Soft Mode, "Relaxor," and Glassy-Type Dynamics in the Solid Solution $Rb_{1-x}(ND_4)_xD_2PO_4$

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We have investigated the various phase boundaries in the (x,T) phase diagram of the solid solution $Rb_{1-x}(ND_4)_xD_2PO_4$ by means of the nonlocal NMR probe ^{87}Rb. Clear evidence for soft-mode behavior was found for the phase transitions to the long-range-ordered ferroelectric ($x=0.15$) and antiferroelectric ($x=0.95$) phases, whereas thermally activated behavior was observed for the deuteron glass composition $x=0.50$. However, the composition $x=0.70$ exhibits a diffuse phase transition to "long-range" antiferroelectric order and a "relaxor" type dynamics.

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It is a well known fact in the theory of phase transitions (PT) that in a mathematical sense only infinite size systems lead to stable solutions for the ordered phases. In these systems the spatial correlation length ξ of the local order diverges at T_c and is infinite below T_c. The correlation function, e.g., for a system of spins S_i can be written as [1]

$$g(\mathbf{R}_i-\mathbf{R}_j)=[\langle S_iS_j\rangle_T]_{\mathrm{av}}\propto\exp(-|\mathbf{R}_i-\mathbf{R}_j|/\xi)\,,\quad |\mathbf{R}_i-\mathbf{R}_j|\to\infty\,, \tag{1}$$

where $|\mathbf{R}_i-\mathbf{R}_j|$ is the distance between the spins S_i and S_j. From this one can define a macroscopic order parameter

$$P^2=\lim_{|\mathbf{R}_i-\mathbf{R}_j|\to\infty} g(\mathbf{R}_i-\mathbf{R}_j)\,. \tag{2}$$

However, real systems are never infinite and finite size effects as, e.g., grain-size-dependent transition temperatures in ceramics or other heterogeneous systems are well known in technical applications. Moreover, many effects in "homogeneous" systems which are attributed to defects may also be finite size effects as, e.g., the occurrence of ferroelectric 180° domains to compensate the surface charges produced by the spontaneous electric polarization.

In this Letter we report on the experimental evidence for finite size effects in $Rb_{1-x}(ND_4)_xD_2PO_4$ which is a disordered system with broken translational invariance and competing ferroelectric (FE) and antiferroelectric (AFE) interactions. We will show that different average cluster or nanometric domain sizes are characteristic for the phase-transition behavior of these systems in a certain concentration range. Specifically we show that, depending on the ammonium content parameter x, there can be a long-range-ordered FE or AFE phase exhibiting typical soft-mode behavior, a long-range-ordered AFE glass —which is called in recent literature a "relaxor" phase [2]—and is reminiscent of a spin glass in an external magnetic field, or a short-range-ordered glass with or without long-range-ordered FE islands. The finite size concerns here the correlation length ξ introduced in Eq. (1) which in some of the above cases does not diverge at T_c but remains finite.

The solid solution $Rb_{1-x}(NH_4)_xH_2PO_4$ and its deuterated analog $Rb_{1-x}(ND_4)_xD_2PO_4$, henceforth designated as RADP-X and D-RADP-X ($X=100x$), respectively—which first have been investigated by Courtens [3] who discovered the glassy character—have proven to be extremely rich in features for studying problems of the above-mentioned kinds. In the last decade many studies have been performed on this system. For a review see Höchli, Knorr, and Loidl [4]. However, a real breakthrough in the understanding was achieved when the pseudospin random-bond random-field model of Pirc and co-workers [5,6] was able to explain the NMR line shapes of the acid deuterons in D-RADP-44 [7], as well as, the Tl^{++} ESR line shapes of Tl doped RADP-70 [8]. This analysis revealed unambiguously the glassy character of the system, and also confirmed the thermally activated behavior of the dynamics observed in earlier T_1 measurements [9,10]. A further proof of the glassy character was the observation of a bifurcation between the field-cooled and zero-field-cooled static dielectric susceptibility in D-RADP-60 at 61 K [11].

The Edwards-Anderson order parameter q_{EA} defined in this model, which can be written as the second moment of the probability distribution function of the time averaged local polarization p,

$$q_{\mathrm{EA}}=\int_{-1}^{-1}W(p)p^2dp,\quad p=\frac{1}{\tau}\int_0^\tau p(t)dt\,, \tag{3}$$

cannot, by itself, distinguish between a random freezeout and a locally correlated freezeout of the protons or deuterons on the biased hydrogen bonds. The length over which the protons are coherently frozen out in one of the six Slater configurations [12] without violating the ice rules has been derived from the diffuse diffracted x-ray intensity in RADP. It is 2.0 nm [13], a value which is definitely longer than the average proton-proton distance, and definitely shorter than the typical size of conventional domains. A similar value has been estimated from our ^{87}Rb NMR line shape analysis in the glass phase of D-RADP-50 [14,15].

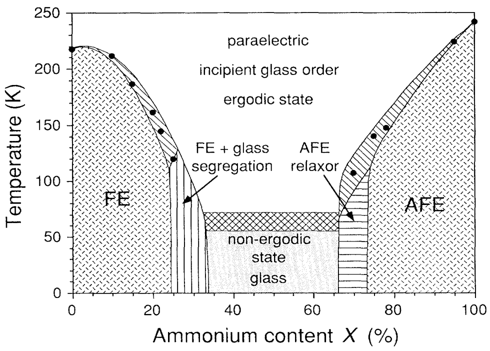

FIG. 1. Phase diagram of D-RADP-X as obtained from ^{87}Rb NMR. The filled circles correspond to the mean $\bar{T}_c$'s. Note that all phase boundaries are diffuse.

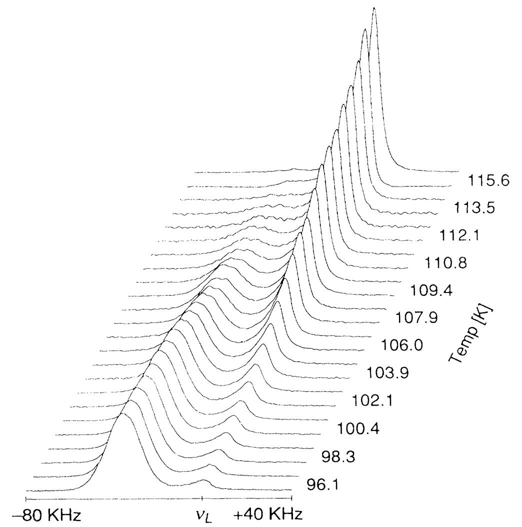

FIG. 2. Temperature dependence of the ^{87}Rb $-1/2 \leftrightarrow +1/2$ NMR spectrum in the PE-AFE coexistence region for D-RADP-70 ($\mathbf{B}_0 \| c$). The line at $\nu_L = 98$ MHz corresponds to PE volume fractions and the line at -38 kHz to AFE regions.

The reason why NMR spectroscopy is so successful in the D-RADP-X system is the existence of local and nonlocal NMR probes in this system. While the covalently bonded deuteron sees only the local polarization, but not the polarization of the neighboring deuterons, the ionically bonded Rb observes a range of about ±2 lattice constants [14,16] and is thus capable of distinguishing between different spatial correlations of deuteron order. Furthermore, the characteristic time scale of NMR for time averaging is in the order of ms, and can be extended to the order of 100 s by means of 2D NMR exchange measurements. It can thus be considered as a quasistatic investigation method.

Figure 1 shows the phase diagram of D-RADP-X as obtained from ^{87}Rb NMR measurements. The different phases can be unambiguously discriminated by their characteristic orientational dependence of the quadrupole perturbed NMR line shapes [14] or by their characteristic relaxation behavior.

The filled circles represent the average transition temperatures, whereas the diagonally hatched areas indicate the temperature region where both the ordered and the disordered phases coexist [17]. Figure 2 shows a series of ^{87}Rb NMR spectra for different temperatures in the coexistence region of D-RADP-70. The temperature dependence of the measured volume fractions fits very well to an error function which implies a Gaussian distribution of transition temperatures. From the diagonally hatched areas in Fig. 1 one can see that the width of the diffuse PT is increasing towards the center of the phase diagram. In the glass region of the phase diagram the transition from the ergodic thermodynamic state into the nonergodic one is indicated by the cross-hatched area. At present the exact transition temperatures are not known since the predicted instability [5], i.e., at 55 K for D-RADP-50, has not yet been observed by means of NMR. The observed transition in the inhomogeneous NMR line shape takes place at higher temperatures, i.e., between 130 and 90 K for D-RADP-50. In the same temperature region the dynamics of the system becomes polydispersive, whereas it is monodispersive above 120 K [15].

The dynamic behavior of the system is obtained independently from the characteristic temperature dependence of the longitudinal ^{87}Rb NMR relaxation time T_1. All Rb T_1 measurements published so far on the RADP system have a serious deficiency, since they do not take into account that the magnetization recovery $M(t)$ is inherently nonexponential in the case of quadrupolar relaxation [18]. For the central line of ^{87}Rb$(I = \frac{3}{2})M(t)$ can be written as

$$M(t) = M_\infty \left\{ 1 - a \sum_{k=1,2} \exp[-(2W_k t)^\beta] \right\}, \tag{4}$$

where W_1 and W_2 are the relaxation rates at the Larmor frequency ω_L and at $2\omega_L$, respectively. The stretched exponent β describes the distribution of relaxation rates of the independently relaxing clusters, i.e., the heterogeneity of the sample. This choice was made for reasons of tractability knowing that $M(t)$ is rather insensitive to the particular shape of the distribution function. The parameters W_1, W_2, and β are obtained from a nonlinear computer fit of the function (4) to the measured $M(t)$'s. For reliable results $M(t)$ had to be measured over 5 to 6 orders of magnitude in time. Furthermore, a good signal-to-noise ratio and an excellent baseline stability of the pulsed NMR spectrometer was required. The resulting parameters $\tau_1 = 1/2W_1$ and $\tau_2 = 1/2W_2$ are shown as a function of the inverse temperature $(1000/T)$ for the compositions $x = 0.15$, and 0.70 together with 0.50 in Figs. 3, and 4, respectively.

The relaxation rates $W_k = \langle A_k^2 \rangle J_k(\omega)$ are usually described by a product of the mean square amplitude fluc-

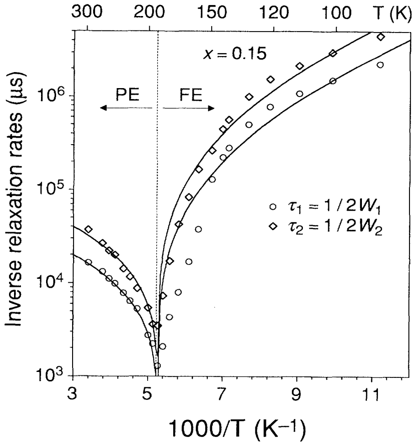

FIG. 3. ^{87}Rb inverse relaxation rates τ_1 and τ_2 vs $1/T$ in D-RADP-15. The solid lines are calculated.

tuations of the relevant elements of the electrical field gradient (EFG) tensor, and a normalized spectral density. In the case of an uncorrelated thermally activated motion it is assumed that $\langle A_k^2 \rangle$ is temperature independent, while $J_k(\omega)$ is the Fourier transform of the normalized single particle autocorrelation function:

$$J_k = \tau_c/[1+(k\omega_L\tau_c)^2], \quad k=1,2, \tag{5}$$

where τ_c is given by the Arrhenius law. This leads to the well known T_1 minimum for $\omega_L\tau_c=1$ which separates the fast motion regime $\omega_L\tau_c \ll 1$, where $J_k=\tau_c$, from the slow motion regime $\omega_L\tau_c \gg 1$, where $J_k = 1/k^2\omega_L^2\tau_c$. For our case this means that the ratio τ_2/τ_1 increases by a factor of 4 on going from the fast motion to the slow motion regime, provided that the system remains monodispersive. In the case of a polydispersive system with a Kohlrausch-Williams-Watts- (KWW-) type single-particle autocorrelation function $F(t)=\exp[-(t/\tau_0)^\alpha]$ this factor of 4 is reduced and equals $2^{(1+\alpha)}$ $(0<\alpha\leq 1)$ [19]. Note that the two stretched exponents α and β, see Eq. (4), describe different probability distributions $\rho(\tau_c)d\tau_c$ and $\sigma(W_k)dW_k$, respectively, which need not be equal.

The theory of NMR spin-lattice relaxation for the classical PT's in the KH$_2$PO$_4$ (KDP) family has been worked out by Blinc *et al.* [20] and is reviewed in detail in [21,22]. The model they use is based on a collective coordinate representation of the hydrogen bond fluctuations connected with a soft-lattice mode. This model predicts a minimum of "T_1" at T_c, but no dispersion of the relaxation on either side of the minimum. This is indeed observed in the case of D-RADP-15, Fig. 3, where the solid lines are a fit of the theory [20,21] to our τ_k data points. The fit is excellent in the PE phase and quite good in the FE phase in view of the diffusiveness of the PT. Thus the soft-mode character of the PT is confirmed for D-RADP-15. In a similar way, the absence of τ_k dispersion

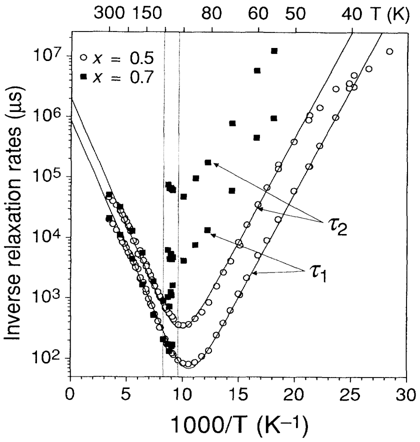

FIG. 4. ^{87}Rb inverse relaxation rates τ_1 and τ_2 vs $1/T$ at $\nu_L=98.163$ MHz in D-RADP-50 and -70. The solid lines are calculated on the basis of thermally activated motions with $E_a=81$ meV and $\tau_\infty=0.5\times10^{-13}$ s.

in the AFE phase is evidence for the AFE soft-mode character of the first-order PT in D-RADP-95 [17]. Here the discontinuity of the τ_k at T_c is a consequence of the discontinuity of the AFE order parameter η, since the τ_k are proportional to $1/(1-\eta^2)$.

In contrast to this "soft-mode" behavior, the dynamics in the compositions D-RADP-50 and -70 is slowing down from 10^{13} Hz to the 1 Hz region (Fig. 4). In the fast motion regime both crystals show an identical relaxation behavior with $\tau_1/\tau_2=\langle A_2^2\rangle/\langle A_1^2\rangle$, whereas this ratio is considerably greater in the slow motion regime, as predicted above for the thermally activated motion. Since the order in the low temperature phase of D-RADP-70 is unambiguously of "long-range" AFE type (Fig. 2)—long in comparison with the observation range of the NMR probe—we have discovered here a "relaxor" type antiferroelectric. The first-order character of the diffuse PT manifests itself by the discontinuous change in τ_k at T_c (by a factor of about 100). In the coexistence range of the PE and AFE phases the corresponding τ_k of both phases could be obtained from the fits, however, with reduced accuracy. In contrast to this behavior $\tau_k(T)$ does not show any discontinuity for D-RADP-50. In the slow motion regime the behavior of both compositions can be described by the Arrhenius law $\tau_c=\tau_\infty\exp(E_a/k_BT)$ with the same activation energies E_a, but with inverse attempt frequencies τ_∞ which differ by a factor of 100. Since this difference is not present in the fast motion regime it corresponds to a gap in the single particle autocorrelation time of D-RADP-70 extending from 10^{-9} to 10^{-7} s.

On the FE side of the phase diagram we have also measured the compositions $x=0.20$, 0.25, and 0.30. While D-RADP-20 still undergoes a complete FE phase transition, the transitions for $x=0.25$ and 0.30 affect only

25% or 10%, respectively, of the volume. The other parts of the volume exhibit short-range glass order with the corresponding dynamics. It seems that the FE clusters or microdomains are still large enough to retain some soft-mode character. At present it is not clear whether this phase segregation is intrinsic or a result of defects or composition striations originating from crystal growth.

To summarize, we have shown that the short-range glass phase in the (x,T) phase diagram of D-RADP-X is sandwiched between a heterogeneous FE+glass state and a homogeneous AFE relaxor phase ("long-range"-ordered glass) which is characterized by the following features: (a) Diffuse PT's with coexistence of both the disordered high temperature phase and the long-range ordered AFE low temperature phase; (b) nanometric domain sizes which substantially exceed the observation range of ± 1.5 nm of the ^{87}Rb NMR probe; and (c) a tremendous slowing down of the deuteron intrabond motion on lowering the temperature, which continues below T_c, in contrast to the "soft-mode" behavior.

Furthermore, we have identified the soft-mode character of the PT's for $x=0.15$ and $x=0.95$. From this behavior we conclude that the spatial correlation $\xi(x)$ of the deuteron order in any of the six Slater configurations has a minimum different from zero in the center of the phase diagram, whereas, it diverges for $x \rightarrow 0$ and $x \rightarrow 1$ for the corresponding FE or AFE Slater configurations. The observed finite size effects in D-RADP-X can thus be assigned to the finite value of the correlation length $\xi(x)$.

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