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# NMR determination of the Edwards-Anderson order parameter in the deuterated pseudo-spin-glass $\mathrm{Rb}_{1-x}(\mathrm{ND}_4)_x\mathrm{D}_2\mathrm{PO}_4$: Anisotropy and concentration dependence of the $\mathrm{ND}_4{}^+$ deuteron second moment

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We measured the rotationally averaged $\mathrm{ND}_4{}^+$ deuteron second moment in deuterated mixed single crystals $\mathrm{Rb}_{1-x}(\mathrm{ND}_4)_x\mathrm{D}_2\mathrm{PO}_4$ with $x=0.22$, 0.44, 0.78, and pure $\mathrm{ND}_4\mathrm{D}_2\mathrm{PO}_4$. We found that the linewidths of the mixed systems show a strong dependence on the crystal's orientation with respect to the external magnetic field. We interpret the temperature dependence of the $\mathrm{ND}_4{}^+$ second moment as due to the slowing down of the O—D. . .O intrabond motions. We also show that, in the temperature region above the glass transition, the second moment may be proportional either to the first or to the second powers of the Edwards-Anderson order parameter, depending on the crystal orientation. We were able to fit our experimentally obtained $q_{\mathrm{EA}}$ to a theoretical value obtained by Pirc, Tadic, and Blinc from the random-field random-bond Sherrington-Kirkpatrick Ising model. A comparison between similar measurements in pure and in mixed systems verifies that the strong orientational dependence of the linewidth is a property unique to the mixed systems.

## I. INTRODUCTION

The mixed normal and isotropically substituted crystals, $\mathrm{Rb}_{1-x}(\mathrm{NH}_4)_x\mathrm{H}_2\mathrm{PO}_4$ (RADP) and $\mathrm{Rb}_{1-x}(\mathrm{ND}_4)_x\mathrm{D}_2\mathrm{PO}_4$ (D-RADP), respectively, represent frustrated H-bond or D-bond systems with random competing ferroelectric (FE) and antiferroelectric (AFE) interactions due to random substitution of $\mathrm{Rb}^+$ ions for ammonium $\mathrm{NH}_4{}^+$ or $\mathrm{ND}_4{}^+$ ions.[1,2] The temperature of the paraelectric (PE)-to-FE transition is lowered by the substitution of a small concentration of $\mathrm{NH}_4{}^+$ or $\mathrm{ND}_4{}^+$ ions ($x \lesssim 0.2$). In contrast, for much larger $\mathrm{NH}_4{}^+$ or $\mathrm{ND}_4{}^+$ concentrations ($x \gtrsim 0.8$) an AFE transition occurs. However, in the intermediate range of $x$, no long-range order is observed in the low-temperature phase, and the system forms a frozen proton or deuteron pseudo-spin-glass state somewhat similar to a magnetic spin glass.[2].

The most important similarity between proton-spin-glass (PSG) and magnetic spin-glass (MSG) systems is that both MSG and PSG are quench-disordered systems[3,4] in which interactions between spins in the MSG (or the electric dipole moments in the PSG) prevent the formation of either a ferromagnetic or antiferromagnetic ground state in the MSG (or the formation of a FE or AFE ground state in the PSG) and thus lead to frustration. However, there are also distinguishing features that are unique to the PSG. One fundamental difference arises from the larger concentration of substitutional impurities in a proton PSG system. This feature results in an intrinsic random field that becomes the source of the smearing out of the temperatures of the glass transition.[3] Thus the Edwards-Anderson order parameter, which is a unique characteristic of the spin-glass state, is nonzero even at temperatures substantially above the theoretical glass-transition temperature $T_G$. Experimental evidence from dielectric and birefringence studies[1,5] has shown that the dielectric susceptibility $\epsilon$ has a gradual rather than a sharp singularity-type peak at $T=T_G$. Such behavior is in contrast to that of the magnetic spin-glass systems, which typically display a singularity in the low-field, low-frequency magnetic susceptibility $\chi$ at $T_G$.[4] Furthermore, other experimental techniques exhibit a similar smearing out of the glass transition. For instance, nuclear magnetic resonance (NMR) studies of $^{87}\mathrm{Rb}$ in D-RADP (Refs. 6 and 7) have shown that the Edwards-Anderson (EA) order parameter $q_{\mathrm{EA}}$ is still nonzero at temperatures far above $T_G$ (e.g., room temperature).

Recently, Blinc *et al.*[8] observed the deuteron resonance of $\mathrm{ND}_4{}^+$ in $\mathrm{Rb}_{0.56}(\mathrm{ND}_4)_{0.44}\mathrm{D}_2\mathrm{PO}_4$. In particular, they measured the temperature dependence of the NMR linewidth of $\mathrm{ND}_4{}^+$ at one crystal orientation [$\sphericalangle(c,\mathbf{H}_0)=150°$, where $\sphericalangle(c,\mathbf{H}_0)$ means the angle between the crystal $c$ axis and the external magnetic field $\mathbf{H}_0$]. They found a nonzero $q_{\mathrm{EA}}$ at temperatures much higher than $T_G$, consistent with earlier $^{87}\mathrm{Rb}$ NMR experiments.[6] Similar $q_{\mathrm{EA}}$ studies have been reported recently for $^{87}\mathrm{Rb}$ and the O—D $\cdots$ O acid deuterons in an $x=0.5$ pseudo-spin-glass crystal.[7] In order to understand the roles of the $\mathrm{ND}_4{}^+$ and the N—D—O bonds in forming a glassy state, and thus to better clarify the relationship between the order parameter and the linewidths, we extended this linewidth study to include measurements at other crystal orientations for various $\mathrm{ND}_4{}^+$ concentrations. In particular, we measured the orientation dependence of the second moment in four single-crystal samples [$x=0.22$, 0.44, 0.78, and 1.0 (pure D-ADP)]. We found that the second moment may be proportional to either first or second powers of the EA order parameter $q_{\mathrm{EA}}$, depending on the crystal orientation with respect to the external field. This dependence of the linewidth on $q_{\mathrm{EA}}$ is responsible for the observed $\mathrm{ND}_4{}^+$ line broadening in the temperature region above $T_G$. We were able to fit our experimentally obtained $q_{\mathrm{EA}}$ to a theoretical value obtained from the random-field random-bond Ising-model mean-field theory.[3,9] A comparison between similar experiments in pure and in mixed systems verifies that the orientational dependence of the linewidth is a property unique to the mixed systems.

## II. THEORETICAL BACKGROUND

Pirc, Tadic, and Blinc recently developed a theoretical model[3] to describe proton pseudo-spin-glass systems. Their model is based upon the fact that occupancy of the double potential well of the O—H · · · O protons in hydrogen-bonded ferroelectrics is mathematically similar to the Ising problem for a spin-$\frac{1}{2}$ nucleus. (The bonding proton is commonly called a pseudospin.) In particular, for PSG systems like RADP, Pirc *et al.*[9] and Akseniv *et al.*[10] employ a random-bond version of this model consisting of a transverse tunneling field plus an additional interaction term describing the local random longitudinal fields resulting from the random substitution of $\mathrm{Rb}^+$ for $\mathrm{ND_4}^+$. The Hamiltonian of such a system is

$$H=-\tfrac{1}{2}\sum_{i,j}J_{ij}S_i^zS_j^z-\Omega\sum_i S_i^x-\sum_i(E+f_i)S_i^z\ , \tag{1}$$

where $\Omega$ represents the tunneling frequency of the O—D · · · O deuterons[9,11] and $S_i$ represents the pseudospins corresponding to the two equilibrium positions of the deuterons within the O—D · · · O bonds. The coupling constant $J_{ij}$ represents the random bond (interaction) between the pseudospins, and $E$ and $f_i$ are, respectively, the homogeneous and random local longitudinal fields at nuclear site $i$. The term $f_i$ is nonzero in the PSG system but vanishes in pure D-ADP or pure D-RDP because of the absence of substitutional disorder. The independent distributions of $J_{ij}$ and $f_i$ can be described by Gaussian probability densities[3,9]

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

$$D(f_i)=\frac{1}{\sqrt{2\pi\Delta}}\exp\left[-\frac{f_i^2}{2\Delta}\right]\ , \tag{2b}$$

where $J^2=\tilde{J}^2/N=\langle J_{ij}^2\rangle$ and $\Delta=\tilde{\Delta}/N=\langle f_i^2\rangle$ are the variances of the random-bond and random-field distributions, respectively. Furthermore, $\Delta$ depends on the $\mathrm{ND_4}^+$ concentration $x$ and is typically of the form[3,12]

$$\Delta\propto x(1-x)\ . \tag{3}$$

This mean-field-theory model has been employed to predict the glass transition in the RADP and RADA systems and has also been successful in interpreting some PSG properties.

By modeling the dueteron occupation within the O—D · · · O bonds as pseudospins, this model can be treated easily using spin-glass theories. Following the Sherrington-Kirkpatrick (SK) method,[13] Pirc *et al.*[3] obtained an integral equation to describe the Edwards-Anderson order parameter in the PSG system

$$q_{\mathrm{EA}}=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\exp\left[-\frac{z^2}{2}\right]\times\tanh^2\left[\frac{\tilde{J}}{k_BT}\left[q_{\mathrm{EA}}+\frac{\Delta}{\tilde{J}^2}z\right]^{1/2}\right]dz\ . \tag{4}$$

## III. ELECTRIC-FIELD GRADIENT OF $\mathrm{ND_4}^+$ IN D-RADP SYSTEMS

In general, for nuclei with a nonzero quadrupole moment ($I>\frac{1}{2}$), the NMR frequencies of individual nuclei reflect the values of the electric-field gradient (EFG) tensors at the particular nuclear sites. The observed inhomogeneous line is a convolution (usually treated as Gaussian) of the individual NMR lines. In the case of ammonium ions in the D-RADP or D-ADP systems, rotational motion exchanges the four deuterons within an $\mathrm{ND_4}^+$ group and averages out a large part of the EFG tensor.[8,12,14] Therefore, the observed $\mathrm{ND_4}^+$ deuteron inhomogeneous linewidth is rotationally averaged, as is common to a number of ammonium compounds. This fast reorientational motion narrows the inhomogeneous line above 120 K in D-RADP systems. Hence, this rotationally averaged $\mathrm{ND_4}^+$ deuteron spectrum does not reflect the values of the actual EFG tensors of the individual deuteron sites in the $\mathrm{ND_4}^+$ ion; rather, it represents the EFG tensor averaged over the four deuteron sites.

The EFG tensor at an $\mathrm{ND_4}^+$ site is determined mainly by the surrounding N—D—O bonds. There are eight surrounding oxygens of which four will form N—D—O bonds to a given $\mathrm{ND_4}^+$ group.[8,12] The formation of N—D—O bonds affects the ordering of the O—D—O bonds (i.e., the O—D · · · O deuteron occupancy) and is responsible for the formation of the AFE phase in D-ADP.[15-17] An individual $\mathrm{PO_4}^{3-}$ oxygen may form one short N · · · D—O or one long N—D · · · O bond to an $\mathrm{ND_4}^+$ group, corresponding to the ammonium deuteron's being closer to or further away from the oxygen, respectively. (Here we use N · · · D—O and N—D · · · O to represent the short and long bonds, respectively.) Any $\mathrm{PO_4}^{3-}$ oxygens forming a short N · · · D—O bond will tend to keep the acid deuterons away from this oxygen in order to minimize the potential energy, thereby resulting in polarization of the adjacent O—D · · · O bonds, as illustrated in Fig. 1. In contrast, formation of a long N—D · · · O bond to a $\mathrm{PO_4}^{3-}$ oxygen allows the acid deuteron to stay closer to the oxygen, thereby polarizing the O—D · · · O bonds in the opposite manner (Fig. 1). The formation of short and long bonds is accompanied by a shift in the $\mathrm{ND_4}^+$ position, resulting in a small $\mathrm{ND_4}^+$ tetrahedral distortion, which is the source of the $\mathrm{ND_4}^+$ EFG.

Because of the relatively fast O—D · · · O intrabond motion in the PE phase of D-ADP, the whole $\mathrm{ND_4}^+$ ground experiences a thermally averaged EFG in which the short and long N—D—O bonds are also averaged. An x-ray study[18] reveals that each $\mathrm{ND_4}^+$ ion in the AFE

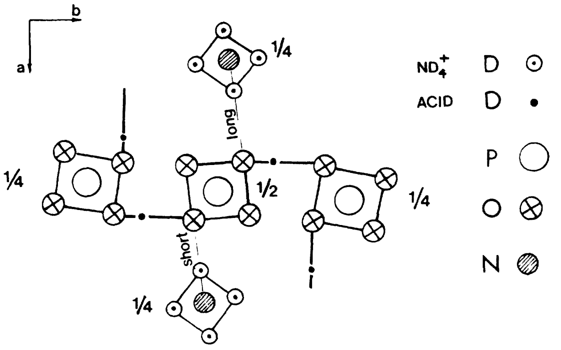

FIG. 1. Schematic structure of D-ADP. Each oxygen in a $PO_4^{3-}$ group links one N—D · · · O and one O—D · · · O bond. The numbers $(\frac{1}{4},\frac{1}{2})$ in the figure indicate the locations of the centers of the corresponding tetrahedra along the crystal $z$ direction (perpendicular to plane of figure).

phase is shifted from its equivalent PE-phase lattice site to an off-center position. This shift results from the formation of two long and two short N—D—O bonds to the adjacent $PO_4^{3-}$ groups, as mentioned earlier. The sublattice polarization results from the correction of the long and short N—D—O bonds with the O—D · · · O bond ordering.

The random substitution of $Rb^+$ for $ND_4^+$ changes the above picture. In the mixed D-RADP systems, some oxygen atoms still form N—D—O bonds with accompanying O—D · · · O order, while other oxygen atoms now have $Rb^+$ neighbors, resulting in an absence of the N—D—O bonds. Since the change in the effective local polarization due to substitution of a $Rb^+$ for an $ND_4^+$ is spatially random, the spatial average of this polarization will be undetectable in a microscopic observation. Nevertheless, this local polarization can be detected in a macroscopic measurement like NMR, since the EFG is very sensitive to changes in local electric fields or polarizations. At higher temperatures the mixed system becomes more like the PE system because of the rapid O—D · · · O intraband motions. At lower temperatures, however, O—D · · · O bond freezeout causes a glasslike state to appear. Since the $ND_4^+$ and N—D · · · O bonds have such important correlation with the O—D · · · O ordering, it is clear that $ND_4^+$ NMR can serve as a useful probe in revealing the spin-glass properties of the D-RADP systems

## IV. DEPENDENCE OF ORDER PARAMETER ON ANISOTROPIC SECOND MOMENT $\sigma^2$

In the high-temperature region both pure D-ADP and mixed D-RADP are in the paraelectric phase. The inhomogeneous line shape of the deuteron $ND_4^+$ reflects thermal averaging and is narrower. This paraelectric-phase linewidth can be described by a second moment $\sigma_0^2$. In the mixed systems the line broadening increases at lower temperatures due to the gradual freeze-out of the O—D · · · O intrabond motions and should be observable at temperatures substantially above $T_G$, as mentioned earlier. The inhomogeneous linewidth can be viewed as a superposition of frequency-shifted lines arising from $ND_4^+$ ions in different clusters (having different polarizations). We consider the second moment $\sigma^2$ of the inhomogeneous line of the $ND_4^+$ deuterons to consist of two terms: (1) a temperature-independent part $\sigma_0^2$ corresponding to the second moment in the high-temperature PE phase and (2) a temperature-dependent part $(\sigma')^2$ due to the freeze-out of the intrabond motions.

To relate the temperature-dependent broadening $(\sigma')^2$ to the order parameter $q_{EA}$, we need to take into account the four N—D—O bonds connecting to a particular $ND_4^+$. From Sec. III, we know that these N—D—O bonds (long or short) depend on the ordering of the four adjacent O—D · · · O bonds, since both types of bonds share the connecting oxygens. The NMR frequency shift of the deuterons for each $ND_4^+$ ion due to the O—D · · · O freeze-out is thus given by

$$\Delta\nu_2^\alpha = \sum_{i=1}^{4} ( A_i p_i + B_i p_i^2 + \cdots ) , \tag{5}$$

where $\alpha$ indicates the $\alpha$th $ND_4^+$ ion, $p_i$ is the local bond order parameter representing the individual O—D · · · O polarizations, and $i$ refers to the four different O—D · · · O bonds near a given $ND_4^+$ group. In general $A_i$ and $B_i$ are anisotropic with respect to crystal orientation. At most orientations the linear term is much bigger than the quadratic term, in which case

$$\Delta\nu_2^\alpha = \sum_{i=1}^{4} A_i p_i \ . \tag{6}$$

If we form an average over the whole crystal, we get

$$\Delta\nu_2 = \overline{\Delta\nu_2^\alpha} = \sum_{i=1}^{4} \overline{A_i p_i} = 0 \ , \tag{7}$$

since there is no bulk polarization $(\bar{p}_i = 0)$ because of the absence of long-range order. The temperature-dependent part $(\sigma')^2$ of the second moment in this case is due to the cluster polarization and is given by

$$\begin{aligned}(\sigma')^2 = \overline{(\Delta\nu_2^\alpha)^2} &= \overline{\left[\sum_{i=1}^{4} A_i p_i\right]^2} \\ &= \sum_{i,j=1}^{4} \overline{A_i A_j p_i p_j} = \sum_i \overline{A_i^2 p_i^2} \ . \end{aligned} \tag{8}$$

Note, $\overline{(\Delta\nu_2^\alpha)^2}$ is zero at high temperatures, where the rapid thermal motions cause the individual cluster polarizations to average to zero. Replica symmetry requires all $\overline{p_i^2}$ to be equal[3] so that we may replace $p_i^2$ by a constant $q_{EA}$, the Edwards-Anderson order parameter,[19] and take it out of the summation. Thus

$$(\sigma')^2 = \overline{\sum_i A_i^2} q_{EA} = \sigma_1^2 q_{EA} \ . \tag{9}$$

Equation (9) indicates that $(\sigma')^2$ is directly proportional to the EA order parameter $q_{EA}$, as has also been found for this linear case by Blinc *et al.*[8]

On the other hand, in some particular crystal orientations (e.g., $c \| \mathbf{H}_0$ for the rotationally averaged $ND_4^+$ case), the linear term $A_i p_i$ almost vanishes due to crystal symmetry.[11,20] In this case $A_i \ll B_i$ and we then need to consider the quadratic term,

$$\Delta\nu_2^\alpha \equiv \sum_{i=1}^{4} B_i p_i^2 \tag{10}$$

and

$$\Delta\nu_2 = \overline{\Delta\nu_2^\alpha} = \overline{\sum_{i=1}^{4} B_i p_i^2} = \sum_{i=1}^{4} B_1 q_{\mathrm{EA}} \equiv \sigma_2 q_{\mathrm{EA}} \ , \tag{11}$$

which is nonzero. Therefore, in this orientation

$$(\sigma')^2 = \sigma_2^2 q_{\mathrm{EA}}^2 \ , \tag{12}$$

which is proportional to $q_{\mathrm{EA}}^2$.

Since $q_{\mathrm{EA}} \ll 1$ at temperatures well above $T_G$ it follows that

$$q_{\mathrm{EA}} \gg q_{\mathrm{EA}}^2 \ . \tag{13}$$

Even when the linear and quadratic coefficients are comparable ($A_i \approx B_i$), Eq. (13) guarantees that the linear term will dominate the second moment.

## V. EXPERIMENTAL RESULTS

### A. Experimental features

We performed NMR studies at $\nu_0 = 12.5$ MHz on the $ND_4^+$ deuterons in $Rb_x(ND_4)_{1-x}D_2PO_4$ mixed single crystals with $ND_4^+$ concentrations $x = 0.22$, 0.44, 0.78, and 1.0 (pure D-ADP). The pure D-ADP crystal was obtained from a commercial source (Quantum Technologies, Florida) with the deuteration level quoted to be about 90%. Moisture contamination was avoided by keeping the samples in a dry container before the experiments.

The inhomogeneous linewidths were obtained from Fourier transforms of the NMR free induction decays (FID's). At lower temperatures the data was obtained from Fourier-transformed spin echoes rather than FID's, since the FID's are too short at the lower temperatures.

The measurements were performed in a variable-temperature liquid-$N_2$ cryostat. The temperature controller uses two sensors: one to control the current of a heating coil wound outside the sample chamber and another to read out the temperature near the sample. The temperature variation was typically less than ±0.5 K during each measurement.

### B. $ND_4^+$ quadrupole coupling constant

We measured the orientational dependence of the quadrupolar line splitting for all four crystals and found, from the EFG tensor components, that the crystal $c$ axis remains the symmetry axis at temperatures above the transition, thus indicating that the tetrahedral structure of the PE phase is not altered as the temperature decreases. We measured the quadrupolar coupling constants of the $ND_4^+$ deuterons in all three mixed samples using Volkoff's method[21] and found that they are nearly the same for all three mixed samples over a large temperature range. The value of $e^2qQ/h^2$ ($\simeq 3.7$ kHz) is approximately equal to that for pure D-ADP in the high-temperature PE phase and is also close to the value for D-ADA.[11] This uniformity in the quadrupolar coupling constants probably reflects a similarity in the underlying crystal structures in which the lattice parameters are comparable. Our linewidths, measured at $\nu_0 = 12.5$ MHz, are not much broader than those at $\nu_0 = 41.46$ MHz (reported in Ref. 8) and certainly show no $1/\nu_0$ dependence as would be expected if there were a significant second-order quadrupole effect on the rotationary averaged $ND_4^+$ deuteron spectrum.

### C. Orientation dependence of linewidths in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$

Figure 2 shows the temperature dependence of the second moment $\sigma^2$ of the $ND_4^+$ deuterons for the mixed pseudo-spin-glass sample D-RADP with $x = 0.44$. In contrast to the nearly-temperature-independent quadrupolar coupling constant, the linewidths of the mixed samples increase significantly as the temperature decreases starting below about 240 K. For the two curves shown in the figure, the tetrahedral axis is perpendicular to the external magnetic field $\mathbf{H}_0$ but the orientation of the crystal $c$ axis with respect to the $\mathbf{H}_0$ is different (0° and 30°). We chose these two orientations because they correspond to two different approximations [Eqs. (9) and (12)] in the dependence of the linewidth on the corresponding parameter $q_{\mathrm{EA}}$.

The $\mathbf{c} \| \mathbf{H}_0$ curve corresponds to the situation in which the linear term $A_i = 0$ and the quadratic term $B_i \neq 0$. As discussed in Sec. II the second moment for this orienta-

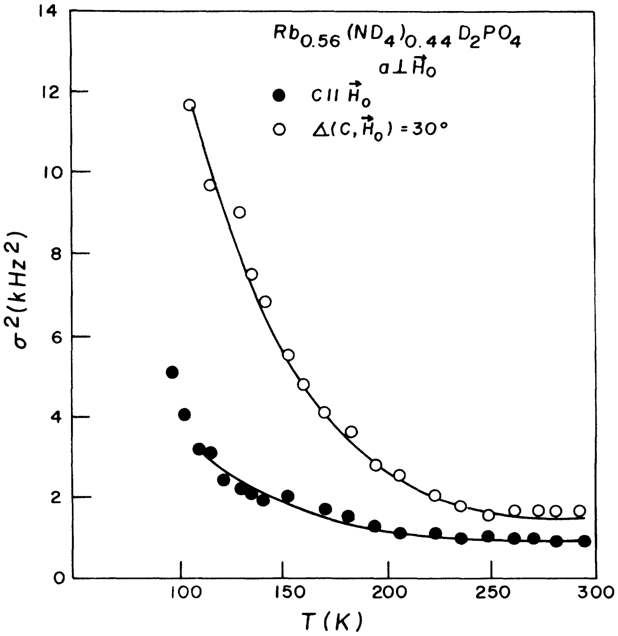

FIG. 2. Temperature dependence of second moment $\sigma^2$ for the $x = 0.44$ sample at two orientations. The solid curves are fits to the data points. Note that the $c \| \mathbf{H}_0$ curve shows much less broadening than does the $\measuredangle(c, \mathbf{H}_0) = 30°$ curve.

tion is proportional to $q_{\mathrm{EA}}^2$ [Eq. (12)]. In contrast, for $\sphericalangle(c,\mathbf{H}_0)=30°$, the linear term is dominant so that the second moment is proportional to $q_{\mathrm{EA}}$ [Eq. (9)] for this orientation. Since the order parameter is much less than unity at temperatures far above the glass transition temperature, we see that $q_{\mathrm{EA}} \gg q_{\mathrm{EA}}^2$ at these temperatures. Therefore, we expect that the linewidth for $c \| \mathbf{H}_0$ should be much less than for $\sphericalangle(c,\mathbf{H}_0)=30°$ and should start to broaden at much lower temperatures. The experimental confirmation of this expectation is displayed in Fig. 2. We performed similar experiments for several other orientations, and our results also show a similar broadening, which increases as the temperature is lowered. For all these orientations, the measured linewidths are significantly larger than that observed for $c \| \mathbf{H}_0$. Since the freeze-out of the O—D · · · O intrabond motion is a gradual process in structural deuteron spin-glass systems, the order parameter $q_{\mathrm{EA}}$, which is a measure of the strength of the local polarization within a cluster, is expected to be nonzero well above $T_G$. The gradually increasing linewidths observed in Fig. 2 reflect this feature.

### D. Evaluation of the order parameter $q_{\mathrm{EA}}$ for $x=0.44$

Section V C contains experimental results for the temperature dependence of the second moment that agree qualitatively with our expectation for the temperature dependence of the order parameter. Since the temperature dependence of the order parameter for the pseudospin-glass systems is theoretically predictable, as described in Eq. (4) for the random-bond random-field Ising model, it is possible to compare the experimentally obtained order parameter $q_{\mathrm{EA}}$ with theory. Such comparison will provide confirmation of the validity of the theoretical model. Also, since the freeze-out of the O—D · · · O ordering is related to $q_{\mathrm{EA}}$, the comparison can verify the assumption that the freeze-out of the O—D · · · O bonds is the actual source of the temperature-dependent part of the second moment $\sigma^2$.

We can derive the experimental order parameter $q_{\mathrm{EA}}$ from our $\sigma^2$-versus-$T$ curves in Fig. 2, according to Eqs. (9) and (12). Specifically, for $c \| \mathbf{H}_0$,

$$q_{\mathrm{EA}}=[(\sigma')^2/\sigma_2^2)]^{1/2} , \tag{14a}$$

and for $\sphericalangle(c,\mathbf{H}_0)=30°$,

$$q_{\mathrm{EA}}=(\sigma')^2/\sigma_1^2 . \tag{14b}$$

To determine $q_{\mathrm{EA}}$ requires a knowledge of $\sigma_1^2$ or $\sigma_2^2$. In principle, these parameters can be determined by measuring the linewidth at temperatures much below $T_G$, where the order parameter $q_{\mathrm{EA}}$ is close to unity. However, there are two experimental difficulties in performing such measurements. First, at substantially lower temperatures the slowing down of the $\mathrm{ND_4}^+$ rotational motion results in a substantial intramolecular contribution to the $\mathrm{ND_4}^+$ linewidth, thus effectively prohibiting an accurate determination of the contribution from O—D · · · O bonds. Second, the $\mathrm{ND_4}^+$ signal strength decreases rapidly as the temperature decreases below 130 K; this decrease is accompanied by a gradual increase in the O—D · · · O deuteron signal. (This phenomenon has been observed and reported earlier[9] but is still unexplained.) Such weakening of the $\mathrm{ND_4}^+$ signal substantially affects the accuracy of the linewidth determination. For these reasons we used an alternative approach to estimate $\sigma_1^2$ and $\sigma_2^2$ for the two orientations.

Our approach is based on the recognition that the maximum displacement of the individual $\mathrm{ND_4}^+$ frequencies in the spin-glass system is approximately the same as the maximum quadrupolar splitting $\mathrm{ND_4}^+$ in the AFE phase of the pure D-ADP, where all the O—D · · · O deuterons are ordered. At 206 K (a few degrees below the AFE transition occurring at $T_c \approx 215$ K in our pure D-ADP sample) we measured in the pure D-ADP crystal maximum quadrupole splittings $\delta\nu$ of approximately 8 kHz for $c \| \mathbf{H}_0$ and 10 kHz for $\sphericalangle(c,\mathbf{H}_0)=30°$. These splittings are much larger than the individual linewidths. Each of the coefficients $\sigma_1^2(30°)$ and $\sigma_2^2(0°)$ is then estimated by equating it to the square of the corresponding $\delta\nu/2$. This approach gives good precision provided that the temperature-dependent part of the linewidth is much larger than the temperature-independent part.

The experimental results for $q_{\mathrm{EA}}$ are plotted in Fig. 3. The individual data points are taken from Fig. 2 using Eq. (14), and the theoretical curve is determined from Eq. (4). To obtain numerically the $q_{\mathrm{EA}}$-versus-$T$ curve we used an iteration method in which $\Delta/\tilde{J}^2$ is varied and $\tilde{J}/k_B$ is held constant. From mean-field theory, the quantity $\tilde{J}/k_B$ in Eq. (4) equals $T_G$ and is a stable replica-symmetry-breaking solution.[9] Even though the original second moments for the two orientations are far apart (Fig. 2), we found, using the value $T_G=70$ K, which is in the range (60–90 K) of theoretical values re-

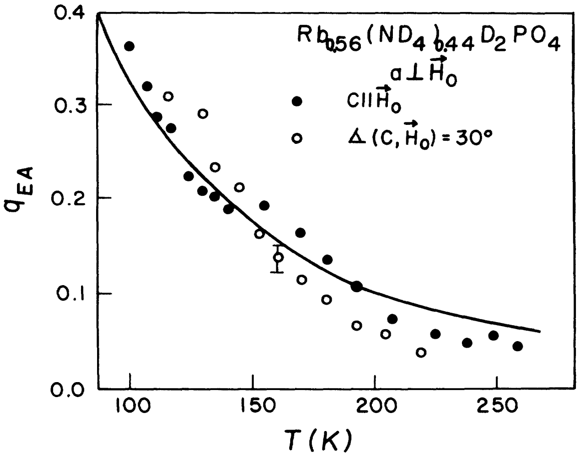

FIG. 3. Temperature dependence of the order parameter $q_{\mathrm{EA}}$ of $\mathrm{Rb_{0.56}(ND_4)_{0.44}D_2PO_4}$. The experimental data are derived from the curves shown in Fig. 2 using Eq. (14). The theoretical curve is obtained from Eq. (4) using $\tilde{J}/K_B=70$ K and $\Delta/\tilde{J}^2=1.0$. Note that the $q_{\mathrm{EA}}$ values obtained from both crystal orientations lie on the same curve.

ported in the literature,[3,8,9] that the experimental data from *both* orientations can be approximately described by a *single* curve (that for which $\Delta/\tilde{J}^2=1.0$). This result is in agreement with the fact that the Edwards-Anderson order parameter, which is dominated in mixed pseudo-spin-glass systems by the O—D···O freeze-out mechanism, should be independent of the crystal orientation. This feature becomes more evident if we make a comparison between the orientational dependences in Figs. 2 and 3. The temperature dependence for 0° and 30° in $\sigma^2$, shown in Fig. 2, certainly cannot be described by one curve. In contrast, the nearly-orientational-independent $q_{\rm EA}$ for the two orientation shown in Fig. 3 is describable by a single curve. This large difference gives strong evidence that the dominant contribution to the $ND_4^+$ line broadening is from the O—D···O motions.

The small discrepancy between the theoretical curve and the experimental data may arise from several sources. First, the experimental data in Fig. 3 appears to deviate slightly from the theoretical curve at temperatures above 220 K. This small discrepancy is not too surprising, since the integral equation for $q_{\rm EA}$ [Eq. (4)] is an approximation whose validity decreases at temperatures far above the transition. Also, our precision in determining the experimental values for $q_{\rm EA}$ is poor at these high temperatures, where the temperature-dependent portion of the linewidth is a small fraction of the total linewidth. Furthermore, there may be a small error due to approximations in estimating $\sigma_1^2$ and $\sigma_2^2$. This error may not be significant at higher temperatures, where $q_{\rm EA}$ is very small, but may become more significant as $q_{\rm EA}$ increases at lower temperatures. In addition, slower $ND_4^+$ reorientations may make a small contribution to the line broadening, especially at lower temperatures, since the $ND_4^+$ deuteron $T_1$ minimum has been determined to occur at about 160 K.[8] Nevertheless, it seems clear that the *dominant* contribution to the data of Figs. 2 and 3 arises from O–D···O freeze-out.

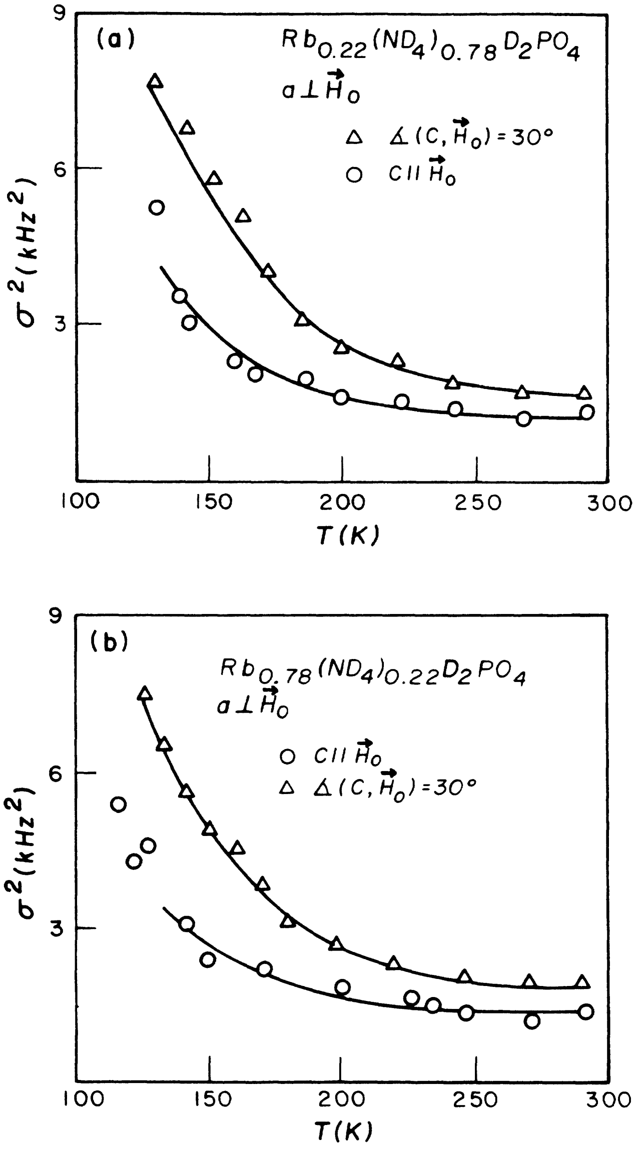

FIG. 4. Temperature dependence of $\sigma^2$ for (a) $x=0.22$ and (b) $x=0.78$. Both figures show an orientational dependence similar to that of Fig. 2.

### E. Dependence of Δ on $ND_4^+$ concentration

Figures 4(a) and 4(b) show the temperature dependence of the second moment $\sigma^2$ for the other two mixed samples ($x=0.22$ and 0.78). Both samples show an orientational dependence similar to that of Fig. 2 for the $x=0.44$ sample.

From the fitting procedure for $q_{\rm EA}$ described in Sec. V D, we can determine the value of the parameter Δ for $x=0.44$. Since Δ depends on the $ND_4^+$ concentration, we may use this experimentally obtained Δ to provide a further check on the validity of the theory. Since Δ is proportional to $x(1-x)$, [Eq. (3)], the $x=0.22$ and 0.78 samples should have precisely the same value of Δ. Their Δ can be determined from the following formula, assuming $\tilde{J}$ is known for each sample:

$$\left[\frac{\Delta}{\tilde{J}^2}\right]_{x=0.22}=\left[\frac{\Delta}{\tilde{J}^2}\right]_{x=0.78}=\left[\frac{\Delta}{\tilde{J}^2}\right]_{x=0.44}\times\left[\frac{(\tilde{J}/k_B)^2_{0.44}}{(\tilde{J}/k_B)^2_{0.22}}\right]\times\left[\frac{0.22\times0.78}{0.44\times0.56}\right]. \qquad (15)$$

The parameter $\tilde{J}$ can be determined from a knowledge of $T_G$ ($\tilde{J}/k_B=T_G$). Since mean-field theory predicts that the glass transition temperature should be 10–20 K higher for those concentrations ($x=0.22$ and 0.78) corresponding to the boundaries of the pseudo-spin-glass region in the phase diagram[9] than for $x=0.44$, we assigned the value 85 K to $T_G$ for the $x=0.22$ and 0.78 samples, which is 15 K above the value (70 K) for the $x=0.44$

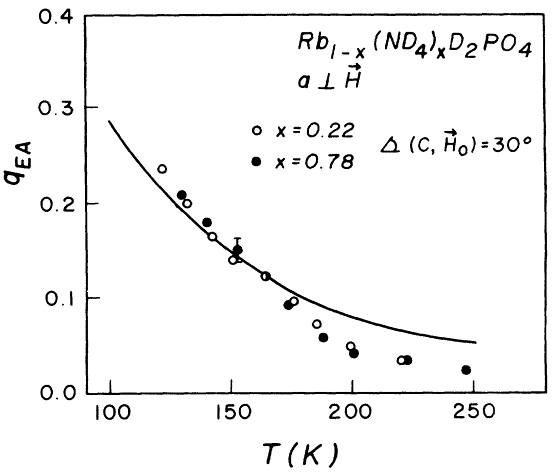

FIG. 5. Temperature dependence of order parameter $q_{EA}$ determined from $x=0.78$ and 0.22 samples for $\sphericalangle(c,\mathbf{H}_0)=30°$. The experimental data points are obtained from Fig. 4. The theoretical curve, obtained from Eq. (4) with $\tilde{J}/k_B=85$ K and $\Delta/\tilde{J}=0.44$, is identical for both $x=0.22$ and 0.78.

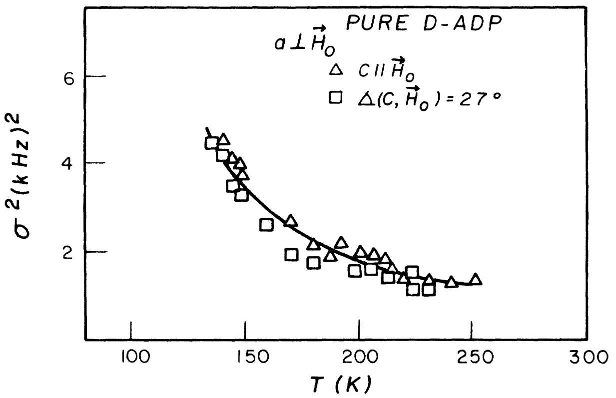

FIG. 6. Temperature dependence of $\sigma^2$ in pure D-ADP for two orientations $[\sphericalangle(c,\mathbf{H}_0)=0°,27°]$. The data show very little orientational dependence for the two orientations.

sample. Substituting these values into Eq. (15), we obtain

$$\left[\frac{\Delta}{\tilde{J}^2}\right]_{x=0.22}=\left[\frac{\Delta}{\tilde{J}^2}\right]_{x=0.78}=0.44\ . \qquad (16)$$

We used these values and Eq. (4) to obtain a "theoretical" curve for $q_{EA}$ (the solid curve of Fig. 5). In Fig. 5 the $x=0.22$ and 0.78 data are reasonably well described by this curve, in approximate agreement with the predictions of Eqs. (4) and (15).

### F. Second moments in pure D-ADP

For comparison we also include here a plot of $\sigma^2$ versus $T$ measured for two orientations in the pure D-ADP sample (Fig. 6). In contrast to the results for the mixed crystals (Figs. 2 and 4), the two sets of data are very close to each other, indicating that there is very little orientational dependence. The orientation, $\sphericalangle(c,\mathbf{H}_0)=27°$, was chosen because individual lines are further apart and, thus, easier to resolve at this orientation. The absence of an orientational dependence in the pure crystal and its presence in the mixed crystals suggest that the orientational dependence is a property of the pseudo-spin-glass. The temperature dependence of linewidths in this pure system may be explained by the slowing down of the thermal fluctuations of the N—D—O bonds, which are related to the sublattice polarization.[22]

## VI. CONCLUSIONS AND DISCUSSIONS

In this paper, we have reported our measurements of the anisotropy and temperature dependence of the rotationally averaged $ND_4^+$ second moment in mixed D-RADP as well as in pure D-ADP. From these measurements we determined the Edwards-Anderson order parameter $q_{EA}$ in the pseudo-spin-glass (PSG) phase. We interpret the temperature-dependent part of the second moment in the mixed crystals as arising from the gradual freezing of the O—D · · · O motions.

We neglected the intramolecular contribution to the line broadening arising from the slowing down of the $ND_4^+$ reorientational motions. This treatment is justified, since the intramolecular interactions are motionally narrowed by the relatively rapid $ND_4^+$ reorientations at all temperatures of our measurements. Furthermore, we found that the inhomogeneous linewidth of the $ND_4^+$ deuterons is several times larger than the homogeneous linewidth in all these samples at all the temperatures of our measurements, suggesting that the homogeneous linewidth is motionally narrowed.[8]

A comparison of our experimental results with the random-bond random-field SK Ising model proposed in Ref. 9 indicates that this mean-field-theory model is fairly good in describing the order parameter in these proton pseudo-spin-glass systems.

One limitation of this model, however, is that it does not predict sharp variations in certain physical properties, such as $q_{EA}$, which would be expected to occur for $ND_4^+$ concentrations ($x$) corresponding to the boundary of the pseudo-spin-glass phase. As a result, knowledge of the $ND_4^+$ concentration $x$ or of $q_{EA}$ in this region will not determine unambiguously whether a mixed sample is in a PSG or in a weakly ordered state.

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