

The effect of hydrostatic pressure on thermodynamic characteristics of $\text{NH}_3\text{CH}_2\text{COOH}\cdot\text{H}_2\text{PO}_3$ type ferroelectric materials

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The model of $\text{NH}_3\text{CH}_2\text{COOH}\cdot\text{H}_2\text{PO}_3$, modified by taking into account the piezoelectric coupling between the ordering structure elements and the strains ε_i , ε_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_2PO_4 family was made in [1, 2], for quasio-ne-dimensional CsH_2PO_4 type ferroelectrics — in [3], for monoclinic RbD_2PO_4 — in [4], for RbH_2SO_4 crystal — in [5].

In [6], on the basis of the proposed model of deformed $\text{NH}_3\text{CH}_2\text{COOH}\cdot\text{H}_2\text{PO}_3$ (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 ε_{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 [6, 7] (figure 1). Dipole moments \mathbf{d}_{qf} (q is the number of a primitive cell, $f = 1, \dots, 4$) are ascribed to the protons on the bonds. In the ferroelectric phase, the dipole moments compensate each other (\mathbf{d}_{q1} with \mathbf{d}_{q3} , \mathbf{d}_{q2} with \mathbf{d}_{q4}) 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}_{qf} 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_{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}_{short} and long-range \hat{H}_{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 [6],

$$\hat{H} = NU_{\text{seed}} + \hat{H}_{\text{short}} + \hat{H}_{\text{MF}}, \quad (2.1)$$

where N is the total number of primitive cells.

The U_{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 ε_i and ε_j ($j = i + 3$):

$$\begin{aligned} U_{\text{seed}} = v \left[\frac{1}{2} \sum_{i,i'=1}^3 c_{ii'}^{E0}(T) \varepsilon_i \varepsilon_{i'} + \frac{1}{2} \sum_{j=4}^6 c_{jj}^{E0}(T) \varepsilon_j^2 + \sum_{i=1}^3 c_{i5}^{E0}(T) \varepsilon_i \varepsilon_5 + c_{46}^{E0}(T) \varepsilon_4 \varepsilon_6 \right. \\ \left. - \sum_{i=1}^3 e_{2i}^0 \varepsilon_i E_2 - e_{25}^0 \varepsilon_5 E_2 - e_{14}^0 \varepsilon_4 E_1 - e_{16}^0 \varepsilon_6 E_1 - e_{34}^0 \varepsilon_4 E_3 - e_{36}^0 \varepsilon_6 E_3 \right. \\ \left. - \frac{1}{2} \chi_{11}^{\varepsilon 0} E_1^2 - \frac{1}{2} \chi_{22}^{\varepsilon 0} E_2^2 - \frac{1}{2} \chi_{33}^{\varepsilon 0} E_3^2 - \chi_{31}^{\varepsilon 0} E_3 E_1 \right]. \quad (2.2) \end{aligned}$$

Here, parameters $c_{ii'}^{E0}(T)$, $c_{i5}^{E0}(T)$, $c_{46}^{E0}(T)$, $c_{jj}^{E0}(T)$, e_{ii}^0 , e_{ij}^0 , $\chi_{ii}^{\varepsilon 0}$, $\chi_{31}^{\varepsilon 0}$ ($i' = 1, 2, 3$) correspond to the so-called “seed” elastic constants, piezoelectric stresses and dielectric susceptibilities, respectively, v is the volume of a primitive cell.

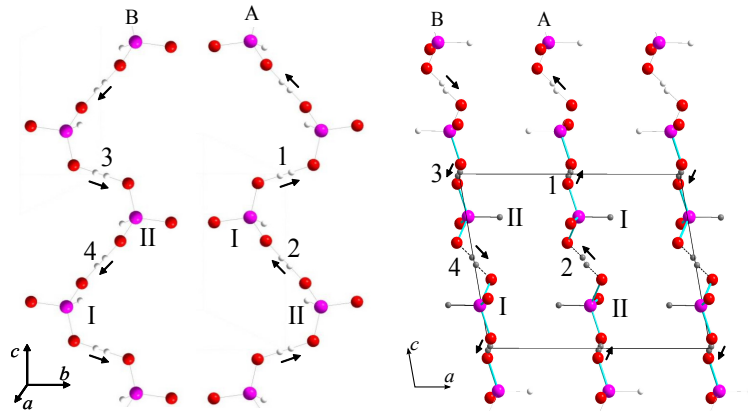


Figure 1. (Color online) Orientations of vectors \mathbf{d}_{qf} in the primitive cell in the ferroelectric phase [6, 7].

The Hamiltonian of short-range interactions

$$\hat{H}_{\text{short}} = -2w \sum_{qq'} \left(\frac{\sigma_{q1} \sigma_{q2}}{2} + \frac{\sigma_{q3} \sigma_{q4}}{2} \right) (\delta_{\mathbf{R}_q \mathbf{R}_{q'}} + \delta_{\mathbf{R}_q + \mathbf{R}_c, \mathbf{R}_{q'}}). \quad (2.3)$$

In (2.3) σ_{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’’, \mathbf{R}_c 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 $\varepsilon_i, \varepsilon_j$:

$$w = w^0 + \sum_{i=1}^3 \delta_i \varepsilon_i + \sum_{j=4}^6 \delta_j \varepsilon_j. \quad (2.4)$$

Hamiltonian \hat{H}_{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 $J_{ff'} = \sum_{qq'} J_{ff'}(qq')$ at $\mathbf{k} = 0$ are linearly expanded over the strains $\varepsilon_i, \varepsilon_j$; and can be written as:

$$\hat{H}_{\text{MF}} = NH^0 + \hat{H}_s, \quad (2.5)$$

where

$$\begin{aligned} H^0 &= \frac{1}{8} J_{11}^0 (\eta_1^2 + \eta_3^2) + \frac{1}{8} J_{22}^0 (\eta_2^2 + \eta_4^2) + \frac{1}{4} J_{13}^0 \eta_1 \eta_3 + \frac{1}{4} J_{24}^0 \eta_2 \eta_4 + \frac{1}{4} J_{12}^0 (\eta_1 \eta_2 + \eta_3 \eta_4) + \frac{1}{4} J_{14}^0 (\eta_1 \eta_4 + \eta_2 \eta_3) \\ &+ \frac{1}{8} \left(\sum_{i=1}^3 \psi_{11i} \varepsilon_i + \sum_{j=4}^6 \psi_{11j} \varepsilon_j \right) (\eta_1^2 + \eta_3^2) + \frac{1}{8} \left(\sum_{i=1}^3 \psi_{22i} \varepsilon_i + \sum_{j=4}^6 \psi_{22j} \varepsilon_j \right) (\eta_2^2 + \eta_4^2) \\ &+ \frac{1}{4} \left(\sum_{i=1}^3 \psi_{13i} \varepsilon_i + \sum_{j=4}^6 \psi_{13j} \varepsilon_j \right) \eta_1 \eta_3 + \frac{1}{4} \left(\sum_{i=1}^3 \psi_{24i} \varepsilon_i + \sum_{j=4}^6 \psi_{24j} \varepsilon_j \right) \eta_2 \eta_4 \\ &+ \frac{1}{4} \left(\sum_{i=1}^3 \psi_{12i} \varepsilon_i + \sum_{j=4}^6 \psi_{12j} \varepsilon_j \right) (\eta_1 \eta_2 + \eta_3 \eta_4) + \frac{1}{4} \left(\sum_{i=1}^3 \psi_{14i} \varepsilon_i + \sum_{j=4}^6 \psi_{14j} \varepsilon_j \right) (\eta_1 \eta_4 + \eta_2 \eta_3), \\ \hat{H}_s &= - \sum_q \left(\mathcal{H}_1 \frac{\sigma_{q1}}{2} + \mathcal{H}_2 \frac{\sigma_{q2}}{2} + \mathcal{H}_3 \frac{\sigma_{q3}}{2} + \mathcal{H}_4 \frac{\sigma_{q4}}{2} \right). \end{aligned} \quad (2.6)$$

In (2.6), the following notations are used:

$$\begin{aligned} \mathcal{H}_1 &= \frac{1}{2} J_{11} \eta_1 + \frac{1}{2} J_{12} \eta_2 + \frac{1}{2} J_{13} \eta_3 + \frac{1}{2} J_{14} \eta_4 + \mu_{13}^x E_1 + \mu_{13}^y E_2 + \mu_{13}^z E_3, \\ \mathcal{H}_2 &= \frac{1}{2} J_{22} \eta_2 + \frac{1}{2} J_{12} \eta_1 + \frac{1}{2} J_{24} \eta_4 + \frac{1}{2} J_{14} \eta_3 - \mu_{24}^x E_1 - \mu_{24}^y E_2 + \mu_{24}^z E_3, \\ \mathcal{H}_3 &= \frac{1}{2} J_{11} \eta_3 + \frac{1}{2} J_{12} \eta_4 + \frac{1}{2} J_{13} \eta_1 + \frac{1}{2} J_{14} \eta_2 - \mu_{13}^x E_1 + \mu_{13}^y E_2 - \mu_{13}^z E_3, \\ \mathcal{H}_4 &= \frac{1}{2} J_{22} \eta_4 + \frac{1}{2} J_{12} \eta_3 + \frac{1}{2} J_{24} \eta_2 + \frac{1}{2} J_{14} \eta_1 + \mu_{24}^x E_1 - \mu_{24}^y E_2 - \mu_{24}^z E_3. \end{aligned} \quad (2.7)$$

In (2.7), $\mu_{13}^{x,y,z} = \mu_1^{x,y,z} = \mu_3^{x,y,z}$, $\mu_{24}^{x,y,z} = \mu_2^{x,y,z} = \mu_4^{x,y,z}$ 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:

$$G = NU_{\text{seed}} + NH^0 + Nv \sum_{i=1}^3 \sigma_i \varepsilon_i - k_B T \sum_q \left[2 \ln \text{Sp} e^{-\beta \hat{H}_q^{(2)}} - \sum_{f=1}^4 \ln \text{Sp} e^{-\beta \hat{H}_{qf}^{(1)}} \right], \quad (2.8)$$

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

$$\hat{H}_q^{(2)} = -2w \left(\frac{\sigma_{q1} \sigma_{q2}}{2} + \frac{\sigma_{q3} \sigma_{q4}}{2} \right) - \frac{y_1 \sigma_{q1}}{\beta} - \frac{y_2 \sigma_{q2}}{\beta} - \frac{y_3 \sigma_{q1}}{\beta} - \frac{y_4 \sigma_{q4}}{\beta}, \quad (2.9)$$

$$\hat{H}_{qf}^{(1)} = -\frac{\bar{y}_f \sigma_{qf}}{\beta}, \quad (2.10)$$

where such notations are used:

$$y_f = \beta(\Delta_1 + \mathcal{H}_f), \quad \bar{y}_f = \beta\Delta_f + y_f. \quad (2.11)$$

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

$$\frac{\text{Sp} \sigma_{qf} e^{-\beta \hat{H}_q^{(2)}}}{\text{Sp} e^{-\beta \hat{H}_q^{(2)}}} = \frac{\text{Sp} \sigma_{qf} e^{-\beta \hat{H}_{qf}^{(1)}}}{\text{Sp} e^{-\beta \hat{H}_{qf}^{(1)}}}. \quad (2.12)$$

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

$$\begin{aligned} \eta_{1,3} &= \frac{1}{D} (\sinh n_1 \pm \sinh n_2 + a^2 \sinh n_3 \pm a^2 \sinh n_4 + a \sinh n_5 + a \sinh n_6 \mp a \sinh n_7 \pm a \sinh n_8) \\ &= \tanh \frac{\bar{y}_{1,3}}{2}, \\ \eta_{2,4} &= \frac{1}{D} (\sinh n_1 \pm \sinh n_2 - a^2 \sinh n_3 \mp a^2 \sinh n_4 \mp a \sinh n_5 \pm a \sinh n_6 + a \sinh n_7 + a \sinh n_8) \\ &= \tanh \frac{\bar{y}_{2,4}}{2}, \end{aligned} \quad (2.13)$$

where

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

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

$$\begin{aligned} n_1 &= \frac{1}{2}(y_1 + y_2 + y_3 + y_4), & n_2 &= \frac{1}{2}(y_1 + y_2 - y_3 - y_4), & n_3 &= \frac{1}{2}(y_1 - y_2 + y_3 - y_4), \\ n_4 &= \frac{1}{2}(y_1 - y_2 - y_3 + y_4), & n_5 &= \frac{1}{2}(y_1 - y_2 + y_3 + y_4), & n_6 &= \frac{1}{2}(y_1 + y_2 + y_3 - y_4), \\ n_7 &= \frac{1}{2}(-y_1 + y_2 + y_3 + y_4), & n_8 &= \frac{1}{2}(y_1 + y_2 - y_3 + y_4). \end{aligned}$$

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

$$\begin{aligned} y_1 &= \frac{1}{2} \ln \frac{1 + \eta_1}{1 - \eta_1} + \beta v_{11} \eta_1 + \beta v_{12} \eta_2 + \beta v_{13} \eta_3 + \beta v_{14} \eta_4 + \frac{\beta}{2} (\mu_{13}^x E_1 + \mu_{13}^y E_2 + \mu_{13}^z E_3), \\ y_2 &= \beta v_{12} \eta_1 + \frac{1}{2} \ln \frac{1 + \eta_2}{1 - \eta_2} + \beta v_{22} \eta_2 + \beta v_{14} \eta_3 + \beta v_{24} \eta_4 + \frac{\beta}{2} (-\mu_{24}^x E_1 - \mu_{24}^y E_2 + \mu_{24}^z E_3), \\ y_3 &= \beta v_{13} \eta_1 + \beta v_{14} \eta_2 + \frac{1}{2} \ln \frac{1 + \eta_3}{1 - \eta_3} + \beta v_{11} \eta_3 + \beta v_{12} \eta_4 + \frac{\beta}{2} (-\mu_{13}^x E_1 + \mu_{13}^y E_2 - \mu_{13}^z E_3), \\ y_4 &= \beta v_{14} \eta_1 + \beta v_{24} \eta_2 + \beta v_{12} \eta_3 + \frac{1}{2} \ln \frac{1 + \eta_4}{1 - \eta_4} + \beta v_{22} \eta_4 + \frac{\beta}{2} (\mu_{24}^x E_1 - \mu_{24}^y E_2 - \mu_{24}^z E_3), \end{aligned}$$

where $v_{ff'} = \frac{J_{ff'}}{4}$.

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:

$$g = \frac{G}{N} = U_{\text{seed}} + H^0 - 2 \left(w^0 + \sum_{i=1}^3 \delta_i \varepsilon_i + \sum_{j=4}^6 \delta_j \varepsilon_j \right) - \frac{1}{2} k_B T \sum_{f=1}^4 \ln(1 - \eta_f^2) - 2k_B T \ln D + 2k_B T \ln 2 + v p \sum_{i=1}^3 \varepsilon_i. \quad (3.1)$$

From equilibrium conditions, we have obtained equations for the strains ε_i , ε_j :

$$\begin{aligned} -p &= c_{11}^{E0} \varepsilon_1 + c_{12}^{E0} \varepsilon_2 + c_{13}^{E0} \varepsilon_3 + c_{15}^{E0} \varepsilon_5 - e_{21}^0 E_2 - \frac{2\delta_1}{v} + \frac{2\delta_1}{vD} M_\varepsilon - \frac{\psi_{111}}{8v} (\eta_1^2 + \eta_3^2) - \frac{\psi_{131}}{4v} \eta_1 \eta_3 \\ &\quad - \frac{\psi_{221}}{8v} (\eta_2^2 + \eta_4^2) - \frac{\psi_{241}}{4v} \eta_2 \eta_4 - \frac{\psi_{121}}{4v} (\eta_1 \eta_2 + \eta_3 \eta_4) - \frac{\psi_{141}}{4v} (\eta_1 \eta_4 + \eta_2 \eta_3), \quad (l = 1, 2, 3), \\ 0 &= c_{51}^{E0} \varepsilon_1 + c_{52}^{E0} \varepsilon_2 + c_{53}^{E0} \varepsilon_3 + c_{55}^{E0} \varepsilon_5 - e_{25}^0 E_2 - \frac{2\delta_5}{v} + \frac{2\delta_5}{vD} M_\varepsilon - \frac{\psi_{115}}{8v} (\eta_1^2 + \eta_3^2) - \frac{\psi_{135}}{4v} \eta_1 \eta_3 \\ &\quad - \frac{\psi_{225}}{8v} (\eta_2^2 + \eta_4^2) - \frac{\psi_{245}}{4v} \eta_2 \eta_4 - \frac{\psi_{125}}{4v} (\eta_1 \eta_2 + \eta_3 \eta_4) - \frac{\psi_{145}}{4v} (\eta_1 \eta_4 + \eta_2 \eta_3), \\ 0 &= c_{44}^{E0} \varepsilon_4 + c_{46}^{E0} \varepsilon_6 - e_{14}^0 E_1 - e_{34}^0 E_3 - \frac{2\delta_4}{v} + \frac{2\delta_4}{vD} M_\varepsilon - \frac{\psi_{114}}{8v} (\eta_1^2 + \eta_3^2) - \frac{\psi_{134}}{4v} \eta_1 \eta_3 \\ &\quad - \frac{\psi_{224}}{8v} (\eta_2^2 + \eta_4^2) - \frac{\psi_{244}}{4v} \eta_2 \eta_4 - \frac{\psi_{124}}{4v} (\eta_1 \eta_2 + \eta_3 \eta_4) - \frac{\psi_{144}}{4v} (\eta_1 \eta_4 + \eta_2 \eta_3), \\ 0 &= c_{46}^{E0} \varepsilon_4 + c_{66}^{E0} \varepsilon_6 - e_{16}^0 E_1 - e_{36}^0 E_3 - \frac{2\delta_6}{v} + \frac{2\delta_6}{vD} M_\varepsilon - \frac{\psi_{116}}{8v} (\eta_1^2 + \eta_3^2) - \frac{\psi_{136}}{4v} \eta_1 \eta_3 \\ &\quad - \frac{\psi_{226}}{8v} (\eta_2^2 + \eta_4^2) - \frac{\psi_{246}}{4v} \eta_2 \eta_4 - \frac{\psi_{126}}{4v} (\eta_1 \eta_2 + \eta_3 \eta_4) - \frac{\psi_{146}}{4v} (\eta_1 \eta_4 + \eta_2 \eta_3), \end{aligned} \quad (3.2)$$

here, such a notation is used

$$M_\varepsilon = 2a^2 \cosh n_3 + 2a^2 \cosh n_4 + a \cosh n_5 + a \cosh n_6 + a \cosh n_7 + a \cosh n_8.$$

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

$$\begin{aligned} P_1 &= e_{14}^0 \varepsilon_4 + e_{16}^0 \varepsilon_6 + \chi_{11}^{\varepsilon 0} E_1 + \chi_{31}^{\varepsilon 0} E_3 + \frac{1}{2v} [\mu_{13}^x (\eta_1 - \eta_3) - \mu_{24}^x (\eta_2 - \eta_4)], \\ P_2 &= e_{21}^0 \varepsilon_1 + e_{22}^0 \varepsilon_2 + e_{23}^0 \varepsilon_3 + e_{25}^0 \varepsilon_5 + \chi_{22}^{\varepsilon 0} E_2 + \frac{1}{2v} [\mu_{13}^y (\eta_1 + \eta_3) - \mu_{24}^y (\eta_2 + \eta_4)], \\ P_3 &= e_{34}^0 \varepsilon_4 + e_{66}^0 \varepsilon_6 + \chi_{33}^{\varepsilon 0} E_3 + \chi_{31}^{\varepsilon 0} E_1 + \frac{1}{2v} [\mu_{13}^z (\eta_1 - \eta_3) + \mu_{24}^z (\eta_2 - \eta_4)]. \end{aligned} \quad (3.3)$$

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

$$\begin{aligned} \chi_{11,33}^\varepsilon &= \chi_{11,33}^{\varepsilon 0} + \frac{\beta}{2v\Delta_{1,3}} \{ (\mu_{13}^{x,z})^2 [\bar{D}\lambda_{24} - (\lambda_{13}\lambda_{24} - \lambda^2)\varphi_{24}^-] + (\mu_{24}^{x,z})^2 [\bar{D}\lambda_{13} - (\lambda_{13}\lambda_{24} - \lambda^2)\varphi_{13}^-] \\ &\quad \mp 2\mu_{13}^{x,z}\mu_{24}^{x,z} [\bar{D}\lambda + (\lambda_{13}\lambda_{24} - \lambda^2)\beta v_2^-] \}, \end{aligned} \quad (3.4)$$

$$\Delta_{1,3} = \bar{D}^2 - \bar{D}(\lambda_{24}\varphi_{13}^- + \lambda_{13}\varphi_{24}^- + 2\lambda\beta v_2^-) + (\lambda_{13}\lambda_{24} - \lambda^2)[\varphi_{13}^-\varphi_{24}^- - (\beta v_2^-)^2],$$

$$\begin{aligned} \chi_{22}^\varepsilon &= \chi_{22}^{\varepsilon 0} + \frac{\beta}{2v\Delta_2} \{ (\mu_{13}^y)^2 [\bar{D}\kappa_{13} - (\kappa_{13}\kappa_{24} - \kappa^2)\varphi_{24}^+] + (\mu_{24}^y)^2 [\bar{D}\kappa_{24} - (\kappa_{13}\kappa_{24} - \kappa^2)\varphi_{13}^+] \\ &\quad - 2\mu_{13}^y\mu_{24}^y [\bar{D}\kappa + (\kappa_{13}\kappa_{24} - \kappa^2)\beta v_2^+] \}, \end{aligned} \quad (3.5)$$

$$\Delta_2 = \bar{D}^2 - \bar{D}(\kappa_{13}\varphi_{13}^+ + \kappa_{24}\varphi_{24}^+ + 2\kappa\beta v_2^+) + (\kappa_{13}\kappa_{24} - \kappa^2)[\varphi_{13}^+\varphi_{24}^+ - (\beta v_2^+)^2].$$

Here, the following notations are used:

$$\begin{aligned}\tilde{D} &= \cosh(y_{13} + y_{24}) + a^2 \cosh(y_{13} - y_{24}) + 2a \cosh y_{13} + 2a \cosh y_{24} + a^2 + 1, \\ \varphi_{13}^\pm &= \frac{1}{1 - \eta_{13}^2} + \beta v_1^\pm, \quad \varphi_{24}^\pm = \frac{1}{1 - \eta_{24}^2} + \beta v_3^\pm; \\ v_l^\pm &= v_l^{0\pm} + \left(\sum_{i=1}^3 \psi_{li}^\pm \varepsilon_i \pm \sum_{j=4}^6 \psi_{lj}^\pm \varepsilon_j \right), \quad (l = 1, 2, 3), \quad v_1^{0\pm} = \frac{1}{4}(J_{11}^0 \pm J_{13}^0); \quad \psi_{1i}^\pm = \frac{1}{4}(\psi_{11i} \pm \psi_{13i}), \\ v_2^{0\pm} &= \frac{1}{4}(J_{12}^0 \pm J_{14}^0); \quad \psi_{2i}^\pm = \frac{1}{4}(\psi_{12i} \pm \psi_{14i}); \quad v_3^{0\pm} = \frac{1}{4}(J_{22}^0 \pm J_{24}^0); \quad \psi_{3i}^\pm = \frac{1}{4}(\psi_{22i} \pm \psi_{24i}), \\ \lambda_{13} &= 1 + a^2 + 2a \cosh y_{13}, \quad \lambda_{24} = 1 + a^2 + 2a \cosh y_{24}, \quad \lambda = 1 - a^2, \\ \kappa_{13} &= \cosh(y_{13} + y_{24}) + a^2 \cosh(y_{13} - y_{24}) + 2a \cosh y_{13} - \eta_{13}^2 \tilde{D}, \\ \kappa_{24} &= \cosh(y_{13} + y_{24}) + a^2 \cosh(y_{13} - y_{24}) + 2a \cosh y_{24} - \eta_{24}^2 \tilde{D}, \\ \varkappa &= \cosh(y_{13} + y_{24}) - a^2 \cosh(y_{13} - y_{24}) - \eta_{13} \eta_{24} \tilde{D}.\end{aligned}$$

Based on (3.3), we have obtained expressions for isothermic coefficients of piezoelectric stress e_{2l} ($l = 1, 2, 3, 5$) of GPI:

$$\begin{aligned}e_{2l} &= \left(\frac{\partial P_2}{\partial \varepsilon_l} \right)_{E_2} = e_{2l}^0 + \frac{\mu_{13}^y}{v} \frac{\beta}{\Delta_2} [(\psi_{11} \eta_{13} + \psi_{21} \eta_{24}) \tau_1^\psi + (\psi_{21} \eta_{13} + \psi_{31} \eta_{24}) \tau_2^\psi - 2\delta_l \tau_1^\delta] \\ &\quad - \frac{\mu_{24}^y}{v} \frac{\beta}{\Delta_2} [(\psi_{11} \eta_{13} + \psi_{21} \eta_{24}) \tau_2^\psi + (\psi_{21} \eta_{13} + \psi_{31} \eta_{24}) \tau_3^\psi - 2\delta_l \tau_2^\delta],\end{aligned}\quad (3.6)$$

where

$$\begin{aligned}\tau_1^\psi &= \tilde{D} \kappa_{13} - (\kappa_{13} \kappa_{24} - \varkappa^2) \varphi_{24}^+, \quad \tau_2^\psi = \tilde{D} \varkappa + (\kappa_{13} \kappa_{24} - \varkappa^2) \beta v_2^+, \quad \tau_3^\psi = \tilde{D} \kappa_{24} - (\kappa_{13} \kappa_{24} - \varkappa^2) \varphi_{13}^+, \\ \tau_1^\delta &= [\tilde{D} - (\kappa_{24} \varphi_{24}^+ + \varkappa \beta v_2^+)] \rho_{13} + (\varkappa \varphi_{24}^+ + \kappa_{13} \beta v_2^+) \rho_{24}, \\ \tau_2^\delta &= [\tilde{D} - (\kappa_{13} \varphi_{13}^+ + \varkappa \beta v_2^+)] \rho_{24} + (\varkappa \varphi_{13}^+ + \kappa_{24} \beta v_2^+) \rho_{24}, \\ \rho_{13} &= [a^2 \sinh(y_{13} - y_{24}) + a \sinh y_{13}] - \eta_{13} M, \\ \rho_{24} &= [-a^2 \sinh(y_{13} - y_{24}) + a \sinh y_{24}] - \eta_{24} M, \\ M &= a^2 \cosh(y_{13} - y_{24}) + a \cosh y_{13} + a \cosh y_{24} + a^2.\end{aligned}$$

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

$$\begin{aligned}c_{ij}^E &= \left(\frac{\partial \sigma_i}{\partial \varepsilon_j} \right)_{E_2} = c_{ij}^{E0} - \frac{2\beta}{v \Delta_2} \{ (\psi_{1i} \eta_{13} + \psi_{2i} \eta_{24}) (\psi_{1j} \eta_{13} + \psi_{2j} \eta_{24}) \tau_1^\psi \\ &\quad + [(\psi_{1i} \eta_{13} + \psi_{2i} \eta_{24}) (\psi_{2j} \eta_{13} + \psi_{3j} \eta_{24}) + (\psi_{2i} \eta_{13} + \psi_{3i} \eta_{24}) (\psi_{1j} \eta_{13} + \psi_{2j} \eta_{24})] \tau_2^\psi \\ &\quad + (\psi_{2i} \eta_{13} + \psi_{3i} \eta_{24}) (\psi_{2j} \eta_{13} + \psi_{3j} \eta_{24}) \tau_3^\psi \} + \frac{4\beta \delta_i}{v \Delta_2} [(\psi_{1j} \eta_{13} + \psi_{2j} \eta_{24}) \tau_1^\delta + (\psi_{2j} \eta_{13} + \psi_{3j} \eta_{24}) \tau_2^\delta] \\ &\quad + \frac{4\beta \delta_j}{v \Delta_2} [(\psi_{1i} \eta_{13} + \psi_{2i} \eta_{24}) \tau_1^\delta + (\psi_{2i} \eta_{13} + \psi_{3i} \eta_{24}) \tau_2^\delta] \\ &\quad - \frac{8\beta \delta_i \delta_j}{v \tilde{D} \Delta_2} [(\rho_{13} \varphi_{13}^+ + \rho_{24} \beta v_2^+) \tau_1^\delta + (\rho_{24} \varphi_{24}^+ + \rho_{13} \beta v_2^+) \tau_2^\delta] \\ &\quad - \frac{4\beta \delta_i \delta_j}{v \tilde{D}^2} \{ [2a^2 \cosh(y_{13} - y_{24}) + a \cosh y_{13} + a \cosh y_{24} + 2a^2] \tilde{D} - 2M^2 \}.\end{aligned}\quad (3.7)$$

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 s_{ij}^E , which

is reciprocal to matrix of elastic constants c_{ij}^E :

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

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

$$\chi_{22}^\sigma = \chi_{22}^\varepsilon + \sum_l e_{2l} d_{2l}, \quad (3.9)$$

isothermal constants of piezoelectric strain

$$h_{2l} = \frac{e_{2l}}{\chi_{22}^\varepsilon}, \quad (3.10)$$

isothermal constants of piezoelectric strain

$$g_{2l} = \frac{d_{2l}}{\chi_{22}^\sigma}. \quad (3.11)$$

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

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

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):

$$\Delta C^\sigma = T \left(\frac{\partial S}{\partial T} \right)_\sigma. \quad (3.13)$$

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 $v_f^{0\pm}$ ($f = 1, 2, 3$);
- deformational potentials δ_i, ψ_{fi}^\pm ($f = 1, 2, 3; i = 1, \dots, 6$);
- effective dipole moments $\mu_{13}^x; \mu_{24}^x; \mu_{13}^y; \mu_{24}^y; \mu_{13}^z; \mu_{24}^z$;
- “seed” dielectric susceptibilities $\chi_{ii}^{\varepsilon 0}, \chi_{31}^{\varepsilon 0}$ ($i = 1, 2, 3$);

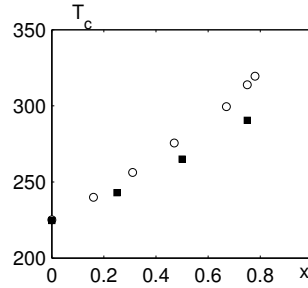


Figure 2. Phase transition temperature T_c vs deuterium concentration x obtained in $\text{GPI}_{1-x}\text{DGPI}_x$: ○ [12]; ■ [13].

- “seed” coefficients of piezoelectric stress $e_{2i}^0, e_{25}^0, e_{14}^0, e_{16}^0, e_{34}^0, e_{36}^0$;
- “seed” elastic constants $c_{i'i'}^{E0}, c_{jj}^{E0}, c_{i5}^{E0}, c_{46}^{E0}$ ($i = 1, 2, 3; i' = 1, 2, 3; j = 4, 5, 6$).

The volume of a primitive cell of GPI is the $\nu_{0,0} = 0.601 \cdot 10^{-21} \text{ cm}^3$, $\nu_{0,808} = 0.6114 \cdot 10^{-21} \text{ cm}^3$.

Figure 2 shows the dependences of the phase transition point T_c of $\text{GPI}_{1-x}\text{DGPI}_x$ on the deuterium concentration x , which are obtained in [12] and [13] and do not agree with each other. The concentration dependence of T_c [12] can be approximated by curve $T_c(x) = 225(1 + 0.382x + 0.193x^2) \text{ K}$, which is a theoretical curve of $T_c(x)$. Since the papers [12, 14] also present a concentration dependence of spontaneous polarization and dielectric permittivity of the mixed $\text{GPI}_{1-x}\text{DGPI}_x$ compounds, in our further analysis we decided to use $T_c(x)$ published in [12].

In [9], the temperature $T_c = 322.85 \text{ K}$ 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 $\nu_f^{0\pm}$ we use $\tilde{\nu}_1^{0+} = \tilde{\nu}_2^{0+} = \tilde{\nu}_3^{0+} = 2.643 \text{ K}$, $\tilde{\nu}_1^{0-} = \tilde{\nu}_2^{0-} = \tilde{\nu}_3^{0-} = 0.2 \text{ K}$, where $\tilde{\nu}_f^{0\pm} = \nu_f^{0\pm}/k_B$. The parameters $\nu_f^{0\pm}$ do not depend on concentration x .

The calculated parameters w^0 of the $\text{GPI}_{1-x}\text{DGPI}_x$ crystals are $w_0/k_B = 820 \text{ K}$ at $x = 0$ and 1323.6 K at $x = 0.808$.

The optimal values of the deformational potentials δ_i at $x = 0.0$ are $\tilde{\delta}_1 = 500 \text{ K}$, $\tilde{\delta}_2 = 600 \text{ K}$, $\tilde{\delta}_3 = 500 \text{ K}$, $\tilde{\delta}_4 = 150 \text{ K}$, $\tilde{\delta}_5 = 100 \text{ K}$, $\tilde{\delta}_6 = 150 \text{ K}$; $\tilde{\delta}_i = \delta_i/k_B$. At $x = 0.808$, they are $\tilde{\delta}_i(0.808) = 0.337\tilde{\delta}_i(0)$.

The optimal values of the ψ_{fi}^{\pm} are as follows: $\tilde{\psi}_{f1}^+ = 87.9 \text{ K}$, $\tilde{\psi}_{f2}^+ = 237.0 \text{ K}$, $\tilde{\psi}_{f3}^+ = 103.8 \text{ K}$, $\tilde{\psi}_{f4}^+ = 149.1 \text{ K}$, $\tilde{\psi}_{f5}^+ = 21.3 \text{ K}$, $\tilde{\psi}_{f6}^+ = 143.8 \text{ K}$, $\tilde{\psi}_{fi}^- = 0 \text{ K}$, where $\tilde{\psi}_{fi}^{\pm} = \psi_{fi}^{\pm}/k_B$. At $x = 0.808$, they are $\psi_{fi}^{\pm}(0.808) = 0.337\psi_{fi}^{\pm}(0)$.

The effective dipole moments in the paraelectric phase are equal to $\mu_{13} = (0.4, 4.02, 4.3) \cdot 10^{-18} \text{ esu}\cdot\text{cm}$, $\mu_{24} = (-2.3, -3.0, 2.2) \cdot 10^{-18} \text{ esu}\cdot\text{cm}$ and do not depend on deuteration. In the ferroelectric phase, the y -component of the first dipole moment increases on deuteration as $\mu_{13\text{ferro}}^y(x) = 3.82(1 + 0.062x) \times 10^{-18} \text{ esu}\cdot\text{cm}$, and at $x = 0.808$, it is $\mu_{13\text{ferro}}^y(x = 0.808) = 4.01 \cdot 10^{-18} \text{ esu}\cdot\text{cm}$.

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

$$\begin{aligned}
 e_{21}^0 &= e_{22}^0 = e_{23}^0 = e_{25}^0 = e_{14}^0 = e_{16}^0 = e_{34}^0 = e_{36}^0 = 0.0 \frac{\text{esu}}{\text{cm}^2}; \\
 \chi_{11}^{\varepsilon 0} &= 0.1, \quad \chi_{22}^{\varepsilon 0}(x = 0.0) = 0.403, \quad \chi_{22}^{\varepsilon 0}(x = 0.808) = 2.2, \quad \chi_{33}^{\varepsilon 0} = 0.5, \quad \chi_{31}^{\varepsilon 0} = 0.0; \\
 c_{11}^{E0} &= 26.91 \cdot 10^{10} \frac{\text{dyn}}{\text{cm}^2}, \quad c_{12}^{E0} = 14.5 \cdot 10^{10} \frac{\text{dyn}}{\text{cm}^2}, \quad c_{13}^{E0} = 11.64 \cdot 10^{10} \frac{\text{dyn}}{\text{cm}^2}, \quad c_{15}^{E0} = 3.91 \cdot 10^{10} \frac{\text{dyn}}{\text{cm}^2}, \\
 c_{22}^{E0} &= [64.99 - 0.04(T - T_c)] \cdot 10^{10} \frac{\text{dyn}}{\text{cm}^2}, \quad c_{23}^{E0} = 20.38 \cdot 10^{10} \frac{\text{dyn}}{\text{cm}^2}, \quad c_{25}^{E0} = 5.64 \cdot 10^{10} \frac{\text{dyn}}{\text{cm}^2}, \\
 c_{33}^{E0} &= 24.41 \cdot 10^{10} \frac{\text{dyn}}{\text{cm}^2}, \quad c_{35}^{E0} = -2.84 \cdot 10^{10} \frac{\text{dyn}}{\text{cm}^2}, \quad c_{55}^{E0} = 8.54 \cdot 10^{10} \frac{\text{dyn}}{\text{cm}^2}, \\
 c_{44}^{E0} &= 15.31 \cdot 10^{10} \frac{\text{dyn}}{\text{cm}^2}, \quad c_{46}^{E0} = -1.1 \cdot 10^{10} \frac{\text{dyn}}{\text{cm}^2}, \quad c_{66}^{E0} = 11.88 \cdot 10^{10} \frac{\text{dyn}}{\text{cm}^2}.
 \end{aligned}$$

Now, let us focus on the obtained results and analyse the effect of hydrostatic pressure $p = -\sigma_1 = -\sigma_2 = -\sigma_3$ on 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.

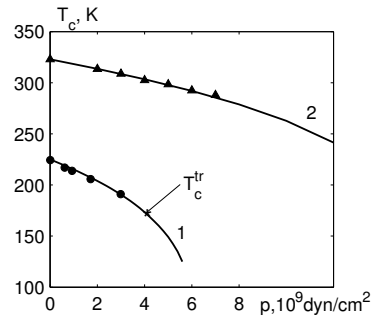


Figure 3. The pressure dependence of the temperature T_c of $\text{GPI}_{1-x}\text{DGPI}_x$ at different x : 0.00 — 1; • [8]; 0.808 — 2; ▲ [9].

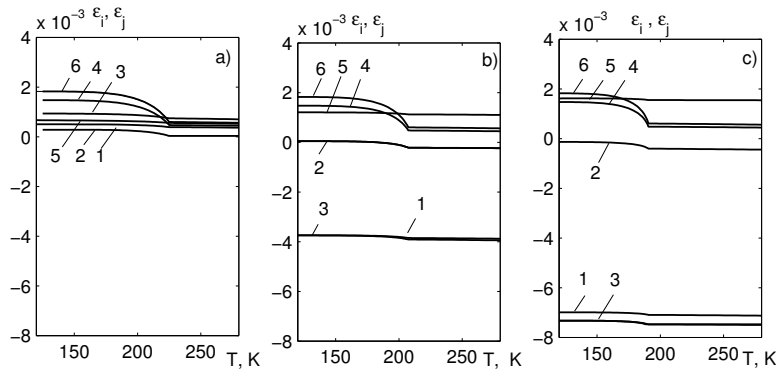


Figure 4. Temperature dependences of the strains of GPI: ε_1 — 1, ε_2 — 2, ε_3 — 3, ε_4 — 4, ε_5 — 5 and ε_6 — 6 at different values of pressure p (10^9 dyn/cm 2): 0.0 — a); 1.7 — b); 3.0 — c).

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 $p = 3.5 \cdot 10^9$ 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 ε_i , ε_j of GPI crystal at different values of hydrostatic pressure p are presented in figure 4. The strains ε_1 , ε_3 and ε_5 are practically independent of temperature in both phases, but the strains ε_2 , ε_4 and ε_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 ε_1 and ε_3 , but the other strains depend on p very little (figure 5).

In figure 6 (a), the temperature dependences of spontaneous polarization of GPI crystal are presented, in figure 6 (b) — for $\text{GPI}_{0.192}\text{DGPI}_{0.808}$ 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 3), it becomes a transition of the first order. In the case of crystal $\text{GPI}_{0.192}\text{DGPI}_{0.808}$, 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 $\text{GPI}_{0.192}\text{DGPI}_{0.808}$ 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]

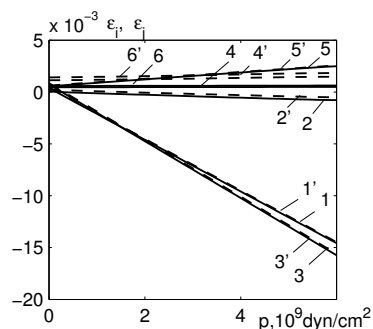


Figure 5. The dependences of the strains of GPI on the pressure at the temperature $T = 205$ K: ε_1 — 1, ε_2 — 2, ε_3 — 3, ε_4 — 4, ε_5 — 5, ε_6 — 6; and at $T = 245$ K: ε_1 — 1', ε_2 — 2', ε_3 — 3', ε_4 — 4', ε_5 — 5', ε_6 — 6'.

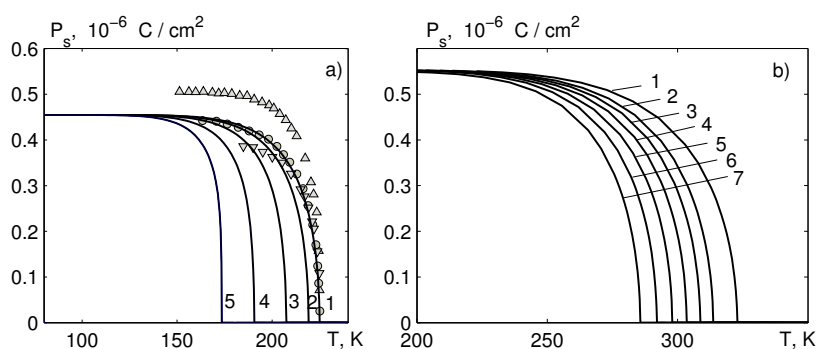


Figure 6. Temperature dependences of the spontaneous polarization of GPI (a) at different values of hydrostatic pressure p , (10^9 dyn/cm 2): 0.0 — 1, \circ [14], Δ [15], \square [16], ∇ [17]; 0.9 — 2; 1.7 — 3; 3.0 — 4; 4.0 — 5; of GPI $_{0.192}$ DGPI $_{0.808}$ (b) at different values of hydrostatic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

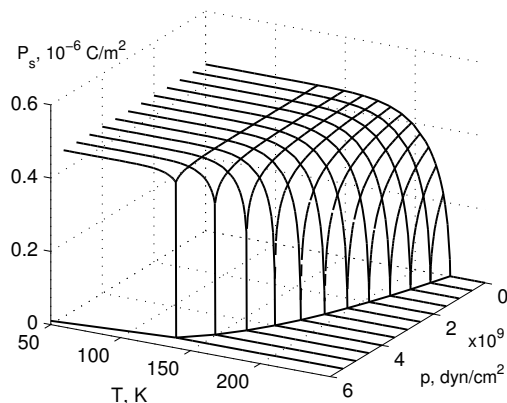


Figure 7. Temperature-pressure dependence of the spontaneous polarization of GPI.

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

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

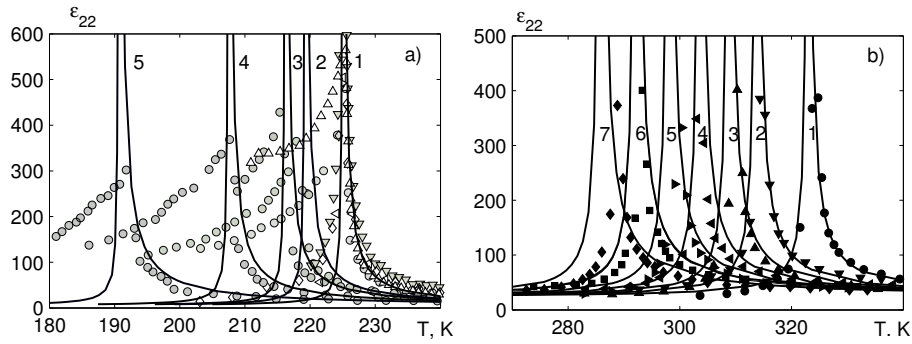


Figure 8. Temperature dependences of the static dielectric permittivity ϵ_{22}^{ϵ} of GPI crystal (a) at different values of hydrostatic pressure p , (10^9 dyn/cm²): 0.0 — 1, \diamond [12], ∇ [17], Δ [15], \square [16], \circ [8]; 0.6 — 2, \circ [8]; 0.9 — 3, \circ [8]; 1.7 — 4, \circ [8]; 3.0 — 5, \circ [8]; and of GPI_{0.192}DGPI_{0.808} (b) at different values of hydrostatic pressure p , (10^9 dyn/cm²): 0.0 — 1, \bullet [9]; 2.0 — 2, \blacktriangledown [9]; 3.0 — 3, \blacktriangle [9]; 4.0 — 4, \blacktriangleleft [9]; 5.0 — 5, \blacktriangleright [9]; 6.0 — 6, \blacksquare [9]; 8.0 — 7 \blacklozenge [9].

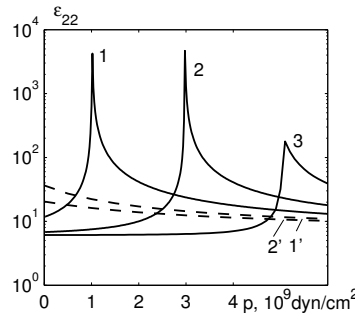


Figure 9. Pressure dependences of the dielectric permittivity ϵ_{22} of GPI crystal at different values of temperature T , K: 245 — 2'; 235 — 1'; 215 — 1; 191 — 2; 159 — 3.

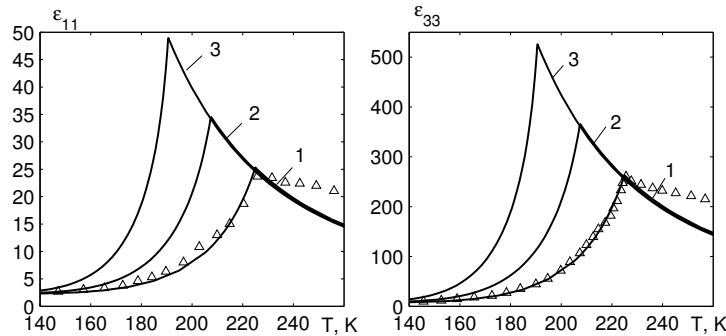


Figure 10. Temperature dependences of the dielectric permittivities ϵ_{11} and ϵ_{33} of GPI crystal at different values of hydrostatic pressure p , (10^9 dyn/cm²): 0.0 — 1, Δ [15]; 1.7 — 2; 3.0 — 3.

of pressure p , but in ferroelectric phase, permittivity ϵ_{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 ϵ_{11} and ϵ_{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 ϵ_{11} and ϵ_{33} increase with an increase of pressure, and maximum values shift to lower temperatures. In the paraelectric phase, ϵ_{11} and ϵ_{33} decrease with

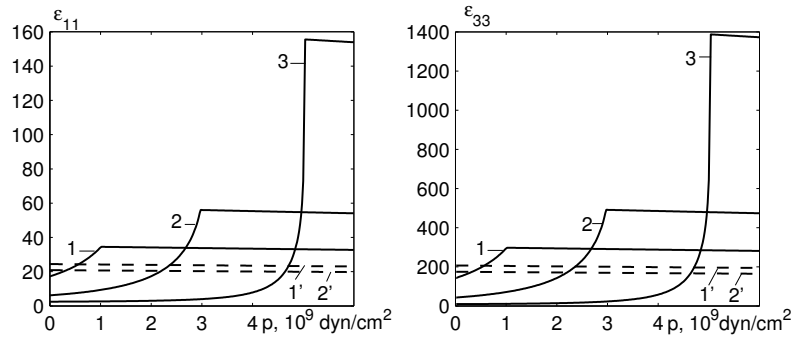


Figure 11. Pressure dependences of the dielectric permittivities ϵ_{11} and ϵ_{33} at different values of temperature T , K: 245 — 2'; 235 — 1'; 215 — 1; 205 — 2; 185 — 3.

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 $(\epsilon_{22}^{\epsilon})^{-1}$ of GPI and $\text{GPI}_{0.192}\text{DGPI}_{0.808}$ 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

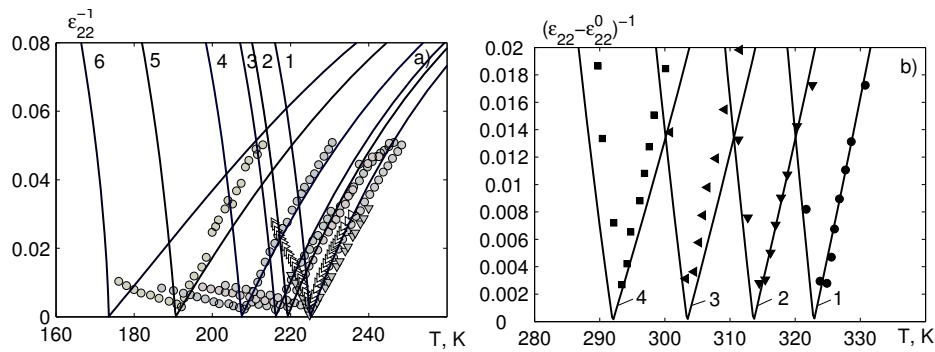


Figure 12. Temperature dependences of the inverse dielectric permittivity $(\epsilon_{22}^{\epsilon})^{-1}$ of GPI crystal (a) at different values of hydrostatic pressure p , (10^9 dyn/cm 2): 0.0 — 1, ∇ [17], \triangleright [18], \circ [8]; 0.6 — 2, \circ [8]; 0.9 — 3, \circ [8]; 1.7 — 4, \circ [8]; 3.0 — 5, \circ [8]; 4.0 — 6; and $\text{GPI}_{0.192}\text{DGPI}_{0.808}$ (b) at different values of hydrostatic pressure p , (10^9 dyn/cm 2): 0.0 — 1, \bullet [9], 2.0 — 2, \blacktriangledown [9], 4.0 — 3, \blacktriangleleft [9], 6.0 — 4, \blacksquare [9].

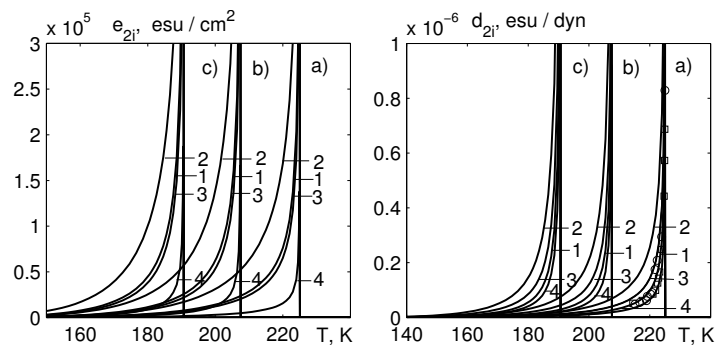


Figure 13. Temperature dependences of the coefficients of piezoelectric stress e_{2i} , e_{25} and strain d_{2i} , d_{25} : 1 — e_{21} , d_{21} \square [16], 2 — e_{22} , d_{22} , 3 — e_{23} , d_{23} \circ [16], 4 — e_{25} , d_{25} of GPI crystal at different values of pressure p , (10^9 dyn/cm 2): 0.0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

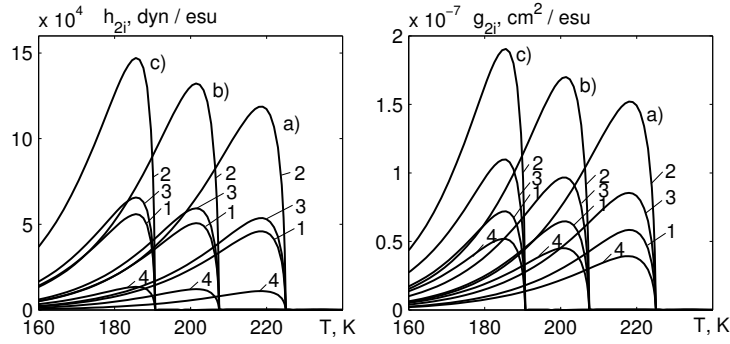


Figure 14. Temperature dependences of the constants of piezoelectric stress h_{2i} , h_{25} and strain g_{2i} , g_{25} : 1 — h_{21} , g_{21} , 2 — h_{22} , g_{22} , 3 — h_{23} , g_{23} , 4 — h_{25} , g_{25} of GPI crystal at different values of pressure p , (10^9 dyn/cm 2): 0 — a); 1.7 — b); 3 — c).

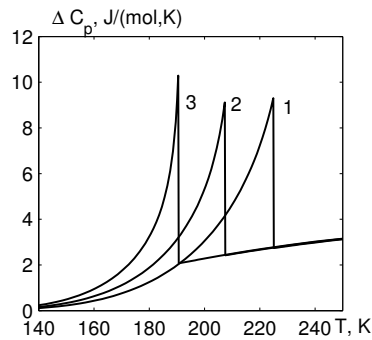


Figure 15. Temperature dependences of ΔC_p at different values of hydrostatic pressure p , (10^9 dyn/cm 2): 0.0 — 1; 0.9 — 2; 1.7 — 3; 3.0 — 4.

at small values of hydrostatic pressure p . As was written above, disagreement in ferroelectric phase for $(\epsilon_{22}^e)^{-1}$ 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_{2i} 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_{2i} , d_{2i} , 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 ΔC_p . In the paraelectric phase, the value of ΔC_p practically does not change with an increase of pressure p , but in the ferroelectric phase, the value of ΔC_p increases with pressure.

5. Conclusions

In this paper, the effect of hydrostatic pressure on phase transition and physical characteristics of the $\text{GPI}_{1-x}\text{DGPI}_x$ crystals is studied in the frames of two-particle cluster approximation within the modified proton ordering model of GPI type quasideimensional ferroelectrics with hydrogen bonds, which takes into account the piezoelectric coupling with the strains ϵ_i , ϵ_j in the ferroelectric phase. We have determined how the strains ϵ_i , ϵ_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.

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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 тисків, використано модифіковану модель $\text{NH}_3\text{CH}_2\text{COOH}\cdot\text{H}_2\text{PO}_3$ (GPI) шляхом врахування п'єзоелектричного зв'язку структурних елементів, які впорядковуються, з деформаціями ε_i , ε_j . В наближенні двочастинкового кластера розраховано компоненти вектора поляризації та тензора статичної діелектричної проникності механічно затиснутого і вільного кристалів, їх п'єзоелектричні та теплові характеристики. Досліджено вплив гідростатичного тиску на фазовий перехід та фізичні характеристики кристалу. Отримано добрий кількісний опис експериментальних даних для цих кристалів.

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