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Changes of anisotropy of dilatative and optical properties of DGN crystal at ferroelectric phase transition

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Abstract. Temperature dependences of the linear dimension $L(T)$ and the optical path difference $D(T)$ of the ferroelectric diglycine nitrate crystals, $(\text{NH}_2\text{CH}_2\text{COOH})_2\cdot\text{HNO}_3$, have been measured for three principal directions of optical indicatrix in the range of 130÷295 K including the phase transition point $T_c = 206$ K. Temperature dependences of the refractivity $n(T) - 1$, refraction $R(T)$, and degrees of dilatative and optical anisotropies, $A_\alpha(T)$ and $A_{n-1}(T)$ have been calculated on the basis of the experimental dependences $L(T)$ and $D(T)$.

Minima of the temperature dependences of spontaneous electrostriction coefficients $Q_{ij}^{(s)}(T)$, anisotropy degrees of dilatative (A_α) and refractive (A_{n-1}) characteristics close to T_c temperature show the relative disordering of DGN crystal in the temperature range near T_c . The temperature dependence of refraction $R(T)$ of the crystal testifies the increase of dipole-dipole interaction with decreasing temperature in the wide range 295÷130 K.

Keywords: ferroelectric crystals, phase transition, anisotropy of physical properties

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1. Introduction

The crystal of diglycine nitrate (DGN), $(\text{NH}_2\text{CH}_2\text{COOH})_2\cdot\text{HNO}_3$, is ferroelectric below the phase transition temperature $T_c = 206$ K belonging to the space group Pa , and above this temperature it becomes paraelectric with the center symmetry space group $P2_1/a$ [1,2]. It was suggested from the dielectric and specific heat measurements that the phase transition of this crystal is of order-disorder type [1]. Structural arrangement of two glycine molecules as well as a hydrogen bond between them and a mechanism of the phase transition were found to be fairly similar to the well-known triglycine sulphate crystals (TGS). The spontaneous polarization vector P_s of DGN crystal lies in the symmetry plane (101) [2] and is equal to $1.4\cdot 10^{-2}$ C/m² at 123 K [1].

It was shown in the investigation of optical properties of DGN crystal [3] that b -axis of the crystal is perpendicular to the symmetry plane and coincides with n_m -direction of the optical indicatrix. The angle between the spontaneous polarization vector P_s and n_p -axis is equal to $17.2^\circ \pm 0.5^\circ$. Principal magnitudes of birefringence of DGN for the wavelength $\lambda = 632.8$ nm are the following, $\Delta n_g = n_m - n_p = 0.079$, $\Delta n_m = n_g - n_p = 0.141$, $\Delta n_p = n_g - n_m = 0.070$. The crystal is transparent in the spectral range of 245÷1900 nm.

The aim of present investigation was to study the peculiarities of temperature behavior of degree of anisotropy of physical properties of DGN crystal in the range including phase transition point T_c .

2. Experimental

The samples of DGN single crystal were grown by the slow evaporation method. Optically transparent samples of DGN crystal were prepared in the form of rectangular blocks cut along the principal directions of optical indicatrix with typical dimensions of about 5÷10 mm.

The thermal linear expansion of DGN crystal was measured using the quartz dilatometer by the electric capacitor method [4]. The rate of temperature change of the samples during cooling run was 1 K/min. The sensitivity of dilatometer δL being a function of distance between capacitor plates was equal to $\delta L \approx 5$ nm in our case. This corresponds to the relative error $\delta(\delta L/L) \leq 10^{-6}$ of the elongation $\delta L/L$.

The dispersion of refractive index $n(\omega)$ of DGN crystals was measured with an accuracy of $\delta n = 2\cdot 10^{-4}$ by the immersion method using the refractive index dispersion data for appropriate immersion liquid using the Pulfrich refractometer.

Temperature measurements of the optical path difference $D(T)$ were performed using the laser interferometer of the Jamin type [5]. Two interfering light beams were passing through the sample of the thickness L_i and through the same thickness of air. The measurements of temperature dependence of light intensity were performed in the scanning mode in the heating regime. Since the relative temperature changes of the optical path difference $D_{ij} = L_i(n_j - 1)$ can be presented in the form [6],

$$\frac{\delta D_{ij}}{D_{ij}} = \frac{\delta L_i}{L_i} + \frac{\delta n_j}{(n_j - 1)}, \quad (1)$$

we have calculated the relative temperature changes of refractivity $\delta n_j/(n_j - 1)$ on the basis of relative temperature changes of $\delta D_{ij}/D_{ij}$ and $\delta L_i/L_i$ ($i, j = g, m, p$).

The temperature dependence of spontaneous polarization $P_s(T)$ of DGN crystal was measured using the known method of pyroelectric current integration [7].

3. Results and discussion

Temperature expansion of DGN crystals in the wide temperature range 130–293 K is characterized by the positive coefficients of linear and volume thermal expansion, $\alpha_i = d/dT(\delta L/L)_i$ and $\beta = (\alpha_g + \alpha_m + \alpha_p)$, respectively (Fig. 1). The character of temperature anomalies of $(\delta L/L)_i$ and dV/V corresponds to the continuous type of phase transition (Fig. 1). Linear approximations of the relative change of crystal's dimensions $(\delta L/L)_i$ and dV/V from paraelectric to ferroelectric phase are shown in Fig. 1

(dashed lines). The spontaneous changes of linear dimensions $(\delta L/L)_i^{(s)}$ are negative for the direction along m -half-axis of optical indicatrix ($i = m$) and are positive for p - and g -half-axes (Fig. 1).

The coefficients of linear and volume spontaneous electrostriction, Q_{ij} and Q_V respectively, were calculated on the basis of the following relations [7]:

$$(\delta L/L)_i^{(s)} = Q_{ij}^{(s)} \cdot P_j^2 = Q_{ij}^{(s)} \cdot P_s^2,$$

$$(\delta V/V)^{(s)} = Q_V^{(s)} \cdot P_s^2. \quad (2)$$

It is seen from Fig. 2 that the characteristics of temperature dependences of the square of spontaneous polarization P_s^2 and spontaneous change of the volume $(\delta V/V)^{(s)}$ are different. Similar relation was found for the dependences $P_s^2(T)$ and $(\delta L/L)_i^{(s)}(T)$. These differences are displayed also in the temperature dependence of $Q_V^{(s)}$ coefficient as its decrease with approaching T_c in ferroelectric phase (Fig. 2).

Taking into account that the spontaneous polarization P_s is a primary order parameter in the proper ferroelectric DGN, the non-constancy of $Q_V^{(s)}$ coefficient near T_c testifies that the $(\delta V/V)^{(s)}$ value is not a “good” secondary order parameter. From the viewpoint of microscopic structure of ferroelectric crystal the spontaneous polarization P_s is associated with the certain electrically charged structure elements, whereas the spontaneous deformation $(\delta V/V)^{(s)}$ reflects peculiarities of the integrated microscopic structure. One can also interpret the observed minimal magnitude of the electrostriction coefficients $Q_V^{(s)}$ and $Q_{ij}^{(s)}$ in the temperature region close to T_c as being caused by the weakened correlation be-

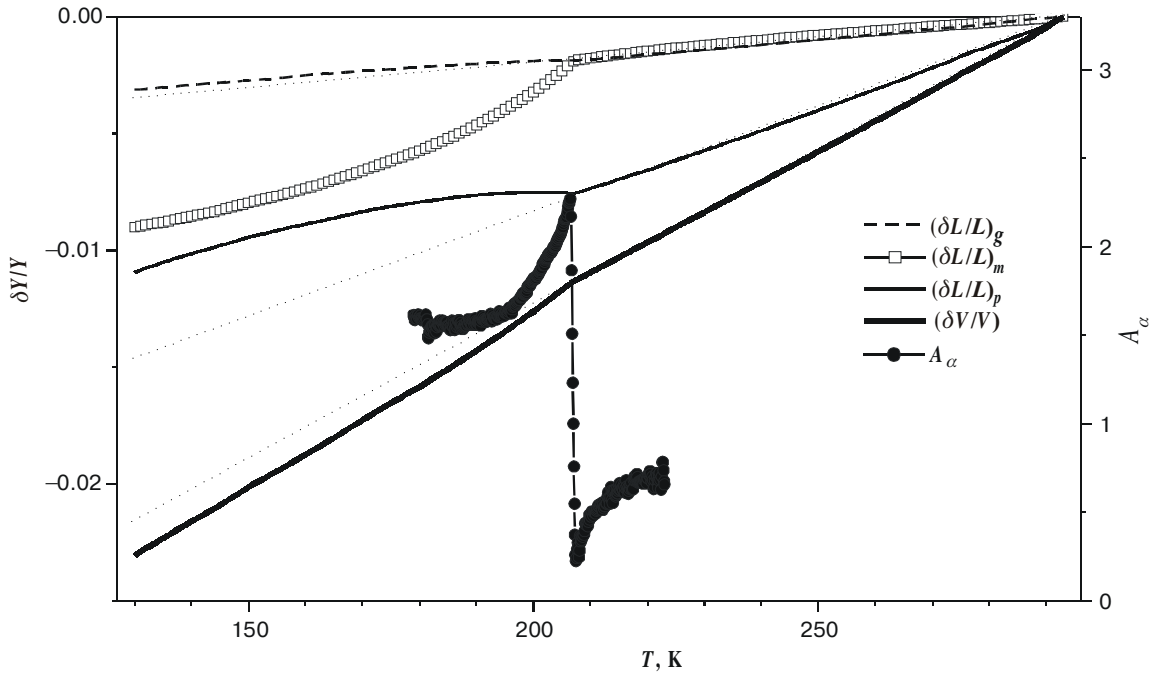


Fig. 1. Temperature dependences of the relative changes of linear dimensions $(\delta L/L)_i$ ($i = g, m, p$), volume $\delta V/V$ and degree of anisotropy A_α of DGN crystal in the range of 130–293 K.

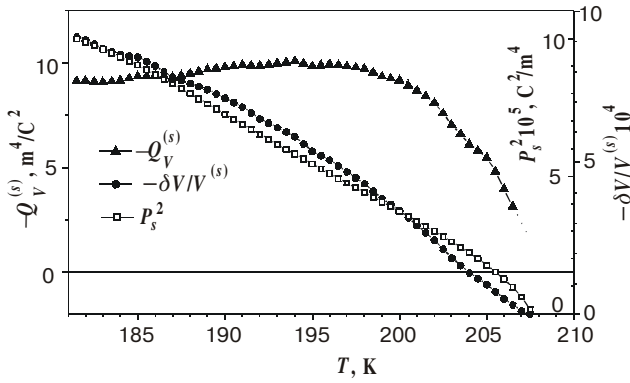


Fig. 2. Temperature dependences of the square of spontaneous polarization P_s^2 , relative spontaneous change of volume $(\delta V/V)^{(s)}$ and coefficients of spontaneous electrostriction $Q_V^{(s)}$ for DGN crystal.

tween these certain electrically charged elements mentioned above and the remained structure elements of the crystal.

The degree of anisotropy of thermal expansion of DGN crystal can be presented similarly to the definition from [8] using only one value A_α which depends on three coefficients of linear expansions α_i :

$$A_\alpha = \frac{|\alpha_g - \alpha_m| + |\alpha_m - \alpha_p| + |\alpha_p - \alpha_g|}{|\alpha_g + \alpha_m + \alpha_p|}. \quad (3)$$

The temperature dependence of $A_\alpha(T)$ (Fig. 1) shows more high level of the anisotropy degree A_α in ferroelectric phase ($T < T_c$) than that one in paraelectric phase ($T > T_c$). Thus, the continuous phase transition in DGN crystal leads to the sharp change of the level of anisotropy degree A_α of thermal linear expansion. Besides, the pronounced maximum and minimum of the temperature dependence of $A_\alpha(T)$ at T_c are observed in the range of 190–220 K. Similar decrease of the anisotropy degree A_α was observed for DMAGaS crystal in the range of paraelectric phase near T_c point of continuous phase transition [8]. Therefore one can suppose that the minimum at T_c of the temperature dependence of $A_\alpha(T)$ in paraelectric phase is a common peculiarity of phase transitions in ferroelectric crystals testifying for the relative disorder of crystal structure. Similar anomalous temperature behavior of $A_\alpha(T)$ in the form of maximum at T_c is characteristic for ferroelectric phase (Fig. 1). Such pre-transitional

anomalous temperature changes of $A_\alpha(T)$ in DGN crystal are as deviation from the simple theoretical (classical) constancy of the temperature dependence $A_\alpha(T)$ in one structural phase of a crystal with continuous phase transition.

Spectral-interference studies have shown that the dispersion of refractive indices $n(\omega)$ of DGN crystal is normal and monotonous in the photon energy range of 1.77–3.10 eV. Analysis of the photon energy dependence of refractive indices $n(\omega)$ in the range under study shows, that this dependence can be satisfactorily described by the single oscillator Sellmeier-like formula

$$\{n(\omega) - 1\}^{-1} = (\omega_0^2 - \omega^2)/(k\omega_0\Delta\omega_0) = a - b\omega^2, \quad (4)$$

where ω_0 , k , and $\Delta\omega_0$ are resonance photon energies, absorption index ($\hat{n} = n + ik$), and spectral width of the effective oscillator's band, respectively [8]. The coefficients a , b , ω_0 , and $k\Delta\omega_0$ derived from the dispersion of principal refractive indices of DGN crystals at room temperature are presented in Table 1. The principal refractive indices of DGN crystal were found to be equal to $n_p = 1.450$, $n_m = 1.530$, $n_g = 1.592$ for the wavelength $\lambda = 632.8$ nm ($\omega = 1.96$ eV) of He-Ne-laser used in this study for measurement of the temperature dependences of optical path differences $\delta D/D(T)$.

It is seen from Fig. 3 that the principal refractive indices n_i increase with decreasing temperature. Clear temperature anomalies of the values $\{\delta n/(n-1)\}_i$ observed at $T_c = 206$ K are characteristic for continuous phase transitions. Relative spontaneous changes of the refractivity $\{\delta n/(n-1)\}_i^{(s)}$ are positive, that leads to the positive coefficients of spontaneous quadratic electrooptic effect $G_{ij}^{(s)}$:

$$\{\delta n/(n-1)\}_i^{(s)} = G_{ij}^{(s)} \cdot P_j^2 = G_{ij}^{(s)} \cdot P_s^2. \quad (5)$$

Taking into account the magnitudes of $\{\delta n/(n-1)\}_i^{(s)}$ at 130 K (Fig. 3) and the magnitude of spontaneous polarization $P_s = 1.4 \cdot 10^{-2}$ C/m² at 123 K [1] one can obtain the magnitudes of the corresponding coefficients $G_{ij}^{(s)}$ being in the range of 11–15 m⁴/C².

The temperature changes of electron refractions $(\delta R/R)_i$ along three principal directions of optical indicatrix characterizing the electron subsystem of DGN crystal have been calculated by the relation

$$\frac{\delta R_i}{R_i} = \frac{\delta V}{V} + \frac{6n_i}{(n_i+1)(n_i^2+2)} \frac{\delta n_i}{(n_i-1)} \quad (6)$$

Table 1. The coefficients a , b , ω_0 , and $k\Delta\omega_0$ of the formula (4) for DGN crystal at room temperature.

Principal direction of optical indicatrix	a	b , eV ⁻²	ω_0 , eV	$k\Delta\omega_0$, eV
g	1.74588	0.01513	10.74	6.15
m	1.93162	0.01182	12.78	6.62
p	2.26731	0.01178	13.87	6.12

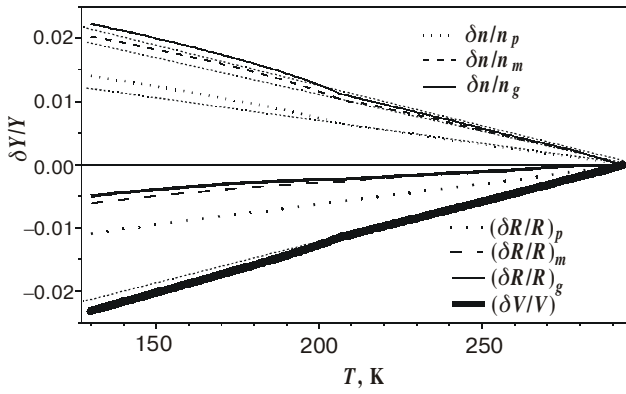


Fig. 3. Temperature dependences of the relative change of refractivity $\delta n_i/(n_i - 1)$ ($i = p, m, g$), volume $\delta V/V$ and corresponding refractions $(\delta R/R)_i$ for DGN crystal. Thin dashed lines are the linear approximations of corresponding dependences from paraelectric into ferroelectric phase.

derived from the known Lorentz-Lorenz relation (7) for the crystals of cubic structure with relatively strong Lorentz-Lorenz dipole-dipole interaction [5]:

$$R_i = \frac{(n_i^2 - 1)M}{(n_i^2 + 2)\rho}. \quad (7)$$

Here M is the molar mass and ρ is the density of the crystal. The relative temperature change of the nonpolarized refraction $\delta R/R$ was calculated as an arithmetically averaged value of three polarized refractions $\delta R_i/R_i$. Such the space averaged electron refraction R is the sum of similarly averaged electron polarizabilities for all elements of microscopic crystal structure over one mole of a substance [5], and therefore this value is expected to be rather temperature independent.

It is seen from Fig. 3 that the molar refractions R_i calculated by the formula (7) decrease monotonously with decreasing temperature in the range of 295÷130 K. Taking into account the definition of the parameter R mentioned above, the observed essential temperature dependence of $\delta R/R$ is rather unexpected. From the other viewpoint, if one supposes the relatively weak dipole-dipole interaction in DGN crystal, then the following relations take place for characteristics R' and $\delta R'/R'$ [5]:

$$R' = \frac{(n^2 - 1)M}{3\rho}, \quad (8)$$

$$\frac{\delta R'}{R'} = \frac{\delta V}{V} + \frac{2n}{(n+1)(n-1)} \frac{\delta n}{n}. \quad (9)$$

Our investigations have shown that the value $\delta R'/R'$ is almost independent on temperature for DGN crystal. Therefore, in the frame of accepted suggestion of temperature independence of electron refraction for DGN crystal in wide temperature range, one can conclude the absence of Lorentz-Lorenz dipole-dipole interaction in this material. But such the explanation is not acceptable because the absence of dipole-dipole interaction in the closed packed substance like DGN crystal is rather impossible. In the frame of suggestion of temperature independence of the additive part of electron refraction R (sum of all non-interacted electron polarizabilities) the obtained temperature coefficient of refraction, $d/dT(\delta R/R) = (4,0 \div 4,5) \cdot 10^{-5} \text{ K}^{-1}$ (Table 2), calculated on the basis of the relation (7), can be explained by the increase of dipole-dipole interaction in the crystal with decreasing temperature in the wide temperature range 295÷130 K. In fact as it is seen from the equations (7) and (8) for the given magnitudes of n , M and ρ the relation $R < R'$ takes place. It means that the refraction R can decrease with increasing Lorentz-Lorenz dipole-dipole interaction.

The decrease of Lorentz-Lorenz dipole-dipole interaction with increasing temperature agrees qualitatively with the corresponding decrease of crystal's density. Therefore the ratio of two coefficients $d/dT(\delta R/R)$ and $d/dT(\delta V/V)$ can also serve for the quantitative evaluation of temperature change of Lorentz-Lorenz dipole-dipole interaction in various ferroelectrics:

$$K = \frac{d/dT(\delta R/R)}{d/dT(\delta V/V)} \quad (10)$$

It is known that the refraction R possessing a dimensionality of volume is approximately equal to the b -correction in Van-der-Waals equation, which is equal to the proper volume of molecules for one mole of substance. It is seen from the equation (7) that the ratio of the characteristic volume of electron subsystem of one mole R and the whole volume V_M of one mole of substance ($m = M$) can be presented in the form:

$$R/V_M = \frac{n^2 - 1}{n^2 + 2} \quad (11)$$

So, the ratio R/V_M is proportional to the refractive index n .

Table 2. Characteristic coefficients of temperature changes of volume V , refraction R and refractivity $(n - 1)$ of DGN crystal in paraelectric (207÷293 K) and ferroelectric (130–207 K) phases.

	$d/dT(\delta V/V), \text{K}^{-1}$	$d/dT(\delta R/R), \text{K}^{-1}$	$d/dT(\delta n/(n - 1), \text{K}^{-1})$	$\frac{d/dT(\delta R/R)}{d/dT(\delta V/V)}$
207÷293 K	$1.30 \cdot 10^{-4}$	$4.0 \cdot 10^{-5}$	$-1.1 \cdot 10^{-4}$	0.308
130÷207 K	$1.47 \cdot 10^{-4}$	$4.6 \cdot 10^{-5}$	$-1.3 \cdot 10^{-4}$	0.313

To evaluate the temperature changes of anisotropy of optical indicatrix of DGN crystal we have introduced the single parameter A_{n-1} (degree of refractivity's anisotropy) similarly to the analogous value A_α for thermal linear expansion (3):

$$A_{n-1} = \frac{|n_g - n_m| + |n_m - n_p| + |n_p - n_g|}{|n_g + n_m + n_p - 3|}. \quad (12)$$

It has been stated that the degree of optical anisotropy A_{n-1} of DGN crystal increases with decreasing temperature in the wide range of 295÷130 K (Fig. 4). On the background of monotonous temperature change of the degree of optical anisotropy $A_{n-1}(T)$ (dashed straight line in Fig. 4) the relative decrease of this parameter in the range of $\delta T \approx 30$ K centered by T_c temperature is seen in Fig. 4. This relatively small decrease of A_{n-1} can testify the approach of valence electron subsystem of DGN crystal to the more isotropic and/or disordered state in the range near T_c . The characters of temperature anomalies of the relative dilatation $(dL/L)_i$ and refractivity $[\delta n/(n-1)]_i$ near T_c are similar (Fig. 1,3). Therefore the temperature behaviors of the corresponding degrees of anisotropy A_α and A_{n-1} near T_c should be similar. Taking into account the form of the temperature dependence $A_{n-1}(T)$ (Fig. 4) one can forecast that the temperature dependence of the absolute value of dA_{n-1}/dT will be similar to the temperature dependence of $A_\alpha(T)$ (Fig. 1) discussed earlier.

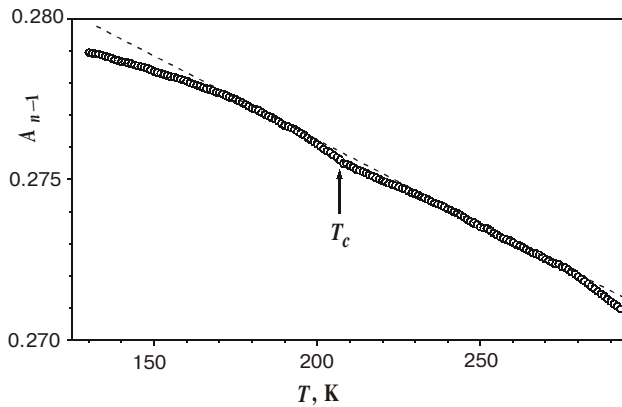


Fig. 4. Temperature dependence of the degree of optical anisotropy $A_{n-1}(T)$ for DGN crystal. The dashed straight line is the background level for the dependence $A_{n-1}(T)$ in the whole temperature range.

4. Conclusions

1. Decrease of the spontaneous electrostriction coefficients $Q_V^{(s)}$ and $Q_{ij}^{(s)}$ with approaching temperature to the phase transition point T_c in ferroelectric phase of DGN crystal can be caused by the weakened correlation between (a) the crystal's structure elements forming the spontaneous polarization P_s and (b) the remained structure elements.

2. Relative temperature decrease of the degrees of anisotropy of linear thermal expansion A_α and refractivity A_{n-1} of DGN crystal in the range of paraelectric phase close to T_c ($T_c \pm T_c + 10$ K) testifies the crystal structure to become to more isotropic and/or relatively disordered.

3. In the frame of suggestion of temperature independence of the additive part of electron refraction R the observed positive temperature coefficient of refraction $d/dT(\delta R/R)$ can be caused by the increase of the Lorentz-Lorenz dipole-dipole interaction with decreasing temperature in the wide range of 295÷130 K including paraelectric and ferroelectric phases of DGN.

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