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The influence of hydrostatic pressure on DADP-type antiferroelectrics

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We study the effects of hydrostatic pressures on deuterated $ND_4D_2PO_4$ type antiferroelectric crystals. Within the four-particle cluster approximation the free energy of the crystals is calculated, and an equation for the transition temperature and explicit expressions for static dielectric permittivities of the crystals are derived. Model pressure dependences of the effective dipole moments of unit cells are proposed. Some peculiarities of the dipole moment formation in these hydrogen bonded crystals are elucidated. In particular, we show the importance of mutual polarization of the dipole moments. The theory parameters providing a satisfactory description of the experimental data for pressure dependences of transition temperature and dielectric characteristics of the considered crystals are found.

Key words: *DADP, antiferroelectrics, pressure, dielectric permittivity, phase transition*

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1. Introduction

Ammonium dihydrogen phosphate $NH_4H_2PO_4$ (ADP) and ammonium dihydrogen arsenate $NH_4H_2AsO_4$ (ADA) are those members of the KH_2PO_4 family of hydrogen bonded crystals which undergo antiferroelectric phase transitions, and it is still not clear what is the origin of this phase transition: Is it triggered by the ordering of protons on hydrogen bonds [1–5], or are the whole H_2PO_4 groups ordering units [6,7]?

High pressure studies are a tool which can shed some light on this problem, in particular, give some information about the role of hydrogen bonds and especially of their geometric parameters in the phase transition and a polarization mechanism in crystals.

Experimentally, the influence of external pressure on these crystals is studied much less than on ferroelectric representatives of the family. However, it is known that transition temperature $T_{\rm N}$ in $NH_4H_2PO_4$, $ND_4D_2PO_4$, $NH_4H_2AsO_4$

and $ND_4D_2AsO_4$ decreases with hydrostatic pressure linearly at low pressures [8,9] (see table 1). The transition temperatures in arsenates are higher than in phosphates, but the coefficients $(\partial T_N/\partial p)_0$ in $ND_4D_2PO_4$ (DADP) and $ND_4D_2AsO_4$ (DADS) are nearly equal. At higher pressures in $NH_4H_2PO_4$ the dependence of $T_N(p)$ becomes nonlinear, and at $p = 33$ kbar the transition temperature in this crystal turns to zero (the ordered phase disappears) [10].

Under the uniaxial pressure $p = -\sigma_3$ the transition temperature in undeuterated $NH_4H_2PO_4$ decreases, too, and this decrease is faster than under hydrostatic pressure [11].

Table 1. Transition temperature at ambient pressure and the initial slope $(\partial T_N/\partial p)_0$ of some antiferroelectrics. The data are taken from [9].

crystal	T_{N0}	$(\partial T_N/\partial p)_0$
$NH_4H_2PO_4$	151.2	-3.4
$ND_4D_2PO_4$	235.1	-1.4
$NH_4H_2AsO_4$	216	-1.97
$ND_4D_2AsO_4$	304	-1.45

In antiferroelectrics of the $NH_4H_2PO_4$ type, a pronounced first order phase transition takes place, accompanied by a significant temperature hysteresis and jumps of both the transverse and longitudinal static dielectric permittivities. The transverse permittivity in $NH_4H_2AsO_4$ and $ND_4D_2AsO_4$ is much higher than in $NH_4H_2PO_4$ and $ND_4D_2PO_4$, respectively.

Transverse permittivity of $NH_4H_2PO_4$, $NH_4H_2AsO_4$ and $ND_4D_2AsO_4$ decreases with pressure in the paraelectric phase and slightly increases in the antiferroelectric phase [9,10]. It should be noted that in arsenates this decrease in ε_1 at $T > T_N$ is fairly fast (in the deuterated form faster than in the undeuterated one).

The influence of pressure on the crystal structure of the KH_2PO_4 family of antiferroelectrics has almost not been studied. However, it is known that the transition temperature in $NH_4H_2PO_4$ and $ND_4D_2PO_4$, as well as in KH_2PO_4 and KD_2PO_4, is a linear function of the H-site distance δ – a separation between two possible positions of a hydrogen on the bond O-H...O – and turns to zero in $NH_4H_2PO_4$ at $\delta_c = 0.2$Å [12–14]. Furthermore, at equal δ with an accuracy of 0.01Å the transition temperatures in KH_2PO_4, $K(H_{1-x}D_x)_2PO_4$, $NH_4H_2PO_4$, and $ND_4D_2PO_4$ coincide.

In the paraelectric phase, an $NH_4H_2PO_4$ crystal is isomorphic to KH_2PO_4 [15–17]. This fact, along with the similarity of temperature and pressure dependences of several physical characteristics of the two crystals, implies the necessity to look for a unified description of high pressure effects in them.

In our recent papers [18–20] we developed an approach which allows us to describe consistently the influence of hydrostatic and uniaxial $p = -\sigma_3$ pressures (pressures which do not lower the crystals symmetry) on deuterated ferroelectric crystals of the KH_2PO_4 family. This approach is based on the model of strained

KH_2PO_4 type crystals proposed earlier by Stasyuk *et al.* [23,24]. In [21,22] we also studied the influence of external pressures on the $ND_4D_2PO_4$ type antiferroelectrics.

In the present paper we slightly change the model (namely, in the way we model the pressure dependence of the Slater energies) and propose a new simple way to describe the polarization processes in antiferroelectric crystals. These changes allow us to describe the experiment for the pressure dependences of dielectric characteristics of a $ND_4D_2AsO_4$ crystal [1] [9], reduce the number of free parameters and to reproduce within the proton ordering model the universality of the transition temperature vs H-site distance dependence in several crystals of this family [12–14].

2. The model of strained DADP type antiferroelectrics

We consider a system of deuterons moving on hydrogen O-D. . . O bonds in the $ND_4D_2PO_4$ type crystals to which an external hydrostatic pressure and electric field E_i $(i = 1, 2, 3)$ along one of the crystallographic axis a, b, c are applied.

The calculations are performed within the four-particle cluster approximation which allows one to take into account the strong short-range correlations between deuterons adequately. The four-particle cluster Hamiltonian of such a system, with the effective long-range interactions (dipole-dipole as well as indirect deuteron-deuteron interactions via lattice vibrations) taken into account in the mean field approximation, reads [21,22]:

$$\begin{aligned}\hat{H}^i_{q4} &= V\left[\frac{\sigma_{q1}}{2}\frac{\sigma_{q2}}{2} + \frac{\sigma_{q2}}{2}\frac{\sigma_{q3}}{2} + \frac{\sigma_{q3}}{2}\frac{\sigma_{q4}}{2} + \frac{\sigma_{q4}}{2}\frac{\sigma_{q1}}{2}\right] + \\ &+ U\left[\frac{\sigma_{q1}}{2}\frac{\sigma_{q3}}{2} + \frac{\sigma_{q2}}{2}\frac{\sigma_{q4}}{2}\right] + \Phi\frac{\sigma_{q1}}{2}\frac{\sigma_{q2}}{2}\frac{\sigma_{q3}}{2}\frac{\sigma_{q4}}{2} - \sum_f \frac{z^i_{qf}}{\beta}\frac{\sigma_{qf}}{2}.\end{aligned} \tag{1}$$

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 cell.

The parameters of short-range configurational interactions $V = (\varepsilon - w_1)/2$, $U = (\varepsilon + w_1)/2$, $\Phi = 2\varepsilon - 8w + 2w_1$ are the functions of the Slater energies $\varepsilon = \varepsilon_s - \varepsilon_a$, $w = \varepsilon_1 - \varepsilon_a$, $w_1 = \varepsilon_0 - \varepsilon_a$, where ε_a, ε_s, ε_1, and ε_0 are the energies of the lateral, up-down, single-ionized and double-ionized deuteron configurations, respectively. Let us mention that the energy of lateral configurations in these antiferroelectric crystals is the lowest.

The fields z^i_{qf} include the effective cluster fields Δ^i_{qf} created by the sites neighbouring to the qf-th site, external electric field E_i, and the long-range deuteron-deuteron interactions taken into account in the mean field approximation

$$z^i_{qf} = \beta[-\Delta^i_{qf} + \sum_{q'f'} J_{ff'}(qq')\frac{\langle\sigma_{q'f'}\rangle}{2} + \mu^i_{qf}E_i], \tag{2}$$

[1]In our earlier paper [21,22] we did not perform calculations for $ND_4D_2AsO_4$, but only for $ND_4D_2PO_4$.

The influence of external pressure on the considered system is modelled on the basis of the ideas of [23,24] and [25] in the following way.

It is known that the Slater energies ε, w, 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

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

dependence of the D-site distance δ of $ND_4D_2PO_4$ and $ND_4D_2AsO_4$ crystals on hydrostatic pressure (according to [26,27] the variation of δ with pressure in KH_2PO_4 and KD_2PO_4 is linear, indeed, only 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 the pressure influence on the energy parameters of the model. Those mechanisms we take 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. We obtain

$$\varepsilon = \varepsilon^0\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big] + \sum_{i=1}^{3}\delta_{1i}\varepsilon_i, \quad w = w^0\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big] + \sum_{i=1}^{3}\delta_{2i}\varepsilon_i,$$
$$w_1 = w_1^0\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big] + \sum_{i=1}^{3}\delta_{3i}\varepsilon_i. \qquad (3)$$

(in our earlier works we did not take into account the influence of the pressure changes in the D-site distance on the Slater energies), and

$$J_{ff'}(qq') = J^{(0)}_{ff'}(qq')\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big] + \sum_{j=1}^{3}\psi^j_{ff'}(qq')\varepsilon_j. \qquad (4)$$

Here $S = S_{11} + 2S_{12} + 2S_{13} + S_{22} + 2S_{23} + S_{33}$; S_{ij} are the elastic compliances of the crystals. To avoid an explicit dependence of the Hamiltonian on pressure p, we express the latter in terms of the resulting strain $\sum_j \varepsilon_j$.

It is understood that above the transition point $\delta_{k1} = \delta_{k2}$, and $\psi^1_{ff'}(qq') = \psi^2_{ff'}(qq')$. In the above expansions we take into account only the diagonal components of strain tensor ε_1, ε_2, ε_3 and neglect piezoelectric strains ε_4, ε_5, ε_6 which must arise if an electric field is applied (piezomodules d_{14}, d_{25}, d_{36} are different from zero).

In [23,24] Stasyuk *et al.* showed that if one takes into account the lattice strains and neglects the changes with pressure in the dipole moment of hydrogen bond $\mu = e\delta$, then application of external pressure to ferroelectric crystals of the DKDP type leads to renormalization of the created by long range interactions mean fields by terms proportional to the mean values of quasispins $\eta_{qf} = \langle\sigma_{qf}\rangle$ and strains ε_i. The same follows from (4) in the mean field approximation if $\delta_1/\delta_0 = 0$.

Taking into account the symmetry of the mean values of quasispins $\langle\sigma_{qf}\rangle = \eta^i_{qf} = \mathrm{Sp}\{\sigma_{qf}\exp(-\beta\hat{H}^i_{q4})\}/\mathrm{Sp}\exp(-\beta\hat{H}^i_{q4})$:

$$\eta^{x,y}_{q13} = -\eta^{x,y}_{q1} = \eta^{x,y}_{q3}, \quad \eta^{x,y}_{q24} = \eta^{x,y}_{q2} = -\eta^{x,y}_{q4}, \quad \eta^{z}_{q14} = \eta^{z}_{q1} = \eta^{z}_{q4}, \quad \eta^{z}_{q23} = \eta^{z}_{q2} = \eta^{z}_{q3},$$

and effective dipole moments

$$\mu_1 = \mu_3^1 = -\mu_1^1,\ \mu_2 = \mu_2^2 = -\mu_4^2,\ \mu_2^1 = \mu_4^1 = \mu_1^2 = \mu_3^2 = 0,\ \mu_3 = \mu_1^3 = \mu_2^3 = \mu_3^3 = \mu_4^3,$$

presenting η^i_{qf} as a sum of two terms: a modulated spontaneous part and a uniaxial one induced by the external electric field

$$\begin{aligned}
&\eta^i_{qf} = \eta_f \mathrm{e}^{i\boldsymbol{k}_Z\boldsymbol{R}_q} + \eta_{fE_i},\\
&\eta = -\eta_1 = \eta_2 = \eta_3 = -\eta_4;\\
&\eta_{3E_1} = -\eta_{1E_1}, \quad \eta_{2E_1} = -\eta_{4E_1}; \quad \eta_{3E_2} = -\eta_{1E_2}, \quad \eta_{2E_2} = -\eta_{4E_2};\\
&\eta_{1E_3} = \eta_{2E_3} = \eta_{3E_3} = \eta_{4E_3}
\end{aligned}$$

($\boldsymbol{k}_Z = \frac{1}{2}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3)$, $\boldsymbol{b}_1$, $\boldsymbol{b}_2$, $\boldsymbol{b}_3$ are the basic vectors of the reciprocal lattice, $\mathrm{e}^{i\boldsymbol{k}_Z\boldsymbol{R}_q} = \pm 1$), we exclude the cluster fields Δ^i_{qf} from the expressions for z^i_{qf}, the symmetry of which is the same as of the corresponding η^i_{qf}. For this purpose, we use the condition that the mean values $\langle\sigma_{qf}\rangle$, calculated within the four-particle and single-particle cluster approximation, that is, with Hamiltonian (1) and with

$$\hat{H}^i_{qf} = -\frac{z^i_{qf} - \Delta^i_{qf}}{\beta}\frac{\sigma_{qf}}{2}, \tag{5}$$

must coincide. We obtain

$$\begin{aligned}
z^x_{q13} &= \frac{1}{2}\ln\frac{1+\eta^x_{q13}}{1-\eta^x_{q13}} + \beta[\nu_a(\boldsymbol{k}_Z)\eta\mathrm{e}^{i\boldsymbol{k}_Z\boldsymbol{R}_q} + \nu_a(0)\eta_{13E_1} + \frac{\mu_1 E_1}{2}],\\
z^x_{q24} &= \frac{1}{2}\ln\frac{1+\eta^x_{q24}}{1-\eta^x_{q24}} + \beta[\nu_a(\boldsymbol{k}_Z)\eta\mathrm{e}^{i\boldsymbol{k}_Z\boldsymbol{R}_q} + \nu_a(0)\eta_{24E_1}],\\
z^y_{q13} &= \frac{1}{2}\ln\frac{1+\eta^y_{q13}}{1-\eta^y_{q13}} + \beta[\nu_a(\boldsymbol{k}_Z)\eta\mathrm{e}^{i\boldsymbol{k}_Z\boldsymbol{R}_q} + \nu_a(0)\eta_{13E_2}],\\
z^y_{q24} &= \frac{1}{2}\ln\frac{1+\eta^y_{q24}}{1-\eta^y_{q24}} + \beta[\nu_a(\boldsymbol{k}_Z)\eta\mathrm{e}^{i\boldsymbol{k}_Z\boldsymbol{R}_q} + \nu_a(0)\eta_{24E_2} + \frac{\mu_2 E_2}{2}],\\
z^z_{q14} &= \frac{1}{2}\ln\frac{1+\eta^z_{q14}}{1-\eta^z_{q14}} + \beta[-\nu_a(\boldsymbol{k}_Z)\eta\mathrm{e}^{i\boldsymbol{k}_Z\boldsymbol{R}_q} + \nu_a(0)\eta_{E_3} + \frac{\mu_3 E_3}{2}],\\
z^z_{q23} &= \frac{1}{2}\ln\frac{1+\eta^z_{q23}}{1-\eta^z_{q23}} + \beta[\nu_a(\boldsymbol{k}_Z)\eta\mathrm{e}^{i\boldsymbol{k}_Z\boldsymbol{R}_q} + \nu_a(0)\eta_{E_3} + \frac{\mu_3 E_3}{2}],
\end{aligned} \tag{6}$$

where the averages η^i_{qf} are

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

and

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

The quantities $\nu_a(\boldsymbol{k})$ where $\boldsymbol{k} = \boldsymbol{k}_Z, 0)$ and $\nu_c(0)$ are the eigenvalues

$$\nu_a(\boldsymbol{k}) = \nu_a^0(\boldsymbol{k})\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{i=1}^{3}\varepsilon_i\Big] + \sum_i \psi_{ai}(\boldsymbol{k})\varepsilon_i, \;\; \nu_c(0) = \nu_c^0(0)\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{i=1}^{3}\varepsilon_i\Big] + \sum_i \psi_{ci}(0)\varepsilon_i,$$
$$\nu_a^0(\boldsymbol{k}) = \frac{1}{4}[J_{11}^{(0)}(\boldsymbol{k}) - J_{13}^{(0)}(\boldsymbol{k})]; \quad \nu_c^0(0) = \frac{1}{4}[J_{11}^{(0)}(0) + 2J_{12}^{(0)}(0) + J_{13}^{(0)}(0)],$$
$$\psi_{ai}(\boldsymbol{k}) = \frac{1}{4}[\psi_{11}^{i}(\boldsymbol{k}) - \psi_{13}^{i}(\boldsymbol{k})]; \quad \psi_{ci}(0) = \frac{1}{4}[\psi_{11}^{i}(0) + 2\psi_{12}^{i}(0) + \psi_{13}^{i}(0)],$$

of the long-range interaction matrix Fourier-transforms

$$J_{ff'}^{(0)}(\boldsymbol{k}) = \sum_{\boldsymbol{R}_q - \boldsymbol{R}_{q'}} J_{ff'}^{(0)}(qq')\mathrm{e}^{-\boldsymbol{k}(\boldsymbol{R}_q - \boldsymbol{R}_{q'})}, \;\; \psi_{ff'}^{i}(\boldsymbol{k}) = \sum_{\boldsymbol{R}_q - \boldsymbol{R}_{q'}} \psi_{ff'}^{i}(qq')\mathrm{e}^{-\boldsymbol{k}(\boldsymbol{R}_q - \boldsymbol{R}_{q'})}.$$

The strains ε_i and the order parameter $\eta = \lim_{E_1\to 0}\eta^i$ are to be determined from the thermodynamic equilibrium conditions

$$\frac{1}{\bar{v}}\frac{\partial f}{\partial \eta} = 0; \quad \frac{1}{\bar{v}}\frac{\partial f}{\partial \varepsilon_i} = -p_i. \tag{7}$$

where f is the free energy of a crystal when no electric field is applied

$$f = \frac{F}{N} = \frac{\bar{v}}{2}\sum_{ij} c_{ij}^{0}\varepsilon_i\varepsilon_j - [2w - \varepsilon] + 2\nu_a(\boldsymbol{k}_Z)\eta^2 + 2T\ln\frac{2}{(1-\eta^2)\,D}, \tag{8}$$

$c_{ij}^{(0)}$ are the so-called "seed" elastic constants of a crystal, describing the elasticity of a "host" lattice – a fictitious lattice without deuterons; $\bar{v} = v/k_{\mathrm{B}}$; v is the cell volume, k_{B} is the Boltzmann constant; $D = 1 + a + d + \cosh 2z + 4b\cosh z$, $z = \dfrac{1}{2}\ln\dfrac{1+\eta}{1-\eta} + \beta\nu_a(\boldsymbol{k}_Z)\eta$.

The system of equations for η and ε_i reads:

$$\eta = \frac{1}{D}(\sinh 2z + 2b\sinh z), \quad -p_i = \sum_j c_{ij}^{0}\varepsilon_j - F_{\mathrm{deu}} \tag{9}$$

where

$$F_{\mathrm{deu}} = \frac{2\delta_{2i} - \delta_{1i}}{\bar{v}} + \frac{2}{\bar{v}}\Big(\psi_{ai}(\boldsymbol{k}_Z) - \frac{2}{S}\frac{\delta_1}{\delta_0}\nu_a^0(\boldsymbol{k}_Z)\Big)\eta^2 -$$
$$-\frac{2}{\bar{v}D}\left(4b\Big(\delta_{2i} - \frac{2}{S}\frac{\delta_1}{\delta_0}w^0\Big)\cosh z + a\Big(\delta_{1i} - \frac{2}{S}\frac{\delta_1}{\delta_0}\varepsilon^0\Big) + d\Big(\delta_{3i} - \frac{2}{S}\frac{\delta_1}{\delta_0}w_1^0\Big)\right) *$$

is a contribution of the deuteron subsystem to crystal elasticity. Since determination of this contribution lies beyond the scope of the present paper, we may safely consider instead of (9) the system

$$\eta = \frac{1}{D}(\sinh 2z + 2b \sinh z), \quad -p_i = \sum_j c_{ij}\varepsilon_j \tag{10}$$

where c_{ij} are elastic constants of the whole crystal, being determined from an experiment.

The temperature of the first order phase transition is found from the following condition for the values of thermodynamic potential $g(\eta, T, p) = f + \bar{v}\sum_i \varepsilon_i p_i$

$$g(\eta, T_{\mathrm{N}}, p) = g(0, T_{\mathrm{N}}, p), \tag{11}$$

the order parameter and lattice strains obeying the system (10).

3. Dielectric properties of strained DADP type antiferroelectrics

It is assumed that the polarization of a crystal is triggered by the deuteron ordering, therefore,

$$P_i = \sum_f \frac{\mu^i_{qf}}{v}\frac{\langle\sigma_{qf}\rangle}{2}.$$

Different from the zero macroscopic polarization of antiferroelectric crystals is determined by those parts of the mean values of quasispins which are induced by the external electric field

$$P_1 = 2\frac{\mu_1}{v}\eta_{13E_1}, \quad P_2 = 2\frac{\mu_2}{v}\eta_{24E_2}, \quad P_3 = \frac{4\mu_3}{v}\eta_{E_3}. \tag{12}$$

Differentiating (12) with respect to E_i one can easily obtain the expressions for the corresponding static dielectric susceptibilites of a clamped ($\varepsilon_i = \mathrm{const}$) crystal of the $ND_4D_2PO_4$ type

$$\begin{aligned}
\chi^{\varepsilon}_{1,2}(0,T,p) &= \left(\frac{\partial P_{1,2}}{\partial E_{1,2}}\right)_{\varepsilon_i} = \frac{\beta\mu^2_{1,2}}{2v}\left[\frac{2\varkappa_1}{D - 2\varkappa_1\varphi^\eta_1} + \frac{2\varkappa_2}{D - 2\varkappa_2\varphi^\eta_1}\right]; \\
\chi^{\varepsilon}_{3}(0,T,p) &= \left(\frac{\partial P_3}{\partial E_3}\right)_{\varepsilon_i} = \frac{\beta\mu^2_3}{v}\frac{4\varkappa_3}{D - 2\varkappa_3\varphi^\eta_3};
\end{aligned} \tag{13}$$

where we use the notations

$$\begin{aligned}
&\varkappa_1 = 1 + b\cosh z, \ \varkappa_2 = \cosh 2z + b\cosh z - \eta^2 D, \ \varkappa_3 = a + b\cosh z; \\
&\varphi^\eta_1 = \frac{1}{1-\eta^2} + \beta\nu_a(0), \quad \varphi^\eta_3 = \frac{1}{1-\eta^2} + \beta\nu_c(0),
\end{aligned}$$

and, thereupon, the static dielectric permittivities

$$\varepsilon_i^{\varepsilon}(0,T,p) = \varepsilon_{i\infty} + 4\pi\chi_i^{\varepsilon}(0,T,p). \tag{14}$$

Let us note that in the paraelectric phase at ambient pressure and at $w, w_1 \to \infty$, (13) coincides with the corresponding expressions of [2,3] and [28,29].

The static dielectric permittivities of the mechanically free crystal (p =const) $\varepsilon_i^F(0,T,p)$ are related to (14) by [30]

$$\begin{aligned} \varepsilon_1^F(0,T,p) &= \varepsilon_1^{\varepsilon}(0,T,p) + 4\pi d_{14}^2 c_{44}^E, \\ \varepsilon_2^F(0,T,p) &= \varepsilon_2^{\varepsilon}(0,T,p) + 4\pi d_{25}^2 c_{55}^E, \\ \varepsilon_3^F(0,T,p) &= \varepsilon_3^{\varepsilon}(0,T,p) + 4\pi d_{36}^2 c_{66}^E, \end{aligned} \tag{15}$$

where d_{ij} are the piezomodules, and c^E are the elastic constants of a short-circuited crystal [31].

Our main task is to determine the pressure dependences of the effective dipole moments μ_i. In the case of ferroelectrics KD_2PO_4 and RbD_2PO_4, a satisfactory quantitative description of temperature curves of the spontaneous polarization and a longitudinal static dielectric permittivity at different values of hydrostatic pressure have been obtained by means of the following simple expressions [32]:

$$\frac{1}{\mu_1}\frac{\partial\mu_1}{\partial p} = \frac{1}{\delta}\frac{\partial\delta}{\partial p} + \frac{1}{a}\frac{\partial a}{\partial p}, \quad \frac{1}{\mu_3}\frac{\partial\mu_3}{\partial p} = \frac{1}{\delta}\frac{\partial\delta}{\partial p} + \frac{1}{c}\frac{\partial c}{\partial p}, \tag{16}$$

found on the basis of the model assumptions about the mechanism of polarization in hydrogen-bonded crystals of this type: The effective dipole moment μ_i, created by displacements of heavy ions and, perhaps, by redistribution of electronic density which are, in turn, triggered by the deuteron ordering, is proportional to δa_i, where a_i is the corresponding lattice constant.

Using (16), for the pressure dependences of coefficients $f_i = \mu_i^2/v$ we obtain

$$k_{f1} = \left(\frac{\partial f_1}{\partial p}\right)_{p=0} = f_1^{(0)}\left[2\frac{\delta_1}{\delta_0} + \frac{\varepsilon_1 - \varepsilon_2 - \varepsilon_3}{p}\right], \tag{17}$$

$$k_{f3} = \left(\frac{\partial f_3}{\partial p}\right)_{p=0} = f_3^{(0)}\left[2\frac{\delta_1}{\delta_0} + \frac{\varepsilon_3 - \varepsilon_1 - \varepsilon_2}{p}\right]. \tag{18}$$

In our earlier work [21,22] we used (17) and (18) to predict the possible pressure dependences of dielectric permittivities of $ND_4D_2PO_4$, for which no experimental results were available; at that moment we were not aware of the data for $ND_4D_2AsO_4$ [9]. However, our later numerical calculations showed that for $ND_4D_2AsO_4$ (to which large dipole moments and rapid changes in dielectric permittivity with external pressure are particular [9]), expressions (17) and (18) do not yield a good description of experimental data, though qualitatively the behaviour of dielectric permittivity with pressure is reproduced.

We believe that in this case in order to improve an agreement with the experimental data, as an additional mechanism of dipole moment formation, one should take into account mutual polarization of the dipoles created by the deuteron ordering.

We estimate the contribution of this mechanism to the pressure dependence of the dipole moment from the following speculations.

Consider a simple model of a polarized lattice, when each unit cell possesses a dipole moment, whose size is much less than the distances between the dipoles (the distances between the nearest dipoles are the lattice constants a and c). Up to the terms linear in the external field, the transverse polarization of an antiferroelectric crystal (naturally, induced by this external field) reads:

$$P_1 = \frac{2\mu_1}{v}\frac{\partial \eta_{13E_1}}{\partial E_{01}}E_{01} = \frac{\mu_1^2}{v}\tilde{\chi}_1 E_{01} = \frac{d_1}{v}, \tag{19}$$

where (see (13))

$$\tilde{\chi}_1 = \frac{1}{2}\left[\frac{2\varkappa_1}{D - 2\varkappa_1\varphi_1^\eta} + \frac{2\varkappa_2}{D - 2\varkappa_2\varphi_1^\eta}\right], \tag{20}$$

d_1 is the transverse dipole moment of a unit cell, v is the unit cell volume, and μ_1 is the effective dipole moment.

To find μ_1 we take into account the fact that the field acting on a dipole is different from the external one E_{01}, but also includes a field created by other dipoles of a crystal. Assuming that the dipole moment of the i-th unit cell $\boldsymbol{d}_i$ is proportional to the entire field

$$\boldsymbol{d}_i = \hat{\alpha}\left(\boldsymbol{E}_0 + \sum_j \frac{3(\boldsymbol{n}_{ij}\boldsymbol{d}_j)\boldsymbol{n}_{ij} - \boldsymbol{d}_j}{R_{ij}^3}\right), \tag{21}$$

($\hat{\alpha}$ is the polarizability tensor, $\boldsymbol{n}_{ij}$ is the unit vector directed from the dipole $\boldsymbol{d}_j$ to $\boldsymbol{d}_i$; R_{ij} is the distance between these dipoles). We neglect a finiteness of the crystal volume, and assume that all the dipoles, as well as the field created by them, are oriented along the external field E_{01}. Then the internal field is

$$d\sum_j \frac{3\cos^2\beta_{ij} - 1}{R_{ij}^3}; \tag{22}$$

β is the angle between vectors $\boldsymbol{n}_{ij}$ and $\boldsymbol{d}_j$, determined by

$$\cos\beta_{ij} = \frac{(\boldsymbol{n}_{ij}\boldsymbol{d}_{ij})}{d} = \frac{x}{\sqrt{x^2+y^2+z^2}};$$

(x, y, z) are the Cartesian coordinates of the dipole $\boldsymbol{d}_j$ if $\boldsymbol{d}_i$ is placed in the origin. Substituting the latter expression into (21), we obtain

$$d_1 = \frac{\alpha_1 E_{01}}{1 - \alpha_1 K_1}; \qquad K_1 = \sum_{\boldsymbol{R}} \frac{2x^2 - y^2 - z^2}{(x^2+y^2+z^2)^{5/2}} = \sum_{n_1 n_2 n_3} \frac{2a^2n_1^2 - b^2n_2^2 - c^2n_3^2}{(a^2n_1^2 + b^2n_2^2 + c^2n_3^2)^{5/2}}, \tag{23}$$

a, b, c are lattice constants; n_1, n_2, n_3 are numerals, and $n_1^2+n_2^2+n_3^2 \neq 0$. Comparing (23) and (19) and differentiating the obtained expression with respect to pressure, we find that

$$\mu_1^2 = \frac{1}{\tilde{\chi}_1}\frac{\alpha_1}{1-\alpha_1 K_1}, \quad \frac{1}{\mu_1^2}\frac{\partial \mu_1^2}{\partial p} = \frac{1}{\alpha_1}\frac{\partial \alpha_1}{\partial p}\left[1+\tilde{\chi}_1 K_1 \mu_1^2\right] + \tilde{\chi}_1 \mu_1^2 \frac{\partial K_1}{\partial p},$$

where

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

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

Here we neglect the variation of $\tilde{\chi}_1$ with pressure, which is very weak, indeed. It turns out that to find K_1 and $\partial K_1/\partial p$, we may consider only the values of $n_i = -2, -1 \ldots 2$ (we take into account only two surroundings of a site).

The value of $\frac{1}{\alpha_1}\frac{\partial \alpha_1}{\partial p}$ is chosen 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, namely:

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

Therefore, with a sufficient accuracy we can think that coefficient k_{f1} of the considered antiferroelectrics reads:

$$k_{f1} = \left[2\left(1+\tilde{\chi}_1 K_1 (\mu_1^0)^2\right)\left(\frac{\delta_1}{\delta_0}+\frac{\varepsilon_1}{p}\right) + \tilde{\chi}_1 (\mu_1^0)^2 \frac{\partial K_1}{\partial p} - \frac{\varepsilon_1+\varepsilon_2+\varepsilon_3}{p}\right], \tag{24}$$

where μ_1^0 is the effective dipole moment of a unit cell at ambient pressure.

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

$$\chi_1(0,T,p) = (1-\alpha_1 K_1)\frac{\mu_1^2}{v}\tilde{\chi}_1 = \frac{\mu_1^2}{v}\frac{\tilde{\chi}_1}{1+\mu_1^2 \tilde{\chi}_1 K_1}. \tag{25}$$

Let us mention that the difference between (13) and (25) is larger, the stronger the crystal lattice differs from the cubic one; at $a=c$, $K_1 \equiv 0$.

Similarly, for a longitudinal susceptibility we obtain

$$\chi_3(0,T,p) = (1-\alpha_3 K_3)\frac{\mu_3^2}{v}\tilde{\chi}_3 = \frac{\mu_3^2}{v}\frac{\tilde{\chi}_3}{1+\mu_3^2 \tilde{\chi}_3 K_3}. \tag{26}$$

where

$$\tilde{\chi}_3 = \frac{4\varkappa_3}{D-2\varkappa_3 \varphi_3^{\eta}}.$$

$$k_{f_3} = \left[2\left(1+\tilde{\chi}_3 K_3(\mu_3^0)^2\right)\left(\frac{\delta_1}{\delta_0}+\frac{\varepsilon_3}{p}\right)+\tilde{\chi}_3(\mu_3^0)^2\frac{\partial K_3}{\partial p}-\frac{\varepsilon_1+\varepsilon_2+\varepsilon_3}{p}\right]\tilde{\chi}_3, \qquad (27)$$

and the expressions for K_3 and $\partial K_3/\partial p$ read:

$$K_3 = \sum_{n_1n_2n_3}\frac{-a^2n_1^2-b^2n_2^2+2c^2n_3^2}{(a^2n_1^2+b^2n_2^2+c^2n_3^2)^{5/2}}, \quad r_3 = -a^2n_1^2-b^2n_2^2+2c^2n_3^2;$$

$$\frac{\partial K_3}{\partial p}p = \sum_{n_1n_2n_3}\frac{-a^2n_1^2(2R^2+5r_3)\varepsilon_1-b^2n_2^2(2R^2+5r_3)\varepsilon_2+c^2n_3^2(4R^2-5r_3)\varepsilon_3}{R^{7/2}}.$$

The differences between k_{f_1} and k_{f_3}, calculated from (17) and (24), and from (18) and (27), respectively, are more significant, the larger effective dipole moments μ_i are. Since the longitudinal moments of ferroelectrics KD_2PO_4 and RbD_2PO_4 are comparatively small, their pressure dependences calculated from (18) and (27) practically coincide. The main contribution to these dependences results from the term $\dfrac{1}{\alpha_3}\dfrac{\partial\alpha_3}{\partial p}$, that is, they are determined by the pressure changes in the D-site distances, whereas the mutual polarization of dipoles is unimportant here.

4. Numerical analysis

With the help of the presented theory we are going to describe the effects of hydrostatic pressure in highly deuterated antiferroelectric crystals $ND_4D_2PO_4$ and $ND_4D_2AsO_4$.

For a numerical estimate of the temperature and pressure dependences of the calculated above physical characteristics of the crystals, we need to set the values of the following parameters:

- Slater energies ε^0, w^0, w_1^0, parameters of the long-range interactions $\nu_a(\boldsymbol{k}_Z)$, $\nu_a(0)$, $\nu_c(0)$, constants $f_3^{(0)} = (\mu_3^{(0)})^2/v^0$ and $f_1^{(0)+} = (\mu_1^{(0)})^2/v^0$ which occur in the expressions for longitudinal and transverse permittivities, respectively. All these parameters correspond to unstrained crystals.

- deformation potentials δ_{ij}, $\psi_{aj}(\boldsymbol{k}_Z)$, $\psi_{aj}(0)$ i $\psi_{cj}(0)$, ratio δ_1/δ_0 which describes the rate of the pressure changes in the D-site distance δ.

- elastic constants c_{ij},

As parameters describing an unstrained state of $ND_4D_2PO_4$, we choose those found in [21,28,29] and which provide a satisfactory agreement with the experimental data for the transition temperature, specific heat, static and dynamic dielectric permittivities of the crystal at the atmospheric pressure. The corresponding parameters for $ND_4D_2AsO_4$ were found in [32]. Everywhere, $w_1 \to \infty$. The calculations were performed for $N(H_{1-x}D_x)_4(H_{1-x}D_x)_2PO_4$ with $T_{N0} = 235K$, for which the dependence of the transition temperature T_N on hydrostatic pressure is known [8] (hereafter, it is denoted simply as $ND_4D_2PO_4$.)

The deformation potentials δ_{ij}, $\psi_{aj}(\boldsymbol{k}_Z)$, $\psi_{aj}(0)$ and $\psi_{cj}(0)$, as well as parameter δ_1/δ_0 are determined by fitting the theoretical results for the pressure dependence of the transition temperature of the crystals to the corresponding experimental data [2].

As our calculations show, the deformation potentials δ_{ij} can be safely put equal to zero. This means that the contribution of the lattice strains to the pressure dependence of the Slater energies is negligibly small, and the latter results mainly from the pressure changes in the D-site distance δ.

However, that is not the case for the parameters of long-range interactions. Here we have to set the values of the deformation potentials $\psi_{aj}(\boldsymbol{k}_Z)$, $\psi_{aj}(0)$, and $\psi_{cj}(0)$. The $\psi_{aj}(\boldsymbol{k}_Z)$ enter the equation for order parameter (9), whereas the $\psi_{aj}(0)$, and $\psi_{cj}(0)$ occur only in expressions for dielectric permittivities.

We tried to set the values of $\psi_{aj}(\boldsymbol{k}_Z)$ in a consistent way, estimating them from the relation

$$\frac{\psi_{ai}(\boldsymbol{k}_Z)(\mathrm{ND_4D_2PO_4})}{\psi_{ai}(\boldsymbol{k}_Z)(\mathrm{ND_4D_2AsO_4})} = \frac{\nu_a^0(\boldsymbol{k}_Z)(\mathrm{ND_4D_2PO_4})}{\nu_a^0(\boldsymbol{k}_Z)(\mathrm{ND_4D_2AsO_4})}. \tag{28}$$

Since the values of dielectric permittivities are not very sensitive to small changes in parameters $\nu_a(0) = \nu_a^0(0)[1 - 2/S\delta_1/\delta_0 \sum_i \varepsilon_i] + \sum_i \psi_{ai}(0)\varepsilon_i$ or $\nu_c(0) = \nu_c^0(0)[1 - 2/S\delta_1/\delta_0 \sum_i \varepsilon_i] + \sum_i \psi_{ci}(0)\varepsilon_i$, for the sake of simplicity we assume that $\psi_{ai}(0) = \psi_{ci}(0) = 0$.

As elastic constants of $\mathrm{ND_4D_2PO_4}$ we take the elements of a matrix inverse to the elastic compliances matrix s_{ij}^E, measured at ambient pressure [31]. As far as $\mathrm{ND_4D_2AsO_4}$ is concerned, the corresponding experimental data are available only for an undeuterated form [33]. Taking into account the fact that elastic constants of deuterated crystals are, as a rule, higher that those of their undeuterated forms, we fix the values of deformation potentials $\psi_{ai}(\boldsymbol{k}_Z)$ calculated with (28), and obtain an agreement with the experimental dependence $T_{\mathrm{N}}(p)$ by changing c_{ij} from c_{ij}^+ of the undeuterated crystal up to $\sim 1.5c_{ij}^+$. Since no experimental data for the elastic constants of the crystals in the ordered phase are 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 the theory parameters which yield the best agreement of the theoretical results with the available experimental data for the temperature and pressure dependences of thermodynamic and dielectric characteristics of the considered crystals are given in tables 2 and 3. Further experimental pressure studies of these crystals will help us to find more precise values of the theory parameters.

In numerical calculations we minimize the thermodynamic potential with respect to the order parameter η and find the strains ε_i from the three latter equa-

[2]Actually, the ratio δ_1/δ_0 is not supposed to be a fitting parameter, for it can be measured experimentally, as it was for ferroelectric KDP and DKDP crystals. However, since no $\delta(p)$ dependence for DADP or DADA has been reported yet, we treat δ_1/δ_0 as a free parameter of the theory.

Table 2. The theory parameters for two crystals, $\psi_{ai} = \psi_{ai}(\boldsymbol{k}_Z)$.

crystal	$T_{\mathrm{N}0}$	ε^0	w^0	$\nu_a^0(\boldsymbol{k}_Z)$	$\nu_a^0(0)$	$\nu_c^0(0)$	$f_1^{(0)}$	$f_3^{(0)}$
	(K)							
$ND_4D_2PO_4$	235	77	709	85.75	-54	-17	837	245
$ND_4D_2AsO_4$	286.3	105	810	103.65	-38.5		1720	

crystal	$\partial T_{\mathrm{N}}/\partial p$	δ_1/δ_0	ψ_{a1}^-	ψ_{a2}^-	ψ_{a3}^-	ψ_{a1}^+	ψ_{a3}^+
	(K/kbar)	(10^{-3}kbar^{-1})	(K)				
$ND_4D_2PO_4$	-1.4	-3.65	-165	-175	80	-170	80
$ND_4D_2AsO_4$	-1.35	-3.0	-160	-180	90	-170	90

Table 3. Elastic constants c_{ij} (units of 10^5bar) for the two crystals.

crystal	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-}
$ND_4D_2PO_4$	6.59	0.53	1.92	3.28	6.24	0.4	1.66	6.4	1.5	3.48
$ND_4D_2AsO_4$	6.4	0.9	2.4	3.85	6.4	0.9	2.4	6.3	2.2	3.85

tions (10); the transition temperature is determined from condition (11). Results of the numerical calculations are given in the figures below.

In figure 1 we plot the dependence of the phase transition temperature of $ND_4D_2PO_4$ and $ND_4D_2AsO_4$ on hydrostatic pressure along with experimental points of [8,9]. Naturally, a perfect fit of theoretical results to the experimen-

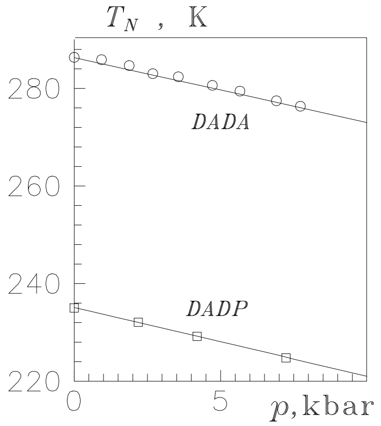

Figure 1. The transition temperature of $ND_4D_2PO_4$ and $ND_4D_2AsO_4$ as a function of hydrostatic pressure. Experimental points are taken from [8] – □ and [9] – ○.

tal data is obtained. At pressures below 10 kbar, the dependences $T_{\mathrm{N}}(p)$ are linear with nearly equal coefficients $k_T = \partial T_{\mathrm{N}}/\partial p = -1.4$ K/kbar.

It should be noted that the points of T_{N} vs δ at different values of hydrostatic pressure (the pressure dependence of δ is calculated with the help of δ_1/δ_0 from table 2) of the two antiferroelectrics considered here, as well as the corresponding points of the ferroelectrics KD_2PO_4, RbD_2PO_4, KD_2AsO_4, and RbD_2AsO_4 under hydrostatic pressure and of $K(H_{0.13}D_{0.87})_2PO_4$ under uniaxial pressure $p = -\sigma_3$ lie on a single line [34]. It means that the universality of the transition temperature vs H-site distance dependence observed experimentally in [12–14] is reproduced in this theory, and even expanded to other crystals of this family and to uniaxial pressure $p = -\sigma_3$.

In figure 2 we present temperature curves of the transverse static dielectric permittivity $\varepsilon_1(0, T, p)$ of $ND_4D_2AsO_4$ at different values of hydrostatic pressure along with the experimental points of [9]. The experimental data correspond to a clamped crystal [9], therefore, the theoretical values of $\varepsilon_1(0, T, p)$ were calculated with (14).

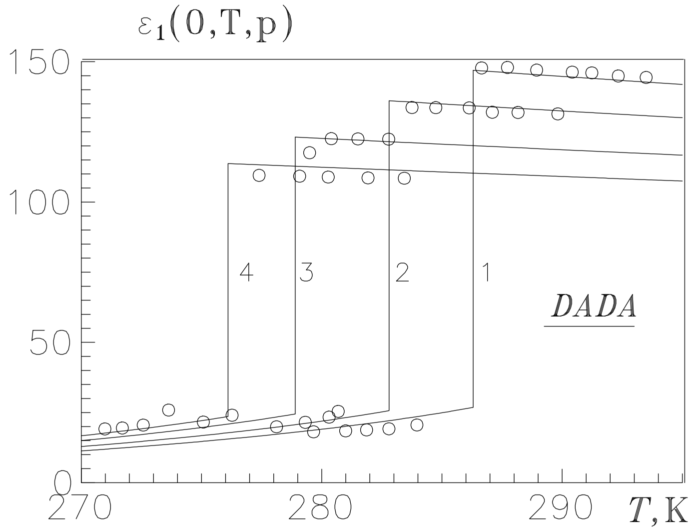

Figure 2. The temperature dependence of the transverse static dielectric permittivity of $ND_4D_2AsO_4$ at different values of external hydrostatic pressure p(kbar): a) 1 – 0.001; 2 – 2.62; 3 – 5.6; 4 – 7.68. Experimental points are taken from [9].

For $ND_4D_2AsO_4$, as well as for other arsenates (KH_2AsO_4 [35] and $NH_4H_2AsO_4$ [9]), the high values of the transverse dielectric permittivity in the paraelectric phase, as compared with those in the corresponding phosphates, are peculiar. The transverse permittivity in $ND_4D_2AsO_4$decreases with pressure fairly fast, whereas a decrease of the transition temperature is comparatively slow. The coefficient k_{f1} was calculated from (24), which provides a satisfactory agreement with the experimental data at temperatures far from critical. In the antiferroelectric phase $\varepsilon_1(0, T, p)$ slightly increases with pressure.

In figure 3 we give the temperature curves of the transverse $\varepsilon_1(0, T, p)$ and longitudinal $\varepsilon_3(0, T, p)$ static dielectric permittivities of $ND_4D_2PO_4$ at different values of hydrostatic pressure along with the experimental points [31] for ambient pressure. Unfortunately, we are not aware of any experimental work, where the pressure influence of dielecrtic characteristics of deuterated DADP was studied; therefore, the presented graphs only illustrate the plausible pressure dependences of $\varepsilon_1(0,T,p)$ and $\varepsilon_3(0,T,p)$. Theoretical values of the permittivities of a free crystal were calculated from (15), using the experimental data for elastic compliances c_{44}^E and c_{66}^E and for piezomodules d_{14} and d_{36} of [31]. Since in $ND_4D_2PO_4$ $d_{14} \ll d_{36}$, the difference between the values of longitudinal permittivity of free and clamped crystals is several times larger than that between the values of the transverse one. The quantities k_{f1} and k_{f3} were calculated from (24) and (27). For $\varepsilon_1(0,T,p)$ a fair description of experimental data is obtained, whereas for $\varepsilon_3(0,T,p)$ an agreement with the experiment is somewhat worse. Perhaps, this agreement can be improved if one explicitly takes into account the influence of piezoelectric strain ε_6.

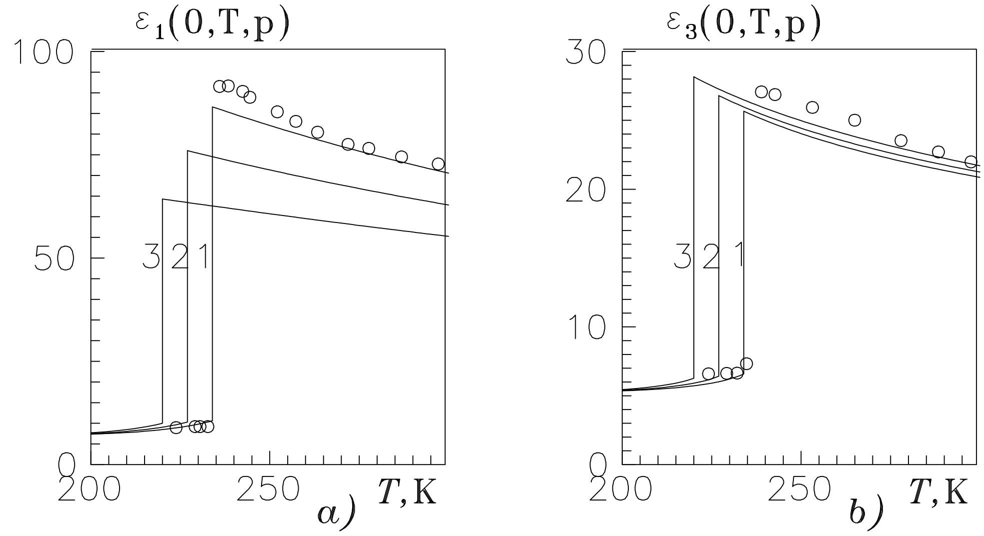

Figure 3. The transverse (a) and longitudinal (b) static dielectric permittivities of $ND_4D_2PO_4$ as functions of temperature at different values of hydrostatic pressure p(kbar): 1, ○ [31] – 0.001; 2 – 5; 3 – 10.

As one can see, the dependences of transverse static dielectric permittivities of $ND_4D_2PO_4$ and $ND_4D_2AsO_4$ on hydrostatic pressure are similar – a strong decrease in $\varepsilon_1(0,T,p)$ in the paraelectric phase and a weak increase in the antiferroelectric phase. The pressure changes in the longitudinal permittivity are mainly the shifts to lower temperatures due to the lowering of the transition temperature. Besides, $\varepsilon_3(0,T,p)$ slightly decreases with pressure in the both phases.

5. Concluding remarks

In this paper we propose a theory of strained by hydrostatic pressure antiferroelectric deuterated crystals of the $ND_4D_2PO_4$type. It should be noted that the theory can be easily generalized to the case of uniaxial pressure $p = -\sigma_3$ and other pressures which do not lower the system symmetry. In fact, for this purpose one should only change the system of equations for the lattice strains (10).

Within the four-particle cluster approximation in the short-range interactions and the mean field approximation in the long-range interactions we derived an equation for the transition temperature and explicit expressions for dielectric characteristics of the crystals. A set of free parameters was found, providing a good agreement between the presented theory and the available experimental data. An importance of the D-site distance in the phase transition and a dielectric response of the crystals is shown. We have also shown that as an essential mechanism of the dipole moment formation in these crystals, one should take into account the processes of mutual polarization of dipole moments of unit cells.

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Вплив гідростатичного тиску на антисегнетоелектрики типу DADP

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В роботі досліджується вплив гідростатичного тиску на дейтеровані антисегнетоелектричні кристали типу $ND_4D_2PO_4$. В наближенні чотиричастинкового кластера розраховано вільну енергію системи, отримано рівняння для температури фазового переходу, а також явні вирази для статичних діелектричних проникливостей кристалів. Запропоновано модельні баричні залежності ефективних дипольних моментів елементарних комірок. З'ясовано деякі особливості утворення дипольного моменту в кристалах з водневими зв'язками цього типу. Зокрема, показано важливість процесів взаємної поляризації диполів.

Знайдено набір параметрів теорії, який забезпечує задовільний кількісний опис експериментальних даних для залежностей від тиску температури переходу й діелектричних характеристик кристалів, що розглядаються.

Ключові слова: *DADP, антисегнетоелектрики, тиск, діелектрична проникливість, фазовий перехід*

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