# Transitional structure in potassium dideuterophosphate crystals during the phase transition

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A multilayer transitional structure has been observed at the time of the ferroelectric phase transition in crystals of potassium dideuterophosphate (DKDP) by a method of x-ray topography using synchrotron radiation. Layers of the paraelectric and ferroelectric phases with a period of 120–500 $\mu$m arise in the direction perpendicular to the tetragonal axis. It is suggested that this structure results from the simultaneous effect of the anisotropy represented by the spontaneous elongation of the crystal and the decrease in the phase-transition temperature as the pressure rises.

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The phase transitions in crystals of the potassium dihydrogen phosphate (KDP) group remain the subject of unflagging interest. New diffraction methods[1-7] have made it possible to carry out progressively more accurate measurements of the jumps in the spontaneous polarization, the elements of the domain structure, the thermal hysteresis, the parameters of the transition, the critical pressures and fields, etc. On the other hand, no information of any sort is available on the structure of the crystal at the temperature corresponding to the jump in the transition parameter, and the mechanism for this transition remains a mystery.

In this letter we are reporting an effort to learn something about these questions. The ferroelectric phase transition was observed by a method of x-ray diffraction topography through the use of synchrotron radiation. Specifically, the synchrotron radiation was provided by the VÉPP-3 electron storage ring at Novosibirsk. The measurement procedure has been described in a recent paper.[6] We used a television system with a cw x-ray vidicon. The good collimation of the primary beam (the convergence angle was $\sim 0.5''$), the continuous spectrum, the high luminosity, and the use of position-sensitive detectors all contributed to provide new opportunities for studying the mechanism for the phase transition by observing the dynamics of the actual crystal structure. The luminosity of our method is far better than that of such advanced methods of $\gamma$ diffractometry,[2] time-of-flight and two-crystal neutron diffractometry,[3,7] and ordinary x-ray diffractometry.[1,5] Furthermore, the use of ordinary detectors, which average the detected radiation over space, makes it difficult to observe spatial inhomogeneities.

We studied samples of $X$-cut crystals of KDP and potassium dideuterophosphate (DKDP) ($KH_2PO_4$ and $KD_2PO_4$). The temperatures of the respective ferroelectric transitions are 123 and 212 K. The dimensions of the samples were about $10 \times 5 \times 0.5$ mm. The distance from the sample to the window of the x-ray vidicon was varied up to 300 mm.

At the transition from the high-temperature paraelectric phase to the low-temperature ferroelectric phase, the tetragonal unit cell undergoes an orthorhombic distortion; the crystal acquires a spontaneous polarization along the direction of the tetragonal axis (the $z$ axis); and one or two systems of domains appear.[1] An angular mismatch of the oppositely charged cells leads to a twinning and to the appearance on the diffraction pattern (topogram) of two or three images of the crystal in the ferroelectric phase.[6] High-quality crystals generally exhibit two images, which result from two systems of oppositely charged domains. The stresses at the domain boundaries and at domain complexes can be seen on the $X$-cut topograms as bands running parallel to the $z$ axis and crossing the entire thickness of the crystal.[6]

We observed an unusual pattern during the transition in the DKDP cyrstals. The images of the crystal in the ferroelectric phase were suddenly cut by narrow white fringes running perpendicular to the $z$ axis ($f$ in Fig. 1). Simultaneously, the same pattern appeared at the position corresponding to the image of the crystal in the paraelectric phase, but the fringes had the inverse contrast ($p$ in Fig. 1). The period of the fringes was 120–500 $\mu$m, falling off with the deterioration in the quality of the crystal after cycling through the phase transition several times and after the application of external electric fields to the crystal. At the transition from the paraelectric phase to the ferroelectric phase the transition mechanism repeats itself, but in this case the regions which "drop out" of the central image appear simultaneously as periodic black fringes in the two images due to the twinning of the crystal. After a certain number of fringes have appeared on the image (in some cases, the fringes cover the entire image), the main phase-transition front appears on the side toward which they are propagating (4 in Fig. 1). Advancing through the crystal, this front "erases"

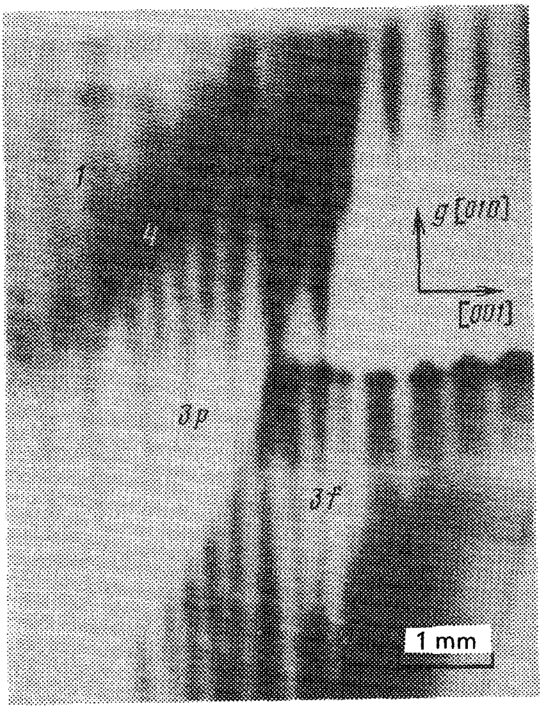

FIG. 1. The moment of the phase transition in an $X$-cut crystal of potassium dideuterophosphate (DKDP). 1–The part of the crystal which is in the paraelectric phase; 2–the part which has converted to the ferroelectric phase (the second image lies outside the vidicon window); 3–region of the transitional structure containing alternating layers of paraelectric ($p$) and ferroelectric ($f$) phases; 4–the main phase-transition front. The (200) reflection. The arrows show the arrangement of the crystallographic axes and of the diffraction vector $g$.

the periodic structure, leaving an ordinary image of the crystal in the ferroelectric or paraelectric phase.

This structure, periodic along the $z$ axis, exists in the DKDP crystals only during the phase transition; it disappears when the crystal becomes paraelectric or ferroelectric. Analysis of the contrast in the images and a study of the transition from the reflections in which the diffraction vector makes an angle with the fringes in the structure lead to suggestions regarding a model for the transition: The transitional structure consists of alternating layers of paraelectric and ferroelectric phases; domains of both signs exist in the ferroelectric phase. The mechanism for the appearance of this periodic structure can be explained in terms of the decrease in the temperature of the phase transition upon an increase in the pressure in the crystal and in terms of a spontaneous-elongation anisotropy.[4] A local change in the pressure (or stress) occurs near a region in the crystal in which the phase transition has occurred. The maximum of the spontaneous relative elongation along the tetragonal axis causes the new-phase layer to propagate perpendicular to this axis. To examine the transition mechanism, we assume that the crystal is, for example, in the paraelectric phase at a temperature near the left-hand edge of the thermal-hysteresis loop. If a jump to the ferroelectric phase occurs somewhere, a ferroelectric layer arises perpendicular to the $z$ axis, and beside this ferroelectric layer another layer (or zone) of elevated pressure appears in which the transition is delayed. Since the temperature field in this case is a long-range field in comparison with the stress field, a very slight lowering of the crystal temperature will lead to the appearance of a structure consisting of alternating layers of paraelectric and ferroelectric phases. If the crystal is homogeneous from the standpoint of defects and is plane-parallel, we should observe a structure with a constant period. These arguments regarding the transition mechanism also apply to the transition from the ferroelectric phase to the paraelectric phase.

A study of two $X$-cut KDP crystals failed to reveal a transitional structure. In this case the transition front erases the image of the crystal in one phase, forming the other without the zone of an intermediate multilayer structure. It may be that the resolution of our television system (20-40 $\mu$m) was not sufficient in this case and that the fringe pattern was masked by the constrast of the visible transition front. Since both the jump in the transition parameter[7] and the spontaneous relative elongation along the $z$ axis ($7.5 \times 10^{-4}$ and $1 \times 10^{-4}$ at atmospheric pressure for DKDP and KDP, respectively[4]) are much higher for the DKDP crystals, the observable effect should also be greater.

The occurence of a macroscopic phase structure near the transition point has been detected previously by optical methods in KDP crystals[8] and in quartz crystals at the $\beta$–$\alpha$ transition.[9] A cellular structure with cells elongated along the optic axis of the crystal was observed and suggests that these cells might be interpreted as the nucleating centers of domains. In our case, in contrast, the alternating layers of the two phases are arranged perpendicular to the direction of the domain walls.

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