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INFLUENCE OF  $\sigma_1 - \sigma_2$  STRESS ON PHASE TRANSITION  
AND PHYSICAL PROPERTIES OF  $KD_2PO_4$ -TYPE HYDROGEN  
BONDED FERROELECTRICS

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**Вплив одновісного тиску  $\sigma_1 - \sigma_2$  на фазовий перехід і фізичні властивості сегнетоелектриків з водневими зв'язками типу  $KD_2PO_4$**

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**Анотація.** На основі запропонованої раніше моделі вивчається вплив одновісної напруги  $\sigma_1 - \sigma_2$  на фазовий перехід і фізичні властивості сегнетоелектрика  $KD_2PO_4$ . В кластерному наближенні з врахуванням короткосяжних і далекосяжних взаємодій та тиску  $\sigma_1 - \sigma_2$  розраховано і досліджено теплові, діелектричні і п'єзоелектричні характеристики  $KD_2PO_4$ , проведено детальний числовий аналіз отриманих результатів. Розраховано і досліджено температурні і баричні залежності спонтанної поляризації, поздовжньої і поперечної статичних діелектричних проникливостей і п'єзоелектричних коефіцієнтів. Проведено детальний числовий аналіз впливу одновісного тиску на фазовий перехід. Вивчаються індуковані тиском  $\sigma_1 - \sigma_2$  фазові переходи.

**Uniaxial pressure  $\sigma_1 - \sigma_2$  influence on phase transition and physical properties of the  $KD_2PO_4$ -type hydrogen bonded ferroelectrics**

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**Abstract.** On the basis of proposed earlier model we study the effects of applied uniaxial pressure  $\sigma_1 - \sigma_2$  on the physical properties of  $KD_2PO_4$  ferroelectrics. In the cluster approximation, taking into account the short-range and long-range interactions and the uniaxial stress  $\sigma_1 - \sigma_2$  we calculate and study thermal, dielectric, and piezoelectric characteristics of a  $KD_2PO_4$  crystal. A thorough numerical analysis of the obtained results is performed. The temperature and pressure dependences of spontaneous polarization, longitudinal and transverse static dielectric permittivities and piezoelectric coefficients are investigated. The phase transition induced by pressure  $\sigma_1 - \sigma_2$  is studied.

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## 1. Introduction

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

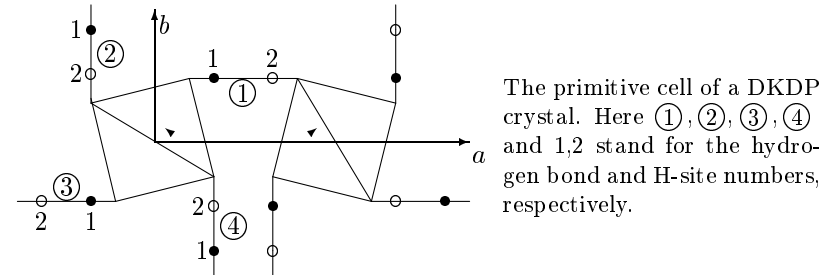
In [1,2] the model of a strained  $KD_2PO_4$  crystal was proposed. This model takes into account not only the deuteron-deuteron interaction but also coupling of deuterons with optic and acoustic vibrations of heavy atoms and with orientational vibrations of  $PO_4$  groups. Resulting from the lattice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

In [5], we presented the results of experimental studies of deuteration and uniaxial  $p = -\sigma_3$  and  $p = -\sigma_1$  stresses influence on temperature and wavelength dependences of the birefringence and transition temperature of  $KD_2PO_4$  crystals. On the basis of the model [1,2], we studied the effects of uniaxial  $p = -\sigma_3$  and  $p = -\sigma_1 = -\sigma_2$  pressures on the phase transition, thermal, dielectric and elastic properties of highly deuterated  $KD_2PO_4$  crystals. We performed a numerical analysis of the obtained theoretical results and studied the dependence of calculated thermodynamic and dielectric characteristics on the theory parameters. The obtained results were compared with the available experimental data and earlier theoretical calculations [3,4] of the hydrostatic pressure effects.

In the present paper, we study the influence of  $\sigma_1 - \sigma_2$  stress on the phase transition, thermal, dielectric, and piezoelectric properties of  $KD_2PO_4$  type ferroelectrics.

## 2. Thermodynamical properties. Four particle cluster approximation.

Let us consider a system of deuterons moving on  $O - D - \dots O$  bonds in a crystal of  $KD_2PO_4$  type. The primitive cell of Bravais lattice of this crystal is composed of the two neighbouring  $PO_4$  tetrahedra with four hydrogen bonds attached to one of them (A-type tetrahedron). Hydrogen bonds going to another (B-type) tetrahedron belong to four nearest structural elements surrounding it.



The Hamiltonian of deuteron subsystem of a  $KD_2PO_4$  crystal when mechanical stress  $\sigma_{12}$  and external electric field  $E_i$  ( $i = 1, 2, 3$ ) along the crystallographic axes  $a, b, c$  are applied has the following form:

$$\begin{aligned} \hat{H}_i = & \frac{\bar{v}N}{2} \sum_{mn} c_{mn}^{(0)} \varepsilon_m \varepsilon_n - \frac{1}{2} \sum_{qf} 2 \mu F_f^i \frac{\langle \sigma_{qf} \rangle}{2} + \\ & + \sum_{\substack{q_1 q_2 \\ q_3 q_4}} \left\{ \frac{1}{2} \sum_{ff'} V_{ff'} \frac{\sigma_{qff}}{2} \frac{\sigma_{qf'f'}}{2} + \Phi \frac{\sigma_{q_1 1}}{2} \frac{\sigma_{q_2 2}}{2} \frac{\sigma_{q_3 3}}{2} \frac{\sigma_{q_4 4}}{2} \right\} \times \\ & \times \{ \delta_{q_1 q_2} \delta_{q_1 q_3} \delta_{q_1 q_4} + \delta_{q_1+r_2, q_2} \delta_{q_1+r_3, q_3} \delta_{q_1+r_4, q_4} \} - \\ & - \sum_{qf} 2 \mu F_f^i \frac{\sigma_{qf}}{2} - \sum_{qf} \mu_{fi} E_i \frac{\sigma_{qf}}{2}. \end{aligned} \quad (2.1)$$

The Hamiltonian (2.1) describes the short range configurational interactions between deuterons near tetrahedra of “A” and “B” type;  $\mathbf{r}_f$  is a relative position vector of a deuteron on a hydrogen bond. Two eigenvalues of Ising spin  $\sigma_{qf} = \pm 1$  are assigned to two equilibrium positions of a deuteron on the  $f$ -th bond in the  $q$ -th unit cell.  $c_{mn}^{(0)}$  are the “seed” elastic constants;  $\varepsilon_m$  are the components of the strain tensor;  $\bar{v} = \frac{v}{k_B}$ ,  $v$  – is the unit cell volume;  $k_B$  is the Boltzmann constant.  $F_f^i$  are internal fields created by, first, effective long-range forces, including as well

an indirect interaction between deuterons through lattice vibrations and second, by a stress  $\sigma_{12} = \sigma_1 - \sigma_2$ ;  $\mu = e\delta$  is the dipole moment of a hydrogen bond;  $\delta$  is a distance between two D-sites on a hydrogen bond.

In the case of unstrained crystal

$$\eta^{(1)} = \langle \sigma_{q1} \rangle = \langle \sigma_{q2} \rangle = \langle \sigma_{q3} \rangle = \langle \sigma_{q4} \rangle. \quad (2.2)$$

If the external stress  $\sigma_{12}$  is applied, the hydrogen bonds directed along the  $a$  axis are contracted, while those directed along the  $b$  axis are expanded. The deuteron arrangement is characterized by two parameters

$$\eta_{13}^{(1)} = \langle \sigma_{q1} \rangle = \langle \sigma_{q3} \rangle, \quad \eta_{24}^{(1)} = \langle \sigma_{q2} \rangle = \langle \sigma_{q4} \rangle. \quad (2.3)$$

The static and dynamic properties of a  $KD_2PO_4$  crystal will be considered in the four-particle cluster approximation. In terms of density matrices [6] it reads :

$$\rho_0 = \frac{e^{-\beta \hat{H}_i}}{\text{Sp } e^{-\beta \hat{H}_i}} = \frac{e^{-\beta \hat{H}_4^A}}{\text{Sp } e^{-\beta \hat{H}_4^A}} \cdot \frac{e^{-\beta \hat{H}_4^B}}{\text{Sp } e^{-\beta \hat{H}_4^B}}, \quad \beta = \frac{1}{T}, \quad (2.4)$$

where  $H_4^A$ ,  $H_4^B$  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, we can consider the static and dynamic properties of the  $KD_2PO_4$  crystal on the basis of  $H_4^A$  solely.

$$\hat{H}_4^{iA} = \sum_q \hat{H}_{4q}^{iA} = \quad (2.5)$$

$$= \sum_q \left\{ V \left( \frac{\sigma_{q1} \sigma_{q2}}{2} + \frac{\sigma_{q2} \sigma_{q3}}{2} + \frac{\sigma_{q3} \sigma_{q4}}{2} + \frac{\sigma_{q4} \sigma_{q1}}{2} \right) + \right. \\ \left. + (U + 2\sigma_{12} \varepsilon_{12}) \frac{\sigma_{q1} \sigma_{q3}}{2} + (U - 2\sigma_{12} \varepsilon_{12}) \frac{\sigma_{q2} \sigma_{q4}}{2} + \right. \\ \left. + \Phi \frac{\sigma_{q1} \sigma_{q2} \sigma_{q3} \sigma_{q4}}{2} - \hat{H}_4^i(q) \right\},$$

$$\hat{H}_4^z(q) = \frac{z_{13}^z}{\beta} \left( \frac{\sigma_{q1}}{2} + \frac{\sigma_{q3}}{2} \right) + \frac{z_{24}^z}{\beta} \left( \frac{\sigma_{q2}}{2} + \frac{\sigma_{q4}}{2} \right), \quad (2.6)$$

$$\hat{H}_4^x(q) = \frac{z_1^x}{\beta} \frac{\sigma_{q1}}{2} + \frac{z_3^x}{\beta} \frac{\sigma_{q3}}{2} + \frac{z_{24}^x}{\beta} \left( \frac{\sigma_{q2}}{2} + \frac{\sigma_{q4}}{2} \right),$$

$$\hat{H}_4^y(y) = \frac{z_3^y}{\beta} \left( \frac{\sigma_{q1}}{2} + \frac{\sigma_{q3}}{2} \right) + \frac{z_2^y}{\beta} \frac{\sigma_{q2}}{2} + \frac{z_4^y}{\beta} \frac{\sigma_{q4}}{2}.$$

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

The effective fields  $z^i$  have the following symmetry :

$$\begin{aligned} z_{13}^z &= \beta [-\Delta_{13} + (\nu + \bar{\nu} + 2\psi_c \varepsilon_{12}) \eta_{13}^{(1)z} + (\nu - \bar{\nu}) \eta_{24}^{(1)z} + \mu_3 E_3], \\ z_{24}^z &= \beta [-\Delta_{24} + (\nu - \bar{\nu}) \eta_{13}^{(1)z} + (\nu + \bar{\nu} - 2\psi_c \varepsilon_{12}) \eta_{24}^{(1)z} + \mu_3 E_3]; \\ z_1^x &= \beta [-\Delta_1 + 2(\nu_1 + \psi_1 \varepsilon_{12}) \eta_1^{(1)x} + 2(\nu_3 + \psi_3 \varepsilon_{12}) \eta_3^{(1)x} + \\ &\quad + 4\nu_2 \eta_{24}^{(1)x} + \mu_1 E_1], \\ z_3^x &= \beta [-\Delta_3 + 2(\nu_3 + \psi_3 \varepsilon_{12}) \eta_1^{(1)x} + 2(\nu_1 + \psi_1 \varepsilon_{12}) \eta_3^{(1)x} + \\ &\quad + 4\nu_2 \eta_{24}^{(1)x} - \mu_1 E_1], \\ z_{24}^x &= \beta [-\Delta_{24} + 2\nu_2 (\eta_1^{(1)x} + \eta_3^{(1)x}) + 2(\nu_1 + \nu_3 - \psi_c \varepsilon_{12}) \eta_{24}^{(1)x}]; \\ z_{13}^y &= \beta [-\Delta_{13} + 2(\nu_1 + \nu_3 + \psi_c \varepsilon_{12}) \eta_{13}^{(1)y} + 2\nu_2 (\eta_2^{(1)y} + \eta_4^{(1)y})], \\ z_2^y &= \beta [-\Delta_2 + 4\nu_2 \eta_{13}^{(1)y} + \\ &\quad + 2(\nu_1 - \psi_1 \varepsilon_{12}) \eta_2^{(1)y} + 2(\nu_3 - \psi_3 \varepsilon_{12}) \eta_4^{(1)y} + \mu_2 E_2], \\ z_4^y &= \beta [-\Delta_4 + 4\nu_2 \eta_{13}^{(1)y} + \\ &\quad + 2(\nu_3 - \psi_3 \varepsilon_{12}) \eta_2^{(1)y} + 2(\nu_1 - \psi_1 \varepsilon_{12}) \eta_4^{(1)y} - \mu_2 E_2], \end{aligned}$$

where

$$\nu_1 = \frac{J_{11}}{4}, \quad \nu_2 = \frac{J_{12}}{4}, \quad \nu_3 = \frac{J_{13}}{4},$$

$$\nu = \nu_1 + 2\nu_2 + \nu_3, \quad \bar{\nu} = \nu_1 - 2\nu_2 + \nu_3, \quad \psi_c = \psi_1 + \psi_3$$

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

$$\mu_1 = \mu_{11} = -\mu_{31}, \quad \mu_{21} = \mu_{41} = 0, \quad \mu_2 = \mu_{22} = -\mu_{42}, \quad \mu_{12} = \mu_{32} = 0.$$

$J_{ff'}$  is a long-range dipole-dipole interaction between deuterons;  $\delta_{12}$ ,  $\psi_1$ ,  $\psi_3$  are the so-called deformation potentials.

The single-particle deuteron Hamiltonians when the stress  $\sigma_{12}$  and electric field  $E_i$  are applied have the following form:

$$\begin{aligned} \hat{H}_{1,3}^{(1)z} &= -\frac{\bar{z}_{13}^z}{\beta} \frac{\sigma_{q1,3}}{2}, \quad \hat{H}_{2,4}^{(1)z} = -\frac{\bar{z}_{24}^z}{\beta} \frac{\sigma_{q2,4}}{2}, \\ \hat{H}_{1,3}^{(1)x} &= -\frac{\bar{z}_{1,3}^x}{2} \frac{\sigma_{q1,3}}{2}, \quad \hat{H}_{2,4}^{(1)x} = -\frac{\bar{z}_{2,4}^x}{\beta} \frac{\sigma_{q2,4}}{2}, \\ \hat{H}_{1,3}^{(1)y} &= -\frac{\bar{z}_{13}^y}{2} \frac{\sigma_{q1,3}}{2}, \quad \hat{H}_{2,4}^{(1)y} = -\frac{\bar{z}_{2,4}^y}{\beta} \frac{\sigma_{q2,4}}{2}. \end{aligned} \quad (2.7)$$

Expressions for  $\bar{z}_{13}^z, \dots, \bar{z}_{2,4}^y$  can be obtained from (7) by replacing  $\Delta_{13}, \dots, \Delta_4$  with  $2\Delta_{13}, \dots, 2\Delta_4$ .

The strain  $\varepsilon_{12}$  induced by the stress  $\sigma_{12}$  changes the constants of deuteron-deuteron interaction, namely, the three and single-particle configurations split into two different groups with the energies  $w^\pm = w \pm \pm\delta_{12}\varepsilon_{12}$ , where the parameter  $\delta_{12}$  describes the rate of changes in the energy  $w$  with the strain  $\varepsilon_{12}$ . Energies of the other deuteron configurations remain unchanged.

The single particle distributions function calculated within the four-particle cluster approximation read

$$\begin{aligned}\eta_{13}^{(1)z} &= \frac{1}{D^z} [\sinh(z_{13}^z + z_{24}^z) + d \sinh(z_{13}^z - z_{24}^z) + 2bc_{12} \sinh z_{13}^z], \\ \eta_{24}^{(1)z} &= \frac{1}{D^z} [\sinh(z_{13}^z + z_{24}^z) - d \sinh(z_{13}^z - z_{24}^z) + 2\frac{b}{c_{12}} \sinh z_{24}^z], \\ \eta_3^{(1)x} &= \frac{1}{D^x} (\sinh A_1^x + d \sinh A_2^x \pm 2a \sinh A_3^x) \pm \\ &\quad \pm \frac{b}{c_{12}} (\sinh A_5^x \pm \frac{b}{c_{12}} \sinh A_6^x + 2bc_{12} \sinh A_7^x), \\ \eta_{24}^{(1)x} &= \frac{1}{D^x} (\sinh A_1^x - d \sinh A_2^x + \frac{b}{c_{12}} \sinh A_5^x - \frac{b}{c_{12}} \sinh A_6^x), \\ \eta_{13}^{(1)y} &= \frac{1}{D^y} (\sinh B_1^y - d \sinh B_2^y + bc_{12} \sinh B_7^y + bc_{12} \sinh B_8^y), \\ \eta_4^{(1)y} &= \frac{1}{D^y} (\sinh B_1^y + d \sinh B_2^y \pm 2a \sinh B_4^y) + \\ &\quad + 2\frac{b}{c_{12}} (\sinh B_6^y \pm bc_{12} \sinh B_7^y \mp 2bc_{12} \sinh B_8^y),\end{aligned}\quad (2.8)$$

where we use the notations

$$\begin{aligned}D^z &= \cosh(z_{13}^z + z_{24}^z) + d \cosh(z_{13}^z - z_{24}^z) + 2a + 2bc_{12} \cosh z_{13}^z + \\ &\quad + 2\frac{b}{c_{12}} \cosh z_{24}^z, \\ D^x &= \cosh A_1^x + d \cosh A_2^x + 2a \cosh A_3^x + 2\frac{b}{c_{12}} \cosh A_5^x + \\ &\quad + 2bc_{12} \cosh A_7^x, \\ D^y &= \cosh B_1^y + d \cosh B_2^y + 2a \cosh B_4^y + 2\frac{b}{c_{12}} \cosh B_6^y + \\ &\quad + 2bc_{12} \cosh B_8^y,\end{aligned}\quad (2.9)$$

and

$$\begin{aligned}A_2^x &= 2(z_1^x + z_3^x \pm 2z_{24}^x), & A_3^x &= 2(z_1^x - z_3^x), \\ A_5^x &= 2(z_1^x - z_3^x \pm 2z_{24}^x), & A_7^x &= 2(z_1^x + z_3^x),\end{aligned}$$

$$\begin{aligned}B_1^y &= 2(z_{13}^y \pm z_2^y \pm z_4^y), & B_4^y &= 2(z_2^y - z_4^y), \\ B_6^y &= 2(z_2^y + z_4^y), & B_7^y &= 2(2z_{13}^y \pm z_2^y \mp z_4^y), \\ a &= \exp(-\beta\varepsilon), & b &= \exp(-\beta w), & d &= \exp(-\beta w_1), & c_{12} &= \exp(-\beta\delta\varepsilon_{12}).\end{aligned}\quad (2.10)$$

After  $\Delta_{13}, \dots, \Delta_7$  had been excluded from (2.7), the quantities  $z_{13}^z, \dots, z_4^y$  read:

$$\begin{aligned}z_{13}^z &= \frac{1}{2} \ln \frac{1 + \eta_{13}^{(1)}}{1 - \eta_{13}^{(1)}} + \frac{\beta}{2} \left[ (\nu + \bar{\nu} + \psi_c \varepsilon_{12}) \eta_{13}^{(1)z} + (\nu - \bar{\nu}) \eta_{24}^{(1)z} + \mu_3 E_3 \right], \\ z_{24}^z &= \frac{1}{2} \ln \frac{1 + \eta_{24}^{(1)}}{1 - \eta_{24}^{(1)}} + \frac{\beta}{2} \left[ (\nu - \bar{\nu}) \eta_{13}^{(1)z} + (\nu + \bar{\nu} - \psi_c \varepsilon_{12}) \eta_{24}^{(1)z} + \mu_3 E_3 \right], \\ z_3^x &= \frac{1}{2} \ln \frac{1 + \eta_1^{(1)x}}{1 - \eta_1^{(1)x}} + \beta(\nu_3 + \psi_3 \varepsilon_{12}) \eta_1^{(1)x} + \beta(\nu_3 + \psi_3 \varepsilon_{12}) \eta_3^{(1)x} + \\ &\quad + 2\beta\nu_2 \eta_{24}^{(1)x} \pm \frac{\beta}{2} \mu_1 E_1, \\ z_{24}^x &= \frac{1}{2} \ln \frac{1 + \eta_{24}^{(1)x}}{1 - \eta_{24}^{(1)x}} + \beta\nu_2 (\eta_1^{(1)x} + \eta_3^{(1)x}) + \beta(\nu_1 + \nu_3 - \psi_c \varepsilon_{12}) \eta_{24}^{(1)x}, \\ z_{13}^y &= \frac{1}{2} \ln \frac{1 + \eta_{13}^{(1)y}}{1 - \eta_{13}^{(1)y}} + \beta(\nu_1 + \nu_3 + \psi_c \varepsilon_{12}) \eta_{13}^{(1)y} + \beta\nu_2 (\eta_2^{(1)y} + \eta_4^{(1)y}), \\ z_4^y &= \frac{1}{2} \ln \frac{1 + \eta_2^{(1)y}}{1 - \eta_2^{(1)y}} + 2\beta\nu_2 \eta_{13}^{(1)y} + \beta(\nu_3 - \psi_3 \varepsilon_{12}) \eta_2^{(1)y} + \\ &\quad + \beta(\nu_3 - \psi_3 \varepsilon_{12}) \eta_4^{(1)y} \pm \frac{\beta}{2} \mu_2 E_2.\end{aligned}$$

The free energy of a crystal calculated within the four-particle cluster approximation is equal to

$$\begin{aligned}f^z &= \frac{\bar{\nu}}{2} c^{(0)} \varepsilon_{12}^2 - 2T \ln 2 + \frac{1}{2} (\nu + \bar{\nu}) [(\eta_{13}^{(1)z})^2 + (\eta_{24}^{(1)z})^2] + \\ &\quad + \frac{1}{2} (\nu - \bar{\nu}) \eta_{13}^{(1)z} \eta_{24}^{(1)z} + \psi_c \varepsilon_{12} [(\eta_{13}^{(1)z})^2 - (\eta_{24}^{(1)z})^2] - \\ &\quad - T \ln [1 - (\eta_{13}^{(1)z})^2] [1 - (\eta_{24}^{(1)z})^2] - 2T \ln D^z.\end{aligned}\quad (2.11)$$

The thermodynamic potential is equal to

$$g^z = f^z - \bar{\nu} \sigma_{12} \varepsilon_{12}.\quad (2.12)$$

Thermodynamic equilibrium conditions under the mechanical stress  $\sigma_{12}$  have the following form:

$$\frac{\partial f^z}{\partial \eta_{13}^{(1)z}} = 0, \quad \frac{\partial f^z}{\partial \eta_{24}^{(1)z}} = 0, \quad \frac{1}{\bar{v}} \frac{\partial f^z}{\partial \varepsilon_{12}} = \sigma_{12}. \quad (2.13)$$

Hence, the set of equations for  $\eta_{13}^{(1)z}$ ,  $\eta_{24}^{(1)z}$  and  $\varepsilon_{12}$  can be found:

$$\eta_{13}^{(1)z} = \frac{\eta_{13}^z}{D^z}; \quad \eta_{24}^{(1)z} = \frac{\eta_{24}^z}{D^z}, \quad (2.14)$$

$$\begin{aligned} \sigma_{12} &= c^{(0)} \varepsilon_{12} - \frac{\psi_c}{\bar{v}} [(\eta_{13}^{(1)z})^2 - (\eta_{24}^{(1)z})^2] + \\ &+ \frac{2\delta_{12}}{\bar{v}D^z} (2bc_{12} \cosh z_{13}^z - 2\frac{b}{c_{12}} \cosh z_{24}^z), \\ c^{(0)} &= \frac{1}{2} (c_{11}^0 - c_{12}^0). \end{aligned}$$

In the paraelectric phase, the equation (2.14) is simplified and the following relation between  $\sigma_{12}$  and  $\varepsilon_{12}$  is obeyed:

$$\sigma_{12} = c^{(0)} \varepsilon_{12} - \frac{b\delta_{12}b \sinh \beta \delta_{12} \varepsilon_{12}}{\bar{v}(1 + 2a + 2 + 4b \cosh \beta \delta_{12} \varepsilon_{12})}. \quad (2.15)$$

At the first order phase transition, the state of a crystal changes abruptly. The transition temperature  $T_c$  is determined from the set of equations

$$\begin{aligned} f[\eta_{13}^{(1)}(T_c), \eta_{24}^{(1)}(T_c), \varepsilon_{12}, T_c] &= f(0, 0, \varepsilon_{12}, T_c), \\ \eta_{13}^{(1)}(T_c) &= \Psi_1[\eta_{13}^{(1)}(T_c), \eta_{24}^{(1)}(T_c), \varepsilon_{12}, T_c], \\ \Psi_1[\eta_{13}^{(1)}(T_c), \eta_{24}^{(1)}(T_c), \varepsilon_{12}, T_c] &= \frac{m_{13}(T_c)}{D(T_c)}, \\ \eta_{24}^{(1)}(T_c) &= \Psi_2[\eta_{13}^{(1)}(T_c), \eta_{24}^{(1)}(T_c), \varepsilon_{12}, T_c], \\ \Psi_2[\eta_{13}^{(1)}(T_c), \eta_{24}^{(1)}(T_c), \varepsilon_{12}, T_c] &= \frac{m_{24}(T_c)}{D(T_c)}. \end{aligned} \quad (2.16)$$

The polarization of the  $KD_2PO_4$  crystals is determined in the following way:

$$\begin{aligned} P_3 &= \frac{\mu_3}{v} (\eta_{13}^{(1)} + \eta_{24}^{(1)}) = \\ &= \frac{2\mu_3}{vD^z} \{ \sinh(z_{13}^z + z_{24}^z) + bc_{12} \sinh z_{13}^z + \frac{b}{c_{12}} \sinh z_{24}^z \}. \end{aligned} \quad (2.17)$$

Let us study now the elastic properties of a  $KD_2PO_4$  crystal. From (2.14) we obtain the expression for the renormalized elastic constant at

constant polarization:

$$\begin{aligned} c_{11}^p &= \left( \frac{\partial \sigma_1}{\partial \varepsilon_1} \right)_P = c^{(0)} - \frac{2\psi_c}{\bar{v}DT} [\eta_{13}^{(1)} (\theta_{13} + t_{13}) - \eta_{24}^{(1)} (\theta_{24} + t_{24})] - \\ &- \frac{2\delta_{12}^2}{\bar{v}DT} (2bc_{12} \cosh z_{13} + 2\frac{b}{c_{12}} \cosh z_{24}) + \frac{2}{\bar{v}D^2T} M^2, \\ c_{12}^p &= \left( \frac{\partial \sigma_1}{\partial \varepsilon_2} \right)_p = -c_{11}^p, \quad c_{22}^p = \left( \frac{\partial \sigma_2}{\partial \varepsilon_2} \right)_p = c_{11}^p, \end{aligned} \quad (2.18)$$

Here the notations are used

$$\begin{aligned} \theta_{13} &= \psi_c (\eta_{13}^{(1)} \mathfrak{x}_{13} - \eta_{24}^{(1)} s) + t_{13}, \\ \theta_{24} &= \psi_c (\eta_{13}^{(1)} s - \eta_{24}^{(1)} \mathfrak{x}_{24}) + t_{24}, \\ \mathfrak{x}_{13} &= \cosh(z_{13} + z_{24}) + d \cosh(z_{13} - z_{24}) + \\ &+ 2bc_{12} \cosh z_{13} - \eta_{13}^{(1)} m_{13}, \\ \mathfrak{x}_{24} &= \cosh(z_{13} + z_{24}) + d \cosh(z_{13} - z_{24}) + \\ &+ 2\frac{b}{c_{12}} \cosh z_{24} - \eta_{24}^{(1)} m_{13}, \\ s &= \cosh(z_{13} + z_{24}) - d \cosh(z_{13} - z_{24}) - \eta_{13}^{(1)} m_{24}, \\ t_{13} &= -2bc_{12} \delta_{12} \sinh z_{13} + \eta_{13}^{(1)} M, \\ t_{24} &= 2\frac{b}{c_{12}} \delta_{12} \sinh z_{24} + \eta_{24}^{(1)} M, \\ M &= \delta_{12} \left( 2bc_{12} \cosh z_{13} - 2\frac{b}{c_{12}} \cosh z_{24} \right). \end{aligned} \quad (2.19)$$

The renormalized elastic constant of unstrained crystals in paraelectric phase is equal to:

$$\tilde{c}_{11}^{p+} = \frac{\partial \sigma_1}{\partial \varepsilon_1} \Big|_{\varepsilon_{12}=0} = c^{(0)} - \frac{8\beta(\delta_{12})^2 b}{\bar{v}(1 + 2a + d + 4b)}. \quad (2.20)$$

Using the relations (2.14) and (2.17), we get expressions for piezoelectric constants related to the  $\varepsilon_{12}$  strain.

The coefficient of piezoelectric stress has the following form

$$\begin{aligned} e_{31} &= \left( \frac{\partial P_3}{\partial \varepsilon_1} \right)_{E_3} = - \left( \frac{\partial \sigma_1}{\partial E_3} \right)_{\varepsilon_{12}} = \frac{\mu_3 \beta}{v \Delta} \{ D(\theta_{13} + \theta_{24}) + \\ &+ \varphi_{13}^\eta (\theta_{13} s - \theta_{24} \mathfrak{x}_{13}) + \varphi_{24}^\eta (\theta_{24} s - \theta_{13} \mathfrak{x}_{24}) + \\ &+ \varphi_{1-4}^\eta [\theta_{24}^\eta (\mathfrak{x}_{13} - s) - \theta_{13} (s - \mathfrak{x}_{24})] \}, \\ e_{32} &= -e_{31}, \end{aligned} \quad (2.21)$$

where

$$\Delta = D^2 - D(\varphi_{13}^\eta \mathfrak{a}_{13} + \varphi_{24}^\eta \mathfrak{a}_{24} + 2\varphi_{1-4}^\eta s) + [\varphi_{13}^\eta \varphi_{24}^\eta - (\varphi_{1-4}^\eta)^2] (\mathfrak{a}_{13}\mathfrak{a}_{24} - s^2), \quad (2.22)$$

$$\varphi_{13}^\eta = \frac{1}{1 - \eta_{13}^{(1)2}} + \frac{1}{2T} (\nu + \bar{\nu}) + \frac{1}{T} \psi_c \varepsilon_{12}, \quad (2.23)$$

$$\varphi_{24}^\eta = \frac{1}{1 - \eta_{24}^{(1)2}} + \frac{1}{2T} (\nu + \bar{\nu}) - \frac{1}{T} \psi_c \varepsilon_{12},$$

$$\varphi_{1-4}^\eta = \frac{1}{2T} (\nu - \bar{\nu}).$$

Using the relations (2.14), we get the following systems of equations for  $d_{13i} = (\partial \eta_{13}^{(1)} / \partial \sigma_i)_{E_3}$ ,  $d_{24i} = (\partial \eta_{24}^{(1)} / \partial \sigma_i)_{E_3}$ ,  $s_{1i}^E = (\partial \varepsilon_1 / \partial \sigma_i)_{E_3}$ ,  $s_{2i}^E = (\partial \varepsilon_2 / \partial \sigma_i)_{E_3}$ , ( $i = 1, 2$ ).

$$\begin{pmatrix} N_{11} & N_{12} & -N_{13} \\ N_{21} & N_{22} & -N_{23} \\ -h_{13} & -h_{14} & c_{11}^p \end{pmatrix} \begin{pmatrix} d_{131} \\ d_{241} \\ s_{11}^E - s_{12}^E \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad (2.24)$$

$$\begin{pmatrix} N_{11} & N_{12} & -N_{13} \\ N_{21} & N_{22} & -N_{23} \\ -h_{13} & -h_{14} & c_{11}^p \end{pmatrix} \begin{pmatrix} d_{132} \\ d_{242} \\ s_{12}^E - s_{22}^E \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix},$$

where

$$\begin{aligned} N_{11} &= D - (\varphi_{13}^\eta \mathfrak{a}_{13} + \varphi_{1-4}^\eta s); \\ N_{12} &= -(\varphi_{1-4}^\eta \mathfrak{a}_{13} + \varphi_{24}^\eta s); \quad N_{13} = \beta \theta_{13}, \\ N_{21} &= -(\varphi_{13}^\eta s + \varphi_{1-4}^\eta \mathfrak{a}_{24}); \\ N_{22} &= D - (\varphi_{1-4}^\eta s + \varphi_{24}^\eta \mathfrak{a}_{24}); \quad N_{23} = \beta \theta_{24}, \\ h_{13} &= \frac{2}{\bar{\nu} D} (\varphi_{13}^\eta \theta_{13} + \varphi_{1-4}^\eta \theta_{24}); \quad h_{24} = \frac{2}{\bar{\nu} D} (\varphi_{1-4}^\eta \theta_{13} + \varphi_{24}^\eta \theta_{24}). \end{aligned} \quad (2.25)$$

and now we find the expression for the coefficient of piezoelectric strain

$$\begin{aligned} d_{31} &= \left( \frac{\partial P_3}{\partial \sigma_1} \right)_{E_3} = e_{31} (s_{11}^E - s_{12}^E), \\ d_{32} &= \left( \frac{\partial P_3}{\partial \sigma_2} \right)_{E_3} = e_{32} (s_{22}^E - s_{12}^E), \end{aligned} \quad (2.26)$$

where  $s_{11}^E - s_{12}^E$  is the elastic compliance at constant field.

$$s_{11}^E - s_{12}^E = s_{22}^E - s_{12}^E = \frac{1}{c_{11}^p - h_{13}e_{13} - h_{24}e_{24}}, \quad (2.27)$$

$$\begin{aligned} e_{13} &= \frac{\mu_3}{\nu} \frac{\beta}{\Delta} [D\theta_{13} - \theta_{13}(\varphi_{14}^\eta s + \varphi_{24}^\eta \mathfrak{a}_{24}) + \theta_{24}(\varphi_{1-4}^\eta \mathfrak{a}_{13} + \varphi_{24}^\eta s)], \\ e_{24} &= \frac{\mu_3}{\nu} \frac{\beta}{\Delta} [D\theta_{24} + \theta_{13}(\varphi_{13}^\eta s + \varphi_{1-4}^\eta \mathfrak{a}_{24}) - \theta_{24}(\varphi_{1-4}^\eta s + \varphi_{13}^\eta \mathfrak{a}_{13})], \end{aligned}$$

$$e_{31} = e_{13} + e_{24}.$$

Let us consider now the thermal properties of a  $KD_2PO_4$  crystal under the stress  $\sigma_{12}$ . In ferroelectric phase the entropy of the crystals per one mole calculated on the basis (2.11), has the following form:

$$\begin{aligned} S &= R[2 \ln 2 + 2 \ln D + \ln(1 - \eta_{13}^{(1)2}) + \\ &+ \ln(1 - \eta_{24}^{(1)2}) + 2T\varphi_{13}^T \eta_{13}^{(1)} + 2T\varphi_{24}^T \eta_{24}^{(1)} + 2\frac{\bar{M}}{D}], \end{aligned} \quad (2.28)$$

where

$$\begin{aligned} \bar{M} &= \frac{w_1}{T} d \cosh(z_{13} - z_{24}) + \\ &+ \frac{w}{T} (2bc_{12} \cosh z_{13} + 2\frac{b}{c_{12}} \cosh z_{24}) + 2\frac{\varepsilon}{T} a + \frac{\varepsilon_{12}}{T} M, \\ \varphi_{13}^T &= -\frac{1}{T^2} \left[ \frac{1}{2}(\nu + \bar{\nu})\eta_{13}^{(1)} + \frac{1}{2}(\nu - \bar{\nu})\eta_{24}^{(1)} + \psi_c \varepsilon_{12} \eta_{13}^{(1)} \right], \\ \varphi_{24}^T &= -\frac{1}{T^2} \left[ \frac{1}{2}(\nu - \bar{\nu})\eta_{13}^{(1)} + \frac{1}{2}(\nu + \bar{\nu})\eta_{24}^{(1)} - \psi_c \varepsilon_{12} \eta_{24}^{(1)} \right]. \end{aligned} \quad (2.29)$$

The molar specific heat at constant pressure we calculate, differentiating the entropy (2.28):

$$\Delta C^\sigma = -RT \left( \frac{\partial S}{\partial T} \right)_\sigma = \Delta C^\varepsilon + RT q^p (\alpha_1 - \alpha_2), \quad (2.30)$$

where  $\Delta C^\varepsilon$  is the molar specific heat at constant strains, and

$$\Delta C^\varepsilon = RT (+q^{P,\varepsilon} + q_{13}^\varepsilon p_{13}^\sigma + q_{24}^\varepsilon p_{24}^\sigma). \quad (2.31)$$

Here we use the following notations:

$$\begin{aligned} q^{P,\varepsilon} &= -\frac{2}{DT} \{ T\varphi_{13}^T [\gamma_{13} + (q_{13} - \eta_{13}^{(1)} \bar{M})] + \\ &+ T\varphi_{24}^T [\gamma_{24} + (q_{24} - \eta_{24}^{(1)} \bar{M})] + N - \frac{\bar{M}^2}{D} \}, \\ q^P &= \frac{2}{\bar{\nu} DT} \{ -T\varphi_{13}^T \theta_{13} - T\varphi_{24}^T \theta_{24} - \\ &- \psi_c \eta_{13}^{(1)} (q_{13} - \eta_{13}^{(1)} \bar{M}) + \psi_c \eta_{24}^{(1)} (q_{24} - \eta_{24}^{(1)} \bar{M}) + \lambda - \frac{\bar{M} M}{D} \}, \end{aligned} \quad (2.32)$$

$$q_{13}^{\varepsilon} = -\frac{2}{D}(\varphi_{13}^{\eta}\gamma_{13} + \varphi_{1-4}^{\eta}\theta_{24}),$$

$$q_{24}^{\varepsilon} = -\frac{2}{D}(\varphi_{1-4}^{\eta}\gamma_{13} + \varphi_{24}^{\eta}\theta_{24}),$$

where

$$N = 2\left(\frac{\varepsilon}{T}\right)^2 a + 2\left(\frac{w + \delta_{12}\varepsilon_{12}}{T}\right)^2 bc_{12} \cosh z_{13} +$$

$$+ 2\left(\frac{w - \delta_{12}\varepsilon_{12}}{T}\right)^2 \frac{b}{c_{12}} \cosh z_{24} + \left(\frac{w_1}{T}\right)^2 d \cosh(z_{13} - z_{24}), \quad (2.33)$$

$$q_{13} = 2\frac{w + \delta_{12}\varepsilon_{12}}{T}bc_{12} \sinh z_{13} + \frac{w_1}{T}d \sinh(z_{13} - z_{24}),$$

$$q_{24} = 2\frac{w - \delta_{12}\varepsilon_{12}}{T}\frac{b}{c_{12}} \sinh z_{13} - \frac{w_1}{T}d \sinh(z_{13} - z_{24}),$$

$$\lambda = \delta_{12}\left[\frac{w + \delta_{12}\varepsilon_{12}}{T} 2bc_{12} \cosh z_{13} - \frac{w - \delta_{12}\varepsilon_{12}}{T} 2\frac{b}{c_{12}} \cosh z_{24}\right],$$

$$\gamma_{13} = T\varphi_{13}^T \mathfrak{a}_{13} + T\varphi_{24}^T s + q_{13} - \eta_{13}^{(1)} \bar{M},$$

$$\gamma_{24} = T\varphi_{13}^T s + T\varphi_{24}^T \mathfrak{a}_{24} + q_{24} - \eta_{24}^{(1)} \bar{M}.$$

From the system of equations obtained from (2.14)

$$\begin{pmatrix} N_{11} & N_{12} & -N_{13} \\ N_{21} & N_{22} & -N_{23} \\ -h_{13} & -h_{14} & c_{11}^p \end{pmatrix} \begin{pmatrix} p_{13}^{\sigma} \\ p_{24}^{\sigma} \\ \alpha \end{pmatrix} = \begin{pmatrix} \gamma_{13} \\ \gamma_{24} \\ -p \end{pmatrix} \quad (2.34)$$

we get an expression for a pyroelectric coefficient at  $\sigma = \text{const}(\alpha = \alpha_1 - \alpha_2)$

$$p^{\sigma} = \frac{\mu_3}{v} (p_{13}^{\sigma} + p_{24}^{\sigma}) = p^{\varepsilon} + e_{31} \alpha, \quad (2.35)$$

$$p^{\varepsilon} = \frac{\mu_3}{v} \frac{1}{\Delta} \left[ \begin{vmatrix} \gamma_{13} & N_{12} \\ \gamma_{24} & N_{22} \end{vmatrix} + \begin{vmatrix} N_{11} & \gamma_{13} \\ N_{21} & \gamma_{24} \end{vmatrix} \right], \quad (2.36)$$

$$\alpha = \frac{-p + p_{13}^{\varepsilon} h_{13} + p_{24}^{\varepsilon} h_{24}}{c_{11}^p - h_{13} \varepsilon_{13} - h_{24} e_{24}}.$$

In (2.34)  $p$  is thermal pressure

$$p = -\left(\frac{\partial \sigma_1}{\partial T}\right)_{P, \varepsilon} = q^P. \quad (2.37)$$

Let us determine the static dielectric susceptibility of a  $KD_2PO_4$  crystal along the  $c$ -axis under the  $\sigma_{12}$  stress. We consider the case of mechanically clamped crystal.

$$\chi_3^{\varepsilon}(0, T, \sigma_{12}) = \frac{\mu_3^2}{v} \frac{1}{2T} \frac{1}{\Delta} [D(\mathfrak{a}_{13} + \mathfrak{a}_{24} + 2s) -$$

$$- (\varphi_{13} + \varphi_{24} - 2\varphi_{1-4}) (\mathfrak{a}_{13}\mathfrak{a}_{24} - s^2)]. \quad (2.38)$$

In the case of unstrained crystal

$$\chi_3^{\sigma}(0, T, \sigma_{12}) = \chi_3^{\varepsilon}(0, T, \sigma_{12}) + e_{31} [d_{31} - d_{32}]. \quad (2.39)$$

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

$$\chi_1^{-}(0, T, \sigma_{12}) = \frac{\mu_1^2}{v} \frac{1}{T} \times \quad (2.40)$$

$$\times \frac{4(a + b/c_{12} \cosh z_{24})}{D - 2(a + \frac{b}{c_{12}} \cosh z_{24}) \left[ (1 - \eta_{13}^{(1)2})^{-1} + \beta(\nu_1 - \nu_3 + (\psi_1 - \psi_3)\varepsilon_{12}) \right]}.$$

In paraelectric phase

$$\chi_{11}^{+}(0, T, \sigma_{12}) = \quad (2.41)$$

$$= \frac{\mu_1^2}{v} \frac{1}{T} \frac{4(a + b/c_{12})}{1 + 2bc_{12} + d - 2\beta\left(a + \frac{b}{c_{12}}\right)[(\nu_1 - \nu_3) + (\psi_1 - \psi_3)\varepsilon_{12}]}.$$

If electric field is directed along  $y$ -axis,

$$\chi_2^{-}(0, T, \sigma_{12}) = \frac{\mu_2^2}{v} \frac{1}{T} \times \quad (2.42)$$

$$\times \frac{4(a + bc_{12} \cosh z_{13})}{D - 2(a + bc_{12} \cosh z_{13}) \left[ (1 - \eta_{24}^{(1)2})^{-1} + \beta(\nu_1 - \nu_3 - (\psi_1 - \psi_3)\varepsilon_{12}) \right]}.$$

$$\chi_2^{+}(0, T, \sigma_{12}) =$$

$$= \frac{\mu_2^2}{v} \frac{1}{T} \frac{4(a + bc_{12})}{1 + 2\frac{b}{c_{12}} + d - 2\beta(a + bc_{12})[(\nu_1 - \nu_3) - (\psi_1 - \psi_3)\varepsilon_{12}]}.$$

### 3. Discussion

For numerical estimate of mechanical stress  $\sigma_{12}$  and temperature dependences of the characteristics, calculated in the previous section, we use the values of theory parameters, obtained in [7]. These values provide a good description of experimental data for thermodynamic and dynamic

characteristics of  $KD_2PO_4$ :  $\varepsilon = 93K$ ,  $w = 840K$ ,  $w_1 = \infty$ ,  $\nu = 37,44 K$ ,  $\bar{\nu} = 16 K$ ,  $T_c = 219,7K$ .

Strain  $\varepsilon_{12}$  changes the energies of one and three-particle deuteron configurations  $w$ . First of all, the change in energy is caused by the changes in the D-site distance:  $\Delta w/w \sim 2\Delta\delta/\delta$ , hydrostatic pressure  $\Delta\delta/\delta \sim 1\%/kbar$ . [2]. The changes of O-O and D-D distances are accompanied by the rotation of  $PO_4$  tetrahedra. Since the symmetrized stress  $\sigma_{12}$  does not lead to the tetrahedra rotation, and the changes in hydrogen bond length are approximately twice as ones in hydrostatic pressure case at the same value of external stress, then at  $\sigma_{12}$  stress  $\Delta\delta/\delta \sim 2\%/kbar$ , and, therefore,  $\Delta w/w \sim 4\%/kbar$ . Taking into account the fact, that for  $KD_2PO_4$ ,  $\tilde{c} = \frac{\partial\sigma_{12}}{\partial\varepsilon_{12}}|_{\varepsilon_{12}=0} \approx 5 \cdot 10^5$  bar, we get  $\delta_{12} = 3 \cdot 10^4 K$ . In this paper we take  $\delta_{12} = 3.024 \cdot 10^4 K$ ; in order to study the influence of this parameter on the form of a phase diagram we also take  $\delta = 3.3 \cdot 10^4$ ;  $3.6 \cdot 10^4$ ;  $3.8 \cdot 10^4 K$ .

The "seed" elastic constant is taken to be equal to  $c^{(0)} = 55 \cdot 10^5$  bar. From the chosen values of parameters and the condition of thermodynamic potential minimum it follows that  $\psi_{\varepsilon_{12}}$  should be equal to  $6 \cdot 10^3 K$ .

In fig.1 we show the phase diagram in the case of  $\delta_{12} = 3,024 \cdot 10^4 K$ , and  $\delta_{12} = 3.3 \cdot 10^4$ ;  $3.6 \cdot 10^4$ ;  $3.8 \cdot 10^4 K$ , respectively; the curve, separating regions I and II, corresponds to the first order phase transition in  $\eta_{13}^{(1)}$  and  $\eta_{24}^{(1)}$  parameters, and the curves, separating I and III, II and IV regions, correspond to the first order phase transition in  $\sigma_{12}$  stress. As one can see, the transition temperature  $T_c$  decreases with stress  $\sigma_{12}$ , and slightly depends on the value of  $\delta_{12}$ . The phase diagrams consists of three phases:

- 1) the phase I, where  $\eta_{13}^{(1)} = \eta_{24}^{(1)} = 0$  and  $\varepsilon_{12}^I$
- 2) the ferroelectric phase II, where  $\eta^{(1)} \neq \eta_{24}^{(1)} \neq 0, \varepsilon_{12}^{II}$
- 3) the phase III with  $\eta_{12}^{(1)} = \eta_{24}^{(1)} = 0, \varepsilon_{12}^{III}$

Point k in phase diagram corresponds to the critical point, where the phase transition in stresses disappears. When  $\delta_{12}$  increases, the value of  $T_k$  increases and that of  $\sigma_{12}^k$  decreases. At larger values of  $\delta_{12}$  parameter, the phase III shifts into the smaller stresses. At  $\delta_{12} = 3.8 \cdot 10^4$  the ferroelectric phase is absent.

In fig.2 we plot the dependences  $\varepsilon_{12}(\sigma_{12})$ , calculated on the basis of (2.14) at the temperatures of 175K (curve 1), 205(2), 250(3). Peculiar to these curves is the possibility of two extrema and bend point existence. The value of stress corresponding to the point can be determined from the condition:  $g(\varepsilon_{12}^{I,II}) = g(\varepsilon_{12}^{III})$ . At this stress, a pressure induced first

order phase transition in the uniaxial stress is possible. The transition stress  $\sigma_{12}^0$  depends on the values of  $\delta_{12}, w, T$  and  $c^{(0)}$  parameters. The  $\delta_{12}$  decreases when  $w, c^{(0)}$  decrease or  $\delta_{12}$  increases. It should be noted that two extrema may appear if the relation

$$\frac{\beta\delta_{12}^2}{c^{(0)}} > 2 * v[(1 + 2a + d)^2 - 4b^2](1 + 2a + d)^2$$

is obeyed.

At  $c^{(0)} = 55 \cdot 10^4$  bar, this condition is satisfied when  $\delta_{12} > 26200K$ . In the curve 1, the first of strain jump of  $\Delta^T\varepsilon_{12}$  corresponds to the ferroelectric transition, and the second one  $\Delta^\sigma\varepsilon_{12}$ -to the transition in stress;  $\Delta^T\varepsilon_{12} \ll \Delta^\sigma\varepsilon_{12}$ . Temperature dependence of the strain  $\varepsilon_{12}$  at different values of  $\sigma_{12}$  stress (0.001kbar-curve1', 1-2', 3-3', 5-4', 6-5') is shown in fig.2a. At stresses, below  $\sigma_{12}$ , the strain  $\varepsilon_{12}$  slightly increases with temperature; at  $T = T_c$  the  $\sigma_{12}$  has a discontinuity (the size of this discontinuity increases with  $\sigma_{12}$ ). At  $\sigma_{12} = 6kbar$  the strain  $\varepsilon_{12}$  decreases with temperature, then has a discontinuity of  $\Delta$  and increases. That is a behaviour usual in the paraelectric phase.

In fig. 3a, 3b we depict the stress and temperature dependences of  $P_3$ . When  $\sigma_{12}$  increases, the value of polarization and the size of polarization discontinuity  $\Delta P_3$  at  $T = T_c$  decreases. However, at low temperatures, when the saturation takes place, the polarization does not depend on the stress except for a jump at  $\sigma_{12}^0$ .

In figs. 4a and 4b we plot the dependences of elastic constants  $c_{11}^p$  at constant polarization on stress  $\sigma_{12}$  and temperature. At low temperatures ( $T_1=175K$ , curve 1),  $c_{11}^p$  does not depend on temperature (phase II); at higher temperatures the increase in, causes the decrease in  $c_{11}^p$ . At  $\sigma_{12} = \sigma_{12}^0$ , the elastic constant  $c_{11}^p$  decreases with a discontinuity, the values of which  $\Delta^\sigma c_{11}^p$  decreases with temperature. At I-III transition,  $\Delta^\sigma c_{11}^p = 0$ .

In the phase III, the elastic constant increases with stress  $\sigma_{12}$ .  $c_{11}^p$  decreases with temperature at all values of stress, and changes abruptly at  $T = T_c$ . The size of discontinuity increases with stress.

In fig. 5a and 5b the stress and temperature dependences of the coefficient of piezoelectric stress  $e_{31}$ , is shown. The coefficient differs from zero only in the phase II. It decreases with stress, reaching its minimum at the ferroelectric phase transition stress. The value of  $\Delta^T e_{31}$  decreases with temperature and becomes zero at  $T \lesssim 150K$ . At certain value of  $\sigma_{12}$ ,  $e_{31}$  starts to decrease and reaches its minimal value at  $T = T_c$ . This minimal value decreases with pressure. At temperatures lower than 175K the  $e_{31}$  is equal to zero. The coefficient of piezoelectric strain  $d_{31}$  has a similar stress and temperature dependences (see figs.6a,6b).

The stress and temperature dependences of the entropy  $S$  are pre-



sented in figs. 7a and 7b respectively. The entropy increases with stress (curve 2,3); at  $\sigma_{12} = \sigma_{12}^0$ ,  $S$  decreases with a discontinuity of  $\Delta^\sigma S$ . The value of discontinuity decreases with temperature in the phase I and becomes zero at  $T = T_k$  and  $\sigma_{12} = \sigma_{12}^k$ . Further increase in stress (the phase III) causes the decrease in the entropy. At temperatures  $203.1K < T < 219.7K$  and stress, which corresponds to the line, separating the phases I and II, the entropy increases with a discontinuity of  $\Delta^T S$ , and  $\Delta^T S \approx \Delta^\sigma S$ . At temperatures below  $T_c$  (curve 1) and  $\sigma_{12} = \sigma_{12}^0$ , the entropy increases with discontinuity  $\Delta^\sigma S$  and decreases in the phase III. At  $T < 150K$  and stresses  $\sigma_{12} < \sigma_{12}^0$ , the entropy does not depend on stress. At constant stress, an increase in temperature causes an increase in  $S$ , then the discontinuous increase by  $\Delta^T S$  at  $T = T_c$  and, then, a weak linear increase of  $S$  in the phase I. The value of  $\Delta^T S$  slightly decreases with  $\sigma_{12}$ . In the temperature curve of the entropy the discontinuity  $\Delta^\sigma S$  takes place, at  $\sigma_{12} = 6kbar$

The stress and temperature dependences of the static dielectric permittivity  $\varepsilon_3^\varepsilon(0, T, \sigma_{12})$  of a clamped crystal are depicted in figs. 8a and 8b respectively. At  $T > T_c$  (curve 3) the permittivity is a decreasing function of stress (up to  $\sigma_{12}^0$ ); it decreases with a discontinuity at  $\sigma_{12} = \sigma_{12}^0$  (the size of discontinuity  $\Delta^\sigma \varepsilon_3^\varepsilon$  decreases with temperature and becomes zero at the critical point). At temperatures  $203.1K < T < 219.7K$  (curve 2) the permittivity increases with stress, then increases with a discontinuity of  $\Delta^T \varepsilon_3^\varepsilon$  at  $T = T_c$ .  $\varepsilon_3^\varepsilon$  decreases when  $\sigma_{12}$  increases up to  $\sigma_{12}^0$  and decreases with a discontinuity of  $\Delta^\sigma \varepsilon_3^\varepsilon$  at  $\sigma = \sigma_{12}^0$ . At  $T = 175K$  (curve 1) the permittivity increases when  $\sigma_{12}$  increases up to  $\sigma_{12}^0$ . The magnitude of the permittivity at 175K is much smaller than that at 205K (curve 2). At  $\sigma_{12} = \sigma^0$   $\varepsilon_3^\varepsilon$  increases with a discontinuity. In the phase III the permittivity slightly varies with stress. The maximum value of the permittivity increases and its position shifts to lower temperatures when the stress increases up to  $\sigma_{12} = 5, 6kbar$ . At  $\sigma = 6kbar$   $\varepsilon_3^\varepsilon$  decreases linearly with temperature and increases with a small discontinuity at  $\sigma_{12} = \sigma_{12}^0$ . The size of this discontinuity is equal to zero at the critical point.

Let us consider now the stress and temperature dependences of transverse static dielectric permittivities  $\varepsilon_1(O, T, \sigma_{12})$  and  $\varepsilon_2(O, T, \sigma_{12})$ . The value of  $l_a = \nu_1 - \nu_3 = 21K$  parameter, which describes the long-range interactions, is taken from [8], where the transverse properties of the unstrained  $KD_2PO_4$  crystals  $\sigma_{12}$  are studied. The value of  $\psi_a$  can be estimated from  $\psi_a = \frac{1}{\varepsilon_{12}} \left( \frac{T}{2} \frac{1+b\varepsilon_{12}}{a+\frac{b}{\varepsilon_{12}}} - l_a \right)$ . In what follows  $\psi_a = 12000K$ .

In figs. 9a and 9b we show the stress and temperature dependences of  $\varepsilon_1(0, T, \sigma_{12})$ . At  $T > T_c$ ,  $\varepsilon_1$  slightly decreases when the stress increases from zero to  $\sigma_{12}^0$ ; at  $\sigma = \sigma_{12}^0$  it decreases with a discontinuity, the size of

which  $\Delta^\sigma \varepsilon_1$  decreases with temperature and becomes zero at the critical point. The  $\varepsilon_1$  increases with stress, at  $203.1K < T < 219.7K$  and has a discontinuity of  $\Delta^T \varepsilon_1$  at  $T = T_c$ . The  $\varepsilon_1$  slightly decreases when stress increases up to  $\sigma_{12}^0$  and has discontinuity of  $\Delta^\sigma \varepsilon_1$  at  $\sigma_{12} = \sigma_{12}^0$  (curve 2). At  $T = 175K$  (curve 1) the permittivity increases with stress and has a discontinuity at  $\sigma_{12} = \sigma_{12}^0$ . An increase in temperature causes an increase in  $\varepsilon_1$ . In the paraelectric phase, the permittivity  $\varepsilon_1$  linearly decreases with temperature at all strains, and  $\varepsilon_1(0, 001kbar) > \varepsilon_1(5kbar)$ .

The stress and temperature dependences of  $\varepsilon_2(O, T, \sigma_{12})$  are depicted in figs. 10a and 10b, respectively. At  $T > T_c$ , it slightly increases with stress, having a discontinuity at  $\sigma_{12} = \sigma_{12}^0$ . The size of discontinuity decreases with temperature and becomes zero at the critical point. At  $203,1K < T < 219.7K$ ,  $\varepsilon_2$  decreases with stress, has a discontinuity  $\Delta^T \varepsilon_2$  at  $T = T_c$ , then slightly increases and decreases with a discontinuity of  $\Delta^T \varepsilon_2$  at  $\sigma_{12} = \sigma_{12}^0$  (curve 2). At 170 K,  $\varepsilon_2$  also increases with stress up to  $\sigma_{12}^0$ , and has a discontinuity of  $\Delta^\sigma \varepsilon_2$  at  $\sigma_{12} = \sigma_{12}^0$ . In the phase III the permittivity decreases with stress,  $\varepsilon_2(175K) < \varepsilon_2(250K)$ . At stresses  $\sigma_{12} < 5.6kbar$  (curves 1'-4') the increase in temperature in the ferroelectric phase causes the sharp increase in  $\varepsilon_2$ , at  $T = T_c$  the permittivity has a discontinuity, which value  $\Delta^T \varepsilon_2$  increases with stress. In the paraelectric phase,  $\varepsilon_2$  linearly decreases with temperature and  $\varepsilon_2(0, 001kbar) < \varepsilon_2(5kbar)$ . At  $\sigma_{12} = 6kbar$  (curve 5') the permittivity increases with pressure almost linearly, has a discontinuity of  $\Delta^\sigma \varepsilon_2$  at  $\sigma_{12} = \sigma_{12}^0$  ( $\Delta^\sigma \varepsilon_2$  is equal to zero at the critical point). The further increase in temperature causes the decrease in  $\varepsilon_2$ .

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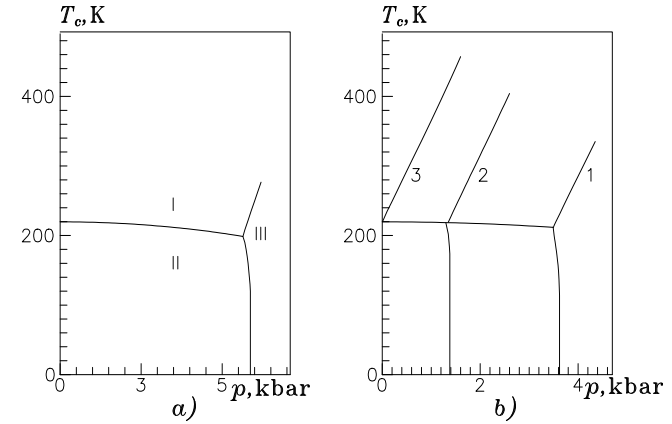


Figure 1: The phase diagrams of a  $KD_2PO_4$  crystal at different values of  $\delta_{12}(K)$ : (a)-30240K; (b): 1-33000, 2-36000, 3-38000.

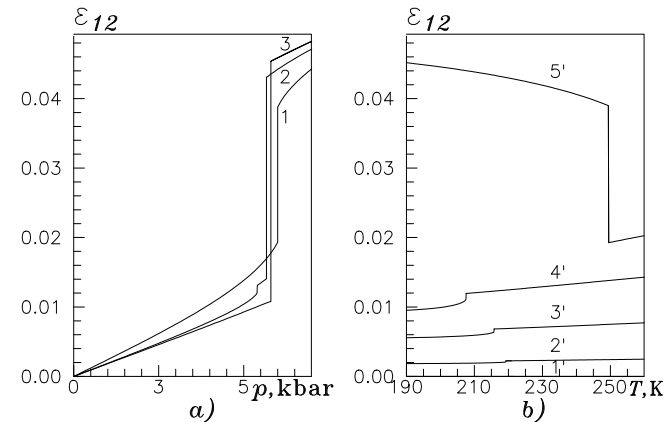


Figure 2: The strain  $\varepsilon_{12}$  of a  $KD_2PO_4$  crystal as a function of: (a) pressure at different temperatures  $T(K)$ : 1-175, 2-205, 3-250; and (b) temperature at different pressures  $p$  (kbar): 1'-0.001, 2'-1, 3'-3, 4'-5, 5'-6.

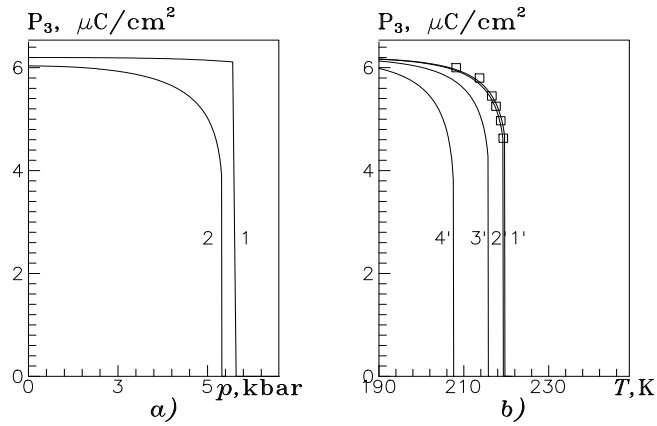


Figure 3: The spontaneous polarization of a  $\text{KD}_2\text{PO}_4$  crystal as a function of: (a) pressure at different temperatures  $T$ (K): 1-175, 2-205; and (b) temperature at different pressures  $p$  (kbar): 1'-0.001, 2'-1, 3'-3, 4'-5.

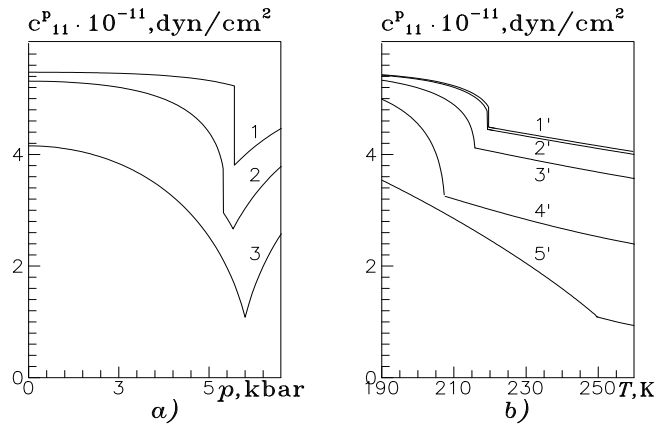


Figure 4: The elastic constants  $c_{11}^p$  of a  $\text{KD}_2\text{PO}_4$  crystal as a function of: (a) pressure at different temperatures  $T$ (K): 1-175, 2-205, 3-250; and (b) temperature at different pressures  $p$  (kbar): 1'-0.001, 2'-1, 3'-3, 4'-5, 5'-6.

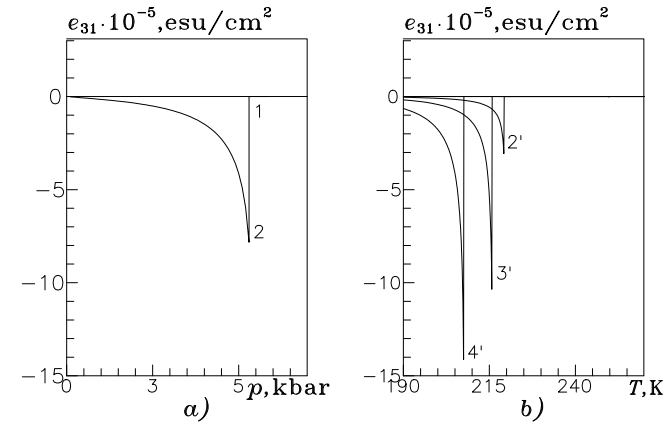


Figure 5: The coefficients of piezoelectric stress  $e_{31}$  of a  $\text{KD}_2\text{PO}_4$  crystal as a function of: (a) pressure at different temperatures  $T$ (K): 1-175, 2-205; and (b) temperature at different pressures  $p$  (kbar): 1'-0.001, 2'-1, 3'-3, 4'-5.

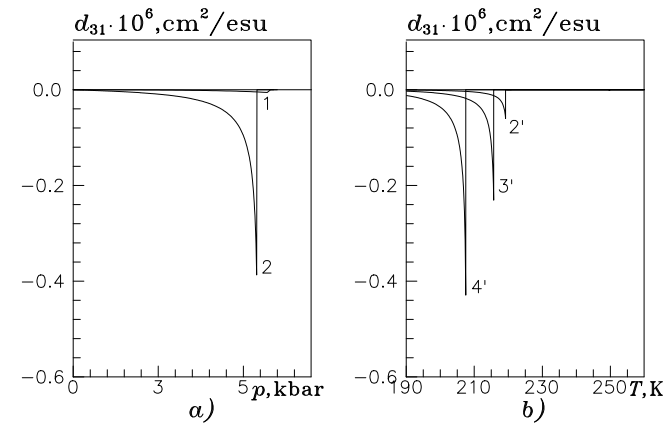


Figure 6: The constants of piezoelectric strain  $d_{31}$  of a  $\text{KD}_2\text{PO}_4$  crystal as a function of: (a) pressure at different temperatures  $T$ (K): 1-175, 2-205; and (b) temperature at different pressures  $p$  (kbar): 1'-0.001, 2'-1, 3'-3, 4'-5.

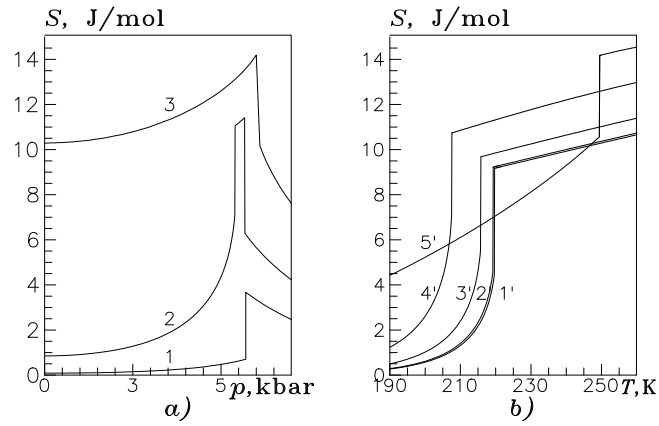


Figure 7: The entropy of a  $\text{KD}_2\text{PO}_4$  crystal as a function of: (a) pressure at different temperatures  $T$  (K): 1–175, 2–205, 3–250; and (b) temperature at different pressures  $p$  (kbar): 1'–0.001, 2'–1, 3'–3, 4'–5, 5'–6.

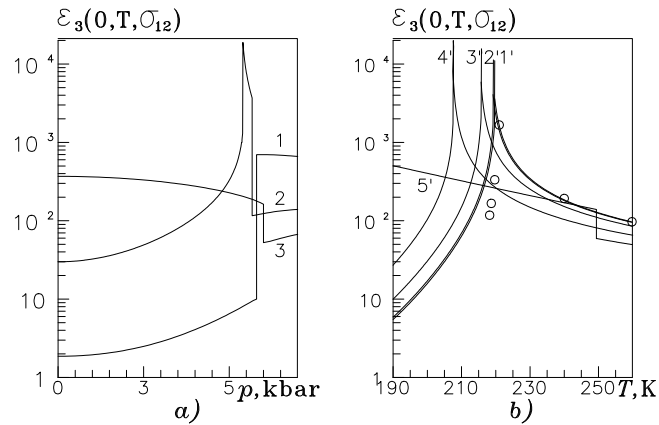


Figure 8: The static dielectric permittivity  $\varepsilon_3^\varepsilon$  of a  $\text{KD}_2\text{PO}_4$  crystal as a function of: (a) pressure at different temperatures  $T$  (K): 1–175, 2–205, 3–250; and (b) temperature at different pressures  $p$  (kbar): 1'–0.001,  $\circ$  [10]; 2'–1; 3'–3; 4'–5; 5'–6.

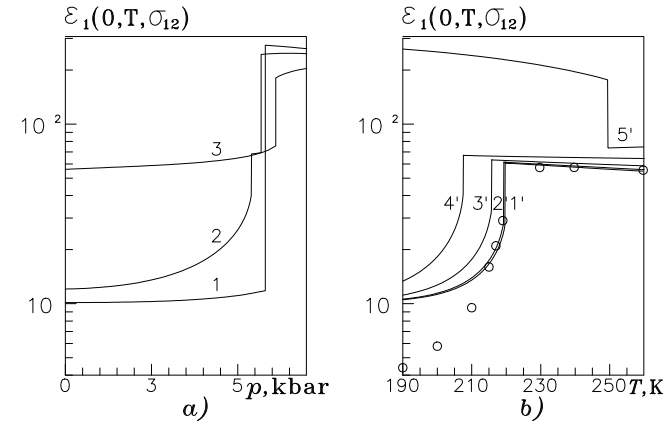


Figure 9: The static dielectric permittivity  $\varepsilon_1$  of a  $\text{KD}_2\text{PO}_4$  crystal as a function of: (a) pressure at different temperatures  $T$  (K): 1–175, 2–205, 3–250; and (b) temperature at different pressures  $p$  (kbar): 1'–0.001,  $\circ$  [11]; 2'–1; 3'–3; 4'–5; 5'–6.

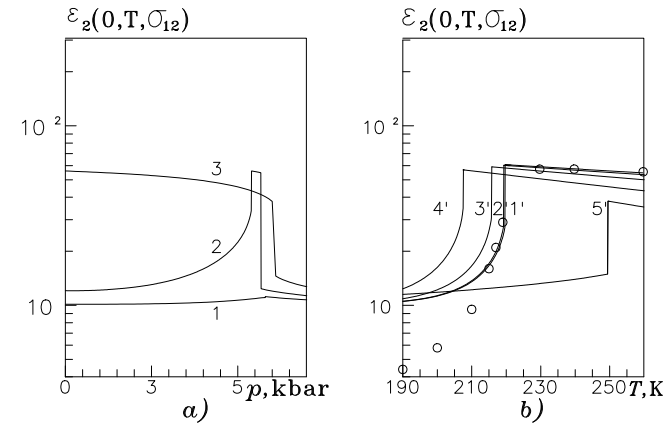


Figure 10: The static dielectric permittivity  $\varepsilon_2$  of a  $\text{KD}_2\text{PO}_4$  crystal as a function of: (a) pressure at different temperatures  $T$  (K): 1–175, 2–205, 3–250; and (b) temperature at different pressures  $p$  (kbar): 1'–0.001,  $\circ$  [11]; 2'–1; 3'–3; 4'–5; 5'–6.

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Вплив одновісного тиску  $\sigma_1 - \sigma_2$  на фазовий перехід і фізичні властивості сегнетоелектриків з водневими зв'язками типу  $\text{KD}_2\text{PO}_4$

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