^{14}N NMR study of the role of the N-D···O bonds in the deuteron glass transition

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^{14}N spin-lattice relaxation-time measurements in $Rb_{0.28}(ND_4)_{0.72}D_2PO_4$ provide direct evidence for the fast exchange averaging of the ''long'' and ''short'' N-D···O hydrogen bonds between the ND_4 group and the four surrounding PO_4 groups. This exchange and the associated distortion of the ND_4 tetrahedron induced by the ''acid'' deuteron intra-O-D···O motion determine the ^{14}N spin-lattice relaxation-time minimum around 78 K. The glass transition is not affected by the slowing down of the rotations of the ND_4 groups but reflects the gradual freeze-out of the O-D···O deuterons between the two equilibrium sites in the O-D···O bonds. [S0163-1829(99)10025-0]

I. INTRODUCTION

It is well known that substitutionally disordered solid solutions of ferroelectric RbD_2PO_4 (DRDP) and antiferroelectric $ND_4D_2PO_4$ (DADP) form at intermediate ammonium concentrations[1–9] $0.22 \leqslant x \leqslant 0.75$ a deuteron glass phase. This phase shows no macroscopic symmetry change on cooling and no long-range order down to the lowest temperatures investigated. In contrast to magnetic spin glasses the cusp in dielectric susceptibility is rounded[1–9] and the freezing takes place over an unusually large temperature interval far above the nominal glass transition temperature T_G.[10,11] For $x \leqslant 0.22$, on the other hand, a transition to an inhomogeneous ferroelectric and for $x \geqslant 0.75$ a transition to an inhomogeneous antiferroelectric phase is observed[10] in $Rb_{1-x}(ND_4)_xD_2PO_4$ systems at lower temperatures.

Whereas it is by now well established[10,11] that the deuteron glass transition is connected with a random freeze-out of the motion of the O-D···O deuterons between the two equilibrium sites in the O-D···O hydrogen bonds, much less is known about the role of the ND_4 groups in this transition.[12,13] It has been suggested that the ''acid'' deuterons freeze-out may be triggered by the rotational ordering of the ND_4 groups which mediate the interactions between different O-D···O bonds and—in contrast to the Rb ions—tend to induce antiferroelectric rather than ferroelectric ordering of the four ''acid'' deuterons around a given PO_4 group.

In order to check on the possible relation between the glassy freeze-out of the acid deuterons and the rotational freeze-out of the ND_4 groups, we have decided to measure the ^{14}N($I=1$) quadrupole perturbed NMR spectra and the ^{14}N and ND_4 deuterons spin-lattice relaxation times T_1 in a $Rb_{0.28}(ND_4)_{0.72}D_2PO_4$ single crystal as a function of temperature.

The idea of the experiment is as follows: In an isolated perfect ND_4^+ tetrahedron the electric-field gradient (EFG) tensor at the ^{14}N site is zero by symmetry. In an ADP crystal the EFG tensor at the ^{14}N site is mainly determined by the four N-D···O hydrogen bonds formed by the ND_4 group to the surrounding PO_4 groups (Fig. 1). In pure ADP each oxygen in the PO_4 group shares one O-D···O and one N-D···O hydrogen bond.[14] The N-D···O bonds may be ''short'' or ''long.''[14] The formation of the N-D···O bonds affects the ordering of the deuterons in the O-D···O bonds. The short N-D···O bond will tend to keep the acid deuteron away from the oxygen, i.e., it will push the deuteron to the ''far'' equilibrium site in the O-D···O bond. In contrast the formation of a long N-D···O bond should allow the acid deuteron to stay at the equilibrium site ''close'' to the H bond sharing oxygen (Fig. 1). The formation of short and long H bond should result in a small distortion of the ND_4 tetrahedron[15] and a finite electric-field gradient (EFG) tensor at the ^{14}N site. In $Rb_{1-x}(ND_4)_xD_2PO_4$ systems, some oxygen atoms will form N-D···O bonds while other oxygens will have Rb^+ neighbors, resulting in the absence of N-D···O bonds.

Because of the fast O-D···O intrabond deuteron motion the long and short N-D···O bonds and the ^{14}N EFG tensor should be exchange averaged at high temperatures. At lower temperatures a freeze-out is expected to take place.

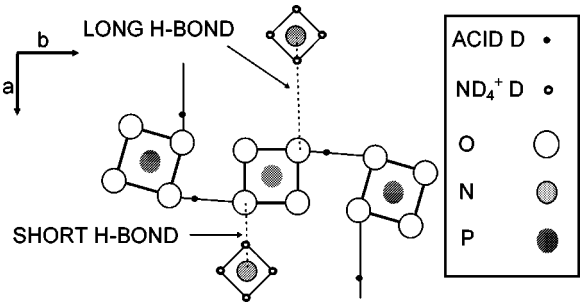

FIG. 1. Schematic projection of the structure of $ND_4D_2PO_4$ on the a-b plane. Each oxygen in a given PO_4 group shares two hydrogen bonds. It is linked by one O-D···O bond to the neighboring PO_4 group and by a N-D···O bond to the neighboring ND_4 group. Depending on the position of the deuteron in the O-D···O bonds the N-D···O bond is either short or long.

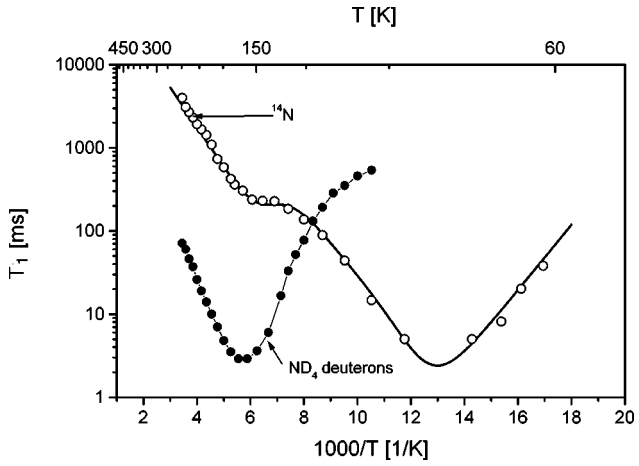

FIG. 2. Temperature dependence of the ^{14}N and ND_4 deuteron spin-lattice relaxation times T_1. The solid line shows the fit to Eqs. (1),(2a) and (2b).

By monitoring the ^{14}N T_1 and line shape we could thus get direct evidence for the existence of long and short N-D$\cdots$O bonds and gain additional information on the N-D$\cdots$O as well as O-D$\cdots$O dynamics and glass freeze-out. The measurements of the ND_4 deuteron T_1 should on the other hand show the possible role of the ND_4 rotational freeze-out on the ND_4 distortion and the deuteron glass transition.

II. EXPERIMENT

The ^{14}N NMR spectra have been measured at a Larmor frequency $\nu(^{14}\mathrm{N}) = 27.458$ MHz using the $90°(x)-90°(y)$ spin echo pulse sequence. The ^{14}N and ND_4 deuteron spin-lattice relaxation times T_1 have been obtained with the $90°-180°$ pulse sequence.

The temperature dependence of the ^{14}N and ND_4 deuteron spin-lattice relaxation times are shown in Fig. 2. The ^{14}N T_1 decreases on cooling down from room temperature, exhibits a shoulder between 175 and 158 K, and then continues to decrease with decreasing temperature until it reaches a broad minimum around 78 K. After that it starts to increase with decreasing T.

The ^{14}N T_1 ''shoulder'' around 175–158 K coincides with the ND_4 deuteron T_1 minimum (Fig. 2) due to the rotational freeze-out of the ND_4 groups. The much deeper ^{14}N T_1 minimum around 78 K is, on the other hand rather close to the acid deuteron T_1 minimum indicating the onset of the freeze-out of the intrabond O-D$\cdots$O deuteron motion.[9–11]

III. DISCUSSION

The above-^{14}N T_1 temperature dependence can be fitted to a model where the high-T part of the ^{14}N T_1 is determined by ND_4 rotation and low-T part by the O-D$\cdots$O acid deuteron intrabond motion inducing the exchange between long and short N-D$\cdots$O bonds:

$$\left(\frac{1}{T_1}\right)_{\mathrm{N}} = \left(\frac{1}{T_1}\right)_{\mathrm{rot,ND_4}} + \left(\frac{1}{T_1}\right)_{\mathrm{acid\ D}}, \qquad (1)$$

where

$$\left(\frac{1}{T_1}\right)_{\mathrm{rot,ND_4}} = A\left(\frac{\tau_{\mathrm{rot}}}{1+\omega_L^2\tau_{\mathrm{rot}}^2} + \frac{2\tau_{\mathrm{rot}}}{1+4\omega_L^2\tau_{\mathrm{rot}}^2}\right) \qquad (2a)$$

and

$$\left(\frac{1}{T_1}\right)_{\mathrm{acid\ D}} = B\left(\frac{\tau_{\mathrm{acid}}}{1+\omega_L^2\tau_{\mathrm{acid}}^2} + C\frac{2\tau_{\mathrm{acid}}}{1+4\omega_L^2\tau_{\mathrm{acid}}^2}\right). \qquad (2b)$$

Here we have $\tau_{\mathrm{rot}} = \tau_{0,\mathrm{rot}}\exp(E_{\mathrm{a,rot}}/kT)$ with $\tau_{0,\mathrm{rot}} = 1.4\ 10^{-12}$ s and $E_{\mathrm{a,rot}} = 153$ meV, whereas $\tau_{\mathrm{acid}} = \tau_{0,\mathrm{acid}}\exp(E_{\mathrm{a,acid}}/kT)$ with $\tau_{0,\mathrm{acid}} = 3.3\ 10^{-13}$ s and $E_{\mathrm{a,acid}} = 78$ meV. The constant $A = 1.6\ 10^5\ \mathrm{s}^{-2}$ describes the ^{14}N-deuteron dipolar coupling, the constant $B = 2.0\ 10^7\ \mathrm{s}^{-2}$ an ^{14}N EFG tensor fluctuation and the constant $C = 1$.

The above results show not only that the ND_4 rotation is much slower than the O-D$\cdots$O deuteron intrabond motion but also that the hypothetical exchange averaging of the long and short N-D$\cdots$O bonds due to acid deuteron intrabond O-D$\cdots$O motion really exists and dominates the ^{14}N T_1 at lower temperatures. The observed activation energy for the averaging of the long and short N-D$\cdots$O bonds $E_a = 78$ meV is very nearly the same as that obtained from the acid deuteron T_1 intrabond motion studies in $Rb_x(ND_4)_{1-x}D_2PO_4$ (Ref. 9) and pure KD_2PO_4.[16] This means that the N-D$\cdots$O bond character exchange is indeed driven by the O-D$\cdots$O intrabond deuteron motion and not by ND_4 rotations.

We may thus conclude the following:

(1) The most effective source of the ^{14}N spin-lattice relaxation—as measured by the depth of the low-T T_1 minimum—is the fluctuation in the EFG tensor at the ^{14}N sites induced by the ''biased'' exchange of the long and short N-D$\cdots$O bond characters and the resulting change is the distortion of the ND_4 tetrahedron. This fluctuation is driven by the fast O-D$\cdots$O acid deuteron intrabond motion.

(2) At higher temperatures this motion is too fast as compared to the ^{14}N Larmor frequency and the much slower ND_4 rotation becomes rate determining for the ^{14}N T_1. This rotation amounts to an exchange of deuterons positions in the distorted ND_4 tetrahedron and results in fluctuations in the ^{14}N deuteron dipolar coupling. The correlation times for the ND_4 rotation and the long and short N-D$\cdots$O bond character exchange fluctuations are compared in Fig. 3.

(3) The fact that the activation energy $E_a = 78$ meV for the exchange between long and short N-D$\cdots$O bonds is practically the same as the one for the deuteron intrabond O-D$\cdots$O$\leftrightarrow$O$\cdots$D-O motion in this systems as well as in KD_2PO_4, where there are no ND_4 groups, demonstrates that these two processes are not affected by the freeze-out of the ND_4 rotation. The glass transition is thus driven by the freeze-out of the O-D$\cdots$O intrabond motion mediated in part by the N-D$\cdots$O bond character exchange and not by the slowing down of the rotations of the ND_4 groups.

The above statements are supported by the temperature dependence of the ^{14}N NMR spectra (Fig. 4). At room tem-

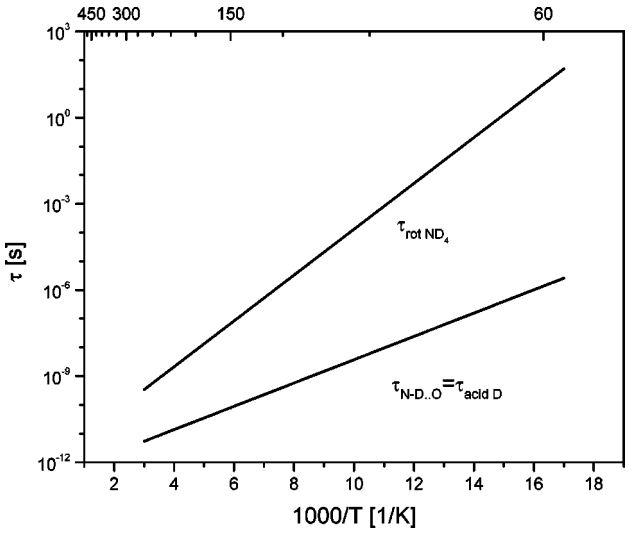

FIG. 3. The temperature dependence of the correlation times for the ND_4 rotation $\tau_{\mathrm{rot,ND_4}}$ and the exchange averaging of the long and short N-D$\cdots$O bond characters $\tau_{\mathrm{exchN\text{-}D\cdots O}}=\tau_{\mathrm{acid,D}}$.

perature the quadrupole splitting between the two $^{14}\mathrm{N}|-1\rangle \rightarrow|0\rangle$ and $|0\rangle\rightarrow|1\rangle$ satellite transitions amounts to about 35 kHz at this orientation. This means that even at room temperature the ND_4 tetrahedron is distorted as indeed assumed in deriving Eq. (2a). What is even more significant is the T-dependent broadening of the two ^{14}N doublet components between room temperature and 120 K, i.e., in the region where both the ND_4 rotation as well as the O-D$\cdots$O

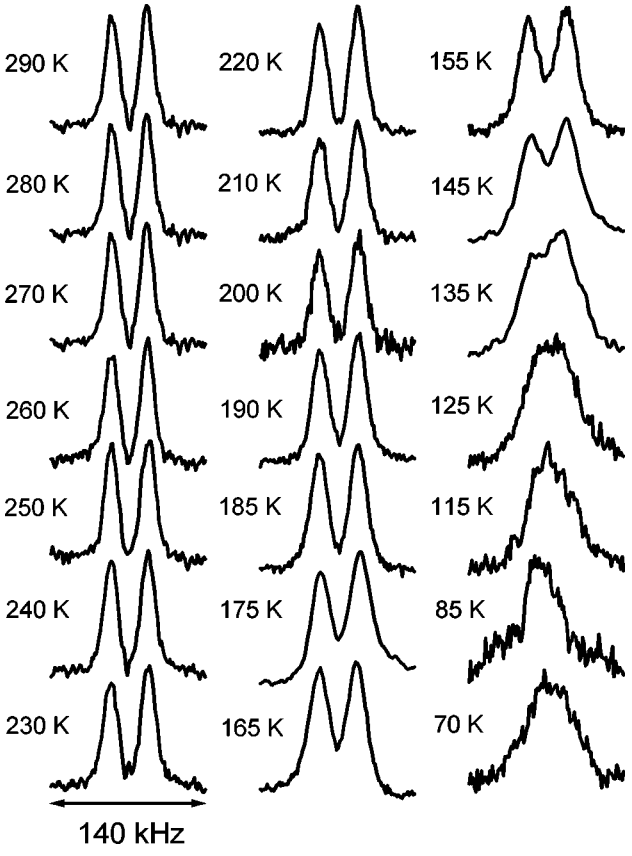

FIG. 4. ^{14}N quadrupole perturbed NMR spectra of $Rb_{0.28}(ND_4)_{0.72}D_2PO_4$ at different temperatures.

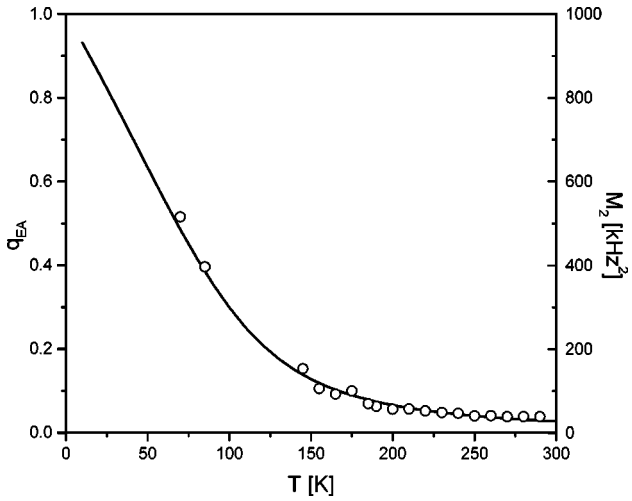

FIG. 5. Temperature dependence of the second moment M_2 and the Edwards-Anderson glass order parameter q_{EA} as derived from the ^{14}N NMR spectra of $Rb_{0.28}(ND_4)_{0.72}D)2PO_4$. The solid line shows the fit to the random-bond–random-field pseudospin Ising model (Ref. 17).

intrabond motion is fast on the NMR time scale (Fig. 3). This broadening is inhomogeneous as shown by the Hahn T_2^{-1} and is indicative of a glass transition smeared out by the presence of random fields.[17]

The local polarization distribution function[11]

$$W(p)=\frac{1}{N}\sum_i \delta(p-p_i) \tag{3}$$

is no longer a delta function at $p=0$ but is characteristic of the glassy state and gradually broadens with decreasing T. Here $p=\langle S_i^z\rangle$ where the pseudospin $S_i^z=\pm 1$ describes the two possible positions of the deuteron in the O-D$\cdots$O bond.

The second moment of $W(p)$ is just the Edwards-Anderson glass order parameter

$$q_{EA}=\int W(p)p^2dp=\frac{1}{N}\sum_{i=1}^{N}\langle S_i\rangle^2 \tag{4}$$

which is simply related to the second moment of the inhomogeneously broadened ^{14}N NMR line. The EFG tensor at the ^{14}N site is—as already mentioned—determined by the four N-D$\cdots$O bonds to the four PO_4 oxygens hydrogen bonded to a given ND_4. The nature of these N-D$\cdots$O bonds in turn depends on the state of order of the acid deuterons in all four O-D$\cdots$O bonds which take part in the N-D$\cdots$O bonding scheme. The ^{14}N NMR frequency shift induced by the acid deuteron ''freeze-out'' is given by

$$\nu-\nu_0=\sum_{i=1}^{4} C_i p_i+\cdots . \tag{5}$$

Since there is no macroscopic polarization, the random average of expression (5) is zero. The random average of $(\nu-\nu_0)^2$ is, however, nonzero. The second moment of the inhomogeneous ^{14}N frequency distribution M_2 is thus in view of Eq. (4) simply proportional to the Edwards-Anderson order parameter

$$M_2 = \alpha q_{EA}. \tag{6}$$

The temperature dependence of M_2 and q_{EA} obtained from the broadening of the ^{14}N doublet components is shown in Fig. 5. It can be seen that q_{EA} is different from zero already at room temperature, i.e., far above the nominal ''random bond'' glass transition temperature $T_G \sim 90$ K. The result can be fitted by the random-bond–random field pseudospin Ising model[17] with a random-bond variance $J = 110$ K and a random-field variance $\Delta/J^2 = 0.2$ The fact that $q_{EA} \neq 0$ even for $T \gg T_G = J/k$ is due to the random-field smearing $\Delta \neq 0$ of the deuteron glass transition. The above results agree with the conclusions derived from ^{14}N T_1 data as well as with previous observations in deuteron and proton glasses[10–13] that a nonzero Edwards-Anderson order parameter develops far above the nominal glass transition T_G.

[1] Z. Trybula and J. Stankowski, Condens. Matter Phys. **1**, 311 (1998), and references therein; see, also, Z. Trybula, J. Stankowski, L. Szczepanska, R. Blinc, A. Weiss, and N. S. Dalal, Physica B **153**, 143 (1988).

[2] V. H. Schmidt, J. T. Wang, and P. Schnackenberg, Jpn. J. Appl. Phys., Suppl. **24**, 944 (1985).

[3] V. H. Schmidt, Ferroelectrics **72**, 157 (1987).

[4] Z. Kutnjak, R. Pirc, A. Levstik, I. Levstik, C. Filipič, R. Blinc, and R. Kind, Phys. Rev. B **50**, 12 421 (1994).

[5] T. K. Song, S. E. Moon, K. H. Noh, S. I. Kwun, H. K. Shin, and J. J. Kim, Phys. Rev. B **50**, 6637 (1994).

[6] E. Courtens, Ferroelectrics **72**, 229 (1987), and references therein.

[7] S. Hayase, H. Sakashita, and H. Terauchi, Ferroelectrics **72**, 245 (1987), and references therein.

[8] P. Prelovšek and R. Blinc, J. Phys. C **15**, L985 (1982).

[9] R. Blinc, D. C. Ailion, B. Günther, and S. Žumer, Phys. Rev. Lett. **57**, 2826 (1986).

[10] N. Korner, C. Pfammatter, and R. Kind, Phys. Rev. Lett. **70**, 1283 (1993).

[11] R. Blinc, J. Dolinšek, R. Pirc, B. Tadić, B. Zalar, R. Kind, and O. Liechti, Phys. Rev. Lett. **63**, 2248 (1989).

[12] R. Blinc, J. Dolinšek, V. H. Schmidt, and D. C. Ailion, Europhys. Lett. **6**, 55 (1988).

[13] S. Chen and D. C. Ailion, Phys. Rev. B **42**, 5945 (1990).

[14] R. O. Keelig, Jr. and R. Pepinsky, Z. Kristallogr. **106**, 236 (1955).

[15] T. Chiba, Bull. Chem. Soc. Jpn. **38**, 490 (1975).

[16] R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1975), and references therein.

[17] R. Pirc, B. Tadić, and R. Blinc, Phys. Rev. B **36**, 8607 (1987).