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Nuclear spin-lattice relaxation of dipolar order caused by paramagnetic impurities

G. B. Furman, A. M. Panich, A. Yochelis, E. M. Kunoff, and S. D. Goren
Department of Physics, Ben-Gurion University, Be'er-Sheva, Israel

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We show that the relaxation function of the dipolar order is given by $\exp[-(t/T_{1d}^a)^\alpha]\exp(-t/T_{1d}^b)$ where T_{1d}^a and T_{1d}^b are spin-lattice relaxation times: T_{1d}^a due to direct interaction of a given nuclear spin with paramagnetic centers and T_{1d}^b due to indirect interaction with the paramagnetic centers through neighboring nuclear spins. For a homogeneous distribution of paramagnetic centers and nuclear spins, $\alpha = D/6$ where D is the sample dimensionality. For an inhomogeneous distribution, the sample is divided into d-dimensional subsystems, each containing one paramagnetic center, yielding $\alpha = (D+d)/6$. The dipolar relaxation is measured in fluorinated graphite. Data from this experiment and from CaF_2 doped with Mn^{2+} in the literature are consistent with this model. [S0163-1829(97)04501-3]

I. INTRODUCTION

In solids containing nuclear spins (I) coupling with spins (S) of paramagnetic impurities (PI's), the dipole-dipole interactions (DDI's) play the dominant role in the spin-lattice relaxation[1–5]. On the one hand, the DDI's between nuclear spins and PI's causes the direct spin-lattice relaxation of the nuclear-spin system. Since, after excitation of the nuclear-spin system the interaction with the PI's is stronger than that with the neighboring nuclear spins, the local nuclear magnetization reaches its equilibrium state at a faster rate near the PI's[1–5]. Consequently, during the relaxation process the nuclear magnetization is spatially inhomogeneous. This induces the spatial diffusion of the nuclear-spin energy by flip-flop transitions due, on the other hand, to DDI's between nuclear spins[1–5].

The case of spin diffusion and the role of the DDI's between PI's has been considered in detail (see, for example, Refs. 2,5) and it was shown that for nuclear spin $I=1/2$, the time dependence of the growth of the nuclear magnetization is exponential, or a sum of a limited number of exponentials.[2,5]

In the diffusionless limit,[6] the Zeeman order of the three-dimensional nuclear-spin system relaxes to equilibrium with the lattice nonexponentially and has the form $\exp[-(t/T_1)^{1/2}]$, where T_1 is the spin-lattice relaxation time of the Zeeman order. More recently, the theory of direct relaxation was extended to include the case of a sample with arbitrary space dimension.[7,8] For a homogeneous distribution of PI's and nuclei, the relaxation function of the Zeeman order is described by $\exp[-(t/T_1)^{D/6}]$, where D is the space dimension of the sample. In the inhomogeneous case, the sample is regarded as consisting of subsystems, each of which includes a PI with neighboring nuclei and possesses a local magnetization, packed in a d-dimensional space. The relaxation process of the Zeeman order evolves as $\exp[-(t/T_1)^{(D+d)/6}]$. This behavior has been observed for samples of one, two, and three dimensions.[7,8]

Proceeding from the study of the spin-lattice relaxation of the Zeeman order, an experimental study of the relaxation of the dipolar order (DO) due to impurities was carried out.[9] The characteristic time for decay of the DO, T_{1d}, was found to depend strongly on the type of impurities and their concentration and could be either longer or shorter than the spin-lattice relaxation time T_1 of the Zeeman order.[9] The authors noted that their measurements were reported to provide information for the development of a theory. However, no theory for spin-lattice relaxation of dipolar order via PI's has as yet been reported. The main purpose of the present paper is to develop such a theory which we then compare with two experiments. The first is our NMR study of two-dimensional fluorinated graphite $(C_{1.47}F)_n$, the results of which are presented here and the second is Humphries and Day's study on CaF_2 doped with paramagnetic Mn^{2+}.[9]

II. THEORY

Let us consider a spin system consisting of nuclear and PI spins, localized in a high external magnetic field $\vec{H}_0$, at positions $\vec{r}_\mu$ and $\vec{r}_j$, respectively. Here the Greek indices indicate the nuclei and the Latin the impurities.

The dynamics of the system under consideration and its relaxation can be described by a solution of the equation for the state operator $\rho(t)$ $(\hbar=1)$

$$i\frac{d\rho(t)}{dt}=[\mathcal{H}(t),\rho(t)] \tag{1}$$

with Hamiltonian

$$\mathcal{H}(t)=\omega_I\sum_\mu I_\mu^z+\omega_S\sum_j S_j^z+\mathcal{H}_{II}+\mathcal{H}_{IS}+\mathcal{H}_{SS}, \tag{2}$$

where ω_I and ω_S are the Zeeman frequencies of the nuclei and impurities, $\omega_I \ll \omega_S$. $\mathcal{H}_{II}$ is the secular part of the nuclear dipole-dipole interaction Hamiltonian

$$\mathcal{H}_{II}=\sum_\mu \mathcal{H}_\mu^d, \tag{3}$$

$$\mathcal{H}_\mu^d=\sum_{\nu\neq\mu} D_{\mu\nu} r_{\mu\nu}^{-3}\left[I_\mu^z I_\nu^z-\frac{1}{4}(I_\mu^+ I_\nu^- + I_\mu^- I_\nu^+)\right], \tag{4}$$

$$D_{\mu\nu}=\gamma^2(1-3\cos^2\theta_{\mu\nu}), \tag{5}$$

$r_{\mu\nu}^{-3}$ and $\theta_{\mu\nu}$ are the spherical coordinates of the vector $\vec{r}_{\mu\nu}$ concerning the μth and νth nuclei in a coordinate system with the z axis along the external magnetic field. Since $\omega_I \ll \omega_S$, in the impurity-nuclear dipole-dipole interaction Hamiltonian $\mathcal{H}_{SI}$ we retain the terms which give the dominant contribution to the relaxation process:

$$\mathcal{H}_{SI}=\sum_{\mu j} r_{\mu j}^{-3} S_j^z (F_{\mu j} I_\mu^+ + F_{\mu j}^* I_\mu^-), \tag{6}$$

$$F_{\mu j}=-\tfrac{3}{4}\gamma_I\gamma_S \sin 2\theta_{\mu j}\exp(-i\phi_{\mu j}). \tag{7}$$

$\mathcal{H}_{SS}$ describes the dipole-dipole interaction between the PI's spins. Since in a high external magnetic field $\omega_I \gg \omega_{\text{loc}}^d$ where ω_{loc}^d is a local field at the position of the nuclear spins, most of the energy of the nuclear-spin system belongs to Zeeman order which is characterized by the averaged value of nuclear magnetization oriented along the external magnetic field $\vec{H}$. It is possible to transfer this Zeeman order into dipolar order by the use of adiabatic demagnetization in the rotating frame[10] or by a pair of phase-shifted pulses.[11] After this transformation, each nuclear-spin is oriented along an internal local field and most of the energy of the nuclear-spin system resides in the nuclear dipolar reservoir.

The evolution equation for the local dipolar energy will be derived by using the method of the nonequilibrium state operator,[12,13] which gives

$$\frac{d\langle \mathcal{H}_\mu^d\rangle}{dt}=(\beta_\mu^d-\beta_S)\int_0^1 d\lambda \int_{-\infty}^0 dt e^{-\varepsilon t}\langle K_\mu(\lambda,t)K_\mu\rangle. \tag{8}$$

Here the thermodynamic average $\langle \dots \rangle$ corresponds to an average with the quasiequilibrium state operator ρ in the high-temperature approximation:

$$\rho=Z^{-1}\left[1-\sum_\mu \beta_\mu\mathcal{H}_\mu^d-\beta_S\mathcal{H}_S\right], \tag{9}$$

where

$$\mathcal{H}_S=\omega_S\sum_j S_j^z+\mathcal{H}_{IS}+\mathcal{H}_{SS}$$

and

$$Z=\mathrm{Tr}\left(\exp\left[-\sum_\mu \beta_\mu\mathcal{H}_\mu^d-\beta_S\mathcal{H}_S\right]\right). \tag{10}$$

β_μ is the local inverse spin temperature of the nuclear dipole-dipole interaction reservoir. For a sufficiently large heat capacity and short spin-lattice relaxation time of the PI spin system, the inverse spin temperature of the PI's, β_S, can be replaced by the inverse temperature of the lattice β_{ℓ}. The definition of K_μ is given by

$$K_\mu=i[\mathcal{H}_{IS},\mathcal{H}_\mu^d], \tag{11}$$

$$K_\mu(\lambda,t)=V(\lambda,t)K_\mu V^+(\lambda,t), \tag{12}$$

$$V(\lambda,t)=\exp\left[\lambda\left(\sum_\mu \beta_\mu\mathcal{H}_\mu^d+\beta_S\mathcal{H}_S\right)\right]\exp[it(\mathcal{H}_S+\mathcal{H}_{II})]. \tag{13}$$

Taking into account that in the high temperature approximation

$$\langle\mathcal{H}_\mu^d\rangle=-\beta_\mu^d\mathrm{Tr}(\mathcal{H}_\mu^d\mathcal{H}_\mu^d), \tag{14}$$

we obtain

$$\frac{d\beta_\mu^d}{dt}=-\sum_j W_{\mu j}(\beta_\mu^d-\beta_{\ell}) \tag{15}$$

where $W_{\mu j}$ is the transition probability per unit time,

$$W_{\mu j}(\omega)=r_{\mu j}^{-6}A_{\mu j}+\sum_\nu r_{\nu j}^{-6}B_{\nu j}^\mu, \tag{16}$$

$$A_{\mu j}(\omega)=\frac{1}{2\pi}F_{\mu j}(\omega)F_{\mu j}(\omega)^*\int_{-\infty}^{\infty}dt f_\mu(t) \times\langle\{S_j^z(t)S_j^z\}\rangle/\mathrm{Tr}(S_j^z)^2, \tag{17}$$

$$B_{\nu j}^\mu(\omega)=\frac{1}{2\pi}F_{\nu j}(\omega)F_{\nu j}(\omega)^*\int_{-\infty}^{\infty}dt g_{\mu\nu}(t) \times\langle\{S_j^z(t)S_j^z\}\rangle/\mathrm{Tr}(S_j^z)^2, \tag{18}$$

$$f_\mu(t)=\sum_\nu r_{\mu\nu}^{-6}D_{\mu\nu}^2\left[\langle I_\mu^+I_\mu^-(t)I_\nu^zI_\nu^z(t)\rangle +\frac{1}{4}\langle I_\mu^zI_\mu^z(t)I_\nu^+I_\nu^-(t)\rangle\right]\Big/ P_\mu, \tag{19}$$

$$g_{\mu\nu}(t)=r_{\mu\nu}^{-6}D_{\mu\nu}^2\left[\langle I_\mu^zI_\mu^z(t)I_\nu^+I_\nu^-(t)\rangle +\frac{1}{4}\langle I_\mu^+I_\mu^-(t)I_\nu^zI_\nu^z(t)\rangle\right]\Big/ P_\mu, \tag{20}$$

$$P_\mu(t)=\sum_\nu r_{\mu\nu}^{-6}D_{\mu\nu}^2\left[\langle I_\mu^zI_\mu^zI_\nu^zI_\nu^z\rangle+\frac{1}{8}\langle I_\mu^+I_\mu^-I_\nu^+I_\nu^-\rangle\right], \tag{21}$$

$$S_j^z(t)=\exp(i\mathcal{H}_S t)S_j^z\exp(-i\mathcal{H}_S t), \tag{22}$$

$$I_\mu^\kappa(t)=\exp(i\mathcal{H}_{II}t)I_\mu^\kappa\exp(-i\mathcal{H}_{II}t) \quad \kappa=z,+,-. \tag{23}$$

From Eq. (16) we can see that the transition probability $W_{\mu j}$ contains two terms : the first term corresponds to direct interaction of a given nuclear-spin I with the PI and the second to indirect relaxation via neighboring nuclear spins which transfer dipole energy to the PI. We note that the second term has no diffusional character. Since the local inverse temperature β_μ^d is distributed throughout the sample and depends on position, in order to obtain a quantity which connects with the experimentally observable component of the magnetization corresponding to the dipolar order, a suitable averaging procedure must be performed.[8] To carry out this averaging procedure, we introduce two models of the nuclei and PI distribution:[8] (a) a homogeneous distribution over the sample and (b) a model in which the sample can be considered as consisting of subsystems, each of which includes a PI surrounded by nuclear spins.

In the homogeneous distribution, Eq. (15) has the solution

$$\beta^d_\mu(t)=\beta^d_\mu(\infty)+[\beta^d_\mu(0)-\beta^d_\mu(\infty)]\exp\left(-\sum_{j=1}^{N_p} W_{\mu j}t\right), \tag{24}$$

where $\beta^d_\mu(\infty)$ is the equilibrium local inverse temperature and N_p is the number of PI's in the sample. If all the local inverse temperatures of dipolar order are equal at the initial moment and in the equilibrium state, the value to be averaged

$$R_{\mathrm{hom}}(t)=\frac{1}{N_n}\sum_{\mu=1}^{N_n}\left\langle \exp\left(-\sum_{j=1}^{N_p} W_{\mu j}t\right)\right\rangle_V \tag{25}$$

is a normalized relaxation function which can be obtained in the experiment. The average $\langle\ \ldots\ \rangle_V$ is an average over the sample. Let all the transition probabilities $W_{\mu j}$ be indentical and independent and, for the sake of simplicity, let us neglect the detailed angular dependence. Thus, in the continuous medium approximation, we have

$$R_{\mathrm{hom}}(t)=\left\{\frac{1}{V_L}\int_0^{V_L} dV\left\langle \exp\left[-\frac{At}{r^6}-\frac{1}{V_L}\int_\delta^{V_L} dV\frac{Bt}{r^6}\right]\right\rangle\right\}, \tag{26}$$

where A and B are the average over all angles

$$A=\langle A_{\mu j}\rangle_{\theta_{\mu j}\phi_{\mu j}} \tag{27}$$

and

$$B=\langle B^\mu_{\nu j}\rangle_{\theta_{\nu j}\phi_{\nu j}}. \tag{28}$$

Considering the indirect relaxation mechanism via neighboring nuclei, we introduce the radius of the diffusion barrier δ,[5,6] which is of the order of $(\gamma_p/\gamma_n)^{1/3}r_0$, here γ_p and γ_n are the gyromagnetic ratio of the PI and nuclei, respectively, and r_0 is distance between neighboring nuclei.

In the limit as $N_p\rightarrow\infty$, $V_L\rightarrow\infty$, and $N_p/V_L=C_p$, the PI concentration, we have[8]

$$R_{\mathrm{hom}}(t)=\exp\left[-\left(\frac{t}{T^a_{1d}}\right)^{D/6}\right]\exp\left[-\left(\frac{t}{T^b_{1d}}\right)\right], \tag{29}$$

where

$$(T^a_{1d})^{-1}=A\left[\frac{2\pi^{D/2}\Gamma(1-D/6)C_p}{D\Gamma(D/2)}\right], \tag{30}$$

$$(T^b_{1d})^{-1}=\frac{2\pi^{D/2}BC_p}{D\Gamma(D/2)(6-D)\delta^{(6-D)}}, \tag{31}$$

and $\Gamma(z)$ is the gamma function. In the inhomogeneous distribution, we assume that any given nucleus is influenced by one PI, so the sample can be divided up into N_p regions of influence (subsystems), each of which includes only one PI surrounded by nuclear spins. In this case the local inverse dipolar temperature of the jth subsystem obeys the equation

$$\frac{d\beta^d_{\mu j}}{dt}=-W_{\mu j}(\beta^d_{\mu j}-\beta_\ell). \tag{32}$$

We perform an average of the solution of Eq. (32) in two steps: an average over all distances between nuclei and the jth PI

$$\beta^d_j(t)=\frac{1}{N_j}\sum_{\mu=1}^{N_j}\langle\beta^d_{\mu j}(t)\rangle_V \tag{33}$$

where N_j is the number of nuclei in the jth subsystem, followed by an average of Eq. (33) over the volume of the subsystems v,

$$\beta^d(t)=\frac{1}{N_p}\sum_{j=1}^{N_p}\langle\beta^d_j(t)\rangle_v\,. \tag{34}$$

Assuming that all nuclei in the subsystem interact with the impurity independently and that all subsystems are independent and identical, for the normalized relaxation function in an inhomogeneous case we have the following expression:

$$R_{\mathrm{inhom}}(t)=\frac{1}{N_p}\sum_{j=1}^{N_p}\left\langle\frac{1}{N_j}\sum_{\mu=1}^{N_j}\langle\exp(-W_{\mu j}t)\rangle_V\right\rangle_v. \tag{35}$$

Using assumptions analogous to those in the homogeneous case and the fact that the radius of the diffusion barrier, δ, is much smaller than the characteristic size of the subsystem l, in the continuous medium approximation Eq. (35) becomes

$$R_{\mathrm{inhom}}(t)=\exp\left(-\frac{t}{T^b_{1d}}\right)\exp\left(-C_p\int_0^{V_L}dV\left[1-\exp\left\{-C_n\int_0^V dv\,(1-e^{-At/r^6})\right\}\right]\right), \tag{36}$$

where

$$(T^b_{1d})^{-1}=\frac{2\pi^{D/2}BC_n}{D\Gamma(D/2)(6-D)\delta^{(6-D)}}\,. \tag{37}$$

Changing the integration variables V and v and integrating by parts, Eq. (36) yields the following expression:

$$R_{\mathrm{inhom}}(t)=\exp[-E\Psi t^{(D+d)/6}]\exp\left[-\left(\frac{t}{T^b_{1d}}\right)\right], \tag{38}$$

where

$$E=\frac{4\pi^{(D+d)/2}}{\Gamma(D/2)\Gamma(d/2)Dd}A^{(D+d)/6}C_pC_n \tag{39}$$

and

$$\Psi=\frac{d}{D+d}\int_0^\infty d[\xi^{(D+d)/6}]\exp[-f(\xi)][1-\exp(-\xi)],\tag{40}$$

$$f(\xi)=\xi^{-d/6}[1-\exp(-\xi)]+\Gamma(1-d/6,\xi),\tag{41}$$

$$\xi=At/l^6,\tag{42}$$

where $\Gamma(z,\xi)$ is the incomplete gamma function. For a long-time approximation ($t\gg T_2$, the spin-spin relaxation time) and sufficiently small size of subsystems, it follows that $\xi\gg 1$ and $\lim_{\xi\to\infty}f(\xi)=0$. If, in addition, the concentration of nuclear-spin is small enough, from Eqs. (38)–(42) we have

$$R_{\mathrm{inhom}}(t)=\exp\left[-\left(\frac{t}{T_{1d}^a}\right)^{(D+d)/6}\right]\exp\left[-\left(\frac{t}{T_{1d}^b}\right)\right],\tag{43}$$

where

$$(T_{1d}^a)^{-1}=A\left[\frac{4\pi^{(D+d)/2}C_pC_n\Gamma[1-(D+d)/6]}{D(D+d)\Gamma(D/2)\Gamma(d/2)}\right]^{6/(D+d)}.\tag{44}$$

In the two limiting cases, when the radius of the diffusion barrier is large ($T_{1d}^a\ll T_{1d}^b$) or small ($T_{1d}^a\gg T_{1d}^b$) enough, only one exponent from Eqs. (29) or (43) plays an important role. In the former case, the dipolar relaxation via PI's depends on their concentration,[9] whereas in the latter case it is PI-concentration independent.[14] The dipolar relaxation may thus be either larger or smaller than the spin-lattice relaxation time of Zeeman order in both the laboratory and rotating frames, T_1 and $T_{1\rho}$, respectively.[9]

III. EXPERIMENTAL RESULTS AND DISCUSSION

The sample of $C_{1.47}F$ was prepared by R.Yazami by fluorination of pitch-coke derived carbons heat treated at 1100–2500 °C as described in Ref. 15. ^{19}F relaxation times have been measured at 28.05 MHz with a Tecmag solid state NMR spectrometer at room temperature. T_1 has been measured using a $\pi-\tau-\pi/2$ sequence, $T_{1\rho}$ with a $\pi/2(0)$ long (90) spin-locking $T_{1\rho}$ pulse sequence and T_{1d} using a modified Jeener echo method with phase cycling: $\pi/2(x)-\tau_1-\pi/4(y)-\tau-\pi/4(y)-\tau_2-\mathrm{acq}(-y)$ and $\pi/2(-x)-\tau_1-\pi/4(y)-\tau-\pi/4(y)-\tau_2-\mathrm{acq}(y)$ (Refs. 11 and 16) [here acq($\pm y$) are the signal acqusitions in the $\pm y$ of y directions; the phase of the pulses is shown in the parentheses]. The length of the $\pi/2$ pulse was 1.6 μs.

X-ray and NMR analyses show that the structure of $(C_xF)_n$ for $x<3$ consists of carbon layers corrugated due to sp^3 hybridization and with covalent C-F bonds symmetrically lined up from both sides perpendicular to this plane.[15,17–22] The thickness of the layers is 5.7–6 Å. The fluorine atoms in $(C_xF)_n$ form a quasi-two-dimensional lattice and therefore $D=2$. Fluorinated graphite contains localized paramagnetic centers due to broken bonds with unpaired electrons created in the fluorination process.[22,23]

^{19}F NMR measurements yield the values of T_1, $T_{1\rho}$, and T_{1d} are on the order of 10 ms, 1 ms, and 20 μs, respectively.

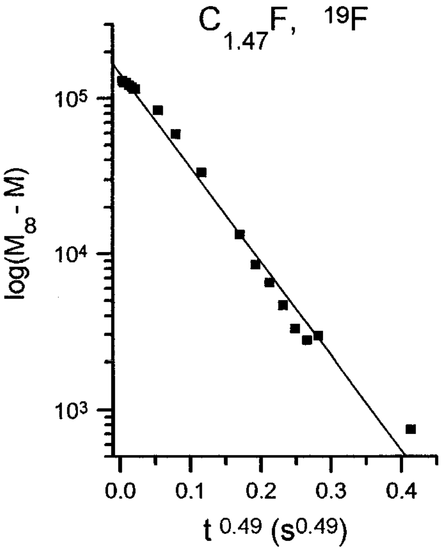

FIG. 1. Log of ^{19}F nuclear magnetization in laboratory frame in $(C_{1.47}F)$ as a function of $t^{0.49}$. Solid line is an apparent linear fit.

We note that values of T_1 in dipolar coupled systems without paramagnetic impurities and molecular mobility are, as a rule, not less than several hundred milliseconds. In our experiment, T_1 is much shorter, evidently due to relaxation through paramagnetic centers. The measurements of T_1 and $T_{1\rho}$ show that the magnetization decay $M(t)$ in both the laboratory and rotation frames may be described by expression (34) of Ref. 8 with $T_1=7.9$ ms and $\alpha=0.49$, and $T_{1\rho}=0.72$ ms and $\alpha=0.5$, respectively (Figs. 1 and 2). To interpret the $T_{1\rho}$ results, we estimate $H_1\sim 30$ G from the length of a $\pi/2$ pulse, which is much greater than the local magnetic field, H_d, estimated at 7.5 G from the fluorine linewidth measurement of $\sim$30 kHz. In this case, the spins are confined to the H_1 direction giving $d=1$ for $T_{1\rho}$ just as for T_1. Thus, our measurements of $\alpha\approx 1/2$ are both consistent with the theory for inhomogeneous distribution of paramagnetic centers in a two-dimensional system without spin diffusion.[8]

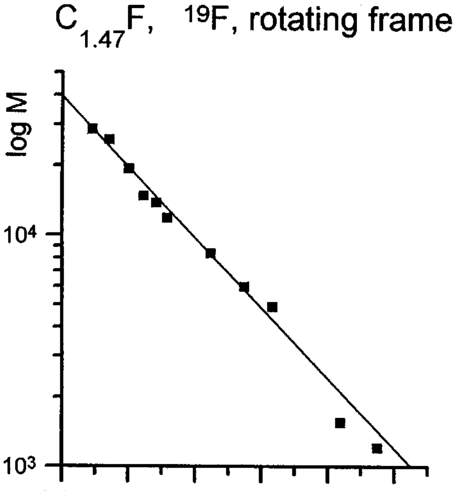

FIG. 2. Log of ^{19}F nuclear magnetization in rotating frame in $(C_{1.47}F)$ as a function of $t^{0.5}$. Solid line is an apparent linear fit.

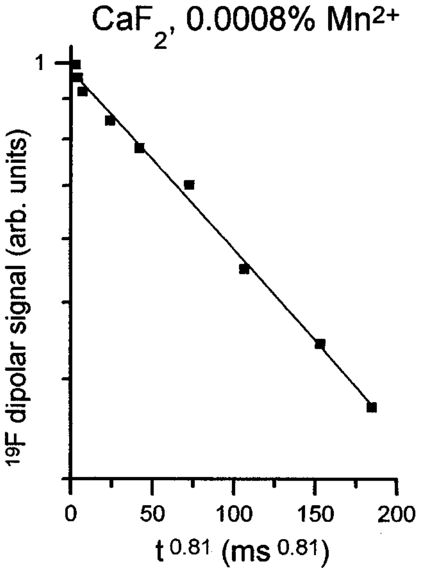

FIG. 3. Log of ^{19}F dipolar signal in CaF$_2$ in the Jeener experiment of Ref. 9 as a function of $t^{0.81}$. Solid line is an apparent fit to expression (37).

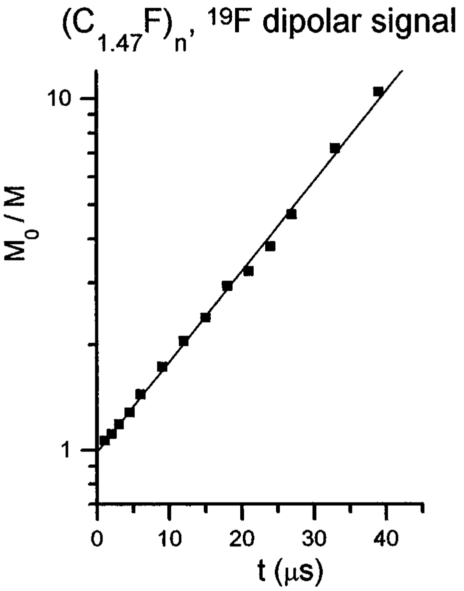

FIG. 4. Log of ^{19}F dipolar signal in (C$_{1.47}$F) in the Jeener experiment as a function of t. Solid line is an apparent linear fit.

The same situation is realized in ^{19}F NMR at Larmor frequency 23 MHz in CaF$_2$ doped with paramagnetic Mn^{2+}, where the decay of the magnetization in the rotating frame also fit a stretched exponential with $\alpha = 1/2$. This was attributed to relaxation via paramagnetic impurities with spin diffusion-vanishing or diffusion-limited conditions.[9]

We now consider the Jeneer echo experiments. For CaF$_2$ doped with 0.0008% of Mn^{2+}, nonexponential decay has been observed at 4.2 K for the magnetic field parallel to the [100] crystalline axis. We note that the second pulse of the Jeener sequence performs a transformation of the spin system from Zeeman order, which is characterized by alignment of spins along the external magnetic field, into dipolar order with alignment of spins in the local field produced by their neighbors. In this case the magnetization is confined to the plane perpendicular to the external magnetic field, so that $d = 2$ and $D = 3$ according to the structure of CaF$_2$. For an inhomogeneous distribution of PI's, $\alpha = (D + d)/6 = 5/6 = 0.83$. Fitting the Jeener echo decay to expression (43) yields good agreement with experiment for $T_{1d}^{a} = 710$ ms, $\alpha = 0.81$, and infinite T_{1d}^{b} (Fig. 3). This means that only the first exponent in Eq. (43) plays an important role and relaxation is via direct interaction of the nuclear-spin with the PI.

For (C$_{1.47}$F)$_n$ with $D = 2$, the ^{19}F Jeener echo decay is seen to be essentially exponential, yielding $T_{1d}^{b} = 17.2$ μs (Fig. 4). In this case, the major contribution is due to the second exponent in Eq. (43) and indirect relaxation is therefore the dominant process of the $I_\mu - I_\nu - S$ type. This is very likely due to the large fluorine content in the sample and strong dipole-dipole coupling of fluorine spins, whose local magnetic field is ~7.5 G as derived above. Thus we show that both direct and indirect relaxation of nuclear-spin with PI's may be obtained experimentally, depending on the system.

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