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# Optical and dilatative properties of diglycine nitrate crystals

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## Abstract

Investigation of the thermal linear expansion  $L(T)$  and temperature dependences of the interference optical path difference  $D(T)$  have been carried out for diglycine nitrate (DGN) crystals,  $(\text{NH}_2\text{CH}_2\text{COOH})_2\cdot\text{HNO}_3$ , in the range of 130-295K. Minimums of the temperature dependences of anisotropy degrees of dilatative ( $A_L$ ) and refractive ( $A_{n-1}$ ) characteristics near  $T_c = 206\text{K}$  show effective disordering of the crystal at phase transition.

**Keywords:** ferroelectrics, dilatative and refractive properties

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## Introduction

Majority of investigations of physical properties of DGN crystal is related to studies of spontaneous polarization, dielectric permittivity [1-3], elastic and electromechanical properties [4]. Optical properties of DGN crystal are less studied [5].

The aim of this investigation was to measure the dispersion of principal refractive indices  $n_i(\lambda)$  of DGN crystal in the wavelength range of its transparency and temperature dependences of thermal linear expansion and refractive indices in the range of 130 – 295K, to study the anomalies of temperature dependences near  $T_c$  temperature of spontaneous electrostriction coefficients, coefficients of spontaneous quadratic electrooptic effect, and the degree of anisotropy of linear expansion and principal refractive indices, and to compare the

character of these anomalies with already obtained ones for other ferroelectric crystals of order-disorder type: TGS [6,7], GPI [7,8], DMAAS [9], and DMAGaS [10].

## Experimental

The thermal linear expansion of DGN crystal was measured using the quartz dilatometer by the known electric capacitor method. The rate of the temperature change of crystal studied at cooling run was 1 K/min. The sensitivity of dilatometer  $dL$  depended on the distance between capacitor plates which was equal to  $dL \approx 5$  nm in our case. This corresponds to the relative error  $d(\delta L)/L \leq 10^{-6}$  of lengthening  $\delta L/L$ .

The dispersion of refractive index  $n(\lambda)$  of DGN crystals was measured by the immersion method using the refractive index dispersion data for the appropriate immersion liquid

measured by the Pulfrich refractometer with an accuracy of  $dn = 2 \cdot 10^{-4}$  [11].

The temperature measurements of optical path difference were performed using the laser interferometer of Jamen type and interference of two light beams, one of which has passed through a sample of the thickness  $L_i$  and another one – through the same thickness of the air. The measurements of temperature dependence of light intensity were carried out in the scanning mode in the heating regime. Since the relative changes of optical path difference  $D_{ij} = L_i \cdot (n_j - 1)$  can be presented in the form [6-10],

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

we have calculated the temperature dependences of the variable part of refractive index  $\delta n_j / (n_j - 1)$  on the basis of the temperature dependences of  $\delta D_{ij} / D_{ij}$  and  $\delta L_i / L_i$ .

### Results and discussion

Temperature expansion of DGN crystals in wide temperature range 130-293K is characterized by positive coefficients of the thermal linear expansion  $\alpha_i$  and volume expansion coefficient  $\gamma = \sum \alpha_i$  (Fig. 1).

Similarly to the presentation of results for the DMAGaS crystal in [10], temperature dependences of the degrees of anisotropy of thermal linear expansion  $A_L(T)$  and  $A_\alpha(T)$  for DGN crystal are shown in Fig. 1. Here, the parameters  $A_L$  and  $A_\alpha$  were calculated by the formulas

$$A_L = \sum_{i \neq j}^3 \frac{|(\delta L / L)_i - (\delta L / L)_j|}{|(\delta L / L)_i| + |(\delta L / L)_j|}, \quad (2)$$

$$A_\alpha = \sum_{i \neq j}^3 \frac{|\alpha_i - \alpha_j|}{|\alpha_i| + |\alpha_j|}. \quad (3)$$

The common feature of the dependences  $A_L(T)$  and  $A_\alpha(T)$  is relatively wide minimum in the range close to  $T_c$  temperature (Fig. 1). Two maximums of the dependence  $A_\alpha(T)$  are caused by a sharp decrease of denominator in the

relation (3) due to reaching zero magnitudes of  $\alpha_p$  and  $\alpha_g$  at the temperatures 204 and 207K (Fig. 1). The similar result (minimum of  $A_\alpha(T)$  dependence at  $T_c$ ) was already observed for DMAGaS crystal [10]. Taking into account this fact one can suppose that the minimum of temperature dependence of  $A_L(T)$  and  $A_\alpha(T)$  is a common peculiarity of phase transitions of ferroelectric crystals testifying to the relative disordering crystal structure.

Spectral-interference studies have shown that the dispersion of refractive indices of DGN crystal is normal and monotonous in the range of 400-700nm. The analysis of the frequency dependence of refractive indices  $n(\omega)$  in the range under study shows, that this dependence can be satisfactorily described by the one-oscillator Selmeier-like formula [11]. The principal refractive indices of the 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 of He-Ne-laser used in this study to measure the temperature dependences of optical path differences  $\delta D / D(T)$ .

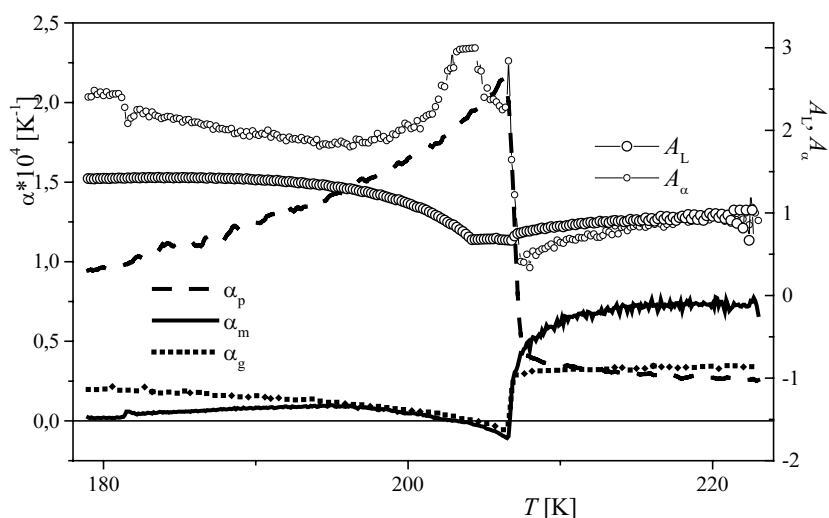
It is seen from Fig. 2 that the principal refractive indices  $n_i$  ( $i = p, m, g$ ) increase when temperature decreases. Clear temperature anomalies of the values  $\{\delta n / (n - 1)\}_i$  characteristic for continuous phase transitions are seen at  $T_c = 206$ K. Spontaneous changes of refractive indices  $\{\delta n / (n - 1)\}_i^{(s)}$  are positive. This means the positive coefficients of spontaneous quadratic electrooptic effect  $G_{is}$ :

$$\{\delta n / (n - 1)\}_i^{(s)} = G_{is} \cdot P_s^2. \quad (4)$$

Magnitudes of the corresponding coefficients  $G_{is}$  of spontaneous quadratic electrooptic effect are in the range of 11 - 15 m<sup>4</sup>/C<sup>2</sup>.

Temperature dependences of the relative changes of principal refractions  $(\delta R / R)_i$  for the DGN crystal are calculated by the relation

$$\frac{\delta R_i}{R_i} = \frac{\delta V}{V} + \frac{6n_i}{(n_i + 1)(n_i^2 + 2)} \frac{\delta n_i}{(n_i - 1)}, \quad (5)$$



**Fig. 1.** Temperature dependences of the coefficients of thermal linear expansion  $\alpha_i$  ( $i = p, m, g$ ) and degrees of anisotropy  $A_L$  and  $A_\alpha$  for the DGN crystal.

derived from the known Lorentz-Lorenz relation [12],

$$R_i = \frac{(n_i^2 - 1)M}{(n_i^2 + 2)\rho}, \quad (6)$$

using the temperature dependences of the relative change of volume  $\delta V/V$  and refractive indices  $\{\delta n/(n - 1)\}_i$  (Fig. 2). Here  $M$  is molar mass and  $\rho$  is density of the crystal. It is seen from Fig. 2 that the molar refractions  $R_i$  decrease monotonously when the temperature decreased in the range of 295-130K. It is known that the Lorentz-Lorenz relation in the form of (6) can be used only in the case of crystals with cubic symmetry and/or isotropic materials [12]. Moreover in the case of low density substances (gas for instance) the refraction  $R$  and refractive index  $n$  relate one to the other according to another relation,

$$R = \frac{(n^2 - 1)M}{3\rho}. \quad (7)$$

In this case the relative change of refraction  $\delta R/R$  can be written in the form:

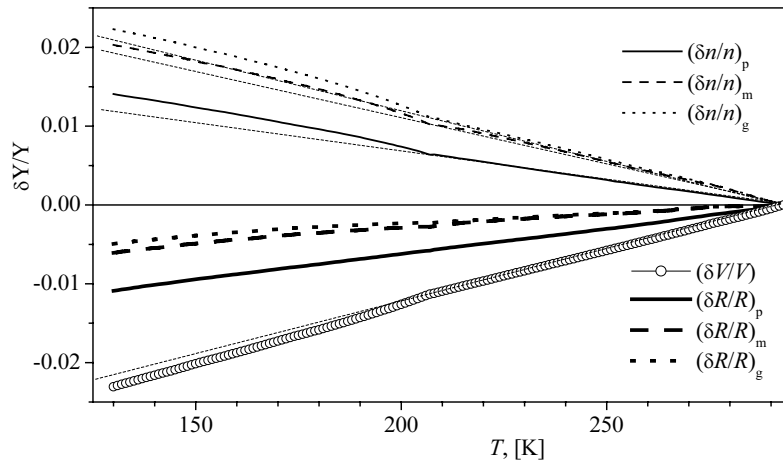
$$\frac{\delta R}{R} = \frac{\delta V}{V} + \frac{2n}{(n+1)(n-1)} \frac{\delta n}{n}. \quad (8)$$

The temperature dependences of polarized

refractions,  $\delta R_i/R_i$  ( $i = p, m, g$ ), and nonpolarized,  $\delta R/R$ , calculated by the formula (8) are shown in Fig. 3. Relative temperature change of the nonpolarized refraction,  $\delta R/R$ , was calculated as the mean arithmetic value of three polarized refractions,  $\delta R_i/R_i$ . It is seen from Fig. 3 that this value, presenting the crystal as a whole, is almost independent on temperature in the wide range 130-293K. The space averaged electron refraction of the crystal  $R$  is the sum of electron polarizabilities for all elements of microscopic crystal structure over one mole of a substance [12], and therefore this value has to be a rather temperature independent parameter. Therefore, one could consider more realistic the independence of the mean value  $\delta R/R$  on temperature (Fig. 3) than the case of decreasing this value with temperature decrease (Fig. 2).

Such a viewpoint agrees better with typical inverse proportionality on temperature of the probability of radiative transition between electron states of a molecule being proportional to the refraction  $R$ .

The other explanation of the dependence  $\delta R/R(T)$  observed in Fig. 2 can be connected with the temperature change of the only



**Fig. 2.** Temperature dependences of the relative change of the variable part of refractive indices  $\delta n_i/(n_i - 1)$  ( $i = p, m, g$ ), volume  $\delta V/V$  and corresponding refractions  $(\delta R/R)_i$  for DGN crystal. The values  $(\delta R/R)_i$  are calculated by the formula (5). Thin dashed lines are linear approximations of corresponding dependences from paraelectric into the ferroelectric phase.

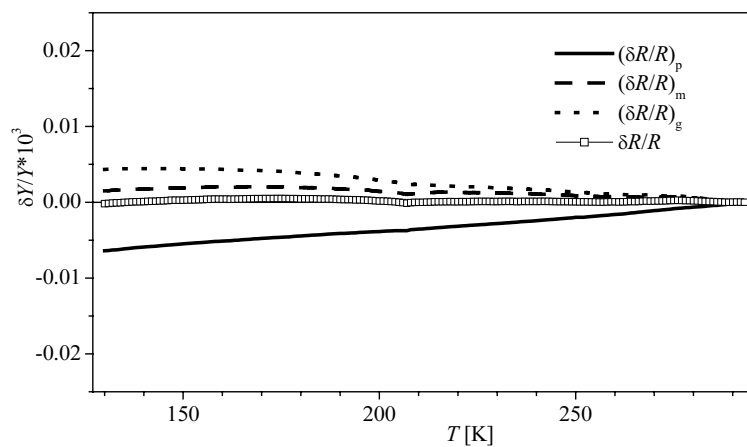
Lorentz-Lorenz dipole-dipole interaction in the wide temperature range 130 – 295K. Comparing the formulas (6) and (7) one can conclude that refraction  $R$  decreases when the Lorentz-Lorenz dipole-dipole interaction increases. Then the temperature dependence  $\delta R/R(T)$  observed in Fig.2 can be as the result of the decreasing Lorentz-Lorenz dipole-dipole interaction when the temperature increases. This explanation of the experimental results is the most realistic.

It is known that the refraction  $R$ , possessing a dimensionality of volume, is equivalent to the

$b$ -correction in Van-der-Vaals equation, which is equal to the proper volume of one mole of a substance [13]. Thus, the magnitude of refraction  $R$  can be identified with the volume of the electron subsystem corresponding to one mole of a substance. Presenting the formula (7) in the form

$$(n - 1) = (R/V) \cdot [3/(n + 1)] \sim R/V, \quad (9)$$

one can see that the variable part of refractive index  $(n - 1)$  is approximately equal to the ratio  $R/V$  of two volumes: the volume  $R$  of electron subsystem for one mole of substance and the



**Figure 3.** Temperature dependences of the relative change refractions  $(\delta R/R)_i$  for DGN crystal. The values  $(\delta R/R)_i$  are calculated by the formula (8).

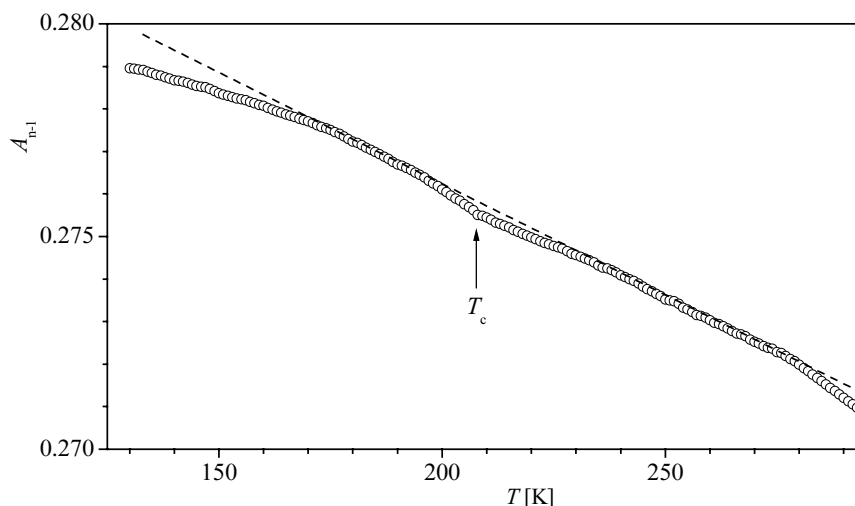


Figure 4. Temperature dependence of the degree of optical anisotropy  $A_{n-1}(T)$  for the DGN crystal. The dashed straight line is a background level for the dependence  $A_{n-1}(T)$  in the whole temperature range.

volume  $V$  of one mole of substance as a whole.

To describe temperature changes of anisotropy of optical indicatrix of DGN crystal we have introduced only one parameter  $A_{n-1}$  of the degree of anisotropy of variable part of refractive index similarly to the analogous value  $A_L$  for thermal linear expansion (2):

$$A_{n-1} = \sum_{\substack{i,j=1 \\ i \neq j}}^3 \frac{|(n_i - 1) - (n_j - 1)|}{(n_i - 1) + (n_j - 1)}. \quad (10)$$

The degree of optical anisotropy  $A_{n-1}$  of the DGN crystal increases when the temperature decreased in the wide range of 295-130K (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) one can see the relative decrease of this parameter in the vicinity of the phase transition temperature  $T_c$  of the width  $\Delta T \approx 30$ K. This decrease of  $A_{n-1}$  testifies the approach of the electron subsystem of the crystal to more isotropic, disordered state and agrees with expected consequences of reorientation of separate structure elements of the DGN crystal at the phase transition ( $\text{NO}_3$  and glycine complexes).

## Conclusions

1. The relative temperature decrease of the degrees of anisotropy  $A_L$ ,  $A_\alpha$  and  $A_{n-1}$  of the DGN crystal on approaching  $T_c$  in the range of  $T_c \pm 10$ K testifies the crystal structure to be more isotropic and disordered.
2. Monotonous decrease of the molar refraction  $R$  of DGN at the temperature decrease from 295 to 130K is obtained when using the known Lorentz-Lorenz formula. This temperature dependence of  $R$  can be explained by the decreasing Lorentz-Lorenz dipole-dipole interaction when the temperature increased.

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