Reduced nuclear magnetic relaxation by paramagnetic impurities in one dimension

Peter M. Richards
Sandia Laboratories, Albuquerque, New Mexico 87185*
(Received 15 May 1979)

The paramagnetic-impurity contribution to NMR relaxation of a diffusing nucleus is shown to be proportional to c^2 in one dimension as opposed to c in three dimensions, where c is the impurity concentration. The mechanism is thus not expected to be important for one-dimensional superionic conductors except at high doping levels, whereas it is significant even in nominally "pure" three-dimensional superionics. This brings into question the interpretation of recent NMR results in supposedly one-dimensional β-eucryptite as being due to paramagnetic impurities.

I. INTRODUCTION

In a previous publication,[1] referred to as I, we discussed nuclear-magnetic-resonance (NMR) relaxation of rapidly diffusing ions by paramagnetic impurities. This has been shown[2] to be a major source of relaxation in superionic conductors even for nominally "pure" samples.[3] The analysis in I assumed the diffusion could be described by a self-avoiding random walk. That is, in a walk of N steps, N different lattice sites are visited and, on the average, NZc paramagnetic ions are encounted, where $Zc << 1$ is the probability that the ion has an impurity for a nearest neighbor (Z is the number of nearest-neighbor sites, c is the impurity concentration). This is a reasonable approximation for a three-dimensional (3-D) lattice, but it clearly breaks down in one dimension. In this paper we treat the 1-D problem which, aside from its academic interest, is important because several superionic conductors have channel structures which suggest predominantly 1-D hopping. In particular β-eucryptite ($LiAlSiO_4$) is a well-documented 1-D system[4] whose NMR relaxation[5] has been attributed[6] to paramagnetic impurities.

The major result is that the relaxation rate $T_{1,2}^{-1}$ due to impurities is greatly reduced in one dimension: whereas $T_{1,2}^{-1} \propto Zc$ in three dimensions, we find $T_{1,2}^{-1} \propto Z^2c^2$ in one dimension. [T_1 and T_2 are the longitudinal (spin lattice) and transverse relaxation times, respectively.] Thus paramagnetic impurities are likely to be important in a true 1-D material only at very high concentrations of the order of 1% while in three dimensions appreciable effects can be expected[2] for c of the order of a few ppm. Further, any characteristic "magnetic tagging" peak[2] in the linewidth T_2^{-1} versus temperature θ can occur only at θ's very much larger than for corresponding 3-D systems.

Physically the result is easy to understand. For a 1-D walk of N steps only a number of the order of $\sqrt{N}$ different sites are encountered on the average. Thus one must take $(Zc)^{-2}$ steps, rather than $(Zc)^{-1}$ for the self-avoiding walk, before encountering an impurity. Hence the relaxation time is at least as long as τ/Z^2c^2, where τ is the jump time, since relaxation cannot proceed until the nucleus diffuses to the vicinity of a paramagnetic ion. Once the diffusing ion reaches the impurity, however, the overwhelming probability is that its successive encounters will be with the same impurity; so if several encounters are required for relaxation, the concentration dependence is of the form $T_{1,2} \sim \tau/Z^2c^2 + T'$, where T' is the time required to make the necessary number of encounters beyond one and is independent of c. Thus the relaxation rate is proportional to c^2 only if $T' << \tau/Z^2c^2$, but which, we argue below, is likely to be the case in most instances. (An implicit assumption is that the paramagnetic impurity is substitutional at a non-mobile-ion site, e.g., Fe^{3+} for Al^{3+} in $LiAlSiO_4$, and thus does not block the 1-D conduction channel.) A further difference from the 3-D self-avoiding walk is that the relaxation is highly nonexponential. This and the above points are treated quantitatively in Sec. II.

II. THEORY

It will be shown that in practically all cases of physical interest the relaxation rate is limited by the time it takes a diffusing nucleus to make its first encounter. Thus consider first for simplicity the situation in which relaxation is effectively instantaneous once the ion reaches the neighborhood of an impurity. The relaxation function is then given by

$$\phi(t) = \int_0^\infty dt' \, P_1(t') \Theta(t - t') \quad , \tag{1}$$

where $\Theta(t - t')$ is the unit step function which is zero for $t > t'$, $P_1(t')$ is the normalized probability that it takes the nucleus a time t' to make its first encounter with a paramagnetic ion, and $\phi(t)$ is the nuclear magnetization at time t normalized to its value at $t = 0$. The sense of Eq. (1) is that the average magnetization immediately decays to zero when $t = t'$, the time

of the first encounter, and remains zero for all future time $t > t'$. The probability $P_1(t')$ is decomposed into

$$P_1(t') = \sum_{N=0}^{\infty} P_1(N)\rho(N|t') \quad , \tag{2}$$

where $P_1(N)$ is the probability that an impurity is first encountered at the Nth step of a random walk and $\rho(N|t')$ is the probability that N steps are taken in the time t'. This latter probability is given[7] by a Poisson distribution which approaches a δ function [$\rho(N|t') = 0$ unless $t' = N\tau$] for $t'/\tau >> 1$ so that Eq. (1) may be rewritten

$$\phi(t) = \sum_{N=0}^{\infty} P_1(N)\Theta(t - N\tau) \quad . \tag{3}$$

We further express $P_1(N)$ as

$$P_1(N) = \sum_{k=1}^{N} (Zc)(1 - Zc)^{k-1} R(k,N) \quad . \tag{4}$$

Here $Zc(1 - Zc)^{k-1}$ is the probability that one must visit $k-1$ different lattice sites before reaching an impurity at the kth site and $R(k,N)$ is the probability that it takes N steps of the walk to visit k different sites.

For the self-avoiding walk $R(k,N) = \delta_{k,N}$ whereupon use of Eq. (4) in Eq. (3) gives (in three dimensions)

$$\phi(t) \approx e^{-Zct/\tau} \quad , \tag{5}$$

for $Zc << 1$ and $(1 - Zc)^{t/\tau} \approx e^{-Zct/\tau}$. Equation (5) gives the well-known result $1/T_{1,2} = Zc/\tau$ in the region where relaxation is limited by the time it takes the nucleus to diffuse to an impurity and also shows that the decay is exponential. (Note that we are considering a discrete hopping model and only nearest-neighbor electron-nuclear spin interactions so that certain considerations[8] based on a continuum diffusion equation and r^{-6} interaction are not relevant here.)

The situation is considerably different for the 1-D problem at hand where $R(k,N)$ is equivalent to the probability that the point $x = ka$ (a is the jump distance) is *first* visited at the Nth step of a random walk which starts at $x = 0$. This is given in the textbook[7] by

$$R(k,N) = (k/N)P(k,N) \quad , \tag{6}$$

where $P(k,N)$ is the familiar probability that a particle is at the point $x = ka$ after the Nth step,

$$P(k,N) = 2^{-N} N!/(N - k/2)!(N + k/2)! \quad . \tag{7}$$

We insert Eqs. (6) and (4) into Eq. (3), convert the sums to integrals and use the continuum approximation

$$P(k,N) = (2\pi N)^{-1/2} \exp(-k^2/2N) \quad ,$$

valid for $N >> 1$. The result for $t/\tau >> 1$ and $Zc << 1$ is (in one dimension)

$$\phi(t) = e^{T} \mathrm{efrc}(\sqrt{T}) \quad , \tag{8}$$

where erfc is the complementary error function and T is a dimensionless time given by $T = \frac{1}{2}Z^2c^2t/\tau$. Since ϕ is a function of T we see that the characteristic decay time is proportional to τ/Z^2c^2 which confirms the physical argument in the Introduction. For $T >> 1$, $\phi(t) \approx (\pi T)^{-1/2}$, while $\phi(t) \approx 1 - 2(T/\pi)^{1/2}$ for $T << 1$.

The function given by Eq. (8) is plotted in Fig. 1 which shows that it is highly nonexponential. It is more nearly exponential when plotted versus $\sqrt{T}$, but the resulting semilog plot still shows sizeable curvature during the first decade of decay. The long-time $(\pi T)^{-1/2}$ approximation is good to within 10% for $T \geq 4$.

If relaxation is not complete after the first encounter, we must consider successive interactions with paramagnetic ions. Since the average distance to the next impurity is of the order of a/Zc, the preceding analysis shows that of the order of $1/Z^2c^2$ steps are required to make an encounter with an ion other than the one first visited. On the other hand, the starting point is revisited[7] on the order of $\sqrt{N}$ times in a walk of N steps. Thus the nucleus will interact with the original impurity about $1/Zc$ times before it encounters a different relaxer, so it is a good approximation to consider encounters with only one ion as long as $Zc << 1$.

To account for noninstantaneous relaxation at the impurity site, we replace the unit step function in Eq.

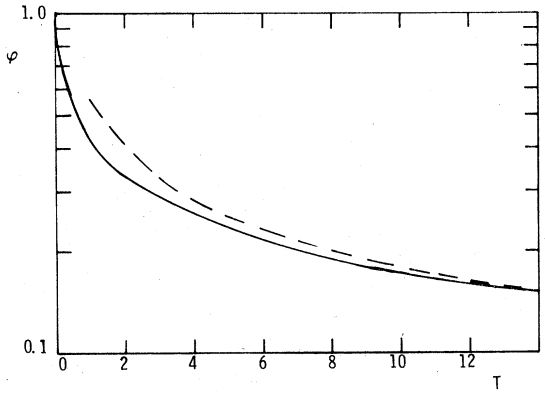

FIG. 1. Relaxation function ϕ vs reduced time $T = \frac{1}{2}Z^2c^2t/\tau$ for case of instantaneous relaxation once impurity is encountered. Dashed curve is $\phi = (\pi T)^{-1/2}$.

(1) by a relaxation function $\psi(t-t')$ defined as

$$\Theta(t-t') \rightarrow \psi(t-t') = \begin{cases} 1, & t < t' \\ \phi_0(t-t'), & t > t' \end{cases}, \quad (9)$$

where $\phi_0(t-t')$ is the relaxation function for a nucleus which is in the neighborhood of an impurity at $t'=0$ and which encounters no other impurities during its subsequent random walk. Standard Kubo-Tomita theory[9] may be used to express this relaxation function as

$$\phi_0(t_1) = \left\langle \exp\left[i \int_0^{t_1} \Delta\omega(t_2) p(0,t_2)\, dt_2 \right] \right\rangle , \quad (10)$$

where $\Delta\omega(t_2)$ is a fluctuating perturbation which has the properties $\langle \Delta\omega(t_2) \rangle_{av} = 0$ and

$$\langle \Delta\omega(t_2)\Delta\omega(t_3) \rangle_{av} = \langle \Delta\omega^2 \rangle e^{-|t_2-t_3|/\tau_c} , \quad (11)$$

in which τ_c is the spin-lattice relaxation time of the paramagnetic impurity. The brackets $\langle\ \rangle_{av}$ in Eq. (11) are averages over the electron-spin coordinates and over the angles of the vector $\vec{r}$ between the nucleus and the nearest-neighbor impurity site in the case of an anisotropic (dipolar) interaction. The quantity $p(0,t_2)$ in Eq. (10) is unity if the nucleus is at the origin of a random walk at time t_2 and zero otherwise. The brackets $\langle\ \rangle$ in Eq. (10) imply an average both over the impurity spin $\langle\ \rangle_{av}$ and over $p(0,t_2)$ [the average $\langle p(0,t_2) \rangle = P(0,t_2)$ as given by Eq. (7)]. For simplicity, nonsecular terms [containing oscillations at ω_0 and $\omega_e (\omega_e >> \omega_0)$, the respective NMR and ESR frequencies] have been omitted from Eq. (10). Thus the treatment is limited either to calculation of transverse relaxation T_2 in the low-temperature region where $\omega_0\tau, \omega_0\tau_c >> 1$ so that secular terms dominate or to T_2 and spin-lattice relaxation T_1 at high temperatures where $\omega_e\tau_c << 1$ and the spectral densities are independent of frequency. This is a convenient but not serious restriction since the basic physics is contained within the model and nonsecular terms can be added in a relatively straightforward manner.

An expression similar to Eq. (10) was treated in I.

TABLE I. Characteristic 1-D decay rates $1/T'$ of $\phi_0(t_1)$, given by $\phi_0(t_1/T') = 1/e$, for three cases, in none of which is $\phi_0(t_1)$ a simple exponential. T' is the time required for relaxation *after* the first impurity is encountered. τ and τ_c are the hopping and impurity spin-lattice relaxation times, respectively.

Case	(i)	(ii)	(iii)
conditions	$\tau_c >> t_1$	$\tau_c << \tau$	$\tau << \tau_c << t_1$
$1/T'$	$0.16\langle\Delta\omega^2\rangle\tau$	$0.32\langle\Delta\omega^2\rangle^2\tau_c^2\tau$	$0.32\langle\Delta\omega\rangle^2\tau^2\tau_c$

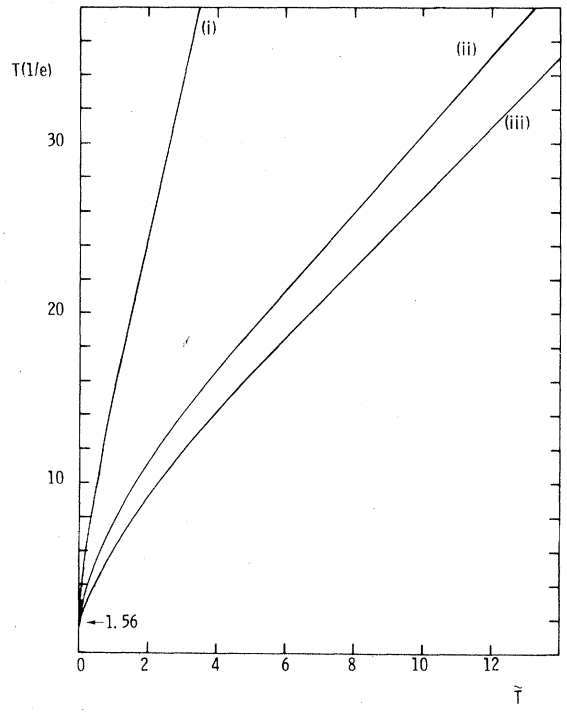

FIG. 2. Reduced time $T(1/e)$ for overall decay of magnetization to $1/e$ of its initial value vs normalized time $\tilde{T}$ which characterizes time for decay of magnetization after impurity has been encountered. $\tilde{T}$ is equal to $\lambda^{-1} = \frac{1}{2}Z^2c^2/\Delta\omega^2\tau^2$, $\Gamma^{-1} = Z^2c^2/\Delta\omega^4\tau_c^2\tau^2$, and $\Gamma'^{-1} = Z^2c^2/\Delta\omega^4\tau^3\tau_c$ for cases (i), (ii), (iii), respectively. To convert $T(1/e)$ to units of real time, multiply by $2\tau/Z^2c^2$ where τ is the hopping time.

But there it was assumed that each encounter involves a different paramagnetic ion so that $\langle \Delta\omega(t_2)\Delta\omega(t_3) \rangle_{av} = 0$ if the times t_2 and t_3 refer to different encounters, i.e., the encounters are statistically independent. Here we must be more careful since each encounter involves the same ion, and thus the encounters are independent only in the limit of rapid electronic relaxation, $\tau_c << \tau$.

We treat three limiting cases (i) $t_1 << \tau_c$, (ii) $\tau_c << \tau$, (iii) $\tau << \tau_c << t_1$. Expressions for the characteristic decay rates $1/T'$ of $\phi_0(t_1)$, which is nonexponential, are summarized in Table I. The reader may confine his attention to Table I and Fig. 2 and skip the remainder of this section if he is interested in results only.

1. $t_1 << \tau_c$

In (i) $\Delta\omega(t_2)$ is constant so that

$$\phi_0(t_1) = \langle e^{i\Delta\omega t^*} \rangle , \quad (12)$$

where t^* is the amount of time spent at the origin in

a walk of duration t_1 and is given by

$$t^* = \sum_{i=0}^{n} \tau_i \ , \tag{13}$$

with τ_i the duration of the ith return visit ($i=0$ refers to the fact that the nucleus is originally at the origin) and n is the number of times the nucleus returns to the origin in a walk of t_1/τ steps. Since the normalized probability that a particle stays at the origin for a time between τ_i and $\tau_i + d\tau_i$ before hopping is $e^{-\tau/\tau_i} d\tau_i/\tau$ and since the durations of each visit are statistically independent, the averages over τ_i may be performed at once with the result

$$\phi_0(t_1) = \sum_{n=1}^{\infty} S(n,t_1/\tau) \langle (1 - i\Delta\omega\tau)^{-n} \rangle_{\text{av}} \ , \tag{14}$$

where $S(n,N)$ is the probability that a particle returns to the origin $n-1$ times (and thus is at the origin at total of n times) in a walk of N steps.

As noted in Sec. I, $\phi(t)$ is expected to differ significantly from the instant relaxation approximation of Eq. (1) only if a very large number of encounters are required to produce relaxation, and the results to be presented justify this. Thus only the case $\Delta\omega\tau << 1$ is of interest whereby the bracket $\langle\ \rangle_{\text{av}}$ in Eq. (14) becomes

$$\langle (1 - i\Delta\omega\tau)^{-n} \rangle_{\text{av}} \approx \langle e^{in\Delta\omega\tau} \rangle_{\text{av}} \approx e^{-n^2 \langle \Delta\omega^2 \rangle \tau^2/2} \ , \tag{15}$$

where the first approximate equality stems from $\Delta\omega\tau << 1$ and the second is the standard[9] Gaussian approximation for a function which satisfies Eq. (11) with $\tau_c \to \infty$. The required probability is[7]

$$S(n,N) = P(n-1, N-n+1) \ , \tag{16}$$

where $P(n', N-n')$, given by Eq. (6), is the probability of being at the point $n'a$ after $N-n'$ steps [$n-1$ is on the right-hand side of Eq. (16) because $S(n,N)$ is defined as the probability for $n-1$ returns].

By using Eq. (15) in Eq. (14) and, similar to the derivation of Eq. (8), converting the sum in Eq. (14) to an integral with the continuum approximation to $S(n,N)$, we obtain

$$\phi_0(t_1) = (1 + \langle \Delta\omega^2 \rangle \tau t_1)^{-1/2} \ . \tag{17}$$

In deriving Eq. (17) an additional approximation, valid for $N = t_1/\tau >> 1$, has been made in Eq. (16) that $P(n-1, N-n+1) \approx P(n-1,N)$ for values of n which contribute to Eq. (14). The final result for case (i) is achieved by inserting Eq. (17) in Eqs. (9) and (1) whereby

$$\phi(t) = 1 - \int_0^T du\, f(u) \{1 - [1 + \lambda(T-u)]^{-1/2}\} \ , \tag{18}$$

with $T = \frac{1}{2} Z^2 c^2 t/\tau$ as in Eq. (8), $\lambda = 2\langle \Delta\omega^2 \rangle \tau^2 / Z^2 c^2$, and

$$f(u) = -\frac{d}{du} [e^u \text{erfc}(\sqrt{u})] \ .$$

Equation (18) is identical to Eq. (8) for $\lambda >> 1$ which confirms the above statement that only the case $\langle \Delta\omega^2 \rangle \tau^2 << 1$ (that is $\langle \Delta\omega^2 \rangle \tau^2 \lesssim Z^2 c^2$) is of interest. Figure 2 shows computed values of T for which $\phi(t) = 1/e$ as a function of λ.

2. $\tau_c << \tau$

For case (ii) the encounters are statistically independent of one another since the spin-correlation time τ_c is much less than the hopping time τ. The situation is then the same as if the walk were self-avoiding and thus

$$\phi_0(t_1) = \left\langle \prod_{i=0}^{n} e^{-\langle \Delta\omega^2 \rangle \tau_c \tau_i} \right\rangle = \langle e^{-\langle \Delta\omega^2 \rangle \tau\tau_c (n+1)} \rangle \ , \tag{19}$$

for $\langle \Delta\omega^2 \rangle \tau\tau_c << 1$, where we have used the conventional line narrowing approximation[9]

$$\left\langle \exp\left[i \int_0^{\tau_i} \Delta\omega(\tau')\, d\tau' \right] \right\rangle_{\text{av}} \approx e^{-\langle \Delta\omega^2 \rangle \tau_c \tau_i}$$

for $\tau_i >> \tau_c$ and $\langle \Delta\omega^2 \rangle \tau_c^2 << 1$ and where, as in Eq. (13), n is the number of returns to the origin in a walk of $N = t_1/\tau$ steps. The average implied in Eq. (19) is with respect to the probability $S(n,N)$, and we find by applying the same methods and approximations used for case (i)

$$\phi_0(t_1) = e^{\langle \Delta\omega^2 \rangle^2 \tau_c^2 \tau t_1/2} \text{erfc}(\langle \Delta\omega^2 \rangle \tau_c \tau^{1/2} t_1^{1/2}/2^{1/2}) \ , \tag{20}$$

from which it follows, as in going from Eq. (17) to Eq. (18),

$$\phi(t) = 1 - \int_0^T du\, f(u) [1 - e^{\Gamma(T-u)} \text{erfc}(\Gamma(T-u))^{1/2}] \ , \tag{21}$$

with $\Gamma = (\langle \Delta\omega^2 \rangle \tau_c \tau / Zc)^2$.

Apart from the functional forms, a major difference between Eqs. (20) and (17) is that the characteristic rate in units of τ^{-1} for decay of $\phi_0(t_1)$ is proportional to α in Eq. (17) [case (i)] and to α^2 in Eq. (20) [case (ii)]. Here we define $\alpha << 1$ as the amount of relaxation per encounter [$\alpha = \frac{1}{2} \langle \Delta\omega^2 \rangle \tau^2$ in case (i) and $\alpha = \langle \Delta\omega^2 \rangle \tau\tau_c$ in case (ii)]. Thus $\phi_0(t_1)$ decays much more rapidly in (i) than in (ii), the physical explanation being that the encounters add coherently to the relaxation in (i) and incoherently in (ii). The $1/e$ decay time for $\phi(t)$ is given in Fig. 2 as a function of Γ.

3. $\tau << \tau_c << t_1$

Case (iii) is intermediate between the complete coherence of (i) and total incoherence of (ii). With

$\tau \ll \tau_c$ there is negligible time dependence of $\Delta\omega(\tau')$ during a given encounter so that

$$\phi_0(t_1) \approx \left\langle \prod_{i=0}^{n} e^{i\Delta\omega(t_i)\tau_i} \right\rangle = \left\langle \exp\left[i \sum_{i=0}^{n} \Delta\omega(t_i)\tau \right] \right\rangle , \quad (22)$$

where t_i is the time of the ith encounter, of which there are $n+1$ altogether and the second equality comes from taking the average over τ_i for $\Delta\omega\tau \ll 1$. If a Gaussian process is assumed, the above reduces to

$$\left\langle \exp\left[i \sum_{i=0}^{n} \Delta\omega(t_i)\tau \right] \right\rangle = \exp\left[-\tfrac{1}{2} \langle \Delta\omega^2 \rangle \tau^2 \sum_{ij} e^{-|t_i - t_j|/\tau_c} P(0,ij) \right] , \quad (23)$$

where $P(0,ij)$, the probability that the origin is revisited at both the ith and jth steps of the walk, is given by

$$P(0,i,j) = \begin{cases} P(0,i)P(0,j-i), & j > i , \\ P(0,j)P(0,i-j), & j < i . \end{cases} \quad (24)$$

The result of using Eqs. (24) and (23) in Eq. (22) and making the usual summation-to-integration and continuum approximations is

$$\phi_0(t_1) \approx \exp\left[-\frac{\langle \Delta\omega^2 \rangle \tau \tau_c^{1/2}}{2\sqrt{\pi}} t_1^{1/2} \times \int_0^1 \frac{du}{(1-u)^{1/2}} \operatorname{erf}\left(\frac{t_1}{\tau_c} u \right) \right] , \quad (25)$$

which reduces to

$$\phi_0(t_1) \approx e^{-\langle \Delta\omega^2 \rangle \tau \tau_c^{1/2} t_1^{1/2} / \sqrt{\pi}} , \quad (26)$$

for $t_1 \gg \tau_c$. Thus the decay rate of t_1 has the same dependence on $\langle \Delta\omega^2 \rangle$ as for the incoherent process of case (ii), but it is enhanced over (ii) by the factor $\tau_c/\tau \gg 1$ which expresses coherence of different encounters which take place within τ_c. As in the previous two examples the overall relaxation function is

$$\phi(t) = 1 - \int_0^T du\, f(u) \times \left\{ 1 - \exp\left[-\left(\frac{2\Gamma'(T-u)}{\pi} \right)^{1/2} \right] \right\} , \quad (27)$$

where $\Gamma' = (\tau/\tau_c)\Gamma$ with Γ as in Eq. (21). The $1/e$ decay time for Eq. (27) is also shown in Fig. 2.

III. DISCUSSION

It has been pointed out[2] that relaxation by paramagnetic impurities can be identified by a maximum in the linewidth (T_2^{-1}) versus temperature. This occurs because $T_2 \approx T_0 + T'$, where T_0 is the time for the nucleus to diffuse to the site of its first encounter and T' is the time to make the additional number of encounters required for relaxation. T_0 is proportional to the jump time τ but T' is proportional to τ^{-1} at least for the self-avoiding walk in the limit $\tau \ll \tau_c$. The reason for $T' \propto \tau^{-1}$ is that the percentage amount of relaxation per encounter is of the order of $\Delta\omega^2\tau^2$ so that a time proportional to $(1/\Delta\omega^2\tau^2) \times \tau$ is needed. Thus at low temperatures where $\Delta\omega\tau \gg 1$, $T_2 \approx T_0 \propto \tau$ while $T_2 \approx T' \propto \tau^{-1}$ at high temperature where $\Delta\omega\tau \ll 1$, and a maximum rate occurs at a temperature such that $\Delta\omega\tau \sim 1$. (Note that $\Delta\omega$ here refers to the electronic-nuclear spin coupling, *not* to the smaller nuclear-nuclear dipole interaction so that the magnetic tagging peak is at a temperature higher than that associated with the onset of motional narrowing of the rigid-lattice dipole-dipole width.)

For the 3-D self-avoiding walk both T_0 and T' are inversely proportional to the impurity concentration c so that the temperature $\theta_{\max}$ of the T_2^{-1} maximum is independent of c. This is not the case in one dimension where we have seen that T_0 is proportional to $1/c^2$ and T' is independent of c. Table II gives T_2^{-1} for $\tau \ll \tau_{\max}$, $\tau = \tau_{\max}$, and $\tau \gg \tau_{\max}$ where $\tau_{\max} = \tau(\theta_{\max})$ for cases (i)–(iii) both in one and three dimensions, the latter from results of I. Note that in cases (i) and (ii) the maximum T_2^{-1} is proportional to Zc independent of dimension and that T_2^{-1} is independent of c for $\tau \ll \tau_{\max}$ in one dimension. The 1-D tagging peak occurs at a hopping time τ_m such that $\tau_m \propto Zc$ for (i) and (ii) and $\tau_m \propto (Zc)^{2/3}$ for (iii). A typical figure is $Zc \sim 10^{-4}$ for an undoped reagent grade sample so that the temperature of the linewidth peak corresponds to a hopping time more than 2 orders of magnitude shorter than expected for a 3-D system. This is illustrated in Fig. 3 where we show T_2^{-1} versus temperature θ in cases (i) and (iii) for one and three dimensions using $\Delta\omega = 10^8$ sec^{-1}, $Zc = 10^{-4}$, an activated $\tau = 2 \times 10^{-13} \exp(\Delta/\theta)$sec with $\Delta = 0.5$ eV, and $\tau_c \to \infty$ for (i) and $\tau_c = (300/\theta)^2 \times 10^{-6}$ sec for (iii). The latter τ_c is reasonable for an isolated S-state paramagnetic ion relaxing via Raman processes with phonons. The 3-D rate is independent of τ_c for $\tau_c \gg \tau$ (which corresponds to $\theta \gtrsim 450$ K in the present example) since successive encounters are uncorrelated because they involve different impurities. But correlation persists for the full τ_c in one dimension, even for $\tau_c \gg \tau$, since the same paramagnetic spin is met at each encounter, and there is considerable difference between the 1-D curves for (i) and (iii). Both 1-D

TABLE II. Relaxation rate T_2^{-1} for cases (i)–(iii) in one and three dimensions. τ_{max} is hopping time at maximum T_2^{-1}.

	τ_{max}	$T_2^{-1}(\tau \ll \tau_{max})$	$T_2^{-1}(\tau = \tau_{max})$	$T_2^{-1}(\tau \gg \tau_{max})$
(i) $\tau_c \gg T_2$				
1 D	$2.7Zc/\langle\Delta\omega^2\rangle^{1/2}$	$0.15\langle\Delta\omega^2\rangle\tau$	$0.050Zc\langle\Delta\omega^2\rangle^{1/2}$	$3.1\tau/Z^2c^2$
3 D	$0.83/\langle\Delta\omega^2\rangle^{1/2}$	$Zc\langle\Delta\omega^2\rangle\tau$	$0.35Zc\langle\Delta\omega^2\rangle^{1/2}$	τ/Zc
(ii) $\tau \gg \tau_c$				
1 D	$Zc/\langle\Delta\omega^2\rangle\tau_c$	$0.31\langle\Delta\omega^2\rangle^2\tau_c^2\tau$	$0.066Zc\langle\Delta\omega^2\rangle\tau_c$	$3.1\tau/Z^2c^2$
3 D	[a]	$Zc\langle\Delta\omega^2\rangle\tau_c$	[a]	τ/Zc
(iii) $\tau \ll \tau_c \ll T_2$				
1 D	$1.9(Zc)^{2/3}/\langle\Delta\omega^2\rangle^{2/3}\tau_c^{1/3}$	$0.31\langle\Delta\omega^2\rangle^2\tau_c\tau^2$	$0.11(Zc)^{4/3}\langle\Delta\omega^2\rangle^{2/3}\tau_c^{1/3}$	$3.1\tau/Z^2c^2$
3 D	$0.83/\langle\Delta\omega^2\rangle^{1/2}$	$Zc\langle\Delta\omega^2\rangle\tau$	$0.35Zc\langle\Delta\omega^2\rangle^{1/2}$	τ/Zc

[a]If the condition $\tau \gg \tau_c$ is maintained, there is no maximum in three dimensions for T_2^{-1} vs τ. Rather T_2^{-1} approaches the limiting value $Zc\langle\Delta\omega^2\rangle\tau_c$ for $\langle\Delta\omega^2\rangle\tau\tau_c << 1$.

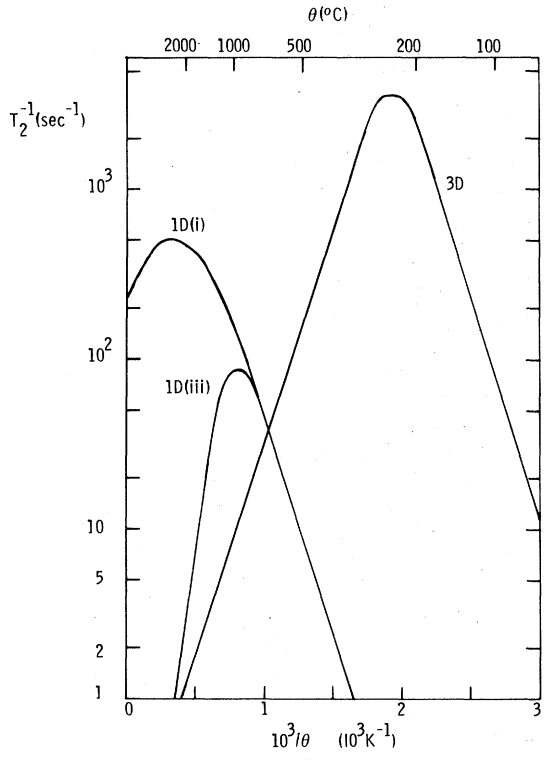

FIG. 3. Predicted transverse relaxation rate T_2^{-1} vs temperature θ for parameters described in text. Curves 3D, 1D(i), and 1D(iii) correspond to the 3-D self-avoiding walk and to cases (i) and (iii) for the 1-D system. The 3-D curve is independent of τ_c [same for (i) and (iii)] as long as $\tau << \tau_c$ except well below T_2^{-1} maximum.

and 3-D rates are independent of τ_c in the low temperature (long τ) region where only one encounter is required and relaxation is thus determined by the time to diffuse to an impurity.

The main conclusion is that except for samples very heavily doped with paramagnetic impurities one would not expect to see a 1-D linewidth maximum in the normal temperature range, and the impurity contribution to relaxation is negligible. Relaxation of ^{7}Li in β-eucryptite has been interpreted as due to paramagnetic impurities mainly because of the anomalous T_1:T_2 ratio at high temperature.[3,6,10] The present results seem to suggest, however, that either the relaxation is not dominated by impurities in spite of the T_1:T_2 ratio or that the diffusion is not 1-D in spite of the large anisotropy of the ionic conductivity.[4] The model here assumes simple 1-D diffusion of a single ion on a chain of equivalent sites, whereas particle interactions and correlations as well as inequivalent sites may be important in β-eucryptite.[5] However, these effects are believed to slow the rate of diffusion and thus make paramagnetic impurities even less important. Indeed if the mean-square displacement $\langle x^2\rangle$ of a labeled particle satisfies $\langle x^2\rangle \propto t^{1/2}$ as predicted in another publication,[11] we would expect T_2^{-1} to be proportional to c^4 rather than c^2.

The results given here have direct consequences which can be checked by experiments on intentionally doped samples, providing a suitable system (if it is not β-eucryptite) can be found. The relaxation rates should vary as c^2 and decays should be nonexponential.

Note added in proof. Equation (8) agrees with a result obtained recently for relaxation of excitations by traps.[12]

ACKNOWLEDGMENT

This work was sponsored by the U.S. DOE under Contract No. DE-AC04-76DP00789.

---

*A DOE facility.

[1]P. M. Richards, Phys. Rev. B 18, 6358 (1978).

[2]R. D. Hogg, S. P. Vernon, and V. Jaccarino, Phys. Rev. Lett. 39, 481 (1977).

[3]D. M. Follstaedt and R. M. Biefeld, Phys. Rev. B 18, 5928 (1978).

[4]U. V. Alpen, H. Schulz, G. H. Talat, and H. Bohm, Solid State Commun. 23, 911 (1977).

[5]D. M. Follstaedt and P. M. Richards, Phys. Rev. Lett. 37, 1571 (1976).

[6]P. M. Richards and D. M. Follstaedt, in Proceedings of XXth Congress Ampere, Tallinn, USSR, August 1978 (to be published).

[7]W. Feller, *An Introduction to Probability Theory and Its Applications,* 3rd ed. (Wiley, New York, 1968), Vol. 1.

[8]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford, New York, 1961), p. 378.

[9]R. Kubo and K. Tomita, J. Phys. Soc. Jpn. 9, 888 (1954).

[10]In β-eucryptite and other Li-ion conductors, one finds $T_1/T_2 \approx 4$ at high temperatures for the $I=\frac{3}{2}$ ^{7}Li resonance. This is to be expected for $I=\frac{3}{2}$ if the coupling is to unlike (electronic) spins, but not for coupling to like spins or to fluctuating electric field gradients, if only the central $\frac{1}{2}$, $-\frac{1}{2}$ transition of a quadrupole-split spectrum is observed. See Ref. 3 and references therein for details.

[11]P. M. Richards, Phys. Rev. B 16, 1393 (1977).

[12]D. L. Huber, Phys. Rev. B 20, 2307 (1979).