Effects of vibrational optical activity in the reflection spectra of crystals for the frequency regions of nondegenerate vibrations

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A new method for studying crystal gyrotropy by reflection vibrational spectra is proposed. The gyrotropy, connected with the dipole-active nondegenerate vibrations, excites a reflected wave polarized normal to the incident wave. This phenomenon is called in this paper reflection nondegenerate vibrational optical activity. Despite the existence of birefringence, the intensity of this wave provides information about the gyration tensor and about the frequencies of the nondegenerate vibrations. A Fresnel-type boundary problem has been solved for reflection and refraction at the air—birefringent-gyrotropic-crystal boundary. The dielectric permittivity tensor near the optically active nondegenerate vibrations has been obtained, and the selection rules at the manifestation of these vibrations in the above-mentioned phenomenon have been found. The peculiarities of the same phenomenon and of the normal electro-magnetic waves in different classes of biaxial and uniaxial crystals have been studied.

I. INTRODUCTION

The reflection vibrational spectra of gyrotropic crystals are studied in this paper. It is well known (see, for example, Refs. 1—4) that in gyrotropic crystals two effects are observed during the propagation of light along the optical axis: (1) circular dichroism (CD), i.e., the difference in absorption coefficients for left- and right-hand circularly polarized electromagnetic waves, and (2) optical rotation (OR) of the polarization plane, caused by the difference in the refractive indices for circularly polarized waves. Another effect has been treated in Ref. 5, namely, the gyrotropic modulation of the reflection spectra of liquids, thin films, and isotropic crystals.

Naturally, the gyrotropic effects are particularly dominant in the frequency regions near the electronic or vibrational resonances of the system; near the frequency of the nuclear vibrations in the molecules or the crystal, the vibrational circular dichroism (VCD) and vibrational optical rotatory dispersion (VORD) can be observed (see, for example, Refs. 6—9). However, while the contribution of degenerate vibrations in uniaxial crystals may be studied successfully by VCD for electromagnetic waves that propagate along the optical axis,[10] the contribution of nondegenerate vibrations to VCD is always masked by the birefringence effects.[6,7] Birefringence causes considerable differences $\Delta n = n_1 - n_2$ in the refractive indices for the two normal electromagnetic waves that propagate in a given direction **S**. The order of magnitude of the gyrotropic contributions to the quantity Δn is $(a/\lambda)^2$, and being 10^{-6}—10^{-8} in the visible and infrared regions, these corrections are negligible (here λ is the wavelength of the electromagnetic wave, and a is the dimension of the structural unit, the lattice constant, for example). At the same time, the two normal electromagnetic waves are left- and right-hand elliptically polarized and the ellipticity is on the order of $a/\lambda \approx 10^{-3}$ to 10^{-4}.[2,6]

A method for studying VOA for nondegenerate vibrations by the crystal reflection spectra is proposed in this work. It is called reflection nondegenerate VOA. The linearly polarized s or p wave incident on the crystal excites two elliptic waves that propagate in different directions due to birefringence. The boundary conditions require that the reflected wave have both polarizations s and p. It is interesting to note that in our case no additional boundary conditions (ABC's) (see Ref. 2) are needed if the gyrotropic terms proportional to $(a/\lambda)^2$ are neglected in the refractive indices of the two elliptic waves. The electric field intensity E_2 for the second reflected wave with polarization different from that of the incident wave is of the order of $E_2 \sim (a/\lambda)E_i$, E_i being the intensity of the incident wave. However, measurements of the "new" wave E_2 are carried out in the initial medium (air) and they are considerably facilitated by the polarization differences in E_2 and E_i. The experimental results demonstrate that similar studies in the excitonic region of CdS and other crystals are completely real.[11]

The situation investigated in this paper is, in principle, analogous to that considered in Ref. 5. There are, however, some essential differences between Ref. 5 and our paper, which can be defined as follows: (a) Our calculations concern anisotropic birefringent crystals. The plane of incidence and of reflection is perpendicular to the crystal optical axis, and birefringence is essential, but it is not an obstacle to the manifestation of vibrational gyrotropy. (b) We discuss the reflection of electromagnetic waves in the infrared region with frequencies near those of crystal nondegenerate vibrations.

For the sake of simplicity we have restricted ourselves to a discussion of nonabsorbing crystals alone. There are no essential difficulties in expanding the area of our research and including absorbing anisotropic crystals as well. In the latter case, however, we will have to take into account the attenuation of nondegenerate vibrations and its influence on the refractive indices and the gyrotropic terms.

The outline of this paper is as follows: The next section contains a general scheme of the proposed new method for the study of vibrational crystal gyrotropy. Section III treats the boundary problem at the air—gyrotropic-crystal boundary. Section IV produces the calculations of the dielectric permittivity near the frequency of the nondegenerate vibrations. Section V contains the selection rules for reflection nondegenerate VOA, while Sec. VI discusses the peculiarities of reflection nondegenerate VOA in different crystal classes.

II. GENERAL SCHEME OF THE REFLECTION NONDEGENERATE VOA METHOD

A study of gyrotropy usually consists of measuring or calculating the difference between the quantities characterizing the response of the crystal to left- or right-hand circularly polarized electromagnetic waves. Our method however, concentrates on the study of the reflection of a linearly polarized wave (Fig. 1). In order to obtain a new polarization in the reflected wave as a result of gyrotropy alone, the plane of incidence is chosen normal to the crystallographic axis of the crystal (in uniaxial crystals, it is normal to the optical axis). The crystallographic axis itself is parallel to the reflecting crystal boundary. The polarizer filters an electromagnetic wave with s or p polarization. The reflected wave contains both polarizations: (1) The main part of the polarized beam has polarization coinciding with the incident (s or p); (2) a beam with a relatively weak intensity $I_n \approx (a/\lambda)^2 I_0$ (where I_0 is the intensity of the incident wave), has a polarization perpendicular to the primary (p or s).

As will be shown in the following sections, the appearance of a reflected wave with a new polarization is a pure gyrotropic effect, which can be observed despite birefringence. The data about the intensity of this wave carry information about the optical activity of the crystal, and in particular, about the frequency region of nondegenerate vibrations.

Naturally, the study of the reflected beam with new polarization obtained after the filtering of the reflected wave through the crossed analyzer involves considerable difficulties, caused by its weak intensity. This necessitates the use of high-quality polarizers and analyzers which will filter electromagnetic waves with a precisely fixed polarization. Similar investigations[11,12] in the excitonic region were carried out with a photon-counter technique. In the vibrational region, additional difficulties may arise as a result of the absence of sensitive infrared detectors.

Overcoming these difficulties, however, can be very promising for it may create conditions for the study of the contribution to gyrotropy of nondegenerate vibrations with vibrational electric dipole moment directed along the optical axis.

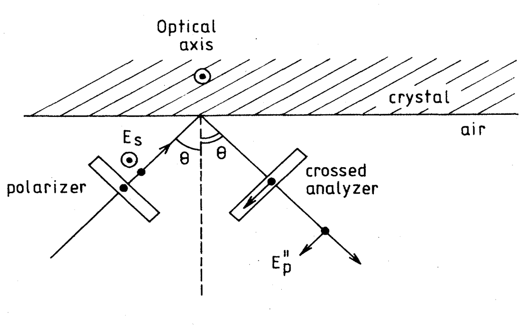

FIG. 1. Schematic of the reflection nondegenerate VOA method. The linearly polarized electromagnetic wave E_s (or E_p) is reflected by a gyrotropic crystal. The plane of incidence is perpendicular to the crystallographic (optical) axis. The result of gyrotropy is a reflected wave with new polarization E_p'' (or E_s'') transmitted by the crossed analyzer.

III. REFLECTION NONDEGENERATE VOA BOUNDARY PROBLEM

We shall in this section consider the reflection at the plane boundary formed by air (refractive index $n=1$) and a dielectric gyrotropic uniaxial or biaxial crystal. Excluded are crystals from the point groups C_1, C_2, and C_s, in which some of the principal axes of the dielectric permittivity tensor ϵ_{ij} are not correlated with the crystallographic axes. We consider the following situation: The incident electromagnetic wave is linearly polarized and the plane of incidence is normal to a crystallographic axis. The matrix element $\mathbf{p}$ of the electric dipole moment for the studied nondegenerate vibration is directed along the same axis X (Fig. 2). The electromagnetic wave frequency ω is near the frequency ω_s of the dipole-active vibration. The normal electromagnetic waves a and b propagate in the crystal due to birefringence. These waves may have also transverse and longitudinal electric field components.[2,4,11] The normal electromagnetic waves satisfy the Maxwell equations in a dielectric medium without external currents and charges:

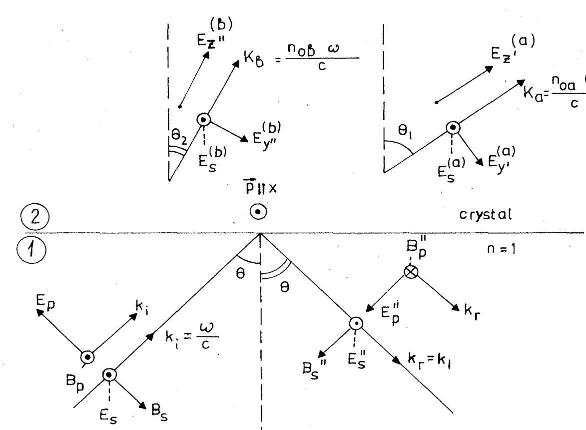

FIG. 2. Reflected and refracted electromagnetic waves at the boundary air-birefringent gyrotropic crystal. The plane of incidence is perpendicular to the crystallographic axis x and to the nondegenerate vibration's electric dipole moment $\mathbf{p}$. $\mathbf{k}_i, \mathbf{k}_r$ are wave vectors of the reflected waves; $\mathbf{k}_a, \mathbf{k}_b$ are wave vectors of the refracted waves; n_{0a}, n_{0b} are corresponding refractive indices (the refraction law $\sin\theta/\sin\theta_{1,2} = n_{0a,b}$ is valid). The components $E_s, E_s'', E_s^{(a)}, E_s^{(b)}$ and the vector $\mathbf{p}$ are parallel. Refracted waves are elliptic polarized and possess 2 or 3 electric field components.

$$\mathrm{rot}\mathbf{E}=-\frac{\partial \mathbf{B}}{\partial t},\quad \mathrm{div}\mathbf{D}=0\ ,$$
$$\mathrm{rot}\mathbf{B}=\mu_0\frac{\partial \mathbf{D}}{\partial t},\quad \mathrm{div}\mathbf{B}=0\ . \qquad (1)$$

The relation $\mathbf{D}=\epsilon\mathbf{E}$ between the electric displacement $\mathbf{D}$ and the electric field intensity $\mathbf{E}$ is as usually given by the dielectric permittivity tensor $\epsilon_{ij}(\omega,\mathbf{k})$. We seek the solution of (1) as plane waves:

$$\mathbf{E}=\mathbf{E}_0 e^{i(\omega t-\mathbf{k}\cdot\mathbf{r})},\quad \mathbf{D}=\mathbf{D}_0 e^{i(\omega t-\mathbf{k}\cdot\mathbf{r})}\ ,$$
$$\mathbf{B}=\mathbf{B}_0 e^{i(\omega t-\mathbf{k}\cdot\mathbf{r})} \qquad (2)$$

and obtain the following system:

$$\mathbf{B}_0=\frac{1}{\omega}\mathbf{k}\times\mathbf{E}_0,\quad \mathbf{k}\cdot\mathbf{D}_0=0,\quad \mathbf{k}\cdot\mathbf{B}_0=0\ , \qquad (3)$$

$$\mathbf{D}_0=-\frac{1}{\mu_0\omega^2}\mathbf{k}\times(\mathbf{k}\times\mathbf{E}_0)$$
$$=\frac{1}{\mu_0\omega^2}(k^2\mathbf{E}_0-\mathbf{k}\cdot\mathbf{E}_0\mathbf{k})\ . \qquad (4)$$

The relation between the electric displacement $\mathbf{D}_0$ and the electric field component $E_0^{\perp}$ perpendicular to $\mathbf{k}$ may be expressed by the two-dimensional tensor of the perpendicular dielectric permittivity $\epsilon^{\perp}(\omega,\mathbf{k})$,[2,4] and more specifically by its principal values n_{0l}^2, $l=a,b$:

$$\mathbf{D}_0=\epsilon^{\perp}(\omega,\mathbf{k})E_0^{\perp}\rightarrow\mathbf{D}_{0l}=\epsilon_0 n_{0l}^2(\omega,\mathbf{k})E_{0l}^{\perp}\ ,$$
$$\epsilon_0=8.85\times10^{-12}\ \mathrm{F/m}\ . \qquad (5)$$

We shall employ Eqs. (4) and (5) and the fact that according to the second equation in (3) the vector $\mathbf{D}$ has no components parallel to $\mathbf{k}$ (we consider waves for which $D_0\neq0$). The following relation is thus obtained:

$$\frac{n_{0l}^2\omega^2}{c^2}=k_l^2\ , \qquad (6)$$

as well as simultaneous equations for the electric field components E_0^l of the normal electromagnetic wave corresponding to n_{0l} (Ref. 2, Sec. 2):

$$\sum_j\left[\frac{\epsilon_{ij}(\omega,\mathbf{k})}{\epsilon_0}-n_{0l}^2(\omega,\mathbf{k})\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right]\right]E_{0j}^l=0\ . \qquad (7)$$

For frequencies near the frequencies of the nondegenerate vibrations, in the expansion in k of the refractive indices $n_{0l}(\omega,\mathbf{k})$, there are no linear terms, and the quadratic and higher-order terms may be neglected.[4,6,7] In such a case, i.e., when $n_{0l}(\omega,\mathbf{k})\equiv n_{0l}(\omega)$, and the plane incidence and the wave vectors $\mathbf{k}_l$ are normal to the matrix element of the electric dipole moment $\mathbf{p}$ (Fig. 2), one of the principal axes of the tensor $\epsilon^{\perp}(\omega,\mathbf{k})$ coincides with the $\mathbf{p}$ direction,[5] and the corresponding principal value n_{0a}^2 has a resonance for the frequency of the nondegenerate vibration ω_s. In uniaxial crystals, the second principal value n_{0b}^2 is independent of the $\mathbf{k}_l$ direction but in lower symmetry crystals n_{0b}^2 is a two-dimensional tensor (without resonance for ω_s).

There are also two reflected waves: s polarized and p polarized. We shall show that four waves, appearing in reflection and refraction, suffice to satisfy the following boundary conditions at the air-crystal boundary:

$$E_{1t}=E_{2t},\quad D_{1n}=D_{2n}\ ,$$
$$B_{1t}=B_{2t},\quad B_{1n}=B_{2n}\ , \qquad (8)$$

where the indices t and n denote the vector components tangential and normal to the boundary (we assume the crystal is not magnetic, i.e., $\mu_r=\mu/\mu_0=1$). By taking into account the first equation (3) as well as (5) and (6), the boundary conditions (8) may be expressed by the following system of six equations (see Fig. 2):

$$E_s^{(a)}+E_s^{(b)}=E_s+E_s''\ , \qquad (9a)$$

$$E_{y'}^{(a)}\cos\theta_1+E_{y''}^{(b)}\cos\theta_2+E_{z'}^{(a)}\sin\theta_1+E_{z''}^{(b)}\sin\theta_2$$
$$=-(E_p+E_p'')\cos\theta\ , \qquad (9b)$$

$$n_{0a}^2E_{y'}^{(a)}\sin\theta_1+n_{0b}^2E_{y''}^{(b)}\sin\theta_2=(E_p''-E_p)\sin\theta\ , \qquad (9c)$$

$$n_{0a}E_{y'}^{(a)}+n_{0b}E_{y''}^{(b)}=E_p''-E_p\ , \qquad (9d)$$

$$n_{0a}E_s^{(a)}\cos\theta_1+n_{0b}E_s^{(b)}\cos\theta_2=(E_s-E_s'')\cos\theta\ , \qquad (9e)$$

$$n_{0a}E_s^{(a)}\sin\theta_1+n_{0b}E_s^{(b)}\sin\theta_2=(E_s+E_s'')\sin\theta\ . \qquad (9f)$$

In this system the intensities E_s and E_p of the incident wave are given and the independent variables are four since between the quantities $E_s^{(a)},E_{y'}^{(a)},E_{z'}^{(a)}$ and $E_s^{(b)},E_{y''}^{(b)},E_{z''}^{(b)}$ there exist relations such as (7). The boundary problem is a generalization of the well-known Fresnel problem in the case where the second medium is an anisotropic birefringent crystal. It is readily shown that the conditions for consistency of six equations with four unknowns are reduced to the known refraction laws for the ordinary and extraordinary waves:

$$\frac{\sin\theta}{\sin\theta_1}=n_{0a},\quad \frac{\sin\theta}{\sin\theta_2}=n_{0b}\ . \qquad (10)$$

Hence equations (9a) and (9f) on one hand, and (9c) and (9d) on the other hand, turn out to be identical and the problem is reduced to solving a system of four linear equations in four unknowns. Our next program includes the following stages: (1) finding the form of the dielectric permittivity $\epsilon(\omega,\mathbf{k})$ that contains information about the gyrotropy of the nondegenerate vibration; (2) finding the intensity of the reflected wave with polarization differing from that of the incident wave, i.e., finding the functions $E_s''(E_p)$ and $E_p''(E_s)$.

IV. DIELECTRIC PERMITTIVITY FOR THE FREQUENCY REGION OF NONDEGENERATE VIBRATIONS

The perpendicular dielectric permittivity $\epsilon^{\perp}(\omega,\mathbf{k})$ in the frequency region of the nondegenerate vibrations has been found in Ref. 6. This work uses the model of intramolecular vibrations in a molecular crystal but the results may be generalized for any optical vibration in the crystal; see also Refs. 2 and 4. However, as far as the boundary conditions (9) comprise transverse and longitudinal electric field components, we have to know the complete dielectric permittivity $\epsilon(\omega,\mathbf{k})$. As shown in Ref. 2, Sec. IV the definition of tensor $\epsilon(\omega,\mathbf{k})$ via tensor $\epsilon^{\perp}(\omega,\mathbf{k})$ in the common case is not unique. In our case, however, this problem may be solved because the following conditions hold (see Ref. 2, Chap. IV, and Ref. 13); we are interested in the dielectric permittivity $\epsilon(\omega,\mathbf{k})$ in the frequency region of an isolated nondegenerate resonance ω_s by neglecting the terms of quadratic and higher powers in k.

Using the procedure described elsewhere,[2,14] we shall find the tensor $\epsilon(\omega,\mathbf{k})$ in the coordinate system $(x||\mathbf{p},y',z'||\mathbf{k})$. The following relations have been obtained[6] for the tensor $\epsilon^{\perp}(\omega,\mathbf{k})$:

$$\epsilon^{\perp}_{xx}(\omega,\mathbf{k})=\epsilon_0\left[a_1-\frac{p^2}{\epsilon_0\hbar v}\frac{2\omega_s}{\omega^2-\omega_s^2}\right],\quad \epsilon^{\perp}_{y'y'}=\epsilon_0 a_2 \tag{11a}$$

$$\epsilon^{\perp}_{xy}(\omega,\mathbf{k})=\epsilon^{\perp *}_{y'x}(\omega,\mathbf{k})=-i\frac{pk\tilde{D}_{y'z'}}{\hbar v}\frac{2\omega_s}{\omega^2-\omega_s^2}, \tag{11b}$$

where $\mathbf{p}$ is the electric dipole moment matrix elements for the given vibration induced in the crystal unit cell, and v is the unit-cell volume. The quantities $\tilde{D}_{y'z'}$ and $\tilde{D}_{z'z'}$ (*vide infra*) represent the matrix elements for the same nondegenerate vibration of the sum of electric quadrupole moment and the magnetic dipole moment. The quantity a_1 expresses the contribution to the refractive index n_{0a}^2 by the remaining—different from ω_s—electronic and vibrational excitations in the crystal with matrix elements of the electric dipole moment along the X axis. Similar contributions a_y and a_z provide the dipole-active excitations with matrix elements along the crystallographic axes Y and Z, respectively. In the chosen coordinate system (X,Y',Z') the quantity (a_y,a_z) transforms as a symmetric tensor with components $a_{y'y'}=a_2$, $a_{z'z'}=a_3$, and $a_{y'z'}=a_{z'y'}$ (see next section). In the proximity of ω_s the quantities a_1,a_2,a_3 may be considered as frequency independent. To calculate the dielectric permittivity $\epsilon(\omega,\mathbf{k})$ we shall introduce the quantities

$$b_{ij}=\frac{\epsilon^{\perp}_{ij}}{\epsilon_0}-\delta_{ij},\quad i,j=1,2\ (x\equiv 1,\ y'\equiv 2,\ z'\equiv 3) \tag{12a}$$

$$b_{13}=b_{31}^{*}=-i\frac{pk\tilde{D}_{z'z'}}{\epsilon_0\hbar v}\frac{2\omega_s}{\omega^2-\omega_s^2}, \tag{12b}$$

$$b_{23}=b_{32}=a_{y'z'},\quad b_{33}=a_3 \tag{12c}$$

where δ_{ij} is the Kronecker symbol. The quantity a_3 further turns out to be nonessential.

According to Refs. 2 and 14, the dielectric permittivity tensor is expressed by the quantities introduced above as follows:

$$\epsilon_{ij}(\omega,\mathbf{k})=\epsilon_0\left[\delta_{ij}+\sum_l d_{il}^{-1}b_{lj}\right],\quad d_{ij}=\delta_{ij}-b_{i3}\delta_{j3}. \tag{13}$$

The following form is thus obtained for the tensor:

$$\frac{\epsilon_{ij}(\omega,\mathbf{k})}{\epsilon_0}=\left\|\begin{matrix}\dfrac{\epsilon^{\perp}_{xx}}{\epsilon_0} & \dfrac{\epsilon^{\perp}_{xy'}}{\epsilon_0}+\dfrac{b_{13}a_{y'z'}}{1-a_3} & \dfrac{b_{13}}{1-a_3}\\ \dfrac{\epsilon^{\perp}_{y'x}}{\epsilon_0}+\dfrac{b_{13}^{*}a_{y'z'}}{1-a_3} & \dfrac{\epsilon^{\perp}_{y'y'}}{\epsilon_0}+\dfrac{a_{y'z'}^2}{1-a_3} & \dfrac{a_{y'z'}}{1-a_3}\\ \dfrac{b_{13}^{*}}{1-a_3} & \dfrac{a_{y'z'}}{1-a_3} & \dfrac{1}{1-a_3}\end{matrix}\right\|. \tag{14}$$

It should be emphasized that the resonance ω_s of the tensor $\epsilon(\omega,\mathbf{k})$ as well as of the tensor $\epsilon^{\perp}(\omega,\mathbf{k})$ coincides with the Coulomb exciton frequency (Ref. 2, Sec. 1) which appears in the absorption and Raman spectra.

V. SELECTION RULES FOR REFLECTION NONDEGENERATE VOA

The terms in (14) which express gyrotropy are linear in k, i.e., these are the terms $\epsilon^{\perp}_{xy'}$ and b_{13}. The selection rules studied in the present section refer to dipole-active nondegenerate vibrations $(\mathbf{p}||x)$ for which the quantities (11b) and (12b) are nonvanishing. In the analysis we shall use the results published elsewhere.[15]

In fact, whether the nondegenerate dipole active vibrations appear in reflection VOA depends on the quantities $\tilde{D}_{yz}$ and $\tilde{D}_{zz}$ being nonvanishing. These quantities are measured in a coordinate system (X,Y,Z) related to the crystallographic axes, and the wave vector k of the normal electromagnetic wave is considered to make an angle α with the axis Y (Fig. 3). By Q_{yz},Q_{yy},Q_{zz} we shall denote the corresponding electric quadrupole moment components (the symmetrical parts of the quantities $\tilde{D}_{yz}$ and $\tilde{D}_{zz}$) and by M_x the matrix element of the magnetic dipole moment of the vibration (i.e., the antisymmetric part of the quantity $\tilde{D}_{yz}$). By taking into account the known transformation rules for the tensor components from a coordinate system (X,Y,Z) (correlated with the crystallographic axes), to the system (x,y',z') (correlated with the wave vector k), the following relations are readily obtained:

$$\tilde{D}_{y'z'}=M_x-Q_{yz}\cos(2\alpha)+\tfrac{1}{2}(Q_{yy}-Q_{zz})\sin(2\alpha), \tag{15}$$

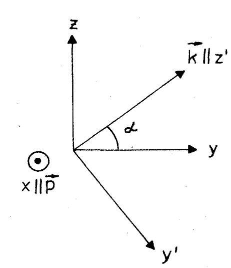

FIG. 3. Two systems of coordinate axes perpendicular to the vibration's electric dipole moment $\mathbf{p}$. The axes (y,z) are the crystallographic axes.

$$\widetilde{D}_{z'z'}=Q_{yz}\sin(2\alpha)$$
$$+\tfrac{1}{2}[Q_{yy}+Q_{zz}+(Q_{yy}-Q_{zz})\cos(2\alpha)] \ . \qquad (16)$$

The corresponding selection rules based on formulas (15) and (16) are listed in Table I for the nondegenerate optically active vibrations from the different crystal classes. It should be noted that the quantity $p_x\widetilde{D}_{y'z'}$ is related to the transverse components of the electric field intensity and the quantity $p_x\widetilde{D}_{z'z'}$ is related via the component ϵ_{31} to the longitudinal electric field in the normal waves.

When analyzing the crystal gyrotropy, the gyration tensor g_{ml} is often used (see Refs. 2–4, 6, and 15). In the coordinate system employed here at $\mathbf{k}||z'$ the following relations hold:[2,5]

$$\epsilon^{\perp}_{xy'}\sim ikg_{z'z'}, \quad b_{13}\sim -ikg_{y'z'} \ . \qquad (17a)$$

The quantity $\epsilon^{\perp}_{xy'}$ proportional to $g_{z'z'}$ is related only to the symmetric part of the gyration tensor. This part defines the optical rotation.[16,17,4,6] The quantity b_{13}, proportional to the off-diagonal element $g_{y'z'}$ depends on both the symmetric and the antisymmetric parts of the gyration tensor.

The selection rules for the gyration tensor's symmetric part have been studied in Ref. 15. These rules may be used via the tensor component transformations to obtain all the expressions in Table I for the quantity $\epsilon^{\perp}_{xy}$ and the α-dependent parts of b_{13}.

The antisymmetric part of the gyration tensor is nonvanishing only in pyroelectric groups,[2,17] being in the groups C_{3v},C_{4v},C_{6v} the only nonvanishing part (for this reason the gyrotropy in these groups usually is called weak). The antisymmetric part does not affect the optical rotation but, together with its symmetric part, it defines equally the elliptic polarization of the normal electromagnetic waves. Namely, it is the antisymmetric part of g_{ml} that defines the addend in (16):

$$\Delta b_{13}\sim \tfrac{1}{2}p_x(Q_{yy}+Q_{zz}) \ . \qquad (17b)$$

As may be traced in the subsequent Sec. VI, the phenomenon reflection nondegenerate VOA provides information both about the symmetric and the antisymmetric parts of the gyration tensor.

We shall calculate also the quantities a_2, a_3, and $a_{y'z'}$ that are featured in (14). Recall that the quantities (a_y,a_z) represent the contributions to the dielectric permittivity of dipole active vibrations with matrix-element components for the electric dipole moment along the crystallographic axes (Y,Z). The following relations are readily obtained:

$$a_{y'y'}=a_2=a_y\sin^2\alpha+a_z\cos^2\alpha \ , \qquad (18a)$$

$$a_{z'z'}=a_3=a_y\cos^2\alpha+a_z\sin^2\alpha \ , \qquad (18b)$$

$$a_{y'z'}=a_{z'y'}=\tfrac{1}{2}(a_y-a_z)\sin 2\alpha \ . \qquad (18c)$$

In uniaxial crystals, the dipole moment of the nondegenerate vibration is directed parallel to the threefold, fourfold, sixfold symmetry axis, i.e., in our case along the X axis. The refractive indices in the plane normal to the X axis are isotropic $a_y=a_z=a$. This simplifies substan-

TABLE I. Selection rules for nondegenerate reflection VOA, connected to the nondegenerate optically active vibrations in gyrotropic crystal point groups (crystal classes C_1,C_2,C_3 are not included). The matrix element $p_x\equiv p_{1,2,3}$ and the plane of incidence are considered perpendicular (Fig. 2).

		Nonzero components[a]				
Point group	Nondegenerate dipole-active vibration	Electric dipole moment	Electric quadrupole moment	Magnetic dipole moment	$\epsilon_{xy'}\approx p_x\widetilde{D}_{y'z'}=p_x[M_x-Q_{yz}\cos 2\alpha+\frac{1}{2}(Q_{yy}-Q_{zz})\sin 2\alpha]$	$b_{13}\sim p_x\widetilde{D}_{z'z'}=p_x[Q_{yz}\sin 2\alpha+\frac{1}{2}(Q_{yy}+Q_{zz})+\frac{1}{2}(Q_{yy}-Q_{zz})x\cos 2\alpha]$
$D_2(222)$	B_3	p_1	Q_{23}	M_1	$p_1(M_1-Q_{23}\cos 2\alpha)$	$p_1Q_{23}\sin 2\alpha$
	B_2	p_2	Q_{13}	M_2	$-p_2(M_2+Q_{13}\cos 2\alpha)$	$p_2Q_{13}\sin 2\alpha$
	B_1	p_3	Q_{12}	M_3	$p_3(M_3-Q_{12}\cos 2\alpha)$	$p_3Q_{12}\sin 2\alpha$
$C_{2v}(mm2)$	A_1	p_3	Q_{11},Q_{22},Q_{33}		$\frac{1}{2}p_3(Q_{11}-Q_{22})\sin 2\alpha$	$p_3(Q_{11}\cos^2\alpha+Q_{22}\sin^2\alpha)$
	B_1	p_1	Q_{13}	M_2		
	B_2	p_2	Q_{23}	M_1		
$C_{(3)}(3),C_{(4)}(4),C_6(6)$	A	p_3	$Q_{11}+Q_{22},Q_{33}$	M_3	p_3M_3	$\frac{1}{2}p_3(Q_{11}+Q_{22})$
$C_{3v}(3m),C_{4v}(4mm),C_{6v}(6mm)$	A_1	p_3	$Q_{11}+Q_{22},Q_{33}$			$\frac{1}{2}p_3(Q_{11}+Q_{22})$
$D_3(32),D_4(422),D_6(622)$	A_2	p_3		M_3	p_3M_3	
$S_4(\bar{4})$	B	p_3	$Q_{11}-Q_{22},Q_{12}$		$p_3[\frac{1}{2}(Q_{11}-Q_{22})\sin 2\alpha-Q_{12}\cos 2\alpha]$	$p_3[Q_{12}\sin 2\alpha+(Q_{11}-Q_{12})\cos 2\alpha]$
$D_{2d}(\bar{4}2m)$	B_2	p_3	Q_{12}		$-p_3Q_{12}\cos 2\alpha$	$p_3Q_{12}\sin 2\alpha$

[a]Coordinate system (1,2,3) is related to the crystallographic axes, while for the system (x,y',z') we have $\mathbf{p}||x$, $\mathbf{k}||z'$ (Fig. 3). The indices (1,2,3) in the table and in Sec. III are different. The angle α is included between the wave-vector direction for refracted wave and crystallographic axis $y\equiv 2$.

tially formula (18) and the dielectric permittivity tensor (14):

$$a_{y'y'}=a_{z'z'}=a,\quad a_{y'z'}=0\ .$$

VI. PECULIARITIES OF THE REFLECTION NONDEGENERATE VOA IN DIFFERENT CRYSTAL CLASSES

A. Crystal classes C_{3v}, C_{4v}, C_{6v}

As seen from Table I, the gyrotropy in these classes produces only a longitudinal electric field. This facilitates substantially the theoretical treatment and the experimental studies. A phenomenon similar to that considered here (see Ref. 11 and references therein) has been investigated namely in the C_{6v} crystal group. It is intriguing that in these classes no gyrotropy occurs if the light propagates along the optical axis; for this reason in Ref. 11 as in our case the plane of incidence is perpendicular to the optical axis.

We shall first consider the properties of normal electromagnetic waves. We shall define the a-wave components by setting $n_{0l}=n_{0a}$ in system (7) and $\epsilon^{\perp}_{xy}\equiv 0$ in tensor (14) (see Table I). The following relations between the electric field components for the normal electromagnetic wave are readily obtained:

$$E^{(a)}_{y'}=0,\quad E^{(a)}_{z'}=b^{(a)}_{13}E^{(a)}_{s}\ . \tag{19}$$

The second refracted wave b that propagates in a direction defined by the second equation in (10) at $n^2_{0b}=a_2$ turns out to be a linearly polarized (ordinary) wave:[11]

$$E^{(b)}_{y''}\neq 0,\quad E^{(b)}_{s}=E^{(b)}_{z''}=0\ . \tag{20}$$

In the crystal classes considered, the system of equations (9) has the following form (the quantities $E_s'', E_p'', E^{(a)}_s, E^{(b)}_{y''}$ will be considered as unknowns):

$$-E_s''+E^{(a)}_s=E_s\ , \tag{21a}$$

$$E_s''\cos\theta+E^{(a)}_s n_{0a}\cos\theta_1=E_s\cos\theta\ , \tag{21b}$$

$$E_p''\cos\theta+E^{(b)}_{y''}\cos\theta_2+E^{(a)}_s b^{(a)}_{13}\sin\theta_1=-E_p\cos\theta\ , \tag{21c}$$

$$E^{(b)}_{y''}n_{0b}-E_p''=-E_p\ . \tag{21d}$$

Let the incident wave be s polarized ($E_p=0$). The electric fields for the four waves are easily obtained:

$$E_s''=E_s\frac{n_{0a}\cos\theta_1-\cos\theta}{n_{0a}\cos\theta_1+\cos\theta},\quad E^{(a)}_s=E_s\frac{2\cos\theta}{n_{0a}\cos\theta_1+\cos\theta}\ , \tag{22}$$

$$E_p''(E_s)=-E_s\frac{b^{(a)}_{13}n_{0b}\sin 2\theta/n_{0a}}{(n_{0a}\cos\theta_1+\cos\theta)(n_{0b}\cos\theta+\cos\theta_2)}\ , \tag{23}$$

$$E^{(b)}_{y''}=E_p''(E_s)/n_{0b}\ . \tag{24}$$

Formulas (22) coincide with the well-known Fresnel formulas for reflected and refracted s waves for a refractive index n_{0a}. The gyrotropy excites p-polarized reflected and refracted waves. The amplitudes of these waves, proportional to the quantity b_{13} are in the order of a/λ from the amplitude of the incident wave E_s and increase for frequencies near the resonance $\omega\approx\omega_s$ of b_{13}. The dependence of $E_p''(E_s)$ on the angle of incidence θ contains several parameters and the detailed analytical examination is difficult; the factor $\sin(2\theta)$ is however particularly essential: It increases from zero for a normal incidence to unity for $\theta=\pi/4$ and vanishes again at $\theta=\pi/2$.

An important peculiarity of the point groups considered is observed if the incident wave is p polarized ($E_s=0$). In such a case gyrotropy is of no importance; i.e., the Fresnel formulas hold for reflection and refraction of p waves with a refractive index n_{0b} and no reflected and refracted s waves appear:

$$E_s''(E_p)=E^{(a)}_s(E_p)=0\ , \tag{25}$$

$$E_p''=-E_p\frac{n_{0b}\cos\theta-\cos\theta_2}{n_{0b}\cos\theta+\cos\theta_2}\ , \tag{26}$$

$$E^{(b)}_{y''}=-E_p\frac{2\cos\theta}{n_{0b}\cos\theta+\cos\theta_2}\ . \tag{27}$$

Thus, in crystals from the groups C_{3v}, C_{4v}, C_{6v}, nondegenerate VOA will be observed in a plane of incidence normal to the optical axis only for s waves, the quantities b_{13}, n_{0a}, and n_{0b} in the most important formula (23) will be independent of the angle of incidence θ (however, b_{13} and n_{0a} depend on the frequency ω of the incident wave).

B. Crystal classes with $\epsilon^{\perp}_{xy}\neq 0$

In the remaining classes comprising Table I, the normal electromagnetic waves have two transverse components of the electric field (besides the possible longitudinal component), and the end of the electric field vector E depicts an ellipsoid with time. The normal electromagnetic a wave with a refractive index $n^2_{0a}=\epsilon^{\perp}_{xx}/\epsilon_0$ has a very long X axis of the ellipsoid while the other components are expressed in the following way in terms of $E^{(a)}_s$:

$$E^{(a)}_{y'}=\frac{\epsilon^{\perp}_{xy'}}{\epsilon^{\perp}_{y'y'}-\epsilon^{\perp}_{xx}}E^{(a)}_s=\delta_a E^{(a)}_s\ , \tag{28a}$$

$$E^{(a)}_{z'}=(b^{(a)}_{13}-a^{(a)}_{y'z'}\delta_a)E^{(a)}_s\ . \tag{28b}$$

In the normal electromagnetic wave b with a refractive index $n^2_{0b}=a^{(b)}_2$ the ellipsoid axis Y is very long:

$$E^{(b)}_{y''}=\frac{\epsilon^{\perp}_{y''y''}-\epsilon^{\perp}_{xx}}{\epsilon^{\perp}_{xy''}}E^{(b)}_s=\frac{1}{\delta_b}E^{(b)}_s\ , \tag{29a}$$

$$E^{(b)}_{z''}=-a^{(b)}_{y''z''}E^{(b)}_{y''}=-\frac{a^{(b)}_{y''z''}}{\delta_b}E^{(b)}_s\ . \tag{29b}$$

The quantities δ_a and δ_b are in the order of magnitude $a/\lambda\approx 10^{-3}-10^{-4}$ and as shown elsewhere[5] they may serve as a measure for gyrotropic effects relative to the birefringence. (Occasional coincidence of the refractive indices $n_{0a}=n_{0b}$ for which no birefringence is observed is not studied in this work. The treatment in Ref. 5 is valid for that situation, too.) We shall use relations (28) and

(29) in system (9) and we shall neglect throughout the terms of the order of k^2 [as adopted also when deriving (28) and (29)]. Further, for uniaxial crystals we obtain once again the equalities (22), (26), and (27) that express the Fresnel formulas. The effects of reflection nondegenerate VOA, i.e., the appearance of a reflected wave with polarization different from that of the incident wave are described by the following two formulas:

$$E_p''(E_s)=E_s\delta_a\frac{2\cos\theta[n_{0a}(\cos\theta_2-a^{(b)}_{y''z''}\sin\theta_2)-n_{0b}(\cos\theta_1-a^{(a)}_{y'z'}\sin\theta_1+\kappa\sin\theta_1)]}{(n_{0a}\cos\theta_1+\cos\theta)(n_{0b}\cos\theta+\cos\theta_2-a^{(b)}_{y''z''}\sin\theta_2)}\,, \tag{30}$$

$$E_s''(E_p)=E_p\delta_b\frac{2\cos\theta(n_{0b}\cos\theta_2-n_{0a}\cos\theta_1)}{(n_{0a}\cos\theta_1+\cos\theta)(n_{0b}\cos\theta+\cos\theta_2-a^{(b)}_{y''z''}\sin\theta_2)}\,, \tag{31}$$

where

$$\kappa=b_{13}/\delta_a\,. \tag{32}$$

Unlike the situation in Sec. VI A, active in reflection VOA are the incident waves in both s and p polarizations. The effect considered here exists even under normal incidence $\theta=\theta_1=\theta_2=0$. In this case the two formulas assume the form

$$E_p''(E_s)=-E_s\frac{2\epsilon^{\perp}_{xy'}/\epsilon_0}{(n_{0a}+1)(n_{0b}+1)(n_{0a}+n_{0b})}\,, \tag{33a}$$

$$E_s''(E_p)=E_p\frac{2\epsilon^{\perp}_{xy''}/\epsilon_0}{(n_{0a}+1)(n_{0b}+1)(n_{0a}+n_{0b})}\,. \tag{33b}$$

In both polarizations, maximum effect is produced at the frequencies $\omega\approx\omega_s$ ($\epsilon^{\perp}_{xy}$ resonances).

In the D_2 and C_{2v} crystals (see Table I) the orientation of the crystallographic axes (Y,Z) with respect to the boundary plane of the crystal plays and important role. In the D_2 class at $\theta=0$, if the boundary plane contains the axes (X,Y), the angle $\alpha=\pi/2$ (see Fig. 3), and the quantities $\epsilon^{\perp}_{xy'}$ and $\epsilon^{\perp}_{xy''}$ are proportional to the sum M_1+Q_{23} and $b_{13}=0$. If the plane (XZ) is the boundary one and $\theta=0$, then $\alpha=0$ and $\epsilon^{\perp}_{xy'},\epsilon^{\perp}_{xy''}\sim p_1(M_1-Q_{23})$; compare with Ref. 15. For other cuts of the crystal or for oblique incidence, nonvanishing will be simultaneously $\epsilon^{\perp}_{xy'},\epsilon^{\perp}_{xy''},b_{13}$.

In the C_{2v} class, according to the selection rules, nondegenerate VOA will be observed only if the plane of incidence is perpendicular to the polar axis of the crystal and the frequency ω is near the frequencies ω_{A_1} of the totally symmetric vibrations. If, however, the boundary plane contains also the second crystallographic axis, for normal incidence $\theta=0$ the quantity $\epsilon^{\perp}_{xy}\sim\sin2\alpha=0$ and according to Sec. VI A reflection VOA would not appear.

In uniaxial crystals the quantities $\epsilon^{\perp}_{xy'}$ and $\epsilon^{\perp}_{xy''}$ differ only because of the different wave vector values k_l [see formula (6)]:

$$k_a=n_{0a}\frac{\omega}{c}\quad(\text{for }\epsilon^{\perp}_{xy'})\,,$$
$$k_b=n_{0b}\frac{\omega}{c}\quad(\text{for }\epsilon^{\perp}_{xy''}) \tag{34}$$

and the quantities n_{0a}, n_{0b}, and $\epsilon^{\perp}_{xy},b_{13}$ are independent of the angle of incidence θ (with the exception of the dependence on θ for the last two quantities in the crystal classes S_4 and D_{2d}). Formulas (30) and (31) may be expressed suitably by the angles θ, θ_1, and θ_2; see formula (10):

$$E_p''(E_s)=E_s\delta_a\frac{2\cos\theta(n_{0a}\cos\theta_2-n_{0b}\cos\theta_1-\kappa n_{0b}\sin\theta_1)}{(n_{0a}\cos\theta_1+\cos\theta)(n_{0b}\cos\theta+\cos\theta_2)}$$
$$=E_s\delta_a\frac{\sin2\theta[\sin(\theta_2-\theta_1)\cos(\theta_1+\theta_2)-\kappa\sin^2\theta_1]}{\sin(\theta+\theta_1)\sin(\theta+\theta_2)\cos(\theta-\theta_2)}\,, \tag{35}$$

$$E_s''(E_p)=E_p\delta_b\frac{2\cos\theta(n_{0b}\cos\theta_2-n_{0a}\cos\theta_1)}{(n_{0a}\cos\theta_1+\cos\theta)(n_{0b}\cos\theta+\cos\theta_2)}$$
$$=E_p\delta_b\frac{\sin2\theta\sin(\theta_1-\theta_2)}{\sin(\theta+\theta_1)\sin(\theta+\theta_2)\cos(\theta-\theta_2)}\,. \tag{36}$$

The two quantities (35) and (36) vanish with increasing angle of incidence up to $\theta=\pi/2$. The analytic expression of the quantity (36) shows that it retains its sign regardless of θ but may have a maximum at an angle of incidence θ_{max}, which is a root of the equation (the lengthy and standard calculations will be discarded here):

$$(n^2_{0a}-\sin^2\theta_{max})^{1/2}=\frac{[n^2_{0b}\cos\theta_{max}+(n^2_{0b}-\sin^2\theta_{max})^{1/2}]\cos\theta_{max}}{(n^2_{0b}-\sin^2\theta_{max})^{1/2}-\cos\theta_{max}}\,. \tag{37}$$

Evidently, the frequency dependence of the refractive index n_{0a} will generate a frequency shift of the angle θ_{max}.

In the crystals of the classes D_3, D_4, and D_6 (the gyrotropic effect in the reflection spectra for crystals of these classes have been reported elsewhere[18] for electromagnetic waves propagating along the optical axis and not normal to it, as in the case under consideration here), the quantity $\kappa\sim b_{13}\equiv0$; see Table I. Besides the simplification of dependence (35) for such crystals, the quantity $E_p''(E_s)$ may vanish when relation (38) is fulfilled:

$$\theta_1+\theta_2=\frac{\pi}{2}\,. \tag{38}$$

Such a vanishing effect of the reflection nondegenerate VOA is an analog of the reflection at the Brewster angle and it will be observed for an angle of incidence θ_{min} of the s-polarized light, defined by the equality

$$\sin\theta_{\min}=n_{0a}n_{0b}(n_{0a}^2+n_{0b}^2)^{-1/2} \tag{39}$$

[evident if the quantity on the right-hand side of (39) is less than unity].

C. Nondegenerate VOA in the refracted waves

The considerations discussed thus far refer to a possibility that because of gyrotropy the reflected electromagnetic wave should possess two polarizations. Evidently, such a phenomenon may appear also in the refracted (and transmitted by the crystal) electromagnetic wave. Formula (24) illustrates the possibility of obtaining a b-type wave in refraction of an s-polarized wave, the new b wave corresponding to p polarization in the C_v groups. For completeness we shall write down two formulas without analysis, thus supplementing formulas (30) and (31) in classes with $\epsilon_{xy}^{\perp}\neq 0$, referring to waves refracted in the crystal and having a "new" polarization:

$$E_s^{(a)}(E_p)=E_p\delta_a\frac{2\cos\theta(n_{0b}\cos\theta_2+\cos\theta)}{(n_{0a}\cos\theta_1+\cos\theta)(n_{0b}\cos\theta+\cos\theta_1-a_{y''z''}^{(b)}\sin\theta_2)}\,, \tag{40}$$

$$E_{y''}^{(b)}(E_s)=-E_s\delta_b\frac{2\cos\theta[n_{0a}\cos\theta+\cos\theta_1+(\kappa-a_{y'z'}^{(a)})\sin\theta_1]}{(n_{0a}\cos\theta_1+\cos\theta)(n_{0b}\cos\theta+\cos\theta_1-a_{y''z''}^{(b)}\sin\theta_2)}\,. \tag{41}$$

Two important effects will be noted.

(1) Because of birefringence the two waves a and b are separated, and the greater the difference in the refracted indices $n_{0a}-n_{0b}$, the stronger is this wave-separation effect. Evidently, this may favor a study of the wave with the new polarization.

(2) In crystal classes in which the normal electromagnetic waves may also have longitudinal components, the direction of the Poynting vectors $\mathbf{S}=\mathbf{E}\times\mathbf{H}$ of the refracted electromagnetic waves differs from the direction of $\mathbf{k}$, defined by equality (10) with angles in the order of magnitude of δ_a,δ_b.

VII. CONCLUSION

A method for studying the vibrational gyrotropy of uniaxial and biaxial crystals by their reflection spectra is proposed in this work. The method is devoted to the study of gyrotropy induced by nondegenerate vibrations. To eliminate the masking birefringence effect which manifests itself in their frequency region, a special geometry was chosen. Unlike the vibrational circular dichroism (VCD), linearly polarized waves should be used in the method proposed here, and the signal studied in the reflected light is polarized normal to the polarization of the incident wave. Similar gyrotropic effects must exist also in the infrared transmission spectra of crystals as well as in the case of multibeam interference from thin gyrotropic crystal plates.

When studying gyrotropy induced by nondegenerate vibrations, we obtain two types of information: (1) that of a purely spectroscopic nature, namely, the frequencies and the matrix elements of the electric dipole and quadrupole moments as well as the magnetic dipole moment of the nondegenerate vibrations, and (2) the peculiarities of the normal electromagnetic waves (see Ref. 11). Relatively simple connections between these two types of information have been obtained in this work and these connections may turn out to be useful when studying different linear and nonlinear processes with polariton participation in gyrotropic crystals.

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