

Nuclear spin-lattice relaxation via paramagnetic impurities in solids with arbitrary space dimension

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(Received 17 March 1995)

We extend the theory of growth of the nuclear magnetization in the presence of paramagnetic impurities and the absence of spin diffusion to the case of solids with arbitrary space dimension D . We show that the rate of growth of the magnetization is proportional to $\exp(-At^\alpha)$ where t is the time and α is a fractional power which depends on the concentration and distribution of the paramagnetic centers and the magnetic nuclei. In the homogeneous distribution, $\alpha = D/6$. In the inhomogeneous distribution, the sample can be regarded as consisting of subsystems packed in the d -dimensional space of the sample, each of which includes a paramagnetic center surrounded by nuclei. This model results in the expression $\alpha = (D+d)/6$. Experimental data are presented for both of these cases.

INTRODUCTION

The effect of paramagnetic centers on the nuclear-spin relaxation has been the subject of many studies.¹⁻⁸ The growth of the nuclear magnetization in the presence of dilute magnetic impurities is found to be proportional to $t^{1/2}$ for very short times following an excitation pulse sequence and under conditions that inhibit spin diffusion. Including all times,⁵⁻⁸ the time dependence has the form $\exp[-(t/T_1)^{1/2}]$; this reduces to the expression originally derived by Blumberg⁴ for very short times. Observation of a time dependence of $t^{1/3}$ in layered materials related to the high-temperature superconductors^{9,10} instigated an extension of the Blumberg theory to D dimensions. For the case of a homogeneous distribution of paramagnetic centers in the absence of spin diffusion, the magnetization growth was found to be proportional to $t^{D/6}$.⁹ This has been observed experimentally for systems of two and three dimensions.^{9,10}

More recently, the Blumberg theory was further extended to include the case of a higher concentration of paramagnetic centers.¹¹ A multiparamagnetic-center model was used to calculate the time dependence of the magnetization at short times after application of an excitation pulse sequence. The sample was divided into regions of influence^{4,5} of D dimensions, each containing only one paramagnetic center. These regions are packed in the d -dimensional space of the sample. The resulting time dependence of the magnetization is $t^{(D+d)/6}$. For example, in a strong magnetic field (as in the experiment considered here) the magnetic moments of the regions are aligned with the external magnetic field so that $d=1$ and the powers obtained are $\frac{1}{3}$, $\frac{1}{2}$, and $\frac{2}{3}$ for one-, two-, and three-dimensional systems, respectively. These time dependences have been observed experimentally and reported in Ref. 11.

In this work, the theory of the growth of the nuclear magnetization in samples of arbitrary dimension¹¹ is gen-

eralized to all times following an excitation pulse sequence for samples with high concentrations of paramagnetic centers. We consider two cases: homogeneous distribution of the paramagnetic centers and nuclei and inhomogeneous distribution. In the former, the magnetization is found to be proportional to $\exp\{-At^{D/6}\}$ and in the latter to $\exp\{-Bt^{(D+d)/6}\}$. We present experimental data exhibiting both cases in the experimental section of this paper.

THEORY

Let us consider a sample containing nuclear spins coupling with paramagnetic centers by dipole-dipole interaction, placed in a high external magnetic field. After excitation of the nuclear-spin system, a local magnetization will be changed most rapidly near the paramagnetic centers. This leads to spatial distribution of the magnetization resulting in spatial diffusion of the nuclear-spin energy. For sufficiently small concentrations of the nuclear spins c_n ,⁴ or when the magic angle condition is met in the rotating frame,¹² this diffusion is negligible, and only direct relaxation processes take place.

Assuming that the dominant nuclear relaxation mechanism is that of the paramagnetic centers, the Hamiltonian of this system is

$$H = \omega_I \sum_{\mu} I_{z\mu} + \omega_S \sum_j S_{zj} + H_{SS} + H_{IS}, \quad (1)$$

where ω_I and ω_S are the Zeeman frequencies of the nuclei and paramagnetic impurities respectively. H_{SS} is the dipole-dipole interaction Hamiltonian of the paramagnetic impurities and H_{IS} describes the dipole-dipole interaction between the nuclei and the paramagnetic impurities, which, for $\omega_I \ll \omega_S$, has a part that gives the dominant contribution to the relaxation process:

$$H_{IS} \propto \sum_{j,\mu} (F_{j\mu} S_{zj} I_{+\mu} + F_{j\mu}^* S_{zj} I_{-\mu}), \quad (2)$$

where

$$F_{j\mu} = -\frac{3}{4} \frac{\gamma_I \gamma_S}{r_{j\mu}^3} \sin^2 \theta_{j\mu} \exp\{-i\varphi_{j\mu}\}, \quad (3)$$

$r_{j\mu}$, $\theta_{j\mu}$, and $\varphi_{j\mu}$ are the spherical coordinates of the vector $\mathbf{r}_{j\mu}$ concerning the j^{th} paramagnetic impurity and the μ^{th} nucleus in a coordinate system with the z axis along the applied external field. Here the Greek indices indicate the positions of the nuclei and the Latin those of the impurities. If the heat capacity of the paramagnetic impurities is large or if the spin-lattice relaxation time of the impurities is very short, it is reasonable to consider only the relaxation process with constant inverse spin temperature of the impurities equal to that of the lattice: $\beta_S = \beta_L$.

The evolution equation for the local nuclear magnetization $m_\mu(t)$ will be derived by using the method of the nonequilibrium statistical operator^{13,14} which gives, in the absence of spin diffusion,

$$\frac{d\langle H_I^\mu \rangle}{dt} = (\beta_I^\mu - \beta_S) \int_0^1 d\lambda \int_{-\infty}^{\infty} dt e^{-\varepsilon t} \langle K_\mu(\lambda, t) K_\mu \rangle, \quad (4)$$

where β_I^μ is the local inverse spin temperature of the nuclear-spin system,

$$K_\mu = i[H_{IS}, H_I^\mu], \quad (5)$$

$$K_\mu(\lambda, t) = U(\lambda, t) K_\mu U^\dagger(\lambda, t), \quad (6)$$

$$U(\lambda, t) = \exp \left[\lambda \left[\beta_S H_S + \sum_\mu \beta_I^\mu H_I^\mu \right] \right] \times \exp \left[it \left[H_S + \sum_\mu H_I^\mu \right] \right], \quad (7)$$

and, after the integration in Eq. (4) is performed, we set $\varepsilon = 0$,¹³ $H_I^\mu = \omega_I I_{z\mu}$, and $H_S = \omega_S \sum_j S_{zj}$. After some transformations, Eq. (4) reduces to following form, which is more convenient for practical computations and consideration:

$$\frac{dm_\mu}{dt} = -\pi \varphi_\mu(\omega_I) (m_\mu - m_{\mu 0}), \quad (8)$$

where $m_{\mu 0}$ is the local magnetization at equilibrium,

$$\varphi_\mu(\omega) = \frac{1}{2\pi} \sum_j F_{j\mu} F_{j\mu}^* \times \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \{S_{zj}(t), S_{zj}\} \rangle / \text{Tr} S_{zj}^2 \quad (9)$$

is the spectral density of the correlation function of the z component of the impurity's spin,

$$S_{zj}(t) = \exp\{iH_{SS}t\} S_{zj} \exp\{-iH_{SS}t\}, \quad (10)$$

and $\{A, B\} = AB + BA$. The thermodynamic average $\langle \dots \rangle$ in Eq. (9) corresponds to an average of the quasiequilibrium density matrix in the high-temperature approximation:

$$\rho = Z^{-1} \left[1 - \beta_S H_S - \sum_\mu \beta_I^\mu H_I^\mu \right], \quad (11)$$

where

$$Z = \text{Tr} \rho. \quad (12)$$

To calculate the spectral density $\varphi_\mu(\omega)$, the correlation function $\langle \{S_{zj}(t), S_{zj}\} \rangle$ is needed. We assume that in the high-temperature approximation this correlation is exponential with a correlation time τ :

$$\langle \{S_{zj}(t), S_{zj}\} \rangle = \langle S_{zj}^2 \rangle \exp\{-|t|/\tau\}. \quad (13)$$

Since the local magnetization $m_\mu(t)$ is distributed throughout the sample and depends on position, in order to obtain a quantity observable by experiment a suitable averaging procedure must be performed. This averaging is strongly dependent on the concrete model that is used to describe the distribution of the nuclei and impurities. Let us consider two models of the distribution: (a) a regular distribution throughout the sample¹² and (b) a model in which the sample can be regarded as consisting of subsystems, each of which includes a paramagnetic impurity surrounded by nuclear spins.^{4,5}

Homogeneous distribution model

In this case, the nuclear spins interact with the impurities independently and Eq. (8) has the solution

$$m_\mu(t) = m_\mu(\infty) + [m_\mu(0) - m_\mu(\infty)] \exp\{-\pi \varphi_\mu(\omega_I) t\}. \quad (14)$$

The observed quantity is the global magnetization $M(t)$, which can be obtained from the local magnetization $m_\mu(t)$ by a spatial average over the variables $r_{j\mu}$ and $\theta_{j\mu}$:

$$M(t) = \frac{1}{N_n} \sum_{\mu=1}^{N_n} \langle m_\mu(t) \rangle_{\text{av}}, \quad (15)$$

where N_n is the number of nuclei in the sample and $\langle \dots \rangle_{\text{av}}$ denotes the average over all distances $r_{j\mu}$ between impurities and nuclei and angles $\theta_{j\mu}$ between the vector $\mathbf{r}_{j\mu}$ and the external magnetic field. If all of the local magnetizations are equal at the initial moment and at equilibrium, then

$$M(t) = M(\infty) + [M(0) - M(\infty)] \frac{1}{N_n} \times \sum \exp\{-\pi \langle \varphi_\mu(\omega_I) \rangle_{\text{av}} t\}, \quad (16)$$

and the quantity to be averaged,

$$R(t) = \frac{1}{N_n} \sum_{\mu=1}^{N_n} \exp\{-\pi \langle \varphi_\mu(\omega_I) \rangle_{\text{av}} t\}, \quad (17)$$

is a normalized relaxation function of the global magnetization. Let us suppose that all quantities $\varphi_\mu(\omega_I)$ are independent and that they are all identical. Then, neglecting the detailed angular dependence⁴ and assuming that the continuous medium approximation is valid,¹⁵ we have

$$R(t) = \left[\frac{1}{V_L} \int_0^{V_L} dV \exp\left\{ \frac{-at}{r^6} \right\} \right]^{N_p}, \quad (18)$$

where N_p is the number of paramagnetic impurities in the sample, V_L is the volume of the sample, and

$$a = \frac{2}{3}S(S+1)(\gamma_p\gamma_n)^2 \sin^2(2\theta) \frac{\tau}{1+\omega_I^2\tau^2}. \quad (19)$$

In the limit as $N_p \rightarrow \infty$, $V_L \rightarrow \infty$, and $N_p/V_L = C_p$, the impurity concentration, we have

$$R(T) = \left[1 - \frac{C_p}{N_p} \int_0^{V_L} dV \left[1 - \exp \left\{ \frac{-at}{r^6} \right\} \right] \right]^{N_p} \\ \cong \exp \left[-C_p \int_0^\infty dV \left[1 - \exp \left\{ \frac{-at}{r^6} \right\} \right] \right]. \quad (20)$$

After integrating Eq. (20) by parts, we obtain

$$R(t) = \exp \{ -At^{D/6} \}, \quad (21)$$

where

$$A = \frac{2\pi^{D/2}\Gamma(1-D/6)}{D\Gamma(D/2)} a^{D/6} C_p, \quad (22)$$

$\Gamma(z)$ is the gamma function, and D is the dimensionality of space of the sample. In the case of $D=3$, Eq. (21) reduces to the results obtained in Refs. 5–8 and 12 and, for short times, the magnetization has a $t^{D/6}$ time dependence in agreement with experimental and theoretical results.⁹ We note that A is proportional to C_p , the concentration of impurity centers.

Subsystem model

The main difference between the homogeneous distribution model and the subsystem model is that in the latter any given nucleus is influenced primarily by one paramagnetic impurity, so that the sample may be divided up into subsystems, each of which includes only one impurity surrounded by nuclear spins.^{4,5} In this case it is

necessary to modify Eq. (8) to

$$\frac{dm_{\mu j}}{dt} = -\pi\varphi_j^\mu(\omega_I)(m_{\mu j} - m_{0j}), \quad (23)$$

where

$$\varphi_j^\mu(\omega) = \frac{1}{2\pi} F_{j\mu} F_{j\mu}^* \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \{S_{zj}(t)S_{zj}\} \rangle / \text{Tr}S_{zj}^2. \quad (24)$$

To obtain the magnetization of the j^{th} subsystem, the solution of Eq. (23) must be averaged over all distances between nuclei and the j^{th} paramagnetic impurity

$$M_j(t) = \frac{1}{N_j} \sum_{\mu=1}^{N_j} \langle m_{\mu j}(t) \rangle_{\text{av}\mu}, \quad (25)$$

where the prime denotes that the summation is only over the nuclei that are in the j^{th} subsystem, and N_j is the number of nuclei in the j^{th} subsystem.

To calculate the global magnetization, it is necessary to average Eq. (25) over the volume of the subsystems:

$$M(t) = \frac{1}{N_p} \sum_{j=1}^{N_p} \langle M_j(t) \rangle_{\text{av}j}, \quad (26)$$

where N_p is the number of impurities in the sample.

Assuming that all nuclei in the subsystem interact with the impurity independently and that all subsystems are independent and identical, we have

$$M(t) = M(\infty) + [M(0) - M(\infty)]R(t), \quad (27)$$

where

$$R(t) = \frac{1}{N_p} \sum_{j=1}^{N_p} \left\langle \frac{1}{N_j} \sum_{\mu=1}^{N_j} \langle \exp \{ -\pi\varphi_{\mu j}(\omega_I)t \} \rangle_{\text{av}\mu} \right\rangle_{\text{av}j}. \quad (28)$$

Under assumptions analogous to those in the preceding section in the continuous medium approximation, Eq. (28) becomes

$$R(t) = \exp \left\{ -C_p \int_0^{V_L} dV \left[1 - \exp \left\{ -C_n \int_0^V d\nu (1 - e^{-at/r^6}) \right\} \right] \right\}. \quad (29)$$

Changing the integration variables and integrating by parts, Eq. (29) yields the following expression for the relaxation function:

$$R(t) = \exp(-Bt^{(D+d)/6}I), \quad (30)$$

where

$$B = \frac{4\pi^{(D+d)/2}}{D d \Gamma(D/2) \Gamma(d/2)} a^{(D+d)/6} C_p C_n, \quad (31)$$

d and D are the dimensionality of space of the subsystems and the sample, respectively, and

$$I = \frac{d}{D+d} \int_0^\infty d\xi (\xi^{(D+d)/6}) e^{-f(\xi)} (1 - e^{-\xi}), \quad (32)$$

$$f(\xi) = \xi^{-D/6} (1 - e^{-\xi}) + \Gamma(1 - d/6, \xi), \quad (33)$$

and $\Gamma(z, \xi)$ is the incomplete gamma function.

In the limit as $\xi \gg 1$ ($\xi \equiv at/l^6$, that is, for a long time t and small size of subsystems l) and $C_n \ll 1$, the power of the exponent in Eq. (32) approaches zero: $\lim_{\xi \rightarrow \infty} f(\xi) = 0$ and

$$R(t) = \exp \left\{ -B \frac{d}{D+d} \Gamma \left[1 - \frac{D+d}{6} \right] t^{(D+d)/6} \right\}. \quad (34)$$

In the case of short times t and $C_p \ll 1$, Eq. (30) reduces to the results obtained in Ref. 11. We note also that the coefficients A and B , from Eqs. (21) and (30), respectively, can be extracted from the slope of the log of the magnetization as a function of t^α , where, for a homogeneous distribution of impurity centers, $\alpha = D/6$ and, for the subsystem model, $\alpha = (D+d)/6$. Both A and B are propor-

tional to the impurity ion concentration C_p , which can thus be determined, and to a , given in Eq. (19). This equation gives the dependence of A and B on the correlation time τ , which is in turn dependent on the sample temperature and the resonance frequency. Determination of A and B as a function of temperature and frequency will thus yield the correlation time function $\tau(T, \omega)$.

EXPERIMENTAL RESULTS

We have studied the growth of the magnetization following a saturation pulse sequence in samples falling in both categories discussed above and have obtained results consistent with our theory. In the copper oxides, copper atoms are paramagnetic centers distributed uniformly throughout the sample. In this section we present the results of ^1H NMR in $\text{H}_x\text{Y}_2\text{BaCuO}_5$, where $x=1.21$. At this concentration, the dipolar interactions between the protons and the copper atoms were shown to be two dimensional in nature.⁹

In Fig. 1 we show the growth of the proton nuclear magnetization in $\text{H}_x\text{Y}_2\text{BaCuO}_5$ for $x=1.21$. To emphasize the nature of this growth, we have plotted the logarithm of the magnetization as a function of $t^{1/2}$ and $t^{1/3}$ in (a) and (b), respectively. In Fig. 1(a), the solid line

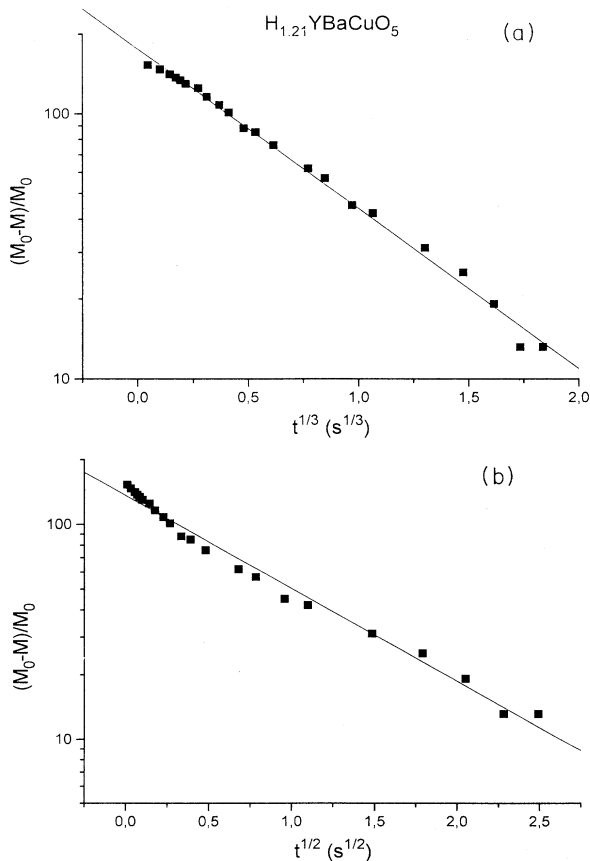


FIG. 1. Log (base 10) of normalized nuclear magnetization of protons in $\text{H}_{1.21}\text{YBaCuO}_5$ as a function of (a) $t^{1/3}$ and (b) $t^{1/2}$. The solid line is a least-squares fit to (a) $A \exp\{-Bt^{1/3}\}$ and (b) $A \exp\{-Bt^{1/2}\}$.

is the result of a least-squares fit of the data to the function $A \exp\{-Bt^{1/3}\}$ and is seen to be a very good fit, while 1(b), which shows the same data with a fit to $A \exp\{-Bt^{1/2}\}$ is not appropriate. Thus, for a sample with $D=2$ we obtain the dependence of the magnetization growth predicted by our theory, $\exp\{-Bt^{D/6}\}$.

In Fig. 2 we present results for the case of inhomogene-

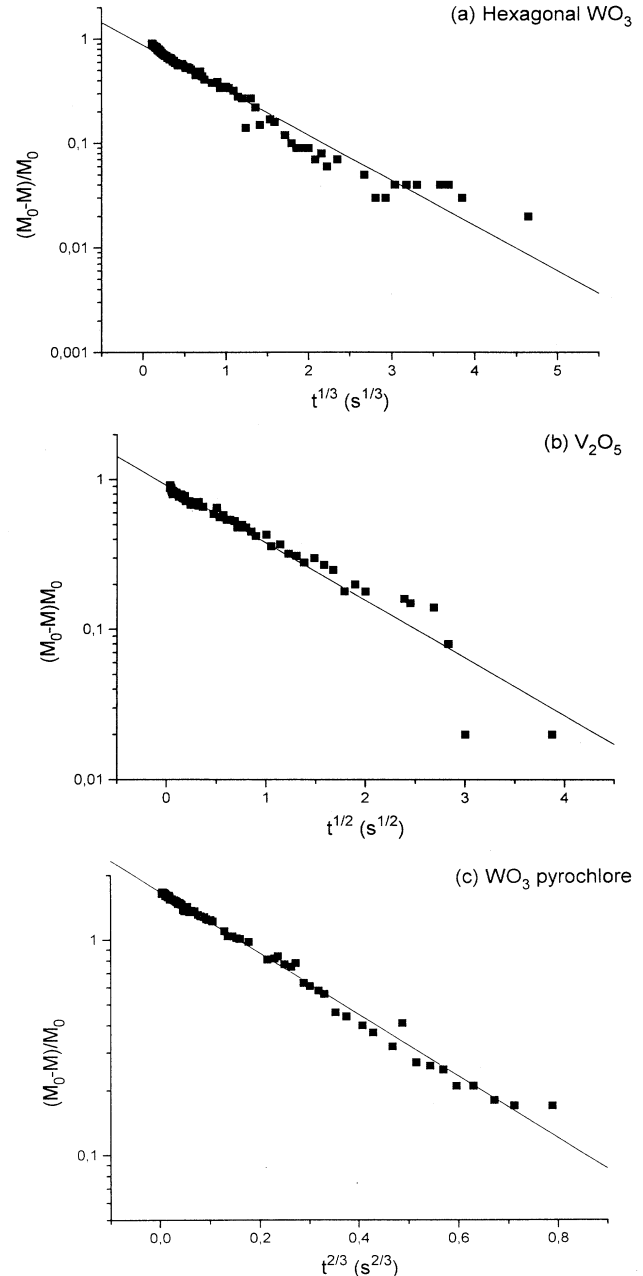


FIG. 2. Log (base 10) of normalized nuclear magnetization of protons in (a) hexagonal WO_3 at 180 K as a function of $t^{1/3}$ (b) V_2O_5 as a function of $t^{1/2}$, and (c) WO_3 Pyrochlore D_2O at 230 K as a function of $t^{2/3}$. Note that in Ref. 11 a least-squares fit was made of these data to $A \exp\{-Bt^\alpha\}$ with α as a free parameter, and the values $\alpha=0.316$, 0.497 , and 0.667 were obtained for the data of (a), (b), and (c), respectively.

ous distribution of magnetic impurities. Samples doped with small quantities of paramagnetic centers and with effective spacial dimensions $D=1, 2$, and 3 were prepared, corresponding to Figs. 2(a), 2(b), and 2(c) respectively. Experimental details are given in Ref. 11. Since the magnetic moments of the subsystems are aligned with the external magnetic field, $d=1$, and the nuclear magnetization of protons is seen to decay as $\exp\{- (Bt)^{(D+d)/6}\}$ for all three samples.

In addition to our own experimental work, we present some data taken from the literature. Kryukov *et al.*¹⁶ measured the ^{169}Tm NMR in $\text{TmBa}_2\text{Cu}_3\text{O}_{6.4}$ and studied the magnetization recovery after a 90° - 180° pulse sequence. They found that the magnetization grows as $\exp\{- (Bt)^{1/3}\}$. Due to the lamellar nature of this compound, $D=2$ and the paramagnetic centers are distributed homogeneously throughout the sample. Their results are thus explained by our theory.

In a continuation of the work on ^{169}Tm NMR in $\text{TmBa}_2\text{Cu}_3\text{O}_x$, Teplov and co-workers studied the effects of high-temperature annealing and quenching on their samples.¹⁷ They found that as the concentration of paramagnetic centers in the sample is decreased, either by oxygenation, long-time room-temperature annealing, or lowering the sample temperature, the exponent α changes from $1/3$ to $1/2$. They explain that this is because of a change in dimensionality of the sample from 2 to 3 , but we propose a different explanation, as we see no other evidence for a change of sample dimensionality. As the concentration of paramagnetic centers decreases, their distribution in the sample changes from a homogeneous to an inhomogeneous one. When this happens, the expression for α changes from $D/6$ to $(D+d)/6$. In this case, the sample dimensionality D is 2 , and, following a $\pi/2$ - π pulse sequence, the magnetic moments of the subsystems are constrained to one dimension along the magnetic field, so that the subsystem dimensionality $d=1$; thus α changes from $1/3$ to $1/2$.

In view of this explanation, we must consider an alternate interpretation of the data presented in Ref. 9 for H-doped Y_2BaCuO_5 . In that paper, it was suggested that increasing the H concentration made the sample three dimensional, resulting in $\alpha=1/2$. Another possibility is that the increased H concentration decreases the concentration of paramagnetic centers sufficiently that they may be distributed inhomogeneously in a sample that is still two dimensional. In this case, $\alpha=(D+d)/6=1/2$. The correct interpretation may be determined by studying the distribution of the paramagnetic centers using ESR, which we intend to do.

The data of Fig. 3 were taken from Ref. 18 in which the ^{19}F NMR of CaF_2 ($0.05 \text{ mol } \% \text{ Eu}^{2+}$) was measured in two experiments. The first experiment used an eight-pulse sequence in order to quench the spin diffusion. This cycle, like the magic angle spinning used in the experiments of Hartman and co-workers,^{8,12} averages the effects of the paramagnetic impurities. The nuclear spins thus effectively interact with all the paramagnetic impurities, and the system may be described by the homogeneous distribution model. In this case, the magnetization decays as $\exp\{- (Bt)^{D/6}\}$ with $D=3$ as shown in these

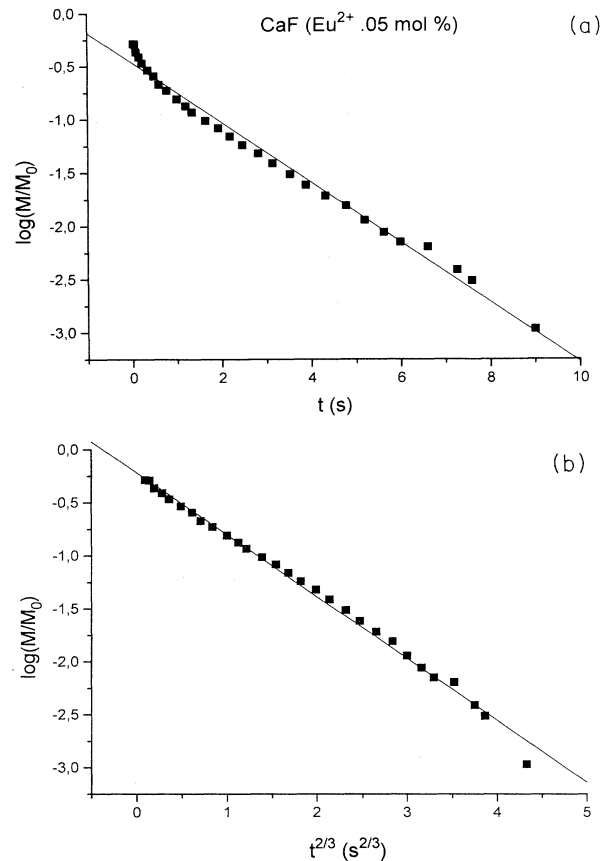


FIG. 3. Log (to base 10) of the amplitude $S(t)$ of the ^{19}F signal of $\text{CaF}(\text{Eu}^{2+} - 0.05 \text{ mol } \%)$ in the spin-locking experiment of Ref. 18 as a function of $\alpha =$ (a) t and (b) $t^{2/3}$. The solid line is a least-squares fit to $A \exp\{-Bt^\alpha\}$.

papers.^{8,12,16,17} Mehring, Raber, and Sinnig also present data from a spin-locking experiment on the same doped CaF_2 sample. Although the authors write that the magnetization decays exponentially, we show in Fig. 3(a) that this is not the case, as the log of the magnetization plotted as a function of pulse separation does not give a straight line. A straight line is obtained in Fig. 3(b), in which we plot the log of the magnetization as a function of $t^{2/3}$. In the spin-locking experiment, each nucleus is primarily affected by only one paramagnetic center and the magnetic moment of the subsystem is constrained to one direction with the effective field in the rotating frame. The subsystem dimensionality is thus $d=1$ and, for a three-dimensional sample, $D=3$, so the magnetization grows as $[1 - \exp\{- (Bt)^{(D+d)/6}\}]$, consistent with our theory for a sample with inhomogeneous distribution of paramagnetic impurities.

Humphries and Day¹⁹ also studied CaF_2 doped with paramagnetic impurities. They find that for a sample with $0.016 \text{ mol } \% \text{ Mn}^{2+}$ the nuclear magnetization is proportional to $\exp(-t^{1/2})$ in a spin-locking experiment. This is in agreement with our theory for a three-dimensional sample with a homogeneous distribution of paramagnetic centers. They also present data from two

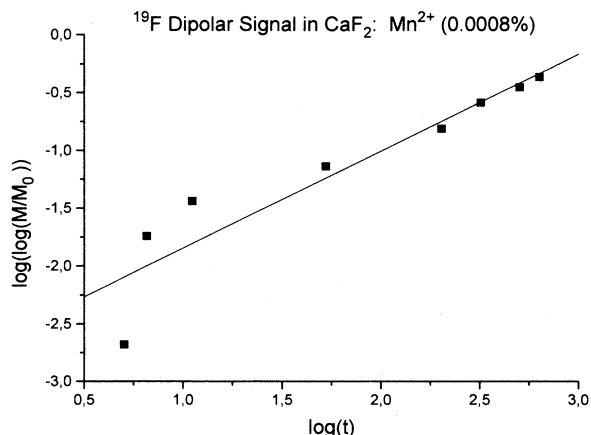


FIG. 4. Log of log (to base 10) of the ^{19}F dipolar signal of CaF_2 (Mn^{2+} —0.0008 mol %) in the Jeneer method experiment of Ref. 19 as a function of $\log_{10}(t)$. The solid line is an apparent linear least-squares fit yielding slope $\alpha=0.840$ or $5/6$.

experiments which measure the decay of the ^{19}F signal from an ordered dipolar state using the methods of adiabatic demagnetization in the rotating frame and of Jeneer, both of which are described there in detail. In their Fig. 6, one sees the nonexponential behavior of the ^{19}F signal for CaF_2 doped to 0.0008 mol % Mn^{2+} . At this low a concentration, the paramagnetic ions are probably distributed inhomogeneously in the sample, so that

the time dependence of the magnetization is given by Eq. (34). In these experiments, the magnetization is confined to the plane perpendicular to the external field resulting in a subsystem dimension $d=2$. For a three-dimensional sample, one should find $\alpha=(2+3)/6=5/6$. To test this, the data of Fig. 6 from Ref. 19 was digitized, and a linear least-squares fit was made to the \log_{10} of $\log_{10}(M)$ as a function of $\log_{10}(t)$ as seen in Fig. 4. The slope of this graph is α and is found to be 0.84, which is extremely close to $5/6$, consistent with our theory.

CONCLUSIONS

We have shown that the growth of the nuclear magnetization towards equilibrium in a sample with paramagnetic centers following a pulse sequence depends on both the spacial dimensionality D of the sample and whether the nucleus is affected by only one or many paramagnetic centers. In the former case the magnetization evolves as $\exp\{-(Bt)^{(D+d)/6}\}$ and in the latter as $\exp\{-(At)^{D/6}\}$. Experimental data has been presented for the homogeneous distribution case for $D=1,2$ and for the subsystem model with $D=1,2,3$ and $d=1,2$, which can be explained by our theory. We are presently conducting nuclear quadrupole resonance experiments in samples doped with paramagnetic centers to include the case $d=3$ for the subsystem model, since, in the absence of a magnetic field, there is no preferred direction for the magnetization.

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