Glasslike Thermal Properties and Isotope Effect in $Rb_{1-x}(NH_4)_xH_2PO_4$ Mixed Crystals

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Low-temperature thermal conductivity and time-dependent specific heat have been measured on mixed crystals of $Rb_{1-x}(NH_4)_xH_2PO_4$ ($x=0.35,0.72$), in the composition range in which an electric dipole glass state forms below ~100 K. Glasslike excitations have been observed. In the fully deuterated isomorph with $x=0.62$, however, the thermal conductivity is that of a crystal, and glasslike excitations are only seen in the specific heat at very long times. This striking isotope effect shows that the low-energy excitations in these crystals relate to tunneling of protons or deuterons, respectively.

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Common to all amorphous solids is a spectrum of low-energy excitations; their density of states is nearly independent of the chemical composition, and so is their coupling to the lattice waves. Tunneling states of atoms or groups of atoms is the most likely, though still unproven, explanation for these excitations. In particular, their apparent universality has remained extremely puzzling. These excitations are not restricted to structural glasses, but have also been identified in a variety of disordered crystalline solids, for example in $(KBr)_{1-x}(KCN)_x$ [1,2]. In these crystals, the *elastic* quadrupolar interaction between the cyanide molecule ions leads to the formation of an orientational glass phase at low temperatures. It has been argued [3] that a fraction of these ions retain a quasirotational mobility to perform a tunneling motion in this phase, thus leading to the low-energy, glasslike excitations. In this Letter, we report that the same kind of excitations can also exist in crystals which freeze into an *electric* dipolar glass at low temperatures. Through isotopic substitution, we establish the crucial participation of protons (or deuterons) in these excitations. This is the first time that these low-energy excitations can be so distinctly modified and labeled.

Rubidium ammonium dihydrogen phosphate (RADP) solid solutions are mixtures of the two components RbH_2PO_4 and $NH_4H_2PO_4$ which undergo a ferroelectric (FE) and antiferroelectric (AFE) phase transition, respectively, at the same critical temperature $T_c=148$ K [4]. The RADP (x,T) phase diagram is well documented: For $0.22<x<0.74$, random competition between FE and AFE orderings of acid $O-H\cdots O$ protons promoted by the random substitution of NH_4 produces disorder in the hydrogen-bond network, leading to an electric dipole or proton glass at low temperatures. In this concentration range, structural transformations are replaced by a collective freezing of the acid protons. The same electric dipole glass formation has been observed in the deuterated isomorph of RADP, called DRADP, in which all protons have been replaced by deuterons [5].

Thermal conductivity was measured below 40 K with a steady-state temperature-gradient technique, and above 30 K with the 3ω method, an ac technique [6]. Specific heat between 0.05 and 2.0 K was measured with the transient heat-pulse technique using thin carbon films as fast thermometers [1]. Thermal relaxations were followed in the quasiadiabatic time window between $0.1\ \text{ms}<t<10$ s. Single crystals of protonated RADP ($x=0.35$ and 0.72) and deuterated DRADP ($x=0.62$) were selected from the same batches studied earlier [7]. Nearly identical results were obtained for the two RADP samples. The data for the $x=0.35$ crystal have been omitted here for clarity, but can be found in Ref. [8].

The thermal conductivity of the RADP mixed crystals resembles closely that of structural glasses, as illustrated in Fig. 1 through a comparison with measurements on amorphous silica (a-SiO_2). Below 1 K, the thermal conductivity varies as $T^{1.8}$; in all structural glasses, the exponent ranges between 1.8 and 2.0. Above ~10 K, the high-temperature regime is approached, in which the conductivity becomes practically independent of temperature, as is also typical for glasses [9]. For comparison the thermal conductivity expected for well-ordered dielectric (i.e., electrically insulating) single crystals is also shown in Fig. 1 using crystalline RDP (RbH_2PO_4) and KDP [8,10] (KH_2PO_4) as examples (note the inflection near 100 K in KDP, which signals the ferroelectric phase tran-

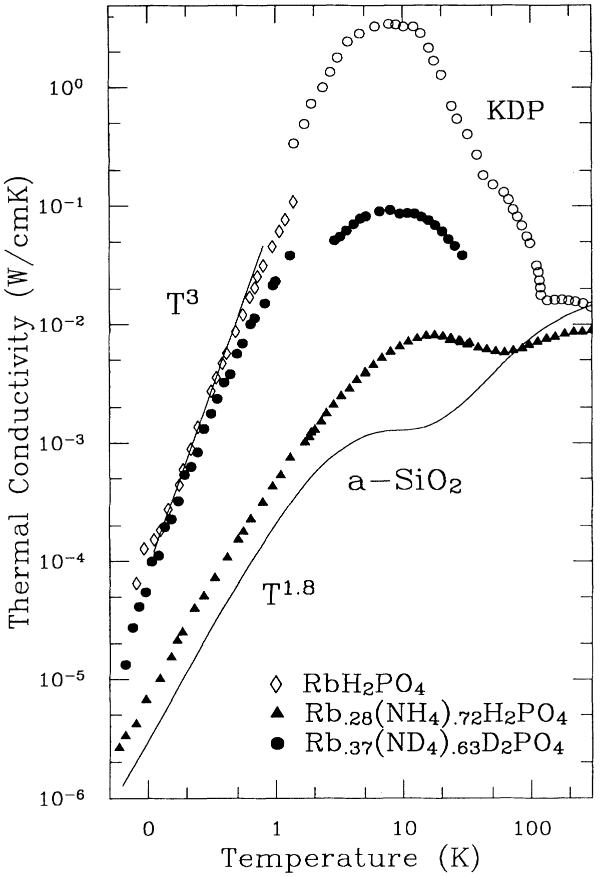

FIG. 1. Thermal conductivity of $Rb_{1-x}(NH_4)_xH_2PO_4$ mixed crystals for $x=0$ (RDP) and for $x=0.72$ (RADP) and also for its fully deuterated isomorph with $x=0.62$. The break in the latter data around 1 K is caused by uncertainties in the geometry of the short and stubby sample, which had to be remounted for the two temperature ranges. Data for RADP with $x=0.35$ are almost identical to those for RADP with $x=0.72$ and have been omitted for clarity [8]. Data for (KDP) single crystal [8,10] and for amorphous silica (a-SiO_2) are shown for comparison. The line labeled T^3 is close to the boundary-limited conductivities predicted from the speeds of sound and sample diameters in RDP, KDP, and DRADP.

sition at 122 K in this solid). Below a few degrees K, the thermal conductivities vary closely to T^3, and their magnitudes agree with the assumption that the phonons are scattered solely at the sample boundaries (Casimir effect). The deuterated DRADP ($x=0.62$), by contrast to RADP, has a thermal conductivity that is crystalline; see Fig. 1. It shows evidence of some defect scattering above a few degrees K. At lower temperatures, however, boundary scattering prevails. Qualitatively similar results have been reported previously on another sample of DRADP ($x=0.48$), for $2\ \mathrm{K} < T < 40\ \mathrm{K}$ [11]. The crystal-like thermal conductivity was about one half that reported here, indicating somewhat stronger defect scattering.

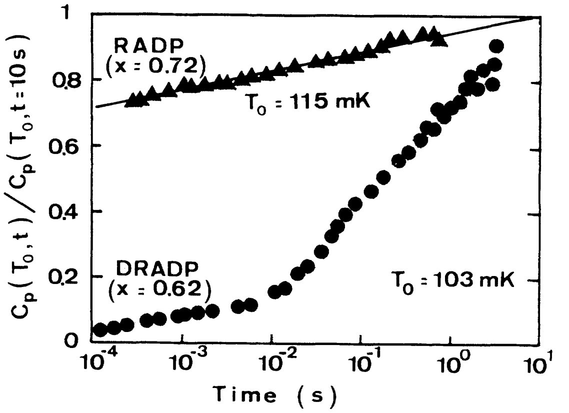

FIG. 2. Time-dependent specific heats for RADP $x=0.72$ at 115 mK and for DRADP $x=0.62$ at 103 mK, normalized to the long-time (10 s) specific heat. Details of extracting the spectral density $\bar{P}$ from such measurements are contained in Ref. [1].

Specific-heat measurements reveal a similarly striking influence of substituting deuterium for hydrogen in these mixed crystals. Figure 2 shows typical traces of the time dependence of the specific heat $C_p(T,t)$ normalized to the long-time specific heat (at $t=10$ s), at an initial temperature of 115 mK. Over nearly 4 orders of magnitude in time, $C_p(T,t)$ of the RADP sample varies linearly with the logarithm of time, as predicted by the so-called tunneling model for structural glasses [12], and as observed not only there, but also in quadrupolar glasses. From best fits to the data obtained on the two RADP samples between 0.06 and 0.5 K, values of the spectral density of the tunneling states $\bar{P}=0.5\times10^{45}\ \mathrm{J^{-1}m^{-3}}$ ($x=0.35$) and $0.8\times10^{45}\ \mathrm{J^{-1}m^{-3}}$ ($x=0.72$) were determined (the method is described in detail in Ref. [1]). These values are close to that reported for a-SiO_2 [13] ($\bar{P}=0.8\times10^{45}\ \mathrm{J^{-1}m^{-3}}$). In the deuterated sample, the time dependence of the specific heat is very different; see Fig. 2: For times less than 10^{-2} s, the normalized specific heat is much smaller than in RADP. A very rapid rise sets in at 10^{-2} s, showing a logarithmic dependence for times exceeding $\sim5\times10^{-2}$ s. The greatly reduced density of tunneling states relaxing at times shorter than 10^{-2} s agrees with the observation that the thermal conductivity of the DRADP shows no sign of bulk scattering below a few K. Figure 3 displays the temperature variation of the specific heat in RADP and DRADP at selected measuring times between 0.1 ms and 1 s. For the RADP mixed crystal, an expression of the form

$$C_p(T,t)=\frac{\pi^2 k_B^2}{12\rho}\bar{P}T[\ln(4t/\tau_{\min})]+c_D T^3+C_{\mathrm{exc}} \qquad (1)$$

was used to fit the data, dropping the subscript on T_0. Here the first term is the prediction of the tunneling model [12], where $\rho=1.92\ \mathrm{g\,cm^{-3}}$ is the mass density, and $\tau_{\min}$ the minimum relaxation time (to be determined from the experiment); the second term is the Debye pre-

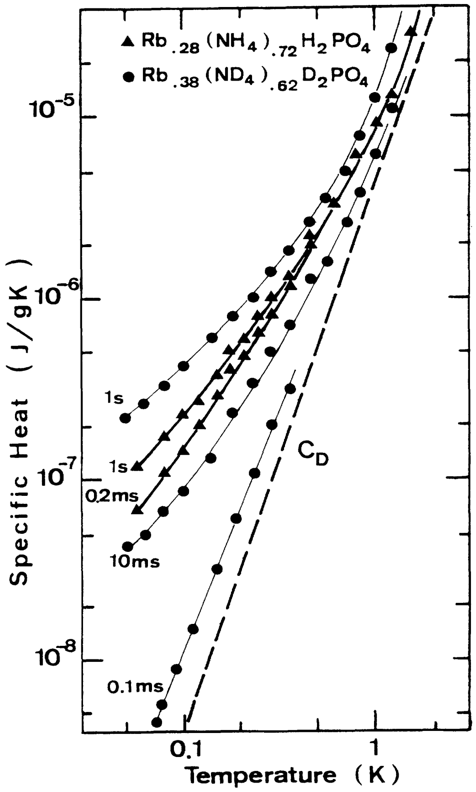

FIG. 3. Specific heat of $Rb_{1-x}(NH_4)_xH_2PO_4$ mixed crystals at selected measuring times for $x=0.72$ and for its deuterated isomorph with $x=0.62$. For the proton glass ($x=0.72$), the $C_p(T,t)$ data were fitted using Eq. (1) (heavy lines). For the deuterated sample, the thin lines are guides for the eyes only. The data calculated from the initial temperature rise for DRADP at $t=0.1$ ms are close to the elastic limit $C_D=(4.3\times10^{-6}\ \mathrm{J\,g^{-1}K^{-4}})T^3$ (dashed line) which has been derived from the low-temperature elastic constants for RADP ($x=0.35$) [14]. Data for $x=0.35$ are nearly identical to those for $x=0.72$ and have been omitted for clarity (see Ref. [8]).

diction, with $c_D=4.3\times10^{-6}\ \mathrm{J\,g^{-1}K^{-4}}$ calculated from the low-temperature elastic constants of the tetragonal phase. An excess term which is independent of the measuring time was found to be necessary for a good fit, as is well known also for structural glasses [15]. For RADP, it was determined as $C_{\mathrm{exc}}=(4\times10^{-6}\ \mathrm{J\,g^{-1}K^{-5/2}})T^{3/2}$. The two heavy solid curves in Fig. 3 for $t=2\times10^{-4}$ s and 1 s were obtained with $\tau_{\min}=5\ \mu$s and the $\bar{P}$ given above. In the deuterated DRADP crystal, the specific heat at 10^{-4} s is almost equal to the Debye value; see Fig. 3. A term linear in T, and of a magnitude as known for glasses (and comparable to that in RADP), evolves only at longer times ($t>10^{-2}$ s). Then, however, its time dependence is much stronger.

These observations show that the electric dipole glass RADP has low-energy excitations very similar to those common to structural glasses, with regards to both the spectral density $P(E)$ and the relaxation-time spectrum $P(\tau)$ of the tunneling states. In that sense, RADP resembles a growing number of disordered crystals, as for example, the quadrupolar glass $(KBr)_{1-x}(KCN)_x$. What is novel, however, is that isotopic substitution in RADP leads to drastic changes in these excitations, even though there are remnants of glasslike excitations, as observed at long measuring times of the specific heat. Such changes have never been achieved in structural glasses by any means, and even in the quadrupolar glasses they have required changes in the chemical composition [say, by varying x in $(KBr)_{1-x}(KCN)_x$].

This drastic isotope effect on the low-energy excitations indicates the crucial role played by the protons or deuterons in the crystals. Since proton intrabond tunneling along the $O-H\cdots O$ bonds linking phosphate groups is an important ingredient in the electric ordering occurring in members of the KDP family, it is suggestive to also view the glasslike, low-energy excitations in RADP as being caused by proton tunneling in the dipole glass, in which the majority of the dipoles is somehow immobilized, like the CN^- ions in the quadrupolar glass $(KBr)_{1-x}(KCN)_x$ [3]. The change of the spectral distribution of the tunneling states and their relaxation times upon deuteration can be understood qualitatively with this picture. We assume, for the purpose of illustration, that the protons (or deuterons) with mass m are tunneling through a barrier of height V between potential minima separated by the distance δ. We use the standard expression for the tunnel splitting Δ_0 for the double-well potential, $\Delta_0\propto\exp-(2mV\delta^2/\hbar^2)^{1/2}$. In members of the KDP family, both V and δ change somewhat upon deuteration (Ubbelohde effect [16]). Lawrence and Robertson [17] determined $V=3260\ \mathrm{cm}^{-1}$ (wave numbers) and $4110\ \mathrm{cm}^{-1}$, and $\delta=0.364$ and 0.446 Å for KDP and DKDP, respectively. Using the same values for our case, we determine a ratio of $\Delta_0(H)/\Delta_0(D)\sim120$. Thus, deuteration is expected to shift the density of tunneling states to very low temperatures (far below the lowest temperatures reached in our specific-heat measurements). In the tunneling model proposed for glasses [12], the minimum relaxation time $\tau_{\min}$ of the tunneling states varies as Δ_0^{-3}. Thus, very large changes of the relaxation times (by a factor of $120^3\sim10^6$) can be expected upon deuteration, in qualitative agreement with our experimental findings. This supports the picture that the low-energy, glasslike excitations in these dipolar glasses are related to the tunneling of protons or deuterons, although it provides no insight into what causes the spectral density of these states in RADP to be so similar to that of all structural glasses.

To conclude, we have observed that a mere isotopic substitution in disordered crystal RADP can lead to striking changes of its low-energy, glasslike excitations. We believe this to be the first time that a crystal in the orientational glass state has been shown to contain low-energy excitations to which the tunneling model applies only in a limited sense. That is to say, that the spectral density of the tunneling states and their relaxation-time distribution differ significantly from those usually found in structural glasses. We expect that a study of the controlled changes of the tunneling states in RADP and DRADP will lead to a better understanding of the nature of these excitations, and beyond that may contribute to our understanding of the lattice vibrations of structural glasses.

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