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ND_4 Deuteron NMR and the Smearing of the Glass Transition in $Rb_{1-x}(ND_4)_xD_2PO_4$.

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Abstract. – The broadening of the rotationally averaged ND_4^+ deuteron lines in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ due to the gradual «acid» deuteron freeze-out allows for a direct determination of the Edwards-Anderson pseudospin glass order parameter q far above the nominal glass transition temperature T_G. The data provide strong evidence for a model where the basic difference between magnetic spin glasses and proton or deuteron pseudospin glasses is the presence of an inherent random field resulting from the substitutional disorder. This field acts as an ordering field conjugate to the pseudospin glass order parameter q and is responsible for the smearing of the deuteron glass transition.

A frozen proton pseudospin glass phase has been recently observed at low temperatures in mixed solid solutions $Rb_{1-x}(NH_4)_xH_2PO_4$ of ferroelectric RbH_2PO_4 (RbDP) and antiferroelectric $NH_4H_2PO_4$ (ADP) for $0.22 \leq x \leq 0.74$ [1, 2]. In contrast to magnetic spin glasses the cusp in the dielectric susceptibility is rounded [1, 2] and the freezing takes place over an unusually large-temperature interval [1-4] far above the glass transition temperature T_G [5, 6]. The microscopic origin of this behaviour—which points towards a basic difference between spin glasses and proton glasses—is still a subject of intensive research.

The ferroelectric (FE) transition in RbDP is connected with the ordering of the «acid» O-H‥O protons into the two polar H_2PO_4 Slater configurations, whereas the antiferroelectric (AFE) transition in ADP involves a different type of «acid» O-H‥O ordering. Here the O-H‥O protons order into the four «lateral» H_2PO_4 Slater configurations [7]. X-ray diffraction results [8, 9] have shown that in ADP each NH_4 ion is shifted below T_c to an off-centre position by forming two shorter and two longer N-H‥O hydrogen bonds with the four surrounding PO_4 tetrahedra.

The microscopic origin of the difference in the O-H‥O proton ordering [10] in FE RbDP and AFE ADP is an NH_4-mediated indirect pseudospin-type interaction between «acid» O-H‥O protons belonging to different PO_4 groups [11-13]. When a PO_4 oxygen is connected to an NH_4 group by a «short» N-H‥O bond, it tends to keep the «acid» proton in the O-H‥O bond in the «far» position, whereas it tends to keep the «acid» proton in the «close» position nearby if the N-H…O bond is «long». The requirement that two adjacent N-H…O bonds be short is incompatible with the FE ordering of protons around the PO_4 groups, but is compatible with AFE ordering. This indirect proton-proton coupling is random in $Rb_{1-x}(NH_4)_xH_2PO_4$. There, the NH_4 ions also induce a tilt in the double-well potentials of those O-H…O bonds, where one oxygen is N-H…O bonded, while the other neighbours on a Rb ion. This tilt can be simulated by a random field acting on the O-H…O pseudospins [14].

In the paraelectric phase of deuterated ADP all ND_4 groups in the unit cell are equivalent (1). The environment of each ND_4^+ ion is identical and axially symmetric along the crystal c-axis on the time scale of the NMR experiment. This is so because of the fast intrabond motion of the «acid» deuterons between the two possible equilibrium sites in the O-D…O bonds. In view of the fast hindered rotation [14] of the ND_4^+ groups—which is, however, much slower than the O-D…O intrabond motion—each D site in a given ammonium ion experiences the same time-averaged electric-field gradient (EFG) tensor which is axially symmetric. Such a behaviour has been indeed observed in paraelectric DADP (see (1)) and DADA [10], where the ND_4 deuteron quadrupole coupling constant e^2qQ/h has been found to be 3.6 kHz and the asymmetry parameter is zero $\eta = (V_{XX} - V_{YY})/V_{ZZ} = 0$.

In the AFE phase the situation is radically different. The freeze-out of the «acid» O-D…O deuteron intrabond motion at T_c results in a nonaxially symmetric environment and the «static» formation of two «short» and two «long» N-H…O bonds for a given ND_4^+ off-center site. This results in a nonzero value of the asymmetry parameter η. Above 110 K the hindered rotation of the ND_4^+ ion is still fast enough so that all four deuterons in a given ND_4 group experience the same rotationally averaged EFG tensor. Any one of the four AFE domains has an ND_4^+ deuteron EFG tensor, whose direction cosines have the same c component, but whose projections on the (a, b)-plane differ in view of the asymmetric positions that the ND_4 ions occupy relative to the four oxygens to which they are hydrogen bonded. This is indeed what has been found below T_c in DADP (see (1)) and DADA [10]. Here all ND_4^+ EFG tensors [10] are characterized by the quadrupole coupling constant $e^2qQ/h = 8.1$ kHz and the asymmetry parameter $\eta = 0.87$.

The observation of the rotationally averaged ND_4^+ deuteron EFG tensor in $Rb_{1-x}(ND_4)_xD_2PO_4$ should thus allow for a high-resolution study of the gradual O-D…O «acid» deuteron freeze-out and the role of the ND_4^+ ions in this pseudospin glass transition.

The temperature and angular dependences of the ND_4^+ deuteron Fourier transform NMR spectra have been measured for a series of mixed $Rb_{1-x}(ND_4)_xD_2PO_4$ single crystals at $\nu_L(^2H) = 41.462$ MHz using a $90°(x) - 90°(y)$ spin echo sequence. The width of the 90° pulse was 4 μs. Quadrature detection was used. The homogeneous linewidth T_2^{-1} was measured by the Hahn echo and the spin-lattice relaxation time T_1 by the $(180 \div 90)°$ pulse sequence.

The temperature dependence of the ND_4^+ deuteron lineshapes for $\bar{a} \perp \bar{H}_0$, $\sphericalangle\, \bar{c}, \bar{H}_0 = 150°$ and $x = 0.44$ are shown in fig. 1. Between room temperature ($T = 17$ °C) and $T = -115$ °C the spectrum is a doublet which can be described as a superposition of two Gaussians displaced by 3.9 kHz. The width of the two Gaussians slowly increases with decreasing temperature, whereas their separation and position are practically temperature independent. Due to the increase in the linewidth of the two Gaussians, the doublet splitting disappears below -120 °C and only a single «broad» line remains. At still lower temperatures the ND_4 rotation slows down so much that the ND_4^+ spectrum is not anymore rotationally averaged and additional fine structure due to the «rigid» lattice spectra of the ND_4^+ deuterons appears.

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(1) Unpublished work from this laboratory.

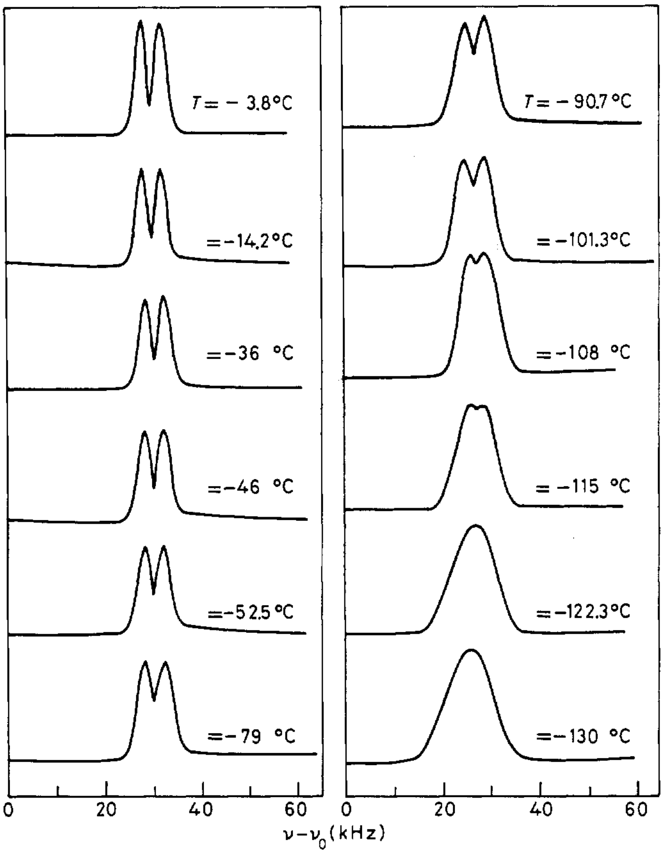

Fig. 1. – Temperature dependence of the ND_4^+ deuteron NMR lineshapes in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ for $\vec{a} \perp \vec{H}_0$, $\sphericalangle\, \vec{c}, \vec{H}_0 = 150°$. $\nu_0(^2H) = 41.46$ MHz.

The ND_4^+ doublet splitting observed at room temperature in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ 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 paraelectric phase at the ammonium site if all «acid» deuterons move fast between the two equilibrium sites in the O-D...O bonds. What is highly unusual—and very different from the situation in deuterated ADA—is the temperature-dependent broadening of the doublet components between + 17 °C and − 115 °C. The broadening is inhomogeneous—as shown by Hahn echo measurements—and anisotropic as expected if it is due to the gradual «freeze-out» of the «acid»-deuteron intrabond motion. At room temperature the homogeneous linewidth is ~ 700 Hz and the inhomogeneous 2.6 kHz, whereas at ~ 130 °C these two values are 900 Hz and 9.6 kHz, respectively. This cannot be due to the onset of the rotational freeze-out of the ND_4 groups as we are in the interval from + 17 °C to − 117 °C on the high-temperature side of the T_1 minimum (fig. 2) and thus in the fast-motion regime, where $\omega_L \tau_{rot} \ll 1$. An additional argument in favour of this statement is provided by the fact that the activation energy for ND_4 rotation is about 160 meV, whereas the activation energy for the observed ND_4 line broadening—if one tries to describe this as a thermally activated process—would amount to only 25 meV. It is thus safe to conclude that the observed ND_4^+ broadening is due to a gradual «freeze-out» of the «acid»-deuteron intrabond motion far above the glass

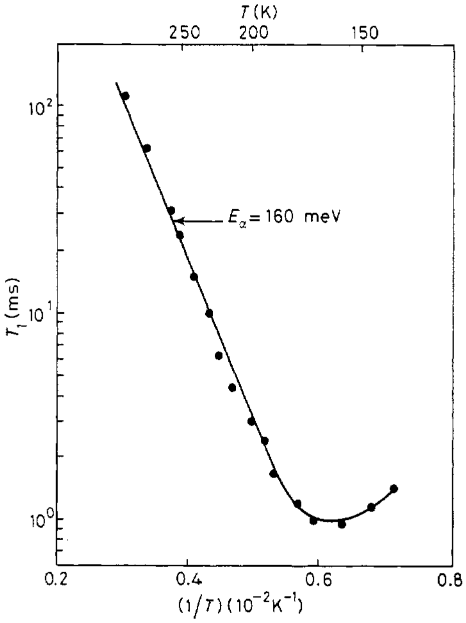

Fig. 2. – Temperature dependence of the ND_4^+ deuteron spin-lattice relaxation time T_1 in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ for $\vec{a} \perp \vec{H}_0$, $\sphericalangle\, \vec{c}, \vec{H}_0 = 150°$.

transition $T_G \approx 90$ K. It should be noted that above T_c in pure KD_2PO_4-type crystals the «acid» deuterons move between the two equilibrium sites in the O-D...O bonds with a rate $(10^{10} \div 10^{11})$ Hz and this motion «freezes-out» only below T_c.

The observed «acid» deuteron «freeze-out» far above T_G in $Rb_{1-x}(ND_4)_xD_2PO_4$ for $x = 0.44$ can be understood as a result of a random field smearing of the deuteron glass transition [14, 15]. The variance of the random field induced by the substitutional disorder acts as an ordering field conjugate to the Edwards-Anderson spin glass order parameter [15] and induces a finite value of this order parameter far above the nominal transition temperature T_G. This results in a random gradual O D $\cdots$ O deuteron freeze-out which in turn produces a broadening of the NMR line.

The effect on the ND_4^+ NMR lineshape far above T_G can be described by a temperature-dependent inhomogeneous broadening $(\sigma_1^2 q)$ which is proportional to the Edwards-Anderson order parameter and thus reflects the biasing of the O-D...O deuteron intrabond motion

$$I = I_0 \exp\left[-(\nu - \nu_0)^2/2(\sigma_0^2 + \sigma_1^2 q)\right]. \tag{1}$$

The lineshape is Gaussian far above T_G. The temperature-independent broadening σ_0^2 reflects the inherent width of the ND_4 line in the paraelectric phase.

The biasing effect can be derived as follows. The EFG tensor at the ND_4^+ site is influenced by the four N-D...O bonds to the four phosphate oxygens hydrogen bonded to the given ammonium ion. This contribution depends on the state of order of the deuterons in all four O-D...O bonds which take part in the N-H—O bonding scheme. The frequency shift induced by the acid deuteron «freeze-out» is thus given by

$$\nu - \nu_0 = \sum_{i=1}^{4} C_i p_i + \ldots, \tag{2}$$

where the local bond order parameter $p_i = \langle S_i^z \rangle$ measures the amount of deuteron ordering between the two equilibrium sites $S^z = \pm 1$ in the i-th O-D...O bond. NMR measures the random average of eq. (2)

$$\overline{\nu - \nu_0} = \overline{\sum_{i=1}^{4} C_i p_i} = 0\,, \tag{3a}$$

which is zero in a pseudospin glass where

$$\overline{p_i} = \frac{1}{N} \sum_{i=1}^{N} \langle S_i^z \rangle = 0\,, \tag{3b}$$

in view of the absence of long-range ordering. The deuteron «freeze-out» $\langle S_i^z \rangle \neq 0$ results, however, in a line broadening

$$\sigma^2 = \overline{(\nu - \nu_0)^2} = \overline{\left(\sum_{i=1}^{4} C_i p_i \right)^2} = \sigma_1^2 q\,, \tag{4}$$

which is directly proportional to the Edwards-Anderson order parameter q. It should be noted that the four $C_i p_i$ values in the sum (3a) are essentially uncorrelated. This is so as any path joining two acid deuterons in the sum crosses at least two phosphate groups, so that there is at least one intervening acid H-bond.

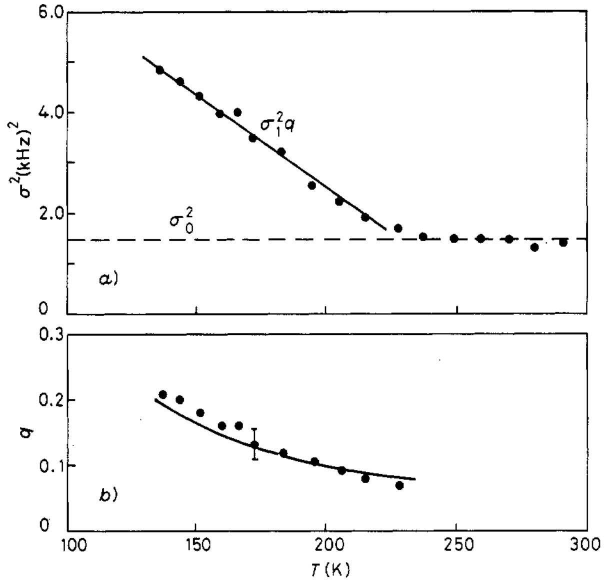

Fig. 3. – *a*) Temperature dependence of the ND_4^+ line broadening $\sigma_1^2 q$ in the interval from room T to $-117\,°C$ for $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$. *b*) Temperature dependence of the Edwards-Anderson order parameter q for $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ as determined from the linewidth data. The experimental points can be fitted to the theoretical curve (eq. (5)) for $\Delta/\tilde{J}^2 = 1.3$ and $\tilde{J}/k_B = 60$ K. ● experiment; —— theory.

According to eqs. (1) and (4) we can separate (fig. 3*a*)) the total width of the ND_4^+ line into a temperature-independent (σ_0^2) and a temperature-dependent part ($\sigma_1^2 q$). Using the data of pure DADP (see [1]) we can estimate σ_1^2 at $\measuredangle\, c, \overline{H} = 150°$ from the difference between the maximum ND_4^+ splitting below T_c—where all the acid protons are ordered—and the width at room temperature as $\sigma_1 \approx 4$ kHz. The resulting T-dependence of q is shown in fig. 3*b*).

The theoretical temperature dependence of q can be derived from the random bond-random field Sherrington-Kirkpatrick-type Ising model of spin glasses [15] as

$$q = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \exp[-x^2/2]\,\mathrm{tgh}^2\left(\frac{\tilde{J}}{kT}\sqrt{q+\Delta/\tilde{J}^2}\,x\right)\mathrm{d}x\,, \tag{5}$$

where $\tilde{J} = J\sqrt{N}$, J^2 is the variance of the random bond and Δ the variance of the random field distributions [15, 16]. For $\Delta \neq 0$, q is $\neq 0$ even for $T > T_G$, whereas $q = 0$ for $T > T_G$ if $\Delta = 0$. The least-square fit of eq. (5) to the experimental data allows for an independent determination of $\tilde{J}$ and Δ. We have measured a whole series of mixed deuterated solid solutions $Rb_{1-x}(ND_4)_xD_2PO_4$ with different ammonium concentrations (see (^{1})) and found that $0.4 \leqslant \Delta/\tilde{J}^2 \leqslant 1.3$ and $90\ \mathrm{K} \geqslant \tilde{J}/k_B \geqslant 60\ \mathrm{K}$. For $x = 0.44$ the theoretical T-dependence of q for $\Delta/\tilde{J}^2 = 1.3$ and $\tilde{J}/k_B = 60$ K agrees (fig. 3*b*)) rather well with the one obtained from the T-dependence of the line-broadening thus yielding strong support for the random field smearing [15] of the glass transition in $Rb_{1-x}(ND_4)_xD_2PO_4$ systems. The q-values vary from $q = 0.08$ at 227 K to $q = 0.21$ at 143 K, whereas the Almeida-Thouless replica symmetry breaking transition [15] T_G occurs in these systems below 90 K.

It should be noted that the above results obtained for deuteron glasses agree with previous observations in proton glasses [5, 6] that a nonzero Edwards-Anderson order parameter develops far above T_G. We believe that a random field smearing of the glass transition occurs in proton glasses as well.

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