Effects arising in glycine phosphite (GPI) ferroelectrics under the action of the shear stresses \( \sigma_5 \) and \( \sigma_6 \) and the electric field \( E_1 \) have been studied in the framework of a modified model that accounts for the piezoelectric coupling between the ordered structural elements and the strains \( \varepsilon_j \). The components of the polarization vectors and the tensor of static dielectric permittivity are calculated in the two-particle cluster approximation for mechanically clamped crystals. The corresponding piezoelectric and thermal parameters are also determined. The influence of the simultaneous action of the stress \( \sigma_5 \) and the field \( E_1 \), as well as the stress \( \sigma_6 \) and the field \( E_1 \), on the physical parameters of the GPI ferroelectric crystals and the phase transition in them is analyzed.

**Keywords:** ferroelectrics, phase transition, dielectric permittivity, piezoelectric moduli, shear stress.

1. **Introduction**

The study of the phenomena that arise under the action of mechanical stresses and external electric fields is one of the challenging problems in the physics of ferroactive compounds. In particular, it concerns the crystals of glycine phosphite (GPI), which belongs to ferroactive materials with hydrogen bonds [1].

The influence of the transverse electric field \( E_1 \) on the dielectric permittivity \( \varepsilon_{33} \) of a GPI crystal was experimentally studied in works [2–4]. The cited authors showed that the application of the field \( E_1 \) resulted in a decrease of the ferroelectric phase transition temperature.

The model of a deformed GPI crystal was developed in work [5] on the basis of the proton model [3]. It considers the piezoelectric coupling between a proton and lattice subsystems. This model served as a basis to study the influence of the transverse electric fields \( E_1 \) and \( E_3 \) on the dielectric and piezoelectric properties of GPI [6]. In particular, the abovementioned experimental data obtained for the temperature dependence of the transverse dielectric permittivity \( \varepsilon_{33} \) in the presence of the field \( E_3 \) [3] were described correctly at the quantitative level. It was found that the influence of the field \( E_1 \) is qualitatively similar to that of the field \( E_3 \), but it is an order of magnitude weaker.

In work [7], the GPI model [6] was modified to describe the case where the shear stresses \( \sigma_4 \), \( \sigma_5 \), and \( \sigma_6 \) are applied to the GPI crystal in the absence of an electric field. It was found that the appearance of the shear stress \( \sigma_4 \) or \( \sigma_6 \) in the ferroelectric phase gives rise to the emergence of the spontaneous polarization along the axes \( OX \) and \( OZ \), and the transverse permeabilities \( \varepsilon_{11} \) and \( \varepsilon_{33} \) tend to infinity at the temperature \( T_c \). The stresses \( \sigma_4 \) and \( \sigma_6 \) were found to produce similar effects at the qualitative level.

In this work, in the framework of a modification of the model [4] of a deformed GPI crystal, the mutual action of the electric field \( E_1 \) and the stresses \( \sigma_5 \) and \( \sigma_6 \) on the phase transition in the crystals of this type and their thermodynamic and static dielectric parameters are studied.

2. **Model Hamiltonian**

Let us consider a system of protons that move in the GPI crystal along the O–H,...,O bonds. The latter form zigzag chains along the \( c \)-axis of the crys-
tal. Let us assign the dipole moment $\mathbf{d}_{qf}$ to the proton at the $f$-th bond ($f = 1, ..., 4$). In the ferroelectric phase, the dipole moments are mutually compensated ($\mathbf{d}_{q1}$ with $\mathbf{d}_{q3}$ and $\mathbf{d}_{q2}$ with $\mathbf{d}_{q4}$) in the $Z$- and $X$-directions but simultaneously mutually added in the $Y$-direction, thus generating a spontaneous polarization. The vectors $\mathbf{d}_{qf}$ are oriented at certain angles with respect to the crystallographic axes and have the longitudinal and transverse components with respect to the $b$-axis (see Fig. 1).

The Hamiltonian of the proton subsystem in GPI consists of the “seed” and pseudospin parts. The “seed” energy $U_{\text{seed}}$ is associated with the lattice of heavy ions and does not depend explicitly on the proton subsystem configuration. The pseudospin part of the Hamiltonian makes allowance for the short-range, $H_{\text{short}}$, and long-range, $H_{\text{MF}}$, proton-proton interactions near the HPO$_3$ tetrahedra, as well as the effective interaction with the electric fields $E_1$, $E_2$, and $E_3$. Hence,

$$
\hat{H} = NU_{\text{seed}} + \hat{H}_{\text{short}} + \hat{H}_{\text{MF}} + \hat{H}_E,
$$

where $N$ is the total number of primitive cells in the Bravais lattice.

The quantity $U_{\text{seed}}$ is the seed energy consisting of the elastic, piezoelectric, and dielectric components, which are expressed in terms of the electric fields $E_i$ ($i = 1, 2, 3$) and the strains $\varepsilon_j$ ($j = 1, 2, 3, 4, 5, 6$), so that

$$
U_{\text{seed}} = \frac{3}{2} \varepsilon_1^0 \varepsilon_1 E_2 - \frac{3}{2} \varepsilon_2^0 \varepsilon_2 E_1 - \frac{3}{2} \varepsilon_3^0 \varepsilon_3 E_1 - \frac{1}{2} \varepsilon_4^0 E_2^2 - \frac{1}{2} \varepsilon_5^0 E_3^2 - \frac{1}{2} \varepsilon_6^0 E_1^2.
$$

Here, the parameters $\sigma_j$ ($j = 1, 2, 3, 4$) is the $z$-component of the operator for the pseudospin located at the $f$-th bond in the $q$-th cell; the first and second Kronecker deltas correspond to the proton interaction in the chains located near the HPO$_3$ tetrahedra of types I and II, respectively; and $\mathbf{R}_c$ is the lattice radius vector directed along the $c$-axis. The contributions of the interaction between protons located around the tetrahedra of different types to the configuration energy are assumed to be identical, as well as the average values of pseudospins $\langle \sigma_j \rangle$ related to the tetrahedra of different types. The quantities $w_1$ and $w_2$ describe short-range interactions of protons in the chains. We can expand them in series in the strains $\varepsilon_j$ and confine the expansions to the linear terms,

$$
w_{1,2} = w_0^0 + \sum_l \delta_l \varepsilon_l \pm \delta_4 \varepsilon_4 \pm \delta_6 \varepsilon_6 \quad (l = 1, 2, 3, 5).
$$

The mean-field Hamiltonian $\hat{H}_{\text{MF}}$ describes long-range dipole-dipole interactions and indirect (through lattice vibrations) proton-proton interactions. Accounting for the expansion of the Fourier transforms of the interaction constants $J_{f'f} = \sum_{qq'} J_{f'f}(qq')$ at $q = 0$ in series in the strains $\varepsilon_j$ and confining the expansions to the linear terms,

$$
J_{11} = J_1^0 + \sum_l \psi_{11} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6,
$$

$$
J_{12} = J_2^0 + \sum_l \psi_{14} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6,
$$

$$
J_{13} = J_3^0 + \sum_l \psi_{15} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6,
$$

$$
J_{15} = J_5^0 + \sum_l \psi_{31} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6,
$$

$$
J_{16} = J_6^0 + \sum_l \psi_{31} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6,
$$

$$
J_{23} = J_3^0 + \sum_l \psi_{14} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6,
$$

$$
J_{25} = J_5^0 + \sum_l \psi_{31} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6,
$$

$$
J_{26} = J_6^0 + \sum_l \psi_{31} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6,
$$

$$
J_{35} = J_5^0 + \sum_l \psi_{31} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6,
$$

$$
J_{36} = J_6^0 + \sum_l \psi_{31} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6,
$$

$$
J_{56} = J_6^0 + \sum_l \psi_{31} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6.
$$

where

\[ H^+_J = J^0 + 2 \sum_l \psi_{12l} \varepsilon_l \pm \psi_{144} \varepsilon_4 \pm \psi_{126} \varepsilon_6, \]

\[ H^-_J = J^0 + 2 \sum_l \psi_{14l} \varepsilon_l \pm \psi_{144} \varepsilon_4 \pm \psi_{146} \varepsilon_6, \]

\[ H^0 = J^0_{22} + 2 \sum_l \psi_{22l} \varepsilon_l \pm \psi_{224} \varepsilon_4 \pm \psi_{226} \varepsilon_6, \]

we obtain the term \( \hat{H}_{MF} \) in the form

\[ \hat{H}_{MF} = NH^0 + \hat{H}_s, \tag{5} \]

where

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

\[ + \frac{1}{4} J_{13} \eta_1 \eta_2 + J_{24} \eta_2 \eta_4 + \frac{1}{4} J_{12} (\eta_1 \eta_2 + \eta_3 \eta_4) + \]

\[ + \frac{1}{4} J_{14} (\eta_1 \eta_4 + \eta_2 \eta_3) \tag{6} \]

and

\[ \hat{H}_s = - \sum_q \left( \hat{H}_1 \frac{\sigma_q^1}{2} + \hat{H}_2 \frac{\sigma_q^2}{2} + \hat{H}_3 \frac{\sigma_q^3}{2} + \hat{H}_4 \frac{\sigma_q^4}{2} \right). \tag{7} \]

In formula (7), the following notations were used:

\[ \hat{H}_f = \sum_{f=1}^{4} \frac{1}{2} J_{ff} \eta_f \quad (f = 1 \div 4). \]

The fourth term in Eq. (1), \( \hat{H}_E \), describes the interaction of pseudospins with electric fields,

\[ \hat{H}_E = \sum_{f=1}^{4} H_{Ef} \frac{\sigma_f^q}{2}, \tag{8} \]

where

\[ H_{E1,3} = \pm \mu^x_1 E_1 + \mu^y_1 E_2 \pm \mu^z_1 E_3, \]

\[ H_{E2,4} = \pm \mu^x_2 E_1 - \mu^y_2 E_2 \pm \mu^z_2 E_3, \]

\[ \mu^x_1, y_1 \; \mu^y_1, y_2 \; \mu^z_1, y_2 \; \mu^x_2, y_2 \; \mu^y_2, y_2 \; \mu^z_2, y_2 \]

are effective dipole moments per pseudospin.

When calculating the thermodynamic and dynamic parameters of ferroactive compounds of the GPI type, let us apply the two-particle cluster (TPC) approximation. In this approximation, the thermodynamic potential of GPI under the action of the shear stresses \( \sigma_{5,6} \) looks like

\[ G = NU_{seed} + NH^0 - \sum_{j=5}^{6} \sigma_j \varepsilon_j - \]

\[ - k_B T \sum_q \left[ 2 \ln \text{Sp} e^{-\beta \hat{H}_q^{(2)}} - \sum_{f=1}^{4} \ln \text{Sp} e^{-\beta \hat{H}_q^{(1)}} \right]. \tag{9} \]

Here, \( \hat{H}_q^{(2)} \) and \( \hat{H}_q^{(1)} \) are the two- and one-particle Hamiltonians given by the following expressions:

\[ \hat{H}_q^{(2)} = -2 \left( w_1 \frac{\sigma_q^1}{2} + w_2 \frac{\sigma_q^2}{2} \right) - \sum_{f=1}^{4} \frac{y_f \sigma_q^f}{2}, \tag{10} \]

\[ \hat{H}_q^{(1)} = - \frac{y_f \sigma_q^f}{2}, \tag{11} \]

where the following notations were used:

\[ y_f = \beta (\Delta_f + \hat{H}_f + H_{Ef}), \quad \bar{y}_f = \beta \Delta_f + y_f. \]

The quantities \( \Delta_f \) are effective fields created by neighbor links located beyond the cluster boundaries. In the cluster approximation, the fields \( \Delta_f \) are determined from the self-consistency condition

\[ \frac{\text{Sp} \sigma_q^f e^{-\beta \hat{H}_q^{(2)}}}{\text{Sp} e^{-\beta \hat{H}_q^{(2)}}} = \frac{\text{Sp} \sigma_q^f e^{-\beta \hat{H}_q^{(1)}}}{\text{Sp} e^{-\beta \hat{H}_q^{(1)}}}. \tag{12} \]

Then, on the basis of Eq. (12), we obtain expressions for the average values of the pseudospin, \( \langle \sigma_q^f \rangle \), in the cases of two- and one-particle Hamiltonians. By excluding the parameters \( \Delta_f \), we obtain the following relations:

\[ \eta_3 = \frac{1}{D} \left[ \sinh n_1 \pm \sinh n_2 + a^2 \sinh n_3 \pm \right. \]

\[ \pm a^2 \sinh n_4 \mp aa_{46} \sinh n_5 + \frac{a}{a_{46}} \sinh n_6 \mp \]

\[ \mp aa_{46} \sinh n_7 \pm \frac{a}{a_{46}} \sinh n_8 \right], \]

\[ \eta_4 = \frac{1}{D} \left[ \sinh n_1 \pm \sinh n_2 - a^2 \sinh n_3 \mp \right. \]

\[ \mp a^2 \sinh n_4 \mp aa_{46} \sinh n_5 \pm \frac{a}{a_{46}} \sinh n_6 + \]

\[ \mp aa_{46} \sinh n_7 + \frac{a}{a_{46}} \sinh n_8 \right]. \]
\[ D = \cosh n_1 + \cosh n_2 + a^2 \cosh n_3 + \]
\[ + a^2 \cosh n_4 + aa_{46} \cosh n_5 + \frac{a}{a_{46}} \cosh n_6 + \]
\[ + aa_{46} \cosh n_7 + \frac{a}{a_{46}} \cosh n_8, \]

where
\[ a = \exp \left[ -\beta \left( w^0 + \sum_{l=1}^{3} \delta_l \varepsilon_l \right) \right], \]
\[ a_{46} = \exp \left[ -\beta (\delta_4 \varepsilon_4 + \delta_6 \varepsilon_6) \right], \]
\[ n_1 = \frac{1}{2} (y_1 + y_2 + y_3 + y_4), \]
\[ n_2 = \frac{1}{2} (y_1 + y_2 - y_3 - y_4), \]
\[ n_3 = \frac{1}{2} (y_1 - y_2 + y_3 - y_4), \]
\[ n_4 = \frac{1}{2} (y_1 - y_2 - y_3 + y_4), \]
\[ n_5 = \frac{1}{2} (y_1 - y_2 + y_3 + y_4), \]
\[ n_6 = \frac{1}{2} (y_1 + y_2 - y_3 - y_4), \]
\[ n_7 = \frac{1}{2} (-y_1 + y_2 + y_3 + y_4), \]
\[ n_8 = \frac{1}{2} (y_1 + y_2 - y_3 + y_4), \]

and
\[ y_f = \frac{1}{2} \ln \frac{1 + \eta_f}{1 - \eta_f} + \frac{\beta}{2} H_f + \frac{\beta}{2} \mu_f E. \]

3. Thermodynamic Parameters of GPI

In order to obtain the dielectric, piezoelectric, and elastic parameters of GPI, let us use formula (9) to calculate the thermodynamic potential per primitive cell,

\[ g = \frac{G}{N} = U_{\text{seed}} + H^0 - 2 \left( w^0 + \sum \delta \varepsilon \right) + \]
\[ + 2k_B T \ln 2 - Nv \sum_{j=5}^{6} \sigma_j e_j - \frac{1}{2} k_B T \sum_{j=1}^{4} \ln (1 - \eta_j^2) - \]
\[ - 2k_B T \ln D, \quad l = 1, 2, 3, 5. \]  

By differentiating this expression with respect to the fields \( E_i \), we obtain the following formulas for the polarizations \( P_i \):

\[ P_1 = e_{14}^0 e_4 + e_{16}^0 e_6 + \chi_{11}^0 E_1 + \]
\[ + \frac{1}{2v} [\mu_{13}^\rho (\eta_1 - \eta_3) - \mu_{24}^\rho (\eta_2 - \eta_4)], \]  
\[ P_2 = e_{21}^0 e_1 + e_{22}^0 e_2 + e_{23}^0 e_3 + e_{25}^0 e_5 + \chi_{22}^0 E_2 + \]
\[ + \frac{1}{2v} [\mu_{13}^\eta (\eta_1 + \eta_3) - \mu_{24}^\eta (\eta_2 + \eta_4)], \]  
\[ P_3 = e_{34}^0 e_4 + e_{36}^0 e_6 + \chi_{33}^0 E_3 + \]
\[ + \frac{1}{2v} [\mu_{13}^\kappa (\eta_1 - \eta_3) + \mu_{24}^\kappa (\eta_2 - \eta_4)]. \]

The static isothermal dielectric susceptibilities along the axes of a mechanically clamped GPI crystal look like

\[ \chi_{11}^\omega = \chi_{11}^\omega + \]
\[ + \frac{1}{2v} [\mu_{13}^\rho (\hat{\eta}_{1E_1} - \hat{\eta}_{3E_1}) - \mu_{24}^\rho (\hat{\eta}_{2E_1} - \hat{\eta}_{4E_1})], \]  
\[ \chi_{22}^\sigma = \chi_{22}^\sigma + \]
\[ + \frac{1}{2v} [\mu_{13}^\eta (\hat{\eta}_{1E_2} + \hat{\eta}_{3E_2}) - \mu_{24}^\eta (\hat{\eta}_{2E_2} + \hat{\eta}_{4E_2})], \]  
\[ \chi_{33}^\varepsilon = \chi_{33}^\varepsilon + \]
\[ + \frac{1}{2v} [\mu_{13}^\kappa (\hat{\eta}_{1E_3} - \hat{\eta}_{3E_3}) + \mu_{24}^\kappa (\hat{\eta}_{2E_3} - \hat{\eta}_{4E_3})], \]

where \( \hat{\eta}_{1E_i}, \hat{\eta}_{3E_i}, \hat{\eta}_{2E_i}, \) and \( \hat{\eta}_{4E_i} \) are the solutions of the following system of equations:

\[ \begin{pmatrix}
2D - \chi_{11}^\omega & -\chi_{12}^\omega & -\chi_{13}^\omega & -\chi_{14}^\omega \\
-\chi_{21}^\omega & 2D - \chi_{22}^\omega & -\chi_{23}^\omega & -\chi_{24}^\omega \\
-\chi_{31}^\omega & -\chi_{32}^\omega & 2D - \chi_{33}^\omega & -\chi_{34}^\omega \\
-\chi_{41}^\omega & -\chi_{42}^\omega & -\chi_{43}^\omega & 2D - \chi_{44}^\omega
\end{pmatrix}
\times
\begin{pmatrix}
\hat{\eta}_{1E_1} \\
\hat{\eta}_{2E_2} \\
\hat{\eta}_{3E_3} \\
\hat{\eta}_{4E_4}
\end{pmatrix}
= \begin{pmatrix}
\chi_{11}^\omega \\
\chi_{22}^\omega \\
\chi_{33}^\omega \\
\chi_{44}^\omega
\end{pmatrix}
. \]

Here, the following notations were used:

\[ \chi_{f1} = \chi_{f11}(\phi_1^\omega + \beta \nu_1^\omega) + \chi_{f12}(\beta \nu_2^\omega + \beta \nu_3^\omega) + \]
\[ + \chi_{f13}(\phi_3^\omega + \beta \nu_1^\omega) + \chi_{f14}(\beta \nu_2^\omega + \beta \nu_3^\omega); \]
\[ \chi_{f2} = \chi_{f22}(\nu_2^\omega + \beta \nu_3^\omega) + \chi_{f21}(\beta \nu_2^\omega + \beta \nu_3^\omega) + \]
\[ + \chi_{f23}(\nu_3^\omega + \beta \nu_1^\omega) + \chi_{f24}(\beta \nu_2^\omega + \beta \nu_3^\omega); \]
\[ \chi_{f3} = \chi_{f31}(\phi_3^\omega - \beta \nu_1^\omega) + \chi_{f32}(\nu_2^\omega - \beta \nu_3^\omega) - \]
\[ - \chi_{f33}(\phi_2^\omega - \beta \nu_1^\omega) - \chi_{f34}(\nu_3^\omega - \beta \nu_3^\omega), \]

\[ xf = \kappa_{j12}(\psi^+_i - \beta \eta^+_i) + \kappa_{j11}(\beta \nu^+_i - \beta \bar{\nu}^+_i) - \\
- \kappa_{j14}(\psi^+_i - \beta \eta^+_i) - \kappa_{j13}(\beta \nu^+_i - \beta \bar{\nu}^+_i), \]

\[ \kappa^x = \kappa_{j13} \beta \nu^+_i + \kappa_{j15} \beta \nu^+_i, \]

\[ \kappa^y = \kappa_{j11} \beta \nu^+_i - \kappa_{j12} \beta \nu^+_i, \]

\[ \kappa^z = \kappa_{j13} \beta \nu^+_i + \kappa_{j14} \beta \nu^+_i, \]

\[ \varphi^+_{1,3} = \frac{1}{1 - \eta^+_i}, \]

\[ \varphi^+_{2,3} = \frac{1}{1 - \eta^+_i}, \]

\[ \varphi^+_{1,4} = \frac{1}{1 - \eta^+_i}, \]

\[ \varphi^+_{2,4} = \frac{1}{1 - \eta^+_i}, \]

\[ \kappa_{j13} = \beta \nu^+_i + \kappa_{j14} \beta \nu^+_i, \]

\[ \nu^{0 \pm}_i = \nu^{1 \pm}_i + \sum_{i=1}^{n} \psi^\mp_i \epsilon_i + \psi^\mp_i \epsilon_i, \]

\[ \bar{\nu}^{0 \pm}_i = \psi^{1 \pm}_i + \psi^{1 \pm}_i, \]

\[ \nu^{0 \pm}_i = \frac{1}{4}(\nu^0_{11} \pm \nu^0_{13}), \]

\[ \nu^{0 \pm}_i = \frac{1}{4}(\nu^0_{12} \pm \nu^0_{14}), \]

\[ \nu^{0 \pm}_i = \frac{1}{4}(\nu^0_{22} \pm \nu^0_{24}), \]

\[ \nu^{0 \pm}_i = \frac{1}{4}(\nu^0_{32} \pm \nu^0_{34}), \]

\[ \nu^{0 \pm}_i = \frac{1}{4}(\nu^0_{42} \pm \nu^0_{44}), \]

\[ \kappa_{j11} = (l^+_1 + l^+_3) - \bar{\eta}_1(l^+_1 + l^+_3) - \bar{\eta}_1(l^+_1 + l^+_3), \]

\[ \kappa_{j12} = (l^+_1 + l^+_5 - \eta_1(l^+_1 + l^+_5 + l^+_7 + l^+_8), \]

\[ \kappa_{j13} = \pm(l^+_2 + l^+_5 + l^+_6 - \eta_2(l^+_2 + l^+_5 + l^+_7 - l^+_8), \]

\[ \kappa_{j14} = \pm(l^+_2 + l^+_5 + l^+_6 - \eta_2(l^+_2 + l^+_5 + l^+_7 - l^+_8), \]

\[ \kappa_{j11} = (l^+_3 + l^+_5 - \eta_2(l^+_3 + l^+_5 + l^+_6), \]

\[ \kappa_{j12} = (l^+_3 + l^+_5 + l^+_6 - \eta_2(l^+_3 + l^+_5 + l^+_6), \]

On the basis of relations (14)–(16), we obtain expressions for the isothermal coefficients of piezoelectric strains in GPE, \( e_{1j} \), \( e_{2j} \), and \( e_{3j} \):

\[ e_{1j} = \frac{\partial P_j}{\partial \varepsilon_1} = \]

\[ = \frac{1}{2}\left[ \mu_{13}(\eta_{1\varepsilon_1} - \eta_{3\varepsilon_1}) - \mu_{24}(\eta_{2\varepsilon_1} - \eta_{4\varepsilon_1}) \right], \]

\[ (j = 4, 6), \]

\[ e_{2j} = \frac{\partial P_j}{\partial \varepsilon_2} = \]

\[ = \frac{1}{2}\left[ \mu_{13}(\eta_{1\varepsilon_1} + \eta_{3\varepsilon_1}) - \mu_{24}(\eta_{2\varepsilon_1} + \eta_{4\varepsilon_1}) \right], \]

\[ (j = 4, 6), \]

\[ e_{3j} = \frac{\partial P_j}{\partial \varepsilon_3} = \]

\[ = \frac{1}{2}\left[ \mu_{13}(\eta_{1\varepsilon_1} - \eta_{3\varepsilon_1}) + \mu_{24}(\eta_{2\varepsilon_1} - \eta_{4\varepsilon_1}) \right], \]

\[ (j = 4, 6), \]

Here, \( \eta_{1\varepsilon_1}, \eta_{2\varepsilon_1}, \eta_{3\varepsilon_1}, \) and \( \eta_{4\varepsilon_1} \) are the solutions of the following system of equations:

\[ \begin{pmatrix} 2D - \chi_{11} & -\chi_{12} & -\chi_{13} & -\chi_{14} \\
-\chi_{21} & 2D - \chi_{22} & -\chi_{23} & -\chi_{24} \\
-\chi_{31} & -\chi_{32} & 2D - \chi_{33} & -\chi_{34} \\
-\chi_{41} & -\chi_{42} & -\chi_{43} & 2D - \chi_{44} \end{pmatrix} \times \]

\[ \begin{pmatrix} \eta_{1\varepsilon_1} \\
\eta_{2\varepsilon_1} \\
\eta_{3\varepsilon_1} \\
\eta_{4\varepsilon_1} \end{pmatrix} = \begin{pmatrix} \chi_{11}' \\
\chi_{12}' \\
\chi_{13}' \\
\chi_{14}' \end{pmatrix}, \]

where the following notations were applied:

\[ \chi_{1i} = \beta(\psi^+_i \varphi_{j11} + \psi^+_i \varphi_{j12})(\eta_1 + \eta_3) + \]

\[ + \beta(\psi^+_i \varphi_{j11} + \psi^+_i \varphi_{j12})(\eta_2 + \eta_4) + \]

\[ + \beta(\psi^+_i \varphi_{j13} + \psi^+_i \varphi_{j14})(\eta_1 - \eta_3) + \]

\[ + \beta(\psi^+_i \varphi_{j13} + \psi^+_i \varphi_{j14})(\eta_2 - \eta_4) + \]

\[ + 2\beta(\rho_1 + \rho_2), \]

\[ \psi^{1 \pm}_i = \frac{1}{4}(\psi^{1 \pm}_i \pm \psi^{1 \pm}_i), \]

\[ \psi^{1 \pm}_i = \frac{1}{4}(\psi^{1 \pm}_i \pm \psi^{1 \pm}_i), \]

\[ \rho_{13} = -2(l^+_5 + l^+_6 + l^+_7 + l^+_8), \]

\[ \rho_{12} = -l^+_5 + l^+_7 + l^+_8 + l^+_6, \]

\[ \rho_{14} = 2(l^+_5 + l^+_6 + l^+_7 + l^+_8), \]

\[ \rho_{14} = l^+_5 + l^+_6 + l^+_7 + l^+_8, \]

\[ \rho_{14} = l^+_5 + l^+_6 + l^+_7 + l^+_8, \]
\[ \nu_{3+4} = a^2 \sinh n_3 \pm a^2 \sinh n_4, \]
\[ \nu_{3+4} = a^2 \cosh n_3 + a^2 \cosh n_4. \]

The molar entropy of the proton subsystem equals
\[
S = \frac{R}{4} \left\{ -2 \ln 2 + \sum_{f=1}^{4} \ln (1 - \eta_f) + 2 \ln D - \frac{2}{3} \left[ \beta \nu_1^+(\eta_1 + \nu_3) + \beta \nu_2^-(\eta_1 - \nu_3) + 2 \beta \nu_2^+(\eta_1 + \nu_3)(\eta_2 + \eta_4) + 2 \beta \nu_3^-(\eta_2 + \eta_4) + \beta \nu_3^+(\eta_2 - \eta_4) + 4 \beta \nu_4^-(\eta_2 - \eta_4) \right] + 4 \nu_f T D M \right\}. \]  (25)

Here, \( R \) is the universal gas constant. The heat capacity of the proton subsystem in a GPI crystal at a constant pressure can be found by differentiating entropy (25).

4. Comparison of the Results of Numerical Calculations with Experimental Data

The values of some microscopic parameters are required to numerically calculate the temperature dependences of the dielectric and piezoelectric parameters of GPI. These are the parameter of the short-range interaction \( \nu_0 \); the parameters of long-range interactions \( \nu_f^\pm \) (\( f = 1, 2, 3 \)); the deformation potentials \( \delta_1 \) and \( \psi_f^\pm \) (\( i = 1, ..., 6 \)); the effective dipole moments \( \mu_{13}^A, \mu_{24}^B, \mu_{13}^B, \mu_{24}^A, \mu_{13}^C \); the “seed” dipole electric susceptibilities \( \kappa_{13}^A \); the “seed” piezoelectric strain coefficients \( c_{ij}^{E0} \); and the elastic constants \( c_{ij}^{E0} \).

In order to determine the required values, we used the experimental temperature dependences of the following physical parameters of GPI: \( P_c(T) \) [8], \( C_p(T) \) [9], \( \epsilon_{11}^H, \epsilon_{22}^H, \epsilon_{33}^H \), \( d_{21} \), and \( d_{23} \) [10]. The volume of the primitive GPI unit cell was taken equal to \( V_0 = 0.601 \times 10^{-21} \text{ cm}^3 \).

The optimal values obtained for the parameters \( \nu_f^\pm = \nu_f^\pm / k_B \) of long-range interactions are \( \nu_1^+ = \nu_2^+ = \nu_3^+ = 3.065 \text{ K} \) and \( \nu_1^- = \nu_2^- = \nu_3^- = 0.05 \text{ K} \). The parameter of the short-range interaction \( \nu_0 \) in the GPI crystal was calculated to equal to \( \nu_0 / k_B = 800 \text{ K} \). The optimal values found for the deformation potentials \( \delta_1 = \delta_1 / k_B = 500 \text{ K} \), \( \delta_2 = 600 \text{ K} \), \( \delta_3 = 500 \text{ K} \), \( \delta_4 = 150 \text{ K} \), \( \delta_5 = 100 \text{ K} \), and \( \delta_6 = 150 \text{ K} \); and the optimal values for \( \psi_f^\pm = \psi_f^\pm / k_B \) are \( \psi_{f1} = 93.6 \text{ K} \), \( \psi_{f2} = 252.5 \text{ K} \), \( \psi_{f3} = 110.7 \text{ K} \), \( \psi_{f4} = 22.7 \text{ K} \), \( \psi_{f5} = \psi_{f6} = 79.5 \text{ K} \).

The effective dipole moments in the paraphase are \( \mu_{13} = (0.4, 0.45, 4.3) \times 10^{-18} \text{ esu cm} \) and \( \mu_{24} = (-2.3, -3.0, 2.2) \times 10^{-18} \text{ esu cm} \). In the ferrophase, the \( y \)-component of the first dipole moment equals \( \mu_{13}^{y \text{ferro}} = 3.82 \times 10^{-18} \text{ esu cm} \).

The values of the “seed” piezoelectric strain coefficients \( c_{ij}^{E0} \), the “seed” dielectric susceptibilities \( \kappa_{ij}^A \), and the “seed” elastic constants \( c_{ij}^{E0} \) are as follows: \( c_{11}^{E0} = 0.0 \text{ esu/cm}^2 \), \( \chi_{11}^H = 0.1, \chi_{22}^H = 0.403, \chi_{33}^H = 0.5 \), \( \chi_{11}^H = 0.0, \chi_{12}^{E0} = 269.1 \text{ kbar}, \chi_{12}^{E0} = 145 \text{ kbar}, \chi_{13}^{E0} = 116.4 \text{ kbar}, \chi_{15}^{E0} = 30.1 \text{ kbar}, \chi_{22}^{E0} = [649.9 - 0.4(T - T_c)] \text{ kbar}, \chi_{12}^{E0} = 203.8 \text{ kbar}, \chi_{13}^{E0} = 56.4 \text{ kbar}, \chi_{15}^{E0} = 241.4 \text{ kbar}, \chi_{22}^{E0} = -28.4 \text{ kbar}, \chi_{13}^{E0} = 85.4 \text{ kbar}, \chi_{15}^{E0} = 153.1 \text{ kbar}, \chi_{22}^{E0} = -11 \text{ kbar}, \) and \( \epsilon_{66}^{E0} = 118.8 \text{ kbar} \).

Now, let us consider how the thermodynamic parameters of the GPI crystal are changed, when the shear stresses \( \sigma_5 \) and \( \sigma_6 \) and the electric field \( E_1 \) are applied simultaneously. The main mechanism of the influence of the shear stresses \( \sigma_5 \) and \( \sigma_6 \) on the thermodynamic parameters of the GPI crystal is associated with a specific temperature behavior of the order parameters \( \eta_f \) at various stresses. The stress \( \sigma_5 \) in the \( XZ \)-plane of the crystal does not affect the symmetry of the parameters, which are only shifted along the temperature axis in this case. On the other hand, the action of the stress \( \sigma_5 \) in the \( XY \)-plane of the crystal leads to the relations \( \eta_1 = \eta_2 = \eta_4 = \eta_6 \).

Furthermore, the order parameters become smeared, which testifies to the disappearance of the phase transition from the ferroelectric phase into the paraelectric one.

If the shear stress \( \sigma_6 \) is applied in the absence of the electric field (curves 63 in all figures), the crystal symmetry decreases, and two sublattices (chain A and chain B) become non-equivalent (see work [7]). As a result, the interactions between pseudospins become stronger in chain A and weaker in chain B. The enhancement of interactions in either sublattice at a cer-
tain stress $\sigma_6$ initiates a phase transition into the ferroelectric phase and elevates the temperature $T_c$. In the figures to follow, the curves marked with the numbers 5 and 6 correspond to the applied mechanical stresses $\sigma_5$ and $\sigma_6$, respectively, the superscripts indicate the stress values (in kbar units), and the subscripts mean the field strength magnitudes (in MV/m units).

The temperature dependences of the GPI crystal polarization $P_2$ at various values of the stress $\sigma_5$, $\sigma_6$ and the electric field strength $E_1$ are shown in Fig. 2 (left panel). The combined action of those factors only leads to a shift of the curve $P_2(T)$ along the temperature axis. The polarization curve corresponding to a field strength of 4 MV/m and the stress $\sigma_5 = 0$ (curve $5^0_1$) is the most shifted toward low temperatures, whereas curve $5^6_1$ is the most shifted toward high temperatures. The growth of the field strength $E_1$ shifts the curves $P_2(T)$ to the left from curve $5^0_1$, and the growth of the stress $\sigma_5$ to the right from it.

If the stress $\sigma_6$ and the electric field $E_1$ are applied, the phase transition becomes smeared (Fig. 2, right panel). If only the field or the stress is applied, the polarization curves $P_2(T)$ – curves $5^1_1$ and $5^2_1$, respectively – are zeroed at the phase transition temperature. At the same time, the combined action of the field $E_1$ and the stress $\sigma_6$ results in the disappearance of the phase transition temperature and the phase transition smearing.

If the stress $\sigma_6$ and the electric field $E_1$ are applied to the crystal, the polarizations $P_1$ and $P_3$ are induced (Fig. 3). If only the stress $\sigma_6$ is applied, those polarizations are zeroed at the phase transition temperature. If only the field $E_1$ is applied or the stress $\sigma_6$ and the electric field $E_1$ are applied together, the polarizations $P_1$ and $P_3$ are smeared at this temperature.

Under the action of the stress $\sigma_6$ and the electric field $E_1$, the curves $P_3(T)$ are positive and increase with the temperature. Then they reach a maximum and, afterward, decrease. The polarizations $P_3$ in this case are negative. They at first decrease to a minimum and then increase as the temperature grows further. The simultaneous growth of the field and the stress leads to an increase of the polarization magnitude. The induced polarization $P_3$ is much larger than the polarization $P_1$ obtained at the same values of the stress $\sigma_6$ and the electric field $E_1$. The induced polarizations arise because two sublattices become non-equivalent under the action of the stress $\sigma_6$. Therefore, the dipole moments of two sublattices in the $XZ$ and $XY$, respectively, planes are not compensated.

Figure 4 (left panel) demonstrates the temperature dependences of the inverse dielectric permittivity $\varepsilon_{22}^{-1}$ of the GPI crystal, if the stress $\sigma_5$ and the electric field $E_1$ are applied. The combined action of those factors only shifts the $\varepsilon_{22}^{-1}(T)$ curves along the temperature axis. The growth of the field strength $E_1$ shifts the $\varepsilon_{22}^{-1}(T)$ curves to the left and the growth of the stress $\sigma_5$ to the right from curve $5^0_6$. In the absence of the field and the stress, the longitudinal permeability diverges at the point $T_c$, but if they are applied, the maxima of $\varepsilon_{22}^{-1}$ become finite.

If the stress $\sigma_6$ and the electric field $E_1$ are applied to the crystal (Fig. 4, right panel), then curves $6^0_6$, $6^1_6$, and $6^2_6$ for the inverse permeability $\varepsilon_{22}^{-1}$ are zeroed at $T = T_c$. The combined action of the stress $\sigma_6$ and the
Fig. 4. Temperature dependences of the inverse dielectric constant $\varepsilon_{22}^{-1}$ of the GPI crystal at various values of the stresses $\sigma_j$ and the electric field $E_1$

Fig. 5. Temperature dependences of the dielectric constant $\varepsilon_{11}$ of the GPI crystal at various values of the stresses $\sigma_j$ and the electric field $E_1$

Fig. 6. Temperature dependences of the dielectric constant $\varepsilon_{33}$ of the GPI crystal at various values of the stresses $\sigma_j$ and the electric field $E_1$

Fig. 7. Temperature dependences of the piezoelectric strain coefficient $e_{21}$ of the GPI crystal at various values of the stresses $\sigma_j$ and the electric field $E_1$

Fig. 8. Temperature dependences of the piezoelectric strain coefficient $e_{1j}$ of the GPI crystal at various values of the stresses $\sigma_j$ and the electric field $E_1$

Fig. 9. Temperature dependences of the piezoelectric strain coefficient $e_{3j}$ of the GPI crystal at various values of the stresses $\sigma_j$ and the electric field $E_1$

If the stress $\sigma_5$ and the field $E_1$ are applied to the crystal, there arises a jump of the permittivities $\varepsilon_{11}$ and $\varepsilon_{33}$ at the phase transition temperature. These
jumps decrease and shift to higher temperatures with the growth of the stress $\sigma_5$ (Figs. 5 and 6). As was found in work [6], the reduction of $T_c$ and the growth of $\varepsilon_{33}$ in the ferroelectric phase occur due to a partial disordering of protons in the chain of type B (see Fig. 1) under the action of the field $E_1$.

If only the field $E_1$ is applied, each of the permeabilities $\varepsilon_{11}$ and $\varepsilon_{33}$ has a jump, and their maxima become smaller and more round as the stress $\sigma_6$ increases (Figs. 5 and 6). At the stress magnitudes exceeding 1 kbar, the curves $\varepsilon_{11}(T)$ and $\varepsilon_{33}(T)$ are smeared and there appear two maxima in them. If only the stress $\sigma_6$ is applied to the crystal, the permeability curves $\varepsilon_{11}(T)$ and $\varepsilon_{33}(T)$ behave as for the longitudinal permeability. The joint action of the stress $\sigma_6$ and the field $E_1$ makes the permeabilities $\varepsilon_{11}$ and $\varepsilon_{33}$ finite, and their values decrease with the increasing field.

The temperature dependences of the piezoelectric strain coefficient $e_{21}$ for the GPI crystal under the action of the stress $\sigma_5$ and the field $E_1$ are shown in Fig. 7. If only the field $E_1$ is applied to the crystal, the curves $e_{21}(T)$ shift to lower temperatures and become finite. At the combined action of the stress $\sigma_5$ and the field $E_1$, the curves $e_{21}(T)$ shift toward higher temperatures as the stress $\sigma_5$ grows, and the negative $e_{21}$-maxima become some smaller.

The temperature dependences of the piezoelectric moduli $e_{11}$ (Fig. 8) and $e_{33}$ (Fig. 9) under the action of the stress $\sigma_5$ and the field $E_1$ are similar. At temperatures close to the phase transition one, the combined action of the stress $\sigma_5$ and the field $E_1$ leads to a drastic increase of the negative values of $e_{11}$ and the positive values of $e_{33}$. At the combined action of the stress $\sigma_6$ and the field $E_1$, the curves for the piezoelectric moduli $e_{11}$ and $e_{33}$ are smeared, and the paraphase values of those parameters are induced. Another specific feature consists in the change of the signs of the transverse piezoelectric coefficients $e_{1j}$ and $e_{3j}$ near $T_c$, which is associated with an almost complete disordering of protons in chain B near $T_c$.

As one can see from Figs. 8 and 9 (curves $6_0^\pm$), the temperature dependences $e_{1j}(T)$ and $e_{3j}(T)$ diverge at the $T_c$ point. It occurs because, if the stress $\sigma_6 \neq 0$, small strain changes $d\varepsilon_4$ and $d\varepsilon_6$ are accompanied by a temperature change $dT_c$ and a shift of the curves $P_1(T)$ and $P_3(T)$ to higher temperatures. Since $dP_1/dT \rightarrow \infty$ near the phase transition temperature, $dP_1/d\varepsilon_4 \rightarrow \infty$ and $dP_1/d\varepsilon_6 \rightarrow \infty$.

Fig. 10. Temperature dependences of $\Delta C_p$ of the GPI crystal at various values of the stresses $\sigma_j$ and the electric field $E_1$.

The temperature dependences of $\Delta C_p$ of the GPI crystal, when the stress $\sigma_5$ and the field $E_1$ are applied, are shown in Fig. 10 (left panel). In this case, the curves $\Delta C_p(T)$ become shifted toward lower temperatures and their maxima decrease. The reduction of the field $E_1$ leads to the growth of the $\Delta C_p(T)$ maximum.

If the stress $\sigma_6$ and the field $E_3$ are applied, the jump of $\Delta C_p$ becomes smeared as the stress $\sigma_6$ increases (Fig. 10, right panel).

5. Conclusions

In this work, the influence of the combined action of the stresses $\sigma_5$ and $\sigma_6$ and the electric field $E_1$ on the phase transition in and the physical parameters of the quasi-one-dimensional GPI ferroelectric has been studied. The research was performed in the framework of a modified model for the proton ordering in quasi-one-dimensional ferroelectrics with hydrogen bonds of the GPI type with regard for the piezoelectric coupling with the strains $\varepsilon_j$ in the ferroelectric phase in the two-particle cluster approximation. It is found that the application of the shear stress $\sigma_5$ substantially increases the strain $\varepsilon_5$ and insignificantly the strain $\varepsilon_3$, whereas the stress $\sigma_6$ increases only the strain $\varepsilon_6$. It is also found that the action of the stresses $\sigma_5$ and $\sigma_6$ and the field $E_1$ affects the thermodynamic parameters of the GPI crystal by changing the temperature behavior of the order parameters.

The results of numerical calculations show how the changes in the temperature dependences of the thermodynamic parameters depend on the signs of the
stresses $\sigma_j$ and the electric field $E_1$ under the combined action on those factors. In particular, if the stress $\sigma_5$ and the field $E_1$ are applied to the crystal, the temperature dependences of thermodynamic parameters become shifted along the temperature axis toward lower temperatures. The combined application of the stress $\sigma_6$ and the field $E_1$ results in the appearance of a number of interesting effects, e.g., the smearing of the polarization $P_2$ and the disappearance of the phase transition, the emergence of the dielectric permittivity $\varepsilon_{22}$ and the piezoelectric stress coefficient $e_{21}$, and the smearing of the piezoelectric strain constant $h_{21}$.

No additional parameters are used when carrying out the numerical calculations of thermodynamic parameters accounting for the shear stresses and the field $E_1$, as compared with the calculations performed for the case without the account for those external factors. Therefore, the temperature dependences obtained in this work for the thermodynamic parameters of the GPI crystal have a predictive character.