Calculation of refractive indices for complicated crystals

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Abstract

The method of calculation of refractive indices for complicated crystals in the frame of "oriented gas" model are proposed and made on the basis of known magnitudes of anisotropic polarizability of chemical bonds between atoms. Principal refractive indices and optical indicatrix orientations of DGN crystal in para- and ferroelectric phases calculated in the frame of "oriented gas" model and experimentally observed have been found to be close to one another.

Keywords: crystals, refractive indices

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Introduction

Investigation of electronic properties of ferroelectric crystals promotes the studying of corresponding microscopic mechanisms of ferroelectric phenomena. Therefore the calculations of parameters of electron polarization for these objects at light propagation (polarizability Π, refraction R and refractive index n) are useful. Most of ferroelectric crystals are complicated and are low-symmetry objects. Therefore, the first principal electron band calculations for such objects have not been made up till now. In such circumstances the calculations of polarizabilitiy (refraction) of elementary unit cell of crystals on the basis of known polarizabilities of corresponding chemical bonds and the additive scheme of polarizabilities (ideal gas model) can be useful [1].

In this paper we have calculated the principal refractive indices n_i ($i = p, m, g$) of the ferroelectric crystal diglycine nitrate (DGN), $(NH_2CH_2COOH)_2{\cdot}HNO_3$, on the basis of known chemical bond's polarizabilities between the constituting atoms of the elementary unit cell.

It is known from the papers [2-4] that DGN crystal is ferroelectric below 206K, belonging to the space group Pa, and above the transition temperature it becomes paraelectric with the space group $P2_1/a$. Spontaneous polarization vector P_s of DGN lies in the symmetry plane (101). Parameters of the elementary unit cell of DGN are shown in Table 1 [5].

Table 1. Parameters of the elementary unit cell of DGN crystal [5]

Temperature K	Space group	a nm	b nm	c nm	β degrees	V_c nm^3	Z	ρ g/cm^3
295 K	$P2_1/a$	0,9459	0,5172	0,9225	97,19	0,4478	2	1,580
123 K	Pa	0,9485	0,5132	0,9089	97,89	0,4382	2	1,615

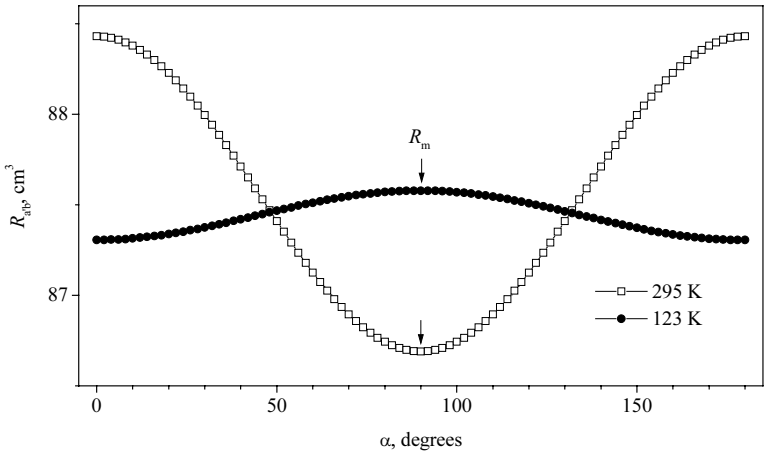

Figure 1. Dependencies of the component $R_{a'b}$ of refraction tensor of unit cell of DGN on the angle α between direction of light polarization and *a*'-axis of unit cell in the plane *a*'*b*.

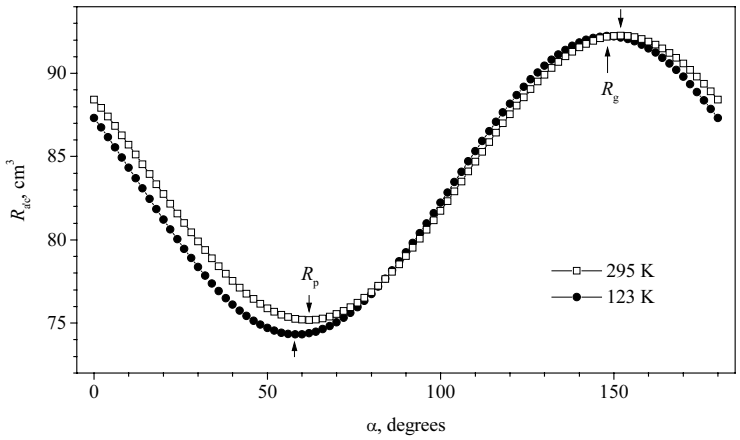

Figure 2. Dependencies of the component $R_{a'c}$ of refraction tensor of unit cell of DGN on the angle α between direction of light polarization and *a*'-axis of unit cell in the plane *a*'*c*.

Method of calculations

It is known that polarizability of *i*-th structure element Π_{ij} is determined by its dipole moment p_i, arising under an influence of the electric field E_j:

$$p_i = \Pi_{ij} E_j \qquad (1)$$

The molar refraction R is determined by the separate polarizabilities Π_{ij}. In the case of high-symmetry cubic crystals and isotropic media polarizability connected with the refractive index n by the Lourents-Lourentz formula,

$$R = (4\pi N_A/3)\sum_{ij}\Pi_{ij} = \frac{(n^2-1)M}{(n^2+2)\rho}, \qquad (2)$$

where N_A, M, and ρ are the Avogadro number, molar weight and density, respectively.

In our calculations we have used the model of ideal gas, which is based on the arithmetic summation of the projections of longitudinal, $R_{ij}^{(l)}$, and transversal, $R_{ij}^{(t)}$, polarizabilities of all the chemical bonds of a crystal's elementary unit cell (see Table 2).

In the case of low-symmetry objects like the DGN crystal, the formula (2) is approximate. To obtain more exact relation between the refractive index n and polarizabilities of chemical bonds $\sum_{ij}\Pi_{ij}$ one has to calculate the effective electric field acting on a molecule using the Lourents–Lourentz correction. One

Table 2. Longitudinal $R^{(l)}$ and transversal $R^{(t)}$ refractions (polarizabilities) of chemical bonds of the $(NH_2CH_2COOH)_2 \cdot HNO_3$ molecule [6]

Bond	$R_{ij}^{(l)}$ cm^3	$R_{ij}^{(t)}$ cm^3
C-H	1,64	1,64
C-C	2,45	0,66
C-O	2,24	1,16
C=O	5,8	(3,53+1,16)/2
N-H	1,26	2,09
N-C	1,44	1,74
O-H	(1,63+1,78)/2	
NO_3^-	11,0	

can expect that in low-symmetry crystals such formulas will be different for different crystallo-physical directions. In the present study the refractive indices calculations of DGN crystal were performed using formula (2), i.e. without taking into account the possible anisotropy of the Lourents-Lourentz correction.

As the elementary unit cell of DGN crystal (Z=2) consists of two formula units $(NH_2CH_2COOH)_2 \cdot HNO_3$ the refraction of unit cell R_{ij} in the j-direction of light polarization can be presented in the form:

$$R_{ij} = \frac{(n_j^2 - 1)MZ}{(n_j^2 + 2)\rho} \qquad (3)$$

The calculation of the refraction of unit cell R_{ij} for certain j-direction of light polarization was conducted by means of summation the refractions R_{ij} for all (N) chemical bonds of the cell by the formula

$$R_{ij} = \sum^{N} R_{ij} = \sum^{N} [R_{ij}^{(l)} \cos^2 \alpha_{ij} + R_{ij}^{(t)} (1 - \cos^2 \alpha_{ij})] \qquad (4)$$

where α_{ij} is the angle between axes of chemical bond and chosen direction. The magnitudes $R_{ij}^{(l)}$ and $R_{ij}^{(t)}$ were taken from the paper [6]. The orientation of chemical bonds in the unit cell of DGN (α_{ij}-angles) was obtained on the basis of reference data on its crystalline structure in paraelectric (T=295K) and ferroelectric (T=123K) phases [5].

Results and discussion

Calculated angular dependencies of the refraction $R(\alpha)$ of elementary unit cell of DGN for the planes $a'b$ and $a'c$ which are perpendicular to the crystallographic directions c and b, respectively, are shown in Figures 1 and 2. Extremal magnitudes of these dependencies correspond to the magnitudes of the elementary unit cell refractions along the principal directions of optical indicatrix (R_p, R_m, R_g) (Figure 3).

The orientation of the calculated optical indicatrix of DGN crystal in paraelectric phase

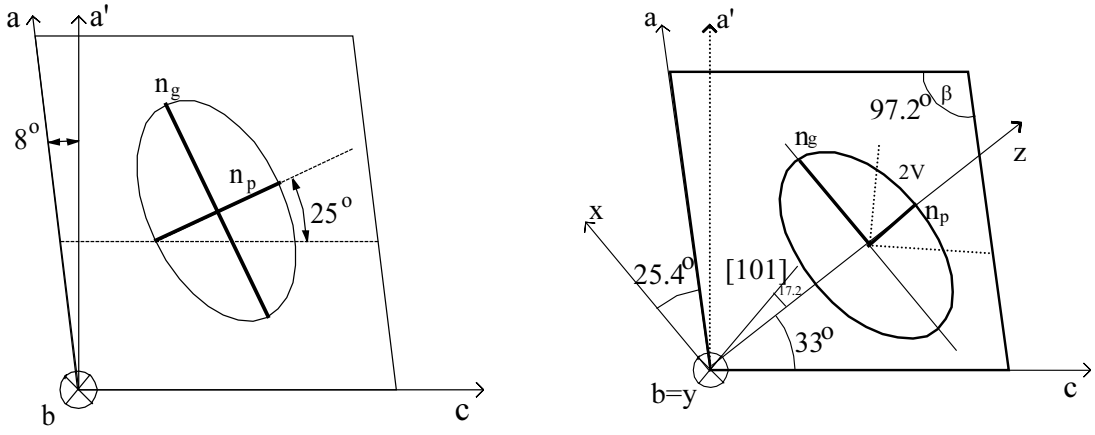

Figure 3. Projections of the unit cell of DGN perpendicularly to the crystallographic direction b and the orientation of corresponding cut of optical indicatrix: (a) - calculated in this work, (b) - experimentally observed [7].

Table 3. Magnitudes of principal refractions R_j of elementary unit cell of DGN crystal and principal refractive indices n_i in para- and ferroelectric phases, calculated by formula (2) and obtained in experiment

Principal directions *j* of optical indicatrix	Refractions R_j,cm^3		Refractive indices n_j		
	Calculation (for white light)		Calculation (for white light)		Experiment λ = 632,8 nm
	T = 295 K	T = 123 K	T = 295 K	T = 123 K	T = 295 K
p	75,19	74,32	1,470	1,476	1,451
m	86,69	87,58	1,556	1,578	1,530
g	92,26	92,23	1,600	1,616	1,592

at room temperature agrees satisfactorily with the experimental data. The calculated angle between the crystallographic *c*-axis and principal directions of optical indicatrix is equal to 25° (Figure 3), when the experimental one is equal to 32° [7]. The orientation of the calculated R_m-component coincides with the crystallographic *b*-axis, which is in the same time the two fold symmetry axes (*2*/*m*-point group symmetry of monoclinic class). The calculation shows that the orientation of optical indicatrix in the ferroelectric phase (*m*-point group of symmetry of monoclinic class) changes essentially relating its orientation in the paraelectric phase. The angle between n_p-axis and crystallographic *c*-axis is already equal to 20°. This result agrees with the symmetry of the crystal in the paraelectric phase allowing a rotation of the optical indicatrix in the *m*-plane of symmetry.

The calculated refractions of unit cell R_{ij} of DGN crystal and refractive indices n_j (3) for the principal directions of the optical indicatrix *p*, *m*, *g* are shown in Table 3. Magnitudes of crystal density at the corresponding temperatures T_p = 295 K and T_f = 123 K are taken from [5] (see Table 1). The molar mass of DGN is equal to *M*=213g. Although calculated and experimentally measured refractive indices differ noticeably (calculated magnitudes are greater than experimental ones by 1–5%), but the calculation adequately reproduces not only the relation between the indicatrix axes, $n_p < n_m < n_g$, but a negative optical sign of DGN crystal (n_p-axis indicatrix is a bisectrix of the acute angle between the optical axes of DGN [7]). It is necessary to mark that possible dependence of anisotropic refractions of chemical bonds on its length has not been taken into account in the given calculation. Note that in the given calculations the possible dependence of polarizability on the length of chemical bonds was not taken into account at different temperatures – 295K and 123K.

Conclusions

1. Principal refractive indices and optical indicatrix orientations of DGN crystal in para– and ferroelectric phases calculated in the frame of "oriented gas" model and experimentally observed have been found to be close to one another.
2. The main characteristic of refractive indices indicatrix of DGN crystal are already formed by the corresponding structure elements on the level of an elementary unit cell.

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