

External pressure influence on ferroelectrics and antiferroelectrics of the KH_2PO_4 family: A unified model

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Within the four-particle cluster approximation for the proton ordering model, we study effects of external pressures which do not lower the crystals symmetry on deuterated ferroelectrics and antiferroelectrics of KH_2PO_4 family. The theory provides a satisfactory description of the available experimental data for transition temperature and static dielectric properties of the crystals and the experimentally observed universality of the transition temperature vs D-site distance dependence. Importance of the D-site distance in the phase transition and dielectric response of the hydrogen bonded crystals is shown. [S0163-1829(99)00813-9]

Potassium dihydrogen phosphate KH_2PO_4 (KDP) is a prototype for a well-known family of hydrogen bonded crystals undergoing ferroelectric or antiferroelectric structural phase transitions. For years, since the so-called proton ordering (or tunneling) model was proposed in 1966,^{1,2} it has been generally accepted that these phase transitions are triggered by ordering of protons on hydrogen bonds. This ordering leads to displacements of heavy ions, hence the spontaneous polarization arises. The tunneling model also easily explains the observed isotope effects in these crystals—an increase in the transition temperature with deuteration—attributing it to a decrease in tunneling integral as protons are replaced with deuterons. The subsequent results of Raman scattering experiments,^{3,4} however, raised serious doubts about the validity of the proton ordering model. Another approach was proposed,⁵ according to which not just protons, but the whole H_2PO_4 groups, play the role of ordering units. There is also the theory of the so-called geometric isotope effect, in which the shift in the transition temperature with deuteration is attributed not to the decrease in tunneling, but to the changes in the geometry of hydrogen bonds, namely, to an increase in the separation δ between two possible hydrogen sites on a bond and/or in H-bond length. Nevertheless, the tunneling model still remains the most elaborated and widely used approach to the description of the phase transitions in the KDP family crystals, including also mixed crystals of $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ type^{6,7} where the spin-glass phase is found.

Naturally, the high-pressure studies are not able to unambiguously establish the mechanism of the phase transitions in these crystals. However, since they are the only means to continuously vary the hydrogen bonds parameters as well as the interparticle interactions in the system, the pressure studies happen to be the best tool to study the dependences of crystal characteristics on the H-bond geometry and, thereby, to explore the role of hydrogen bonds subsystem in the physics involved.

For instance, it is known that hydrostatic pressure reduces the transition temperatures in all KDP-type crystals,⁸ as well as the H-site distance and the H-bond length.^{9,10} By means of neutron-scattering technique, Nemes *et al.*¹¹ found out that in four crystals of this family having a three-dimensional

network of hydrogen bonds, namely KDP, KD_2PO_4 (DKDP), and two antiferroelectrics $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) and $\text{ND}_4\text{D}_2\text{PO}_4$ (DADP), the dependences of transition temperatures on H-site distances almost coincide, that is, the isotope effect in these crystals is suppressed when δ is kept constant. Furthermore, it was asserted that in crystals with one-dimensional (PbHPO_4), two-dimensional (squaric acid $\text{H}_2\text{C}_4\text{O}_4$), and three-dimensional (the above-mentioned KDP, DKDP, ADP, and DADP) H-bonds network, transition temperature falls to zero at the same value of δ of approximately 0.2 Å.

Usually, the decrease in the transition temperature in KDP family crystals with pressure is explained within the proton ordering (tunneling) model in the mean-field approximation assuming a decrease in the parameter of hydrogen-hydrogen interaction J and an increase in the tunneling integral (see the book by Blinc¹² and Samara's review⁸). A more adequate description of pressure effects in these crystals has been obtained in the four-particle cluster approximation by Blinc¹³ and Torstveit.¹⁴ The derivatives of transition temperature, spontaneous polarization, and Curie constant with respect to hydrostatic pressure for KDP and DKDP were successfully described. However, since then a lot of new experimental data on the pressure effects has become available for other crystals of KDP family¹⁵⁻²⁰ and for uniaxial pressures,²¹ not to mention the observed universality of the T_C vs δ dependence.¹¹

Therefore, it seems worthwhile to re-examine the ability of the conventional proton ordering model to consistently describe pressure effects on several ferroelectric and antiferroelectric crystals of KDP family. Particularly, studies of uniaxial pressures may give a better insight into the problem of phase transition and/or polarization mechanism in these crystals. For the sake of simplicity we restrict our consideration with deuterated crystals strained by pressures which do not lower the crystals symmetry: hydrostatic and uniaxial $p = -\sigma_3$. In order to study the pressure dependences of static dielectric properties, simple models of dipole moment formation in these crystals are suggested. We shall also verify whether the universality of the transition temperature vs D-site distance dependences observed in KD_2PO_4 and $\text{ND}_4\text{D}_2\text{PO}_4$ strained by hydrostatic pressure can be ac-

counted for in this model and whether it is obeyed by other crystals of this family under hydrostatic or uniaxial pressure.

I. THE MODEL

We consider a deuteron subsystem of a ferroelectric (FE) or an antiferroelectric (AFE) crystal of KH_2PO_4 family with a general formula MeD_2XO_4 , where $\text{Me} = \text{K, Rb, ND}_4$, $\text{X} = \text{P, As}$. The crystals are assumed to possess the tetragonal symmetry in the paraelectric phase. In our calculations we use the model of strained KH_2PO_4 -type crystals by Stasyuk *et al.*,²² as well as some ideas of the previous theories by Blinc¹³ and Torstveit.¹⁴ In Refs. 22 and 23, the influence of the B_1 symmetry uniaxial pressure $\sigma_1 - \sigma_2$ on the DKDP-type ferroelectrics was considered, and a possibility of the pressure induced phase transition within a monoclinic phase was shown. In the present work, we consider only pressures which do not lower the system symmetry: hydrostatic or uniaxial $p = -\sigma_3$ applied along the ferroelectric axis c .

We perform our calculations within the four-particle cluster approximation which allows one to take adequately into account the strong short-range correlations between deuterons. The four-particle cluster Hamiltonian of the system has the following conventional form:

$$H_q = V \left[\frac{\sigma_{q1}}{2} \frac{\sigma_{q2}}{2} + \frac{\sigma_{q2}}{2} \frac{\sigma_{q3}}{2} + \frac{\sigma_{q3}}{2} \frac{\sigma_{q4}}{2} + \frac{\sigma_{q4}}{2} \frac{\sigma_{q1}}{2} \right] + U \left[\frac{\sigma_{q1}}{2} \frac{\sigma_{q3}}{2} + \frac{\sigma_{q2}}{2} \frac{\sigma_{q4}}{2} \right] + \Phi \frac{\sigma_{q1}}{2} \frac{\sigma_{q2}}{2} \frac{\sigma_{q3}}{2} \frac{\sigma_{q4}}{2} - \sum_{f=1}^4 \frac{z_{qf}^i}{\beta} \frac{\sigma_{qf}}{2}, \quad (1)$$

where two eigenvalues of the Ising spin $\sigma_{qf} = \pm 1$ are assigned to two equilibrium positions of a deuteron on the f th bond in the q th cell, tunneling being neglected. Depending on the choice of the theory parameters, Hamiltonian (1) can describe both the ferroelectric and antiferroelectric ordering. The antiferroelectric ordering can be obtained only if the long-range interactions are taken into account.²⁴

Each PO_4 tetrahedron in a crystal of the KH_2PO_4 family is oriented such that two of its edges are parallel to the ab plane; an ‘‘upper’’ and a ‘‘lower’’ oxygen of two neighboring PO_4 groups are linked by a hydrogen bond with a double-minima potential well. Configurations with two hydrogens in potential wells being close to upper (or lower) oxygens of a given PO_4 group and with the hydrogens on the two other bonds being close to the neighboring tetrahedra are called ‘‘up’’ (or ‘‘down’’) configurations and assigned energy ε_s . Configuration with two hydrogens close to an upper and a lower oxygen, with only one (or three) hydrogens close to a given group, and with four hydrogens (or without any) are called lateral (energy ε_a), single ionized (ε_1), and double ionized (ε_0), respectively. It is usually assumed that the energies of up-down configurations in ferroelectric crystals and of lateral configurations in antiferroelectric ones are the lowest.

Parameters V , U , and Φ , different for ferro- and antiferroelectric crystals, describe the short-range correlations between deuterons. They are chosen such that Hamiltonian (1)

reproduces the energy levels of the Slater-type model for KDP (see, for instance, Ref. 12)—the Slater energies ε , w , and w_1 ($\varepsilon \ll w \ll w_1$), determined by the energies of up-down ε_s , lateral ε_a , single-ionized ε_1 , and double-ionized ε_0 deuteron configurations:

$$\begin{aligned} & \text{FE} \\ & V = -\frac{w_1}{2}, \\ & U = -\varepsilon + \frac{w_1}{2}, \\ & \Phi = 4\varepsilon - 8w + 2w_1; \\ & \varepsilon = \varepsilon_a - \varepsilon_s, \\ & w = \varepsilon_1 - \varepsilon_s, \\ & w_1 = \varepsilon_0 - \varepsilon_s; \\ & \text{AFE} \\ & V = \frac{\varepsilon - w_1}{2}, \\ & U = \frac{\varepsilon + w_1}{2}, \\ & \Phi = 2\varepsilon - 8w + 2w_1; \\ & \varepsilon = \varepsilon_s - \varepsilon_a, \\ & w = \varepsilon_1 - \varepsilon_a, \\ & w_1 = \varepsilon_0 - \varepsilon_a. \end{aligned}$$

The fields z_{qf}^i include the effective cluster fields Δ_{qf}^i created by the sites neighboring to the qf th site, external electric field E_i applied along one of the crystallographic axes, and the long-range deuteron-deuteron interactions (dipole-dipole and indirect via lattice vibrations) taken into account in the mean-field approximation

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

The Slater energies ε ,^{25,26} w ,¹⁴ w_1 , and the components of the long-range interaction matrix $J_{ff'}(qq')$ are proportional to the square of the separation between two possible positions of a deuteron on a bond—D-site distance δ . Assuming the linear dependence of the D-site distance δ in all MeD_2XO_4 crystals on hydrostatic and uniaxial $p = -\sigma_3$ pressure

$$\delta = \delta_0 + \delta_1 p \quad (3)$$

(according to Refs. 9 and 10, the variation of δ with hydrostatic pressure in KD_2PO_4 is linear indeed, except that δ_0 and δ_1 are temperature dependent), we expand ε , w , w_1 , and $J_{ff'}(qq')$ in powers of *pressure* up to the linear terms. However, there can be other mechanisms of pressure influence on the energy parameters of the model, like, for instance, changes in distances between the dipoles due to the lattice deformation affect $J_{ff'}(qq')$. We take these mechanisms into account by expanding ε , w , w_1 , and $J_{ff'}(qq')$ in powers of *components of lattice strain tensor* up to the linear terms, so that

TABLE I. Changes in the Slater energies due to the strains of different symmetries. (The strain symmetry is indicated in parentheses.)

Level	ε_4 (E)	ε_5 (E')	ε_6 (B ₂)	$\varepsilon_1 - \varepsilon_2$ (B ₁)
ε			$\delta_{16}\varepsilon_6$	
ε			$-\delta_{16}\varepsilon_6$	
w		$\delta_{25}\varepsilon_5$		$-\delta_{27}(\varepsilon_1 - \varepsilon_2)$
w		$-\delta_{25}\varepsilon_5$		$-\delta_{27}(\varepsilon_1 - \varepsilon_2)$
w	$\delta_{24}\varepsilon_4$			$\delta_{27}(\varepsilon_1 - \varepsilon_2)$
w	$-\delta_{24}\varepsilon_4$			$\delta_{27}(\varepsilon_1 - \varepsilon_2)$
w_1				

$$\begin{aligned}\varepsilon &= \varepsilon^0 \left[1 - \frac{2}{S} \frac{\delta_1}{\delta_0} \sum_{j=1}^3 \varepsilon_j \right] + \sum_{i=1}^3 \delta_{1i} \varepsilon_i, \\ w &= w^0 \left[1 - \frac{2}{S} \frac{\delta_1}{\delta_0} \sum_{j=1}^3 \varepsilon_j \right] + \sum_{i=1}^3 \delta_{2i} \varepsilon_i, \\ w_1 &= w_1^0 \left[1 - \frac{2}{S} \frac{\delta_1}{\delta_0} \sum_{j=1}^3 \varepsilon_j \right] + \sum_{i=1}^3 \delta_{3i} \varepsilon_i,\end{aligned}\quad (4)$$

and

$$J_{ff'}(qq') = J_{ff'}^{(0)}(qq') \left[1 - \frac{2}{S} \frac{\delta_1}{\delta_0} \sum_{j=1}^3 \varepsilon_j \right] + \sum_{j=1}^3 \psi_{ff'}^j(qq') \varepsilon_j. \quad (5)$$

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

In Eqs. (4) and (5) we take into account only the diagonal components of the strain tensor. As symmetry analysis shows,²² these strains do not split degenerate energy levels, whereas the nondiagonal components of the strain tensor can partially remove this degeneracy.²² The changes in the Slater energy levels caused by strains of different symmetries are presented in Table I.

Hereafter, we consider only a longitudinal electric field E_3 in ferroelectric crystals and a transverse one E_1 in antiferroelectric crystals. It brings about the following symmetry of the quasispin mean values, effective dipole moments μ_{qf}^i , and effective fields z_{qf}^i :

$$\begin{aligned}\text{FE} \\ \eta^f &\equiv \langle \sigma_{q1} \rangle = \langle \sigma_{q2} \rangle = \langle \sigma_{q3} \rangle = \langle \sigma_{q4} \rangle; \\ \mu_3 &\equiv \mu_{q1}^3 = \mu_{q2}^3 = \mu_{q3}^3 = \mu_{q4}^3; \\ z^f &\equiv z_{q1}^3 = z_{q2}^3 = z_{q3}^3 = z_{q4}^3; \\ \text{AFE} \\ \eta_{q13}^a &\equiv -\langle \sigma_{q1} \rangle = \langle \sigma_{q3} \rangle, \\ \eta_{q24}^a &\equiv -\langle \sigma_{q4} \rangle = \langle \sigma_{q2} \rangle, \\ \mu_1 &\equiv -\mu_{q1}^1 = \mu_{q3}^1, \\ \mu_{q2}^1 &= \mu_{q4}^1 = 0, \\ z_{q13}^a &\equiv -z_{q1}^1 = z_{q3}^1, \\ z_{q24}^a &\equiv z_{q2}^1 = -z_{q4}^1.\end{aligned}$$

The order parameter (mean value of the quasispin) of a ferroelectric crystal is uniform, whereas that of an antiferroelectric crystal should be presented as the sum of a spontaneous modulated part and of a field-induced uniform part:

$$\begin{aligned}\eta_{qf}^a &= \eta_f^a e^{ik_Z R_q} + \eta_{fE}^a, \\ \eta^a &= -\eta_1^a = \eta_2^a = \eta_3^a = -\eta_4^a, \\ \eta_{13E}^a &\equiv \eta_{3E}^a = -\eta_{1E}^a, \\ \eta_{24E}^a &\equiv \eta_{2E}^a = -\eta_{4E}^a.\end{aligned}$$

Here $k_Z = (\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)/2$; $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are the basic vector of the reciprocal lattice; the factor $e^{ik_Z R_q} = \pm 1$ denotes two sublattices of an antiferroelectric.

Now we shall proceed with the conventional cluster approach calculations, excluding the effective fields Δ from z by making use of the self-consistency condition. The condition states that the mean values of the quasispins calculated with the four-particle Hamiltonian (1) and with the one-particle Hamiltonian

$$H_{qf}^{(1)} = - \left(\frac{z_{qf}^i}{\beta} - \Delta_{qf}^i \right) \frac{\sigma_{qf}}{2} \quad (6)$$

must coincide. We obtain

$$\text{FE} \\ z^f = \frac{1}{2} \ln \frac{1 + \eta^f}{1 - \eta^f} + \beta \nu_c(0) \eta^f + \frac{\beta \mu_3 E_3}{2},$$

$$\text{AFE} \\ z_{q13}^a = \frac{1}{2} \ln \frac{1 + \eta_{q13}^a}{1 - \eta_{q13}^a} + \beta \left[\nu_a(\mathbf{k}_Z) \eta^a e^{ik_Z R_q} + \nu_a(0) \eta_{13E}^a + \frac{\mu_1 E_1}{2} \right],$$

$$z_{q24}^a = \frac{1}{2} \ln \frac{1 + \eta_{q24}^a}{1 - \eta_{q24}^a} + \beta [\nu_a(\mathbf{k}_Z) \eta^a e^{ik_Z R_q} + \nu_a(0) \eta_{24E}^a],$$

with

$$\begin{aligned}\nu_c(0) &= \frac{1}{4} [J_{11}(0) + 2J_{12}(0) + J_{13}(0)] \\ &= \nu_c^0(0) \left[1 - \frac{2}{S} \frac{\delta_1}{\delta_0} \sum_{j=1}^3 \varepsilon_j \right] + \sum_i \psi_{ci}(0) \varepsilon_i, \\ \nu_a(\mathbf{k}) &= \frac{1}{4} [J_{11}(\mathbf{k}) - J_{13}(\mathbf{k})] \\ &= \nu_a^0(\mathbf{k}) \left[1 - \frac{2}{S} \frac{\delta_1}{\delta_0} \sum_{j=1}^3 \varepsilon_j \right] + \sum_i \psi_{ai}(\mathbf{k}) \varepsilon_i\end{aligned}$$

being the eigenvalues of Fourier transforms of the long-range interaction matrices.

Now the free energy of strained crystals can be calculated (here $E_i = 0$).

$$\begin{aligned}
& \text{FE} \\
f^f &= \frac{\bar{v}}{2} \sum_{ij} c_{ij}^{(0)} \varepsilon_i \varepsilon_j - 2w + 2\nu_c(0) [\eta^f]^2 \\
& + 2T \ln \frac{2}{(1-[\eta^f]^2)D^f}, \\
& \text{AFE} \\
f^a &= \frac{\bar{v}}{2} \sum_{ij} c_{ij}^{(0)} \varepsilon_i \varepsilon_j - 2w + \varepsilon + 2\nu_a(\mathbf{k}_Z) [\eta^a]^2 \\
& + 2T \ln \frac{2}{(1-[\eta^a]^2)D^a};
\end{aligned} \tag{7}$$

$c_{ij}^{(0)}$ are the so-called ‘‘seed’’ elastic constants of a crystal, describing the elasticity of a ‘‘host’’ lattice—a fictitious lattice without deuterons; $\bar{v} = v/k_B$; v is the unit cell volume, and

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

$$D^a = \cosh 2z^a + 4b \cosh z^a + a + d + 1,$$

$$a = \exp(-\beta\varepsilon),$$

$$b = \exp(-\beta w),$$

$$d = \exp(-\beta w_1).$$

Terms like $S_{66}h_{36}^2P_3^2$ and $\sum_i q_{i3}\varepsilon_i P_3^2$, which usually occur in the free energy when one considers the piezoelectric coupling and electrostriction effect (h_{36} is the piezomodule, and q_{i3} are the electrostriction coefficients), are taken into account in our expressions by $2\nu_c(0)[\eta^f]^2$ {or $2\nu_a(\mathbf{k}_Z)[\eta^a]^2$ }.

The order parameter and lattice strains are to be determined from the thermodynamic equilibrium conditions

$$\frac{1}{\bar{v}} \frac{\partial f}{\partial \eta} = 0;$$

$$\frac{1}{\bar{v}} \frac{\partial f}{\partial \varepsilon_i} = -p_i,$$

$p_i = (p, p, p)$ for the hydrostatic pressure, and $p_i = (0, 0, p)$ for the uniaxial pressure $p = -\sigma_3$, leading to the following system of equations:

$$\eta^{f,a} = \frac{1}{D^{f,a}} (\sinh 2z^{f,a} + 2b \sinh z^{f,a}), \tag{8}$$

$$-p_i = \sum_{j=1}^3 c_{ij}^{(0)} \varepsilon_j - F_{f,a}^i \left(\varepsilon_i, \eta^{f,a}, \frac{\delta_1}{\delta_0} \right), \tag{9}$$

where

$$\begin{aligned}
F_f^i &= \frac{2}{\bar{v}} \left(\delta_{2i} - \frac{2}{S} \frac{\delta_1}{\delta_0} w^0 \right) - \frac{2}{\bar{v}} \left(\psi_{ci}(0) - \frac{2}{S} \frac{\delta_1}{\delta_0} \nu_c^0(0) \right) [\eta^f]^2 \\
& + \frac{2}{\bar{v}D^f} \left[4b \left(\delta_{2i} - \frac{2}{S} \frac{\delta_1}{\delta_0} w^0 \right) \cosh z^f \right. \\
& + 2a \left(\delta_{1i} - \frac{2}{S} \frac{\delta_1}{\delta_0} \varepsilon^0 \right) + d \left(\delta_{3i} - \frac{2}{S} \frac{\delta_1}{\delta_0} w_1^0 \right) \left. \right]; \\
F_a^i &= \frac{2}{\bar{v}} \left(\delta_{2i} - \frac{2}{S} \frac{\delta_1}{\delta_0} \omega^0 \right) - \frac{1}{\bar{v}} \left(\delta_{1i} - \frac{2}{S} \frac{\delta_1}{\delta_0} \varepsilon^0 \right) \\
& - \frac{2}{\bar{v}} \left(\psi_{ai}(\mathbf{k}_Z) - \frac{2}{S} \frac{\delta_1}{\delta_0} \nu_a^0(\mathbf{k}_Z) \right) [\eta^a]^2 \\
& + \frac{2}{\bar{v}D^a} \left[4b \left(\delta_{2i} - \frac{2}{S} \frac{\delta_1}{\delta_0} w^0 \right) \cosh z^a \right. \\
& + a \left(\delta_{1i} - \frac{2}{S} \frac{\delta_1}{\delta_0} \varepsilon^0 \right) + d \left(\delta_{3i} - \frac{2}{S} \frac{\delta_1}{\delta_0} w_1^0 \right) \left. \right]
\end{aligned}$$

are the contributions of deuteron subsystems to crystals elasticity. Since determination of these contributions lies beyond the scope of the present paper, we may consider instead of Eq. (9) the system

$$-p_i = \sum_{j=1}^3 c_{ij} \varepsilon_j; \tag{10}$$

electrostriction is neglected; c_{ij} are the elastic constants of the whole crystal, being determined from an experiment.

The first-order phase transition temperature can be found from the following condition on the values of the thermodynamic potential $g(\eta, T, p)$

$$g(\eta^f(\text{or } \eta^a), T_C(\text{or } T_N), p) = g(0, T_C(\text{or } T_N), p). \tag{11}$$

It is assumed that the polarization of the crystal, triggered by deuteron ordering, is related to the mean values of quasipons as

$$P_i = \sum_f \frac{\mu_{qf}^i}{v} \frac{\langle \sigma_{qf} \rangle}{2},$$

with summation going over all sites of a unit cell (summation over a primitive cell would give a sublattice polarization). Taking into account the system symmetry, we can write that

$$\begin{aligned}
& \text{FE} \\
P_3 &= \frac{4\mu_3}{v} \eta^f, \\
& \text{AFE} \\
P_1 &= \frac{2\mu_1}{v} \eta_{13E}^a.
\end{aligned} \tag{12}$$

It is the variation of the effective dipole moments μ_i with pressure that governs the pressure dependences of dielectric characteristics of the crystals. Determination of this variation will be deferred till the next section.

TABLE II. The theory parameters for the considered crystals.

Crystal	T_{C0} (K)	$\partial T_C / \partial p$ (K/kbar)	δ_1 / δ_0 (10^{-3} kbar $^{-1}$)	ε^0	w^0	ν^0 ^a	ψ_1^- ^a	ψ_2^- ^a	ψ_3^- ^a	ψ_1^+ ^a	ψ_3^+ ^a	f^0 ^b	μ_3^{0-}/v ($\mu\text{C}/\text{cm}^2$)
KD ₂ PO ₄	220	-2.0 Ref. 16	-6.4	92.0	830	38.0	130	110	-560	120	-560	76	
KD ₂ PO ₄	220	-2.5 Ref. 15	-7.4	92.0	830	38.0	130	110	-560	120	-560		1.55
K(H _{0.13} D _{0.87}) ₂ PO ₄ ^c	210	-12.5 Ref. 21	-35.0	87.6	785	37.05	120	100	-545	110	-545		1.49
K(H _{0.16} D _{0.84}) ₂ PO ₄ ^d	208	-3.0 Ref. 15	-9.3	87.6	785	36.0	110	90	-545	100	-545		
RbD ₂ PO ₄	207.3	-3.7 Ref. 18	-10.7	95.9	828	29.9	110	90	-450	100	-450	13.5	
KD ₂ AsO ₄	159.7	-1.6 Ref. 19	-6.0	73.0	800	21.6	80	60	-220	70	-220		
RbD ₂ AsO ₄	169.8	-2.7 Ref. 19	-8.5	77.8	795	23.3	100	80	-210	90	-210		
ND ₄ D ₂ PO ₄	235.0	-1.4 Ref. 39	-4.9	77.0	709	85.75	310	290	-500	290	-560		
ND ₄ D ₂ AsO ₄	286.3	-1.4 Ref. 20	-4.4	105.0	810	103.65	380	360	-680	370	-680	1400	

^a $\nu^0 = \nu_c^0(0)$ and $\psi_i = \psi_{ci}(0)$ for ferroelectrics; $\nu^0 = \nu_a^0(\mathbf{k}_Z)$ and $\psi_i = \psi_{ai}(\mathbf{k}_Z)$ for antiferroelectrics. ψ_i^- and ψ_i^+ are the values of the deformation potentials below and above transition point, respectively.

^b $f^0 = (\mu_3^0)^2/v$ for ferroelectrics and $f^0 = (\mu_1^0)^2/v$ for antiferroelectrics.

^cValues of $\partial T_C / \partial p$ and δ_1 / δ_0 for this crystal correspond to uniaxial pressure $p = -\sigma_3$.

^dValues of deuteration x for K(H_{1-x}D_x)₂PO₄ crystals are nominal.

Differentiation of Eq. (12) with respect to E_3 or E_1 at $\partial \varepsilon_i / \partial E_j = 0$ (the strains are independent of the electric field) yields the expressions for static dielectric permittivities of clamped crystals.

$$\begin{aligned} & \text{FE} \\ \varepsilon_3^f(T, p) &= \varepsilon_{3\infty}^f + 4\pi \frac{\beta \mu_3^2}{v} \frac{4\chi_3^f}{D^f - 2\varphi_3^f \chi_3^f}, \\ & \text{AFE} \\ \varepsilon_1^a(T, p) &= \varepsilon_{1\infty}^a + 4\pi \frac{\beta \mu_1^2}{v} \left(\frac{\chi_1^a}{D^a - 2\chi_1^a \varphi_1^a} + \frac{\chi_2^a}{D^a - 2\chi_2^a \varphi_1^a} \right); \end{aligned} \quad (13)$$

$\varepsilon_{i\infty}$ are high-frequency contributions to the permittivities, and

$$\chi_3^f = \cosh 2z^f + b \cosh z^f - [\eta^f]^2 D^f,$$

$$\chi_1^a = 1 + b \cosh z^a,$$

$$\chi_2^a = \cosh 2z^a + b \cosh z^a - [\eta^a]^2 D^a;$$

$$\varphi_3^f = \frac{1}{1 - [\eta^f]^2} + \beta \nu_c(0),$$

$$\varphi_1^a = \frac{1}{1 - [\eta^a]^2} + \beta \nu_a(0).$$

It should be noted that at ambient pressure above T_{N0} , if $w \rightarrow \infty$ and $w_1 \rightarrow \infty$ the obtained expression for ε_1^a coincides with that of Havlin.²⁷

Permittivities of mechanically free crystals are related to those of clamped crystals by

$$\tilde{\varepsilon}_3^f(p, T) = \varepsilon_3^f(p, T) + 4\pi \left(\sum_{i=1}^3 e_{3i} d_{3i} + e_{36} d_{36} \right),$$

$$\tilde{\varepsilon}_1^a(p, T) = \varepsilon_1^a(p, T) + 4\pi d_{14}^2 c_{44};$$

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

II. THE FITTING PROCEDURE

We need to set the values of the following theory parameters for each of the considered MeD_2XO_4 ($Me = K, Rb, ND_4$, $X = P, As$) crystals:

- Slater energies $\varepsilon^0, w^0, w_1^0$ for both FE and AFE crystals, eigenvalues of Fourier transforms of the long-range interaction matrices $\nu_a^0(\mathbf{k}_Z)$ for AFE and $\nu_c^0(0)$ for FE (these parameters describe the unstrained state of crystals);

- the eigenvalue $\nu_a^0(0)$ for AFE crystals, the effective dipole moments $\mu_i^{(0)}$ for FE and AFE crystals (they determine magnitudes of dielectric characteristics at atmospheric pressure);

- the elastic constants c_{ij} ;

- the ratio δ_1 / δ_0 and so-called deformation potentials δ_{ij} for both types of crystals, $\psi_{ci}(0)$ for FE crystals and $\psi_{ai}(\mathbf{k}_Z)$ for AFE crystals (these parameters determine the pressure dependence of the transition temperatures);

- the slopes $\partial \mu_i / \partial p$ for both types of crystals, $\psi_{ai}(0)$ for AFE crystals (they determine the pressure dependence of the dielectric properties).

Values of the parameters relevant to the unstrained crystals have been found earlier.²⁸⁻³⁰ They provide quantitative description of experimental data for the transition temperatures, spontaneous polarization, dielectric permittivities and specific heat of the crystals at ambient pressure. In the present work, those values were slightly adjusted so that they corresponded to the deuteration levels for which the values of $\partial T_C / \partial p$ or $\partial T_N / \partial p$ were available. Everywhere we neglected contributions of double-ionized deuteron configurations, putting $w_1^0 \rightarrow \infty$ and $\delta_{3i} = 0$.

The ratio δ_1 / δ_0 describing the rate of the pressure changes in the D-site distance is the only theory parameter different for hydrostatic and uniaxial pressures. For all crystals and pressures, we treat δ_1 / δ_0 as a free parameter. In the case of KD₂PO₄ with $T_{C0} = 220$ K and $\partial T_C / \partial p = -2.5$ K/kbar, for which the dependence of spontaneous polarization on hydrostatic pressure is reported,¹⁵ the adopted value of δ_1 / δ_0 (see Table II) is more or less close to that calculated with the available structural data by Nelmes⁹ cor-

TABLE III. Elastic constants (units of 10^5 bar) of the considered crystals.

Crystal	T_{C0}	c_{11}^+	c_{12}^+	c_{13}^+	c_{33}^+	c_{11}^-	c_{12}^-	c_{13}^-	c_{22}^-	c_{23}^-	c_{33}^-
KD ₂ PO ₄	220	6.14	-0.71	1.05	4.82	6.14	-0.71	1.0	6.14	1.1	4.3
K(H _{0.13} D _{0.87}) ₂ PO ₄	210 ^a	6.93	-0.78	1.22	5.45	6.8	-0.78	1.0	6.99	1.0	5.3
RbD ₂ PO ₄		6.85	-0.1	1.3	5.2	6.85	-0.1	1.3	6.85	1.2	5.2
KD ₂ AsO ₄		6.5	0.8	1.36	4.9	6.6	0.8	1.33	6.5	1.37	4.9
RbD ₂ AsO ₄		4.9	-1.92	0.48	3.8	4.98	-1.92	0.48	4.978	0.48	3.8
ND ₄ D ₂ PO ₄		6.28	0.39	1.9	3.25	6.28	0.39	1.6	6.28	1.59	3.25
ND ₄ D ₂ AsO ₄		6.4	0.9	2.4	3.85	6.4	0.9	2.4	6.3	2.2	3.85

^aDifference between elastic constants of K(H_{0.13}D_{0.87})₂PO₄ and K(H_{0.16}D_{0.84})₂PO₄ crystals with $T_{C0} = 210$ K and $T_{C0} = 208$ K, respectively, is neglected.

responding to a sample with $T_{C0} = 222$ K, and $\partial T_C / \partial p = -2.9$ K/kbar.

In our calculations, the deformation potentials δ_{ij} were equal to zero. It means that the contribution of lattice strains to the pressure dependence of the Slater energies was neglected, and the latter was assumed to result mainly from the pressure-induced changes in the D-site distance δ . That accords with the earlier theories^{13,14} where no other mechanism of pressure effects on the Slater energies was taken into account.

Unlike the Slater energies, the parameters of the long-range interactions are essentially influenced by the lattice strains. To estimate the values of the deformation potentials $\psi_{c_j}(0)$ and $\psi_{a_j}(\mathbf{k}_Z)$, which describe this influence, we use the fact that, loosely speaking, the dipole-dipole part of the long-range interactions, and the part which describe the lattice mediated interactions are proportional to a^{-3} and a^{-6} , respectively²⁵ (a is the lattice constant). This yields $\sum_i \psi_{c_i}(0) \varepsilon_i \approx -(3+6) \nu_c^0(0) \varepsilon_1$, depending on the relative weights of the two parts of long-range interactions. The best fit to the experimental dependence of the transition temperature of KD₂PO₄ on hydrostatic pressure is obtained if

$$2\psi_{c_1}(0) + \psi_{c_3}(0) \frac{\sum_j S_{3j}}{\sum_j S_{1j}} \approx -8\nu_c^0(0) \quad (14)$$

above the transition point. For the other crystals the values of $\psi_{c_i}(0)$ or $\psi_{a_i}(\mathbf{k}_Z)$ can be set consistently, using the relations

$$\frac{\psi_{c_1}(0) \text{ [or } \psi_{a_1}(\mathbf{k}_Z)](MeD_2XO_4)}{\psi_{c_1}(0)(KD_2PO_4)} = \frac{\nu_c^0(0) \text{ [or } \nu_a^0(\mathbf{k}_Z)](MeD_2XO_4)}{\nu_c^0(0)(KD_2PO_4)}, \quad (15)$$

whereas $\psi_{c_3}(0)$ [or $\psi_{a_3}(\mathbf{k}_Z)$] can be found from Eq. (14). Since the crystals for which the experimental $\partial T_C / \partial p$ are known might be of different, although high, deuteration levels, the adopted values of deformation potentials $\psi_{c_i}(0)$ [or $\psi_{a_i}(\mathbf{k}_Z)(0)$] slightly differ from those calculated with Eq. (15).

Since values of the transverse dielectric permittivity of an antiferroelectrics are not very sensitive to small changes in the parameter

$$\nu_a(0) = \nu_a^0(0) \left(1 - \frac{2}{S} \frac{\delta_1}{\delta_0} \sum_i \varepsilon_i \right) + \sum_i \psi_{a_i}(0) \varepsilon_i,$$

for the sake of simplicity we assume that $\psi_{a_i}(0) = 0$.

Due to the lack of the necessary experimental data, the choice of values of elastic constants is not quite plain. For instance, for K(H_{1-x}D_x)₂PO₄ the elastic constants at ambient pressure are available only for deuteration $x=0$ and $x=0.89$ above the transition point.^{31,32} The required values of c_{ij} for the crystals with different values of x were obtained by linear extrapolation (interpolation) of the data of Ref. 31 for $x=0.89$ and of Ref. 32 for an undeuterated sample KH₂PO₄. It also should be mentioned that, usually, the elastic constants c_{11} and c_{33} are measured fairly accurately, and the data of different sources are close to each other. As far as c_{12} and c_{13} , are concerned, their values are much lower than those of c_{11} and c_{33} , and different measurements give different results (see, for instance, Ref. 33). Besides, for KD₂AsO₄, ND₄D₂PO₄, and RbD₂AsO₄ the data of only one measurement are available (Ref. 34 for KD₂AsO₄, Ref. 35 for ND₄D₂PO₄, and Ref. 36 for RbD₂AsO₄). Therefore, in calculations for these crystals we fix the values of c_{11} and c_{33} of Refs. 34–36, whereas the agreement with the experimental dependence of $T_C(p)$ was obtained by varying c_{12} and c_{13} around the experimental values.

For RbD₂PO₄ and ND₄D₂AsO₄ the corresponding experimental data are available only for undeuterated forms.^{37,38} Taking into account the fact that elastic constants of deuterated crystals are usually close to those of their undeuterated analogs, for RbD₂PO₄ and ND₄D₂AsO₄ we obtain an agreement with the experimental dependence $T_C(p)$ by slight changing c_{ij} near that of the undeuterated crystals. Since no experimental data for the elastic constants of the crystals in the ordered phase is available, we calculated the transition temperature of these crystals at different pressures and different but close to c_{ij}^+ trial values of c_{ij}^- , choosing those which provide the best fit to the experimental data.

The values of deformation potentials and elastic constants yielding the best fit of theoretical dependences of transition temperature on pressure to experimental data are given in Tables II and III, respectively. The number of varied parameters could be reduced if we knew the elastic constants and the variation of the D-site distance with pressure in crystals with the same deuteration as in the samples for which data for the pressure dependences of other characteristics are available. However, we would like to emphasize that devia-

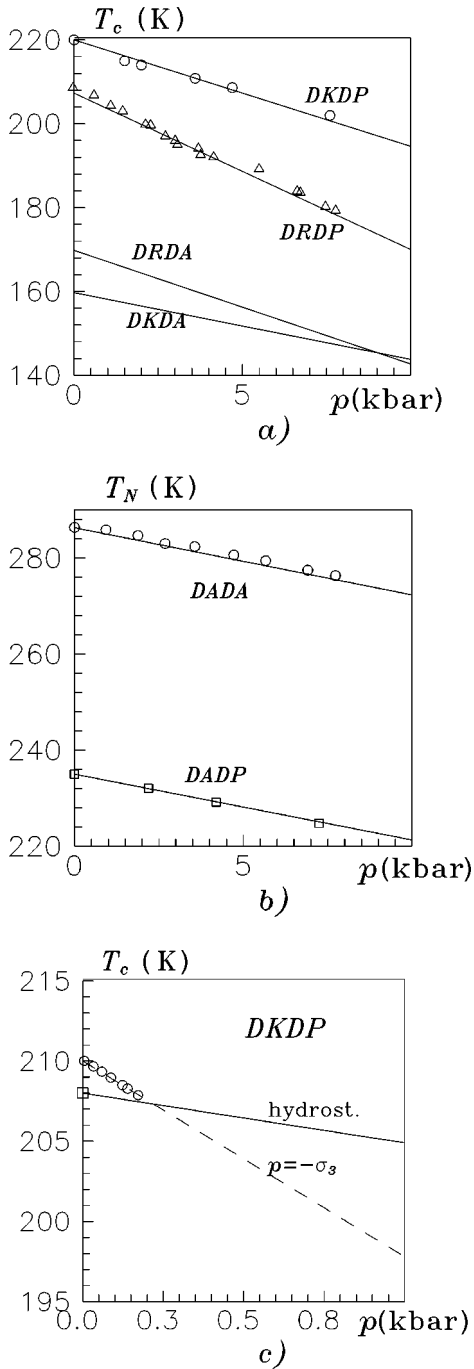


FIG. 1. Pressure dependence of transition temperature: (a) \circ , Ref. 15: KD_2PO_4 ; \triangle , Ref. 18: RbD_2PO_4 (tetragonal); KD_2AsO_4 ; RbD_2AsO_4 ; (b) \square , Ref. 39: $\text{ND}_4\text{D}_2\text{PO}_4$, and \circ , Ref. 20: $\text{ND}_4\text{D}_2\text{AsO}_4$; (c) \circ , $\text{K}(\text{H}_{1-x}\text{D}_x)_2\text{PO}_4$ with nominal values of x : 0.87 ($T_{C0}=210$ K)(\circ), Ref. 21, dashed line; 0.84 ($T_{C0}=208$ K)(\square), Ref. 15, solid line.

tion of the adopted values of the elastic constants from the experimental data is slight. Performed adjustment of the elastic constants changes the theoretical values of the slopes $\partial T_C/\partial p$ within only a few percents, and is not necessary if a reasonable tolerance for $\partial T_C/\partial p$ is allowed. The theoretical pressure dependences of transition temperatures are mainly determined by the changes in the D-site distance (via δ_1/δ_0) and, to a lesser degree, by a lattice strains counterpart in the pressure dependence of the long-range interactions [via $\psi_{ci}(0)$ or $\psi_{ai}(\mathbf{k}_Z)$].

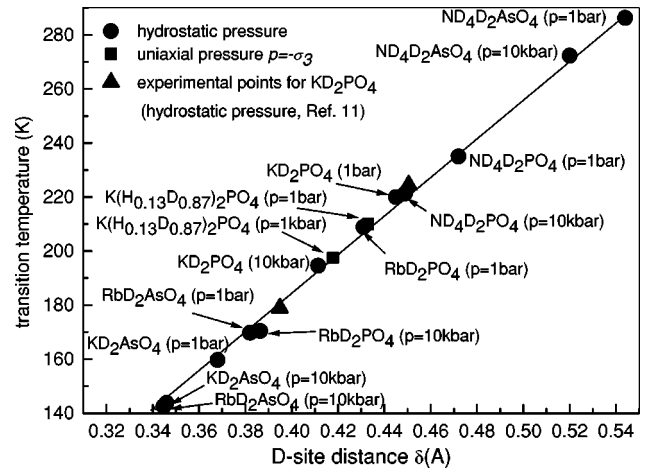


FIG. 2. Transition temperature vs D-site distance dependence for several deuterated crystals of the KH_2PO_4 family.

In numerical calculations we minimize the thermodynamic potential with respect to the order parameter η and find the strains ε_i from Eqs. (10); the transition temperature is determined from the condition (11). Results of the calculations are given in the figures below.

In Figs. 1(a) and 1(b) we plot the dependences of the phase transition temperature of the six MeD_2XO_4 ($\text{Me} = \text{K}, \text{Rb}, \text{ND}_4$, $\text{X} = \text{P}, \text{As}$) crystals on hydrostatic pressure along with the experimental points. Naturally, a perfect fit of theoretical results to the experimental data is obtained. No experimental point for KD_2AsO_4 or RbD_2AsO_4 is presented, but the theoretical slopes $\partial T_C/\partial p$ for these crystals agree with the corresponding data of Ref. 19.

Transition temperature vs uniaxial pressure $p = -\sigma_3$ line is presented in Fig. 1(c) along with the experimental points of Ref. 21 and a theoretical curve for the hydrostatic pressure. A rapid decrease in transition temperature with the uniaxial pressure $p = -\sigma_3$ was detected;²¹ to describe it, a negative value of δ_1/δ_0 was used in calculations. The fact that variation of T_C with uniaxial pressure is more pronounced than with hydrostatic is understandable, since the uniaxial pressure deforms the crystal stronger than the hydrostatic pressure does. The unexpected outcome of the fitting process is the prediction that the uniaxial pressure $p = -\sigma_3$ shortens the hydrogen bonds and D-site distances ($\delta_1/\delta_0 < 0$): one would rather expect the pressure applied along the c axis to expand the D bonds lying in the ab plane. One of the possible explanations of this shortening is that $p = -\sigma_3$ pressure flattens PO_4 tetrahedra along the c axis, thereby enlarging their projection on the ab plane and reducing the distances between oxygens of different PO_4 groups. Another reason for such elongation could be a rotation of PO_4 tetrahedra around the c axis in a direction opposite to the direction in which they rotate under hydrostatic pressure.^{9,10} However, these conjectures should await an experimental verification.

Universality of the transition temperature vs D-site distance dependence is clearly manifested in Fig. 2. The values of δ are calculated using the values of the ratio δ_1/δ_0 from Table II, which provide the correct slopes $\partial T_C/\partial p$ and assuming a universal $T_{C0}(\delta)$ dependence for all these crystals at atmospheric pressure. As one can see, the points $T_C(\delta)$

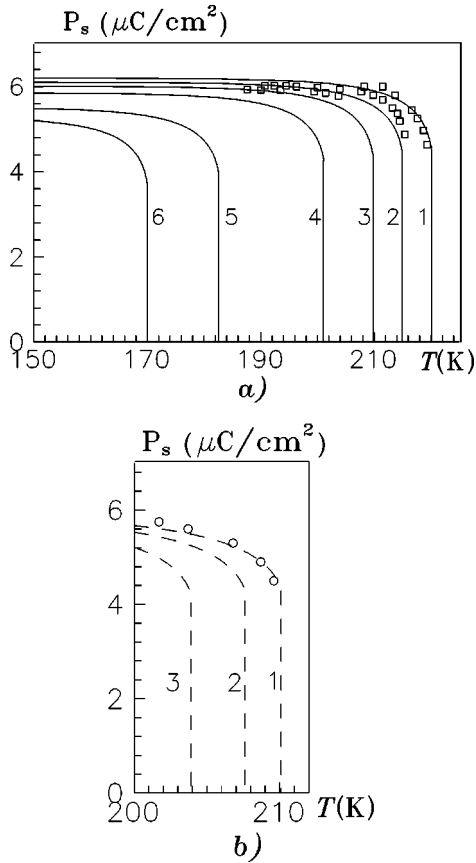


FIG. 3. Spontaneous polarization of KD_2PO_4 (a) and $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ (b) crystals as a function of temperature at different values of external pressure p (kbar): (a) ($T_{C0} = 220$ K, $\partial T_C/\partial p = -2.5$ K/kbar) 1 – 0.001; 2 – 2.07; 3 – 4.14; 4 – 7.6; 5 – 15.0; 6 – 20.0. (b) ($T_{C0} = 210$ K) 1 – 0.001; 2 – 0.2; 3 – 0.5. Solid and dashed lines correspond to hydrostatic and uniaxial $p = -\sigma_3$ pressures, respectively. Experimental points are taken from Ref. 15 (\square) and Ref. 40 (\circ).

and $T_N(\delta)$ plotted for several ferroelectric and antiferroelectric crystals of KH_2PO_4 family, strained either by hydrostatic or uniaxial pressure, lie on a single line. Therefore the proton ordering model not only describes the universal T_C vs δ dependence¹¹ observed in KD_2PO_4 and $\text{ND}_4\text{D}_2\text{PO}_4$ under hydrostatic pressure, but also predicts that this dependence is obeyed also by the other crystals of the family strained by hydrostatic pressure as well as by the $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ strained by uniaxial pressure $p = -\sigma_3$. This fact again emphasizes the importance of the D-site distance in the phase transition in hydrogen bonded crystals and supports our assumption that pressure $p = -\sigma_3$ reduces δ .

Now we shall discuss pressure effects on the dielectric properties of the crystals. The slopes $\partial\mu_i/\partial p$ can be determined without introducing into the theory any extra fitting parameter on the basis of the following speculations. Even though these speculations are not quite rigorous, they do have two virtues: they are simple and their predictions agree fairly well with the experiment.

It is believed that the deuteron ordering in the system results in displacements of heavy ions and electron density which contribute to crystal polarization. Since, when ordered, a deuteron shifts from its central position on a hydro-

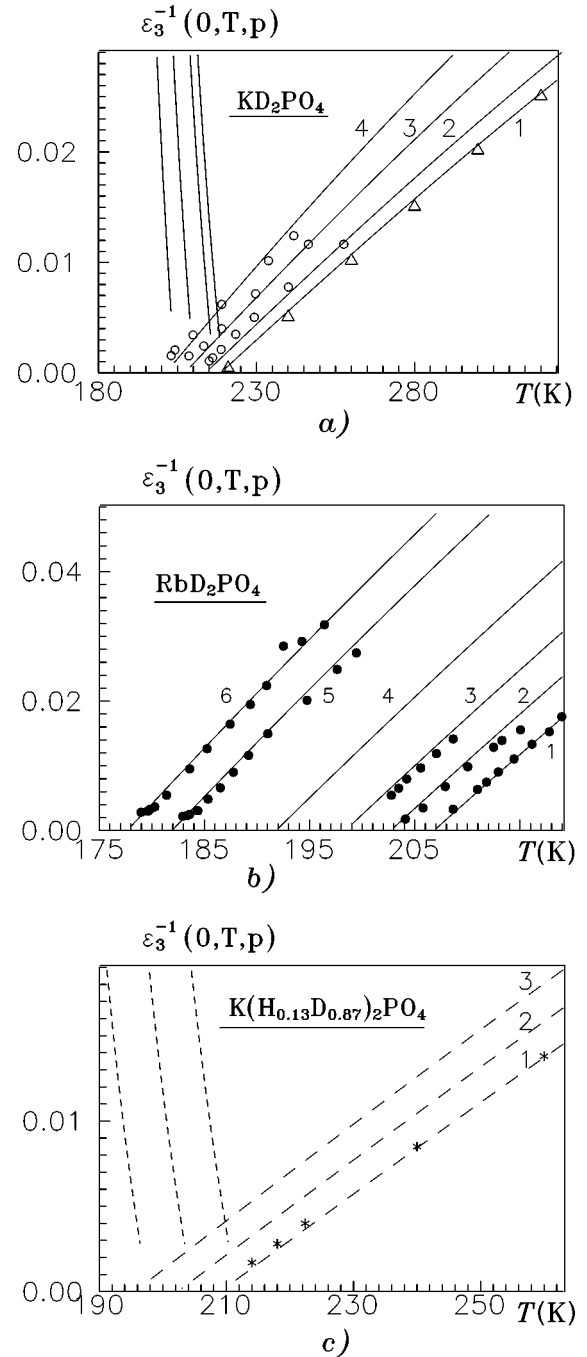


FIG. 4. The temperature dependence of the inverse static longitudinal dielectric permittivity of KD_2PO_4 (a), RbD_2PO_4 (b), and $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ (c) crystals at different values of external pressure p (kbar): (a) ($T_{C0} = 220$ K, $\partial T_C/\partial p = -2$ K/kbar) 1 – 0.001; 2 – 3.6; 3 – 4.7; 4 – 7.6; (b) 1 – 0.001; 2 – 1.1; 3 – 2.25; 4 – 4.0; 5 – 6.63; 6 – 7.76; (c) 1 – 0.001; 2 – 0.5, 3 – 1. Experimental points are taken from: Ref. 41 (\triangle), Ref. 16 (\circ), Ref. 18 (\bullet), and Ref. 42 ($*$). Solid and dashed lines correspond to hydrostatic and uniaxial $p = -\sigma_3$ pressures, respectively.

gen bond to the off-central one by a distance $\delta/2$, it seems reasonable to assume that the heavy ions displacements are also proportional to δ . This idea was used in the previous theories.^{13,14} In the present work we also assume that μ_i is proportional to the corresponding lattice constant a_i , reflecting an intuitively understood fact that the larger molecule is, the greater dipole moment arises in it. This yields

$$\frac{1}{\mu_i^0} \frac{\partial \mu_i}{\partial p} = \frac{\delta_1}{\delta_0} + \frac{\varepsilon_i}{p}. \quad (16)$$

In Fig. 3 we plot the temperature curves of spontaneous polarization of $\text{K}(\text{H}_{1-x}\text{D}_x)_2\text{PO}_4$ crystals at different values of hydrostatic and uniaxial $p = -\sigma_3$ pressures. As one can see, the model pressure dependence (16) of the effective dipole moment μ_3 provides a satisfactory description of a decrease in saturation polarization with hydrostatic pressure. Since we accepted a negative value of δ_1/δ_0 for a uniaxial pressure $p = -\sigma_3$, then, according to Eq. (16), effective dipole moment μ_3 and thereby the spontaneous polarization is expected to decrease with this pressure. Unfortunately, no direct experimental data for the uniaxial pressure $p = -\sigma_3$ on the spontaneous polarization of KD_2PO_4 is available.

In Fig. 4 we present the temperature dependences of the inverse static dielectric permittivity of KD_2PO_4 and RbD_2PO_4 crystals at different values of hydrostatic pressure and of $\text{K}(\text{H}_{0.13}\text{D}_{0.87})_2\text{PO}_4$ at different $p = -\sigma_3$ pressures. Difference between permittivities of clamped and free crystals is neglected. Unfortunately, experimental data for non-zero pressures are available only for the hydrostatic one.^{16,41} As one can see, the model dependences (16) well describe a decrease in the Curie constant with hydrostatic pressure. Due to the adopted negative value of δ_1/δ_0 , uniaxial pressure $p = -\sigma_3$ is expected to lower the Curie constant as well.

Hence, similarly to the pressure dependence of the transition temperature, the pressure dependences of dielectric permittivity and spontaneous polarization of these ferroelectrics are also governed by the parameter δ_1/δ_0 , indicating the crucial role of the D-site distance in the dielectric response of the hydrogen bonded crystals.

Let us consider now the pressure effects on the dielectric properties of antiferroelectric crystals of the KH_2PO_4 family. The antiferroelectric crystals of this family are characterized by the large values of transverse effective dipole moments of unit cell. The permittivity $\varepsilon_1(T, p)$ of $\text{ND}_4\text{D}_2\text{AsO}_4$ exhibits a strong variation with pressure,²⁰ and the slopes (16) describe the experimental data only qualitatively. It means that the mechanism of dipole moment formation in these crystals is somewhat different from that described above for the ferroelectric crystals, or rather there must be some other factor in addition to ion shifts due to the deuteron ordering. We assume that there exists interaction between large dipole moments of unit cells (we call this mutual polarization), which changes their magnitude and the character of their pressure dependence. Let us consider a simple model in which a unit cell i is assigned a dipole moment \mathbf{d}_i ; the size of the dipoles is much smaller than the distance between them. Up to the terms linear in external field E_{01} , the transverse polarization of an antiferroelectric crystal (naturally, induced by this external field) reads

$$P_1 = \frac{2\mu_1}{v} \frac{\partial \eta_{13E}^a}{\partial E_{01}} E_{01} = \frac{\mu_1^2}{v} \tilde{\chi}_1 E_{01} = \frac{d_1}{v}, \quad (17)$$

where [see Eq. (13)]

$$\tilde{\chi}_1 = \frac{\beta \chi_1^a}{D^a - 2\chi_1^a \varphi_1^a} + \frac{\beta \chi_2^a}{D^a - 2\chi_2^a \varphi_1^a},$$

d_1 is the transverse dipole moment of a unit cell.

We assume that the magnitude of the dipole moment is proportional to a complete electric field acting on it. This field differs from the external field \mathbf{E}_0 but include also the internal field created by other dipoles of the crystal

$$\mathbf{d}_k = \hat{\alpha} \left(\mathbf{E}_0 + \sum_l \frac{3(\mathbf{n}_{kl}\mathbf{d}_l)\mathbf{n}_{kl} - \mathbf{d}_l}{R_{kl}^3} \right), \quad (18)$$

where $\hat{\alpha}$ is the polarizability tensor; \mathbf{n}_{kl} is the unit vector directed from the k th dipole \mathbf{d}_k to the l th dipole \mathbf{d}_l , and R_{kl} is the distance between the dipoles; summation goes over all unit cell of a crystal. If all dipoles are directed along the external field, and the magnitudes of the dipoles are all the same, then Eq. (18) can be solved, and, for instance, for transverse dipole moment we obtain

$$d_1 = \frac{\alpha_1 E_{01}}{1 - \alpha_1 K_1}, \quad (19)$$

$$K_1 = \sum_{n_1 n_2 n_3} \frac{2a^2 n_1^2 - b^2 n_2^2 - c^2 n_3^2}{(a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2)^{5/2}},$$

a, b, c are the lattice constants and n_1, n_2, n_3 are integers such that $n_1^2 + n_2^2 + n_3^2 \neq 0$. From Eqs. (17) and (19) it follows that

$$\mu_1^2 = \frac{1}{\tilde{\chi}_1} \frac{\alpha_1}{1 - \alpha_1 K_1}.$$

Differentiating this equation with respect to pressure and choosing the value of the derivative $\partial \alpha_1 / \partial p$ so that it corresponds to the rate of the pressure changes in the square of effective dipole moment μ_1^2 in the case when the mutual polarization of dipoles is not taken into account ($K_1 = 0$), namely,

$$\frac{1}{\alpha_1} \frac{\partial \alpha_1}{\partial p} = 2 \left(\frac{\delta_1}{\delta_0} + \frac{\varepsilon_1}{p} \right),$$

we obtain

$$\frac{1}{\mu_1^2} \frac{\partial \mu_1^2}{\partial p} = \frac{1}{\alpha_1} \frac{\partial \alpha_1}{\partial p} (1 + \tilde{\chi}_1 K_1 \mu_1^2) + \tilde{\chi}_1 \mu_1^2 \frac{\partial K_1}{\partial p}, \quad (20)$$

where

$$\frac{\partial K_1}{\partial p} p = \sum_{n_1 n_2 n_3} \frac{a^2 n_1^2 (4R^2 - 5r_1) \varepsilon_1 - (2R^2 + 5r_1) (b^2 n_2^2 \varepsilon_2 + c^2 n_3^2 \varepsilon_3)}{R^7},$$

$$R = \sqrt{a^2 n_1^2 + b^2 n_2^2 + c^2 n_3^2}, \quad r_1 = 2a^2 n_1^2 - b^2 n_2^2 - c^2 n_3^2,$$

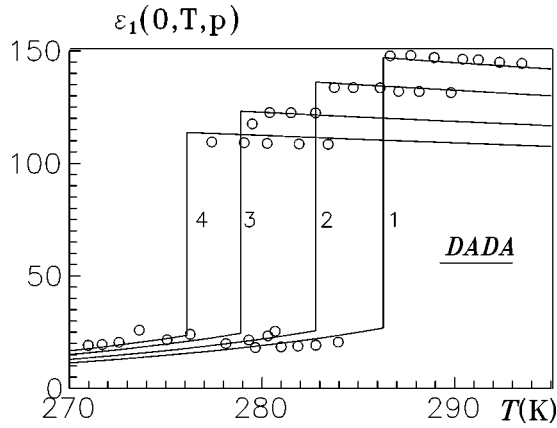


FIG. 5. The temperature dependence of the transverse static dielectric permittivity of $\text{ND}_4\text{D}_2\text{AsO}_4$ at different values of external hydrostatic pressure p (kbar): 1 – 0.001; 2 – 2.62; 3 – 5.6; 4 – 7.68. Experimental points are taken from Ref. 20.

and the pressure dependence of $\tilde{\chi}_1$ is neglected. One can see, that the terms in $\partial\mu_1^2/\partial p$ describing the influence of mutual polarization (via K_1 and $\partial K_1/\partial p$) are proportional to μ_1^2 and, therefore, are unessential for crystals with small dipole moments such as μ_3 in KD_2PO_4 or RbD_2PO_4 .

The dielectric susceptibility should be now determined as a derivative of polarization with respect to a complete field $E_1 = E_{01} + d_1 K_1 = E_{01}/(1 - \alpha_1 K_1)$. Then, instead of Eq. (13), we obtain

$$\varepsilon_1^a(0, T, p) = \varepsilon_{1\infty}^a + 4\pi \frac{\mu_1^2}{v} \frac{\tilde{\chi}_1}{1 + \mu_1^2 \tilde{\chi}_1 K_1}. \quad (21)$$

Let us mention that the difference between Eqs. (13) and (21) is the larger, the stronger the crystal lattice differs from a cubic one; at $a = b = c$, $K_1 \equiv 0$.

In Fig. 5 we plot the temperature curves of the transverse dielectric permittivity of $\text{ND}_4\text{D}_2\text{AsO}_4$ (DADA) at different values of hydrostatic pressure along with the experimental points by Gesi.²⁰ In calculations, we use $\nu_a^0(0) = -35$ K and a value of the piezomodule d_{14} corresponding to an undeuterated sample.³⁸

The pressure dependence of the coefficient μ_1^2 calculated with Eq. (20) provides a fair description of a decrease in ε_1^a in the paraelectric phase as well as of a slow increase in the antiferroelectric phase, showing thereby an importance of the mutual polarization mechanism in the dielectric response of these crystals. It should be noted that there can also be other mechanisms of pressure influence on the dipole moments of hydrogen bonded crystals, neglected here: rotation of PO_4 tetrahedra around the c axis, shortening of N-H-O bonds in antiferroelectrics, etc. It can also be important that the dielectric permittivity of DADA (Ref. 20) is measured at $\nu = 10^5$ Hz, which belongs to the region of the piezoelectric resonance.

In a similar way, one describes also the variation with hydrostatic pressure of the transverse dielectric permittivity of DKDP given by

$$\varepsilon_1^f(T, p) = \varepsilon_{1\infty}^f + 4\pi \frac{\beta \mu_1^2}{v} \frac{2\kappa_1^f}{D^f - 2\kappa_1^f \varphi_1^f}$$

[where $\kappa_1^f = a + b \cosh z^f$ and $\varphi_1^f = (1 - [\eta^f]^2)^{-1} + \beta \nu_a(0)$] — a decrease with pressure in the paraelectric phase and an

increase in the ferroelectric phase observed recently by Dr. A. G. Slivka of Uzhgorod State University.⁴³

III. CONCLUDING REMARKS

We presented a unified approach allowing one to describe the effects of hydrostatic and uniaxial pressures on the phase transition and static dielectric properties of deuterated ferroelectrics and antiferroelectrics of KDP family. We also studied pressure influence on dielectric relaxation in these crystals. Results of these studies will be published elsewhere.

The calculations performed within the proton ordering model in the framework of the four-particle cluster approximation confirm the ability of the proton ordering model to describe the behavior of KDP-type crystals under external pressure. It should be noted that the theory can be easily generalized to the cases of other pressures, including those which lower the crystals symmetry, in particular,²³ $\sigma_1 - \sigma_2$. The proposed scheme of choosing the theory parameters allows one to describe the influence of different pressures on a transition temperature and static dielectric properties of the crystals. The main parameter which determines the pressure dependences of the transition temperature, spontaneous polarization and static dielectric permittivities is the ratio δ_1/δ_0 , which is the rate of the pressure induced changes in the D-site distance. Our calculations show that the universality of the transition temperature vs D-site distance dependence observed experimentally in some of the crystals deformed by hydrostatic pressure is obeyed also by the other crystals of the family and also under the uniaxial pressure $p = -\sigma_3$. The theory predicts that this uniaxial pressure should shorten the hydrogen bonds and the D-site distance, even though this pressure is applied along the axis perpendicular to the plane in which the hydrogen bonds lie. The suggested model pressure dependences of the effective dipole moments of unit cells provide a satisfactory agreement with experimental data for the effects of hydrostatic pressure on the dielectric properties of the crystals. We show that for the antiferroelectric crystals of the family with large values of transverse dipole moments, one should take into account processes of mutual polarization of unit cell dipoles. For the ferroelectrics with small longitudinal moments those processes are not important. Further dielectric and structural measurements of the pressure effects, especially of uniaxial pressures, on the KDP family crystals will allow to ascertain the values of the theory parameters, verify its predictions about the possible changes in the H-bond geometry and dielectric properties of the crystals.

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