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Stretched-exponential nuclear magnetization recovery in the proton pseudo-spin-glass $Rb_{1-x}(NH_4)_xH_2AsO_4$

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The proton spin-lattice recovery function at high magnetic fields and the nuclear magnetization decay in the rotating frame are nonexponential in the incipient proton glass $Rb_{1-x}(NH_4)_xH_2AsO_4$. The results can be described by a stretched-exponential correlation and magnetization-recovery function with the distribution parameter n in $\alpha = 1 - n$ varying from zero at room temperature to 0.25 at 100 K and 0.4 at temperatures below 12 K. The same values of n are obtained at high magnetic fields and in the rotating frame.

I. INTRODUCTION

It is well known[1] that RbH_2AsO_4 is ferroelectric ($T_c = 110$ K), whereas $NH_4H_2AsO_4$ is antiferroelectric ($T_c = 216$ K) at low temperatures. In the high-temperature paralectric phase ($T > T_c$) the two systems are isomorphous and the "acid" protons are dynamically disordered between the two equilibrium sites in the O—H —O bonds linking the various PO_4 groups into a three-dimensional network. Depending on whether we introduce an alkali ion like Rb or an $NH_4{}^+$ ion into the structure, different H_2AsO_4 proton configurations are stabilized resulting in ferroelectric or antiferroelectric proton ordering at low temperatures.[1]

Dielectric measurements have recently shown[2] the presence of glassy behavior in $Rb_{1-x}(NH_4)_xH_2AsO_4$ with $x = 0.31$. The maximum of the dielectric losses at microwave frequencies occurs at $T_G = 58$ K. The temperature dependences of the real and imaginary parts of the dielectric constant seem to be analogous to those observed in $Rb_{1-x}(NH_4)_xH_2PO_4$ by Courtens.[3] It thus seems that the mixed rubidium-ammonium dihydrogen arsenate crystal represents a proton pseudo-spin-glass[3] with randomly competing ferro- and antiferroelectric interactions somewhat similar to those in magnetic spin glasses.[3] The O—H—O-bonded "acid" proton is the basic two-position-reversible electric dipole and plays here a role similar to that of the electronic spin in magnetic spin glasses.

The most characteristic property[4] of the glassy state is the dramatic increase in the time scale for structural relaxation which reflects the extreme slowing down of the motional processes leading to atomic rearrangements. The slow relaxation is not of a simple exponential form and cannot be described with a single relaxation time. Dielectric and shear-stress relaxation data are often represented by the "stretched-exponential" or the Kohlrausch-Williams-Watts formula[5]

$$g_\alpha(t) = \exp[-(t/\tau)^\alpha] \text{ with } 0 < \alpha < 1 \ , \qquad (1)$$

which can be applied rather universally[5] to a broad class of disordered materials. The above expression is expected to hold[6] if relaxation is due to diffusion of defects with a fractal waiting-time distribution, i.e., if the time sequence of local motional events is self-similar, like points in a fractal Cantor set.[7,8] Kinetic models in "ultrametric spaces" which describe hierarchical patterns of energy barriers also lead[4,8] to Eq. (1). Very recently, it has been predicted[9] that stretched-exponential relaxation is a general property of systems with a large number of quasidegenerate ground states where the "valley-bottom" free energies are independent random variables.[9]

In order to check this prediction and to throw further light on the dynamics of proton pseudo-spin glasses[3] we decided to investigate the temperature dependence of the proton spin-lattice relaxation in a powdered $Rb_{1-x}(NH_4)_xH_2AsO_4$ single crystal at high fields and in the rotating frame in the low-temperature region. We also decided to investigate the form of the proton magnetization recovery toward equilibrium. Similar studies have already been performed[10] on the rubidium ($I = \frac{3}{2}$) and deuterium ($I = 1$) nuclei in $Rb_{1-x}(ND_4)_xD_2PO_4$ and on rubidium[11] in $Rb_{1-x}(NH_4)_xH_2PO_4$. The presence of a nonzero quadrupole moment—while useful[10] in separating resonances of "ammonium" and acid deuterons—has, however, so far prevented a systematic study of the form of the magnetization recovery in view of the fact that the spin-lattice relaxation of quadrupolar nuclei is inherently nonexponential. The proton ($I = \frac{1}{2}$) spin-lattice relaxation process does not suffer from this deficiency and is strictly exponential if the atomic fluctuations can be characterized by a single correlation time. We thus hoped that proton spin-lattice relaxation and magnetization-recovery data will be able to settle the question of whether a stretched-exponential form determines relaxation processes in incipient pseudo-spin-glasses like $Rb_{1-x}(NH_4)_xH_2AsO_4$ or not.

II. STRETCHED-EXPONENTIAL SPIN-LATTICE RELAXATION AND MAGNETIZATION RECOVERY

An autocorrelation function of the stretched-exponential type—Eq. (1)—represents, in fact, a whole distribution

$\rho(\tau')$ of microscopic correlation times τ':

$$g_a(t) = \exp[-(t/\tau_c)^a] = \int_0^\infty \rho(\tau') e^{-t/\tau'} d\tau' \ . \tag{2}$$

It is thus not surprising that the dependence of the spin-lattice relaxation rate on the Larmor frequency or the correlation time τ is here very different from the one obtained for a correlation function of the simple Bloembergen-Purcell-Pound (BPP) type where $g(t) = e^{-t/\tau_c}$. The spectral density of expression (1) at the nuclear Larmor frequency ω_L,

$$J_a(\omega_L) = \int_{-\infty}^{+\infty} e^{i\omega_L t} g_a(t) dt \tag{3}$$

can be expressed as

$$J_a(\omega_L) = \frac{2\tau_c}{a} \int_0^\infty x^{1/a-1} \cos(\omega_L \tau_c x^{1/a}) e^{-x} dx \ , \tag{4}$$

where $x = (t/\tau_c)^a$. Using

$$\cos y = \sum_{n=0}^{\infty} (-1)^n \frac{y^{2n}}{(2n)!}$$

this becomes

$$J_a(\omega_L) = \frac{2\tau_c}{a} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n)!} \Gamma\left(\frac{2n+1}{a}\right) (\omega_L \tau_c)^{2n} \ , \tag{5}$$

where we introduced the Γ function, e.g.,

$$\int_0^\infty x^{1/a-1} e^{-x} dx = \Gamma\left(\frac{1}{a}\right) \ .$$

In the "fast-motion" regime, where $\omega_L \tau_c \ll 1$, one thus finds

$$J_a(\omega_L) = \frac{2\tau_c}{a} \Gamma\left(\frac{1}{a}\right) \neq f(\omega_L), \ \ \omega_L \tau_c \ll 1 \ . \tag{6}$$

In the extreme "slow-motion" regime, where $\omega_L \tau_c \gg 1$ one gets from expression (3) with $z = \omega_L t$ by partial integration the asymptotic expression

$$J_a(\omega_L) \approx \frac{2a}{\omega_L^{1+a} \tau_c^a} \int_0^\infty z^{a-1} \sin z \, dz \ , \tag{7}$$

yielding

$$T_1 \propto \omega_L^{1+a} \tau_c^a, \ \ 0 < a = 1 - n < 1 \ . \tag{8}$$

It should be noted that in this limit expansion (5) is not very useful in view of very slow convergence. It is thus preferable to use in this limit the asymptotic expressions (7) and (8). The larger n is—and the smaller a is—the broader is the spectrum of relaxation times $\rho(\tau')$. Expressions (3) and (5) still yield a minimum in the T_1 vs $\omega_L \tau_c$ plot. The minimum, however, does not occur anymore at $\omega_L \tau_c = 1$ as in the BPP case, where $a = 1$ and $n = 0$. The minimum is asymmetric and becomes very flat as $n \rightarrow 1$ and $a \rightarrow 0$.

If the motion is thermally activated so that

$$\tau_c = \tau_0 \exp(E/kT) \ , \tag{9}$$

the T_1 vs $1/T$ plot will be asymmetric too: The high-T side of the minimum where $\omega_L \tau_c \ll 1$ will yield an activation energy E_a, whereas the low-T side will yield a smaller apparent activation energy $E' = aE$.

The random free-energy model[9,12] also predicts a nonexponential magnetization-recovery function which should at long times exhibit a stretched-exponential behavior:

$$M(t) = M_0(1 - e^{-(t/T_1)^a}) \ . \tag{10}$$

A similar stretched exponential magnetization relaxation recovery is also predicted[13] by the percolation model[13] of the glass transition, where the proton magnetization-recovery function

$$F(t) = \frac{M_0 - M(t)}{M_0}$$
$$= \int P(T_1^{-1}) \exp(-t/T_1) d(T_1^{-1}) = e^{-(t/T_1)^a} \tag{11}$$

is a weighted average of recovery functions for the various clusters. Here the probability distribution of spin-lattice relaxation rates $P(T_1^{-1})$ is related to the cluster probability distribution[13] $g(\xi)$ by

$$P(T_1^{-1}) dT_1^{-1} = g(\xi) d\xi \ , \tag{12}$$

where ξ is a typical cluster size and T_1 depends on the cluster surface-to-volume ratio and thus on the cluster size ξ.

III. EXPERIMENT

The proton spin-lattice relaxation time T_1 was measured with the saturation recovery pulse sequence with a $\pi/2$ pulse duration of about 2 μs at 50 MHz. The rotating-frame relaxation time $T_{1\rho}$ was measured with the spin-locking pulse sequence of duration τ at $H_1 = 2$, 5, and 8 G. The temperature was varied between 100 and 4.2 K. For each experimental point several free-induction decays (FID's) were accumulated in order to obtain a signal-to-noise ratio better than 70:1. These averaged FID's were then split into 33 slices ("windows") each at a different time delay t.

These data, along with the equilibrium magnetization FID's were then used to generate the magnetization relaxation recovery functions.

IV. RESULTS

The results of the spin-lattice relaxation measurements were analyzed by fitting the magnetization-recovery function

$$F(t,\tau) = F_0(t) \exp[-(\tau/T_1)^{l-n}] \ . \tag{13}$$

Here $F_0(t)$ is the shape of the observed FID which is not a Gaussian in view of the presence of two types of protons in the sample: the "frozen in" NH_4^+ protons and the "acid" protons. The shape of $F_0(t)$ does not change from 70 to 4 K. For each window (identified by its t_w value), $F_{\exp}(t_w, \tau)$ was plotted semilogarithmically versus τ^{1-n}. The parameter n was varied until the best straight line was obtained. This was done for all windows. The least-squares fit to these data yielded the average value of T_1^{1-n} used to calculate T_1.

In the rotating frame the results are somewhat more complicated. All measured decays have two components, a "fast" ($T_{1\rho}^f$) and a "slow" ($T_{1\rho}^s$) one. The fast com-

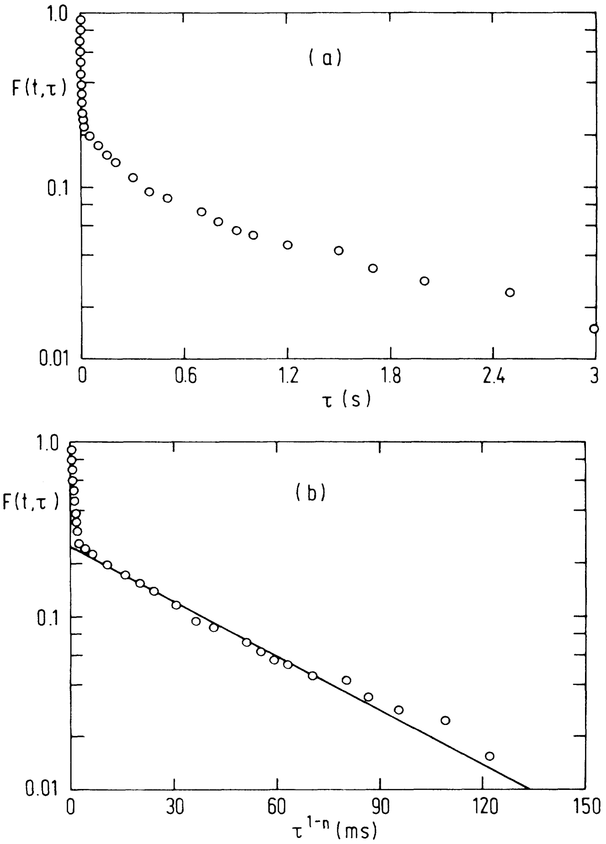

FIG. 1. Nuclear magnetization-recovery function in the rotating frame: (a) semilogarithmic plot of $F(t,\tau)$ vs τ, and (b) semilogarithmic plot of $F(t,\tau)$ vs τ^{1-n}. Here $T=4.2$ K, $t=12$ μsec, and $H_1=2$ G.

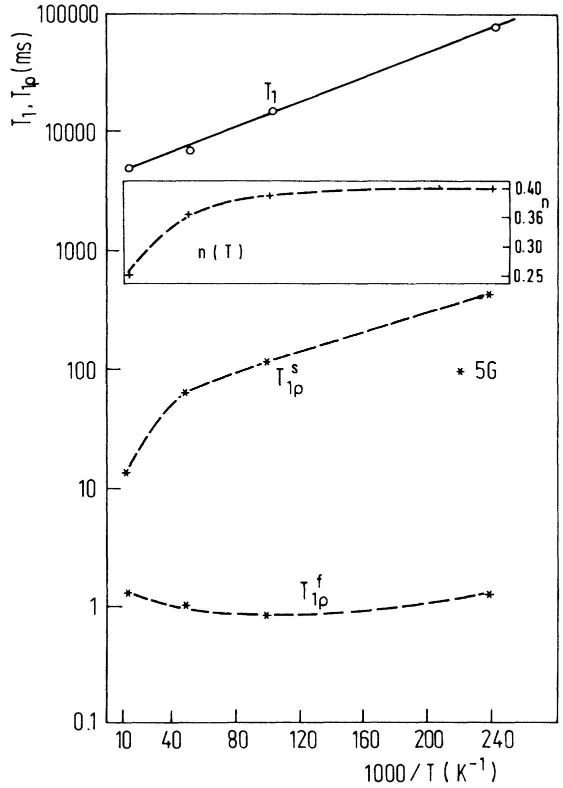

FIG. 2. Temperature dependence of (a) the proton spin-lattice relaxation time T_1 at high magnetic fields, (b) the slowly ($T^s_{1\rho}$) and the fast ($T^f_{1\rho}$) decaying component of the proton spin-lattice relaxation time in the rotating frame, and (c) the distribution parameter n, characterizing the stretched exponential exponent $\alpha=1-n$ in the nuclear magnetization-recovery function.

ponent—which is independent of temperature—seems to be due to either cross relaxation to ^{75}As and ^{87}Rb nuclei or to cross relaxation to a "tunneling" energy reservoir of the $NH_4{}^+$ protons. The slow component is, on the other hand, temperature dependent and has a characteristic recovery similar to the spin-lattice relaxation recovery. The $T_{1\rho}$ results were thus fitted to

$$F(t,\tau)=F_0^f(t)\exp(-\tau/T^f_{1\rho})+F_0^s(t)\,\exp[-(\tau/T^s_{1\rho})^{1-n}]\ , \tag{14}$$

resulting in a good agreement with experiment (Fig. 1).

The value of the parameter n obtained from rotating-frame data is the same as that obtained from magnetization-recovery data at high fields for the same temperature. The value of n varies from $n=0.25$ ($\alpha=0.75$) at 100 K to $n=0.4$ ($\alpha=0.6$) at 4 K. At room temperature $n=0$ and $\alpha=1$ (Fig. 2).

$\log_{10}T_1$ is linear in $10^3/T$ from 100 down to 4 K. The huge difference between T_1 and $T_{1\rho}$ demonstrates that we are in the slow-motion regime where expressions (7) and (8) are valid. In this temperature interval the proton T_1 is increasing with decreasing temperature as expected for the case of Eq. (8), where $\omega_L\tau\gg1$ and $T_1\propto\tau^{1-n}$ with $\tau=\tau_0\exp(E/kT)$. The magnitude of the slow $T_{1\rho}$ component $T^s_{1\rho}$ as well increases with decreasing temperature. Again $\log_{10}T^s_{1\rho}$ is linear in $10^3/T$ from 74 to 4.2 K. The apparent activation energy derived from the slopes of the T_1 and $T_{1\rho}$ vs $10^3/T$ plots is $\alpha E\approx1.06$ meV, $E=1.77$ meV. This value of E is much lower than the one found[10] for ND_4 rotation ($E=160$ meV) or D_3PO_4 diffusion ($E=78$ meV) in $Rb_{1-x}(ND_4)_xD_2PO_4$ and may indicate the importance of tunneling.

The above data thus show that the nuclear magnetization recovery in the incipient proton glass $Rb_{1-x}(NH_4)_xH_2AsO_4$ is nonexponential in the 100- to 4-K temperature range both at high fields and in the rotating frame. The results can be described by a stretched exponential magnetization recovery function with a temperature-dependent parameter α. The temperature dependence of this distribution parameter $\alpha=1-n$ shows the broadening of the distribution of microscopic correlation times $\rho(\tau')$ with decreasing temperature.

It should be noted that within a recent model[12]—where the spin-glass transition appears as a percolation threshold in eigenstate space—$\alpha=2/(2+\Theta)$ with Θ being the fractal random-walk exponent $d_w=2+\Theta$. The model predicts that Θ is zero at very high temperatures (i.e., $\alpha=1$), whereas it tends to 4 and α to $\frac{1}{3}$ as the percolation threshold is approached, thus reproducing the trend observed here.

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