

THEORY OF PHYSICAL PROPERTIES OF FERRO- AND ANTIFERROELECTRICS OF THE KH_2PO_4 FAMILY RELATED TO STRAINS u_4 AND u_5

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UDC 536, 538.95
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An extension of the proton tunneling model is proposed in order to study piezoelectric, elastic, and dielectric properties of ferro- and antiferroelectrics of the KH_2PO_4 family, which are connected to the shear strains u_4 and u_5 . Expressions for a number of relevant physical characteristics of those crystals in the paraelectric phase are obtained in the four-particle cluster approximation for short-range interactions and in the molecular field approximation for long-range ones. Due to a proper selection of the values for the fitting parameters of the theory, a good agreement between theoretical and experimental results for ferroelectrics KH_2PO_4 and antiferroelectrics $\text{NH}_4\text{H}_2\text{PO}_4$ is achieved.

good agreement of the theory and experiment has been obtained.

Fundamental results for deuterated ferroelectrics of the KDP family, when the strains u_4 and u_5 are present, were obtained in [2, 3]. In those works, strain molecular fields, induced by piezoelectric interaction, were indicated and a splitting, due to the deformations of the configuration energies of deuterons near a PO_4 tetrahedron, was calculated. We shall extend the first result of those works to include the case of ADP-antiferroelectrics. Concerning the second result, we propose another splitting of proton configuration energies around a PO_4 tetrahedron. It differs substantially from that of [2]. The main difference is that in [2], the condition of one proton on one H-bond was required to be held at the energy splitting of single-ionized configurations, separately for each of two PO_4 tetrahedron groups, which differ according to different spatial orientations of tetrahedrons comprised. We think that this demand is more rigorous than it is necessary, with the necessary requirement being the fulfillment of the condition of one proton on one H-bond for all tetrahedrons in whole. Moreover, the energy of lateral configurations was not split in [2].

In general, we propose an extension of the proton tunneling model for the investigation of dielectric, piezoelectric, and elastic properties, connected to the u_4 and u_5 strains, of ferroelectrics and antiferroelectrics of the KDP-family. Relevant physical properties of those crystals in the paraelectric phase are calculated. The results of the proposed theory are compared with corresponding experimental data for KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ crystals.

Introduction

The structure of ferroelectrics of the KH_2PO_4 - (KDP-) type and of antiferroelectrics of the $\text{NH}_4\text{H}_2\text{PO}_4$ - (ADP-) type, which compose a family of KDP crystals, has the symmetry of the non-centrosymmetric point group D_{2d} in the high-temperature paraelectric phase. Therefore, those crystals possess piezoelectric properties. In this work, the physical properties of such crystals, connected to the shear strains $u_4 = 2u_{bc}$ and $u_5 = 2u_{ac}$ in a tetragonal coordinate system (a, b, c) , are studied. The theoretical aspects of the scope of those physical phenomena in the crystals concerned are not developed enough at the microscopic level. In particular, a corresponding extension of the proton tunneling model and a study, within its framework, of dielectric, piezoelectric, and elastic properties of the KDP-family crystals, connected to the shear strains u_4 and u_5 , are dealt with. The urgency of theoretical studies in this direction is caused by a manifestation of the piezoelectric interaction under the action of external electric fields and mechanical stresses of a certain symmetry on the crystal. They are also necessary for investigating striction effects. Note that an extension of the proton tunneling model, taking into account the shear strain $u_6 = 2u_{ab}$, has been proposed in [1]. Relevant physical properties of KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ crystals have been investigated in it, and a

1. Model Hamiltonian of the KDP-Family Crystals under Strains u_4 and u_5

Consider a ferro- or antiferroelectric of the KDP family in the (x, y, z) coordinate system, also denoted as $(1, 2, 3)$, which coincides with a tetragonal $(\bar{1}42d)$

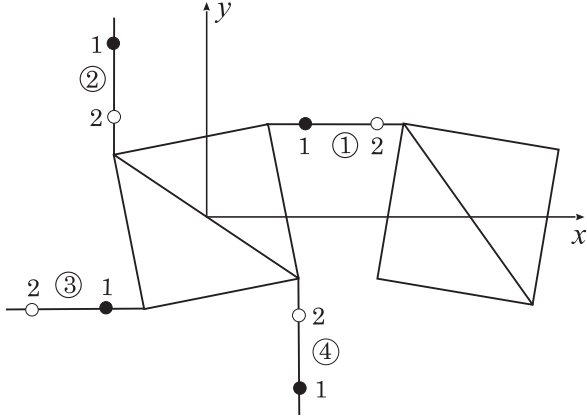


Fig. 1. Scheme of a primitive cell of a KDP-family crystal. Encircled numbers enumerate hydrogen bonds. Non-encircled numbers enumerate possible proton positions [occupied (solid) or empty (hollow)] on a hydrogen bond. One of the possible proton configurations is depicted

crystallographic one (a, b, c) . The mechanical shear stresses $\sigma_4 = \sigma_{yz}$ and $\sigma_5 = \sigma_{xz}$ as well as an electric field $\mathbf{E} = (E_1, E_2, 0)$ are applied to the crystal. They induce independently contributions to the polarization $\mathcal{P} = (\mathcal{P}_1, \mathcal{P}_2, 0)$ and to the corresponding strains u_4 and u_5 of the crystal. Those two strains, for the sake of convenience, will be united into a strain vector $\mathbf{u} = (u_4, u_5, 0)$. Note that the \mathbf{u} strains affect identically both sublattices of the ADP-antiferroelectric. Let the contributions to the Hamiltonian of the proton subsystem, quadratic in strain and field, are negligible.

The total model Hamiltonian \hat{H} of ferro- and antiferroelectrics includes the “bare” and pseudospin parts. The “bare” part describes a lattice of heavy ions and does not depend explicitly on the proton subsystem configuration. The pseudospin part makes allowance for short- and long-range interactions of protons near the PO_4 tetrahedrons, which tunnel along hydrogen bonds, and the effective interaction with the field \mathbf{E} :

$$\hat{H} = N_{\text{p.c.}} U_{\text{bare}} + \hat{H}_{\text{MF}} + \hat{H}_{\text{short}} - 2\Omega \sum_{\mathbf{n}, f} \hat{S}_f^x(\mathbf{n}) - \sum_{\mathbf{n}, f} (\boldsymbol{\mu}_f \mathbf{E}) \hat{S}_f^z(\mathbf{n}). \quad (1)$$

Here, $N_{\text{p.c.}}$ is the total number of primitive cells. A primitive cell is composed by two adjacent PO_4 tetrahedrons with 4 hydrogen bonds belonging to one of them (see Fig. 1). $\hat{S}_f^\alpha(\mathbf{n})$ is an α -component of the pseudospin operator $\hat{\mathbf{S}}_f(\mathbf{n})$, $\alpha = x, z$, $f = 1 \dots 4$, which describes a proton state on the f -th hydrogen bond in

the \mathbf{n} -th primitive cell. The eigenvalues of the operator $\hat{S}_f^z(\mathbf{n}) = \mp \frac{1}{2}$ correspond to two possible equilibrium positions of a proton on the bond (see positions 1 and 2 in Fig. 1). 2Ω is the energy of a proton tunneling along the hydrogen bond. It is taken independent of the shear strains u_4 and u_5 , at each of which the relevant pair of hydrogen bonds rotates without essential changes of its geometrical dimensions. Moreover, taking into account the aspects of symmetry, the dependence of the tunnel energy on such strains can be shown to be only even. $\boldsymbol{\mu}_f = (\mu_f^1, \mu_f^2, \mu_f^3)$ is the effective dipole moment of a primitive cell per one hydrogen bond. Its components obey the relations [4–8]

$$\mu_1^1 = -\mu_3^1 = \mu_1, \quad \mu_2^1 = \mu_4^1 = 0;$$

$$\mu_4^2 = -\mu_2^2 = \mu_2, \quad \mu_1^2 = \mu_3^2 = 0.$$

U_{bare} is the “bare” energy of a primitive cell of the crystal, expressed through the electric field \mathbf{E} and the strains \mathbf{u} [1–3]. It comprises elastic, piezoelectric, and electric parts:

$$U_{\text{bare}} = v \sum_{i=4}^5 \left(C_{ii}^{E0}(T) \frac{u_i^2}{2} - e_{j(i)i}^0 E_{j(i)} u_i - \varepsilon_0 \chi_{j(i)j(i)}^0 \frac{E_{j(i)}^2}{2} \right). \quad (2)$$

Hereafter, for convenience and to write expressions with indices in a compact form, a function $j(i) = i - 3$ is introduced. The parameters $C_{ii}^{E0}(T)$, $e_{j(i)i}^0$, and $\chi_{j(i)j(i)}^0$ are the so-called bare elastic constant, bare piezoelectric tension factor, and bare dielectric susceptibility, respectively, T is the absolute temperature, v is the primitive cell volume, ε_0 is the dielectric constant. The “bare” physical characteristics are responsible for the temperature behavior of ultimate ones in the temperature range far from the phase transition point T_c . On the basis of the analysis of experimental data [9], the “bare” elastic constant $C_{ii}^{E0}(T)$ is taken as follows:

$$C_{ii}^{E0}(T) = c_{ii}^{E0} - \mathcal{K}_{ii}^{\text{para}}(T - T_c)\theta(T - T_c), \quad i = 4, 5,$$

where $\mathcal{K}_{ii}^{\text{para}} \geq 0$ and $\theta(T - T_c)$ is the theta function. The coefficient $\mathcal{K}_{ii}^{\text{para}}$ can be characterized as making allowance, phenomenologically, for the high-temperature anharmonicity of the lattice. The constant c_{ii}^{E0} is

conveniently interpreted as a relevant value of the elastic constant at the phase transition point.

$$\begin{aligned} \hat{H}_{\text{MF}} = & \frac{1}{2} \sum_{\mathbf{n}_1, f_1} \sum_{\mathbf{n}_2, f_2} J_{f_1 f_2}(\mathbf{n}_1, \mathbf{n}_2) \times \\ & \times \langle \hat{S}_{f_1}^z(\mathbf{n}_1) \rangle \langle \hat{S}_{f_2}^z(\mathbf{n}_2) \rangle - \sum_{\mathbf{n}_1, f_1} \times \\ & \times \left(\sum_{\mathbf{n}_2, f_2} J_{f_1 f_2}(\mathbf{n}_1, \mathbf{n}_2) \langle \hat{S}_{f_2}^z(\mathbf{n}_2) \rangle + 2(\boldsymbol{\psi}_{f_1} \mathbf{u}) \right) \hat{S}_{f_1}^z(\mathbf{n}_1) \end{aligned} \quad (3)$$

is the mean field Hamiltonian of long-range dipole-dipole and indirect (mediated by lattice vibrations [10, 11]) interproton interactions and of the mean field that is linear in the strains \mathbf{u} [2, 3] and is induced by the piezoelectric interaction. $\boldsymbol{\psi}_f = (\psi_f^1, \psi_f^2, 0)$ is the vector of parameters of the strain molecular field affecting the f -th hydrogen bond. The components of that vector obey the relations

$$\psi_1^1 = -\psi_3^1 = \psi_4 \geq 0, \quad \psi_2^1 = \psi_4^1 = 0;$$

$$\psi_4^2 = -\psi_2^2 = \psi_5 \geq 0, \quad \psi_1^2 = \psi_3^2 = 0.$$

$$\hat{H}_{\text{short}} = 2 \sum_{\mathbf{n}} \left(\hat{H}_{\text{tetra}}(\mathbf{n}) + \Delta \hat{H}_{4,5}(\mathbf{n}) \right) \quad (4)$$

is the Hamiltonian of short-range interactions between protons near the PO_4 tetrahedrons, linear with respect to the strains. $\hat{H}_{\text{tetra}}(\mathbf{n})$ is the Hamiltonian of the proton interaction near the PO_4 tetrahedron of the KDP-family crystal, and it does not include induced strains. Since all further calculations are carried out for the paraelectric phase, it can be written as follows:

$$\begin{aligned} \hat{H}_{\text{tetra}}(\mathbf{n}) = & V \left[\hat{S}_1^z(\mathbf{n}) \hat{S}_2^z(\mathbf{n}) + \hat{S}_2^z(\mathbf{n}) \hat{S}_3^z(\mathbf{n}) + \right. \\ & \left. + \hat{S}_3^z(\mathbf{n}) \hat{S}_4^z(\mathbf{n}) + \hat{S}_1^z(\mathbf{n}) \hat{S}_4^z(\mathbf{n}) \right] + \\ & + U \left[\hat{S}_1^z(\mathbf{n}) \hat{S}_3^z(\mathbf{n}) + \hat{S}_2^z(\mathbf{n}) \hat{S}_4^z(\mathbf{n}) \right] + \Phi \prod_{f=1}^4 \hat{S}_f^z(\mathbf{n}). \end{aligned} \quad (5)$$

The proton correlation energies U, V, Φ around the tetrahedron are connected to the ferroelectric energies ε, w, w_1 of the extended Slater–Takagi model [10, 12]:

$$U = -\varepsilon + \frac{1}{2} w_1, \quad V = -\frac{1}{2} w_1, \quad \Phi = 4\varepsilon - 8w + 2w_1,$$

which are introduced on the basis of the configuration energies

$$\varepsilon = \bar{\varepsilon}_a - \bar{\varepsilon}_s, \quad w = \bar{\varepsilon}_1 - \bar{\varepsilon}_s, \quad w_1 = \bar{\varepsilon}_0 - \bar{\varepsilon}_s.$$

To describe the antiferroelectric ordering of the ADP type in the proton model, other corresponding energies are introduced [12]:

$$\tilde{\varepsilon} = \bar{\varepsilon}_s - \bar{\varepsilon}_a, \quad \tilde{w} = \bar{\varepsilon}_1 - \bar{\varepsilon}_a, \quad \tilde{w}_1 = \bar{\varepsilon}_0 - \bar{\varepsilon}_a.$$

The correspondence between ferro- and antiferroelectric energies is easy to write:

$$\varepsilon = -\tilde{\varepsilon}, \quad w = \tilde{w} - \tilde{\varepsilon}, \quad w_1 = \tilde{w}_1 - \tilde{\varepsilon}, \quad (6)$$

which may lead to the expressions for the energies U, V, Φ in the antiferroelectric approach. Moreover, this correspondence makes it possible to use theoretical results of ferro- and antiferroelectric approaches simultaneously for the ferro- and antiferroelectric crystals of the KDP family in the phase of their structural isomorphism.

A correction $\Delta \hat{H}_{4,5}(\mathbf{n})$ to the Hamiltonian of the proton configuration interactions near the PO_4 tetrahedron, which is linear in u_4 and u_5 , was obtained as a result of the consideration of all possible linear splittings of proton configuration energies $\bar{\varepsilon}_s, \bar{\varepsilon}_a, \bar{\varepsilon}_1, \bar{\varepsilon}_0$ near it (see Table 1) which are stipulated by a symmetry of those strains.

The Hamiltonian $\Delta \hat{H}_{4,5}(\mathbf{n})$ equals the total configuration energy of the protons near the tetrahedron, $\sum_{s_1 s_2 s_3 s_4} \hat{N}_{s_1 s_2 s_3 s_4}(\mathbf{n}) \delta \Lambda_{4,5}(s_1 s_2 s_3 s_4)$, but the proton energy in a strain molecular field

$$\begin{aligned} & -\frac{\delta_{a4} + \delta_{14}}{2} u_4 \left(\hat{S}_1^z(\mathbf{n}) - \hat{S}_3^z(\mathbf{n}) \right) - \\ & -\frac{\delta_{a5} + \delta_{15}}{2} u_5 \left(\hat{S}_4^z(\mathbf{n}) - \hat{S}_2^z(\mathbf{n}) \right), \end{aligned}$$

which is allowed for in \hat{H}_{MF} : $\psi_i = \psi_{0i} + (\delta_{ai} + \delta_{1i})/2$. Here, ψ_{0i} has the sense of a strain molecular field parameter, existing in [2, 3].

$\hat{N}_{s_1 s_2 s_3 s_4}(\mathbf{n}) = \prod_{f=1}^4 \left(\frac{1}{2} + s_f \hat{S}_f^z(\mathbf{n}) \right)$ is the operator of a four-particle configuration [10, 12], where s_f stands for the sign of an eigenvalue of the $\hat{S}_f^z(\mathbf{n})$ operator in

a specific “ $s_1s_2s_3s_4$ ” configuration: $s_f = “+”$ or “ $-$ ”. Therefore, the Hamiltonian $\Delta\hat{H}_{4,5}(\mathbf{n})$ reads:

$$\begin{aligned} \Delta\hat{H}_{4,5}(\mathbf{n}) = & -4\delta_{1a4}u_4 \left[\hat{S}_1^z(\mathbf{n})\hat{S}_2^z(\mathbf{n})\hat{S}_4^z(\mathbf{n}) - \right. \\ & \left. -\hat{S}_2^z(\mathbf{n})\hat{S}_3^z(\mathbf{n})\hat{S}_4^z(\mathbf{n}) \right] - \\ & -4\delta_{1a5}u_5 \left[\hat{S}_1^z(\mathbf{n})\hat{S}_3^z(\mathbf{n})\hat{S}_4^z(\mathbf{n}) - \hat{S}_1^z(\mathbf{n})\hat{S}_2^z(\mathbf{n})\hat{S}_3^z(\mathbf{n}) \right]. \end{aligned} \quad (7)$$

We note that, for the consistent reproduction of the piezoelectric phenomenon in the framework of those model speculations, the inequality $\psi_i \geq |\delta_{1ai}|$ must be held. The parameter $\delta_{1ai} = (\delta_{1i} - \delta_{ai})/2$ may be of an arbitrary finite value.

2. Four-Particle Cluster Approximation

Strong short-range correlations in the KDP-family crystals, together with the lattice structure features, make it natural to use the four-particle cluster approximation for short-range interactions [10,12] when calculating the electric thermodynamic potential (the Gibbs electric function). For long-range interactions, the molecular field approximation has been already done. In those approximations, the electric thermodynamic potential of the KDP-family crystal per a primitive cell has the form

$$\begin{aligned} g_{2E}(T, u_i, E_{j(i)}, X, P_{in.f}, X_{in.f}) = \\ = U_{\text{bare}} + \frac{1}{8} \sum_{f_1, f_2} J_{f_1 f_2}(0) P_{in.f_1} P_{in.f_2} - \\ - \frac{2}{\beta} \ln \frac{Z_4}{4} - \frac{1}{2\beta} \sum_{f=1}^4 \ln(1 - Q_f^2) \end{aligned} \quad (8)$$

in the paraelectric phase, where $Q_f = \sqrt{P_{in.f}^2 + (X + X_{in.f})^2}$, $\beta = 1/(k_B T)$, k_B is the Boltzmann constant, $J_{f_1 f_2}(0)$ is a Fourier-transformation matrix of the long-range interactions, $J_{f_1 f_2}(0) = \sum_{\mathbf{n}_1 - \mathbf{n}_2} J_{f_1 f_2}(\mathbf{n}_1, \mathbf{n}_2)$, $Z_4 = \text{Sp} \left[e^{-\beta \hat{H}_4} \right]$ is the four-particle statistical sum. The four-particle Hamiltonian \hat{H}_4 is given by

$$\hat{H}_4 = \hat{H}_{\text{tetra}} + \Delta\hat{H}_{4,5} + 2\Gamma \sum_{f=1}^4 \hat{S}_f^x +$$

$$+ \sum_{f=1}^4 \left(\eta_{in.f} \hat{S}_f^x + C_{in.f} \hat{S}_f^z \right). \quad (9)$$

Here, \hat{H}_{tetra} and $\Delta\hat{H}_{4,5}$ designate Hamiltonians (5) and (7), respectively, without the dependence on \mathbf{n} , Γ is a variational field independent of external factors, while $C_{in.f}$ and $\eta_{in.f}$ are induced variational fields ($C_{in.f}|_{\mathbf{E}=0, \mathbf{u}=0} = 0$, $\eta_{in.f}|_{\mathbf{E}=0, \mathbf{u}=0} = 0$). Note that, when deriving the electric thermodynamic potential (8), the relations

$$\langle 2\hat{S}_f^x(\mathbf{n}) \rangle = X + X_{in.f}, \quad \langle 2\hat{S}_f^z(\mathbf{n}) \rangle = P_{in.f},$$

$$X_{in.f} \Big|_{\substack{\mathbf{E}=0 \\ \mathbf{u}=0}} = 0, \quad P_{in.f} \Big|_{\substack{\mathbf{E}=0 \\ \mathbf{u}=0}} = 0$$

were taken into consideration.

The unknown variables X , $P_{in.f}$, and $X_{in.f}$ are determined by minimizing potential (8):

$$\frac{\partial g_{2E}}{\partial X} \Big|_{\substack{\mathbf{E}=0 \\ \mathbf{u}=0}} = 0, \quad \frac{\partial g_{2E}}{\partial P_{in.f}} = \frac{\partial g_{2E}}{\partial X_{in.f}} = 0. \quad (10)$$

For further calculations, an expression for the four-particle statistical sum is needed. Let us write it down as follows: $Z_4 = \sum_{i=1}^{16} e^{-\beta(\mathcal{E}_{pi} + \mathcal{E}_{in.i})}$. Here, \mathcal{E}_{pi} are the eigenvalues of the Hamiltonian $\hat{H}_4|_{\mathbf{E}=0, \mathbf{u}=0}$. The method of calculations and their results can be found elsewhere [7,8]. $\mathcal{E}_{in.i}$ is a contribution to the Hamiltonian (9)

T a b l e 1. Splitting of the proton configuration energies near a PO_4 tetrahedron of the KDP-family crystal, stipulated by the shear strains u_4 and u_5 . (The coefficients δ_{ai} and δ_{1i} were selected to provide $\delta_{a4} = \delta_{a5} \geq 0$ and $\delta_{14} = \delta_{15} \geq 0$)

Configuration “ $s_1s_2s_3s_4$ ”	Energy	Energy variation $\delta\Lambda_{4,5}(s_1s_2s_3s_4)$
“++++”	ε_s	0
“----”		0
“+- -+”	ε_a	$-\delta_{a4}u_4 - \delta_{a5}u_5$
“-+ +-”		$\delta_{a4}u_4 + \delta_{a5}u_5$
“- - ++		$\delta_{a4}u_4 - \delta_{a5}u_5$
“+ + --”		$-\delta_{a4}u_4 + \delta_{a5}u_5$
“- + ++”	ε_1	$\delta_{14}u_4$
“+ - ++”		$-\delta_{15}u_5$
“+ + -+”		$-\delta_{14}u_4$
“+ + +-”		$\delta_{15}u_5$
“- - -+”		$-\delta_{15}u_5$
“- - +-”		$\delta_{14}u_4$
“- + --”		$\delta_{15}u_5$
“+ - --”		$-\delta_{14}u_4$
“- + -+”	ε_0	0
“+ - +-”		0

eigenvalues, dependent on external factors, with $\mathcal{E}_{\text{in},i}|\mathbf{E}=0,\mathbf{u}=0 = 0$. For further calculations, it is enough to find it to an accuracy of the second order in the fields $C_{\text{in},f}$ and $\eta_{\text{in},f}$.

Using the conditions of minimum (10), we get a system of transcendental equations for the variables $P_{\text{in},f}$ and $X_{\text{in},f}$:

$$P_{\text{in},f} = -\frac{2}{\beta Z_4} \frac{\partial Z_4}{\partial C_{\text{in},f}},$$

$$X_{\text{in},f} = -\frac{2}{\beta Z_4} \frac{\partial Z_4}{\partial \eta_{\text{in},f}} - X. \quad (11)$$

The fields $C_{\text{in},f}$ and $\eta_{\text{in},f}$, contained in that system, are found by resolving the equations for the single-particle average values of pseudospins:

$$C_{\text{in},f} = \frac{P_{\text{in},f}}{2\beta Q_f} \ln \frac{1-Q_f}{1+Q_f} - \frac{1}{4} \sum_{f_1=1}^4 J_{ff_1}(0) P_{\text{in},f_1} - (\psi_f \mathbf{u}) - \frac{1}{2} (\boldsymbol{\mu}_f \mathbf{E}),$$

$$\eta_{\text{in},f} = \frac{X + X_{\text{in},f}}{2\beta Q_f} \ln \frac{1-Q_f}{1+Q_f} - 2\Gamma - \Omega. \quad (12)$$

In the limits $\mathbf{E} \rightarrow 0$ and $\mathbf{u} \rightarrow 0$ in Eqs. (11) and expressions (12), we deduced an equation for X and an expression for Γ . They are coincide with those in [7, 8].

3. Dielectric, Piezoelectric, and Elastic Properties

Let us calculate dielectric, piezoelectric, and elastic properties of the KDP-family crystals in the paraelectric phase. This calculation was performed starting from the equations of state and on the basis of the system of equations (11).

Putting down the dielectric and elastic equations of state from the electric thermodynamic potential (8)

$$\mathcal{P}_{j(i)} = -\frac{1}{\bar{v}} \left(\frac{\partial g_{2E}}{\partial E_{j(i)}} \right)_{T,u},$$

$$\sigma_i = \frac{1}{\bar{v}} \left(\frac{\partial g_{2E}}{\partial u_i} \right)_{T,E}, \quad i = 4, 5,$$

where \bar{v} is a primitive cell volume in the paraphase, the expressions for the equilibrium polarization $\mathcal{P}_{j(i)}$ and the

equilibrium stress σ_i are

$$\mathcal{P}_{j(i)} = e_{j(i)i}^0 u_i + \varepsilon_0 \chi_{j(i)j(i)}^0 E_{j(i)} + \frac{1}{2\bar{v}} \sum_{f=1}^4 P_{\text{in},f} \mu_f^{j(i)} \quad (13)$$

and

$$\sigma_i = C_{ii}^{E0}(T) u_i - e_{j(i)i}^0 E_{j(i)} - \frac{1}{\bar{v}} \sum_{f=1}^4 P_{\text{in},f} \psi_f^{j(i)} - \frac{2}{\bar{v}\beta Z_4} \frac{\partial Z_4}{\partial u_i}, \quad (14)$$

respectively.

From (13) and (14), making use of system (11), we found the isothermal dielectric susceptibility of a free crystal ($\sigma_i = \text{const}$):

$$\chi_{j(i)j(i)}^{T\sigma} = \frac{1}{\varepsilon_0} \left(\frac{\partial \mathcal{P}_{j(i)}}{\partial E_{j(i)}} \right)_{T,\sigma} \Bigg|_{\substack{\mathbf{E}=0 \\ \mathbf{u}=0}} =$$

$$= \chi_{j(i)j(i)}^{Tu} + \frac{(e_{j(i)i}^T)^2}{\varepsilon_0 C_{ii}^{TE}}, \quad i = 4, 5, \quad (15)$$

which is expressed through the isothermal dielectric susceptibility of a strained crystal ($u_i = \text{const}$)

$$\chi_{j(i)j(i)}^{Tu} = \frac{1}{\varepsilon_0} \left(\frac{\partial \mathcal{P}_{j(i)}}{\partial E_{j(i)}} \right)_{T,u} \Bigg|_{\substack{\mathbf{E}=0 \\ \mathbf{u}=0}} =$$

$$= \chi_{j(i)j(i)}^0 + \frac{\mu_{j(i)}^2}{2\varepsilon_0 \bar{v}} \frac{\mathcal{R}_1(1,1,1)}{\mathcal{R}_1(1,1,1) \bar{A}_{1\nu_1} - 1}, \quad (16)$$

the isothermal piezoelectric tension factor

$$e_{j(i)i}^T = - \left(\frac{\partial \sigma_i}{\partial E_{j(i)}} \right)_{T,u} \Bigg|_{\substack{\mathbf{E}=0 \\ \mathbf{u}=0}} =$$

$$= \left(\frac{\partial \mathcal{P}_{j(i)}}{\partial u_i} \right)_{T,E} \Bigg|_{\substack{\mathbf{E}=0 \\ \mathbf{u}=0}} =$$

$$= e_{j(i)i}^0 + \frac{\mu_{j(i)}}{\bar{v}} \frac{\delta_{1ai} \mathcal{R}_1(-1,1,-1) + \psi_i \mathcal{R}_1(1,1,1)}{\mathcal{R}_1(1,1,1) \bar{A}_{1\nu_1} - 1}, \quad (17)$$

and the isothermal elastic constant at a fixed field

$$c_{ii}^{TE} = \left(\frac{\partial \sigma_i}{\partial u_i} \right)_{T,E} \bigg|_{\substack{\mathbf{E} = 0 \\ \mathbf{u} = 0}} = c_{ii}^{E0} - \mathcal{K}_{ii}^{\text{para}}(T - T_c)\theta(T - T_c) - \left[\frac{\psi_i^2 \mathcal{R}_1(1, 1, 1) + 2\psi_i \delta_{1ai} \mathcal{R}_1(-1, 1, -1) + \delta_{1ai}^2 \mathcal{R}_1^2(-1, 1, -1) \bar{A}_{1\nu_1}}{\mathcal{R}_1(1, 1, 1) \bar{A}_{1\nu_1} - 1} - \delta_{1ai}^2 \mathcal{R}_1(-1, -1, 1) \right] \frac{2}{\bar{v}}. \quad (18)$$

Here, the following notations are introduced:

$$\mathcal{R}_1(s_1, s_2, s_3) = \frac{1}{Z_4} \left\{ \sum_{i=7}^8 [\varkappa(\mathcal{E}_{pi}, w) \mathcal{U}_6^2(\mathcal{E}_{pi} - \varepsilon) + s_3 2\varkappa(\mathcal{E}_{pi}, \varepsilon) \mathcal{U}_5^2(\mathcal{E}_{pi} - \varepsilon)] + \sum_{i=1}^4 \sum_{j=7}^8 \varkappa(\mathcal{E}_{pi}, \mathcal{E}_{pj}) \prod_{k=1}^2 [\sqrt{2} \mathcal{U}_2(\mathcal{E}_{pi}) \mathcal{U}_5(\mathcal{E}_{pj} - \varepsilon) + s_k \mathcal{U}_3(\mathcal{E}_{pi}) \mathcal{U}_6(\mathcal{E}_{pj} - \varepsilon)] + \sum_{i=5}^6 \varkappa(\mathcal{E}_{pi}, w) \mathcal{U}_6^2(\mathcal{E}_{pi}) + \sum_{i=14}^{15} \varkappa(\mathcal{E}_{pi}, w) \mathcal{U}_6^2(\mathcal{E}_{pi} - w_1) \right\},$$

$$\varkappa(\lambda_1, \lambda_2) = \frac{e^{-\beta\lambda_1} - e^{-\beta\lambda_2}}{\lambda_1 - \lambda_2}, \quad \mathcal{U}_2(\lambda) = \frac{2\sqrt{2}\Gamma\lambda(\lambda - w_1)}{\Phi(\lambda)},$$

$$\mathcal{U}_3(\lambda) = \frac{\lambda(\lambda - \varepsilon)(\lambda - w_1)}{\Phi(\lambda)}, \quad \mathcal{U}_5(\lambda) = \frac{2\Gamma}{\sqrt{4\Gamma^2 + \lambda^2}},$$

$$\mathcal{U}_6(\lambda) = \frac{\lambda}{\sqrt{4\Gamma^2 + \lambda^2}},$$

$$\Phi(\lambda) = \left\{ (\lambda - \varepsilon)^2 (\lambda - w_1)^2 (4\Gamma^2 + \lambda^2) + \right.$$

$$\left. + 4\lambda^2 \Gamma^2 [2(\lambda - w_1)^2 + (\lambda - \varepsilon)^2] \right\}^{\frac{1}{2}},$$

$$\bar{A}_{1\nu_1} = \frac{1}{2\beta X} \ln \frac{1 - X}{1 + X} - \frac{\nu_1}{4}, \quad \nu_1 = J_{11}(0) - J_{13}(0).$$

Other isothermal piezoelectric and elastic characteristics for this case can be calculated using the already found parameters and taking advantage of the well-known formulae (see, e.g., [9]). Thus, we obtained a full kit of physical parameters for the paraelectric phase, which describe dielectric, piezoelectric, and elastic properties of ferro- and antiferroelectrics of the KDP family, providing the strains u_4 and u_5 . Note that all calculated characteristics, related to the strain u_4 , coincide with their counterparts related to the strain u_5 if the relevant parameters of the theory are equal. Note also that the dielectric susceptibility (16) is identical to the relevant results of [7, 8, 13].

4. Numerical Analysis and Comparison with Experiment. Discussion of the Results Obtained

Numerical analysis aims at the most accurate theoretical description of the experimental data concerned for KH_2PO_4 ferroelectrics and $\text{NH}_4\text{H}_2\text{PO}_4$ antiferroelectrics in the paraelectric phase.

The optimal values of the parameters Ω , ε , w , and ν_1 for a KH_2PO_4 crystal and the parameters Ω , $\tilde{\varepsilon}$, \tilde{w} , and ν_1 for a $\text{NH}_4\text{H}_2\text{PO}_4$ one are taken from [7, 8] and [13], respectively. They provide a good description of the phase transition, thermal and dielectric characteristics of those crystals, beyond taking into account the piezoelectric interaction. Therefore, those values were selected for current calculations. In so doing, the values of the parameters ε and w for a $\text{NH}_4\text{H}_2\text{PO}_4$ crystal were reevaluated through the relevant values of the parameters $\tilde{\varepsilon}$ and \tilde{w} , making use of formulae (6). The parameter w_1 , similarly to what has been done in [7, 8, 13], was determined according to the relation $w_1 = 4w - 2\varepsilon$, which corresponds to the equation $\Phi = 0$. Note that the selected values of the theoretical parameters lead to the following temperatures of phase transitions in crystals: $T_c = 122.751$ K in KH_2PO_4 [7, 8] and $T_c = 148$ K in $\text{NH}_4\text{H}_2\text{PO}_4$ [13].

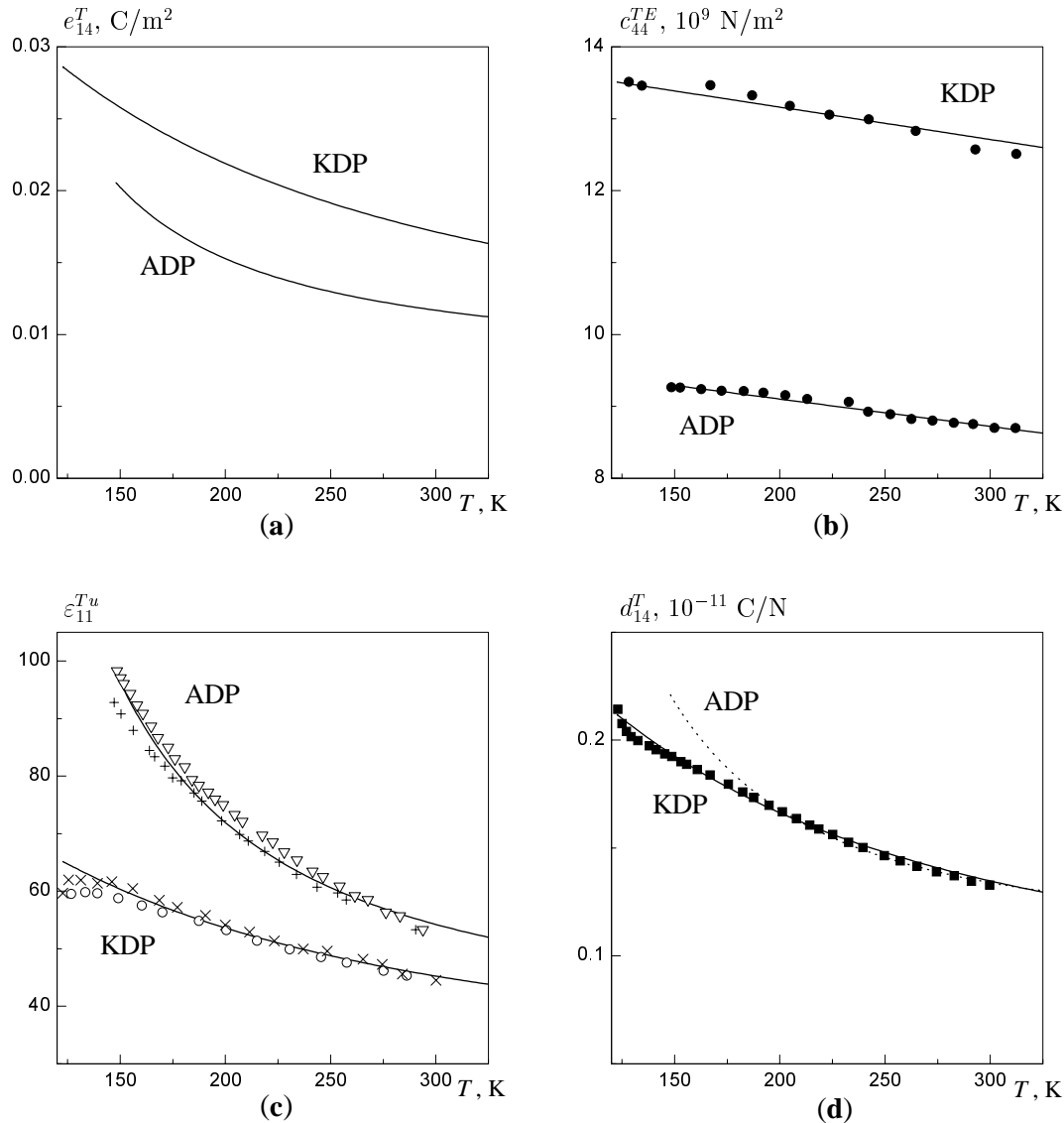


Fig. 2. Temperature dependences of the piezoelectric, elastic, and dielectric physical characteristics of KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ crystals in the paraelectric phase. Experimental data: \bullet [9], \circ [5], \times [16], ∇ [17], $+$ [18], \blacksquare [19]

The parameters ψ_4 and δ_{1a4} were determined providing the best fit of the theoretical results to relevant experimental data, the majority of them being depicted in Fig. 2. The remaining theoretical parameters were evaluated simultaneously. In so doing, the constant c_{44}^{E0} and the factor $\mathcal{K}_{44}^{\text{para}}$ were determined according to the most accurate consistence of theoretical and experimental results for the temperature dependence of the elastic constant c_{44}^{TE} near T_c ($T - T_c \leq 20$ K) and far from T_c ($T - T_c > 20$ K), respectively. In turn, the “bare” constants e_{14}^0 and χ_{11}^0 were determined from the experimental temperature dependences of the

piezofactor e_{14}^T [9, 20] and the dielectric permittivity $\epsilon_{11}^{Tu} = 1 + \chi_{11}^{Tu}$, respectively, in a high-temperature region far from T_c . The following values for the primitive cell volume have been taken: $\bar{v} = 191.127 \times 10^{-30}$ m³ in KDP crystals [14] and $\bar{v} = 210.994 \times 10^{-30}$ m³ in ADP ones [15]. The values of the theoretical parameters for the KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ crystals are quoted in Table 2.

In Fig. 2, the temperature dependences of “principal” characteristics, namely, piezoelectric e_{14}^T , elastic c_{44}^{TE} , and dielectric ϵ_{11}^{Tu} ones, for KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ crystals are shown, as well as a piezomodulus d_{14}^T

Table 2. Values of theoretical parameters for KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ crystals

Crystal	w , K	ε , K	Ω , K	ν_1 , K	ψ_4 , K	δ_{1a4} , K	c_{44}^{E0} , $10^9 \frac{\text{N}}{\text{m}^2}$	$\mathcal{K}_{44}^{\text{para}}$, $10^9 \frac{\text{N}}{\text{m}^2 \cdot \text{K}}$	e_{14}^0 , $\frac{\text{C}}{\text{m}^2}$	χ_{11}^0	μ_1 , $10^{-30} \text{ C} \cdot \text{m}$
KH_2PO_4	600	55	138	40	30	5	13.51	0.0045	0.0065	25.6	13.07
$\text{NH}_4\text{H}_2\text{PO}_4$	530	-40	84	70	10	2	9.3	0.0038	0.0075	32.8	12.12

calculated making use of them. In general, we have a good agreement between the theory and experiment. Theoretical values of the piezomodulus d_{14}^T at ambient temperature coincide well with relevant experimental data [9, 20] for both crystals. From Fig. 2, it is seen that, near T_c , the temperature behaviors of the depicted dielectric and piezoelectric constants of the ADP crystal are sharper than those of the KDP one.

Note that, in a high-temperature region far from T_c , it is impossible to fit well the theoretical elastic constant c_{44}^{TE} at $\mathcal{K}_{44}^{\text{para}} = 0$ with experiment, because it saturates in this case ($c_{44}^{TE} \rightarrow c_{44}^{E0}$). It means that the lattice anharmonicity, taken into account phenomenologically, plays an important role at such temperatures.

A distinction between the theoretical temperature dependences of the dielectric permittivities $\varepsilon_{11}^{T\sigma} = 1 + \chi_{11}^{T\sigma}$ and ε_{11}^{Tu} for the KDP and ADP crystals is very small. It amounts no more than 0.02% of the permittivities themselves. Such a distinction is unnoticeable experimentally. It is also the case for the theoretical values of the elastic constants c_{44}^{TE} and c_{44}^{TP} of those crystals.

Concluding Remarks

In this work, an extension of the proton tunneling model, which makes it possible to study, in a linear approximation, the influences of the stresses σ_4 , σ_5 and the electric field $\mathbf{E} = (E_1, E_2, 0)$ on physical characteristics of ferro- and antiferroelectrics of the KDP family, has been proposed. The extended model makes allowance, at the microscopic level, for the contribution to the proton subsystem energy linear in the strains u_4 and u_5 . A high-temperature anharmonicity of the lattice in the paraelectric phase is taken into account phenomenologically.

In general, this model, provided the proper selection of the theoretical parameter values is done, makes it possible to describe adequately and quantitatively the experimental data concerning the temperature dependences of the full kit of dielectric, piezoelectric, and elastic parameters, connected to the strains u_4 and u_5 , of the KH_2PO_4 ferroelectrics and $\text{NH}_4\text{H}_2\text{PO}_4$ antiferroelectrics in the paraelectric phase.

To summarize, it should be noted that, for an adequate reproduction of the complete physical picture of piezoelectric and elastic phenomena in ferro- and antiferroelectric phases of the KDP-family crystals, a striction has to be taken into account.

This work was supported by the State Foundation for Fundamental Investigations of the Ukrainian Ministry in Affairs of Science and Technology (Project No.02.07/00310).

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Received 01.07.03.

Translated from Ukrainian by O.I.Voitenko

ТЕОРІЯ ПОВ'ЯЗАНИХ З ДЕФОРМАЦІЯМИ u_4 І u_5
 ФІЗИЧНИХ ВЛАСТИВОСТЕЙ СЕГНЕТО-
 І АНТИСЕГНЕТОЕЛЕКТРИКІВ СІМ'Ї KN_2PO_4

Б.М. Лісний, Р.Р. Левуцький

Р е з ю м е

Запропоновано розвинення протонної моделі з тунелюванням для дослідження п'єзоелектричних, пружних та діе-

лектричних властивостей, які пов'язані із зсувними деформаціями u_4 та u_5 , сегнетоелектриків і антисегнетоелектриків сім'ї KN_2PO_4 . В наближенні чотиричастинкового кластера за короткодійними та молекулярного поля за далекодійними взаємодіями отримано вирази для відповідного ряду фізичних характеристик цих кристалів у параелектричній фазі. Належним вибором значень параметрів теорії досягнуто доброго узгодження теоретичних та експериментальних результатів для сегнетоелектрика KN_2PO_4 і антисегнетоелектрика $\text{NH}_4\text{H}_2\text{PO}_4$.