A modified proton ordering model of glycinium phosphite ferroelectric, which involves the piezoelectric coupling of the proton and lattice subsystems, is used for the investigation of the electrocaloric effect. The model also accounts for the dependence of the effective dipole moment on a hydrogen bond on an order parameter, as well as a splitting of parameters of the interaction between pseudospins in the presence of shear stresses. In the two-particle cluster approximation, the influence of longitudinal and transverse electric fields on components of the polarization vector and the dielectric permittivity tensor, as well as on thermal characteristics of the crystal, is calculated. Longitudinal and transverse electrocaloric effects are studied. The calculated electrocaloric temperature change is quite small, about 1 K; however, it can change its sign under the influence of a transverse field.

Keywords: ferroelectrics, phase transition, dielectric permittivity, electric field effect, electrocaloric effect.

1. Introduction

As is known, NH$_3$CH$_2$COOH·H$_2$PO$_3$ crystal (glycinium phosphite – GPI) belongs to the family of ferroelectrics with hydrogen bonds [1, 2]. At room temperature, this crystal is in the paraelectric phase and has a monoclinic structure (space group P2$_1$/a) [3–5]. But, at the temperature about 225 K, the crystal passes to the ferroelectric phase (space group P2$_1$). At that, there appear simultaneously ferroelectric ordering of dipole moments along the crystallographic b axis and the antiferroelectric ordering in the (b,c) plane. As a result, the crystal is sensitive to the influence of both: longitudinal and transverse electric fields. In particular, in [6, 7] it was experimentally discovered that its transverse permittivity $\varepsilon_{zz}$ in the ferroelectric phase greatly increases under the influence of a transverse field $E_z$. In addition, dielectric properties of the crystal greatly depend on hydrostatic [8] and uniaxial [9] pressures. These peculiarities make GPI crystals of interest for studies.

In [6, 10], a pseudospin proton ordering model was proposed for the theoretical study of dielectric properties of GPI crystals, which takes the orientation of dipole moments in an unit cell into account. Based on this model, the transverse field effect on the permittivity $\varepsilon_{zz}$ was qualitatively properly explained.

In [11], this model was developed by considering the lattice strains and piezoelectric coupling of the proton and lattice subsystems (deformed proton ordering model). This made it possible to calculate expressions for the spontaneous polarization, static dielectric permittivity tensor, piezoelectric coefficients, elastic constants, and molar heat capacity of the crystal and to obtain the good explanation of experimental data for these characteristics. In addition, based on a modified GPI model, the effects of transverse fields $E_x$ and $E_z$ [12] of hydrostatic [13] and uniaxial [14] pressures on the phase transition and thermodynamic characteristics of GPI crystals, as well as
Longitudinal and Transverse Electrocaloric Effects

Experimental data [16] show that, in the presence of longitudinal field $E_y$, the phase transition smears, and the temperature dependence of the longitudinal permittivity $\varepsilon_{yy}(T)$ has rounded maximum. At the same time, in the model proposed in [11], the effective dipole moments with different values of longitudinal components in the para- and ferroelectric phases are used for the description of $\varepsilon_{yy}(T)$. This leads to the appearance of a break on the curve $\varepsilon_{yy}(T)$ instead of a smoothed maximum in the presence of the field $E_y$. Therefore, in [17] for a proper description of the phase transition smearing, the model [11] was modified. It was supposed that the effective dipole moment on a hydrogen bond depends on the order parameter on this bond, because this parameter continuously depends on the temperature near the phase transition point. This made it possible to quantitatively describe the effect of the field $E_y$.

In [18], the model of GPI proposed in [11] was modified with regard for the splitting of parameters of the interaction between pseudospins under shear stresses $\varepsilon_4$ and $\varepsilon_6$. This enabled the study of the effects of shear stresses $\sigma_4$ and $\sigma_6$ on the phase transition and on dielectric and piezoelectric characteristics of the crystal.

It is interesting to investigate also the electrocaloric (EC) effect, which is a change the temperature $\Delta T$ of the crystal at an adiabatic change of the applied electric field $E_y$ or $E_z$, on the basis of the deformed proton ordering model. In the present paper, we will simultaneously consider the dependence of the effective dipole moment on a hydrogen bond on the order parameter on this bond, as well as a splitting of parameters of the interaction between pseudospins under shear stresses.

2. The Model of GPI Crystal

The proton ordering model of GPI [11, 18] can be understood from Fig. 1, where a unit cell in the ferroelectric phase is shown. For a better understanding of the model, the only phosphite groups are shown in the figure. Protons, which are localized on O–H..., O bonds between the phosphite groups HPO$_3^-$, form zigzag chains along the crystallographic c-axis of the crystal. Dipole moments $d_{4f}/(f = 1, ..., 4)$ are ascribed to the protons on the bonds. In the ferroelectric phase, the dipole moments compensate one another ($d_{q1}$ with $d_{q2}$ and $d_{q4}$) in the directions $Z$ and $X (X \perp (b, c), Y \parallel b, Z \parallel c)$, and simultaneously supplement one another in the direction $Y$, creating the spontaneous polarization.

The pseudospin variables $\sigma_4$, ..., $\sigma_6$ describe a re-orientation of the dipole moments of the base units: $d_{4f} = \mu_f \sigma_4$. The mean values $\langle \sigma_4 \rangle = \frac{1}{2}(n_a - n_b)$ are connected with differences in the occupancies of the two possible molecular positions, $n_a$ and $n_b$.

Hereinafter for convenience, we use the notations $1, 2$, and $3$ instead of $x$, $y$, and $z$, respectively, for components of vectors and tensors. The Hamiltonian of the proton subsystem of GPI, which involves the short-range and long-range interactions and the applied mechanical stresses and electric fields $E_1$, $E_2$, $E_3$ along positive directions of the Cartesian axes $X$, $Y$, and $Z$, can be written in such a way:

$$
\hat{H} = N\varepsilon_{\text{seed}} + \hat{H}_{\text{short}} + \hat{H}_{\text{long}} + \hat{H}_E + \hat{H}_{E}^3,
$$

(2.1)

where $N$ is the total number of primitive cells. The term $U_{\text{seed}}$ in (2.1) is the “seed” energy, which relates to the heavy ion sublattice and does not explicitly depend on the configuration of the proton subsystem. It includes the elastic, piezoelectric, and dielectric parts expressed in terms of electric fields $E_i$ ($i = 1, 2, 3$) and strains $\varepsilon_j$ ($j = 1, ..., 6$):

$$
U_{\text{seed}} = \frac{\nu}{2} \sum_{i=1}^{6} \varepsilon_i^0 c_{ij}^0(T)\varepsilon_j - \sum_{i=1}^{3} \sum_{j=1}^{6} \varepsilon_i E_i - \sum_{i=1}^{3} \sum_{j=1}^{6} \frac{1}{2} \chi_{ij}^0 E_i E_j.
$$

(2.2)

The parameters $c_{ij}^0(T)$, $\varepsilon_i^0$, $\chi_{ij}^0$ are so called “seed” elastic constants, “seed” coefficients of piezoelectric...
In the paraelectric phase, all coefficients \( \chi^0, \chi^0_H \) are given by:

\[
\chi^0 = \begin{pmatrix}
c^1_{11} & c^1_{12} & c^1_{13} & 0 & c^1_{15} & 0 \\
c^1_{12} & c^1_{22} & c^1_{23} & 0 & c^1_{25} & 0 \\
c^1_{13} & c^1_{23} & c^1_{33} & 0 & c^1_{35} & 0 \\
c^1_{15} & c^1_{25} & c^1_{35} & 0 & c^1_{55} & 0 \\
0 & 0 & 0 & c^0_E & 0 & c^0_F \\
0 & 0 & 0 & 0 & c^0_E & 0
\end{pmatrix},
\]

where \( l = 1, 2, 3, 5 \). The third term in (2.1) describes the long-range dipole-dipole interactions and indirect (through the lattice vibrations) interactions between protons, which are taken into account in mean field approximation:

\[
\hat{H}_{\text{long}} = \frac{1}{2} \sum_{f,f',\ell} J_{ff'} \langle \sigma_{qf} \rangle \langle \sigma_{q'f'} \rangle - \sum_{f,f'} J_{ff'} \langle \sigma_{qf} \rangle \langle \sigma_{qf} \rangle.
\]  

(2.6)

The Fourier transforms of the interaction constants \( J_{ff'} = \sum_q J_{ff'}(q^q) \) at \( k = 0 \) are linearly expanded with respect to the strains \( \varepsilon_j \):

\[
\hat{J}_{ff'} = \hat{J}_{ll'}^0 + \sum_j \psi_{ff',j} \varepsilon_j.
\]

In view of the symmetry of the crystal, the parameters \( \hat{J}_{ff'} \) are given by:

\[
\hat{J}_{11} = \hat{J}_{11}^0 + \sum_l \psi_{11} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6,
\]

\[
\hat{J}_{13} = \hat{J}_{13}^0 + \sum_l \psi_{13} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6,
\]

\[
\hat{J}_{13} = \hat{J}_{13}^0 + \sum_l \psi_{12} \varepsilon_l \pm \psi_{14} \varepsilon_4 \pm \psi_{16} \varepsilon_6,
\]

\[
\hat{J}_{24} = \hat{J}_{24}^0 + \sum_l \psi_{23} \varepsilon_l \pm \psi_{24} \varepsilon_4 \pm \psi_{26} \varepsilon_6,
\]

(2.7)

As one can see from (2.5), (2.7), the parameters \( w \) and most of \( J_{ff'} \) split in the presence of shear strains \( \varepsilon_4, \varepsilon_6 \). As a result, (2.6) can be written as:

\[
\hat{H}_{\text{long}} = NH^0 - \sum_{q} \sum_{f=1}^{4} \mathcal{H}_f \sigma_{qf},
\]

where

\[
H^0 = \sum_{f,f'=1}^{4} \frac{1}{8} J_{ff'} \eta_f \eta_{f'}, \quad \mathcal{H}_f = \sum_{f'=1}^{4} \frac{1}{2} J_{ff'} \eta_{f'}.
\]

(2.8)
The fourth term in (2.1) describes the interactions of pseudospins with the external electric field:

\[ H_E = -\sum_{qf} \mu_f E \frac{\sigma_{qf}}{2}. \]  

(2.10)

Here, \( \mu_1 = (\mu_{13}^x, \mu_{13}^y, \mu_{13}^z) \), \( \mu_3 = (-\mu_{13}^x, \mu_{13}^y, -\mu_{13}^z) \), \( \mu_2 = (-\mu_{24}^x, -\mu_{24}^y, \mu_{24}^z) \), and \( \mu_4 = (\mu_{24}^x, -\mu_{24}^y, -\mu_{24}^z) \) are the effective dipole moments per one pseudospin.

The term \( \hat{H}_E \) in Hamiltonian (2.1) is introduced in the present model for the first time. It accounts for the above-mentioned dependence of the longitudinal components of dipole moments on the mean value of the pseudospin \( s_f \):

\[ \hat{H}_E = -\sum_{qf} s_f^2 \mu_f E_2 \frac{\sigma_{qf}}{2} = \sum_{qf} \left( \frac{1}{N} \sum_{q'} \sigma_{q'f} \right)^2 \frac{\mu_f E_2 \sigma_{qf}}{2} \]

(2.11)

Here corrections to the dipole moments \( s_f^2 \mu_f \) are used instead of \( s_f \mu_f \) because of the symmetry considerations, the energy should not change, when the field and all pseudospins change their sign.

The term \( \hat{H}_E \), as well as long-range interactions, is taken into account in the mean field approximation:

\[ \hat{H}_E = -\sum_{qf} \left( \frac{1}{N} \sum_{q'} \sigma_{q'f} \right)^2 \frac{\mu_f E_2 \sigma_{qf}}{2} = \]

\[ = -\frac{1}{N^2} \sum_{qf} \sum_{q'} \sigma_{qf} \sigma_{q'f} \frac{\mu_f E_2 \sigma_{qf}}{2} \]

\[ \approx -\frac{1}{N^2} \sum_{qf} \sum_{q'} \left( \sigma_{qf} + \sigma_{q'f} + \sigma_{q'f} \right) n_f^2 - 2 n_f^2 \mu_f E_2 = \]

\[ = -\sum_{qf} \left( 3 \sigma_{qf} n_f^2 - 2 n_f^2 \mu_f E_2 \right) = \]

\[ = -3 \sum_{qf} \frac{\sigma_{qf}}{2} \eta_f^2 \mu_f E_2 + N \sum_{f=1}^4 \eta_f^4 \mu_f E_2. \]  

(2.12)

The two-particle cluster approximation for short-range interactions is used for the calculation of field effects in GPI. In this approximation, the thermodynamic potential under stresses \( \sigma_j \) is given by:

\[ G = N U_{\text{seed}} + NH^0 + N \sum_{f=1}^4 \eta_f^4 \mu_f E_2 - N v \sum_{j=1}^6 \sum_{f=1}^4 \sigma_j \varepsilon_j - \]

\[ - k_B T \sum_q \left\{ 2 \ln \text{Sp} e^{-\beta H_2^{(q)}} - 4 \sum_{j=1}^6 \ln \text{Sp} e^{-\beta H_{4j}^{(q)}} \right\}. \]  

(2.13)

where the following notations are used:

\[ \text{Sp}\{ \ldots \} = \sum_{\sigma_1 = \pm 1} \sum_{\sigma_2 = \pm 1} \sum_{\sigma_3 = \pm 1} \sum_{\sigma_4 = \pm 1}, \]

\[ \beta = \frac{1}{k_B T}, \quad k_B \text{ is the Boltzmann constant, } \hat{H}_2^{(2)} \text{ and } \hat{H}_{4j}^{(1)} \text{ are the effective two-particle and one-particle Hamiltonians:} \]

\[ \hat{H}_2^{(2)} = H_{sh} - \sum_{f=1}^4 \eta_f \sigma_{qf} \]  

(2.14)

\[ \hat{H}_{4j}^{(1)} = - \frac{\gamma_f}{\beta} \sigma_{qf}, \]

(2.15)

\[ H_{sh} = -2 \left( w_1^2 \sigma_{q1} \sigma_{q2}^2 + w_2^2 \sigma_{q3} \sigma_{q4}^2 \right), \]

(2.16)

\[ \gamma_f = \beta (\Delta_f + H_f + \mu_f E + 3 n_f^2 \mu_f E_2), \]

(2.17)

The symbols \( \Delta_f \) are the effective fields created by the neighboring bonds from outside of the cluster. In the cluster approximation, the fields \( \Delta_f \) can be determined from the condition of minimum of the thermodynamic potential \( \delta G / \delta \Delta_f = 0 \), which gives the self-consistency condition that states that the mean values of the pseudospins \( \langle \sigma_{qf} \rangle = \eta_f \) calculated with the two-particle and one-particle Gibbs distributions, respectively, should coincide:

\[ \eta_f = \frac{\text{Sp} \sigma_{qf} e^{-\beta H_2^{(2)}}}{\text{Sp} e^{-\beta H_2^{(2)}}} = \frac{\text{Sp} \sigma_{qf} e^{-\beta H_{4j}^{(1)}}}{\text{Sp} e^{-\beta H_{4j}^{(1)}}}. \]  

(2.18)

Using (2.18) with the one-particle distribution function \( \eta_f = \text{th}(\gamma_f / 2) \), the effective fields \( \Delta_f \) are expressed through the order parameters \( \eta_f \)

\[ \Delta_f = \frac{1}{2 \beta} \ln 1 + \frac{1}{1 - \eta_f} - \frac{1}{2} H_f - \frac{1}{2} (\mu_f E + 3 n_f^2 \mu_f E_2), \]

Then \( \gamma_f \) are given by:

\[ \gamma_f = \frac{1}{2} \ln 1 + \frac{1}{1 - \eta_f} + \frac{4}{\beta} \sum_{j=1}^6 \eta_f^4 \mu_f E_2 + \frac{1}{2} (\mu_f E + 3 n_f^2 \mu_f E_2). \]

The first equality (2.18) yields the system of equations for the order parameters \( \eta_f \):

\[ \eta_f = \frac{1}{2} \text{Sp} \left\{ \sigma_{qf} e^{-\beta H_{sh} + \sum_{j=1}^6 \gamma_f \eta_f^4 \mu_f E_2} \right\}. \]  

(2.19)
where $Z$ is the two-particle partition function.

$$Z = \text{Sp} e^{-\beta H_{sh} + \sum_{i=1}^{4} \frac{y_i \varepsilon_i}{2}}. \quad (2.20)$$

3. Thermodynamic Characteristics of GPI

Let us write the thermodynamic potential per unit cell in the form

$$g = \frac{G}{N} = U_{\text{seed}} + H^0 + \sum_{f=1}^{4} \eta_f^j \mu_f^j E_2 - v \sum_{j=1}^{6} \sigma_j \varepsilon_j +$$

$$+ 4 k_B T \ln 2 - \frac{1}{2} k_B T \sum_{f=1}^{4} \ln (1 - \eta_f^2) - 2 k_B T \ln Z. \quad (3.1)$$

From the condition of minimum of the thermodynamic potential, we have

$$\left( \frac{\partial g}{\partial \varepsilon_j} \right)_{E_i, \sigma_j} = 0.$$

Taking (2.19) into account, we get a system of equations for the strains $\varepsilon_j$:

$$\sigma_j = \sum_{j'=1}^{6} e_{jj'}^0(T) \varepsilon_{j'} - \frac{3}{2} e_{ij}^0 \varepsilon_i -$$

$$- \frac{2M_l}{v Z} - \sum_{f,f'=1}^{4} \psi_{ff'} \eta_f \eta_{f'} \cdot \quad (3.2)$$

Here, the following notation is used:

$$M_l = \text{Sp} \left\{ 2 \left( \frac{\sigma_{qf}}{2} \frac{\sigma_{qf}}{2} + \delta_{2f} \frac{\sigma_{qf}}{2} \frac{\sigma_{qf}}{2} \right) e^{-\beta H_{sh} + \sum_{j=1}^{4} \frac{y_j \varepsilon_j}{2}} \right\}$$

Differentiating the thermodynamic potential with respect to the fields $E_i$, one can get the expressions for components of the polarization $P_i$:

$$P_1 = e_{14}^0 \varepsilon_4 + e_{16}^0 \varepsilon_6 + \chi_{10}^0 E_1 +$$

$$+ \frac{1}{2v} \left[ \mu_{13}^f (\eta_1 - \eta_3) - \mu_{24}^f (\eta_2 - \eta_4) \right],$$

$$P_2 = e_{21}^0 \varepsilon_1 + e_{22}^0 \varepsilon_2 + e_{23}^0 \varepsilon_3 + e_{25}^0 \varepsilon_5 + \chi_{20}^0 E_2 +$$

$$+ \frac{1}{2v} \left[ \mu_{13}^f (\eta_1 - \eta_3) - \mu_{24}^f (\eta_2 - \eta_4) \right] + \frac{1}{2v} \sum_{f=1}^{4} \eta_f \mu_f^j \cdot \quad (3.3)$$

$$P_3 = e_{34}^0 \varepsilon_4 + e_{36}^0 \varepsilon_6 + \chi_{30}^0 E_3 +$$

$$+ \frac{1}{2v} \left[ \mu_{13}^f (\eta_1 - \eta_3) - \mu_{24}^f (\eta_2 - \eta_4) \right] \cdot \quad (3.4)$$

The components of the isothermal dielectric susceptibility tensor of mechanically clamped or free crystal GPI can be found by the numerical differentiation of components of the polarization vector with respect to components of the field at a constant strain or constant stress, respectively:

$$\chi_{ii}^\sigma = \lim_{E_i \to 0} \left( \frac{\partial P_i}{\partial E_i} \right)_{E_j, \sigma_j}, \quad \chi_{ii}^{\sigma f} = \lim_{E_i \to 0} \left( \frac{\partial F_i}{\partial E_i} \right)_{E_j, \sigma_j}.$$

The molar entropy of the proton subsystem (here, $R$ is the gas constant) is given by:

$$S = - \frac{N_A}{4} \left( \frac{\partial q}{\partial T} \right)_{\eta_f, \varepsilon_i} = R \left\{ - 4 \ln 2 + \frac{1}{2} \sum_{f=1}^{4} \ln (1 - \eta_f) +$$

$$+ 2 \ln Z - \frac{2R}{Z} \right\} \left( \sum_{f=1}^{4} \frac{J_{ff} + 3 \eta_f^2 \mu_f^j E_2}{2} \right) \cdot \quad (3.4)$$

where such notation is used:

$$H_{2\varepsilon} = - H_{sh} + \sum_{f=1}^{4} \left( \sum_{j=1}^{4} J_{ff} + \eta_f \right),$$

$$+ \frac{1}{2} \left( \mu_f E + 3 \eta_f^2 \mu_f^j E_2 \right) \cdot \quad (3.5)$$

The molar heat capacity of the proton subsystem of GPI crystals can be found by the numerical differentiation of entropy (3.4):

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

The total specific heat is considered to be the sum of the proton and lattice contributions:

$$C = \Delta C^\sigma + C_{\text{lattice}}. \quad (3.6)$$

The lattice contribution near $T_c$ is approximated by the linear dependence

$$C_{\text{lattice}} = C_0 + C_1 (T - T_c). \quad (3.7)$$

The corresponding lattice contribution to the entropy near $T_c$ is then

$$S_{\text{lattice}} = \int \frac{C_{\text{lattice}}}{T} dT = (C_0 - C_1 T_c) \ln (T) + C_1 T. \quad (3.8)$$

Hence, the total entropy as a function of the temperature and the field component $E_i$ reads

$$S_{\text{total}}(T, E_i) = S + S_{\text{lattice}}. \quad (3.9)$$
Solving (3.9) with respect to the temperature at $S_{\text{total}}(T, E_i) = \text{const}$ and two values of the field, one can calculate the electrocaloric temperature shift (as seen in Fig. 10)

$$\Delta T = T(S_{\text{total}}, E_i(2)) - T(S_{\text{total}}, E_i(1)).$$

(3.10)

The electrocaloric temperature change can be calculated also, by using the known formula

$$\Delta T = - \int_0^V \frac{TV}{C} \left( \frac{\partial P_i}{\partial T} \right) dE_i,$$

(3.11)

where $V = vN_A/4$ is the molar volume.

4. Results of Numerical Calculations. Discussion

For the numerical calculation of the dielectric characteristics of GPI, we use the parameters determined in [18] and earlier in [11] from the condition of agreement of the calculated characteristics with experimental data. At that, experimental data on the temperature dependences of the spontaneous polarization $P_s(T)$ [19], molar dielectric constant $C_p(T)$ [20], components of the dielectric permittivity $\varepsilon_{ii}$ [21, 22], $\varepsilon_{0}$, $\varepsilon_{\infty}$ [1], piezoelectric coefficients $d_{21}$, $d_{23}$[22], as well as the strain potentials, were taken into account as well. The optimal values of the theory parameters are given below.

The parameter of the short-range interactions $\omega_0/k_B = 800$ K.

The parameters of the long-range interactions:

- $J_{13}^0 = J_{12}^0 = J_{22}^0 = 6.23$ K,
- $J_{13}^0 = J_{14}^0 = J_{24}^0 = 6.03$ K,

where $J_{ij}^0 = J_{ff}^0/k_B$.

Strain potentials:

- $\delta_1 = 500$ K, $\delta_2 = 600$ K, $\delta_3 = 500$ K, $\delta_4 = 150$ K, $\delta_5 = 100$ K, $\delta_6 = 150$ K; $\delta_i = \delta_i/k_B$;
- $\psi_{ff1} = 187.3$ K, $\psi_{ff2} = 505.1$ K, $\psi_{ff3} = 221.3$ K, $\psi_{ff5} = 45.4$ K,
- $\psi_{114} = \psi_{124} = \psi_{224} = \psi_{116} = \psi_{126} = \psi_{226} = 317.8$ K,
- $\psi_{134} = \psi_{144} = \psi_{244} = \psi_{136} = \psi_{146} = \psi_{246} = 0.0$ K.

where $\psi_{ffij} = \psi_{ffij}/k_B$.

Components of the effective dipole moments

- $\mu_{13}^x = 0.4 \times 10^{-18}$ esu-cm; $\mu_{13}^y = 4.05 \times 10^{-18}$ esu-cm;
- $\mu_{13}^z = 4.2 \times 10^{-18}$ esu-cm; $\mu_{24}^x = 2.3 \times 10^{-18}$ esu-cm;
- $\mu_{24}^y = 3.0 \times 10^{-18}$ esu-cm; $\mu_{24}^z = 2.2 \times 10^{-18}$ esu-cm.

Corrections to the effective dipole moments $\mu_1^* = \mu_1^2 = -0.25 \times 10^{-18}$ esu-cm and $\mu_4^* = \mu_4^2 = 0$ esu-cm are found in the present paper from the condition of agreement of the calculated saturation polarization with experimental data.

The volume of a unit cell of GPI is $v = 0.601 \times 10^{-21}$ cm$^3$.

The “seed” coefficients of the piezoelectric stress $\sigma_{ij}$, “seed” dielectric susceptibilities $\chi_{ij}$, and “seed” elastic constants $c_{ij}$ are obtained as follow: $c_{11}^0 = 0.0$ cm$^2$/esu; $\chi_{11} = 0.1$, $\chi_{22} = 0.403$, $\chi_{33} = 0.5$, $\chi_{12} = 0.0$; $c_{11}^0 = 269.1$ kbar, $c_{12}^0 = 145$ kbar, $c_{13}^0 = 116.4$ kbar, $c_{22}^0 = 39.1$ kbar, $c_{23}^0 = 649.9 - 0.4(T - T_c)$ kbar, $c_{33}^0 = 203.8$ kbar, $c_{23}^0 = 56.4$ kbar, $c_{23}^0 = 244.1$ kbar, $c_{35}^0 = -28.4$ kbar, $c_{35}^0 = 85.4$ kbar, $c_{34}^0 = 153.1$ kbar, $c_{36}^0 = -11$ kbar, $c_{46}^0 = 118.8$ kbar.

The parameters of lattice contribution to the molar heat capacity $c_0$ (see (3.7)): $c_0 = 147.5$ J/(mol K), $c_1 = 0.45$ J/(mol K).

Let us investigate firstly, how the present theory describes the dielectric properties of GPI. In the absence of a field, the spontaneous polarization $P_s$ monotonically and continuously decreases with increasing the temperature and goes to zero at the temperature $T_c$ (Fig. 2, curve 0). For comparison, we also present the temperature dependences calculated in [17] $P_s(T)$ (curve 0) with regard for the dependence of the effective dipole moment $\mu(\eta)$ on the order parameter, but omitting the splittings of the parameters $\mu$ and $J_{ff}$ in the presence of shear strains. Besides, we present the temperature dependences calculated in [18] $P_s(T)$ (curve 0) in view of the splittings of the parameters $\mu$ and $J_{ff}$, but not accounting for $\mu(\eta)$.

The longitudinal electric field $E_2$ smears the phase transition. As a result, the curve $P_s(T)$ becomes smoothed (Fig. 2, curves 0, 40). In this and next figures in the notations of the curves “a, b, c,” number $a$ means a value of an external field in MV/m, indices $y$ and $z$ mean the directions of the field ($E_y$, $E_z$).

The transverse field $E_3$ induces the polarization component $P_3$ (Fig. 3) and lowers the temperature $T_c$, as it is shown in Fig. 4. In a weak transverse field, the phase transition remains the second order one. At
that, the temperature dependence $P_2(T)$ is qualitatively similar to the case of $E_3 = 0$ MV/m (Fig. 2, curves $4^z$, $5^z$), the curve $P_5(T)$ has a sharp bend at $T_c$ (Fig. 3, curves $2^z$, $4^z$, $5^z$). In the fields stronger than some critical $E^{tr} \approx 5.9$ MV/m (tricritical point), the phase transition becomes the first order one (dashed curve in Fig. 4). As a result, the components $P_2(T)$ and $P_3(T)$ have a break at $T_c$ (curves $6^c$, $6.5^c$, $7^c$ in Fig. 2 and 3).

In the absence of a field, the longitudinal dielectric permittivities of mechanically free $\varepsilon_{22}^\sigma$ and clamped $\varepsilon_{22}^\epsilon$ crystals go to infinity at $T_c$ (Fig. 5, solid 1 and dashed $1'$ curves, respectively; as well as Fig. 6, curves 0, solid and dashed, respectively). In the paraelectric phase, the permittivities $\varepsilon_{22}^\sigma$ and $\varepsilon_{22}^\epsilon$ coincide. For comparison, we also present the temperature dependences $\varepsilon_{22}^\sigma(T)$ calculated in [17] (Fig. 5, curves 2, $2'$) with regard for $\mu(\eta)$, but omitting the splittings of the parameters $w$ and $J_{ff}^{c}$ in the presence of shear strains. In addition, we give the temperature dependences calculated in [18] $\varepsilon_{22}^{\sigma,c}(T)$ (Fig. 5, curves 3, $3'$), by considering the splittings of the parameters $w$ and $J_{ff}^{c}$, but not accounting for $\mu(\eta)$.

In the presence of a longitudinal electric field $E_2$, the curves $\varepsilon_{22}^{\sigma,c}(T)$ are smoothed (Fig. 6, curves $1''$, $2''$, $3''$, $4''$, $5''$, $6''$, $7''$).
In a weak transverse field $E_3 < E_{tr}$, the longitudinal dielectric permittivity of a mechanically free crystal $\varepsilon_{22}^\sigma$ goes to infinity at $T_c$ (Fig. 6, solid lines $\sigma^1, \sigma^5$), whereas the permittivity of a clamped crystal $\varepsilon_{22}^\tau$ is finite (Fig. 6, dashed lines $\tau^1, \tau^5$). Curves $\varepsilon_{22}^\sigma(T)$ and $\varepsilon_{22}^\tau(T)$ do not coincide even in the paraelectic phase. In a strong field $E_3 > E_{tr}$, owing to the first-order phase transition, the permittivities $\varepsilon_{22}^\sigma$ both become finite and decrease with increasing the field strength (Fig. 6, curves $\sigma^6, \sigma^5, \sigma^7$).

In the absence of a field, the transverse dielectric permittivities of mechanically free $\varepsilon_{22}^\sigma$ and clamped $\varepsilon_{22}^\tau$ crystals are finite and have sharp bends at $T_c$ (Fig. 8, solid line 0 and, very close to it, dashed line 0, respectively). In the paraelectric phase, the permittivities $\varepsilon_{33}^\sigma$ and $\varepsilon_{33}^\tau$ coincide. For comparison, we present the temperature dependences $\varepsilon_{33}^\sigma(T)$ [17] (Fig. 8, curve $\sigma'$) with taking $\mu(\eta)$ into account, but not considering the splittings of the parameters $w$ and $J_{ff'}$ in the presence of shear strains.

In the presence of a longitudinal field, the curves $\varepsilon_{33}^\sigma(T)$ and $\varepsilon_{33}^\tau$ also become smoothed (Fig. 8, solid and dashed curves $\tau'$). In the presence of a transverse field, the transverse dielectric permittivities $\varepsilon_{33}^\sigma$ greatly increase in the ferroelectric phase in comparison with the case of $E_3 = 0$, and curve $\varepsilon_{33}^\sigma(T)$ has a break at $T_c$ (Fig. 8, curves $\tau^1, \tau^5$). As was shown in [25], such increase of $\varepsilon_{33}^\sigma$ is related to the disordering of pseudospins in the chain “B” (see Fig.1) at the influence of the field $E_3$. The maximum value of $\varepsilon_{33}^\sigma$ goes to infinity, when $E_3 \to E_{tr}$. In a strong field $E_3 > E_{tr}$ owing to the first-order phase transition, the permittivities $\varepsilon_{33}^\sigma$ decrease again with increasing the field strength (Fig. 8, curves $\sigma^6, \sigma^5, \sigma^7, \sigma^8$).

In the presence of the field $E_3$, experimental curves $\varepsilon_{33}^\sigma(T)$ are smoothed near $T_c$ and have no any break (Fig. 9). In order to explain such behavior of the transverse permittivity, we calculated $\varepsilon_{33}^\sigma(T)$, by supposing that an internal electric field $E_2$ appears together with the applied external field $E_3$. It turned out that it is possible to achieve the satisfactory description of the temperature dependence of $\varepsilon_{33}^\sigma$, by supposing that $E_2 \sim 0.07E_3$ (Fig. 9, solid black line).
Temperature dependences of the transverse dielectric permittivities of mechanically free $\varepsilon_{33}^\sigma$ (solid lines) and clamped $\varepsilon_{33}^\sigma$ (dashed lines) GPI crystals at different values of the fields $E_2$ and $E_3$; symbols $\circ$ are experimental data [1] at the zero field.

Temperature dependences of the dielectric permittivity $\varepsilon_{33}^\sigma$ at different values of the field strength $E_3$ (MV/m): 0.0 – 1 ($\bigcirc$); 1.0 – 2 ($\square$); 2.0 – 3 ($\bigcirc$); 3.0 – 4 ($\bigodot$); 4.0 – 5 ($\bigtriangleup$) [7] and at the applied simultaneously longitudinal field $E_2 = 0.07E_3$. Red dashed curves 1’–5’ [25] of the permittivity $\varepsilon_{33}^\sigma$ at the same values of $E_3$ and at the field $E_2 \sim 0.05E_3$ applied simultaneously.

Fig. 10. Temperature dependences of the molar entropy of GPI at different values of the fields $E_2$ and $E_3$.

In this figure, the permittivity calculated in [25] of a mechanically clamped crystal $\varepsilon_{33}^\sigma$ is shown at different values of the field $E_3$ and at applied simultaneously longitudinal field $E_2 = 0.07E_3$. We note that the $y$-components of the effective dipole moment was considered in [25] to be the same in the paraelectric and ferroelectric phases. It is necessary to note that the phase transition temperature for the sample in [7] was 222 K. For the explanation of the experimental data [7], we supposed that the values of all interactions in this sample are proportional to the values of corresponding interactions in the sample with $T_c = 225$ K: $w(222$ K) = $k\bar{w}(225$ K), $\psi_{ij}^< (222$ K) = $k\bar{\psi}_{ij}^< (225$ K), $\delta_i(222$ K) = $k\delta_i(225$ K), $\psi_f^>(222$ K) = $k\psi_f^>(225$ K), $\mu_f(222$ K) = $k\mu_f(225$ K), where $k = 0.987 \approx 222/225$. All another parameters are such as for the sample with $T_c = 225$ K.

The longitudinal field $E_2$ decreases the entropy of a crystal in the whole temperature interval (Fig. 10, curve 50°), inasmuch as it increases the ordering of pseudospins in both sublattices, “A” and “B” (Fig. 1). The transverse field $E_3$ also decreases the entropy, but only in the paraelectric phase. In the ferroelectric phase in the weak fields $E_3 < E^m$, the entropy increases owing to a disordering of pseudospins in sublattice “B” under the influence of the field $E_3$ (Fig. 10, curve 4°). The strong field $E_3 > E^m$ overturns the pseudospins in sublattice “B” and orders them in its direction. As a result, the entropy decreases again (Fig. 10, curve 50°).

The effect of the fields $E_2$ and $E_3$ on the molar heat capacity is mainly similar to the effect of these fields on the dielectric properties: the field $E_2$ smoothes the curve $C(T)$ near $T_c$ (Fig. 11, curve 4°), whereas the field $E_3$ lowers $T_c$ (Fig. 11, curves 4°, 5°, 6°, 6.5°, 7°).

As one can see from the previous figures, the present model, which simultaneously involves $\mu(\eta)$ and the splittings of the interaction parameters $w$ and $J_{ij}$ in the presence of shear strains, practically reproduces the results of previous calculations [17] and...
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Fig. 11. Temperature dependences of the heat capacity of GPI at different values of the fields $E_2$ and $E_3$. Symbols ⌂ are experimental data [20]. Solid line presents the result of calculations, the dashed line corresponds to the lattice contribution.

Fig. 12. Temperature dependence of the electrocaloric temperature change $\Delta T$ of GPI crystal at different values of the field $E_2$.

[18], as well as satisfactorily describes the experimental data for dielectric characteristics and the effect of electric fields on the dielectric permittivity. Therefore, this model can be suitable for the investigation of the electrocaloric effect in GPI crystals.

Let us firstly examine the longitudinal EC effect. In Fig. 12, 13, a change of the temperature $\Delta T$ of the crystal at the adiabatic change of the applied electric field $E_2$ at different values of the initial temperature and the field $E_2$ are presented. In the weak fields ($E_2 < 1$ MV/m) at the initial temperature $T = T_c = 225$ K, the temperature change follows the law $\Delta T \sim E_2^{2/3}$ (green curve in Fig. 13); at

$T < T_c$, $\Delta T \sim E_2$ (blue curves in Fig. 13); at $T > T_c$, $\Delta T \sim E_2^3$ (red curves in Fig. 13). At stronger fields $E_2 > 1$ MV/m, the dependences $\Delta T(E_2)$ deviate from the mentioned laws and reach the saturation at $E_2 \gg 50$ MV/m. The longitudinal EC effect is positive in the whole temperature interval.

In the case of adiabatic application of a transverse field $E_3$, the electrocaloric temperature change $\Delta T$ can be positive or negative (Fig. 14, 15). At the initial temperatures $T \geq T_c$, the transverse EC effect is qualitatively similar to the longitudinal EC effect: in the weak fields $\Delta T \sim E_3^2$ (green and red curves in Fig. 15). At strong fields, the dependences $\Delta T(E_3)$ deviate from the quadratic law and reach the saturation at $E_3 \gg 50$ MV/m. At the initial temperatures $T < T_c$ in the weak fields $E_3 < E^c$, the temperature of the crystal nonlinearly lowers with increasing the field strength (blue curves in Fig. 15). This is connected with the above-mentioned disordering of pseudospins in sublattice "B" under influence of the field $E_3$ that leads to increasing the entropy at a constant temperature (Fig. 10, curve $4^c$) and to the adiabatic (at a constant entropy) lowering of the temperature. In addition, as one can see from Fig. 3, in the ferroelectric phase the the polarization component $P_3$ increases with the temperature, i.e., $\partial P_3 / \partial E_3 > 0$. Then $\Delta T < 0$, according to (3.11). At a further strengthening of the field ($E_3 > E^c$), as was said above, the pseudospins in sublattice "B" turn over and order in the direction of field that leads to decreasing the entropy at a constant temperature (Fig. 10, curve $5^c$) and an isentropic increase of the temperature.

5. Conclusions

The simultaneous consideration of the dependence of the effective dipole moment of a hydrogen bond on the order parameter on this bond $\mu(\eta)$, as well as the splittings of the interaction parameters $w$ and $J_{ff}$ in the presence of shear strains, practically reproduces the results of previous calculations of the dielectric characteristics with regard for only $\mu(\eta)$ or only the splitting of $w$ and $J_{ff}$.

At the weak field $E_2$ in the ferroelectric phase, an electrocaloric temperature change $\Delta T$ linearly increases with the field, in the paraelectric phase – quadratically, and at the initial temperature $T = T_c$ – by the law $\Delta T \sim E_2^{2/3}$. At strong fields, the dependence $\Delta T(E_2)$ deviates from these laws and reaches the saturation at $E_2 \gg 50$ MV/m.

The transverse EC effect is qualitatively similar to the longitudinal EC effect, whereas, in the ferroelectric phase, it can be negative. This is connected with the antiferroelectric ordering in the plane $(a, c)$ below $T_c$.

It should be noted that the present deformed proton ordering model is suitable for studies of the barocaloric, piezocaloric, and multicaloric effects in GPI crystals.

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Abstract

The present study investigates the longitudinal and transverse electrocaloric effects in the ferroelectric GPI crystal. The crystallographic structure and Dielectric properties of GPI were characterized. The influence of electric fields and hydrostatic pressure on the thermodynamic characteristics of the crystal were evaluated. The deformation effects on the crystal were observed. The influence of uniaxial pressures on the thermodynamic properties of GPI was investigated. The dynamic properties of GPI were studied. The phase transitions and deformation effects were characterized. The study provides insights into the electrocaloric phenomena in GPI crystal.