

HYDROSTATIC PRESSURE INFLUENCE ON PHASE TRANSITION AND PHYSICAL PROPERTIES OF KD_2PO_4 -TYPE FERROELECTRICS

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On the basis of proposed earlier model the effects of applied hydrostatic pressure on the physical properties of DKDP type crystals are studied. Within the cluster approximation for proton model the dielectric, thermal and elastic characteristics of considered crystals are calculated. Detailed numerical analysis of obtained results is performed. It is shown that under the proper choice of the theory parameters, a satisfactory description of experimental results for the pressure dependencies of spontaneous polarization, static dielectric permittivities and transition temperature is obtained. To explain the experimental determined behaviour of elastic constants the anharmonic effects must be taken into account.

1. Introduction

The ferroelectric properties of a potassium dihydrogen phosphate (KDP) were discovered about sixty years ago, but despite decades of intensive studies the mechanism of a phase transition in it remains a problem.

This compound is known as a typical substance of hydrogen bonded crystals, which undergo ferroelectric structural phase transitions. The main feature of phase transitions in crystals of this family is a remarkable isotope effect at transition temperature. It is strongly affected by deuteration, increasing from 123K in KDP to 220K in its deuterated isomorph KD_2PO_4 (DKDP). To account for this large isotopic effect the tunnelling proton model was introduced and has become the established basis for models of phase transitions of this kind (see [1, 2] and references therein).

In accordance with this model, the phase transition is triggered by proton ordering; the latter makes heavy atoms shift along the polar axis from their paraelectric positions, hence a spontaneous polarization arises. In high temperature phase H-atoms are disordered over two possible sites on a hydrogen bond and order onto one of those sites below T_c . It was assumed that protons, moving in the double well potential, tunnel between its two minima. The isotope effect is explained in terms of differences in tunnelling matrix elements, arising from the mass difference between H and D atoms: tunnelling prevents ordering; thus the larger tunnelling frequency

(the lighter a particle), the lower transition temperature. In completely deuterated DKDP crystal tunnelling effects are practically negligible, so the model reduces to the regular order-disorder one.

As far as the static dielectric and thermal properties are concerned, the tunnelling model provides a satisfactory quantitative fit to experimental data. It should be mentioned, that short range correlations between hydrogen atoms play an essential if not crucial role in the phase transition. Therefore, any result obtained in a way when these correlations are not taken into account adequately (e.g. in the mean field approximation) is subject to doubt. The four particle cluster approximation, used, for instance, in [3–5] seems to be appropriate here. It has been shown that one can find a set of fitting parameters, which yields a good quantitative description of the isotope effect on T_c , Curie constant, as well as on the temperature behaviour of entropy and spontaneous polarization [5]. Tunneling was found to be effectively suppressed by short-range correlations. Based on this statement calculations were performed in the [6, 7], where the order-disorder model was used in the whole range of deuteron concentrations. The sets of free parameters, allowing one to describe the temperature and concentration dependencies of all static dielectric (including transverse and longitudinal permittivities) and thermal properties, were found. The number of theory parameters was much less than that of characteristics described.

While the static properties were considered, heavy atoms were assumed to follow hydrogen motions instantaneously, and the polarization was directly determined by the level of H-ordering. Yet when the dynamics of the system is considered, this assumption is not appropriate anymore. Then a proton-phonon model with the motion of protons in the H-bonds coupled to the motion of heavy ions, especially to the optic mode along the polar axis, was proposed. Two modes appear in the system if the interaction of protons with only one optic mode is assumed; the instability of the crystal against the lower of them (the soft mode ω_-) leads to a phase transition. Both modes were detected in experiments on Raman scattering in KDP in $x(yx)y$ geometry. It was found out that, first, the soft mode is heavily overdamped in the whole temperature region, but can be made underdamped by application of high pressure [9]. Second, in this geometry the corresponding mode in DKDP crystal is absent [10]. Both facts are quantitatively accounted for by the soft mode model, giving a strong experimental evidence for it.

However, there do exist some experimental facts that do not accord with tunnelling (proton-phonon) picture (an excellent review of them is given in [11]).

In particular, the experiments on light scattering in the low frequency region, carried out in $z(yx)\bar{z}$ geometry have revealed [12] that, in contrast to the $x(yx)y$ spectrum, the peak corresponding the soft mode in DKDP does exist. Furthermore, its frequency is larger than that in the KDP crystal, whereas the reverse was expected. In Raman spectra of internal modes region [13] there have been found some peaks (ν_3 and ν_4) which are forbidden, if PO_4 groups are of S_4 symmetry above T_c , but must appear in the case of C_2 symmetry. Besides, it is stated that no evidence for PO_4 groups of C_1 symmetry ("lateral" configurations) had been found.

The very recent experiments on Raman scattering under high pressure asserted [14, 15], that the soft mode frequency ω_- in forward $z(yx)\bar{z} + \delta$ scattering was larger than that in 90deg $x(yx)y$ scattering. Hence, ω_- was found to decrease when the scattering vector increases, although it was supposed to increase, as a frequency of a usual ferroelectric soft mode at Γ point. This result was claimed as that which suggests a breakdown of

the coupled proton-phonon model, since it predicts an unreasonable $\omega - \vec{q}$ relation of the soft mode.

Another model was proposed in order to explain the facts which seem to be inconsistent with tunnelling picture [16, 17]. Within this model, PO_4 groups are assumed to be of C_2 symmetry both below and above T_c ; the phase transition originates from ordering of distorted PO_4 tetrahedrons. The low-lying overdamped peak, which was thought to correspond to the soft mode, is assigned to a libration mode of PO_4 groups now.

Yet it should be mentioned that the order-disorder model of PO_4 dipoles meets some difficulties as well. The first, and the most important one is that it doesn't account for the isotope effects. Usually, the increase in transition temperature is explained in terms of the so-called geometric isotope effect (see below), but the speculations here are rather qualitative, and no quantitative explanation has been developed yet. Besides, there arise some complications, concerning the ice rule constraint (two hydrogens near each PO_4 group and one hydrogen on a bond).

So, now we are in a situation when after the years of investigations, there were developed two different approaches to the problem, and the experimental evidence for and against both of them have been found. The question of how and why the ferroelectric phase transition in KDP crystal occurs in fact, still remains the issue of the day.

Perhaps, an external hydrostatic pressure may become a probe which is able to shed some light on this long-pending problem. External pressure essentially influences physical properties of the crystal [18–24]. In modifying the geometrical parameters of internal crystal structure, we change molecular potentials of the system and thereby significantly change its characteristics. Among the most striking pressure effects is the decrease of the transition temperature and ultimate vanishing of the ordered phase. At p of about 17kbar the transition temperature of KDP crystal falls to zero with an indefinite slope in accordance with the third law of thermodynamics.

Pressure reduces the magnitude of the static dielectric constant and shifts the whole $\varepsilon_c(T)$ curve to the lower temperatures. In the paraelectric phase ε_c obeys the Curie-Weiss law in a wide temperature range, showing a marked discontinuous change at the transition point, so

$$\varepsilon_c = \varepsilon_\infty + \frac{C}{T - T_0},$$

at $T > T_c$. Here T_0 is the Curie-Weiss temperature, which is, for KDP, the same as T_c to within 0.1K. At ambient pressure the Curie constant C decreases with pressure linearly with $d \ln C / dp = -6.6 \pm 0.2\% GPa^{-1}$ in KDP and $-14.3 \pm 1.0\% GPa^{-1}$ in 82% DKDP [21].

Hydrostatic pressure can induce a transition from the ferroelectric to the paraelectric phase. At a constant temperature $\varepsilon_c(p)$ obeys "the Curie-Weiss law" with respect to p :

$$\varepsilon_c = \frac{C^*}{p - p_0}, \quad (1.1)$$

p_0 is strongly temperature dependent, whereas C^* is not so.

The spontaneous polarization P_s decreases with the increase of pressure linearly with $\partial \ln P_s / \partial p = -23.5 \pm 1.5\% GPa^{-1}$ in KDP at 76 K and $-8.7 \pm 1.0\% GPa^{-1}$ at 190 K in 94% DKDP [21]. The pressure influence on P_s arises from the intrinsic changes in P_s due to the changes in the density of dipoles and in dipole momentum as well as from the shift of the whole $P_s(T)$ curve to lower temperatures due to the lowering of T_c . It is clear that the shift in T_c does not affect P_s at temperatures far from the transition point.

The pressure dependencies of all the studied characteristics are found to be strongly dependent on the deuteration level. It is interesting that in KDP crystal $\partial \ln P_s / \partial p$ is much larger than $\partial \ln C / \partial p$, and in DKDP the reverse is true. ([18,21]).

Pressure dependence of the elastic constants C_{ij} of paraelectric KDP-type crystals have been reported in [25]. It was found that in all studied compounds (KDP, DKDP, ADP, DADP) C_{44} and C_{66} constants exhibited an anomalous non-linear (appr. parabolic) behaviour, whereas the others (C_{11} and C_{33}) increased linearly with increasing pressure. One should expect that at points where the constants C_{44} and C_{66} extrapolate to zero the pressure-induced phase transitions take place, although the corresponding pressures (appr. 100kbar) are well beyond the limits of the apparatus used.

A comprehensive analysis of pressure influence on crystal structure of paraelectric KDP-type crystals has been performed by R.J.Nelmes (see [26–32]).

The crystal structure of KDP-type crystals is known to be tetragonal (space group $I4_2d$) in paraelectric phase and orthorhombic (space group $Fdd2$) in the ferroelectric one. The lattice is composed of the PO_4 tetrahedra, an upper and a lower oxygen atom from different PO_4 groups being connected by hydrogen bonds. O...O bonds and lines joining H-sites lie almost in the xy -plane; their inclinations to this plane are about 5.5° and 0.56° (in KDP at room temperature) respectively.

The cell-volume compressibility for KDP depends on pressure in a non-linear way. The isothermal pressure derivative $\Delta a / \Delta P$ is 40% lower in the high pressure range than at 1bar, while $\Delta c / \Delta P$ is not perceptibly changed. At low pressure $\Delta a / \Delta P$ and $\Delta c / \Delta P$ are almost equal and slightly altered by temperature and deuteration. The size and the shape of the PO_4 groups remain practically unaltered in the paraelectric phase. They rotate in a direction in which the angle of their orientation around 4-axis increases and, hence, the bond length $2R$ is barely altered. ($2R$ is reduced by only 40% of the fractional changes in a .) The K - K , K - P and P - P distances simply scale with a and c [26,28].

It is known that the deuteration significantly changes geometrical parameters of a hydrogen bond; an increase of T_c is accompanied by a corresponding increase in H-bond length $2R$ and the H-site separation δ . This fact invites the question, whether the isotope effect on T_c may be completely or partially attributable to the changes in the H-bond geometry (so called "geometrical isotopic effect" [33]) without explicit invoking tunnelling motions. In order to answer this question, an experiment with an application of external pressure can be extremely useful, since hydrostatic pressure influences the H-bond structure in the same way as going from the deuterated to undeuterated crystals does.

It has been found [26,28] that the bond parameters δ (H-site separation) and $2R$ vary linearly with temperature at a constant pressure and linearly with pressure at a constant temperature, so

$$\delta(p, T) = \delta(p_0, T_0) + c_1(T - T_0) + c_2(p - p_0) + c_3(p - p_0)(T - T_0),$$

and the same is true for $2R$. It enables one to extrapolate to the critical values δ_c and $2R_c$, appearing at the pressure when the ordered phase vanishes. It turns out that T_c tends to 0K at the same non-zero δ_c of approximately 0.2Å in all the studied compounds, independently of their crystal structure and dimensionality of H-bond framework (1D for PbH_2PO_4 , 2D for the squaric acid $H_2C_4O_4$ and 3D for KDP or DKDP). Moreover, at the same

value of δ (within 0.01Å) both KDP and DKDP have the same transition temperature! It means that deuteration effects are almost completely suppressed when δ is kept constant [30–32].

A comprehensive microscopic theory of high pressure effects in the crystals considered above is not yet developed. Usually, the pressure dependence of ferroelectricity in KDP family crystal is qualitatively accounted for in the framework of tunnelling or coupled proton-phonon models, assuming that the proton tunnelling frequency Ω increases and the dipolar proton-proton interaction J (enhanced by the proton-lattice interaction in the case of the coupled proton-phonon model) decreases with pressure [18, 21]. Within the mean-field approximation the transition temperature is given by the equation

$$4\Omega/J = \tanh(\Omega/kT_c).$$

The equation has solutions (a finite T_c does exist) only if $4\Omega < J$. If 4Ω becomes larger than J at some sufficiently high pressure, the ordered phase must vanish. In the same way the pressure dependencies of the Curie constant and spontaneous polarization are described.

A more appropriate four-particle cluster approximation (FPCA) for the tunnelling model was used in [34]. Effects of both deuteration and external pressure are explained in a consistent way with a quite conservative number of fitting parameters. The free energy calculated numerically from the theory is analysed in terms of Landau expansions in the polarization. It is assumed that energies of non-ionized and singly ionized groups ε and w are in the lowest order proportional to the squared distance δ between H-sites, these parameters being dependent on pressure and deuteration only through their dependence on δ . The pressure dependence of the parameter γ , introduced to describe the long-range dipolar interactions, is governed by δ and by the constant Q_h^L (this constant specifies the contribution to the volume electrostriction due to explicit dependence of the free energy on the lattice constants). Proper choice of δ and Q_h^L gives acceptable agreement with experiment for the logarithmic pressure derivatives of Curie-Weiss temperature, saturation polarization and the Curie-Weiss constant.

In [35] the model of coupled anharmonic oscillators was used to investigate the effects of pressure on the ferroelectric phase transition. It is assumed that the model parameters depend on distance between ions of the lattice according to some power laws. Expressions are obtained for the pressure dependence of the transition temperature within MFA, the theoretical results being in good agreement with the observed experimental findings both for KDP and DKDP.

A rather simple model of a one-dimensional hydrogen bond with a double Morse potential, analogous to that developed in [36] was studied by E.Matsushita and T.Matsubara in [37]. An empirical relation between bond length $2R$ and H-site distance δ was explained. Within this theory, the geometric isotope effect is entirely caused by the tunnelling motion of hydrogen and cannot be a reason, apart from tunnelling, for the shift of T_c with deuteration.

In [38] the dependence of the tunnelling frequency and exchange integral on the H-bond length and pressure with the same potential was examined. It appears that this dependence does not coincide with that assumed in the phenomenological theories. The pressure dependence of the transition temperature calculated within MFA is found to be in good qualitative agreement with experiment.

The purpose of this paper is to reexamine the usefulness of an proton model for a DKDP crystal in describing the behaviour of a crystal under

high hydrostatic pressure. It opens up the series of publications where we study the influence of external hydrostatic and uniaxial of different geometries stresses on the phase transition in crystals of KH_2PO_4 family. Our calculations are based on the model of the strained crystals of this type, proposed in [39,40].

The structure of this paper is the following. In Section 2 the Hamiltonian of the system under consideration is formulated and the equation for the transition temperature as a function of external pressure is derived. In Section 3 and 4 the influence of pressure on elastic constants and piezoelectric modules and on thermal properties of a crystal is studied. Expressions for the longitudinal and transverse components of static dielectric susceptibility tensor are derived in Section 5. Section 6 contains a discussion on the obtained results.

2. Cluster approach

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 the four nearest structural elements surrounding it 1

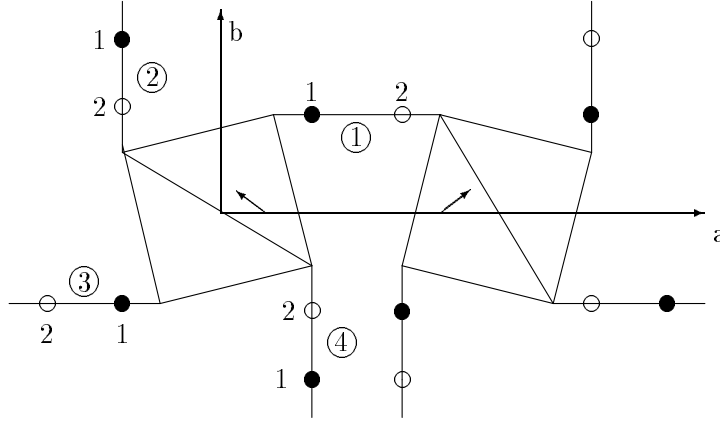


Figure 1. The unit cell of DKDP crystal. Here 1,2 denote H-sites, and 1,2,3,4 in circles stand for the hydrogen bonds numbers.

The Hamiltonian of the system at presence of hydrostatic pressure $-p = \sigma_1 = \sigma_2 = \sigma_3$ and an external electric field E_i ($i = 1, 2, 3$) along the crystallographic axes a, b, c has the following form [39]:

$$H_i = \frac{\bar{v}N}{2} \sum_{ij} c_{ij}^{(0)} \varepsilon_i \varepsilon_j - \sum_{q_j f_j} 2\mu F_{f_j}^i \frac{\langle \sigma_{f_j}(\mathbf{R}_{q_j}) \rangle}{2} +$$

$$+ \sum_{q_1, q_2, q_3, q_4} \left\{ \delta_{\mathbf{R}_{q_1}, \mathbf{R}_{q_2}} \delta_{\mathbf{R}_{q_1}, \mathbf{R}_{q_3}} \delta_{\mathbf{R}_{q_1}, \mathbf{R}_{q_4}} + \delta_{\mathbf{R}_{q_1}+\mathbf{r}_2, \mathbf{R}_{q_2}} \delta_{\mathbf{R}_{q_1}+\mathbf{r}_3, \mathbf{R}_{q_3}} \delta_{\mathbf{R}_{q_1}+\mathbf{r}_4, \mathbf{R}_{q_4}} \right\} \times$$

$$\begin{aligned} & \times \left\{ \frac{1}{2} \sum_{f_i f_j} V_{f_i f_j} \frac{\sigma_{f_i}(\mathbf{R}_{q_i})}{2} \frac{\sigma_{f_j}(\mathbf{R}_{q_j})}{2} + \Phi \frac{\sigma_1(\mathbf{R}_{q_1})}{2} \frac{\sigma_2(\mathbf{R}_{q_2})}{2} \frac{\sigma_3(\mathbf{R}_{q_3})}{2} \frac{\sigma_4(\mathbf{R}_{q_4})}{2} \right\} + \\ & - \sum_{q_j f_j} \left[2\mu F_{f_j}^i \frac{\sigma_{f_j}(\mathbf{R}_{q_j})}{2} + \mu_{f_j i} E_i \frac{\sigma_{f_j}(\mathbf{R}_{q_j})}{2} \right]. \end{aligned} \quad (2.1)$$

The Hamiltonian (2.1) describes the short-range configurational interactions between deuterons near tetrahedra of "A" and "B" type; \mathbf{r}_{f_j} is a relative position vector of a deuteron on a hydrogen bond. Two eigenvalues of Ising spin $\sigma_{f_i}(\mathbf{R}_{q_i}) = \pm 1$ are assigned to two equilibrium positions of a deuteron on the f_i -th bond in the q_i -th unit cell. $c_{ij}^{(0)}$ are the "seed" elastic constants; ε_i are the components of the deformations tensor; $\bar{v} = v/k_B$, v is the unit cell volume; k_B is the Boltzmann constant. $F_{f_j}^i$ are internal fields, created by, first, effective long-range forces, including as well an indirect interaction between deuterons through lattice vibrations, and, second, by a hydrostatic pressure p . They read: [39,40]

$$\begin{aligned} 2\mu F_1^i &= 2\eta_1^{(1)} \left[\frac{J_{11}}{4} + \sum_i \psi_{1i} \varepsilon_i \right] + 2\eta_2^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i} \varepsilon_i \right] + \\ &+ 2\eta_3^{(1)} \left[\frac{J_{13}}{4} + \sum_i \psi_{3i} \varepsilon_i \right] + 2\eta_4^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i} \varepsilon_i \right], \\ 2\mu F_2^i &= 2\eta_1^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i} \varepsilon_i \right] + 2\eta_2^{(1)} \left[\frac{J_{11}}{4} + \sum_i \psi_{1i} \varepsilon_i \right] + \\ &+ 2\eta_3^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i} \varepsilon_i \right] + 2\eta_4^{(1)} \left[\frac{J_{13}}{4} + \sum_i \psi_{3i} \varepsilon_i \right], \\ 2\mu F_3^i &= 2\eta_1^{(1)} \left[\frac{J_{13}}{4} + \sum_i \psi_{3i} \varepsilon_i \right] + 2\eta_2^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i} \varepsilon_i \right] + \\ &+ 2\eta_3^{(1)} \left[\frac{J_{11}}{4} + \sum_i \psi_{1i} \varepsilon_i \right] + 2\eta_4^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i} \varepsilon_i \right], \\ 2\mu F_4^i &= 2\eta_1^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i} \varepsilon_i \right] + 2\eta_2^{(1)} \left[\frac{J_{11}}{4} + \sum_i \psi_{1i} \varepsilon_i \right] + \\ &+ 2\eta_3^{(1)} \left[\frac{J_{12}}{4} + \sum_i \psi_{2i} \varepsilon_i \right] + 2\eta_4^{(1)} \left[\frac{J_{13}}{4} + \sum_i \psi_{3i} \varepsilon_i \right], \end{aligned} \quad (2.2)$$

where $\eta_{f_i}^{(1)} = \langle \sigma_{f_i}(\mathbf{R}_{q_j}) \rangle$; $J_{f_i f_j}$ is a long-range dipole-dipole interaction between deuterons; ψ_{1i} , ψ_{2i} , ψ_{3i} are the so-called deformation potentials; $\mu = e\delta$ is the dipole moment of a hydrogen bond; δ is a distance between two H-sites on a hydrogen bond.

According to [26,28], δ is a linear function both of pressure and temperature, so:

$$\delta = \delta(p_0, T_0) + c_1(T - T_0) + c_2(p - p_0) + c_3(p - p_0)(T - T_0) = \delta_0 + \delta_1 p,$$

with $\delta(p_0, T_0) = 0.387 \text{ \AA}$, $c_1 = -5 \cdot 10^{-5} \text{ \AA/K}$, $c_2 = -3.8 \cdot 10^{-4} \text{ \AA/kbar}$, $c_3 = 4 \cdot 10^{-6} \text{ \AA/K/kbar}$, $p_0 = 16.5 \text{ kbar}$, $T = 295 \text{ K}$ [26]; $\delta_0 > 0$ and $\delta_1 < 0$.

Taking into account the fact that $J_{f_i f_j} = \mu^2 \bar{J}_{f_i f_j}$ we can write:

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

$2 \frac{\delta_1}{\delta_0} = -1.77 \cdot 10^{-2} \text{kbar}^{-1}$ at 250K and slightly decreases with lowering temperature.

The static and dynamic properties of deuterated orthophosphates will be considered in the four-particle cluster approximation. In terms of density matrices [41] it reads:

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

where H_4^{iA} , H_4^{iB} are the four-particle cluster Hamiltonians, which describe behaviour of deuterons near "A" and "B" tetrahedra. Since the equilibrium distribution functions of deuterons around "A" and "B" tetrahedra are equal within the cluster approximation, then we can consider the static and dynamic properties of the KD_2PO_4 crystal on the basis of H_4^{iA} solely.

$$\begin{aligned} H_4^{iA} = & V \left[\frac{\sigma_1 \sigma_2}{2} + \frac{\sigma_2 \sigma_3}{2} + \frac{\sigma_3 \sigma_4}{2} + \frac{\sigma_4 \sigma_1}{2} \right] + U \left[\frac{\sigma_1 \sigma_3}{2} + \frac{\sigma_2 \sigma_4}{2} \right] + \\ & + \Phi \frac{\sigma_1 \sigma_2 \sigma_3 \sigma_4}{2} - \sum_{f_j} \frac{z_{f_j}^i}{\beta} \frac{\sigma_{f_j}}{2}. \end{aligned} \quad (2.5)$$

Here $V = -\frac{w_1}{2}$, $U = -\varepsilon + \frac{w_1}{2}$, $\Phi = 4\varepsilon - 8w + 2w_1$. For the sake of clarity we omitted the index (\mathbf{R}_{q_j}) near the spin operators.

Within the proposed model the energies of deuteron configurations ε , w , and w_1 are assumed to be linear functions of deformations ε_i :

$$\begin{aligned} T < T_c & \quad T > T_c \\ \varepsilon = \varepsilon^0 + \delta_{11}^- \varepsilon_1 + \delta_{12}^- \varepsilon_2 + \delta_{13}^- \varepsilon_3, & \quad \varepsilon = \varepsilon^0 + \delta_{11}^+ (\varepsilon_1 + \varepsilon_2) + \delta_{13}^+ \varepsilon_3, \\ w = w^0 + \delta_{21}^- \varepsilon_1 + \delta_{22}^- \varepsilon_2 + \delta_{23}^- \varepsilon_3, & \quad w = w^0 + \delta_{21}^+ (\varepsilon_1 + \varepsilon_2) + \delta_{23}^+ \varepsilon_3, \\ w_1 = w_1^0 + \delta_{31}^- \varepsilon_1 + \delta_{32}^- \varepsilon_2 + \delta_{33}^- \varepsilon_3, & \quad w_1 = w_1^0 + \delta_{31}^+ (\varepsilon_1 + \varepsilon_2) + \delta_{33}^+ \varepsilon_3. \end{aligned} \quad (2.6)$$

The effective fields $z_{f_j}^i$ have the following symmetry:

$$\begin{aligned} z^z &= \beta \{ -\Delta_3 + 2\nu \eta^{(1)z} + \mu_3 E_3 \}, \\ z_1^x &= \beta \{ -\Delta_1 + 2\nu_1 \eta_1^{(1)x} + 2\nu_3 \eta_3^{(1)x} + 4\nu_2 \eta_{24}^{(1)x} + \mu_1 E_1 \} \\ z_3^x &= \beta \{ -\Delta_3 + 2\nu_3 \eta_1^{(1)x} + 2\nu_1 \eta_3^{(1)x} + 4\nu_2 \eta_{24}^{(1)x} - \mu_1 E_1 \}, \\ z_{24}^x &\equiv z_2^x = z_4^x = \beta \{ -\Delta_{24} + 2\nu_2 [\eta_1^{(1)x} + \eta_3^{(1)x}] + 2[\nu_1 + \nu_3] \eta_{24}^{(1)x} \}, \\ z_{13}^y &\equiv z_1^y = z_3^y = \beta \{ -\Delta_{13} + 2[\nu_1 + \nu_3] \eta_{13}^{(1)y} + 2\nu_2 [\eta_2^{(1)y} + \eta_4^{(1)y}] \}, \\ z_2^y &= \beta \{ -\Delta_2 + 4\nu_2 \eta_{13}^{(1)y} + 2\nu_1 \eta_2^{(1)y} + 2\nu_3 \eta_4^{(1)y} + \mu_2 E_2 \} \\ z_4^y &= \beta \{ -\Delta_4 + 4\nu_2 \eta_{13}^{(1)y} + 2\nu_3 \eta_2^{(1)y} + 2\nu_1 \eta_4^{(1)y} - \mu_2 E_2 \}, \end{aligned} \quad (2.7)$$

where

$$\nu = \frac{\nu_c(0)}{4} \left[1 + 2 \frac{\delta_1}{\delta_0} p \right] + \sum_i \psi_{ci} \varepsilon_i, \quad \nu_j = \frac{\nu_{1j}(0)}{4} \left[1 + 2 \frac{\delta_1}{\delta_0} p \right] + \sum_i \psi_{ji} \varepsilon_i \quad (2.8)$$

are the functions both of pressure p and deformations ε_i ($j = 1, 2, 3$). We took into account, that have taken

$$\begin{aligned} \eta^{(1)z} &= \eta_1^{(1)z} = \eta_2^{(1)z} = \eta_3^{(1)z} = \eta_4^{(1)z}, \\ \eta_{24}^{(1)x} &= \eta_2^{(1)x} = \eta_4^{(1)x}; \quad \eta_{13}^{(1)y} = \eta_1^{(1)y} = \eta_3^{(1)y}, \\ \nu_c^{(0)} &= J_{11}^{(0)} + 2J_{12}^{(0)} + J_{13}^{(0)}; \quad \psi_{ci} = \psi_{1i} + 2\psi_{2i} + \psi_{3i}; \\ \mu_3 &= \mu_{13} = \mu_{23} = \mu_{33} = \mu_{43}, \\ \mu_1 &= \mu_{11} = -\mu_{31}, \quad \mu_{21} = \mu_{41} = 0, \quad \mu_2 = \mu_{22} = -\mu_{42}, \quad \mu_{12} = \mu_{32} = 0. \end{aligned} \quad (2.9)$$

In (2.7) and (2.8) $\Delta_1, \dots, \Delta_4$ are effective fields, resulting from an interaction with neighbouring quasispins outside a cluster. They can be determined from the condition of equality of the mean values of $\langle \sigma_{f_j}(\mathbf{R}_{q_j}) \rangle$ calculated with four- and single-particle Gibbs' distributions with the Hamiltonian (2.5) and with

$$H_{f_j}^i(\mathbf{R}_{q_j}) = -\frac{\bar{z}^i \sigma_{f_j}(\mathbf{R}_{q_j})}{\beta} \frac{1}{2}. \quad (2.10)$$

Expressions for $\bar{z}^z, \dots, \bar{z}_4^y$ can be obtained from (2.7) and (2.8) 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 . The calculation of the mean values

$$\begin{aligned} \langle \sigma_{f_j}(\mathbf{R}_{q_j}) \rangle &= \frac{\text{Sp} \{ \sigma_{f_j}(\mathbf{R}_{q_j}) \exp(-\beta H_4^{iA}(\mathbf{R}_{q_j})) \}}{\text{Sp} \exp(-\beta H_4^{iA}(\mathbf{R}_{q_j}))} = \\ &= \frac{\text{Sp} \{ \sigma_{f_j}(\mathbf{R}_{q_j}) \exp(-\beta H_{f_j}^i(\mathbf{R}_{q_j})) \}}{\text{Sp} \exp(-\beta H_{f_j}^i(\mathbf{R}_{q_j}))} \end{aligned}$$

is straightforward; the obtained expressions are rather cumbersome and therefore omitted here. After $\Delta_1, \dots, \Delta_4$ had been excluded from (2.7) and (2.8) the quantities z^z, \dots, z_4^y read:

$$\begin{aligned} z^z &= \frac{1}{2} \ln \frac{1 + \eta^{(1)z}}{1 - \eta^{(1)z}} + \beta \nu \eta^{(1)z} + \frac{\beta \mu_3 E_3}{2}, \\ z_1^x &= \frac{1}{2} \ln \frac{1 + \eta_1^{(1)x}}{1 - \eta_1^{(1)x}} + \beta \left[\nu_1 \eta_1^{(1)x} + \nu_3 \eta_3^{(1)x} + 2\nu_2 \eta_{24}^{(1)x} + \frac{\mu_1 E_1}{2} \right], \\ z_3^x &= \frac{1}{2} \ln \frac{1 + \eta_3^{(1)x}}{1 - \eta_3^{(1)x}} + \beta \left[\nu_3 \eta_1^{(1)x} + \nu_1 \eta_3^{(1)x} + 2\nu_2 \eta_{24}^{(1)x} - \frac{\mu_1 E_1}{2} \right], \\ z_{24}^x &= \frac{1}{2} \ln \frac{1 + \eta_{24}^{(1)x}}{1 - \eta_{24}^{(1)x}} + \beta \left[\nu_2 [\eta_1^{(1)x} + \eta_3^{(1)x}] + [\nu_1 + \nu_3] \eta_{24}^{(1)x} \right], \\ z_{13}^y &= \frac{1}{2} \ln \frac{1 + \eta_{13}^{(1)y}}{1 - \eta_{13}^{(1)y}} + \beta \left[\nu_2 [\eta_2^{(1)y} + \eta_4^{(1)y}] + [\nu_1 + \nu_3] \eta_{13}^{(1)y} \right], \end{aligned} \quad (2.11)$$

$$z_2^y = \frac{1}{2} \ln \frac{1 + \eta_2^{(1)y}}{1 - \eta_2^{(1)y}} + \beta \left[2\nu_2 \eta_{13}^{(1)y} + \nu_1 \eta_2^{(1)y} + \nu_3 \eta_4^{(1)y} + \frac{\mu_2 E_2}{2} \right],$$

$$z_4^y = \frac{1}{2} \ln \frac{1 + \eta_4^{(1)y}}{1 - \eta_4^{(1)y}} + \beta \left[2\nu_2 \eta_{13}^{(1)y} + \nu_3 \eta_2^{(1)y} + \nu_1 \eta_4^{(1)y} - \frac{\mu_2 E_2}{2} \right].$$

where

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

$$a = \exp(-\beta\varepsilon), \quad b = \exp(-\beta w), \quad d = \exp(-\beta w_1). \quad (2.12)$$

Deformations ε_i and the order parameter $\eta^{(1)z}$ can be determined from conditions of the thermodynamic equilibrium:

$$\frac{1}{\bar{v}} \frac{\partial f^z}{\partial \eta^{(1)}} = 0; \quad \frac{1}{\bar{v}} \frac{\partial f^z}{\partial \varepsilon_1} = \frac{1}{\bar{v}} \frac{\partial f^z}{\partial \varepsilon_2} = \frac{1}{\bar{v}} \frac{\partial f^z}{\partial \varepsilon_3} = -p. \quad (2.13)$$

where f^z is the free energy of the crystal:

$$f_-^z = \frac{F_z}{N} = \frac{\bar{v}}{2} \sum_{ij} c_{ij}^{0-} \varepsilon_i \varepsilon_j - 2 \sum_i \delta_{2i}^- \varepsilon_i + 2\nu [\eta^{(1)z}]^2 +$$

$$+ 2T \ln 2 - 2T \ln(1 - (\eta^{(1)z})^2) - 2T \ln D^z, \quad (2.14)$$

The thermodynamic potential is equal to

$$g^z(\eta^{(1)z}, T, p) = f^z + \bar{v}p \sum_i \varepsilon_i,$$

The set of equations for $\eta^{(1)z}$ and ε_i , has the following form:

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

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

$$-p = c_{12}^{0-} \varepsilon_1 + c_{22}^{0-} \varepsilon_2 + c_{23}^{0-} \varepsilon_3 - 2 \frac{\delta_{22}^-}{\bar{v}} - \frac{2\psi_{c2}}{\bar{v}} [\eta^{(1)z}]^2 + \frac{2}{\bar{v}} \frac{M_2^-}{D^z}, \quad (2.15)$$

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

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

In paraelectric phase the free energy is equal to: ($\varepsilon_1 = \varepsilon_2$)

$$f_+ = \frac{\bar{v}}{2} \{ 2(c_{11}^{0+} + c_{12}^{0+}) \varepsilon_1^2 + c_{33}^{0+} \varepsilon_3^2 + 2c_{13}^{0+} \varepsilon_1 \} -$$

$$- 2 \sum_i \delta_{2i}^+ \varepsilon_i + 2T \ln \frac{2}{D_+},$$

pressure and deformations being connected in the way:

$$-p = (c_{11}^{0+} + c_{12}^{0+}) \varepsilon_1 + c_{13}^{0+} \varepsilon_3 - 2 \frac{\delta_{21}^+}{\bar{v}} + \frac{2}{\bar{v}} \frac{M_1^+}{D_+},$$

$$-p = 2c_{13}^{0+} \varepsilon_1 + c_{33}^{0+} \varepsilon_3 - 2 \frac{\delta_{23}^+}{\bar{v}} + \frac{2}{\bar{v}} \frac{M_3^+}{D_+}, \quad (2.16)$$

where

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

As one can see from equations (2.15) and (2.16) to make deformations ε_i equal to zero at zero pressure, one must assume the parameters δ_{2i} to be temperature dependent. For the sake of simplicity and in order to keep δ_{2i} constant we put deformations ε_i to be equal to zero only at the transition point. Thus the parameters δ_{2i} can be determined from the equation:

$$\delta_{2i}^+ = \frac{2a\delta_{1i}^+}{1 + 2a},$$

a is taken at $T = T_c$. At all other temperatures small residual deformations ($\approx 10^{-6}$) exist at pressure of 1 bar.

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

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

the order parameter and deformations obey the system (2.15).

Polarization of the crystal, when the electric field along the z -axis is applied, is equal to

$$P_3 = 2 \frac{\mu_3}{v} \eta^{(1)z}, \quad (2.18)$$

an effective dipole momentum μ_3 and the unit cell volume v being linear functions of pressure:

$$\mu_3 = \mu_3^{(0)} - k_{\mu_3} p, \quad v = v^{(0)} - k_v p. \quad (2.19)$$

Respectively,

$$P_1 = \frac{\mu_1}{v} [\eta_1^{(1)x} - \eta_3^{(1)x}], \quad P_2 = \frac{\mu_2}{v} [\eta_2^{(1)y} - \eta_4^{(1)y}]. \quad (2.20)$$

3. Elastic and piezoelectric properties

Let us study now how the hydrostatic pressure affects the elastic properties of crystals under consideration. Matrix of elastic constants in ferroelectric phase has the following symmetry:

$$\begin{pmatrix} c_{11}^{p-} & c_{12}^{p-} & c_{13}^{p-} & 0 & 0 & 0 \\ c_{12}^{p-} & c_{22}^{p-} & c_{23}^{p-} & 0 & 0 & 0 \\ c_{13}^{p-} & c_{23}^{p-} & c_{33}^{p-} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44}^{p-} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55}^{p-} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66}^{p-} \end{pmatrix}$$

Its elements, altered by hydrostatic pressure, we calculate, taking into account the deuteron ordering.

$$\begin{aligned} c_{ij}^{p-} &= c_{ij}^{0-} - \frac{4\eta^{(1)}}{\bar{v}DT} [2\psi_{ci}\psi_{cj}\eta^{(1)}\varkappa + \psi_{ci}t_j + \psi_{cj}t_i] - \\ &- \frac{2}{\bar{v}DT} [4b\delta_{2i}^-\delta_{2j}^- \cosh z + 2a\delta_{1i}^-\delta_{1j}^- + d\delta_{3i}^-\delta_{3j}^-] + \frac{2}{\bar{v}D^2T} M_i^- M_j^-. \end{aligned} \quad (3.1)$$

Here we used the following notations:

$$\begin{aligned}\mathfrak{x} &= [\cosh 2z + b \cosh z] - \eta^{(1)}[\sinh 2z + 2b \sinh z]; \\ t_i &= -2b\delta_{2i}^- \sinh z + \eta^{(1)}M_i^-, \end{aligned}$$

In the present approach we cannot determine how the constants c_{44}^{p-} , c_{55}^{p-} , c_{66}^{p-} are changed by external pressure.

In the paraelectric phase the symmetry of elastic constants matrix somewhat changes:

$$\begin{pmatrix} c_{11}^{p+} & c_{12}^{p+} & c_{13}^{p+} & 0 & 0 & 0 \\ c_{12}^{p+} & c_{11}^{p+} & c_{13}^{p+} & 0 & 0 & 0 \\ c_{13}^{p+} & c_{13}^{p+} & c_{33}^{p+} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44}^{p+} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44}^{p+} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66}^{p+} \end{pmatrix}$$

and in the case $w_1 \rightarrow \infty$ ($d = 0$) we have

$$\begin{aligned} c_{11}^{p+} &= c_{11}^{0+} - \frac{2}{\bar{v}D_+T} [4b(\delta_{21}^+)^2 + 2a(\delta_{11}^+)^2 + 8ab(\delta_{11}^+ - \delta_{21}^+)^2], \\ c_{12}^{p+} &= c_{12}^{0+} - \frac{2}{\bar{v}D_+T} [4b(\delta_{21}^+)^2 + 2a(\delta_{11}^+)^2 + 8ab(\delta_{11}^+ - \delta_{21}^+)^2], \\ c_{13}^{p+} &= c_{13}^{0+} - \frac{2}{\bar{v}D_+T} [4b\delta_{21}^+\delta_{23}^+ + 2a\delta_{11}^+\delta_{13}^+ + 8ab(\delta_{11}^+ - \delta_{21}^+)(\delta_{13}^+ - \delta_{23}^+)], \\ c_{33}^{p+} &= c_{33}^{0+} - \frac{2}{\bar{v}D_+T} [4b(\delta_{23}^+)^2 + 2a(\delta_{13}^+)^2 + 8ab(\delta_{13}^+ - \delta_{23}^+)^2]. \end{aligned}$$

Using (2.15) we can calculate the quantities, which characterize the electromechanical properties of a crystal.

In direct piezoelectric effect, coefficients of piezoelectric strain e_{3i} determine a polarization caused by mechanical deformations, and in reverse piezoeffect, a pressure, which, at a given electric field, must be applied to a crystal to maintain it undeformed. They read:

$$e_{3i} = \left(\frac{\partial P_3}{\partial \varepsilon_i} \right)_{E_3} = \frac{\mu_3}{v} \frac{2}{T} \frac{2\psi_{ci}\eta^{(1)}\mathfrak{x} + t_i}{D - 2\varphi\mathfrak{x}}, \quad e_h = e_{31} + e_{32} + e_{33}.$$

where

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

At direct piezoeffect, constants of piezoelectric strain give an increase of an electric field, necessary to maintain polarization constant, if this increase is caused by mechanical deformations. At reverse piezoeffect, they give an increase in pressure due to a polarization, which maintains a crystal undeformed.

$$h_{3i} = - \left(\frac{\partial E_3}{\partial \varepsilon_i} \right)_{P_3} = \frac{2}{\mu_3 D} \varphi (2\psi_{ci}\eta^{(1)}\mathfrak{x} + t_i), \quad h_h = h_{31} + h_{32} + h_{33}.$$

At direct piezoeffect, coefficients of piezoelectric deformations g_{3i} characterize an electric voltage in open circuit at a given pressure, and, at the

reverse effect, deformations, caused by polarization. These constants we find, solving the set of equations:

$$\sum_i c_{ij}^{p-} g_{3j} = h_{3j}; \quad g_h = g_{31} + g_{32} + g_{33}.$$

Constants of piezoelectric deformations describe a change in polarization with pressure at a direct piezoeffect, and a deformation, occurring in a free crystal, when an electric field is applied, at the reverse effect.

$$d_{3j} = \sum_i s_{ij}^{E-} e_{3j}; \quad d_h = d_{31} + d_{32} + d_{33}.$$

Here $s_{11}^{E-}, \dots, s_{33}^{E-}$ are the elastic constants (constants of elastic compliance):

$$\begin{aligned} s_{11}^E &= \frac{1}{\Delta_c} \begin{vmatrix} c_{22}^E & c_{23}^E \\ c_{23}^E & c_{33}^E \end{vmatrix}, \quad s_{12}^E = -\frac{1}{\Delta_c} \begin{vmatrix} c_{12}^E & c_{23}^E \\ c_{13}^E & c_{33}^E \end{vmatrix}, \quad s_{13}^E = \frac{1}{\Delta_c} \begin{vmatrix} c_{12}^E & c_{22}^E \\ c_{13}^E & c_{23}^E \end{vmatrix}, \\ s_{22}^E &= \frac{1}{\Delta_c} \begin{vmatrix} c_{11}^E & c_{13}^E \\ c_{13}^E & c_{33}^E \end{vmatrix}, \quad s_{23}^E = -\frac{1}{\Delta_c} \begin{vmatrix} c_{11}^E & c_{13}^E \\ c_{12}^E & c_{23}^E \end{vmatrix}, \quad s_{33}^E = \frac{1}{\Delta_c} \begin{vmatrix} c_{11}^E & c_{12}^E \\ c_{12}^E & c_{22}^E \end{vmatrix}, \\ \Delta_c &= \begin{vmatrix} c_{11}^E & c_{12}^E & c_{13}^E \\ c_{12}^E & c_{22}^E & c_{23}^E \\ c_{13}^E & c_{23}^E & c_{33}^E \end{vmatrix}, \end{aligned} \quad (3.2)$$

where

$$c_{ij}^{E-} = c_{ij}^{p-} - h_{3i} e_{3j}; \quad i, j = 1, 2, 3.$$

Piezoelectric and elastic characteristics are connected through the following relations:

$$\sum_i s_{ij}^{p-} h_{3j} = g_{3j}; \quad \sum_i c_{ij}^{E-} d_{3j} = e_{3j};$$

Let us note that all piezoelectric coefficients, calculated above (i.e. e_{3i} , h_{3i} , g_{3i} , d_{3i}) are equal to zero in paraelectric phase.

4. Thermal properties

Let us consider now the thermal properties of a deuteron subsystem of a KD_2PO_4 crystal.

In ferroelectric phase the entropy per one mol has the following form:

$$\begin{aligned} S^- &= \left(\frac{\partial f_-}{\partial T} \right)_{\eta^{(1)}, \varepsilon} = \\ &= R \left(-2 \ln 2 + 2 \ln[1 - (\eta^{(1)})^2] + 2 \ln D - \frac{4}{T} \nu [\eta^{(1)}]^2 + 2 \frac{M}{D} \right), \end{aligned} \quad (4.1)$$

where R is the gas constant, and

$$M = M_0^- + \beta \sum_i \varepsilon_i M_i^-, \quad M_0^- = \beta(4w^0 b \cosh z + 2\varepsilon^0 a + w_1^0 d).$$

In the paraelectric phase

$$S^+ = R \left\{ -2 \ln 2 + 2 \ln D_+ + \frac{2}{D_+} (M_0^+ + 2\beta\varepsilon_1 M_1^+ + \beta\varepsilon_3 M_3^+) \right\}.$$

The molar specific heat at constant pressure we calculate, differentiating the entropy (4.1):

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

In the result:

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

where ΔC^ε is the molar specific heat at constant deformations, and

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

Quantities, occuring in (4.2) and (4.3) are the following:

$$\begin{aligned} q_i^P &= - \left(\frac{\partial S}{\partial \varepsilon_i} \right)_{P,T} && \text{heat of deformations at a constant polarization;} \\ q^\varepsilon &= - \left(\frac{\partial S}{\partial P_3} \right)_{\varepsilon,T} && \text{heat of polarization at constant deformations;} \\ p^P &= \left(\frac{\partial P_3}{\partial T} \right)_p && \text{pyroelectric coefficient at a constant pressure} \\ \alpha_i &= \left(\frac{\partial \varepsilon_i}{\partial T} \right)_p && \text{coefficients of the thermal expansion.} \end{aligned}$$

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

where the notations were used:

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

From (2.15) we obtain:

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

where

$$p^\varepsilon = -\frac{\mu_3}{v} \frac{2}{T} \frac{2\eta^{(1)}\beta\nu\varkappa - [q - \eta^{(1)}M]}{D - 2\varphi\varkappa},$$

and the thermal expansion coefficients obey the system of equations:

$$\sum_j c_{ij}^E \alpha_j = -p_i + p^\varepsilon h_{3i};$$

$\alpha = \alpha_1 + \alpha_2 + \alpha_3$, and p_i is a thermal pressure.

$$p_i = \left(\frac{\partial p}{\partial T} \right)_{P_3, \varepsilon} = q_i^P.$$

In paraelectric phase

$$\alpha_{1,2} = \frac{-p_1^+ c_{33}^{p+} + p_3^+ c_{13}^{p+}}{[c_{11}^{p+} + c_{12}^{p+}]c_{33}^{p+} - 2[c_{13}^{p+}]^2} + \alpha_1^0, \quad \alpha_3 = \frac{2p_1^+ c_{11}^{p+} - p_3^+ [c_{11}^{p+} + c_{12}^{p+}]}{[c_{11}^{p+} + c_{12}^{p+}]c_{33}^{p+} - 2[c_{13}^{p+}]^2} + \alpha_3^0, \quad (4.5)$$

The constant terms, which describe contributions of the lattice anharmonicity, have been added to the right-hand sides of (4.5).

5. Dielectric susceptibility

Let us determine the static dielectric susceptibility along the z -axis at presence of hydrostatic pressure. Consider, at first, the 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 :

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

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

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

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:

$$\begin{aligned} \chi_1^{\varepsilon-}(0, T, p) &= \frac{1}{2} \left(\frac{\partial P_1}{\partial E_1} \right)_{\varepsilon, E_1=0} = . \\ &= \frac{\mu_1^2}{v} \frac{1}{T} \frac{2(a + b \cosh z)}{D - 2(a + b \cosh z)\{[1 - (\eta^{(1)})^2]^{-1} + \beta[\nu_1 - \nu_3]\}}. \end{aligned} \quad (5.2)$$

In paraelectric phase

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

At presence of hydrostatic pressure the x - and y - directions remain equivalent; therefore, in the paraelectric phase the static dielectric susceptibility still is isotropic in the xy -plane:

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

6. Discussion

Before going into the discussion of the proposed in previous sections theory, let us note that, strictly speaking, this theory can be valid for a completely deuterated KD_2PO_4 crystal only, whereas the vast majority of experimental data concern the crystals, deuterated partially. Nevertheless, as the relaxational character of dielectric dispersion in $K(H_{1-x}D_x)_2PO_4$ crystals implies, tunnelling effects in them are most likely suppressed by the short-range correlations between hydrogens. So at least in the case of high deuteration, we are allowed to neglect tunnelling and apply the theory to $K(H_{1-x}D_x)_2PO_4$ crystals as well. In [6,7] it has been shown that under the proper choice of free parameters one can get a satisfactory description of a number of thermodynamic characteristics of considered crystals at ambient pressure.

For a numerical estimate of the pressure and temperature dependencies of dielectric, elastic, piezoelectric and thermal characteristics of KD_2PO_4 crystals obtained in previous sections it is necessary to set the values of the cluster parameters ε , w , w_1 , long range interaction parameters $\nu_c(0)$, dipole moments per unit cell μ_c and μ_a , deformation potentials δ_{ij} , ψ_{cj} and "seed" elastic constants c_{ij}^0 . As the theory parameters for undeformed $K(H_{1-x}D_x)_2PO_4$ we took those obtained in [6,7]. The deformation potentials were chosen such that the best agreement with experimental data was attained for the variation of transition temperature T_c , spontaneous polarization P_s and longitudinal static dielectric permittivity $\varepsilon_3(0, T, p)$ with pressure (see Table 1).

x	T_c	ε^0	w^0	$\nu_c(0)/4$	δ_{11}^-	δ_{12}^-	δ_{13}^-	ψ_{c1}^-	ψ_{c2}^-	ψ_{c3}^-	δ_{11}^+	δ_{13}^+	ψ_{c1}^+	ψ_{c3}^+
0.98	218	92.0	830	37.39	-45	-55	885	-105	-95	50	-50	800	-105	50
0.87	210	87.6	785	36.80							-50	800	-95	390
0.84	208	87.0	770	36.63							-50	800	-95	590

Table 1. Parameters of the theory (all in K) at different deuteration.

$\mu_c^- = 3.625 \cdot 10^{-18}$ esu, $\mu_c^+ = 2.931 \cdot 10^{-18}$ esu, $\mu_a^- = 2.837 \cdot 10^{-18}$ esu, $w_1 \rightarrow \infty$. Further experimental study of transverse dielectric, piezoelectric, elastic and thermal characteristics as functions of hydrostatic pressure is required to define the values of deformation potentials more precisely.

It should be mentioned that amount of deuteration is difficult to determine exactly: the discrepancies in $T_c(x)$ dependence reported by different authors reach 10%. In this work we used the data by E.N.Volkova (see [6] and references therein).

The experimental values of the elastic constants are available for the $K(H_{1-x}D_x)_2PO_4$ crystals only with $x = 0$ $x = 0.89$ above T_c [43]. Nevertheless, we can estimate the values of c_{ij}^+ at $x = 0.98, 0.87, 0.84$, assuming their linear dependence on deuteration. Those data were taken as the "seed" elastic constants c_{ij}^{0+} . Since the values of elastic constants of ferroelectric DKDP were not available at all, we carried out 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-} , providing the best fit to experimental data is given in Table 2.

We met some difficulties, trying to solve the system of equations (2.15) by Newton-Raphson method directly. Instead, we had to minimize the thermodynamical potential $g(\eta^{(1)z}, T, p)$ with respect to the order parameter $\eta^{(1)z}$ and determine the deformations ε_i from the three latter equations of (2.15). The transition point was found from the (2.17) criterion.

x	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-}
0.98	6.14	-0.71	1.05	4.82	6.24	-0.71	1.05	6.0	1.0	4.82
0.87	6.93	-0.78	1.22	5.45						

Table 2. The "seed" elastic constants c_{ij}^0 (units of 10^{11} dyn/cm²) for $K(H_{1-x}D_x)_2PO_4$ crystals at different deuterations.

In figure 2 the calculated pressure dependence of the transition temperature on of $K(H_{1-x}D_x)_2PO_4$ crystal for $x = 0.98, 0.87$, and 0.84 is shown along with experimental data [21, 24]. Up to 25kbar, T_c decreases with pressure linearly as $T_c(p) = T_c - k_T p$, $k_T(0.98) = 2.02$ K/kbar, $k_T(0.87) = 2.67$ K/kbar, $k_T(0.84) = 3.02$ K/kbar. The further raising of pressure leads to the deviation of $T_c(p)$ dependence from linearity, and the slope $|\partial T_c / \partial p|$ significantly increases. Calculations show that at $p \approx 65$ kbar the transition temperature falls to zero, so the ordered phase disappears.

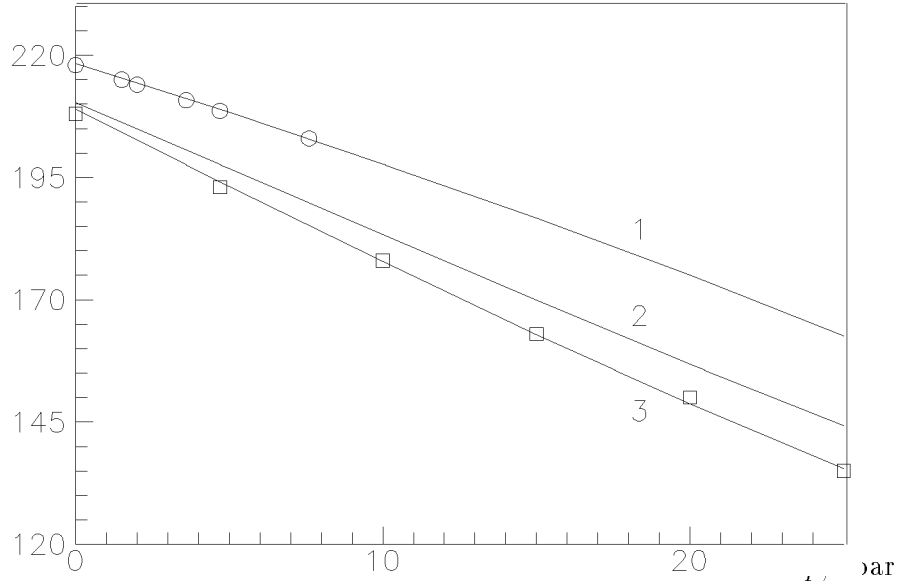


Figure 2. The transition temperature of $K(H_{1-x}D_x)_2PO_4$ crystals as a function of pressure at different deuteration levels x : 1, \circ [24] – 0.98; 2 – 0.87; 3, \square [21] – 0.84

In figures 3 the variation of deformations ε_i with pressure at $T = 190$ K and $x = 0.98$ is depicted. The absolute values of ε_i increase with pressure linearly do not perceptibly change with temperature except for the abrupt jumps at the transition point. Our calculations give the linear decrease in the unit cell volume with the hydrostatic pressure:

$$v = (0.3892 - k_v p) \cdot 10^{-21} \text{ cm}^3, \quad k_v = 0.0017 \text{ cm}^3/\text{kbar},$$

$$\bar{v} = v/k_B = (2.82 - k_{\bar{v}} p) \text{ K/kbar}, \quad k_{\bar{v}} = 0.0095 \text{ K/kbar}^2,$$

what agrees with the experimental result of [28] $k_v = 0.0013 \text{ cm}^3/\text{kbar}$.

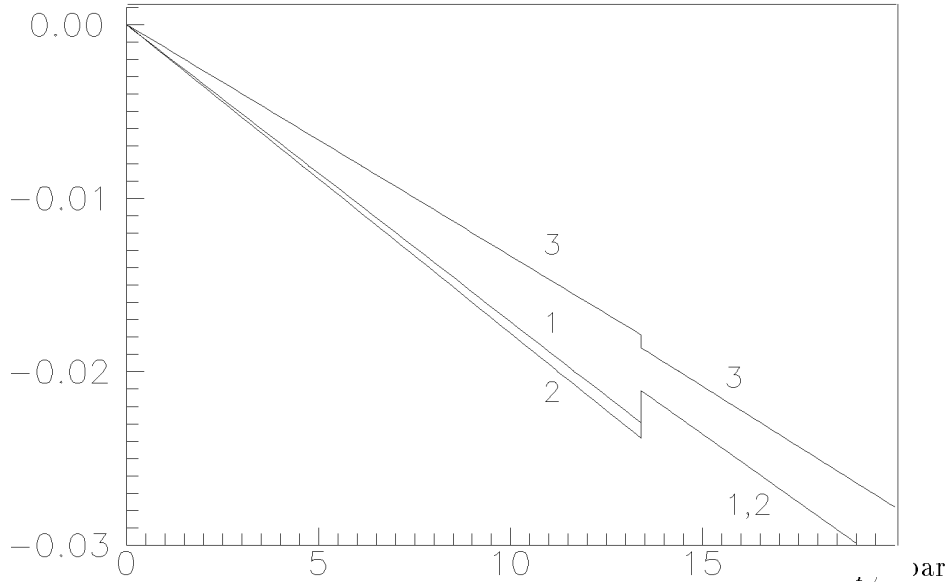


Figure 3. The deformations ε_i of a $K(H_{0.02}D_{0.98})_2PO_4$ crystal as functions of pressure at 190K: 1 – ε_1 ; 2 – ε_2 ; 3 – ε_3 .

Pressure reduces the values of cluster parameters ε , w , as well as of the long-range interaction parameter ν . Analytically, these dependencies are expressed as follows:

$$\varepsilon = \varepsilon^0 - k_\varepsilon p, \quad w = w^0 - k_w p, \quad \nu = \nu_c(0)/4 - k_\nu p$$

with

	$x \backslash T(K)$	100	200	230	300
k_ε (K/kbar)	0.98	0.985	1.005	0.955	0.958
	0.84			0.835	0.916
k_w (K/kbar)	0.98	0.562	0.572	0.550	0.553
	0.84			0.481	0.483
k_ν (K/kbar)	0.98	0.455	0.411	0.416	0.382
	0.84			1.034	1.007

The energy of a non-ionized group ε decreases with pressure much more rapidly than does the energy of a single-ionized group w . At $x = 0.98$

$\partial \ln \varepsilon / \partial p = -1.09\%/\text{kbar}$ and $\partial \ln w / \partial p = -0.069\%/\text{kbar}$ at $T < T_c$;
 $\partial \ln \varepsilon / \partial p = -1.04\%/\text{kbar}$ and $\partial \ln w / \partial p = -0.066\%/\text{kbar}$ at $T > T_c$;
(compare with the result of [34] $\partial \ln \varepsilon / \partial p = \partial \ln w / \partial p = -1.9\%/\text{kbar}$ in both phases).

Influence of hydrostatic pressure on the spontaneous polarization P_s vs temperature curves of $K(H_{1-x}D_x)_2PO_4$ was studied by G.A.Samara in [21], where the data for $P_s(T)$ for $x = 0.94$ and $T_c = 220$ K at $p = 0, 2.07$ and 4.14 kbar are presented. According to table I of this paper the value of $P_s(T)$ at 190 K is $6.15 \pm 0.10 \mu\text{C}/\text{cm}^2$. However, in [42] (also by G.A.Samara) it is asserted that at nearly the same transition temperature of 219.8 ± 0.1 K deuteration is $x = 0.98$ with a saturation polarization of $6.21 \pm 0.07 \mu\text{C}/\text{cm}^2$. Furthermore, at all temperatures $P_s(T)$ at $x = 0.94$ [21] is greater than $P_s(T)$ at $x = 0.98$ [42], whereas the reverse is expected. Since the dependence of T_c on deuteration x obtained in [42] is in agreement with the independent data of E.N.Volkova (see [6]), we assumed that in [21] x had been merely understated – its more precise value should be about 1.0.

The calculated dependencies of spontaneous polarization P_s on temperature at different pressures and on pressure at different temperatures along with experimental points of [21] are plotted in figs.4 and 5. A good description of experimental data is obtained at $\mu_c^- = \bar{\mu}_c^- - k_\mu^- p$, with $k_\mu = 0.051 \cdot 10^{-18} \text{esu} \cdot \text{cm}/\text{kbar}$, (or, $d \ln \mu_c^- / dp = -1.07\%/\text{kbar}$ (compare with $d \ln \mu_c^- / dp = -1.2\%/\text{kbar}$ of Samara [21])). As one can see, an increase in pressure leads to a decrease in P_s saturation value, while the jump of P_s at the transition point hardly depends on pressure. The strength of the first-order transition increases with pressure.

In figs.6-9 the temperature dependencies of piezoelectric coefficients e_{3i} , d_{3i} , h_{3i} and g_{3i} of $K(H_{0.02}D_{0.98})_2PO_4$ crystal at different pressures are depicted. In the paraelectric phase all piezocoefficients are equal to zero. When the temperature tends to T_c the magnitudes of e_{3i} and d_{3i} sharply increase, and abrupt jumps of them are found at the transition point. Pressure reduces the size of the jumps. The temperature range ΔT 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 , d_{31} , d_{32} are negative, and those of e_{33} , e_h , \dots , d_{33} , d_h are positive. This fact is consistent with the statement that the sign of resultant piezoelectric coefficients e_h, \dots, d_h determines the direction of the transition temperature shift with pressure.

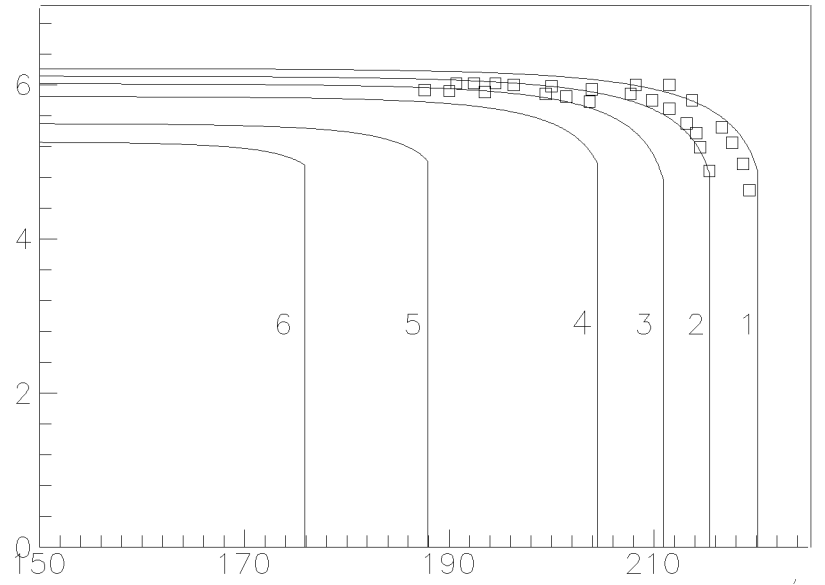


Figure 4. The spontaneous polarization of a KD_2PO_4 crystal as a function of temperature at different pressures p (kbar): 1, - 0.001; 2, - 2.07; 3, - 4.14; 4, - 7.6; 5 - 15.0; 6 - 20.0. Experimental data are taken from [21].

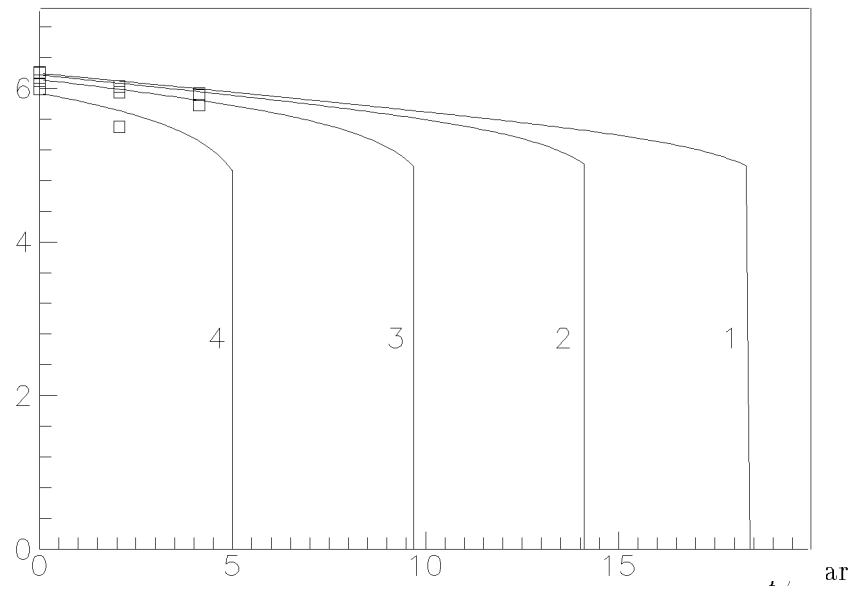


Figure 5. The spontaneous polarization of a KD_2PO_4 crystal as a function of pressure at different temperatures T (K): 1, - 170; 2, - 190; 3, - 200; 4, - 210. Experimental data are taken from [21].

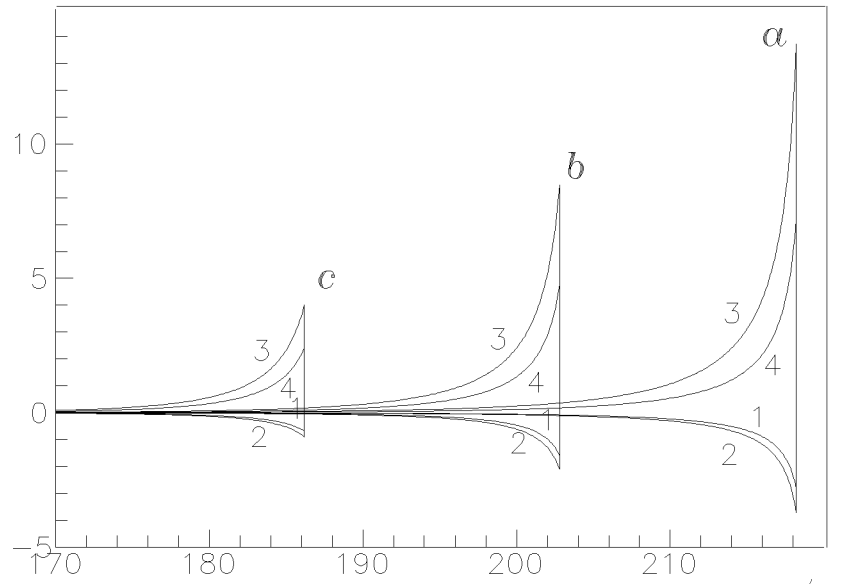


Figure 6. The coefficients of piezoelectric strain e_{3i} and e_h of a $K(H_{0.02}D_{0.98})_2PO_4$ crystal as functions of temperature at different pressures p (kbar): $a - 0.001$; $b - 7.6$; $c - 15$; 1 - e_{31} ; 2 - e_{32} ; 3 - e_{33} ; 4 - e_h .

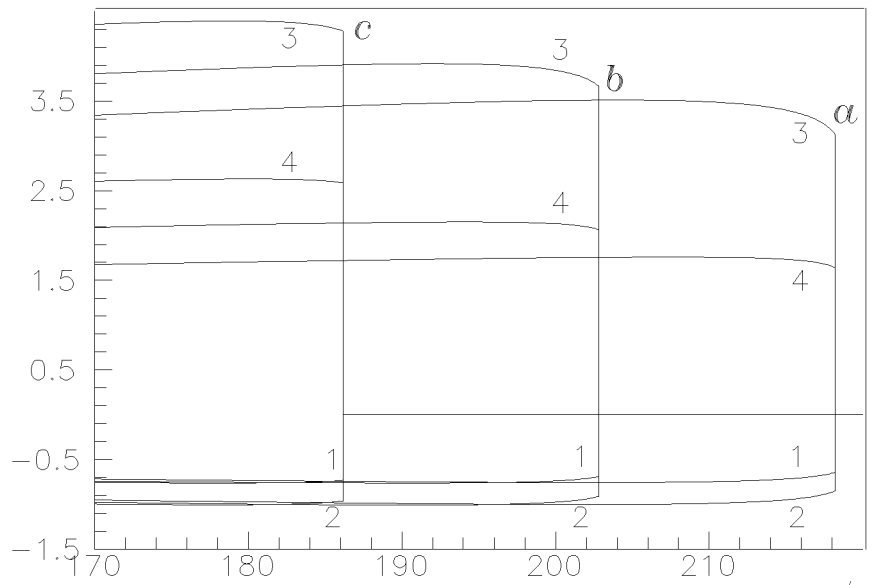


Figure 7. The constants of piezoelectric strain h_{3i} and h_h of a $K(H_{0.02}D_{0.98})_2PO_4$ crystal as functions of temperature at different pressures p (kbar): $a - 0.001$; $b - 7.6$; $c - 15$; 1 - h_{31} ; 2 - h_{32} ; 3 - h_{33} ; 4 - h_h .

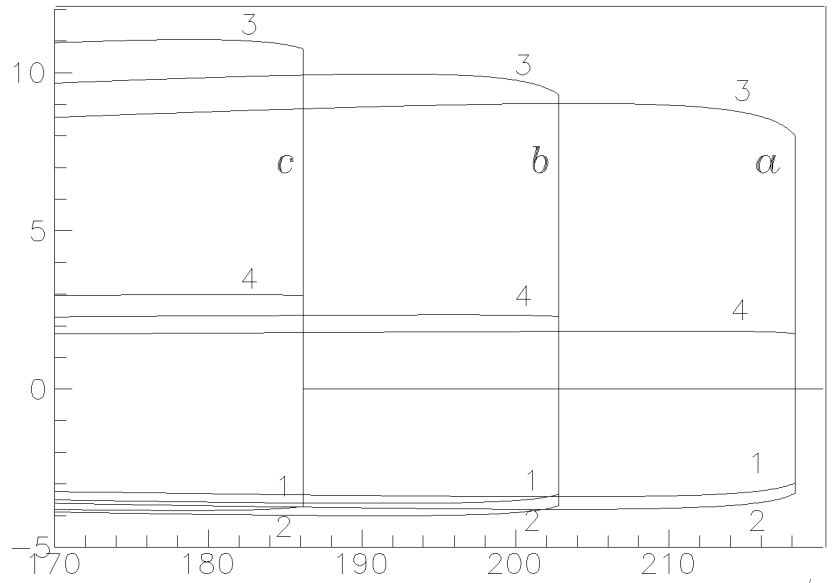


Figure 8. The coefficients of piezoelectric deformations g_{3i} and g_h of a $K(H_{0.02}D_{0.98})_2PO_4$ crystal as functions of temperature at different pressures p (kbar): *a* – 0.001; *b* – 7.6; *c* – 15; 1 – g_{31} ; 2 – g_{32} ; 3 – g_{33} ; 4 – g_h .

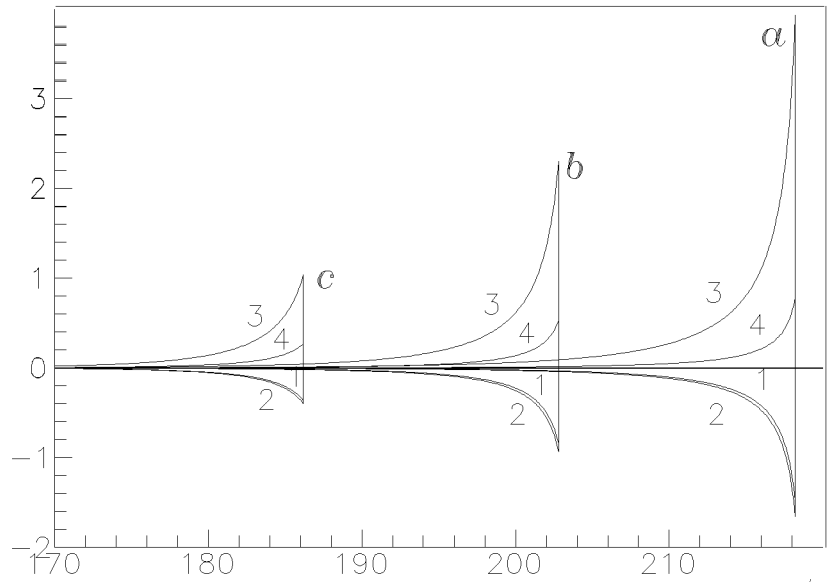


Figure 9. The constants of piezoelectric deformations d_{3i} and d_h of a $K(H_{0.02}D_{0.98})_2PO_4$ crystal as functions of temperature at different pressures p (kbar): *a* – 0.001; *b* – 7.6; *c* – 15; 1 – d_{31} ; 2 – d_{32} ; 3 – d_{33} ; 4 – d_h .

In figure 10 we plotted the variation of the attributed to the deuteron ordering part of specific heat of $K(H_{1-x}D_x)_2PO_4$ crystals with temperature at different pressures and the experimental points of [44]. As can be seen, at $p=1\text{bar}$ a good agreement with experimental data is obtained. In the ferroelectric phase ΔC^p increases sharply with temperature and decreases with a discontinuity at $T = T_c$. The peak values of ΔC^p in the high pressure range are smaller than those at 1bar. In the paraelectric phase the specific heat hardly depends on either pressure or temperature.

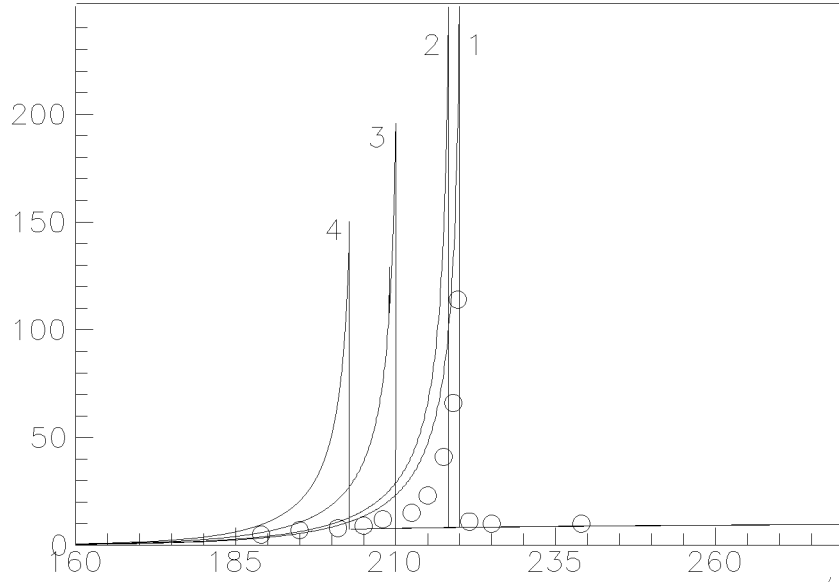


Figure 10. The specific heat of $K(H_{1-x}D_x)_2PO_4$ crystal as a function of temperature at different pressures $p(\text{kbar})$: 1, \circ [44] – 0.001 ($x = 1.00$); 2 – 0.001 ($x = 0.98$); 3 – 4.14; 4 – 7.6.

The influence of hydrostatic pressure on the temperature dependence of dielectric permittivity of $K(H_{1-x}D_x)_2PO_4$ crystals was studied in [21–24]. The measurements were carried out on crystals with $x = 0, 0.35$ and 0.82 [21], with $x = 0$ and 0.82 in [22], with $x = 0$ in [23], and with $x = 0, 0.35$ and 1.0 in [24]. Unfortunately, in [24] data at ambient pressure are absent. Extrapolation of the linear ε_3^{-1} vs pressure dependence, derived from [24] data gives the values of $\varepsilon_3^{-1}(0, T, p)$ at 1bar, which are, however, 25–30% higher than those given in [45–47]. Choosing the values of deformation potentials δ_{ij} and ψ_{cj} , we tried to get the best fit to the experimental data at 1 bar and to describe $\varepsilon_3^{-1}(0, T, p)$ vs temperature curves at all other non-zero pressures with approximately equal errors.

In figure 11 the temperature dependence of inverse longitudinal dielectric permittivity of 0.98% KD_2PO_4 crystal at different pressures along with the experimental points of [21, 42, 48] is shown. As can be seen, in the paraelectric phase the Curie-Weiss law is obeyed in a wide temperature range at different pressures. A good agreement with experimental data is obtained if $f_c^+ = (\mu_c^+)^2/v_k = 155$, $\mu_c^+ = (2.931 - k_\mu^+ p) \cdot 10^{-18}$ esu·cm and

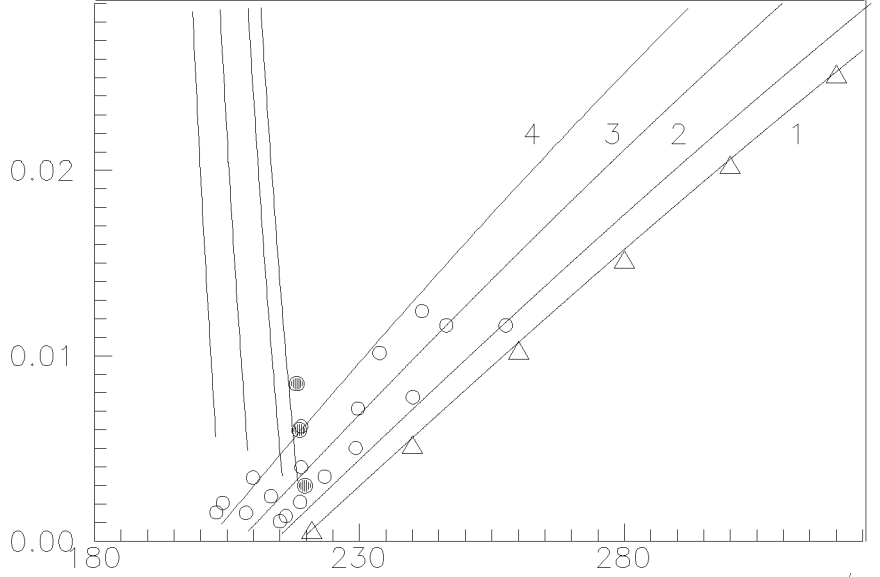


Figure 11. The inverse longitudinal dielectric permittivity of the $K(H_{0.02}D_{0.98})_2PO_4$ crystal as a function of temperature at different pressures p (kbar): 1 – 0.001; 2 – 3.6; 3 – 4.7; 4 – 7.6. The experimental points are taken from [46] – \triangle , [48] – \bullet and from [21] – \circ .

$k_\mu^+ = 5 \cdot 10^{-3}$ esu·cm/kbar ($d \ln \mu_c^+ / dp = -0.17\%/\text{kbar}$). It should be noted that the slope of the $\varepsilon_3^{-1}(0, T, p)$ curves does not depend on the values of the deformation potentials.

In the ferroelectric phase $\varepsilon_3^{-1}(0, T, p)$ depends on pressure in a non-linear way. We took $f_c^- = (\mu_c^-)^2 / v_k = 244.7 - k_f p$, with $k_f = 5.99 \text{ kbar}^{-1}$. Calculations predict a much more rapid increase in $\varepsilon_3^{-1}(0, T, p)$ than that observed experimentally in [24]. We may explain the discrepancies between theory and experiment in the ferroelectric phase, assuming that in the measurements the crystal was probably not converted into a single domain.

The data of [21] are rather contradictory. The slopes of $\varepsilon_3^{-1}(0, T, p)$ vs T lines at 1bar and at 4.14kbar for $x = 0.82$ (figure 2 from [21]) are smaller than those at $p = 1.8, 5.0, 10.0, 15.0, 20.0, 25.0$ kbar, calculated on the basis of figure 7 from [21]. The magnitude of $\varepsilon_3^{-1}(0, T, p)$ at $p = 1.8 \text{ kbar}$ is greater than that at $p = 4.18 \text{ kbar}$. The dependence $\varepsilon_3^{-1}(0, T, p)$ on pressure at $T = 204 \text{ K}$, calculated on the basis of the expression (1.1), taken from [21], also does not agree with the picture presented in figure 7 of [21].

The temperature dependence of the inverse longitudinal dielectric permittivity of $K(H_{0.16}D_{0.84})_2PO_4$ crystal at different pressures is shown in figure 12 along with the experimental points of [21]. It should be noted that in [21] it is stated that the transition temperature of $T_c = 208 \text{ K}$ corresponds to $x = 0.82$. However, on the basis of E.N.Volkova (see [6]) data, we take for the deuteration $x = 0.84$.

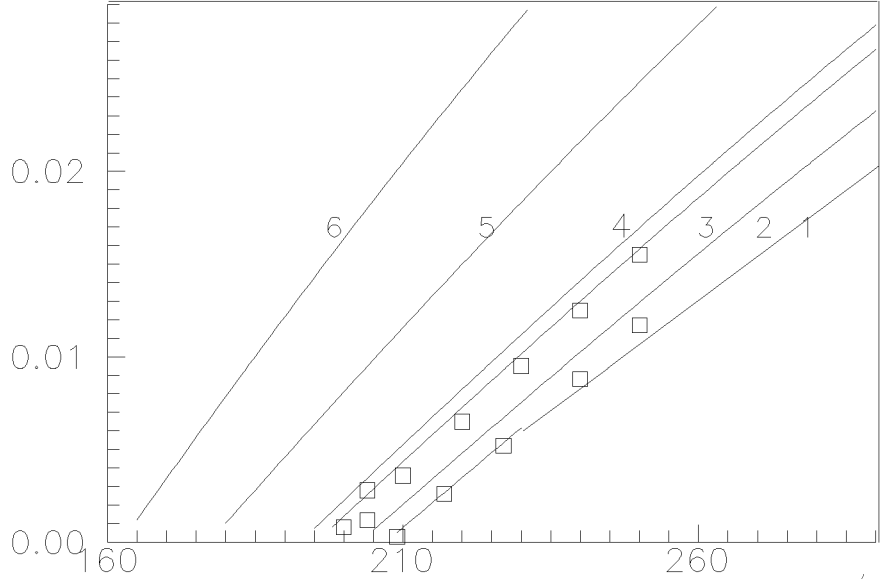


Figure 12. The inverse longitudinal dielectric permittivity of $K(H_{0.16}D_{84})_2PO_4$ crystal as a function of temperature at different pressures p (kbar): 1 – 0.001; 2 – 1.8; 3 – 4.14; 4 – 5.0; 5 – 10.0; 6 – 15.0. The experimental points are taken from [21].

Concluding remarks

On the basis of the previously proposed model of a strained crystal of DKDP type [39,40], we study the influence of hydrostatic pressure on the phase transition, thermodynamic, elastic, piezoelectric and dielectric properties of these crystals. Both short-range and long-range interactions between hydrogens are taken into account. Theoretical results are compared with available experimental data. It is shown that under the proper choice of fitting parameters the theory provides a satisfactory description of variation of studied characteristics with pressure. Unfortunately, the experimental data mainly concern spontaneous polarization and longitudinal dielectric constant, whereas any information about the pressure dependence of, say, transverse permittivity or specific heat is absent. To determine the theory parameters more precisely, a detailed experimental study of DKDP crystal responses as functions of pressure is needed.

We hope, that the present and following works will draw attention to this problem. Such investigations would give us one more chance to understand finally the origin of the phase transition in these crystals.

Acknowledgements

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ВПЛИВ ГІДРОСТАТИЧНОГО ТИСКУ НА ФАЗОВИЙ ПЕРЕХІД І ФІЗИЧНІ ВЛАСТИВОСТІ СЕГНЕТОЕЛЕКТРИКІВ ТИПУ KD_2PO_4

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На основі запропонованої раніше моделі досліджується вплив гідростатичного тиску на фізичні властивості кристалу типу KD_2PO_4 . В кластерному наближенні розраховано діелектричні, пружні і теплові характеристики кристалу, що досліджується, проведено детальний числовий аналіз отриманих результатів. Показано, що при належному виборі параметрів теорії має місце задовільний опис експериментальних результатів для баричних залежностей спонтанної поляризації, продовжної статичної діелектричної проникливості та температури фазового переходу. Для пояснення експериментально визначеної поведінки пружних сталей слід враховувати ангармонічні ефекти.