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Electrogyration and Piezogyration in $NaClO_3$

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Abstract

A method is developed for measuring electrogyration and piezogyration effects in polar crystals. The influence of linear electro-optic and piezo-optic effects is discussed in detail. By the use of different directions of measurement, the tensorial behaviour of the induced gyration is proved unequivocally. The magnitudes of the electrogyration and piezogyration coefficients are 10^{-16} m V^{-1} and 10^{-15} m^2 N^{-1} respectively. The relations between constants measured under different thermodynamic conditions are considered. An analysis of results on the basis of a coupled oscillator model reveals a strong sensitivity of induced gyration to changes in the arrangement of the oscillators.

I. Introduction

Optical activity arises from variations of the radiation field within the structural unit of the material. Hence the magnitude of the gyration coefficient g is usually smaller than the refractive power $n^2 - 1$ by a factor a/λ, where a is a length of molecular dimension and λ the wavelength of light (Born, 1972). Miller (1973) has demonstrated that the changes in birefringence and optical activity induced by electric fields should be related by the same factor. He estimated a value of $\Delta g = 6{\cdot}6 \times 10^{-16}$ m V^{-1}. Measurements on more than thirty alums (Weber & Haussühl, 1976) and nitrates of alkaline earths (Weber & Haussühl, 1977) of point group $m3$ exhibit a surprisingly wide variation of Δg, about three orders of magnitude, but the average value agrees with the predicted one. As all published experimental results on polar crystals are several orders of magnitude higher, Miller (1973) suggested that they are influenced by the dominant linear electro-optic effect. Here we investigate these influences in detail to obtain reliable experimental results in order to decide whether in polar and centrosymmetric crystals different contributions to the electrogyration effect exist, or if the previous results are due to experimental errors.

Only a few papers on the changes of optical activity caused by mechanical stress have been published. Meyers & Vedam (1965) have investigated the influence of hydrostatic pressure on the optical rotation in α-quartz, sodium chlorate, benzil, and ethylenediamine sulphate. Their results reveal that the magnitude of the piezogyration coefficients is indeed smaller than the piezo-optic effect by a factor a/λ. Using uniaxial stresses instead of hydrostatic pressure, it is possible to obtain all components of the piezogyration tensor. However, their determination is disturbed by the piezo-optic effect similarly to the way the electrogyration measurements are disturbed by the linear electro-optic effect.

The problem in measuring electrogyration and piezogyration is to recognize that part of an induced rotation which originates in the induced birefringence. This must be separated from the intrinsic gyration effect, which may be achieved using the following method.

The samples under investigation are mounted between two polarizers. An expression is developed for the change in the intensity of light traversing this optical system as a function of the changes in azimuth η and ellipticity θ which occur in the light wave between crystal and analyser. Appropriate formulas relating these quantities to the induced birefringence and optical activity are obtained by an expansion of η and θ in a power series with the variables ρ (rotatory power) and δ (linear birefringence). Although $NaClO_3$ has cubic symmetry, an initial birefringence has to be taken into account because the samples used show small strain-induced double refractions. If sufficiently small electric fields and mechanical stresses are employed, only first-order terms of the power series are needed. It will be shown that the intrinsic gyration effect can be separated from the influence of the induced birefringence by varying the azimuth of the incident linear wave. A further check is obtained by applying a d.c. biasing voltage in appropriate directions, allowing a variation of the initial birefringence to be made by means of the linear electro-optic effect. As a final proof of the correct interpretation of the recorded intensity changes, different directions of the light beam, the electric field, and the mechanical stress are employed and the tensorial anisotropy is examined. The last test is possible only in cubic crystals, since optical activity is only easily observable in directions without linear birefringence. We therefore chose $NaClO_3$ with point symmetry 23 as a suitable crystal for our investigation.

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II. Theoretical considerations

Two practicable methods are known for describing the influence of an optically active and birefringent crystal on a light wave. Jones (1948) has developed a matrix method and Pancharatnam (1957) has used geometric calculations by means of the Poincaré sphere. Both theories, as well as electro-optic and piezo-optic effects, are described in the survey on crystal optics by Ramachandran & Ramaseshan (1961). The basic equations are summarized below.

(*a*) *Optical activity and birefringence*

An optically active crystal with cubic symmetry rotates a linearly polarized wave through the angle

$$\rho = (\pi l/\lambda n)\, g. \tag{1}$$

Here l is the length of the specimen and n the index of refraction. The scalar parameter of gyration is defined by

$$g = \mathbf{G}.\mathbf{s} = g_{ij}\, s_i\, s_j,$$

where $\mathbf{G}$ is the gyration vector with components $G_i = g_{ij} s_j$, s_i are components of the unit vector of wave propagation and g_{ij} is an axial tensor of second rank.

The birefringence of an otpically anisotropic medium is described by

$$\delta = (2\pi/\lambda)(n' - n'')\, l, \tag{2}$$

where n' and n'' are the refractive indices for the two linear modes of the crystal.

If both properties are present two elliptically polarized waves propagate through the crystal. The axial ratio of the ellipses is $\pm\tan\alpha$ with

$$\tan 2\alpha = \delta/2\rho, \tag{3a}$$

and their relative path difference is given by

$$\omega = (\delta^2 + 4\rho^2)^{1/2}. \tag{3b}$$

In passing through an optically active and birefringent crystal a linear wave becomes elliptically polarized. By means of the Poincaré sphere, Sliker (1964) has developed appropriate formulas which describe the ellipticity θ and the azimuth η of the emergent wave in terms of α, ω, and the original vibration direction η_0:

$$\sin 2\theta = \sin 2\alpha[\cos 2\eta_0 \cos 2\alpha(1 - \cos\omega) + \sin 2\eta_0 \sin\omega],$$

$$\tan 2\eta = \tan 2\eta_0 \cos\omega + \cos 2\alpha \sin\omega \times (\sin^2 2\alpha + \cos^2 2\alpha\, \cos\omega - \tan 2\eta_0 \cos 2\alpha\, \sin\omega)^{-1}. \tag{4}$$

The angles η_0 and η are referred to a principal vibration direction within the crystal. In principle, the determination of the electrogyration effect is possible by measuring the θ and η of a sample in a strong static electric field. This method has recently been employed by Schamburov & Romanova (1976) with α-quartz. Nevertheless, in the light of theoretical considerations (Miller, 1973) their results seem to be too high to represent the intrinsic electrogyration effect accurately. We believe that it is difficult to achieve a sufficiently high quality and fineness of adjustment of the optical components to ensure reliable results in static experiments. These sources of trouble are avoided to a great extent by the dynamic method employed in this work.

(*b*) *Induced changes*

For an application of the above equations in dynamic experiments measurable changes of θ and η are needed as functions of the external electric fields and mechanical stresses. Under the prevailing experimental conditions the calculations can be shortened by the reasonable assumptions that the induced birefringence exceeds the induced gyration ($\Delta\delta \gg \Delta\rho$) and $2\rho \gg \delta$. The latter holds for a light propagation nearly parallel to an optical axis and in an isotropic medium. In cubic crystals δ arises from internal strains. The validity of both approximations will be demonstrated by experimental data. Assuming only small changes we obtain from (3):

$$\Delta\alpha = (1/4\rho)\,\Delta\delta \quad \text{and} \quad \Delta\omega = (\delta/2\rho)\,\Delta\delta + 2\Delta\rho. \tag{5}$$

Expanding (4) in terms of the variables α and ω and inserting (5) we obtain

$$\Delta\theta = (\sin\rho/2\rho)\sin(2\eta_0 + \rho)\,\Delta\delta, \tag{6}$$

and

$$\Delta\eta = \frac{1}{4\rho}\left[1 - \frac{\sin 2\rho}{2\rho} - \frac{\sin^2\rho}{\rho}\,\sin(4\eta_0\, 2\rho)\right]\delta\Delta\delta + \Delta\rho. \tag{7}$$

Thus the change $\Delta\theta$ of the light wave emergent from the crystal is only a function of the induced birefringence $\Delta\delta$, whereas the variation $\Delta\eta$ is due to the induced gyration $\Delta\rho$ as well as to a birefringent term $\delta\Delta\delta$. From (7) it is obvious that a direct determination of $\Delta\rho$ is possible by the measurement of $\Delta\eta$, when the initial birefringence δ of the sample is zero. But as $\Delta\delta$ is expected to be about 10^3 times greater than $\Delta\rho$, even very small values of δ are able to disturb the measurements to a considerable extent and it is not possible to neglect the term $\delta\Delta\delta$ in real crystals with cubic symmetry. In the next section we demonstrate that, in the experimental set-up used, a further quantity must also be considered, namely

$$2\theta\Delta\theta = (\sin^2\rho/4\rho^2)[1 - \cos(4\eta_0 + 2\rho)]\,\delta\Delta\delta. \tag{8}$$

Now we must relate the variables $\Delta\delta$ and $\Delta\rho$ in (6)–(8) to the electric-field components E_k and the mechanical-stress components σ_{kl}. Differentiating (1) and (2) gives

$$\Delta\rho = (\pi/\lambda)[\Delta g/n - (g/n^2)\,\Delta n + (g/n)\,\Delta l/l]\,l, \qquad (9)$$

and

$$\Delta\delta = (2\pi/\lambda)[\Delta n' - \Delta n'' + (n' - n'')\,\Delta l/l]\,l. \qquad (10)$$

The induced changes Δn and $\Delta l/l$, where $\Delta l/l$ describes the deformation ε_{ij}, are defined by (Nye, 1957).

$$\Delta a_{ij} = r_{ijk}\,E_k + q_{ijkl}\,\sigma_{kl}, \qquad (11)$$

where $\Delta a_{ii} = -(2/n^3)\,\Delta n_i$, when reference is made to the principal axes coordinate system of the crystal and

$$\varepsilon_{ij} = d_{klj}\,E_k + s_{ijkl}\,\sigma_{kl}. \qquad (12)$$

In the same manner we define

$$\Delta g_{ij} = s_{ijk}\,E_k + w_{ijkl}\,\sigma_{kl}. \qquad (13)$$

The quantities entering (11)–(13) are components of the following tensors:

r_{ijk}: linear electro-optic
q_{ijkl}: piezo-optic
d_{klj}: inverse piezoelectric
s_{ijkl}: elastic compliance
s_{ijk}: electrogyration
w_{ijkl}: piezogyration.

In order to avoid long unwieldy formulas we omit an explicit substitution of (9)–(13) into (6)–(8). The numbers of independent components in (11)–(13) are equal for tensors of the same rank. Using matrix notation (Nye, 1957) the nonvanishing electrogyration and piezogyration coefficients in point symmetry group 23 are $s_{41} = s_{52} = s_{63}$ and $w_{11} = w_{22} = w_{33}$, $w_{12} = w_{23} = w_{31}$, $w_{13} = w_{21} = w_{32}$, $w_{44} = w_{55} = w_{66}$ respectively.

(*c*) *Thermodynamic relations*

In most common electro-optic experiments the crystals under investigation are mechanically free so that the stress is zero. An electric field of low frequency then causes a strain by the inverse piezoelectric effect. This in turn changes the gyration tensor by an effect which may be called elastogyration. In full notation we write

$$\Delta g_{ij} = (s^{\varepsilon}_{ijk} + w^{*}_{ijmn}\,d_{kmn})\,E_k. \qquad (14)$$

s^{ε}_{ijk} describes the so-called primary and $w^{*}_{ijmn}d_{kmn}$ the secondary effect. The elastogyration coefficients w^{*}_{ijkl} are obtained by the relation

$$\Delta g_{ij} = w_{ijkl}\,\sigma_{kl} = w_{ijkl}\,c_{klmn}\,\varepsilon_{mn} = w^{*}_{ijmn}\,\varepsilon_{mn},$$

where c_{klmn} are the stiffness constants.

In piezogyration measurements a distinction can be made between electrically free ($\mathbf{E}$ = constant) and electrically clamped (polarization $\mathbf{P}$ = constant) conditions. In practice, the electric field is kept constant. The stress then produces the polarization $\mathbf{P}$ by the direct piezoelectric effect which in turn changes g_{ij}:

$$\Delta g_{ij} = (w^{P}_{ijkl} + s^{*}_{ijm}\,d_{mkl})\,\sigma_{kl}. \qquad (15)$$

Again, w^{P}_{ijkl} can be called the primary and $s^{*}_{ijm}\,d_{mkl}$ the secondary effect. s^{*}_{ijk} is defined by

$$\Delta g_{ij} = s^{*}_{ijk}\,P_k = s^{*}_{ijk}\,\kappa_0\,\chi_{kl}\,E_l = s_{ijl}\,E_l.$$

Here κ_0 is the permittivity of a vacuum and χ_{kl} the dielectric susceptibility tensor. In (11)–(15) the summation convention applies (Nye, 1957).

For a complete thermodynamic consideration thermal effects must also be taken into account. In dynamic measurements, such as those carried out in this work, electric fields and mechanical stress produce changes ΔT in the crystal temperature by the electrocaloric and piezocaloric effects respectively. ΔT in turn changes the gyration tensor. We have developed the relation between adiabatic and isothermal constants by standard thermodynamic methods (Nye, 1957). The results are

$$\begin{aligned} s^{T}_{ijk} - s^{S}_{ijk} &= (\partial g_{ij}/\partial T)\,p_k(T/C), \\ w^{T}_{ijkl} - w^{S}_{ijkl} &= (\partial g_{ij}/\partial T)\,\alpha_{kl}(T/C). \end{aligned} \qquad (16)$$

The superscripts denote experimental conditions of constant temperature T and constant entropy S respectively. $\partial g_{ij}/\partial T$ describes the temperature dependence of the gyration tensor, C the specific heat of the crystal, p_k the pyroelectric constant, and α_{kl} the thermal expansion.

III. Measurements

(*a*) *Experimental procedure*

The measurements are performed by a dynamic lock-in technique with apparatus partly described earlier (Weber & Haussühl, 1974). Additional information about the experimental set-up is given in Fig. 1. Oscillating electric fields at *ca* 500 Hz and uniaxial

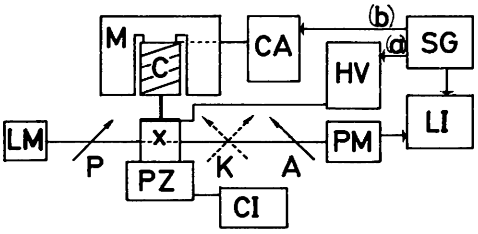


Fig. 1. Schematic diagram of the experimental arrangement. *LM* light source with monochromator; *P* polarizer; *x* crystal; *K* Babinet compensator, only used for measurements of induced birefringence; *A* analyser; *PM* photomultiplier; *SG* sine-wave generator; *LI* lock-in. (*a*) For electrogyration measurements: *HV* a.c. and d.c. high-voltage supply. (*b*) For piezogyration measurements: *CA* current amplifier; *C* coil with pin; *M* magnet; *PZ* piezoelectric cell; *CI* charge amplifier and indicator.

pressure oscillations at *ca* 100 Hz are applied to rectangular samples of $1–3 \times 10^{-6}$ m^3 volume. The pressure is produced by passing a current at 100 Hz through a coil in a magnetic field. The coil is supported by a pin which rests on the crystal and transmits the pressure, measured in turn by a piezoelectric cell. Some difficulties occur with the distribution of the stress within the sample. However, it is possible to check its homogeneity by examining the piezo-optical response at different points of the specimen. Troubles of this kind do not arise in the application of electric fields. In appropriate directions of measurement a static biasing field is applied additionally to the dynamic field and to the pressure.

The induced ellipticity $\Delta\theta$ of the emergent light is measured in the usual way by mounting a $\lambda/4$ plate and an analyser behind the sample. When the elliptically polarized light emergent from the sample passes directly through the analyser, the observed intensity is (Ramachandran & Ramaseshan, 1961)

$$I = I_0(1 - \cos 2\theta \cos 2\varphi)/2.$$

I_0 denotes the incident light intensity and φ is a measure of the angle between the principal directions of the light ellipse and the analyser. Assuming only small values for θ we deduce

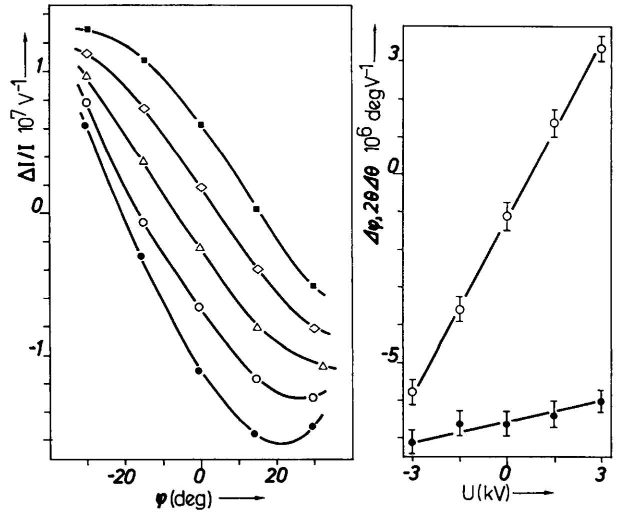
$$\Delta I = I_0(\sin 2\varphi\, \Delta\varphi + 2\theta \cos 2\varphi\, \Delta\theta),$$

where $\Delta\varphi$ is equal to $\Delta\eta$ in (7). The changes of the light intensity, ΔI, are compared with those produced by a Faraday cell mounted between crystal and analyser. Typical examples of ΔI signals *versus* angle φ are shown in Fig. 2(*a*). Values of $\Delta\varphi$ and $2\theta\Delta\theta$ derived from these curves depend linearly on the biasing field (Fig. 2*b*). This dependence is not observed in those directions where the linear electro-optic effect is zero. Thus we conclude that the biasing field influences $\Delta\eta$ and $2\theta\Delta\theta$ measurements by a change of the initial birefringence δ contained in (7) and (8).

(*b*) *Experimental examination of theoretical formulas*

Equations (7) and (9) reveal that the linear electro-optic or the piezo-optic effect influences the determination of the electrogyration or the piezogyration tensor in a rather complex way. In practice most troubles occur from the $\delta\Delta\delta$ term in (7) and special experimental care must be taken to separate these disturbances from the intrinsic induced gyration $\Delta\rho$. Recently Rogers (1977) has reported a method for a dynamic measurement of electrogyration effects in α-quartz on the basis of Jones's matrices. However, he has neglected any influence of the linear electro-optic effect and therefore his experiments result in unreasonably high values for the electrogyration coefficients. This example once more stresses the necessity for a detailed experimental test of formulas describing induced gyration measurements.

As a first step we checked the dynamic method by measuring the linear electro-optic and piezo-optic effects. The induced ellipticity $\Delta\theta$ was determined as a function of the rotatory power ρ for three different positions of the polarizer: (1) perpendicular to **E** ($\eta_0 = 0$); (2) diagonal to **E** ($\eta_0 = 45°$), the appropriate position for measuring the induced birefringence in crystals without optical activity; and (3) observation of the condition $\eta_0 = 45° - \rho/2$, for which maximal $\Delta\theta$ values are produced.



(*a*) (*b*)

Fig. 2. Measurable quantities in electrogyration experiments (**E**‖[001]; **k**‖[110]). (*a*) Intensity changes *versus* analyser position φ. Biasing voltage in kV: ● −3·0, ○ −1·5, △ 0·0, ◇ 1·5, ■ 3·0. (*b*) $\Delta\varphi$ (full circles) and $2\theta\Delta\theta$ (open circles) *versus* biasing voltage *U*.

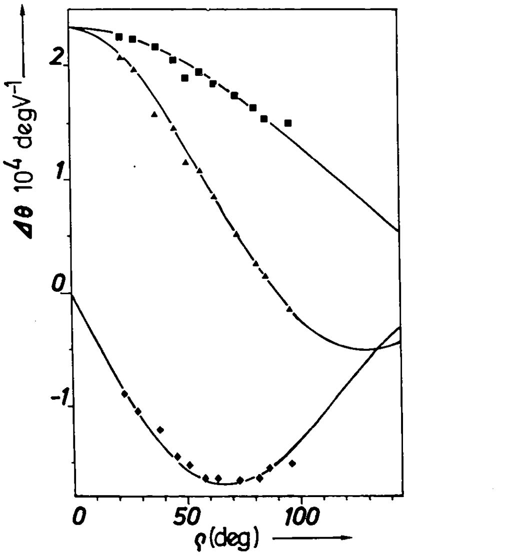


Fig. 3. Induced ellipticity $\Delta\theta(E)$ *versus* rotatory power ρ at different polarizer positions η_0: ◆ 0°, ▲ 45°, ■ 45° $-\rho/2$ (experimental values); ——: calculated according to equation (5) with an averaged value $\Delta\delta$.

The variation of ρ was achieved by using specimens of different length and varying the wavelength in such a small range that a constant electro-optic coefficient could be assumed. Fig. 3 demonstrates that the experimental values fit equation (6) very well. Thus it is possible to determine linear electro-optic and piezo-optic constants on the basis of this simple relation. The results are shown in Fig. 4 and are compared with previous measurements which had been made using static methods.

For studying the influence of the birefringence on induced gyration measurements in detail, $\Delta\eta$ as well as $2\theta\Delta\theta$ is determined as functions of the polarizer position and of the biasing field. This is illustrated in Fig. 5(*a*) and (*b*) by typical results from electrogyration experiments. The validity of the approximations involved in (7) and (8) is examined by the following tests: (1) $\Delta\eta$ and $2\theta\Delta\theta$ measurements must yield the same $\delta\Delta\delta$ values; (2) $\delta\Delta\delta$ depends linearly on the biasing field; and (3) $\Delta\rho$ is independent of the biasing field.

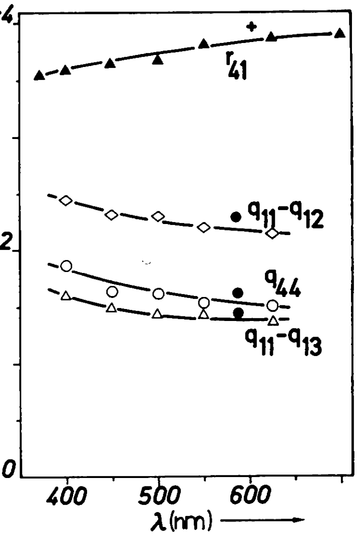


Fig. 4. Linear electro-optic (r_{mn}) and piezo-optic (q_{mn}) constants *versus* wavelength. Units: r_{mn} 10^{-13} m V^{-1}; q_{mn} 10^{-12} m^2 N^{-1}. + Pockels (1894), ● Ramachandran & Chandrasekharan (1951).

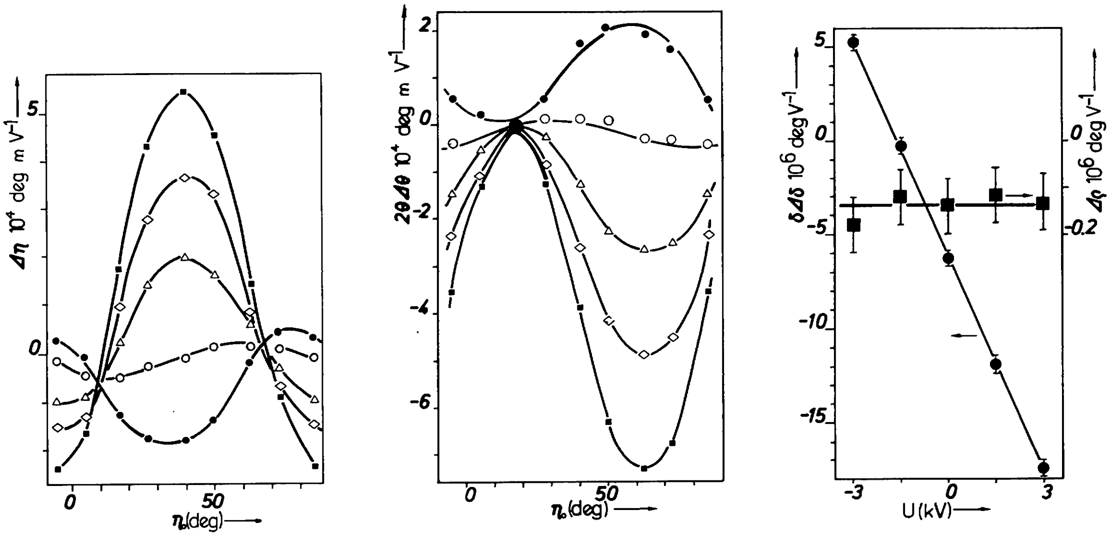
With the values of Fig. 5(*a*) and (*b*) this test is performed in Fig. 5(*c*). The above-mentioned conditions are fulfilled within the limits of experimental accuracy.

We emphasize that the intrinsic electrogyration effect $\Delta\rho$ contributes only slightly to the total change $\Delta\eta$. Therefore, a relatively large error adheres to $\Delta\rho$ (Fig. 5*c*), and it is necessary to repeat the measurement several times.

The results demonstrate that our formulas (7) and (8) describe the experimental observations fairly well. They are therefore a suitable basis for a successful determination of electrogyration and piezogyration coefficients.

(*c*) *Determination of signs*

To ensure the correct signs and designations of the tensor components, the enantiomorphic form of $NaClO_3$ used as well as the orientation of the crystallographic axes must be considered. The enantiomorphic form can be recognized by the sign of the optical activity. In sodium chlorate dextrorotation is correlated with the absolute configuration **A** (Ramachandran & Chandrasekaran, 1957), which is characterized by an anticlockwise arrangement of the ClO_3^- planes (Wooster, 1953). Such a crystal rotates a linear



(*a*) (*b*) (*c*)

Fig. 5. Electrogyration effect (**E**∥[001], **k**∥[110]). (*a*) $\Delta\eta$ and (*b*) $2\theta\Delta\theta$ *versus* azimuth η_0 (notation of biasing voltage as in Fig. 1). (*c*) $\delta\Delta\delta$ and $\Delta\rho$ *versus* biasing voltage. $\delta\Delta\delta$ values computed from (*a*) and (*b*) coincide in (*c*).

Table 1. *Directions of measurement*

$\mathbf{E}_{ac}$: measuring electric field; $\boldsymbol{\sigma}$: mechanical stress; $\mathbf{E}_{dc}$: biasing electric field; $\mathbf{k}$: wave normal; r_{mn}: linear electro-optic, q_{mn}: piezo-optic, s_{mn}: electrogyration, and w_{mn}: piezogyration coefficients.

Number	$\mathbf{E}_{ac}$	$\boldsymbol{\sigma}$	$\mathbf{E}_{dc}$	$\mathbf{k}$	r_{mn}	q_{mn}	s_{mn}	w_{mn}
1	[001]	–	[001]	[110]	r_{41}		s_{41}	
2	[001]	–	[001]	$[1\bar{1}0]$	$-r_{41}$		$-s_{41}$	
3	[111]	–	–	[111]	–		$2\sqrt{3}s_{41}/3$	
4	–	[100]	–	[010]		$q_{11}-q_{12}$		w_{13}
5	–	[100]	–	[001]		$q_{11}-q_{13}$		w_{12}
6	–	[110]	–	[001]		q_{44}		$(w_{12}+w_{13})/2$
7	–	$[1\bar{1}0]$	[001]	[110]		$(2q_{11}-q_{12}-q_{13}+2q_{44})/4$		$(w_{12}+w_{13})/4+(w_{11}-w_{44})/2$
8	–	[001]	[001]	[110]		$(2q_{11}-q_{12}-q_{13})/2$		$(w_{12}+w_{13})/2$
9	–	$[1\bar{1}0]$	$[11\bar{2}]$	[111]		$(2q_{11}-q_{12}-q_{13}+4q_{44})/6$		$(w_{12}+w_{13})/3+(w_{11}-w_{44})/3$

polarization clockwise when looking towards the light source. In this investigation only specimens of the configuration A are used. The coordinate axes are defined with the aid of the piezoelectric effect. According to Collins & Bloembergen (1964) in crystals of configuration A the (111) face of a slab, cut perpendicular to [111], develops a positive charge for a longitudinal stress. Thus the constant d_{14} is positive and the orientation is easily tested by measuring the piezoelectric voltage. With this convention the linear electro-optic constant r_{41} is found to be negative. In a further step we have checked the relative signs of d_{14} and r_{41}. With a Jamin interferometer, absolute retardation measurements can be made. The quantities obtained with this method are deduced by substituting $\Delta n'' = 0$ and $n'' = 1$ into equation (10). With an electric field in [001], a light beam in [110] and the vibration directions nearly parallel and perpendicular to **E**, we determined a negative ratio $(n-1)d_{14}/[0\cdot 5n^3 r_{41} - (n-1)d_{14}]$. This indicates opposite signs for d_{14} and r_{41}. A final check was carried out using the piezo-optic effect. Ramachandran & Chandrasekharan (1951) have reported the piezo-optic constants $q_{11} - q_{12} = -2\cdot 28$ and $q_{11} - q_{13} = -1\cdot 43 \times 10^{-12}$ m^2 N^{-1}. Their notations are referred to a coordinate system which had been determined by intensity inequalities of suitable reflections in Laue patterns. We have measured the same ratio of the piezo-optic constants in samples which had been orientated using a piezoelectric device.

IV. Results

In Table 1 all directions of measurement used are listed with the corresponding tensor components. They were obtained with rectangular shaped crystals of the three different orientations [100][010][001], $[110][1\bar{1}0]$-[001], and $[1\bar{1}0][\bar{2}11][111]$. For each orientation two samples with different dimensions were prepared to allow control measurements to be made. The electrogyration measurements with electric field and light propagation parallel to [111] (No. 3) are of special interest since no linear electro-optic effect occurs. This allows a further check of the results obtained in directions where the linear electro-optic effect disturbs the determination of $\Delta\rho$.

A comparison of results with linear electro-optic, piezo-optic, piezoelectric, and elastic constants shows that the contributions $g\Delta n$ and $g\Delta l/l$ in (9) to the total induced rotation $\Delta\rho$ are negligibly small compared to the errors of measurement. This observation is discussed in § V in terms of a microscopic model, in contrast to (9), which is deduced from a phenomenological theory of induced gyration effects.

The electrogyration constants s_{ijk} and the piezogyration constants w_{ijkl} summarized in Fig. 6 represent averaged values obtained from the different measurements in Table 1. The quoted limits of error are no indication of a poor agreement between the theoretical and experimental values for the tensorial anisotropy of the effects. They also occur in different specimens with the same combination of tensor components. An exhaustive examination of these errors by measurements in several samples indicates that there seems to

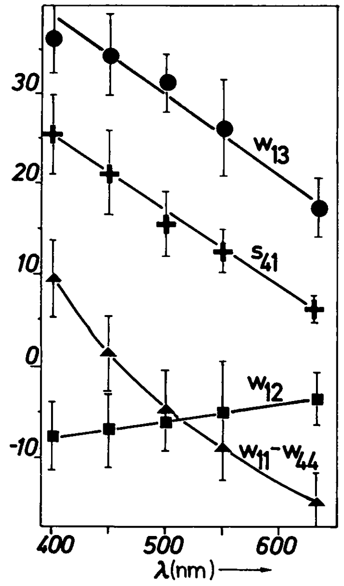


Fig. 6. Electrogyration (s_{mn}) and piezogyration (w_{mn}) constants *versus* wavelength. Units: s_{mn} 10^{-16} m V^{-1}, w_{mn} 10^{-15} m^2 N^{-1}.

be a fundamental limit for the determination of electrogyration and piezogyration effects in polar crystals. This limit may arise from an additional distortion by the initial and induced birefringence which is explained qualitatively as follows.

In considering the influences of an initial double refraction, we assumed a homogeneously strained crystal, which is an oversimplification. In practice we must consider a crystal with inhomogeneous birefringence. When such a sample is cut into small slices, each one may be homogeneously strained with any direction of the principal axes. Hurwitz & Jones (1941) have proved that such a set of birefringent elements can be replaced by one retardation and one rotatory plate. Therefore, the inhomogeneity of a sample produces an additional non-intrinsic optical activity. Superposition of an induced birefringence onto the initial one changes the inhomogeneity, and thus the observable rotatory power must also change. We did not try to identify this misleading effect. Nevertheless, both the electrogyration effect and the piezogyration effect exhibit such a high anisotropy that the tensor character of these properties is unequivocally proved.

The complete set of tensor components cannot be obtained by transverse piezogyration measurements alone. As can be seen from Table 1, w_{11} and w_{44} occur only as the difference $w_{11} - w_{44}$. However, the hydrostatic pressure measurements of Meyers & Vedam (1967) allow the sum $w_{11} + w_{12} + w_{13}$ to be computed and thus a separation of w_{11} and w_{44} in our experiments. All tensor components are listed in Table 2 together with the elastogyration coefficients w^*_{ij}. The latter quantities are not only necessary for estimating the secondary electrogyration effect but are also of interest in elasto-optic experiments with ultrasonic waves. A positive constant indicates that a linearly polarized wave rotates anticlockwise when looking towards the light source. The signs given are valid for a dextrorotatory crystal.

Table 2. *Electrogyration* (s_{mn}), *piezogyration* (w_{mn}), *and elastogyration* (w^*_{mn}) *constants of* NaClO$_3$

Units: s_{mn} 10^{-16} m V^{-1}, w_{mn} 10^{-15} m^2 N^{-1}, w^*_{mn} 10^{-4}.

λ(nm)	400	450	500	550	633
s_{41}	22·5	21·7	15·6	12·7	6·6
w_{11}	−33·4	−31·6	−29·2	−24·1	−16·3
w_{12}	−7·8	−6·9	−5·9	−5·1	−3·0
w_{13}	36·4	34·7	31·7	26·4	17·3
w_{44}	−42·9	−33·2	−24·9	−15·3	−2·0
w_h†	−4·8	−3·8	−3·4	−2·8	−2·1
w^*_{11}	−12·3	−11·5	−10·7	−8·8	−5·9
w^*_{12}	−3·4	−3·0	−2·5	−2·2	−1·3
w^*_{13}	11·8	11·4	10·4	8·8	5·7
w^*_{44}	−4·9	−3·8	−2·9	−1·8	−0·2

† $w_h = w_{11} + w_{12} + w_{13}$ (Meyers & Vedam, 1967).

Using equations (14)–(15) we computed the following differences in the constants measured under free and clamped conditions: $s^{\sigma}_{41} - s^{\varepsilon}_{41} = 0{\cdot}5 w^*_{44} d_{14} = -1{\cdot}5 \times 10^{-16}$ m V^{-1} (12%); $w^E_{44} - w^P_{44} = 2 s^*_{41} d_{14} = 0{\cdot}8 \times 10^{-15}$ m^2 N^{-1} (6%). In NaClO$_3$ the differences for the further piezogyration constants vanish. In both kinds of measurements the influence of the secondary effect is only about 10%. Equation (16) shows that isothermal and adiabatic electrogyration constants differ only in pyroelectric crystals but not in NaClO$_3$. The corresponding differences in piezogyration constants are smaller than 10^{-19} m^2 N^{-1}. Thus, isothermal and adiabatic measurements of induced gyration effects are equal in practice.

V. Discussion

A suitable coupled-oscillator model describing the optical activity has been developed by Chandrasekhar (1960). Two charges, separated by a distance d, oscillate perpendicular to the line joining them. The angle between both vibration directions is θ. Then the rotation ρ of a linearly polarized light wave is given by

$$\rho = N \frac{e^4 f^2 \sin 2\theta}{4\pi m^2 d^2 c^2} \frac{\lambda_0^4 \lambda^2}{(\lambda^2 - \lambda_0^2)^2}.$$

Here N is the number of oscillators per unit volume, e the charge and m the mass of an electron, λ_0 the wavelength at resonance, f the oscillator strength, and c the velocity of light *in vacuo*. Differentiating the above equation yields

$$\frac{\Delta\rho}{\rho} = \frac{\Delta N}{N} + 2\frac{\Delta f}{f} + 2\cot 2\theta\,\Delta\theta - 2\frac{\Delta d}{d} + \frac{4\lambda^2}{\lambda^2 - \lambda_0^2}\frac{\Delta\lambda_0}{\lambda_0}. \quad (17)$$

On the basis of a harmonic-oscillator model the refractive index is given by (Born, 1972)

$$n^2 - 1 = N \frac{e^2 f}{mc^2} \frac{\lambda_0^2 \lambda^2}{\lambda^2 - \lambda_0^2},$$

and its change according to

$$\Delta n = \frac{n^2 - 1}{2n} \left(\frac{\Delta N}{N} + \frac{\Delta f}{f} + \frac{2\lambda^2}{\lambda^2 - \lambda_o^2} \frac{\Delta\lambda_0}{\lambda_0} \right). \quad (18)$$

A comparison of (17) with (18) reveals that the induced rotation $\Delta\rho$ may be partly expressed in terms of Δn:

$$\frac{\Delta\rho}{\rho} = \frac{4n}{n^2 - 1}\Delta n - \frac{\Delta N}{N} - 2\frac{\Delta d}{d} + 2\cot 2\theta\,\Delta\theta. \quad (19)$$

Now Δn, $\Delta N/N$, and $\Delta d/d$ in (19) are computed from the linear electro-optic, piezo-optic, inverse piezoelectric, and elastic effects. The difference between these contributions and the total effect describes the 'geometric term' $2\cot 2\theta\Delta\theta$. As a representative example we chose the [110] direction for light propagation and [001] for electric field and mechanical stress respectively. The results are shown in Table 3. They are evaluated with the aid of the piezoelectric and elastic constants measured by Bechmann (1951) and Haussühl (1964) respectively. In both cases nearly the whole effect is expressed by the geometric term. In centrosymmetric crystals this contribution is the only one which does not vanish when electric fields are applied. Therefore, we conclude that there is no essential difference for electrogyration effects between crystals with and without a centre of symmetry.

Ramachandran (1951) has pointed out that the orientation of the O_3^{2-} planes is mainly responsible for the optical activity of $NaClO_3$. Therefore, the microscopic rotation $\Delta\theta$ of (19) may be identified as a tipping of these planes. The coupled-oscillator model in the form used is obviously too simple for a further interpretation of the measured effects by structural properties. Nevertheless, the above analysis shows that the effects are caused by a twisting of specific structural units under external influences rather than by a change of resonance wavelengths or oscillator strengths. This sensitivity of induced gyration effects on small changes of atomic parameters suggests that they may be successfully applied in the investigation of ferroelectric and ferroelastic phase transitions, where such small displacements occur.

Regarding the dispersion of the induced optical activity, the existence of two oscillators with resonances at 90 and 185 nm has to be taken into account (Chandrasekhar, 1960). Whereas the optical activity is mainly influenced by the resonance wavelength at 90 nm, the strong increase of electrogyration and piezogyration with decreasing wavelengths indicates that both induced effects are mainly caused by the 185 nm oscillators. The experimental data are not exact enough for a detailed analysis of the dispersion behaviour.

In conclusion we note that it is not possible to achieve reliable results for electrogyration and piezogyration constants without a careful examination of the birefringence effects. Although the equations describing these influences are tested with a cubic crystal they are of general interest because the approximations involved, $2\rho \gg \delta$ and $\Delta\delta \gg \Delta\rho$, are also valid in birefringent crystals with a light beam nearly parallel to the optical axis. It is worth while noting that experimental determination of related effects, such as the nonlinear optical activity, which has been recently studied theoretically (Ovander & Petrenko, 1977), may be subjected to disturbances similar to those encountered in the electrogyration and piezogyration measurements in this paper.

Table 3. *Single contributions to the electrogyration and piezogyration effect* ($\sigma \parallel \mathbf{E} \parallel [001]$; $\mathbf{k} \parallel [110]$)

$\Delta\rho/\rho$	$\Delta n 4n/(n^2-1)$	$-\Delta N/N$	$-2\Delta d/d$	$2\cot 2\theta\Delta\theta$
Electrogyration ($\times 10^{-11}$ m V^{-1})				
−4·61	−0·16	0·0	−0·17	−4·28
Piezogyration ($\times 10^{-10}$ m^2 N^{-1})				
−4·98	−0·19	0·13	0·05	−4·97

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References

Bechmann, R. (1951). *Proc. Phys. Soc. (London)*, B**66**, 323–337.

Born, M. (1972). *Optik*. Berlin: Springer.

Chandrasekhar, S. (1960). *Proc. R. Soc. London Ser. A*, **259**, 531–553.

Collins, F. A. & Bloembergen, N. (1964). *J. Chem. Phys.* **40**, 3479–3492.

Haussühl, S. (1964). *Phys. Kondens. Mater.* **3**, 139–145.

Hurwitz, H. Jr & Jones, R. C. (1941). *J. Opt. Soc. Am.* **31**, 493–499.

Jones, R. C. (1948). *J. Opt. Soc. Am.* **38**, 671–685.

Meyers, M. B. & Vedam, K. (1965). *J. Opt. Soc. Am.* **55**, 1180–1181.

Meyers, M. B. & Vedam, K. (1967). *J. Opt. Soc. Am.* **57**, 1146–1148.

Miller, A. (1973). *Phys. Rev. B*, **8**, 5902–5908.

Nye, J. F. (1957). *Physical Properties of Crystals*. Oxford Univ. Press.

Ovander, L. N. & Petrenko, A. D. (1977). *Sov. Phys. Solid State*, **19**, 195–199.

Pancharatnam, S. (1957). *Proc. Indian Acad. Sci. Sect. A*, **46**, 280–302.

Pockels, F. (1894). *Abh. Ges. Wiss. Göttingen*, **39**, 1–204.

Ramachandran, G. N. (1951). *Proc. Indian Acad. Sci. Sect. A*, **33**, 309–315.

Ramachandran, G. N. & Chandrasekharan, V. (1951). *Proc. Indian Acad. Sci. Sect. A*, **33**, 199–215.

Ramachandran, G. N. & Chandrasekaran, K. S. (1957). *Acta Cryst.* **10**, 671–675.

Ramachandran, G. N. & Ramaseshan, S. (1961). In *Encyclopedia of Physics*, edited by S. Flügge. Berlin: Springer.

Rogers, A. J. (1977). *Proc. R. Soc. London Ser. A*, **353**, 177–192.

Schamburov, V. A. & Romanova, N. F. (1976). *Krist. Tech.* **11**, 885–897.

Sliker, T. R. (1964). *J. Opt. Soc. Am.* **54**, 1348–1351.

Weber, H. J. & Haussühl, S. (1974). *Phys. Status Solidi B*, **65**, 633–639.

Weber, H. J. & Haussühl, S. (1976). *Acta Cryst.* A**32**, 892–895.

Weber, H. J. & Haussühl, S. (1977). *Z. Kristallogr.* **146**, 303–307.

Wooster, W. A. (1953). *Rep. Prog. Phys.* **16**, 62–82.