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Deuteron NMR study of dynamics and of coexistence of paraelectric and ferroelectric phases in $Rb_{0.90}(ND_4)_{0.10}D_2AsO_4$

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The deuteron glass $Rb_{1-x}(ND_4)_xD_2AsO_4$ (DRADA) is a mixed crystal of RbD_2AsO_4 (DRDA) and $ND_4D_2AsO_4$ (DADA). Deuteron nuclear magnetic resonance has been performed on the acid and ammonium deuterons. The crystal studied has an ammonium concentration ($x = 0.10$) that puts it in the coexistence region of the phase diagram. Line-shape measurements of the ammonium deuterons show the coexistence of the ferroelectric (FE) and paraelectric (PE) phases as the temperature is lowered below the ferroelectric-phase-transition temperature T_c. The acid deuteron line shape on the other hand is found to broaden as the temperature is reduced but is unaffected by the ferroelectric transition. Spin-lattice-relaxation measurements have been performed and the activation energies for the relaxation processes have been computed. The relaxation-rate anomaly for acid deuterons in the ferroelectric-transition range indicates a short correlation length for the FE phase in the coexistence region of the phase diagram.

I. INTRODUCTION

Proton and deuteron glasses are pseudospin glasses observed in hydrogen-bonded mixed crystals of ferroelectric and antiferroelectric systems. Since its discovery by Courtens[1] many experimental studies viz. dielectric,[2-5] optical,[6-8] electron paramagnetic resonance[9-12] (EPR), and nuclear magnetic resonance[13-19] (NMR) have been carried out on various ammonium concentrations to investigate proton glass behavior and study the dynamics involved in the two kinds of proton or deuteron ordering. The deuteron glasses $Rb_{1-x}(ND_4)_xD_2PO_4$ (DRADP) and $Rb_{1-x}(ND_4)_xD_2AsO_4$ (DRADA) are two systems in this family of mixed crystals that are studied most often. Experiments have also been performed[20,21] on systems with Rb replaced by K, but these crystals are harder to grow. Depending upon the amount of ammonium present, the system could have a ferroelectric, antiferroelectric, or proton glass transition as the temperature is lowered. A phase diagram for the RADA mixed system was obtained by Trybula *et al.*[22] and by DeLooze *et al.*[23] for the deuterated counterpart. Dielectric measurements[2] on these same crystals also show the coexistence of ferroelectric (FE) and paraelectric (PE) phases for ammonium concentrations $0.04 < x < 0.16$ at temperatures below the ferroelectric-phase-transition temperature T_c.

Spin-glass and pseudospin-glass behavior is generally considered to require randomness and frustration. In DRADA, the randomness lies in the Rb^+ and ND_4^+ cation placement. The frustration lies in two inconsistent tendencies for ordering of the $O—D\cdots O$ deuteron "pseudospins." In ferroelectric RbD_2AsO_4 (DRDA), if one looks down along c, the deuterons in $O—D\cdots O$ bonds lying along $a(b)$ are near the tops (bottoms) of AsO_4 groups, or vice versa for reversed domains. In antiferroelectric $ND_4D_2AsO_4$ (DADA) two adjacent $N—D\cdots O$ bonds (viewed along c) of a given ND_4^+ ion are short and the other two adjacent $N—D\cdots O$ bonds are long. A given $O—D\cdots O$ bond shares oxygens with one short and one long $N—D\cdots O$ bond, with the $O—D$ near the long bond and the $D\cdots O$ near the short bond. This arrangement puts one deuteron near the top, and one near the bottom of each AsO_4 group, which is inconsistent with ferroelectric ordering. In a mixed crystal, these inconsistent ordering schemes favored by the arsenate and ammonium ions cause frustration and inhibit or prevent either ferroelectric or antiferroelectric ordering.

In order to investigate the nature of coexistence in these crystals we decided to perform ^2H NMR on the ammonium and acid deuterons in DRADA for an ammonium concentration on the low x side of the phase diagram. Because of the quadrupole moment of the deuteron and its interaction with the local electric-field gradient (EFG), the splitting of the NMR line for the acid deuteron makes it convenient to study the acid and ammonium deuterons independently.

In this work we performed spin-lattice relaxation measurements for both the acid and ammonium deuterons on a single mixed crystal of DRADA with $x = 0.10$. In addition, the deuteron line shape was studied for the acid and ammonium deuterons. Evidence of coexistence is seen in the ammonium deuteron spectra but could not be seen in the acid deuteron spectra. The activation energies were calculated from the spin-lattice-relaxation times for the ammonium and acid deuterons on the high-temperature side of the Bloembergen-Purcell-Pound (BPP)-like T_1 minimum.

II. EXPERIMENTAL

The experiment was performed on a deuterated single crystal of DRADA, with $x = 0.10$. The ammonium concentration was determined from dielectric measurements[2] by comparing the ferroelectric-transition temperature with the phase diagram[23] published for deuterated samples of the RADA family. The crystal was oriented with

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the dc magnetic field $\mathbf{H}_0$ perpendicular to the ferroelectric c axis (z direction) and along one of the other two (a or b) crystallographic axes. ^{2}H spin-lattice-relaxation times and spectra were measured at 28 MHz.

A Fourier transform 90° saturation pulse sequence was used. This sequence consisted of a number of 90° pulses with equal spacing τ. Responses to the first few pulses were discarded, and the remaining responses were averaged. This procedure was repeated for several τ of order T_1, and the deviation of the pulse response from the equilibrium (long τ) response was plotted vs τ on semilog paper. We defined T_1 as the τ value at the $1/e$ point on the best straight line through the data.

The acid and ammonium deuterons were excited independently by making use of the splitting in the acid deuteron line at $\Theta_z = 0°$. At this orientation the X—bond deuterons (with O—D $\cdots$ O bonds nearly along H_0) have resonance lines near 80 kHz above and below the center of the spectrum, while the Y-bond deuterons have lines near 40 kHz above and below the spectrum center. The ammonium deuterons in the fast motion limit have a splitting of only 4 kHz. Both lines for these ammonium deuterons were excited by a 90° pulse (22 μs) at the center of the spectrum. One of the two Y-bond acid deuteron lines was excited by a 90° pulse (16 μs, $\sqrt{2}$ shorter as required for such asymmetric excitation) 40 kHz below the spectrum center. The crystal was placed in a continuous flow low-temperature cryostat and the temperature was measured using a calibrated type-K thermocouple.

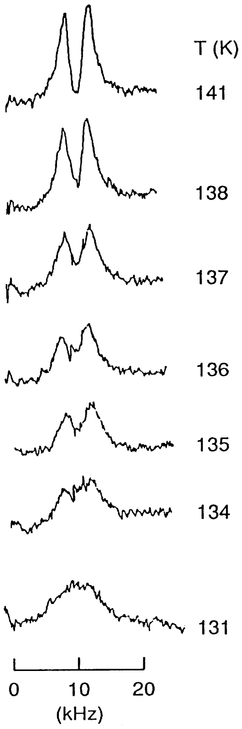

FIG. 1. Temperature dependence of the ND_4^+ deuteron NMR line shapes in $Rb_{0.90}(ND_4)_{0.10}D_2AsO_4$ for $\underline{a}\|\mathbf{H}_0, \underline{c}\perp\mathbf{H}_0, \nu=28$ MHz.

III. RESULTS AND DISCUSSION

The temperature dependence of the ND_4^+ deuteron Fourier transform NMR spectra is shown in Fig. 1. From 300 to 135 K the spectrum exhibits a doublet which can be described as a superposition of two Gaussians displaced by 4 kHz. The doublet arises from the paraelectric portion of the crystal where the deuterons are still mobile. The width of the Gaussians increases with decreasing temperature, but their separation and position are practically temperature independent. This broadening is a result of the random bias fields that get stronger as the temperature is lowered. At still lower temperatures the ND_4 rotation should slow down to the extent that we should see the rigid lattice spectra of the ND_4^+ deuterons because the spectrum is no longer rotationally averaged. However, the NMR signal at this point was too small to analyze. The ND_4 spectra in Fig. 1 show a superposition of lines from the FE and PE portions of the sample. The doublet described above corresponds to the PE portion while the single broad line in the background is due to the FE portion. The gradual disappearance of the doublet at 131 K where the single broad line grows to its full size indicates that below this temperature a greater portion of the crystal is in the FE phase. Contributions to the spectra from the PE phase were too small to be detected due to the poor signal-to-noise ratio at lower temperatures. This result is consistent with the presence of coexistence below T_c as determined from dielectric measurements[2] which show that the ferroelectric transition begins at 146 K and is mostly complete at 120 K.

The ND_4^+ doublet splitting observed at room temperature in DRADA is analogous to the one found in pure deuterated ADP. It is compatible with the axially symmetric ND_4^+ EFG tensor expected to be found in the PE phase at the ammonium site if all the acid deuterons move fast between the two equilibrium sites in the O—D $\cdots$ O bonds. From spin-lattice-relaxation times for the ND_4 deuterons, the activation energy for the reorientation process of the ammonium deuterons is found to be 150 meV from Fig. 2, where we plot the spin-lattice-relaxation time T_1 for the ND_4^+ deuterons as a function of temperature. This activation energy is similar to that reported by Blinc *et al.*[18] for the ammonium deuterons in the phosphate deuteron glass (160 meV). The T_1 minimum for the ammonium deuterons is driven by ammonium reorientations. The activation energy can also be computed from the T_1 minimum, where for $\Delta m = \pm 1$ and ± 2 transitions, we have $\omega\tau = 0.6$ and

$$\tau = \tau_0 \exp(-E_a/kT) \; , \tag{1}$$

where τ_0 is the preexponential factor which we assume is approximately 5×10^{-14} s. Using Eq. (1) with $T = 160$ K from Fig. 2, the activation energy is found to be 145 meV, in good agreement with the previous result.

Figure 3 shows the spin-lattice-relaxation times for the acid deuterons. In the case of pure KD_2PD_4 (DKDP), there are three principal mechanisms[24] for deuteron spin-lattice relaxation. One component of relaxation, due

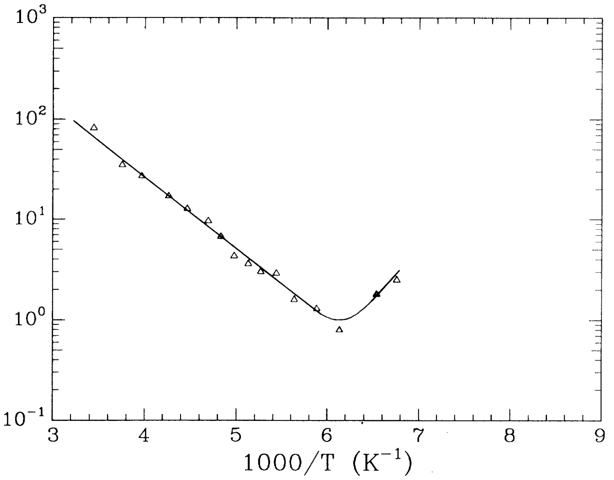

FIG. 2. Temperature dependence of the spin-lattice-relaxation times T_1 for the ammonium deuterons in $Rb_{0.90}(ND_4)_{0.10}D_2AsO_4$.

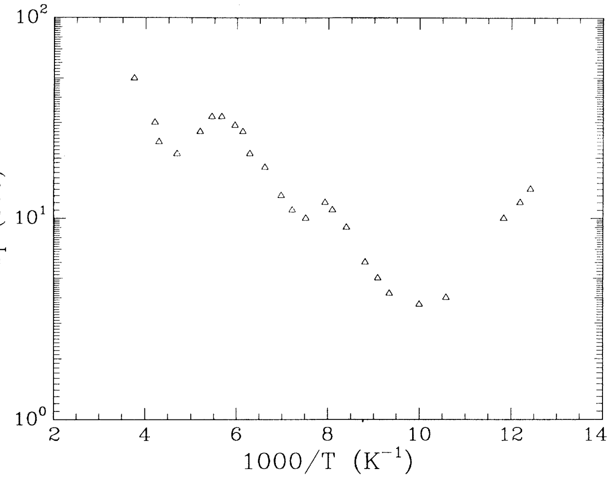

FIG. 3. Temperature dependence of the spin-lattice-relaxation time T_1 for the acid deuterons in $Rb_{0.90}(ND_4)_{0.10}D_2AsO_4$.

to spin diffusion to paramagnetic impurities, is not seen in these measurements because it is small compared to the intrabond jump relaxation mechanism discussed below. Another mechanism seen in DKDP, due to the interaction of the deuteron quadrupole moment with the electric-field gradient fluctuations caused by deuterons jumping between the acid O—D · · · O bonds with two orthogonal orientations, was not seen at the low temperatures used in these experiments. The third component of relaxation in DKDP, the only one seen in these measurements, is due to deuteron jumps within O—D · · · O bonds.

The highest-temperature T_1 minimum in Fig. 3 is due to mixing between the deuterons within the two orthogonal orientations of the O—D · · · O bonds, i.e., interbond motion. There are two spin-lattice-relaxation-rate constants for the nonsymmetrically excited Y-bond system, namely $3P_1$ and P_1+2P_2. If we assume one of these rates predominates and its inverse is T_1, and if we further assume the same rate constant predominates for the X-bond deuterons, we obtain the following comparison of apparent T_1 for the slow (low-temperature) and fast (high-temperature) X-Y mixing regimes. In the slow mixing regime, the decay time is T_{1s}. In the fast mixing regime, the deviation of the response from its equilibrium value is nonexponential and follows the relation

$$S_{\max}-S(\tau)=[2\exp(\tau/T_{1s})-1]^{-1} . \qquad (2)$$

The apparent T_1 from this curve is $T_{1s}/2$ evaluated from the initial slope, or $0.62T_{1s}$ from a straight line through the $1/e$ point. From Fig. 3, the highest-temperature T_1 value is only 32% of the value obtained by extrapolation of the slow mixing regime slope. The difference can be attributed to the lower relaxation rate for the X-bond deuterons.[24]

A second small anomaly seen around 133 K is due to the ferroelectric transition. At this temperature we see from the ND_4^+ deuteron spectra shown in Fig. 1 that the doublet disappears as a result of the appearance of the ferroelectric phase. The increase in T_1 below 133 K occurs because spin diffusion of acid deuterons in the FE phase to the relaxing deuterons in the PE phase slows the T_1 process. The existence of this spin diffusion shows that the correlation length of FE phase regions is less than the spin-diffusion range.

The third broad BPP-like minimum occurs around 100 K due to the extreme slowing down of the O—D · · · O motions, a characteristic of the proton or deuteron glass state. Such an effect is not seen in the pure DRDA or DADA samples which are in completely ordered states at this temperature. This third minimum occurs at a temperature corresponding to the glass transition one expects to see at 28 MHz from dielectric measurements.[2] Below the temperature corresponding to this minimum, the deuteron intrabond motion (O—D · · · O) freezes out on the NMR time scale. The activation energy for deuteron intrabond motion is found to be 65 meV from T_1 measurements shown in Fig. 3, while the activation energy calculated using Eq. (1) with $T=100$ K for the minimum (which is broader than for a BPP minimum) is found to be 90 meV. In order to obtain a lower activation energy from Eq. (1), the third minimum in T_1 would have to occur at lower temperatures. In the case of DRADP, for $x=0.55$, which puts this crystal in the pure deuteron glass regime, Blinc *et al.*[18] found the activation energy for deuteron intrabond motion to be 76 meV. We find that the acid deuteron line in DRADA broadens as the temperature is reduced below the glass transition temperature but is not much affected by the ferroelectric or glass transition.

IV. CONCLUSIONS

In order to study the dynamics of the phase transitions in these mixed crystals, deuteron nuclear magnetic resonance was performed on a deuterated single crystal of RADA with $x=0.10$. Both the acid and ammonium deuterons were excited independently of each other. Analysis of the ammonium deuteron spectra shows the coexistence of ferroelectric and paraelectric phases below T_c. The activation energies of the mechanisms responsible for spin-lattice relaxation were calculated and were in agreement with those calculated for the phosphates. Both the ammonium and acid deuteron spectra show that the ND_4^+ hindered rotation and the position of the deuteron in the O—D $\cdots$ O bond are not much affected by the ferroelectric phase transition. The increase of acid deutron T_1 with decreasing temperature in the ferroelectric transition temperature range shows that the correlation length for ferroelectric regions is short compared to the distance over which spin diffusion is effective. Evidence of the deuteron glass freezing is seen as a broadened minimum in the spin-lattice-relaxation time at low temperatures.

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