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q-DEPENDENT CORRELATION FUNCTIONS AND DIELECTRIC PERMITTIVITIES OF DKDP AND DADP TYPE CRYSTALS. INFLUENCE OF EXTERNAL PRESSURE

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Within the four-particle cluster approximation, we obtain an equation for the $\boldsymbol{q}$-dependent deuteron pair correlation functions of DKDP and DADP crystals to which external hydrostatic and uniaxial σ_3 pressure is applied. Their wavevector, temerature and pressure dependences are studied. Expressions for the dielectric permittivities of the strained crystals are derived. It is shown that under the proper choice of theory parameters, the obtained results agree well with the available experimental data.

1. Introduction

Lately, a great attention has been paid to investigations of external pressure effects in KDP-type crystals. In our recent papers [1–6] we developed an approach (based on the model [7,8]) which allowed one to describe the pressure dependences of the transition temperature, dielectric and thermal properties of deuterated ferroelectrics and antiferroelectrics of DKDP and DADP type. The calculations were carried out within the four particle cluster approximation. It allowed us to take into account the strong short-range correlations between deuterons adequately. A good description of the available experimental data was obtained, and some predictions concerning the effects of uniaxial pressure σ_3 on the considered responses of the crystals were made. Further experimental studies of hydrostatic and, especially, uniaxial pressure influence on these crystals are required to verify our predictions and determine the theory parameters more precisely.

In understanding the nature of phase transitions in KDP type crystals and studying their internal structure, the thermal neutron scattering technique is extremely useful. Since the calculation of neutron cross-sections may be reduced to calculation of appropriate correlation functions [9], to study the latters becomes exceedingly important. Besides that, analytical expressions for correlation functions enable one to calculate the corresponding dielectric susceptibility tensor.

Deuteron $\boldsymbol{q}$-dependent correlation functions of unstrained DKDP and DADP crystals have been calculated in a few papers. Thus, in [10] the equation for the $\boldsymbol{q}$-dependent correlation functions of DKDP and DADP crystals was suggested. No consistent derivation of it was given. The calculations were carried out for the case of $\boldsymbol{q} = 0$ only. The obtained results correspond to the cluster approximation only at $T > T_C$.

The method of calculation of the $\boldsymbol{q}$-dependent correlation functions of paraelectric DKDP for a model with short-range interactions alone was proposed in [11]. In the four-particle cluster approximation, the dielectric susceptibility as a function of wavevector of some directions was calculated, and some numerical results were presented.

The consistent procedure for calculation of $\boldsymbol{q}$-dependent correlation functions of the model of a DKDP crystal with both short-range and long-range interactions (the latter being taken into account in the mean field approximation) in the cluster approximation was proposed in [12]. An equation of the Ornstein-Zernike type for pair correlation functions was derived both for $T > T_{\mathrm{C}}$ and $T < T_{\mathrm{C}}$. Components of the dielectric susceptibilty tensor were calculated for some directions of wavevector.

In this work, following the method of [12], we derive an equation for pair $\boldsymbol{q}$-dependent correlation functions of DKDP and DADP crystals to which external hydrostatic and uniaxial σ_3 pressure is applied. In Section 2, we suggest the unified model of strained DKDP and DADP crystals. In Section 3, the equations for pair correlation functions are derived. In Section 4, the expressions for dielectric permittivities are presented. Results of numerical calculations are given in Section 5.

2. The model

We consider a system of deuterons moving on O-D...O bonds in a crystal of KD_2PO_4 (DKDP) or $ND_4D_2PO_4$(DADP) type. The primitive cell of such a crystal is composed of two neighbouring PO_4 tetrahedra together with four hydrogen bonds attached to one of them ("A" type tetrahedra). Hydrogen bonds going to another ("B" type) tetrahedron belong to four nearest structural elements surrounding it. An external hydrostatic (σ_{h}) or uniaxial stress (σ_3), which does not lower the system symmetry

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

and electric field E_i ($i = 1,2,3$) directed along the crystallographic axes a, b, c are applied.

The Hamiltonian of the system has the following form [7]

$$\hat{H} = \frac{\bar{v}N}{2}\sum_{ij} c_{ij}^{(0)}\varepsilon_i\varepsilon_j - \frac{1}{2}\sum_{qq'}\sum_{ff'} J_{ff'}(qq')\frac{\sigma_{qf}}{2}\frac{\sigma_{q'f'}}{2} + H_{\mathrm{short}} - \sum_{qf} h_{qf}^{i}\frac{\sigma_{qf}}{2}, \tag{2.2}$$

$$\begin{aligned} H_{\mathrm{short}} &= \left\{\frac{1}{2}\sum_{ff'} V_{ff'}\frac{\sigma_{q_f f}}{2}\frac{\sigma_{q_{f'}f'}}{2} + \Phi\frac{\sigma_{q_1 1}}{2}\frac{\sigma_{q_2 2}}{2}\frac{\sigma_{q_3 3}}{2}\frac{\sigma_{q_4 4}}{2}\right\}\times \qquad (2.3)\\ &\times\sum_{q_1,q_2 q_3,q_4}\left\{\delta_{\mathbf{R}_{q_1},\mathbf{R}_{q_2}}\delta_{\mathbf{R}_{q_1},\mathbf{R}_{q_3}}\delta_{\mathbf{R}_{q_1},\mathbf{R}_{q_4}} + \delta_{\mathbf{R}_{q_1}+\mathbf{r}_2,\mathbf{R}_{q_2}}\delta_{\mathbf{R}_{q_1}+\mathbf{r}_3,\mathbf{R}_{q_3}}\delta_{\mathbf{R}_{q_1}+\mathbf{r}_4,\mathbf{R}_{q_4}}\right\};\\ h_{qf}^{i} &= \mu_{qf}^{i}E_i. \end{aligned}$$

Hamiltonian (2.3) describes short-range configurational interactions between deuterons near tetrahedra of "A" and "B" type; $\mathbf{r}_f$ is a relative position vector of a hydrogen bond in a cell. Two eigenvalues of Ising spin $\sigma_{qf} = \pm 1$ are assigned to two equilibrium positions of a deuteron on the f-th bond in the q-th unit cell. $c_{ij}^{(0)}$ are the "seed" elastic constants; ε_i are the components of the strain tensor; $\bar{v} = v/k_{\rm B}$; v is the unit cell volume; $k_{\rm B}$ is the Boltzmann constant.

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

for ferroelectric crystals of DKDP type. Here

$$\begin{aligned} &V = -w_1/2, \quad U = -\varepsilon + w_1/2, \quad \Phi = 4\varepsilon - 8w + 2w_1; \\ &\varepsilon = \varepsilon_a - \varepsilon_s, \quad w = \varepsilon_1 - \varepsilon_s, \quad w_1 = \varepsilon_0 - \varepsilon_s, \end{aligned}$$

ε_s, ε_a, ε_1, ε_0 are the energies of lateral, up-down, single-ionized and double ionized deuteron configurations, respectively. Let us note that the energy ε_s is assumed to be the lowest.

For antiferroelectric crystals of DADP type

$$\begin{aligned} &V = (\varepsilon - w_1)/2, \quad U = (\varepsilon + w_1)/2, \quad \Phi = 2\varepsilon - 8w + 2w_1; \\ &\varepsilon = \varepsilon_s - \varepsilon_a, \quad w = \varepsilon_1 - \varepsilon_a, \quad w_1 = \varepsilon_0 - \varepsilon_a, \end{aligned}$$

the energy of the lateral configurations ε_a is the lowest. Within the proposed model the energies ε, w, and w_1 are assumed to be linear functions of strains ε_i

$$\begin{aligned} \varepsilon &= \delta_{11}\varepsilon_1 + \delta_{12}\varepsilon_2 + \delta_{13}\varepsilon_3 + \varepsilon^{(0)}, \\ w &= \delta_{21}\varepsilon_1 + \delta_{22}\varepsilon_2 + \delta_{23}\varepsilon_3 + w^{(0)}, \\ w_1 &= \delta_{31}\varepsilon_1 + \delta_{32}\varepsilon_2 + \delta_{33}\varepsilon_3 + w_1^{(0)}. \end{aligned} \tag{2.4}$$

We consider only diagonal components of the strain tensor ε_1, ε_2, ε_3, and neglect piezoelectric shear strains ε_4, ε_5, ε_6 arising when the respective electric fields E_1, E_2 and E_3 are applied (the piezomodules d_{14}, d_{25}, d_{36} differ from zero). Therefore, the calculated dielectric susceptibilities will correspond to clamped (ε_i = const) crystals.

$J_{ff'}(qq')$ are the constants of long-range forces (dipole-dipole interactions and indirect interaction between deuterons through lattice vibrations), which we shall take into account in the mean field approximation. Let us note that if one formally expands the constants of the long-range interaction $J_{ff'}(qq')$ in powers of strains up to the linear terms

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

then the obtained expressions for the mean fields

$$æ_{qf} = \sum_{q'f'} \left[\tilde{J}^{(0)}_{ff'}(qq') + \sum_j \psi^j_{ff'}(qq')\varepsilon_j \right] \frac{\eta^{(1)}_{q'f'}}{2} + h^i_{qf}, \tag{2.5}$$

($\eta^{(1)}_{qf} \equiv \langle\sigma_{qf}\rangle^H$, averaging being carried out with the Hamiltonian (2.2)) coincide with those found in [7,8] – the long-range interaction, taken into account in the mean field approximation, is renormalized by terms linear in the mean values of quasispins $\langle\sigma_{qf}\rangle^H$ and strains ε_i, – calculated considering only the lattice strains but neglecting the pressure dependence of the dipole moment of a hydrogen bond $\mu = e\delta$ (δ is the D-site distance on a O-D...O bond).

The pressure dependence of μ can be taken into account in the following way. According to [13,14], δ in KDP and DKDP crystals is a linear function of hydrostatic pressure. Assuming that the character of this dependence on hydrostatic and uniaxial σ_3 stress in DADP crystal and uniaxial stress in DKDP is the same and bearing in mind (2.1) we can write

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

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

$$\begin{aligned}
\tilde{J}^{(0)}_{ff'}(qq') &= J^{(0)}_{ff'}(qq')[1 + 2\frac{\delta_1}{\delta_0}p], \\
æ_{qf} &= \sum_{q'f'} \left[J^{(0)}_{ff'}(qq')[1 + 2\frac{\delta_1}{\delta_0}p] + \sum_j \psi^j_{ff'}(qq')\varepsilon_j \right] \frac{\eta^{(1)}_{q'f'}}{2} + h^i_{qf}. \quad (2.6)
\end{aligned}$$

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

The following calculations will be carried out in the cluster approximation. Considering the structure of the crystals, it is natural to divide the quasispin lattice into the four-particle clusters, vertices of which we choose in the centers of the O-D...O bonds. As

$${}^{f_2}\Delta_{q_1 f_1}$$

we denote an effective field acting on the spin $\sigma_{q_1 f_1}$ from the side of its nearest neighbour f_2. Let us make an identical transformation (the long-range interactions have been taken into account in the mean field approximation)

$$\begin{aligned}
H &= \frac{\bar{v}N}{2}\sum_{ij} c^{(0)}_{ij}\varepsilon_i\varepsilon_j + \frac{1}{2}\sum_{qf}\sum_{q'f'} J_{ff'}(qq')\frac{\langle\sigma_{qf}\rangle^H}{2}\frac{\langle\sigma_{q'f'}\rangle^H}{2} + H', \\
H' &= H_{\mathrm{short}} - \sum_{qf}\frac{\tilde{z}_{qf}}{\beta}\frac{\sigma_{qf}}{2} - \sum_q\sum_{ff'} {}^{f'}\Delta_{qf}\frac{\sigma_{qf}}{2} = \sum_{qf} H^{(1)}_{qf} + \sum_R U_R,
\end{aligned}$$

where H' is the Hamiltonian of the so-called reference system, and

$$\begin{aligned}
H^{(1)}_{qf} &= -\frac{\tilde{z}_{qf}}{\beta}\frac{\sigma_{qf}}{2}; \\
U_R &= V\left[\frac{\sigma_{R1}}{2}\frac{\sigma_{R2}}{2} + \frac{\sigma_{R2}}{2}\frac{\sigma_{R3}}{2} + \frac{\sigma_{R3}}{2}\frac{\sigma_{R4}}{2} + \frac{\sigma_{R4}}{2}\frac{\sigma_{R1}}{2}\right] + \quad (2.7) \\
&+ U\left[\frac{\sigma_{R1}}{2}\frac{\sigma_{R3}}{2} + \frac{\sigma_{R2}}{2}\frac{\sigma_{R4}}{2}\right] + \Phi\frac{\sigma_{R1}}{2}\frac{\sigma_{R2}}{2}\frac{\sigma_{R3}}{2}\frac{\sigma_{R4}}{2} - \sum_{f\in R}\sum_{f'\in\pi_f\in R}\frac{{}^{f'}\Delta_{Rf}}{\beta}\frac{\sigma_{Rf}}{2}.
\end{aligned}$$

The summation in $\sum_R$ is carried out over clusters instead of lattice sites. Hereafter, it is implied that the clusters R, R' belong to the cell q, clusters R_1, R_1' belong to the cell q_1 etc; π_f denotes the set of the nearest neighbours of the site f.

$$\tilde{z}_{qf} = \beta[æ_{qf} - \sum_{f'\in\pi_f} {}^{f'}\Delta_{qf}].$$

Let us define the generating function $\mathcal{F}$ of the reference system as

$$\mathcal{F} = \ln \mathrm{Sp}\ \mathrm{e}^{-\beta H'} = \ln \mathrm{Sp} \left\{ \exp(-\beta \sum_{qf} H^{(1)}_{qf}) \exp\left(-\beta \sum_{R} U_R\right) \right\}. \quad (2.8)$$

Then the free energy of the crystal is equal to

$$F = \frac{v\bar{N}}{2} \sum_{ij} c_{ij} \varepsilon_i \varepsilon_j + \frac{1}{2} \sum_{qf} \sum_{q'f'} J_{ff'}(qq') \frac{\langle \sigma_{qf} \rangle^H}{2} \frac{\langle \sigma_{q'f'} \rangle^H}{2} - \frac{\mathcal{F}}{\beta}. \quad (2.9)$$

Our goal is to calculate the correlation functions (cumulant averages of spin operators products, in particular, single-particle and pair ones) which are related to the free energy in the following way:

$$\langle \sigma_{q_1 f_1} \ldots \sigma_{q_n f_n} \rangle^H_c = \left(\frac{2}{\beta}\right)^n \frac{\delta}{\delta h_{q_1 f_1}} \cdots \frac{\delta(-\beta F)}{\delta h_{q_n f_n}}. \quad (2.10)$$

respectively, the correlation functions of the reference system are

$$\langle \sigma_{q_1 f_1} \ldots \sigma_{q_n f_n} \rangle^c = \left(\frac{2}{\beta}\right)^n \frac{\delta}{\delta æ_{q_1 f_1}} \cdots \frac{\delta \mathcal{F}}{\delta æ_{q_n f_n}}. \quad (2.11)$$

From (2.8)-(2.11) it follows that the single-particle correlation functions of the reference and general systems coincide $\langle \sigma_{qf} \rangle^H = \langle \sigma_{qf} \rangle$, whereas for the pair correlation functions the following relations hold

$$\langle \sigma_{q_1 f_1} \sigma_{q_2 f_2} \rangle^H_c = \sum_{q_3 f_3} \langle \sigma_{q_1 f_1} \sigma_{q_3 f_3} \rangle^c \left[\delta_{q_3 q_2} \delta_{f_3 f_2} - \frac{\beta}{4} \sum_{q_4 f_4} J_{f_3 f_4}(q_3 q_4) \langle \sigma_{q_3 f_3} \sigma_{q_2 f_2} \rangle^c \right]^{-1}. \quad (2.12)$$

Let us introduce the notations

$$\langle (\ldots) \rangle_0 \equiv \frac{\mathrm{Sp}\{(\ldots) \exp(-\beta \sum_{qf} H^{(1)}_{qf})\}}{\mathrm{Sp} \exp(-\beta \sum_{qf} H^{(1)}_{qf})},$$

$$F^{(1)}_{qf} \equiv \ln \mathrm{Sp} \exp(-\beta H^{(1)}_{qf}) = \ln 2 \cosh \frac{\tilde{z}_{qf}}{2}.$$

Then

$$\mathcal{F} = \sum_{qf} F^{(1)}_{qf} + \ln \left\langle \exp[-\beta \sum_R U_R] \right\rangle_0. \quad (2.13)$$

We restrict our consideration to the first order of the cluster expansion, that is

$$\ln \left\langle \exp[-\beta \sum_R U_R] \right\rangle_0 \simeq \sum_R \ln \langle \exp[-\beta U_R] \rangle_0. \quad (2.14)$$

Then, the generating function $\mathcal{F}$ becomes

$$\mathcal{F} = \sum_R \ln \mathrm{Sp} \exp[-\beta H^{(4)}_R] - \sum_{qf} F^{(1)}_{qf} = \sum_R F^{(4)}_R - \sum_{qf} F^{(1)}_{qf}, \quad (2.15)$$

where

$$H_R^{(4)} = V\left[\frac{\sigma_{R1}}{2}\frac{\sigma_{R2}}{2} + \frac{\sigma_{R2}}{2}\frac{\sigma_{R3}}{2} + \frac{\sigma_{R3}}{2}\frac{\sigma_{R4}}{2} + \frac{\sigma_{R4}}{2}\frac{\sigma_{R1}}{2}\right] + \tag{2.16}$$
$$+ U\left[\frac{\sigma_{R1}}{2}\frac{\sigma_{R3}}{2} + \frac{\sigma_{R2}}{2}\frac{\sigma_{R4}}{2}\right] + \Phi\frac{\sigma_{R1}}{2}\frac{\sigma_{R2}}{2}\frac{\sigma_{R3}}{2}\frac{\sigma_{R4}}{2} - \sum_{f\in R}\frac{z_{Rf}}{\beta}\frac{\sigma_{Rf}}{2}$$

is the four-particle cluster Hamiltonian. Here we use the fact that since each site of the given lattice belongs to two neighbouring clusters then

$$\sum_{qf}(\ldots) = \frac{1}{2}\sum_R\sum_{f\in R}(\ldots).$$

The fields z_{Rf} are

$$z_{Rf} = \beta[æ_{Rf} - \sum_{f'\in\pi_f\notin R}{}^{f'}\Delta_{Rf}] = \beta[æ_{Rf} - \Delta_{Rf}], \tag{2.17}$$

the sum contains effective fields created by the neighbouring quasispins outside the cluster; for the lattice considered, Δ_{Rf} is an effective field created by the whole neighbouring cluster R', which also contains the site Rf. Let us note that

$$\tilde{z}_{Rf} = \beta[æ_{Rf} - \sum_{f'\in\pi_f}{}^{f'}\Delta_{Rf}] = \beta[æ_{Rf} - \Delta_{R'f} - \Delta_{Rf}], \tag{2.18}$$

the field $\Delta_{R'f}$ is created by the spins of the cluster R.

From the condition of a minimum of the generating function $\mathcal{F}$ with respect to Δ_{Rf}

$$\frac{\partial\mathcal{F}}{\partial\Delta_{Rf}} = 0 \tag{2.19}$$

it follows that

$$\frac{\partial F_R^{(4)}}{\partial æ_{Rf}} = \beta\frac{\partial F_R^{(4)}}{\partial z_{Rf}} = \frac{\partial F_{Rf}^{(1)}}{\partial æ_{Rf}} = \beta\frac{\partial F_R^{(1)}}{\partial\tilde{z}_{Rf}}; \quad \frac{\partial F_{R'}^{(4)}}{\partial æ_{Rf}} = \frac{\partial F_{R'f}^{(1)}}{\partial æ_{Rf}}, \tag{2.20}$$

and

$$\langle\sigma_{Rf}\rangle = \frac{2}{\beta}\frac{\partial F_R^{(4)}}{\partial æ_{Rf}} = \frac{2}{\beta}\frac{\partial F_R^{(1)}}{\partial æ_{Rf}}, \tag{2.21}$$

(provided that the site f belongs to the clusters R and R'), that is, the mean values of spins, calculated with the single-particle Hamiltonian $H_{qf}^{(1)}$ and the four-particle one $H_R^{(4)}$, must coincide. The relations (2.21) comprise the system of equations for the unknown fields Δ_{Rf}.

If no electric field is applied, the quantities z_{Rf} are uniform, that is,

DKDP

$$z^f \equiv z_{R1} = z_{R2} = z_{R3} = z_{R4} = z_{R'1} = z_{R'2} = z_{R'3} = z_{R'4} =$$
$$= \beta[-\Delta + \nu_c(0)\eta^{(1)}], \tag{2.22}$$

DADP

$$z_R^a = -z_{R1} = z_{R2} = z_{R3} = -z_{R4} = \beta[-\Delta_R + \nu_a(\mathbf{k}_Z)\eta_R^{(1)}] = z_{R'}^a,$$

where

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

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

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

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

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

($\mathbf{k}_Z = (\mathbf{b}_1+\mathbf{b}_2+\mathbf{b}_3)/2$, $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are the basic vectors of the reciprocal lattice; the averages $\langle\sigma_{Rf}\rangle$ are equal for both R and R' clusters and obey the relations

DKDP

$$\eta^{(1)} = \eta_{R1}^{(1)} = \eta_{R2}^{(1)} = \eta_{R3}^{(1)} = \eta_{R4}^{(1)} = \eta_{R'1}^{(1)} = \eta_{R'2}^{(1)} = \eta_{R'3}^{(1)} = \eta_{R'4}^{(1)}, \tag{2.23}$$

DADP

$$\eta_R^{(1)} = -\eta_{R1}^{(1)} = \eta_{R2}^{(1)} = \eta_{R3}^{(1)} = -\eta_{R4}^{(1)} = \eta^{(1)}\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_q} = \eta_{R'}^{(1)};$$

the factor $\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_q} = \pm 1$ denotes two sublattices of antiferroelectric DADP crystal.

The fields z_{Rf} are determined from the condition (2.21). In the uniform case

DKDP

$$z^f = \frac{1}{2}\ln\frac{1+\eta^{(1)}}{1-\eta^{(1)}} + \beta\nu_c(0)\eta^{(1)}; \tag{2.24}$$

DADP

$$z_R^a = z^a\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_q} = \Big[\frac{1}{2}\ln\frac{1+\eta^{(1)}}{1-\eta^{(1)}} + \beta\nu_a(\mathbf{k}_Z)\eta^{(1)}\Big]\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_q}.$$

Let us now calculate the averages $\langle\sigma_{Rf}\rangle$ and $\langle\sigma_{Rf}\sigma_{Rf'}\rangle$ (the intracluster correlation functions), provided that (2.22)–(2.24) hold:

DKDP

$$\eta^{(1)} = \frac{\sinh 2z^f + 2b\sinh z^f}{D^f}, \tag{2.25}$$

$$\eta^{(2)} = \langle\sigma_{R1}\sigma_{R2}\rangle = \langle\sigma_{R2}\sigma_{R3}\rangle = \langle\sigma_{R3}\sigma_{R4}\rangle = \langle\sigma_{R4}\sigma_{R1}\rangle = \frac{\cosh 2z^f - d}{D^f},$$

$$\eta^{(2)'} = \langle\sigma_{R1}\sigma_{R3}\rangle = \langle\sigma_{R2}\sigma_{R4}\rangle = \frac{\cosh 2z^f - 2a + d}{D^f};$$

DADP

$$\eta_R^{(1)} = \frac{\sinh 2z_R^a + 2b\sinh z_R^a}{D^a}, \tag{2.26}$$

$$\eta^{(2)} = \langle\sigma_{R1}\sigma_{R4}\rangle = \langle\sigma_{R2}\sigma_{R3}\rangle == \frac{a - d + \cosh z_R^a - 1}{D^a},$$
$$\eta^{(2)'} = -\langle\sigma_{R1}\sigma_{R2}\rangle = -\langle\sigma_{R3}\sigma_{R4}\rangle = \frac{-a + d + \cosh z_R^a - 1}{D^a},$$
$$\eta^{(2)''} = -\langle\sigma_{R1}\sigma_{R3}\rangle = -\langle\sigma_{R2}\sigma_{R4}\rangle = \frac{-a - d + \cosh z_R^a + 1}{D^a}.$$

The quantities $\eta^{(2)}$ are even functions of z_R and do not depend on q;

$$a = \exp[-\beta\varepsilon]; \quad b = \exp[-\beta w]; \quad d = \exp[-\beta w_1];$$
$$D^f = \cosh 2z^f + 4b\cosh z^f + 2a + d;$$
$$D^a = \cosh 2z^a + 4b\cosh z^a + a + d + 1.$$

Let us also introduce some notations for the cumulant averages which will be used in the following sections

DKDP

$$F_0^f = 1 - (\eta^{(1)})^2, \quad F_1^f = \eta^{(2)} - (\eta^{(1)})^2, \quad F_2^f = \eta^{(2)'} - (\eta^{(1)})^2, \tag{2.27}$$

DADP

$$F_0^a = 1 - (\eta_R^{(1)})^2, \quad F_1^a = \eta^{(2)} - (\eta_R^{(1)})^2, \tag{2.28}$$
$$F_2^a = -\eta^{(2)'} + (\eta_R^{(1)})^2, \quad F_3^a = -\eta^{(2)''} + (\eta_R^{(1)})^2.$$

If no electric field is applied, the free energy of a crystal reads:

DKDP

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

DADP

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

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

$$\frac{1}{\bar{v}}\frac{\partial f}{\partial\eta^{(1)}} = 0; \quad \frac{1}{\bar{v}}\frac{\partial f}{\partial\varepsilon_i} = -p_i. \tag{2.29}$$

(with $p_i(\mathrm{h}) = (p, p, p), \quad p_i(3) = (0, 0, p)$), namely, from the equations

DKDP

$$\eta^{(1)} = \frac{1}{D^f}(\sinh 2z^f + 2b\sinh z^f),$$
$$-p_i = \sum_j c_{ij}^{(0)}\varepsilon_j - 2\frac{\delta_{2i}}{\bar{v}} - \frac{2\psi_{ci}}{\bar{v}}[\eta^{(1)}]^2 + \frac{2}{\bar{v}}\frac{M_i^f}{D^f}, \tag{2.30}$$

DADP

$$\eta^{(1)} = \frac{1}{D^a}(\sinh 2z^a + 2b\sinh z^a),$$
$$-p_i = \sum_j c_{ij}^{(0)}\varepsilon_j - \frac{2\delta_{2i} - \delta_{1i}}{\bar{v}} - \frac{2\psi_{ai}(\mathbf{k}_Z)}{\bar{v}}[\eta^{(1)}]^2 + \frac{2}{\bar{v}}\frac{M_i^a}{D^a}, \tag{2.31}$$

where $M_i^f = 4b\delta_{2i}\cosh z^f + 2a\delta_{1i} + d\delta_{3i}$, $M_i^a = 4b\delta_{2i}\cosh z^a + a\delta_{1i} + d\delta_{3i}$.

As one can see from equations (2.30) and (2.31), the strains ε_i are equal to zero at ambient pressure only if we assume the temperature dependence of the parameters δ_{2i} in the form

$$\delta_{2i}^{+} = \frac{2a\delta_{1i}^{+}}{1+2a}, \tag{2.32}$$

in the paraelectric phase of a DKDP crystal and

$$\delta_{2i}^{+} = \delta_{1i}^{+}\frac{4b+3a+2}{2a+4} \tag{2.33}$$

in the paraelectric phase of a DADP crystal and in a more complicated form in the ordered phases. In order to keep δ_{2i} constant and for the sake of simplicity we assumed that (2.32) and (2.33) are satisfied only at the transition points, that is,

DKDP

$$\delta_{2i}^{+} = \frac{2\exp(-\beta_{\mathrm{C}}\varepsilon)\delta_{1i}^{+}}{1+2\exp(-\beta_{\mathrm{C}}\varepsilon)}, \tag{2.34}$$

DADP

$$\delta_{2i}^{+} = \delta_{1i}^{+}\frac{4\exp(-\beta_{\mathrm{N}}w)+3\exp(-\beta_{\mathrm{N}}\varepsilon)+2}{2\exp(-\beta_{\mathrm{N}}\varepsilon)+4}, \tag{2.35}$$

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

3. Equation for $\boldsymbol{q}$-dependent correlation functions

In this Section, following the procedure suggested in [12] for DKDP-type crystal at ambient pressure, we derive an equation of Ornstein-Zernike type for the $\boldsymbol{q}$-dependent pair correlation functions of strained DKDP and DADP crystals.

We need to calculate

$$b_{f_1f_2}(R_1R_2) \equiv \langle\sigma_{R_1f_1}\sigma_{R_2f_2}\rangle^c = \frac{4}{\beta^2}\frac{\delta^2\mathcal{F}}{\delta æ_{R_1f_1}\delta æ_{R_2f_2}}. \tag{3.1}$$

Differentiating the expression for the single particle correlation function (2.21)

$$b_{R_1f_1} = \langle\sigma_{R_1f_1}\rangle = 2\frac{\partial F_{R_1}^{(4)}}{\partial z_{R_1f_1}} = 2\frac{\partial F_{R_1f_1}^{(1)}}{\partial \tilde{z}_{R_1f_1}}$$

with respect to $æ_{R_2f_2}$, we get:

$$\langle\sigma_{R_1f_1}\sigma_{R_2f_2}\rangle^c = \frac{4}{\beta}\frac{\partial^2 F_{R_1f_1}^{(1)}}{\partial\tilde{z}_{R_1f_1}\partial\tilde{z}_{R_1f_1}}\frac{\partial\tilde{z}_{R_1f_1}}{\partial æ_{R_2f_2}} = \frac{4}{\beta}\sum_{g\in R_1}\frac{\partial^2 F_{R_1}^{(4)}}{\partial z_{R_1f_1}\partial z_{R_1g}}\frac{\partial z_{R_1g}}{\partial æ_{R_2f_2}}; \tag{3.2}$$

summation in (3.2) goes over all sites of the cluster R_1. Let us introduce the following notations:

$$z'_{f_1f_2}(R_1R_2) \equiv \frac{1}{\beta}\frac{\partial \bar{z}_{R_1f_1}}{\partial æ_{R_2f_2}}; \qquad \Delta'_{f_1f_2}(R_1R_2) \equiv \frac{\partial \Delta_{R_1f_1}}{\partial æ_{R_2f_2}}.$$

$$F^{(4)}_{f_1f_2}(R_1) \equiv 4\frac{\partial^2 F^{(4)}_{R_1}}{\partial z_{R_1f_1}\partial z_{R_1f_2}} = \langle \sigma_{R_1f_1}\sigma_{R_1f_2}\rangle^c,$$

$$F^{(1)}_{f_1f_2}(R_1) \equiv 4\frac{\partial^2 F^{(1)}_{R_1f_1}}{\partial \tilde{z}^2_{R_1f_1}}\delta_{f_1f_2}, \quad P_{f_1f_2}(R_1) = \left[\hat{F}^{(4)}(R_1)\right]^{-1}_{f_1f_2}. \quad (3.3)$$

Then, according to (2.17) and (2.18),

$$\frac{1}{\beta}\frac{\partial z_{R_1f_1}}{\partial æ_{R_2f_2}} = z'_{f_1f_2}(R_1R_2) + \Delta'_{f_1f_2}(R_1R_2). \quad (3.4)$$

Equation (3.2) can be written as

$$\sum_{g\in R_1}[\delta_{f_1g} - P_{f_1g}(R_1)F^{(1)}_{f_1f_1}(R_1)]z'_{gf_2}(R_1R_2) = -\Delta'_{f_1f_2}(R_1R_2). \quad (3.5)$$

Relation analogous to (3.5) for the cluster R'_1 which also contains the spin f_1 reads:

$$\sum_{g\in R'_1}[\delta_{f_1g} - P_{f_1g}(R'_1)F^{(1)}_{f_1f_1}(R'_1)]z'_{gf_2}(R'_1R_2) = -\Delta'_{f_1f_2}(R'_1R_2). \quad (3.6)$$

Let us now return to the uniform systems with (2.22) and (2.23); for the intracluster correlation functions $\eta^{(2)}_{f_1f_2}$ and $\eta^{(1)}_{R_1f_1}$ occurring in $P_{f_1f_2}(R_1)$ the relations (2.25) and (2.26) are obeyed, and the matrices $P_{f_1f_2}(R_1)$ and $P_{f_1f_2}(R'_1)$ coincide. The $F^{(4)}_{ff'}(R)$ matrix of DADP contains only even functions of $\eta^{(1)}_{qf}$ and $\eta^{(1)}_{q'f}$; therefore, we can omit the factors $\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_q}$ and $\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_{q'}}$. Adding equation (3.5) to (3.6), taking the factors $\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_q}$ and $\mathrm{e}^{i\mathbf{k}_Z\mathbf{R}_{q'}}$. Adding equation (3.5) to (3.6), taking into account the relation

$$b_{f_1f_2}(R_1R_2) = F^{(1)}_{f_1f_1}(R_1)z'_{f_1f_2}(R_1R_2),$$

which follows from (3.2), and the fact that

$$-[\Delta'_{f_1f_2}(R_1R_2) + \Delta'_{f_1f_1}(R'_1R_2)] = z'_{f_1f_2}(R_1R_2) - \delta_{f_1f_2}(\delta_{R_1R_2} + \delta_{R'_1R_2}),$$

(f_1 is the common site of the clusters R_1 and R'_1), we get

$$-\delta_{f_1f_2}(\delta_{R_1R_2} + \delta_{R'_1R_2}) = \quad (3.7)$$

$$= \sum_{R=R_1,R'_1}\sum_{g\in R}{}' \left\{\delta_{f_1g}\left[\frac{1}{F^{f,a}_0} - P^{f,a}_{f_1f_1}(R)\right] - P^{f,a}_{f_1g}(R)\right\} b_{gf_2}(RR_2),$$

where in the sum $\sum_{R=R_1,R_1'}\Sigma'_{g\in R}$ the term with $g=f_1$ occurs only once. The matrix $\hat{P}^f(R_1)$ has the following elements

$$\hat{P}^f(R_1)=\hat{P}^f(R_1')=\begin{pmatrix} P_0^f & P_1^f & P_2^f & P_1^f \\ P_1^f & P_0^f & P_1^f & P_2^f \\ P_2^f & P_1^f & P_0^f & P_1^f \\ P_1^f & P_2^f & P_1^f & P_0^f \end{pmatrix}, \tag{3.8}$$

where

$$P_0^f=\frac{F_0^f(F_0^f+F_2^f)-2(F_1^f)^2}{(F_0^f-F_2^f)((F_0^f+F_2^f)^2-4(F_1^f)^2)},\quad P_1^f=\frac{F_1^f}{(F_0^f+F_2^f)^2-4(F_1^f)^2},$$
$$P_2^f=\frac{2(F_1^f)^2-F_2^f(F_0^f+F_2^f)}{(F_0^f-F_2^f)((F_0^f+F_2^f)^2-4(F_1^f)^2)},$$

whereas

$$[\hat{P}^a(R_1)]^{-1}=[\hat{P}^a(R_1')]^{-1}=\begin{pmatrix} F_0^a & F_1^a & F_2^a & F_3^a \\ F_1^a & F_0^a & F_3^a & F_2^a \\ F_2^a & F_3^a & F_0^a & F_1^a \\ F_3^a & F_2^a & F_1^a & F_0^a \end{pmatrix}. \tag{3.9}$$

It is convenient to Fourier transform equation (3.7) in positions vectors of cells $\mathbf{R}_q$:

$$P_{fg}(\mathbf{q})\equiv\sum_R P_{fg}(R)\mathrm{e}^{-i\boldsymbol{q}\boldsymbol{R}_q}\mathrm{e}^{-i\boldsymbol{q}(\boldsymbol{r}_f-\boldsymbol{r}_g)}, \tag{3.10a}$$

$$b_{fg}(\boldsymbol{q})\equiv\sum_{R_1-R_2} b_{fg}(R_1R_2)\mathrm{e}^{-i\boldsymbol{q}(\boldsymbol{R}_{q_1}-\boldsymbol{R}_{q_2})}\mathrm{e}^{-i\boldsymbol{q}(\boldsymbol{r}_f-\boldsymbol{r}_g)} \tag{3.10b}$$

Let us note that the sum in (3.10a) contains only two nonzero terms with $R=R_1$ and $R=R_1'$, f_1 being the common site of the clusters R_1 and R_1'. Then instead of (3.7), we get

$$-\delta_{f_1f_2}=\sum_{g=1}^{4}\left\{\frac{\delta_{f_1g}}{F_0^{f,a}}-P_{f_1g}^{f,a}(\boldsymbol{q})\right\}b_{gf_2}(\boldsymbol{q}), \tag{3.11}$$

where

$$P^{f,a}(\boldsymbol{q})=\begin{pmatrix} 2P_0^{f,a} & P_1^{f,a}(\boldsymbol{q}) & P_2^{f,a}(\boldsymbol{q}) & P_3^{f,a}(\mathbf{q}) \\ P_1^{f,a}(\boldsymbol{q}) & 2P_0^{f,a} & P_4^{f,a}(\boldsymbol{q}) & P_5^{f,a}(\boldsymbol{q}) \\ P_2^{f,a}(\boldsymbol{q}) & P_4^{f,a}(\boldsymbol{q}) & 2P_0^{f,a} & P_6^{f,a}(\boldsymbol{q}) \\ P_3^{f,a}(\boldsymbol{q}) & P_5^{f,a}(\boldsymbol{q}) & P_6^{f,a}(\boldsymbol{q}) & 2P_0^{f,a} \end{pmatrix};$$

$$P_0^{f,a}=\frac{1}{1-(\eta^{(1)})^2},$$
$$P_1^{f,a}(\boldsymbol{q})=2P_1^{f,a}\cos\frac{q_x+q_y+q_z}{4},\quad P_2^{f,a}(\boldsymbol{q})=2P_2^{f,a}\cos\frac{q_x}{2},$$
$$P_3^{f}(\boldsymbol{q})=2P_1^{f}\cos\frac{q_x-q_y+q_z}{4},\quad P_3^{a}(\boldsymbol{q})=2P_3^{a}\cos\frac{q_x-q_y+q_z}{4},$$
$$P_4^{f}(\boldsymbol{q})=2P_1^{f}\cos\frac{q_x-q_y-q_z}{4},\quad P_4^{a}(\boldsymbol{q})=2P_3^{a}\cos\frac{q_x-q_y-q_z}{4},$$
$$P_5^{f,a}(\boldsymbol{q})=2P_2^{f,a}\cos\frac{q_y}{2},\quad P_6^{f,a}(\boldsymbol{q})=2P_1^{f,a}\cos\frac{q_x+q_y-q_z}{4},$$

(q_x, q_y, q_z are projections of the dimensionless wavevector on the basic vectors of the tetragonal unit cell; $q_i \in [-\pi, \pi]$). Relations (3.11) comprise a close set of equations for the $\boldsymbol{q}$-dependent correlation functions of the reference systems corresponding to strained DKDP and DADP crystals.

4. Dielectric permittivity

Obtained in the previous section pair correlation function $b_{f_1 f_2}(\boldsymbol{q})$ of the reference system enables one to calculate the correlation function of the general system $b^H_{f_1 f_2}(\boldsymbol{q})$ related to the former by (2.12), and hence the components of $\mathbf{q}$-dependent static dielectric susceptibilities of a clamped ($\varepsilon_i =$ const) crystal. We need to calculate:

$$\chi_{ij}(\boldsymbol{q}, T, p) = \frac{\beta}{4v} \sum_{ff'} \mu^i_f \mu^j_{f'} b^H_{ff'}(\boldsymbol{q}), \tag{4.12}$$

where

$$\begin{aligned} &\mu_1 = \mu^1_3 = -\mu^1_1, \quad \mu^1_2 = \mu^1_4 = 0, \\ &\mu_2 = \mu^2_2 = -\mu^2_4, \quad \mu^2_1 = \mu^2_3 = 0, \\ &\mu_3 = \mu^3_1 = \mu^3_2 = \mu^3_3 = \mu^3_4, \end{aligned}$$

are effective dipole moment of unit cells, assumed to be linear functions of pressure, and

$$\hat{b}^H(\boldsymbol{q}) = \left\{ \hat{b}^{-1}(\boldsymbol{q}) - \frac{\beta}{4} \hat{J}(\boldsymbol{q}) \right\}^{-1}$$

in the mean-field approximation used. With the help of the eigenfunctions $W_{f\mu}(\boldsymbol{q})$ and eigenvalues $b_\mu(\boldsymbol{q})$ of the $\hat{b}^H(\boldsymbol{q})$ matrix, we can get the following expressions for the transverse and longitudinal diagonal elements of the dielectric susceptibility tensor:

$$\begin{aligned} \chi_1(\boldsymbol{q}, T, p) &= \frac{\beta \mu_1^2}{v} \sum_\mu b_\mu(\boldsymbol{q}) \left[W_{1\mu}(\boldsymbol{q}) - W_{3\mu}(\boldsymbol{q}) \right]^2; \\ \chi_2(\boldsymbol{q}, T, p) &= \frac{\beta \mu_2^2}{v} \sum_\mu b_\mu(\boldsymbol{q}) \left[W_{2\mu}(\boldsymbol{q}) - W_{4\mu}(\boldsymbol{q}) \right]^2; \\ \chi_3(\boldsymbol{q}, T, p) &= \frac{\beta \mu_3^2}{v} \sum_\mu b_\mu(\boldsymbol{q}) [\sum_f W_{f\mu}(\boldsymbol{q})]^2. \end{aligned}$$

Essential simplification occurs when the matrices $\hat{P}(\boldsymbol{q})$ (and thereby $\hat{b}^{-1}(\boldsymbol{q})$) and $\hat{J}(\boldsymbol{q})$ have the same symmetry. Then

$$b_\mu(\boldsymbol{q}) = \frac{1}{\tilde{P}_\mu(\boldsymbol{q}) - [1 - (\eta^{(1)})^2]^{-1} - \beta \nu_\mu(\boldsymbol{q})/4},$$

$\tilde{P}_\mu(\boldsymbol{q})$, $\nu_\mu(\boldsymbol{q})$ being the eigenvalues of $\hat{P}(\boldsymbol{q})$ and $\hat{J}(\boldsymbol{q})$ matrices.

In what follows we consider only the case of $\boldsymbol{q} = 0$, looking for the expressions for the static susceptibilities of the crystals. It should be mentioned that due to the non-analytical properties of the $J(\boldsymbol{q})$ matrix at $q \to 0$, the values of susceptibilities in the center of Brillouin zone essentially depend on the direction along which the transition $q \to 0$ takes place, for instance, $\boldsymbol{q} = (0, 0, q_z \to 0)$ and $\boldsymbol{q} = (q_x \to 0, q_y \to 0, 0)$.

If we neglect the non-analytical properties of the $J(\boldsymbol{q})$ matrix, then

$$W(0) = \frac{1}{2}\begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix}$$

is the common system of eigenvectors of $\hat{J}(\boldsymbol{q})$ and $\hat{P}(\boldsymbol{q})$ matrices, and

$$\begin{aligned}
&\nu_{1,3}(0) = J_{11}(0) + J_{13}(0) \pm 2J_{12}(0); \quad \frac{\nu_1(0)}{4} = \nu_c(0); \\
&\nu_{2,4}(0) = J_{11}(0) - J_{13}(0); \quad \frac{\nu_2(0)}{4} = \nu_a(0); \\
&\tilde{P}^f_{1,3}(0) = 2(P^f_0 \pm 2P^f_1 + P^f_2), \quad \tilde{P}^a_{1,3}(0) = 2(P^a_0 + P^a_2 \pm (P^a_1 + P^a_3)), \\
&\tilde{P}^f_{2,4}(0) = 2(P^f_0 - P^f_2), \quad \tilde{P}^a_{2,4}(0) = 2(P^a_0 - P^a_2 \pm (P^a_1 - P^a_3))
\end{aligned}$$

are their eigenvalues. Hence, we get the following expressions for the static susceptibilities of the crystals:

<u>DKDP</u>

$$\begin{aligned}
&\chi^\varepsilon_{1,2}(0, T, p) = \frac{\beta\mu^2_{1,2}}{v}\frac{2æ_3}{D^f - 2æ_3\varphi^\eta_1}, \\
&\chi^\varepsilon_3(0, T, p) = \frac{\beta\mu^2_3}{v}\frac{2æ_2}{D^f - 2\varphi^\eta_3 æ_2};
\end{aligned} \tag{4.13}$$

<u>DADP</u>

$$\begin{aligned}
&\chi^\varepsilon_{1,2}(0, T, p) = \frac{\beta\mu^2_{1,2}}{2v}\left[\frac{2æ_1}{D^a - 2æ_1\varphi^\eta_1} + \frac{2æ_2}{D^a - 2æ_2\varphi^\eta_1}\right], \\
&\chi^\varepsilon_3(0, T, p) = \frac{\beta\mu^2_3}{v}\frac{2æ_3}{D^a - 2æ_3\varphi^\eta_3};
\end{aligned} \tag{4.14}$$

Here we introduce the notations:

$$æ_1 = 1 + b\cosh z, \ æ_2 = \cosh 2z + b\cosh z - [\eta^{(1)}]^2 D, \ æ_3 = a + b\cosh z,$$

and

$$\varphi^\eta_1 = \frac{1}{1 - [\eta^{(1)}]^2} + \beta\nu_a(0), \quad \varphi^\eta_3 = \frac{1}{1 - [\eta^{(1)}]^2} + \beta\nu_c(0).$$

Let us note that the expressions for the dielectric susceptibilities coincide with those obtained in [1–5] by means of a different method.

Dielectric permittivity is related to susceptibility as

$$\varepsilon^\varepsilon_i(0, T, p) = \varepsilon_{i\infty} + 4\pi\chi^\varepsilon_i(0, T, p). \tag{4.15}$$

Since the values of the piezoelectric constants d_{ij} of a DADP crystal are fairly large, to compare our results with the experimental data, we need to calculate the dielectric permittivities of a free crystal $\varepsilon_i^F(0,T,p)$, which are usually measured. The "free" permittivities of DADP are related to "clamped" ones by the formulas

$$\begin{aligned}\varepsilon_1^F(0,T,p) &= \varepsilon_1^\varepsilon(0,T,p) + 4\pi\frac{d_{14}^2}{s_{44}^E},\\ \varepsilon_2^F(0,T,p) &= \varepsilon_2^\varepsilon(0,T,p) + 4\pi\frac{d_{25}^2}{s_{55}^E},\\ \varepsilon_3^F(0,T,p) &= \varepsilon_3^\varepsilon(0,T,p) + 4\pi\frac{d_{36}^2}{s_{66}^E},\end{aligned} \tag{4.16}$$

where d_{ij} are the piezoelectric constants, and s^E are the elastic shear compliances of a short circuited crystal [20]. In case of DKDP the difference between permittivities of clamped and free crystal is negligibly small.

5. Numerical analysis

The formulas for the $\boldsymbol{q}$-dependent correlation functions and dielectric permittivities as well as the systems of equations for the order parameters and strains (2.30) and (2.31) contain the following fitting parameters

- ε^0, w^0, $w_1^0 \to \infty$, $\nu_c^0(0)$, $f_1^{0)} = (\mu_1^{(0)})^2/v$, $f_3^{0)} = (\mu_3^{(0)})^2/v$ for both DKDP and DADP, $\nu_a^0(\mathbf{k}_Z)$, $\nu_a^0(0)$ for DADP – relevant for unstrained crystals;
- δ_{1i}, δ_{2i}, $\psi_{ci}(0)$, δ_1/δ_0, $\partial\mu_1/\partial p$, $\partial\mu_3/\partial p$ for DKDP and DADP, $\psi_{ai}(\mathbf{k}_Z)$, $\psi_{ai}(0)$ for DADP – the so-called deformation potentials, and
- $c_{ij}^{(0)}$ – the "seed" elastic constants.

Their values, chosen as described below are given in Tables 1, 2, 3.

The values of ε^0, w^0, $\nu_c^0(0)$ for DKDP and $\nu_a(\mathbf{k}_Z)$ for DADP have been found in [6,15,16]. They provide a satisfactory description of the temperature dependences of static and dynamic dielectric permittivities, spontaneous polarization, specific heat at ambient pressure as well as values of transition temperatures of the crystals.

The values of the deformation potentials δ_{1i} of DKDP and DADP, $\psi_{ci}(0)$ of DKDP and $\psi_{ai}(\mathbf{k}_Z)$ of DADP have been chosen in [1–5]. They yield a good fit to the available experimental data for variation of transition temperature, spontaneous polarization, longitudinal dielectric permittivity of DKDP and transition temperature of DADP with hydrostatic pressure. The values of δ_{2i} parameters were determined from the criteria (2.34) and (2.35). The dependence of the D-site distance δ on hydrostatic pressure in DKDP has been reported in [13,14]. The value of δ_1/δ_0 in the case of DADP was found from the available data for the $T_{\mathrm{N}}(\delta)$ and $T_{\mathrm{N}}(p)$ dependences [17,18]. In the case of the uniaxial pressure σ_3, the δ_1/δ_0 parameter was chosen such that a good fit to the reported in [4] $T_{\mathrm{C}}(\sigma_3)$ dependence was obtained. Let us mention that the transition temperature $T_{\mathrm{C}}(T_{\mathrm{N}})$ decreases with the uniaxial pressure σ_3 several times more rapidly that with hydrostatic σ_{h}:

DKDP

$$\delta_1/\delta_0(\sigma_\mathrm{h}) = -0.89 \cdot 10^{-5}\mathrm{bar}^{-1}, \quad \delta_1/\delta_0(\sigma_3) = -0.7 \cdot 10^{-4}\mathrm{bar}^{-1},$$
$$\frac{\partial T_\mathrm{C}}{\partial p}(\sigma_\mathrm{h}) = -2.67\ \mathrm{K/kbar}, \quad \frac{\partial T_\mathrm{C}}{\partial p}(\sigma_3) = -13.9\ \mathrm{K/kbar},$$

DADP

$$\delta_1/\delta_0(\sigma_\mathrm{h}) = -3.35 \cdot 10^{-6}\ \mathrm{bar}^{-1}, \quad \delta_1/\delta_0(\sigma_3) = -1.75 \cdot 10^{-5}\mathrm{bar}^{-1},$$
$$\frac{\partial T_\mathrm{N}}{\partial p}(\sigma_\mathrm{h}) = -1.4\ \mathrm{K/kbar}, \quad \frac{\partial T_\mathrm{N}}{\partial p}(\sigma_3) = -9.0\ \mathrm{K/kbar}.$$

The values of $\psi_{ai}(0)$ and $\psi_{ci}(0)$ for DADP crystal hardly affect the dielectric responses of the crystals, so we put them equal to zero. The chosen value of derivative $\partial\mu_3/\partial p$ provides a good description of the dependences of spontaneous polarization and longitudinal static dielectric permittivity on hydrostatic pressure in the case of DKDP. As far as $\partial\mu_1/\partial p$ in DKDP and both $\partial\mu_3/\partial p$ and $\partial\mu_1/\partial p$ in DADP crystals are concerned, no appropriate experimental data are available to determine their values. The values of the elastic constants of paraelectric DKDP and DADP crystals were reported in [19,20]. Those values were taken as "seed" elastic constants $c_{ij}^{(0)}$.

Further experimental studies of hydrostatic and uniaxial pressure effects are required to ascertain the values of the theory parameters.

Table 1. The theory parameters (in K) for unstrained crystals.

	T_C	ε^0	w^0	$\nu_a^0(\mathbf{k}_Z)$	$\nu_a^0(0)$	$\nu_c^0(0)$
DKDP	210	87.5	785			36.8
DADP	235	77	709	85.5	-54	-17

Table 2. The deformation potentials (in K) for DKDP [1–4] and DADP [5,6] crystals; $\mathbf{k} = 0$ for DKDP and $\mathbf{k} = \mathbf{k}_Z$ for DADP.

	δ_{11}^-	δ_{12}^-	δ_{13}^-	δ_{11}^+	δ_{13}^+	$\psi_1^-(\mathbf{k})$	$\psi_2^-(\mathbf{k})$	$\psi_3^-(\mathbf{k})$	$\psi_1^+(\mathbf{k})$	$\psi_3^+(\mathbf{k})$
DKDP	-45	-55	885	-50	800	-85	-105	250	-95	390
DADP	-38	-46	741	-42	665	-180	-252	112	-239	109

Table 3. The "seed" elastic constants (units of $10^{11}\mathrm{dyn/cm}^2$) of a DKDP [19] and DADP [20] crystals.

	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-}
DKDP	6.93	-0.78	1.22	5.45	6.93	-1.78	1.22	6.0	1.1	5.0
DADP	6.59	0.53	1.92	3.28	6.24	0.4	1.66	6.4	1.5	3.48

In figure 1 we depict the wavevector dependences of some pair correlation functions of a DKDP crystal at different values of hydrostatic pressure and temperature.

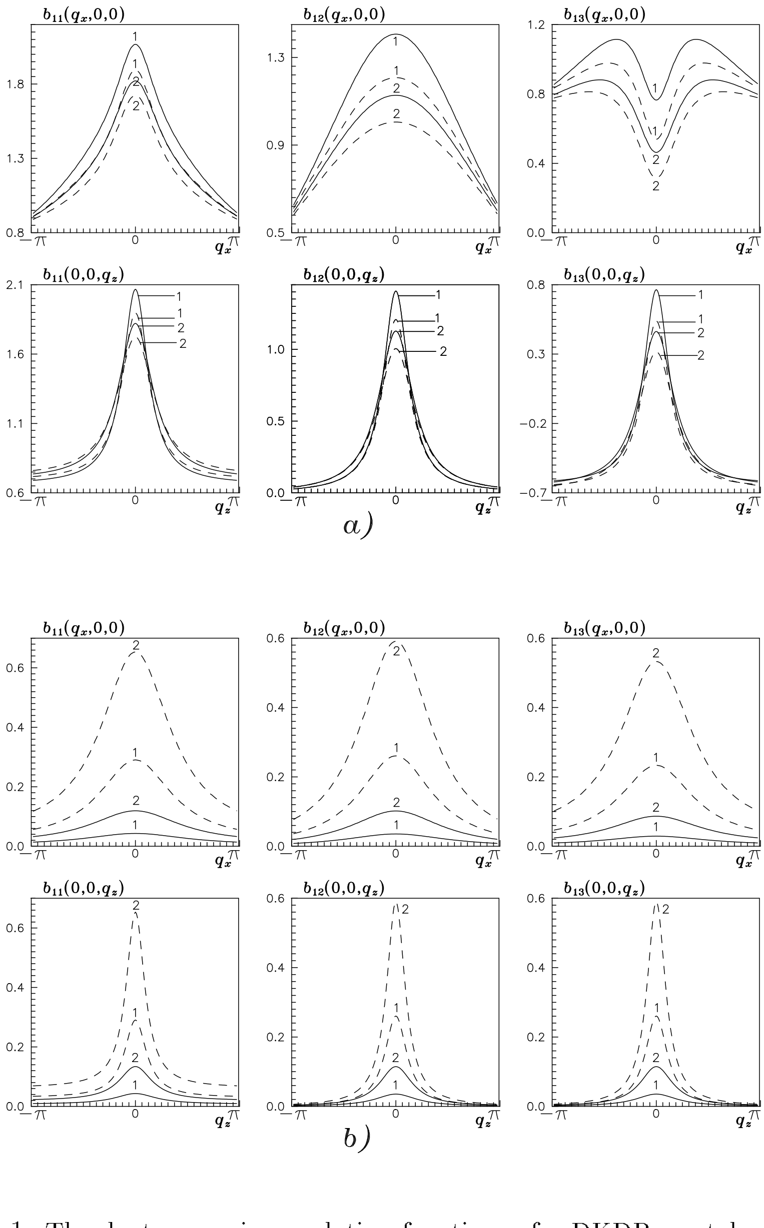

Figure 1. The deuteron pair correlation functions of a DKDP crystal as functions of wavevector at different values of temperature T(K): a) 1 – 190, 2 – 200; b) 1 – 220; 2 – 250 and hydrostatic pressure p(kbar): solid lines – 0.001, dashed lines – 10.

As one can see, $b_{11}(\boldsymbol{q}) > b_{12}(\boldsymbol{q}) > b_{13}(\boldsymbol{q})$. Overall, the correlation functions have maxima in the center of the Brillouin zone, except for the $b_{11}(q,0,0)$ which has a minimum at $q=0$. The amplitude of spin correlations increases when temperature approaches T_{C}. Therefore, an increase in temperature and increase in pressure in the paraelectric phase and decrease in temperature and decrease in pressure in the ferroelectric phase influence the correlations in a similar way, because all of them move the system from the transition point. A strong anisotropy of correlation functions is observed along the $(q,0,0)$ and $(0,0,q)$ directions; that agrees with the result of [11].

In figure 2 we plot the wavevector dependences of the pair correlation functions of a DADP crystal at different values of hydrostatic pressure and temperature at $T > T_{\mathrm{N}}$. Here, also $b_{11}(\boldsymbol{q}) > b_{12}(\boldsymbol{q}) > b_{13}(\boldsymbol{q})$. However, the maxima of $b_{12}(q,0,0)$ and $b_{13}(q,0,0)$ shift from the center to the boundary of Brillouin zone. Furthermore, $b_{12}(\boldsymbol{q})$ and $b_{13}(\boldsymbol{q})$ increase with pressure and temperature.

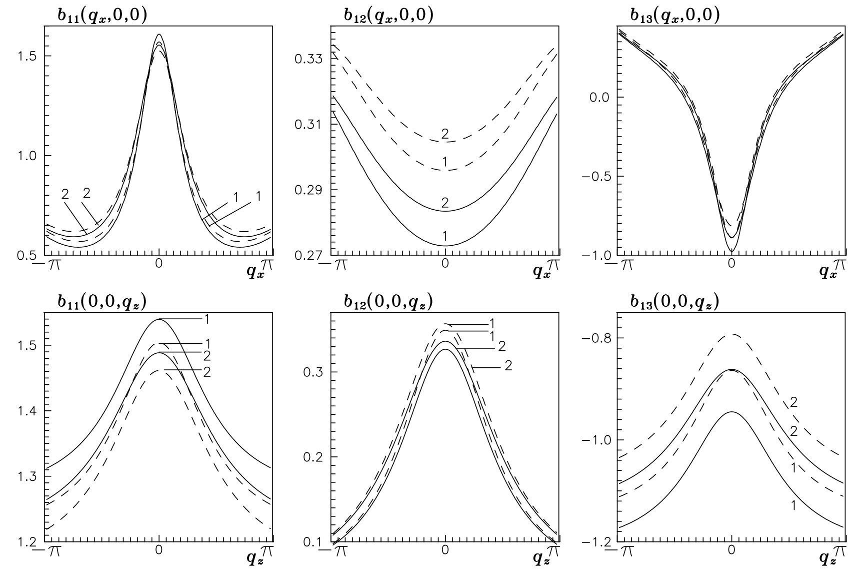

Figure 2. The deuteron pair correlation functions of a DADP crystal as functions of wavevector at different values of temperature T(K): 1 – 240, 2 – 270 and hydrostatic pressure p(kbar): solid lines – 0.001, dashed lines – 10.

The temperature dependence of the inverse longitudinal dielectric permittivity $\varepsilon_3^{-1}(0,T,p)$ of a DKDP crystal at different hydrostatic and uniaxial $-p=\sigma_3$ pressures is plotted in figures 3 and 4, respectively. In figure 4 we also depicted the $\varepsilon_3^{-1}(0,T,p)$ curve at hydrostatic pressure of 1 kbar.

As can be seen, in the paraelectric phase the Curie-Weiss law is obeyed in a wide temperature range at different pressures, the Curie constant decreasing with hydrostatic pressure and being independent of uniaxial pressure. The main effect of the uniaxial pressure is the shift of the transition point and, thereby, of the whole $\varepsilon_3(T)$ curve to lower temperatures. Therefore, at constant ΔT, the $\varepsilon_3(0,T,p)$ almost does not depend on pressure in the paraelectric phase and only slightly varies in the ferroelectric phase.

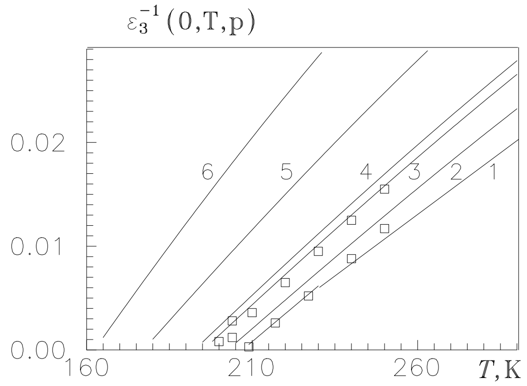

Figure 3. The inverse longitudinal dielectric permittivity of a KD_2PO_4 crystal as a function of temperature at values of hydrostatic pressure p(kbar): $1-0.001$; $2-1.8$; $3-4.14$; $4-5.0$; $5-10.0$; $6-15.0$. The experimental points are taken from [21].

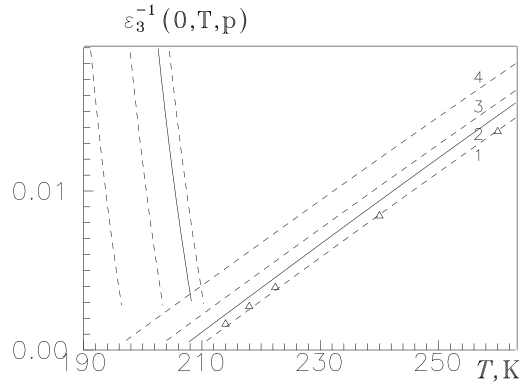

Figure 4. The temperature dependence of the inverse longitudinal static dielectric permittivity $\varepsilon_3^{-1}(0,T,p)$ of a DKDP crystal at different values of uniaxial σ_3 (dashed lines) pressure p(kbar): 1, $\triangle$ [22], – 0.001; 2,4 – 1; 3 – 0.5. The solid line corresponds to hydrostatic pressure of 1 kbar.

In figures 5 and 6 we plot the calculated temperature dependences of the static transverse $\varepsilon_1(0,T,p)$ and longitudinal $\varepsilon_3(0,T,p)$ permittivities of a DADP crystal at different pressures along with the experimental points for the ambient pressure. We are not aware of any experimental measurement of pressure effects on dielectric characteristics of deuterated DADP.

Theoretical values of "free" permittivities are calculated using relations (4.16) and experimental data for appropriate piezoelectric constants and elastic shear compliances [20]. Since in DADP crystal $d_{36} \gg d_{14}$, the difference between clamped and free values of the longitudinal permittivity is several times larger than that of transverse permittivity. A good description of experimental data is obtained for $\varepsilon_1(0,T,p)$, while for $\varepsilon_3(0,T,p)$ a small discrepancy between theory and experiment is observed. Probably, we could remove the discrepancy by explicit taking into account of shear strain ε_6.

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

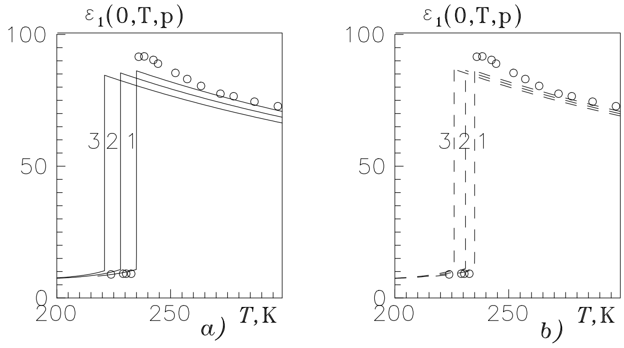

Figure 5. The temperature dependence of the transverse static dielectric permittivity of an $ND_4D_2PO_4$ crystal at different pressures p(kbar): a) (hydrostatic) 1, ○ [20] – 0.001; 2 – 5; 3– 10; b) (uniaxial σ_3) 1, ○ [20] – 0.001; 2 –0.5; 3– 1.

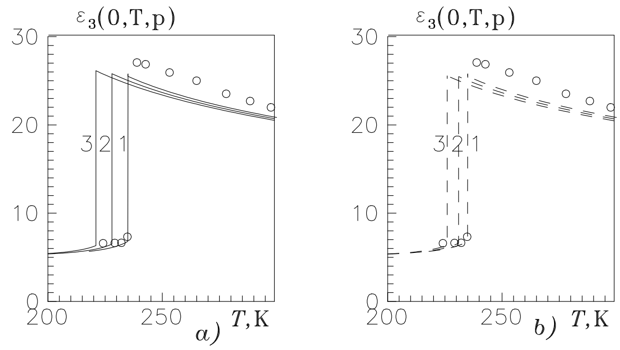

Figure 6. The temperature dependence of the longitudinal static dielectric permittivity of an $ND_4D_2PO_4$ crystal at different pressures p(kbar): a) (hydrostatic) 1, ○ [20] – 0.001; 2 – 5; 3 – 10; b) (uniaxial σ_3) 1, ○ [20] – 0.001; 2 – 0.5; 3 – 1.

Conclusions

In this paper, on the basis of previously proposed model [1–6], we study the influence of external hydrostatic and uniaxial σ_3 pressure on the $\boldsymbol{q}$-dependent pair correlation functions and dielectric properties of DKDP and DADP crystals. In the four-particle cluster approximation, we derive an equation for these functions and find expressions for static dielectric permittivities of these crystals as functions of pressure and temperature. Theoretical results are compared with available experimental data. It is shown that under the proper choice of fitting parameters, the theory provides a satisfactory description of variation of studied characteristics with hydrostatic pressure.

We also state the possible changes in the dielectric properties of DKDP and DADP crystals with the uniaxial pressure, assuming some plausible changes in the crystal structure with pressure. The main feature of the predicted effects is that even low uniaxial stress can induce a significant shift of the transition temperature, whereas the intrinsic changes in the responses of DKDP and DADP crystals (i.e. beyond the shift) are rather small.

It is necessary to carry out comprehensive experimental studies of the uniaxial pressure effects on these crystals, especially on their structure. We hope that these measurements will allow us to define the theory parameters more precisely and verify our predictions.

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***q*-ЗАЛЕЖНІ КОРЕЛЯЦІЙНІ ФУНКЦІЇ І ДІЕЛЕКТРИЧНІ ПРОНИКЛИВОСТІ КРИСТАЛІВ ТИПУ DKDP І DADP. ВПЛИВ ЗОВНІШНЬОГО ТИСКУ**

А.П.Моїна

В наближенні чотиричастинкового кластера отримано рівняння для ***q***-залежних парних кореляційних функцій дейтронів кристалів DKDP і DADP, до яких прккладено зовнішній гідростатичний чи одновісний σ_3 тиск. Досліджуються їх залежності від хвильового вектора, температури та тиску. Знайдено вирази для статичних діелектричних проникливостей деформованих кристалів, що розглядаються. Показано, що при належному виборі параметрів теорії, отримані результати задовільно узгоджуються з наявними експериментальними даними.