UNIAXIAL PRESSURE INFLUENCE ON KH_2PO_4–TYPE FERROELECTRICS

I. V. Stasyuk[1], R. R. Levitskii[1], A. P. Moina[1], I. R. Zachek[2], A. S. Duda[1],
M. O. Romanyuk[3], V. J. Stadnyk[3], Ye. V. Shcherbina[4]

[1] *Institute for Condensed Matter Physics, 1 Svientsitskii Str., Lviv, UA–79011, Ukraine*
[2] *State University "Lvivs'ka Politekhnika", 12 Bandera Str., Lviv, UA–79646, Ukraine*
[3] *Ivan Franko National University of Lviv, 50 Drahomanov Str., Lviv, UA–79005, Ukraine*
[4] *Institute for Single Crystals, 60 Lenin Pr., Kharkiv, UA–61141, Ukraine*

(Received March 12, 1999)

We performed experimental investigations of deuteration and uniaxial $p = -\sigma_i'$ pressure influence on temperature dependence of the birefringences and transition temperature of $K(H_{1-x}D_x)_2PO_4$ crystals. On the basis of the previously proposed model for a strained KD_2PO_4 crystal, we study the effects of uniaxial $p = -\sigma_3$ pressure on the phase transition and static dielectric properties of highly deuterated $K(H_{1-x}D_x)_2PO_4$ crystals. The obtained theoretical results are compared with the available experimental data and earlier theoretical calculations, concerning the hydrostatic pressure effects. The role of D–site distance in the phase transition and dielectric response of the crystals is discussed.

Key words: uniaxial pressure, ferroelectrics, KDP, birefringence, phase transition.

PACS number(s): 77.84.Fa, 77.80.Bh, 78.20.Fm

I. INTRODUCTION

Recently, a great attention has been paid to the investigation of the effects caused by hydrostatic pressure in ferroelectric crystals with hydrogen bonds of the KH_2PO_4 family. Hydrostatic pressure is known to lower down the transition temperature, spontaneous polarization and Curie constant of these crystals. However, the influence of uniaxial stresses on these crystals can be even more essential. Relative ions displacements in uniaxially strained crystals are several times larger. In contrast to hydrostatic pressure, uniaxial pressure can lower the crystal symmetry and 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 deuteron–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 fields which act on deuterons are calculated. In [3] within this model we studied the hydrostatic pressure influence on the physical properties of highly deuterated $K(H_{1-x}D_x)_2PO_4$ type ferroelectrics and $ND_4D_2PO_4$ type antiferroelectrics. It has been shown that under the proper choice of the theory parameters, a satisfactory description of the available experimental data for the pressure 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 pressures influence on the temperature dependence of the birefringences and transition temperature of $K(H_{1-x}D_x)_2PO_4$ crystals. On the basis of the model [1,2], we study the effects of uniaxial $p = -\sigma_3$ pressure on the phase transition and dielectric properties of highly deuterated $K(H_{1-x}D_x)_2PO_4$ crystals. We perform a numerical analysis of the obtained theoretical results and compare them with the available experimental data and earlier theoretical calculations [3] of the hydrostatic pressure effects.

II. EXPERIMENTAL RESULTS

In this section we present the results of experimental study of the influence of uniaxial pressures $p = -\sigma_i'$ applied along the axes of the $Fdd2$ (in the ferroelectric phase) or $F\bar{4}2d$ (in the paraelectric phase) unit cell on the temperature dependences of the birefringence in KDP and DKDP crystals. The x' and y' axes of the $F\bar{4}2d$ cell (face centered with 8 formula units) are 45^0 rotated with respect to the x and y axes of the standard body centered $I\bar{4}2d$ unit cell containing 4 formula units. Pressures reffered to the $F\bar{4}2d$ and $I\bar{4}2d$ cells are related by

$$\sigma_1' = \frac{\sigma_1 + \sigma_2 - 2\sigma_6}{4}, \quad \sigma_2' = \frac{\sigma_1 + \sigma_2 + 2\sigma_6}{4}, \quad \sigma_3' = \sigma_3.$$

Transition temperature of the DKDP crystal at ambient pressure is 210 K, which corresponds to a nominal value of deuteration of $x = 0.87$.

The birefringence at given wavelength λ, temperature T and pressure p is

$$\Delta n(\lambda, T, p) = \frac{k\lambda}{d(T,p)}, \tag{1}$$

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

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 a diagonal position between two crossed nicols. Uniaxial pressure was produced by a 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.

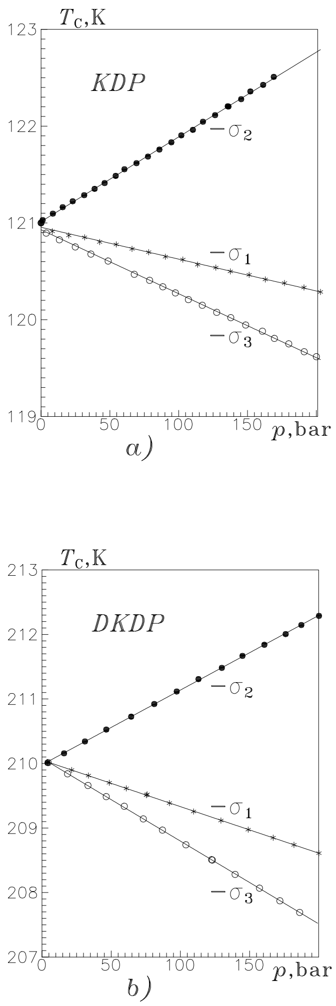


Fig. 1. The pressure dependence of the transition temperature of KDP (**a**) and DKDP (**b**) crystals; $*$ — $p=-\sigma_1'$, $\bullet$ — $p=-\sigma_2'$, and $\circ$ — $p=-\sigma_3$.

Variation of the birefringence with temperature and pressure was measured by recording the changes in the interference pattern minima with pressure at constant temperature. 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 $30'$.

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 the accuracy of 0.05 K. Crystals were cooled down to the ferroelectric phase, then pressure was applied, and the birefrinegences were measured at slow heating of the sample up to the paraelectric phase.

A separate question is whether there is a phase transition in these crystals under pressures $p=-\sigma_1'$ or $p=-\sigma_2'$ at all. These pressures include the shear stress σ_6. When the signs of spontaneous and induced by the shear stress σ_6 strains ε_6 are opposite, the system appears in a metastable state [4]; therefore, in the case of the pressure $p=-\sigma_1'$ (why not σ_2' is explained in Section IV) we are possibly dealing not with a true phase transition but with a certain transition from a metastable to a stable state. Henceforth, for the cases of pressures $p=-\sigma_1'$ and $p=-\sigma_2'$ we use the term "transition temperature" meaning the temperature of the abrupt changes in the studied characteristics.

In Fig. 1 we plot the experimental points of transition temperature vs uniaxial pressures $p=-\sigma_1'$, $p=-\sigma_2'$, $p=-\sigma_3$ in KDP and DKDP crystals. As one can see, the transition temperature is lowered down by $p=-\sigma_1'$ and $p=-\sigma_3$ pressures and raised up by $p=-\sigma_2'$. Unlike hydrostatic pressure, variation of the transition temperature with uniaxial pressures in more pronounced in deuterated DKDP rather than in KDP (see Table 1).

	$p=-\sigma_1'$	$p=-\sigma_2'$	$p=-\sigma_3$	hydrostatic
KDP	-3.0	8.0	-7.0	-4.6
DKDP	-7.0	11.0	-12.0	-3.0

Table 1. Experimental pressure derivatives of the transition temperature dT_C/dp for two crystals (units of K/kbar). The data in the last column were taken from Samara's work [5].

In Fig. 2 we present the experimental curves of the temperature dependence of birefringences Δn_x and Δn_y in KDP and DKDP crystals at $\lambda=500$ nm and at different values of uniaxial pressures. The birefringences decrease with temperature in the ferroelectric phase, jump up at the transition point, and, again decrease in the paraelectric phase. In deuterated DKDP variation of Δn_x and Δn_y with temperature is essentially non–linear. Above T_C, Δn_x=Δn_y, that is, the crystals are optically uniaxial.

The uniaxial pressure $p=-\sigma_3$ increases Δn_x and Δn_y both in KDP and DKDP crystals, whereas the influence of $p=-\sigma_1'$ and $p=-\sigma_2'$ pressures is reverse: $p=-\sigma_1'$ decreases Δn_y and so does $p=-\sigma_2'$ to Δn_x(remember that $p=-\sigma_1'$ and $p=-\sigma_3$ decrease the transition temperature, whereas $p=-\sigma_2'$ increases). External pressure may either weaken or enhance variation of the birefringences with temperature (see the values of $d\Delta n_i/dT$ in Table 2).

	KDP				DKDP			
	atmosph.	$p=-\sigma_1'$	$p=-\sigma_2'$	$p=-\sigma_3$	atmosph.	$p=-\sigma_1'$	$p=-\sigma_2'$	$p=-\sigma_3$
$\delta\Delta n_x$	1.25		2.1	1.3	0.8		0.75	1.1
$\delta\Delta n_y$	8.1	10.4		6.4	2.66	2.92		2.61
$\delta\Delta n_z$	5.25		5.2	4.8	1.8	1.84	1.78	
$\mathrm{d}\Delta n_x/\mathrm{d}T$	-1.29		−1.6	−1.09	−0.28		−0.25	−0.52
$\mathrm{d}\Delta n_y/\mathrm{d}T$	-2.26	−2.49		−2.01	−0.23	−0.19		−0.39
$\mathrm{d}\Delta n_z/\mathrm{d}T$	0.75	0.83	0.6		0.58	0.75	0.36	

Table 2. Jumps of birefringences $\delta\Delta n_i$ (units of 10^{-4}) at the transition points and the temperature derivatives $\mathrm{d}\Delta n_i/\mathrm{d}T$ (units of $10^{-5}\mathrm{K}^{-1}$) of the two crystals at different pressures ($p=-\sigma_i=200$ bar). The values of the slopes $\mathrm{d}\Delta n_1/\mathrm{d}T$ and $\mathrm{d}\Delta n_2/\mathrm{d}T$ are given for the temperatures just above the transition points.

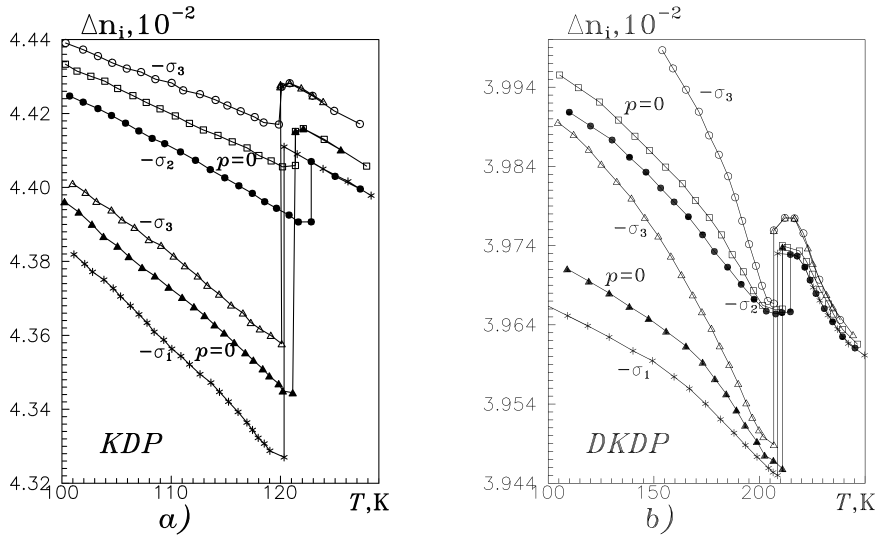


Fig. 2. The temperature dependence of the birefringences Δn_x (upper groups of curves) and Δn_y (lower groups of curves) of KDP (**a**) and DKDP (**b**) crystals at $\lambda = 500$ nm and at different pressures: ● — $p=-\sigma_2'=200$ bar; □ and ▲ — atmospheric pressure; △ and ○ — $p=-\sigma_3=200$ bar; $*$ — $p=-\sigma_1'=200$ bar.

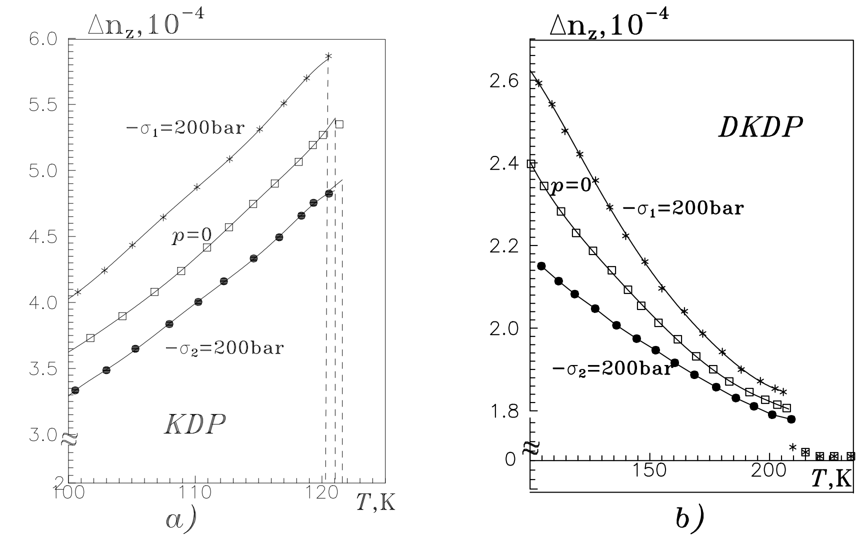


Fig. 3. The temperature dependence of the birefringence Δn_z of KDP (**a**) and DKDP (**b**) crystals at $\lambda = 500$ nm and at different pressures: ● — $p=-\sigma_2'=200$ bar; $*$ — $p=-\sigma_1'=200$ bar, and □ — atmospheric pressure.

The temperature dependence of the birefringence Δn_z at ambient pressure and at $p = -\sigma_1' = 200$ bar and $p = -\sigma_2' = 200$ bar in KDP and DKDP crystals is given in Fig. 3. In the paraelectric phase at atmospheric pressure, where the crystals are optically uniaxial, Δn_z=0. However, under pressure $p = -\sigma_1'$ the small non–zero values of the birefringence Δn_z persist in a narrow temperature range after its jump at the "transition point".

Below T_C, Δn_z decreases with temperature in KDP and increases in DKDP. In both crystals Δn_z is raised up by $p = -\sigma_1'$ and lowered down by $p = -\sigma_2'$. The values of jumps in Δn_z at the transition points and the slopes $\mathrm{d}\Delta n_z/\mathrm{d}T$ at different pressures are given in Table 2.

On the basis of the obtained data and using the relations

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

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

$$\delta(\Delta n_x)_{\sigma_2'} = \frac{1}{2}[n_y^3\pi_{22} - n_z^3\pi_{32}]\sigma_{12} + s_{12}[n_y - n_z]\sigma_{12} = \pi_{12}^0\sigma_2',$$

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

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

$$\delta(\Delta n_z)_{\sigma_2'} = \frac{1}{2}[n_x^3\pi_{12} - n_y^3\pi_{22}]\sigma_{32} + s_{32}[n_x - n_y]\sigma_{32} = \pi_{32}^0\sigma_2'$$

we calculated the combined piezooptic constants π_{ij}^0 of KDP and DKDP crystals (see Table 3). The coefficients of KDP increase and those of DKDP decrease as temperature tends to T_C in the ferroelectric phase.

	T (K)	π_{12}^0	π_{13}^0	π_{31}^0	π_{32}^0	π_{21}^0	π_{23}^0
KDP	85	−3.7	4.5	4.0	−2.4	−3.4	3.1
	120	−9.0	13.5	6.0	−4.6	−27.1	21.2
DKDP	100	6.5	18.0	12.5	−9.8	−11.5	15.1
	200	−1.5	2.8	3.0	−1.6	-3.5	5.5

Table 3. The combined piezooptic constants of KDP and DKDP crystals at different temperatures.

III. THEORY

We restrict our theoretical consideration to the pressures which do not lower the crystal symmetry: hydrostatic and uniaxial $p = -\sigma_3$.

Calculations are performed within the proton ordering model in the four–particle cluster approximation. It allows us to take into account the short–range correlations between deuterons adequately. The cluster Hamiltonian reads

$$\hat{H}_{q4}^i = V\left[\frac{\sigma_{q1}}{2}\frac{\sigma_{q2}}{2} + \frac{\sigma_{q2}}{2}\frac{\sigma_{q3}}{2} + \frac{\sigma_{q3}}{2}\frac{\sigma_{q4}}{2} + \frac{\sigma_{q4}}{2}\frac{\sigma_{q1}}{2}\right]$$

$$+ U\left[\frac{\sigma_{q1}}{2}\frac{\sigma_{q3}}{2} + \frac{\sigma_{q2}}{2}\frac{\sigma_{q4}}{2}\right] \qquad (2)$$

$$+ \Phi\frac{\sigma_{q1}}{2}\frac{\sigma_{q2}}{2}\frac{\sigma_{q3}}{2}\frac{\sigma_{q4}}{2} - \sum_f \frac{z_{qf}^i}{\beta}\frac{\sigma_{qf}}{2};$$

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 cell.

In Hamiltonian (2), z_{qf}^i are the effective fields which include the long range interactions taken into account in the mean field approximation, external electric field E_i and effective cluster fields Δ_{qf}^i created by sites neighboring to the qf–th one but not belonging to the q–th cluster:

$$z_{qf}^i = \beta\big[-\Delta_{qf}^i + \sum_{q'f'} J_{ff'}(qq')\frac{\langle\sigma_{q'f'}\rangle}{2} + \mu_{qf}^i E_i\big]. \qquad (3)$$

The long range interactions $J_{ff'}(qq')$ include the dipole–dipole and lattice mediated deuteron–deuteron interactions. To determine how pressure influences the parameters of the long range interactions, one should take into account two possible mechanisms of this influence: i) via the changes in the interparticle distances, and ii) via the changes in the D–site distance δ. In the mean field approximation, the lattice strains counterpart is fields linear in strains and mean values of quasispins. Their form has been found in [1,2]. It should be mentioned that this form is exactly the same as that if one formally expands the components of the long–range interaction matrix in diagonal components of the strain tensor up to the linear terms. The counterpart which describes the influence of the pressure induced changes in the D–site distance δ is obtained by taking into account the fact that parameters of the long range interactions $J_{ff'}$ are proportional to μ^2; $\mu \sim \delta$ is a dipole moment of a hydrogen bond. According to [6,7], in KDP and DKDP δ is a linear function of hydrostatic pressure. Assuming the same character of its dependence on pressure $p = -\sigma_3$

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

we obtain

$$J_{ff'}(qq') = J^{(0)}_{ff'}(qq')\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big] + \sum_{j=1}^{3}\psi^{j}_{ff'}(qq')\varepsilon_j. \tag{4}$$

We take into account only the diagonal components of the strain tensor, To avoid explicit dependence of the Hamiltonian on pressure, we expressed pressure in terms of the resulting strain $\varepsilon_1 + \varepsilon_2 + \varepsilon_3$. Here $S = \sum_{ij} S_{ij}$ for hydrostatic pressure and $S = \sum_j S_{3j}$ for the uniaxial $p = -\sigma_3$ pressure; S_{ij} is the matrix of elastic compliances. The parameters $\psi^j_{ff'}(qq')$ are the same for all non–lowering the system symmetry pressures applied to a given crystal, whereas the ratio δ_1/δ_0 is different for hydrostatic and uniaxial pressures.

Parameters

$$V = -\frac{w_1}{2},\ U = -\varepsilon + \frac{w_1}{2},\ \Phi = 4\varepsilon - 8w + 2w_1$$

in the Hamiltonian (2), being the functions of the Slater energies ε, w, and w_1, describe the short range correlations between the quasispins. The Slater energies are defined as differences between energies of the so–called “up/down” (with deuterons in positions close to upper/lower oxygens of a given PO_4 group) ε_s, “lateral” ε_a, single ionized ε_1 and double ionized ε_0 deuteron configurations

$$\varepsilon = \varepsilon_a - \varepsilon_s, \quad w = \varepsilon_1 - \varepsilon_s, \quad w_1 = \varepsilon_0 - \varepsilon_s.$$

At $\delta = 0$ $\varepsilon_a = \varepsilon_s = \varepsilon_0 = \varepsilon_1$, since with deuterons in the centers of hydrogen bonds, there is no sense to distinguish between different configurations. Besides, the transformation $\delta \to -\delta$ transforms all deuteron configurations to the ones with the same energies: “up” configurations to “down” configurations, “right lateral” to “left lateral”, positive ionized (with three or four deuterons) to negative ionized (with one deuteron or without any). Hence, ε, w, and w_1 are even functions of δ and turn to zero at $\delta = 0$. Taking into account only the quadratic terms of the $\varepsilon(\delta)$, $w(\delta)$, and $w_1(\delta)$ dependences, we model variation of the Slater energies with pressure similarly to (4)

$$\begin{aligned}
\varepsilon &= \varepsilon^0\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big] + \sum_{i=1}^{3}\delta_{1i}\varepsilon_i,\\
w &= w^0\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big] + \sum_{i=1}^{3}\delta_{2i}\varepsilon_i,\\
w_1 &= w_1^0\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big] + \sum_{i=1}^{3}\delta_{3i}\varepsilon_i,
\end{aligned} \tag{5}$$

where via the terms $\sum_i \delta_{ji}\varepsilon_i$ we describe the influence of factors other than variation of D–site distance δ with pressure. Amongst them there are pressure dependences of the the hydrogen bond length, and of the inclination ϕ of the line connecting D–sites to the ab plane, rotation of PO_4 groups around the c–axis, etc.

The mean values of quasispins $\eta^i_f = \langle\sigma_{qf}\rangle_{E_i}$ are

$$\begin{aligned}
\eta^z &= \frac{1}{D^z}\left[\sinh 2z^z + 2b\sinh z^z\right],\\
\eta^x_{1,3} &= \frac{1}{D^x}\left[\sinh A_1 + d\sinh A_2 \pm 2a\sinh A_3 + b(2\sinh A_4 \pm \sinh A_5 \pm \sinh A_6)\right],\\
\eta^x_{24} &= \frac{1}{D^x}\left[\sinh A_1 - d\sinh A_2 + b(\sinh A_5 - \sinh A_6)\right],\\
\eta^y_{13} &= \frac{1}{D^y}\left[\sinh B_1 - d\sinh B_2 + b(\sinh B_4 - \sinh B_6)\right],\\
\eta^y_{2,4} &= \frac{1}{D^y}\left[\sinh B_1 + d\sinh B_2 \pm 2a\sinh B_3 + b(2\sinh B_4 \pm \sinh B_5 \pm \sinh B_6)\right],
\end{aligned} \tag{6}$$

where

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

$$D^x = \cosh A_1 + d\cosh A_2 + 2a\cosh A_3 + b(2\cosh A_4 + \cosh A_5 + \cosh A_6),$$

$$D^y = \cosh B_1 + d\cosh B_2 + 2a\cosh B_3 + b(2\cosh B_4 + \cosh B_5 + \cosh B_6);$$

$$A_{1,2} = \frac{z_1^x + z_3^x}{2} \pm z_{24}^x, \quad A_{3,4} = \frac{z_1^x \mp z_3^x}{2}, \quad A_{5,6} = \frac{z_1^x - z_3^x}{2} \pm z_{24}^x;$$

$$B_{1,2} = \pm z_{13}^y + \frac{z_2^y + z_4^y}{2}, \quad B_{3,4} = \frac{z_2^y \mp z_4^y}{2}, \quad B_{5,6} = \pm z_{13}^y + \frac{z_2^y + z_4^y}{2};$$

a, b, and d are Gibbs' factors

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

Here we took into account the fact that under the considered pressures and in electric fields E_i, the following relations are obeyed:

$$\eta^z = \eta_1^z = \eta_2^z = \eta_3^z = \eta_4^z, \ \eta_{24}^x = \eta_2^x = \eta_4^x, \ \eta_{13}^y = \eta_1^y = \eta_3^y;$$

$$z^z = z_1^z = z_2^z = z_3^z = z_4^z, \ z_{24}^x = z_2^x = z_4^x, \ z_{13}^y = z_1^y = z_3^y;$$

$$\mu_3 = \mu_{13} = \mu_{23} = \mu_{33} = \mu_{43};$$

$$\mu_1 = \mu_{11} = -\mu_{31}, \ \mu_{21} = \mu_{41} = 0;$$

$$\mu_2 = \mu_{22} = -\mu_{42}, \ \mu_{12} = \mu_{32} = 0.$$

Within the cluster approximation, the fields Δ_{qf}^i 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) and with the one–particle deuteron Hamiltonians

$$H_{qf}^i = -\frac{z_{qf}^i - \beta\Delta_{qf}^i}{\beta}\frac{\sigma_{qf}}{2}. \qquad (7)$$

Excluding Δ_{qf}^i from z_{qf}^i given by (3), we get

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

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

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

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

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

where $\nu_j = [J_{1j}(0)]/4$, and ν is the eigenvalue of the long range interactions matrix Fourier transform

$$\nu = \nu_c^{(0)}(0)[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{i=1}^{3}\varepsilon_i] + \sum_{i=1}^{3}\psi_{ci}(0)\varepsilon_i,$$

$$\nu_c^{(0)}(0) = \frac{1}{4}\left[J_{11}^{(0)}(0) + 2J_{12}^{(0)}(0) + J_{13}^{(0)}(0)\right];$$

$$\psi_{ci} = \frac{1}{4}\left[\psi_{1i}(0) + 2\psi_{2i}(0) + \psi_{3i}(0)\right].$$

The free energy of the crystal in the four–particle cluster approximation can be written as (here $E_i = 0$; in this case the symmetry of the quasispin mean values is as that in the field E_3)

$$f = \frac{\bar{v}}{2}\sum_{ij} c_{ij}^{(0)}\varepsilon_i\varepsilon_j - 2\sum_i \delta_{2i}\varepsilon_i + 2\nu\eta^2 + 2T\ln\frac{2}{(1-\eta^2)D}; \qquad (8)$$

here $D = \lim_{E_3\to 0} D^z$, $z = \lim_{E_3\to 0} z^z$, $\eta = \lim_{E_3\to 0}\eta^z$; $c_{ij}^{(0)}$ are the "seed" elastic constants corresponding to a fictitious lattice without deuterons; ε_i are the components of the strain tensor; $\bar{v} = v/k_{\mathrm{B}}$; v is the unit cell volume; k_{B} is the Boltzmann constant.

Equation for the order parameter η we obtain minimizing the free energy with respect to η

$$\eta = \frac{1}{D}(\sinh 2z + 2b\sinh z), \qquad (9)$$

whereas to find the lattice strains we use obvious relations

$$-p_i = \sum_j c_{ij}\varepsilon_j, \tag{10}$$

where c_{ij} are the elastic constants of the crystal determined from an experiment; $p_i = (p,p,p)$ for the hydrostatic pressure, and $p_i = (0,0,p)$ for the uniaxial pressure $p = -\sigma_3$. The thermodynamic potential is

$$g = f + \bar{v}\sum_i \varepsilon_i p_i, \tag{11}$$

The temperature of the first order phase transition $T_{\rm C}$ is determined from the criterion that:

$$g(\eta, T_{\rm C}, p) = g(0, T_{\rm C}, p). \tag{12}$$

Polarization of the crystal, resulting from the deuteron ordering, is proportional the the mean values of quasispins

$$P_1 = \frac{\mu_1}{v}[\eta_1^x - \eta_3^x], \quad P_2 = \frac{\mu_2}{v}[\eta_2^y - \eta_4^y], \quad P_3 = 2\frac{\mu_3}{v}\eta^z. \tag{13}$$

Variation of effective dipole moments μ_1 and μ_3 with pressure governs the pressure dependence of static dielectric characteristics of the crystals.

Let us determine the static dielectric permittivities of a $K(H_{1-x}D_x)_2PO_4$–type crystal in the presence of external pressure. For a clamped crystal (ε_i =const) we have

$$\varepsilon^\varepsilon_{1,2}(0,T,p) = \varepsilon_{1,2\infty} + 4\pi\left(\frac{\partial P_{1,2}}{\partial E_{1,2}}\right)_\varepsilon\Bigg|_{E_{1,2}=0}$$

$$= \varepsilon_{1,2\infty} + 4\pi\frac{\beta\mu_{1,2}^2}{v}\frac{2æ_1}{D - 2æ_1\varphi_a};$$

$$\varepsilon^\varepsilon_3(0,T,p) = \varepsilon_{3\infty} + 4\pi\left(\frac{\partial P_3}{\partial E_3}\right)_\varepsilon\Bigg|_{E_3=0}$$

$$= \varepsilon_{3\infty} + 4\pi\frac{\beta\mu_3^2}{v}\frac{2æ_3}{D - 2\varphiæ_3}, \tag{14}$$

where

$$æ_1 = a + b\cosh z; \quad æ_3 = \cosh 2z + b\cosh z - \eta^2 D;$$

$$\varphi = \frac{1}{1-\eta^2} + \beta\nu, \quad \varphi_a = \frac{1}{1-\eta^2} + \beta[\nu_1 - \nu_3]$$

In the case of a free crystal (p=const),

$$\varepsilon_1^p(0,T,p) = \varepsilon_1^\varepsilon(0,T,p) + 4\pi e_{14}d_{14},$$

$$\varepsilon_3^p(0,T,p) = \varepsilon_3^\varepsilon(0,T,p) + 4\pi\left(\sum_{i=1}^3 e_{3i}d_{3i} + e_{36}d_{36}\right),$$

e_{ij} and d_{ij} are crystal piezomodules.

IV. DISCUSSION

The only available experimental data concerning the uniaxial pressure $p = -\sigma_3$ effects on the studied crystals is on the dependence of the transition temperature presented in the previous section. Thus we can only 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 pressure 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 pressure; the actual peculiarities of this dependence are quite difficult to predict theoretically. Nevertheless, we thought it necessary to describe the possible changes in characteristics of these crystals induced by uniaxial pressure, considering the variation of the D–site distance δ with pressure (δ_1/δ_0) as a free parameter. Our goal was to draw attention to this problem and stimulate a further experimental investigation of hydrostatic and uniaxial pressure effects on physical properties of H–bonded ferroelectrics.

In order to describe an unstrained state of a $K(H_{0.13}D_{0.87})_2PO_4$ crystal, we need to set the values of the cluster parameters ε^0, w^0, w_1^0, long–range interaction parameters $\nu_c^{(0)}(0)$, and the effective dipole moment per unit cell $\mu_3^{(0)}$. To describe the pressure dependence of transition temperature, we also need the values of the deformation potentials δ_{ij}, $\psi_{ci}(0)$, the ratio δ_1/δ_0, and the elastic constants c_{ij}. Variation with pressure of the dielectric characteristics of the crystal is governed by the derivative $\partial\mu_3/\partial p$.

The values of ε^0, w^0, w_1^0, $\nu_c^{(0)}(0)$, $\mu_3^{(0)}$, providing a satisfactory description of a number of characteristics of a $K(H_{1-x}D_x)_2PO_4$ crystal at ambient pressure in a wide range of deuterations, have been found in [8,9].

The ratio δ_1/δ_0 which is the rate of the pressure–induced changes in the D–site distance is the most important parameter in determining the pressure dependence of the transition temperature. The deformation potentials $\psi_{ci}(0)$, being the same in the cases of hydrostatic and uniaxial pressures applied, describe the contributions of lattice strains into the pressure dependence of the eigenvalue of the long range interaction matrix Fourier transform ν. The values of δ_1/δ_0, δ_{ij} and $\psi_{ci}(0)$ are chosen such that the dependences best fit to the experimentally found $T_{\rm C}(p)$ were obtained. We put the parameters δ_{ij} equal to zero, that is, take into account only the influence on the Slater energies of changes in the D–site distance and neglect all other possible factors. That accords also with the results of the previous studies [10,11] where no mechanism of pressure influence the Slater energies but via pressure the dependence of δ was taken into account.

An unexpected outcome of the fitting is that we should assume the negative value of δ_1/δ_0 for the uniaxial pressure $p = -\sigma_3$. It means that this pressure shortens the D–site distance, although, being applied along the axis perpendicular to the plane in which the hydrogen bonds lie, it is expected to expand the bonds. We may assume that $p = -\sigma_3$ pressure flattens PO_4 tetrahedra along the c–axis, thereby enlarging their projection on the ab–plane and reducing the distances between oxygens of different PO_4 groups, but this assumption should await its experimental verification. We treated δ_1/δ_0 as a free parameter in the case of hydrostatic pressure too, because the available experimental data by Nelmes [6,7] for the $\delta(p)$ dependence correspond to a crystal with a different deuteration level ($T_{C0} = 222$ K and different slope $\partial T_C/\partial p = -3$ K/kbar.

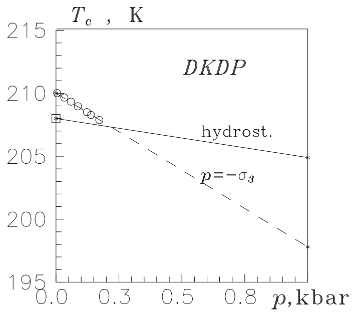


Fig. 4. Variation of the transition temperature of KD_2PO_4 crystal with hydrostatic and uniaxial $p = -\sigma_3$ pressures.

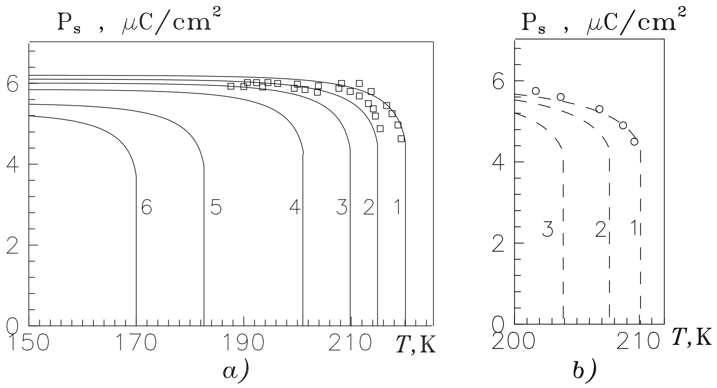


Fig. 5. Spontaneous polarization of $K(H_{1-x}D_x)_2PO_4$ crystals as a function of temperature at different values of hydrostatic (a) and uniaxial $p = -\sigma_3$ (b) pressures p(kbar): a) ($x = 0.98$) 1 — 0.001; 2 — 2.07; 3 — 4.14; 4 — 7.6; 5 — 15.0; 6 — 20.0. b) ($x = 0.87$) 1 — 0.001; 2 — 0.2; 3 — 0.5. Experimental points are taken from [5] — □ and [14] — ○ (for $x = 0.84$).

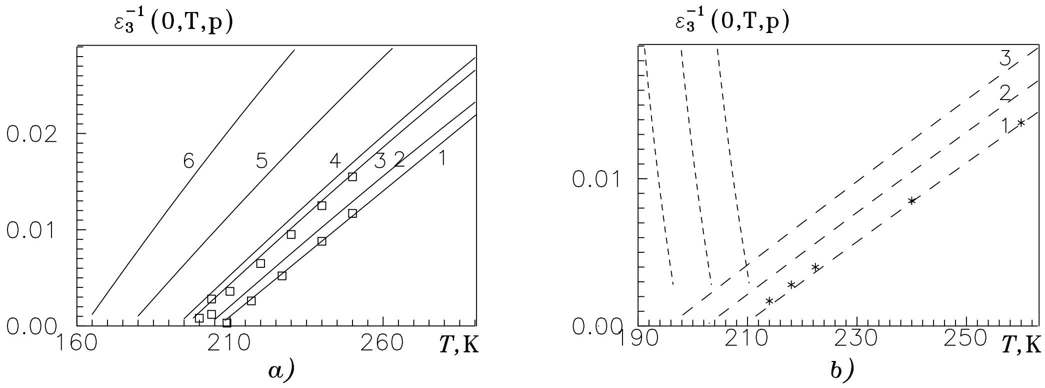


Fig. 6. The temperature dependence of the inverse longitudinal static dielectric permittivity $\varepsilon_3^{-1}(0,T,p)$, of $K(H_{0.13}D_{0.87})_2PO_4$ at different pressures p(kbar): 1 — 0.001; 2 — 1.8; 3 — 4.14; 4 — 5.0; 5 — 10.0; 6 — 15.0; b) 1 — 0.001; 2,4 — 1; 3 — 0.5. Experimental points are taken from [5] — □ and [15] — △. Points of [15] correspond to $x = 0.86$.

T_{C0} (K)	$\partial T_C/\partial p$ (K/kbar)	δ_1/δ_0 ($kbar^{-1}$)	ε^0	w^0	$\nu_c^0(0)$	ψ_{c1}^-	ψ_{c2}^-	ψ_{c3}^-	ψ_{c1}^+	ψ_{c3}^+
			(K)							
210	−12.5	−33.5	87.6	785	37.05	120	100	−545	110	−545
208	−3.0	−9.8	87.6	785	36.0	110	90	−545	100	−545

Table 4. The theory parameters for two crystals. The values of $\partial T_C/\partial p$ and δ_1/δ_0 for the crystals with T_{C0} = 210 K and T_{C0} = 208 K correspond to the uniaxial $p = -\sigma_3$ and hydrostatic pressures, respectively.

c_{11}^+	c_{12}^+	c_{13}^+	c_{33}^+	c_{11}^-	c_{12}^-	c_{13}^-	c_{22}^-	c_{23}^-	c_{33}^-
6.93	−0.78	1.22	5.45	6.8	−0.78	1.0	6.99	1.0	5.3

Table 5. The elastic constants (units of 10^{11}dyn/cm^2). The difference between the elastic constants of crystals with T_{C0} = 210 K and T_{C0} = 208 K is neglected.

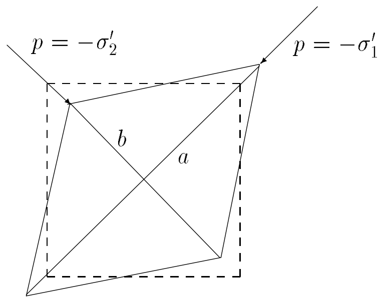
Experimental values of the elastic constants of a $K(H_{1-x}D_x)_2PO_4$ crystal for $x = 0.89$ at temperatures above the transition point are reported in [12]. Since the values of elastic constants of ferroelectric DKDP are not available at all, we carried out the calculations of T_C, ε_i and other characteristics at different pressures and different trial values of c_{ij}^- close to c_{ij}^+. The set of $c_{ij}^\pm$, providing the best fit to experimental data is given in Table 4.

Results of numerical calculations are presented in Figs. 4–6. The solid and dashed lines correspond to the characteristics of a crystal under hydrostatic and $p = -\sigma_3$ pressures, respectively.

Transition temperature vs. uniaxial pressure $p = -\sigma_3$ line is presented in Fig. 4 along with the experimental points of Section II and a theoretical line for hydrostatic pressure. The linear dependences of the transition temperature on both pressures are obtained. Variation of T_C with uniaxial pressure is more pronounced than with hydrostatic, and this is understandable since the uniaxial pressure deforms the crystal more strongly than so hydrostatic pressure does. As has been mentioned above, in order to describe a decrease in transition temperature with the uniaxial pressure $p = -\sigma_3$, the negative value of δ_1/δ_0 was used in calculations. It should be noted that the accepted values of δ_1/δ_0 for hydrostatic and uniaxial $p = -\sigma_3$ pressures yield the universal transition temperature vs D–site distance δ dependence for the two pressures. Calculations performed for other crystals of this family MeD_2XO_4, where Me = K, Rb, ND_4, X = P, As, revealed that universality holds for these crystals too [13].

It is interesting to discuss also the effects of pressures $p = -\sigma_1'$ and $p = -\sigma_2'$ which do lower the crystal symmetry. As we have already mentioned, these pressures were applied along the axes of the $Fdd2$ unit cell, that is, not along the hydrogen bonds. Schematically, the experiment geometry is presented in the figure below. Here a and b are the lattice constants; hydrogen bonds go along the rhomb sides. By dotted lines we denoted a square–shaped projection of the paraelectric tetragonal unit cell on the ab plane.

The signs of spontaneous and induced by pressure $p = -\sigma_2'$ strain ε_6 coincide, which is reflected by increase in the transition temperature. In this case, the observed transition is a true phase transition, since in the presence of the stress σ_6 the minimum of the thermodynamic potential at η of the same sign as that of σ_6 is deeper than the opposite minimum [4]. The same behavior one should find if pressure is applied to a paraelectric sample, which is then cooled down. On the contrast, the signs of these strains in the case of pressure $p = -\sigma_1'$ must be opposite, and the observed experimentally decrease in the temperature of jumps of birefringence corresponds to a decrease in temperature of a certain transition between the induced by stress σ_6 metastable state and stable state. Of course, this transition is biased by stresses σ_1 and σ_2.



The slopes $\partial\mu_3/\partial p$ and $\partial f_3/\partial p$ can be determined without introducing into the theory any extra fitting parameter on the basis of the following speculations. It is believed that the deuteron ordering in the system results in the displacements of heavy ions and electron density which contribute to crystal polarization. Since, when ordered, deuteron shifts from its central position on a hydrogen bond to the off–central one by the distance $\delta/2$, it seems reasonable to suppose that the heavy ions displacements are also proportional to δ. This idea was used in the previous theories [10,11]. Here, we also assume that μ_3 is proportional to the corresponding lattice constant c. This yields

$$\frac{1}{\mu_3^0}\frac{\partial\mu_3}{\partial p} = \frac{\delta_1}{\delta_0} + \frac{\varepsilon_3}{p}, \quad \frac{1}{f_3^0}\frac{\partial f_3}{\partial p} = 2\frac{\delta_1}{\delta_0} + \frac{\varepsilon_3 - \varepsilon_1 - \varepsilon_2}{p}. \tag{15}$$

In Fig. 5b we plot the temperature curves of spontaneous polarization of a $K(H_{0.13}D_{0.87})_2PO_4$ crystal at different values of uniaxial $p = -\sigma_3$ pressures. At ambient pressure, the calculated $P_s(T)$ dependence is an agreement with the experimental results of [14] ($x = 0.84$). The curves presented in Fig. 5a illustrate that model dependence (15) of the effective dipole moment μ_3 provides a satisfactory description of a decrease in saturation polarization of a completely deuterated crystal KD_2PO_4 with hydrostatic pressure. Since we accepted a negative value of δ_1/δ_0 for a uniaxial pressure $p = -\sigma_3$, then, according to (15), the effective dipole moment μ_3 and thereby the spontaneous polarization are expected to decrease with this pressure. Unfortunately, no direct experimental data for the uniaxial pressure $p = -\sigma_3$ on the spontaneous polarization of KD_2PO_4 is available to verify our predictions.

The temperature dependence of the inverse longitudinal dielectric permittivity $\varepsilon_3^{-1}(0,T,p)$ of a $K(H_{0.13}D_{0.87})_2PO_4$ crystal at different pressures $p = -\sigma_3$ is plotted in figure 6a. At ambient pressure, the calculated dependence $\varepsilon_3^{-1}(0,T,p)$ is in agreement with the experimental data of [14] for $x = 0.84$. The theory predicts that the magnitude of $\varepsilon_3(0,T,p)$ should decrease with pressure, but the main pressure effect here is the shift of the transition point and, thereby, of the $\varepsilon_3(T)$ curves to lower temperatures. Fig. 6b illustrate the variation of $\varepsilon_3^{-1}(0,T,p)$ with hydrostatic pressure. As one can see, the model dependence (15) equally well describes a decrease in the Curie constant with hydrostatic pressure.

V. CONCLUDING REMARKS

In our previous work [3] within the earlier proposed model we studied the influence of hydrostatic pressure on the physical properties of $K(H_{1-x}D_x)_2PO_4$ crystals. In the present paper within the same model we consider the uniaxial $p = -\sigma_3$ pressure effects on the phase transition and dielectric properties of these crystals. A detailed theory of the other pressure effects will be given elsewhere.

We performed experimental measurements of uniaxial $p = -\sigma_i'$ pressures influence on the temperature dependence of the birefringence in KH_2PO_4 and KD_2PO_4 crystals. It has been revealed that the transition temperature decreases with $p = -\sigma_3$ and $p = -\sigma_1'$ pressures but increases with $p = -\sigma_2'$.

Since the only available experimental data are for the pressure dependence of the transition temperature and some optical characteristics, we can only 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 D–site distance δ with the pressure δ_1/δ_0 as a free parameter.

Further experimental studies of the uniaxial pressure effects on these crystals, especially on their structure will allow us to define the theory parameters more precisely and check our predictions.

In [3] as well as here it was shown 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 dielectric characteristics of ferroelectric crystals of the 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 possibly the microscopic model itself.

ACKNOWLEDGEMENTS

This work was supported by the Foundation for Fundamental Investigations of the Ukrainian Ministry in the Affairs of Science and Technology, Project No 2.04/171.

[1] I. V. Stasyuk, I. N. Biletskii, Bull. Acad. Sci. USSR, Phys. Ser. **4**, 79 (1983).
[2] I. V. Stasyuk, I. N. Biletskii, O. N. Styahar, Ukr. Fiz. Zh. **31**, 567 (1986).
[3] I. V. Stasyuk, R. R. Levitskii, I. R. Zachek, A. P. Moina, A. S. Duda, Cond. Matt. Phys. (Lviv) iss. 8, 129 (1996).
[4] I. V. Stasyuk, R. R. Levitskii, I. R. Zachek, A. P. Moina, A. S. Duda, preprint ICMP–99–25E, Lviv (1999).
[5] G. A. Samara, Ferroelectrics **22**, 925 (1979).
[6] R. J. Nelmes, Ferroelectrics **71**, 87 (1987).
[7] J. E. Tibbals, R. J. Nelmes, G. J. McIntyre, J. Phys. C **15**, 37 (1982).
[8] R. R. Levitskii, I. R. Zachek, I. Ye. Mits, preprint ITP–87–114R, Kiev, 1987.
[9] R. R. Levitskii, I. R. Zachek, Ye. V. Mits, preprint ITP–87–115R, Kiev, 1987.
[10] R. Blinc, B. Žekš, Helv. Phys. Acta **41**, 701 (1968).
[11] S. Torstveit, Phys. Rev. B **20**, 4431 (1979).
[12] L. A. Shuvalov, A. V. Mnatsakanyan, Sov. Phys. Crystallogr. **11**, 210 (1966).
[13] I. V. Stasyuk, R. R. Levitskii, A. P. Moina, Phys. Rev. B **59**, 8530 (1999).
[14] M. Chabin, E. Giletta, Ferroelectrics **15**, 149 (1977).
[15] M. Chabin, E. Giletta, Phys. Status Solidi B **100**, K77 (1980).

ВПЛИВ ОДНОВІСНОГО ТИСКУ НА СЕҐНЕТОЕЛЕКТРИКИ ТИПУ KH_2PO_4

І. В. Стасюк[1], Р. Р. Левицький[1], А. П. Моїна[1], І. Р. Зачек[2], А. С. Дуда[1],
М. О. Романюк[3], В. Й. Стадник[3], Є. В. Щербина[4]
[1]*Інститут фізики конденсованих систем, вул. Свєнціцького, 1, Львів, 79011, Україна*
[2]*Державний Університет "Львівська політехніка", вул. С. Бандери, 12, Львів, 79646, Україна*
[3]*Львівський національний університет імені Івана Франка, вул. Драгоманова, 50, Львів, 79005, Україна*
[4]*Інтситут монокристалів НАН України, просп. Леніна. 60, Харків, 61141, Україна*

Проведено експериментальні дослідження впливу дейтерування й одновісних тисків на температурні залежності двозаломлень і температури переходу кристалів типу $K(H_{1-x}D_x)_2PO_4$. На основі запропонованої раніше моделі деформованого кристала типу KD_2PO_4 досліджено вплив одновісного тиску $p=-\sigma_3$ на фазовий перехід і статичні діелектричні властивості високодейтерованих кристалів $K(H_{1-x}D_x)_2PO_4$. Отримані теоретичні результати порівняно з наявними експериментальними даними і попередніми теоретичними розрахунками для випадку гідростатичного тиску. Обговорено роль віддалі між положеннями рівноваги дейтрона на зв'язку у фазовому переході та діелектричному відгуку кристалів.