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Spin-Diffusion Limitations for High-Sensitivity NMR Techniques*

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The experimental sensitivity attainable in employing such high-sensitivity NMR techniques as double nuclear resonance and rotating-frame relaxation can be limited by spin-diffusion rates within the bulk detected spin system. We develop a diffusion kernel solution to the driven spin-diffusion equation and calculate the detected-system magnetization decay rate induced by a dilute concentration of pumping centers. Our results show that spin-diffusion suppression of the induced decay rate depends only upon local parameters, is independent of concentration of pumping centers, and, in all systems whose experimental study has thus far been reported, would produce at most a 10% effect. These particular conclusions apply only to the case of completely dispersed pumping centers, but the general approach can be extended to treat aggregated systems. Our description of the spin-diffusion behavior yields results in agreement with existing experimental data, but in disagreement with previous theoretical treatments.

I. INTRODUCTION

Extraordinary sensitivity for detection and study of very dilute concentrations of defect states in solids is provided by the techniques of nuclear magnetic double resonance (DNR) and of rotating-frame relaxation, $(1/T_{1\rho})$, induced by slow atomic motions. Both methods involve the same principle; an easily detected bulk nuclear resonance in the sample, which we refer to as the detected system, is adiabatically demagnetized to very low spin temperatures, and this cold detected system is brought into thermal contact with hot defect states which we refer to as pumping centers. In both cases, the

bulk detected spin system serves as an integrating detector of the energy transferred from the pumping-center defect being studied.

In the case of rotating-frame (or zero-field) relaxation experiments, spatial coordinates describing the defect are driven by the lattice dynamics and the defect couples to the bulk spins by magnetic dipole or quadrupolar interactions with a more or less broad spectrum characterized by the average jump time of the defect. Slichter and Ailion^{1,2} used this method to study the motion of free vacancies in Li metal at low temperatures; the technique was employed more recently by Kumano and Hanabusa³ and by Wagner and Moran^{4,5} to study the motions and

interactions of localized-defect complexes in the alkali halides. In the latter experiments, for example, average Li^7 atomic jump times in excess of 10^3 sec could be measured as the reorientation of vacancies bound to divalent ions in LiF contributed to Li^7 ($1/T_{1\rho}$).

In the DNR technique, which was first proposed by Hartmann and Hahn,⁶ the defect state is a rare-species nuclear spin which is kept hot by the application of an appropriate rf field; nuclear dipole-dipole interactions couple the rare-pumped spins to the bulk detected spins via a sharp frequency spectrum corresponding to the rare-resonance effective-field Larmor frequency. Several groups⁷⁻¹⁴ have used the DNR method to study a variety of rare nuclear resonances in solids. As an example of the sensitivity of the DNR technique, the DNR cross-relaxation studies by Lang and Moran^{14,15} of isotopically enriched Li^7F showed detections of the dilute Li^6 resonance at unity signal-to-noise ratio in a data-acquisition time 10^{-10} of that required with signal-averaging methods. Similar experimental sensitivities have been reported more recently by Spencer, Schmid, and Slichter^{16,17} in observing Na^{23} quadrupolar splittings in Ag-doped NaCl .

The sensitivities to dilute defect states in both techniques depends not only on the ability of the hot pumping centers to transfer energy to neighboring nuclear spins, but also upon the ability of these local spins to transport that energy into the bulk of the sample. Bloembergen¹⁸ first treated the latter process, which is called spin diffusion, and its importance has been recognized primarily in nuclear relaxation by paramagnetic impurities.¹⁹⁻²² The relative weakness and short range of the defect-state interactions with bulk spins in the DNR and ($1/T_{1\rho}$) experiments discussed in this paper makes the situation qualitatively different from that for paramagnetic centers. Slusher and Hahn²³ have treated the spin-diffusion process for zero-field double-resonance experiments, and they conclude that the net energy transfer from a single pumped center is increasingly suppressed by spin-diffusion effects as the defect-state concentrations are reduced below a certain critical value. Our experiments,¹⁴ however, did not confirm this behavior, and subsequent other studies,^{5,17} both here and elsewhere, indicate that the pumping-center net-energy-transfer rate is independent of pumped-center concentration.

The purpose of this paper is to develop a more satisfactory treatment of the spin-diffusion process appropriate to the DNR and ($1/T_{1\rho}$) experiments in order to determine, for any given system, what limitations finite spin-diffusion rates may place upon experimental sensitivities. We use a simple phenomenological model and examine in particular

the magnetization decay rate induced by the pumping centers as a function of local parameters. In this treatment, we use a diffusion-kernel approach to eliminate solving the spatial-diffusion profile in favor of a local integral equation. The advantages are that the detailed relaxation behavior can be described approximately by simple analytic expressions, the derived relaxation rates depend only on local parameters, systems involving aggregated defect states can be similarly treated, and the approach is valid even for systems with such high local-energy inputs that perturbation approaches are inapplicable.

In Sec. II, we develop the necessary notation and relationships with experimentally observed quantities, and we derive the local integral equation from the diffusion problem. In Sec. III, we obtain the approximate local spin-temperature solutions, average magnetization behavior, and relaxation rates for dispersed pumping centers. In Sec. IV, we compare our results with experimental data and obtain the general consequences regarding experimental sensitivities and, finally, provide a brief summary.

II. SPIN-DIFFUSION EQUATION

A. Local Spin Temperature

Following the notation of SH, we denote the local inverse of the bulk detected spin temperature by $\beta_D(\mathbf{r}, t)$; local spin temperature means that the spin system has approximate local equilibrium between its Zeeman and dipolar energies. The total detected-system spin energy is given by

$$E_D = -C_D(H_D^2 + H_I^2) k^{-1} \int \beta_D(\mathbf{r}, t) dV, \quad (1)$$

where C_D is the detected-system Curie constant, H_D is the effective external magnetic field strength, H_I is the detected spin local field, and k is Boltzmann's constant. The precise definitions of C_D , H_D , and H_I are given in many references,^{1,8,14} and their calculation for specific experimental samples is detailed, for example, in earlier papers¹⁴ from this laboratory. The free-induction-decay resonance signal is proportional to M_D , the total detected-system magnetization aligned along H_D ,

$$M_D = C_D H_D k^{-1} \int \beta_D(\mathbf{r}, t) dV, \quad (2)$$

where H_D , H_I , E_D , and M_D may refer, as is appropriate, either to lab-frame or to rotating-frame quantities. Since one measures the time dependence of the relative signal $M_D(t)/M_D(0)$, Eq. (2) implies that we need investigate only the local inverse temperature $\beta_D(\mathbf{r}, t)$.

We assume a simple isotropic model for the system in which the behavior of $\beta_D(\mathbf{r}, t)$ is described by the driven diffusion equation,

$$d_t \beta_D(\mathbf{r}, t) = - (1/T_1) [\beta_D(\mathbf{r}, t) - \beta_{EQ}] + D \nabla^2 \beta_D(\mathbf{r}, t) - W(\mathbf{r}, t) [\beta_D(\mathbf{r}, t) - \beta_P], \quad (3)$$

where the first term represents normal background spin-lattice relaxation to a thermal equilibrium value, the second expresses the spin-diffusion contribution, and the final term gives the local-energy-input rate produced by cross relaxation with the pumping centers described by the pumped temperature β_P . Equation (3) is simplified by defining the inverse temperature β ,

$$\beta(\mathbf{r}, t) = \exp(t/T_1) (\beta_D - \beta_{EQ}), \quad (4)$$

to obtain

$$d_t \beta(\mathbf{r}, t) = D \nabla^2 \beta(\mathbf{r}, t) - W(\mathbf{r}, t) [\beta(\mathbf{r}, t) - \delta\beta], \quad (5)$$

where

$$\delta\beta = \exp(t/T_1) [\beta_P(t) - \beta_{EQ}]. \quad (6)$$

The $\beta(\mathbf{r}, t)$ defined in Eq. (4) has a simple interpretation; the logarithmic decay of β is just the difference between the logarithmic decay of $(\beta_D - \beta_{EQ})$ when only the T_1 relaxation occurs and the logarithmic decay of $(\beta_D - \beta_{EQ})$ when both the T_1 and the defect pumping terms are effective. For example, in the DNR experiments, this is determined by taking the ratio of detected-spin decay rates with and without rare-spin pumping. Alternatively, $\beta(\mathbf{r}, t)$ may represent the detected-spin inverse temperature in the infinite T_1 limit. Although other conditions may be carried through the following treatment with some additional mathematical steps, we consider explicitly hereafter only the important practical case $\beta_P = \beta_{EQ}$, i. e., $\delta\beta \approx 0$ in Eq. (5).

B. Integral Equation Solutions

Our approach to the problem can be greatly simplified by considering the form of the pumping term in Eq. (5), $W(\mathbf{r}, t) \beta(\mathbf{r}, t)$. First, in the systems of interest for the DNR and the $(1/T_1)_P$ experiments, $W(\mathbf{r}, t)$ is a short-range function characterized by a distance of one or two lattice constants and is well described by a time-independent cross-relaxation rate. In contrast to paramagnetic center relaxation phenomena, the interactions characterizing $W(\mathbf{r})$ are weak, i. e., they are only comparable to the detected-spin local fields. Moreover, in assuming a local spin temperature describable by Eq. (3), we have already implicitly assumed a local equilibrium condition in which $\beta(\mathbf{r}, t)$ does not vary significantly over distances on the order of a lattice constant. It is, therefore, both consistent and valid to approximate $\beta(\mathbf{r}, t)$ as spatially constant over the range of $W(\mathbf{r})$. Similarly, one can show that the detailed specific form of $W(\mathbf{r})$ is not crucial provided one chooses a $W(\mathbf{r})$ having the same total local energy-

transfer rate and the same characteristic range as the true cross-relaxation function. We therefore take $W(\mathbf{r})$ to be a Gaussian function centered at each pumping site R_i and write

$$W(\mathbf{r}) \beta(\mathbf{r}, t) \approx \sum_i (1/\tau) \exp[-(R_i - \mathbf{r})^2/\sigma^2] \beta(R_i, t). \quad (7)$$

When the actual form of the cross-relaxation mechanism is known, the characteristic range σ can be obtained by equating second moments of the true cross-relaxation function $W(\mathbf{r})$ and the approximation in Eq. (7),

$$\begin{aligned} & \left[\int \mathbf{r}^2 \exp(-\mathbf{r}^2/\sigma^2) dV \right] \left[\int \exp(-\mathbf{r}^2/\sigma^2) dV \right]^{-1} = \frac{3}{2} \sigma^2 \\ & = \left[\int \mathbf{r}^2 W(\mathbf{r}) dV \right] \left[\int W(\mathbf{r}) dV \right]^{-1}. \end{aligned} \quad (8)$$

In the approximate form expressed by Eq. (7), we note that $\beta(R_i, t)$ is a lower bound to $\beta(\mathbf{r}, t)$ and that a Gaussian $W(\mathbf{r})$ has extremely rapidly decreasing wings. Thus, these approximations will tend to give somewhat more pronounced spin-diffusion suppression of the net cross-relaxation decay rate of β than one would expect from the true system; this is desirable for the purpose of determining a lower bound on the DNR or $(1/T_1)_P$ sensitivity for a particular system. Using the approximation of Eq. (7) in Eq. (5) and assuming a uniform initial temperature, $\beta(\mathbf{r}, t=0) = \beta_0$, one can employ the Gaussian diffusion kernel for the three-dimensional problem to obtain the following solution to Eq. (5):

$$\begin{aligned} \beta(\mathbf{r}, t) = \beta_0 - \left(\frac{1}{\tau} \right) \sum_i \int_0^t \beta(0, t'') \exp \left(\frac{-(R_i - \mathbf{r})^2}{\sigma^2 + 4D(t - t'')} \right) \\ \times [1 + (4D/\sigma^2)(t - t'')]^{-3/2} dt'' \end{aligned} \quad (9)$$

We assume in Eq. (9) that all pumping sites are equivalent and choose one of the R_i 's as the coordinate-system origin, i. e.,

$$\beta(R_i, t) = \beta(R_j, t) = \beta(0, t).$$

The NMR signal is proportional to the average detected-spin magnetization expressed in Eq. (2), and one can carry out the crystal volume average of Eq. (9), assuming sample dimensions large compared to the average spacing between pumping centers, to obtain

$$\begin{aligned} \langle M(t) \rangle &= C_D H_D k^{-1} \langle \beta \rangle_{av} \\ &= C_D H_D k^{-1} \left[\beta_0 - (N_P/V) (\pi^{3/2} \sigma^3/\tau) \right. \\ &\quad \left. \times \int_0^t \beta(0, t') dt' \right], \end{aligned} \quad (10)$$

where (N_P/V) is the average volume density of pumping-center sites. We are, of course, also assuming that the pumping sites are so dilute that there is negligible difference between the total crystal volume and the volume associated only with the detected spins. Thus, the time evolution of $\langle M(t) \rangle$ or, equivalently, $\langle \beta(t) \rangle$ proceeds according to the time derivative of Eq. (10),

$$d_t \langle \beta(t) \rangle = - (N_P/V) (\pi^{3/2} \sigma^3 / \tau) \beta(0, t), \quad (11)$$

which reflects several important features of our problem. First, the average energy-transfer rate specified by $d_t \langle \beta(t) \rangle$ depends solely upon $\beta(0, t)$, the local spin-temperature term within the cross-relaxation range of the hot pumping centers. Second, in the infinitely rapid diffusion limit, the total system maintains a common spin temperature, $\beta(r, t) = \beta(0, t) = \langle \beta(t) \rangle$, which gives

$$d_t \langle \beta \rangle = - (N_P/V) (\pi^{3/2} \sigma^3 / \tau) \langle \beta \rangle \quad \text{as } D \rightarrow \infty. \quad (12)$$

This special case was treated in LM in terms of the characteristic rate $(1/\tau_{cr})$, with which the pumped-site temperature β_p tends to relax toward the detected-spin β and the ratio of pumped-center heat capacity to the detected-spin heat capacity ϵ ,

$$d_t \langle \beta \rangle = - (\epsilon / \tau_{cr}) \langle \beta \rangle. \quad (13)$$

Examining Eqs. (11)–(13), one observes that $\pi^{3/2} \sigma^3$ is the characteristic cross-relaxation volume, $(1/\tau)$ is the average rate at which a detected spin within that volume relaxes toward the pumping-site temperature, and that τ_{cr} , which is one of the quantities measured in the experiments in LM, is related to τ by the expression

$$(\epsilon / \tau_{cr}) = (N_P/V) (\pi^{3/2} \sigma^3) (1/\tau), \quad (14)$$

a result in accord with net energy conservation in the cross-relaxation process. Similar expressions can, of course, also be derived in the case of $(1/T_{1p})$ experiments to relate, for example, the average vacancy-jump time τ_v in the defect-complex reorientation studies of WM to the effective rate $(1/\tau)$ in Eq. (11). In subsequent parts of this paper we shall often use (ϵ / τ_{cr}) simply as a shorthand notation for the expression on the right-hand side of Eq. (14). A third consequence immediately available from Eq. (11) is that, independent of any assumption concerning the actual value of D , when the system evolves from an initial uniform spin temperature, the initial logarithmic derivative is equal to the rapid-diffusion-limit decay rate,

$$d_t \langle \beta \rangle / \langle \beta \rangle \big|_{t=0} = - (N_P/V) (\pi^{3/2} \sigma^3 / \tau) = - (\epsilon / \tau_{cr}). \quad (15)$$

Finally, since the observed decay rate depends upon the local term $\beta(0, t)$ according to Eq. (11), we need to investigate Eq. (9) only for $r=0$; we change variables $t' = t - t''$ to obtain

$$\begin{aligned} \beta(0, t) = \beta_0 - \frac{1}{\tau} \int_0^t \beta(0, t-t') \sum_i \exp\left(\frac{-R_i^2}{\sigma^2 + 4Dt'}\right) \\ \times \left[1 + \left(\frac{4D}{\sigma^2}\right) t'\right]^{-3/2} dt' \quad (16) \end{aligned}$$

III. SPIN-TEMPERATURE SOLUTIONS

A. High-Concentration Limit

The present work considers systems in which the

pumping sites are completely dispersed so that there is no aggregation into clusters. We note that there are two time regimes for the integral on the right-hand side of Eq. (16); we call the rms distance between neighboring pumping centers ΔR , $\Delta R = \langle (R_i - R_j)^2 \rangle_{nn}^{1/2}$, and define T_R to be the spin-diffusion time for half this distance,

$$T_R = \frac{1}{4} (\Delta R^2 / 4D). \quad (17)$$

When $t' \ll T_R$ in Eq. (16), then only the term $R_i = 0$ contributes to the sum in the integral, but when $t' \gg T_R$, the Gaussian profiles in the sum overlap and the sum may be converted into an integral, $\sum_i \rightarrow \int (N_P/V) d^3 R_i$. We obtain approximate solutions to Eq. (16) by breaking the integral into two parts, $t' < T_R$ and $t' > T_R$, using only the $R_i = 0$ term in the former part, and using the integral approximation for the sum in the latter part. By carrying out this procedure, using the more compact notation defined by Eq. (13), and employing a simple change of variables, one obtains

$$\begin{aligned} \beta(0, t) \simeq \beta_0 - \int_0^T R \beta(0, t-t') \{ (1/\tau) [1 + (4D/\sigma^2) t']^{-3/2} \\ - (\epsilon / \tau_{cr}) \} dt' - (\epsilon / \tau_{cr}) \int_0^t \beta(0, t'') dt'' \quad (18) \end{aligned}$$

To obtain Eq. (18) we assumed that neighboring Gaussian profiles in the sum in Eq. (16) did not overlap significantly for $t' < T_R$; this is not true unless ΔR is large compared with σ . Careful evaluation of the first integral in Eq. (18) shows that its value should, in fact, be zero unless $\Delta R \gtrsim 3.5\sigma$. Therefore, we define the pumped-center high-concentration limit by the criterion

$$(N_P/V) = (\Delta R)^{-3} \gtrsim (3.5\sigma)^{-3} \approx \frac{1}{50} \sigma^{-3}, \quad (19)$$

and note that, in the high-concentration limit, only the second integral in Eq. (18) contributes, thus giving the same spin-temperature relaxation rate (ϵ / τ_{cr}) as results from the uniform-temperature approximation leading to Eqs. (12) or (13). Since σ is about one lattice constant, the high-concentration limit of Eq. (19) corresponds to pumped-center concentrations greater than about 2%.

It is important to note that the diffusion in Eq. (16) depends upon the square of the distances to pumped-center sites. Consequently, one expects that relaxation behavior described by Eq. (16) depends strongly on the distribution of local pumped-center densities as well as the volume average density. Although it is outside the scope of the present work, the approach followed in this paper can be directly extended to the problem of aggregated-defect distributions. A treatment of aggregated pumped-center systems and the interesting experimental consequences will be presented in a subsequent publication.

B. Dilute Pumped-Center Limit

In the dilute pumped-center limit, $(N_P/V) \ll \frac{1}{50} \sigma^{-3}$, the first integral on the right-hand side of Eq. (18) does give a finite contribution and tends to suppress the decay rate of $\langle \beta \rangle$ with respect to the high-concentration-limit rate (ϵ/τ_{cr}) . Let us first consider the relaxation behavior for times less than T_R ; we call this the infinite-dilution limit for the pumped centers, i. e., there is negligible overlap of the Gaussian spin-diffusion profiles from neighboring sites. Equation (18) can then be written

$$\beta(0, t) = \beta_0 - (1/\tau) \int_0^t \beta(0, t-t') [1 + (4D/\sigma^2)t']^{-3/2} dt', \quad (20)$$

and, since the term $[1 + (4D/\sigma^2)t']^{-3/2}$ gives a convergent integral, we deduce immediately that the local-temperature term $\beta(0, t)$ decays to a finite constant value over a time interval characterized by $(\sigma^2/2D)$. To find the approximate time dependence, it is convenient to change variables in the integral of Eq. (20) and differentiate to obtain

$$d_t \beta(0, t) = - (1/\tau) \beta(0, t) + (1/\tau) (6D/\sigma^2) \int_0^t \beta(0, t-t') \times [1 + (4D/\sigma^2)t']^{-5/2} dt'. \quad (21)$$

Subject to a later consistency check, we assume that $\beta(0, t-t')$ varies slowly compared with $[1 + (4D/\sigma^2)t']^{-5/2}$ and approximate the integral in Eq. (21) by

$$\begin{aligned} \int_0^t \beta(0, t-t') [1 + (4D/\sigma^2)t']^{-5/2} dt' \\ \approx \beta(0, t) \int_0^t [1 + (4D/\sigma^2)t']^{-5/2} dt' \\ = \beta(0, t) (6D/\sigma^2)^{-1} [1 - (4D/\sigma^2)t]^{-3/2}. \end{aligned} \quad (22)$$

Substituting Eq. (22) into Eq. (21), one finds

$$d_t \beta(0, t) \approx - (1/\tau) [1 + (4D/\sigma^2)t]^{-3/2} \beta(0, t), \quad (23)$$

which gives

$$\beta(0, t) = \beta_0 \exp \left(-\alpha \{1 - [1 + (4D/\sigma^2)t]^{-1/2}\} \right), \quad (24)$$

where

$$\alpha = (\sigma^2/2D)/\tau. \quad (25)$$

The spin-diffusion parameter α represents the ratio of the time required for a local nucleus to lose energy by spin diffusion out of the cross-relaxation volume $(\sigma^2/2D)$, to the time required to gain energy from the pumping center τ . One can take the logarithmic derivative of Eq. (24) to verify that $\beta(0, t)$ varies relatively slowly, as assumed in obtaining Eq. (22), provided that $t \gg (\sigma^2/2D)$, or for all values of t provided that $\alpha \ll 1$. In Sec. IV, we show that the DNR and $(1/T_{1\rho})$ studies reported thus far correspond to $\alpha \ll 1$. When $\alpha \ll 1$, the local term $\beta(0, t)$, according to Eq. (24), never departs significantly from the volume average value $\langle \beta(r, t) \rangle$, and this

behavior assures the validity of normal-mode perturbation treatments such as used by Spencer.¹⁶

In an experiment one observes $d_t \langle \beta \rangle$, for which we substitute the expression in Eq. (24) into Eqs. (12) and (13) to obtain, for times of interest in this infinite-dilution limit,

$$\begin{aligned} d_t \langle \beta \rangle &= - (\epsilon/\tau_{cr}) \beta(0, t) = - (\epsilon/\tau_{cr}) e^{-\alpha} \beta_0 \\ &= - (\epsilon/\tau_{cr}) e^{-\alpha} \langle \beta \rangle, \end{aligned} \quad (26)$$

where the final equality in Eq. (26) uses the pumped-center infinite-dilution limit identity $\langle \beta \rangle = \beta_0$. The most significant consequence of Eq. (26) is that, even for infinitely dilute pumped centers, the average observed decay rate is suppressed only by a factor of $e^{-\alpha}$ relative to the high-concentration-limit rate (ϵ/τ_{cr}) . Therefore, when α is small, spin diffusion never significantly suppresses the net DNR or $(1/T_{1\rho})$ magnetization decay rate regardless of pumped-center concentration, i. e., the pumped-center concentration enters only in the relative heat-capacity term ϵ . This result differs from that of Slusher and Hahn's treatment, which predicts, for any finite value of D , a critical concentration below which the net decay rate becomes increasingly suppressed relative to (ϵ/τ_{cr}) as the pumped-center concentration decreases.

The source of Slusher and Hahn's result is worth comment; in that treatment, the motivation was to understand the role of spin diffusion in systems with relatively high pumped-center concentrations, typically greater than about 100 ppm. At these concentrations and with typical nuclear-spin values for τ_{cr} , D , and the cross-relaxation volume, SH employ a valid approximation where, in effect, one replaces the Gaussian diffusion profiles in Eq. (9) by parabolic profiles centered at the midpoint of the average pumped spin separation ΔR . Close inspection of the SH equations reveals that the critical concentration which results is simply related to that value of ΔR for which the parabolic approximation to the diffusion profile becomes invalid for detected-spin positions near the pumped-center site. When one uses the SH treatment to describe the behavior for larger values of ΔR , the theoretically predicted local-temperature term $\beta(0, t)$ becomes substantially smaller than the true value. Since the net decay rate depends critically upon $\beta(0, t)$, as indicated in Eq. (12), the SH calculation gives a highly suppressed magnetization decay rate.

C. General Solutions

We now assume that the spin-diffusion time between neighboring pumped-center sites is long compared with $(\sigma^2/2D)$, but small compared to the time scale over which the magnetization decay is observed. We find approximate solutions to Eq. (18)

by assuming that $\beta(0, t)$ varies only slightly over a time interval T_R so that we can again factor $\beta(0, t - t')$ out of the first integral on the right-hand side of Eq. (18). Evaluating the integral, we then obtain

$$\beta(0, t) \approx \beta_0 - (\alpha - \epsilon T_R / \tau_{cr}) \beta(0, t) - (\epsilon / \tau_{cr}) \int_0^t \beta(0, t'') dt'', \quad (27)$$

which has the solution

$$\beta(0, t) = \beta(0, T_R) \exp \left[-(\epsilon / \tau_{cr}) \times (1 + \alpha - \epsilon T_R / \tau_{cr})^{-1} (t - T_R) \right]. \quad (28)$$

The constant $\beta(0, T_R)$ is given approximately by setting $t = T_R$ in Eq. (24), and we can evaluate the term $\epsilon T_R / \tau_{cr}$ by using Eqs. (17), (25), and (14),

$$\epsilon T_R / \tau_{cr} = (\pi^{3/2} \sigma^3 / \Delta R^3 \tau) (\Delta R^3 \tau) (\Delta R^2 / 16 D) = (\pi^{3/2} \sigma / 8 \Delta R) \alpha. \quad (29)$$

Since we are concerned here with the dilute pumped-center situation, $(\sigma / \Delta R) \ll 1$, we can subsequently neglect $\epsilon T_R / \tau_{cr}$ in comparison with α as indicated by Eq. (29).

We can now employ Eq. (10) to calculate the average spin-temperature behavior by using Eq. (24) for $t < T_R$ and Eq. (28) for $t > T_R$:

$$\langle \beta \rangle \approx \beta_0 [1 - (\epsilon / \tau_{cr}) e^{-\alpha} t], \quad t < T_R \quad (30)$$

$$\langle \beta \rangle = \langle \beta(T_R) \rangle \exp \left[-(\epsilon / \tau_{cr}) (1 + \alpha)^{-1} (t - T_R) \right], \quad t > T_R \quad (31)$$

where $\langle \beta(T_R) \rangle$ in Eq. (31) is obtained from Eq. (30) by setting $t = T_R$. It is easy to show in this dilute pumped-center limit that $\langle \beta(T_R) \rangle$ is smaller than β_0 by a negligible amount, and we will henceforth use the approximation $\langle \beta(T_R) \rangle = \beta_0$.

It is convenient to define an average magnetization decay rate $(1/T_1)$ produced by DNR pumping at localized rare spins or, in the T_{1p} experiments, produced by localized spin-lattice relaxation centers. We obtain $(1/T_1)$ by taking the logarithmic derivative of $\langle \beta(t) \rangle$ given in Eqs. (30) and (31),

$$(1/T_1) = -(d_t \langle \beta \rangle) / \langle \beta \rangle = (\epsilon / \tau_{cr}) e^{-\alpha}, \quad t < T_R \quad (32)$$

and

$$(1/T_1) = (\epsilon / \tau_{cr}) (1 + \alpha)^{-1}, \quad t > T_R. \quad (33)$$

For any system in which $\alpha \ll 1$, the long- and short-time decay rates given above are equal, and the magnetization decays exponentially at a rate suppressed only by a factor of $(1 + \alpha)^{-1}$ relative to the high-density limit rate (ϵ / τ_{cr}) . We emphasize again that this result is obtained only for the case of completely dispersed pumping centers and is not true in general for systems where the pumped centers are aggregated to produce local high-density regions.

IV. EXPERIMENTAL COMPARISONS

A. DNR Experiments

We first consider the DNR rotating-frame results of LM¹⁴ who measured the cross-relaxation rate $(1/\tau_{cr})$ for the Li⁶-Li⁷ system in LiF. One can use the theory developed by Khutsisvili²¹ or by Slusher and Hahn¹³ to estimate $(1/\tau_{cr})$, modifying for the "three-spin system" appropriate to LiF. One finds, to a sufficiently good approximation for our purposes, that the cross-relaxation rate can be described in terms of the Van Vleck second moments of the pumped spins and the detected spins, $\Delta\omega_p^2$ and $\Delta\omega_D^2$, respectively, by

$$(1/\tau_{cr}) \approx \Delta\omega_p^2 / \Delta\omega_D; \quad (34)$$

this represents the maximum cross-relaxation rate corresponding to adiabatically demagnetized detected spins and for pumped-spin rf field strengths less than $(\Delta\omega_p / \gamma_p)$. We use the approximate correspondence between the detected spin T_2 and $\Delta\omega_D$ to write the Li⁶ and Li⁷ second moments as $(1/T_{27})^2$ and $[I_6(I_6 + 1)/I_7(I_7 + 1)] (\gamma_6/\gamma_7)^2 (1/T_{27})^2$, respectively, and we find from Eq. (34)

$$(1/\tau_{cr})_{Li^6-Li^7} \leq \frac{3}{40} (1/T_{27}) = \frac{1}{320} (\mu\text{sec})^{-1}, \quad (35)$$

using the powdered sample value $T_{27} = 25 \mu\text{sec}$. The result in Eq. (35) includes the Li⁶ cross-relaxation path which proceeds through the F¹⁹ dipole-dipole system, a process which the LM results show to be important; the value of $320 \mu\text{sec}$ is in good agreement with the measured value.

One can obtain a value for σ by approximating the dipole-dipole cross-relaxation coupling rate as an isotropic function $W_0(d/r)^6$, where d is the nearest-neighbor distance; using the expression in Eq. (8), one finds

$$\sigma = 1.4d = a, \quad (36)$$

where a is the fcc lattice constant. The diffusion constant D can be estimated from the treatments of Bloembergen¹⁸ or others,^{13,21} or from the more detailed considerations of Redfield and Yu²⁴; a reasonably good estimate appears to be given by

$$D \approx (a^2 / 12 T_2). \quad (37)$$

For the LiF lattice and DNR conditions set so that the heat capacity per spin of the pumped and detected species are equal, one can use Eq. (14) and the relation expressed in Eqs. (35) and (36) to find

$$(1/\tau) = (1/\tau_{cr}) (\pi^{3/2} \sigma^3)^{-1} (a^3/4) \approx 1/20 \tau_{cr} \approx \frac{1}{270} (1/T_{27}) \text{ for Li}^6\text{-Li}^7 \text{ DNR}. \quad (38)$$

Thus, the α given by Eq. (25) can be expressed variously using Eqs. (36)–(38),

$$\alpha = \frac{(\sigma^2/2D)}{\tau} \simeq (1/5T_2) (\pi^{3/2}\tau_{cr})^{-1} \simeq 0.05 \text{ for Li}^6\text{-Li}^7 \text{ DNR,} \quad (39)$$

from which it is apparent that the spin-diffusion suppression in the DNR Li⁶-Li⁷ experiments of LM is negligible. Experimental results of the Li⁶-Li⁷ DNR magnetization decay are shown in Fig. 1. The circles are data for a 7.4%-Li⁶ sample, which is well within the high-density limit, and the triangles are data for a 0.008%-Li⁶ sample. The time scale is normalized to account for the concentration dependence which enters simply in the heat-capacity ratio ϵ ; we obtain ϵ for each sample as described in LM and take $t' = \epsilon t$. The experimental conditions for both samples in Fig. 1 were set to give $\tau_{cr} = 0.9$ msec in the high-concentration sample. The solid line in Fig. 1 shows the theoretical high-density-limit result, which is indistinguishable from the theoretical dilute-limit results, for $\tau_{cr} = 0.9$ msec, on the scale of this figure. The dotted line is calculated from the Slusher-Hahn treatment for the 0.008%-Li⁶ system.

The approximate expression given in Eq. (39), $\alpha \simeq (1.5T_2) (\pi^{3/2}\tau_{cr})^{-1}$, shows that α will be small compared to unity as long as the detected spin T_2 is shorter than the pumped-spin cross-relaxation time. This will certainly be true for all systems in which the gyromagnetic ratio and spin number of the pumped spins remains comparable to or smaller than that of the detected spins. If the pumped-spin gyromagnetic ratio is very large, however, it is possible that τ_{cr} would be short com-

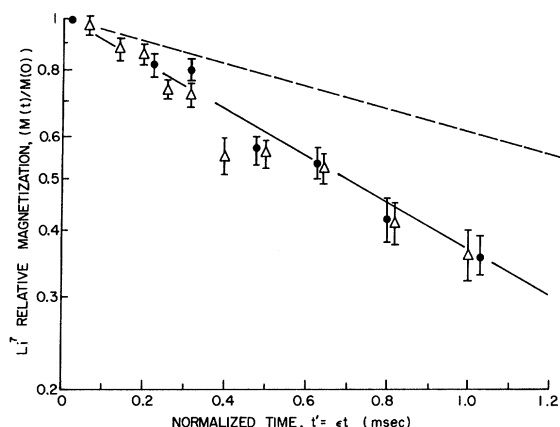


FIG. 1. Li⁷ magnetization versus time for Li⁶-Li⁷ DNR experiments in LiF. The time scale is normalized to the Li⁶-Li⁷ relative heat capacity ϵ ; $t' = \epsilon t$. Experimental conditions are set to produce a Li⁶ cross-relaxation time of 0.9 msec. The circles are for 7.4% Li⁶ and the triangles for 0.008% Li⁶.

pared with the T_2 of detected spins and, consequently, $\alpha > 1$. Experimental DNR studies reported thus far^{6,8,12,14,17,25} in a variety of materials all correspond to the former case and measured values give $\tau_{cr} > 10 T_{2D}$ for these systems. Thus, one has a limit $\alpha < 0.1$ in all experiments so far reported, and spin-diffusion suppression factors should be negligibly small as is consistent with the experimental observations.

The basic physical reason that no further spin-diffusion suppression effects appear, once the system passes out of the high-concentration limit, can be understood as follows. There is only a very short period of time, about $\sigma^2/2D$, during which the local cross-relaxation volume can be heated with respect to the bulk spins, and this produces the $(1 + \alpha)^{-1}$ suppression effect shown in Eq. (33). For longer times, the volume into which the spin energy diffuses can increase proportional to $t^{3/2}$, whereas the total energy input can increase no faster than t . Consequently, there is no additional local-heating effect and thus no further suppression of the average magnetization decay rate. This behavior is the basis for the validity of the spin-diffusion criterion proposed by McArthur *et al.*²⁵ for their Ca⁴³-F¹⁹ DNR experiments and, since $\alpha \ll 1$ for this system, local spin-heating effects should be negligible, as was experimentally found to be the case.

B. Slow Atomic Motion Experiments

In the rotating-frame relaxation experiments of Wagner and Moran,^{4,5} the atomic jumps corresponding to the reorientation of vacancies bound to divalent impurities in LiF induced large Li⁷ relaxation rates. The measured $(1/T_1)$ versus temperature is shown in Fig. 2 for this system; the cross-relaxation volume associated with the complex is quite large, $\sigma \approx 1.7a$, as the vacancy complex effectively interacts directly with about thirty Li⁷ nuclei. The largest values of $(1/T_1)$ shown in Fig. 2 for the 100-ppm Mg²⁺-doped sample imply a minimum value for τ , $\tau > 3 \times 10^{-3}$ sec. Using Eqs. (25) and (37) and the powder-average T_2 of 25 μ sec for the Li⁷ resonance, one obtains the bound $\alpha \leq 10^{-1}$. Thus, for the dispersed divalent-ion-vacancy complexes, the relaxation-rate suppression according to Eq. (33) would be always less than 10%. The lower curve in Fig. 2 shows the results for a sample having a divalent-ion concentration less than about 9 ppm as determined from ionic conductivity and Z-center formation studies. The ratio of $(1/T_1)$ for the two samples compared with the bound on the ratio of divalent-ion concentrations shows there is, consistent with the predictions of the present treatment, no observable spin-diffusion suppression of $(1/T_1)$ at the lower concentration.

In this LiF system the Li⁷ relaxation was domi-

nated by quadrupolar interactions with the reorienting vacancy. The results of the WM experiments showed that strong fluctuating quadrupole interactions produce a variety of spin-level isolation effects and this precludes more general semiquantitative statements about α than can be obtained directly from the particular experimental data. However, in the case of nuclei which have zero, or at least a very small, quadrupole moment, the dominant relaxation comes from the magnetic dipole-dipole interaction and, for this situation, some interesting general conclusions can be drawn. The theoretical result¹ for slow atomic motions is that, on the average, at most only one nucleus relaxes each time the moving entity jumps. If we call the average jump time τ_v , then we must have

$$\tau \geq (\pi^{3/2} \sigma^3 / a^3) \tau_v, \quad (40)$$

from which, again using Eqs. (25) and (37), we can find

$$\alpha \leq (a/\sigma) (T_2/\tau_v). \quad (41)$$

Since $\sigma \approx a$, we see from Eq. (41) that α remains small giving, consequently, no spin-diffusion suppression of the magnetization decay rate, provided

that $\tau_v \gg T_2$. Moreover, as τ_v becomes smaller so that $\tau_v \approx T_2$ then, as discussed by WM, the interactions effectively become motionally narrowed and the relaxation rate decreases to give a longer τ than that described by Eq. (40). Thus it would appear, at least when nuclear dipole-dipole interactions dominate the relaxation mechanism, that minor spin-diffusion suppression of $(1/T_1)$ occurs only for jump times near T_2 ; it is just for this regime that no adequate theory exists² to describe the relaxation behavior even for free vacancies or in the high-density limit.

C. Summary

In high-sensitivity NMR experiments which rely upon cross-relaxation energy transfers from a low concentration of dispersed pumping centers to a bulk nuclear-spin system, spin-diffusion processes cause no detectable effects in the high-density limit. This limit is defined by the average separation between pumping centers being less than about 3.5σ , where σ is the characteristic radius describing the direct cross-relaxation volume. In the dilute pumped-center limit, on the other hand, spin-diffusion processes suppress the average magnetization decay rate relative to that calculated for a uniform spin-temperature (high-density limit) system. This suppression is characterized by the local parameter $\alpha = (\sigma^2/2D)/\tau$, where τ is the characteristic time with which a detected-system spin within the cross-relaxation volume relaxes toward the pumped-center temperature and $(\sigma^2/2D)$ is the characteristic time for detected-system energy to diffuse out of the direct cross-relaxation volume. In this dilute-center limit, the average relaxation behavior can be described in two time regimes; for times less than required for diffusion half-way between neighboring pumped centers, the average magnetization of the detected system relaxes according to the infinite-dilution limit in which the suppression factor is $e^{-\alpha}$. For longer times, the temperature profiles expanding from neighboring pumped centers begin to overlap substantially and the relaxation-rate suppression becomes $(1 + \alpha)^{-1}$. For experimental purposes, only the long-time behavior is of interest because the net observed magnetization decay during the short-time period is always negligibly small. Detailed consideration of the NMR systems reported thus far shows that α could not be expected to exceed 0.1; therefore, the relaxation-rate suppression caused by finite spin-diffusion rates can largely be ignored, and one is justified in employing the uniform spin-temperature approximation. These results are derived for dispersed pumped centers, are not dependent upon the average concentration of pumped-center sites, and are in good agreement with experimental results. However, if the pumped

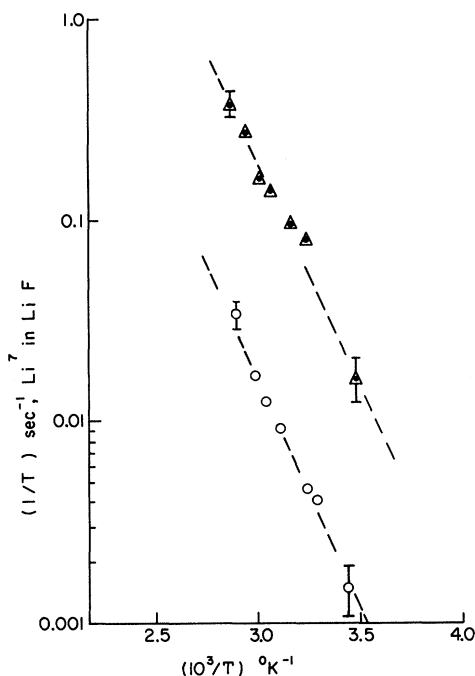


FIG. 2. Li^7 magnetization decay rate $(1/T_1)$ versus inverse temperature in LiF for rotating-frame relaxation induced by motion of bound-vacancy-divalent-ion complexes. The triangles are for 100-ppm Mg^{++} doping, and the circles are for a divalent-ion concentration less than 9 ppm.

centers are aggregated into clusters of local high density, then spin-diffusion suppression is expected to be much more severe; this situation can be de-

scribed within the framework of our approach to the spin-diffusion equations and will be the subject of a subsequent publication.

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Electron-Impact Desorption of Ions from Polycrystalline Tungsten*

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A cylindrical magnetic spectrometer has been constructed to study the electron-impact desorption of ions and neutrals from solid surfaces. The instrument has high-energy resolution and sensitivity and allows the determination of the charge-to-mass ratio of the emitted ions. The apparatus has been applied to the study of polycrystalline tungsten with O₂, CO, CO₂, H₂, N₂, and H₂O adsorbed. The ions which have been observed are O⁺ from O₂/W, CO/W, and CO₂/W; CO⁺ from CO/W; and H⁺ from H₂/W and H₂O/W. The ion energy distributions, ionic and total desorption cross sections, threshold energies, and other experimental results are presented and discussed.

I. INTRODUCTION

The process of the emission of ions by electron bombardment was first reported by Dempster in

1918.¹ However, before 1964, little was known about the mechanism involved in the electron-impact desorption of ions and neutrals from solid surfaces. In 1964, Redhead² and Menzel and