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E. Courtens. Competing structural orderings and transitions to glass in mixed crystals of $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$. Journal de Physique Lettres, 1982, 43 (6), pp.199-204. 10.1051/jphyslet:01982004306019900 . jpa-00232031

HAL Id: jpa-00232031

<https://hal.science/jpa-00232031>

Submitted on 1 Jan 1982

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Classification

Physics Abstracts

61.40D — 77.80D — 64.70E — 78.20F

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

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(Reçu le 17 décembre 1981, accepté le 25 janvier 1982)

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 $0 \leq x \leq 0,35$. 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 antiferroelectric 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 $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ 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_2PO_4 (RDP) and $\text{NH}_4\text{H}_2\text{PO}_4$ (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 (~ 20 μ 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 , $dT_c/dx \simeq -300$ 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 (~ 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 $r_{63} \equiv \rho_{63} \epsilon_0 (\epsilon'_{33} - 1)$. 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 $\Delta\epsilon_{33} = \epsilon_{cw} - \epsilon'_{33}$.

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 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 ($\epsilon'' \neq 0$) in both $\epsilon_{ii}(\omega)$. Below T_g , $\epsilon'_{ii}(\omega)$ decreases markedly with increasing ω and decreasing T . Remembering that r_{63} is proportional to $\epsilon'_{33}(\omega = 0)$, 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 algorithm.

Quite salient is the broad maximum in ϵ_{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 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 $\Delta\epsilon_{33} = \epsilon_{CW} - \epsilon_{33}$ 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 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-

trophy required is provided by the crystal itself. The first-orderness of the $\text{M} \rightarrow \text{FE}$ 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^+ perturbors. 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 $\text{PE} \rightarrow \text{M}$ 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.

H. J. Scheel contributed by his careful crystal growth and in discussions, P. Bayer patiently helped with delicate technical aspects, and H. Weibel provided some exploratory ε_{33} measurements and technical advice. Many thanks are expressed to all of them, as well as to A. Barattoff, K. A. Müller, D. Sherrington and R. H. Swendsen for stimulating conversations.

References

- [1] For recent theoretical reviews, see ANDERSON, P. W., *J. Appl. Phys.* **49** (1978) 1599 ;
BRÉZIN, E., GERVAIS, J. L. and TOULOUSE, G., *Phys. Rep.* **67** No. 1 (1980) ;
BINDER, K., *Proceedings of the EPS Conference on Condensed Matter*, Antwerp, 1980 (Plenum Press, New York) to be published.
- [2] MYDOSH, J. A., *Proceedings of the International Conference on Disordered Systems and Localization*, Rome, 1981 (Springer, Heidelberg) to be published, and references therein.
- [3] KANZIG, W., HART, H. R. and ROBERTS, S., *Phys. Rev. Lett.* **13** (1964) 543.
- [4] FISCHER, B. and KLEIN, M. W., *Phys. Rev. Lett.* **37** (1976) 756.
- [5] MALETTA, H. and FELSCH, W., *Phys. Rev. B* **20** (1979) 1245.
- [6] MATTHIAS, B. and MERZ, W., *Helv. Phys. Acta* **19** (1946) 227.
- [7] SCHEEL, H. J. and COURTENS, E., to be published.
- [8] SLATER, J. C., *J. Chem. Phys.* **9** (1941) 16.
- [9] MEGAW, H. D., *Ferroelectricity in Crystals* (Methuen, London) 1957, Chap. 3.
- [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.
- [11] BASTIE, P., LAJZEROWICZ, J. and SCHNEIDER, J. R., *J. Phys. C* **11** (1978) 1203 and references therein.
- [12] BLINC, R. and ZEKS, B., *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam) 1974, p. 94-96.
- [13] ZWICKER, B. and SCHERRER, P., *Helv. Phys. Acta* **17** (1944) 346 ;
VALLADE, M., *Phys. Rev. B* **12** (1975) 3755.

- [14] Abbreviated subscripts are used, and the axes are those of the tetragonal phase throughout.
 - [15] See, e.g. COURTENS, E., *J. Phys.* **C 14** (1981) L-37.
 - [16] EDWARDS, S. F. and ANDERSON, P. W., *J. Phys.* **F 5** (1975) 965.
 - [17] PARISI, G. and TOULOUSE, G., *J. Physique Lett.* **41** (1980) L-361.
 - [18] GABAY, M. and TOULOUSE, G., *Phys. Rev. Lett.* **47** (1981) 201.
 - [19] STAUFFER, D., *Phys. Rep.* **54** (1979) 1.
 - [20] COURTENS, E., GAMMON, R. and ALEXANDER, S., *Phys. Rev. Lett.* **43** (1979) 1026.
 - [21] Another example might be provided by the « rotational » system $\text{KBr}_{1-x}(\text{CN})_x$ [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.
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