The effect of hydrostatic pressure on thermodynamic characteristics of NH$_3$CH$_2$COOH-H$_2$PO$_3$ type ferroelectric materials

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The model of NH$_3$CH$_2$COOH-H$_2$PO$_3$, modified by taking into account the piezoelectric coupling between the ordering structure elements and the strains $\epsilon_i$, $\epsilon_j$, is used for investigation of the effects that appear under external pressures. Within two-particle cluster approximation, the components of polarization vector and static dielectric permittivity tensor of the mechanically clamped and free crystals, their piezoelectric and thermal characteristics are calculated. The effect of hydrostatic pressure on the phase transition and the calculated physical characteristics of the crystal is studied. A good quantitative description of experimental data for these crystals is obtained.

**Key words:** ferroelectrics, phase transition, dielectric permittivity, piezoelectric coefficients, hydrostatic pressures

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1. Introduction

The study of the effects that appear under external pressures is one of the urgent problems in the physics of ferroelectric materials. External pressures can be a powerful tool for a purposeful influence on their physical characteristics and can be used in technological processes. The study of the behaviour of ferroelectrics under external pressures enabled us to better understand the mechanisms of phase transitions in these materials.

It is necessary to note that an acceptable description of an external hydrostatic pressure effect on the phase transition and physical characteristics for many ferroelectric crystals of KH$_2$PO$_4$ family was made in [1, 2], for quasione-dimensional CsH$_2$PO$_4$ type ferroelectrics — in [3], for monoclinic RbD$_2$PO$_4$ — in [4], for RbH$_2$SO$_4$ crystal — in [5].

In [6], on the basis of the proposed model of deformed NH$_3$CH$_2$COOH-H$_2$PO$_3$ (GPI) type ferroelectrics, the dielectric, piezoelectric, elastic and thermal characteristics of these crystals were calculated in the two-particle cluster approximation and a good quantitative description of the available experimental data for these characteristics was obtained. The effect of electric fields on dielectric properties of GPI ferroelectric was investigated in [7]. A satisfactory quantitative description of the corresponding experimental data was obtained at the proper choice of the model parameters. An experimental study of hydrostatic pressure effect on the physical properties of GPI type crystals was carried out in [8, 9]. Calculation of the static dielectric permittivities and investigation of the electric field $E_3$ on the permittivity $\varepsilon_{33}$ of GPI crystal was carried out in [10, 11] within the phenomenological Landau theory.

In the present work, the hydrostatic pressure effect on the phase transition, thermodynamic, dielectric, piezoelectric and elastic characteristics of this type of crystals is studied based on the model of a deformed GPI crystal [6].
2. Model Hamiltonian

We consider the system of protons in GPI, localized on O-H...O bonds between phosphite groups HPO$_3$, which form zigzag chains along the $c$-axis of the crystal \[ \text{figure 1}\]. Dipole moments $\mathbf{d}_{af}$ ($q$ is the number of a primitive cell, $f = 1, \ldots, 4$) are ascribed to the protons on the bonds. In the ferroelectric phase, the dipole moments compensate each other ($\mathbf{d}_{a1}$ with $\mathbf{d}_{a3}$, $\mathbf{d}_{a2}$ with $\mathbf{d}_{a4}$) in the directions $Z$ and $X$ ($X \perp (b, c)$, $Y \parallel b$, $Z \parallel c$), and simultaneously supplement each other in the direction $Y$, creating a spontaneous polarization. Vectors $\mathbf{d}_{af}$ are oriented at some angles to crystallographic axes and have longitudinal and transverse components along the $b$-axis. Herein below, for components of vectors and tensors we often use the notations 1, 2 and 3 instead of $x$, $y$ and $z$ for convenience. The Hamiltonian of proton subsystem of GPI, which takes into account the short-range and long-range interactions, applied hydrostatic pressure $p = -\sigma_i$ ($i = 1, 2, 3$) and electric fields $E_1$, $E_2$, $E_3$ along positive directions of the Cartesian axes $OX$, $OY$ and $OZ$, consists of “seed” and pseudospin parts. The “seed” energy $U_{\text{seed}}$ corresponds to the heavy ion sublattice and does not depend explicitly on the configuration of the proton subsystem. The pseudospin part takes into account the short-range $\hat{H}_{\text{short}}$ and long-range $\hat{H}_{\text{MF}}$ interactions of protons near tetrahedra HPO$_3$, as well as the effective interaction with the electric fields $E_1$, $E_2$ and $E_3$. Therefore \[ \hat{H} = N U_{\text{seed}} + \hat{H}_{\text{short}} + \hat{H}_{\text{MF}}, \]

where $N$ is the total number of primitive cells.

The $U_{\text{seed}}$ corresponds to the “seed” energy, which includes the elastic, piezoelectric and dielectric parts, expressed in terms of electric fields $E_i$ ($i = 1, 2, 3$) and strains $\epsilon_i$ and $\epsilon_j$ ($j = i + 3$):

\[
U_{\text{seed}} = \frac{1}{2} \sum_{i',i=1}^{3} c_{i'i}^{E}(T) \epsilon_i \epsilon_{i'} + \frac{1}{2} \sum_{j=4}^{6} c_{ij}^{E}(T) \epsilon_j^2 + \sum_{i=1}^{3} c_{i3}^{E}(T) \epsilon_i \epsilon_3 + c_{45}^{E}(T) \epsilon_4 \epsilon_5 + c_{46}^{E}(T) \epsilon_4 \epsilon_6 \\
- \sum_{i=1}^{3} \epsilon_{i2} \epsilon_i E_2 - \epsilon_{25} \epsilon_5 E_2 - \epsilon_{44} \epsilon_4 E_1 - \epsilon_{16} \epsilon_6 E_1 - \epsilon_{34} \epsilon_4 E_3 - \epsilon_{36} \epsilon_6 E_3 \\
- \frac{1}{2} \chi_{11} \epsilon_1^2 - \frac{1}{2} \chi_{22} \epsilon_2^2 - \frac{1}{2} \chi_{33} \epsilon_3^2 - \chi_{31} \epsilon_3 E_1. \tag{2.2}
\]

Here, parameters $c_{i'i}^{E}(T)$, $c_{i3}^{E}(T)$, $c_{45}^{E}(T)$, $c_{46}^{E}(T)$, $\epsilon_{i2}$, $\chi_{ii}$, $\chi_{31}$ ($i' = 1, 2, 3$) correspond to the so-called “seed” elastic constants, piezoelectric stresses and dielectric susceptibilities, respectively, $v$ is the volume of a primitive cell.

![Figure 1. (Color online) Orientations of vectors $\mathbf{d}_{af}$ in the primitive cell in the ferroelectric phase](image)

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The Hamiltonian of short-range interactions

\[
\hat{H}_{\text{short}} = -2w \sum_{qq'} \left( \frac{\sigma_{q1} \sigma_{q'2}}{2} + \frac{\sigma_{q3} \sigma_{q'4}}{2} \right) \left( \delta_{R_q, R_{q'}} + \delta_{R_q + R_{q'}, R_{q'}} \right).
\]  

(2.3)

In (2.3) \( \sigma_{qf} \) is the \( z \)-component of pseudospin operator that describes the state of the \( f \)-th bond \((f = 1, 2, 3, 4) \), in the \( q \)-th cell. The first Kronecker delta corresponds to the interaction between protons in the chains near the tetrahedra HPO\(_3\) of type “I”, while the second one — near the tetrahedra HPO\(_3\) of type “II”. \( R_q \) is the lattice vector along \( c \)-axis. The contributions into the energy of interactions between protons near tetrahedra of different type, as well as the mean values of the pseudospins \( \eta_f = \langle \sigma_{qf} \rangle \), which are related to tetrahedra of different type, are equal.

 Parameter \( w \), which describes the short-range interactions within the chains, is expanded linearly into a series over strains \( \varepsilon_i, \varepsilon_j \):

\[
w = w^0 + \sum_{i=1}^{3} \delta_i \varepsilon_i + \sum_{j=4}^{6} \delta_j \varepsilon_i.
\]  

(2.4)

Hamiltonian \( \hat{H}_{\text{MF}} \) of the long-range dipole-dipole interactions and indirect (through the lattice vibrations) interactions between protons in the mean field approximation takes into account that Fourier transforms of interaction constants \( J_{ff'} = \sum_{q} J_{ff'}(qq') \) at \( k = 0 \) are linearly expanded over the strains \( \varepsilon_i, \varepsilon_j \); and can be written as:

\[
\hat{H}_{\text{MF}} = NH^0 + \hat{H}_s,
\]  

(2.5)

where

\[
H^0 = \frac{1}{8} J_{11} (\eta_1^2 + \eta_2^2) + \frac{1}{8} J_{22} (\eta_1^2 + \eta_2^2) + \frac{1}{4} J_{12} (\eta_1 \eta_3 + \eta_2 \eta_4) + \frac{1}{4} J_{24} (\eta_1 \eta_3 + \eta_2 \eta_4) + \frac{1}{4} J_{14} (\eta_1 \eta_4 + \eta_2 \eta_3)
\]

\[
+ \frac{1}{8} \left( \sum_{i=1}^{3} \psi_{1i} \varepsilon_i + \sum_{j=4}^{6} \psi_{1j} \varepsilon_j \right) \eta_1 \eta_3 \eta_4 + \frac{1}{8} \left( \sum_{i=1}^{3} \psi_{2i} \varepsilon_i + \sum_{j=4}^{6} \psi_{2j} \varepsilon_j \right) \eta_2 \eta_4
\]

\[
+ \frac{1}{4} \left( \sum_{i=1}^{3} \psi_{12} \varepsilon_i + \sum_{j=4}^{6} \psi_{12} \varepsilon_j \right) (\eta_1 \eta_2 + \eta_3 \eta_4) + \frac{1}{4} \left( \sum_{i=1}^{3} \psi_{14} \varepsilon_i + \sum_{j=4}^{6} \psi_{14} \varepsilon_j \right) (\eta_1 \eta_4 + \eta_2 \eta_3).
\]

\[
\hat{H}_s = -\sum_{q} \left( \mathcal{H}_1 \frac{\sigma_{q1}}{2} + \mathcal{H}_2 \frac{\sigma_{q2}}{2} + \mathcal{H}_3 \frac{\sigma_{q3}}{2} + \mathcal{H}_4 \frac{\sigma_{q4}}{2} \right).
\]  

(2.6)

In (2.6), the following notations are used:

\[
\mathcal{H}_1 = \frac{1}{2} J_{11} \eta_1 + \frac{1}{2} J_{12} \eta_2 + \frac{1}{2} J_{13} \eta_3 + \frac{1}{2} J_{14} \eta_4 + \mu^x_{13} E_1 + \mu^y_{13} E_2 + \mu^z_{13} E_3,
\]

\[
\mathcal{H}_2 = \frac{1}{2} J_{22} \eta_2 + \frac{1}{2} J_{23} \eta_3 + \frac{1}{2} J_{24} \eta_4 - \mu^x_{24} E_1 - \mu^y_{24} E_2 + \mu^z_{24} E_3,
\]

\[
\mathcal{H}_3 = \frac{1}{2} J_{13} \eta_3 + \frac{1}{2} J_{14} \eta_4 - \mu^x_{13} E_1 - \mu^y_{13} E_2 + \mu^z_{13} E_3,
\]

\[
\mathcal{H}_4 = \frac{1}{2} J_{24} \eta_4 + \frac{1}{2} J_{23} \eta_3 - \mu^x_{24} E_1 + \mu^y_{24} E_2 - \mu^z_{24} E_3.
\]  

(2.7)

In (2.7), \( \mu^x_{13} = \mu^x_{14} = \mu^x_{23} = \mu^x_{24} \), \( \mu^y_{13} = \mu^y_{14} = \mu^y_{23} = \mu^y_{24} \), \( \mu^z_{13} = \mu^z_{14} = \mu^z_{23} = \mu^z_{24} \) are the effective dipole moments per one pseudospin. The two-particle cluster approximation is used for calculation of the thermodynamic and dielectric characteristics of GPI. In this approximation, thermodynamic potential is given by:

\[
G = NU_{\text{seed}} + NH^0 + Nw \sum_{i=1}^{3} \varepsilon_i - k_B T \sum_{q} \left[ 2 \ln \text{Sp} e^{-\beta H^0_{q}} - \frac{4}{4} \ln \text{Sp} e^{-\beta H^{(i)}_{q}} \right],
\]  

(2.8)
where $\hat{H}_q^{(2)}, \hat{H}_q^{(1)}$ are two-particle and one-particle Hamiltonians:

$$
\hat{H}_q^{(2)} = -2\omega \left( \frac{\sigma_{q1} \sigma_{q2}}{2} + \frac{\sigma_{q3} \sigma_{q4}}{2} \right) - \frac{y_1 \sigma_{q1}}{\beta} + \frac{y_2 \sigma_{q2}}{\beta} - \frac{y_3 \sigma_{q3}}{\beta} - \frac{y_4 \sigma_{q4}}{\beta},
$$

$$(2.9)$$

$$
\hat{H}_q^{(1)} = -\frac{y_f \sigma_{af}}{\beta},
$$

$$(2.10)$$

where such notations are used:

$$
y_f = \beta(\Delta_f + \cal{H}_f), \quad \bar{y}_f = \beta \Delta_f + y_f.
$$

$$(2.11)$$

Here, $\Delta_f$ are the effective cluster fields created by the neighboring bonds from outside the cluster. In the cluster approximation, the fields $\Delta_f$ can be determined from the self-consistency condition: the mean values of the pseudospins $\langle \sigma_{af} \rangle$ calculated with the two-particle and one-particle Gibbs distribution, respectively, should coincide:

$$
\frac{\text{Sp} \sigma_{af} e^{-\beta \hat{H}_q^{(2)}}}{\text{Sp} e^{-\beta \hat{H}_q^{(2)}}} = \frac{\text{Sp} \sigma_{af} e^{-\beta \hat{H}_q^{(1)}}}{\text{Sp} e^{-\beta \hat{H}_q^{(1)}}}.
$$

$$(2.12)$$

Hence, based on $$(2.12), with taking into account $$(2.9) and $(2.10), we obtain

$$
\eta_{1,3} = \frac{1}{D} (\sinh n_1 \pm \sinh n_2 + a^2 \sinh n_3 \pm a^2 \sinh n_4 + a \sinh n_5 + a \sinh n_6 \mp a \sinh n_7 \pm a \sinh n_8)
$$

$$
= \tanh \frac{\bar{y}_{1,3}}{2},
$$

$$
\eta_{2,4} = \frac{1}{D} (\sinh n_1 \pm \sinh n_2 - a^2 \sinh n_3 \mp a^2 \sinh n_4 \pm a \sinh n_5 \pm a \sinh n_6 \mp a \sinh n_7 \mp a \sinh n_8)
$$

$$
= \tanh \frac{\bar{y}_{2,4}}{2},
$$

$$(2.13)$$

where $D = \cosh n_1 + \cosh n_2 + a^2 \cosh n_3 + a^2 \cosh n_4 + a \cosh n_5 + a \cosh n_6 + a \cosh n_7 + a \cosh n_8$,

$$
a = \exp \left[ -\frac{1}{k_B T} \left( w^0 + \sum_{i=1}^{3} \delta_i E_i + \sum_{j=4}^{6} \delta_j E_j \right) \right],
$$

$$
n_1 = \frac{1}{2} (y_1 + y_2 + y_3 + y_4), \quad n_2 = \frac{1}{2} (y_1 + y_2 - y_3 - y_4), \quad n_3 = \frac{1}{2} (y_1 - y_2 + y_3 - y_4),
$$

$$
n_4 = \frac{1}{2} (y_1 - y_2 - y_3 + y_4), \quad n_5 = \frac{1}{2} (y_1 - y_2 + y_3 + y_4), \quad n_6 = \frac{1}{2} (y_1 + y_2 + y_3 - y_4),
$$

$$
n_7 = \frac{1}{2} (-y_1 + y_2 + y_3 + y_4), \quad n_8 = \frac{1}{2} (-y_1 + y_2 - y_3 - y_4).
$$

Taking into consideration $(2.11), (2.13)$, we exclude the parameters $\Delta_f$ and write the relations:

$$
y_1 = \frac{1}{2} \ln \left( \frac{1 + \eta_1}{1 - \eta_1} \right) + \beta \nu_{11} \eta_1 + \beta \nu_{12} \eta_2 + \beta \nu_{13} \eta_3 + \beta \nu_{14} \eta_4 + \frac{\beta}{2} (\mu^0_{13} E_1 + \mu^0_{13} E_2 + \mu^0_{13} E_3),
$$

$$
y_2 = \beta \nu_{12} \eta_1 + \frac{1}{2} \ln \left( \frac{1 + \eta_2}{1 - \eta_2} \right) + \beta \nu_{22} \eta_2 + \beta \nu_{14} \eta_3 + \beta \nu_{24} \eta_4 + \frac{\beta}{2} (\mu^0_{24} E_1 - \mu^0_{24} E_2 + \mu^0_{24} E_3),
$$

$$
y_3 = \beta \nu_{13} \eta_1 + \beta \nu_{14} \eta_2 + \frac{1}{2} \ln \left( \frac{1 + \eta_3}{1 - \eta_3} \right) + \beta \nu_{11} \eta_3 + \beta \nu_{12} \eta_4 + \frac{\beta}{2} (\mu^0_{13} E_1 + \mu^0_{13} E_2 - \mu^0_{13} E_3),
$$

$$
y_4 = \beta \nu_{14} \eta_1 + \beta \nu_{24} \eta_2 + \beta \nu_{12} \eta_3 + \frac{1}{2} \ln \left( \frac{1 + \eta_4}{1 - \eta_4} \right) + \beta \nu_{22} \eta_4 + \frac{\beta}{2} (\mu^0_{24} E_1 - \mu^0_{24} E_2 - \mu^0_{24} E_3),
$$

where $\nu_{ff'} = J_{ff'}$.

At the absence of external electric fields

$$
\eta_1 = \eta_3 = \eta_{13}, \quad \eta_2 = \eta_4 = \eta_{24}, \quad y_1 = y_3 = y_{13}, \quad y_2 = y_4 = y_{24}.
$$
3. Thermodynamic characteristics of GPI

To calculate the dielectric, piezoelectric and elastic characteristics of the GPI we use the thermodynamic potential per one primitive cell obtained in the two-particle cluster approximation:

\[
g = \frac{G}{N} = U_{\text{seed}} + H^0 - 2 \left( \sum_{i=1}^{3} \delta_i E_i + \sum_{j=4}^{6} \delta_j E_j \right) - \frac{1}{2} k_B T \sum_{j=1}^{4} \ln (1 - \eta_j^2)
\]

\[-2k_B T \ln D + 2k_B T \ln 2 + \nu p \sum_{i=1}^{3} E_i. \tag{3.1}\]

From equilibrium conditions, we have obtained equations for the strains \(e_i, e_j:\)

\[-p = c_{11}^E e_1 + c_{12}^E e_2 + c_{13}^E e_3 + c_{15}^E e_5 - c_{20}^E E_2 - \frac{2\delta_1}{v} + \frac{2\delta_1}{v} M_x - \frac{\psi_{111}}{4v} (\eta_1^2 + \eta_2^2) - \frac{\psi_{131}}{4v} \eta_1 \eta_3\]

\[-\frac{\psi_{222}}{8v}(\eta_1^2 + \eta_2^2) - \frac{\psi_{244}}{4v} \eta_2 \eta_4 - \frac{\psi_{125}}{4v} (\eta_1 \eta_2 + \eta_3 \eta_4) - \frac{\psi_{145}}{4v} (\eta_1 \eta_4 + \eta_2 \eta_3), \ (l = 1, 2, 3),\]

\[0 = c_{51}^E e_1 + c_{52}^E e_2 + c_{53}^E e_3 + c_{55}^E e_5 - c_{25}^E E_2 - \frac{2\delta_5}{v} + \frac{2\delta_5}{v} M_x - \frac{\psi_{115}}{8v} (\eta_1^2 + \eta_2^2) = \frac{\psi_{135}}{4v} \eta_1 \eta_3\]

\[-\frac{\psi_{222}}{8v}(\eta_1^2 + \eta_2^2) - \frac{\psi_{244}}{4v} \eta_2 \eta_4 - \frac{\psi_{125}}{4v} (\eta_1 \eta_2 + \eta_3 \eta_4) - \frac{\psi_{145}}{4v} (\eta_1 \eta_4 + \eta_2 \eta_3),\]

\[0 = c_{44}^E e_4 + c_{46}^E e_6 - c_{14}^E E_1 - c_{34}^E E_3 - 2\delta_4 + \frac{2\delta_4}{v} M_x - \frac{\psi_{114}}{8v} (\eta_1^2 + \eta_3^2) - \frac{\psi_{134}}{4v} \eta_1 \eta_3,\]

\[-\frac{\psi_{222}}{8v}(\eta_1^2 + \eta_2^2) - \frac{\psi_{244}}{4v} \eta_2 \eta_4 - \frac{\psi_{125}}{4v} (\eta_1 \eta_2 + \eta_3 \eta_4) - \frac{\psi_{145}}{4v} (\eta_1 \eta_4 + \eta_2 \eta_3),\]

\[0 = c_{46}^E e_4 + c_{66}^E e_6 - c_{16}^E E_1 - c_{36}^E E_3 - \frac{2\delta_6}{v} + \frac{2\delta_6}{v} M_x - \frac{\psi_{116}}{8v} (\eta_1^2 + \eta_2^2) - \frac{\psi_{136}}{4v} \eta_1 \eta_3,\]

\[-\frac{\psi_{222}}{8v}(\eta_1^2 + \eta_2^2) - \frac{\psi_{244}}{4v} \eta_2 \eta_4 - \frac{\psi_{125}}{4v} (\eta_1 \eta_2 + \eta_3 \eta_4) - \frac{\psi_{145}}{4v} (\eta_1 \eta_4 + \eta_2 \eta_3). \tag{3.2}\]

Here, such a notation is used

\[M_x = 2a^2 \cosh n_3 + 2a^2 \cosh n_4 + a \cosh n_5 + a \cosh n_6 + a \cosh n_7 + a \cosh n_8.\]

Differentiating (3.1) over the fields \(E_i,\) we get the expressions for polarizations \(P_i:\)

\[P_1 = e_1^0 e_4 + e_1^0 e_6 + \chi_{11}^{E0} E_1 + \chi_{31}^{E0} E_3 + \frac{1}{2v} [\mu_{13}^l (\eta_1 - \eta_3) - \mu_{12}^l (\eta_1 - \eta_2)],\]

\[P_2 = e_1^0 e_1 + e_2^0 e_2 + e_3^0 e_3 + e_5^0 e_5 + \frac{1}{2v} [\mu_{13}^l (\eta_1 - \eta_3) - \mu_{12}^l (\eta_1 - \eta_2)],\]

\[P_3 = e_1^0 e_4 + e_6^0 e_6 + \chi_{33}^{E0} E_1 + \chi_{31}^{E0} E_3 + \frac{1}{2v} [\mu_{13}^l (\eta_1 - \eta_3) + \mu_{12}^l (\eta_1 - \eta_2)]. \tag{3.3}\]

Static isothermic dielectric susceptibilities of the mechanically clamped crystal GPI are given by:

\[\chi_{11,33}^{E} = \chi_{11,33}^{E0} + \frac{\beta}{2\nu\Delta_{1,3}} \left( (\mu_{13}^x) \Delta_{1,3} (\lambda_{1,3} \lambda_{1,2} - \lambda_3^2) \psi_{24}^+ \right) + (\mu_{13}^x) \Delta_{1,3} (\lambda_{1,3} \lambda_{1,2} - \lambda_3^2) \psi_{13}^+\]

\[\Delta_{1,3} = \frac{\beta}{2\nu\Delta_{1,2}} \left( (\mu_{13}^x) \Delta_{1,3} (\lambda_{1,3} \lambda_{1,2} - \lambda_3^2) \psi_{24}^+ \right) + (\mu_{13}^x) \Delta_{1,3} (\lambda_{1,3} \lambda_{1,2} - \lambda_3^2) \psi_{13}^+\]

\[\chi_{22}^{E} = \chi_{22}^{E0} + \frac{\beta}{2\nu\Delta_{2}} \left( (\mu_{13}^x) \Delta_{1,3} (\lambda_{1,3} \lambda_{1,2} - \lambda_3^2) \psi_{24}^+ \right) + (\mu_{13}^x) \Delta_{1,3} (\lambda_{1,3} \lambda_{1,2} - \lambda_3^2) \psi_{13}^+\]

\[\Delta_{2} = \frac{\beta}{2\nu\Delta_{2}} \left( (\mu_{13}^x) \Delta_{1,3} (\lambda_{1,3} \lambda_{1,2} - \lambda_3^2) \psi_{24}^+ \right) + (\mu_{13}^x) \Delta_{1,3} (\lambda_{1,3} \lambda_{1,2} - \lambda_3^2) \psi_{13}^+. \tag{3.5}\]
Here, the following notations are used:

\[ \mathcal{D} = \cosh(y_{13} + y_{24}) + a^2 \cosh(y_{13} - y_{24}) + 2a \cosh y_{13} + 2a \cosh y_{24} + a^2 + 1, \]

\[ \phi_{13}^\pm = \frac{1}{1 - \eta_{13}^2} + \beta \nu_{13}^\pm, \quad \phi_{24}^\pm = \frac{1}{1 - \eta_{24}^2} + \beta \nu_{24}^\pm; \]

\[ \nu_1^{0\pm} = \nu_1^{0\pm} + \left( \sum_{i=1}^{3} \psi_{i1}^0 \epsilon_i + \sum_{j=4}^{6} \psi_{j1}^0 \epsilon_j \right), \quad (l = 1, 2, 3), \quad \nu_2^{0\pm} = \frac{1}{4} (\nu_{12}^0 + \nu_{14}^0); \quad \nu_3^{0\pm} = \frac{1}{4} (\nu_{22}^0 + \nu_{24}^0); \quad \nu_4^{0\pm} = \frac{1}{4} (\nu_{22}^0 + \nu_{24}^0). \]

\[ \lambda_{13} = 1 + 2a \cosh y_{13}, \quad \lambda_{24} = 1 + a^2 + 2a \cosh y_{24}, \quad \lambda = 1 - a^2, \]

\[ \kappa_{13} = \cosh(y_{13} + y_{24}) + a^2 \cosh(y_{13} - y_{24}) + 2a \cosh y_{13} - \eta_{13}^2 \mathcal{D}, \]

\[ \kappa_{24} = \cosh(y_{13} + y_{24}) + a^2 \cosh(y_{13} - y_{24}) + 2a \cosh y_{24} - \eta_{24}^2 \mathcal{D}, \]

\[ \kappa = \cosh(y_{13} + y_{24}) - a^2 \cosh(y_{13} - y_{24}) - \eta_{13} \eta_{24} \mathcal{D}. \]

Based on (3.2), we have obtained coefficients for isothermic piezoelectric stress \( e_{2l} \) (\( l = 1, 2, 3 \)) of GPI:

\[
e_{2l} = \left[ \frac{\partial \mathcal{P}_2}{\partial E_1} \right]_{E_2} = e_{2l}^0 + \frac{\mu_{13}^\pm \beta}{v \Delta_2} \left[ (\psi_{11} \eta_{13} + \psi_{21} \eta_{24}) \tau_1^{\psi} + (\psi_{21} \eta_{13} + \psi_{31} \eta_{24}) \tau_2^{\psi} - 2\delta_1 \tau_1^\delta \right]
- \frac{\mu_2^\pm \beta}{v \Delta_2} \left[ (\psi_{11} \eta_{13} + \psi_{21} \eta_{24}) \tau_2^{\psi} + (\psi_{21} \eta_{13} + \psi_{31} \eta_{24}) \tau_3^{\psi} - 2\delta_2 \tau_2^\delta \right],
\]

where

\[
\tau_1^{\psi} = \mathcal{D} \kappa_{13} - (\kappa_{13} \kappa_{24} - \kappa^2) \phi_{24}^{\pm}, \quad \tau_2^{\psi} = \mathcal{D} \kappa + \kappa_{13} \kappa_{24} - \kappa^2 \phi_{13}^{\pm}, \quad \tau_3^{\psi} = \mathcal{D} \kappa_{24} - (\kappa_{13} \kappa_{24} - \kappa^2) \phi_{13}^{\pm},
\]

\[
\tau_1^\delta = \mathcal{D} \kappa_{13} + (\kappa_{13} \kappa_{24} - \kappa^2) \beta \nu_{13}^{\pm}, \quad \tau_2^\delta = \mathcal{D} \kappa + (\kappa_{13} \kappa_{24} - \kappa^2) \beta \nu_{13}^{\pm}, \quad \tau_3^\delta = \mathcal{D} \kappa_{24} - (\kappa_{13} \kappa_{24} - \kappa^2) \beta \nu_{13}^{\pm},
\]

\[
\rho_{13} = [a^2 \sinh(y_{13} - y_{24}) + a \sinh y_{13}] - \eta_{13} M,
\]

\[
\rho_{24} = [-a^2 \sinh(y_{13} - y_{24}) + a \sinh y_{24}] - \eta_{24} M,
\]

\[
M = a^2 \cosh(y_{13} - y_{24}) + a \cosh y_{13} + a \cosh y_{24} + a^2.
\]

Proton contribution to elastic constants of GPI is found by differentiating (3.2) over strains at a constant field:

\[
c_{ij}^E = \left[ \frac{\partial \sigma_{ij}}{\partial E_1} \right]_{E_2} = c_{ij}^{E0} - \frac{2 \beta}{v \Delta_2} \left[ (\psi_{11} \eta_{13} + \psi_{21} \eta_{24}) (\psi_{1j} \eta_{13} + \psi_{2j} \eta_{24}) \tau_1^{\psi} \right.
+ \left[ (\psi_{11} \eta_{13} + \psi_{21} \eta_{24}) (\psi_{2i} \eta_{13} + \psi_{3i} \eta_{24}) + (\psi_{2i} \eta_{13} + \psi_{3i} \eta_{24}) (\psi_{1j} \eta_{13} + \psi_{2j} \eta_{24}) \right] \tau_2^{\psi}
+ \left. (\psi_{21} \eta_{13} + \psi_{31} \eta_{24}) (\psi_{1j} \eta_{13} + \psi_{2j} \eta_{24}) \tau_3^{\psi} \right]
+ \frac{4 \beta \delta_1}{v \Delta_2} \left[ (\psi_{11} \eta_{13} + \psi_{21} \eta_{24}) \tau_1^\delta + (\psi_{21} \eta_{13} + \psi_{31} \eta_{24}) \tau_2^\delta \right]
+ \frac{4 \beta \delta_2}{v \Delta_2} \left[ (\psi_{11} \eta_{13} + \psi_{21} \eta_{24}) \tau_1^\delta + (\psi_{21} \eta_{13} + \psi_{31} \eta_{24}) \tau_2^\delta \right]
- \frac{8 \beta \delta_1 \delta_2}{v \Delta_2} \left[ (\rho_{13} \phi_{13} + \rho_{24} \phi_{24}) \tau_1^\delta + (\rho_{24} \phi_{24} + \rho_{13} \phi_{13}) \tau_2^\delta \right]
- \frac{4 \beta \delta_1 \delta_2}{v \Delta_2} \left[ 2a^2 \cosh(y_{13} - y_{24}) + a \cosh y_{13} + a \cosh y_{24} + 2a^2 \mathcal{D} - 2M^2 \right].
\]

Other dielectric, piezoelectric and elastic characteristics of GPI can be found using the expressions established above. In particular, the matrix of isothermal elastic compliance at a constant field \( c_{ij}^E \), which
The effect of hydrostatic pressure is reciprocal to matrix of elastic constants $c_{ij}^E$:

$$\hat{C}^E = \begin{pmatrix} c_{11}^E & c_{12}^E & c_{13}^E & c_{15}^E \\ c_{12}^E & c_{22}^E & c_{23}^E & c_{25}^E \\ c_{13}^E & c_{23}^E & c_{33}^E & c_{35}^E \\ c_{15}^E & c_{25}^E & c_{35}^E & c_{55}^E \end{pmatrix}, \quad \hat{S}^E = (\hat{C}^E)^{-1},$$

isothermal coefficients of piezoelectric strain

$$d_{2l} = \sum_{l'} s_{ll'}^E e_{2l'}, \quad (l, l' = 1, 2, 3, 5), \quad (3.8)$$

isothermal dielectric susceptibility of a mechanically free crystal

$$\chi_2'' = \chi_2'' + \sum_l c_{2l} d_{2l}, \quad (3.9)$$

isothermal constants of piezoelectric strain

$$h_{2l} = \frac{e_{2l}}{\chi_2''}, \quad (3.10)$$

isothermal constants of piezoelectric strain

$$g_{2l} = \frac{d_{2l}}{\chi_2''}. \quad (3.11)$$

Let us consider thermal characteristics of GPI crystal. Molar entropy of the proton subsystem:

$$S = \frac{R}{4} \left[ -2 \ln 2 + \ln(1 - \eta_{13}) + \ln(1 - \eta_{24}) + 2 \ln D - 2(\beta v_1^2 \eta_{13} + \beta v_2^2 \eta_{24}) \eta_{13} \\
- 2(\beta v_3^2 \eta_{13} + \beta v_4^2 \eta_{24}) \eta_{24} + \frac{4w}{T D} M \right], \quad (3.12)$$

here, $R$ is the gas constant.

The molar heat capacity of a proton subsystem of GPI crystals can be found numerically from the entropy (3.12):

$$\Delta C'' = T \left( \frac{\partial S}{\partial T} \right)_{\sigma}. \quad (3.13)$$

4. **Comparison of the results of numerical calculations with the experimental data**

To calculate the temperature dependences of dielectric and piezoelectric characteristics of GPI, which are calculated below, we need to set certain values of the following parameters:

- parameter of short-range interactions $w^0$;
- parameters of long-range interactions $\nu_0^{f+}$ ($f = 1, 2, 3$);
- deformational potentials $\delta_i, \psi_i^f$ ($f = 1, 2, 3; i = 1, \ldots, 6$);
- effective dipole moments $\mu_{13}^f; \mu_{24}^f; \mu_{13}^f; \mu_{24}^f; \mu_{13}; \mu_{24}$;
- "seed" dielectric susceptibilities $\chi_0^{0 i}, \chi_0^{0 i} (i = 1, 2, 3)$;
The volume of a primitive cell of GPI is the $v_{0.0} = 0.601 \cdot 10^{-21} \text{cm}^3$, $v_{0.808} = 0.6114 \cdot 10^{-21} \text{cm}^3$.

Figure [2] shows the dependences of the phase transition point $T_c$ of $\text{GPI}_{1-x} \text{DGPI}_x$ on the deuteron concentration $x$, which are obtained in [12] and [13], and do not agree with each other. The concentration dependence of $T_c$ is approximated by the curve $T_c(x) = 225(1 + 0.382x + 0.193x^2)$ K, which is a theoretical curve of $T_c(x)$. Since the papers [12, 14] also present a concentration dependence of $T_c$, which are obtained in [12] and [13] and do not agree with each other. The concentration dependence of $T_c(x)$ is presented in [12].

In [9], the temperature $T_c = 322.85$ K is stated, that corresponds to the concentration $x = 0.808$ in our model. The values of the given theory parameters are determined at the study of the static properties of [6]. The optimal values of long-range interactions $\nu f_{ij}$ we use $\nu f_1 = \nu f_3 = 2.643$ K, $\nu f_2 = \nu f_5 = 0.2$ K, where $\nu f_{ij}$ do not depend on concentration $x$.

The calculated parameters $\nu f_{ij}$ of the $\text{GPI}_{1-x} \text{DGPI}_x$ crystals are $\nu f_0/k_B = 820$ K at $x = 0$ and 1323.6 K at $x = 0.808$.

The optimal values of the deformational potentials $\delta_i$ at $x = 0$ are $\delta_1 = 500$ K, $\delta_2 = 600$ K, $\delta_3 = 500$ K, $\delta_4$ = 150 K, $\delta_5$ = 100 K, $\delta_6$ = 150 K, $\delta_i = \delta_i/k_B$. At $x = 0.808$, they are $\delta_i(0.808) = 0.337\delta_i(0)$.

The optimal values of the $\psi^\pm_{f_0}$ are as follows: $\psi^+_{f_1} = 87.9 K$, $\psi^+_{f_2} = 238.0 K$, $\psi^+_{f_3} = 103.8 K$, $\psi^+_{f_4} = 149.1 K$, $\psi^+_{f_5} = 21.3 K$, $\psi^+_{f_6} = 143.8 K$, $\psi^-_{f_1} = 0 K$, where $\psi^\pm_{f_0} = \psi^\pm_{f_0}/k_B$. At $x = 0.808$, they are $\psi^\pm_{f_0}(0.808) = 0.337\psi^\pm_{f_0}(0)$.

The effective dipole moments in the paraelectric phase are equal to $\mu_{13} = (0.4, 4.02, 4.3) \cdot 10^{-18} \text{esu-cm}$, $\mu_{24} = (2.3, -3.0, 2.2) \cdot 10^{-18} \text{esu-cm}$ and do not depend on deuteration. In the ferroelectric phase, the $y$-component of the first dipole moment increases on deuteration as $\mu_{13}^{\text{ferro}}(x = 0.808) = 4.01 \cdot 10^{-18} \text{esu-cm}$.

“Seed” coefficients of piezoelectric stress, dielectric susceptibilities and elastic constants

| $c_{21}^0 = c_{22}^0 = c_{23}^0 = c_{45}^0 = c_{14}^0 = c_{16}^0 = c_{36}^0 = 0.0$ | $\text{esu/cm}$ |
| $\chi_{31}^{E_{20}} = 0.1$, $\chi_{22}^{20}(x = 0.0) = 0.403$, $\chi_{33}^{20}(x = 0.808) = 2.2$, $\chi_{33}^{E_{30}} = 0.5$, $\chi_{31}^{E_{30}} = 0.0$ | $\text{esu/cm}$ |
| $c_{11}^{O} = 26.91 \cdot 10^{10}$ | $\text{dyne/cm}^2$, $c_{12}^{O} = 14.5 \cdot 10^{10}$ | $\text{dyne/cm}^2$, $c_{13}^{O} = 11.64 \cdot 10^{10}$ | $\text{dyne/cm}^2$, $c_{35}^{O} = 3.91 \cdot 10^{10}$ | $\text{dyne/cm}^2$ |
| $c_{22}^{O} = [64.99 - 0.04(T - T_c)] \cdot 10^{10}$ | $\text{dyne/cm}^2$, $c_{23}^{O} = 20.38 \cdot 10^{10}$ | $\text{dyne/cm}^2$, $c_{24}^{O} = 5.64 \cdot 10^{10}$ | $\text{dyne/cm}^2$ |
| $c_{33}^{E_{20}} = 24.41 \cdot 10^{10}$ | $\text{dyne/cm}^2$, $c_{35}^{E_{20}} = -2.84 \cdot 10^{10}$ | $\text{dyne/cm}^2$, $c_{35}^{E_{30}} = 8.54 \cdot 10^{10}$ | $\text{dyne/cm}^2$, $c_{44}^{E_{40}} = 15.31 \cdot 10^{10}$ | $\text{dyne/cm}^2$, $c_{46}^{E_{40}} = -1.1 \cdot 10^{10}$ | $\text{dyne/cm}^2$ |

Let us focus on the obtained results and analyse the effect of hydrostatic pressure $p = -\sigma_1 = -\sigma_2 = -\sigma_3$ on the thermodynamic characteristics of $\text{GPI}_{1-x} \text{DGPI}_x$.

The pressure dependences of temperature $T_c$ of $\text{GPI}_{1-x} \text{DGPI}_x$ at $x = 0.0$ and $x = 0.808$ are presented in figure [3].
The effect of hydrostatic pressure

Figure 3. The pressure dependence of the temperature $T_c$ of GPI$_{1-x}$DGPI$_x$ at different $x$: 0.00 — 1; ● [8]; 0.808 — 2; ▲ [9].

Figure 4. Temperature dependences of the strains of GPI: $\varepsilon_1$ — 1, $\varepsilon_2$ — 2, $\varepsilon_3$ — 3, $\varepsilon_4$ — 4, $\varepsilon_5$ — 5 and $\varepsilon_6$ — 6 at different values of pressure $p$ ($10^9$ dyn/cm$^2$): 0.0 — a); 1.7 — b); 3.0 — c).

The calculated dependences $T_c(p)$ at the established theory parameters quantitatively well describe the experimental data [8, 9]. Applying a hydrostatic pressure to the crystals decreases their transition temperature $T_c(p)$. The rate of decreasing of transition temperature with an increase of pressure at $x = 0.00$ is $dT_c/dp = -11$ K/kbar [8] up to the pressure $p = 3.510^9$ dyn/cm$^2$ and the corresponding temperature $T_c = 180$ K, and at higher pressures $T_c$ decreases nonlinearly; at $x = 0.808$, the rate of a decrease is $dT_c/dp = -5.0$ K/kbar [9].

Temperature dependences of the strains $\varepsilon_i, \varepsilon_j$ of GPI crystal at different values of hydrostatic pressure $p$ are presented in figure 4. The strains $\varepsilon_1, \varepsilon_3$ and $\varepsilon_5$ are practically independent of temperature in both phases, but the strains $\varepsilon_2, \varepsilon_4$ and $\varepsilon_6$ slightly decrease with temperature in the ferroelectric phase and are almost independent of temperature in the paraelectric phase.

Pressure $p$ leads to a significant increase of absolute values of the strains $\varepsilon_1$ and $\varepsilon_3$, but the other strains depend on $p$ very little (figure 5).

In figure 5(a), the temperature dependences of spontaneous polarization of GPI crystal are presented, in figure 6(b) — for GPI$_{0.192}$DGPI$_{0.808}$ at different values of hydrostatic pressure $p$; in figure 7 — the temperature-pressure dependences of spontaneous polarization of GPI crystal. An increase of $p$ leads to the change of the phase transition order.

At low pressures, the phase transition is a transition of the second order, but at high pressures, starting with $p \approx 4$ dyn/cm$^2$ (tricritical point in figure 5), it becomes a transition of the first order. In the case of crystal GPI$_{0.192}$DGPI$_{0.808}$, even at high pressures, there is a second order phase transition. An increase of $p$ leads to a slight decrease of the polarization $P_s$ in the whole temperature range.

Temperature dependences of the longitudinal static dielectric permittivity of GPI and GPI$_{0.192}$DGPI$_{0.808}$ crystals at different values of pressure are presented in figure 8(a) and 8(b), respectively. The results of theoretical calculations quantitatively well agree with experimental data [8, 9].
Figure 5. The dependences of the strains of GPI on the pressure at the temperature $T = 205$ K: $\varepsilon_1 = 1$, $\varepsilon_2 = 2$, $\varepsilon_3 = 3$, $\varepsilon_4 = 4$, $\varepsilon_5 = 5$, $\varepsilon_6 = 6$; and at $T = 245$ K: $\varepsilon_1 = 1'$, $\varepsilon_2 = 2'$, $\varepsilon_3 = 3'$, $\varepsilon_4 = 4'$, $\varepsilon_5 = 5'$, $\varepsilon_6 = 6'$.

Figure 6. Temperature dependences of the spontaneous polarization of GPI (a) at different values of hydrostatic pressure $p$ (10$^9$ dyn/cm$^2$): 0.0 — 1, $\circ$ [14], $\triangle$ [15], $\square$ [16], $\triangledown$ [17]; 0.9 — 2; 1.7 — 3; 3.0 — 4; 4.0 — 5; of GPI$_{0.192}$DGPI$_{0.808}$ (b) at different values of hydrostatic pressure $p$ (10$^9$ dyn/cm$^2$): 0.0 — 1; 2.0 — 2; 3.0 — 3; 4.0 — 4; 5.0 — 5; 6.0 — 6; 7.0 — 7.

Figure 7. Temperature-pressure dependence of the spontaneous polarization of GPI.

in the paraelectric phase at small values of hydrostatic pressure $p$. Disagreement in ferroelectric phase for $\varepsilon_{22}^C$ is connected with domain reorientation contribution to permittivity, which is not taken into account in our theory.

The dependences of dielectric permittivity $\varepsilon_{22}$ of GPI crystal on hydrostatic pressure at different values of temperature are presented in figure 9. In the paraelectric phase, $\varepsilon_{22}$ decreases with an increase
The effect of hydrostatic pressure

Figure 8. Temperature dependences of the static dielectric permittivity $\varepsilon_{22}$ of GPI crystal (a) at different values of hydrostatic pressure $p$, ($10^9$ dyn/cm$^2$): 0.0 — 1, $\circ$ [12], $\triangledown$ [17], $\triangle$ [15], $\square$ [14], $\circ$ [8]; 0.6 — 2, $\circ$ [8]; 0.9 — 3, $\circ$ [8]; 1.7 — 4, $\circ$ [8]; 3.0 — 5, $\circ$ [8]; and of GPl$_{0.193}$DGPl$_{0.808}$ (b) at different values of hydrostatic pressure $p$, ($10^9$ dyn/cm$^2$): 0.0 — 1, $\circ$ [9]; 2.0 — 2, $\triangledown$ [9]; 3.0 — 3, $\triangle$ [9]; 4.0 — 4, $\blacktriangle$ [9]; 5.0 — 5, $\blacktriangledown$ [9]; 6.0 — 6, $\blacksquare$ [9]; 8.0 — 7 $\blacklozenge$ [9].

Figure 9. Pressure dependences of the dielectric permittivity $\varepsilon_{22}$ of GPI crystal at different values of temperature $T$, K: 245 — 2'; 235 — 1'; 215 — 1; 191 — 2; 159 — 3.

Figure 10. Temperature dependences of the dielectric permittivities $\varepsilon_{11}$ and $\varepsilon_{33}$ of GPI crystal at different values of hydrostatic pressure $p$, ($10^9$ dyn/cm$^2$): 0.0 — 1, $\triangle$ [15]; 1.7 — 2; 3.0 — 3.

of pressure $p$, but in ferroelectric phase, permittivity $\varepsilon_{22}$ increases up to the phase transition pressure, and then decreases.

Temperature dependences of transverse static dielectric permittivities of GPI crystal at different values of hydrostatic pressure are presented in figure 10 and pressure dependences of dielectric permittivity $\varepsilon_{11}$ and $\varepsilon_{33}$ at different values of temperature — in figure 11. Notations 1', 2' in figure 11 are used for the curves in a paraelectric phase. The values of $\varepsilon_{11}$ and $\varepsilon_{33}$ increase with an increase of pressure, and maximum values shift to lower temperatures. In the paraelectric phase, $\varepsilon_{11}$ and $\varepsilon_{33}$ decrease with
an increase of pressure \( p \), but in ferroelectric phase, transverse permittivities increase up to the phase transition pressure, and then decrease.

Temperature dependences of the inverse dielectric permittivity \((\varepsilon^{-1})\) of GPI and GPI\(_{0.192}\)DGPI\(_{0.808}\) crystals at different values of pressure \( p \) are presented in figure 12(a) and 12(b), respectively. The results of theoretical calculations quantitatively well agree with experimental data \[8, 9\] in the paraelectric phase.

**Figure 12.** Temperature dependences of the inverse dielectric permittivity \((\varepsilon^{-1})\) of GPI crystal (a) at different values of hydrostatic pressure \( p \), \( (10^9 \text{ dyn/cm}^2) \): 0.0 — 1, \( \blacklozenge \) \[17\], \( \blacklozenge \) \[18\]; 0.6 — 2, \( \bullet \) \[8\]; 0.9 — 3, \( \bullet \) \[8\]; 1.7 — 4, \( \blacklozenge \) \[8\]; 3.0 — 5, \( \bullet \) \[8\]; 4.0 — 6; and GPI\(_{0.192}\)DGPI\(_{0.808}\) (b) at different values of hydrostatic pressure \( p \), \( (10^9 \text{ dyn/cm}^2) \): 0.0 — 1, \( \blacklozenge \) \[9\], 2.0 — 2, \( \blacklozenge \) \[9\], 4.0 — 3, \( \bullet \) \[9\], 6.0 — 4, \( \bullet \) \[9\].

**Figure 13.** Temperature dependences of the coefficients of piezoelectric stress \( e_{2i} \), \( e_{25} \) and strain \( d_{2i} \), \( d_{25} \): 1 — \( e_{21} \), \( d_{21} \) \[16\], 2 — \( e_{22} \), \( d_{22} \), 3 — \( e_{23} \), \( d_{23} \) \[16\], 4 — \( e_{25} \), \( d_{25} \) of GPI crystal at different values of pressure \( p \), \( (10^9 \text{ dyn/cm}^2) \): 0.0 — a); 1.7 — b); 3.0 — c).
The effect of hydrostatic pressure

Figure 14. Temperature dependences of the constants of piezoelectric stress \( h_{2i}, h_{25} \) and strain \( g_{2i}, g_{25} \):
1 — \( h_{21}, g_{21} \), 2 — \( h_{22}, g_{22} \), 3 — \( h_{23}, g_{23} \), 4 — \( h_{25}, g_{25} \) of GPI crystal at different values of pressure \( p \), (10^9 dyn/cm^2): 0 — a); 1.7 — b); 3 — c).

Figure 15. Temperature dependences of \( \Delta C_p \) at different values of hydrostatic pressure \( p \), (10^9 dyn/cm^2): 0.0 — 1; 0.9 — 2; 1.7 — 3; 3.0 — 4.

at small values of hydrostatic pressure \( p \). As was written above, disagreement in ferroelectric phase for \((e_{22})^{-1}\) is connected with the domain reorientation contribution to permittivity, which is not taken into account in our theory.

Temperature dependences of the coefficients of piezoelectric stress \( e_{2i}, e_{25} \) and strain \( d_{2i}, d_{25} \) of GPI crystal at different values of pressure \( p \) are presented in figure 13 and the temperature dependences of the constants of piezoelectric stress \( h_{2i}, h_{25} \) and strain \( g_{2i}, g_{25} \) — in figure 14.

Hydrostatic pressure practically does not influence the magnitude of the \( e_{3i}, e_{35} \) and \( d_{3i}, d_{35} \), but just shifts their maxima to lower temperatures. An increase of the pressure \( p \) leads to an increase of magnitude of the piezoelectric coefficients \( h_{2i}, h_{25} \) and \( g_{2i}, g_{25} \).

Figure 15 shows temperature dependences of pseudospin contribution on heat capacity \( \Delta C_p \). In the paraelectric phase, the value of \( \Delta C_p \) practically does not change with an increase of pressure \( p \), but in the ferroelectric phase, the value of \( \Delta C_p \) increases with pressure.

5. Conclusions

In this paper, the effect of hydrostatic pressure on phase transition and physical characteristics of the GPI_{1-x}DGPI_x crystals is studied in the frames of two-particle cluster approximation within the modified proton ordering model of GPI type quasione-dimensional ferroelectrics with hydrogen bonds, which takes into account the piezoelectric coupling with the strains \( e_i, e_j \) in the ferroelectric phase. We have determined how the strains \( e_i, e_j \) are changed under hydrostatic pressure. These changes of the strains lead to a pressure dependence of the parameters of interactions and, consequently, to a pressure dependence of the transition temperature and other characteristics of these crystals. At low pressures, the phase transition in our model of GPI is a transition of the second order, but at high pressures, starting from
some critical pressure, it becomes a transition of the first order in the nondeuterated crystal. In the case of deuterated crystal, even at high pressures, there is the second order phase transition. The pressure effect in the nondeuterated crystal is much stronger than in a deuterated crystal. A good quantitative description of the observed pressure and temperature dependences of the considered characteristics has been obtained in paraelectric phase at small values of pressure at the proper choice of the model parameters.

References

1. Stasyuk I.V., Levitskii R.R., Moina A.P., Slivka A.G., Velychko O.V., Field and Deformational Effects in Complex Ferroelectric Compounds, Grazhda, Uzhgorod, 2009 (in Ukrainian).
2. Levitskii R.R., Zachek I.R., Vdovych A.S., Stasyuk I.V., J. Phys. Stud., 2013, 17, 4703 (in Ukrainian).
3. Levitskii R.R., Zachek I.R., Vdovych A.S., J. Phys. Stud., 2012, 16, 4702 (in Ukrainian).
4. Zachek I., Levitskii R., Vdovych A., Ferroelectrics, 2013, 444, 67, doi:10.1080/00150193.2013.786481.
5. Zachek I.R., Levitskii R.R., Vdovych A.S., J. Phys. Stud., 2015, 19, 3703 (in Ukrainian).
6. Zachek I.R., Shchur Ya., Levitskii R.R., Vdovych A.S., Physica B, 2017, 520, 164, doi:10.1016/j.physb.2017.06.015.
7. Zachek I.R., Levitskii R.R., Vdovych A.S., Stasyuk I.V., Condens. Matter Phys., 2017, 20, 23706, doi:10.5488/CMP.20.23706.
8. Yasuda N., Sakurai T., Czapla Z., J. Phys.: Condens. Matter, 1997, 9, L347, doi:10.1088/0953-8984/9/25/003.
9. Yasuda N., Kaneda A., Czapla Z., J. Phys.: Condens. Matter, 1997, 9, L447, doi:10.1088/0953-8984/9/33/002.
10. Stasyuk I., Czapla Z., Dacko S., Velychko O., J. Phys.: Condens. Matter, 2004, 16, 1963, doi:10.1088/0953-8984/16/12/006.
11. Balashova E.V., Lemanov V.V., Pankova G.A., Fiz. Tverd. Tela, 2007, 49, 331 (in Russian).
12. Nayeem J., Wakahayashi H., Kikutu T., Yamazaki T., Nakatani N., Ferroelectrics, 2002, 269, 153, doi:10.1080/71716051.
13. Shikanai F., Yamasaki M., Komukae M., Osaka T., J. Phys. Soc. Japan., 2003, 72, 325, doi:10.1143/JPSJ.72.325.
14. Nayeem J., Kikutu T., Nakatani N., Matsui F., Takeda S.-N., Hattori K., Daimon H., Ferroelectrics, 2006, 332, 13, doi:10.1080/00150190500309064.
15. Dacko S., Czapla Z., Baran J., Drozd M., Phys. Lett. A, 1996, 223, 217, doi:10.1016/S0375-9601(96)00698-6.
16. Wiesner M., Phys. Status Solidi B, 2003, 238, 68, doi:10.1002/pssb.200301750.
17. Tchukvinskyi R., Cach R., Czapla Z., Dacko S., Phys. Status Solidi A, 1998, 165, 309, doi:10.1002/(SICI)1521-396X(199801)165:1<309::AID-PSSA309>3.0.CO;2-U.
18. Baran J., Bator G., Jakubas R., Slecz M., J. Phys.: Condens. Matter, 1996, 8, 10647, doi:10.1088/0953-8984/8/49/049.

Вплив гідростатичного тиску на термодинамічні характеристики сегнетоактивних матеріалів типу \( \text{NH}_3\text{CH}_2\text{COOH}\cdot\text{H}_2\text{PO}_3 \)

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Для дослідження ефектів, що виникають під дією зовнішніх тиску, використано модифіковану модель \( \text{NH}_3\text{CH}_2\text{COOH}\cdot\text{H}_2\text{PO}_3 \) (GPI) шляхом врахування п'єзеелектричного зв'язку структурних елементів, які впорядковуються, деформації \( \varepsilon_i, \varepsilon_j \). В наближенні двочастинкового кластера розраховано компоненти вектора поляризації та тензора статичної діелектричної проникності механічно затиснутого і вільного кристалів, їх п'єзеелектричні та теплові характеристики. Дослідження вплив гідростатичного тиску на фазовий перехід та фізичні характеристики кристалу. Отримано добрі кількісні опис експериментальних даних для цих кристалів.

Ключові слова: сегнетоелектрики, фазовий перехід, діелектрична проникність, п'єзеелектричні коефіцієнти, гідростатичний тиск.