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Thermodynamics and dielectric properties of the $NH_4H_2PO_4$ type antiferroelectrics

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Within the framework of the proton model we study thermodynamic and static dielectric properties of the ADP type antiferroelectrics with taking into account the tunnelling effects of protons on hydrogen bonds. In the four-particle cluster approximation for the short-range interactions and in the mean field approximation for the long-range interactions we calculate the free energy, entropy, and components of static dielectric susceptibility of the crystals. We also get the system of equations for the sublattice proton order parameter and an equation for the phase transition temperature. We find the values of the theory parameters for the $NH_4H_2PO_4$ and $NH_4H_2AsO_4$ crystals and get a good agreement between the theoretical results and the corresponding experimental data for the temperature dependences of the spontaneous sublattice polarization, proton specific heat, longitudinal and transverse static dielectric permittivities of the crystals.

Key words: *ADP, tunnelling, cluster approximation, phase transition, dielectric permittivity*

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1. Introduction

The phase transition in ammonium dihydrogen phosphate – $NH_4H_2PO_4$ (ADP) has been known for over sixty years. Initially it was attributed to the rotation of ammonium groups and was considered to be totally different from the ferroelectric transitions in KH_2PO_4 (KDP) type crystals. First, Nagamiya [1] has established an antiferroelectric character of the transition and showed that many of its characteristics can be described within the Slater model for KDP, only assuming a negative value of the Slater energy ε. He also proposed a scheme of proton ordering below the transition temperature (T_N) that leads to an antiferroelectric arrangement of electric dipoles along the x (or y) axis. Later, such a character of the ordered structure in ADP was experimentally confirmed [2].

However, the assumptions made by Nagamiya cannot describe an actual phase transition in ADP, since at negative ε both ferroelectric and antiferroelectric dipole orderings in the (xy) plane are possible [3,4]. Ishibashi et al. [3,4] showed that the dipole ordering [1,2] observed in ADP in the model modified by Nagamiya Slater can be stabilized just by taking into account a long range interaction within the mean field approximation.

The ADP type crystals above the temperature of the antiferroelectric phase transition are isomorphic to the KDP type crystals as they are above the ferroelectric transition temperature (space group $I\bar{4}2d$ with four molecules in a unit cell [5]). The PO_4 groups and ammonium groups NH_4 are linked by a three-dimensional network of hydrogen bonds. The bonds O–H...O are shorter than N–H...O bonds, more stable, and less temperature dependent. At the transition into the antiferroelectric phase the tetragonal symmetry of the crystal is changed to an orthorhombic one (space group $P2_12_12_1$). The directions of crystallographic axes or the number of molecules per unit cell are not changed. Groups of NH_4–PO_4 tetrahedra are polarized perpendicularly to the z-axis with alternating directions of the dipole moments of the neighbouring (along the z-axis) groups [1,2].

The ADP type crystals undergo a clear first order phase transition accompanied by the jumps of both dielectric permittivities and specific heat. Optical measurements showed [6] that below the transition temperature there arises a superstructure in ADP: a center of the body-centered tetragonal unit cell, equivalent at $T \geqslant T_N$ to its vertices, is not equivalent to them below T_N.

The statistical theory of the phase transitions in ADP type crystals, based on the principles of the proton ordering model proposed in [7–9] for the KH_2PO_4 type crystals, was developed in [4,10]. In [4] the free energy of the proton system was calculated within the four-particle cluster approximation, and possible types of proton ordering were established. It was shown that in addition to the known version of the ferroelectric ordering of protons on the bonds between the PO_4 groups, the antiferroelectric ordering described by Nagamiya [1] is realized at certain conditions. It was noted that a crucial role in the antiferroelectric ordering is played by the long range interactions. In [10] the thermodynamic and dielectric characteristics of deuterated $ND_4D_2PO_4$ type crystals were calculated within the proton ordering model for $NH_4H_2PO_4$ [4] without tunnelling.

The study of dynamic aspects of the phase transition in ADP was initiated in [11], where the proton-lattice interactions were taken into account, and the existence of a soft mode in the excitation spectrum of $NH_4H_2PO_4$ was shown. The energy of the soft mode at the transition point tends to zero at $\boldsymbol{k} \rightarrow \boldsymbol{k}_z$ ($\boldsymbol{k}_z$ is the wave vector of the z-point of the Brillouin zone). This accords with the data of quasielastic neutron scattering in $ND_4D_2PO_4$ [12]. Later [13], the dynamic dielectric susceptibility tensor of the KDP family crystals was calculated using the Bloch method within a similar model that took into account an actual structure of the crystals.

In [14] the proton ordering model for the KDP ferroelectrics was modified to the antiferroelectrics case in a somewhat different way than in [4,10]. The calculations [14] were based on the four-sublattice Slater model for ADP [3], and proton tunnelling was not taken into account. Later [15], the static and dynamic behaviour of the antiferroelectric $NH_4H_2PO_4$ type crystals was studied using the two-time temperature Green functions for the four-sublattice pseudospin model [14] with taking into account the spin-phonon interaction and proton tunnelling.

The dynamics of the KDP family crystals was studied in [16] within the four-particle cluster approximation within the framework of the approach developed in [17,18]. It has been shown for the first time that dynamic characteristics of these crystals are essentially affected by an effective tunnelling parameter, renormalized by short range interactions. Later this fact was noted in [19].

Hence, the antiferroelectric transition in the $NH_4H_2PO_4$ type crystals can be described within the proton ordering model for the KH_2PO_4 type ferroelectrics, provided the lowest energy is the energy of the lateral proton configurations, not of the up/down configurations, and (the necessary condition) the long range interactions are present. Undoubtedly, this character of the proton configuration in ADP results mainly from the presence of the NH_4 ions and additional N–H. . . O hydrogen bonds. Qualitatively it can be described as follows [20]. Each oxygen atom is linked by hydrogen bonds with another oxygen atom of a neighbouring NH_4 ammonium group. In the low temperature phase the NH_4 ion shifts from the central position so that two hydrogen bonds linking the nitrogen atom of this group with oxygens become longer than the two others [5]. If the atom O is linked to N by a longer bond, then the proton on the O–H. . . O bond is near the oxygen atom, and vice versa, at the short N–H. . . O bond, the proton on the O–H. . . O bonds is remote. Hence, the additional hydrogen bonds change the proton configuration. A microscopic theory of these effects was proposed in [20]. It has been shown that these effects can be reduced to an effective antiferroelectric interaction between the protons on the O–H. . . O bonds – lateral configurations have a lower energy.

Thus the proton ordering model [4], is the most consistent for the ADP type crystals. However, in the above mentioned papers where this model used, a study of the physical properties of the ADP type crystals is not complete. Particularly, the thermodynamic and static dielectric characteristics of $NH_4H_2PO_4$ and $NH_4H_2AsO_4$ (ADA) antiferroelectrics have not been calculated with taking into account proton tunnelling. Such a study would allow to explore the role of proton tunnelling more thoroughly. Neither there has been developed a consistent approach which would allow to determine the optimal values of the model parameters for a simultaneous description of all thermodynamic and static dielectric characteristics of ADP type antiferroelectrics. To fill these gaps is the main task of the present paper.

The calculations will be performed within the framework of the proton ordering model with tunnelling within the cluster approximation for the short range interactions and in the mean field approximation for the long range interactions. Numerical analysis will be carried out using the fitting procedure [21,22] proposed earlier for the ferroelectric KDP type crystals, modified to the antiferroelectric ADP type crystals. The obtained results will be compared with the experimental data.

2. Hamiltonian. Cluster approximation

We consider a system of protons which move on the O–H...O-bonds in an antiferroelectric crystal of the $NH_4H_2PO_4$ type. A primitive cell of two equivalent Bravais sublattices that are polarized in opposite directions is formed by two neighbouring tetrahedra PO_4 along with four hydrogen bonds attached to one of them. Hydrogen bonds attached to the other tetrahedron belong to the four nearest structural elements surrounding it. Positions and numbering of the potential mimima on the hydrogen bonds in the primitive cell are schematically shown in figure 1.

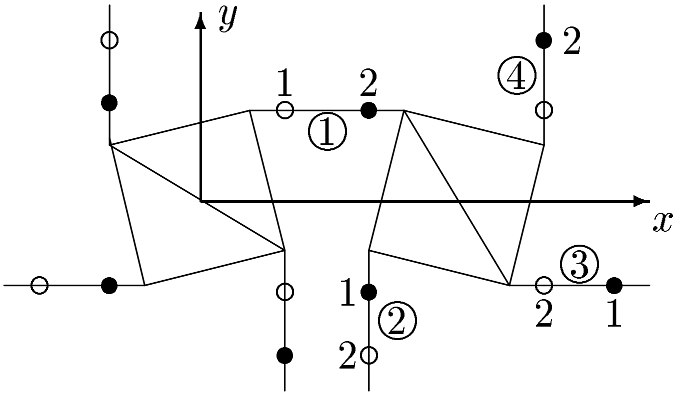


Figure 1. Sublattice primitive cell in the antiferroelectric $NH_4H_2PO_4$ type crystal. Labels ①, ②, ③ and ④ numerate hydrogen bonds; numbers 1 and 2 mark equilibrium proton sites ∘ on a bond. One of the possible antiferroelectric configurations of the protons • is shown.

An effective Hamiltonian of the proton subsystem of the ADP type antiferroelectric crystal that takes into account short range and long range proton interactions as well as proton tunnelling reads [4]:

$$\begin{aligned}\hat{H} \;=\;& -2\Omega\sum_{\boldsymbol{n},f}\hat{S}^x_f(\boldsymbol{n}) - \frac{1}{2}\sum_{\boldsymbol{n}_1,\boldsymbol{n}_2}\sum_{f_1,f_2}J_{f_1f_2}(\boldsymbol{n}_1,\boldsymbol{n}_2)\hat{S}^z_{f_1}(\boldsymbol{n}_1)\hat{S}^z_{f_2}(\boldsymbol{n}_2)\\ &+\sum_{\substack{\boldsymbol{n}_1,\boldsymbol{n}_2\\ \boldsymbol{n}_3,\boldsymbol{n}_4}}\Big\{\frac{1}{2}\sum_{f_1,f_2}V_{f_1f_2}\hat{S}^z_{f_1}(\boldsymbol{n}_1)\hat{S}^z_{f_2}(\boldsymbol{n}_2)+\Phi\hat{S}^z_1(\boldsymbol{n}_1)\hat{S}^z_2(\boldsymbol{n}_2)\hat{S}^z_3(\boldsymbol{n}_3)\hat{S}^z_4(\boldsymbol{n}_4)\Big\}\\ &\times\{\delta_{\boldsymbol{n}_1,\boldsymbol{n}_2}\delta_{\boldsymbol{n}_1,\boldsymbol{n}_3}\delta_{\boldsymbol{n}_1,\boldsymbol{n}_4}+\delta_{\boldsymbol{n}_1+\boldsymbol{r},\boldsymbol{n}_2+\boldsymbol{r}}\delta_{\boldsymbol{n}_1+\boldsymbol{r},\boldsymbol{n}_3+\boldsymbol{r}}\delta_{\boldsymbol{n}_1+\boldsymbol{r},\boldsymbol{n}_4+\boldsymbol{r}}\}. \qquad (2.1)\end{aligned}$$

Here the first term describes the tunnelling of protons on the O–H...O bonds (2Ω is the tunnelling frequency); the second term is the long range interaction between protons ($J_{f_1f_2}(\boldsymbol{n},\boldsymbol{n})=0$) that also includes their interaction via lattice vibrations [11,23]; the third term presents the short range configurational correlations between the protons within the primitive cells. $\hat{S}^\alpha_f(\boldsymbol{n})$ is the α-component ($\alpha=x,z$) of a pseudospin operator that describes a state of the proton on the f-th hydrogen bond ($f=1,2,3,4$) in $\boldsymbol{n}$-th cell: the eigenvalues of the operator $\hat{S}^z_f(\boldsymbol{n})$ correspond to the two equilibrium proton positions on a bond; $\boldsymbol{r}$ is a relative position vector of a tetrahedron in a primitive cell. Constants of the short range interaction have the following symmetry

$$V_{12} = V_{23} = V_{34} = V_{41} = V, \quad V_{13} = V_{24} = U, \quad V_{ff} = 0.$$

They are related to the configurational energies $\tilde{\varepsilon} = \overline{\varepsilon}_s - \overline{\varepsilon}_a, \tilde{w} = \overline{\varepsilon}_1 - \overline{\varepsilon}_a, \tilde{w}_1 = \overline{\varepsilon}_0 - \overline{\varepsilon}_a$ of the four-particle cluster [4]:

$$V = \frac{1}{2}(\tilde{\varepsilon} - \tilde{w}_1), \quad U = \frac{1}{2}(\tilde{\varepsilon} + \tilde{w}_1), \quad \Phi = 2\tilde{\varepsilon} - 8\tilde{w} + 2\tilde{w}_1, \tag{2.2}$$

where $\overline{\varepsilon}_0, \overline{\varepsilon}_1, \overline{\varepsilon}_a, \overline{\varepsilon}_s$ are the energies of the possible proton configurations around a PO_4 group.

Due to the strong short range correlations in the ADP type crystals and the peculiarities of the crystal structure, it is most natural to use in the calculations the four-particle cluster approximation for the short range interactions and the mean field approximation for the long range interactions.

In these approximations, the free energy of the $NH_4H_2PO_4$ type crystal, with the four-particle Hamiltonians within the primitive cell chosen as a cluster being equivalent, reads [4]:

$$\begin{aligned} F &= -\frac{1}{\beta}\sum_{\boldsymbol{n}}\left(2\ln \mathrm{Sp}\;[\mathrm{e}^{-\beta\hat{H}_4(\boldsymbol{n})}] - \sum_{f=1}^{4}\ln \mathrm{Sp}\;[\mathrm{e}^{-\beta\hat{H}_{1f}(\boldsymbol{n})}]\right) \\ &\quad + \frac{1}{2}\sum_{\boldsymbol{n}_1,\boldsymbol{n}_2}\sum_{f_1,f_2} J_{f_1f_2}(\boldsymbol{n}_1,\boldsymbol{n}_2)\langle\hat{S}^z_{f_1}(\boldsymbol{n}_1)\rangle\langle\hat{S}^z_{f_2}(\boldsymbol{n}_2)\rangle. \end{aligned} \tag{2.3}$$

Here $\beta = 1/k_{\mathrm{B}}T$, k_{B} is the Boltzmann constant; T is the absolute temperature, whereas the four-particle $\hat{H}_4(\boldsymbol{n})$ and single-particle $\hat{H}_{1f}(\boldsymbol{n})$ Hamiltonians of the cluster are given by expressions

$$\begin{aligned} \hat{H}_4(\boldsymbol{n}) &= \sum_{f=1}^{4}\left(-2\Omega + \frac{1}{2}\eta_f(\boldsymbol{n})\right)\hat{S}^x_f(\boldsymbol{n}) + \frac{1}{2}\sum_{f_1,f_2=1}^{4} V_{f_1f_2}\hat{S}^z_{f_1}(\boldsymbol{n})\hat{S}^z_{f_2}(\boldsymbol{n}) \\ &\quad + \Phi\prod_{f=1}^{4}\hat{S}^z_f(\boldsymbol{n}) + \sum_{f=1}^{4}(\Delta_f(\boldsymbol{n}) - \gamma_f(\boldsymbol{n}))\hat{S}^z_f(\boldsymbol{n}), \\ \hat{H}_{1f}(\boldsymbol{n}) &= (-2\Omega + \eta_f(\boldsymbol{n}))\hat{S}^x_f(\boldsymbol{n}) + (2\Delta_f(\boldsymbol{n}) - \gamma_f(\boldsymbol{n}))\hat{S}^z_f(\boldsymbol{n}). \end{aligned} \tag{2.4}$$

In (2.4) the effect of proton correlations on the tunnelling is taken into account via the parameter $\eta_f(\boldsymbol{n})$; ($\eta_f(\boldsymbol{n})$ is an average "transverse" field acting on the given proton from the side of the nearest neighbours). In its turn, $\Delta_f(\boldsymbol{n})$ is the consistency parameter for the short range forces which determines the effect of protons of the neighbouring cells on the f-th proton in the $\boldsymbol{n}$-th cell ($\Delta_f(\boldsymbol{n})$ is an average "longitudinal" field); $\gamma_f(\boldsymbol{n})$ is the effective field created by the long range interactions

$$\gamma_f(\boldsymbol{n}) = \sum_{\boldsymbol{n}_1,f_1} J_{ff_1}(\boldsymbol{n},\boldsymbol{n}_1)\langle\hat{S}^z_{f_1}(\boldsymbol{n}_1)\rangle.$$

Parameters $\eta_f(\boldsymbol{n})$ and $\Delta_f(\boldsymbol{n})$ are found by minimization of the free energy

$$\frac{\partial F}{\partial \eta_f(\boldsymbol{n})} = \frac{\partial F}{\partial \Delta_f(\boldsymbol{n})} = 0. \tag{2.5}$$

Taking into account (2.3) and (2.4), we can rewrite the condition (2.5) as

$$\mathrm{Sp}\,[\hat{\rho}_4(\boldsymbol{n})\hat{S}^{\alpha}_f(\boldsymbol{n})] = \mathrm{Sp}\,[\hat{\rho}_{1f}(\boldsymbol{n})\hat{S}^{\alpha}_f(\boldsymbol{n})], \quad \alpha = x, y, \tag{2.6}$$

where

$$\hat{\rho}_4(\boldsymbol{n}) = \frac{\exp[-\beta\hat{H}_4(\boldsymbol{n})]}{Z_4(\boldsymbol{n})}, \qquad \hat{\rho}_{1f}(\boldsymbol{n}) = \frac{\exp[-\beta\hat{H}_{1f}(\boldsymbol{n})]}{Z_{1f}(\boldsymbol{n})},$$
$$Z_4(\boldsymbol{n}) = \mathrm{Sp}\,\mathrm{e}^{-\beta\hat{H}_4(\boldsymbol{n})}, \qquad Z_{1f}(\boldsymbol{n}) = \mathrm{Sp}\,\mathrm{e}^{-\beta\hat{H}_{1f}(\boldsymbol{n})}.$$

Equations (2.6) are called the self-consistency equations: the mean value of each component of the pseudospin $P_{\boldsymbol{n}f} \equiv \langle\hat{S}^z_f(\boldsymbol{n})\rangle$, $X_{\boldsymbol{n}f} \equiv \langle\hat{S}^x_f(\boldsymbol{n})\rangle$ should not depend on the density matrix (four- or single-particle) it was calculated with. Hence, to find the cluster parameters we can use either the condition of the free energy minimum or equation (2.6).

In order to calculate the free energy (2.3), we need to find eigenvalues of the four- and single particle cluster Hamiltonians (2.4). The eigenvalues of the single-particle Hamiltonians $\hat{H}_{1f}(\boldsymbol{n})$ are easily obtained after rotation transformation for the pseudospin operators, so that the terms linear in $\hat{S}^x_f(\boldsymbol{n})$ are excluded from $\hat{H}_{1f}(\boldsymbol{n})$. Then, the corresponding single-particle partition function is obtained

$$\begin{aligned} Z_{1f}(\boldsymbol{n}) &= 2\cosh\left(\beta\sqrt{K_f(\boldsymbol{n})}\right), \\ K_f(\boldsymbol{n}) &= (A_f(\boldsymbol{n}) + \frac{1}{2}\gamma_f(\boldsymbol{n}))^2 + (2\Gamma_f(\boldsymbol{n}) + \Omega)^2. \end{aligned} \tag{2.7}$$

For the sake of convenience, here we introduce the new variational fields

$$A_f(\boldsymbol{n}) = \Delta_f(\boldsymbol{n}) - \gamma_f(\boldsymbol{n}), \qquad \Gamma_f(\boldsymbol{n}) = -\Omega + \frac{\eta_f(\boldsymbol{n})}{4}.$$

Having calculated the single-particle averages $P_{\boldsymbol{n}f}$, $X_{\boldsymbol{n}f}$ and having solved the system of these two equations, we obtain the fields $A_f(\boldsymbol{n})$ and $\Gamma_f(\boldsymbol{n})$

$$\begin{aligned} A_f(\boldsymbol{n}) &= \frac{P_{\boldsymbol{n}f}}{2\beta\sqrt{P^2_{\boldsymbol{n}f} + X^2_{\boldsymbol{n}f}}} \ln\frac{1 - \sqrt{P^2_{\boldsymbol{n}f} + X^2_{\boldsymbol{n}f}}}{1 + \sqrt{P^2_{\boldsymbol{n}f} + X^2_{\boldsymbol{n}f}}} - \frac{\gamma_f(\boldsymbol{n})}{2}, \\ \Gamma_f(\boldsymbol{n}) &= \frac{X_{\boldsymbol{n}f}}{4\beta\sqrt{P^2_{\boldsymbol{n}f} + X^2_{\boldsymbol{n}f}}} \ln\frac{1 - \sqrt{P^2_{\boldsymbol{n}f} + X^2_{\boldsymbol{n}f}}}{1 + \sqrt{P^2_{\boldsymbol{n}f} + X^2_{\boldsymbol{n}f}}} - \frac{\Omega}{2}. \end{aligned} \tag{2.8}$$

The proposed by Nagamiya [1] antiferroelectric ordering of protons around the PO_4 groups in the ADP crystals, when the antiferroelectric spontaneous polarization is directed along the x axis, is realized at the following relations between the pseudospin mean values

$$\begin{aligned}
&-P_{\boldsymbol{n}1} = P_{\boldsymbol{n}2} = P_{\boldsymbol{n}3} = -P_{\boldsymbol{n}4}\,, \\
&X_{\boldsymbol{n}1} = X_{\boldsymbol{n}2} = X_{\boldsymbol{n}3} = X_{\boldsymbol{n}4} \equiv X.
\end{aligned} \tag{2.9}$$

Using the found in [4,11] spatial dependence of the proton ordering parameter

$$P_{\boldsymbol{n}f} = P_f \mathrm{e}^{\mathrm{i}\boldsymbol{k}_z\boldsymbol{n}},$$

where $\boldsymbol{k}_z = \frac{1}{2}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3)$, $\boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3$ are the basic vectors of the lattice, reciprocal to the the body-centered tetragonal lattice, and the exponent can have only two values $\mathrm{e}^{\mathrm{i}\boldsymbol{k}_z\boldsymbol{n}} = \pm 1$, that correspond to the two sublattices, and from the relations (2.9), (2.8) we find

$$\begin{aligned}
&-P_1 = P_2 = P_3 = -P_4 \equiv P; \\
&\gamma_f(\boldsymbol{n}) = \gamma_f \mathrm{e}^{\mathrm{i}\boldsymbol{k}_z\boldsymbol{n}}, \qquad \gamma_f = \frac{1}{2}\nu_a P_f, \qquad \nu_a = J_{11}(\boldsymbol{k}_z) - J_{13}(\boldsymbol{k}_z), \\
&J_{f_1f_2}(\boldsymbol{k}) = \sum_{\boldsymbol{n}-\boldsymbol{n}_0} J_{f_1f_2}(\boldsymbol{n}, \boldsymbol{n}_0)\mathrm{e}^{-\boldsymbol{k}(\boldsymbol{n}-\boldsymbol{n}_0)}; \\
&A_f(\boldsymbol{n}) = A_f \mathrm{e}^{\mathrm{i}\boldsymbol{k}_z\boldsymbol{n}}, \qquad -A_1 = A_2 = A_3 = -A_4 \equiv A; \\
&\Gamma_1(\boldsymbol{n}) = \Gamma_2(\boldsymbol{n}) = \Gamma_3(\boldsymbol{n}) = \Gamma_4(\boldsymbol{n}) \equiv \Gamma.
\end{aligned} \tag{2.10}$$

The variational fields A and Γ read

$$\begin{aligned}
A &= \frac{P}{2\beta Q}\ln\frac{1-Q}{1+Q} - \frac{1}{4}\nu_a P, \\
\Gamma &= \frac{X}{4\beta Q}\ln\frac{1-Q}{1+Q} - \frac{\Omega}{2}, \\
& Q = \sqrt{P^2 + X^2}.
\end{aligned} \tag{2.11}$$

It is more difficult to find the eigenvalues of the four-particle Hamiltonian $\hat{H}_4(\boldsymbol{n})$. We perform a unitary transformation of the initial matrix of the Hamiltonian $\hat{H}_4(\boldsymbol{n})$, using the fact that its symmetry groups are isomorphic to the point group D_{4h} in the paraelectric phase ($T > T_N : A = 0, P = 0$) and to its subgroup D_2 (see [24,25]) in the antiferroelectric phase ($T < T_N : A \neq 0, P \neq 0$). After the transformation, subtracting a constant value from the obtained matrix (this does not affect the subsequent results), we obtain a quasidiagonal form of the matrix $\bar{H}_4$ of the Hamiltonian $\hat{H}_4$ [26]:

$$\bar{H}_4 = \bar{H}_{4af}\theta(T_N - T) + \bar{H}_{4p}\theta(T - T_N). \tag{2.12}$$

Here

$$\bar{H}_{4af} = \tilde{B}_1 \oplus \tilde{B}_2 \oplus \tilde{B}_3 \oplus \tilde{B}_4,$$

$$\tilde{B}_1=\left(\begin{array}{ccccccc} -2A & 0 & 0 & 2\Gamma & 0 & 0 & 0 \\ 0 & 2A & 0 & 0 & 2\Gamma & 0 & 0 \\ 0 & 0 & \tilde{\varepsilon} & \sqrt{2}\Gamma & \sqrt{2}\Gamma & 0 & 0 \\ 2\Gamma & 0 & \sqrt{2}\Gamma & \tilde{w}-A & 0 & \sqrt{2}\Gamma & \sqrt{2}\Gamma \\ 0 & 2\Gamma & \sqrt{2}\Gamma & 0 & \tilde{w}+A & \sqrt{2}\Gamma & \sqrt{2}\Gamma \\ 0 & 0 & 0 & \sqrt{2}\Gamma & \sqrt{2}\Gamma & \tilde{w}_1 & 0 \\ 0 & 0 & 0 & \sqrt{2}\Gamma & \sqrt{2}\Gamma & 0 & 0 \end{array}\right),$$

$$\tilde{B}_2=\left(\begin{array}{ccc} \tilde{\varepsilon} & \sqrt{2}\Gamma & \sqrt{2}\Gamma \\ \sqrt{2}\Gamma & \tilde{w}-A & 0 \\ \sqrt{2}\Gamma & 0 & \tilde{w}+A \end{array}\right), \ \tilde{B}_3=\left(\begin{array}{ccc} 0 & \sqrt{2}\Gamma & \sqrt{2}\Gamma \\ \sqrt{2}\Gamma & \tilde{w}-A & 0 \\ \sqrt{2}\Gamma & 0 & \tilde{w}+A \end{array}\right),$$

$$\tilde{B}_4=\left(\begin{array}{ccc} \tilde{w}-A & 0 & \sqrt{2}\Gamma \\ 0 & \tilde{w}+A & \sqrt{2}\Gamma \\ \sqrt{2}\Gamma & \sqrt{2}\Gamma & \tilde{w}_1 \end{array}\right), \qquad (2.13)$$

and

$$\begin{aligned} &\bar{H}_{4p} = \tilde{B}_{p1}\oplus\tilde{B}_{p2}\oplus\tilde{B}_{p3}\oplus\tilde{B}_{p4}\oplus\tilde{B}_{p3}\oplus\tilde{B}_{p4}\oplus\tilde{B}_{p5}\oplus\tilde{B}_{p6}\oplus\tilde{B}_{p4}, \\ &\tilde{B}_{p1} = \left(\begin{array}{cccc} \tilde{\varepsilon} & 0 & 2\Gamma & 0 \\ 0 & 0 & 2\sqrt{2}\Gamma & 0 \\ 2\Gamma & 2\sqrt{2}\Gamma & \tilde{w} & 2\Gamma \\ 0 & 0 & 2\Gamma & \tilde{w}_1 \end{array}\right), \ \tilde{B}_{p2} = \left(\begin{array}{cc} \tilde{\varepsilon} & 2\Gamma \\ 2\Gamma & \tilde{w} \end{array}\right), \\ &\tilde{B}_{p3} = \left(\begin{array}{cc} 0 & 2\Gamma \\ 2\Gamma & \tilde{w} \end{array}\right), \ \tilde{B}_{p4}=\tilde{w}, \ \tilde{B}_{p5}=0, \ \tilde{B}_{p6} = \left(\begin{array}{cc} \tilde{w}_1 & 2\Gamma \\ 2\Gamma & \tilde{w} \end{array}\right). \end{aligned} \qquad (2.14)$$

Let us note that the matrix $\bar{H}_{4af}$ is equivalent to the corresponding matrix obtained earlier in [25].

Solving the eigenvalues problem for the $\bar{H}_{4af}$ and $\bar{H}_{4p}$ matrices, we obtain the following equations

$$\begin{aligned} &E^7 + E^6 k_6 + E^5 k_5 + E^4 k_4 + E^3 k_3 + E^2 k_2 + E k_1 + k_0 = 0, \\ &E^3 + E^2 l_2 + E l_1 + l_0 = 0, \\ &E^3 - 2\tilde{w}E^2 + E d_1 + 4\Gamma^2\tilde{w} = 0, \\ &E^3 + E^2 m_2 + E m_1 + m_0 = 0, \end{aligned} \qquad (2.15)$$

in the antiferroelectric phase and $E_{p1}, E_{p2}, E_{p3}, E_{p4}$ are the roots of the equation:

$$\begin{aligned} &E^4 + E^3(-\tilde{w} - \bar{w}_1) + E^2(\tilde{w}_1\tilde{\varepsilon} + \tilde{w}\bar{w}_1 - 16\Gamma^2) \\ &\qquad + E(12\Gamma^2\bar{w}_1 - \tilde{w}_1\tilde{w}\tilde{\varepsilon}) - 8\Gamma^2\tilde{w}_1\tilde{\varepsilon} = 0, \\ &E_{p5,6} = \frac{1}{2}\Big(\tilde{w} + \tilde{\varepsilon} \pm \sqrt{(\tilde{w}-\tilde{\varepsilon})^2 + 16\Gamma^2}\Big), \\ &E_{p7(10),8(11)} = \frac{1}{2}\Big(\tilde{w} \pm \sqrt{\tilde{w}^2 + 16\Gamma^2}\Big), \\ &E_{p9,12,16} = \tilde{w}; \qquad E_{p13} = 0, \\ &E_{p14,15} = \frac{1}{2}\Big(\tilde{w}_1 + \tilde{w} \pm \sqrt{(\tilde{w}_1 - \tilde{w})^2 + 16\Gamma^2}\Big) \end{aligned} \qquad (2.16)$$

in the paraelectric phase. Here we use the following notations

$$
\begin{aligned}
k_0 &= -16\Gamma^2 A^2 \tilde{w}_1 \tilde{w} \tilde{\varepsilon},\\
k_1 &= 4A^4 \tilde{\varepsilon} \tilde{w}_1 + 32\Gamma^4 \tilde{w}_1 \tilde{\varepsilon} - 4A^2 \tilde{w}^2 \tilde{w}_1 \tilde{\varepsilon} + 32A^2\Gamma^2 \tilde{w} \bar{w}_1,\\
k_2 &= 4A^2(\tilde{w}^2 \bar{w}_1 + 2\tilde{w}_1 \tilde{w} \tilde{\varepsilon}) - 4A^4 \bar{w}_1 - 48\Gamma^4(\tilde{\varepsilon} + \tilde{w})\\
&\quad + 12\Gamma^2 \tilde{w}_1 \tilde{w} \tilde{\varepsilon} - 16A^2\Gamma^2(3\tilde{w} + \bar{w}_1),\\
k_3 &= -A^2(4\tilde{w}^2 + 5\tilde{\varepsilon}\tilde{w}_1 + 8\tilde{w}\bar{w}_1) - 4\Gamma^2(4\tilde{w}\bar{w}_1 + 3\tilde{w}_1\tilde{\varepsilon})\\
&\quad + 4A^4 + 32\Gamma^2 A^2 + 64\Gamma^4 + \tilde{w}^2 \tilde{w}_1 \tilde{\varepsilon},\\
k_4 &= A^2(8\tilde{w} + 5\bar{w}_1) - \tilde{w}^2 \bar{w}_1 - 2\tilde{w}_1 \tilde{w} \tilde{\varepsilon} + 4\Gamma^2(5\tilde{w} + 4\bar{w}_1),\\
k_5 &= \tilde{w}^2 + 2\tilde{w}\bar{w}_1 + \tilde{\varepsilon}\tilde{w}_1 - 5A^2 - 20\Gamma^2, \qquad k_6 = -2\tilde{w} - \bar{w}_1;\\
l_0 &= -\tilde{\varepsilon}\tilde{w}^2 + \tilde{\varepsilon}A^2 + 4\Gamma^2\tilde{w}, \qquad l_1 = \tilde{w}^2 + 2\tilde{w}\tilde{\varepsilon} - A^2 - 4\Gamma^2,\\
l_2 &= -2\tilde{w} - \tilde{\varepsilon}; \qquad m_0 = -\tilde{w}_1\tilde{w}^2 + \tilde{w}_1 A^2 + 4\Gamma^2\tilde{w},\\
m_1 &= \tilde{w}^2 + 2\tilde{w}\tilde{w}_1 - A^2 - 4\Gamma^2, \qquad m_2 = -2\tilde{w} - \tilde{w}_1;\\
d_1 &= \tilde{w}^2 - A^2 - 4\Gamma^2; \qquad \bar{w}_1 = \tilde{w}_1 + \tilde{\varepsilon}.
\end{aligned}
$$

Hence, the problem of finding the free energy in the cluster approximation is reduced to diagonalization of the matrices (2.13) and (2.14), or to solving the corresponding seventh and third order algebraic equations (2.15) in the low-temperature phase and the fourth order equation (2.16) in the high-temperature phase.

3. Spontaneous sublattice polarization and some thermodynamic characteristics of the $NH_4H_2PO_4$ type antiferroelectrics

Spontaneous polarization of the primitive cells of two equivalent, polarized in the opposite directions along the x axis sublattices of the ADP type crystal is related to the ordering of protons of the hydrogen bonds linking the PO_4 groups [1,2,20]. Within the proton ordering model, we have a general expression, relating the spontaneous polarization of sublattice primitive cells of the ADP type antiferroelectrics $\mathcal{P}_x(\boldsymbol{n})$ with the parameters of proton ordering $P_{\boldsymbol{n}f}$

$$
\mathcal{P}_x(\boldsymbol{n}) = \frac{\mu_x}{v}\Big(\frac{P_{\boldsymbol{n}3}}{2} - \frac{P_{\boldsymbol{n}1}}{2}\Big) = \frac{\mu_x}{v} P \mathrm{e}^{\mathrm{i}\boldsymbol{k}_z\boldsymbol{n}}. \tag{3.1}
$$

The expression (3.1) yields the following polarizations along the x-direction for the first and the second sublattices, respectively

$$
\mathcal{P}_{xI} = \mathcal{P}, \quad \mathcal{P}_{xII} = -\mathcal{P}, \quad \mathcal{P} = \frac{\mu_x}{v} P.
$$

Here μ_x is the effective dipole moment of a hydrogen bond along the x axis, v is the primitive cell volume.

Let us consider some thermodynamic characteristics of the system. The free energy of the proton subsystem of the $NH_4H_2PO_4$ type crystal per one mole is obtained from (2.3), taking into account (2.7), (2.9), (2.10), (2.15), (2.16)

$$
f = RT\big(-\ln Z_4 + 2\ln Z_1 + \frac{\beta}{4}\nu_a P^2\big), \tag{3.2}
$$

where R is the gas constant,

$$Z_4 = \sum_{i=1}^{16} \exp(-\beta E_i), \qquad E_i \text{ are roots of (2.15)},$$
$$Z_1 = 2\cosh(\beta\sqrt{K}), \qquad K = (A + \frac{\nu_a}{4}P)^2 + (2\Gamma + \Omega)^2.$$

Entropy of the proton subsystem is given by the expression

$$S = -\frac{f}{T} + R\beta\Big(\frac{1}{4}\nu_a P^2 + \frac{1}{Z_4}\sum_{i=1}^{16}\exp(-\beta E_i)E_i + 2\sqrt{K}\tanh(\beta\sqrt{K})\Big). \tag{3.3}$$

The expression for specific heat is too cumbersome to be presented here. Besides, it can be found by numerical differentiation of entropy with respect to temperature.

All physical characteristics of the considered system contain the variational parameters A and Γ. From the condition of the free energy minimum (3.2) we obtain the following system equations for P and X, with which they are related by (2.11):

$$\begin{cases} P = \frac{1}{2Z_4}\sum\limits_{i=1}^{16}\exp(-\beta E_i)E_{iA}\,, \\ X = \frac{1}{4Z_4}\sum\limits_{i=1}^{16}\exp(-\beta E_i)E_{i\Gamma}\,. \end{cases} \tag{3.4}$$

Here we introduce the following notations

$$\begin{aligned}
E_{iA} &= -\frac{E_i^5 k_{5A} + E_i^4 k_{4A} + E_i^3 k_{3A} + E_i^2 k_{2A} + E_i k_{1A} + k_{0A}}{7E_i^6 + 6E_i^5 k_6 + 5E_i^4 k_5 + 4E_i^3 k_4 + 3E_i^2 k_3 + 2E_i k_2 + k_1},\\
k_{0A} &= -32\Gamma^2 A\tilde{w}_1\tilde{w}\tilde{\varepsilon}\,, \quad k_{1A} = 16A^3\tilde{\varepsilon}\tilde{w}_1 - 8A\tilde{w}^2\tilde{w}_1\tilde{\varepsilon} + 64A\Gamma^2\tilde{w}\bar{w}_1,\\
k_{2A} &= 8A(\tilde{w}^2\bar{w}_1 + 2\tilde{w}_1\tilde{w}\tilde{\varepsilon}) - 16A^3\bar{w}_1 - 32A\Gamma^2(3\tilde{w} + \bar{w}_1),\\
k_{3A} &= -2A(4\tilde{w}^2 + 5\tilde{\varepsilon}\tilde{w}_1 + 8\tilde{w}\bar{w}_1) + 16A^3 + 64\Gamma^2 A,\\
k_{4A} &= 2A(8\tilde{w} + 5\bar{w}_1), \qquad k_{5A} = -10A, \qquad i = \overline{1,7};\\
E_{iA} &= \frac{2A(E_i - \tilde{\varepsilon})}{3E_i^2 + 2E_i l_2 + l_1}, \qquad i = \overline{8,10};\\
E_{iA} &= \frac{2AE_i}{3E_i^2 - 4\tilde{w}E_i + d_1}, \qquad i = \overline{11,13};\\
E_{iA} &= \frac{2A(E_i - \tilde{w}_1)}{3E_i^2 + 2E_i m_2 + m_1}, \qquad i = \overline{14,16};\\
E_{i\Gamma} &= -\frac{E_i^5 k_{5\Gamma} + E_i^4 k_{4\Gamma} + E_i^3 k_{3\Gamma} + E_i^2 k_{2\Gamma} + E_i k_{1\Gamma} + k_{0\Gamma}}{7E_i^6 + 6E_i^5 k_6 + 5E_i^4 k_5 + 4E_i^3 k_4 + 3E_i^2 k_3 + 2E_i k_2 + k_1},\\
k_{0\Gamma} &= -32A^2\Gamma\tilde{w}_1\tilde{w}\tilde{\varepsilon}, \qquad k_{1\Gamma} = 128\Gamma^3\tilde{w}_1\tilde{\varepsilon} + 64A^2\Gamma\tilde{w}\bar{w}_1\,,\\
k_{2\Gamma} &= -192\Gamma^3\bar{w}_1 + 24\Gamma\tilde{w}_1\tilde{w}\tilde{\varepsilon} - 32A^2\Gamma(3\tilde{w} + \bar{w}_1),\\
k_{3\Gamma} &= 8\Gamma(4\tilde{w}\bar{w}_1 + 3\tilde{w}_1\tilde{\varepsilon}) - 64\Gamma A^2 - 256\Gamma^3,\\
k_{4\Gamma} &= 8\Gamma(5\tilde{w} + 4\bar{w}_1), \qquad k_{5\Gamma} = -40\Gamma, \qquad i = \overline{1,7};
\end{aligned}$$

$$E_{i\Gamma} = \frac{8\Gamma(E_i - \tilde{w})}{3E_i^2 + 2E_i l_2 + l_1}, \qquad i = \overline{8,10};$$
$$E_{i\Gamma} = \frac{8\Gamma(E_i - \tilde{w})}{3E_i^2 - 4\tilde{w}E_i + d_1}, \qquad i = \overline{11,13};$$
$$E_{i\Gamma} = \frac{8\Gamma(E_i - \tilde{w})}{3E_i^2 + 2E_i m_2 + m_1}, \qquad i = \overline{14,16}.$$

In the high-temperature phase ($T > T_N$) the obtained characteristics have a simpler form. Thus, the free energy (3.2) in this temperature range after taking into account (2.16) reads

$$f_p = RT\Big(- \ln Z_{4p} + 2\ln\cosh\left(\beta(2\Gamma + \Omega)\right) + 2\ln 2\Big),$$

where

$$\begin{aligned} Z_{4p} &= \sum_{i=1}^{4} \mathrm{e}^{-\beta E_{pi}} + \kappa(\tilde{\varepsilon}) + 2\kappa(0) + \kappa(\tilde{w}_1) + 3\mathrm{e}^{-\beta\tilde{w}} + 1, \\ \kappa(\lambda) &= 2\mathrm{e}^{-\frac{\beta}{2}(\tilde{w}+\lambda)} \cosh\left(\frac{\beta}{2}\sqrt{(\tilde{w}-\lambda)^2 + 16\Gamma^2}\right). \end{aligned}$$

Entropy of the proton system is now given by

$$\begin{aligned} S_p &= -\frac{f_p}{T} + \frac{R\beta}{Z_{4p}}\Big(Z_{4p}(4\Gamma + 2\Omega)\tanh\left(\beta(2\Gamma + \Omega)\right) \\ &\quad + \sum_{i=1}^{4} \exp(-\beta E_{pi})E_{pi} + \zeta(\tilde{\varepsilon}) + 2\zeta(0) + \zeta(\tilde{w}_1) + 3\tilde{w}\mathrm{e}^{-\beta\tilde{w}}\Big). \end{aligned} \tag{3.5}$$

Here for the sake of brevity we introduce the function $\zeta(\lambda)$:

$$\begin{aligned} \zeta(\lambda) &= \mathrm{e}^{-\frac{\beta}{2}(\tilde{w}+\lambda)}\Big[(\tilde{w}+\lambda)\cosh\left(\frac{\beta}{2}\sqrt{(\tilde{w}-\lambda)^2 + 16\Gamma^2}\right) \\ &\quad - \sqrt{(\tilde{w}-\lambda)^2 + 16\Gamma^2}\sinh\left(\frac{\beta}{2}\sqrt{(\tilde{w}-\lambda)^2 + 16\Gamma^2}\right)\Big]. \end{aligned}$$

In the paraelectric phase we have only one variation parameter Γ

$$\Gamma = \frac{1}{4\beta}\ln\frac{1-X}{1+X} - \frac{\Omega}{2},$$

which is found from the equation for X

$$X = -\frac{Z_{4p\Gamma}}{4Z_{4p}}, \tag{3.6}$$

where

$$\begin{aligned} Z_{4p\Gamma} &= \sum_{i=1}^{4} \mathrm{e}^{-\beta E_{pi}} E_{pi\Gamma} + \xi(\tilde{\varepsilon}) + 2\xi(0) + \xi(\tilde{w}_1), \\ E_{pi\Gamma} &= \frac{(32E_{pi}^2 - 24\bar{w}_1 E_{pi} + 16\tilde{w}_1\tilde{\varepsilon})\Gamma}{4E_{pi}^3 - 3(\bar{w}_1 + \tilde{w})E_{pi}^2 + 2(\tilde{w}\bar{w}_1 + \tilde{w}_1\tilde{\varepsilon} - 16\Gamma^2)E_{pi} + 12\Gamma^2\bar{w}_1 - \tilde{\varepsilon}\tilde{w}\tilde{w}_1}, \\ \xi(\lambda) &= -\frac{16\Gamma}{\sqrt{(\tilde{w}-\lambda)^2 + 16\Gamma^2}}\mathrm{e}^{-\frac{\beta}{2}(\tilde{w}+\lambda)}\sinh\left(\frac{\beta}{2}\sqrt{(\tilde{w}-\lambda)^2 + 16\Gamma^2}\right). \end{aligned}$$

Continuity condition for the free energy at the first order phase transition and the system of equations (3.4) yield another the system of equations for the temperature of the antiferroelectric phase transition T_N

$$\begin{cases} f(X,P,T_N) = f_p(X,T_N), \\ P = \frac{1}{2Z_4}\sum\limits_{i=1}^{16}\exp(-\beta E_i)E_{iA}\,, \\ X = \frac{1}{4Z_4}\sum\limits_{i=1}^{16}\exp(-\beta E_i)E_{i\Gamma}\,. \end{cases} \tag{3.7}$$

Here all temperature dependent quantities are taken at $T = T_N$.

Hence, in this section we obtain the expressions for the antiferroelectric spontaneous polarization, free energy and entropy of the $NH_4H_2PO_4$ type antiferroelectrics and the system of equations for variational parameters and phase transition temperature. To find these characteristics one needs to solve the system of two transcendent equations for X and P and at the same time to find the eigenvalues of the four-particle cluster Hamiltonian.

4. Static dielectric susceptibility tensor of the $NH_4H_2PO_4$ type antiferroelectrics

Let us consider now the static dielectric properties of the proton model for the $NH_4H_2PO_4$ type antiferroelectrics. In a weak external constant electric field $\mathbf{E} = (E_x, E_y, E_z)$, the model Hamiltonian of the proton system reads

$$\hat{H}_{\mathbf{E}} = \hat{H} + \hat{V}.$$

Here $\hat{H}$ is given by (2.1), whereas $\hat{V}$ describes the interaction of protons with electric field $\mathbf{E}$; this interaction in the present case has a similar form as that for the KH_2PO_4 type crystals [22,27]

$$\hat{V} = -\sum_{\mathbf{n},f}(\boldsymbol{\mu}_f\mathbf{E})\hat{S}^z_f(\mathbf{n}),$$

where $\boldsymbol{\mu}_f = (\mu^x_f, \mu^y_f, \mu^z_f)$ is the effective dipole moment of the f-th hydrogen bond. Its components obey the following relations

$$\begin{gathered} -\mu^x_1 = \mu^x_3 = \mu_x, \qquad -\mu^y_4 = \mu^y_2 = \mu_y\,; \\ \mu^y_1 = \mu^y_3 = \mu^x_4 = \mu^x_2 = 0; \\ \mu^z_1 = \mu^z_2 = \mu^z_3 = \mu^z_4 = \mu_z\,. \end{gathered}$$

They follow from the symmetry of the hydrogen bonds system and the character of the proton ordering in the electric field.

For the four-particle and single-particle Hamiltonians of the cluster approximation in the field $\mathbf{E}$ we have

$$\hat{H}_{4\mathbf{E}}(\boldsymbol{n}) \;\; = \;\; \hat{H}_4(\boldsymbol{n}) + \sum_{f=1}^{4}(\eta_{f\mathbf{E}}\hat{S}^x_f(\boldsymbol{n}) + A_{f\mathbf{E}}\hat{S}^z_f(\boldsymbol{n})),$$

$$\begin{aligned}\hat{H}_{1f\mathbf{E}}(\boldsymbol{n}) &= \hat{H}_{1f}(\boldsymbol{n}) + 2\eta_{f\mathbf{E}}\hat{S}_f^x(\boldsymbol{n}) \\ &\quad + 2\left(A_{f\mathbf{E}} + \frac{1}{4}\sum_{f_1=1}^{4} J_{ff_1}(0)P_{f_1\mathbf{E}} + \frac{1}{2}\boldsymbol{\mu}_f\mathbf{E}\right)\hat{S}_f^z(\boldsymbol{n}). \qquad (4.1)\end{aligned}$$

Here $\hat{H}_4(\boldsymbol{n})$ and $\hat{H}_{1f}(\boldsymbol{n})$ are the known Hamiltonians (2.4), whereas $\eta_{f\mathbf{E}}$ and $A_{f\mathbf{E}}$ are the variational fields created by the external electric field, so that

$$\eta_{f\mathbf{E}} = A_{f\mathbf{E}} = 0 \quad \text{at} \quad \mathbf{E} = 0.$$

Taking into account (2.9) and (2.10), we use the following representation of the pseudospin mean values in the field $\mathbf{E}$:

$$\begin{aligned}&\langle 2\hat{S}_f^x(\mathbf{n})\rangle = X + X_{f\mathbf{E}}\,, \qquad \langle 2\hat{S}_f^z(\mathbf{n})\rangle = P_{\mathbf{n}f} + P_{f\mathbf{E}}\,,\\ &X_{f\mathbf{E}}|_{\mathbf{E}=0} = 0, \qquad P_{f\mathbf{E}}|_{\mathbf{E}=0} = 0, \qquad f = \overline{1,4}.\end{aligned}$$

Polarization of antiferroelectric crystals different from zero emerges only in an external field. It is related to the quasispin mean values as

$$\mathcal{P}_x = \frac{\mu_x}{2v}(P_{3\mathbf{E}} - P_{1\mathbf{E}}), \qquad \mathcal{P}_y = \frac{\mu_y}{2v}(P_{2\mathbf{E}} - P_{4\mathbf{E}}), \qquad \mathcal{P}_z = \frac{\mu_z}{2v}\sum_{f=1}^{4} P_{f\mathbf{E}}\,.$$

Therefore, to find the static dielectric susceptibility tensor of the $NH_4H_2PO_4$ type crystals

$$\chi_{\alpha\beta} = \frac{1}{\varepsilon_0}\frac{\mathrm{d}\mathcal{P}_\alpha}{\mathrm{d}E_\beta}\bigg|_{\mathbf{E}=0}, \qquad \alpha,\beta = x,y,z,$$

ε_0 is the electric constant, we need to find the derivatives $P_{f\alpha} = \frac{\mathrm{d}P_{f\mathbf{E}}}{\mathrm{d}E_\alpha}\Big|_{\mathbf{E}=0}$. We can do so from the self-consistency equations for $X_{f\mathbf{E}}$ and $P_{f\mathbf{E}}$. These equations are differentiated with respect to the components E_α of the field $\mathbf{E}$; after that the field is put equal to zero ($\mathbf{E} = 0$). For the derivatives $P_{f\alpha}$ ($\alpha = x,y,z$) we get a linear system of equations

$$\begin{cases} P_{f\alpha} = \sum\limits_{f_1=1}^{4} R_{ff_1}A_{f_1\alpha} + \sum\limits_{f_1=1}^{4} M_{ff_1}\eta_{f_1\alpha}\,, \\ X_{f\alpha} = \sum\limits_{f_1=1}^{4} M_{ff_1}A_{f_1\alpha} + \sum\limits_{f_1=1}^{4} N_{ff_1}\eta_{f_1\alpha}\,, \end{cases}$$

where

$$\begin{aligned}A_{f\alpha} &= A_{11}P_{f\alpha} + A_{12f}X_{f\alpha} - \frac{1}{4}\sum_{f_1=1}^{4} J_{ff_1}(0)P_{f_1\alpha} - \frac{1}{2}\mu_f^\alpha\,,\\ \eta_{f\alpha} &= A_{12f}P_{f\alpha} + A_{22}X_{f\alpha}\,.\end{aligned}$$

Here we use the notations

$$X_{f\alpha} = \frac{\mathrm{d}X_{f\mathbf{E}}}{\mathrm{d}E_\alpha}\bigg|_{\mathbf{E}=0}, \qquad A_{f\alpha} = \frac{\mathrm{d}A_{f\mathbf{E}}}{\mathrm{d}E_\alpha}\bigg|_{\mathbf{E}=0}, \qquad \eta_{f\alpha} = \frac{\mathrm{d}\eta_{f\mathbf{E}}}{\mathrm{d}E_\alpha}\bigg|_{\mathbf{E}=0}.$$

The equation coefficients are

$$
\begin{aligned}
R_{ff_1} &= -\frac{2}{\beta Z_4}\frac{\partial^2 Z_{4\mathbf{E}}}{\partial A_{f\mathbf{E}}\partial A_{f_1\mathbf{E}}}\bigg|_{\substack{A_{f\mathbf{E}}=0\\ A_{f_1\mathbf{E}}=0}} + \frac{1}{2}\beta P_f P_{f_1}\,,\\
M_{ff_1} &= -\frac{2}{\beta Z_4}\frac{\partial^2 Z_{4\mathbf{E}}}{\partial A_{f\mathbf{E}}\partial \eta_{f_1\mathbf{E}}}\bigg|_{\substack{A_{f\mathbf{E}}=0\\ \eta_{f_1\mathbf{E}}=0}} + \frac{1}{2}\beta P_f X,\\
N_{ff_1} &= -\frac{2}{\beta Z_4}\frac{\partial^2 Z_{4\mathbf{E}}}{\partial \eta_{f\mathbf{E}}\partial \eta_{f_1\mathbf{E}}}\bigg|_{\substack{\eta_{f\mathbf{E}}=0\\ \eta_{f_1\mathbf{E}}=0}} + \frac{1}{2}\beta X^2,
\end{aligned}
\tag{4.2}
$$

$$
\begin{aligned}
A_{11} &= \frac{X^2}{2\beta Q^3}\ln\frac{1-Q}{1+Q} - \frac{P^2}{\beta Q^2(1-Q^2)},\\
A_{22} &= \frac{P^2}{2\beta Q^3}\ln\frac{1-Q}{1+Q} - \frac{X^2}{\beta Q^2(1-Q^2)},\\
A_{12} &= -\frac{PX}{2\beta Q^3}\ln\frac{1-Q}{1+Q} - \frac{PX}{\beta Q^2(1-Q^2)},\\
& -A_{121} = A_{122} = A_{123} = -A_{124} \equiv A_{12}\,,
\end{aligned}
$$

where $Z_{4\mathbf{E}} = \mathrm{Sp}\,\mathrm{e}^{-\beta\hat{H}_{4E}}$ is the four-particle partition function under the external field. Solving these linear systems, we find the components of the static dielectric susceptibility tensor of the proton model for the ADP type antiferroelectrics. In the chosen reference system (figure 1) this tensor is diagonal

$$
\chi_{\alpha\beta} = \frac{\mu_\alpha^2(1+\delta_{\alpha z})}{2v\varepsilon_0}\frac{D_{\alpha\alpha}}{D_\alpha}\delta_{\alpha\beta}\,, \qquad \alpha,\beta = x,y,z. \tag{4.3}
$$

Here

$$
D_\alpha = \begin{vmatrix}
a_{1\alpha}-1 & a_{2\alpha} & a_{3\alpha} & a_{4\alpha}\\
a_{2\alpha} & a_{1\alpha}-1 & a_{4\alpha} & a_{3\alpha}\\
b_{1\alpha} & b_{2\alpha} & b_{3\alpha}-1 & b_{4\alpha}\\
b_{2\alpha} & b_{1\alpha} & b_{4\alpha} & b_{3\alpha}-1
\end{vmatrix},
$$

$$
D_{\alpha\alpha} = \begin{vmatrix}
R_{1\alpha} & a_{2\alpha} & a_{3\alpha} & a_{4\alpha}\\
R_{2\alpha} & a_{1\alpha}-1 & a_{4\alpha} & a_{3\alpha}\\
M_{1\alpha} & b_{2\alpha} & b_{3\alpha}-1 & b_{4\alpha}\\
M_{2\alpha} & b_{1\alpha} & b_{4\alpha} & b_{3\alpha}-1
\end{vmatrix}, \quad \alpha = x,y;
$$

$$
D_{zz} = 1, \quad D_z = \frac{-(1-M_zA_{12})^2 + N_zA_{22} + R_zN_zA_{12}^2}{R_z(1-N_zA_{22}) + M_z^2A_{22}} + A_{11} - \frac{1}{4}\nu_z\,.
$$

At the same time

$$
\begin{aligned}
a_{1\alpha} &= R_{1\alpha}(A_{11}+\frac{1}{4}\nu_\alpha)+M_{1\alpha}A_{12}\,, \qquad & a_{3\alpha} &= R_{1\alpha}A_{12}+M_{1\alpha}A_{22}\,,\\
a_{2\alpha} &= R_{2\alpha}(A_{11}+\frac{1}{4}\nu_\alpha)+M_{2\alpha}A_{12}\,, \qquad & a_{4\alpha} &= R_{2\alpha}A_{12}+M_{2\alpha}A_{22}\,,\\
b_{1\alpha} &= M_{1\alpha}(A_{11}+\frac{1}{4}\nu_\alpha)+N_{1\alpha}A_{12}\,, \qquad & b_{3\alpha} &= M_{1\alpha}A_{12}+N_{1\alpha}A_{22}\,,\\
b_{2\alpha} &= M_{2\alpha}(A_{11}+\frac{1}{4}\nu_\alpha)+N_{2\alpha}A_{12}\,, \qquad & b_{4\alpha} &= M_{2\alpha}A_{12}+N_{2\alpha}A_{22}\,,
\end{aligned}
$$

$$
\begin{aligned}
&R_{1\alpha}=R_{11}-R_{13}\,, \qquad M_{1\alpha}=-M_{11}-M_{13}\,, \qquad N_{1\alpha}=N_{11}+N_{13}\,,\\
&R_{2\alpha}=R_{14}-R_{12}\,, \qquad M_{2\alpha}=-M_{12}-M_{14}\,, \qquad N_{2\alpha}=N_{12}+N_{14}\,,\\
&\nu_\alpha=J_{11}(0)-J_{13}(0), \qquad \alpha=x,y;
\end{aligned}
$$

$$
\begin{aligned}
&R_z=R_{11}+R_{12}+R_{13}+R_{14}\,, \qquad N_z=N_{11}-N_{12}-N_{13}+N_{14}\,,\\
&M_z=-M_{11}+M_{12}+M_{13}-M_{14}\,, \qquad \nu_z=J_{11}(0)+2J_{12}(0)+J_{13}(0)\,.
\end{aligned}
$$

To find the coefficients $R_{f_1f_2}$, $M_{f_1f_2}$, $N_{f_1f_2}$ defined in (4.2) it suffices to find the partition function up to the second order in small fields $\eta_{f\mathbf{E}}$ and $A_{f\mathbf{E}}$, applying the perturbation theory to the Hamiltonian $\hat{H}_{4\mathbf{E}}$. Let us have

$$
E_{i\mathbf{E}}=E_i+E_i^{(1)}+E_i^{(2)}, \qquad i=\overline{1,16};
$$

then from (4.2) we obtain

$$
\begin{aligned}
R_{f_1f_2} &= -\frac{2}{Z_4}\sum_{i=1}^{16}\mathrm{e}^{-\beta E_i}\left(\beta\frac{\partial E_i^{(1)}}{\partial A_{f_1\mathbf{E}}}\frac{\partial E_i^{(1)}}{\partial A_{f_2\mathbf{E}}}-\frac{\partial^2 E_i^{(2)}}{\partial A_{f_1\mathbf{E}}\partial A_{f_2\mathbf{E}}}\right)+\frac{\beta}{2}P_{f_1}P_{f_2}\,,\\
M_{f_1f_2} &= -\frac{2}{Z_4}\sum_{i=1}^{16}\mathrm{e}^{-\beta E_i}\left(\beta\frac{\partial E_i^{(1)}}{\partial A_{f_1\mathbf{E}}}\frac{\partial E_i^{(1)}}{\partial \eta_{f_2\mathbf{E}}}-\frac{\partial^2 E_i^{(2)}}{\partial A_{f_1\mathbf{E}}\partial \eta_{f_2\mathbf{E}}}\right)+\frac{\beta}{2}P_{f_1}X,\\
N_{f_1f_2} &= -\frac{2}{Z_4}\sum_{i=1}^{16}\mathrm{e}^{-\beta E_i}\left(\beta\frac{\partial E_i^{(1)}}{\partial \eta_{f_1\mathbf{E}}}\frac{\partial E_i^{(1)}}{\partial \eta_{f_2\mathbf{E}}}-\frac{\partial^2 E_i^{(2)}}{\partial \eta_{f_1\mathbf{E}}\partial \eta_{f_2\mathbf{E}}}\right)+\frac{\beta}{2}X^2.
\end{aligned}
$$

Analytical results of such calculations are extremely cumbersome. The expressions for (4.2) in the high-temperature phase ($T\geqslant T_N$: $P=0$, $A=0$, $M_{f_1f_2}=0$, $A_{12}=0$, $R_{12}=R_{14}$) are much simpler. For the static dielectric susceptibility tensor (4.3) in this phase we have

$$
\bar{\chi}_{\alpha\beta}=\frac{(\mu_\alpha)^2(1+\delta_{\alpha z})}{2v\varepsilon_0}\frac{\delta_{\alpha\beta}}{-1/\bar{R}_\alpha+\bar{A}_{11}-\nu_\alpha/4}, \qquad \alpha,\beta=x,y,z. \tag{4.4}
$$

Here

$$
\bar{A}_{11} = \frac{1}{2\beta X}\ln\frac{1-X}{1+X},
$$

$$
\begin{aligned}
\bar{R}_\alpha &= \frac{1}{Z_{4p}}\left[\sum_{i=1}^{4}\sum_{j=7}^{8}\frac{(\mathrm{e}^{-\beta E_{pi}}-\mathrm{e}^{-\beta E_{pj}})(\sqrt{2}U_{2i}U_{7j}+U_{3i}U_{8j})^2}{E_{pi}-E_{pj}}\right.\\
&+\sum_{i=5}^{6}\frac{(\mathrm{e}^{-\beta E_{pi}}-\mathrm{e}^{-\beta\tilde{w}})U_{6i}^2}{E_{pi}-\tilde{w}}+2\sum_{i=7}^{8}\frac{(\mathrm{e}^{-\beta E_{pi}}-1)U_{7i}^2}{E_{pi}}\\
&\left.+\sum_{i=7}^{8}\frac{(\mathrm{e}^{-\beta E_{pi}}-\mathrm{e}^{-\beta\tilde{w}})U_{8i}^2}{E_{pi}-\tilde{w}}+\sum_{i=14}^{15}\frac{(\mathrm{e}^{-\beta E_{pi}}-\mathrm{e}^{-\beta\tilde{w}})U_{15i}^2}{E_{pi}-\tilde{w}}\right], \qquad \alpha=x,y,\\
\bar{R}_z &= \frac{1}{Z_{4p}}\left[\sum_{i=1}^{4}\sum_{j=5}^{6}\frac{(\mathrm{e}^{-\beta E_{pi}}-\mathrm{e}^{-\beta E_{pj}})(2U_{1i}U_{5j}+U_{3i}U_{6j})^2}{E_{pi}-E_{pj}}\right.\\
&\left.+2\sum_{i=7}^{8}\frac{(\mathrm{e}^{-\beta E_{pi}}-\mathrm{e}^{-\beta\tilde{w}})U_{8i}^2}{E_{pi}-\tilde{w}}+\sum_{i=14}^{15}\frac{(\mathrm{e}^{-\beta E_{pi}}-\mathrm{e}^{-\beta\tilde{w}})U_{15i}^2}{E_{pi}-\tilde{w}}\right].
\end{aligned}
$$

The quantities U_{ij} read

$$
\begin{aligned}
&U_{1i}=\frac{2\Gamma E_{pi}(E_{pi}-\tilde{w}_1)}{\Psi(E_{pi})}, \qquad U_{2i}=\frac{2\sqrt{2}\,\Gamma(E_{pi}-\tilde{w}_1)(E_{pi}-\tilde{\varepsilon})}{\Psi(E_{pi})},\\
&U_{3i}=\frac{E_{pi}(E_{pi}-\tilde{w}_1)(E_{pi}-\tilde{\varepsilon})}{\Psi(E_{pi})}, \qquad U_{4i}=\frac{2\Gamma E_{pi}(E_{pi}-\tilde{\varepsilon})}{\Psi(E_{pi})},\\
&\Psi(E_{pi})=\Big((E_{pi}-\tilde{w}_1)^2(E_{pi}-\tilde{\varepsilon})^2(8\Gamma^2+E_{pi}^2)\\
&\qquad\qquad +4\Gamma^2E_{pi}^2((E_{pi}-\tilde{\varepsilon})^2+(E_{pi}-\tilde{w}_1)^2)\Big)^{\frac{1}{2}}, \qquad i=\overline{1,4};\\
&U_{5i}=\frac{2\Gamma}{\sqrt{4\Gamma^2+(E_{pi}-\tilde{\varepsilon})^2}}, \qquad U_{6i}=\frac{E_{pi}-\tilde{\varepsilon}}{\sqrt{4\Gamma^2+(E_{pi}-\tilde{\varepsilon})^2}}, \qquad i=5,6;\\
&U_{7i}=\frac{2\Gamma}{\sqrt{4\Gamma^2+E_{pi}^2}}, \qquad U_{8i}=\frac{E_{pi}}{\sqrt{4\Gamma^2+E_{pi}^2}}, \qquad i=7,8;\\
&U_{14i}=\frac{2\Gamma}{\sqrt{4\Gamma^2+(E_{pi}-\tilde{w}_1)^2}}, \qquad U_{15i}=\frac{E_{pi}-\tilde{w}_1}{\sqrt{4\Gamma^2+(E_{pi}-\tilde{w}_1)^2}}, \qquad i=14,15.
\end{aligned}
$$

Now we easily get the components of the static dielectric permittivity tensor

$$\varepsilon_{\alpha\beta}(0,T)=\varepsilon_\alpha(\infty,T)\delta_{\alpha\beta}+\chi_{\alpha\beta} \quad (\alpha,\beta=x,y,z),$$

where $\varepsilon_\alpha(\infty,T)$ is the corresponding high-frequency contribution.

The found components of the static dielectric permittivity tensor of the ADP type antiferroelectrics (4.3) in the limiting case $\Omega\to 0$ ($\eta=0$, $\Gamma=0$, $X=0$) yield the tensor of the static dielectric permittivity for the deuterated $ND_4D_2PO_4$ type antiferroelectrics

$$\chi_{\alpha\beta}^D=\frac{\beta(\mu_\alpha)^2(1+\delta_{\alpha z})}{2v\varepsilon_0}\left(\frac{\mathcal{F}_{1\alpha}}{\mathcal{D}_a-2\mathcal{F}_{1\alpha}\varkappa_\alpha}+\frac{\mathcal{F}_{2\alpha}}{\mathcal{D}_a-2\mathcal{F}_{2\alpha}\varkappa_\alpha}\right)\delta_{\alpha\beta}\,, \tag{4.5}$$

$$
\begin{aligned}
&\mathcal{D}_a = 2\cosh^2(\beta A) + 4\mathrm{e}^{-\beta\tilde{w}}\cosh(\beta A) + \mathrm{e}^{-\beta\tilde{\varepsilon}} + \mathrm{e}^{-\beta\tilde{w}_1},\\
&\mathcal{F}_{1x} = \mathcal{F}_{1y} = 1 + \mathrm{e}^{-\beta\tilde{w}}\cosh(\beta A),\\
&\mathcal{F}_{2x} = \mathcal{F}_{2y} = \cosh(2\beta A) + \mathrm{e}^{-\beta\tilde{w}}\cosh(\beta A) - P^2\mathcal{D}_a\,,\\
&\mathcal{F}_{1z} = \mathcal{F}_{2z} = \mathrm{e}^{-\beta\tilde{w}}\cosh(\beta A) + \mathrm{e}^{-\beta\tilde{\varepsilon}},\\
&\varkappa_\alpha = \frac{1}{1-P^2} + \frac{\beta}{4}\nu_\alpha\,, \qquad \alpha = x, y, z.
\end{aligned}
$$

These results for $\chi^D_{\alpha\alpha}$ accord with the corresponding expressions found in [28] as well as with the results of [29] for the paraelectric phase. At $\tilde{w}, \tilde{w}_1 \to \infty$ the obtained formulas for $\chi^D_{\alpha\alpha}$ agree with those found in [14,27].

Hence, we obtain new analytical results for the components of the static dielectric permittivity tensor of the proton model of the $NH_4H_2PO_4$ type antiferroelectrics in the four-particle cluster approximation with taking into account proton tunnelling on the hydrogen bonds. In the classical limit (zero tunnelling) they transform to the components of the static dielectric permittivity tensor of deuterated $ND_4D_2PO_4$ type crystals which accord with the results of other sources.

5. Numerical analysis and comparison with experimental data

In this section we shall perform a numerical analysis of the obtained theoretical results for thermodynamic and static dielectric characteristics of the ADP type antiferroelectric crystals. Our goal is a systematic study of the dependence of the above characteristics on the theory parameters in order to set the optimal values of the parameters which would provide a good quantitative agreement between the theory and the experiment for two crystals: $NH_4H_2PO_4$ and $NH_4H_2AsO_4$. The mentioned study is carried out using the proposed in [21,22] fitting procedure for the KDP type crystals, modified to the case of antiferroelectrics. We use the experimental data given in table 1 and in the figures below. The obtained results for the $NH_4H_2PO_4$ and $NH_4H_2AsO_4$ crystals are given in table 2 and in the figures.

Thus, the theoretical formulas for thermodynamic and static dielectric characteristics of the ADP type antiferroelectrics contain five independent theory parameters Ω, $\tilde{\varepsilon}$, $\tilde{w}$, $\tilde{w}_1$, and ν_a. Since the energy $\tilde{w}_1$ of the least probable proton configurations with four or with none protons near a given tetrahedron is very large, it is often put equal to infinity $\tilde{w}_1 \to \infty$ (see [14,27–29]). We can assume that $\tilde{w}_1 = 4\tilde{w} - \tilde{\varepsilon}$ (see [9,27]), since values of $\tilde{w}_1$, larger than this, hardly affect the calculated physical characteristics. This choice of the energy $\tilde{w}_1$ yields $\Phi = 0$ that approximately corresponds to two-particle character of the short-range correlations between protons [27,33]. In the Hamiltonian (2.1) and in all previous formulas the correlations were presented in a more general form.

Thus, we have only four independent parameters Ω, $\tilde{\varepsilon}$, $\tilde{w}$, and ν_a. For each taken set of these parameters, the equations (3.4), (2.15), (3.7) were solved numerically and T_N, the temperature dependence of the proton ordering parameter $P(T)$, its saturation value $P_s = P(T_s)$ and jump $P_c = P(T_N)$ at the transition point were found. The obtained results were compared with the corresponding experimental data for

Table 1. Experimental data for the ADP type crystals.

	$NH_4H_2PO_4$	$NH_4H_2AsO_4$
T_N, K	145.13 [30], 148 [31–34] 149 [38], 150 [39]	216 [34–37]
S_N, J/(mol·K)	4.47 [38]	4.24 [37]
v, 10^{-30} m^3	210.846 (152 K), 212.852 (296 K) [40] 210.994 (T_N) [41] 210.288 (110 K), 210.656 (147 K) [39]	228.444 (293 K) [42]

$NH_4H_2PO_4$ and $NH_4H_2AsO_4$: namely, with T_N, ratio of the sublattice polarization jump $\mathcal{P}_c$ to saturation polarization $\mathcal{P}_s$ ($\mathcal{P}_c/\mathcal{P}_s = P_c/P_s$), and the temperature dependence of $\mathcal{P}(T)$. The final selection of the parameters Ω, $\tilde{\varepsilon}$, $\tilde{w}$, and ν_a was made using the condition of the best agreement between the theoretical and the experimental results for the temperature dependence of proton subsystem specific heat $\Delta C(T)$ and for the transition temperature $S_N = S(T_N + 0)$. The specific heat $\Delta C(T)$ was calculated by numerical differentiation of entropy (3.3) with respect to temperature. Experimental specific heat of proton subsystem was obtained by subtracting a lattice contribution from the total specific heat; the contribution was found by a linear approximation. After that, we calculated the static dielectric characteristics with the obtained as described values of the model parameters.

Experimental temperature dependences of the primitive cell volumes are weak (see table 1) and approximated by a constant value $v(T) = v$ in numerical calculations. We take $v = 210.994\ 10^{-30}$ m^3 [41] for $NH_4H_2PO_4$ and $v = 228.444\ 10^{-30}$ m^3 [42] for $NH_4H_2AsO_4$.

Table 2. Sets of the model parameters $\Omega, \tilde{\varepsilon}, \tilde{w}, \nu_a, \nu_x, \nu_z$ for the ADP type crystals and the calculated physical characteristics.

N	$\tilde{w}$, K	$\tilde{\varepsilon}$, K	Ω, K	ν_a , K	T_N , K	P_c/P_s	S_N , J/(mol·K)
1_{ADP}	570	40	84	224.7	148.0	0.93	4.53
2_{ADA}	700	50	46	332.12	216.0	0.93	5.17
3	700	–10	180	472.2	216.0	0.90	4.90

Table 2. Sets of the model parameters. Continuation.

N	ν_x, K	$\mu_x \cdot 10^{30}$, C·m	$\bar{\mu}_x \cdot 10^{30}$, C·m	$\varepsilon_x(\infty)$	$\bar{\varepsilon}_x(\infty)$	ν_z, K	$\mu_z \cdot 10^{30}$, C·m	$\varepsilon_z(\infty)$	$\bar{\varepsilon}_z(\infty)$
1	70	5.77	12.12	11	33.8	50	7.98	11	12
2	240	4.98	9.96	16	56	40	4.32	9.8	9.8
3	390	5.28	10.57	16	53	40	2.98	9.7	11.1

Components of the static dielectric permittivity tensor $\varepsilon_\alpha(0,T) \equiv \varepsilon_{\alpha\alpha}(0,T)$ ($\alpha = x, z$) of the $NH_4H_2PO_4$ type antiferroelectric were calculated with (4.5), where the temperature dependence of the high-frequency contribution $\varepsilon_\alpha(\infty,T)$ was approximated as

$$\varepsilon_\alpha(\infty,T) = \varepsilon_\alpha(\infty)\theta(T_N - T) + \bar{\varepsilon}_\alpha(\infty)\theta(T - T_N),$$

since this dependence should be weak [21,28]. The corresponding values of $\varepsilon_\alpha(\infty)$ and $\bar{\varepsilon}_\alpha(\infty)$ along with the values of ν_α and μ_α, (see table 2) were chosen by fitting to the experiment. Later we shall separately consider each of the crystals.

The theory parameters for $NH_4H_2PO_4$ were chosen by fitting to the most probable value $T_N = 148$ K from table 1. Besides, the only available experimental temperature dependence of sublattice spontaneous polarization $\mathcal{P}(T)$ are the calculations performed in [43] (see figure 2) from the experimental data for an electrooptic effect and from a qualitative estimate made in [44]. Therefore, at the fitting procedure we tried to obtain a very large jump of P_c, close to the saturation value P_s, approximately yielding $P_c/P_s \approx 0.93$.

Eventually, according to the above described fitting procedure we obtained for $NH_4H_2PO_4$ a set 1 of the model parameters in table 2. As tables 1 and 2 show, we have a good agreement for the values of T_N and S_N. Discrepancy between theory and experiment is about 1–2 % for the sublattice spontaneous polarization (figure 2) and up to 10 % for the specific heat (figure 3) that does not exceed an experimental error. The set 1 of the model parameters also provides a good description of experimental dielectric permittivities $\varepsilon_x(0,T)$ and $\varepsilon_z(0,T)$ (figures 4, 5) with about 1–2 % deviation from the experiment, which is within limits of dispersion of the experimental points.

It should be noted that we obtained different values of the effective dipole moment μ_x for the transverse dielectric permittivity in different phases. Even at the optimal value of ν_x that sets the ratio of the dipole moments in two phases, the value of μ_x below T_N determined from the experimental sublattice spontaneous polarization [43] is twice smaller than the value of $\bar{\mu}_x$ above T_N (see table 2).

Let us discuss now the theoretical results for the $NH_4H_2AsO_4$ crystal. Unfortunately, here no experimental estimate for sublattice spontaneous polarization is avail-

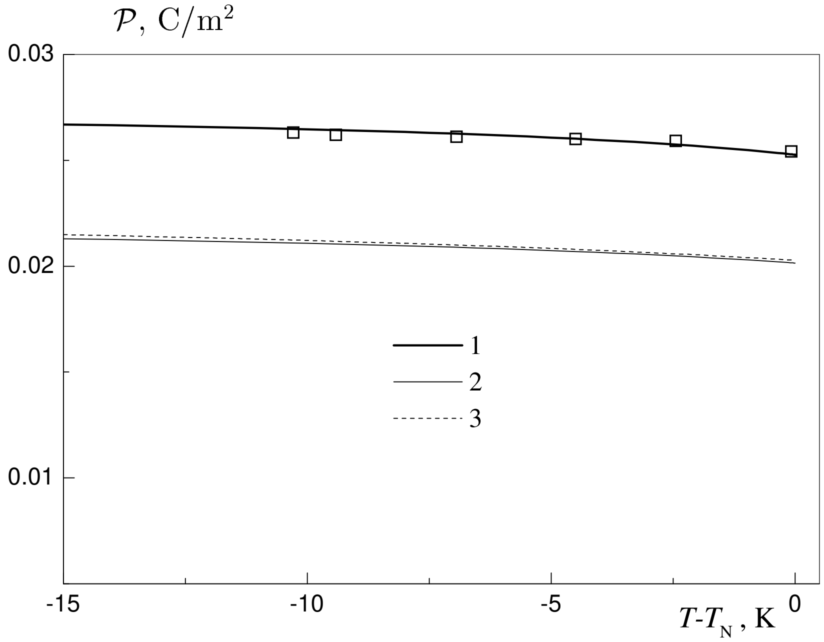


Figure 2. Temperature dependence of sublattice spontaneous polarization of the $NH_4H_2PO_4$ and $NH_4H_2AsO_4$ crystals. Lines are theoretical results obtained for the sets 1–3 of the theory parameters from table 2. Symbols □ mark experimental points for $NH_4H_2PO_4$ taken from [43].

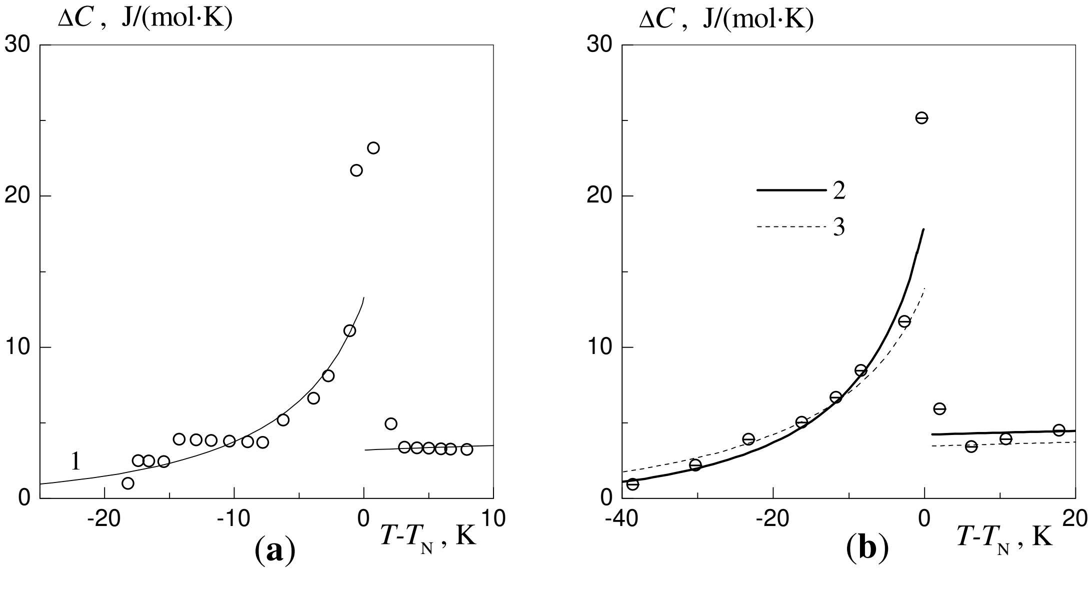
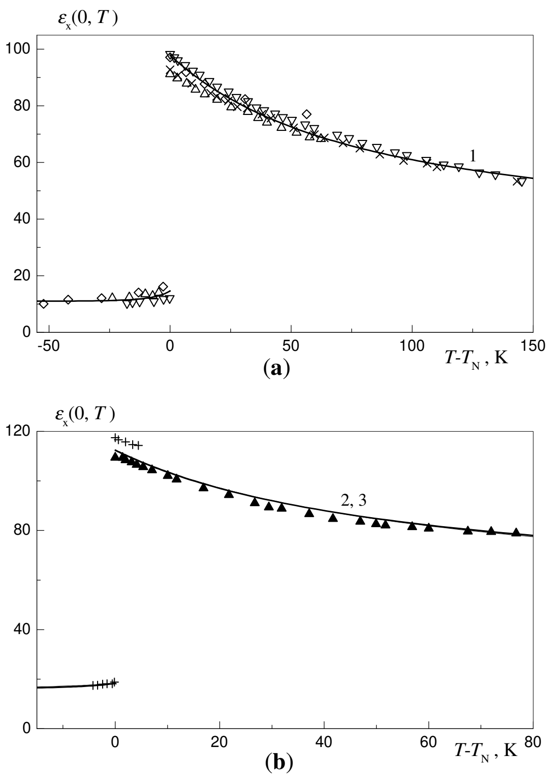


Figure 3. Temperature dependence of the specific heat of the proton subsystem of $NH_4H_2PO_4$ (a) and $NH_4H_2AsO_4$ (b). Lines are theoretical results for the sets of the model parameters 1 (a) and 2, 3 (b) (see table 2). Points are experimental data of: ⊖ – [37], ∘ – [38].



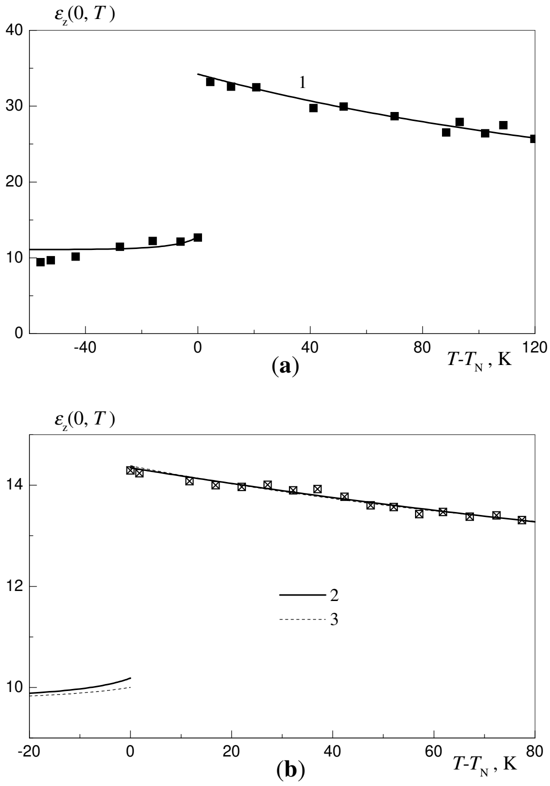


Figure 4. Temperature dependence of static transverse dielectric permittivity of the $NH_4H_2PO_4$ (a) and $NH_4H_2AsO_4$ (b) crystals. Lines are theoretical results for the sets of the model parameters 1 (a) and 2, 3 (b) (see table 2). Points are experimental data of: $\triangle$ – [30], $\diamond$ – [31], $\triangledown$ – [32], $\times$ – [33], $+$ – [35], ▲ – [36].

Figure 5. Temperature dependence of static longitudinal dielectric permittivity of the $NH_4H_2PO_4$ (a) and $NH_4H_2AsO_4$ (b) crystals. Lines are theoretical results for the sets of the model parameters 1 (a) and 2, 3 (b) (see table 2). Points are experimental data of: ■ – [31], ⊠ – [36].

able. Therefore, the main attention in the fitting procedure is concentrated on the description of specific heat $\Delta C(T)$ (see figure 3). To obtain the ratio $P_c/P_s \approx 0.93$ was not a major task of the fitting; we kept it only as a tentative approximation. The found set 2 of the theory parameters in table 1 provides a good agreement of the theory (within the experimental error limits) with the available experimental data for T_N and $\Delta C(T)$, however yielding a rather large deviation (about 20%) of the theoretical value of S_N from the experimental estimate made in [37] (see tables 1 and 2).

As one would expect, the set 2 also gives a good description of experimental dielectric permittivities $\varepsilon_x(0,T)$ and $\varepsilon_z(0,T)$ of $NH_4H_2AsO_4$ (see figures 4, 5) with the deviation from the experiment within limits of the experimental error. Here we also obtain different values of the effective dipole moment μ_x above and below T_N – $\bar{\mu}_x/\mu_x = 2$ (see table 2). The temperature dependence of sublattice spontaneous polarization $\mathcal{P}(T)$ of the $NH_4H_2AsO_4$ crystal calculated with the value of μ_x found by fitting to $\varepsilon_x(0,T)$ is somewhat smaller than the spontaneous polarization of $NH_4H_2PO_4$ (see figure 2).

Here the theoretical study of the $NH_4H_2AsO_4$ crystal might be finished, if not a certain unexpected and interesting experimental fact. In [45] using the EPR it was established that in the disordered phase of the $NH_4H_2AsO_4$ crystal the number of up-down configurations of the H_2AsO_4 radicals is larger than that of the lateral configurations. It means that the configurational energy $\tilde{\varepsilon}$ in $NH_4H_2AsO_4$ can be negative. The fact that the positive energy $\tilde{\varepsilon}$ is not a necessary condition for the antiferroelectric ordering has been mentioned already in [46]. It has been shown that a strong long range interaction along the x or y axis can stabilize an antiferroelectric ordering, provided a certain critical positive value of the Slater energy is not exceeded. In view of this, Havlin et al [14,27], describing the static dielectric permittivities of $NH_4H_2AsO_4$ within a "two-level" proton ordering model without tunnelling, used a negative value of $\tilde{\varepsilon}$ and obtained a good agreement with the experiment. Recently, Matsushita and Matsubara [20] have shown that the effective taking account of the NH_4 groups' influence on protons of the O–H…O groups in the ADP type crystals yields that the energy $\tilde{\varepsilon}$ should only be larger than a certain non-zero negative value.

In view of all the mentioned facts, in our fitting procedure we attempted to find a set of the model parameters with a negative value of $\tilde{\varepsilon}$. Such a set is presented in table 2 – set 3. In figures 2, 4, 5 we can see that the spontaneous polarization $\mathcal{P}(T)$ and dielectric characteristics of $NH_4H_2AsO_4$ can be equally well described by either of the sets 2 and 3. However, the corresponding specific heats $\Delta C(T)$ calculated with these sets of parameters are essentially different (see figure 3). Analysis of the obtained results shows that for negative $\tilde{\varepsilon}$ one should assume a significant tunnelling Ω (set 3) in order to obtain polarization $\mathcal{P}(T)$ and specific heat $\Delta C(T)$ close to those found with the set 2 and close to the experiment (see [26]). From physical point of view, this means the following phase transition mechanisms at negative $\tilde{\varepsilon}$: a significant tunnelling destroys the ground state ferroelectric configuration created by the short range interactions, whereas the long range interactions establish an antiferroelectric ordering. However, the existence of this mechanisms can be verified only with new experimental studies; in particular, the results of [45] should be confirmed. Therefore, at present it is difficult to unambiguously choose between the sets 2 and 3 for $NH_4H_2AsO_4$. However, since the theoretical specific heat for the set 2 accords with the experiment better than the specific heat obtained with the set 3, and since the dynamics of the ADP is of a relaxational character [28], we would rather assume that the set 2 is the most suitable for describing the $NH_4H_2AsO_4$ crystal.

As has been mentioned in [9,21,22,48,49], the cluster approximation for a Hamiltonian with non-commuting operators yields an unphysical behaviour of the physical characteristics in a certain region of low temperatures. We also obtain the unphysical behaviour for the physical characteristics of the proton ordering model for $NH_4H_2PO_4$ type crystals. The character of this behaviour is practically the same as that described in [9,21,22,48,49]. It should be only mentioned that the temperature where this behaviour emerges is about 80 K for the sets 1, 2 and 110 K for the set 3.

6. Conclusions

In this paper, using the four-particle cluster approximation for the short range interactions and the mean field approximation for the long range interactions for the proton ordering model with tunnelling, we obtain new theoretical results for thermodynamic and static dielectric characteristics of the $NH_4H_2PO_4$ type antiferroelectrics.

Using the ideas developed in [21,22], we propose a fitting procedure for the $NH_4H_2PO_4$ type antiferroelectrics. The found during this procedure with making use of experimental data for the temperature dependences of spontaneous sublattice polarization and proton specific heat sets of the model parameters for the $NH_4H_2PO_4$ and $NH_4H_2AsO_4$ crystals also yield a good agreement with experiment for the transverse and longitudinal components of the static dielectric permittivity of the crystals.

We show that the antiferroelectric phase transition in $NH_4H_2AsO_4$ can be described also if the lowest energy of the short range configurations is the energy of ferroelectric ordering ($\tilde{\varepsilon} < 0$). However, a final determination of a sign of the energy $\tilde{\varepsilon}$ for $NH_4H_2AsO_4$ requires additional experimental and theoretical studies.

The obtained theoretical results are a ponderable evidence for an adequacy of the proton ordering model with tunnelling [4] to the antiferroelectric $NH_4H_2PO_4$ type crystals.

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Термодинаміка та діелектричні властивості антисегнетоелектриків типу $NH_4H_2PO_4$

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В рамках протонної моделі досліджуються термодинамічні та статичні діелектричні властивості антисегнетоелектричних кристалів типу ADP з врахуванням ефектів тунелювання протонів на водневих зв'язках. В наближенні чотиричастинкового кластера по короткосяжних і молекулярного поля по далекосяжних взаємодіях розраховано вільну енергію, ентропію, компоненти тензора статичної діелектричної сприйнятливості, отримано систему рівнянь для параметра протонного впорядкування підгратки та рівняння для температури фазового переходу. Знайдено значення параметрів теорії для кристалів $NH_4H_2PO_4$ та $NH_4H_2AsO_4$ і отримано добре узгодження результатів теоретичного розрахунку з відповідними експериментальними даними для температурних залежностей спонтанної поляризації підгратки, протонної теплоємності, поздовжньої і поперечної статичних діелектричних проникностей цих кристалів.

Ключові слова: *ADP, тунелювання, кластерне наближення, фазовий перехід, діелектрична сприйнятливість*

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