tilde{I}_\alpha}{\partial t}=D\,\nabla^2 I_\alpha-\frac{C_\alpha}{r^6}\tilde{I}_\alpha\quad , \tag{21}$$

where the distance dependence is explicitly given as $\eta_\alpha(r)=C_\alpha/r^6$. Equation (21) is identical to that treated extensively by others[6,7,9,10] except for the more general definition of C_α through (19) and (20) which allows for an arbitrary value of $W\tau_c$. Their results could be carried over immediately if it weren't for the combined effects of spin and particle diffusion. For $r > b$ there is both particle and spin diffusion, but only particle diffusion can take place for $r < b$. Here b is the critical distance below which spin diffusion cannot occur because the local field of the paramagnetic impurity changes too rapidly between sites to allow for energy-conserving spin flips.[7] An explicit expression for b is given in Ref. 7 and is repeated here in Eq. (43). We thus have an r-dependent D given by

$$D(r)=\begin{cases} D_S+D_P\ , & r>b \\ D_P\ , & r<b \end{cases} \tag{22}$$

where $D_P=\frac{1}{6}Wa^2$ is the particle (hopping) diffusion coefficient and $D_S\approx\frac{1}{6}a^2T_{20}^{-1}$ is the spin-diffusion coefficient with T_{20} the rigid lattice (low-temperature, nonmotionally narrowed) transverse relaxation time. The assumption that spin and particle diffusion are simply additive ignores the effect of hopping on the dynamics of mutual spin flips and is thus likely to be quite crude in general. However, in the region where $D_S \gtrsim D_P$ and spin diffusion is thus important there is little motional narrowing ($T_2 \approx T_{20}$), at least for Li_5AlO_4 whose relaxation we treat in detail, so that the above description is deemed adequate.

The following treatment parallels that of Rorschach.[7] A stead-state solution is obtained to Eq. (21) subject to the condition that $\tilde{I}_\alpha$ is held at some nonequilibrium value ΔI at a large distance R from the impurity. Under steady-state conditions the rate at which spins are relaxed within the volume equals the flow of spin current across the surface at R, and thus

$$4\pi R^2 D(R)\left(\frac{\partial \tilde{I}_\alpha}{\partial r}\right)_R=\frac{1}{T_\alpha}\int_{a_0}^{R}4\pi r^2\,dr\,\tilde{I}_\alpha(r)\ , \tag{23}$$

where the right-hand side of (23) serves as the definition of T_α as the relaxation time of the total spin contained within the sphere of influence of the impurity. In the limit of R much greater than the characteristic lengths of the problem a_0, b, and

$$\beta\equiv[C_\alpha/(D_S+D_P)]^{1/4}\ ,$$

the left-hand side of (23) is independent of R, and the right-hand side is approximately $\Delta I V_0/T_\alpha$, where $V_0=\frac{4}{3}\pi R^3$ is the volume of the impurity's sphere of influence. Thus,

$$\frac{1}{T_\alpha}=\frac{4\pi N(D_P+D_S)}{\Delta I}\lim_{R\to\infty}\left(R^2\frac{\partial\tilde{I}_\alpha}{\partial R}\right)\ , \tag{24}$$

where we have assumed that $V_0^{-1}=N$, the number of impurities per cm^3.

The steady-state solution to (21) and (22) which satisfies the boundary condition

$$\lim_{r\to\infty}\tilde{I}_\alpha(r)=\Delta I$$

is, as in Ref. 7,

$$\tilde{I}_\alpha(r)=BI_{1/4}\left(\frac{\beta^2}{2r^2}\right)+\Delta I\,\Gamma(\tfrac{3}{4})\left(\frac{\beta^2}{4}\right)^{1/4}I_{-1/4}\left(\frac{\beta^2}{2r^2}\right)\ , \tag{25}$$

where $I_\nu(z)$ is the Bessel function of imaginary argument and $\Gamma(z)$ is the γ function. From (25) we have

$$\lim_{r\to\infty}r^2\frac{\partial\tilde{I}_\alpha(r)}{\partial r}=-4B\left(\frac{\beta^2}{4}\right)^{1/4}\frac{1}{\Gamma(\frac{1}{4})}\ ,$$

and thus

$$\frac{1}{T_\alpha}=-\frac{16\pi N(D_P+D_S)}{\Delta I}\,\frac{B(\frac{1}{4}\beta^2)^{1/4}}{\Gamma(\frac{1}{4})}\ . \tag{26}$$

The constant B is determined by the following matching and boundary conditions: (i) $\tilde{I}_\alpha$ and $D(r)\partial\tilde{I}_\alpha/\partial r$ are continuous at the radius b where $D(r)$ changes from D_S+D_P to D_P. (ii) $\partial\tilde{I}_\alpha/\partial r=0$ at $r=a_0$ since there is no diffusion to distances closer than a_0, the nearest-neighbor distance between impurity and nuclear-spin sites. Since Rorschach treated spin diffusion only and tacitly assumed $b>a_0$, his results correspond to using condition (ii) only with $a_0=b$.

In the region $a_0<r<b$ we have

$$\tilde{I}_\alpha(r)=B'I_{1/4}\left(\frac{\beta'^2}{2r^2}\right)+B''I_{-1/4}\left(\frac{\beta'^2}{2r^2}\right)\ , \tag{27}$$

where $\beta'=(C_\alpha'/D_P)^{1/4}$ as opposed to

$$\beta=[C_\alpha/(D_P+D_S)]^{1/4}\ .$$

Note that C_α' in general differs from C_α since in applying Eq. (19) the hopping rate W should be $6(D_P+D_S)/a^2$ for $r>b$ whereas $W=6D_P/a^2$ for $r<b$. Equation (25) holds for $r>b$. Application of conditions (i) and (ii) to Eqs. (25) and (27) is straightforward, and the resulting expression for the relaxation rate is

$$\frac{1}{T_\alpha}=8\pi N\beta(D_P+D_S)\frac{\Gamma(\frac{3}{4})}{\Gamma(\frac{1}{4})}\times\frac{qI_{3/4}(\delta)-I_{-1/4}(\delta)}{qI_{-3/4}(\delta)-I_{1/4}(\delta)}\ , \tag{28}$$

where $\delta = \beta^2/2b^2$ and

$$q = \frac{\beta^2}{\beta'^2}\left(1 + \frac{D_S}{D_P}\right)\frac{k_1}{k_2} \tag{29}$$

with

$$k_1 = I_{-1/4}(\delta') - \frac{I_{3/4}(\delta_a)}{I_{-3/4}(\delta_a)} I_{1/4}(\delta') \ ,$$

$$k_2 = I_{3/4}(\delta') - \frac{I_{3/4}(\delta_a)}{I_{-3/4}(\delta_a)} I_{-3/4}(\delta') \ ,$$

in which $\delta' = \beta'^2/2b^2$, $\delta_a = \beta'^2/2a_0^2$. In the limit $D_P << D_S$, we find $q >> 1$ and (28) reduces to Eq. (10) of Ref. 7. If $D_P >> D_S$, then $\delta \approx \delta'$ and $\beta \approx \beta'$, and (29) simplifies to

$$\frac{1}{T_\alpha} = \gamma \pi N \beta D_P \frac{\Gamma(\frac{3}{4})}{\Gamma(\frac{1}{4})} \frac{I_{3/4}(\delta_a)}{I_{-3/4}(\delta_a)} \ , \tag{30}$$

which is the same as Eq. (10) of Ref. 7 except for b replaced by a_0. Thus, as expected, in this case the solution is independent of b and given by that for a spatially independent $D = D_P$ with diffusion allowed down to the distance a_0.

For rapid particle diffusion $\delta_a << 1$ and Eq. (30) reduces to

$$1/T_\alpha = \tfrac{4}{3}\pi N a_0 \eta_\alpha(a_0) \ , \tag{31}$$

which is the same as Eq. (12) apart from a constant of the order of unity, so there is no fundamental difference between the continuum and nearest-neighbor models in this case. On the other hand, for very slow spin and particle diffusion $\delta >> 1$ and since $I_\nu(\delta)$ is independent of ν for $\delta >> 1$, Eq. (28) becomes[6]

$$1/T_\alpha = 8.5 N (D_S + D_P)[C_\alpha/(D_S + D_P)]^{1/4} \tag{32}$$

which differs from Eq. (10) for $\langle f_\alpha \rangle << 1$ by the $[C_\alpha/(D_S + D_P)]^{1/4}$ dependence.

IV. INCLUSION OF NUCLEAR DIPOLE-DIPOLE COUPLING

At low (which often just means room) temperature the NMR line is not motionally narrowed and the paramagnetic impurity contribution to $1/T_2$ is masked by the rigid-lattice rate. Hence a complete description of the observed T_2 must include the effect of internuclear dipole-dipole coupling, which is responsible for the low-temperature transverse relaxation. (Nuclear dipole coupling may also influence T_1 strongly at some temperatures but not at others, depending on the precise conditions as discussed later.)

Within the framework of the Kubo-Tomita perturbation approach,[12] the nuclear dipole-dipole contribution is additive in the following sense. The methods of Ref. 12 show that

$$\phi_\alpha(t) = \exp\left[-\int_0^t (t - t') G_\alpha(t')\, dt'\right] \ , \tag{33}$$

where $\phi_\alpha(t)$ is the relaxation function [for $\alpha = 0$ (T_1) or $\alpha = \pm 1$ (T_2)] of the net nuclear spin of the sample and $G_\alpha(\tau)$ contains terms which are proportional to

$$\langle [H_{\text{tot}}'(\tau), I_\alpha][H_{\text{tot}}'(0), I_{-\alpha}] \rangle \ ,$$

where $H_{\text{tot}}'(\tau)$ is the total (nuclear-electronic plus nuclear-nuclear) perturbation and time dependence includes hopping motion by making the interaction parameters experienced by the nucleus functions of time [i.e., in Eq. (1) $A_{\alpha\beta}(\vec{r}) \rightarrow A_{\alpha\beta}(\tau)$ via $\vec{r} = \vec{r}(\tau)$]. One need only observe that there are no interference terms, so that

$$\begin{aligned} \langle [H_{\text{tot}}'(\tau), I_\alpha][H_{\text{tot}}'(0), I_{-\alpha}] \rangle &= \langle [H_{n-n}'(\tau), I_\alpha][H_{n-n}'(0), I_{-\alpha}] \rangle \\ &\quad + \langle [H_{e-n}'(\tau), I_\alpha][H_{e-n}'(0), I_{-\alpha}] \rangle \ , \end{aligned} \tag{34}$$

in order to establish

$$\phi_\alpha(t) = \phi_\alpha^{n-n}(t)\, \phi_\alpha^{e-n}(t) \ , \tag{35}$$

where the symbols *n-n* and *e-n* stand for the internuclear and nucleus-paramagnetic impurity couplings, respectively. The absence of interference terms involving $H_{e-n}' H_{n-n}'$ comes from the fact that such terms would contain averages of the product of one electronic spin operator and three nuclear-spin operators which vanish in the high-temperature limit of interest (high temperature here meaning that there is negligible spin polarization).

The nucleus-impurity relaxation function is what has been calculated in the preceding sections,

$$\phi_\alpha^{e-n}(t) = e^{-t/T_\alpha^{e-n}} \ , \tag{36}$$

where we now use the superscript to indicate that T_α previously derived is for the *e-n* process only.

A simple expression to account for motional narrowing of the *n-n* process is[13]

$$\phi_1^{n-n} = \exp\left[-\langle \Delta\omega^2 \rangle \int_0^t dt' (t - t') e^{-Wt'}\right] \ , \tag{37}$$

where $\langle \Delta\omega^2 \rangle$ is the secular second moment and W is the hopping rate as before. Nonsecular terms are important only for sufficiently rapid hopping that $W \gtrsim \omega_0$, and we assume that when this occurs $1/T_2^{e-n} >> 1/T_2^{n-n}$ so that the *n-n* process is negligible. Equations (35)–(37) suggest that an effective T_2 be defined as the solution to

$$1 = \frac{T_2}{T_2^{e-n}} + \langle \Delta\omega^2 \rangle \int_0^{T_2} dt' \, (T_2 - t') e^{-Wt'} \ . \tag{38}$$

In the strong-narrowing limit $T_2^{-1} << \langle \Delta\omega^2 \rangle^{1/2}$, we have the additive result

$$1/T_2 = 1/T_2^{e-n} + \langle \Delta\omega^2 \rangle / W \ .$$

As long as $\omega_0 T_{1,2} >> 1$, *n-n* contributions to T_1 and nonsecular *n-n* contributions to T_2 produce an additional rate which adds simply to $1/T_{1,2}^{e-n}$.

Sufficient conditions for the *e-n* process to dominate T_1 at high temperature and the *n-n* one to dominate at low temperature are

$$Zc \, \langle \Delta\omega^2 \rangle_{e-n} >> \langle \Delta\omega^2 \rangle_{n-n}$$

and

$$Zc << \langle \Delta\omega^2 \rangle_{n-n} / \omega_0^2 \ ,$$

where $\langle \Delta\omega^2 \rangle_{e-n}$ and $\langle \Delta\omega^2 \rangle_{n-n}$ measure strengths of the mean square *e-n* and *n-n* couplings, respectively. The first condition comes from taking

$$1/T_1^{e-n} \approx Zc \, \langle \Delta\omega^2 \rangle_{e-n} / W \ ,$$

$$\frac{1}{T_1^{n-n}} \approx \langle \Delta\omega^2 \rangle_{n-n} / W$$

at high temperatures where $\omega_0 << W$. The second one comes from the assumed low-temperature formulae

$$1/T_1^{e-n} \sim ZcW \ ,$$

$$1/T_1^{n-n} \sim (\langle \Delta\omega^2 \rangle_{n-n} / \omega_0^2) \, W \ ,$$

with the former a consequence of Eq. (10) and the latter the standard Bloembergen-Purcell-Pound (BPP) expression[14] for $\omega_0 >> W$.

V. COMPARISON WITH PbF$_2$:Mn

The dominant *e-n* interaction in this system is an isotropic nearest-neighbor transferred hyperfine $\hbar A \, \vec{I} \cdot \vec{S}$ with[15] $A = 1.5 \times 10^8$ sec^{-1}, so the treatment of Sec. II is appropriate. Equations (A4) and (A5) reduce to

$$G_0(t) = \tfrac{2}{3} A^2 S(S+1) \cos\omega_e t e^{-t/\tau_c} \ , \qquad (39a)$$

$$G_1(t) = \tfrac{1}{3} A^2 S(S+1)(1 + e^{-i\omega_e t}) e^{-t/\tau_c} \qquad (39b)$$

for $\omega_e >> \omega_0$, where ω_e and ω_0 are the EPR and NMR frequencies, respectively. It is claimed in Ref. 3 that the electronic relaxation rate $1/\tau_c$ is negligible over the whole temperature range. In this case $(W\tau_c >> 1)$ use of Eq. (39b) in (4) and (7) gives

$$\langle f_1 \rangle = \mathrm{Re} \int_0^\infty du \, e^{-u} \exp\left[-y \left(\tfrac{1}{2} u^2 - i \frac{u}{x} + \frac{1 - e^{-iux}}{x^2} \right) \right] \qquad (40)$$

with $y = \frac{1}{3} A^2 S(S+1)/W^2$, $x = \omega_e / W$. Only the real part Re is considered since a frequency shift is not of concern. The linewidth data of Ref. 3 are compared with Eqs. (10), (38), and (39b) in Fig. 1 for $c = 3 \times 10^{-4}$ (the lowest concentration studied), $Z = 4$ and $\omega_e / 2\pi = 63$ GHz (corresponding to the NMR frequency of 90 MHz). The hopping time $1/W$ is taken from the work of Boyce, Mikkelsen, and O'Keefe[16] who inferred it from conductivity data. The only adjustable parameter is $\langle \Delta\omega^2 \rangle$ which we choose to give the observed low-temperature value of

$$\gamma_N [\Delta H (T \to 0)]_{\mathrm{pp}} = \sqrt{3} \, \langle \Delta\omega^2 \rangle^{1/2} / 2^{3/2} \ ,$$

where

$$\Delta H_{\mathrm{pp}} = (2/\sqrt{3})(1/\gamma_N T_2)$$

is the peak-to-peak width of the absorption derivative curve and γ_N is the ^{19}F gyromagnetic ratio.

The features of note in Fig. 1 are the pronounced minimum and maximum. These, as observed by Hogg, Vernon, and Jaccarino are characteristic signatures of the presence of paramagnetic impurities. The minimum linewidth occurs when the impurity

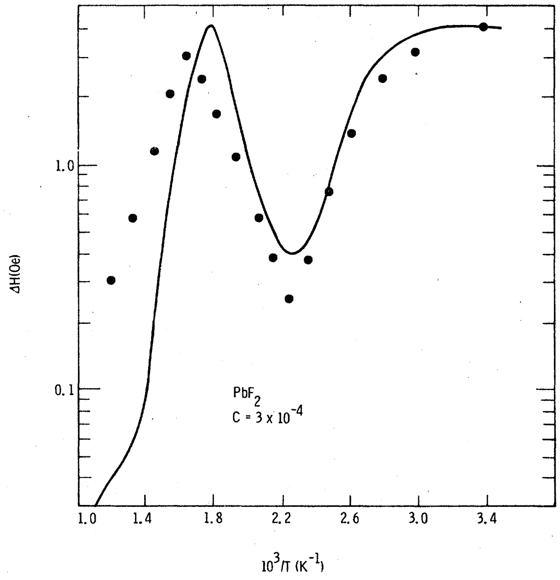

FIG. 1. Linewidth of Mn-doped PbF$_2$. Curve is theory with parameters chosen as explained in text. Points are data of Ref. 3 for Mn concentration $c = 3 \times 10^{-4}$.

rate $ZcW \propto e^{-U/k_BT}$ in the slow-motion regime catches up, as temperature is increased, with the motionally narrowed dipole contribution $\langle \Delta\omega^2 \rangle / W \propto e^{U/k_BT}$. The linewidth therefore reaches a local minimum at a temperature $T_{\min}$ given roughly by

$$k_B T_{\min} \approx 2U / \ln(Zc\nu_0^2 / \langle \Delta\omega^2 \rangle) \ ,$$

where ν_0 and U are the "attempt" frequency (prefactor) and activation energy, respectively, of the hopping rate. The maximum occurs when the effective fluctuation rate (which is just W as long as $W\tau_c >> 1$) matches the perturbation frequency $A[\frac{1}{3}S(S+1)]^{1/2}$. At this point one switches from the slow-hopping limit $\langle f \rangle << 1$ of Eq. (10) to the fast-hopping regime of Eq. (12). The characteristic temperature $T_{\max}$ is given by

$$k_B T_{\max} \approx 2U / \ln[3Zc/A^2 S(S+1)] \ .$$

Agreement is seen to be fairly good up to the temperature at which $\Delta H_{\rm pp}$ is a maximum. The theory, however, underestimates $\Delta H_{\rm pp}$ by about a factor of 7 at the highest temperature. At this temperature the n-n contribution is negligible and the theoretical value is the same as the BPP expression

$$\frac{1}{T_2} = \frac{1}{3} A^2 S(S+1) ZcW^{-1} \left(1 + \frac{1}{1+\omega_e^2/W^2} \right) \ ,$$

where here, as opposed to the above qualitative description of $T_{\max}$, we have included the nonsecular contribution involving ω_e.

VI. COMPARISON WITH Li_5AlO_4

Follstaedt and Biefeld[4] have recently reported ^{7}Li T_1 and T_2 measurements over a broad range of temperature in Li_5AlO_4. Although the samples wer nominally "pure," the observed high-temperature relation (for $\omega_0 << W$) $T_1 \approx 4T_2$ is strongly suggestive of relaxation via paramagnetic impurities when only the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition of the quadrupole split levels is observed in $I = \frac{3}{2}$ ^{7}Li. One would expect[17] $T_1 = T_2$ for $I = \frac{3}{2}$ if the relaxation were via fluctuating electric field gradients, but

$$T_1 = (I + \tfrac{1}{2})^2 T_2 = 4T_2$$

for $I = \frac{3}{2}$ for coupling to electron spins.[18] Subsequent room-temperature EPR measurements[5] revealed about 150 ppm (assuming $S = \frac{5}{2}$) paramagnetic ions substituted for Al with linewidths narrow enough to be detected.

For the lowest temperature at which $T_1 \approx 4T_2$, we estimate $\omega_e >> W$ which rules out an isotropic $\hbar A\, \vec{I} \cdot \vec{S}$ interaction as responsible for the relaxation. This is because Eqs. (39) show that $T_1/T_2 \sim \omega_e^2/W^2$ for $\omega_e >> W$. Thus, we are led to consider classical e-n dipole coupling, the important terms of which are those involving $S_z I_z$ and $S_z I_\pm$ since they do not require the energetically unfavorable (for $\omega_e >> W$) flip of an electron spin. Equations (A4) and (A5) then give

$$G_0(t) = \tfrac{2}{5} S(S+1) \gamma_e^2 \gamma_N^2 \hbar^2 r^{-6} \cos\omega_0 t \, e^{-t/\tau_c} \quad (41a)$$

$$\begin{aligned} G_1(t) = {} & \tfrac{1}{5} S(S+1) \gamma_e^2 \gamma_N^2 \hbar^2 r^{-6} e^{-t/\tau_c} \\ & + 2[I(I+1) - \tfrac{1}{4}] \tfrac{1}{5} S(S+1) \gamma_e^2 \gamma_N^2 \hbar^2 \\ & \times r^{-6} e^{-i\omega_0 t} e^{-t/\tau_c} \end{aligned} \quad (41b)$$

for an angular average of the dipolar interaction

$$\tfrac{1}{2} \gamma_e \gamma_N \hbar^2 [\vec{I} \cdot \vec{S}/r^3 - 3(\vec{I} \cdot \vec{r})(S \cdot \vec{r})/r^5]$$

at a distance r from the impurity where γ_e and γ_N are the electronic and nuclear gyromagnetic ratios. The factor $2[I(I+1) - \frac{1}{4}]$ is introduced to account for the enhancement of transverse fluctuations in the T_2 process when only the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition is observed.[18] [Such considerations are not needed for nuclei without a quadrupole moment and were not included in Eqs. (39) for the study of $I = \frac{1}{2}$ ^{19}F.] Note that for $\omega_0/W << 1$ or $\omega_0 \tau_c << 1$, $e^{-i\omega_0 t}$ and $\cos\omega_0 t$ may be replaced by unity for times of importance and then Eqs. (41) give $G_1(t) = (I + \frac{1}{2})^2 G_0(t)$ which guarantees $T_1 = 4T_2$ for $I = \frac{3}{2}$ in the high-temperature region.

From Eqs. (19) and (21) we obtain

$$C_0' = \tfrac{2}{5} S(S+1) \gamma_e^2 \gamma_N^2 \hbar^2 \frac{\tau_c{}^*}{1 + \omega_0^2 \tau_c{}^{*2}} \ , \quad (42a)$$

$$\begin{aligned} C_1' = {} & [I(I+1) - \tfrac{1}{4}] C_0' \\ & + \tfrac{1}{5} S(S+1) \gamma_e^2 \gamma_N^2 \hbar^2 \tau_c{}^* \ , \end{aligned} \quad (42b)$$

where the effective rate $\tau_c{}^*$ is given by $1/\tau_c{}^* = 1/\tau_c + W$ and where we have considered only the real part in C_1'. The primes on C_0' and C_1' indicate that they are for the region $r < b$ in which only particle diffusion is considered and $W = D_P/6a^2$. For C_0 and C_1, used for $r > b$, one simply replaces W in Eqs. (42) with $W \rightarrow (1/6a^2)(D_P + D_S)$.

The barrier-to-spin-diffusion distance b is taken from Ref. 7,

$$b = (3 \langle \mu_P \rangle / \gamma_N \hbar I)^{1/4} a \ , \quad (43)$$

where $\langle \mu_P \rangle$, the effective impurity moment which is "static" during the spin-diffusion time T_{20}, is given by

$$\langle \mu_P \rangle^2 = \tfrac{1}{3}\gamma_e^2 \hbar^2 S(S+1) \times \left[\frac{2}{\pi} \tan^{-1}\left(\frac{2\pi\tau_c}{T_{20}} \right) + \tfrac{1}{3} S(S+1)\gamma_e^2 \hbar^2 H^2 / k_B^2 T^2 \right] \tag{44}$$

with H the applied field. For reasonable values of τ_c and T_{20} the second term in square brackets of (44) is negligible at room temperature and above.

We attempt to fit T_1 for the parameters $a_0 = a = 2.5$ Å, $S = \frac{5}{2}$, $\gamma_N = 1.04 \times 10^4$ Oe^{-1} -sec^{-1}, $\gamma_e = 1.76 \times 10^7$ Oe^{-1} sec^{-1}, $T_{20} = 10^{-4}$ sec (see Fig. 5) appropriate to ^{7}Li resonance in the α phase of Li_5AlO_4 with spin $\frac{5}{2}$, $g = 2$ paramagnetic impurities. In the high-temperature region $1/T_1$ is given by Eq. (31) and its maximum value is at $\omega_0 \tau_c{}^* = 1$ from Eq. (42a). We then choose the concentration to give the observed maximum rate at 21.5 MHz, which yields $Na_0^3 = 5.9 \times 10^{-5}$, equivalent to 350 ppm substitution for Al. The activation energy is taken to be 0.96 eV from measurements of conductivity in an argon atmosphere.[19] If we assume that $W\tau_c \gg 1$ at the T_1 minimum so that $\tau_c{}^* \approx 1/W$, the attempt frequency (prefactor of W) is 1.6×10^{13} sec^{-1}.

We then obtain the electronic spin-lattice relaxation time τ_c by fitting the data at the lowest temperatures where spin diffusion is dominant. This gives $\tau_c = 2.7 \times 10^{-7}$ sec at room temperature for the 21.5-MHz data and the barrier given by Eqs. (43) and (44).

The results of this fit for 21.5 MHz are shown in Fig. 2, where we have taken $\tau_c \propto T^{-2}$, as expected for high-temperature Raman processes, and τ_c independent of temperature T in curves (a) and (b), respectively. Neither of these is very satisfactory since they produce too slow a decrease of $1/T_1$ on the low-temperature side of the T_1 minimum. The reason is that this short $a\,\tau_c$ plays a significant influence on the effective correlation time $\tau_c{}^*$ of Eqs. (42a) at temperatures not much below that of the T_1 minimum. This may be seen by noting the good fit for $10^3/T < 1.6$ obtained by setting $\tau_c \gg 1/W$ and thereby $\tau_c{}^* \approx 1/W$ at all temperatures [curve (d) of Fig. 2]. The situation is improved somewhat by assuming $b = a$, i.e., neglecting the barrier to diffusion, instead of the prediction of Eqs. (43) and (44) $b = 3.6a$. This increases τ_c to 2.4×10^{-6} sec in order to fit the room-temperature, 21.5-MHz data, and the result of a constant τ_c of this value is shown as curve (c). The room-temperature values of τ_c quoted above are consistent with the observed ESR width of 6 Oe, which implies $\tau_c \gtrsim 10^{-8}$ sec.

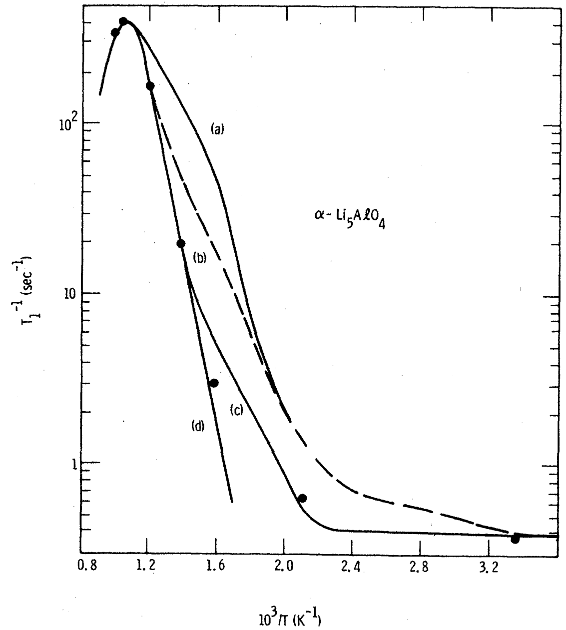

FIG. 2. Spin-lattice relaxation rate of α-Li_5AlO_4 at 21.5 MHz. Points are data of Ref. 4. Curves are theory for (a) $\tau_c = 2.7 \times 10^{-7}(300/T)^2$ sec, given by Eqs. (43) and (44). (b) $\tau_c = 2.7 \times 10^{-7}$ sec, b given by Eqs. (43) and (44). (c) $\tau_c = 2.4 \times 10^{-6}$ sec, $b = a$ (no barrier to spin diffusion). (d) $\tau_c \gg 1/W$ (impurity effectively has infinite spin-lattice relaxation time). Further details of parameters are contained in text.

The frequency dependence at the T_1 minimum is shown in Fig. 3 for the three experimental frequencies. A BPP $T_1 \propto \omega_0$ dependence is observed in agreement with the calculation. It may be worthwhile to note, however, that the dependence is sensitive to the interaction strength. The result of increasing the coefficient of $\tau_c{}^*/(1 + \omega_0^2 \tau_c{}^{*2})$ in Eq. (42a) by a fac-

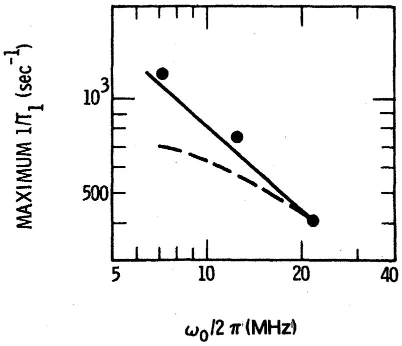

FIG. 3. Relaxation rate at temperature of T_1 minimum vs NMR frequency. Points are data of Ref. 4 for α-Li_5AlO_4. Solid line: interaction strength, as used in curves of Fig. 2, is classical dipolar at nearest-neighbor distance appropriate to α-Li_5AlO_4. Dashed line: interaction strength 10 times greater than for solid line. Concentration is adjusted to give agreement at 21.5 MHz.

tor of 10 over its classical dipolar value is shown as the dashed curve in Fig. 3, which is normalized to maintain agreement at 21.5 MHz. The weaker frequency dependence arises from the relaxation rate having a weaker-than-linear dependence on interaction strength for large values of $\eta_0(a)$ as may be seen by analogy with Eqs. (10) and (11).

The low-temperature frequency dependence can also be sensitive to the parameters as shown in Fig. 4. The BPP result $T_1 \propto \omega_0^2$ is satisfied only if $\eta_0(b)T_{20} << 1$ so that a spin requires many encounters at the barrier distance b to be relaxed. An $\omega_0^{1/2}$ dependence results from the opposite extreme $\eta_0(b)T_{20} >> 1$ and is seen to exist for $b=a$, $\tau_c = 2.4\times 10^{-6}$ sec [curve (a) of Fig. 4] as used to fit the room-temperature, 21.5-MHz data in the neglect of a barrier to spin diffusion. The values used for curves (a) and (b) in Fig. 2 which utilize Eqs. (43) and (44) give an intermediate dependence shown as curve (b) in Fig. 4. The rather sparse data fall between these latter two cases.

In regard to frequency dependence it is interesting to observe the differences between T_1 data[4] for the α and β phases of Li_5AlO_4. The calculation presented here is independent of details of the lattice structure and hopping processes and therefore makes no distinction between the two phases since both have the same coordination numbers and nearly the same values of a and a_0. The experiments, however, show a significant difference. In the β phase the minimum T_1 is nearly independent of frequency yet shows a stronger $T_1 \propto \omega_0^{1.8}$ dependence at low temperature. Within the context of the present model this could be accounted for by a larger interaction and a longer τ_c than in the α phase. The larger interaction would violate the condition $\eta_0(a_0) << \omega_0$ at the temperature of the T_1 minimum and thereby lead to a weaker frequency dependence as depicted in Fig. 3. Conversely, a longer τ_c could increase the barrier radius b [see Eq. (44)] and thereby reduce $\eta_0(b)T_{20}$, even though the interaction at nearest-neighbor distance is larger, to the point where $\eta_0(b)T_{20} << 1$ is satisfied. Although the differences could in principle be interpreted in this manner, it obviously would be desirable to see if they were a direct consequence of a more detailed model which took account of, for example, the fact that there are five inequivalent Li^+ positions in the α phase and only two in the β phase.

Figure 5 presents the predicted T_2 at 21.5 MHz for the same parameters used to fit T_1 in Fig. 2 together with the data[4] on α-Li_5AlO_4. Agreement is found only at the highest temperatures. At lower temperatures, T_2 is not at all described by the conventional motional narrowing process. Instead of decreasing when $WT_{20} \approx 1$, the rate actually shows an initial increase and does not start to fall until $WT_{20} \approx 10$. The fact that normal motional narrowing does seem to apply to $I = \frac{1}{2}$ ^{19}F in PbF_2:Mn (Fig. 1) suggests that the discrepancy may be attributed to quadrupole effects such as some mixing-in of non $\frac{1}{2} \rightarrow -\frac{1}{2}$ transitions which are not accounted for in the present treatment.

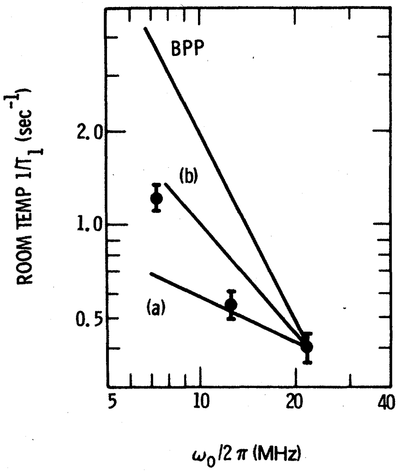

FIG. 4. Room-temperature relaxation rate vs NMR frequency. Points are data of Ref. 4 for α-Li_5AlO_4. (a) $\tau_c = 2.4\times 10^{-6}$ sec, $b=a$ (no barrier to spin diffusion). (b) $\tau_c = 2.1\times 10^{-7}$ sec, b given by Eqs. (43) and (44). Curve labeled BPP is $T_1 \propto \omega_0^2$ result of BPP at low temperatures.

VII. SUMMARY AND CONCLUSIONS

A theory of NMR relaxation in superionic conductors by paramagnetic impurities has been developed in a manner which allows for an arbitrary ratio $W\tau_c$ of paramagnetic relaxation time to hopping time. Thus, the entire temperature range can be treated. Two types of interactions were considered: nearest-

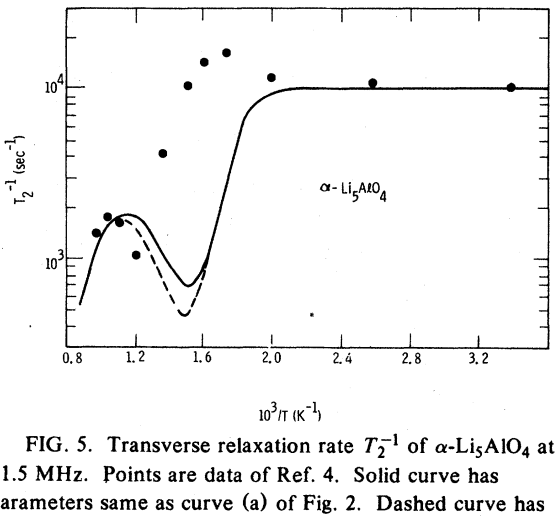

FIG. 5. Transverse relaxation rate T_2^{-1} of α-Li_5AlO_4 at 21.5 MHz. Points are data of Ref. 4. Solid curve has parameters same as curve (a) of Fig. 2. Dashed curve has parameters same as curve (d) of Fig. 2.

neighbor only and long-range dipole-dipole. For the former a discrete hopping model was used. In the latter case a classical diffusion equation was assumed. Solution of this equation followed the methods of Rorschach[7] but extended the range of validity by allowing the aforementioned arbitrary value of $W\tau_c$ and both particle and spin diffusion.

An example of the nearest-neighbor-only interaction is likely to be PbF_2:Mn where there is a strong transferred hyperfine interaction. Good quantitative agreement was obtained over most of the range for the temperature-dependent linewidth without any adjustable parameters for the lowest concentration studied in Ref. 3. However, the theoretical linewidth is too small at the highest temperatures.

The classical dipole case was applied to data on Li_5AlO_4. The low-temperature frequency dependence could be reproduced with reasonable choices of the parameters, but the short values of electronic spin-lattice relaxation time τ_c interfere with the temperature dependence below the T_1 minimum. A much better fit of the high-temperature data is obtained if the rate τ_c^{-1} is taken as negligible compared with the hopping rate. It would then be difficult, however, to explain the low- (room-)temperature data since, with such a long τ_c the paramagnetic impurity mechanisms would be very weak because the effective correlation time becomes too much greater than the NMR precession time and because the barrier distance to spin diffusion b becomes too large. The possibility exists that the room temperature T_1 is dominated by other mechanisms such as coupling of the quadruple moment to phonons, but these should be frequency independent. A further discrepancy is in the line narrowing which does not occur until a much higher temperature than predicted and may be indicative of additional quadrupole effects which complicate T_2.

In conclusion, the theory is probably adequate to describe situations where simple uncorrelated activated hopping processes occur. [As noted in connection with Eq. (6) we have treated only the case where hopping is described by a simple, uncorrelated random walk.] The lack of agreement at high temperature in PbF_2:Mn may, for example, be indicative of a true difference between the effective hopping time for a nucleus to jump away from the vicinity of an impurity site and that for describing the bulk conductivity. In this case it might appear that the former time is longer than the latter in the sublattice-melting region. If deviations can be so attributed to features of correlated hopping,[20] then the present theory serves a useful purpose in telling when one can and cannot say that strong correlations are in evidence.

In situations where the electronic spin-lattice relaxation time and spin diffusion are important there may be difficulties. It would be desirable to have ESR measurements of τ_c and an independent measure, possibly by satellite NMR, of the barrier to spin diffusion in relevant compounds to assess further the theory.

ACKNOWLEDGMENT

This work was supported by the U. S. Department of Energy under Contract No. AT(29-1)789.

APPENDIX A: PERTURBATION THEORY OF RELAXATION FUNCTION

For the interaction of Eq. (1), the equation of motion is

$$\begin{aligned}\frac{dI_\alpha(t)}{dt} &= i\sum_{\alpha'\beta} A_{\alpha'\beta}S_{\alpha'}(t)[I_\beta(t),I_\alpha(t)] - i\alpha\omega_0 I_\alpha(t)\\ &= i\sum_{\alpha'\beta} A_{\alpha'\beta}S_{\alpha'}(t)k_{\beta\alpha}I_{\alpha+\beta}(t)\ ,\end{aligned}\tag{A1}$$

where, with $\alpha=0, \pm1$ standing for the components I_z, $I_\pm$, the commutators give for the nonzero components of $k_{\alpha\beta}$: $k_{1,-1}=-k_{-1,1}=2$, $k_{10}=-k_{01}=k_{0,-1}=-k_{-1,0}=1$. By iterating (A1) twice we obtain

$$\begin{aligned}\tilde{I}_\alpha(t+\tau) =& -i\sum_{\alpha'\beta'} A_{\alpha'\beta}\int_t^{t+\tau} S_{\alpha'}(t_1)k_{\beta'\alpha}\tilde{I}_{\alpha+\beta'}(t)e^{-i\beta'\omega t_1}\,dt_1\\ &-\sum_{\alpha'\beta}\sum_{\alpha''\beta''} A_{\alpha'\beta'}A_{\alpha''\beta''}\int_t^{t+\tau} dt_1\int_t^{t_1} dt_2 S_{\alpha'}(t_1)S_{\alpha''}(t_2)k_{\beta'\alpha}k_{\beta'',\alpha+\beta'}\tilde{I}_{\alpha+\beta'+\beta''}(t)\\ &\times e^{-i\beta'\omega_0 t_1}e^{-i\beta''\omega_0 t_2}+\cdots\end{aligned}\tag{A2}$$

to second order in the coupling $A_{\alpha\beta}$ where

$$I_\alpha(t)=\tilde{I}_\alpha(t)e^{-i\alpha\omega_0 t}\ .$$

Ultimately we are interested only in the average behavior of the nuclear spin, and this entails a thermal average over the electron-spin coordinates, and an angular average over the spatial coordinates for the case of an anisotropic dipolar interaction. We assume that this averaging can be applied to Eq. (A2) and thereby arrive at

$$\tilde{I}_\alpha(t+\tau) = \tilde{I}_\alpha(t) - \int_t^{t+\tau} dt'\,(\tau - t')\,G_\alpha(t')\,dt'\,\tilde{I}_\alpha(t)$$
$$\approx \tilde{I}_\alpha(t)\exp\left[-\int_t^{t+\tau} dt'\,(\tau - t')\,G_\alpha(t')\,dt'\right] ,$$

where

$$G_0(t') = \tfrac{4}{3}S(S+1)e^{-t'/\tau_c}[\langle|A_{01}|^2\rangle_{\mathrm{av}}\cos\omega_0 t' + 2\langle|A_{11}|^2\rangle_{\mathrm{av}}\cos(\omega_e-\omega_0)t'$$
$$+2\langle|A_{1,-1}|^2\rangle_{\mathrm{av}}\cos(\omega_e+\omega_0)t'] , \tag{A4}$$

$$G_{\pm 1}(t') = \tfrac{2}{3}S(S+1)e^{-t'/\tau_c}(\langle|A_{01}|^2\rangle_{\mathrm{Av}}e^{\mp i\omega_0 t'} + 2\langle|A_{11}|^2\rangle_{\mathrm{av}}e^{\pm i(\omega_e-\omega_0)t'}$$
$$+2\langle|A_{1,-1}|^2\rangle_{\mathrm{av}}e^{\mp i(\omega_e+\omega_0)t'}$$
$$+2\langle|A_{00}|^2\rangle_{\mathrm{av}} + 8\langle|A_{01}|^2\rangle_{\mathrm{av}}\cos\omega_e t') . \tag{A5}$$

In arriving at Eqs. (A4) and (A5) we have used

$$\langle S_\alpha\rangle = 0 ,$$
$$\langle S_\alpha(t_1)S_\beta(t_2)\rangle = \tfrac{1}{3}S(S+1)(1+|\alpha|)e^{-|t_1-t_2|/\tau_c}e^{i\alpha\omega_e(t_1-t_2)}\delta_{\alpha,-\beta}$$

appropriate to high temperature and assumed that the necessary angular averages satisfy

$$\langle A_{\alpha\beta}A_{\alpha'\beta'}\rangle_{\mathrm{av}} = \langle|A_{\alpha\beta}|\rangle^2\rangle_{\mathrm{av}}\delta_{\alpha+\beta,-\alpha'-\beta'} ,$$

which is true for the dipolar interaction. Here ω_e and τ_c are the electronic resonance frequency and relaxation time, respectively. It is through this averaging that Eq. (A3) results. In general, one would find that the right-hand side of (A2) also contains terms $\tilde{I}_{\iota\;\beta'+\beta''}(t)$ with $\beta'+\beta'' \neq 0$.

The second equality in (A3) is the standard approximation[12] employed to extrapolate the first equality to an expression valid for longer times. Replacement of the double integral over $dt_1\,dt_2$ by a single integral occurs by virtue of the fact that the averaging makes any quantity which depends on t_1 and t_2 a function of the single variable $t' = t_1 - t_2$. The reader is referred to Refs. 12 and 6 for further details and discussion of the approximations.

The above results assume that all $\Delta m = \pm 1$ transitions contribute to the resonance (Δm is the change in nuclear Zeeman quantum number) so that the total component of nuclear spin I_α is observed. If, as is often the case for resolved quadrupole splittings, only the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition is observed, one must restrict the expressions to matrix elements such as $\langle\frac{1}{2}|I_+|-\frac{1}{2}\rangle$. One can show[18] that the effect of this on $G_{\pm 1}$ is to multiply the first three terms on the right-hand side of (A5) (those which involve transverse fluctuations) by

$$\langle\tfrac{1}{2}|I^+I^- + I^-I^+|\tfrac{1}{2}\rangle = 2[I(I+1) - \tfrac{1}{4}] .$$

The last two terms, which involve longitudinal fluctuations, are unaffected. The expression for T_1 is unaffected since a common procedure[4] for measuring longitudinal relaxation is to saturate all quadrupole-split lines by a pulse sequence, after which the system is assumed to relax with a common spin temperature.

APPENDIX B: PROBABILITY OF ENCOUNTERING IMPURITIES DURING RANDOM WALK

We derive here Eq. (8) for the probability $P(n|t)$ that in time t a hopping nucleus lands on n sites which are neighbors of paramagnetic impurities. This probability is expressed as

$$P(n|t)=\sum_{M=n}^{\infty} p(n|M)\rho(M|t) \ , \tag{B1}$$

where

$$p(n|M)=(Zc)^n(1-Zc)^{M-n}\frac{M!}{n!(M-n)!} \tag{B2}$$

is the probability that, for a random distribution of impurities, n sites out of M are neighbors of an impurity and $\rho(M|t)$ is the probability that the nucleus lands on M different sites in time t. In (B2) Zc is the probability that any one site is neighbor to an impurity since there are Z nearest-neighbor host sites with a probability c per site of occupation by a paramagnetic ion and we assume $Zc \ll 1$. The probability $\rho(M|t)$ is computed by taking $W\delta t$ as the probability of a jump occurring in a short time δt. The Poisson distribution

$$\rho'(M|t)=\frac{e^{-Wt}(Wt)^M}{M!} \tag{B3}$$

results for the number of successes (jumps) as the number of "attempts" $t/\delta t$ goes to infinity and the probability per attempt $W\delta t$ goes to zero such as to keep the average number of successes Wt finite. Equation (B3) gives the probability $\rho'(M|t)$ of there being M jumps in time t. We assume that for a three-dimensional walk with a large number of nearest-neighbor sites available per jump the fraction of sites which are reached more than once in a walk of M steps is small, so that

$$\rho(M|t)\approx\rho'(M|t) \ . \tag{B4}$$

Use of (B4) and (B2) in (B1) leads to

$$\begin{aligned}P(n|t)&=\frac{(Zc)^n}{n!}\sum_{M=n}^{\infty}(1-Zc)^{M-n}\frac{(Wt)^M}{(M-n)!}e^{-Wt}\\&=(Wt)^n\frac{(Zc)^n}{n!}\sum_{M'=0}^{\infty}(1-Zc)^{M'}\frac{(Wt)^{M'}}{M'!}e^{-Wt}\\&=(Wt)^n\frac{(Zc)^n}{n!}\exp[(1-Zc)Wt]e^{-Wt}\\&=(Wt)^n\frac{(Zc)^n}{n!}e^{-ZcWt} \ .\end{aligned} \tag{B5}$$

APPENDIX C: NON-r^{-6} DEPENDENCE OF $\eta_\alpha(r)$

For small distances $\eta_\alpha(r)$ can vary as r^{-3} under circumstances described in connection with Eq. (20). A solution can be obtained in terms of Bessel functions if we take

$$\langle\eta_\alpha(r)\rangle=\begin{cases}\dfrac{C_\alpha}{r_c^3 r^3} \ , & r\leq r_c\\[2ex] \dfrac{C_\alpha}{r^6} \ , & r>r_c\end{cases} \tag{C1}$$

where

$$r_c=(C_\alpha/a_0^3)^{1/3}[2/G(a_0,0)]^{1/6} \tag{C2}$$

for $W\tau_c \gg 1$ and $\frac{1}{2}G_\alpha(a_0,0)/W^2>1$, the limiting case in which $r_c>a_0$ is realized. (Obviously only $r_c>a_0$ is of concern since a_0 is the distance of closest approach.) The solution to the steady-state equation is

$$D\nabla^2\tilde{I}_\alpha-\eta_\alpha(r)\tilde{I}_\alpha=0 \ , \tag{C3}$$

$$\tilde{I}_\alpha=\begin{cases}A'r^{-1/2}I_1[2\beta^2/(rr_c^3)^{1/2}]+B'r^{-1/2}K_1[2\beta^2/(rr_c^3)^{1/2}] \ , & r<r_c\\ Ar^{-1/2}I_{1/4}(\beta^2/2r^2)+Br^{-1/2}I_{-1/4}(\beta^2/2r^2) \ , & r>r_c\end{cases} \tag{C4}$$

where $\beta=(C_\alpha/D)^{1/4}$ and A', B', A, B are constants to be determined. Since the conditions at $r\rightarrow\infty$ are unaltered by (C1) the relaxation rate is still given by Eq. (26). The boundary conditions are continuity of $\tilde{I}_\alpha$ and $\partial\tilde{I}_\alpha/\partial r$ at r_c as well as the ones used in Sec. IV at a_0 and the spin-diffusion barrier b. There are two cases to consider. (i) $r_c<b$. Here the change in behavior of $\eta_\alpha(r)$ occurs where $D(r)=D_P$. (ii) $r_c>b$. The change in behavior of $\eta_\alpha(r)$ occurs where $D(r)=D_P+D_S$. Application of the boundary conditions leads in either case to four simultaneous equations whose solutions are straightforward, though the resulting expressions involving Bessel functions are lengthy and not repeated here.

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[*] A U. S. Department of Energy facility.

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[20] I am grateful to V. Jaccarino for suggesting this.