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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 biréfringence sont présentées pour $0 \leqslant x \lesssim 0,35$. 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 antiferroelectric constituents. Birefringence and dielectric measurements are reported for $0 \leqslant x \leqslant 0.35$. 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 $0 \leqslant x \lesssim 0.35$. 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 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 ρ_{63} is an electro-optic coefficient. As the latter is nearly constant, the measurement of Δn_{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 µW), 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, $dT_c/dx \simeq -$ 300 K. The saturation polarization remains sizeable, however, practically equal to that of RDP when account is taken of the also observed small decrease of ρ_{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 kV/m). For $x \simeq 0.22$, *no* optical evidence remains of *any* transition towards a phase of lower point symmetry. The field cooled value of Δn_{12} can then be measured with a compensator. At low E_3, it is proportional to E_3, with $\Delta n_{12} = n_0^3 r_{63} E_3$, and $r_{63} \equiv \rho_{63} \varepsilon_0(\varepsilon'_{33} - 1)$. Here, ε_0 is the dielectric permittivity of vacuum, and ε'_{33} is the real part of the dielectric constant along the FE axis. This is shown in figure 1 for $x \simeq 0.34$. Up to the highest field, Δn_{12} remains considerably smaller than the values attained in the FE phase with $x <$ 0.2. The low-temperature

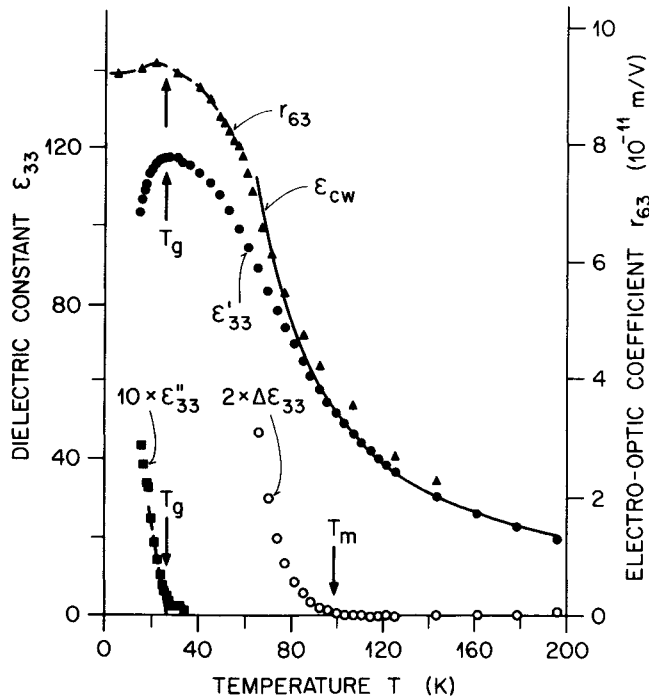Fig. 1. — Right ordinate : the field cooled electro-optic coefficient r_{63} : the dashed line is a guide to the eye. Left ordinate : the real and imaginary parts of the longitudinal dielectric constant at 1 kHz, ε'_{33} and ε''_{33}, respectively (x = 0.34). The solid line is the high-temperature Curie-Weiss fit, while $\Delta\varepsilon_{33} = \varepsilon_{CW} - \varepsilon'_{33}$.

plateau of r_{63}, as well as thermal release of polarization and a number of effects indicating rema-
nence, were suggestive of a transition to a glass phase with a random FE-type condensation.

To characterize the situation further, careful measurements of ε_{33}, the susceptibility associated
with the FE phase of KDP, and of ε_{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
$\varepsilon_{ii}(\omega)$. Below T_g, $\varepsilon'_{ii}(\omega)$ decreases markedly with increasing ω and decreasing T. Remembering
that r_{63} is proportional to $\varepsilon'_{33}(\omega = 0)$, 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
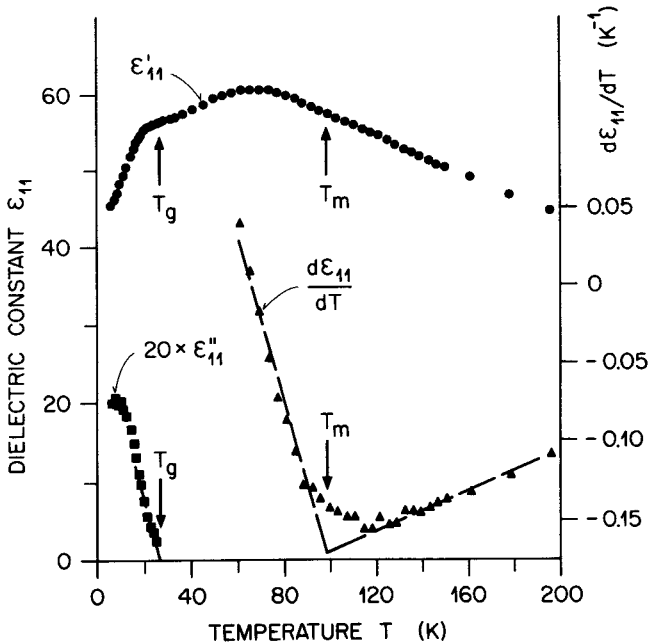below, we propose to name this new phase a « structural glass » (SG).

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

Quite salient is the broad maximum in ε_{11} which occurs much above T_g. The transverse suscepti-
bility 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 ε_{33}. In the PE phase of RDP, ε_{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 ε_{33} from 300
to 100 K is $T_{CW} = 38$ K, significantly higher than $T_g = 27$ K. Below T_m, ε_{33} is smaller than the
extrapolated Curie-Weiss value ε_{CW}; both ε_{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 ferro-
electricity, 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 ε_{33} and ε_{11} on cooling. Remarkably, T_m also corresponds to the inflection point of ε_{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 ~ 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_3^2, 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.
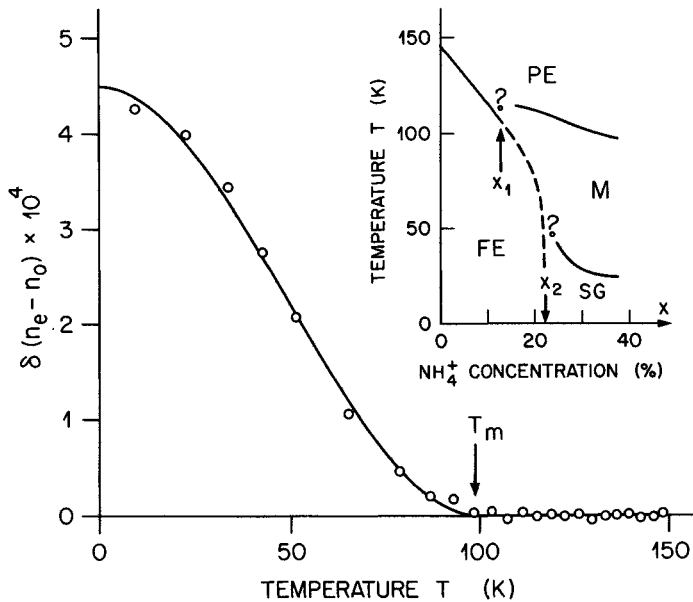

Fig. 3. — The remainder of the tetragonal birefringence $\delta(n_e - n_o)$ after subtraction of the lattice expansion contribution for $x = 0.34$. The solid line is the fit explained in the text. Inset : A tentative phase diagram. Along the dashed line, the transition is clearly first-order, while it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

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 $0.43 \simeq 1 - (1 - x_1)^4$, or $x_1 \simeq 13 \%$, 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 $0.43 \simeq (1 - x_2)^4$, or $x_2 \simeq 19 \%$, 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 $PE \rightarrow M$ 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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