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Competing structural orderings and transitions to glass in mixed crystals of Rb$_{1-x}$(NH$_4$)$_x$H$_2$PO$_4$

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Résumé. — On produit de la frustration dans des cristaux de la famille du KDP par mélange de composants aux tendances ferroélectriques et antiferroélectriques. Des mesures diélectriques et de birefringence sont présentées pour $0 \leq x \leq 0.35$. Elles indiquent un diagramme de phase intéressant, avec une phase vitreuse précédée probablement par une phase mixte pour les concentrations élevées. La compétition au hasard d'interactions à courte portée joue sans doute un rôle important dans ce système, rendant ces verres de véritables analogues structuraux des verres de spin magnétiques.

Abstract. — Frustration is produced in crystals of the KDP family by mixing ferroelectric and anti-ferroelectric constituents. Birefringence and dielectric measurements are reported for $0 \leq x \leq 0.35$. They indicate an interesting phase diagram, with a glassy phase probably preceded by a mixed phase for the upper part of the concentration range investigated. The randomness of the competing short-range interactions is likely to play a major role, making these structural glasses truly analogous to magnetic spin glasses.

Considerable attention is currently being given to systems with random frustration [1]. Experimentally, the interest has concentrated on magnetic spin glasses [2]. Dipolar glasses [3], with frustrated random dipolar interactions [4], have also been investigated. As it would be of interest to know a structural analog of exchange-coupled spin glasses [5], we take here a fresh look at crystals with mixed short-range ferroelectric (FE) and antiferroelectric (AFE) constituents [6]. An experimental study of Rb$_{1-x}$(NH$_4$)$_x$H$_2$PO$_4$ is presented for $0 \leq x \leq 0.35$. Detailed information is given on the upper concentration range, where evidence for a glass transition probably preceded by a mixed phase is obtained.

RbH$_2$PO$_4$ (RDP) and NH$_4$H$_2$PO$_4$ (ADP) form isomorphous tetragonal crystals at ambient temperature. Their lattice parameters match closely, and mixed crystals can apparently be grown over the full range of $x$ [7]. The H-bonds linking PO$_4$ tetrahedra play an important role in the transitions: the ordering of the acid protons in « up-down » Slater configurations [8] produces the FE transition in RDP, whereas « lateral » ordering generates the AFE phase of ADP. The latter presumably occurs because the NH$_4^+$ protons tend to form their own H-bonds with four nearby PO$_4$ groups [9]. This additional bonding manifests itself in many ways, in particular by a distribution coefficient which favours NH$_4^+$ incorporation in the growing crystal [7, 10]. The FE transition of RDP (at $T_c = 146$ K) is believed to be continuous [11]. The FE structure results from condensation of a mode of B$_2$ symmetry at the centre of the Brillouin zone [12] and the...
orthorhombic axes are rotated 45° from the a-axes of the body-centred tetragonal cell. In ADP, the AFE transition \( (T_c = 147 \text{ K}) \) is strongly first-order. The orthorhombic distortion is that of an \( M_{34} \) mode at the M-point [12], with axes parallel to the original tetragonal ones.

The investigation reported here was performed with birefringence, electro-optic, and dielectric measurements. The FE transition produces a spontaneous birefringence [13], given in first-order by \( \Delta n_{12} = n_0^3 \rho_{63} P_3 \) [14]. The polarization along the FE axis is \( P_3 \), \( n_0 \) is an average refractive index, and \( \rho_{63} \) is an electro-optic coefficient. As the latter is nearly constant, the measurement of \( \Delta n_{12} \) gives access to the FE order parameter \( P_3 \). Thin plates were provided with semi-transparent electrodes allowing application of a poling field \( E_3 \). A low power (\( \sim 20 \mu \text{W} \)), slightly focussed He-Ne laser beam (6328 Å) was used. For small \( x \), the paraelectric (PE) to FE transition temperature decreases rapidly with increasing \( x \), \( dT_c/dx \approx -300 \text{ K} \). The saturation polarization remains sizeable, however, practically equal to that of RDP when account is taken of the also observed small decrease of \( \rho_{63} \) with increasing \( x \). For \( x \gtrsim 0.13 \), \( T_c \) decreases even faster and the transition exhibits a first-order birefringence jump on cooling, whereas fringes can still be counted on heating back to the high-temperature phase. With \( E_3 = 0 \), the onset of the new phase is manifested by the sudden appearance of near-forward scattering in the form of a cross produced by domain walls [15]. Near \( x = 0.2 \), it becomes impossible to pole the crystals with the highest fields applied (\( \sim 300 \text{ kV/m} \)). For \( x \approx 0.22 \), no optical evidence remains of \textit{any} transition towards a phase of lower point symmetry. The field cooled value of \( \Delta n_{12} \) can then be measured with a compensator. At low \( E_3 \), it is proportional to \( E_3 \), with \( \Delta n_{12} = n_0^3 \rho_{63} E_3 \), and \( \rho_{63} \equiv \rho_{63} \varepsilon_0 (\varepsilon_{33}' - 1) \). Here, \( \varepsilon_0 \) is the dielectric permittivity of vacuum, and \( \varepsilon_{33}' \) is the real part of the dielectric constant along the FE axis. This is shown in figure 1 for \( x \approx 0.34 \). Up to the highest field, \( \Delta n_{12} \) remains considerably smaller than the values attained in the FE phase with \( x < 0.2 \). The low-temperature

Fig. 1. — Right ordinate : the field cooled electro-optic coefficient \( r_{63} \) : the dashed line is a guide to the eye. Left ordinate : the real and imaginary parts of the longitudinal dielectric constant at 1 kHz, \( \varepsilon_{33} \) and \( \varepsilon_{33}' \), respectively \( (x = 0.34) \). The solid line is the high-temperature Curie-Weiss fit, while \( \Delta \varepsilon_{33} = \varepsilon_{\text{CW}} - \varepsilon_{33}' \).
plateau of $r_{63}$, as well as thermal release of polarization and a number of effects indicating remanence, were suggestive of a transition to a glass phase with a random FE-type condensation.

To characterize the situation further, careful measurements of $\varepsilon_{33}$, the susceptibility associated with the FE phase of KDP, and of $\varepsilon_{11}$ were performed. Results at 1 kHz are shown in figures 1 and 2. The temperature $T_g$ marks the onset of dispersion and dielectric loss ($\varepsilon'' \neq 0$) in both $\varepsilon_i(\omega)$. Below $T_g$, $\varepsilon'_i(\omega)$ decreases markedly with increasing $\omega$ and decreasing $T$. Remembering that $r_{63}$ is proportional to $\varepsilon'_3(\omega = 0)$, the behaviour is strikingly similar to that of spin glasses [2]. All results are compatible with a random FE-type condensation below $T_g$. For reasons explained below, we propose to name this new phase a « structural glass » (SG).

Fig. 2. — Left ordinate : the real and imaginary parts of the transverse dielectric constant at 1 kHz, $\varepsilon'_{11}$ and $\varepsilon''_{11}$, respectively (for $x = 0.34$). Right ordinate : the derivative of $\varepsilon'_{11}$ obtained with a three-point algorithm.

Quite salient is the broad maximum in $\varepsilon_{11}$ which occurs much above $T_g$. The transverse susceptibility derives a large contribution from the polarizability of the acid-proton bonds, which are mainly perpendicular to $c$. This maximum indicates they have reached a degree of ordering which counteracts their ability to contribute to $P_1$ by changing their distribution among the potential wells. A clue to the type of ordering they adopt is given by $\varepsilon_{33}$. In the PE phase of RDP, $\varepsilon_{33}$ follows closely a mean-field Curie-Weiss law [11], and the same is found here at sufficiently high temperatures, above $T_m = 99$ K. The Curie-Weiss temperature obtained by fitting $\varepsilon_{33}$ from 300 to 100 K is $T_{CW} = 38$ K, significantly higher than $T_g = 27$ K. Below $T_m$, $\varepsilon_{33}$ is smaller than the extrapolated Curie-Weiss value $\varepsilon_{CW}$; both $\varepsilon_{CW}$ and the difference $\Delta\varepsilon_{33} = \varepsilon_{CW} - \varepsilon_{33}$ are shown in figure 1. This indicates that progressively more sites are prevented from contributing to ferroelectricity, which also forces $T_g$ below $T_{CW}$. As the effect is not accompanied by appreciable dielectric loss or dispersion, it is reasonable to infer a random AFE-type condensation. Indeed, antiferroelectric clusters do not couple linearly to the applied electric field. The formation of such clusters can be thought as preventing a fraction of the material from contributing to the
growth of $\varepsilon_{33}$ and $\varepsilon_{11}$ on cooling. Remarkably, $T_m$ also corresponds to the inflection point of $\varepsilon_{11}$, which is better seen in the numerical derivative plotted in figure 2.

To further support this conjecture, the change in the natural birefringence of the tetragonal phase [13], $\Delta(n_o - n_e)$, was also measured. Here, $n_o$ and $n_e$ are the ordinary and extraordinary indices, respectively. This change has two causes. Firstly, the lattice anharmonicity produces thermal expansion, leading to a variation of both indices, and of their difference, proportional to density changes. For temperatures above the proton ordering, excellent fits to a Debye function are obtained, with a satisfactory Debye temperature of $\sim 400$ K. Extrapolating the Debye function to lower temperatures, and subtracting the observed $\Delta(n_o - n_e)$, one obtains a remainder $\delta(n_e - n_o)$. In pure KDP, this remainder is known to be proportional to $P_2^2$, and we find this result also for RDP [13]. In pure ADP, for similar symmetry reasons, $\delta(n_e - n_o)$ should be proportional to the square of the AFE order parameter. The onset of $\delta(n_e - n_o)$ on cooling, in the absence of any other symmetry change of the crystal, can thus be interpreted as the development of an Edwards-Anderson order parameter $q$ [16]. Approximately, one would have $q \propto \delta(n_e - n_o)$.

As shown in figure 3, there is indeed an onset at $T_m$. Interestingly, no noticeable change occurs at $T_g$. The solid curve is an empirical fit to $q = 3 \tau^2 - 2 \tau^3$, where $\tau \equiv 1 - T/T_m$. This appears significantly different from the dependence $q = \tau + \tau^2 - \tau^3$ predicted for the Sherrington-Kirkpatrick (SK) Hamiltonian [17]. It suggests that another model might be needed to account for the particular order parameter and/or randomness of the present case. Careful examination of our data at other concentrations indicates the occurrence of this condensation at least for all $x \gtrsim 0.13$. Tentatively, the new phase, if there is one, will be called a mixed phase (M), as roughly-speaking it corresponds to a mixture of paraelectric regions with AFE clusters.

![Fig. 3. — The remainder of the tetragonal birefringence $\delta(n_e - n_o)$ after subtraction of the lattice expansion contribution for $x = 0.34$. The solid line is the fit explained in the text. Inset: A tentative phase diagram. Along the dashed line, the transition is clearly first-order, while it seems continuous elsewhere.](image)

A provisional phase diagram summarizing the present information is shown in the inset of figure 3. The nature of the special points remains to be elucidated. The occurrence of the M region before the SG phase is in line with the recent theoretical result on the Heisenberg SK model in presence of a field [18]. Here, no field needs to be applied to reveal the M region, as the aniso-
tropy required is provided by the crystal itself. The first-orderness of the M $\rightarrow$ FE transition indicates a strong competition between the two phases, which is easy to understand intuitively. It should be noted that approximate values for the concentrations $x_1$ and $x_2$ of figure 3 can be derived by simple percolation reasoning. Considering the PO$_4$ groups as single units, one finds that they are linked by the acid-proton bonds with the topology of the diamond lattice. Each NH$_4^+$ perturbs four PO$_4$ groups forming a tetrahedron of second-nearest neighbours, and conversely, each PO$_4$ is surrounded by four sites available to NH$_4^+$ perturbers. For random substitution, the probability of a PO$_4$ site to remain unperturbed is simply $(1 - x)^4$. We surmise that the percolation of perturbed PO$_4$ groups forces the protons to seek an arrangement leading to AFE-type condensation. Neglecting correlations, the site percolation threshold in the diamond lattice is 0.43 [19], giving $0.43 \approx 1 - (1 - x_1)^4$, or $x_1 \approx 13 \%$, in agreement with observation. On the other hand, the FE phase could be suppressed when the unperturbed groups cease to percolate. Again, neglecting the correlations of perturbed sites, this gives $0.43 \approx (1 - x_2)^4$, or $x_2 \approx 19 \%$, in reasonable agreement with the findings. This emphasizes the possible importance of short-range interactions, but does not prevent long-range models from applying. Indeed, the order parameter $q$ is, by symmetry, linearly coupled to density, and that coupling can have a strong fluctuation-quenching effect due to elasticity, as is now well known for KDP [20]. Since $\delta(n_e - n_o)$ is also expected to be linearly related to density changes, at least the FE $\rightarrow$ M transition might be describable adequately by some mean-field approach. A genuine structural analog of magnetic spin glasses seems to have been discovered here [21]. The system could be called either a ferroelectric, a polar, or a structural glass. The last-mentioned name is preferred. The first one commonly refers to non-crystalline ferroelectrics, and the second one has been used for situations where dipolar interactions were thought important, which is presumably not the case presently, as explained above.

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[10] For this reason, $x$ had to be determined carefully. As the density is a sensitive function of $x$, flotation was used and confirmed by X-ray powder analysis. The latter did not indicate superstructures.


[14] Abbreviated subscripts are used, and the axes are those of the tetragonal phase throughout.


[21] Another example might be provided by the « rotational » system KBr$_{1-x}$(CN)$_x$ [ROWE, J. M., RUSH, J. J., HINKS, D. G. and SUSMAN, S., Phys. Rev. Lett. 43 (1979) 1158, and references therein], if it turns out to be a real glass.