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UNIAXIAL PRESSURE INFLUENCE ON PHASE TRANSITION
AND PHYSICAL PROPERTIES OF HIGHLY DEUTERATED
 $K(H_xD_{1-x})_2PO_4$ -TYPE FERROELECTRICS

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Вплив одновісного тиску на фазовий перехід і фізичні властивості високодейтерованих сегнетоелектриків з водневими зв'язками типу $K(H_xD_{1-x})_2PO_4$

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Анотація. Проведено експериментальне дослідження впливу дейтерування і одновісного механічного тиску на $p = -\sigma_3$ і $p = -\sigma_1$ на температурні і спектральні залежності двозаломлення та температуру фазового переходу. На основі запропонованої раніше моделі деформованого кристалу KD_2PO_4 в рамках кластерного підходу досліджено вплив одновісних $p = -\sigma_3$ і $p = -\sigma_1 = -\sigma_2$ тисків на фазовий перехід, теплові, діелектричні і пружні характеристики високодейтерованих кристалів $K(H_xD_{1-x})_2PO_4$. Отримані результати порівнюються з наявними експериментальними даними і результатами попередніх досліджень ефектів, викликаних гідростатичним тиском.

Uniaxial pressure influence on phase transition and physical properties of highly deuterated $K(H_xD_{1-x})_2PO_4$ -type ferroelectrics

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Abstract. We performed experimental investigations of deuteration and uniaxial $p = -\sigma_3$ and $p = -\sigma_1$ mechanical stress influence on temperature and wavelength dependences of the birefringence and transition temperature of $K(H_xD_{1-x})_2PO_4$ crystals. On the basis of the previously proposed model for a strained KD_2PO_4 crystal, we study the effects of uniaxial $p = -\sigma_3$ and $p = -\sigma_1 = -\sigma_2$ pressures on the phase transition, thermal, dielectric and elastic properties of highly deuterated $K(H_xD_{1-x})_2PO_4$ crystals. The obtained results are compared with available experimental data and earlier theoretical calculations, concerning the hydrostatic pressure effects.

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1. Introduction

Recently, a great attention has been paid to investigation of the effects caused by hydrostatic pressure in ferroelectric crystals with hydrogen bonds. However, the influence of uniaxial stresses on these crystals can be even more essential. In contrast to the hydrostatic pressure, the uniaxial stress can lower the crystal symmetry. Besides, the relative ions displacements in a uniaxially strained crystal are several times larger. The uniaxial stress can induce new phase transitions, in addition to the well studied ferroelectric one.

In [1,2] the model of a strained KD_2PO_4 crystal was proposed. This model takes into account not only the deuterium-deuteron interaction but also coupling of deuterons with optic and acoustic vibrations of heavy atoms and with orientational vibrations of PO_4 groups. Resulting from the lattice strains longitudinal fields, which act on deuterons, are calculated. In [3,4] within this model we studied the hydrostatic pressure influence on the physical properties of highly deuterated $\text{K}(\text{H}_x\text{D}_{1-x})_2\text{PO}_4$ crystals. In the cluster approximation we calculated the dielectric, elastic and thermal responses of the crystals, and carried out a thorough numerical analysis of the obtained results. It has been shown that under the proper choice of the theory parameters, a satisfactory numerical description of the available experimental data for the pressure and temperature dependences of spontaneous polarization, longitudinal static dielectric permittivity and the transition temperature is possible.

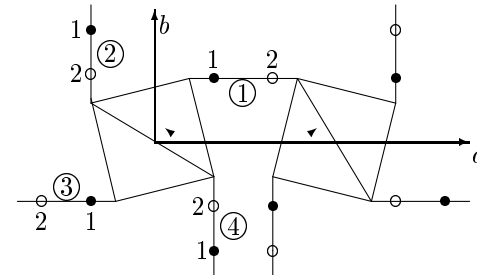
In this paper, we present the results of experimental studies of deuteration and uniaxial $p = -\sigma_3$ and $p = -\sigma_1$ stresses influence on temperature and wavelength spectral dependences of the birefringence and transition temperature of $\text{K}(\text{H}_x\text{D}_{1-x})_2\text{PO}_4$ crystals. On the basis of the model [1,2], we study the effects of uniaxial $p = -\sigma_3$ and $p = -\sigma_1 = -\sigma_2$ pressures on the phase transition, thermal, dielectric and elastic properties of highly deuterated $\text{K}(\text{H}_x\text{D}_{1-x})_2\text{PO}_4$ crystals. We perform a numerical analysis of the obtained theoretical results and study the dependence of calculated thermodynamic and dielectric characteristics on the theory parameters. The obtained results are compared with the available experimental data and earlier theoretical calculations [3,4] of the hydrostatic pressure effects.

2. Four-particle cluster approximation

We consider a system of deuterons moving on O-D...O bonds in a crystal of KD_2PO_4 type. The unit cell of Bravais lattice of such a crystal

is composed of two neighbouring PO_4 tetrahedra together with four hydrogen bonds attached to one of them ("A" type tetrahedra). Hydrogen bonds going to another ("B" type) tetrahedron belong to four nearest structural elements surrounding it (see the figure below). An external stress σ_l ($l = \text{h}, 3, 1+2$) which does not lower the system symmetry is applied:

$$\sigma_{\text{h}} = (-p, -p, -p), \quad \sigma_3 = (0, 0, -p), \quad \sigma_{1+2} = (-p, -p, 0). \quad (2.1)$$



The unit cell of a DKDP crystal. Here ①, ②, ③, ④ and 1, 2 stand for the hydrogen bond and H-site numbers, respectively.

The Hamiltonian of the system when the stress $-p = \sigma_1 = \sigma_2$ or $-p = \sigma_3$ and external electric field E_i ($i = 1, 2, 3$) along the crystallographic axes a, b, c are applied has the following form [1]:

$$\begin{aligned} H_i = & \frac{\bar{v}N}{2} \sum_{ij} c_{ij}^{(0)} \varepsilon_i \varepsilon_j - \sum_{qf} 2\mu F_f^i \frac{\langle \sigma_{qf} \rangle}{2} + \\ & + \sum_{q_1, q_2, q_3, q_4} \{ \delta_{\mathbf{R}_{q_1} \mathbf{R}_{q_2}} \delta_{\mathbf{R}_{q_1} \mathbf{R}_{q_3}} \delta_{\mathbf{R}_{q_1} \mathbf{R}_{q_4}} + \delta_{\mathbf{R}_{q_1} + \mathbf{r}_2 \mathbf{R}_{q_2}} \delta_{\mathbf{R}_{q_1} + \mathbf{r}_3 \mathbf{R}_{q_3}} \delta_{\mathbf{R}_{q_1} + \mathbf{r}_4 \mathbf{R}_{q_4}} \} \\ & \times \left\{ \frac{1}{2} \sum_{ff'} V_{ff'} \frac{\sigma_{qff}}{2} \frac{\sigma_{qf'f'}}{2} + \Phi \frac{\sigma_{q_1 1}}{2} \frac{\sigma_{q_2 2}}{2} \frac{\sigma_{q_3 3}}{2} \frac{\sigma_{q_4 4}}{2} \right\} - \\ & - \sum_{q_j f_j} \left[2\mu F_{f_j}^i \frac{\sigma_{q_j f_j}}{2} + \mu_{f_j i} E_i \frac{\sigma_{q_j f_j}}{2} \right]. \end{aligned} \quad (2.2)$$

The Hamiltonian (2.2) describes the short-range configurational interactions between deuterons near tetrahedra of "A" and "B" type; \mathbf{r}_f is a relative position vector of a hydrogen bond in a cell. Two eigenvalues of Ising spin $\sigma_{qf} = \pm 1$ are assigned to two equilibrium positions of a deuteron on the f -th bond in the q -th unit cell. $c_{ij}^{(0)}$ are the "seed" elastic constants; ε_i are the components of the strain tensor; $\bar{v} = v/k_B$; v is the unit cell volume; k_B is the Boltzmann constant. F_f^i are internal fields, created by, first, effective long-range forces, including as well an

indirect interaction between deuterons through lattice vibrations, and, second, by external pressure [1,2]:

$$\begin{aligned}
2\mu F_1^i &= 2\eta_1^{(1)} \left[\frac{J_{11}}{4} + \sum_i \psi_{1i}\varepsilon_i \right] + 2\eta_2^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i}\varepsilon_i \right] + \\
&\quad + 2\eta_3^{(1)} \left[\frac{J_{13}}{4} + \sum_i \psi_{3i}\varepsilon_i \right] + 2\eta_4^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i}\varepsilon_i \right], \\
2\mu F_2^i &= 2\eta_1^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i}\varepsilon_i \right] + 2\eta_2^{(1)} \left[\frac{J_{11}}{4} + \sum_i \psi_{1i}\varepsilon_i \right] + \\
&\quad + 2\eta_3^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i}\varepsilon_i \right] + 2\eta_4^{(1)} \left[\frac{J_{13}}{4} + \sum_i \psi_{3i}\varepsilon_i \right], \\
2\mu F_3^i &= 2\eta_1^{(1)} \left[\frac{J_{13}}{4} + \sum_i \psi_{3i}\varepsilon_i \right] + 2\eta_2^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i}\varepsilon_i \right] + \\
&\quad + 2\eta_3^{(1)} \left[\frac{J_{11}}{4} + \sum_i \psi_{1i}\varepsilon_i \right] + 2\eta_4^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i}\varepsilon_i \right], \\
2\mu F_4^i &= 2\eta_1^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i}\varepsilon_i \right] + 2\eta_2^{(1)} \left[\frac{J_{11}}{4} + \sum_i \psi_{1i}\varepsilon_i \right] + \\
&\quad + 2\eta_3^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i}\varepsilon_i \right] + 2\eta_4^{(1)} \left[\frac{J_{13}}{4} + \sum_i \psi_{3i}\varepsilon_i \right],
\end{aligned}$$

where $\eta_f^{(1)} = \langle \sigma_{qf} \rangle$; $J_{ff'}$ is a long-range interaction between deuterons; $\psi_{1i}, \psi_{2i}, \psi_{3i}$ are the so-called deformation potentials; $\mu = e\delta$ is a dipole moment of a hydrogen bond; δ is the H-site distance. According to [5,6], δ is a linear function of hydrostatic pressure. Assuming the same character of its dependence on stresses σ_3 and σ_{1+2} and bearing in mind (2.1), we can write:

$$\delta = \delta_0 + \delta_1 p,$$

where $\delta_1 < 0$, $\delta_0 > 0$. Taking into account the fact that $J_{ff'}$ is proportional to μ^2 , we have:

$$J_{ff'} = J_{ff'}^{(0)} [1 + 2\frac{\delta_1}{\delta_0} p]. \quad (2.3)$$

The static and dynamic properties of a deuteron subsystem of a DKDP crystal will be considered in the four-particle cluster approxi-

mation, which in terms of density matrices can be expressed as follows. The cluster Hamiltonian reads: [9]:

$$\rho_0 = \frac{e^{-\beta H_i}}{\text{Sp } e^{-\beta H_i}} = \frac{e^{-\beta H_4^{iA}}}{\text{Sp } e^{-\beta H_4^{iA}}} \frac{e^{-\beta H_4^{iB}}}{\text{Sp } e^{-\beta H_4^{iB}}}, \quad \beta = \frac{1}{T}, \quad (2.4)$$

where H_4^{iA}, H_4^{iB} are the cluster Hamiltonians describing the behaviour of deuterons around "A" and "B" tetrahedra. Since the equilibrium distribution functions of deuterons around "A" and "B" tetrahedra coincide in the cluster approximation [9], the static properties of the KD_2PO_4 crystals will be considered on the basis of the Hamiltonian H_4^{iA} solely:

$$\begin{aligned}
\hat{H}_{q4}^{iA} &= V \left[\frac{\sigma_{q11} \sigma_{q22}}{2} + \frac{\sigma_{q22} \sigma_{q33}}{2} + \frac{\sigma_{q33} \sigma_{q44}}{2} + \frac{\sigma_{q44} \sigma_{q11}}{2} \right] + \\
&\quad + U \left[\frac{\sigma_{q11} \sigma_{q33}}{2} + \frac{\sigma_{q22} \sigma_{q44}}{2} \right] + \Phi \frac{\sigma_{q11} \sigma_{q22} \sigma_{q33} \sigma_{q44}}{2} - \sum_f \frac{z_f^i \sigma_{qf}}{\beta}, \quad (2.5)
\end{aligned}$$

where

$$\begin{aligned}
z^z &= \beta \{ -\Delta_3^z + 2\nu\eta^{(1)z} + \mu_3 E_3 \}, \\
z_{1,3}^x &= \beta \{ -\Delta_1^x + 2\nu_1\eta_1^{(1)x} + 2\nu_3\eta_3^{(1)x} + 4\nu_2\eta_{24}^{(1)x} \pm \mu_1 E_1 \} \\
z_{24}^x &\equiv z_2^x = z_4^x = \beta \{ -\Delta_{24}^x + 2\nu_2[\eta_1^{(1)x} + \eta_3^{(1)x}] + 2[\nu_1 + \nu_3]\eta_{24}^{(1)x} \}, \\
z_{13}^y &\equiv z_1^y = z_3^y = \beta \{ -\Delta_{13}^y + 2[\nu_1 + \nu_3]\eta_{13}^{(1)y} + 2\nu_2[\eta_2^{(1)y} + \eta_4^{(1)y}] \}, \\
z_{2,4}^y &= \beta \{ -\Delta_2^y + 4\nu_2\eta_{13}^{(1)y} + 2\nu_1\eta_2^{(1)y} + 2\nu_3\eta_4^{(1)y} \pm \mu_2 E_2 \},
\end{aligned}$$

and

$$\nu = \frac{\nu_c(0)}{4} [1 + 2\frac{\delta_1}{\delta_0} p] + \sum_i \psi_{ci}\varepsilon_i, \quad \nu_j = \frac{J_{1j}(0)}{4} [1 + 2\frac{\delta_1}{\delta_0} p] + \sum_i \psi_{ji}\varepsilon_i.$$

In (2.5), $\Delta_1, \dots, \Delta_4$ are effective fields, resulting from an interaction with neighbouring quasispins outside a cluster. Here we took into account the fact that under the considered pressures and in fields E_i , the following relations are obeyed:

$$\begin{aligned}
\eta^{(1)z} &= \eta_1^{(1)z} = \eta_2^{(1)z} = \eta_3^{(1)z} = \eta_4^{(1)z}, \\
\eta_{24}^{(1)x} &= \eta_2^{(1)x} = \eta_4^{(1)x}; \quad \eta_{13}^{(1)y} = \eta_1^{(1)y} = \eta_3^{(1)y}, \\
\nu_c(0) &= J_{11}^{(0)} + 2J_{12}^{(0)} + J_{13}^{(0)}; \quad \psi_{ci} = \psi_{1i} + 2\psi_{2i} + \psi_{3i}; \\
\mu_3 &= \mu_{13} = \mu_{23} = \mu_{33} = \mu_{43}, \\
\mu_1 &= \mu_{11} = -\mu_{31}, \quad \mu_{21} = \mu_{41} = 0, \\
\mu_2 &= \mu_{22} = -\mu_{42}, \quad \mu_{12} = \mu_{32} = 0.
\end{aligned} \quad (2.6)$$

The single-particle deuteron Hamiltonians read:

$$H_{qf}^i = -\frac{\bar{z}_f^i}{\beta} \frac{\sigma_{qf}}{2}. \quad (2.7)$$

Expressions for $\bar{z}^z, \dots, \bar{z}_4^y$ can be obtained from (2.5) by replacing $\Delta_1, \dots, \Delta_4$ with $2\Delta_1, \dots, 2\Delta_4$; obviously, their symmetry coincides with that of z^z, \dots, z_4^y .

In (2.5) $V = -\frac{w_1}{2}$, $U = -\varepsilon + \frac{w_1}{2}$, $\Phi = 4\varepsilon - 8w + 2w_1$, where

$$\begin{aligned} T < T_c & & T > T_c \\ \varepsilon = \varepsilon^0 + \delta_{11}^- \varepsilon_1 + \delta_{12}^- \varepsilon_2 + \delta_{13}^- \varepsilon_3, & \quad \varepsilon = \varepsilon^0 + \delta_{11}^+ (\varepsilon_1 + \varepsilon_2) + \delta_{13}^+ \varepsilon_3, \\ w = w^0 + \delta_{21}^- \varepsilon_1 + \delta_{22}^- \varepsilon_2 + \delta_{23}^- \varepsilon_3, & \quad w = w^0 + \delta_{21}^+ (\varepsilon_1 + \varepsilon_2) + \delta_{23}^+ \varepsilon_3, \\ w_1 = w_1^0 + \delta_{31}^- \varepsilon_1 + \delta_{32}^- \varepsilon_2 + \delta_{33}^- \varepsilon_3, & \quad w_1 = w_1^0 + \delta_{31}^+ (\varepsilon_1 + \varepsilon_2) + \delta_{33}^+ \varepsilon_3. \end{aligned}$$

and $\varepsilon^0 = \varepsilon_a - \varepsilon_s$, $w^0 = \varepsilon_1 - \varepsilon_s$, $w_1^0 = \varepsilon_0 - \varepsilon_s$, $\varepsilon_a, \varepsilon_s, \varepsilon_1, \varepsilon_0$ are the deuteron configuration energies; δ_{ij}^\pm are the so-called deformation potentials.

The single-particle deuteron distributions functions read:

$$\eta^{(1)z} = \frac{1}{D^z} [\sinh 2z^z + 2b \sinh z^z] \quad (2.8)$$

$$\eta_{1,3}^{(1)x} = \frac{1}{D^x} [\sinh A_1 + d \sinh A_2 \pm 2a \sinh A_3 + \pm b(\sinh A_5 + \sinh A_6 \pm 2 \sinh A_7)],$$

$$\eta_{24}^{(1)x} = \frac{1}{D^x} [\sinh A_1 - d \sinh A_2 + b(\sinh A_5 - \sinh A_6)],$$

$$\eta_{13}^{(1)y} = \frac{1}{D^y} [\sinh B_1 - d \sinh B_2 + b(\sinh B_7 - \sinh B_8)],$$

$$\eta_{2,4}^{(1)y} = \frac{1}{D^y} [\sinh B_1 + d \sinh B_2 \pm 2a \sinh B_4 \pm \pm b(\pm 2 \sinh B_6 + \sinh B_7 + \sinh B_8)], \quad (2.9)$$

where

$$D^z = \cosh 2z^z + 4b \cosh z^z + 2a + d,$$

$$D^x = \cosh A_1 + d \cosh A_2 + 2a \cosh A_3 + b(\cosh A_5 + \cosh A_6 + 2 \cosh A_7),$$

$$D^y = \cosh B_1 + d \cosh B_2 + 2a \cosh B_3 + b(2 \cosh B_6 + \cosh B_7 + \cosh B_8),$$

and

$$\begin{aligned} A_{1,2} &= \frac{z_1^x + z_3^x}{2} \pm z_{24}^x; & A_3 &= \frac{z_1^x - z_3^x}{2}; \\ A_{5,6} &= \frac{z_1^x - z_3^x}{2} \pm z_{24}^x; & A_7 &= \frac{z_1^x + z_3^x}{2}; \\ B_{1,2} &= \pm z_{13}^y + \frac{z_2^y + z_4^y}{2}; & B_4 &= \frac{z_2^y - z_4^y}{2}; \\ B_{7,8} &= \pm z_{13}^y + \frac{z_2^y + z_4^y}{2}; & B_6 &= \frac{z_2^y + z_4^y}{2}; \end{aligned}$$

$$a = \exp(-\beta\varepsilon), \quad b = \exp(-\beta w), \quad d = \exp(-\beta w_1).$$

Within the cluster approximation, the fields $\Delta_1, \dots, \Delta_4$ are determined from the condition of equality of the mean values $\langle \sigma_{qf} \rangle$ calculated with four- and single-particle Gibbs' distributions, i.e. with the Hamiltonian (2.5) and with (2.7). In the result:

$$z^z = \frac{1}{2} \ln \frac{1 + \eta^{(1)z}}{1 - \eta^{(1)z}} + \beta \nu \eta^{(1)z} + \frac{\beta \mu_3 E_3}{2},$$

$$z_{1,3}^x = \frac{1}{2} \ln \frac{1 + \eta_1^{(1)x}}{1 - \eta_1^{(1)x}} + \beta \left[\nu_1 \eta_1^{(1)x} + \nu_3 \eta_3^{(1)x} + 2\nu_2 \eta_{24}^{(1)x} \pm \frac{\mu_1 E_1}{2} \right],$$

$$z_{24}^x = \frac{1}{2} \ln \frac{1 + \eta_{24}^{(1)x}}{1 - \eta_{24}^{(1)x}} + \beta \left[\nu_2 [\eta_1^{(1)x} + \eta_3^{(1)x}] + [\nu_1 + \nu_3] \eta_{24}^{(1)x} \right],$$

$$z_{13}^y = \frac{1}{2} \ln \frac{1 + \eta_{13}^{(1)y}}{1 - \eta_{13}^{(1)y}} + \beta \left[\nu_2 [\eta_2^{(1)y} + \eta_4^{(1)y}] + [\nu_1 + \nu_3] \eta_{13}^{(1)y} \right],$$

$$z_{2,4}^y = \frac{1}{2} \ln \frac{1 + \eta_2^{(1)y}}{1 - \eta_2^{(1)y}} + \beta \left[2\nu_2 \eta_{13}^{(1)y} + \nu_1 \eta_2^{(1)y} + \nu_3 \eta_4^{(1)y} \pm \frac{\mu_2 E_2}{2} \right],$$

The free energy of the crystal in the four-particle cluster approximation can be written as follows:

$$\begin{aligned} f_z^- &= \frac{F_z}{N} = \frac{\bar{v}}{2} \sum_{ij} c_{ij}^{0-} \varepsilon_i \varepsilon_j - 2 \sum_i \delta_{2i}^- \varepsilon_i + 2\nu [\eta^{(1)z}]^2 + \\ &+ 2T \ln 2 - 2T \ln [1 - (\eta^{(1)z})^2] - 2T \ln D^z, \end{aligned} \quad (2.10)$$

External pressure changes the unit-cell volume:

$$\begin{aligned} v &= (0.3892 + k_v p) \cdot 10^{-21} \text{cm}^3, & \bar{v} &= (2.82 + k_{\bar{v}} p) \text{K}, \\ k_v &= 0.3892 \frac{\varepsilon_1 + \varepsilon_2 + \varepsilon_3}{p}, & k_{\bar{v}} &= 2.82 \frac{\varepsilon_1 + \varepsilon_2 + \varepsilon_3}{p}. \end{aligned}$$

The thermodynamic potential is equal to:

$$\begin{aligned} g^z(1+2) &= f^z(1+2) + \bar{v}p(\varepsilon_1 + \varepsilon_2), \\ g^z(3) &= f^z(3) + \bar{v}p\varepsilon_3. \end{aligned}$$

From the conditions of the thermodynamic equilibrium

$$\frac{1}{\bar{v}} \frac{\partial g^z}{\partial \eta^{(1)}} = 0; \quad \frac{1}{\bar{v}} \frac{\partial g^z}{\partial \varepsilon_i} = 0 \quad (2.11)$$

we find the system of equations for order parameter and strains caused by the external pressure:

$$\underline{-p = \sigma_1 = \sigma_2}$$

$$\eta^{(1)z} = \frac{1}{D^z} (\sinh 2z^z + 2b \sinh z^z), \quad (2.12)$$

$$-p = c_{11}^0 \varepsilon_1 + c_{12}^0 \varepsilon_2 + c_{13}^0 \varepsilon_3 - 2 \frac{\delta_{21}^-}{\bar{v}} - \frac{2\psi_{c1}}{\bar{v}} [\eta^{(1)z}]^2 + \frac{2}{\bar{v}} \frac{M_1^-}{D^z},$$

$$-p = c_{12}^0 \varepsilon_1 + c_{22}^0 \varepsilon_2 + c_{23}^0 \varepsilon_3 - 2 \frac{\delta_{22}^-}{\bar{v}} - \frac{2\psi_{c2}}{\bar{v}} [\eta^{(1)z}]^2 + \frac{2}{\bar{v}} \frac{M_2^-}{D^z},$$

$$0 = c_{13}^0 \varepsilon_1 + c_{23}^0 \varepsilon_2 + c_{33}^0 \varepsilon_3 - 2 \frac{\delta_{23}^-}{\bar{v}} - \frac{2\psi_{c3}}{\bar{v}} [\eta^{(1)z}]^2 + \frac{2}{\bar{v}} \frac{M_3^-}{D^z},$$

$$\underline{-p = \sigma_3}$$

$$\eta^{(1)z} = \frac{1}{D^z} (\sinh 2z^z + 2b \sinh z^z), \quad (2.13)$$

$$0 = c_{11}^0 \varepsilon_1 + c_{12}^0 \varepsilon_2 + c_{13}^0 \varepsilon_3 - 2 \frac{\delta_{21}^-}{\bar{v}} - \frac{2\psi_{c1}}{\bar{v}} [\eta^{(1)z}]^2 + \frac{2}{\bar{v}} \frac{M_1^-}{D^z},$$

$$0 = c_{12}^0 \varepsilon_1 + c_{22}^0 \varepsilon_2 + c_{23}^0 \varepsilon_3 - 2 \frac{\delta_{22}^-}{\bar{v}} - \frac{2\psi_{c2}}{\bar{v}} [\eta^{(1)z}]^2 + \frac{2}{\bar{v}} \frac{M_2^-}{D^z},$$

$$-p = c_{13}^0 \varepsilon_1 + c_{23}^0 \varepsilon_2 + c_{33}^0 \varepsilon_3 - 2 \frac{\delta_{23}^-}{\bar{v}} - \frac{2\psi_{c3}}{\bar{v}} [\eta^{(1)z}]^2 + \frac{2}{\bar{v}} \frac{M_3^-}{D^z},$$

here $M_i^- = 4b\delta_{2i}^- \cosh z^z + 2a\delta_{1i}^- + d\delta_{3i}^-$.

In the paraelectric phase the order parameter is equal to zero, and the following relation between the pressure and the strains is held:

$$\underline{-p = \sigma_1 = \sigma_2}$$

$$-p = (c_{11}^0 + c_{12}^0)\varepsilon_{1,2} + c_{13}^0 \varepsilon_3 - 2 \frac{\delta_{21}^+}{\bar{v}} + \frac{2}{\bar{v}} \frac{M_1^+}{D_+}, \quad (2.14)$$

$$0 = 2c_{13}^0 \varepsilon_1 + c_{33}^0 \varepsilon_3 - 2 \frac{\delta_{23}^+}{\bar{v}} + \frac{2}{\bar{v}} \frac{M_3^+}{D_+},$$

$$\underline{-p = \sigma_3}$$

$$\begin{aligned} 0 &= (c_{11}^0 + c_{12}^0)\varepsilon_{1,2} + c_{13}^0 \varepsilon_3 - 2 \frac{\delta_{21}^+}{\bar{v}} + \frac{2}{\bar{v}} \frac{M_1^+}{D_+}, \\ -p &= 2c_{13}^0 \varepsilon_1 + c_{33}^0 \varepsilon_3 - 2 \frac{\delta_{23}^+}{\bar{v}} + \frac{2}{\bar{v}} \frac{M_3^+}{D_+}, \end{aligned} \quad (2.15)$$

where

$$\begin{aligned} M_i^+ &= 4b\delta_{2i}^+ + 2a\delta_{1i}^+ + d\delta_{3i}^+, \quad M_1^+ = M_2^+, \\ D_+ &= 1 + 4b + 2a + d. \end{aligned}$$

As one can see from the equations (2.12), (2.13), (2.14) and (2.15), the strains ε_i are equal to zero at ambient pressure only if we assume the temperature dependence of the parameters δ_{2i} in the form

$$\delta_{2i}^+ = \frac{2a\delta_{1i}^+}{1 + 2a} = \frac{2\delta_{1i}^+}{\exp(\beta\varepsilon) + 2}$$

in the paraelectric phase and in a more complicated form in the ferroelectric phase. In order to keep δ_{2i} constant and for the sake of simplicity we assumed that

$$\delta_{2i}^+ = \frac{2\delta_{1i}^+}{\exp(\beta_c\varepsilon) + 2} \quad (2.16)$$

($\beta_c = 1/T_c$); thus at pressure of 1 kbar, small residual strains ($\sim 10^{-6}$) exist at all temperatures except for the transition point.

The temperature of the first order phase transition T_c is determined from the criterion that:

$$g^z(\eta^{(1)z}, T_c, p) = g^z(0, T_c, p), \quad (2.17)$$

Polarization of the crystal, resulting from the deuteron ordering, is equal to:

$$\begin{aligned} P_1 &= \frac{\mu_1}{v} [\eta_1^{(1)x} - \eta_3^{(1)x}], \quad P_2 = \frac{\mu_2}{v} [\eta_2^{(1)y} - \eta_4^{(1)y}], \\ P_3 &= 2 \frac{\mu_3}{v} \eta^{(1)z}. \end{aligned} \quad (2.18)$$

3. Elastic and piezoelectric properties

Let us consider now the pressure influence on elastic properties of a $\text{K}(\text{H}_x\text{D}_{1-x})_2\text{PO}_4$ crystal. Here we neglect the anharmonicity of lattice

vibrations. The attributed to a deuteron subsystem parts of elastic constants, related to the pressures $-p = \sigma_1 = \sigma_2$ or $-p = \sigma_3$ are given by the formula:

$$c_{ij}^{p-} = c_{ij}^{0-} - \frac{4\eta^{(1)}}{\bar{v}DT} [\psi_{ci}\theta_j + \psi_{cj}\theta_i - 2ab\delta_{2i}^-\delta_{2j}^-\cosh z + 2a\delta_{1i}^-\delta_{1j}^- + d\delta_{3i}^-\delta_{3j}^-] + \frac{2}{\bar{v}D^2T} M_i^- M_j^-. \quad (3.1)$$

Here we use the following notations:

$$\begin{aligned} \varkappa &= [\cosh 2z + b \cosh z] - \eta^{(1)} [\sinh 2z + 2b \sinh z]; \\ \theta_i &= -2b\delta_{2i}^-\sinh z + \eta^{(1)} M_i^- + 2\psi_{ci}\eta^{(1)z}\varkappa. \end{aligned} \quad (3.2)$$

Making use of the relations (2.12), we calculate the quantities which characterize the electromechanical properties of a crystal.

Coefficients e_{3i} and constants h_{3i} of piezoelectric stress read:

$$e_{3i} = \frac{\mu_3}{v} \frac{2}{T} \frac{\theta_i}{D - 2\varphi\varkappa}, \quad h_{3i} = \frac{2\varphi\theta_i}{\mu_3 D}, \quad (3.3)$$

where

$$\varphi = \frac{1}{1 - [\eta^{(1)}]^2} + \beta\nu.$$

Using (2.12) and taking into account the fact that $(\partial\varepsilon_i/\partial\sigma_j)_{E_i} = s_{ij}^E$ – the elastic compliance constants, we get the systems of equations for the coefficients of piezoelectric strain d_{3i} :

$$d_{3i} = \sum_j s_{ij}^{E-} e_{3j}; \quad -h_{3k} d_{3k} + \sum_j c_{ij}^{p-} s_{ij}^{E-} = \frac{p_k}{p}, \quad (3.4)$$

where $p_k = (p, p, 0)$ at $-p = \sigma_1 = \sigma_2$ i $p_k = (0, 0, p)$ at $-p = \sigma_3$. Compliances s_{ij}^{E-} found from the system (3.4) read:

$$\begin{aligned} s_{11}^E &= \frac{1}{\Delta_c} \begin{vmatrix} c_{22}^E & c_{23}^E \\ c_{23}^E & c_{33}^E \end{vmatrix}, & s_{12}^E &= -\frac{1}{\Delta_c} \begin{vmatrix} c_{12}^E & c_{23}^E \\ c_{13}^E & c_{33}^E \end{vmatrix}, \\ s_{13}^E &= \frac{1}{\Delta_c} \begin{vmatrix} c_{12}^E & c_{22}^E \\ c_{13}^E & c_{23}^E \end{vmatrix}, & s_{22}^E &= \frac{1}{\Delta_c} \begin{vmatrix} c_{11}^E & c_{13}^E \\ c_{13}^E & c_{33}^E \end{vmatrix}, \\ s_{23}^E &= -\frac{1}{\Delta_c} \begin{vmatrix} c_{11}^E & c_{13}^E \\ c_{12}^E & c_{23}^E \end{vmatrix}, & s_{33}^E &= \frac{1}{\Delta_c} \begin{vmatrix} c_{11}^E & c_{12}^E \\ c_{12}^E & c_{22}^E \end{vmatrix}, \\ \Delta_c &= \begin{vmatrix} c_{11}^E & c_{12}^E & c_{13}^E \\ c_{12}^E & c_{22}^E & c_{23}^E \\ c_{13}^E & c_{23}^E & c_{33}^E \end{vmatrix}, & c_{ij}^{E-} &= c_{ij}^{P-} - h_{3i}e_{3j}; \quad i, j = 1, 2, 3. \end{aligned}$$

where $c_{ij}^{E-} = c_{ij}^{P-} - h_{3i}e_{3j}$ is the elastic stiffness at constant electric field.

Constants of piezoelectric strain g_{3i} we find, solving the system

$$\sum_i c_{ij}^{p-} g_{3j} = h_{3i};$$

4. Thermal properties

Let us consider now the thermal properties of a deuteron subsystem of a KD_2PO_4 crystal in presence of stress $-p = \sigma_1 = \sigma_2$ or $-p = \sigma_3$. In the ferroelectric phase the entropy per one mole has the following form:

$$S^- = R \left(2 \ln[1 - (\eta^{(1)})^2] + 2 \ln \frac{D}{2} + 4T\varphi^T \eta^{(1)} + 2 \frac{\bar{M}}{D} \right), \quad (4.1)$$

where R is the gas constant, and

$$\bar{M} = \beta(4wb \cosh z + 2\varepsilon a + w_1 d), \quad \varphi^T = -\frac{1}{T^2} \nu \eta^{(1)}.$$

To calculate the specific heat per one mole at constant pressure we differentiate the entropy (4.1):

$$\Delta C^p = RT \left(\frac{\partial S}{\partial T} \right)_p.$$

In the result:

$$\Delta C^p = \Delta C^\varepsilon - RT \sum_i q_i^P \alpha_i; \quad (4.2)$$

ΔC^ε is molar specific heat at constant strains, and

$$\Delta C^\varepsilon = RT(-q^{P\varepsilon} - q^\varepsilon p^P). \quad (4.3)$$

Using (4.1), we get:

$$\begin{aligned} q_i^P &= \frac{2}{\bar{v}DT} \left\{ -2T\varphi^T \theta_i - 2\psi_{ci}\eta^{(1)z} [q - \eta^{(1)} \bar{M}] + \lambda_i - \frac{\bar{M} M_i}{D} \right\}, \\ q^\varepsilon &= -\frac{\nu}{\mu_3} \frac{2}{D} \varphi^\eta \left[2\varkappa T \varphi^T + (q - \eta^{(1)} \bar{M}) \right], \\ q^{P,\varepsilon} &= -\frac{2}{DT} \left\{ 4T\varphi^T \left[\varkappa T \varphi^T + (q - \eta^{(1)} \bar{M}) \right] + N - \frac{\bar{M}^2}{D} \right\}, \end{aligned}$$

where

$$\begin{aligned} N &= 4 \left(\frac{w}{T} \right)^2 b \cosh z + 2 \left(\frac{\varepsilon}{T} \right)^2 a + \left(\frac{w_1}{T} \right)^2 d, \\ q &= 2 \frac{w}{T} b \sinh z, \quad \lambda_i = -\frac{1}{T} (4wb\delta_{2i}^- \cosh z + 2\varepsilon a \delta_{1i}^- + w_1 d \delta_{3i}^-). \end{aligned} \quad (4.4)$$

From the relations (2.12) we obtain the expression for the pyroelectric coefficient at constant pressure:

$$p^P = p^\varepsilon + \sum_i e_{3i} \alpha_i, \quad (4.5)$$

where

$$p^\varepsilon = \frac{\mu_3}{v} \frac{2}{T} \frac{2\alpha T \varphi^T + [q - \eta^{(1)} \bar{M}]}{D - 2\varphi \eta \alpha}, \quad (4.6)$$

thermal expansion coefficients, attributed to the deuteron subsystem, obey the system of equations:

$$\sum_j c_{ij}^E \alpha_j = -q_i^P + p^\varepsilon h_{3i}. \quad (4.7)$$

In the paraelectric phase:

$$\begin{aligned} \alpha_{1,2} &= \frac{-p_1^+ c_{33}^{p+} + p_3^+ c_{13}^{p+}}{[c_{11}^{p+} + c_{12}^{p+}] c_{33}^{p+} - 2[c_{13}^{p+}]^2} + \alpha_1^0, \\ \alpha_3 &= \frac{2p_1^+ c_{11}^{p+} - p_3^+ [c_{11}^{p+} + c_{12}^{p+}]}{[c_{11}^{p+} + c_{12}^{p+}] c_{33}^{p+} - 2[c_{13}^{p+}]^2} + \alpha_3^0, \end{aligned} \quad (4.8)$$

The constant terms, which describe contributions of the lattice anharmonicity, have been added to the right-hand sides of (4.8).

5. Dielectric susceptibility

Let us determine the longitudinal static dielectric susceptibility of a $K(\text{H}_x\text{D}_{1-x})_2\text{PO}_4$ -type crystal in presence of external pressure. Consider, at first, a clamped crystal ($\varepsilon_i = \text{const}$). In the ferroelectric phase, the expression for $\chi_3^{\varepsilon^-}(0, T, p)$ reads:

$$\chi_3^{\varepsilon^-}(0, T, p) = \left(\frac{\partial P_3^-}{\partial E_3} \right)_{\varepsilon, E_3=0} = \frac{\mu_3^2}{v} \frac{1}{T} \frac{4\alpha}{D - 2\varphi \alpha}. \quad (5.1)$$

In the paraelectric phase:

$$\chi_3^{\varepsilon+}(0, T, p) = \frac{\mu_3^2}{v} \frac{1}{T} \frac{4(1+b)}{2a + 2b + d - 1 - 2\beta\nu_c(1+b)}. \quad (5.2)$$

In the case of a free crystal ($p = \text{const}$),

$$\chi_3^{p-}(0, T, p) = \chi_3^{\varepsilon+}(0, T, p) + \sum_i e_{3i} d_{3i}. \quad (5.3)$$

In the paraelectric phase the longitudinal susceptibilities of clamped and free crystals coincide:

$$\chi_3^{p+}(0, T, p) = \chi_3^{\varepsilon+}(0, T, p)$$

Transverse static dielectric susceptibility (along the x -axis) reads:

$$\begin{aligned} \chi_1^{\varepsilon-}(0, T, p) &= \left(\frac{\partial P_1}{\partial E_1} \right)_{\varepsilon, E_1=0} = \\ &= \frac{\mu_1^2}{v} \frac{1}{T} \frac{2(a+b \cosh z)}{D - 2(a+b \cosh z) \{ [1 - (\eta^{(1)})^2]^{-1} + \beta[\nu_1 - \nu_3] \}}. \end{aligned}$$

In the paraelectric phase:

$$\chi_1^{\varepsilon+}(0, T, p) = \frac{\mu_1^2}{v} \frac{1}{T} \frac{2(a+b)}{1 + 2b + d - 2\beta[\nu_1 - \nu_3](a+b)}. \quad (5.4)$$

The static dielectric susceptibility $\chi_2^{\varepsilon-}(0, T, p)$ read:

$$\begin{aligned} \chi_2^{\varepsilon-}(0, T, p) &= \left(\frac{\partial P_2}{\partial E_2} \right)_{\varepsilon, E_1=0} = \\ &= \frac{\mu_2^2}{v} \frac{1}{T} \frac{2(a+b \cosh z)}{D - 2(a+b \cosh z) \{ [1 - (\eta^{(1)})^2]^{-1} + \beta[\nu_1 - \nu_3] \}}. \end{aligned}$$

In the paraelectric phase:

$$\chi_1^{\varepsilon+}(0, T, p) = \chi_2^{\varepsilon+}(0, T, p)$$

6. Experimental results

In this section we present the results of experimental study of the influence of uniaxial stresses applied along the crystallographic axes c (the optic axis) and a (the perpendicular to the optic axis) on the temperature (70 – 300 K) and wavelength (400 – 700 nm) dependences of the birefringence Δn_y in KDP and DKDP crystals.

The birefringence at given wavelength λ , temperature T and stress σ read:

$$\Delta n(\lambda, T, \sigma) = \frac{k\lambda}{d(T, \sigma)}, \quad (6.5)$$

where k is the interference minimum number; $d(T, \sigma)$ is the thickness of a sample, being a function of temperature (owing to thermal expansion) and stress.

We use the photographic method to record the interference pattern in the focal plane of the ДФС-8 spectrograph. The pattern arises once white light passes through the studied sample placed on the spectrograph axis in the diagonal position between two crossed nicols. Uniaxial stress was produced by the purpose attachment to a nitrogen cryostat. The device allowed one to carry out measurements in wide temperature (77 – 300 K) and wavelength (250 – 800 nm) ranges under pressures up to 1 kbar depending on the sample stability.

Variation of the birefringence with temperature and pressure was measured by recording the changes in the interference pattern minima with pressure at constant temperature. The transition temperature as a function of external pressure was determined by examining the variation of the birefringence magnitude with pressure. Since the phase transitions in KDP and DKDP crystals are of the first order, pronounced changes in the interference pattern are observed at $T = T_c$; the transition temperature was determined with an accuracy of 0.05 K. Orientation of crystals was performed judging from the view of conoscopic patterns as well as using a polarizing microscope. This method allowed one to determine a crystallographic direction to within 30'.

In figure 1 we depicted the wavelength dependence Δn_y of KDP and DKDP crystals (the transition temperature of the DKDP crystal is 213 K what corresponds to 89% deuteration) at different values of σ_1 and σ_3 stresses. It is revealed that Δn_y increases with σ_3 and decreases with σ_1 . Both stresses slightly affect the dispersion $\Delta n_y(\lambda)$. The values of derivatives $d\Delta n_y/d\lambda$ at pressures σ_3 and σ_1 of 200 bar and different temperatures are given in Table 1.

In the figure 2 the pressure dependence of the birefringence Δn_y of KDP and DKDP crystals is plotted (see also Table 1). As temperature in the ferroelectric phase decreases, the changes in of Δn_y of a DKDP crystal increase with pressure; this effect for σ_3 stress is more significant than for σ_1 .

In figure 3 we plotted the temperature dependence of the birefringence Δn_y of KDP and DKDP crystals at different values of pressure. In DKDP the Δn_y is more sensitive to σ_1 than to σ_3 , whereas the reverse is observed in KDP. The magnitude of changes in Δn_y with pressure in KDP and decreases in DKDP as temperature tends to T_c in the ferroelectric phase.

The dependence of the jump of Δn_y at the transition point on stress magnitude and direction is found. in KDP: $\delta\Delta n_y=8.2 \cdot 10^{-4}$ ($\sigma = 0$), $6.4 \cdot 10^{-4}$ ($\sigma_3 = 200$ bar) and $10.4 \cdot 10^{-4}$ ($\sigma_1 = 200$ bar), in DKDP: $2.66 \cdot 10^{-4}$ ($\sigma = 0$), $2.61 \cdot 10^{-4}$ ($\sigma_1 = 200$ bar) and $2.92 \cdot 10^{-4}$ ($\sigma_3 = 200$ bar).

As one can see, the Δn_y in DKDP is much lower than in KDP and its dependence on the stress direction is much weaker.

On the basis of the obtained data and using the relations

$$\delta(\Delta n_y)_{\sigma_x} = \frac{1}{2}[n_x^3\pi_{11} - n_z^3\pi_{31}]\sigma_{21} + s_{12}[n_z - n_x]\sigma_{21} = \pi_{21}^0\sigma_1,$$

$$\delta(\Delta n_y)_{\sigma_z} = \frac{1}{2}[n_z^3\pi_{33} - n_x^3\pi_{13}]\sigma_{23} + s_{23}[n_x - n_z]\sigma_{23} = \pi_{23}^0\sigma_3$$

we calculated the combined piezooptic constants π_{21}^0 and π_{23}^0 of KDP and DKDP crystals (see Table 1).

The coefficients of KDP crystal increase and those of DKDP decrease as temperature tends to T_c in the ferroelectric phase.

| | T (K) | $d\Delta n_y/d\lambda, \sigma_3$ | $d\Delta n_y/d\lambda, \sigma_1$ | $d\Delta n_y/d\sigma_3$ | $d\Delta n_y/d\sigma_1$ | π_{21}^0 | π_{23}^0 |
|------|----------|----------------------------------|----------------------------------|------------------------------|-------------------------|------------------------------|--------------|
| | | $(10^{-5} \text{ nm}^{-1})$ | | $(10^{-7} \text{ bar}^{-1})$ | | $(10^{-7} \text{ bar}^{-1})$ | |
| KDP | 77 | -1.44 | -1.48 | 4.01 | -2.33 | -3.4 | 3.1 |
| | 123 | -1.35 | -1.39 | 11.2 | -12.6 | -27.1 | 21.2 |
| DKDP | 100 | -1.05 | -1.09 | 8.17 | -2.65 | -11.5 | 15.1 |
| | 200 | -1.18 | -1.22 | 1.67 | -1.15 | -3.5 | 5.5 |

Table 1: The wavelength and pressure derivatives of the birefringence and the combined piezooptic constants of KDP and DKDP crystals at different temperatures.

The transition temperature of KDP and DKDP crystals (figure 4) decreases with pressure linearly with: $dT_c/d\sigma_3 = -0.012$ K/kbar, $dT_c/d\sigma_1 = -0.007$ K/kbar in DKDP and -0.007 K/kbar and -0.003 K/kbar in KDP.

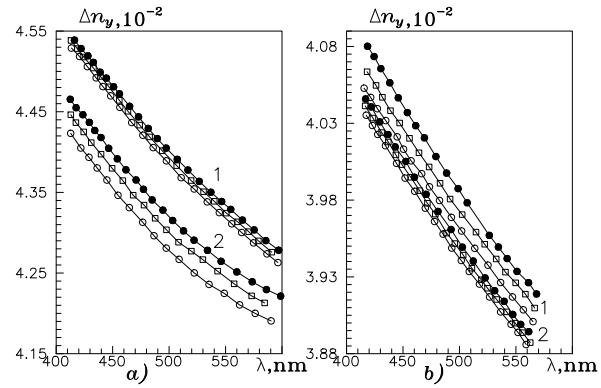


Figure 1: Dispersion of the birefringence Δn_y of KDP (a) and DKDP (b) crystals at different temperatures T (K): a) 1 – 77; 2 – 123; b) 1 – 100; 2 – 200; and pressures \bullet – $\sigma_3=200$ bar; \square – $\sigma_i = 1$ bar; \circ – $\sigma_1=200$ bar.

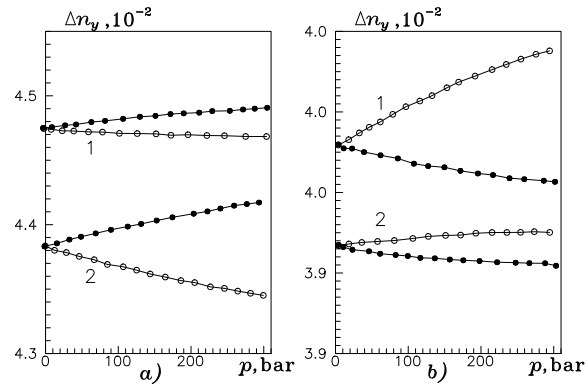


Figure 2: The pressure dependence of the birefringence Δn_y of KDP (a) and DKDP (b) crystals at different temperatures T (K): a) 1 – 77; 2 – 123; b) 1 – 100; 2 – 200. \bullet – σ_3 ; \square – σ_i ; \circ – σ_1 .

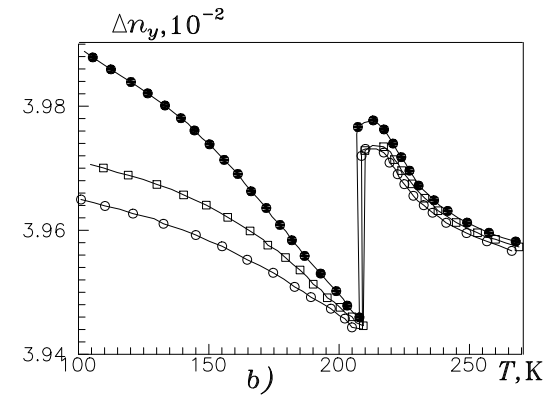
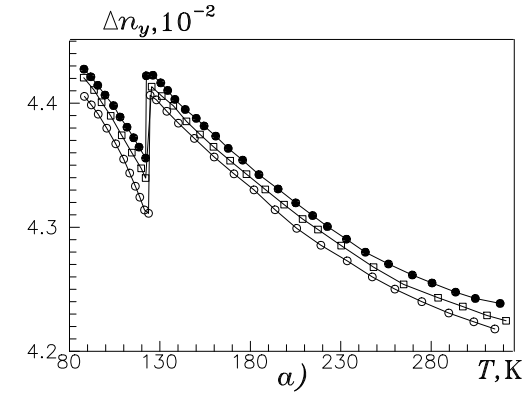


Figure 3: The temperature dependence of the birefringence Δn_y of KDP (a) and DKDP (b) crystals at $\lambda = 500$ nm at different pressures: \bullet – $\sigma_3=200$ bar; \square – $\sigma_i = 1$ bar; \circ – $\sigma_1=200$ bar.

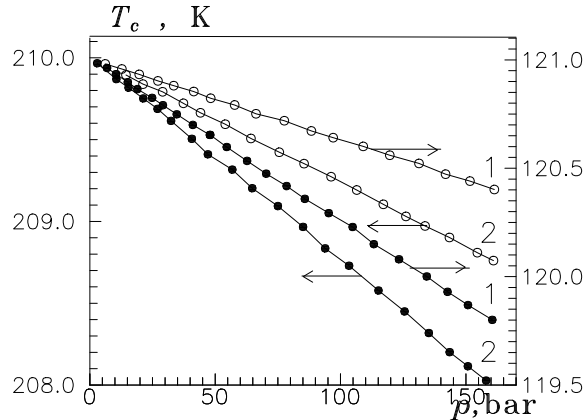


Figure 4: The pressure dependence of the transition temperature of KDP (1) and DKDP (2) crystals; ● - σ_3 ; ○ - σ_1 .

7. Discussion

The only available experimental data concerning the uniaxial pressure effects on the studied crystals are for the presented in the previous section dependence of the transition temperature T_c on the $-p = \sigma_3$ stress. Thus we only can estimate the theory parameters and the corresponding changes in the responses of the uniaxially strained crystals. The experimental studies of these effects are of great importance. It would be very interesting to explore the structure changes in KDP crystals with uniaxial stress and compare them with the changes caused by hydrostatic pressure. There is no experimental information about the dependence of the hydrogen bond geometry on the uniaxial stress; the actual peculiarities of this dependence are very difficult to predict theoretically. Nevertheless, we thought it necessary to describe the possible changes in characteristics of these crystals induced by uniaxial stresses, considering the variation of the H-site distance δ with pressure (δ_1/δ_0) as free parameter.

Our goal was to draw attention to this problem and stimulate further experimental investigation of hydrostatic and uniaxial pressure effects on physical properties of H-bonded ferroelectrics.

In order to study the influence of the strains ε_i , caused by the uniaxial

stress σ_3 or by σ_{1+2} , on the transition temperature, elastic, piezoelectric, thermal and dielectric characteristics of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal, we need to set the values of the cluster parameters ε^0 , w^0 , w_1^0 , long-range interaction parameters $\nu_c(0)$, $\nu_a(0)$, effective dipole moments per unit cell $\mu_c^{(0)}$, $\mu_a^{(0)}$, relevant to the case of an unstrained crystal, as well as the values of the deformation potentials δ_{ij} , ψ_{ci} , ψ_{ai} , the parameter δ_1/δ_0 and the "seed" elastic constants c_{ij}^0 .

The values of ε^0 , w^0 , w_1^0 , $\nu_c(0)$, $\nu_a(0)$, $\mu_c^{(0)}$ and $\mu_a^{(0)}$, providing a satisfactory description of a number of characteristics of a $\text{K}(\text{H}_x\text{D}_{1-x})_2\text{PO}_4$ crystal at ambient pressure, have been found in [7,8]. At $x = 0.87$: $\varepsilon^0 = 87.5$ K, $w^0 = 785$ K, $w_1^0 = \infty$, $\nu_c(0)/4 = 36.8$ K, $\nu_a(0)/4 = 19$ K, $\mu_c^{(0)-} = 3.415510^{-18}$ esu, $\mu_c^{(0)+} = 2.80310^{-18}$ esu, $\mu_a^{(0)} = 2.80010^{-18}$ esu.

The values of the deformation potentials, being the same in the cases of hydrostatic and uniaxial pressures applied, were chosen such that the best agreement with experimental data was obtained for the variation of transition temperature T_c with hydrostatic pressure [3,4]. Those values we use in the present work (see Table 2).

| δ_{11}^- | δ_{12}^- | δ_{13}^- | ψ_{c1}^- | ψ_{c2}^- | ψ_{c3}^- | δ_{11}^+ | δ_{13}^+ | ψ_{c1}^+ | ψ_{c3}^+ |
|-----------------|-----------------|-----------------|---------------|---------------|---------------|-----------------|-----------------|---------------|---------------|
| -45 | -55 | 885 | -97 | -97 | 250 | -50 | 800 | -97 | 390 |

Table 2: The deformation potentials (in K) for a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal.

In the case of $p = -\sigma_3$ stress, the value of δ_1/δ_0 which turned to be the most important fitting parameter was chosen such that the best fit to the experimentally found $T_c(\sigma_3)$ dependence was obtained.

| c_{11}^{0+} | c_{12}^{0+} | c_{13}^{0+} | c_{33}^{0+} | c_{11}^{0-} | c_{12}^{0-} | c_{13}^{0-} | c_{22}^{0-} | c_{23}^{0-} | c_{33}^{0-} |
|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| 6.93 | -0.78 | 1.22 | 5.45 | 6.93 | -1.78 | 1.22 | 6.0 | 1.1 | 5.0 |

Table 3: The "seed" elastic constants (units of 10^{11} dyn/cm²) of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal.

Experimental values of the elastic constants of a $\text{K}(\text{H}_x\text{D}_{1-x})_2\text{PO}_4$ crystal for $x = 0.89$ at temperatures above T_c are reported in [11]. These data have been taken as the "seed" elastic constants c_{ij}^{0+} . Since the values of elastic constants of ferroelectric DKDP are not available at all, we

carried out the calculations of T_c , ε_i and other characteristics at different pressures and different trial values of c_{ij}^{0-} close to c_{ij}^{0+} . The set of $c_{ij}^{0\pm}$, providing the best fit to experimental data is given in Table 3.

Results of numerical calculations are presented in figures 5-15. The solid, long-dashed and short-dashed lines correspond to characteristics of a crystal under stresses σ_h , σ_{1+2} , and σ_3 , respectively.

In figure 5 we showed the calculated dependence of the transition temperature of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal on different pressures at different values of the δ_1/δ_0 parameter along with experimental data for $T_c(\sigma_3)$. The linear dependence $T_c(p) = T_c - k_T p$ is obtained, with

$$\begin{aligned} k_T(3) &= 13.9 \text{ K/kbar at } 2\delta_1/\delta_0 = -1.4 \cdot 10^{-4} \text{ bar}^{-1}, \\ k_T(3) &= -6.3 \text{ K/kbar at } 2\delta_1/\delta_0 = 0.7 \cdot 10^{-4} \text{ bar}^{-1}, \\ k_T(1+2) &= 6.6 \text{ K/kbar at } 2\delta_1/\delta_0 = -0.7 \cdot 10^{-4} \text{ bar}^{-1}, \text{ and} \\ k_T(h) &= 2.67 \text{ K/kbar at } 2\delta_1/\delta_0 = -0.18 \cdot 10^{-4} \text{ bar}^{-1} [5]. \end{aligned}$$

The experimentally determined $T_c(\sigma_3)$ dependence is well described at $2\delta_1/\delta_0 = -1.4 \cdot 10^{-4} \text{ bar}^{-1}$.

In figure 6 we plotted the pressure dependence of strains $\varepsilon_i(l)$ of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal with pressure. The values of ε_i vary with pressure linearly as:

$$\varepsilon_i(1+2) = -k_{\varepsilon_i(1+2)} p, \quad \varepsilon_i(3) = -k_{\varepsilon_i(3)} p,$$

where (units $10^{-3} \text{ kbar}^{-1}$):

$$\begin{aligned} k_{\varepsilon_1(3)}^- &= -0.54, & k_{\varepsilon_2(3)}^- &= -0.57, & k_{\varepsilon_3(3)}^- &= 2.3; \\ k_{\varepsilon_1(3)}^+ &= k_{\varepsilon_2(3)}^+ = 0.4, & k_{\varepsilon_3(3)}^+ &= -2.0, \\ k_{\varepsilon_1(h)}^- &= 1.7, & k_{\varepsilon_2(h)}^- &= 1.8, & k_{\varepsilon_3(h)}^- &= 1.3; \\ k_{\varepsilon_1(h)}^+ &= k_{\varepsilon_2(h)}^+ = 1.4, & k_{\varepsilon_3(h)}^+ &= 1.2, \\ k_{\varepsilon_1(1+2)}^- &= 2.3, & k_{\varepsilon_2(1+2)}^- &= 2.5, & k_{\varepsilon_3(1+2)}^- &= -1.1; \\ k_{\varepsilon_1(1+2)}^+ &= k_{\varepsilon_2(1+2)}^+ = 1.8, & k_{\varepsilon_3(1+2)}^+ &= -0.71. \end{aligned}$$

Calculations do not predict any perceptible changes in ε_i with temperature except for the abrupt jumps at the transition point. Let us note, that the magnitude of the strains does not depend on the δ_1/δ_0 value. The Poisson coefficient is equal to

$$\sigma = \left| \frac{\varepsilon_{1,2}(3)}{\varepsilon_3(3)} \right| = 0.19$$

The dependence of spontaneous polarization of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal on temperature at different stresses σ_3 and σ_{1+2} is given in figures 7a and 7b. For $p = 0.001 \text{ kbar}$ the calculated $P_s(T)$ dependence is an

agreement with the experimental results of [12] ($x = 0.84$). In calculations we put the effective dipole moment μ_3 to decrease with pressure linearly with $\mu_3^- = (3.4155 - k_\mu^- p) \cdot 10^{-18} \text{ esu}$, where $k_\mu^-(3) = 0.07 \text{ esu/kbar}$, $k_\mu^-(1+2) = 0.02 \text{ esu/kbar}$, assuming that $k_\mu^-(3) < k_\mu^-(h)$. In order to determine the values of $k_\mu(3)$ and $k_\mu(1+2)$, we need to know the pressure dependence of $P_s(3)$ and $P_s(1+2)$. However, we are not aware of any experimental measurements of these dependences.

In figure 8 we depicted the polarizations $P_s(h)$, $P_s(3)$ and $P_s(1+2)$ of a $\text{K}(\text{H}_x\text{D}_{1-x})_2\text{PO}_4$ ($x = 0.87$) crystal as functions of $\Delta T = T - T_c$. As one can see, the pressure of 1 kbar reduces only $P_s(3)$, whereas $P_s(h)$ and $P_s(1+2)$ remain almost unchanged.

In figures 9-11 we depicted the temperature dependences of piezoelectric coefficients e_{3i} , d_{3i} , h_{3i} , g_{3i} , ($i = 1, 2, 3$) of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal at stresses σ_3 and σ_{1+2} of 0.001 and 0.2 kbar. Let us note that the magnitudes of the piezocoefficients at low $-p = \sigma_1 = \sigma_2$ or $-p = \sigma_3$ stresses hardly differ. In the paraelectric phase all the considered piezocoefficients are equal to zero. When the temperature tends to T_c the absolute values of e_{3i} and d_{3i} sharply increase and fall to zero abruptly at the transition point; pressure reduces the size of the jumps. The temperature range where e_{3i} and d_{3i} differ from zero, decreases with pressure. Coefficients h_{3i} and g_{3i} increase slightly with temperature and fall to zero with a discontinuity at $T = T_c$; the size of the discontinuity increases with pressure. The values of e_{31} , e_{32}, \dots, g_{31} , g_{32} are negative, and those of e_{33} , e_h, \dots, d_{33} , d_h are positive.

In figure 13 we plotted the variation of the attributed to the deuteron subsystem part of specific heat of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal with temperature at different stresses $-p = \sigma_1 = \sigma_2$ and $-p = \sigma_3$ along with the experimental points for $p = 0.001 \text{ kbar}$. In the ferroelectric phase ΔC^p sharply increases as temperature tends to T_c and decreases with a discontinuity at the transition point. The peak values of ΔC^p in the high pressure range are smaller than those at 0.001 kbar. In the paraelectric phase the specific heat hardly depends on either pressure or temperature.

The temperature dependence of the inverse longitudinal dielectric permittivity $\varepsilon_3^{-1}(0, T, p)$ of the $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal at different pressures $-p = \sigma_3$ and $-p = \sigma_1 - \sigma_2$ is plotted in figures 14a and 14b, respectively. At $p = 0.001 \text{ kbar}$, the calculated dependence $\varepsilon_3^{-1}(0, T, p)$ is in agreement with the experimental data of [12] for $x = 0.84$. In figure 14a we also depicted the $\varepsilon_3^{-1}(0, T, p)$ curve at hydrostatic pressure of 1 kbar. As one can see, the magnitude of $\varepsilon_3(0, T, p)$ decreases with pressure, influence of the uniaxial σ_3 stress being the most significant. However, the main pressure effect here is the shift of the transition point

and, thereby, of the whole $\varepsilon_3(T)$ curve to lower temperatures. Thus at constant ΔT , $\varepsilon_3(0, T, p)$ almost does not depend on pressure in the paraelectric phase and only slightly varies in the ferroelectric phase.

In figure 15 we depicted the temperature dependence of the transverse static dielectric permittivity of a uniaxially σ_3 strained DKDP crystal along with the experimental data [15] for $p = 0.001$ kbar. It should be noted that the character of the changes in $\varepsilon_1(0, T, p)$ with pressure essentially depends on the choice of the free parameters. For instance, $\varepsilon_1(0, T, p)$ decreases with σ_3 at $T > T_c$ and decreases at $T < T_c$, if $\psi_{11} = \psi_{12} = 1000$ K, $\psi_{13} = -1000$ K, and decreases at all temperatures if $\psi_{11} = \psi_{12} = 5000$ K, $\psi_{13} = 10000$ K.

8. Concluding remarks

In our previous works [3,4] within the earlier proposed model we studied the influence of hydrostatic pressure on the physical properties of $K(\text{H}_x\text{D}_{1-x})_2\text{PO}_4$ crystals. In the present paper within the same model we consider the uniaxial $p = -\sigma_3$ and $p = -\sigma_1 = -\sigma_2$ stresses effects on the phase transition, thermodynamic, elastic, piezoelectric and dielectric properties of these crystals.

We performed the experimental measurements of uniaxial $p = -\sigma_3$ and $p = -\sigma_1$ stresses influence on temperature and wavelength dependences of the birefringence in KH_2PO_4 and KD_2PO_4 crystals. It was found out that the $p = -\sigma_3$ and $p = -\sigma_1$ stresses affected the birefringence in different ways: Δn_y increased with $p = -\sigma_3$ and decreased with $p = -\sigma_1$. It is shown that the pressure dependence of the jump of Δn_y at the transition point in DKDP was much lower than in KDP. It was also revealed that the transition temperature decreases with $p = -\sigma_3$ more rapidly than with $p = -\sigma_1$ or with hydrostatic pressure.

Since the only available experimental data are for the pressure dependence of the transition temperature and some optical characteristics, we only can estimate the theory parameters. To compare the present results with the relevant data in the hydrostatic pressure case is of great interest.

In this paper we state the possible changes in the physical properties of DKDP crystals with the uniaxial pressure, considering the variation of the H-site distance δ with pressure (δ_1/δ_0) as free parameter. The main feature of the predicted effects is that even low uniaxial stress can induce significant changes in the responses of the studied crystals.

It is urgent to carry out comprehensive experimental studies of the uniaxial pressure effects on these crystals, especially on their structure.

It will allow us to define the theory parameters more precisely and check our predictions.

The previous [3,4] and present studies show that in the framework of the proton ordering model within the cluster approximation it is possible to obtain a good description of experimental data for the pressure dependence of thermodynamic and dynamic characteristics of ferroelectric crystals of KDP family. We hope that experimental measurements of the hydrostatic and uniaxial pressure effects on the hydrogen-bonded crystals (on KDP in particular) will allow us to clarify the microscopic mechanism of the phase transition in these crystals, correct the theory parameters and maybe the microscopic model itself.

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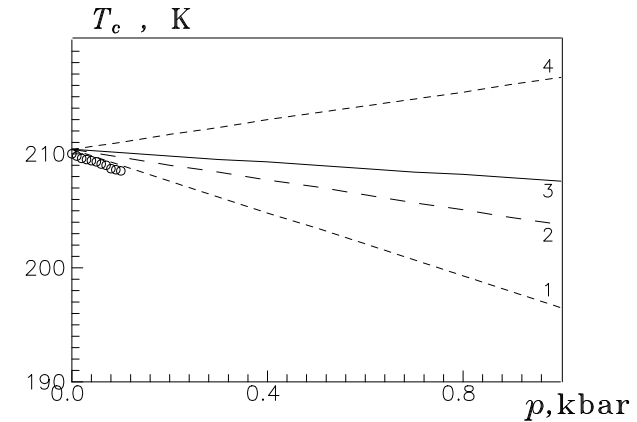


Figure 5: The pressure dependence of the transition temperature T_c of a $K(H_{0.13}D_{0.87})_2PO_4$ crystal under the stresses σ_3 , σ_{1+2} and σ_h at different values of $2\delta_1/\delta_0$ (bar-1): 1 - $-1.4 \cdot 10^{-4}$; 2 - $-0.7 \cdot 10^{-4}$; 3 - $-0.17 \cdot 10^{-4}$ [5] 4 - $0.7 \cdot 10^{-4}$.

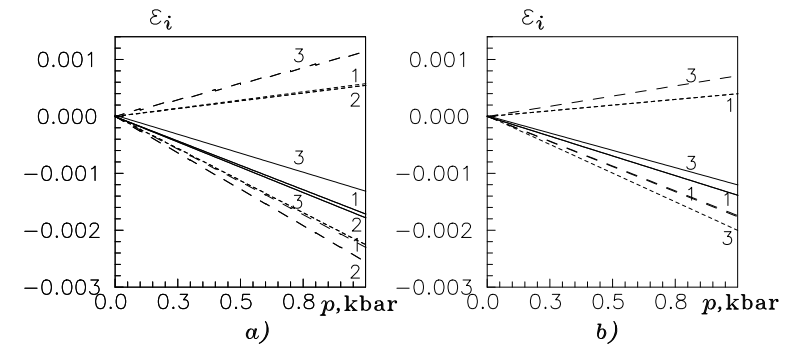


Figure 6: The pressure dependence of the strains $\varepsilon_i(l)$ at $T < T_c$ (a) $i T > T_c$ (b): 1 - $\varepsilon_1(l)$; 2 - $\varepsilon_2(l)$; 3 - $\varepsilon_3(l)$; ($l=3, 1^+2, h$).

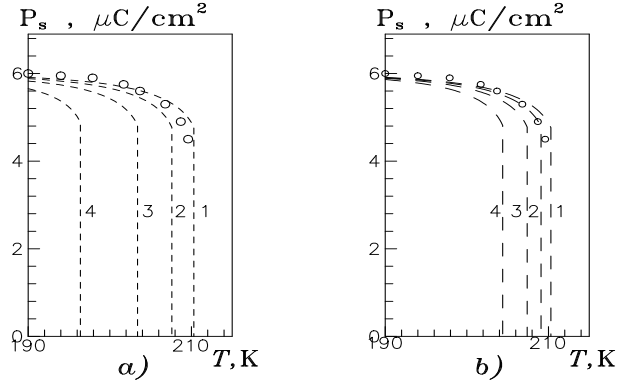


Figure 7: The temperature dependence of the spontaneous polarization $P_s(3)$ (a) and $P_s(1^{+2})$ (b) of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal at different pressures p (kbar): 1, $\circ[12]$ ($x = 0.84$) - 0.001; 2 - 0.2; 3 - 0.5; 4 - 1.0.

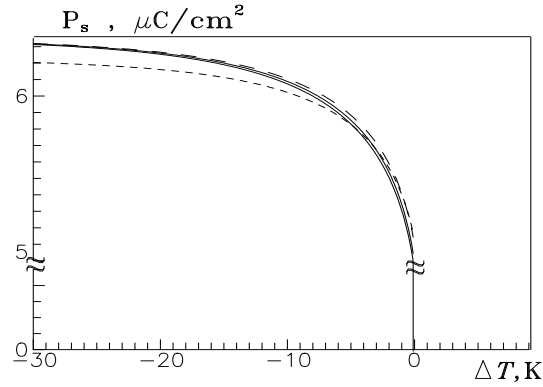


Figure 8: The temperature ($\Delta T = T - T_c$) dependence of the spontaneous polarization $P_s(3)$, $P_s(h)$ and $P_s(1^{+2})$ of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal at different pressures p (kbar): 1 - 0.001; 2 - 1.0.

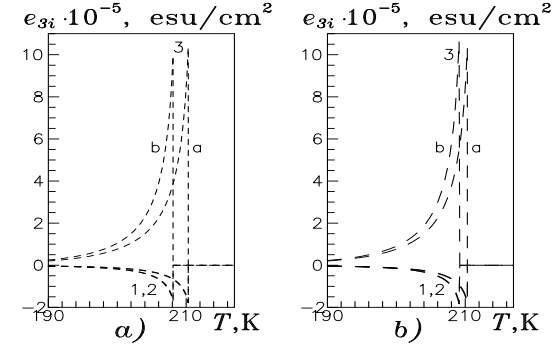


Figure 9: The temperature dependence of the piezoelectric coefficients $e_{3i}(3)$ (a) and $e_{3i}(1^{+2})$ (b) of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal at different pressures p (kbar): 0.001 - a; 0.2 - b. 1 - e_{31} ; 2 - e_{32} ; 3 - e_{33} .

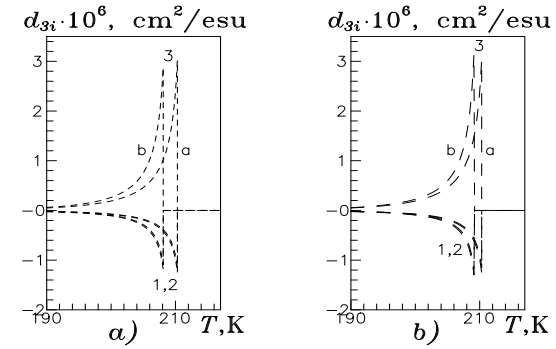


Figure 10: The temperature dependence of the piezoelectric coefficients $d_{3i}(3)$ (a) and $d_{3i}(1^{+2})$ (b) of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal at different pressures p (kbar): 0.001 - a; 0.2 - b. 1 - d_{31} ; 2 - d_{32} ; 3 - d_{33} .

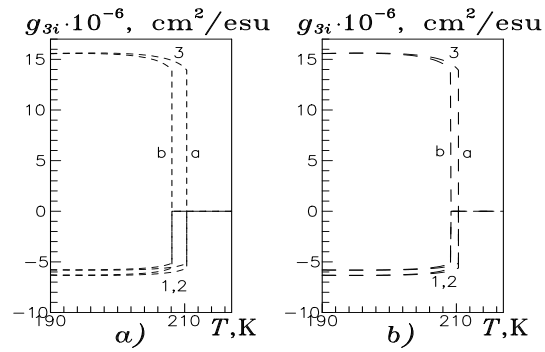


Figure 11: The temperature dependence of the piezocoefficients $g_{3i}(3)$ (a) and $g_{3i}(1+2)$ (b) of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal at different pressures p (kbar): 0.001 - a; 0.2 - b. 1 - g_{31} ; 2 - g_{32} ; 3 - g_{33} .

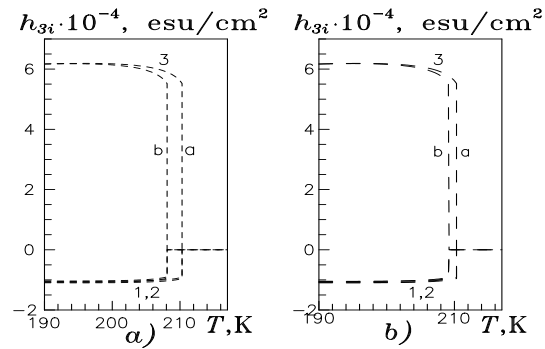


Figure 12: The temperature dependence of the piezocoefficients $h_{3i}(3)$ (a) and $h_{3i}(1+2)$ (b) of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal at different pressures p (kbar): 0.001 - a; 0.2 - b. 1 - h_{31} ; 2 - h_{32} ; 3 - h_{33} .

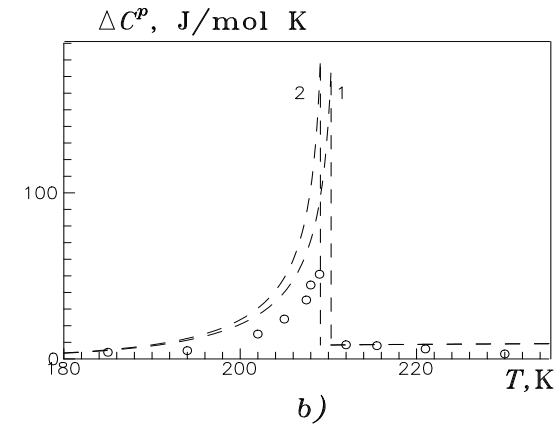
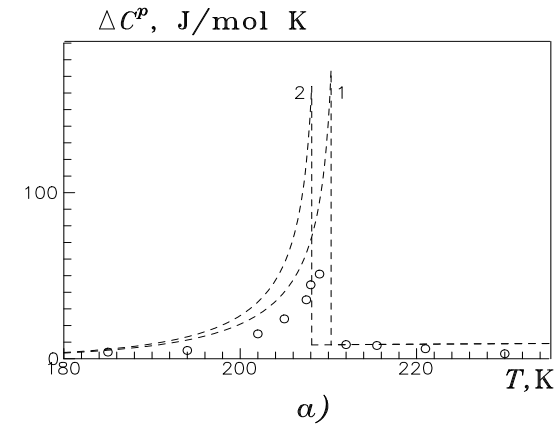


Figure 13: The temperature dependence of the attributed to a deuteron subsystem specific heat ΔC^p of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal at different pressures p (kbar): 1, \circ [13] - 0.001, 2 - 0.2.

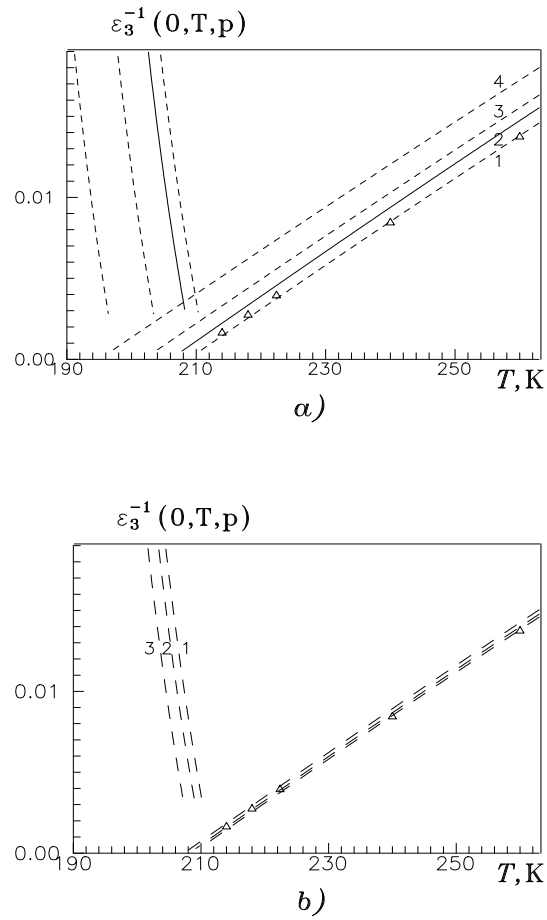


Figure 14: The temperature dependence of the inverse longitudinal static dielectric permittivity $\varepsilon_3^{-1}(0, T, \sigma_3)$, $\varepsilon_3^{-1}(0, T, h)$ (a) and $\varepsilon_3^{-1}(0, T, \sigma_{12})$ (b) of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal at different pressures p (kbar): a) 1, Δ [14], - 0.001; 2, 4 - 1; 3 - 0.5; b) 1, Δ [14] - 0.001; 2 - 0.5.

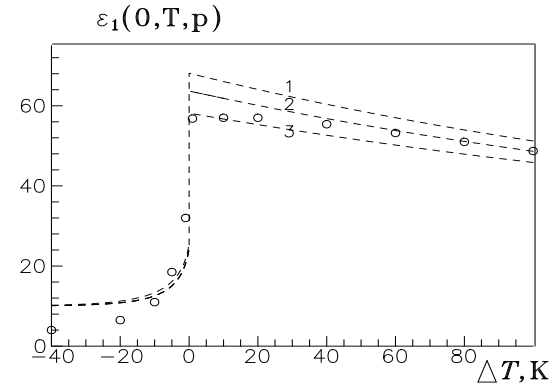


Figure 15: The temperature dependence of the transverse static dielectric permittivity $\varepsilon_1(0, T, \sigma_3)$ of a $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ crystal at different pressures p (kbar) and different values of deformation potentials ψ_{ai} : 1 - 1 kbar, $\psi_{11} = \psi_{12} = 1000$ K, $\psi_{13} = -1000$ K; 2, $\sigma[15] = 0.001$; 3 - 1 kbar, $\psi_{11} = \psi_{12} = -5000$ K, $\psi_{13} = 10000$ K.

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ВПЛИВ ОДНОВІСНОГО ТИСКУ НА ФАЗОВИЙ ПЕРЕХІД І ФІЗИЧНІ
ВЛАСТИВОСТІ ВИСОКОДЕЙТЕРОВАНИХ СЕГНЕТОЕЛЕКТРИКІВ З
ВОДНЕВИМИ ЗВ'ЯЗКАМИ ТИПУ $K(H_xD_{1-x})_2PO_4$

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