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Optical rotation in biaxial, achiral and ferroelectric $NaNO_2$-crystal at 296K.

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Abstract

$NaNO_2$ crystal is biaxial, achiral and ferroelectric ionic solid at room temperature. It belongs to the symmetry class *mm2*. The magnitude and sense of optical rotation with opposite signs are determined in the two optic axis directions, OA1 and OA2, of the crystal model at four wavelengths. The handedness of the crystal structure is in correlation with the optical rotation character of the dominant components of plane polarized light, when it propagates in the directions of both OAs. The directions of the involved OAs are derived from the known refractive indices in the principal axis directions and they deviate with the same angle from the bisector axis, at any one wavelength, in the *mm2* symmetry. Cross products of the wave vector in the propagation direction of light and the electric moments in the other two principal axis directions of the quadric around the NO_2^- ion generate two axial vectors of second rank. The dominating vector of them accommodates the position of *Z*-axis of the indicatrix, which is experimentally observed and lies parallel with the crystallographic *b*-axis. The magnitude of the refractive index in the direction of OA is extracted in polar coordinates from the contributions arising from the principal axis directions of the crystal. The magnitudes of two orthogonal polar vectors, Θ'_{OA} and Θ'_{ZZ}, in the directions of optic axes and the optic normal, respectively, in the quadric of the second electric moments, are iterated to topological equivalence with the net charges of N and O atoms as variables, until the ratio of them reached the inverted ratio of the corresponding refractive indices in the quadric of the optical indicatrix. Both quadrics are representation surfaces of second rank and geometrically three axial ellipsoids. The magnitude and sense of the dominant component of the circularly polarized light in the direction of OA reveal the sense of optical rotation character of crystal. When a plane polarized light travels in the OA1 direction of the absolute crystal structure with a right-handed system of coordinate axes of $NaNO_2$ crystal, a clockwise rotation of +17.2 ° mm $^{-1}$ is observable. The crystal is dextrorotatory. When a plane polarized light propagates in the direction of OA2, the crystal turns left-handed and rotates the plane of light anticlockwise –17.2 ° mm $^{-1}$ and now the crystal is levorotatory when seen against the light source by an observer.

Keywords: $NaNO_2$, optical rotation, biaxial, achiral, refractive indices,second electric and axial vectors.

Introduction

Optical rotation (= circular birefringence) is easy to measure in the uniaxial crystals, when a plane-polarized light travels and vibrates parallel to the optic axis and whose wave normal is perpendicular to it. Then the optical rotation is free of disturbing double refraction (= linear birefringence). In the orthorhombic, monoclinic and triclinic crystals the symmetry is lower than in the uniaxial crystals and the measurement of optical rotation suffers from double refraction, which is usually much stronger than the optical rotation. However, the latter three crystal systems have always two directions, for any one wavelength, along which the light ray travels free of double refraction, but in practice it is not easy to find out those directions in the measurements.

Optical rotation is experimentally measured with a HAUP (High Accuracy Universal Polarimeter) method [1,2] in the birefringent directions of over 20 biaxial and non-centrosymmetric achiral crystals. In $LiH_3(SO_3)_2$ and $NaNO_2$ crystals the optical rotation has been measured close in optic axis directions. [3] A technique of tilting thin plates of crystal with respect to a wave vector of light is later developed and used to modulate birefringence in order to record the rotation and its sign. [4]

The model determinations of optical rotation are basing on the classical coupled oscillator theory, which is an electromagnetic application, originally developed by Max Born, according to which the valence electrons are placed at the equilibrium positions between the atoms. They respond as oscillating dipoles in the field of polarized light wave and induce a secondary field with oscillating dipoles in new directions from the original wave. The interference of the induced waves and dipoles through a crystal may cause the rotation of the plane of polarization. [5] Another type of theory describes the optical polarization with a help of atomic polarizabilities. Reijnhart [6] calculated the magnitudes of dielectric constants, $(\varepsilon_r)_a$, $(\varepsilon_r)_b$ and $(\varepsilon_r)_c$, from the atomic polarizabilities of N and O in the three principal axis directions of $NaNO_2$ crystal and found $(\varepsilon_r)_c$ strongly dependent of the effective polarizability values of nitrogen atoms. He never computed any value for optical rotation, because no observed values were available to compare with at that time. The theory of polarizabilities is further developed by Devarajan and Glazer [7] by including the isotropic polarizability volumes for the atoms in the crystal systems according to Ramachandran. [8,9,10] Glazer and Stadnicka [11] have unified the sum of a number of calculated polarizabilities and the sense of optical rotation with that of the atomic helical arrangement in crystals.

Very few model calculations are performed in the orthorhombic crystals with *mm2* symmetry owing partly to a view that optical rotation must be associated with the enantiomorphic (chiral) crystals. The principal axes, $a < b < c$, are unequal of length but mutually orthogonal. The axes of the indicatrix, $X < Y < Z$, are always mutually orthogonal and coincide with the principal crystallographic axes. The crystals in the *mm2* symmetry are the simplest objects of all biaxial crystals, where a close study of optical rotation can be made, although the axes of the indicatrix can coincide with any of the crystal axes. For examples in the minerals andalusite Al_2SiO_5, with $2V_X$ = 69-88°, $X=c$, $Y=b$, $Z=a$, and monticellite $CaMgSiO_4$, with $2V_X$= 69-88°, $X=b$, $Y=c$, $Z=a$, which both are negative biaxial (-) with the angle $2V_Z > 90°$ due to more complicated crystal structures. [12]

This paper presents model calculations of optical rotation in the $NaNO_2$ crystal. This type of analysis relies on the distribution of net atomic charges and on a possibility to fashion the electric moments in an asymmetric unit of the absolute crystal structure of ionic solid. $NaNO_2$ crystal is an ionic solid at room temperature, where the rule of integer charges is not broken.

[13,14] Na^+ ion has a spherical noble gas core of electrons around the nucleus, which makes it almost nonpolarizable. NO_2^- ions give the crystal polar properties.

The biaxial crystals have two optic axes, which do not coincide with the principal crystallographic axes. The OAs are symmetry related with equal lengths in the unit cell of the $NaNO_2$ crystal. The refractive indices, $n\alpha < n\beta < n\gamma$, are measured at four different wavelengths in the directions of the principal crystallographic axes. The angle between the OA and the bisector axis is calculated from the measured refractive indices and the magnitude of the refractive index in the OA direction is extracted in polar spherical coordinates from the contributions arising from the measured refractive indices and the known angles between the OA and the crystallographic axes in the crystal.

The magnitudes of two polar vectors (electric moments) are computed in the directions of the crystallographic axes and the axial vectors of second rank are generated through the cross products of the wave vector of light and the polar vectors of the crystal. The electric moment in the OA direction is derived from the electric moment of the bisector, which is the crystallographic *b*-axis. The ratios of the refractive indices and the electric moments are defined in the indicatrix and in the quadric of electric moments, respectively. The OAs and the crystallographic *c*-axis are mutually orthogonal, whose magnitudes of electric moments are iterated with the net charges of N and O as variables, until the ratio of them is topologically equivalent with the inverted ratio of the corresponding refractive indices. The iterated electric moments are axial vectors, which can be converted to the gyration tensor components. Their screw rotational character and the handedness can explain the sense of rotation of the circularly polarized light waves according to Fresnel's proposal. [15] The magnitude of optical rotation is obtained from the difference between the two gyration tensor components.

Theoretical and structural basis for model

Sodium nitrite, $NaNO_2$, crystallizes in an orthorhombic symmetry group *mm2* at room temperature. The crystal structure was first examined with X-rays by Ziegler [16] and later on by Carpenter. [17] Kay and Frazer [18] determined the structure in the space group *Im2m* by neutron diffraction and Gohda et al. [19] by anomalous X-ray diffraction techniques at room temperature. Since Sawada *et al.* [20] found ferroelectricity in $NaNO_2$ crystal many properties have been investigated and model calculations carried out on it [14]. The absolute crystal structure with two units of $NaNO_2$ (Z=2) in the right-handed system of coordinate axes is shown in Fig. 1, where the *a-c* and *b-c* planes are mirror planes.

The experimentally measured values of refractive indices of $NaNO_2$ crystal are taken from Mitsui et al. [21] and from Dmitriev *et al.*, where the observed optical orientation is given as *X=a, Y=c and Z=b* and $2V_Z = 62.5°$ at 5325 Å. [22] The values are standing in TABLE I.

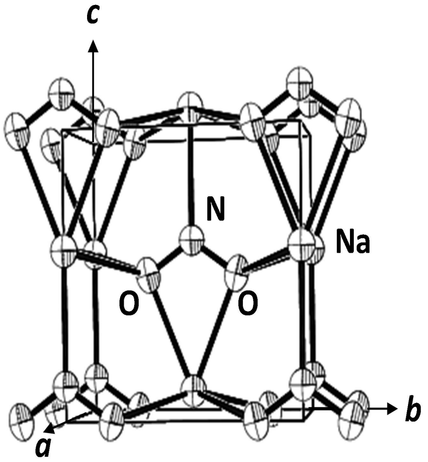


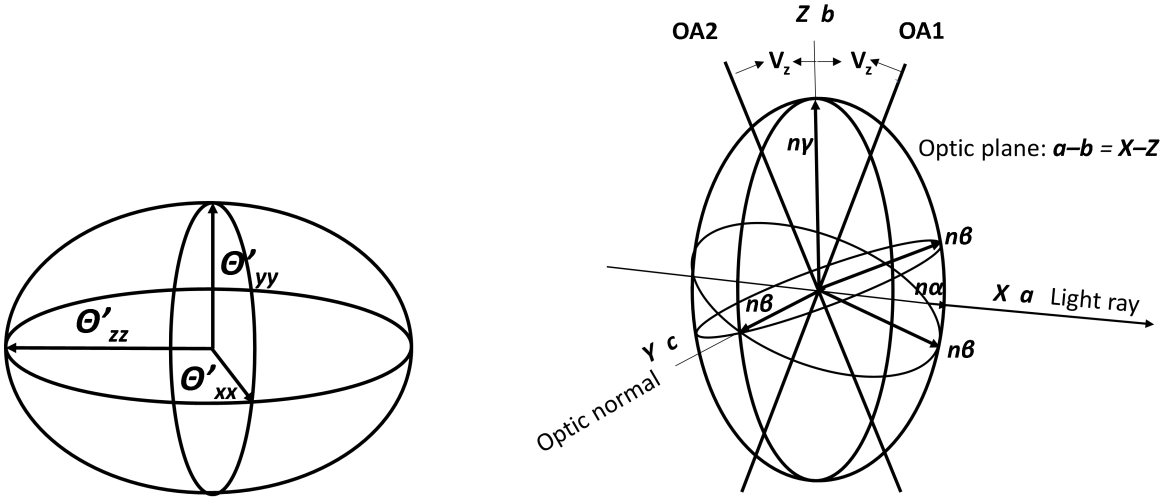
Figure 1. Crystal structure of ferroelectric $NaNO_2$ in space group *Imm2*. [23]

TABLE I. Experimentally measured values of refractive indices of $NaNO_2$ crystal.

λ (Å)	*nα*	*nβ*	*nγ*	Ref.
6328	1.3443	1.4107	1,6510	Mitsui
5325	1.3475	1.4147	1.6643	Dmitriev *et.al.*
5762	1.3455	1.4125	1.6547	"
11523	1.3353	1.4029	1.6319	"

When a light ray travels in a principal *a*-axis direction, which has the lowest magnitude of the refractive indices of $NaNO_2$ crystal, it is possible to design the two circular sections with a radius *nβ*, towards which the optic axes (OAs) are normals as drawn in the Fig. 2(b). The OAs are lying parallel with the crystallographic *b*-axis on the optic plane. The angle $2V_Z$ is an optic angle, which is bisected by the crystallographic *b*-axis. The two-fold *c*-axis is an optic normal and it is always lying perpendicular to the optic plane in the crystals with *mm2* symmetry. Optical rotation is observable and free of disturbing double refraction, when a plane-polarized light traverses in the OA-directions.

The Figs. 2(a) and 2(b) are (exaggerated) positive quadrics and designed with the crystallographic *c*-axis placed horizontally for a better illustration. They are surfaces of second rank with the electric moments (Θ'_{xx}, Θ'_{yy}, Θ'_{zz}) as semiaxes in the nano-quadric in Fig. 2(a) and with the measured refractive indices (*nα, nβ, nγ*) as semiaxes in the indicatrix in Fig. 2(b) of the $NaNO_2$crystal.



2(a) 2(b)

Figure 2. Quadrics of (a) the electric moments of NO_2^- ion and (b) the optical indicatrix of $NaNO_2$.

Model calculations of $NaNO_2$ crystal

The HAUP method was used by Chern and Phillips [24], when the optical rotation of 15.7 ± 0.5 °/mm in the directions of 33° from the *c*-axis on the *a-c* plane of the $NaNO_2$ crystal was experimentally recorded in *m2m* symmetry with the wavelength of 6328 Å. It is also discussed in the dissertation of Chern. [25] The following calculations are only performed for the structure with the refractive indices measured at λ=6328 Å. The results computed in other wavelengths are only summarized in TABLES II, IV and V.

Determination of optic angel ($2V_Z$)

The relationship between the measured refractive indices and the angle V_Z at λ = 6328 Å is reckoned according to the Eq. (1). [12]

$$\cos^2(V_Z) = \frac{n_\alpha^2\,(n_\gamma^2 - n_\beta^2)}{n_\beta^2\,(n_\gamma^2 - n_\alpha^2)} = \frac{1.3443^2\,(1{,}6510^2 - 1.4107^2)}{1.4107^2\,(1.6510^2 - 1.3443^2)} = 0.72725 \qquad \text{Eq. (1)}$$

$$\Rightarrow \cos(V_Z) = 0.85279 \Rightarrow V_Z = 31.483° \Rightarrow 2V_Z \Rightarrow 62.967°$$

The *Z* axis of the indicatrix bisects the optic angle $2V_Z$ and when $2V_Z < 90°$ the $NaNO_2$ crystal is optically positive.

Extraction of index of refraction in OA direction

A radius vector ***r'*** to any point ***P*** *(x,y,z)* lying on the surface of a three-axial ellipsoid of general form, illustrates the orientation of ***r'*** in the indicatrix of the $NaNO_2$ crystal in Fig. 3. [12] The length of the vector ***r'*** can be obtained with the help of polar spherical coordinates, when the angles of ρ and δ are known. There are not existing any predesigned expressions of the polar coordinates for a ready use. They must be separately defined for every distinct structure description. The point coordinates *x,y,z* must not be mixed up with the *X,Y,Z* axes of the indicatrix. The expressions used to extract the contributions to the ordinary length of the vector ***r'*** in polar coordinates from the point coordinates in the principal axis directions of the orthorhombic $NaNO_2$ crystal according to the Fig.3 are the following:

$x = r' \sin\rho \cos\delta,$

$y = r' \cos\rho,$

$z = r' \sin\rho \sin\delta$

and when the magnitude of $r' = (x^2 + y^2 + z^2)^{1/2}$

$$=> 1/r' = \left(\frac{sin^2\rho\, cos^2\delta}{x^2} + \frac{cos^2\rho}{y^2} + \frac{sin^2\rho\, sin^2\delta}{z^2} \right)^{-1/2}. \qquad \text{Eq. (2)}$$

The ordinary length of the vector ***r'*** is not needed in this study, but the Eq. (2) can be utilized to define the length of it as an index of refraction, *n'*, for a plane polarized light propagating parallel to the vector ***r'*** with the wave normal perpendicular to it. In the $NaNO_2$ crystal the angles $\rho = V_Z$ and $\delta = 0$ and when $\sin\delta = 0$ according to Fig. 3 the contribution from the last term in Eq. (3) will be zero and the value of the refractive index *n'* must lie between $n\alpha$ and $n\beta$. The Eq. (3) gives the value of *n'*.

$$1/n' = \left(\frac{sin^2\rho\, cos^2\delta}{n\alpha^2} + \frac{cos^2\rho}{n\beta^2} + \frac{sin^2\rho\, sin^2\delta}{n\gamma^2} \right)^{-1/2} = \left(\frac{sin^2\rho\, cos^2\delta}{n\alpha^2} + \frac{cos^2\rho}{n\beta^2} + 0 \right)^{-1/2} \qquad \text{Eq. (3)}$$

$=> n' = 1.39162.$

The radius vector ***r'*** is perpendicular to the *c*-axis and when the *P-c* plane in Fig.3 is not a mirror plane, the ratio of the two refractive indices, $n\beta /n' = 1.4107/1.39161 = 1.013711$, can be used as a reference in the iteration of the electric moments. The optic angle, $V_Z = \rho$, the refraction indices of $n\beta$ and n' with different wavelengths are written in the TABLE II.

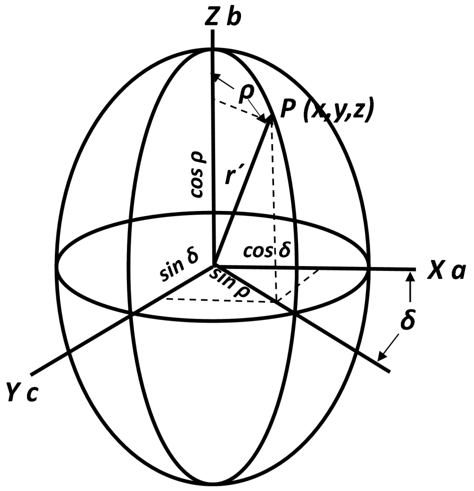


Figure 3. Orientation of radius ***r'*** of indicatrix described with help of the angles of *ρ* and *δ*.

Table II. Angle $V_z = \rho$, two refractive indices and their ratio in $NaNO_2$ at different wavelengths.

$\rho = V_Z$ (°)	$n\beta$	n'	$n\beta/n'$	λ (Å)
31.483	1.4107	1.39162	1.013711	6328
31.258	1.4147	1.39562	1.013671	5325
31.523	1.4125	1.39320	1.013853	5762
32.241	1.4029	1.38262	1.013945	11523

Iteration of second electric moments and net atomic charges

The accurate lattice constants and atomic positional parameters are taken from Gohda et al. [19] and adapted to the *mm2* symmetry with the changed directions of the *b* and *c* axes and coordinates to the space group *Imm2*. They are presented TABLE III.

TABLE III. Lattice constants and atomic coordinates of $NaNO_2$ in the space group *Imm2*.

Lattice constants	*a* = 3.5653 Å	*b* = 5.3846 Å	*c* = 5.5728 Å
Atom	*x*	*y*	*z*
Na	1/2	1/2	0.58670
N	1/2	1/2	0.62112
O1	1/2	0.30448	1/2
O2	1/2	0.69552	1/2

The magnitudes of electric moments in the directions of crystallographic axes are always multiplied by the square of the lattice constants, though they are presented as semi-axes in the Fig. 2(a). The optic axes lie on the *a*-*b* plane and they deviate by the angle V_Z from the *b*-axis in the $NaNO_2$ crystal. The magnitude of the second electric moment in the direction of OA is

$\Theta'_{OA} = \Theta'_{YY}/\cos^2(V_Z)$, when the light ray penetrates the length of $b/\cos(V_Z)$ through the unit cell. The values of the polar second electric moments, Θ'_{OA} and Θ'_{ZZ}, must be defined with respect to the common reference coordinates ($Y_C = Z_C = 1/2$) to make them comparable with each other. In the NO_2 ion the center of charge coincides at the reference coordinate $Y_C = 1/2$ in the crystallographic *b*-axis direction, which is not polar. The Eqs. (4) and (5) give the net values of the second electric moments of Θ'_{YY} and Θ'_{OA}, respectively. But the nitrite ion is polar in the *c*-axis direction and z-coordinates of N and O atoms must be iterated towards the center of the electric moment ($Z_C = 1/2$) according to the Eq. (7). Eq. (6) the gives the magnitude of net electric moment Θ'_{ZZ} with the iterated *z*-coordinates. The Na^+ ion is omitted in these calculations.

$$\Theta'_{YY} = \Sigma e_i\,(y_i^{\,2} - Y_C^{\,2}) \cdot b^{\,2} \qquad \text{Eq. (4)}$$

$$\Theta'_{OA} = \Sigma e_i\,(y_i^{\,2} - Y_C^{\,2}) \cdot [b\,/\,(\cos\,(V_Z)\,]^2 \qquad \text{Eq. (5)}$$

$$\Theta'_{ZZ} = \Sigma e_i\,(z_i^{\,2} - Z_C^{\,2}) \cdot c^{\,2} \qquad \text{Eq. (6)}$$

$$\phi = \Sigma(e_i)/R + \Sigma\,(e_i\,z_i)/R^2 + \Sigma\,(\,e_i\,z_i^2)/R^3 + \Sigma\,(e_i\,z_i^3)/R^4 + \ldots \qquad \text{Eq. (7)}$$

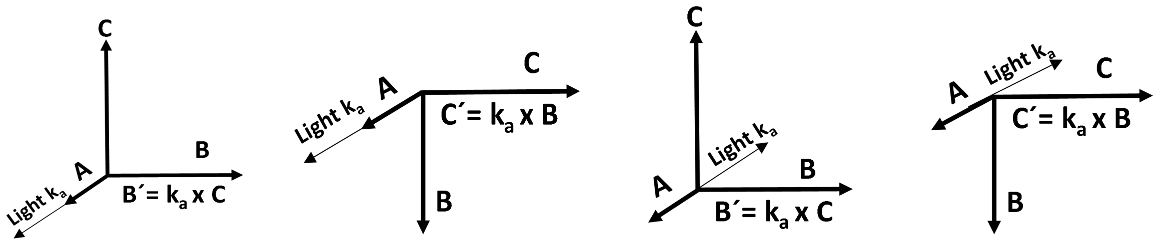
The Eq. (7) is an expression of the total electrostatic potential, $\phi = \Sigma(e_i)/(R/2)$, for a system of point charges, which must be fulfilled in ionic solids with the integer charges on ions. It is originally presented in a polar coordinate system and developed into a power series in a Cartesian coordinate system by Buckingham [26,27]. The Eq. (7) is applied only in the polar *c*-axis direction of $NaNO_2$ and when truncated after the fourth term it is giving the accurate *z*-coordinates for N and O atoms in the iteration. The input values of the net atomic charges, $\Sigma(e_i) = -1$, $R=1$ and the coordinates of N and O from TABLE III into the Eq. (7) starts the iteration against $\phi = -2$ as explained in the Ref. [28]. The iteration separates the center of charge from the center of electric moment ($Z_C = 1/2$) in the nitrite ion. This is repeated with new atomic charges and stopped until the ratio of the second electric moments ($\Theta'_{OA}/\Theta'_{ZZ}$), derived from the quadric in Fig. 2(a), reaches the inverted ratio of the correspondent refractive indices ($n\beta/n'$) from the indicatrix in Fig. 2(b). The two quadrics are standing now in a topological equivalence.

TABLE IV. The summary of the first three and the final steps of the iteration of z-coordinates of N and O atoms with the net charges as variables resulted in the components of second electric moments, Θ'_{OA} and Θ'_{ZZ}, at λ=6328 Å and with the other three wavelengths in $NaNO_2$ crystal. The initial charges of -1/3 were applied to the atoms in the nitrite ion.

λ (Å)	V_Z (°)	Atom	Charge	z	Θ'_{OA} eÅ^2	Θ'_{ZZ} eÅ^2	$\Theta'_{OA}/\Theta'_{ZZ}$	$n\beta/n'$
6328	31.483	N	-1/3	0.621510				
		O	-1/3	0.500300	-1.016035	-1.418783	0.716131	
		N	-.10	0.651486				
		O	-.45	0.530366	-1.371647	-1.416242	0.968512	
		N	-.05	0.658111				
		O	-.475	0.536991	-1.447850	-1.416061	1.022449	
		N	-.05810	0.657033				
		O	-.47095	0.535913	-1.435505	-1.416083	1.013715	1.013711
5325	31.258	N	-.05363	0.657632				
		O	-.473185	0.536512	-1.435427	-1.416082	1.013661	1.013671
5762	31.523	N	-.058778	0.656943				
		O	-.470611	0.535823	-1.435699	-1.416090	1.013847	1.013853
11523	32.241	N	-.07322	0.655026				
		O	-.46339	0.533906	-1.435882	-1.416144	1.013938	1.013945

Refractive indices and handedness of axial vectors

Figs.4(a-d) are schematic presentations of the measurements of refractive indices in $NaNO_2$ crystal with a nonpolar light of accurate wavelength. The polar electric moments, Θ'_{XX}, Θ'_{YY}, and Θ'_{ZZ}, are labelled as **A**, **B** and **C** in the positive directions of the semiaxes of the quadric 2(a) and the axial vectors are denoted by **B'** and **C'**. $\mathbf{k_a}$ is a wave vector of light. The Figs. 4(a) and 4(b) show the measurements of the refractive index in the **B** and **C** axis directions of the absolute crystal structure in the right-handed system of coordinate axes, when light travels in a positive direction of the **A** axis. In the Figs. 4(c) and 4(d) the light ray propagates in a negative **A**-axis direction and turns the coordinate system left-handed as a mirror image of the absolute structure. The handedness of the axial vectors reveals the rotational character of the circularly polarized light rays, when they advance in the axial vectors.



4(a) 4(b) 4(c) 4(d)

Figure 4. Second electric moments, axial vectors and wave vector of light propagating in positive and and negative directions along the crystallographic *a*-axis in $NaNO_2$.

4(a) $\mathbf{B'= k_a \; x \; C}$ follows the left-hand rule with a counterclockwise (n_L) rotation character.

4(b) $\mathbf{C'= k_a \; x \; B}$ follows the right-hand rule with a clockwise (n_R) rotation character.

4(c) $\mathbf{B'= k_a \; x \; C}$ follows the right-hand rule with a clockwise (n_R) rotation character.

4(d) $\mathbf{C'= k_a \; x \; B}$ follows the left-hand rule with a counterclockwise (n_L) rotation character.

The vector cross products form two axial vectors of second rank parallel with both the crystallographic *b*- and *c*-axes, but they bear the magnitudes from the polar vectors in the *c*- and *b*-axis directions, respectively. This is an excellent coincidence with the experimentally observed optical orientation of the indicatrix made by Dmitriev et al. and shown in Fig. 2(b). [22] This means the that the refractive index *nβ* has the parallel orientation with the crystallographic *c*-axis according to Dmitriev et al. [22] and the vector cross products in this study. The ratio of the refraction indices *nβ /n'* was used as a reference, when the second electric moments were calculated and summarized in TABLE IV.

Gyration tensor components g_{12} and g_{33}

The gyration tensor components are axial vectors of second rank. The components of the second electric moments in units eÅ^2, in TABLE IV, are converted to the gyration tensor components in units coulombcentimeter^2 (Ccm^2) according to the Eqs. (8) and (9).

$$g_{12} = \Theta'_{OA} \cdot (-1.602177 \cdot 10^{-19}) \cdot 10^{16}\,\mathrm{Ccm}^2 \qquad \text{Eq. (8)}$$

$$g_{33} = \Theta'_{ZZ} \cdot (-1.602177 \cdot 10^{-19}) \cdot 10^{16}\,\mathrm{Ccm}^2 \qquad \text{Eq. (9)}$$

g_{12} is the faster and dominant component with a higher magnitude than the lower component g_{33}. The values of them are written in TABLE V.

Optical rotation in $NaNO_2$ crystal

According to the theory of optical rotation a plane polarized light is split up into two circularly polarized waves with opposite rotations but with same frequency, when it enters the crystal in the optic axis direction as supposed by Fresnel [15]. The faster of the waves is dominant and the handedness of it determines the sign of optical rotation in the crystal. When a plane polarized light propagates parallel with OA1 in the right-handed coordinate axis system of the absolute crystal structure of $NaNO_2$, the dominant gyration tensor component g_{12}, having the same handedness as the dominant axial vector **B’** in Fig. 4(a), drives the circularly polarized wave component with a counterclockwise rotation (n_L) faster than the slower g_{33} (n_R) does with a clockwise rotation character. The rotation is seen as a positive, clockwise dextrorotation towards the light source by an observer. When a light ray travels in the direction of OA2, it feels the coordinate axis system left-handed, where the dominant g_{12} follows the right-hand rule with the clockwise rotation character (n_R) as the dominant axial vector **B’** in Fig. 4(c) and this is seen as a negative, anticlockwise levorotation towards the light source by an observer. The magnitude and sense of optical rotation per unit path, *d*, in the $NaNO_2$ crystal are given according to Eq. (10). [29]

$$\phi = \frac{\pi \cdot d \cdot (n_L - n_R)}{\lambda} \text{ radians.} \qquad \text{Eq. (10)}$$

The optical rotation and the refractive indices are usually given for the crystal plates with thicknesses of 1 mm and 1 cm, respectively. The magnitude and sense of optical rotation at λ = 6328 Å are expressed in the directions of optic axes, OA1 and OA2, in the unit cell with two asymmetric units in the $NaNO_2$ crystal, according to Eqs. (11) and (12), respectively, and summarized in TABLE V together with the results at other three wavelengths.

$$\text{In OA1: } \phi = \frac{2 \cdot 0.1 \cdot \pi \cdot (g_{12} - g_{33})}{\lambda} = +\,0.30889 \text{ rad. mm}^{-1} = +17.7\ ^\circ \text{ mm}^{-1}. \qquad \text{Eq. (11)}$$

$$\text{In OA2: } \phi = \frac{2 \cdot 0.1 \cdot \pi \cdot (g_{33} - g_{12})}{\lambda} = -\,0.30889 \text{ rad. mm}^{-1} = -\,17.7\ ^\circ \text{ mm}^{-1}. \qquad \text{Eq. (12)}$$

The experimental value of $\phi = 15.7 \pm 0.5\ ^\circ \text{ mm}^{-1}$ at λ = 6328 Å is measured with the HAUP method close to the same OA directions but with opposite rotational senses as in this study. [24]

TABLE V. The summary of the optical rotations calculated from the gyration tensor components, g_{12} and g_{33}, derived from the second electric moments, Θ'_{OA} and Θ'_{ZZ}, in the TABLE IV and through the Eqs. (8-12) at different wavelengths in the two OA directions. The values are given only with three significant numbers, because the fourth decimals of the refractive indices at λ = 6328 Å are estimated from the three-decimal curvature-values in the temperature dependence measurements of refractive indices published by Mitsui *et al.* [21]

Optic axis	Wavelength (Å)	$g_{12} \cdot 10^{-3}$ (Ccm^2)	$g_{33} \cdot 10^{-3}$ Ccm^2)	ϕ (rad. mm^{-1})	ϕ (° mm^{-1})
OA1	6328	2.29993	2.26882	-0.30889	+ 17.7
OA2	“	”	”	”	– 17.7
OA1	5325	2.29981	2.26881	-0.36578	+ 21.0
OA2	“	”	”	”	– 21.0
OA1	5762	2.30024	2.26883	-0.34251	+ 19.6
OA2	“	”	”	”	– 19.6
OA1	11523	2.30054	2.26891	-0.17247	+ 9.90
OA2	”	”	”	”	– 9.90

Discussion

The directions with an intensity maximum of optical rotation with a minimal disturbance from double refraction are not easy to discover in the biaxial crystals. The component of optical gyration tensor in a symmetry group of *mm2* does not reveal enough information about the magnitude of rotation in the involved directions without any application model. The circular sections, which optic axes penetrate, can only be found, when a light ray travels in the direction with the lowest refraction index in the crystal. It is not always the direction of the crystallographic *a*-axis in biaxial crystals. A fortuitous search after optical rotation with maximum intensity in biaxial crystal places great demands. Crystals must be cut normal to optic axis at the both ends to minimize ellipticity in the circularly polarized light, when the optical rotation is measured.

The purpose of this study has been to show that optical rotation can be computed from a point charge model in the biaxial achiral crystal. Net atomic charges in the absolute crystal structure and the accurately measured refractive indices are very essential in this type of analysis in order to find the correct outcome about the magnitude and sense of optical rotation. The parallel orientations of the experimentally observed refractive indices in the indicatrix with the computed magnitudes of axial vectors in the quadric of electric moments make a good start point. It is possible to iterate reliable net charges on N and O atoms under the ionic integer constraints in $NaNO_2$ crystal. The structures with a higher number of atoms in general positions in the unit cell require very accurate X-ray diffraction work, where particularly the low angel reflections with strong intensity can suffer from extinction. It is the intensity decrease, which is associated with the distribution of valence electrons that bring most information about the net atomic charges in crystals.

The frequency of light causes the electron clouds around the atoms to resonate at the same frequency in the measurement of refractive indices and therefore it is often necessary to report the indices of refraction at several wavelengths. The refractive indices of the biaxial crystals can be very rich of information. Unit cells of the biaxial crystals may contain two or more multinuclear systems of ions or molecules. The contributions from them must be included in the total magnitudes of principal electric moments and axial vectors of second rank. The axial vectors with their local handedness of the dominants can saturate the refractive indices by effects, which can change their directions in the indicatrix. The charge density in the NO_2^- ion is highly concentrated in the oxygen atoms in this work. The values of the atomic charges with five or six decimals were needed to get the topological equivalence because of the low value of optical rotation, which can be common in the biaxial crystals. The use of light with a lower wavelength can be favorable in the rotation measurements. Charge densities can be refined from the collected X-ray datasets with superior programs *MOLLY* and *XD* (http://xd.chem.buffalo.edu).

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References

[1] Kaminsky, W., Thomas, P.A. and Glazer A.M. (2002). Z. Kristallogr. 217, 1-7.

[2] Kobayashi, J., Uesu, Y. (1983). J. Appl. Crystallogr. 16, 204-211.

[3] Kobayashi, J., Uesu, Y., Takehara, H. (1983). J. Appl. Crystallogr. 16, 212-219.

[4] Claborn, K., Isborn, C., Kaminsky, W. and Kahr B. (2008). Angew. Chem. Int. Ed. 47, 5706-5717.(Internet: Optical Rotation of Achiral Compounds – Academia.edu).

[5] Born, M., Phys. (1915). Z., 16, 251.

[6] Reijnhart, R., Dissertation, (1970). Technische Hogeschool, Delft (1970). (Internet: P1966-3184.pdf).

[7] Devarajan, V. and Glazer, A. M. (1986). Acta Cryst. A42, 560-569.

[8] Ramachandran, G.N. (1951). Proc. Indian Acad. Sci. A33, 217 - 227.

[9] Ramachandran, G.N. (1951). Proc. Indian Acad. Sci. A33, 309 - 315.

[10] Ramachandran, G.N. (1951). Proc. Indian Acad. Sci. A34, 127 - 135.

[11] Glazer, A.M. and Stadnicka, K. (1986). J. Appl. Crystallogr, 19, 108-122.

[12] Nesse, W.D. (1986). Introduction to Optical Mineralogy, Oxford University Press.

[13] Axe, J.D. (1968). Phys. Rev. 167, 573.

[14] Ravindran, P., Delin, A., Johansson, B. and Eriksson, O. (1999). Phys. Rev. B 59, 1776.

[15] Fresnel, A. (1824). Bull. Soc. Philomath. Paris. pp. 147-158.

[16] Ziegler, G.E. (1931). Phys. Rev. 38, 1040.

[17] Carpenter, G.B. (1952). Acta Cryst. 5, 132.

[18] Kay, M.I. and Frazer, B.C. (1961). Acta Cryst. 14, 56.

[19] Gohda, T., Ichikawa, M., Gustafsson, T. and Olovsson, I. (1996). J. Korean. Phys. Soc. 29, S551-S554.

[20] Sawada, S., Nomura, S., Fuji, S. and Yoshida, I. (1958). Phys. Rev. Lett. 1, 320.

[21] Mitsui, T. Iio, K. Hanazaki, B. and Nakamura, T. (1985). Jpn. J. of Appl. Phys. 24, 272 (On line.).

[22] Dmitriev, V.G., Gurzadyan, G.G. and Nikogosyan, David N. (2013). Handbook of Nonlinear Optical Crystals, 3th Revised Edition, Springer-Verlag.(Internet: Refractive Indices in biaxial NaNO2 crystal).

[23] Farrugia, L.J. (1997). ORTEP-3 for Windows, J. Appl. Crystallogr. 30, 565.

[24] Chern, Mao-Jin. and Phillips, R.A. (1970). J. Op. Soc. Am., 60,1230-1232.

[25] Chern, Mao-Jin., Dissertation, (1972) University of Minnesota, (1972). (Internet: A study of optical activity and Raman scattering in the sodium-nitrite crystals).

[26] Buckingham, A.D. (1959). Q. Rev. Chem.Soc. 13, 183.

[27] Buckingham, A.D. (1970). Physical Chemistry. An Advanced Treatise. Vol. IV, p.349.

[28] Karppinen, M. (2015). Acta Crystallogr. Sect. B 71, 334-341.

[29] Nye, J.F. (1972). Physical Properties of Crystals. Oxford: Clarendon Press.