Pressure-Induced Suppression of the Proton-Glass Phase and Isotope Effects in $Rb_{1-x}(NH_4)_xH_2PO_4$

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(Received 9 March 1987)

The proton-glass phase in $Rb_{0.5}(NH)_{0.5}H_2PO_4$ can be completely suppressed by 5 kbar, and the details of this suppression are indicative of the nonequilibrium nature of the glass transition. There is a large hydrogen isotope effect not only on the dynamic glass-transition temperature but also on its pressure derivative. The results emphasize the importance of the proton's intrabond motion in the freezing dynamics.

There has been much recent interest in the dynamic and static properties of systems in which randomly competing interactions cause the formation of a glassy state at low temperatures. Much of this work has dealt with disordered magnetic systems, especially the spin-glass state.[1] More recently, considerable attention has been given to electric dipolar and quadrupolar glasses such as $Rb_{1-x}(NH_4)_xH_2PO_4$,[2,3] $KBr_{1-x}(CN)_x$,[4] and $KTa_{1-x}Nb_xO_3$.[5,6] On cooling, these systems exhibit a slowing down of the orientational relaxation of their multipoles, ultimately resulting in a frozen-in frustrated multipole state with no long-range orientational order.

The $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP) system has become the most thoroughly investigated and, perhaps, the most understood system among the multipolar glasses.[2,3] Its dynamical response has revealed the full evolution of the freezing dynamics over an extremely large range (≈ 17 orders of magnitude) of frequency.[2] This is a much broader range than is possible for metallic spinglasses, and, consequently, the evolution of the glassy state in RADP is now better established than in any glassy system.

Earlier high-pressure studies have led to a much better understanding of the nature of the competing intermolecular and intramolecular interactions which are responsible for the establishment of long-range order and the onset of many structural phase transitions.[7] Pressure can also be expected to modify the interactions responsible for short-range correlations and thereby to provide new insights into the formation and properties of the glassy state. This consideration was the preliminary motivation for the present work, and the above facts about RADP made this material system an ideal choice.

In this Letter we report the effects of pressure on the properties of an RADP crystal with $x = 0.5$. This composition places this sample in the middle of the compositional domain of the glassy state. It will be shown that the pressure effects are large and that the glassy state is completely suppressed for hydrostatic pressures ≥ 5 kbar. The manner in which the dynamic glass transition temperature (T_g) vanishes, i.e., how $T_g \rightarrow 0$ K, is qualitatively different from the vanishing of ferroelectric (FE) and antiferroelectric (AFE) transitions, a feature which emphasizes the nonequilibrium nature of the glass transition. In combination with earlier data on a deuterated sample, the present results also reveal a large hydrogen isotope effect not only on T_g but also on its pressure derivative, dT_g/dP, thereby emphasizing the importance of the intrabond motion of the proton (deuteron) in the freezing dynamics.

The end members of the RADP system, RbH_2PO_4 and $NH_4H_2PO_4$, transform on cooling to ordered FE and AFE phases, respectively. For compositions $0.2 \leq x \leq 0.75$, there is much convincing evidence for the existence at low temperatures of short-range correlations and the formation of a proton-glass state believed to be associated with the freezing of "pseudospin" $O—H \cdots O$ proton intrabond motion.[2,3,8] The suppression of long-range order in this composition range is a consequence of the frustration of the system caused by the random substitution of NH_4 ions for Rb ions (or vice versa), which introduces random fields which couple to the $O—H \cdots O$ pseudospins.

RADP is analogous to magnetic spin systems in that the elementary excitation in RADP involves the motion of the proton between two equilibrium sites $(S_z = \pm 1)$ along the $O—H \cdots O$ hydrogen bond under ice-rule-like constraints.[8] This motion and its freezing dynamics are determined to a large extent by the details of the double-well potential which describes the two equilibrium sites along the $O—H \cdots O$ bond. Pressure can significantly modify this potential and thereby the glassy behavior of the system. Earlier measurements[9] on a deuterated RADP crystal $(x = 0.48)$ showed that T_g de-

creases with hydrostatic pressure and suggested that it should be possible to suppress the glass state completely (i.e., $T_g \to 0$ K) in undeuterated RADP at a readily accessible pressure. This suppression is demonstrated below.

The combined temperature (4–100 K), hydrostatic pressure (0–8 kbar), and frequency (10^4–10^6 Hz) dependences of the real (ϵ') and imaginary (ϵ'') parts of the dielectric constant were investigated. The samples, in the form of thin plates $\simeq 7$–20 mm^2 in area and 0.6–1.0 mm thick, were cut from clear, solution-grown crystals. The apparatus and techniques were similar to those used earlier.[10] Helium was used as the pressure-transmitting medium. All measurements were made at applied field strengths of ≤ 10 V/cm.

Figure 1 shows some of the results on an a-cut sample. At 1 bar the $\epsilon'_a(T)$ response does not exhibit a cusp, but a characteristic[2] S-shaped curve, and $\epsilon''_a(T)$ exhibits a well-defined, frequency-dependent peak. The peak temperature, T_{max}, shifts to higher temperature with increasing frequency—behavior characteristic of materials which transform to a glassy phase at low temperature.[2,4,5] The strong influence of pressure is clearly seen. With increasing pressure there is a large displacement of the $\epsilon'_a(T)$ and $\epsilon''_a(T)$ responses to lower T.

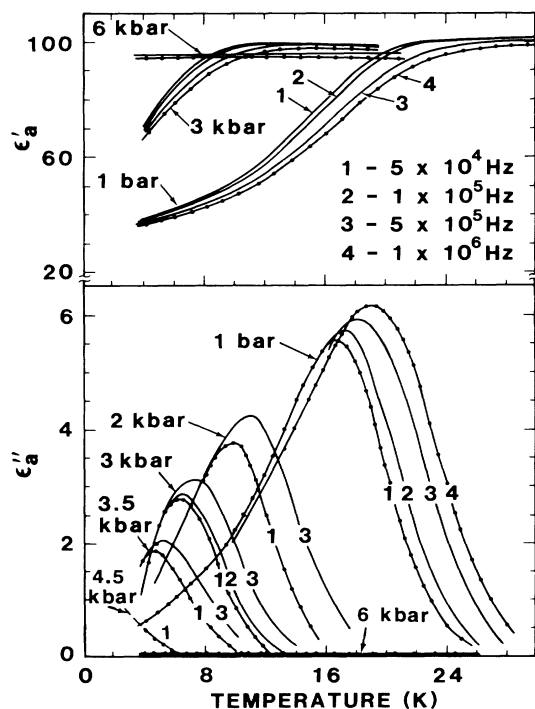Figure 2 shows T_{max} at different frequencies as a func-

tion of pressure. At each frequency the decrease of T_{max} with pressure is linear, and the dispersion of T_{max} with frequency decreases markedly with pressure. We take T_{max} as a measure of T_g. Unfortunately, our pressure apparatus could not be cooled below 4 K and there are no data below this temperature. Extrapolation of the linear $T_g(P)$ responses to higher pressures suggests that the proton-glass phase should vanish by $\simeq 5$ kbar. In support of this suggestion, the 6.0-kbar data in Fig. 1 show no anomaly in either $\epsilon'_a(T)$ or $\epsilon''_a(T)$ down to $\simeq 4$ K and no hint of any impending anomalies at lower T. In fact, at 6 kbar the dielectric loss, and thereby ϵ''_a, become extremely small and frequency independent, as shown in Fig. 1. We take these results to indicate strongly that the proton-glass phase has completely vanished at this pressure.

The results for a c-cut sample were qualitatively similar to the a-cut results in Fig. 1. At 6.0 kbar there is no anomaly and no dispersion in $\epsilon''_c(T)$, and there is no evidence in the data for an impending proton-glass state below 4 K.

As noted above, the strong frequency dispersion exhibited by the dielectric responses (Fig. 1) is characteristic of glassy behavior. Analysis of such results at 1 bar re-
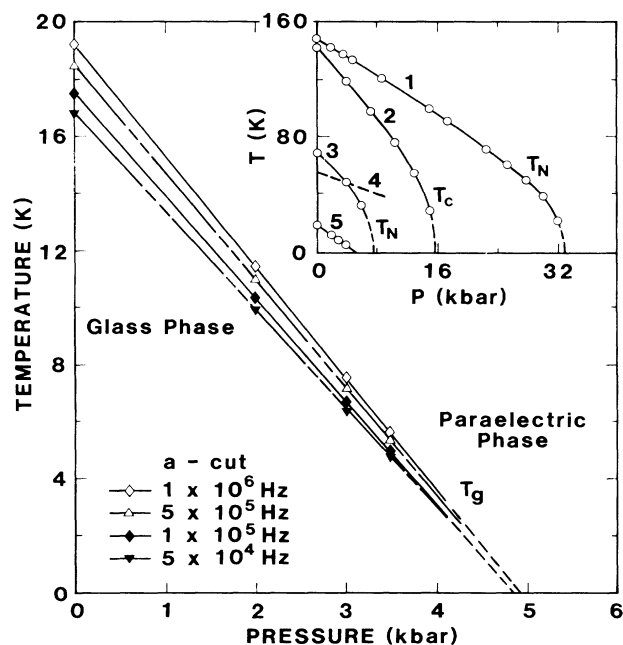

FIG. 1. Temperature dependences of the real (ϵ'_a) and imaginary (ϵ''_a) parts of the a-axis dielectric constant of RADP ($x = 0.5$) measured at different frequencies and hydrostatic pressures.

FIG. 2. Temperature-pressure phase diagram for an RADP crystal showing the pressure dependence of the dynamic glass transition temperature T_g, and the expected vanishing of the glass phase above $\simeq 5$ kbar. Inset: Comparison of the pressure dependences of the dynamic glass (T_g), ferroelectric (T_c), and antiferroelectric (T_N) transition temperatures for several Rb$_{1-x}$(NH$_4$)$_x$H$_2$PO$_4$ crystals. Curves 1–5 correspond to $x = 1$, 0, 0.8, 0.48 (72% D), and 0.5, respectively.

veals that T_{max}, or T_g, increases nearly linearly with the logarithm of the measuring frequency, and there is a broad distribution of relaxation times τ.[2] The present dielectric data thus show that there is a large slowing down of the relaxation with decreasing T. However, these data extend over a relatively small range of frequency, and the question remains as to whether or not the system exhibits a finite "static" freezing temperature. Fortunately, it has been possible to answer this question in the affirmative for RADP. The key is the fact that the dielectric polarization is the fundamental excitation mode in RADP, and this mode is active in Raman and Brillouin scattering, in addition to dielectric susceptibility. This important feature has made it possible to use all three techniques to follow the full evolution of the freezing dynamics over ≈ 17 decades of frequency. Results at 1 bar show[2] that the T dependence of the cutoff (or lowest) frequency v_c of the distribution of relaxers is very well represented over this large frequency range by the phenomenological Vogel-Fulcher equation $v_c = 1/\tau_c = v_0 \exp[-E_c/(T-T_0)]$. Here v_0 is an attempt frequency, E_c is an activation energy in units of temperature, and T_0 is the temperature where all relaxation times diverge, i.e., the "static" glass freezing temperature. A fit of the 1-bar data by this expression yields[2] $v_0 = 3.5 \times 10^{12}$ Hz, $E_c = 268$ K, and $T_0 = 8.7$ K.

Our high-pressure dielectric data do not extend over a broad enough frequency range to allow a meaningful fit by the Vogel-Fulcher equation. Nevertheless, it is possible to make some qualitative remarks about the pressure dependences of E_c and T_0. In the high-T phase the protons are disordered in their potential wells, leading to an effectively symmetric O—H—O bond. On cooling, there is a slowing down of protonic motion, and ultimately the proton freezes in one or the other of the potential minima leading to an elongated asymmetric O—H $\cdots$ O bond. To support this picture we note that there is an expansion of the unit-cell volume of RADP on proton freezing.[2,3] More generally, it is known that in crystals of the KH_2PO_4 (KDP) family, asymmetric H bonds are longer than symmetric ones, and there is lattice expansion on proton ordering.[10] The energy barrier between the two potential minima relates to the activation energy E_c.

Pressure opposes the expansion of the unit-cell volume and should thereby suppress proton freezing, i.e., lower T_g and T_0. Alternatively, pressure can be expected to reduce the H-bond length and favor a more symmetric bond. The shorter the bond, the lower the energy barrier and thereby E_c. The consequence of this barrier lowering is a lower T_g and T_0.

For sufficiently high pressure, we expect that the H bond will become sufficiently short and effectively symmetric, even at the lowest temperatures. In such a circumstance the energy barrier becomes vanishingly small, and there will be no proton freezing,[10] i.e., the glassy

state vanishes. This is, of course, what is observed experimentally (Fig. 1).

It should be emphasized that while the above qualitative picture contains the essential physics of the triggering mechanism for the transition, it is certainly not complete, since it ignores proton-proton correlations and the coupling of the proton motion to the lattice. The cited expansion of the lattice observed on proton freezing illustrates the strength of the latter coupling. Coupling and correlations, whether long or short range, are known to be essential for a detailed understanding of the properties of H-bonded systems[7] including the RADP glasses.[11,12]

The inset in Fig. 2 compares the pressure-induced suppression of the glassy state in RADP with the suppression of the FE state in RbH_2PO_4 (Ref. 13) and AFE state in $NH_4H_2PO_4$.[14] Also shown are results for an $x = 0.8$ RADP crystal and for a partially deuterated (72% D) $x = 0.48$ RADP crystal. The data show an important difference between the glassy "transitions" and the FE and AFE transitions which we now discuss.

For $NH_4H_2PO_4$ and RbH_2PO_4 (curves 1 and 2 in the inset), the magnitude of the slope $dT_{c,N}/dP$ increases with pressure at high pressure with strong indication that the transition temperature vanishes with infinite slope, i.e., $dT_{c,N}/dP \rightarrow -\infty$ as $T_{c,N} \rightarrow 0$ K. This behavior, which is in agreement with the prediction of certain models,[7] is also dictated by the third law of thermodynamics for an *equilibrium first- or second-order phase transition*.[15] The results on the $x = 0.8$ RADP sample (which exhibits an AFE transition) suggest a similar behavior. The response of the $x = 0.5$ RADP sample, on the other hand, is qualitatively different. In this case T_g, which is frequency dependent, decreases linearly with pressure down to ≈ 5 K (Fig. 2) with no hint of any impending increase in the magnitude of dT_g/dP at lower T's. We cannot, of course, completely rule out the possibility of such an increase below 5 K, but experience with other RADP crystals ($x = 0$, 0.8, and 1.0 in Fig. 2) and oxides,[5] as well as the 4.5-kbar $\epsilon_a''(T)$ data in Fig. 1 (and 4-kbar data, not shown), suggest that this is unlikely. The 4.5-kbar data show a sharp rise in ϵ_a'' with decreasing T starting at ≈ 6 K. This signifies an impending glass transition below 4 K, and it suggests that the transition has not completely vanished by 4.5 kbar. Comparison of these data with the $\epsilon_a''(T)$ data at 3 and 3.5 kbar further suggests that T_g for the 4.5-kbar data can be expected to occur 4–5 K below the onset in the sharp rise in $\epsilon_a''(T)$ at ≈ 6 K. This would place T_g for the 4.5-kbar data at ≈ 1–2 K, not inconsistent with the extrapolation of the $T_g(P)$ data in Fig. 2. Thus, the above results strongly indicate that the response of the $x = 0.5$ sample is different from the FE and AFE crystals in the inset in Fig. 2, and we believe that this difference is most likely evidence for the nonequilibrium nature of the transition in this material. We expect the deuterated $x = 0.48$

RADP sample also to exhibit this nonequilibrium response, but the data do not extend to sufficiently high pressure to test this point.

Finally, we note that there is a large hydrogen-isotope effect not only on T_g but also on its pressure derivative. The $x = 0.5$ and $x = 0.48$ (72% D) samples afford a particularly good comparison. The onset of proton freezing in the glass-forming range of RADP is approximately independent of composition so that the small difference in composition between the $x = 0.5$ and $x = 0.48$ samples is essentially insignificant. The differences in T_g and dT_g/dP between the $x = 0.5$ and $x = 0.48$ (72% D) samples, namely the increase in T_g at 10^5 Hz from 17.4 to 56.5 K and the decrease in the magnitude of dT_g/dP from -3.6 to -2.0 K/kbar on deuteration, are thus manifestations of hydrogen-isotope effects. These effects can be qualitatively understood in terms of proton tunneling in the same way as similar effects for FE and AFE transitions.[7] Specifically, the higher T_g and smaller dT_g/dP for the deuterated glass are due to the fact that the deuteron sits deeper in its potential wells than does the proton (lower zero-point energy) and has a much lower probability for tunneling between the two potential wells along the O—$D \cdots O$ bond. Our present results thus again emphasize the important role of the hydrogen-bond potential in triggering the ordering process in KDP-type materials regardless of whether the ordering is long or short range. They also emphasize the usefulness of pressure in studying the ordering process.

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[10]It is not necessary for the barrier to vanish completely. The barrier has to become small enough to allow the proton to move (or tunnel) freely between the two potential minima at all temperatures.

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[15]According to the third law of thermodynamics, the difference in entropy (ΔS) between the two phases goes to zero as $T \to 0$ K. The consequence of this is that $dT_c/dP \to \infty$ as $T_c \to 0$ K. This can be readily seen from the Clausius-Clapeyron equation ($dT_c/dP = \Delta V/\Delta S$, where ΔV is the difference in volume) for a first-order phase transition and from the Ehrenfest equation ($dT_c/dP = VT \Delta \beta/\Delta C_p$, where $\Delta \beta$ and ΔC_p are the differences in thermal expansion and specific heat, respectively) for a second-order phase transition. Recall that the specific heat $T(\partial S/\partial T) \to 0$ as $T \to 0$ K.