Dynamics of Deuteron Glasses as Probed by 2 D Exchange NMR *

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The deuteron intra-bond dynamics of the deuteron glass phase in $Rb_{0.68}(ND_4)_{0.32}D_2AsO_4$ has been studied by 2 D exchange NMR which extends the NMR observation window from the kHz region into the milli-Hertz region. The results show that the $O-D\cdots O$ deuterons are indeed the basic reversible two-position dipoles in the structure and that deuteron intra-bond exchange – and thus dipole reversal transition – occurs deeply in the glass phase well below T_g where 1 D NMR techniques observe only frozen static glassy disorder.

Key Words: Deuteron glasses, 2 D exchange NMR.

I. Introduction

The basic question in the formation of glasses is whether the glass phase is a consequence of a new kind of thermodynamic phase transition or whether the motional freezing is a kinetic phenomenon observed because of the finite observation time of experimental techniques.

One possible answer has been obtained for magnetic spin glasses. Here Edwards and Anderson [1] introduced a statistical model leading to an ergodic-nonergodic phase transition with local freezing but without long-range ordering. Sherrington and Kirkpatrick [2] introduced an infinite range version of this model where the low temperature phase consists of an infinite number of pure states characterized by an infinite number of order parameters. Below the glass transition temperature the free-energy surface is highly degenerate with many global and side minima. The system can be trapped into one of the pure states corresponding to a given minimum. Depending on the potential barrier separating this minimum from other minima the system can either tunnel to another state or stay effectively locked in a given state. In structural glasses such as H-bonded proton and deuteron glasses the Sherrington-Kirkpatrick model has been extended to describe the frozen proton pseudo-spin glass (PG) phase observed in mixed hydrogen-bonded ferro- and antiferroelectric crystals such as $Rb_{1-x}(NH_4)_xH_2PO_4$, commonly abbreviated as RADP. In analogy to spin glasses, the frozen PG state is believed to be due to quenched random interactions between the pseudo-spin degrees of freedom, which represent the equilibrium positions of the protons within the $O-H\cdots O$ bonds. The simplest prototype model of a PG is the tunneling model [3], which has been further refined by introducing local random fields [4]. This field makes the H-bonds asymmetric and introduces glass disorder already far above the nominal glass temperature T_g. In the random field variance-temperature plane [5] there exists a line separating the ergodic phase, described by a single order parameter of the Edwards-Anderson type q_{EA}, from the nonergodic phase, described by an infinite number of order parameters. The random field-random bond model thus first predicts a phase transition at T_g from the paraelectric to an ergodic PG phase and than at lower temperature T_f another transition from the ergodic to a nonergodic PG phase.

Experimental verification of the existence of a phase transition in proton glasses is still far from being conclusive. Experimental determination of the field-cooled (fc) and zero-field-cooled (zfc) static dielectric susceptibilities of the deuteron glass $Rb_{0.4}(ND_4)_{0.6}D_2PO_4$ has shown [6] that above the freezing temperature T_f the two susceptibilities are equal, whereas the splitting of the two branches and a remanent polarization is observed below T_f. Repeating the experiment with ac fields of different frequencies in the range 0.1 to 0.001 Hz has however shown that the temperature, where the splitting of fc and zfc susceptibilities occurs, is frequency dependent. $T_f(\omega)$ was decreasing with decreasing ω.

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NMR lineshape [7–11] and spin-lattice relaxation studies have, on the other side, shown a perfectly static frozen-in disorder of the local H-bond polarization. The Edwards-Anderson order parameter q_{EA} has been determined in a large temperature interval. It has been shown that q_{EA} is non-zero already far above the nominal glass transition temperature T_g, which was found in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ to be around 85 K. This demonstrated the random field smearing of the glass transition from the paraelectric to the ergodic PG phase. q_{EA} could be determined from the second moment M_2 of the quadrupole perturbed Zeeman absorption lineshapes. It is understood that q_{EA}, which is conjugate to the variance of the random field, measures the order of an ergodic system effectively locked in one of the global or side minima of the fractal mountain-like free energy surface in the phase space. The Edwards-Anderson order parameter is – as it is defined – a true static quantity, thus supporting the hypothesis of a phase transition.

The determination of q_{EA} from NMR experimental data would lead to the conclusion that the glassy disorder in H-bonded systems like RADP is completely static, so we are dealing with a thermodynamically stable disordered state. Here we keep in mind that the observation window of the NMR lineshape measuring technique lies in the kHz region. To test the above conclusion, it is necessary to extend the observation window of NMR towards slower motions by several orders of magnitude.. Such an extension is possible by the application of 2 D "exchange" NMR spectroscopy. Here one correlates a certain state of the investigated system in two distinct instants of time. Since the same state is monitored coherently at two successive times, one can detect the internal motions which have time constants corresponding to the time separation between the two observations of the system. The separation time is called mixing time and can be as long as the spin-lattice relaxation time. Since the latter in DRADP mixtures amounts to several hundred seconds for deuteron nuclei at temperatures below 50 K, the observation window of 2 D exchange technique falls in the milli-Hertz region. The application of this technique should elucidate whether the perfectly frozen-in glass disorder – as seen by the NMR lineshape analysis – is a true equilibrium state of the system, or whether it appears to be static only because of the finite observation window of the measurement technique.

II. The Glass Order Parameter

The random bond-random field Ising model Hamiltonian for deuteron glasses can be written as [4, 12]

$$\mathscr{H} = -\tfrac{1}{2}\sum_{ij} J_{ij}\, S_i^z S_j^z - \sum_i h_i S_i^z\,, \tag{1}$$

where J_{ij} denote the infinite range quenched random interactions between the pseudo-spins S_i^z, whereas h_i represents the random longitudinal field at the site i produced by the substitutional disorder. The pseudo-spin variables $S_i^z = \pm 1$ represent the two positions of the deuteron in the O–D···O bond. The random interactions J_{ij} and fields h_i are independently distributed according to their respective Gaussian probability densities

$$D(J_{ij}) = (2\pi J^2)^{-1/2} \exp[-(J_{ij}-J_0)^2/(2J^2)]\,, \tag{2a}$$

$$D(h_i) = (2\pi \Delta)^{-1/2} \exp(-\tfrac{1}{2} h^2/\Delta)\,. \tag{2b}$$

Introducing $J_0 = \tilde{J}_0/N$ and $\tilde{J} = J/N^{1/2}$, where N is the number of lattice sites, one finds that for $h_i = 0$ and $|\tilde{J}_0| > \tilde{J}$ the system undergoes a paraelectric-ferroelectric transition ($\tilde{J}_0 > 0$) or paraelectric-antiferroelectric transition ($\tilde{J}_0 < 0$), whereas for $\tilde{J} \geq |\tilde{J}_0|$ a deuteron glass phase appears below a freezing temperature T_g.

The local polarization of a given H-bond is given by

$$p_i = \langle S_i^z \rangle\,, \tag{3}$$

where the brackets $\langle\ \rangle$ represent a thermodynamic (mean field) average. The average polarization of all bonds in the glass phase vanishes:

$$\bar{p} = \frac{1}{N}\sum_i \langle S_i^z \rangle = [\langle S_i^z \rangle]_{av} = 0\,. \tag{4}$$

Here the brackets $[\ ]_{av}$ denote the disorder average, i.e. the simultaneous average over the distribution of random bonds and random fields, (2a, b). The average square local polarization is, however, different from zero as the bonds are polarized but in a random spatial manner. The free energy of a glassy state in a phase space is believed to be highly degenerate, exhibiting many global and local minima (Figure 1a). The pseudo-spin system can in general visit many of these minima, and the appropriate order parameter to describe such a case is the "multi-valley" order parameter [13]

$$q = \frac{1}{N}\sum_i \Big[\sum_l P_l \langle S_i^z \rangle_l\Big]^2 = \Big[\Big[\sum_l P_l \langle S_i^z \rangle_l\Big]^2\Big]_{av}\,. \tag{5a}$$

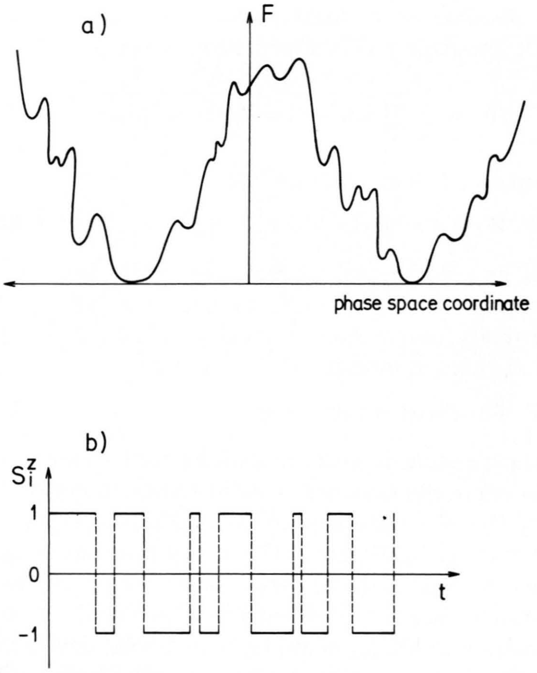

Fig. 1. a) Free energy surface in phase space of a glass state exhibiting degeneracy with many global and side minima. b) Time dependence of the pseudo-spin variable S_i^z, reflecting random jumps of proton or deuteron between two possible sites in the H-bond.

Here P_l is the probability of finding the system in the l-th valley and the summation is over all valleys. An experiment over a short time, however, measures the properties of the system effectively locked in one of the global or local minima. Such a "single-valley" order parameter corresponds to the case of infinitely high barriers ΔU between different valleys. This order parameter is of the "Edwards-Anderson" type

$$q_{\mathrm{EA}} = \frac{1}{N} \sum_i \langle S_i^z \rangle^2 = [\langle S_i^z \rangle^2]_{\mathrm{av}} \tag{5b}$$

and is obtained from the multi-valley order parameter q when all the probabilities P_l are zero except one which is 1.

It is possible to define the glass order parameter also in terms of dynamics. The S_i^z variable assumes in time randomly the values ± 1 (Figure 1b). The time-dependent local polarization is obtained as the time integral of $S_i^z(t)$ over the observation time t_{obs}:

$$p_i(t_{\mathrm{obs}}) = \frac{1}{t_{\mathrm{obs}}} \int_0^{t_{\mathrm{obs}}} S_i^z(t)\, \mathrm{d}t\,. \tag{6}$$

In the limit $t_{\mathrm{obs}} \to \infty$ one obtains the equilibrium polarization p_i, (3). The time-dependent glass order parameter is obtained as an average time-autocorrelation function of S_i^z [13]

$$q(t) = [\langle S_i^z(0)\, S_i^z(t) \rangle_{t'}]_{\mathrm{av}}\,, \tag{7a}$$

where the time average $< >_{t'}$ is performed over an observation time t_{obs}:

$$\langle S_i^z(0)\, S_i^z(t) \rangle_{t'} = \frac{1}{t_{\mathrm{obs}}} \int_0^{t_{\mathrm{obs}}} \mathrm{d}t' \, [S_i^z(t')\, S_i^z(t'+t)]\,. \tag{7b}$$

The Edwards-Anderson (single-valley) order parameter q_{EA} is obtained as the limiting case of $q(t)$ when the barriers between the valleys ΔU diverge and the time t tends to infinity:

$$q_{\mathrm{EA}} = \lim_{t \to \infty} \lim_{\Delta U \to \infty} q(t)\,. \tag{8a}$$

If the barriers stay finite we obtain the multi-valley order parameter q:

$$q = \lim_{t \to \infty} q(t)\,. \tag{8b}$$

Another interesting limit is obtained with regard to t_{obs}. In the limit of infinitely short observation time one observes an "instant-time" picture, where the system is in a single valley and everything is perfectly ordered in the moment of observation, yielding

$$\lim_{t_{\mathrm{obs}} \to \infty} q(t) = 1\,. \tag{8c}$$

In the intermediate case, when t_{obs} is neither infinitely short nor infinitely long, $q(t)$ actually depends on the integration time t_{obs} and will thus depend on the observation window in frequency space of different experimental techniques. What is important is the relation between the frequency windows of experimental techniques and internal molecular motions. Observation of the system with a window much higher in frequency than the frequencies of the molecular motions will probe the system as completely static, whereas the dynamics may appear in observations with the window shifted towards lower frequencies.

In deuteron glasses the glass phase appears as a consequence of the deuteron intra-H-bond motion freeze-out. When observed in an NMR spin-lattice and lineshape experiment the intra-bond motion appears as completely static at temperatures below 70 K. Here one has to take into account that the spin-lattice and lineshape techniques have the observation window in the range $10^8 - 10^3$ Hz. For a check whether the glass disorder is static also on lower time scales it is necessary to apply a technique with an observation window shifted towards lower frequencies. The 2D NMR exchange technique provides a possibility to monitor the O–D···O intrabond exchange down to milli-Hertz frequencies, thus extending the observation window by six orders of magnitude towards slower motions.

III. NMR Observation of Deuteron Intra-Bond Exchange in Deuteron Glasses

a) ^{87}Rb Lineshape Analysis in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$

The average position of a deuteron in a given hydrogen bond can be described by a local polarization p which is defined as the difference between the occupations of the "left" and "right" site of the bond. Random fields make the hydrogen bonds asymmetric and create the difference in populations of the two sites already in the fast intrabond motion limit. Local polarization is distributed over all bonds in the systerm by a probability distribution function $W(p)$ [8] which is defined as

$$W(p) = \frac{1}{N} \sum_i \delta(p - \langle S_i^z \rangle) = [\delta(p - \langle S_i^z \rangle)]_{\text{av}} . \quad (10)$$

For fast intrabond exchange, occurring at high temperatures, $W(p)$ becomes a delta-function at $p = 0$, whereas for slow exchange at low temperatures $W(p)$ becomes double-peaked at $p = \pm 1$. In deuteron glasses one measures with the NMR lineshape the probability distribution $W(p)$ since it modulates the electric field gradient tensor at a given nuclear site and affects the quadrupole-perturbed NMR lineshape. $W(p)$ is related to but not identical with the local field distribution $D(h)$, (2b). The first moment of the distribution function $W(p)$ is the total polarization P, which is zero in the absence of a homogeneous external electric field. The second moment yields in the ergodic glasss phase the Edwards-Anderson order parameter [8]

$$q_{\text{EA}} = \int \mathrm{d}p \, p^2 \, W(p) . \quad (11)$$

The relation between the Larmor frequency of a deuteron positioned at the i-th hydrogen bond is related to the bond polarization $p_i = \langle S_i^z \rangle$ in the simplest case as

$$\nu_i = \nu_0 + \nu_1 \langle S_i^z \rangle . \quad (12)$$

The distribution of local polarizations makes the NMR lineshape $f(\nu)$ inhomogeneously broadened,

$$f(\nu) = \frac{1}{N} \sum_i \delta(\nu - \nu_i) = [\delta(\nu - \nu_i)]_{\text{av}} . \quad (13)$$

Comparing (10) and (13) we find

$$W(p) = \nu_1 f(\nu), \quad \nu = \nu_0 + \nu_1 p . \quad (14)$$

Thus, an experimental determination of the inhomogeneously broadened NMR lineshape $f(\nu)$ yields the probability distribution of local polarization $W(p)$ and, the second moment of $f(\nu)$ gives q_{EA}:

$$\int \mathrm{d}\nu \, f(\nu)(\nu - \nu_0)^2 = \nu_1^2 \, q_{\text{EA}} . \quad (15)$$

The temperature dependence of the Edwards-Anderson order parameter obtained from the second moment of the $^{87}\text{Rb}\ \frac{1}{2} \rightarrow -\frac{1}{2}$ lineshape in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ [8] is displayed in Figure 2. The second moment M_2 is shown as a dashed line. M_2 is scaled to reach the saturation value 1 at low temperatures. The theoretical prediction for q_{EA} is displayed as a solid line. It is seen that between 370 K and 80 K q_{EA}, as determined from the second moment of the resonance line, follows the theoretical prediction, whereas below 70 K M_2 becomes saturated and deviates from the theoretical line for q_{EA}. If one would continue to extract q_{EA} from M_2, q_{EA} would be unity at all temperatures below 70 K, leading to the conclusion that the deuterons are

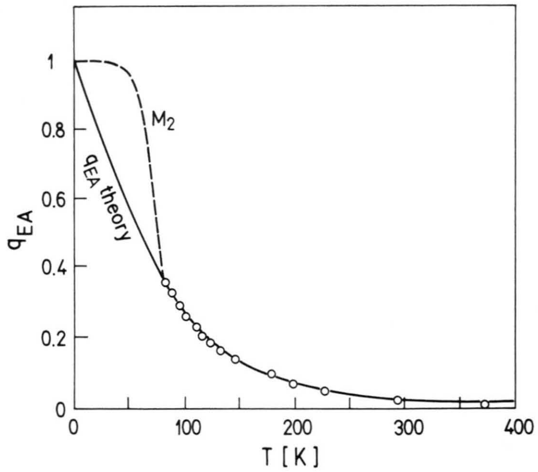

Fig. 2. Temperature dependence of the Edwards-Anderson order parameter q_{EA} as determined from the second moment of $^{87}\text{Rb}\ \frac{1}{2} \rightarrow -\frac{1}{2}$ NMR spectra in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$. The second moment M_2 is shown as a dashed line. The solid line represents a theoretical prediction for q_{EA} using the random bond-random field model.

fully ordered and disorder is completely static. The above conclusion is based on experimental results of NMR lineshape technique which has the observation window in the kHz region. It is interesting to contrast these results with the ones obtained by a 2D NMR exchange technique which is sensitive to several orders of magnitude lower deuteron intrabond exchange frequencies.

b) 2D NMR Exchange of Deuterons in $Rb_{0.68}(ND_4)_{0.32}D_2AsO_4$

In 2D NMR exchange spectroscopy of deuterons in DKDP-type systems one observes at low temperatures slow deuteron intra-H-bond exchange, i.e. jumps of deuterons from one site to the other in the double potential of the H-bond. The jumps are monitored in a time interval, called the mixing time, which determines the observation window of this techniques. The low frequency limit of the window is determined by the spin-lattice relaxation time of deuterons, which is about 200 seconds at temperatures below 40 K. The 2D exchange experiment is thus sensitive to internal motions in the milli-Hertz region.

In a 2D exchange spectrum [14] two kinds of peaks appear, namely diagonal peaks, originating from deuterons which during mixing time did not leave their initial positions in the H-bonds, and cross peaks, where the intensity is coming from those deuterons which jumped from one site to the other during the mixing time. We denote the two sites in the H-bond as A and B and their energy difference as Δ. The inverse deuteron jump rates are

$$K_{AB}^{-1} = \tau_{AB} = \tau_0 \exp\left(\frac{E_a - \Delta/2}{kT}\right) = \tau \exp\left(-\frac{\Delta}{2kT}\right), \tag{16a}$$

$$K_{BA}^{-1} = \tau_{BA} = \tau_0 \exp\left(\frac{E_a + \Delta/2}{kT}\right) = \tau \exp\left(\frac{\Delta}{2kT}\right), \tag{16b}$$

Here E_a stands for the activation energy of the exchange process in a symmetric double-well potential. When the evolution (t_1) and detection (t_2) periods are of negligible duration as compared to the mixing period (t_m) of the 2D experiment one obtains the 2D NMR free induction signal as

$$\begin{aligned} F(t_1, t_2, t_m) = {} & e^{-t_m/T_1}\, e^{-(t_1+t_2)/T_2} \\ & \cdot \{a_{AA}(t_m) \cos\omega_A t_1 \cos\omega_A t_2) \\ & + a_{BB}(t_m) \cos\omega_B t_1 \cos\omega_B t_2) \\ & + a_{AB}(t_m) \cos\omega_A t_1 \cos\omega_B t_2) \\ & + a_{BA}(t_m) \cos\omega_B t_1 \cos\omega_A t_2)\}\,. \end{aligned} \tag{17}$$

The first two terms in the curly brackets give after a 2D Fourier transform the diagonal peaks in the spectrum whereas the last two terms give the cross peaks. The intensities $a_{ij}(t_m)$ are

$$\begin{aligned} a_{AA}(t_m) = {} & [2\,\mathrm{ch}(\Delta/2kT)]^{-2} \\ & \cdot [\exp(\Delta/kT) + \exp(-2(t_m/\tau)\,\mathrm{ch}(\Delta/2kT))], \end{aligned} \tag{18a}$$

$$\begin{aligned} a_{BB}(t_m) = {} & [2\,\mathrm{ch}(\Delta/2kT)]^{-2} \\ & \cdot [\exp(-\Delta/kT) + \exp(-2(t_m/\tau)\,\mathrm{ch}(\Delta/2kT))], \end{aligned} \tag{18b}$$

$$\begin{aligned} a_{AB}(t_m) &= a_{BA}(t_m) \\ &= [2\,\mathrm{ch}(\Delta/2kT)]^{-2}\,[1 - \exp(-2(t_m/\tau)\,\mathrm{ch}(\Delta/2kT))], \end{aligned} \tag{18c}$$

In the glassy state the asymmetries Δ are distributed with a distribution function $\varrho(\Delta)$ which is symmetric $\varrho(\Delta) = \varrho(-\Delta)$. This accounts for the fact that the total polarization in a deuteron glass vanishes. The intensities (18a)–(18c) have to be averaged over $\varrho(\Delta)$. This yields $\overline{a_{AA}}(t_m) = \overline{a_{BB}}(t_m) = 1$, and both diagonal peaks have the same intensities. We introduce $u = \Delta/2kT$ and $x = t_m/\tau$ and get the ratio between the intensities of the cross and diagonal peaks as

$$R(x) = \overline{a_{BA}(x)}/\overline{a_{AA}(x)} = (I_c - I_b(x))/(I_a + I_b(x)), \tag{19}$$

where the bar describes the averaging over $\varrho(u)$ and

$$I_a = \int_{-\infty}^{\infty} \varrho(u)\,\mathrm{ch}^{-2} u \exp(2u)\,du, \tag{20a}$$

$$I_b(x) = \int_{-\infty}^{\infty} \varrho(u)\,\mathrm{ch}^{-2} u \exp(-2x\,\mathrm{ch}\,u)\,du, \tag{20b}$$

$$I_c = \int_{-\infty}^{\infty} \varrho(u)\,\mathrm{ch}^{-2} u\,du. \tag{20c}$$

If all O–D···O bonds are symmetric, so that $\varrho(u) = \delta(u)$, we get

$$R(x) = \mathrm{th}(x) \tag{21}$$

and $R(x \to \infty) = 1$. The ratio $R(x \to \infty)$ is a measurable physical quantity which is very sensitive to the size of the bond asymmetries Δ. For an illustration we take a single bond and compute $R(\infty)$ from (18a)–(18c). We obtain

$$R(\infty) = \frac{a_{BA}(\infty)}{a_{AA}(\infty)} = e^{-\Delta/kT}.$$

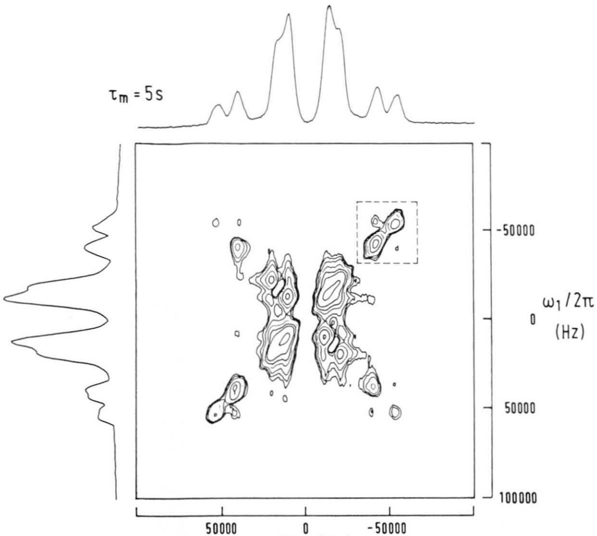

Fig. 3. A 2D O–D···O deuteron exchange spectrum in $Rb_{0.68}(ND_4)_{0.32}D_2AsO_4$ at 40 K and orientation $\vec{a} \perp \vec{H}_0$, $\measuredangle \vec{b}, \vec{H}_0 = 45°$. Mixing time $t_m = 5$ s. The spectrum in the dashed box corresponds to $X_\pm$ bonds.

At $T = 40$ K, kT amounts to 3 meV. Taking $\Delta = 3$ meV, which is a small estimate, we obtain $R(\infty) = 0.37$. A systematic study of $R(x)$ should provide information about H-bond asymmetries which is of key importance in the understanding of the deuteron glass phase.

A 2D exchange experiment has been performed on $Rb_{0.68}(ND_4)_{0.32}D_2AsO_4$ single crystal at an orientation $\vec{a} \perp \vec{H}_0$, $\measuredangle \vec{b}, \vec{H}_0 = 45°$ and deuteron frequency $\nu_0(^2H) = 41.463$ MHz. A 2D deuteron spectrum at $T = 40$ K and mixing time $t_m = 5$ s is shown in Figure 3. The part of the spectrum corresponding to X_+ and X_- bonds is enclosed in a dashed box. Here X_+ and X_- denote the bonds aligned along the crystal a-axis, and subscripts + and − denote whether the "upper" end of the bond is in the positive or negative X-direction. The $X_\pm$ part of the spectrum is displayed in Fig. 4 for different mixing times. It is seen that the cross peaks are growing with increasing mixing time and reach the intensity of the diagonal peaks for $t_m = 30$ s.

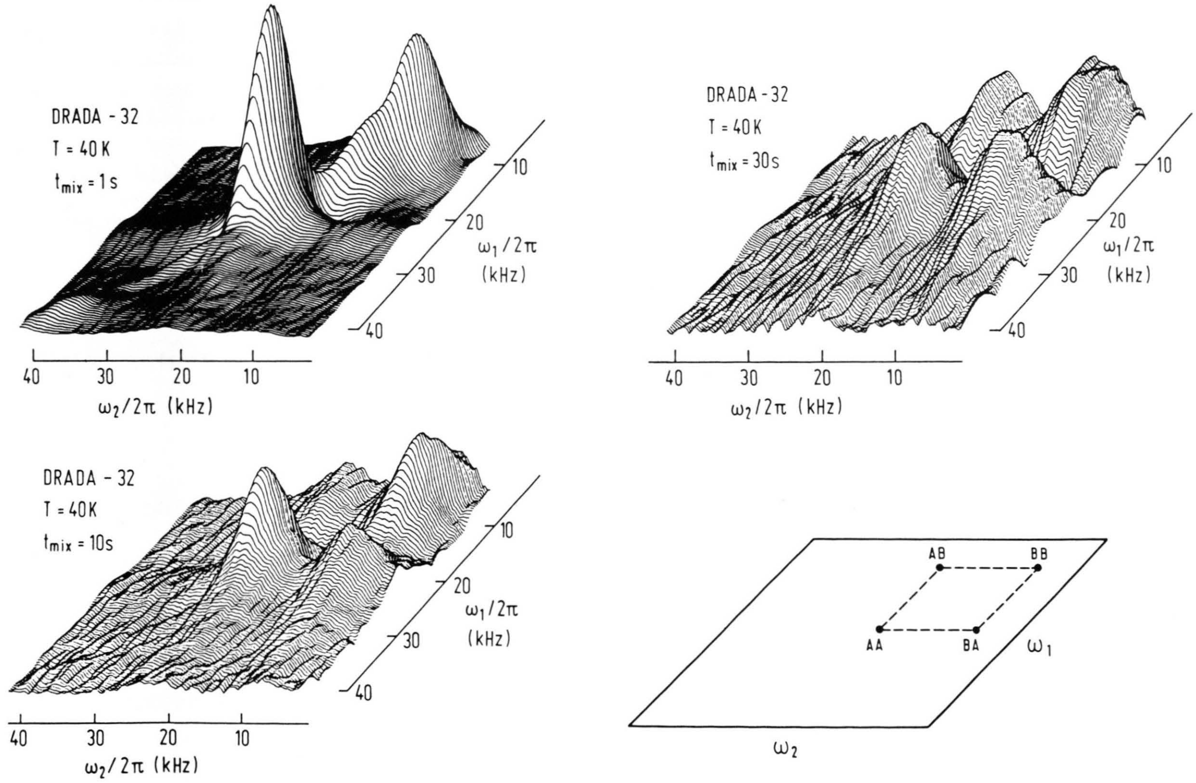

Fig. 4. O–D···O deuteron 2D exchange spectrum in DRADA $x = 0.32$ at 40 K for mixing times 1 s, 10 s, and 30 s. Only the part of the spectrum corresponding to $X_\pm$ bonds (dashed box of Fig. 3) is shown. At long mixing times cross and diagonal peaks have the same intensities. The peak assignation is shown in the lower right corner.

The ratio $R(x) = \overline{a_{BA}}(x)/\overline{a_{AA}}(x)$ is shown in Fig. 5 for different temperatures in the interval from 45 K to 24 K. Interestingly all saturated values of the ratio $R(x \to \infty)$ are equal to 1, which is according to (21) only possible when all the bonds are symmetric. The experimental $R(x)$ curves have been fitted with (21), which is derived for the case of purely symmetric bonds. The corresponding deuteron intrabond exchange time τ is displayed in Figure 6. τ acts as thermally activated, $\tau = \tau_0 \exp(E_a/kT)$ with $E_a = 12.8$ meV and $\tau_0 = 0.43$ s. At $T = 45$ K τ amounts to 14.4 s and at $T = 24$ K it amounts to 236 s, which shows the time scale of the deuteron intrabond exchange. This time scale is very different from the single particle deuteron intrabond jump time $\tau_c = \tau_\infty \exp(E_a/kT)$ with $\tau_\infty = 2.8 \cdot 10^{-12}$ s and $E_a = 74$ meV as determined from deuteron spin-lattice relaxation (T_1) data [15]. The unusually large value of $\tau_0 = 0.43$ s points to the fact that the 2D exchange experiment does not observe a single particle motion but a correlated motion of larger ensemble of particles like clusters or microdomains. This should, however, be accomplished by an increase of the activation energy, which is not observed in this case. The τ_0 and E_a values have been obtained from the assumption of an Arrhenius type thermally activated motion which does not reproduce correctly also the low temperature T_1 data in DRADP $x = 0.44$ [10]. A more elaborate model of O–D···O intra-bond motion seems to be necessary to clarify this point.

The appearance of cross peaks in a 2D exchange experiment proves that the degree of glass disorder observed in an experiment depends on the observation window of that technique. Below 60 K the 1D NMR lineshape technique observes the glass disorder as completely frozen. The same disorder appears as dynamic in the 2D NMR exchange technique which has the observation window six orders of magnitude shifted towards lower frequencies. Ergodicity is broken on short time scales compared to the deuteron intra-bond motion ($t \ll \tau$), whereas ergodicity is restored when $t \gg \tau$. The saturated values $R(\infty) = 1$ can be explained if we take the bond asymmetries Δ to be time dependent. Slow lattice motions make the bonds symmetric in time average on long time scales, whereas bonds are observed as statistically asymmetric in an "instant-time" picture.

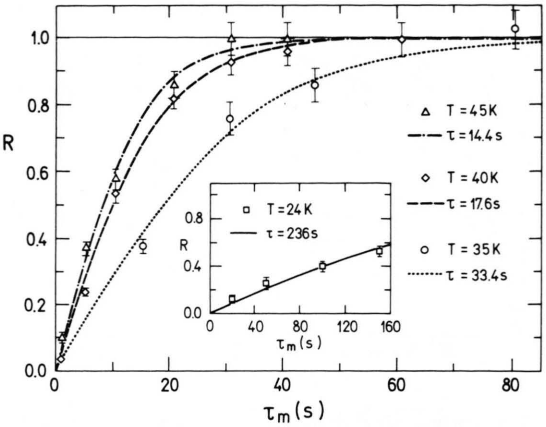

Fig. 5. Experimental ratio of cross peak to diagonal peak intensities versus the mixing time t_m at 45, 40, 35 and 24 K. The curves represent fits with (21), valid for the case of purely symmetric H-bonds. (DRADA $x = 0.32$, $\vec{a} \perp \vec{H}_0$, $\sphericalangle \vec{b}, \vec{H}_0 = 45°$, $\nu_0(^2\mathrm{H}) = 41.463$ MHz).

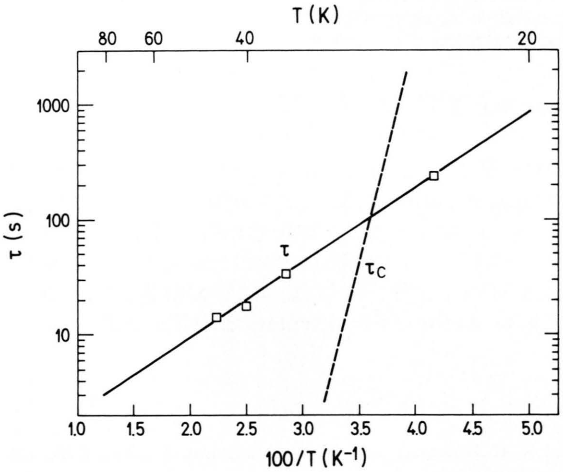

Fig. 6. Temperature dependence of the intra-H-bond deuteron exchange time τ, determined from 2D exchange NMR. The single particle intra-H-bond jump time τ_c, extrapolated from T_1 minimum around 90K is shown as a dashed line.

The same behavior of the cross and diagonal peak intensities ratio can be predicted also from a spin diffusion effect. The spin diffusion time is, however, temperature independent [16], which is to be contrasted with the thermally activated form of τ in Figure 6. Another test to prove or eliminate the presence of spin diffusion is to vary the frequency separation between X_+ and X_- deuteron lines, which can be achieved by changing the orientation of the probe in the magnetic field. The spin diffusion time constant in the weakest case increases as the square of the frequency distance between the lines; $T_{SD} \propto (\Delta\nu)^2$ [16]. Stronger dependencies like $T_{SD} \propto (\Delta\nu)^4$ [16] and ex-

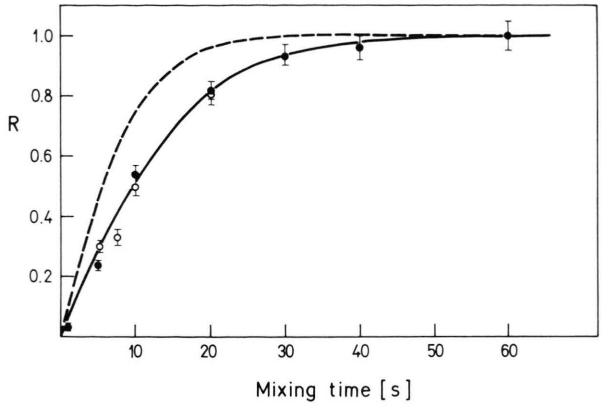

Fig. 7. Experimental ratio of the deuteron cross to diagonal peak intensities versus mixing time t_m at 40 K in DRADA $x = 0.32$. Two experiments have been made at two different orientations. a) $\vec{a} \perp \vec{H}_0$, $\sphericalangle \vec{b}, \vec{H}_0 = 45°$ (full circles) where the $X_\pm$ deuteron line splitting amounts to 11.3 kHz. b) $\vec{a} \perp \vec{H}_0$, $\sphericalangle \vec{b}, \vec{H}_0 = 25°$ (open circles) with $X_\pm$ splitting of 8.7 kHz. The solid line represents the fit $R = \text{th}\, t_m/\tau$ with $\tau = 14.4$ s, the dashed line a calculated curve $R = \text{th}\, t_m/T_{SD}$ which would be obtained at the orientation with splitting 8.7 kHz in case of spin diffusion, assuming quadratic dependence of T_{SD} on the line separation ($T_{SD} \propto (\Delta\nu)^2$).

ponential [17] have been also predicted. We performed two sets of 2D exchange experiments at $T = 40$ K for two different orientations and plot the $R(x)$ curves. The first experiment has been made at the orientation $\vec{a} \perp \vec{H}_0$, $\sphericalangle \vec{b}, \vec{H}_0 = 45°$, where the $X_\pm$ splitting amounts to 11.3 kHz, whereas the second has been made at the orientation $\vec{a} \perp \vec{H}_0$, $\sphericalangle \vec{b}, \vec{H}_0 = 25°$ with $X_\pm$ splitting of 8.7 kHz. At those two orientations $X_\pm$ and $Y_\pm$ lines do not overlap, where $Y_\pm$ denote the bonds in the b-crystallographic direction. The $X_\pm$ splitting at $\sphericalangle \vec{b}, \vec{H}_0 = 45°$ is 30% larger than the one at $\sphericalangle \vec{b}, \vec{H}_0 = 25°$, which should yield in the weakest case ($T_{SD} \propto (\Delta\nu)^2$) an about 70% larger time constant. No change in exchange time has, however, been detected (Fig. 7), ruling out the effects of spin diffusion.

IV. Conclusions

It is now clear why the NMR lineshape and spin-lattice relaxation studies see the glass disorder as completely static. These techniques are sensitive to molecular motions in the $10^8 - 10^3$ Hz window. Due to the frequency scale of molecular motions in glasses these motions appear as frozen static below a certain temperature, and the experiment sees an "instant-time" frozen picture. The degree of glass disorder observed in an experiment depends on the observation window of the experimental technique. The NMR lineshape and 2D exchange results can be explained properly by taking the slow dynamics of the glass phase into account. On observation time scales short compared to the deuteron intrabond motion time ($t \ll \tau$) the deuteron glass phase appears as non-ergodic, the glass disorder looks static and the glass order parameter q_{EA} is different from zero. On longer observation time scales ($t \gg \tau$) slow intrabond exchange recovers ergodicity.

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