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^{31}P NMR spin-lattice relaxation: Structural glass dynamics in $Rb_{1-x}(ND_4)_xD_2PO_4$

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We performed ^{31}P NMR measurements of the temperature-dependent spin-lattice relaxation time in several mixed single crystals of $Rb_{1-x}(ND_4)_xD_2PO_4$ [DRADP] having different ammonium concentration x ($x=0.22$, 0.44, 0.78) as well as in three pure single crystals $(ND_4)D_2PO_4$ [DADP], $(NH_4)H_2PO_4$ [ADP], and RbH_2PO_4 [RDP]. The ^{31}P NMR spin-lattice relaxation-time measurements in mixed crystals show that the phosphorus nuclei are strongly influenced by the gradual slowing down of the motions of protons in the nearby O—D · · · O acid bonds in the structural spin-glass states. In addition to a common T_1 minimum observed in all ammonium-containing systems, a second T_1 minimum is observed in the temperature region of the glass transition in mixed spin-glass systems but not in pure ADP, DADP, or RDP. We attribute this lower temperature T_1 minimum to the extreme slowing down of the O—D · · · O intrabond motion, which is unique to the glass system. In addition, the correlation times and activation energies for the T_1 minima in all samples were determined. A comparison between the pure and mixed systems reveals that the mixed system T_1 minimum must be fit to a distribution of correlation functions but that each pure system requires only a single correlation function. Furthermore, measurements on systems having $x=0.78$ and 0.22 show that ^{31}P NMR can be used to determine the threshold concentrations that characterize the glass phase.

I. INTRODUCTION

Mixed single-crystal $Rb_{1-x}(NH_4)_xH_2PO_4$ [or $Rb_{1-x}(ND_4)_xD_2PO_4$] is a typical substitutionally disordered system in which the random substitution of Rb^+ ions for the ammonium ions in crystals having intermediate ammonium concentration x ($0.22<x<0.75$) affects the O—H · · · O (or O—D · · · O) bonds leading to frustration which thereby destroys the long-range order. At low temperatures the system enters a spin-glass-like state as a result of the freeze-out of O—H · · · O (or O—D · · · O) intrabond motions.[1-4] Since the discovery of the glassy behavior in this system by Courtens,[1] extensive experimental and theoretical research has been done on this and similar substances,[2-12] which shows that these proton glass systems share many common properties with magnetic spin-glass systems and with other glasses.

NMR techniques have been successfully employed in studying of several aspects[5-9] the proton (or deuteron) structural spin-glass systems. Previous NMR studies were mainly focused on studying quadrupolar nuclei [e.g., ^{87}Rb and ^{2}D in $Rb_{1-x}(ND_4)_xD_2PO_4$].[5,7,8] The main advantage of quadrupolar nuclei is that the electric field gradient (EFG) is very sensitive to changes in the nuclear environment; therefore, the quadrupolar interaction can provide a probe for studying either structural variations or molecular motions in the vicinity of the quadrupolar nuclei. Examination of O—D · · · O intrabond motion is specifically important, because its freeze-out is an important characteristic of a spin-glass state. In fact, the earlier O—D · · · O studies by ^{87}Rb and ^{2}D NMR demonstrated that both static and dynamic properties of the proton spin-glass system can be detected by investigating these quadrupolar nuclei.[7]

Many spin-glass properties, such as the freezing of polarization cluster ordering[13] and stretched exponential relaxation behavior,[14] are bulk properties of spin-glass systems and, therefore, should be observable by means of dipolar relaxation of a spin-$\frac{1}{2}$ nucleus. Although in many circumstances dipolar interactions have less effect than quadrupolar interactions on the spin-lattice relaxation rate, there are certain advantages in using a spin-$\frac{1}{2}$ nucleus. In contrast to quadrupolar nuclei, which have several transitions due to unequally spaced energy levels, a spin-$\frac{1}{2}$ nucleus has only a single transition. It is more straightforward and unambiguous to deal with a single-level transition than with multilevel transitions, because it is difficult in many cases to separate effects due to a distribution of correlation times (as often occurs in glass systems) from these multilevel quadrupolar effects.

In this paper, we report temperature-dependent ^{31}P spin-lattice relaxation time T_1 measurements in three $Rb_{1-x}(ND_4)_xD_2PO_4$ mixed single crystals having $x=0.22$, 0.44, and 0.78. For comparison, we also performed similar measurements in three pure single crystals: $(NH_4)H_2PO_4$, $(ND_4)D_2PO_4$, and RbH_2PO_4, which are referred to as ADP, DADP, and RDP, respectively. The phosphorous nucleus ^{31}P has special advantages over the proton as a candidate for studying dipolar interactions in these crystals, since there is only one phosphorus nucleus in each molecule but there are two kinds of protons (NH_4^+ and O—H · · · O protons) whose linewidths overlap. We observed in all our ammonium-containing samples (pure or mixed) a T_1 minimum, occurring at approximately 170 K, which is due to the NH_4^+ (or ND_4^+) reorientational motions. In addition, we observed a second T_1 minimum only in the mixed spin-glass systems in the temperature region of the glass transition. The values of T_1 at the second minimum vary with the ammonium concentration x. We interpret this lower temperature T_1 minimum to be due to the extreme slowing down of the O—H···O intrabond motions, a unique feature of the structural spin-glass system. A comparison between samples with different ammonium concentration shows that it is possible to use ^{31}P NMR studies to detect the threshold concentration for the spin-glass state. In addition, the correlation times and activation energies were determined from the T_1 minima in all samples. Furthermore, we were required to fit our lower temperature T_1 data with a stretched-exponential correlation function, thereby providing further evidence for the glassy nature of the mixed D-RADP systems. The current study is the first structural spin-glass observation using ^{31}P NMR.

II. ^{31}P T_1 MECHANISM IN $\mathrm{Rb}_{1-x}(\mathrm{NH}_4)_x\mathrm{H}_2\mathrm{PO}_4$ AND IN $\mathrm{Rb}_{1-x}(\mathrm{ND}_4)_x\mathrm{D}_2\mathrm{PO}_4$

Spin-lattice relaxation in the mixed solids, $\mathrm{Rb}_{1-x}(\mathrm{NH}_4)_x\mathrm{H}_2\mathrm{PO}_4$ and $\mathrm{Rb}_{1-x}(\mathrm{ND}_4)_x\mathrm{D}_2\mathrm{PO}_4$, is governed by several mechanisms because of its complicated structure and the substitution of Rb^+ for NH_4^+ (or ND_4^+). However, for a particular nucleus (e.g., ^{31}P, ^{87}Rb, etc.), only the neighboring structure affects the relaxation. The role of ^{31}P nuclei in the structure is that they form PO_4^{3-} tetrahedra in which the oxygens link both acid and ammonium protons (or deuterons) by forming O—H···O and N—H···O (or O—D···O and N—D···O) bonds.[5] For the mixed solid solution with Rb^+ substituted for NH_4^+ (or ND_4^+), the PO_4^{3-} positions are not changed substantially.

The intramolecular effects on the ^{31}P relaxation rate of PO_4^{3-} reorientational motions can be neglected, since the dominant oxygen isotope (^{16}O) is not magnetic and does not contribute appreciably to dipolar interactions. At the temperatures of our measurements, we would expect phosphate reorientations to be very infrequent, because of the strong bonding between the oxygens and the protons. Furthermore, reorientations of the PO_4^{3-} tetrahedron about an axis that passes through the ^{31}P nucleus, would not contribute to T_1 at all, since ^{31}P-^{1}H (or ^{31}P-^{2}D) interactions would not then be modulated. Ammonium reorientations or acid motions, on the other hand, would have a relatively weak effect on the ^{31}P relaxation but a strong effect on the ^{1}H (or ^{2}D) relaxation, and is consistent with our observations. The important contributions come from motions of the next-nearest neighbors, the O—H···O protons (or deuterons) and N—H···O protons (or deuterons). This feature suggests that ^{31}P NMR may be able to detect *both* ammonium and O—H···O motions since PO_4^{3-} links both types of bonds.[12] In contrast, previous studies[5,7] show that the ND_4^+ deuteron T_1 detects only the ND_4^+ motions while the O—D···O T_1 detects only the O—D···O motions. Since these two motional minima occur at widely separated temperatures, the same nucleus (^{31}P) can be used to study and resolve both kinds of motions.

The spin-lattice relaxation of ^{31}P arises from fluctuations of the local field $H_{\mathrm{loc}}(t)$, which includes all dipolar interactions of a ^{31}P spin with its neighbors. The Hamiltonian for such an interaction can be written

$$\mathcal{H}=-\gamma\hbar I H_{\mathrm{loc}}(t)\ , \tag{1}$$

where $I=\frac{1}{2}$ for ^{31}P. If only the contributions from neighboring O—H···O and NH_4^+ motions are included, the local field can be expressed as

$$H_{\mathrm{loc}}(t)=H_1(t)+H_2(t)\ , \tag{2}$$

where $H_1(t)$ is the contribution from ammonium protons (or deuterons) and $H_2(t)$ is that from acid protons (or deuterons). The correlation function corresponding to these two types of motions are

$$G(t)=G_1(t)+G_2(t)\ , \tag{3}$$

where the correlation function due to NH_4^+ motion is the conventional exponential

$$G_1(t)=A\exp(-t/\tau_1)\ . \tag{4}$$

The correlation function $G_2(t)$ for O—H···O motions, which describes the occupancy[13,15] exchange for the proton in the double-well potential, was reported[15] to be very small in pure KDP systems including pure ADP and RDP, even at the lowest temperatures measured, but to be much larger[7] in the spin-glass ground state of mixed RADP, due to the O—D···O slowing-down and formation of local clusters. A time-dependent order parameter, similar to the Edwards-Anderson order parameter in magnetic spin glass,[5,16] can be introduced to describe such a correlation, and is given by

$$q(t)\propto\langle p(0)p(t)\rangle\ , \tag{5}$$

where p is the electric dipole moment associated with the well occupancy of an O—H···O proton (or O—D···O deuteron). In pure ADP, DADP, or RDP, $G_2(t)$ [which is proportional to $q(t)$] can be expressed as a single exponential,

$$G_2(t)=B\exp(-t/\tau_2)\ , \tag{6}$$

because it is a single process. This single exponential correlation function also describes the high-temperature phase of the mixed systems, where thermal motion is significant. However, the random formation of locally ordered clusters in the low-temperature spin-glass phase of the mixed crystals destroys the long-range order and results in a distribution of the correlation times. Such a correlation function often can be expressed as a stretched exponential

$$G_2(t)=C\exp(-t/\tau_2)^{\alpha}\ , \tag{7}$$

where the exponent α is less than unity but approaches unity at high temperatures, where rapid thermal intrabond motions destroy the clusters.

Since both Eqs. (4) and (6) are single exponentials, $G(t)$ for pure systems can be expressed as the sum of ammonium (G_1) and acid (G_2) contributions,

$$G(t)=A\exp(-t/\tau_1)+B\exp(-t/\tau_2)\ . \tag{8}$$

Since the two correlation times will usually have different temperature dependences, there exist temperatures for which $\tau_2 \ll \tau_1$ and the first term is dominant, and there exist other temperatures for which the second term is dominant.

In a mixed glass system, on the other hand, the correlation function is

$$G(t)=A\exp(-t/\tau_1)+B\exp[-(t/\tau_2)^{\alpha}] , \tag{9}$$

which also reduces to a single exponential for $\tau_2 \ll \tau_1$. The stretched-exponential term will be dominant when $\tau_2 \gg \tau_1$.

Using the above assumptions for the correlation functions, we can write the spectral density

$$J(\omega)=\int_{-\infty}^{\infty}\exp(-i\omega t)G(t)dt \tag{10}$$

in terms of τ_1 and τ_2. For the pure systems,

$$J(\omega)=a\frac{\tau_1}{1+(\omega\tau_1)^2}+b\frac{\tau_2}{1+(\omega\tau_2)^2} \tag{11}$$

and, for the glass system,

$$J(\omega)=c\frac{\tau_1}{1+(\omega\tau_1)^2}+d\frac{2\tau_2}{\alpha}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n)!}\Gamma\left[\frac{2n+1}{\alpha}\right](\omega\tau_2)^{2n} , \tag{12}$$

where the second term in the above equation was obtained first by Sobal *et al.*[17]

III. EXPERIMENTAL FEATURES

The pure ADP and DADP single crystals were obtained from a commercial source whereas the pure RDP and the mixed samples were provided by Blinc's group in the Jozef Stefan Institute, Ljubljana, Slovenia.

The ^{31}P NMR measurements were performed at $\nu_0=32.5$ MHz using the saturation-recovery pulse sequence. [Since the spin-lattice relation time is very long (≥ 10 s), the saturation-recovery sequence is superior to the inversion-recovery sequence.]

Temperature variation was obtained by the helium flow method using a temperature controller (Lake Shore Cryotronics, Inc., Model DRC-91C). The temperature stability was better than ± 1 K in most of our measurements.

IV. ^{31}P OBSERVATION OF AMMONIUM MOTIONS IN PURE CRYSTALS

Figures 1(a) and 1(b) show the ^{31}P spin-lattice relaxation rate T_1^{-1} as a function of $1/T$. A single Bloembergen Purcell Pound[18] (BPP)-type T_1^{-1} maximum was observed in both ADP and DADP. The slopes on each side of the T_1^{-1} maximum are equal in magnitude, as anticipated for a single correlation time. A single symmetric type T_1 minimum corresponds to either the first or the second term of Eq. (11) being dominant. Since only a single T_1^{-1} maximum, which has been attributed to NH_4^+ reorientations,[15] has been observed, the effects of O—H $\cdots$ O motion on the ^{31}P T_1 relaxation rate can be ruled out at least at these higher temperatures. The fact that no further T_1 minimum is observed in these two pure crystals at lower temperatures suggests that the O—D $\cdots$ O mechanism involves motions that cannot satisfy $\omega\tau_2=1$ at any temperatures studied. Such behavior is common to KDP and DKDP systems.[15] Furthermore, this T_1^{-1} maximum, appearing at 180 and 168 K for pure DADP and ADP, respectively, corresponds to a single activation energy ($E_a=165$ meV for the deuterated and 186 meV for the undeuterated samples). In view of the similarity between these activation energies and that previously obtained from ND_4^+ deuteron data[7,9] as well as the similarity of the temperatures of the ^{31}P and ND_4^+ T_1 minima, we can conclude that this ^{31}P T_1 minimum and the ND_4^+ deuteron T_1 minimum are due to the very same mechanism (i.e., ammonium reorientations[5,7]).

Since this T_1 minimum is driven by the ammonium motions, a noticeable isotope effect is expected when substituting deuterons for the protons. The ND_4^+ tumbling

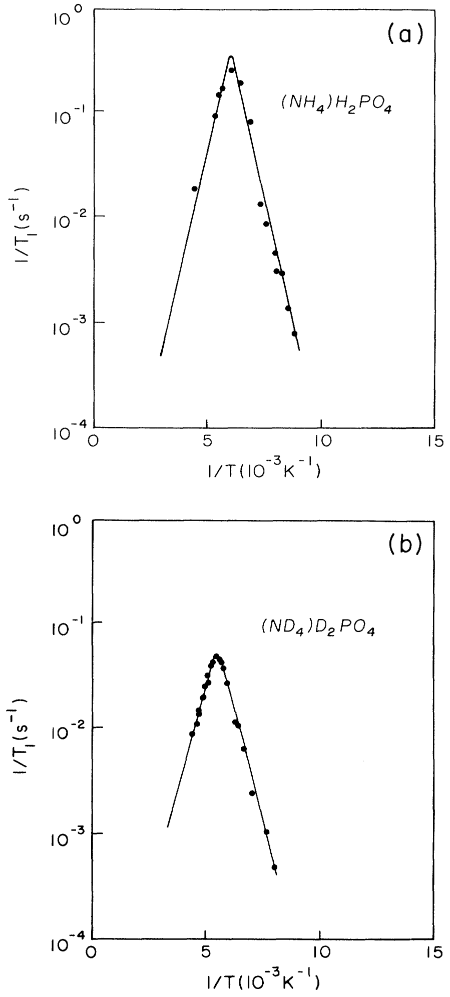

FIG. 1. The spin-lattice relaxation rates as a function of $1/T$ in (a) pure ADP and (b) pure DADP. Note that only a single peak is observed in each case. This peak corresponds to ammonium motions in these compounds. The solid curves are merely to guide the eye.

motion is slower than that of NH_4^+ at a given temperature and corresponds to a longer correlation time. Therefore, it is expected that the T_1 minimum will shift towards a higher temperature for DADP relative to that for ADP, as is observed in our experiments (Fig. 1). In addition, the relaxation rate is also reduced for the deuterated case, since the magnetic moments are considerably smaller for the deuterons than for the protons.

V. ^{31}P OBSERVATION OF BOTH AMMONIUM AND O—D · · · O MOTIONS IN MIXED SPIN-GLASS SYSTEMS

The O—D · · · O motions, characterized by fluctuations of the proton (deuteron) occupancy of the two wells of the double potential-well, behave quite differently in mixed spin-glass systems than in the pure systems. Due to the slowing down of O—D · · · O motions within locally ordered clusters in the mixed crystals, the rate of these slower O—D · · · O motions may be comparable to the Larmor frequency and thus be readily detectable by NMR relaxation techniques.

Figure 2 shows T_1^{-1} for ^{31}P as a function of $1/T$ in the mixed crystal RADP with $x=0.44$. Two T_1^{-1} maxima were observed. The higher-temperature maximum, which appears in the same temperature region as that for pure ADP and DADP, is symmetric (equal slopes) and clearly corresponds to the ammonium motion. This result implies that the correlation time τ_2 is so small that $\omega\tau_2 \ll 1$, so that the second term in Eq. (12) is much smaller than the first term. In addition to this T_1^{-1} maximum at 160 K a second T_1^{-1} maximum appears at lower temperatures where a structural spin-glass transition is expected.[2,7] The temperature corresponding to this T_1^{-1} maximum is very close to that at which the T_1^{-1} maxima for ^{87}Rb and O—D · · · O were observed.[7] This result suggests that all three T_1^{-1} maxima arise from the same mechanism, namely, the slowing down of the O—D · · · O motions, a characteristic of the spin-glass state. As the temperature decreases below that of the high-temperature T_1^{-1} maximum, the slowing down of the O—D · · · O motions effectively increases τ_2, so that the contribution to the relaxation rate from the second term in Eq. (12) increases as the temperature decreases and becomes dominant when $\tau_1 < \tau_2$. Thus, in the lower-temperature region,

$$J(\omega) \propto \frac{2\tau_2}{\alpha} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n)!} \Gamma\left[\frac{2n+1}{\alpha}\right] (\omega\tau_2)^{2n} . \tag{13}$$

On the high-temperature side of the second T_1^{-1} maximum, $\omega\tau_2 < 1$ and only the $n=0$ term is important, so that

$$J(\omega) \propto \frac{2\tau_2}{\alpha} \Gamma\left[\frac{1}{\alpha}\right] \propto \tau_2 . \tag{14}$$

Note that the spectral density depends linearly on τ_2 in this temperature region, as does the usual BPP-type relaxation. However, on the low-temperature side of the maximum, $\omega\tau_2 \gg 1$, and an asymptotic expansion[13] of Eq. (13) yields

$$J(\omega) \propto \omega^{-1-\alpha} \tau_2^{-\alpha} . \tag{15}$$

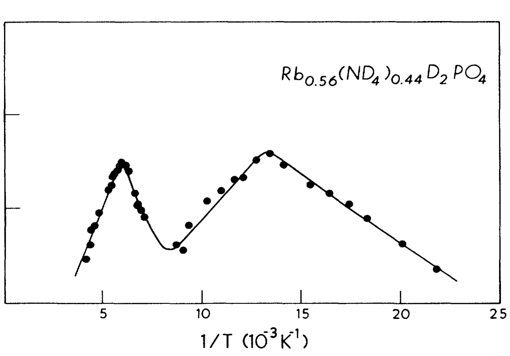

FIG. 2. The spin-lattice relaxation rate as a function of $1/T$ in the mixed single-crystal DRADP having $x=0.44$. Note that two T_1^{-1} maxima were observed in this system. The one at high temperatures is driven by ammonium motions and the one at low temperatures is due to the slowing-down of O—D · · · O motions. The low-temperature one is absent in pure ADP or RDP. The solid curve is merely to guide the eye.

This slope on the lower-temperature side is less steep than that on the high-temperature side as anticipated, since $\alpha < 1$ for the glass state. The asymmetry of the slopes is observed in Fig. 2. Similar features were also observed in the ^{87}Rb and ^{2}D O—D · · · O studies, suggesting that the asymmetric T_1^{-1} maximum is a fundamental property of the spin-glass phase. The differences in slope correspond to differences in the activation energy. The activation energy E_a calculated from the high-temperature slope is 51 meV; while the apparent activation energy E' of the low-temperature slope is 25 meV. From these two activation energies, we determined the exponent α and obtained $\alpha=0.48$. This value of α is consistent with the result obtained directly from the O—D · · · O deuteron measurements, thereby further demonstrating that the O—D · · · O (or O—H · · · O) freeze-out is detectable by ^{31}P NMR. Moreover, our current method of using a spin-$\frac{1}{2}$ nucleus eliminates any ambiguity in distinguishing multilevel transition effects for quadrupolar nuclei in a mixture of O—D · · · O and ammonium deuterons.

It is important to point out that this low-temperature T_1^{-1} peak is observed only in the mixed spin-glass system, and does not appear in either Fig. 1(a) or 1(b). For comparison, we also performed[19] similar ^{31}P measurements on a pure RDP single crystal and observed no T_1^{-1} maximum over the temperature range 180–77 K. Rather, as the temperature was lowered, T_1 was observed to increase monotonically (up to hours in length). This value is several orders of magnitude longer than the value (10 s) observed at the T_1^{-1} maximum in mixed glass systems. The absence of a low-temperature T_1^{-1} maximum in pure RDP clearly rules out the possibility that the low-temperature T_1^{-1} maximum observed in mixed systems might somehow be related simply to motional processes that occur in pure RDP. Hence, we conclude that the second T_1^{-1} maximum is due to the critical slowing-down of the O—D · · · O motions in the PSG state and is a unique property of pseudo-spin-glass systems.

VI. ^{31}P DETECTION OF THE ONSET OF THE PSG STATE

In the last section, we showed that a second T_1^{-1} peak is observed in the low-temperature region associated with the spin-glass transition in a typical glass system ($x=0.44$), and explained this T_1^{-1} maximum as due to the slowing down of O—D · · · O motions. In order to determine experimentally the dependence of the spin-glass state formation on ammonium concentration, we performed similar measurements in two other mixed crystals whose ammonium concentrations ($x=0.22$ and 0.78) represent approximately the two boundaries of the pseudo-spin-glass region. Together with the $x=0.44$ crystal, these measurements spanned the range of ammonium concentrations that can result in spin-glass states in the low-temperature phase.

Figures 3(a) and 3(b) show T_1^{-1} for ^{31}P as a function of $1/T$ for (a) $x=0.22$ and (b) $x=0.78$. In Fig. 3(a) we observed two T_1^{-1} maxima similar to those obtained for $x=0.44$, indicating that, for this sample at this ammonium concentration, the low-temperature state is still a spin-glass phase. In contrast, for the $x=0.78$ crystal [Fig. 3(b)], the low-temperature peak of T_1^{-1} is significantly flatted out, indicating that this ammonium concentration x may correspond to the borderline concentration for a spin-glass state.

Although the two nominal concentrations $x=0.22$ and 0.78 appear to be symmetric about $x=0.5$, the threshold concentration for a glass state is not necessarily symmetric about $x=0.5$. In view of the different transition temperatures for the pure crystals[13,20] ($T_C=242$ K for pure DADP and $T_C=218$ K for pure DRDP), it is clear that the spin-glass phase diagram should be somewhat asymmetric[3] about $x=0.5$, as we have observed in our NMR measurements.

Comparison of the NMR experimental results obtained in the above three mixed crystals with different ammonium concentrations suggests that it is possible to identify the threshold concentration and the onset of a PSG state by measurement of ^{31}P spin-lattice relaxation. It may be that NMR offers the most sensitive technique for detecting the onset of this transition.

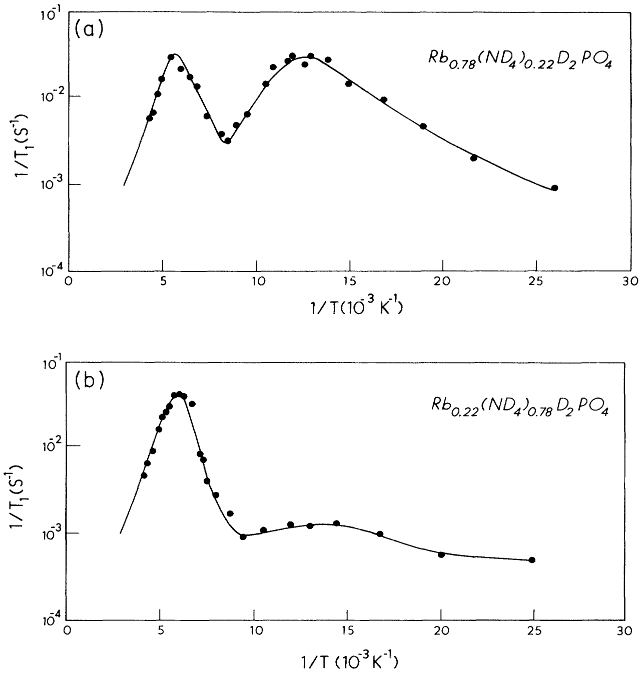

FIG. 3. The spin-lattice relaxation rate as a function of $1/T$ in DRADP mixed single crystals having (a) $x=0.22$ and (b) $x=0.78$. The solid curves are merely to guide the eye.

VII. DISCUSSIONS AND SUMMARY

In this paper, we presented ^{31}P NMR spin-lattice relaxation time measurements in pure single crystals ADP and DADP, as well as in mixed DRADP crystals having three different ND_4^+ concentrations. We demonstrated that the spin-glass properties can be observed by dipolar interactions via a spin-$\frac{1}{2}$ nucleus (^{31}P). The observation of a high-temperature T_1^{-1} maximum is interpreted as arising from fluctuations in dipolar interactions due to ND_4^+ reorientations, which is observable both in pure ADP and RADP. A second low-temperature T_1^{-1} maximum, which is observed only in the spin-glass systems, is due to O—D · · · O motions. We further demonstrated that the onset of the glass state can be detected via the ^{31}P T_1 measurements.

A stretched-exponential fit of the spin-lattice relaxation data in the low-temperature glass states of DRADP is not the only approach for the explanation of non-BPP-type behavior. However, this approach can be justified because of the existence of distributions of correlation times in the glass state.

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