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EXTERNAL PRESSURE INFLUENCE ON PHASE TRANSITION AND PHYSICAL PROPERTIES OF $ND_4D_2PO_4$-TYPE ANTIFERROELECTRICS.

ЛЬВІВ

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Вплив зовнішнього тиску на фазовий перехід і фізичні властивості антисегнетоелектриків типу $ND_4D_2PO_4$.

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Анотація. На основі запропонованої раніше моделі досліджено вплив гідростатичного та одновісного σ_3 тисків на фізичні властивості кристалів типу DADP. В кластерному наближенні розраховано теплові, статичні і динамічні діелектричні характеристики DADP та отримано їх можливі залежності від тисків, що розглядаються. Проведено детальний числовий аналіз отриманих результатів. Показано, що при належному виборі параметрів теорії, отримується задовільний кількісний опис експериментальних даних для залежності температури фазового переходу кристалу DADP від гідростатичного тиску. Встановлено, що ефекти, викликані зовнішніми тисками в кристалах DKDP і DADP, можливо описати в рамках єдиного підходу.

External pressure influence on phase transition and physical properties of $ND_4D_2PO_4$-type antiferroelectrics.

R.R.Levitskii, A.P.Moina, I.R.Zachek

Abstract. On the basis of the proposed microscopic model, we study the effects of hydrostatic and uniaxial σ_3 pressures on the physical properties of a DADP crystal. The thermal, static and dynamic dielectric properties of a considered crystal are investigated within the cluster approximation. A thorough numerical analysis of obtained results is performed. Proper choice of the theory parameters we obtain a satisfactory description of experimental results for pressure dependence of the transition temperature of DADP. On the basis of carried calculations, we obtain possible dependences of physical characteristics on the uniaxial σ_3 and hydrostatic stresses. We show that it is possible to describe the pressure effects on antiferroelectric DADP and ferroelectric DKDP crystals within the same model. Further experimental study of uniaxial and hydrostatic pressure effects on the physical properties of considered crystals is required.

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1. Introduction

Amongst compounds obtained by isomorphic substitution of heavy ions in KH_2PO_4 (KDP), the ammonium salts ($NH_4H_2PO_4$, $NH_4H_2AsO_4$) are of particular interest, for they undergo an antiferroelectric phase transition.

In the paraelectric phase an $NH_4H_2PO_4$ crystal (ADP) is isomorphic to KDP (the space group $I42d$ with four molecules in the unit cell) [1,2]. The PO_4 tetrahedra are connected with each other and with ammonium groups NH_4 by a three-dimensional network of hydrogen bonds. The bonds O-H. . .O are shorter, more stable and less temperature dependent than the bonds N-H. . .O. Transition to the low temperature phase is accompanied by distortion of the unit cell (the space group $P2_12_12_1$); the atoms of nitrogen and phosphorus shift in the direction perpendicular to the c-axis of the crystal; the tetrahedra NH_4 and PO_4 distort and polarize, so that the neighbouring along the c-axis NH_4 and PO_4 groups are polarized in the opposite directions. The number of molecules per unit cell does not change.

In the crystals of ADP type, a clear first-order phase transition is observed, accompanied by a pronounced temperature hysteresis and a discontinuities of both dielectric permittivities [3,4]. The transverse permittivity is much higher than the longitudinal one; its temperature dependence is more pronounced. The crystal possesses piezoelectric properties in the paraelectric phase.

The physical properties of ADP type crystals as well as those of KDP, are strongly affected by deuteration [3–6,10,7–9]. The transition temperature T_N increases from 148 K in ADP to 245 K in completely deuterated $ND_4D_2PO_4$ (DADP). The thermal and dielectric responses change with deuteration correspondingly.

The properties of ADP are perceptibly dependent on external pressure. For instance, the transition temperatures T_N of ADP and DADP as well as of KDP and DKDP crystals decrease with pressure linearly [10] ($\partial T_N/\partial p = -3.4$ K/kbar in ADP, $\partial T_N/\partial p = -1.4$ K/kbar in DADP). At a higher pressure, the decrease of T_N in ADP becomes nonlinear, and T_N becomes zero at $p = 33$ kbar, (the ordered phase vanishes) [11]. The transverse dielectric permittivity of ADP decreases with pressure in the paraelectric phase and increases in the antiferroelectric [11]. The influence of hydrostatic pressure on the elastic properties of the paraelectric ADP has been studied by Fritz [12]. It has been revealed that the elastic constants c_{11} and c_{33} increase with pressure linearly, while the behaviour of c_{44} and c_{66} is nonlinear.

Little data about pressure influence on the crystal structure of ADP are available. However, it is known that the transition temperature of ADP and DADP, as well as of KDP, is a linear function of the distance δ between two H(D)-sites on O-H(D). . .O bond and turns to zero at $\delta_c = 0.2\mathring{A}$ [13–15]. Moreover, at equal (within $0.01\mathring{A}$) δ, the transition temperatures of KDP, DKDP, ADP and DADP crystals coincide.

Interesting information can be obtained from the Raman spectra of these crystals [16,17]. In the antiferroelectric crystals of this type, no critical soft mode in the centre of the Brillouin zone is expected or detected. However, in Raman spectra of ADP, the active proton modes of B_2 and E symmetries are observed. Their temperature dependence is of great interest, for these modes give the dominant contribution to the dielectric permittivity of the crystal. The estimated in [16,17] contribution of the B_2 mode is in agreement with the data of [18] obtained in the ultrahigh frequency region.

Pronounced isotopic dependence of the transition temperature, thermal, and dielectric responses of ADP type antiferroelectrics, the peculiarities of the behaviour of their characteristics in the vicinity of the transition point, and the data of [19,20] suggest the strong connection between the phase transition in these antiferroelectrics and the ordering of protons on O-H. . .O bonds, coupled to the lattice vibrations.

Usually, the antiferroelectric character of proton ordering in ADP is explained under assumption that the lateral (not up-down ones as in the KDP case) proton configurations have the lowest energy, that is, the Slater parameter ε is negative. At first, this idea was proposed by Nagamiya [21]. However, he didn't explain the phase transition. It should be noted that the system with the short-range proton correlations alone has as many as three configurations with the same energy, and only one of these configurations is antiferroelectric [22–24]. The phase transitions can be described only if the long-range proton interactions are taken into account [22]. Senko [25] was not able to explain the phase transition in ADP either, even though he considered the long-range interactions.

The neutron scattering measurements by Hewat (see [16] has proven to be very important for understanding of the phase transition mechanism in ADP. The character of proton ordering found here corresponds to the one assumed by Nagamiya [21]. Existence of the lateral proton configurations in the low-temperature phase of ADP crystals was also affirmed by Raman scattering measurements [26,27]. At the same time, these experiments reveal that at $T > T_N$, groups $H_2PO_4^-$ ($D_2PO_4^-$) have the symmetry C_2, i.e. protons form up-down, not lateral (C_1) configurations. This conclusion was based on the fact that the modes allowed in C_1

symmetry but forbidden in C_2 were not detected in the Raman spectra of $\alpha(\bar{\beta}z)\beta$ geometry. These results agree well with the idea by Schmidt [28] that the antiferroelectricity in ADP type crystals results from additional NH_4-mediated short-range interactions between hydrogens, the Slater energy being positive, rather than from long-range interactions and negative Slater energy.

Apparently, the peculiarities of proton ordering in ADP type crystals result from presence of ammonium ions NH_4 and of additional hydrogen bonds N−H...O. Each oxygen atom in these crystals in connected by H-bonds with another oxygen of a neighbouring PO_4 group and with a nitrogen atom of a neighbouring ammonium group NH_4. The ion NH_4 is shifted to the off-centre position, so that two hydrogen bonds connecting the nitrogen atom of this group with oxygens, become longer than the other two [2]. If an oxygen atom is linked to a nitrogen by the longer bond, then a proton on O−H...O bond, attached to this oxygen, is located in position close to the oxygen, and *vice versa*, if the N−H...O bond is short, the proton on the O−H...O bond is located in positions away from the oxygen. The role of these structural features of ammonium salts is discussed by Matsushita and Matsubara [29]. They show that these features lead to effective antiferroelectric interaction between protons on O−H...O bonds.

The fact that in the paraelectric phase ADP crystal is isomorphic to KDP and the qualitative similarity of pressure and temperature dependences of various physical characteristics of KDP and ADP suggest the necessity to look for a single theory of the phase transitions in these crystals.

At the moment, there exist two different approaches to this problem. According to one of them [22,30], the phase transition takes place due to ordering of H_2PO_4 dipoles, protons forming lateral configurations. The long-range dipole-dipole interactions are essential here.

The other approach [23,24,31,32] is based on the proton ordering model. Using this model, Levitskii *et al* proposed the first consistent statistical theory of ferro- and antiferroelectric crystals of KDP family [23,24]. The theory takes into account the short-range correlations between protons on O−H...O bonds as well as the long-range interactions between them. Within the four-particle cluster approximation, the free energy of proton subsystem is calculated and studied, and the possible types of proton ordering in these crystals are established. It is shown that antiferroelectric transition is possible only if the long-range interactions are taken into account.

According to this model, polarization along the antiferroelectric axes *a* or *b*, induced by electric field, is created by dipole moments of hydrogen bonds directed along the axis along with the displacements of heavy ions in the *b* plane, accompanying proton ordering. Hydrogen bonds attached to a given PO_4 group contribute to polarizations along both *a* and *b* axes. In contrast to this, in [22], polarization is attributed to H_2PO_4 dipoles, where each dipole can be polarized only along one of the *a* or *b* axes. As a result, the expressions for the transverse dielectric permittivity obtained in [23,31] and [22] are different, even though a proper choice of fitting parameters yields a satisfactory description of experimental data in both cases.

Levitskii *et al* [34–36] explored the dynamic aspects of the ADP antiferroelectrics. In [35,36], they thoroughly study the two-sublattice model of ADP, considering two polarized in the opposite directions sublattices of protons tunnelling on O−H...O bonds. In [34], the proton-lattice coupling is also taken into account. It is shown that in the spectrum of ADP excitations, there is a soft mode, which frequency tends to zero at the transition point at $\mathbf{k} \to \mathbf{k}_Z$; $\mathbf{k}_Z$ are the wavevectors of the Z-point in the Brillouin zone. This result is in agreement with the data of quasielastic neutron scattering by ADP [37].

In order to study the dynamic properties of KDP type ferroelectric, the Bloch method is also used (see, for instance [38]). Although this method allows to taken into account tunnelling effects, it does have a very serious drawback, resulting from the mean field approximation involved.

A large part of studies on the dynamics of these crystals is based on the stochastic Glauber model [39]. Yoshimitsu and Matsubara [40], later Havlin *et al* [41] and Levitskii *et al* [42–45] proposed the kinetic model of ferroelectrics and antiferroelectrics of KDP type and used it for the investigation of the transverse and longitudinal relaxation in deuterated DKDP and DADP crystals.

A microscopic theory of the pressure effects in ADP type crystals had not been yet developed. Such a theory would be able to shed some light on the long-pending problem about the nature of the phase transition in these crystals.

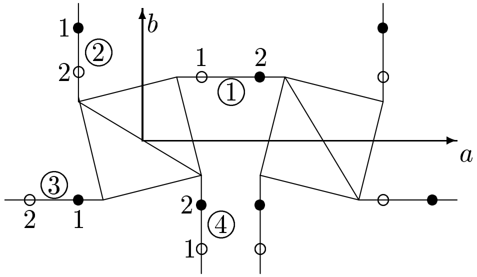
The model of a strained $K(H_{1-x}D_x)_2PO_4$ -type crystal was proposed by Stasyuk in [46,47]. Its quantitative analysis for the case of pressures which do not lower the system symmetry is performed in [48–51]. We found the set of theory parameters providing a satisfactory description of pressure dependences of the transition temperature, spontaneous polarization and longitudinal dielectric permittivity of crystals at different deuteration levels.

Our goal is to apply this theory to a strained DADP crystal and check whether it is possible to describe the pressure effects in ferroelectric and antiferroelectric crystals of the KDP family within a single approach.

2. Cluster approach

We consider a system of deuterons moving on O-D…O bonds in a crystal of $ND_4D_2PO_4$ type. The primitive cell of such a crystal is composed of two neighbouring PO_4 tetrahedra together with four hydrogen bonds attached to one of them (”A” type tetrahedra). Hydrogen bonds going to another (”B” type) tetrahedron belong to four nearest structural elements surrounding it (see the figure below). An external hydrostatic ($\sigma_{\rm h}$) or uniaxial stress (σ_3), which does not lower the system symmetry, is applied

$$\sigma_{\rm h} = (-p, -p, -p), \quad \sigma_3 = (0, 0, -p). \tag{2.1}$$



The unit cell of a DADP crystal. Here ①,②,③,④ and 1,2 stand for the hydrogen bond and H-site numbers, respectively.

When an external stress and electric field E_i ($i = 1, 2, 3$) directed along the crystallographic axes a, b, c are applied, the Hamiltonian of the system has the following form [46]

$$\hat{H}_i = \frac{\bar{v}N}{2}\sum_{ij} c_{ij}^{(0)}\varepsilon_i\varepsilon_j - \frac{1}{2}\sum_{qf} 2\mu F^i_{qf}\frac{\langle\sigma_{qf}\rangle}{2} - \sum_{qf}\left[2\mu F^i_{qf} + \mu_{fi}E_i\right]\frac{\sigma_{qf}}{2} +$$
$$+\sum_{\substack{q_1,q_2\\ q_3,q_4}}\left\{\delta_{\mathbf{R}_{q_1},\mathbf{R}_{q_2}}\delta_{\mathbf{R}_{q_1},\mathbf{R}_{q_3}}\delta_{\mathbf{R}_{q_1},\mathbf{R}_{q_4}} + \delta_{\mathbf{R}_{q_1}+\mathbf{r}_2,\mathbf{R}_{q_2}}\delta_{\mathbf{R}_{q_1}+\mathbf{r}_3,\mathbf{R}_{q_3}}\delta_{\mathbf{R}_{q_1}+\mathbf{r}_4,\mathbf{R}_{q_4}}\right\}\times$$
$$\times\left\{\frac{1}{2}\sum_{ff'} V_{ff'}\frac{\sigma_{q_f f}}{2}\frac{\sigma_{q_{f'} f'}}{2} + \Phi\frac{\sigma_{q_1 1}}{2}\frac{\sigma_{q_2 2}}{2}\frac{\sigma_{q_3 3}}{2}\frac{\sigma_{q_4 4}}{2}\right\} \tag{2.2}$$

Hamiltonian (2.2) describes short-range configurational interactions between deuterons near tetrahedra of ”A” and ”B” type; $\mathbf{r}_f$ is a relative position vector of a hydrogen bond in a cell. 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. $c_{ij}^{(0)}$ are the ”seed” elastic constants; ε_i are the components of the strain tensor; $\bar{v} = v/k_{\rm B}$; v is the unit cell volume; $k_{\rm B}$ is the Boltzmann constant. F^i_f are the internal fields, created by effective long-range forces, which also include an indirect interaction between deuterons through lattice vibrations. Their form in the case of a DKDP crystal has been found in [46,47]. The long-range interaction, taken into account in the mean field approximation, is renormalized by terms linear in the mean values of quasispins $\eta^{(1)}_{qf} = \langle\sigma_{qf}\rangle$ and strains ε_i. Such terms arise if one considers only the lattice strains but neglects the pressure dependence of the dipole moment of a hydrogen bond $\mu = e\delta$ (δ is the D-site distance on a O-D…O bond). However, a similar result is obtained if one formally expands the constants of the long-range interaction $J_{ff'}(qq')$ in powers of strains up to the linear terms

$$J_{ff'}(qq') = \tilde{J}^{(0)}_{ff'}(qq') + \sum_j \psi^j_{ff'}(qq')\varepsilon_j;$$

$$2\mu F^i_{qf} = \sum_{q'f'}[\tilde{J}^{(0)}_{ff'}(qq') + \sum_j \psi^j_{ff'}(qq')\varepsilon_j]\frac{\eta^{(1)i}_{q'f'}}{2}.$$

The pressure dependence of μ can be taken into account in the following way. According to [52,53], δ in KDP and DKDP crystals is a linear function of hydrostatic pressure. Assuming that the character of this dependence on hydrostatic and uniaxial σ_3 stress in DADP crystal is the same and bearing in mind (2.1) we can write

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

Expanding $J_{ff'}$ in terms of pressure and considering the fact that it is proportional to μ^2, we get

$$\tilde{J}^{(0)}_{ff'}(qq') = J^{(0)}_{ff'}(qq')[1 + 2\frac{\delta_1}{\delta_0}p],$$

$$2\mu F^i_{qf} = \sum_{q'f'}\left[J^{(0)}_{ff'}(qq')[1 + 2\frac{\delta_1}{\delta_0}p] + \sum_j \psi^j_{ff'}(qq')\varepsilon_j\right]\frac{\eta^{(1)i}_{q'f'}}{2}. \tag{2.3}$$

Parameters $\psi_{ff'}(qq')$ are the same for all pressures which do not lower the system symmetry, whereas the ratio δ_1/δ_0 is different for hydrostatic and uniaxial stresses.

The static and dynamic properties of a deuteron subsystem of a DKDP crystal will be considered in the four-particle cluster approximation. The cluster Hamiltonian reads

$$\hat{H}^{iA}_{q4} = V\left[\frac{\sigma_{q1}}{2}\frac{\sigma_{q2}}{2} + \frac{\sigma_{q2}}{2}\frac{\sigma_{q3}}{2} + \frac{\sigma_{q3}}{2}\frac{\sigma_{q4}}{2} + \frac{\sigma_{q4}}{2}\frac{\sigma_{q1}}{2}\right] + \tag{2.4}$$
$$+ U\left[\frac{\sigma_{q1}}{2}\frac{\sigma_{q3}}{2} + \frac{\sigma_{q2}}{2}\frac{\sigma_{q4}}{2}\right] + \Phi\frac{\sigma_{q1}}{2}\frac{\sigma_{q2}}{2}\frac{\sigma_{q3}}{2}\frac{\sigma_{q4}}{2} - \sum_f \frac{z^i_{qf}}{\beta}\frac{\sigma_{qf}}{2}.$$

Here $V = (\varepsilon - w_1)/2$, $U = (\varepsilon + w_1)/2$, $\Phi = 2\varepsilon - 8w + 2w_1$; $\varepsilon = \varepsilon_s - \varepsilon_a$, $w = \varepsilon_1 - \varepsilon_a$, $w_1 = \varepsilon_0 - \varepsilon_a$; ε_a, ε_s, ε_1 and ε_0 are the energies of lateral, up-down, single-ionized and double ionized deuteron configurations, respectively. Let us note that the energy of the lateral configurations is the lowest.

Within the proposed model the energies ε, w, and w_1 are assumed to be linear functions of strains ε_i

$$\begin{array}{cc}
T < T_{\rm N} & T > T_{\rm N} \\
\varepsilon = \varepsilon^0 + \delta^-_{11}\varepsilon_1 + \delta^-_{12}\varepsilon_2 + \delta^-_{13}\varepsilon_3, & \varepsilon = \varepsilon^0 + \delta^+_{11}(\varepsilon_1 + \varepsilon_2) + \delta^+_{13}\varepsilon_3, \\
w = w^0 + \delta^-_{21}\varepsilon_1 + \delta^-_{22}\varepsilon_2 + \delta^-_{23}\varepsilon_3, & w = w^0 + \delta^+_{21}(\varepsilon_1 + \varepsilon_2) + \delta^+_{23}\varepsilon_3, \\
w_1 = w^0_1 + \delta^-_{31}\varepsilon_1 + \delta^-_{32}\varepsilon_2 + \delta^-_{33}\varepsilon_3, & w_1 = w^0_1 + \delta^+_{31}(\varepsilon_1 + \varepsilon_2) + \delta^+_{33}\varepsilon_3.
\end{array}$$

We consider only diagonal components of the strain tensor ε_1, ε_2, ε_3, and neglect piezoelectric shear strains ε_4, ε_5, ε_6 arising when the respective electric fields E_1, E_2 and E_3 are applied (the piezomoduli d_{14}, d_{25}, d_{36} differ from zero). This approximation should not affect the values of transition temperature or specific heat calculated at $E_i = 0$, but gives rise to error in calculations of the dielectric responses of the crystal, especially of the longitudinal permittivity $\varepsilon_3(0, T, p)$, since $d_{36} \gg d_{14}$ [4].

Calculation of the mean values

$$\langle\sigma_{qf}\rangle = \frac{{\rm Sp}\left\{\sigma_{qf}\exp\left(-\beta\hat{H}^{iA}_{q4}\right)\right\}}{{\rm Sp}\exp\left(-\beta\hat{H}^{iA}_{q4}\right)},$$

yields

$$\begin{aligned}
\eta^{(1)x,y}_{q13} &= \frac{2\sinh z^{x,y}_{q13}\cosh z^{x,y}_{q24} + 2b\sinh z^{x,y}_{q13}}{D^{x,y}}, \\
\eta^{(1)x,y}_{q24} &= \frac{2\sinh z^{x,y}_{q24}\cosh z^{x,y}_{q13} + 2b\sinh z^{x,y}_{q24}}{D^{x,y}}, \\
\eta^{(1)z}_{q14} &= \frac{a\sinh(z^z_{q14} + z^z_{q23}) + \sinh(z^z_{q14} - z^z_{q23}) + 2b\sinh z^z_{q14}}{D^z}, \\
\eta^{(1)z}_{q23} &= \frac{a\sinh(z^z_{q14} + z^z_{q23}) - \sinh(z^z_{q14} - z^z_{q23}) + 2b\sinh z^z_{q23}}{D^z}.
\end{aligned} \tag{2.5}$$

where

$$\begin{aligned}
D^{x,y} &= 2\cosh z^{x,y}_{q13}\cosh z^{x,y}_{q24} + 2b(\cosh z^{x,y}_{q13} + \cosh z^{x,y}_{q24}) + a + d, \\
D^z &= a\cosh(z^z_{q14} + z^z_{q23}) + \cosh(z^z_{q14} - z^z_{q23}) + \\
&\quad + 2b(\cosh z^z_{q14} + \cosh z^z_{q23}) + d + 1, \\
a &= \exp(-\beta\varepsilon), \quad b = \exp(-\beta w), \quad d = \exp(-\beta w_1).
\end{aligned} \tag{2.6}$$

The effective fields z^i_{qf} have the following form:

$$\begin{aligned}
z^x_{q13} &= \beta[-\Delta^x_{q13} + 2\nu_a(\mathbf{k}_Z)\eta^{(1)}{\rm e}^{i\mathbf{k}_Z\mathbf{R}_q} + 2\nu_a(0)\eta^{(1)}_{13E_1} + \mu_1 E_1], \\
z^x_{q24} &= \beta[-\Delta^x_{q24} + 2\nu_a(\mathbf{k}_Z)\eta^{(1)}{\rm e}^{i\mathbf{k}_Z\mathbf{R}_q} + 2\nu_a(0)\eta^{(1)}_{24E_1}], \\
z^y_{q13} &= \beta[-\Delta^y_{q13} + 2\nu_a(\mathbf{k}_Z)\eta^{(1)}{\rm e}^{i\mathbf{k}_Z\mathbf{R}_q} + 2\nu_a(0)\eta^{(1)}_{13E_2}], \\
z^y_{q24} &= \beta[-\Delta^y_{q24} + 2\nu_a(\mathbf{k}_Z)\eta^{(1)}{\rm e}^{i\mathbf{k}_Z\mathbf{R}_q} + 2\nu_a(0)\eta^{(1)}_{24E_2} + \mu_2 E_2], \\
z^z_{q14} &= \beta[-\Delta^z_{q14} - 2\nu_a(\mathbf{k}_Z)\eta^{(1)}{\rm e}^{i\mathbf{k}_Z\mathbf{R}_q} + 2\nu_c(0)\eta^{(1)}_{E_3} + \mu_3 E_3], \\
z^z_{q23} &= \beta[-\Delta^z_{q23} + 2\nu_a(\mathbf{k}_Z)\eta^{(1)}{\rm e}^{i\mathbf{k}_Z\mathbf{R}_q} + 2\nu_c(0)\eta^{(1)}_{E_3} + \mu_3 E_3],
\end{aligned} \tag{2.7}$$

We took into account the symmetry of the distribution functions $\eta^{(1)i}_{qf}$ and of the bond dipole moments

$$\begin{aligned}
&\eta^{(1)x,y}_{q13} = -\eta^{(1)x,y}_{q1} = \eta^{(1)x,y}_{q3}, \quad \eta^{(1)x,y}_{q24} = \eta^{(1)x,y}_{q2} = -\eta^{(1)x,y}_{q4}, \\
&\eta^{(1)z}_{q14} = \eta^{(1)z}_{q1} = \eta^{(1)z}_{q4}, \quad \eta^{(1)z}_{q23} = \eta^{(1)z}_{q2} = \eta^{(1)z}_{q3}, \\
&\mu_1 = \mu_{31} = -\mu_{11}, \quad \mu_{21} = \mu_{41} = 0, \\
&\mu_2 = \mu_{22} = -\mu_{42}, \quad \mu_{12} = \mu_{32} = 0, \\
&\mu_3 = \mu_{13} = \mu_{23} = \mu_{33} = \mu_{43},
\end{aligned} \tag{2.8}$$

and presented $\eta^{(1)i}_{qf}$ as a sum of two terms: the modulated spontaneous part and the uniform one caused by electric fields

$$\begin{aligned}
&\eta^{(1)i}_{qf} = \eta^{(1)}_f{\rm e}^{i\mathbf{k}_Z\mathbf{R}_q} + \eta^{(1)}_{fE_i}, \\
&\eta^{(1)} = -\eta^{(1)}_1 = \eta^{(1)}_2 = \eta^{(1)}_3 = -\eta^{(1)}_4; \\
&\eta^{(1)}_{3E_1} = -\eta^{(1)}_{1E_1}, \quad \eta^{(1)}_{2E_1} = -\eta^{(1)}_{4E_1}; \quad \eta^{(1)}_{3E_2} = -\eta^{(1)}_{1E_2}, \quad \eta^{(1)}_{2E_2} = -\eta^{(1)}_{4E_2}; \\
&\eta^{(1)}_{1E_3} = \eta^{(1)}_{2E_3} = \eta^{(1)}_{3E_3} = \eta^{(1)}_{4E_3}.
\end{aligned}$$

Here $\mathbf{k}_Z = \dfrac{1}{2}(\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$, $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are the basic vectors of the reciprocal lattice, and ${\rm e}^{i\mathbf{k}_Z\mathbf{R}_q} = \pm 1$.

According to (2.3), the parameters of the long-range interaction are linear functions of strains and pressure

$$\nu_a(\mathbf{k}) = \nu_a^0(\mathbf{k})[1 + 2\frac{\delta_1}{\delta_0}p] + \sum_i \psi_{ai}(\mathbf{k})\varepsilon_i,$$

$$\nu_c(0) = \nu_c^0(0)[1 + 2\frac{\delta_1}{\delta_0}p] + \sum_i \psi_{ci}(0)\varepsilon_i,$$

$$\nu_a^0(\mathbf{k}) = \frac{1}{4}[J_{11}^{(0)}(\mathbf{k}) - J_{13}^{(0)}(\mathbf{k})]; \;\; \nu_c^0(0) = \frac{1}{4}[J_{11}^{(0)}(0) + 2J_{12}^{(0)}(0) + J_{13}^{(0)}(0)],$$

$$\psi_{ai}(\mathbf{k}) = \frac{1}{4}[\psi_{11}^i(\mathbf{k}) - \psi_{13}^i(\mathbf{k})]; \;\; \psi_{ci}(0) = \frac{1}{4}[\psi_{11}^i(0) + 2\psi_{12}^i(0) + \psi_{13}^i(0)].$$

Here $\mathbf{k} = \mathbf{k}_Z, 0$.

In (2.7), Δ_{qf}^i are effective fields, resulting from an interaction with neighbouring quasispins outside a cluster. The fields can be determined from the condition of equality of the mean values $\langle\sigma_{qf}\rangle$ calculated with four- and single-particle Gibbs' distributions, i.e. with Hamiltonian (2.4) and with

$$\hat{H}_{qf}^i = -\frac{\bar{z}_{qf}^i}{\beta}\frac{\sigma_{qf}}{2}, \tag{2.9}$$

respectively. Expressions for $\bar{z}_{qf}^i$ can be obtained from (2.7) by replacing Δ_{qf}^i with $2\Delta_{qf}^i$; obviously, their symmetry coincides with that of z_{qf}^i. After Δ_{qf}^i had been excluded from (2.7), the quantities z_{qf}^i read

$$\begin{aligned}
z_{q13}^x &= \frac{1}{2}\ln\frac{1+\eta_{q13}^{(1)x}}{1-\eta_{q13}^{(1)x}} + \beta[\nu_a(\mathbf{k}_Z)\eta^{(1)}\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_q} + \nu_a(0)\eta_{13E_1}^{(1)} + \frac{\mu_1 E_1}{2}],\\
z_{q24}^x &= \frac{1}{2}\ln\frac{1+\eta_{q24}^{(1)x}}{1-\eta_{q24}^{(1)x}} + \beta[\nu_a(\mathbf{k}_Z)\eta^{(1)}\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_q} + \nu_a(0)\eta_{24E_1}^{(1)}],\\
z_{q13}^y &= \frac{1}{2}\ln\frac{1+\eta_{q13}^{(1)y}}{1-\eta_{q13}^{(1)y}} + \beta[\nu_a(\mathbf{k}_Z)\eta^{(1)}\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_q} + \nu_a(0)\eta_{13E_2}^{(1)}],\\
z_{q24}^y &= \frac{1}{2}\ln\frac{1+\eta_{q24}^{(1)y}}{1-\eta_{q24}^{(1)y}} + \beta[\nu_a(\mathbf{k}_Z)\eta^{(1)}\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_q} + \nu_a(0)\eta_{24E_2}^{(1)} + \frac{\mu_2 E_2}{2}],\\
z_{q14}^z &= \frac{1}{2}\ln\frac{1+\eta_{q14}^{(1)z}}{1-\eta_{q14}^{(1)z}} + \beta[-\nu_a(\mathbf{k}_Z)\eta^{(1)}\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_q} + \nu_c(0)\eta_{E_3}^{(1)} + \frac{\mu_3 E_3}{2}],\\
z_{q23}^z &= \frac{1}{2}\ln\frac{1+\eta_{q23}^{(1)z}}{1-\eta_{q23}^{(1)z}} + \beta[\nu_a(\mathbf{k}_Z)\eta^{(1)}\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_q} + \nu_c(0)\eta_{E_3}^{(1)} + \frac{\mu_3 E_3}{2}].
\end{aligned} \tag{2.10}$$

The strains ε_i and order parameter $\eta^{(1)}$ are determined from the conditions of the thermodynamic equilibrium

$$\frac{1}{\bar{v}}\frac{\partial f}{\partial\eta^{(1)}} = 0; \quad \frac{1}{\bar{v}}\frac{\partial f}{\partial\varepsilon_i} = -p_i. \tag{2.11}$$

with $p_i(\mathrm{h}) = (p,p,p)$, $p_i(3) = (0,0,p)$; f is the free energy of a crystal at zero electric field

$$f = \frac{\bar{v}}{2}\sum_{ij} c_{ij}^0\varepsilon_i\varepsilon_j - [2w-\varepsilon] + 2\nu_a(\mathbf{k}_Z)[\eta^{(1)}]^2 + 2T\ln\frac{2}{(1-[\eta^{(1)}]^2)\,D}, \tag{2.12}$$

where $D = 1+a+d+\cosh 2z+4b\cosh z$, $z = \frac{1}{2}\ln\frac{1+\eta^{(1)}}{1-\eta^{(1)}} + \beta\nu_a(\mathbf{k}_Z)\eta^{(1)}$. The thermodynamic potential is equal to

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

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

$$\begin{aligned}
\eta^{(1)} &= \frac{1}{D}(\sinh 2z + 2b\sinh z),\\
-p_i &= \sum_j c_{ij}^0\varepsilon_j - \frac{2\delta_{2i}-\delta_{1i}}{\bar{v}} - \frac{2\psi_{ai}(\mathbf{k}_Z)}{\bar{v}}[\eta^{(1)}]^2 + \frac{2}{\bar{v}}\frac{M_i}{D},
\end{aligned} \tag{2.13}$$

where $M_i = 4b\delta_{2i}\cosh z^z + a\delta_{1i} + d\delta_{3i}$. As one can see from equations (2.13), the strains ε_i are equal to zero at ambient pressure only if we assume the temperature dependence of the parameters δ_{2i} in the form

$$\delta_{2i}^+ = \delta_{1i}^+\frac{4\exp(-\beta w) + 3\exp(-\beta\varepsilon) + 2}{2\exp(-\beta\varepsilon) + 4} \tag{2.14}$$

(in the limit $w_1 \to \infty$ and $d \to 0$) in the paraelectric phase and in a more complicated form in the ferroelectric phase. In order to keep δ_{2i} constant and for the sake of simplicity we assumed that (2.14) is obeyed only at $T = T_\mathrm{N}$, that is

$$\delta_{2i}^+ = \delta_{1i}^+\frac{4\exp(-\beta_\mathrm{N} w) + 3\exp(-\beta_\mathrm{N}\varepsilon) + 2}{2\exp(-\beta_\mathrm{N}\varepsilon) + 4}, \tag{2.15}$$

($\beta_\mathrm{N} = 1/T_\mathrm{N}$). It means that at pressure of 0.001 kbar, small residual strains ($\sim 10^{-6}$) exist at all temperatures except for the transition point.

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

$$g(\eta^{(1)},T_\mathrm{N},p) = g(0,T_\mathrm{N},p), \tag{2.16}$$

where the order parameter and strains obey the system of equations (2.13).

3. Elastic and thermal characteristics

Matrices of the elastic constants and piezomoduli of a DADP crystal have the following symmetry:

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

and

$$d_{ij}^{p-} = \begin{pmatrix} 0 & 0 & 0 & d_{14}^{p-} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25}^{p-} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36}^{p-} \end{pmatrix}, \quad d_{ij}^{p+} = \begin{pmatrix} 0 & 0 & 0 & d_{14}^{p+} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14}^{p+} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36}^{p+} \end{pmatrix},$$

in the antiferroelectric (the space group $P2_12_12_1$) and paraelectric (the space group $I\bar{4}2d$) phase, respectively. In our approach we can calculate only the c_{11}, c_{12}, c_{13}, c_{22}, c_{23}, and c_{33} components of these matrices. To calculate c_{44}, c_{55}, c_{66}, d_{14}, d_{25}, and d_{36} we must take into account the strains ε_4, ε_5, and ε_6.

Differentiating the free energy (2.12), we get the following expressions for the parts of elastic constants, attributed to a deuteron subsystem $(i, j = 1, 2, 3)$

$$\begin{aligned} \Delta c_{ij}^p &= c_{ij}^p - c_{ij}^0 = \\ &= -\frac{2}{\bar{v}DT}[4b\delta_{2i}\delta_{2j}\cosh z + a\delta_{1i}\delta_{1j} + d\delta_{3i}\delta_{3j}] + \frac{2}{\bar{v}D^2T}M_iM_j - \\ &- \frac{4\eta^{(1)}}{\bar{v}DT}[2\psi_{ai}(\mathbf{k}_Z)\psi_{aj}(\mathbf{k}_Z)\eta^{(1)}\text{æ} + \psi_{ai}(\mathbf{k}_Z)t_j + \psi_{aj}(\mathbf{k}_Z)t_i], \end{aligned} \tag{3.1}$$

Here we use the notations

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

Let us explore now the thermal properties of the strained DADP crystal. The entropy per one mole is equal to

$$S = R\left(2\ln[1 - (\eta^{(1)})^2] + 2\ln\frac{D}{2} + 4T\varphi^T\eta^{(1)} + 2\frac{\bar{M}}{D}\right), \tag{3.2}$$

where R is the gas constant, and

$$\bar{M} = \beta(4wb\cosh z + \varepsilon a + w_1 d), \quad \varphi^T = -\frac{1}{T^2}\nu_a(\mathbf{k}_Z)\eta^{(1)}.$$

To calculate the specific heat of the deuteron subsystem at constant pressure we differentiate the entropy (3.2):

$$\Delta C^p = RT\left(\frac{\partial S}{\partial T}\right)_p = \Delta C^\varepsilon - RT\sum_i q_i^P\alpha_i, \tag{3.3}$$

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

$$\Delta C^\varepsilon = RT(-q^{P\varepsilon} - q^\varepsilon p^P); \tag{3.4}$$

$$\begin{aligned} q_i^P &= \frac{2}{\bar{v}DT}\left\{-2T\varphi^T\theta_i - 2\psi_{ci}\eta^{(1)}[q - \eta^{(1)}\bar{M}] + \lambda_i - \frac{\bar{M}M_i}{D}\right\}, \\ q^\varepsilon &= -\frac{v}{\mu_3}\frac{2}{D}\varphi^\eta\left[2\text{æ}T\varphi^T + (q - \eta^{(1)}\bar{M})\right], \\ q^{P,\varepsilon} &= -\frac{2}{DT}\left\{4T\varphi^T\left[\text{æ}T\varphi^T + (q - \eta^{(1)}\bar{M})\right] + N - \frac{\bar{M}^2}{D}\right\}, \\ p^P &= \frac{\mu_3}{v}\frac{2}{T}\frac{2\text{æ}T\varphi^T + [q - \eta^{(1)}\bar{M}]}{D - 2\varphi^\eta\text{æ}}; \end{aligned}$$

α_i are the thermal expansion coefficients. We use the following notations:

$$\begin{aligned} N &= 4\left(\frac{w}{T}\right)^2 b\cosh z + \left(\frac{\varepsilon}{T}\right)^2 a + \left(\frac{w_1}{T}\right)^2 d, \\ q &= 2\frac{w}{T}b\sinh z, \quad \lambda_i = \frac{1}{T}(4wb\delta_{2i}\cosh z + \varepsilon a\delta_{1i} + w_1 d\delta_{3i}), \\ \varphi^\eta &= \frac{1}{1 - [\eta^{(1)}]^2} + \beta\nu_a(\mathbf{k}_Z), \quad \theta_i = 2\psi_{ai}(\mathbf{k}_Z)\eta^{(1)}\text{æ} + t_i. \end{aligned}$$

4. Dielectric properties

Nonzero polarization in an antiferroelectric crystal arises only if an electric field is applied. Therefore,

$$P_1 = \frac{\mu_1}{v}\eta_{13E_1}^{(1)}, \quad P_2 = \frac{\mu_2}{v}\eta_{24E_2}^{(1)}, \quad P_3 = \frac{2\mu_3}{v}\eta_{E_3}^{(1)}. \tag{4.1}$$

The effective dipole moments μ_i and unit cell volume are assumed to be linear functions of pressure:

$$\mu_i = \mu_i^{(0)} + k_{\mu_i}p, \quad v = v^{(0)} + k_v p.$$

Differentiating (4.1) with respect to E_i, we get the expressions for the corresponding static dielectric susceptibilities of a *clamped* (ε_i = const) crystal

$$\chi^{\varepsilon}_{1,2}(0,T,p) = \left(\frac{\partial P_{1,2}}{\partial E_{1,2}}\right)_{\varepsilon_i} = \frac{\beta\mu^2_{1,2}}{2v}\left[\frac{2\ae_1}{D-2\ae_1\varphi^{\eta}_1} + \frac{2\ae_2}{D-2\ae_2\varphi^{\eta}_1}\right];$$
$$\chi^{\varepsilon}_{3}(0,T,p) = \left(\frac{\partial P_{3}}{\partial E_{3}}\right)_{\varepsilon_i} = \frac{\beta\mu^2_{3}}{v}\frac{2\ae_3}{D-2\ae_3\varphi^{\eta}_3}; \qquad (4.2)$$

Here we introduce the following notations:

$\ae_1 = 1 + b\cosh z;\ \ \ae_2 = \cosh 2z + b\cosh z - [\eta^{(1)}]^2 D;\ \ \ae_3 = a + b\cosh z,$

and

$$\varphi^{\eta}_1 = \frac{1}{1-[\eta^{(1)}]^2} + \beta\nu_a(0), \quad \varphi^{\eta}_3 = \frac{1}{1-[\eta^{(1)}]^2} + \beta\nu_c(0).$$

Dielectric permittivity is related to susceptibility by

$$\varepsilon^{\varepsilon}_i(0,T,p) = \varepsilon_{i\infty} + 4\pi\chi^{\varepsilon}_i(0,T,p). \qquad (4.3)$$

Let us note that in the paraelectric phase at ambient pressure ($\varepsilon_i = 0$) and at $w, w_1 \to \infty$ (4.2) coincides with the corresponding expressions found in [31,32] and [23,44,45].

The "free" dielectric permittivities $\varepsilon^F_i(0,T,p)$ can be calculated by means of the formulas

$$\varepsilon^F_1(0,T,p) = \varepsilon^{\varepsilon}_1(0,T,p) + 4\pi\frac{d^2_{14}}{s^E_{44}},$$
$$\varepsilon^F_2(0,T,p) = \varepsilon^{\varepsilon}_2(0,T,p) + 4\pi\frac{d^2_{25}}{s^E_{55}}, \qquad (4.4)$$
$$\varepsilon^F_3(0,T,p) = \varepsilon^{\varepsilon}_3(0,T,p) + 4\pi\frac{d^2_{36}}{s^E_{66}},$$

where d_{ij} are the piezoelectric constants, and s^E are the elastic shear compliances of a short circuited crystal [4].

5. Relaxational dynamics

In order to study the dynamic responses of a DADP crystal, let us assume that the electric fields E_i in (2.2), (2.4) and (2.9) are time-dependent.

In the spirit of the Glauber approach [39] we assume that the system (2.2) interacts with a heat reservoir which causes spins of the system to change their states randomly with probability $w_{qf}(\ldots,\sigma_{qf},\ldots)$ per unit time. System behaviour is described in terms of probability functions $P(\ldots,\sigma_{qf},\ldots,t)$, which time dependence is governed by the master equation

$$\frac{\mathrm{d}}{\mathrm{d}t}P\{...,\sigma_{qf},...,t\} = -\sum_{qf} w_{qf}\{...,\sigma_{qf},...\}P\{...,\sigma_{qf},...,t\} +$$
$$+\sum_{qf} w_{qf}\{...,-\sigma_{qf},...\}P\{...,-\sigma_{qf},...,t\}, \qquad (5.1)$$

or if rewritten in terms of the mean values of spin products $\langle\prod_f \sigma_{qf}\rangle$

$$-\alpha\frac{\mathrm{d}}{\mathrm{d}t}\langle\prod_f \sigma_{qf}\rangle = \sum_f\langle\prod_{f'}\sigma_{qf'}\left[1-\sigma_{qf}\tanh\frac{1}{2}\beta\mathcal{E}_{qf})\right]\rangle, \qquad (5.2)$$

(the sum here is carried out only over the spins that occur in the product $\prod_{f'}$). The parameter α describes the time scale on which all transitions in the system take place; $\mathcal{E}_{qf}$ denotes the field acting on the qf-th spin.

The local fields $\mathcal{E}_{qf}$ can be easily found from the Hamiltonian (2.4)

$$\mathcal{E}^{(i)}_{q1} = -\frac{V}{2}[\sigma_{q2}+\sigma_{q4}] - \frac{U}{2}\sigma_{q3} - \frac{\Phi}{8}\sigma_{q2}\sigma_{q3}\sigma_{q4} + \frac{z^i_{q1}}{\beta};$$
$$\mathcal{E}^{(i)}_{q2} = -\frac{V}{2}[\sigma_{q1}+\sigma_{q3}] - \frac{U}{2}\sigma_{q4} - \frac{\Phi}{8}\sigma_{q1}\sigma_{q3}\sigma_{q4} + \frac{z^i_{q2}}{\beta};$$
$$\mathcal{E}^{(i)}_{q3} = -\frac{V}{2}[\sigma_{q2}+\sigma_{q4}] - \frac{U}{2}\sigma_{q1} - \frac{\Phi}{8}\sigma_{q1}\sigma_{q2}\sigma_{q4} + \frac{z^i_{q3}}{\beta};$$
$$\mathcal{E}^{(i)}_{q4} = -\frac{V}{2}[\sigma_{q1}+\sigma_{q3}] - \frac{U}{2}\sigma_{q2} - \frac{\Phi}{8}\sigma_{q1}\sigma_{q2}\sigma_{q3} + \frac{z^i_{q4}}{\beta};$$

Bearing in mind (5.2), we expand $\tanh\dfrac{\beta\mathcal{E}_{qf}}{2}$ in powers of spin operators

$$\frac{1}{\alpha}\tanh\frac{\beta\mathcal{E}^{(i)}_{q1}}{2} = M^{(i)}_1\sigma_{q3}[\sigma_{q2}+\sigma_{q4}] + N^{(i)}_1\sigma_{q2}\sigma_{q4} + L^{(i)}_1 +$$
$$+ P^{(i)}_1\sigma_{q3} + Q^{(i)}_1[\sigma_{q2}+\sigma_{q4}] + R^{(i)}_1\sigma_{q2}\sigma_{q3}\sigma_{q4};$$
$$\ldots \qquad (5.3)$$
$$\frac{1}{\alpha}\tanh\frac{\beta\mathcal{E}^{(i)}_{q4}}{2} = M^{(i)}_4\sigma_{q2}[\sigma_{q1}+\sigma_{q3}] + N^{(i)}_4\sigma_{q1}\sigma_{q3} + L^{(i)}_4 +$$
$$+ P^{(i)}_4\sigma_{q2} + Q^{(i)}_4[\sigma_{q1}+\sigma_{q3}] + R^{(i)}_4\sigma_{q1}\sigma_{q2}\sigma_{q3},$$

where

$$\begin{aligned}
P^i_{qf} &= \frac{1}{4\alpha}\left[(a^2-b^2)\gamma_{1f} - 2(1-b^2)\gamma_{2f} - (b^2-d^2)\gamma_{3f}\right],\\
Q^i_{qf} &= \frac{1}{4\alpha}\left[(a^2-b^2)\gamma_{1f} + (b^2-d^2)\gamma_{3f}\right],\\
R^i_{qf} &= \frac{1}{4\alpha}\left[(a^2-b^2)\gamma_{1f} + 2(1-b^2)\gamma_{2f} - (b^2-d^2)\gamma_{3f}\right],\\
L^i_{qf} &= \frac{\sinh z^i_{qf}}{2\alpha}\left[ab\gamma_{1f} + 2b\gamma_{2f} + bd\gamma_{3f}\right],\\
M^i_{qf} &= \frac{\sinh z^i_{qf}}{2\alpha}\left[ab\gamma_{1f} - bd\gamma_{3f}\right],\\
N^i_{qf} &= \frac{\sinh z^i_{qf}}{2\alpha}\left[ab\gamma_{1f} - 2b\gamma_{2f} + bd\gamma_{3f}\right],\\
\gamma_{1f} &= \left[a^2 + b^2 + 2ab\cosh z^i_{qf}\right]^{-1},\\
\gamma_{2f} &= \left[1 + b^2 + 2b\cosh z^i_{qf}\right]^{-1},\\
\gamma_{3f} &= \left[b^2 + d^2 + 2bd\cosh z^i_{qf}\right]^{-1}.
\end{aligned}$$

The quantities $P^{(i)}_{qf}$, $Q^{(i)}_{qf}$, $R^{(i)}_{qf}$ are even functions of z^i_{qf}, and do not depend on q at $E_i = 0$.

Substituting (5.4) into (5.2), and taking into account the symmetry of the deuteron distribution functions in the transverse electric fields E_1 or E_2

$$\begin{aligned}
&\eta^{(1)x,y}_{q13} = -\langle\sigma_{q1}\rangle = \langle\sigma_{q3}\rangle, \quad \eta^{(1)x,y}_{q24} = \langle\sigma_{q2}\rangle = -\langle\sigma_{q4}\rangle,\\
&\eta^{(3)x,y}_{q24} = \langle\sigma_{q3}\sigma_{q4}\sigma_{q1}\rangle = -\langle\sigma_{q1}\sigma_{q2}\sigma_{q3}\rangle,\\
&\eta^{(3)x,y}_{q13} = -\langle\sigma_{q2}\sigma_{q3}\sigma_{q4}\rangle = \langle\sigma_{q1}\sigma_{q2}\sigma_{q4}\rangle,\\
&\eta^{(2)x,y}_{23} = \langle\sigma_{q2}\sigma_{q3}\rangle = \langle\sigma_{q1}\sigma_{q4}\rangle, \quad \eta^{(2)x,y}_{q15} = -\langle\sigma_{q1}\sigma_{q2}\rangle = -\langle\sigma_{q3}\sigma_{q4}\rangle,\\
&\eta^{(2)x,y}_{q4} = -\langle\sigma_{q1}\sigma_{q3}\rangle, \quad \eta^{(2)x,y}_{q6} = -\langle\sigma_{q2}\sigma_{q4}\rangle,
\end{aligned}$$

and in the longitudinal field E_3:

$$\begin{aligned}
&\eta^{(1)z}_{q14} = \langle\sigma_{q1}\rangle = \langle\sigma_{q4}\rangle, \quad \eta^{(1)z}_{q23} = \langle\sigma_{q2}\rangle = \langle\sigma_{q3}\rangle,\\
&\eta^{(3)z}_{q14} = \langle\sigma_{q1}\sigma_{q2}\sigma_{q4}\rangle = \langle\sigma_{q1}\sigma_{q2}\sigma_{q3}\rangle,\\
&\eta^{(3)z}_{q23} = \langle\sigma_{q3}\sigma_{q4}\sigma_{q1}\rangle = \langle\sigma_{q2}\sigma_{q3}\sigma_{q4}\rangle,\\
&\eta^{(2)z}_{q15} = -\langle\sigma_{q1}\sigma_{q2}\rangle = -\langle\sigma_{q3}\sigma_{q4}\rangle, \quad \eta^{(2)z}_{q46} = -\langle\sigma_{q1}\sigma_{q3}\rangle = -\langle\sigma_{q2}\sigma_{q4}\rangle\\
&\eta^{(2)z}_{q2} = \langle\sigma_{q2}\sigma_{q3}\rangle, \quad \eta^{(2)z}_{q3} = \langle\sigma_{q1}\sigma_{q4}\rangle,
\end{aligned}$$

and, respectively, in the fields E_1 or E_2

$$\begin{aligned}
&P^{x,y}_{q1} = P^{x,y}_{q3} = P^{x,y}_{q13}, \quad P^{x,y}_{q2} = P^{x,y}_{q4} = P^{x,y}_{q24},\\
&Q^{x,y}_{q1} = Q^{x,y}_{q3} = Q^{x,y}_{q13}, \quad Q^{x,y}_{q2} = Q^{x,y}_{q4} = Q^{x,y}_{q24},\\
&R^{x,y}_{q1} = R^{x,y}_{q3} = R^{x,y}_{q13}, \quad R^{x,y}_{q2} = R^{x,y}_{q4} = R^{x,y}_{q24},\\
&-L^{x,y}_{q1} = L^{x,y}_{q3} = L^{x,y}_{q13}, \quad L^{x,y}_{q2} = -L^{x,y}_{q4} = L^{x,y}_{q24},\\
&-M^{x,y}_{q1} = M^{x,y}_{q3} = M^{x,y}_{q13}, \quad M^{x,y}_{q2} = -M^{x,y}_{q4} = M^{x,y}_{q24},\\
&-N^{x,y}_{q1} = N^{x,y}_{q3} = M^{x,y}_{q13}, \quad N^{x,y}_{q2} = -N^{x,y}_{q4} = N^{x,y}_{q24},\\
&-z^{x,y}_{q1} = z^{x,y}_{q3} = z^{x,y}_{q13}, \quad z^{x,y}_{q2} = -z^{x,y}_{q4} = z^{x,y}_{q24},
\end{aligned}$$

and in the field E_3:

$$\begin{aligned}
&P^z_{q1} = P^z_{q4} = P^z_{q14}, \quad P^z_{q2} = P^z_{q3} = P^z_{q23},\\
&Q^z_{q1} = Q^z_{q4} = Q^z_{q14}, \quad Q^z_{q2} = Q^z_{q3} = Q^z_{q23},\\
&R^z_{q1} = R^z_{q4} = R^z_{q14}, \quad R^z_{q2} = R^z_{q3} = R^z_{q23},\\
&L^z_{q1} = L^z_{q4} = L^z_{q14}, \quad L^z_{q2} = L^z_{q3} = L^z_{q23},\\
&M^z_{q1} = M^z_{q4} = M^z_{q14}, \quad M^z_{q2} = M^z_{q3} = M^z_{q23},\\
&N^z_{q1} = N^z_{q4} = M^z_{q14}, \quad N^z_{q2} = N^z_{q3} = N^z_{q23},\\
&z^z_{q1} = z^z_{q4} = z^z_{q14}, \quad z^z_{q2} = z^z_{q3} = z^z_{q23},
\end{aligned}$$

we get the eighth order systems of linear differential equations for the time-dependent deuteron distribution functions:
when the fields E_1 or E_2 are applied

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\eta^{(1)x,y}_{q13}\\ \eta^{(1)x,y}_{q24}\\ \eta^{(3)x,y}_{q13}\\ \eta^{(3)x,y}_{q24}\\ \eta^{(2)x,y}_{q15}\\ \eta^{(2)x}_{q23}\\ \eta^{(2)x,y}_{q4}\\ \eta^{(2)x,y}_{q6}\end{pmatrix} = \begin{pmatrix} b_{11}\, b_{12} \ldots b_{18}\\ b_{21}\, b_{22} \ldots b_{28}\\ b_{31}\, b_{32} \ldots b_{38}\\ \vdots \qquad\qquad \vdots\\ \\ \vdots \qquad\qquad \vdots\\ b_{81}\, b_{82} \ldots b_{88}\end{pmatrix}\begin{pmatrix}\eta^{(1)x,y}_{q13}\\ \eta^{(1)x,y}_{q24}\\ \eta^{(3)x,y}_{q13}\\ \eta^{(3)x,y}_{q24}\\ \eta^{(2)x,y}_{q15}\\ \eta^{(2)x}_{q23}\\ \eta^{(2)x,y}_{q4}\\ \eta^{(2)x,y}_{q6}\end{pmatrix} + \begin{pmatrix} b_1\\ b_2\\ b_3\\ \vdots\\ \\ \vdots\\ b_8\end{pmatrix}, \tag{5.4}$$

and in the case of the field E_3:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\eta^{(1)z}_{q14}\\ \eta^{(1)z}_{q23}\\ \eta^{(3)z}_{q14}\\ \eta^{(3)z}_{q23}\\ \eta^{(2)z}_{q15}\\ \eta^{(2)z}_{q2}\\ \eta^{(2)z}_{q3}\\ \eta^{(2)z}_{q46}\end{pmatrix} = \begin{pmatrix} c_{11}\, c_{12} \ldots c_{18}\\ c_{21}\, c_{22} \ldots c_{28}\\ c_{31}\, c_{32} \ldots c_{38}\\ \vdots \qquad\quad \vdots\\ \\ \\ \vdots \qquad\quad \vdots\\ c_{81}\, c_{82} \ldots c_{88}\end{pmatrix}\begin{pmatrix}\eta^{(1)z}_{q14}\\ \eta^{(1)z}_{q23}\\ \eta^{(3)z}_{q14}\\ \eta^{(3)z}_{q23}\\ \eta^{(2)z}_{q15}\\ \eta^{(2)z}_{q2}\\ \eta^{(2)z}_{q3}\\ \eta^{(2)z}_{q46}\end{pmatrix} + \begin{pmatrix}c_1\\ c_2\\ c_3\\ \vdots\\ \\ \\ \vdots\\ c_8\end{pmatrix}, \tag{5.5}$$

The expressions for the coefficients in (5.4) and (5.5) are given in Appendix. These coefficients contain the unknown time-dependent functions z^i_{qf}. In order to determine these functions we can use the consistency condition, which states that the values of $\langle\sigma_{qf}\rangle$ (and thereby of $\mathrm{d}\langle\sigma_{qf}\rangle/\mathrm{d}t$) calculated within the four-particle and the single-particle cluster approximations must coincide. In the latter case $\mathcal{E}_{qf} = \bar{z}^i_{qf}/2$ and, respectively,

$$\frac{\mathrm{d}}{\mathrm{d}t}\eta^{(1)i}_{qf} = -\frac{\eta^{(1)i}_{qf}}{\alpha} + \frac{1}{\alpha}\tanh\frac{\bar{z}^i_{qf}}{2}. \tag{5.6}$$

Let us assume that the electric field $E_i(t) = E_{i0}\exp(-i\omega t)$ is weak and causes only small departures from thermal equilibrium. All the quantities involved may be therefore written as static equilibrium values plus time-dependent fluctuations

$$\begin{aligned}
&\eta^{(1)i}_{qf} = \tilde{\eta}^{(1)}_q + \eta^{(1)i}_f(t), \quad \eta^{(3)i}_{qf} = \tilde{\eta}^{(3)}_q + \eta^{(3)i}_f(t),\\
&\eta^{(2)i}_{q1,5} = \tilde{\eta}'^{(2)} + \eta^{(2)}_{q1,5}(t), \ \ \eta^{(2)i}_{q2,3} = \tilde{\eta}^{(2)} + \eta^{(2)}_{q2,3}(t), \ \ \eta^{(2)i}_{q4,6} = \tilde{\eta}''^{(2)} + \eta^{(2)}_{q4,6}(t),\\
&P^i_{qf} = P^{(0)} + \frac{z^i_f(t)}{2}P^{(1)}_q, \ Q^i_{qf} = Q^{(0)} + \frac{z^i_f(t)}{2}Q^{(1)}_q,\\
&R^i_{qf} = R^{(0)} + \frac{z^i_f(t)}{2}R^{(1)}_q, \ L^i_{qf} = L^{(0)}_q + \frac{z^i_f(t)}{2}L^{(1)},\\
&M^i_{qf} = M^{(0)}_q + \frac{z^i_f(t)}{2}M^{(1)}, \ N^i_{qf} = N^{(0)}_q + \frac{z^i_f(t)}{2}N^{(1)},\\
&z^i_{qf} = \tilde{z}_q + z^i_f(t).
\end{aligned}$$

The time-dependent parts of z^i_{qf} have the following symmetry

$$z^x_{13}(t) = \beta[-\Delta^x_{13}(t) + 2\nu_a(0)\eta^{(1)}_{13E_1}(t) + \mu_1 E_1(t)],$$

$$\begin{aligned}
&z^x_{24}(t) = \beta[-\Delta^x_{24}(t) + 2\nu_a(0)\eta^{(1)}_{24E_1}(t)],\\
&z^y_{13}(t) = \beta[-\Delta^y_{13}(t) + 2\nu_a(0)\eta^{(1)}_{13E_2}(t)],\\
&z^y_{24}(t) = \beta[-\Delta^y_{24}(t) + 2\nu_a(0)\eta^{(1)}_{24E_2}(t) + \mu_2 E_2(t)],\\
&z^z(t) = \beta[-\Delta^z(t) + 2\nu_c(0)\eta^{(1)}_{E_3}(t) + \mu_3 E_3(t)],
\end{aligned}$$

Expressions for $\bar{z}^i_{qf}(t)$ can be obtained from those for $z^i_{qf}(t)$ by replacing $\Delta^i_{qf}(t)$ with $2\Delta^i_{qf}(t)$.

Since at frequencies of external electric field higher than the piezoelectric dispersion frequency ($\sim 10^6$ Hz) the crystal is effectively clamped ($\varepsilon_i = \mathrm{const}$), we assume the strains ε_i to be time-independent.

Let us restrict ourselves to the case of the paraelectric phase where $\tilde{\eta}^{(1)} = \tilde{\eta}^{(3)} = 0$, and $\tilde{z} = 0$,

$$\begin{aligned}
&L^{(0)+} = 0; \quad L^{(1)+} = \frac{1}{\alpha}\left(\frac{ab}{(a+b)^2} + \frac{2b}{(1+b)^2} + \frac{bd}{(b+d)^2}\right),\\
&M^{(0)+} = 0; \quad M^{(1)+} = \frac{1}{\alpha}\left(\frac{ab}{(a+b)^2} - \frac{bd}{(b+d)^2}\right),\\
&N^{(0)+} = 0; \quad N^{(1)+} = \frac{1}{\alpha}\left(\frac{ab}{(a+b)^2} - \frac{2b}{(1+b)^2} + \frac{bd}{(b+d)^2}\right),\\
&P^{(1)+} = 0; \quad P^{(0)+} = \frac{1}{4\alpha}\left(\frac{a-b}{a+b} - 2\frac{1-b}{1+b} - \frac{b-d}{b+d}\right),\\
&Q^{(1)+} = 0; \quad Q^{(0)+} = \frac{1}{4\alpha}\left(\frac{a-b}{a+b} + \frac{b-d}{b+d}\right),\\
&R^{(1)+} = 0; \quad R^{(0)+} = \frac{1}{4\alpha}\left(\frac{a-b}{a+b} + 2\frac{1-b}{1+b} - \frac{b-d}{b+d}\right);
\end{aligned} \tag{5.7}$$

Expanding all the quantities in (5.4) and (5.5) in powers of fluctuations (5.7) up to the linear terms, we obtain separate systems of equations for the equilibrium distribution functions and for their time-dependent parts. The solutions of the former are the static distribution functions $\tilde{\eta}^{(2)}$, $\tilde{\eta}'^{(2)}$, $\tilde{\eta}''^{(2)}$. In the paraelectric phase

$$\tilde{\eta}^{(2)} = \frac{a-d}{D} = -\tilde{\eta}'^{(2)}, \quad \tilde{\eta}''^{(2)} = \frac{2-a-d}{D}, \quad D = 2+a+d+4b.$$

The fluctuation parts of (5.4) and (5.5) are decoupled into separate systems of equations for the single- and three-particle distribution functions and for the pair distribution functions. The system of equations for the single-particle distribution functions occuring in the expressions for the corresponding polarizations (4.1) reads

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\eta^{(1)i}\\ \eta^{(3)i}\end{pmatrix} = \begin{pmatrix}a^{i+}_1 & a^{i+}_3\\ b^{i+}_1 & b^{i+}_3\end{pmatrix}\begin{pmatrix}\eta^{(1)i}\\ \eta^{(3)i}\end{pmatrix} - \frac{\mu_i E_i(t)}{2T}\begin{pmatrix}a^{i+}\\ b^{i+}\end{pmatrix}. \tag{5.8}$$

where $\eta^{(1,3)i}$ are $\eta_{13}^{(1,3)x}$ in the case of E_1 field, $\eta_{24}^{(1,3)y}$ in the case of E_2 field, and $\eta^{(1,3)z}$ in the case of E_3 field. The system coefficients are

$$\begin{array}{lll}
a_1^{x,y+} = b_{11}^{0+} + \beta\nu_a(0)Y_1^+ - \xi_a\Psi_1^+, & a_3^{x,y+} = b_{12}^{0+} - \xi_a b_{12}^{0+}, & a^{x,y+} = \xi_a/\alpha, \\
b_1^{x,y+} = b_{21}^{0+} + \beta\nu_a(0)Y_3^+ - \xi_b\Psi_1^+, & b_3^{x,y+} = b_{22}^{0+} - \xi_b b_{12}^{0+}, & b^{x,y+} = \xi_b/\alpha, \\
a_1^{z+} = c_{11}^{0+} + \beta\nu_c(0)Y_1^+ - \xi_a\Psi_3^+, & a_3^{z+} = c_{12}^{0+} - \xi_a c_{12}^{0+}, & a^{z+} = \xi_a/\alpha, \\
b_1^{z+} = c_{21}^{0+} + \beta\nu_c(0)\overline{Y_3^+} - \overline{\xi_b}\Psi_3^+, & b_3^{z+} = c_{22}^{0+} - \overline{\xi_b}c_{12}^{0+}, & b^{z+} = \overline{\xi_b}/\alpha,
\end{array}$$

provided that

$$\begin{array}{ll}
b_{11}^{0+} = -1/\alpha - P^{(0)+}, & b_{12}^{0+} = R^{(0)+}, \\
b_{21}^{0+} = -2P^{(0)+} + 3R^{(0)+}, & b_{22}^{0+} = -3/\alpha - P^{(0)+}, \\
c_{11}^{0+} = -1/\alpha + P^{(0)+} + 2Q^{(0)+}, & c_{12}^{0+} = R^{(0)+}, \\
c_{21}^{0+} = 2P^{(0)+} + 4Q^{(0)+} + 3R^{(0)+}, & c_{22}^{0+} = -3/\alpha + P^{(0)+} + 2Q^{(0)+},
\end{array}$$

and

$$\begin{array}{l}
Y_1^+ = 2M_1^+\tilde{\eta}^{(2)} - N_1^+\tilde{\eta}''^{(2)} + L_1^+, \\
Y_3^+ = -2M_1^+ + L_1^+\tilde{\eta}''^{(2)} - N_1^+, \\
\overline{Y_3^+} = 2(N_1^+ + M_1^+ + L_1^+)\tilde{\eta}^{(2)} - (L_1^+ + 2M_1^+)\tilde{\eta}''^{(2)} + N_1^+ + 2M_1^+, \\
\xi_a = Y_1^+(Y_1^+ - 2/\alpha)^{-1}, \\
\xi_b = Y_3^+(Y_1^+ - 2/\alpha)^{-1}, \quad \overline{\xi_b} = \overline{Y_3^+}(Y_1^+ - 2/\alpha)^{-1}, \\
\Psi_1^+ = b_{11}^{0+} + \beta\nu_a(0)[Y_1^+ - 1/\alpha] + 1/\alpha, \\
\Psi_3^+ = c_{11}^{0+} + \beta\nu_c(0)[Y_1^+ - 1/\alpha] + 1/\alpha.
\end{array}$$

We need to know the time dependence of the single-particle distribution function $\eta^{(1)i}(t)$. Reducing the system (5.8) to a single second order differential equation, we obtain

$$\begin{aligned}
\eta^{(1)i}(t) = {} & C_1^{i+}e^{-t/\tau_1^{i+}} + C_2^{i+}e^{-t/\tau_2^{i+}} + \\
& + \frac{\mu_i E_i(t)}{2T}k^i\frac{\tau_1^{i+}\tau_2^{i+}}{(1+i\omega\tau_1^{i+})(1+i\omega\tau_2^{i+})}.
\end{aligned} \qquad (5.9)$$

The relaxation times are equal to

$$(\tau_{1,2}^{i+})^{-1} = \frac{1}{2}\{-k_1^i \pm \sqrt{(k_1^i)^2 - 4k_0^i}\},$$

where

$$\begin{array}{l}
k^i = -i\omega l_1^i + l_0^i; \\
l_1^i = -a^{i+}, \quad l_0^i = -\begin{vmatrix} a_3^{i+} & a^{i+} \\ b_3^{i+} & b^{i+} \end{vmatrix}, \quad k_1^i = a_1^{i+} + b_3^{i+}; \quad k_0^i = \begin{vmatrix} a_1^{i+} & a_3^{i+} \\ b_1^{i+} & b_3^{i+} \end{vmatrix}.
\end{array}$$

On the basis of (5.9) we can calculate the dynamic susceptibility of a clamped crystal

$$\chi_i^\varepsilon(\omega,T,p) = \lim_{E_i\to 0}\frac{\mathrm{d}P_i(t)}{\mathrm{d}E_i}, \qquad (5.10)$$

the dependence of polarization P_i on $\eta^{(1)i}(t)$ being given by (4.1). Hence,

$$\chi_i^\varepsilon(\omega,T,p) = \frac{\mu_i^2}{v}\frac{k^i}{T}\prod_{j=1}^{2}\frac{\tau_j^{(i)}}{1+i\omega\tau_j^{(i)}} = \sum_{j=1}^{2}\frac{\chi_j^{(i)}}{1+i\omega\tau_j^{(i)}}. \qquad (5.11)$$

The dynamic permittivity of the clamped crystal is equal to

$$\begin{aligned}
\varepsilon_i'^{\varepsilon+}(\omega,T,p) &= \varepsilon_{i\infty}^+ + \frac{4\pi\chi_1^{i+}}{1+(\omega\tau_1^{i+})^2} + \frac{4\pi\chi_2^{i+}}{1+(\omega\tau_2^{i+})^2}; \qquad (5.12)\\
\varepsilon_i''^{\varepsilon+}(\omega,T,p) &= \frac{4\pi\chi_1^{i+}\omega\tau_1^{i+}}{1+(\omega\tau_1^{i+})^2} + \frac{4\pi\chi_2^{i+}\omega\tau_2^{i+}}{1+(\omega\tau_2^{i+})^2};
\end{aligned}$$

where

$$\chi_{1,2}^{i+} = \pm\frac{\mu_i^2}{vT}\frac{\tau_1^{i+}\tau_2^{i+}}{\tau_2^{i+} - \tau_1^{i+}}\left(l_1^i - \tau_{1,2}^{i+}l_0^i\right),$$

The static permittivity is obtained from (5.12) in the limit $\omega \to 0$:

$$\varepsilon_i^{\varepsilon+}(0,T,p) = \varepsilon_{i\infty} + 4\pi(\chi_1^{i+} + \chi_2^{i+}).$$

6. Discussion

Before discussing the proposed theory for strained crystals, let us mention that recently is has been successfully applied to the description of thermodynamic and dynamic characteristics of partially deuterated crystals as well. Within this theory the averaged parameters

$$\varepsilon^0(x) = (1-x)\varepsilon_{\mathrm{H}}^0 + x\varepsilon_{\mathrm{D}}^0, \quad w^0(x) = (1-x)w_{\mathrm{H}}^0 + xw_{\mathrm{D}}^0 \qquad (6.1)$$

for an $\mathrm{N(H_{1-x}D_x)_4(H_{1-x}D_x)_2PO_4}$ crystal were assumed. Tunnelling effects were neglected. To a great extent, this approximation is validated by the fact that dielectric properties of these crystals are determined by the effective tunnelling parameter [54], which is much smaller than the bare tunnelling parameter. Renormalization of the tunnelling parameter by the short-range correlations leads to suppression of the soft mode, thereby explaining the Debye character of dielectric dispersion observed in these crystals.

The expressions for thermodynamic and dynamic characteristics of unstrained $N(H_{1-x}D_x)_4(H_{1-x}D_x)_2PO_4$ crystals depend on the following free parameters: the cluster parameters ε^0, w^0, $w_1^0 \to \infty$, long-range interaction parameters $\nu_a^0(\mathbf{k}_Z)$, $\nu_a^0(0)$, $\nu_c^0(0)$, effective dipole moments $\mu_1^{(0)}$ and $\mu_3^{(0)}$, and the parameter α, determining the time scale of dynamic processes in the system. To determine the values of these parameters we used the experimental data for the variation of the transition temperature T_N, with deuteration and for the temperature and frequency dependences of permittivities $\varepsilon_1^*(\omega, T, 0)$ and $\varepsilon_3^*(\omega, T, 0)$ [5,6,10,7–9,55–58]. The fitting procedure had three stages. First, using the data for $\varepsilon_1(0,T,0) - \varepsilon_{1\infty}$, $\varepsilon_3(0,T,0) - \varepsilon_{3\infty}$, and T_N we chose the values of ε^0, w^0, $\nu_a^0(\mathbf{k}_Z)$, $\nu_a^0(0)$, and $\nu_c^0(0)$. The choice criterion was the minimal temperature dependence of the $f_1^{(0)} = (\mu_1^{(0)})^2/v$ and $f_3^{(0)} = (\mu_3^{(0)})^2/v$ parameters. Next, on the basis of the data for $\varepsilon_1^*(\omega, T)$ and $\varepsilon_3^*(\omega, T)$, we determined the value of α, which was assumed to be slightly temperature dependent as $\alpha = [P + R(\Delta T - 14)] \cdot 10^{-14}$, $(\Delta T = T - T_\mathrm{N})$. Finally, we found the values of $\varepsilon_{1\infty}$ and $\varepsilon_{3\infty}$. In the Table 1 we present the values of the theory parameters chosen as described and providing the best agreement with experimental data for all studied characteristics of unstrained $N(H_{1-x}D_x)_4(H_{1-x}D_x)_2PO_4$ crystals.

x	T_N	ε^0	w^0	$\nu_a^0(\mathbf{k}_z)$	$\nu_a^0(0)$	$\nu_c^0(0)$	$f_1^{(0)}$	$f_3^{(0)}$	P	R
	(K)								(sec)	(sec/K)
1.00	240	80	720	93.6	-55	-17.5	854	256	6.8	0.0031
0.95	235	77	709	85.5	-54	-17	837	245	6.5	0.0040
0.89	230	73.4	695.8	83.9	-53.2	-16.7	821	235	6.2	0.0050
0.74	216	64.4	663	77.3	-51	-15.5	770	205	5.3	0.0076
0.45	190	47	599	69.6	-47.7	-13.5	672	149	3.7	0.0127
0.00	148	20	500	59.5	-40	-10.0	518	62	1.1	0.0206

Table 1: The theory parameters for unstrained $N(H_{1-x}D_x)_4(H_{1-x}D_x)_2PO_4$ crystals at different deuterations.

The calculations of strained crystals characteristics are performed for the case of $T_\mathrm{N} = 235$ K, that corresponds to the deuteration of $x = 0.95$. The values of the deformation potentials δ_{1i} and $\psi_{ai}(\mathbf{k}_Z)$ can be estimated with the help of values of the corresponding quantities for a DKDP crystal obtained in [48–51], assuming that

$$\frac{\varepsilon^0(\mathrm{DKDP})}{\varepsilon^0(\mathrm{DADP})} = \frac{\delta_{1i}(\mathrm{DKDP})}{\delta_{1i}(\mathrm{DADP})}, \quad \frac{\nu_c^0(0)(\mathrm{DKDP})}{\nu_a^0(\mathbf{k}_Z)(\mathrm{DADP})} = \frac{\psi_{ci}(\mathrm{DKDP})}{\psi_{ai}(\mathbf{k}_Z)(\mathrm{DADP})}. \tag{6.2}$$

The parameters δ_{2i} are determined from the criterion (2.15). It turns out that the difference between the values of $\delta_{1i}(\mathrm{DADP})$ and $\psi_{ai}(\mathbf{k}_Z)(\mathrm{DADP})$ yielding the correct experimentally observed value of $\partial T_\mathrm{N}/\partial p$ and those calculated with the help of (6.2) does not exceed several percent.

	ε^0	δ_{11}^-	δ_{12}^-	δ_{13}^-	δ_{11}^+	δ_{13}^+
DKDP	92.0	-45	-55	885	-50	800
DADP	77	-38	-46	741	-42	665

	$\nu^0(\mathbf{k})$	$\psi_1^-(\mathbf{k})$	$\psi_2^-(\mathbf{k})$	$\psi_3^-(\mathbf{k})$	$\psi_1^+(\mathbf{k})$	$\psi_3^+(\mathbf{k})$
DKDP	37.39	-85	-115	50	-105	50
DADP	85.5	-180	-252	112	-239	109

Table 2: The theory parameters (all in K) for DKDP [48–51] and DADP crystals; $\mathbf{k} = 0$ for DKDP and $\mathbf{k} = \mathbf{k}_Z$ for DADP.

The values of the free parameters for a DKDP crystal found in [48–51] and for DADP providing the best fit to the experimental data are given in Table 2. Further experimental study of dielectric and thermal characteristics of DADP as functions of external pressures of different symmetries is required to ascertain the values of deformation potentials.

The experimental values of the elastic compliances s_{ij}^E of paraelectric DADP are reported in [4]. The elements of the inverse to s_{ij}^E matrix are taken as the "seed" elastic constants c_{ij}^{0+}. Since the experimental values of elastic constants of ferroelectric DADP are not available, we carried out the calculations of T_N, ε_i and other characteristics at different pressures and different trial values of c_{ij}^{0-} close to c_{ij}^{0+}. The set of $c_{ij}^{0\pm}$, providing the best fit to experimental data is given in Table 3.

c_{11}^{0+}	c_{12}^{0+}	c_{13}^{0+}	c_{33}^{0+}	c_{11}^{0-}	c_{12}^{0-}	c_{13}^{0-}	c_{22}^{0-}	c_{23}^{0-}	c_{23}^{0-}
6.59	0.53	1.92	3.28	6.24	0.4	1.66	6.4	1.5	3.48

Table 3: The "seed" elastic constants (units of 10^{11}dyn/cm^2) of a DADP crystal.

We also have to determine the value of the δ_1/δ_0 parameter, describing the rate of a decrease in the D-site distance δ with pressure. In the case of hydrostatic pressure it can be found from the experimentally determined dependences of the transition temperature $T_{\rm N}$ on pressure and δ:

$$T_{\rm N} = T_{\rm N0} + k_T p; \quad T_{\rm N} = k_\delta(\delta - \delta_0),$$

where $T_{\rm N0} = 235$ K is the transition temperature at ambient pressure, $k_T = \partial T_{\rm N}/\partial p = -1.4$ K/kbar [10], $k_\delta = T_{\rm N0}/(\delta_0 - \delta_c)$, δ_0, δ_c are the D-site distances at ambient pressure and at the critical pressure when ordered phase vanishes. According to [13–15], $\delta_0 = 0.45\mathring{A}$, $\delta_c = 0.2\mathring{A}$. Excluding from these relations $T_{\rm N}$, we get

$$\frac{\delta_1}{\delta_0} = \frac{k_T}{T_{\rm N0}}(\frac{\delta_c}{\delta_0} - 1).$$

In the case of the uniaxial stress σ_3 we can use the fact that $k_T \sim \delta_1/\delta_0$ and assume that

$$\frac{\delta_1/\delta_0(\sigma_{\rm h}, {\rm DADP})}{\delta_1/\delta_0(\sigma_3, {\rm DADP})} = \frac{\delta_1/\delta_0(\sigma_{\rm h}, {\rm DKDP})}{\delta_1/\delta_0(\sigma_3, {\rm DKDP})} = \frac{k_T(\sigma_{\rm h}, {\rm DKDP})}{k_T(\sigma_3, {\rm DKDP})}.$$

The experimental values of the slopes $k_T(\sigma_3, {\rm DKDP}) = -13.9$ K/kbar and $k_T(\sigma_{\rm h}, {\rm DKDP}) = -2.67$ K/kbar have been found in [48,51] and [59]. The calculated as described values of the δ_1/δ_0 parameters for DADP crystals are

$$\delta_1/\delta_0(\sigma_{\rm h}) = 3.35 \cdot 10^{-6}{\rm K/kbar} \quad \delta_1/\delta_0(\sigma_3) = -1.75 \cdot 10^{-5}{\rm K/kbar}.$$

The parameters f_1 and f_3 occurring in the expressions for dielectric permittivities are assumed to be linear functions of pressure

$$f_1 \equiv \mu_1^2/v = f_1^{(0)} + k_{f1}p, \quad f_3 \equiv \mu_3^2/v = f_3^{(0)} + k_{f3}p.$$

The coefficients k_f are estimated from the following speculations. It is believed that the effective dipole moment μ_1 or μ_3 is proportional to the H-site distance δ. The moment μ_3 is created by the displacements of heavy ions of phosphorus and ammonium (or potassium) group along the c-axis. The transverse polarization results from the deuteron ordering accompanied by ion displacements in the ab plane. It seems reasonable to assume that $\mu_3 \sim c$ and $\mu_1 \sim a$. Therefore, if $\mu_3 \sim \delta c$ and $\mu_1 \sim \delta a$, then

$$\frac{1}{\mu_1}\frac{\partial\mu_1}{\partial p} = \frac{1}{\delta}\frac{\partial\delta}{\partial p} + \frac{1}{a}\frac{\partial a}{\partial p}, \quad \frac{1}{\mu_3}\frac{\partial\mu_3}{\partial p} = \frac{1}{\delta}\frac{\partial\delta}{\partial p} + \frac{1}{c}\frac{\partial c}{\partial p}. \qquad (6.3)$$

The strains ε are linear functions of pressure, thus

$$\frac{1}{c}\frac{\partial c}{\partial p} = \frac{\varepsilon_3}{p}, \quad \frac{1}{a}\frac{\partial a}{\partial p} = \frac{\varepsilon_1}{p}.$$

The correct dependence of spontaneous polarization of a DKDP crystal on hydrostatic pressure [48,49] is obtained at

$$\frac{1}{\mu_3}\frac{\partial\mu_3}{\partial p} = -1.07\%/{\rm kbar},$$

According to [52] and [48,49]

$$\frac{1}{\delta}\frac{\partial\delta}{\partial p} = -0.89\%/{\rm kbar}, \quad \frac{\varepsilon_3}{p} = -0.12\%/{\rm kbar},$$

that is, for μ_3 of a DKDP crystal, (6.3) is obeyed almost exactly. Assuming that this relation is valid for DADP too, we get

$$k_{f1} = f_1^{(0)}[2\frac{\delta_1}{\delta_0} + \frac{\varepsilon_1 - \varepsilon_2 - \varepsilon_3}{p}], \quad k_{f3} = f_3^{(0)}[2\frac{\delta_1}{\delta_0} + \frac{\varepsilon_3 - \varepsilon_1 - \varepsilon_2}{p}].$$

We are also supposed to determine the values of the deformation potentials $\psi_{ai}(0)$ and $\psi_{ci}(0)$. However, as it has been noted in [31,32] and confirmed by our calculations, $\varepsilon_1(0,T,p)$ and $\varepsilon_3(0,T,p)$ are not very sensitive to small changes in $\nu_a(0)$ or $\nu_c(0)$; therefore, even at high pressures the calculations are performed at $\psi_{ai}(0) = \psi_{ci}(0) = 0$.

We encountered some difficulties when trying to solve the system of equations (2.13) by Newton-Raphson method. Instead, we minimized the thermodynamic potential $g(\eta^{(1)}, T, p)$ with respect to the order parameter $\eta^{(1)}$ and determined the strains ε_i from the last three equations of (2.13). The transition point was found from the (2.16) criterion.

Results of numerical calculations are presented in figures 1-7. In figures 1-5 the solid and dashed lines correspond to characteristics of a crystal under hydrostatic and uniaxial σ_3 stresses, respectively. In figures 6-7 the solid and dashed lines correspond to characteristics of a crystal calculated at different values of hydrostatic pressure.

In figure 1.a we plot the calculated variation of the transition temperature of a DADP crystal with hydrostatic pressure along with the experimental points from [10]. A perfect fit to the points is obtained. A linear decrease in $T_{\rm N}$ with pressure with $k_T = \partial T_{\rm N}/\partial p = -1.4$ K/kbar is observed. In figure 1.b we show the dependence of $T_{\rm N}$ on hydrostatic and uniaxial σ_3 pressures. One can see that $T_{\rm N}$ decreases with σ_3 much more rapidly than with hydrostatic pressure ($k_T = 9.0$ K/kbar). The same effect was observed experimentally in KDP, DKDP [51] and ADP [60] crystals.

Figure 2 shows the pressure dependence of the strains ε_i for a DADP crystal. The absolute values of ε_i increase with pressure linearly. Calculations do not predict any perceptible changes in ε_i with temperature except for the discontinuity at the transition point. The uniaxial pressure deforms the crystal much stronger than the hydrostatic: $\varepsilon_3(3)/\varepsilon_3(h) = 2.2$, $|\varepsilon_{12}(3)/\varepsilon_{12}(h)| = 1.4$.

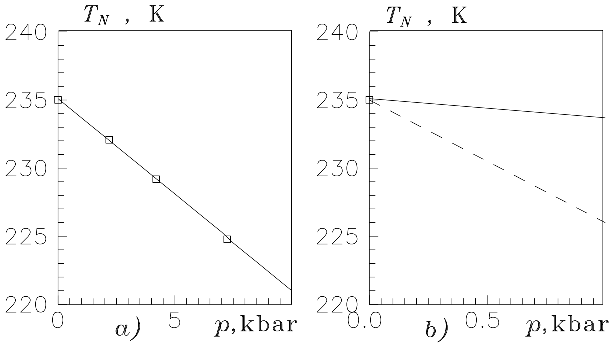


Figure 1: The transition temperature of a $ND_4D_2PO_4$ crystal as a function of pressure. Experimental points are taken from [10].

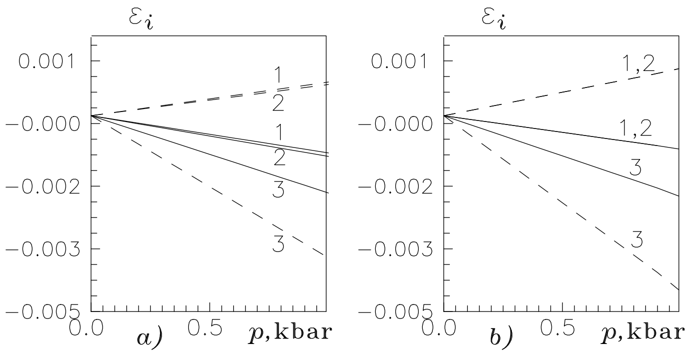


Figure 2: The strains ε_i of an $ND_4D_2PO_4$ crystal as functions of pressure at $T < T_N$ (a) and $T > T_N$ (b): 1 – ε_1; 2 – ε_2; 3 – ε_3.

In figure 3 we plot the variation of the attributed to the deuteron subsystem part of specific heat of a DADP crystal with temperature at different pressures. The experimental points of [9] correspond to a slightly higher level of deuteration. One can see that not only does the pressure shift the whole $\Delta C^p(T)$ curve to lower temperatures, but it also reduces the peak values of the specific heat at the transition points. In the paraelectric phase the specific heat hardly depends on either pressure or temperature.

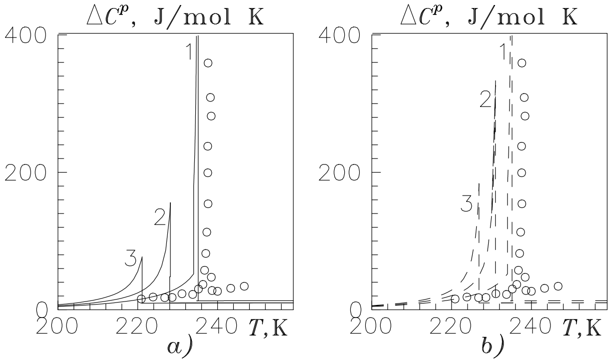


Figure 3: The specific heat of an $ND_4D_2PO_4$ crystal as a function of temperature at different pressures p(kbar): a) 1, ○ [9] – 0.001; 2 – 5; 3 – 10; b) 1, ○ [9] – 0.001; 2 – 0.5; 3 – 1.

In figures 4 and 5 we plot the calculated temperature dependences of the static transverse $\varepsilon_1(0,T,p)$ and longitudinal $\varepsilon_3(0,T,p)$ permittivity of a DADP crystal at different pressures along with the experimental points for the ambient pressure. We are not aware of any experimental measurement of pressure effects on dielectric characteristics of deuterated DADP. Theoretical values of "free" permittivities are calculated using relations (4.4) and experimental data for appropriate piezoelectric constants and elastic shear compliances [4]. Since in DADP crystal $d_{36} \gg d_{14}$, the difference between clamped and free values of the longitudinal permittivity is several times larger than that of transverse permittivity. A good description of experimental data is obtained for $\varepsilon_1(0,T,p)$, while for $\varepsilon_3(0,T,p)$ a small discrepancy between theory and experiment is observed. Probably, we could remove the discrepancy by explicit taking into account of shear strain ε_6.

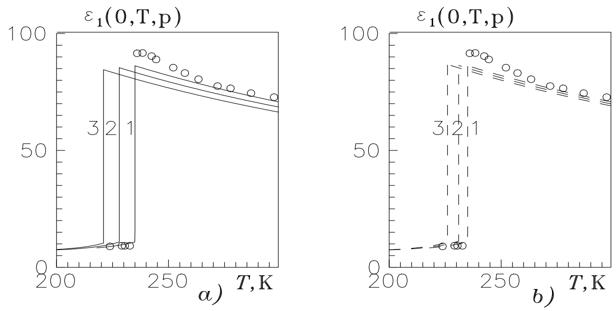


Figure 4: The temperature dependence of the transverse static dielectric permittivity of an $ND_4D_2PO_4$ crystal at different pressures p(kbar): a) 1, ○ [4] – 0.001; 2 – 5; 3 – 10; b) 1, ○ [4] – 0.001; 2 – 0.5; 3 – 1.

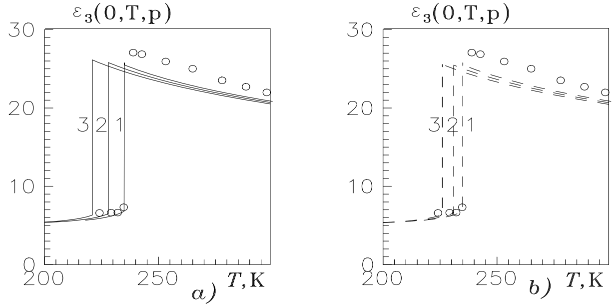


Figure 5: The temperature dependence of the longitudinal static dielectric permittivity of an $ND_4D_2PO_4$ crystal at different pressures p(kbar): a) 1, ○ [4] – 0.001; 2 – 5; 3 – 10; b) 1, ○ [4] – 0.001; 2 – 0.5; 3 – 1.

The main pressure effect is in the shift of the $\varepsilon_i(0,T,p)$ curves to lower temperatures. Besides, $\varepsilon_1(0,T,p)$ and $\varepsilon_3(0,T,p)$ decrease with pressure in the paraelectric phase and increase in the antiferroelectric phase, with the pressure effect being much stronger at $T > T_{\rm N}$.

The figure 6 shows the influence of hydrostatic pressure on the temperature curves of the transverse and longitudinal dynamic permittivities of a DADP crystal.

As numerical calculations show, the main contribution into the $\varepsilon_i(\nu,T,p)$ is going from the first relaxational mode ($\chi_1^{i+} \gg \chi_2^{i+}$), and $\tau_1^i \ll \tau_2^i$ that is, the relaxation is of Debye type. The τ_1^i decrease, and τ_2^i increase with temperature. External pressure slightly increases τ_1^i and hardly changes τ_2^i.

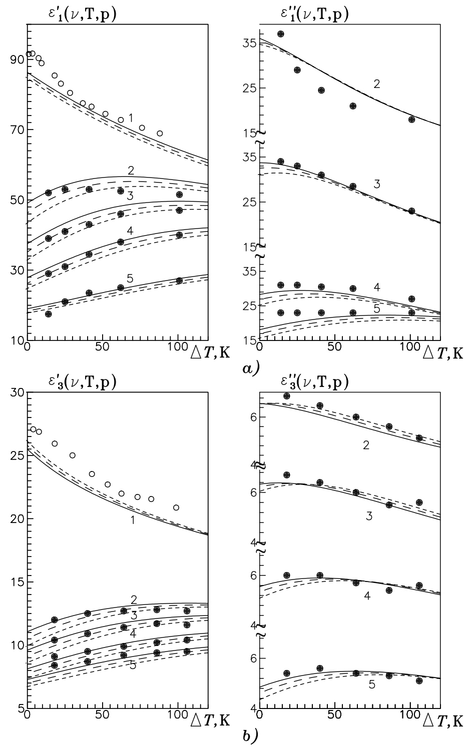


Figure 6: The temperature dependence of the transverse (a) and longitudinal (b) dielectric permittivities of an $ND_4D_2PO_4$ crystal at different frequencies ν(GHz): 1 – 10^{-6}, 2(a) – 150, 2(b) – 262, 3(a) – 210, 3(b) – 330, 4(a) – 300, 4(b) – 437, 5 – 540 and different values of hydrostatic pressures p(kbar): solid lines, ○[4], ●[58]– 0.001; long-dashed lines – 5; short-dashed lines – 10.

The changes in $\varepsilon_1(\nu,T,p)$ and $\varepsilon_3(\nu,T,p)$ with pressure are different ($\nu = \omega/2\pi$). At all frequencies and temperatures above the transition point, pressure reduces $\varepsilon'_1(\nu,T,p)$. The $\varepsilon'_3(\nu,T,p)$ is lowered down by pressure at frequencies higher than the dielectric dispersion frequency, whereas the static longitudinal permittivity $\varepsilon_3'(0,T,p)$ is raised up. The imaginary part of the longitudinal permittivity $\varepsilon_3''(\nu,T,p)$ decreases with pressure at low temperatures and increases at higher; the temperature where the character of the pressure dependence of $\varepsilon_3''(\nu,T,p)$ changes increases with frequency.

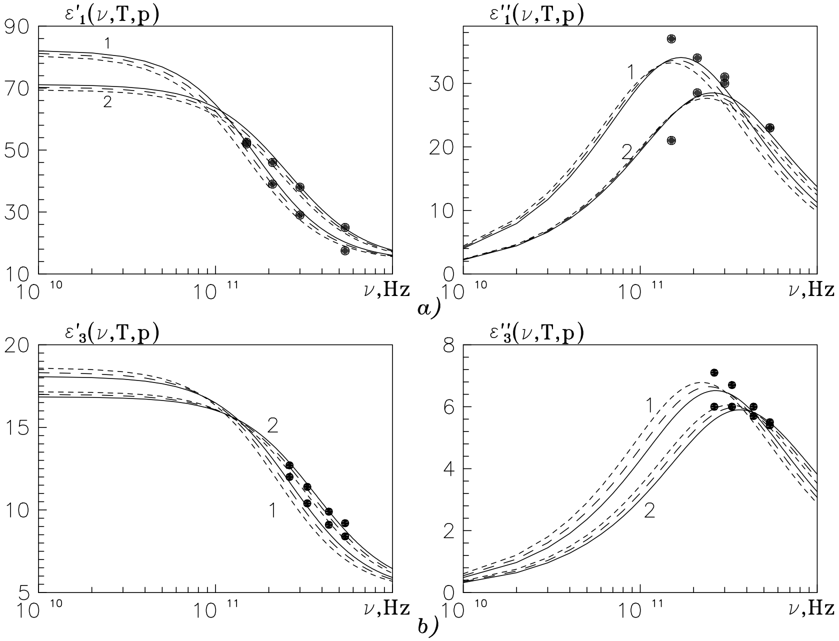


Figure 7: The frequency dependence of the transverse (a) and longitudinal (b) dielectric permittivities of an $ND_4D_2PO_4$ crystal at different values of hydrostatic pressure p(kbar): solid lines, ●[4] – 0.001; long-dashed lines – 5; short-dashed lines – 10 and different temperatures T(K); (a) 1 – 14, 2 – 62; (b) 1 – 18, 2 – 64.

The frequency dependences of dynamic dielectric permittivities $\varepsilon_i(\nu,T,p)$ are plotted in figure 7. One can see that in the region $\sim 10^{11}$ Hz a dispersion of the permittivity is observed; the dispersion frequency of $\varepsilon_1(\nu,T,p)$ is lower than that of $\varepsilon_3(\nu,T,p)$ and increases with temperature. The real part of the longitudinal permittivity $\varepsilon_1'(\nu,T,p)$ decreases with pressure in the whole frequency range, whereas its imaginary part ε_1'' and both real and imaginary parts of the transverse permittivity ε_3' and ε_3'' decrease with pressure at frequencies below that of the dielectric dispersion and increase at higher frequencies. The lower temperature, the stronger this dependence.

Concluding remarks

In our previous papers [48–51] we studied the influence of hydrostatic and uniaxial pressure on the phase transition, thermodynamic, elastic, piezoelectric and dielectric properties of highly deuterated $K(H_{1-x}D_x)_2PO_4$ ferroelectrics. It has been shown that the proper choice of the theory parameters yields a satisfactory description of pressure dependence of these characteristics.

In this paper we explore the pressure effects on DADP-type antiferroelectrics in the framework of the same model. Within the four-particle cluster approximation, considering short-range and long-range interactions between deuterons we calculate the thermodynamic and dielectric characteristics of these crystals as functions of external pressure. We also obtain a good fit to the experimental points for unstrained $N(H_{1-x}D_x)_4(H_{1-x}D_x)_2PO_4$ crystals with different deuterations. Here we describe possible changes in DADP characteristics induced by hydrostatic and uniaxial stresses, assuming some plausible changes in the crystal structure with pressure. The main feature of the predicted effects is that even low uniaxial stress can induce a significant shift of the transition temperature, whereas the intrinsic changes in the responses of DKDP and DADP crystals (i.e. beyond the shift) are rather small.

The previous [48–51] and present studies show that it is possible to describe the pressure effects in antiferroelectric DADP and ferroelectric DKDP crystals within the same approach, based on the proton ordering model.

We hope that experimental measurements of the hydrostatic and uniaxial pressure effects on the hydrogen-bonded ferroelectrics and antiferroelectrics will allow us to verify our predictions. Further studies will help us to clarify the microscopic mechanism of the phase transition in these crystals, correct the theory parameters, and improve the microscopic model itself.

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References

[1] Ueda R. Crystal structure of ammonium dihydrogen phosphate $NH_4H_2PO_4$. // J. Phys. Soc. Jpn., 1948, vol. 3, No 4, p. 328-333.

[2] Keeling R.O. Jr., Pepinsky R. An X-ray diffraction study on the transition in $NH_4H_2PO_4$ at 148^{o}K. // Z. Kristallogr., 1955, vol. 106, No 3, p. 236-285.

[3] Eisner I.Ya. Some electric characteristics of ammonium dihydrogen phosphate single crystals. // Bull. Acad. Sci. USSR Phys. Ser., 1960, vol. 24, No 11, p. 1326-1328 (in Russian).

[4] Mason W.P., Matthias B.T. The piezoelectric, dielectric and elastic properties of $ND_4D_2PO_4$ (deuterated ADP). // Phys. Rev., 1952, vol. 88, No 3, p. 477-479.

[5] Volkova E.N., Izrailenko A.N. Physical properties of ADP-DADP solid solutions. // Sov. Phys. Crystallogr., 1983, vol. 28, No 6, p.716.

[6] Lomova L.G., Sonin A.S. Spontaneous polarization of antiferroelectric ammonium dihydrogen phosphate. // Sov. Phys. Solid State, 1968, vol. 10, No 5, p.1241.

[7] Wiener(Avnear) E., Levin B., Pelah I. Antiferroelectric transitions in $NH_4H_2PO_4$ and $NH_4H_2AsO_4$ studied by infrared absorption. // J. Chem. Phys., 1970, vol. 52, No 6, p. 2891-2900.

[8] Jakubas R., Narowski E., Soboczyk L. Dielectric dispersion in d-ADP. // Solid St. Commun., 1983, vol. 45, No 8, p. 729-732.

[9] Amin M., Strukov B.A. Effects of deuteration on the specific heat of $NH_4H_2PO_4$ (ADP) crystals. // Sov. Phys. Solid State, 1970, vol. 12, p. 1616.

[10] Skalyo J., Jr., Frazer B.C., Shirane G., Daniels W.B. The pressure dependence of the transition temperature in KDP and ADP. // J. Phys. Chem. Solids, 1969, vol. 30, p. 2045-2051.

[11] Samara G.A. Vanishing of the ferroelectric and antiferroelectric states in KH_2PO_4 -type crystals at high pressure. // Phys. Rev. Lett., 1971, vol. 27, No 2, p. 103-106.

[12] Fritz I.J. Anomalous acoustic behaviour of KH_2PO_4-type crystals at high pressure. // Phys. Rev. B, 1976, vol. 13, No 2, p. 705-712.

[13] Piltz R.O., McMahon M.I., Nelmes R.J. Neutron-diffraction studies of the geometric isotope effect in H-ordering transitions. // Ferroelectrics, 1990, vol.108, p. 271-276.

[14] McMahon M.I., Piltz R.O., Nelmes R.J. Neutron-diffraction studies of the relationship between T_c and H-bond dimensions in H-ordering transitions. // Ferroelectrics, 1990, vol. 108, p. 277-282.

[15] Nelmes R.J., McMahon M.I., Piltz R.O., Wright N.G. High pressure neutron-diffraction studies of KH_2PO_4-type phase transitions as T_c tends to 0K. // Ferroelectrics, 1991, vol. 124, p. 355-360.

[16] Lines M.E., Glass A.M. Principles and application of ferroelectric and related materials. Oxford, Clarendon Press, 1977.

[17] Broberg T.W., She C.Y , Wall L.S., Edwards D.F. Longwavelength polarization fluctuations in antiferroelectric $NH_4H_2PO_4$. // Phys. Rev. B, 1972, vol. 6, No 9, p. 3332-3336.

[18] Kaminov I.P. Microwave dielectric properties of $NH_4H_2PO_4$, KH_2AsO_4 and partially deuterated KH_2PO_4. // Phys. Rev., 1965, vol. 138, No 5A, p. 1539-1543.

[19] Genin D.J., O'Reilly D.E., Tsang T. Nuclear and electron paramagnetic resonance studies of antiferroelectric ammonium dihydrogen phosphate. // Phys. Rev., 1968, vol. 167, No 2, p. 445-449.

[20] Dalal N.S., McDowell G.A. Detection by electron paramagnetic resonance of the proton-lattice coupled mode in $KH_2A_5O_4$, $KD_2A_5O_4$ and $NH_4H_2A_5O_4$ ferroelectrics and antiferroelectrics. // Phys. Rev. B, 1972, vol. 5, No 3, p. 1047-1077.

[21] Nagamiya T. On the theory of dielectric, piezoelectric and elastic properties of $NH_4H_2PO_4$. // Progr. Theor. Phys., 1952, vol. 7, No 3, p. 275-284.

[22] Ishibashi Y., Ohya S., Takagi Y. Theory of the phase transition in ADP. // J. Phys. Soc. Jpn., 1972, vol. 33, No 6, p. 1545-1550.

[23] Levitskii R.R., Korinevskii N.A., Stasyuk I.V. Theory of proton ordering in ferroelectrics and antiferroelectrics of orthophosphates type. // Ukr. Fiz. Zh., 1974, vol. 19, No 18, p. 1289-1297 (in Russian).

[24] Levitskii R.R., Korinevskii N.A., Stasyuk I.V. Distribution functions and thermodynamical properties of KD_2PO_4 and $ND_4D_2PO_4$ type crystals. // Phys.Stat.Sol.(b), 1978, vol. 88, No 1, p. 51-63.

[25] Senko H.E. Order-disorder model theory for the ferroelectrics effect in the dihydrogen phosphates. // Phys. Rev., 1961, vol. 121, No 6, p. 1599-1604.

[26] Kasahara M., Tatsuzaki I. Raman scattering in $NH_4H_2PO_4$ and $ND_4D_2PO_4$. // Jap. Journ. Appl. Phys., 1985, vol. 24, Suppl. 24-2, p. 920-922.

[27] Kasahara M., Tokunaga M., Tatsuzaki I. Raman scattering study on the phase transition of $NH_4H_2PO_4$ and $ND_4D_2PO_4$. // J. Phys. Soc. Jpn., 1986, vol. 55, No 1, p. 367-376.

[28] Schmidt V.H., Wang J.T., Schnackenberg P. // Jap. J. Appl. Phys., 1985, vol. 24, Suppl. 24-2, p.944.

[29] Matsushita E., Matsubara T. The role of hydrogen bonds in antiferroelectricity of $NH_4H_2PO_4$. // J. Phys. Soc. Jpn., 1987, vol. 56, No 1, p.200-207.

[30] Tokunaga M. Order-disorder model of PO_4 dipoles for KDP and ADP.

// Jap. Journ. Appl. Phys., 1985, vol. 24, Suppl. 24-2, p. 908-910.

[31] Havlin S., Litov E., Sompolinsky H. Unified model for the transverse electric susceptibility in KH_2PO_4 and $NH_4H_2PO_4$-type crystals. // Phys. Rev. B, 1976, vol. 14, No 3, p. 1297-1302.

[32] Havlin S. Longitudinal and transverse dielectric constants of KDP-type ferro- and antiferroelectrics. // Ferroelectrics, 1987, vol. 71, p. 183-223.

[33] Levitskii R.R., Zachek I.R., Varanitskii V.I. Relaxation dynamics of the orthophosphate type. / Preprint ITF-79-11E, Kiev, 1979, 45p.

[34] Stasyuk I.V., Levitskii R.R. Dynamic theory of hydrogen bonded antiferroelectrics of $NH_4H_2PO_4$ type. // Bull. Ac. Sci. USSR, Phys. Ser., 1971, vol. 35, No 9, p. 1775-1778 (in Russian).

[35] Levitskii R.R., Sorokov S.I. Dynamics of a simple model of antiferroelectrics with order-disorder phase transition. I. Formulation of diagrammatic method. // Ukr. Fiz. Zh., 1980, vol. 24, No 12, p. 1814-1821 (in Russian).

[36] Levitskii R.R., Sorokov S.I. Dynamics of a simple model of antiferroelectrics with order-disorder phase transition. II. Correlation functions and polarization waves. // Ukr. Fiz. Zh., 1980, vol. 25, No 1, p. 10-17 (in Russian).

[37] Meister H., Skalyo J., Frazer B.C., Shirane G. Lattice-dynamical aspects of antiferroelectric phase transition in $ND_4D_2PO_4$. // Phys. Rev., 1969, vol. 184, No 2, p. 550-555.

[38] Blinc R., Žekš B. Soft modes in ferroelectrics and antiferroelectrics. New York, Elseviers, 1974.

[39] Glauber J. Time-dependent statistics of the Ising model. // J. Math. Phys., 1963, vol. 4, No 2, p. 294-307.

[40] Yoshimitsu K., Matsubara T. Relaxation process in ferroelectrics near Curie temperature. // Progr. Theor. Phys., Suppl. Extra Number, 1968, p.109-136.

[41] Havlin S., Litov E., Sompolinsky H. Anomalous temperature dependence of protonic E-mode in KDP-type crystals. // Phys. Lett., 1975, vol. 53A, No 1, p.41-42.

[42] Zachek I.R., Levitskii R.R. Relaxation dynamics of deuterated ferroelectric orthophosphates. // Teor. Mat. Fiz., 1980, vol. 43, No 1, p.128-147 (in Russian).

[43] Levitskii R.R., Zachek I.R., Varanitskii V.I. Relaxation processes in hydrogen bonded ferroelectrics of $K(H_{1-x}D_x)_2PO_4$ -type. // Ukr. Fiz. Zh., 1980, vol. 25, No 12, p.1961-1969 (in Russian).

[44] Levitskii R.R., Mits Ye.V., Zachek I.R. Dynamics and some thermodynamic properties of ferroelectrics such as $ND_4D_2PO_4$. / Preprint ITF-81-137R, Kiev, 1982, 40p. (in Russian).

[45] Levitskii R.R., Mits Ye.V., Zachek I.R., A.A. Volkov, V.G. Kozlov, S.P. Lebedev. Longitudinal and transverse relaxation in $ND_4D_2PO_4$. / Preprint ITF-82-2R, Kiev, 1982, 30p. (in Russian).

[46] Stasyuk I.V., Biletskii I.N. Influence of omnidirectional and uniaxial stress on the ferroelectric phase transition in crystals of KH_2PO_4 type. // Bull. Ac.Sci.USSR. Phys.Ser., 1983, vol. 4, No 4, p. 79-82.

[47] Stasyuk I.V., Biletskii I.N., Styahar O.N Pressure induced pressure phase transition in KD_2PO_4 crystals. // Ukr. Fiz. Zh., 1986, vol. 31, No 4, p. 567-571 (in Russian).

[48] Stasyuk I.V., Levitskii R.R., Zachek I.R , Moina A.P., Hydrostatic and uniaxial pressure effects on phase transition and physical properties of KD_2PO_4-type ferroelectrics.. Four-particle cluster approximation. // Submitted to Mol. Phys. Reports.

[49] I.V. Stasyuk, R.R. Levitskii, I.R. Zachek, A.P. Moina, A.S. Duda. Hydrostatic pressure influence on phase transition and physical properties of KD_2PO_4-type ferroelectrics. // Cond. Matt. Phys., 1996, vol. 8, p. 129-156.

[50] Stasyuk I.V., Levitskii R.R., Zachek I.R , Moina A.P., Duda A.S. Hydrostatic pressure influence on phase transition and physical properties of KD_2PO_4-type ferroelectrics. / Preprint ICMP-96-12E, Lviv, 1996, 42 p.

[51] Stasyuk I.V., Levitskii R.R., Zachek I.R., Duda A.S., Moina A.P., Romanyuk N.O., Stadnyk V.J., Chervony R.G., Shcherbina Ye.V., / Preprint, ICMP-96-18E, Lviv, 1996, 36 p.

[52] Nelmes R.J. Structural studies of KDP and the KDP-type transition by neutron and X-ray diffraction: 1970–1985. // Ferroelectrics, 1987, vol. 71, p. 87-123.

[53] Tibbals J.E., Nelmes R.J., McIntyre G.J. The crystal structure of tetragonal KH_2PO_4 and KD_2PO_4 as a function of temperature and pressure. // J.Phys.C: Solid State. Phys., 1982, vol. 15, p. 37-58.

[54] Levitskii R.R., Stasyuk I.V., Korinevskii N.A. Dynamics of ferroactive crystals of orthophosphate type. // Ferroelectrics, 1978, vol. 21, p.481-483.

[55] B.K. Chaudhuri, S. Ganguli, D. Nath. Calculation of transverse and longitudinal electrical susceptibilities in ADP-type crystals. // J. Indian Pure Appl. Phys., 1980, vol. 18, 573-576.

[56] L.P. Pereverzeva. Peculiarities of dispersion of ε in ferroelectrics with order-disorder phase transitions. // Bull. Acad. Sci. USSR Phys. Ser., 1971, vol. 35, No 12, p. 2613-2614 (in Russian).

[57] A.A.Volkov, G.V.Kozlov, S.P.Lebedev. Critical absorption of electromagnetic radiation in a KDP crystal. // Sov. Phys. Solid State, 1980, vol. 22, p. 1665-

[58] Kozlov V.G., Lebedev S.P., Prokhorov A.M., Volkov A.A. Investigation of ferroelectric excitations in hydrogen-bond crystals using the method of submillimeter spectroscopy. // J. Phys. Soc. Japan, 1980, vol. 49, Suppl., p. 188-190.

[59] Samara G.A. Pressure dependence of the static dielectric properties of $K(H_xD_{1-x})PO_4$ and RbH_2PO_4. // Ferroelectrics, 1979, vol. 22, p. 925-936.

[60] Romanyuk M.O., Stadnyk V.J., Chervony R.G. Unpublished work.

Appendix

The coefficients of the system of equations (5.4) read

$$
\begin{aligned}
b_{11} &= -1/\alpha - P_{13}^{x,y}, & b_{12} &= 0,\\
b_{13} &= R_{13}^{x,y}, & b_{14} &= 0,\\
b_{15} &= -M_{13}^{x,y}, & b_{16} &= M_{13}^{x,y},\\
b_{17} &= 0, & b_{18} &= -N_{13}^{x,y},\\
b_{21} &= 0, & b_{22} &= -1/\alpha - P_{24}^{x,y},\\
b_{23} &= 0, & b_{24} &= R_{24}^{x,y},\\
b_{25} &= -M_{24}^{x,y}, & b_{26} &= M_{24}^{x,y},\\
b_{27} &= -N_{24}^{x,y}, & b_{28} &= 0,\\
b_{31} &= R_{13}^{x,y} + 2R_{24}^{x,y} - 2P_{24}^{x,y}, & b_{32} &= 0,\\
b_{33} &= -3/\alpha - P_{13}^{x,y}, & b_{34} &= 0,\\
b_{35} &= L_{24}^{x,y} + M_{13}^{x,y} - N_{24}^{x,y}, & b_{36} &= L_{24}^{x,y} - M_{13}^{x,y} - N_{24}^{x,y},\\
b_{37} &= 0, & b_{38} &= L_{13}^{x,y},\\
b_{41} &= 0, & b_{42} &= R_{24}^{x,y} + 2R_{13}^{x,y} - 2P_{13}^{x,y},\\
b_{43} &= 0, & b_{44} &= -3/\alpha - P_{24}^{x,y},\\
b_{45} &= L_{13}^{x,y} + M_{24}^{x,y} - N_{13}^{x,y}, & b_{46} &= L_{13}^{x,y} - M_{24}^{x,y} - N_{13}^{x,y},\\
b_{47} &= L_{24}^{x,y}, & b_{48} &= 0,\\
b_{51} &= L_{24}^{x,y} + M_{13}^{x,y} - N_{24}^{x,y}, & b_{52} &= L_{13}^{x,y} + M_{24}^{x,y} - N_{13}^{x,y},\\
b_{53} &= M_{24}^{x,y}, & b_{54} &= M_{13}^{x,y},\\
b_{55} &= -2/\alpha + R_{13}^{x,y} + R_{24}^{x,y}, & b_{56} &= -P_{13}^{x,y} - P_{24}^{x,y},\\
b_{57} &= Q_{24}^{x,y}, & b_{58} &= Q_{13}^{x,y},\\
b_{61} &= L_{24}^{x,y} - M_{13}^{x,y} - N_{24}^{x,y}, & b_{62} &= L_{13}^{x,y} - M_{24}^{x,y} - N_{13}^{x,y},\\
b_{63} &= M_{13}^{x,y}, & b_{64} &= M_{24}^{x,y},\\
b_{65} &= -P_{13}^{x,y} - P_{24}^{x,y}, & b_{66} &= -2/\alpha + R_{13}^{x,y} + R_{24}^{x,y},\\
b_{67} &= -Q_{24}^{x,y}, & b_{68} &= -Q_{13}^{x,y},\\
b_{71} &= 2L_{13}^{x,y}, & b_{72} &= 0,\\
b_{73} &= -2N_{13}^{x,y}, & b_{74} &= 0,\\
b_{75} &= 2Q_{13}^{x,y}, & b_{76} &= -2Q_{13}^{x,y},\\
b_{77} &= -2/\alpha, & b_{78} &= 2R_{13}^{x,y},\\
b_{81} &= 0, & b_{82} &= 2L_{24}^{x,y},\\
b_{83} &= 0, & b_{84} &= -2N_{24}^{x,y},\\
b_{85} &= 2Q_{24}^{x,y}, & b_{86} &= 2Q_{24}^{x,y},\\
b_{87} &= 2R_{24}^{x,y}, & b_{88} &= -2/\alpha;\\
b_1 &= L_{13}^{x,y}, & b_2 &= L_{24}^{x,y},\\
b_3 &= -N_{13}^{x,y}, & b_4 &= -N_{24}^{x,y},\\
b_5 &= -Q_{13}^{x,y} - Q_{24}^{x,y}, & b_6 &= Q_{13}^{x,y} + Q_{24}^{x,y},\\
b_7 &= -2P_{13}^{x,y}, & b_8 &= -2P_{24}^{x,y},
\end{aligned}
$$

The coefficients of the system of equations (5.5) are equal to

$$
\begin{aligned}
c_{11} &= -1/\alpha + Q_{14}^{z}, & c_{12} &= Q_{14}^{z} + P_{14}^{z},\\
c_{13} &= R_{14}^{z}, & c_{14} &= 0,\\
c_{15} &= -M_{14}^{z}, & c_{16} &= M_{14}^{z},\\
c_{17} &= 0, & c_{18} &= -N_{14}^{z},\\
c_{21} &= Q_{23}^{z} + P_{23}^{z}, & c_{22} &= -1/\alpha + Q_{23}^{z},\\
c_{23} &= 0, & c_{24} &= R_{23}^{z},\\
c_{25} &= -M_{23}^{z}, & c_{26} &= 0,\\
c_{27} &= M_{23}^{z}, & c_{28} &= -N_{23}^{z},\\
c_{31} &= R_{14}^{z} + 2R_{23}^{z} + 2Q_{23}^{z}, & c_{32} &= P_{14}^{z} + P_{23}^{z} + Q_{14}^{z} + Q_{23}^{z},\\
c_{33} &= -3/\alpha + Q_{14}^{z}, & c_{34} &= P_{23}^{z} + Q_{23}^{z},\\
c_{35} &= -L_{23}^{z} - M_{23}^{z} - N_{14}^{z}, & c_{36} &= L_{14}^{z},\\
c_{37} &= M_{23}^{z} + N_{23}^{z}, & c_{38} &= -L_{23}^{z} - M_{14}^{z} - M_{23}^{z},\\
c_{41} &= P_{14}^{z} + P_{23}^{z} + Q_{14}^{z} + Q_{23}^{z}, & c_{42} &= R_{23}^{z} + 2R_{14}^{z} + 2Q_{14}^{z},\\
c_{43} &= P_{14}^{z} + Q_{14}^{z}, & c_{44} &= -3/\alpha + Q_{23}^{z},\\
c_{45} &= -L_{14}^{z} - M_{14}^{z} - N_{23}^{z}, & c_{46} &= M_{14}^{z} + N_{14}^{z},\\
c_{47} &= L_{23}^{z}, & c_{48} &= -L_{14}^{z} - M_{14}^{z} - M_{23}^{z},\\
c_{51} &= -L_{23}^{z} - N_{14}^{z} - M_{23}^{z}, & c_{52} &= -L_{14}^{z} - N_{23}^{z} - M_{14}^{z},\\
c_{53} &= -M_{14}^{z}, & c_{54} &= -M_{23}^{z},\\
c_{55} &= -2/\alpha + R_{23}^{z} + R_{14}^{z}, & c_{56} &= -P_{14}^{z},\\
c_{57} &= -P_{23}^{z}, & c_{58} &= Q_{23}^{z} + Q_{14}^{z},\\
c_{61} &= 2M_{23}^{z} + 2N_{23}^{z}, & c_{62} &= 2L_{23}^{z},\\
c_{63} &= 0, & c_{64} &= 2M_{23}^{z},\\
c_{65} &= -2P_{23}^{z}, & c_{66} &= -2/\alpha,\\
c_{67} &= 2R_{23}^{z}, & c_{68} &= -2Q_{23}^{z},\\
c_{71} &= 2L_{14}^{z}, & c_{72} &= 2M_{14}^{z} + 2N_{14}^{z},\\
c_{73} &= 2M_{14}^{z}, & c_{74} &= 0,\\
c_{75} &= -2P_{14}^{z}, & c_{76} &= 2R_{14}^{z},\\
c_{77} &= -2/\alpha, & c_{78} &= -2Q_{14}^{z},\\
c_{81} &= -L_{23}^{z} - M_{14}^{z} - M_{23}^{z}, & c_{82} &= -L_{14}^{z} - M_{23}^{z} - M_{14}^{z},\\
c_{83} &= -N_{14}^{z}, & c_{84} &= -N_{23}^{z},\\
c_{85} &= -Q_{23}^{z} + Q_{14}^{z}, & c_{86} &= -Q_{14}^{z},\\
c_{87} &= -Q_{23}^{z}, & c_{88} &= -2/\alpha + R_{23}^{z} + R_{14}^{z},\\
c_1 &= L_{14}^{z}, & c_2 &= L_{23}^{z},\\
c_3 &= N_{14}^{z} + M_{14}^{z} + M_{23}^{z}, & c_4 &= N_{23}^{z} + M_{14}^{z} + M_{23}^{z},\\
c_5 &= -Q_{14}^{z} - Q_{23}^{z}, & c_6 &= 2Q_{23}^{z},\\
c_7 &= 2Q_{14}^{z}, & c_8 &= -P_{14}^{z} - P_{23}^{z}.
\end{aligned}
$$

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