

## ON AN ADDITIONAL COMPONENT OF SPONTANEOUS POLARIZATION OF A $\text{KH}_2\text{PO}_4$ SINGLE CRYSTAL

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**The pyroelectric coefficient of a KDP (potassium dihydrophosphate) single crystal in nonpolar directions was measured. The data obtained suggest a possible mechanism underlying the appearance of an additional component of spontaneous polarization.**

Earlier studies of various ferroelectrics with point defects [1-3] revealed a common phenomenon: formation of an additional component  $\mathbf{P}_{S_{ad}}$  in the field of the initial matrix  $\mathbf{P}_{S_m}$  at low ( $T < 15$  K) temperatures. It has been found that the vectors  $\mathbf{P}_{S_{ad}}$  and  $\mathbf{P}_{S_m}$  are noncollinear and are related as  $|\mathbf{P}_{S_{ad}}|/|\mathbf{P}_{S_m}| \leq 10^{-4}$ . The component  $\mathbf{P}_{S_{ad}}$  is due to the presence of charged ligands in the matrix. The probable mechanisms of its appearance are a low-temperature phase transition in the subsystem of impurity defects [2] and an ordered localization of protons on excess hydrogen bonds formed at  $T \rightarrow 0$  in the triglycine sulfate structure owing to introduced impurities [3]. A special case is the hydrogen-containing ferroelectric  $\text{KH}_2\text{PO}_4$  (KDP). Even a perfect single crystal of this compound shows an anomalous behavior of the pyroelectric coefficient  $\gamma^\sigma$  with change of sign at 15.3 K [4]. It was suggested in [4] that this phenomenon is due either to different signs of the optical mode contributions or to anomalous behavior of the secondary pyroelectric coefficient. Our investigations of perfect and defect KDP single crystals of different growth prehistory supported the experimental observations reported in [4], but we offered an explanation of the physical mechanism of the anomalous behavior of  $\gamma^\sigma$  in terms of a two-component model of spontaneous polarization. In contrast to the impurity components  $\mathbf{P}_S$  in triglycine sulfate, and lithium niobate and tantalate [1-3], the additional component  $\mathbf{P}_{S_{ad}}$  in KDP stems from low-temperature dynamics of mobile elements of the structure (protons) as in the case of the linear pyroelectric  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , where the formation of spontaneous polarization components in the region of  $T < 110$  K in nonpolar (at room temperature) crystallographic directions is unambiguously related to the vibration dynamics of water molecules [5]. A "polar phase-polar phase" transition in the proton subsystem with  $T_C = 21-23$  K was suggested to be the mechanism of  $\mathbf{P}_{S_{ad}}$  formation in KDP. In order to verify the general character of the statement that the vectors  $\mathbf{P}_{S_{ad}}$  and  $\mathbf{P}_{S_m}$  are noncollinear and to obtain additional data on the mechanism of  $\mathbf{P}_{S_{ad}}$  formation, we measured the pyroelectric coefficient in perfect single crystal specimens of KDP cut both at a right angle and at an angle of  $45^\circ$  (parallel to the [101] and  $[\bar{1}01]$  directions) to the polar axis. The measurement results and their brief discussion are given in the present communication.

A perfect KDP single crystal grown by a conventional (slow) method from a highly pure material was taken for the study. The disk-shaped specimens 12 mm in diameter and 2 mm thick with silver electrodes were cooled prior to the measurement to 1.5 K in a  $0.5 \text{ kW cm}^{-1}$  constant electric field. The pyroelectric coefficient was measured by the static methods [6].

The results of  $\gamma^\sigma$  measurements are demonstrated in Fig. 1. One can see from the figure that the  $\gamma^\sigma(T)$  curves in the [101] and  $[\bar{1}01]$  directions at  $T > 20$  K are a projection of the  $\gamma^\sigma(T)$  curve for the polar cut specimens onto these directions. The coincidence of the temperatures of pyroelectric coefficient sign reversal for all the curves presented indicates that this statement is also valid for the region of  $T < 20$  K. In other words, the KDP crystal studied does not possess polar properties in nonpolar crystallographic directions. Hence, the additional component of spontaneous polarization  $\mathbf{P}_{S_{ad}}$  in this case is collinear with the spontaneous polarization of the  $\mathbf{P}_{S_m}$  matrix, in distinction to the earlier studied cases of doped ferroelectrics [1-3] and the linear pyroelectric  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  [5].

The canonic dependence  $\gamma^\sigma(T)$  of a perfect KDP crystal shown in Fig. 1 by the dashed line is described

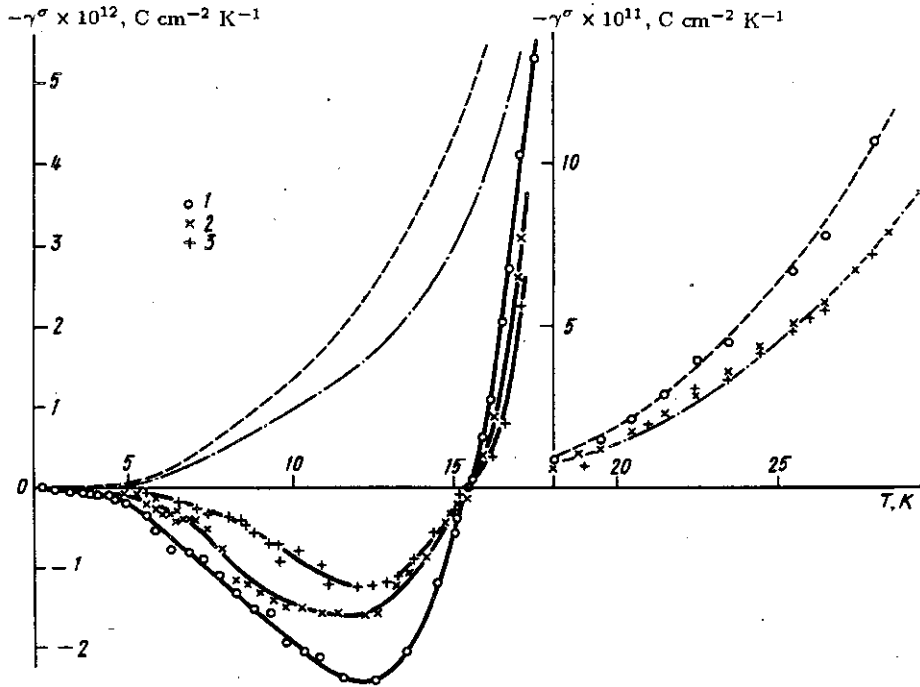


Fig. 1

Temperature dependences of the pyroelectric coefficient of the KDP single crystal in the following crystallographic directions: (1) [001], (2) [101], and (3)  $[\bar{1}01]$ . The dashed line shows the canonic dependence of a perfect crystal, the dot-and-dash line shows its projection onto the [101] and  $[\bar{1}01]$  directions.

by the expression

$$\gamma^\sigma = -5.92 \times 10^{-12} E(44 \text{ K}) - 1.92 \times 10^{-9} E(187.5 \text{ K}) \text{ C cm}^{-2} \text{ K}^{-1} \quad (1)$$

in the temperature range indicated in the figure (here  $E$  is Einstein's function).

The data obtained in this study suggest some additional ideas as regards the mechanism of  $\mathbf{P}_{S_{ad}}$  formation. It seems that proton motion during the assumed phase transition with  $T_C \approx 21 \text{ K}$  changes the charge state of oxygen atoms so that the  $\mathbf{P}_{S_{ad}}$  component arises only in the direction of the polar axis  $c$ . The projections of  $\mathbf{P}_{S_{ad}}$  on the crystallographic axes  $a$  and  $b$  turn out to be zero due to symmetry of the KDP ferroelectric phase. The question of the origin of elementary dipoles responsible for the observed macroscopic polarization  $\mathbf{P}_{S_{ad}}$  requires a complete and conclusive settling. Now we can only assume that these dipoles are formed due to the displacement of protons from the equilibrium position and that the direction of their displacements is opposite to that of the dipoles formed by  $\text{K}^+$  ions and  $\text{H}_2\text{PO}_4^-$  groups which are responsible for  $\mathbf{P}_{S_m}$ .

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