Short-range ordering and freezing in a randomly mixed ferroelectric-antiferroelectric crystal

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X-ray measurements on single-crystals of $Rb_{1-x}(NH_4)_xH_2PO_4$ trace the development of a glasslike state. The absence of macroscopic crystal-symmetry change during freezing is confirmed, while diffuse scattering reveals the growth of very-short-range order. The latter coincides with a compressibility anomaly seen in Brillouin scattering and with dielectric effects suggesting freezing. The system is in many ways analogous to spin-glasses.

The elusive nature of the spin-glass state relates to our experimental inability to directly measure the spin-glass order parameter and its spatial correlations. The difficulty resides in the fact that long-range replica-symmetry breaking has, especially in magnetic systems, at most, indirect structural consequences.[1] Hence there has been a renewed interest in structurally frustrated systems,[2] for example, in orientational or quadrupolar glasses of which KCN-KBr is the most recent example.[3] A major difficulty in the latter case is that a laboratory field coupling linearly to the frustrated ordering parameter is not available. The recent synthesis of a possible polar structural analog to conventional spin-glasses, mixed crystals of the ferroelectric (FE) RbH_2PO_4 (RDP), and of the antiferroelectric (AFE) $NH_4H_2PO_4$ (ADP), provides new hopes for experimental studies.[4] Birefringence observations indicated that the mixed crystals $Rb_{1-x}(NH_4)_xH_2PO_4$ maintain their high-temperature tetragonal symmetry for $0.22 < x < 0.8$, although they exhibit dramatic "freezing" effects as they are cooled below ~ 100 K.[2] The freezing culminates in a remarkable low-frequency dielectric dispersion below ~ 30 K. The crystals are both piezoelectric and electrostrictive. The piezoelectricity linearly couples shear strains to the local polarization while electrostriction links the square of the polarization to the density. These effects being quite strong, local freezing has profound crystallographic consequences. X-ray diffraction and diffuse-scattering results are presented confirming the microscopic nature of the glass state. They indicate progressive freezing of random polarizations on cooling, combined with very short-range clustering, presumably for the compensation of piezoelectrically induced shear strains. In combination with dielectric and Brillouin measurements, they provide a remarkably detailed picture of the freezing into a glasslike state.

The x-ray measurements were performed on a two-axis spectrometer using Cu$K\alpha$ radiation. Diffuse scattering was observed with an apparatus previously described.[5] The $x = 0.35$ RDP-ADP crystal was in the form of a thin (100) plate of size $3 \times 3 \times 0.15$ mm^3. It was annealed at 100 °C for 24 h to relieve strains, then held in the $(h0l)$ scattering plane by a glass fiber attached to one end with a minute amount of GE7031 varnish. Roughly 3 mm^2 of sample were irradiated in a region away from the support to minimize spurious strains. The temperature was varied from 300 to 9 K and stabilized to within 0.01 K. The lattice constants were obtained from the (800) and (008) Bragg peaks (BP). To this effect the pyrolytic graphite monochromator was replaced with a Ge(111) crystal, reducing the (800) instrumental half-width at half maximum (HWHM) from 0.0043 to 0.0012 Å^{-1}.

A systematic search of reciprocal space did not reveal any new low-temperature structures outside the regions of the normal paraelectric (PE) BP's. Special attention was given to $(h0l)$ values where a signature of AFE order would have appeared, such as (302), (207), $(h01)$, and $(10l)$.[6] The excellent chemical mixing was indicated by the absence of modulation of the diffuse background at 300 K. This is a sensitive test as Rb^+ and NH_4^+ have very different form factors. The angle between the crystallographic a and b axes was also checked in the $(hk0)$ plane. It was found equal to 90° within the accuracy of $\pm 0.06°$, and temperature independent with a precision of about $\pm 0.01°$. From all this, one concludes there is no detectable transition to a low-temperature structure of either the FE or the AFE types, thus confirming previous reports.[2,4] Besides these important negative results, measurements of the lattice parameters a and c (Fig. 1) and of diffuse scattering around allowed BP's (Fig. 2) revealed remarkable information.

On cooling, the contraction of the PE phase leads to a change of the unit-cell volume $v = a^2c$ which, in first approximation, is proportional to the internal energy.[7] Fitting $v(T)$ for $T > 100$ K to the appropriate Debye function,[8] one obtains the solid line of Fig. 1(a) and a satisfactory value $\theta = 384$ K for the Debye temperature. Below ~ 80 K, the measurements depart from the fit by an excess volume Δv [Fig. 1(b)]. Below ~ 50 K, the volume actually increases as the temperature is lowered. Crystals of the KH_2PO_4 (KDP) family expand upon proton ordering,[9] asymmetric H bonds being longer than symmetric ones.[10] Hence, the excess volume confirms a progressive asymmetrization of the bonds, in agreement with birefringence and dielectric indications for the onset of local freezing around 100 K.[2,4] Note that the ultimate low-temperature value $\Delta v/v = 0.43 \times 10^{-3}$ is of the same order as typical volume jumps on ordering. For example, cooling ADP through its strongly first-order transition one has

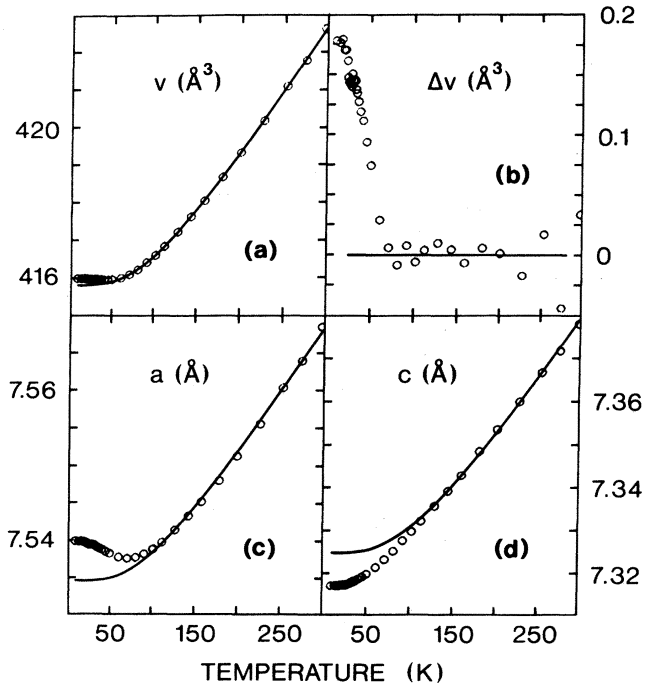

FIG. 1. X-ray diffraction results on cell volume (a) and lattice parameters (c) and (d). The solid lines are fits to the Debye internal energy. The deviation between measurement and fit in (a) is expanded in (b).

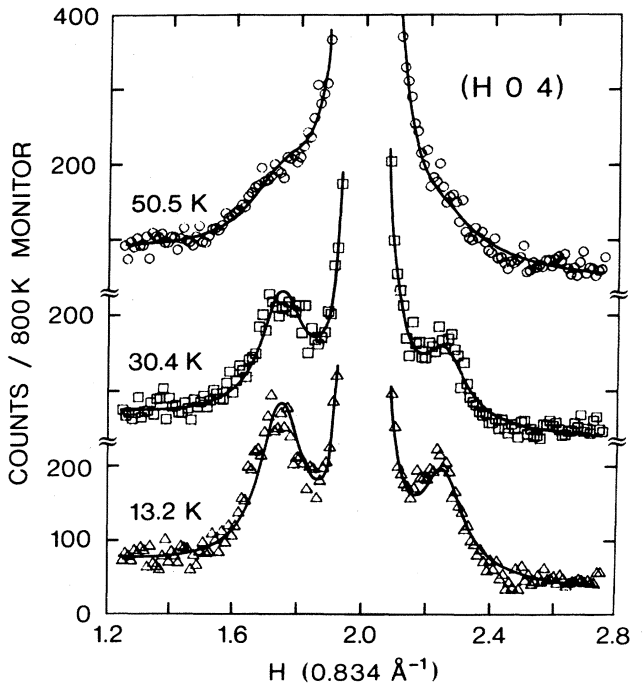

FIG. 2. Diffuse x-ray scattering along $(h04)$. The solid lines are fits as explained in the text.

$\Delta v/v = 2.7\times10^{-3}$,[11] while for KDP $\Delta v/v = 0.6\times10^{-3}$.[12] Similarly, the lattice parameters a and c are expected to exhibit a temperature variation approximately proportional to the internal energy. However, as the c/a ratio is also temperature dependent, the proportionality is less quantitative. This is seen in Figs. 1(c)–1(d), where best Debye fits of the points $T > 110$ K with $\theta = 384$ K are shown. Below ~ 100 K, a departure from the Debye fit is evident, with final low-temperature deviations $\Delta a/a = 5\times10^{-3}$ and $\Delta c/c = -8\times10^{-3}$. A large positive $\Delta a/a$ and a large negative $\Delta c/c$ are specific to the NH_4^+-substituted KDP crystals at their ordering transitions.[9] Microscopically this is related with the specific H bond of the NH_4^+ ions.[6,10] One infers that NH_4^+ ions do progressively freeze below ~ 100 K, although without acquiring an appreciable AFE short-range order that would produce diffuse scattering peaks for $h+k+l$ odd. This freezing is also confirmed by recent NMR proton spin-lattice-relaxation measurements.[13]

Diffuse-scattering equal-intensity contours taken near the (204) reflection at 20 K have an h/l aspect ratio of $\sim 2/1$. The elongation along h recalls the shape typical of ferroelectric fluctuations.[14] Furthermore, broad satellites occur in h scans (Fig. 2). These have been found in the wings of several PE BP's, in particular, (204), (404), and possibly (202) in decreasing order of intensity. Their shifts from the corresponding BP is one-quarter reciprocal-lattice parameter independently of $(h0l)$ and T. Their intensity grows approximately together with the volume anomaly Δv of Fig. 1(b), but remains weak. In Fig. 2, the BP is higher than 10^7 counts/800 K monitor and its instrumental limited HWHM is ~ 0.003 units of h. The largest integrated satellite intensity observed was 10^{-3} times that of the BP. Fitting the satellites and the instrumental wing to Lorentzians, one obtains the solid lines of Fig. 2, and the inverse satellite width ξ plotted in Fig. 3.

Satellites occurring at fixed points of the Brillouin zone indicate a tendency towards a superstructure. As the elastic continuity of the lattice cannot accommodate purely random shears, the satellites are presumably related to a periodic alternation of shears piezoelectrically generated by quasirandomly frozen polarizations. This is consistent with the absence of well-resolved satellites in l scans, as the piezoelectric constant h_{14} is at least an order of magnitude smaller than h_{36} for all KDP-type phosphates, and as furthermore the polarization component P_3 dominates for $x = 0.35$. Our results indicate a quasiperiodicity of four lattice distances. A (001) projection of a possible strain pattern is sketched in the inset of Fig. 3. With a random chemical distribution long-range order does, of course, not establish, as seen from the satellite width. The correlation length increases on cooling but saturates at a value of about two lattice parameters (Fig. 3).

X-ray measurements cannot decide whether the short-range order is static or dynamic, but a quasistatic component seems likely for this random system. In this case, frozen *glass* clusters could extend over distances much beyond the correlation length of the ordered regions, and the appreciable long-range striction illustrated in Fig. 1 can be an important coupling mechanism. It is interesting to note that a peculiar polarization noise has been observed upon field cooling in the region $T \sim 60$ to 40 K.[2] This corrresponds to the temperature region in which Δv is changing rapidly. To examine this region further we checked the stability condition[15] $C = (C_{11}+C_{12})C_{33} - 2xC_{13}^2 > 0$ using Brillouin scattering data. Measurements were performed with an A-ion laser operating on the 5145-Å

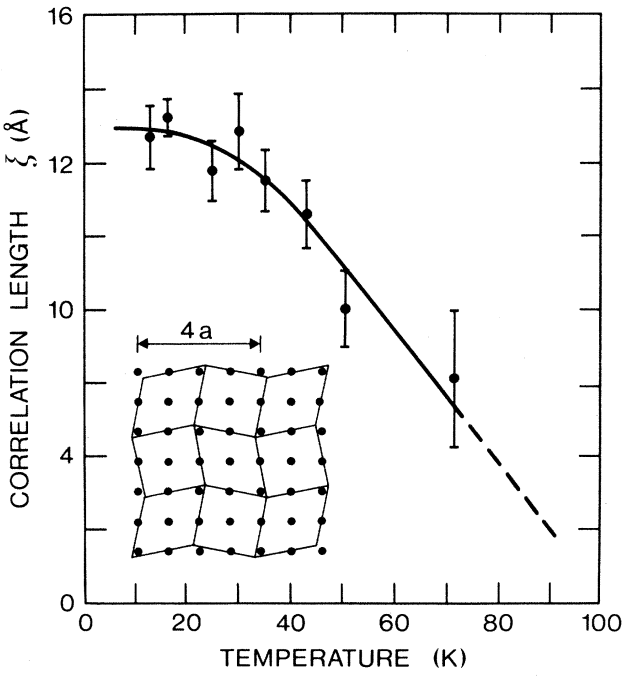

FIG. 3. Correlation length extracted from the satellites of Fig. 2. The error bars correspond to one standard deviation and the line is a guide to the eye which interestingly extrapolates to zero near the onset of freezing at ~100 K. Inset: a possible strain pattern leading to satellites. The dots designate the undistorted configuration and the lines a distorted one.

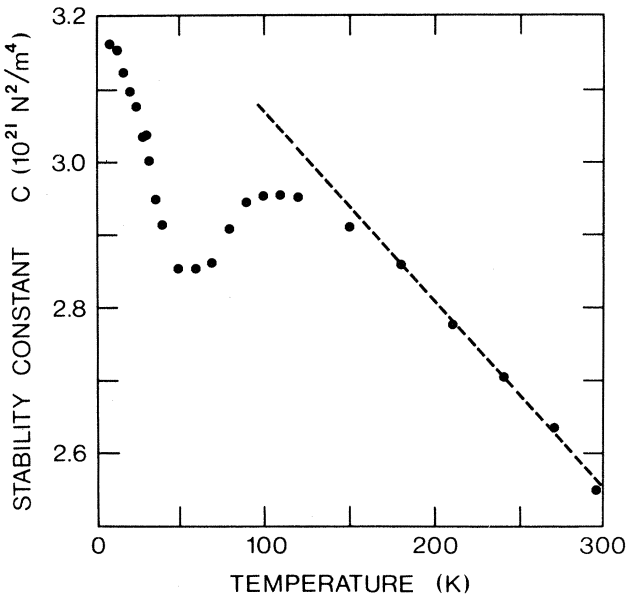

FIG. 4. Stability constant C as determined from Brillouin scattering measurements. The line is a guide to the eye.

line and in 90° scattering geometry. They were complemented by a determination of the T dependence of the refractive indices, so that all elastic constants C_{ij} could be extracted;[16] C is shown in Fig. 4. An appreciable softening in the region of rapid change in Δv is evident. Although there is no x-ray evidence for this, one cannot exclude that a bulk instability related to type 0 (Ref. 15) produces the polarization noise. The Brillouin measurement is microscopic, since it is performed at a finite $q = 2\times10^5$ cm^{-1} fixed by the scattering geometry. As type-0 elastic instabilities are *strictly* restricted to the zone center,[17] a further check at a truly macroscopic scale will be worthwhile.

We have obtained microscopic evidence for freezing and short-range ordering in RADP at $x = 0.35$. The occurrence of these effects at temperatures much above the onset of low-frequency susceptibility dispersion (~30 K) is reminiscent of a recent neutron polarization analysis result on Cu-Mn.[18] Also, as in spin-glasses, one would expect a specific-heat maximum in the region of rapid freezing (~50 to 70 K), and this was recently confirmed in a preliminary experiment.[19] Although much work along the present line remains to be performed, such as the investigation of the x dependence, we now feel confident that mixed crystals of RADP provide in the field of structural transitions a valuable analog and alternative to the magnetic glasses. In view of the piezoelectric and strictive couplings in RADP, the study of this material offers new experimental possibilities and might also reveal rather novel aspects of the freezing into glass.

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