Nuclear Magnetic Resonance in Random Fields: Cluster Formation and Local Dynamics of a Deuteron Glass

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NMR data show that the deuteron "pseudo spin-glass" transition in $Rb_{1-x}(ND_4)_xD_2PO_4$ is not just a simple kinetic slowing down process but is characterized by a gradual condensation of randomly polarized clusters as expected if we deal with a percolation transition in eigenstate space. The results provide novel information on the temperature dependence and distribution of local random fields and their dynamics. The spin-lattice and motional-narrowing data further suggest that the "pseudospin" O—D--O deuteron intrabond motion determines the freezing dynamics.

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The usefulness of NMR for the study of phase transitions in nonrandom systems is based on the fact[1] that the NMR or nuclear quadrupole resonance (NQR) frequency is a function of the order parameter of the transition, which is zero above T_c and nonzero below T_c. In strongly disordered systems[2] such as spin-glasses where there is an infinite number of order parameters the situation is radically different as there is no long-range structural ordering and no sharp change in the NMR or NQR frequency at any temperature. We wish to point out that the NMR technique is nevertheless capable of providing unique information about the distribution and dynamics of local random fields and order parameters in strongly disordered systems as here the quadrupole-perturbed NMR frequency of a given nucleus depends on the local random field p_i:

$$\nu_i(t) = \nu_i(p_i(t)). \tag{1}$$

The use of this technique in magnetic spin-glasses, however, is severely restricted by the fact that the spin-glass transition is greatly disturbed by the finite magnetic field needed for an NMR experiment.

In this Letter we report the results of a deuteron and ^{87}Rb NMR study of the dynamics of local freezing in the deuteron "pseudospin" glass[3] $Rb_{1-x}(ND_4)_xD_2PO_4$ for $x=0.55$, where the magnetic field does not affect the transition. This solid solution[3,4] of ferroelectric RbD_2PO_4 and antiferroelectric $ND_4D_2PO_4$ (which are isostructural in the high-temperature disordered paraelectric phase) represents a frustrated H-bonded system[3,4] with competing ferroelectric and antiferroelectric interactions somewhat similar to a magnetic spin-glass. In the virtual-crystal approximation the system would be incommensurate. The random substitution of NH_4 groups for the rubidium ions introduces a random field which couples linearly to the O—D--O pseudospins and destroys the long-range ordering.

Here we show that the distribution $g(p)$ of the random fields which break the local symmetry of the high-temperature phase can be extracted from the difference between the inhomogeneous and homogeneous NMR line shapes. The NMR line-shape data exclude the simple kinetic slowing-down model and demonstrate the gradual freezeout of finite-size clusters in quasistatic local random fields over a wide temperature range. The spin-lattice relaxation data further show that the local freezing dynamics is determined by the randomly biased freezeout of the O—D--O deuteron intrabond motion which occurs here—in contrast to pure RbD_2PO_4 or $ND_4D_2PO_4$[1]—in self-similar, scale-invariant clusters of events.[5,6]

The deuteron and ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR spectra were measured by Fourier transformation of the off-resonance spin echos of the $Rb_{0.45}(ND_4)_{0.55}D_2PO_4$ single crystal while the homogeneous linewidth was determined from the slope of the plot of spin-echo amplitude versus squared pulse separation. The ^{87}Rb magnetization recovery after a saturation sequence was found to be describable by a "stretched" exponential recovery function at an orientation where in pure RbH_2PO_4 no deviation from an exponential recovery could be detected.

The spin-lattice relaxation results are shown in Fig. 1.

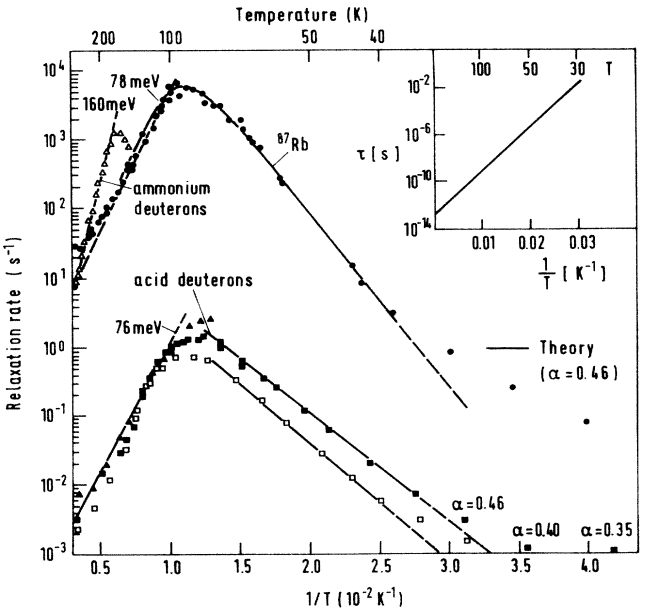

FIG. 1. Temperature dependence of the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$, ND_4^+ deuteron, and O—D--O deuteron spin-lattice relaxation rates T_1^{-1}. The solid lines represent the "stretched exponential" fits with $\alpha = 0.46$. ^{87}Rb T_1: open triangles, $\mathbf{c} \perp \mathbf{H}_0$ (2.0 T), closed circles, $\mathbf{c} \| \mathbf{H}_0$ (4.2 T); ^{2}H T_1: closed triangles, $\mathbf{c} \| \mathbf{H}_0$ (2.0 T), closed squares, $\mathbf{c} \| \mathbf{H}_0$ (4.2 T), open squares, $\mathbf{c} \| \mathbf{H}_0$ (8.45 T). Inset: The temperature dependence of the O—D--O deuteron intrabond correlation-time fitting parameter τ deduced from the "stretched-exponential" fits (Eq. 2) to the O—D--O and ^{87}Rb T_1^{-1} data.

In contrast[1,7] to pure RbD_2PO_4 and $ND_4D_2PO_4$ the temperature dependences of both the O—D--O deuteron and the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ spin-lattice relaxation rates T_1^{-1} show broad, asymmetric, non-Bloembergen-Purcell-Pound type T_1 minima around 90 K. A T_1 minimum in the O—D--O deuteron intrabond NMR relaxation has not been observed so far in any other H-bonded crystal[1] or biological system at any temperature, to the best of our knowledge, and represents a specific effect of the freezeout in this deuteron glass. The temperature and Larmor frequency dependence of the O—D--O deuteron T_1^{-1} can be described by a deuteron autocorrelation function of the stretched-exponential type,[8,9]

$$G(t) = C \exp(-t/\tau)^{\alpha}, \quad 0 < \alpha < 1, \tag{2}$$

as recently predicted for relaxation in Ising spin-glasses.[10] Here $\alpha = 1 - n = 0.46$ above 33 K and decreases below this temperature. At 28 K it reaches $\alpha = 0.40$ and at 24 K $\alpha = 0.35$. It is interesting to note that within the above-mentioned model,[10] where the spin-glass transition appears as a percolation threshold in eigenstate space, $\alpha = 2/(2+\theta)$ with θ the fractal random-walk exponent $d_w = 2 + \theta$. The model predicts that θ is zero at very high temperature (i.e., $\alpha = 1$), whereas it tends to 4 and α to $\frac{1}{3}$ as the percolation threshold T_G is approached at low temperatures,[10] thus reproducing the trend observed here.

The other fitting parameter of Eq. (6), τ, follows a simple exponential temperature dependence $\tau = \tau_0 \times \exp[E_a/kT]$ with an activation energy $E_a = 78$ meV which is the same[1] as found for deuteron intrabond motion—induced by the diffusion of D_3PO_4 defects—in pure KD_2PO_4. The same is true for $\tau_0 = 10^{-13}$ s demonstrating that anomalous diffusion of D_3PO_4 defects is rate determining for O—D--O intrabond motion here as well. Within the limits of experimental error the stretched-exponential law [Eq. (2)] also describes the ^{87}Rb spin-lattice relaxation data with a different proportionality constant given by the square of the fluctuating electric field gradient tensor components and a slightly different α. The value of α agrees with the one derived from the magnetization recovery data.

The shift in the Rb T_1 minimum from 30 K in the undeuterated system[11] to 90 K in the deuterated one demonstrates the importance of the H-bond dynamics in the transition. The τ values deduced from the ^{87}Rb and O—D--O deuteron T_1 fits agree rather well, demonstrating that it is the tremendous slowing down of the deuteron intrabond motion from 10^{-13} s at room temperature to more than 10^{-2} s at 30 K (Fig. 1) that dominates the ^{87}Rb relaxation as well as the freezing dynamics. The elementary reversible electric dipole—analogous to the magnetic spin—is thus here the O—H--O bond, where the deuteron moves between two equilibrium sites $S_z = \pm 1$ under ice-rule-like constraints.[1] The $-ND_4^+$ deuteron relaxation, on the other hand, is of the simple Bloembergen-Purcell-Pound type[12] and induced by $-ND_4^+$ rotations. It does not seem to be affected by the incipient glass transition.

Both the ^{87}Rb and the O—D--O deuteron NMR line shapes are temperature dependent, anisotropic, and inhomogeneously broadened even on the high-temperature side of the T_1 minimum, i.e., in the "fast motion" regime.

The formation of quasistatic, randomly oriented, locally polarized clusters is best seen from the asymmetry of the inhomogeneous ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ line shape [Fig. 2(a)] for $\mathbf{c} \| \mathbf{H}_0$. The homogeneous linewidth (T_2^{-1}) here is less than 1 kHz, whereas the inhomogeneous linewidth $(T_2^{\times})^{-1}$ varies between 5 kHz at room temperature and 20 kHz at 50 K. The kinetic model,[12] on the other hand, predicts $T_2 = T_2^{\times}$ and a symmetric line shape in the line-narrowing regime. The observed asymmetry of the line shape and the fact that $T_2 \gg T_2^{\times}$ thus definitely rule out the simple kinetic slowing-down model and show that the principal source of line broadening is static on a T_2 time scale. The obvious explanation is that nuclei in differently polarized clusters have different resonance frequencies and that ergodicity is broken on the NMR time scale as p—according to Eq. (1)—is nonzero. The distribution of resonance frequencies $f(\nu)$ is then simply related to the spatial distribution $g(p)$ of static random

fields:

$$f(\nu)d\nu = g(p)dp, \tag{3}$$

so that

$$f(\nu) = \frac{g(p)}{|d\nu/dp|}. \tag{4}$$

If the relation $\nu_i = \nu_i(p_i)$ is known, a measurement of the line shape allows for a direct determination of $g(p)$. Expanding the relation $\nu_i = \nu_i(p_i)$ into a Taylor series,

$$\nu_p = \nu_0 + \nu_1 p + \nu_2 p^2 + \ldots, \tag{5}$$

we see that different line shapes are predicted for the O—D--O deuteron case where ν_p is strictly local and linear ($\nu_1 \neq 0$, $\nu_n = 0$, $n > 1$) and $d\nu/dp$ is always nonzero, and the ^{87}Rb case where a term quadratic in p ($\nu_2 \neq 0$) will always be present. For the deuteron case the predicted line shape is, in agreement with experiment, always symmetric. The presence of a term quadratic in p in expressions (5) and (4) for the rubidium case will result in a singularity in $f(\nu)$ for $d\nu/dp = 0$, thus explaining the observed asymmetry in the ^{87}Rb NMR line shape [Fig. 2(a)].

The above line-shape analysis was based on the assumption that the dominant contribution to the inhomogeneous NMR line shape is due to static random fields. In fact the anomalous diffusion of D_3PO_4 defects result in a motion of cluster walls leading to motional averaging effects and a T-dependent line shape. We therefore add to p a rapidly fluctuating part $\Delta p(t)$ so that

$$p_{\text{total}}(t) = p + \Delta p(t). \tag{6}$$

Here p, which includes static and quasistatic contributions, is determined by the average

$$p = t_0^{-1} \int_0^{t_0} p_{\text{total}}(t')dt' \tag{7}$$

over fluctuations which are fast on the time scale corresponding to the rigid-lattice linewidth $t_0 = \Delta\nu_0^{-1}$. The autocorrelation function for the fast fluctuations is, according to T_1 data, of the stretched-exponential type:

$$\langle \Delta p(0)\Delta p(t)\rangle = \langle \Delta p^2\rangle \exp(-t/\tau)^{\alpha}. \tag{8}$$

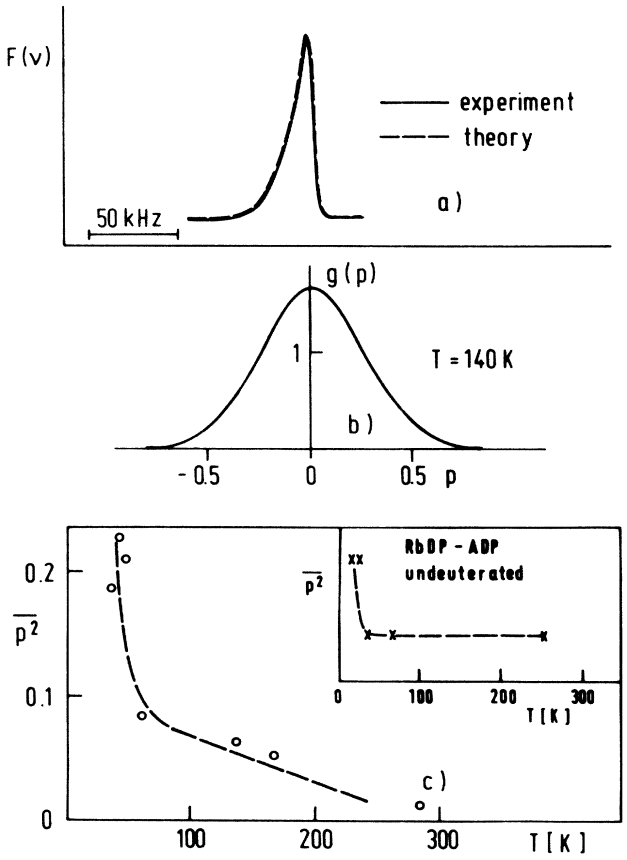

FIG. 2. (a) ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR line shape for $\mathbf{c} \| \mathbf{H}_0$ and $T = 140$ K. The solid line represents the fit by expressions (9) and (10) after convolution with the homogeneous line shape. (b) Static and quasistatic random-field distribution $g(p)$ deduced from the inhomogeneous ^{87}Rb line shape. (c) Temperature dependence of the second moment $\langle p^2\rangle$ of the random-field distribution $g(p)$. The sharp increase at low T follows from Eq. (11) and the τ and α values derived from the T_1 data. The units for p are arbitrary. Inset: The isotope shift in $\langle p^2\rangle$ vs T in an undeuterated sample.

For the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR lineshape at $\mathbf{H} \| \mathbf{c}$ the dominant second-order perturbation is quadratic in p and nonlocal in time.[13] In case of $\langle p^2\rangle > \langle \Delta p^2\rangle$ one finds[14] for a Gaussian distribution of fluctuating random fields

$$f(\nu) = \int g(p) \int \exp\{i2\pi[\nu_0 + \nu_2(p^2 + \langle \Delta p^2\rangle) - \nu]t\} \exp[-(4\pi\nu_{2p})^2 \langle \Delta p^2\rangle u(t)]dt\, dp, \tag{9}$$

$$u(t) = \int_0^t (t - t')\exp(-t'/\tau)^{\alpha} dt'. \tag{10}$$

The above expression represents a convolution of $g(p)$ with a motionally narrowed line-shape function and reduces to Eq. (4) for $\tau \rightarrow \infty$. For $\langle p^2\rangle > \langle \Delta p^2\rangle$ the motional averaging effects are small irrespective of τ and show up only in the tails. The experimental line shape $F(\nu)$ is obtained after convolution of $f(\nu)$ with the width of the homogeneous lines which are Gaussians. The coefficients ν_0, ν_1, ν_2 have been determined from the angular dependence of the line shapes. The dependence of ν_p on the random field p is of the same functional form as the dependence of the corresponding frequency on the spontaneous polarization in pure RbD_2PO_4 though the values of the coefficients are different.[7] The fit between the experimental and theoretical Rb line shapes allows us to deduce the random-field distribution

function $g(p)$ [Fig. 2(b)] which is symmetric around $p=0$. The second moment $\langle p^2\rangle$ of this distribution [Fig. 2(c)] continuously increases from room temperature down to 33 K, i.e., to the lowest temperature where the line shape fit was made. It should be noted that $\langle p^2\rangle$ sharply increases in the same T range where $\alpha \rightarrow \frac{1}{3}$ and where the dielectric data[3,4] indicate the approach to the Vogel-Fulcher "transition" temperature T_0. A similar effect is seen as well in the undeuterated sample at a lower temperature [inset to Fig. 2(c)].

The observed sharp increase in the second moment of the random-field distribution at low temperatures is due to a change in the quasistatic contribution and directly follows from the τ and α values obtained from the spin-lattice relaxation data as

$$\langle p^2\rangle - \langle p^2\rangle_{\text{static}} = 2u(t_0)/t_0^2, \tag{11}$$

and is thus the result of a gradual condensation of randomly polarized clusters on the NMR time scale.

The disorder in this mixed system thus produces two different effects: It introduces a random field component which is static on the NMR time scale in the whole investigated temperature range. In addition it changes the diffusion of D_3PO_4 defects from normal to anomalous, thus resulting in a power-law distribution of waiting times[5] and a time-fractal stretched-exponential behavior of the random-field dynamics. Further investigations are needed to determine whether this is due to a hierarchical array of potential barriers for cluster dynamics or to the fact that the system is for $x=0.55$ close to the percolation limit[15] for D_3PO_4 diffusion.

[1]See, for instance, R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North Holland, Amsterdam, 1974), and references therein.

[2]R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. **53**, 958 (1984), and references therein. See also M. C. Chen and C. P. Slichter, Phys. Rev. B **27**, 278 (1983).

[3]E. Courtens, J. Phys. (Paris), Lett. **43**, L199 (1982). See also E. Courtens, Jpn. J. Appl. Phys. Suppl. **24**, 70 (1985).

[4]H. Terauchi, Jpn. J. Appl. Phys. Suppl. **24**, 75 (1985).

[5]M. F. Schlesinger, J. Stat. Phys. **36**, 639 (1984).

[6]V. S. Dotsenko, J. Phys. C **18**, 6023 (1985).

[7]R. Blinc, M. Mali, and S. Žumer, J. Chem. Phys. **63**, 2898 (1975).

[8]R. Rammal, J. Phys. (Paris) **46**, 1837 (1985).

[9]C. De Dominicis, H. Orland, and F. Lainee, J. Phys. (Paris), Lett. **46**, L463 (1985).

[10]I. A. Campbell, J. Phys. (Paris), Lett. **46**, L1159 (1985).

[11]J. Slak, R. Kind, R. Blinc, E. Courtens, and S. Žumer, Phys. Rev. B **30**, 85 (1984).

[12]N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

[13]J. L. Bjorkstam and M. Villa, Phys. Rev. B **22**, 5025 (1980).

[14]Unpublished work from this laboratory.

[15]S. Robillard and A. M. S. Tremblay, J. Phys. A **19**, 2171 (1986).