Local-Polarization Distribution in Deuteron Glasses

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It is shown that quadrupole-perturbed nuclear magnetic resonance provides a powerful technique to determine the local-polarization distribution and its second moment, the Edwards-Anderson order parameter in proton and deuteron glasses. The experimentally determined local-polarization distributions show the characteristic features predicted by a deuteron-glass model with infinitely ranged random-bond interactions in the presence of quenched random fields. The measurements demonstrate that we deal in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ with a random-field smearing of a random-bond-type pseudo-spin-glass transition and not with a random-field-type freezing or a classical random-bond-type spin-glass transition.

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The question on the existence of a phase transition[1] in real spin glasses is still one of the great open problems in condensed matter physics. This is also true for proton or deuteron pseudo-spin glasses which are characterized by the random freezeout[2,3] of the hydrogen ions between the two possible positions in the O—H--O bonds in mixed solid solutions of hydrogen-bonded ferroelectric and antiferroelectric crystals. In spite of many investigations it is still not clear what is the nature of the observed freezeout. Do we have a pseudo-spin-glass transition of the Ising type[1-3] driven by randomly frustrated competing interactions and occurring at a nonzero transition temperature T_G, or just a strong random-field-type single-particle freezing?

The problem which makes experimental studies of spin glasses as well as proton and deuteron glasses so difficult is that the Edwards-Anderson order parameter q_{EA} characterizing the deuteron glass, as well as magnetic spin glasses, has no macroscopic conjugate field and is therefore hard to measure directly. Here we show that quadrupole-perturbed nuclear magnetic resonance (NMR) allows a direct experimental determination of the average local-polarization distribution function $W(p)$ and its second moment, the Edwards-Anderson order parameter q_{EA}, in proton and deuteron glasses. This is so as the site-averaged distribution of NMR frequencies is a direct measure of the average distribution of the local O—D--O deuteron polarization. We also present a theoretical evaluation of the average distribution of local polarizations $W(p)$ based on the Ising model with infinitely ranged random interactions and quenched random fields. A comparison of the experimentally determined local-polarization distribution function $W(p)$ with the calculated one shows that we indeed find the predicted change of $W(p)$ from a single-peaked form at high temperatures to a double-peaked form at low temperatures and that the above model is—in spite of its simplicity—capable of describing the essential features of the deuteron-glass phase in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ (DRADP). Our results also demonstrate that we deal in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ with a random-field smearing of the deuteron-glass transition and not with a simple random-field-type single-particle freezing or a classical random-bond-type spin-glass transition.

The solid solution $Rb_{1-x}(ND_4)_xD_2PO_4$ of ferroelectric RbD_2PO_4 and antiferroelectric $ND_4D_2PO_4$ represents a randomly frustrated H-bonded system[4] with competing ferroelectric and antiferroelectric interactions. For $0.22 \leq x \leq 0.8$ the system forms, at low temperatures, a "deuteron" glass. The O—D--O bond represents a two position reorientable dipole[4] which can be described[5] by an Ising pseudospin, $S^z = \pm 1$. The Edwards-Anderson order parameter is here defined in analogy to magnetic spin glasses as

$$q_{EA} = \frac{1}{N}\sum_i \langle S_i^z \rangle^2 = [\langle S_i^z \rangle^2]_{AV}, \tag{1}$$

where N is the number of lattice sites, $\langle \cdots \rangle$ represents the thermal average, while $[\cdots]_{AV}$ denotes the disorder average, i.e., the simultaneous average over random bonds and random fields.

The average probability distribution of the local polarization p is defined as

$$W(p) = \frac{1}{N}\sum_i \delta(p - \langle S_i^z \rangle) = [\delta(p - \langle S_i^z \rangle)]_{AV}. \tag{2}$$

Equation (2) implies that $W(p)$ is self-averaging; i.e., the two types of averaging in expression (2) are fully equivalent.

It is trivial to verify that the first moment of the distribution $W(p)$ is the total polarization P, which is zero in the absence of a homogeneous external electric field, while its second moment is just the proton-glass order parameter

$$q_{EA} = \int dp\, p^2 W(p). \tag{3}$$

The relation between the Larmor frequency of a deuteron positioned at the ith hydrogen bond in a mixed

DRADP crystal and the pseudo-spin polarization $\langle S_i^z \rangle$ of this bond can be in the simplest case written as

$$\nu_i = \nu_0 + \nu_1 \langle S_i^z \rangle \tag{4}$$

as long as we are in the fast-motion limit.

If the local polarization $p_i = \langle S_i^z \rangle$ is nonzero due to the presence of random fields or random-bond interactions leading to a glass ordering and making the O—D--O potential asymmetric, quadrupolar nuclei like O—D--O deuterons with different p_i will have different NMR and nuclear quadrupole resonance (NQR) frequencies. This will result in an inhomogeneous broadening of the NMR or NQR lines.

The inhomogeneous deuteron NMR line shape is characterized here by the average frequency distribution function

$$f(\nu) = \frac{1}{N} \sum_i \delta(\nu - \nu_i) = [\delta(\nu - \nu_i)]_{\mathrm{AV}}, \tag{5}$$

where self-averaging has again been assumed.

Comparing Eqs. (2) and (5) we find

$$W(p) = \nu_1 f(\nu), \quad \nu = \nu_0 + \nu_1 p. \tag{6}$$

Thus, an experimental determination of $f(\nu)$ immediately yields the probability distribution of local polarizations $W(p)$. In particular, the second moment of $f(\nu)$ is directly proportional to the Edwards-Anderson glass order parameter, i.e.,

$$\int d\nu f(\nu)(\nu - \nu_0)^2 = \nu_1^2 q_{\mathrm{EA}}. \tag{7}$$

The above considerations can be easily extended to the case where the relation between the O—D--O deuteron Larmor frequency and the pseudo-spin polarization of this bond contains linear and quadratic terms. If quadratic terms are present, $f(\nu) = W(p) \left| d\nu/dp \right|^{-1}$ becomes asymmetric and it is the first moment of $f(\nu)$ which is proportional to q_{EA}.

The situation is somewhat different if the nuclear spin is located at a position i other than the pseudo-spin site in the O—D--O bond. This, for instance, is the case for the Rb nucleus in $Rb_{1-x}(ND_4)_xD_2PO_4$. Here the resonance frequency is linearly perturbed by a group of pseudospins, $j = 1, 2, \ldots, r$, so that we can generalize expression (4) to

$$\nu_i = \nu_0 + \sum_j C_{ij} \langle S_j^z \rangle. \tag{8}$$

The second moment of the distribution function[5] is now given by

$$M_2 = \int d\nu f(\nu)(\nu - \nu_0)^2 = \sum_{jk} [C_{ij} C_{ik} \langle S_j^z \rangle \langle S_k^z \rangle]_{\mathrm{AV}}. \tag{9}$$

One may assume that the coefficients C_{ij} are independent of the site index i, and thus C_{ij} is not a random variable. The remaining average is simply[6]

$$[\langle S_j^z \rangle \langle S_k^z \rangle]_{\mathrm{AV}} = \delta_{jk} [\langle S_j^z \rangle^2]_{\mathrm{AV}} = \delta_{jk} q_{\mathrm{EA}}. \tag{10}$$

From Eq. (10) it immediately follows that $M_2 = C q_{\mathrm{EA}}$, with $C = \sum_{j=1} C_{ij}^2$. All above considerations are valid if the local-dipole-moment fluctuations are fast compared to the rigid lattice quadrupolar splittings. In the slow-motion regime we have to take into account the additional broadening due to the slowing down of the fluctuations via

$$I(\omega) = \int I(\omega, p) W(p)\, dp, \tag{11}$$

where $I(\omega, p)$ is the line shape due to exchange[7] in an asymmetric two-site potential and $W(p)$ is the local-polarization distribution function defined previously. $I(\omega)$ reduces to $f(\nu)$ in the fast-motion limit.

The above considerations are quite general. Let us now be more specific and let us evaluate $W(p)$ for the Ising pseudo-spin model with infinitely ranged random interactions and quenched random fields:[3,8]

$$\mathcal{H} = -\tfrac{1}{2} \sum_{i,j} J_{ij} S_i^z S_j^z - \sum_i f_i S_i^z. \tag{12}$$

Here the random interactions J_{ij} and random fields f_j are assumed to be independently distributed according to their respective Gaussian probability densities:

$$P(J_{ij}) = J^{-1} (2\pi)^{-1/2} \exp(-\tfrac{1}{2} J_{ij}^2 / J^2),$$
$$P(f_i) = (2\pi\Delta)^{-1/2} \exp(-\tfrac{1}{2} f_i^2 / \Delta). \tag{13}$$

In order to perform the average over the disorder in Eqs. (1) and (2) we apply the replica formalism as known from the theory of spin glasses.[1,7] For the replica symmetric phase we obtain the analytic result

$$W(p) = \frac{1}{\beta \tilde{J} [2\pi(q + \tilde{\Delta})]^{1/2}} \frac{1}{1 - p^2} \times \exp\left[-\frac{1}{2} \frac{\operatorname{arctanh}^2(p)}{\beta^2 \tilde{J}^2 (q + \tilde{\Delta})} \right], \tag{14}$$

where $\beta = 1/kT$, $\tilde{J} = J\sqrt{N}$, and $\tilde{\Delta} = \Delta/\tilde{J}^2$, and the value of the order parameter $q = q_{\mathrm{EA}}$ is given by the familiar self-consistency equation[3]

$$q = (2\pi)^{-1/2} \int dz \exp(-z^2/2) \tanh^2[\beta \tilde{J} (q + \tilde{\Delta})^{1/2} z]. \tag{15}$$

In Fig. 1, the distribution function (14) is plotted for $\tilde{\Delta} = 0.35$ and several values of the reduced temperature $T/\tilde{J}$. For $T < T_G \equiv \tilde{J}$, $W(p)$ exhibits a two-peak structure with maxima near $p = \pm 1$. However, $W(p) = 0$ at $p = \pm 1$. At $T \approx T_G$, $W(p)$ flattens out, and for $T > T_G$ becomes a bell-shaped distribution with a maximum at $p = 0$. With increasing temperature the width of $W(p)$ decreases, and for extremely high temperatures it behaves asymptotically as

$$\lim_{T \to \infty} W(p) = \delta(p), \tag{16}$$

which can easily be derived from Eq. (14). Similarly, one can show that in the absence of random fields, i.e., for $\Delta \to 0$, one has $q = 0$ from Eq. (15), and again $W(p)$

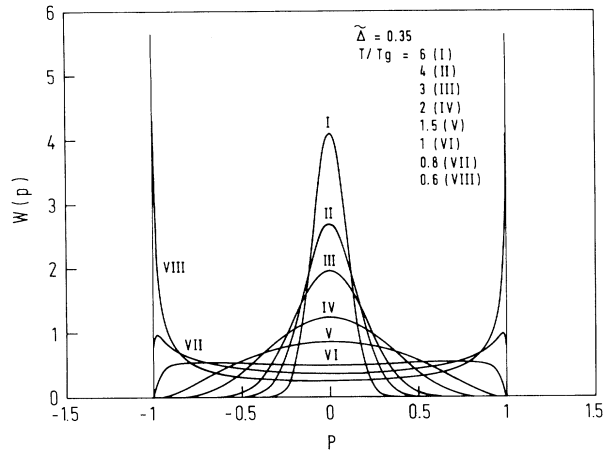

FIG. 1. Temperature dependence of the average local-polarization distribution function $W(p)$ for $\tilde{\Delta}=0.35$ according to expression (14).

$=\delta(p)$ for all temperatures $T > T_G$.

The O—D--O deuteron and ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ quadrupole-perturbed NMR spectra have been measured for deuterated RADP single crystals with $x=0.44$ at an orientation where the relation between ν and p is close to being linear. The inhomogeneous broadening of the spectra has been found to be much larger than the homogeneous linewidth $L(\nu)$ measured by the Hahn echo. $L(\nu)$ has been found to be Gaussian.

The temperature dependence of the Edwards-Anderson order parameter obtained from the second moment of the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ line shapes—after subtracting the contribution due to the homogeneous linewidth—is shown in Fig. 2. The data cannot be fitted by a pure glass-transition model ($\tilde{J}^2 \neq 0$, $\Delta=0$) nor by a pure random-field model ($\tilde{J}^2=0$, $\Delta \neq 0$) for any value of $\tilde{J}$ or Δ. A reasonable fit can, however, be obtained for $\tilde{J}^2 \neq 0$ and $\Delta \neq 0$. This seems to show a random-field smearing of the Ising pseudo-spin-glass transition in $Rb_{1-x}(ND_4)_xD_2PO_4$ as predicted.[3]

It should be noted that all of the above results have been obtained in the fast-motion regime as demonstrated by Rb and deuteron spin-lattice relaxation time data.[2]

To see if the local-polarization distribution function can be extracted from the NMR data we studied the O—D--O deuteron line shapes as a function of temperature (Fig. 3). We selected such an orientation so that the ND_4 deuteron line was well separated from the O—D--O deuteron line. The experimental deuteron line shapes—and $W(p)$—indeed show the predicted change from a single-peaked structure at high temperatures to a double-peaked structure at low temperatures (Fig. 3). Figure 4 shows the theoretical line shapes for the same set of temperatures as the measured spectra (Fig. 3). The theoretical line shapes are evaluated without any

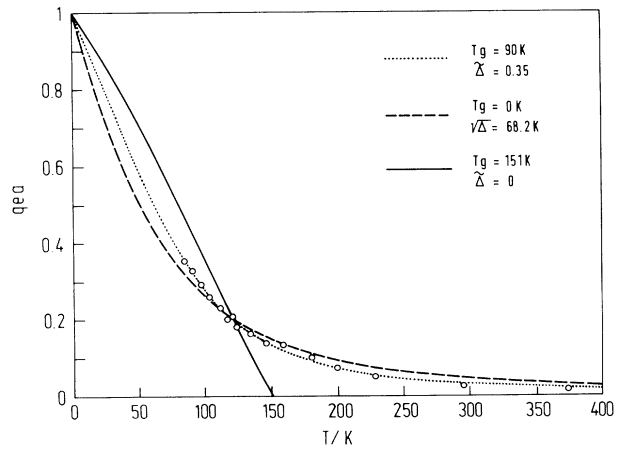

FIG. 2. Temperature dependence of the Edwards-Anderson order parameter q_{EA} as determined from the second moment of the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR spectra in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$. The dotted line represents the calculated temperature dependence for $\tilde{\Delta}=0.35$, $T_G=\tilde{J}=90$ K whereas the dashed line represents the best fit for the pure random-field model $T_G=0$, $\sqrt{\Delta}=68$ K and the solid line the curve for the pure random-bond model with $T_G=151$ K and $\tilde{\Delta}=0$.

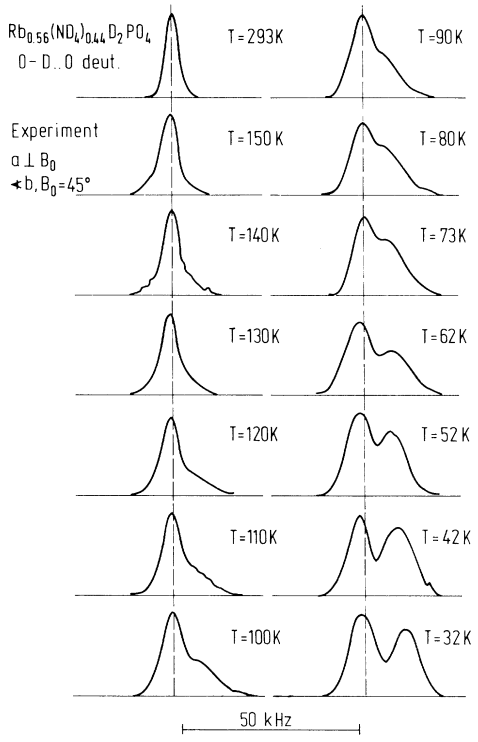

FIG. 3. Temperature dependence of the O—D--O deuteron NMR line shapes for $x=0.44$ and $a \perp B_0$, $\sphericalangle b$, $B_0=45°$ showing the predicted change from a single-peaked $f(\nu)$—and $W(p)$—to a double-peaked $f(\nu)$ and $W(p)$. At this orientation the relation between ν and p is $\nu-\nu_0=\nu_1 p+\nu_2 p^2$ with $\nu_1=5.2$ kHz and $\nu_2=3.3$ kHz resulting in an asymmetric line shape. The relation between ν and p is nonlinear due to the expansion of the H bond on deuteron ordering.

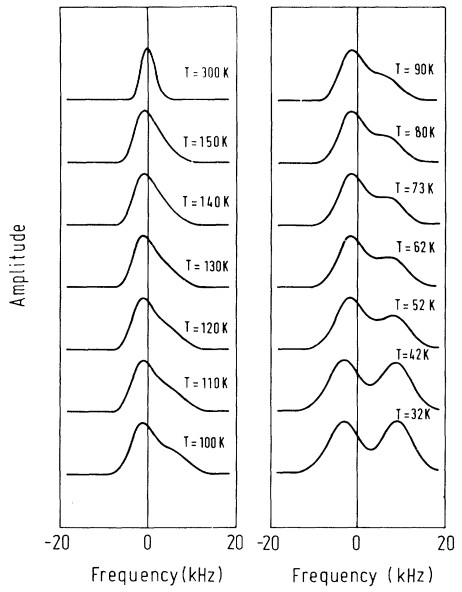

FIG. 4. Theoretical O—D--O deuteron line shapes for the same set of temperatures as the measured spectra in Fig. 3. The line shapes were evaluated using the parameters $\tilde{\Delta}=0.35$ and $\tilde{J}=90$ K obtained from the ^{87}Rb second moment data (Fig. 2). The spectra below 50 K have been corrected for dynamic effects using Eq. (11) and the correlation times from Ref. 2.

free parameters using the $\tilde{J}$ and Δ values obtained from the ^{87}Rb second-moment data (Fig. 2). The dynamic corrections are negligible above 45 K. Below this temperature dynamic effects are taken into account by convoluting $W(p)$ with the chemical exchange line shape $I(\omega,p)$ according to Eq. (11). The correlation time was obtained from the rubidium and deuteron T_1 data[2] so that there are again no free parameters in the fit. It should be noted that due to the rather high value of the Edwards-Anderson order parameter q_{EA} at the crossover between the fast- and the slow-motion regimes the line shape $I(\omega)$ and the extracted $W(p)$ are much less affected by dynamic effects than the second moment.

The deuteron as well as the Rb quadrupole-perturbed NMR data thus clearly demonstrate that we deal in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ with a random-field smearing of a random-bond-type psuedo-spin-glass transition and not with a random-field-type freezing or a classical random-bond-type spin-glass transition. It should be noted that in this model an Almeida-Thouless-type line $T_I(\Delta)$ exists in the temperature-random-field variance plane[3] separating the high-temperature ergodic pseudo-spin-glass phase characterized by a single order parameter $q=q_{EA}$ from the nonergodic low-temperature phase characterized[9] by an order parameter function $q(x)$ with $0\leq x\leq 1$. Further dynamic investigations are needed to check on this point.

It should be stressed that the technique described in this Letter is quite general and not at all restricted to proton glasses. An analogous relation between the local-magnetization distribution function, the NMR-NQR frequency distribution function, and the Edwards-Anderson order parameter can be also derived for magnetic spin glasses though in that case magnetic resonance experiments are more difficult[10] in view of the effect of the magnetic field on the spin-glass transition.

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