Optical properties, reflectance, and transmittance of anisotropic absorbing crystal plates

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The optical properties of strongly absorbing orthorhombic (and higher-symmetry, uniaxial) crystals are considered. Expressions for the amplitude reflection and transmission coefficients of crystal plates with smooth surfaces parallel to principal planes are presented. Equations for the reflectance and transmittance of crystal layers with rough surfaces are also derived. The expressions are presented in a form that facilitates their computational implementation and their ready comparison with the known formulas corresponding to films of isotropic media. A quantitative description of the contribution to the TM-polarized, off-axis infrared absorption spectrum of anisotropic crystal plates due to polar longitudinal-optic modes will be given. The practical interest of the derived equations for their applications in absorption spectroscopy of solids is emphasized.

I. INTRODUCTION

Linear optics of nonmagnetic absorbing crystals is determined by the knowledge of the complex dielectric tensor $\tilde{\varepsilon}(\omega)$ over the spectral range of interest. Conversely, the values of this tensor can be deduced from spectroscopic experiments, namely from measurements of the reflectance and transmittance of crystal samples. The behavior of the dielectric function $\tilde{\varepsilon}(\omega)$ with frequency, in turn, conveys information about the electronic and vibrational structure of the solid.

The phenomena of reflection and refraction of light at the plane boundary of nontransparent isotropic media and the corresponding reflectance and transmittance of films of these materials are discussed in a number of places.[1–4]

From the transmittance of very thin films of cubic crystals, Berreman[5] demonstrated the potentiality of infrared (ir) absorption spectroscopy for the detection of polar longitudinal-optic (LO) modes. These modes also appear in the reflectance spectrum of films deposited on thick dielectric or metallic substrates. The bands only occur for off-normal incidence and for the transverse-magnetic (TM) component of the radiation.

The crystal optics of weakly absorbing anisotropic media is treated in Ref. 2. A study on the reflection and refraction of plane electromagnetic waves at a single basal plane of strongly absorbing uniaxial crystals is given in Ref. 6, and an extention of this study to the case of incidence on a principal face of orthorhombic crystals is included in Refs. 7 and 8. In these latter references it is shown that for anisotropic crystals of symmetry as high or higher than orthorhombic, TM-polarized, off-axis ir reflection spectroscopy on principal plane surfaces of thick crystals can be employed for the determination of the longitudinal frequency of those optic modes polarized perpendicularly to the surface.

In spite of its practical importance there appears to be no readily available general analysis dealing with the reflection and transmission of strongly absorbing anisotropic crystal plates.[9] This will be the main subject of the present work.

For the sake of completeness we shall briefly review in Sec. II the optics of unbounded absorbing crystals. The results of Sec. II will be particularized in Sec. III to the case of light propagation along principal planes of nontransparent crystals with symmetry as high or higher than orthorhombic.

In Sec. IV we shall examine the boundary conditions for plane electromagnetic waves at the plane interface between an absorbing crystal and an optically isotropic medium.

In Sec. V we shall calculate the amplitude reflection and transmission coefficients corresponding to principal faces of absorbing crystals. These coefficients will be employed in Sec. VI to derive the expressions for the reflectance and transmittance of absorbing crystal plates. This section also includes a detailed quantitative description of the absorption bands due to LO modes polarized perpendicularly to the plate which occur in the corresponding TM-polarized, off-axis transmission spectrum. It is shown that the intensity of these bands is enhanced by cooperative resonant effects due to selective reflection at the front surface and true absorption in the bulk of the sample. In the final Sec. VII we will summarize the main results of this work and discuss some of their applications to ir spectroscopy of solids.

II. CRYSTAL OPTICS OF ABSORBING MEDIA

We shall review in this section the propagation of plane electromagnetic waves of a single frequency in absorbing crystals, following closely the treatment given by Landau and Lifshitz[3] for transparent anisotropic media.

For media containing no free charges or currents, Maxwell's equations for the electric field **E**, electric induction **D**, magnetic field **H**, and magnetic induction **B** can be written (in Gaussian units) as

$$\nabla\times\mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t}\ , \tag{1a}$$

$$\nabla\times\mathbf{H}=\frac{1}{c}\frac{\partial\mathbf{D}}{\partial t}\ , \tag{1b}$$

$$\nabla \cdot \mathbf{D} = \nabla \cdot \mathbf{B} = 0 \ . \tag{1c}$$

We shall consider nonmagnetic ($\mathbf{B}=\mathbf{H}$) linear crystals; consequently, the relation between $\mathbf{D}$ and $\mathbf{E}$ is

$$\mathbf{D} = \hat{\epsilon} \cdot \mathbf{E} \ , \tag{2}$$

where $\hat{\epsilon}$ is a tensorial linear integral operator.

For a plane electromagnetic wave of frequency ω propagating in an absorbing crystal, all field vectors can be expressed in a form proportional to $\exp\{i[(\omega/c)\mathbf{n}\cdot\mathbf{r}-\omega t]\}$, where $\mathbf{n}=\mathbf{n}'+i\mathbf{n}''$ ($\mathbf{n}'$ and $\mathbf{n}''$, real vectors) is the (in general complex) wave-normal vector. From Eqs. (1) it follows that the corresponding $\mathbf{n}$, $\mathbf{D}$, and $\mathbf{H}$ vectors are mutually perpendicular, while $\mathbf{E}$ is normal to $\mathbf{H}$; hence the three vectors $\mathbf{n}$, $\mathbf{E}$, and $\mathbf{D}$ must be coplanar. Moreover, for monochromatic plane waves, Maxwell's equations (1) lead to the relation[10]

$$\mathbf{D} = \tilde{n}^2 \mathbf{E} - (\mathbf{n}\cdot\mathbf{E})\mathbf{n} \ , \tag{3}$$

where $\tilde{n}$, the complex magnitude of the wave-normal vector $\mathbf{n}$, is the refractive index.

In absence of spacial dispersion, the Cartesian components of relation (2) become

$$D_i = \sum_k \tilde{\epsilon}_{ik}(\omega) E_k , \quad i,k = x,y,z \ , \tag{4}$$

where

$$\tilde{\epsilon}_{ik}(\omega) = \epsilon'_{ik}(\omega) + i\epsilon''_{ik}(\omega)$$

are the i,k elements of the dielectric tensor $\tilde{\epsilon}=\epsilon'+i\epsilon''$. The real ($\epsilon'$) and imaginary ($\epsilon''$) parts of $\tilde{\epsilon}$ are symmetrical tensors[2,3] and therefore both can be diagonalized into their principal values by an orthogonal transformation to their respective dielectric axes. In crystals of orthorhombic or higher symmetry, ϵ' and ϵ'' have a common system of principal axes. For rhombohedral, tetragonal, and hexagonal (uniaxial) crystals, one of these axes is coincident with the crystallographic axis of symmetry of the third, fourth, or sixth order, respectively, (optical axis). The direction of the other two axes, in a plane perpendicular to the optic axis, is arbitrary and the corresponding pair of principal values for ϵ' and ϵ'' are, respectively, equal. In an orthorhombic crystal all three dielectric axes are coincident with the crystallographic ones.

In the system of principal dielectric axes of crystals with symmetry as high or higher than orthorhombic, relations (4) reduce to

$$D_i = \tilde{\epsilon}_i E_i , \quad i = x,y,z \ . \tag{5}$$

Substitution of these relations in Eq. (3) yields the complex Fresnel equation[2,6]

$$\tilde{n}^2(\tilde{\epsilon}_x \tilde{n}_x^2 + \tilde{\epsilon}_y \tilde{n}_y^2 + \tilde{\epsilon}_z \tilde{n}_z^2) - [\tilde{n}_x^2 \tilde{\epsilon}_x(\tilde{\epsilon}_y+\tilde{\epsilon}_z) + \tilde{n}_y^2 \tilde{\epsilon}_y(\tilde{\epsilon}_x+\tilde{\epsilon}_z) + \tilde{n}_z^2 \tilde{\epsilon}_z(\tilde{\epsilon}_x+\tilde{\epsilon}_y)] + \tilde{\epsilon}_x\tilde{\epsilon}_y\tilde{\epsilon}_z = 0 \ . \tag{6}$$

For a given frequency, Eq. (6) is a fourth-order complex wave-vector surface in the coordinates $\tilde{n}_x, \tilde{n}_y, \tilde{n}_z$ which determines the values of the complex refractive index $\tilde{n}$ as a function of direction. Being the complex Fresnel equation (6) of second order in $\tilde{n}^2$ there will be, in general, two different complex values of $\tilde{n}^2$ corresponding to each direction of propagation.

Some general properties of the complex wave-vector surface (6) can be studied by introducing the complex ray vector $\mathbf{s}$. The direction of $\mathbf{s}$ is parallel to that of the Poynting vector $\mathbf{S}=c(\mathbf{E}\times\mathbf{H})/4\pi$, and its magnitude is such that $\mathbf{n}\cdot\mathbf{s}=1$. The locus of the points $\mathbf{s}$ generate in the coordinates $\tilde{s}_x, \tilde{s}_y, \tilde{s}_z$ a complex ray surface.

The complex wave vector and ray surfaces are in a certain dual relationship. Since the Poynting vector is perpendicular to the complex wave-vector surface,[11] the same is true of $\mathbf{s}$. Hence the ray vector $\mathbf{s}$ of a wave with a given wave-normal $\mathbf{n}$ vector is perpendicular at the corresponding point of the wave-vector surface. As in the case of transparent crystals,[3] the reverse is also valid: the normal to the complex ray surface gives the direction of the corresponding complex wave vectors.

The location of the ray vector relative to the field vectors in the wave is given by[6]

$$\tilde{s}^2(\tilde{\epsilon}_y\tilde{\epsilon}_z \tilde{s}_x^2 + \tilde{\epsilon}_x\tilde{\epsilon}_z \tilde{s}_y^2 + \tilde{\epsilon}_x\tilde{\epsilon}_y \tilde{s}_z^2) - [\tilde{s}_x^2(\tilde{\epsilon}_y+\tilde{\epsilon}_z) + \tilde{s}_y^2(\tilde{\epsilon}_x+\tilde{\epsilon}_z) + \tilde{s}_z^2(\tilde{\epsilon}_x+\tilde{\epsilon}_y)] + 1 = 0 \ , \tag{7}$$

which determines the (fourth-order) complex ray surface. When the direction of $\mathbf{s}$ is given, Eq. (7) is a quadratic equation for $\tilde{s}^2$ which in general has two different complex roots. This implies that two rays with different complex wave vectors can propagate in any direction through the crystal.

For an arbitrary direction of propagation, the two complex refractive indexes $\tilde{n}$ solutions of Eq. (6) are, respectively, associated with the propagation of two waves whose corresponding $\mathbf{D}$ vectors are perpendicular to each other and, in general, elliptically polarized.[2] If the wave-normal vector $\mathbf{n}$ lies on any of the three principal planes determined by the principal dielectric axes, then both modes of propagation are linearly polarized: one with $\mathbf{D}\|\mathbf{E}$ perpendicular to this plane and the other mode with $\mathbf{D}$ (and the corresponding $\mathbf{E}$ vector) laying on it. A similar dual consideration can be done regarding the linear polarization of the $\mathbf{E}$ vector in the two ray modes associated with a given direction of the ray vector $\mathbf{s}$.

III. PROPAGATION OF ELECTROMAGNETIC WAVES ALONG PRINCIPAL PLANES

For simplicity we shall consider the propagation of monochromatic plane waves along principal planes in crystals of symmetry as high or higher than orthorhombic. For a wave propagating along the (x,z) principal plane, $\tilde{\mathbf{n}}_y=0$ and the Fresnel equation (6) gives the following solutions:

$$\tilde{\mathbf{n}}^2=\tilde{\varepsilon}_y \ , \tag{8}$$

corresponding to a wave whose electric field $\mathbf{E}$ vector is perpendicular to the (x,z) plane [transverse-electric (TE) mode], and

$$\frac{\tilde{\mathbf{n}}_x^2}{\tilde{\varepsilon}_z}+\frac{\tilde{\mathbf{n}}_z^2}{\tilde{\varepsilon}_x}=1 \ , \tag{9}$$

associated with a wave whose $\mathbf{E}$ vector lies on the (x,z) plane of propagation [transverse-magnetic (TM) mode].

From Eq. (7) we obtain the corresponding pair of complex ray surfaces:

$$\tilde{\mathbf{s}}^2=1/\tilde{\varepsilon}_y \quad \text{(TE mode)} \ , \tag{10}$$

$$\tilde{\varepsilon}_z\tilde{\mathbf{s}}_x^2+\tilde{\varepsilon}_x\tilde{\mathbf{s}}_z^2=1 \quad \text{(TM mode)} \ . \tag{11}$$

In the case of uniaxial crystals (i.e., for noncubic crystals of symmetry higher than orthorhombic), the TE and TM modes correspond to ordinary and extraordinary waves, respectively.

For TE waves, the complex refractive index $\tilde{\mathbf{n}}_0$ and the complex magnitude of the ray vector $\tilde{\mathbf{s}}_0$, given by Eqs. (8) and (9), are independent of the direction of propagation. From these equations and the condition $\mathbf{n}_0\cdot\mathbf{s}_0=1$, it follows that $\mathbf{n}_0\|\mathbf{s}_0$ and hence $\mathbf{D}_0\|\mathbf{E}_0$. Therefore the TE mode propagates as a wave in an isotropic medium.

For TM waves, the corresponding $\tilde{\mathbf{n}}_e$ and $\tilde{\mathbf{s}}_e$ values are given by Eqs. (9) and (11) and depend on the direction of propagation. Introducing in these equations the (in general complex) angles $\tilde{\theta}_e$ and $\tilde{\theta}'_e$ that $\mathbf{n}_e$ and $\mathbf{s}_e$, respectively, subtend with the z axis, we obtain

$$\frac{1}{\tilde{\mathbf{n}}_e^2}=\frac{\sin^2\tilde{\theta}_e}{\tilde{\varepsilon}_z}+\frac{\cos^2\tilde{\theta}_e}{\tilde{\varepsilon}_x} \ , \tag{12a}$$

$$\frac{1}{\tilde{\mathbf{s}}_e^2}=\tilde{\varepsilon}_z\sin^2\tilde{\theta}'_e+\tilde{\varepsilon}_x\cos^2\tilde{\theta}'_e \ . \tag{12b}$$

Taking into account that $\mathbf{n}_e$ and $\mathbf{s}_e$ are, respectively, perpendicular to the ray surface (11) and wave-vector surface (9), the following relation between $\tilde{\theta}_e$ and $\tilde{\theta}'_e$ is obtained:

$$\frac{\tilde{\mathbf{s}}_x}{\tilde{\varepsilon}_z}=\tan\tilde{\theta}'_e=\frac{\tilde{\varepsilon}_x}{\tilde{\varepsilon}_z}\frac{\tilde{\mathbf{n}}_x}{\tilde{\mathbf{n}}_z}=\frac{\tilde{\varepsilon}_x}{\tilde{\varepsilon}_z}\tan\tilde{\theta}_e \ . \tag{13}$$

For TM polarization, all $\mathbf{n}_e$, $\mathbf{s}_e$, $\mathbf{D}_e$, and $\mathbf{E}_e$ vectors lie on the principal (x,z) plane but, in general, neither $\mathbf{n}_e$ and $\mathbf{s}_e$ [see Eq. (13)] nor are $\mathbf{D}_e$ and $\mathbf{E}_e$ parallel to each other.

IV. BOUNDARY CONDITIONS

In Secs. II and III we considered the propagation of light through unlimited crystals. We shall now study the reflection and refraction of plane electromagnetic waves at the plane interface between an absorbing crystal and a isotropic medium.

When light passes from one medium into another the electromagnetic field vectors must satisfy certain boundary conditions which derive from Maxwell's equations (1), namely the conditions of continuity of the tangential components of $\mathbf{E}$ and $\mathbf{H}$ at the interface between the two media.[1]

For incident (i), reflected (r), and transmitted (t) monochromatic plane waves, the complete homogeneity of the electromagnetic field at the plane interface implies that the components of the wave-normal vectors $\mathbf{n}^{(i)}$, $\mathbf{n}^{(r)}$, and $\mathbf{n}^{(t)}$ along the plane must be equal.

We shall examine now the following situations: case (A) where medium 1, from which the wave is incident, is air and medium 2 is an absorbing crystal, and case (B) where medium 1 is an absorbing crystal and medium 2 is assumed to be isotropic (which could eventually be air or an absorbing body).

Let us consider a crystal of symmetry as high or higher than orthorhombic whose dielectric axes are labeled x, y, and z and whose limiting face is parallel to the principal (x,y) plane. For incident waves laying on the (x,z) plane, the reflected and refracted beams also lay on this plane (see Fig. 1) and the boundary condition that applies to the corresponding wave-normal vectors becomes

$$\tilde{\mathbf{n}}_x^{(i)}=\tilde{\mathbf{n}}_x^{(r)}=\tilde{\mathbf{n}}_x^{(t)} \ . \tag{14}$$

Case (A). Equation (14) leads to the complex Snell's law of refraction

$$\mathbf{n}_x^{(i)}=\mathbf{n}_x^{(r)}=\tilde{\mathbf{n}}_x^{(t)}=\sin\theta_i \ , \tag{15}$$

where θ_i is the angle of incidence.

From Eqs. (8), (9), and (15) it follows that

$$\tilde{\mathbf{n}}_z^{(t)}=(\tilde{\varepsilon}_y-\sin^2\theta_i)^{1/2} \quad \text{(TE mode)} \ , \tag{16}$$

$$\tilde{\mathbf{n}}_z^{(t)}=(\tilde{\varepsilon}_x/\tilde{\varepsilon}_z)^{1/2}(\tilde{\varepsilon}_z-\sin^2\theta_i)^{1/2} \quad \text{(TM mode)} \ . \tag{17}$$

Case (B). In this case Eq. (14) becomes

$$\tilde{\mathbf{n}}_x^{(i)}=\tilde{\mathbf{n}}_x^{(r)}=\tilde{\mathbf{n}}_x^{(t)}=\tilde{\mathbf{n}}\sin\tilde{\theta}_i \ , \tag{18}$$

where now the "angle of incidence" $\tilde{\theta}_i$ may be a complex number, and the complex refractive index $\tilde{\mathbf{n}}$ of the crystal is given by Eq. (8) for TE polarization and by Eq. (12a) with $\tilde{\theta}_e=\tilde{\theta}_i$ for TM waves. From Eqs. (8), (12a), and (18) it follows that

$$\tilde{\mathbf{n}}_z^{(t)}=(\tilde{\varepsilon}_b-\tilde{\varepsilon}_y\sin^2\tilde{\theta}_i)^{1/2} \quad \text{(TE mode)} \ , \tag{19}$$

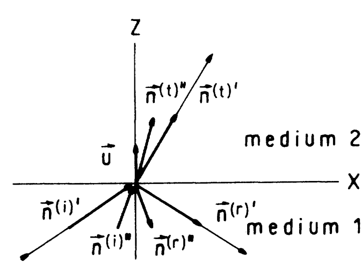

FIG. 1. Wave-normal $\mathbf{n}=\mathbf{n}'+i\mathbf{n}''$ vectors for the incident, reflected, and refracted beams at the interface between an isotropic medium and an absorbing crystal cleaved along a principal plane. Because of the boundary conditions that apply to the situations considered in this work, the field vectors of these beams are in general described by inhomogeneous plane waves proportional to $\exp[i(\omega/c)(\mathbf{n}'+i\mathbf{n}'')\cdot\mathbf{r}]$ with $\mathbf{n}''$ perpendicular to the interface.

$$\tilde{\mathbf{n}}_z^{(t)} = \left[\tilde{\epsilon}_b - \frac{\tilde{\epsilon}_x \tilde{\epsilon}_z}{\tilde{\epsilon}_x + \tilde{\epsilon}_z \cot^2 \tilde{\theta}_i} \right]^{1/2} \quad \text{(TM mode)} , \tag{20}$$

where $\tilde{\epsilon}_b$ is the dielectric constant of the isotropic medium.

V. REFLECTION AND TRANSMISSION AT PRINCIPAL FACES OF ABSORBING CRYSTALS

We can now procede to calculate the components of the reflected and transmitted waves in terms of those of the incident beam. Since an arbitrary incident wave can be resolved into their TE and TM components, we shall consider separately these two cases, (I) and (II), employing a subscript s for the TE mode and p to refer to the TM mode. We shall identify medium 1 with air (of dielectric constant $\epsilon_1 = 1$), medium 2 with the absorbing crystal ($\epsilon_2 = \tilde{\epsilon}$), and medium 3 with an isotropic body ($\epsilon_3 = \tilde{\epsilon}_b$), and will be interested in the reflection and refraction at the interfaces 1-2 and 2-3.

A. Case (I): TE polarization

The boundary condition for the tangential component of **E** is

$$E_{ys}^{(i)} + E_{ys}^{(r)} = E_{ys}^{(t)} . \tag{21}$$

The condition of continuity of the tangential component of **H** can be expressed in terms of the corresponding vector **E** by

$$\tilde{\mathbf{n}}_z^{(i)} (E_{ys}^{(i)} - E_{ys}^{(r)}) = \tilde{\mathbf{n}}_z^{(t)} E_{ys}^{(t)} . \tag{22}$$

Defining the amplitude reflection and transmission coefficients $\tilde{\mathbf{r}}^{(s)}$ and $\tilde{\mathbf{t}}^{(s)}$ by

$$\tilde{\mathbf{r}}^{(s)} = \frac{E_{ys}^{(r)}}{E_{ys}^{(i)}} , \tag{23a}$$

$$\tilde{\mathbf{t}}^{(s)} = \frac{E_{ys}^{(t)}}{E_{ys}^{(i)}} = 1 + \tilde{\mathbf{r}}^{(s)} , \tag{23b}$$

there results from Eqs. (21) and (22) that

$$\tilde{\mathbf{r}}^{(s)} = \frac{\tilde{\mathbf{n}}_z^{(i)} - \tilde{\mathbf{n}}_z^{(t)}}{\tilde{\mathbf{n}}_z^{(i)} + \tilde{\mathbf{n}}_z^{(t)}} , \tag{24a}$$

$$\tilde{\mathbf{t}}^{(s)} = \frac{2\tilde{\mathbf{n}}_z^{(i)}}{\tilde{\mathbf{n}}_z^{(i)} + \tilde{\mathbf{n}}_z^{(t)}} . \tag{24b}$$

B. Case (II): TM polarization

In this case the electric field **E** lies on the plane of incidence (x,z) and it is more convenient to carry out the calculations for the magnetic field, which is along the y axis and satisfies the boundary condition

$$H_{yp}^{(i)} + H_{yp}^{(r)} = H_{yp}^{(t)} . \tag{25}$$

Relating the electric field for the three waves to their associated magnetic fields, the boundary condition that applies to the tangential component of **E** becomes

$$\tilde{\mathbf{s}}_z^{(i)} (H_{yp}^{(i)} - H_{yp}^{(r)}) = \tilde{\mathbf{s}}_z^{(t)} H_{yp}^{(t)} . \tag{26}$$

Defining the amplitude reflection and transmission coefficients $\tilde{\mathbf{r}}^{(p)}$ and $\tilde{\mathbf{t}}^{(p)}$ by

$$\tilde{\mathbf{r}}^{(p)} = \frac{H_{yp}^{(r)}}{H_{yp}^{(i)}} . \tag{27a}$$

$$\tilde{\mathbf{t}}^{(p)} = \frac{H_{yp}^{(t)}}{H_{yp}^{(i)}} = 1 + \tilde{\mathbf{r}}^{(p)} , \tag{27b}$$

we obtain from Eqs. (25) and (26) the relations

$$\tilde{\mathbf{r}}^{(p)} = \frac{\tilde{\mathbf{s}}_z^{(i)} - \tilde{\mathbf{s}}_z^{(t)}}{\tilde{\mathbf{s}}_z^{(i)} + \tilde{\mathbf{s}}_z^{(t)}} , \tag{28a}$$

$$\tilde{\mathbf{t}}^{(p)} = \frac{2\tilde{\mathbf{s}}_z^{(i)}}{\tilde{\mathbf{s}}_z^{(i)} + \tilde{\mathbf{s}}_z^{(t)}} . \tag{28b}$$

Expressions for $\tilde{\mathbf{r}}_{12}$, $\tilde{\mathbf{r}}_{21}$, $\tilde{\mathbf{r}}_{23}$, $\tilde{\mathbf{t}}_{12}$, $\tilde{\mathbf{t}}_{21}$, and $\tilde{\mathbf{t}}_{23}$ in terms of the angle of incidence and the dielectric constants can easily be obtained from Eqs. (24) and (28) and the results of Secs. III and IV. To this purpose, for TE waves, we must replace in Eqs. (24) the values of the z component of the wave-normal vectors given by Eqs. (16) and (19); for TM waves, we must introduce in Eqs. (28) the values of the z components of the ray vectors obtained employing Eqs. (12), (13), (15), and (16).

For thick samples, the refracted wave at the interface 1-2 is completely absorbed by the crystal. The ratio of the reflected and incident intensities (reflectance) corresponding to the s- and p-polarized components are given by the well-known formulas:[6]

$$\mathcal{R}_s = |\tilde{\mathbf{r}}_{12}^{(s)}|^2 = \left| \frac{\cos\theta_i - \tilde{\mathbf{J}}_y}{\cos\theta_i + \tilde{\mathbf{J}}_y} \right|^2 , \tag{29a}$$

$$\mathcal{R}_p = |\tilde{\mathbf{r}}_{12}^{(p)}|^2 = \left| \frac{\tilde{\epsilon}\cos\theta_i - \tilde{\mathbf{J}}_z}{\tilde{\epsilon}\cos\theta_i + \tilde{\mathbf{J}}_z} \right|^2 , \tag{29b}$$

where $\tilde{\mathbf{J}}_y = (\tilde{\epsilon}_y - \sin^2\theta_i)^{1/2}$, $\tilde{\mathbf{J}}_z = (\tilde{\epsilon}_z - \sin^2\theta_i)^{1/2}$, and $\tilde{\epsilon} = (\tilde{\epsilon}_x \tilde{\epsilon}_z)^{1/2}$.

The equation (29a) for the TE reflectance $\mathcal{R}_s$ and the similar equations that apply to the other two principal planes allow the determination of the complex dielectric tensor $\tilde{\epsilon}$, and thus the optical properties of the crystal, from experimental reflectance. This can be performed, for example, by measurements of $\mathcal{R}_s$ at a given frequency and at two (or more) angles of incidence[12,13] or employing the Kramers-Kronig[14–16] dispersion relations on reflectance data at a fixed angle of incidence but covering a range as wide as possible of frequencies.[17,18]

Equation (29b) rewritten in the form

$$\mathcal{R}_p(\omega) = \left| \frac{\tilde{\epsilon}_x^{1/2}(\omega)\cos\theta_i - [1 - (\sin^2\theta_i)/\tilde{\epsilon}_z(\omega)]^{1/2}}{\tilde{\epsilon}_x^{1/2}(\omega)\cos\theta_i + [1 - (\sin^2\theta_i)/\tilde{\epsilon}_z(\omega)]^{1/2}} \right|^2 , \tag{30}$$

shows that if $\tilde{\epsilon}_z(\omega)$ presents a resonance in a frequency region where the behavior of $\tilde{\epsilon}_x(\omega)$ is smooth, then the TM reflectance will exhibit a maximum in the spectral range where $\tilde{\epsilon}_z(\omega)$ is small, that is for the longitudinal frequency

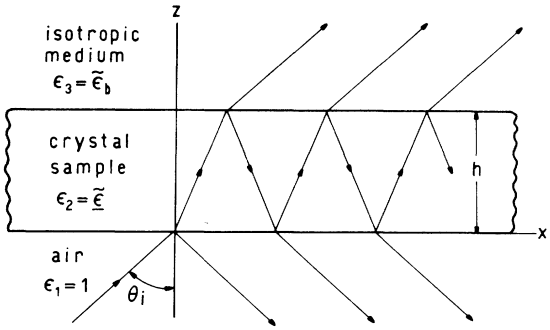

FIG. 2. Multiple reflections and refractions of a plane wave in a plane parallel crystal plate.

of the associated optic mode polarized along the z axis. Hence the frequency of LO modes can be determined from TM, off-axis reflectance measurements in thick crystals.[7,8]

VI. REFLECTANCE AND TRANSMITTANCE OF ABSORBING CRYSTAL PLATES

Because of its practical interest is spectroscopy of solids we shall consider here the reflectance and transmittance of absorbing crystal plates with faces parallel to principal planes. The situation is schematically depicted in Fig. 2, where the optical properties of the three media are as described at the beginning of Sec. V. Both limits of smooth and rough boundary surfaces of the crystal layer will be considered.

For thin crystal plates, the multiple reflection-transmission processes at the 1-2 and 2-3 interfaces cannot be neglected. To deal with this case we shall recourse to the usual procedure of multiple-beam interference employed in optics.[2,4]

From the complex Snell's law (15), we obtain for the complex angle of refraction at the interface 1-2:

$$\tilde{\mathbf{n}}\sin\tilde{\theta}=\sin\theta_i \ , \tag{31}$$

where $\tilde{\mathbf{n}}=\tilde{\mathbf{n}}_0=\tilde{\epsilon}_y^{1/2}$ and $\tilde{\theta}=\tilde{\theta}_0$ for TE polarization, and $\tilde{\mathbf{n}}=\tilde{\mathbf{n}}_e$ [given by Eq. (12a) with $\tilde{\theta}=\tilde{\theta}_e$] for TM polarization. The values of $\tilde{\theta}_0$ and $\tilde{\theta}_e$ are expressed in terms of the angle of incidence θ_i through

$$\sin^2\tilde{\theta}_0=\frac{\sin^2\theta_i}{\tilde{\epsilon}_y} \ , \tag{32a}$$

$$\tan^2\tilde{\theta}_e=\frac{\tilde{\epsilon}_z}{\tilde{\epsilon}_x}\left[\frac{\sin^2\theta_i}{\tilde{\epsilon}_z-\sin^2\theta_i}\right] . \tag{32b}$$

These relations allow us to express the amplitude reflection and transmission coefficients at the interface 2-3 as a function of θ_i:

$$\tilde{\mathbf{r}}_{23}^{(s)}=\frac{\tilde{\mathbf{J}}_y-\tilde{\mathbf{J}}_b}{\tilde{\mathbf{J}}_y+\tilde{\mathbf{J}}_b} \ , \tag{33a}$$

$$\tilde{\mathbf{t}}_{23}^{(s)}=\frac{2\tilde{\mathbf{J}}_y}{\tilde{\mathbf{J}}_y+\tilde{\mathbf{J}}_b} \ , \tag{33b}$$

$$\tilde{\mathbf{r}}_{23}^{(p)}=\frac{\tilde{\epsilon}_b\tilde{\mathbf{J}}_z-\tilde{\epsilon}\tilde{\mathbf{J}}_b}{\tilde{\epsilon}_b\tilde{\mathbf{J}}_z+\tilde{\epsilon}\tilde{\mathbf{J}}_b} \ , \tag{34a}$$

$$\tilde{\mathbf{t}}_{23}^{(p)}=\frac{2\tilde{\epsilon}_b\tilde{\mathbf{J}}_z}{\tilde{\epsilon}_b\tilde{\mathbf{J}}_z+\tilde{\epsilon}\tilde{\mathbf{J}}_b} \ , \tag{34b}$$

where $\tilde{\mathbf{J}}_b=(\tilde{\epsilon}_b-\sin^2\theta_i)^{1/2}$.

The values of $\tilde{\mathbf{r}}_{21}$ and $\tilde{\mathbf{t}}_{21}$ for both TE and TM polarizations can be obtained as the particular cases of Eqs. (33) and (34) corresponding to $\tilde{\epsilon}_b=1$. We can easily verify the following relationships:

$$\tilde{\mathbf{r}}_{21}=-\tilde{\mathbf{r}}_{12} \ , \tag{35}$$

$$\tilde{\mathbf{t}}_{12}\tilde{\mathbf{t}}_{21}=1-\tilde{\mathbf{r}}_{12}^2 \ , \tag{36}$$

which generalize to the case of anisotropic crystals the corresponding relations among the amplitude reflection and transmission coefficients that apply in the case of two adjacent isotropic media.[2,4]

For smooth crystal faces (within the scale of a wavelength of the radiation), the amplitude A_r of the reflected wave (either the electric field for TE polarization or the magnetic field for TM polarization) is given by a series that takes into account multiple-beam interference effects (see Fig. 2):

$$A_r=A_i[\tilde{\mathbf{r}}_{12}+(\tilde{\mathbf{t}}_{12}\tilde{\mathbf{t}}_{21})\tilde{\mathbf{r}}_{23}e^{2i\tilde{\phi}h}+(\tilde{\mathbf{t}}_{12}\tilde{\mathbf{t}}_{21})\tilde{\mathbf{r}}_{21}\tilde{\mathbf{r}}_{23}^2e^{4i\tilde{\phi}h}+(\tilde{\mathbf{t}}_{12}\tilde{\mathbf{t}}_{21})\tilde{\mathbf{r}}_{21}^2\tilde{\mathbf{r}}_{23}^3e^{6i\tilde{\phi}h}+\cdots] \ , \tag{37}$$

where A_i is the amplitude of the incident beam and $\tilde{\phi}h$ is the complex phase acquired by the wave over the thickness h of the layer. The factor $\tilde{\phi}$ in the exponents is given by

$$\tilde{\phi}=\tilde{\phi}_s=\frac{\omega}{c}\tilde{\mathbf{J}}_y \ \ \text{(TE mode)} \ , \tag{38a}$$

$$\tilde{\phi}=\tilde{\phi}_p=\frac{\omega}{c}(\tilde{\epsilon}_x/\tilde{\epsilon}_z)^{1/2}\tilde{\mathbf{J}}_z \ \ \text{(TM mode)} \ . \tag{38b}$$

The amplitude A_t of the wave transmitted by a crystal plate in air is

$$A_t=A_i[(\tilde{\mathbf{t}}_{12}\tilde{\mathbf{t}}_{21})e^{i\tilde{\phi}h}+(\tilde{\mathbf{t}}_{12}\tilde{\mathbf{t}}_{21})\tilde{\mathbf{r}}_{21}^2e^{3i\tilde{\phi}h}+(\tilde{\mathbf{t}}_{12}\tilde{\mathbf{t}}_{21})\tilde{\mathbf{r}}_{21}^4e^{5i\tilde{\phi}h}+\cdots] \ . \tag{39}$$

Introducing into Eqs. (37) and (39) the relations (35) and (36) and summing the series there, results in the following expressions for the amplitude reflection and transmission coefficients:

$$R_A=\frac{A_r}{A_i}=\frac{\tilde{\mathbf{r}}_{12}e^{-i\tilde{\phi}h}+\tilde{\mathbf{r}}_{23}e^{i\tilde{\phi}h}}{e^{-i\tilde{\phi}h}+\tilde{\mathbf{r}}_{12}\tilde{\mathbf{r}}_{23}e^{i\tilde{\phi}h}} \ , \tag{40a}$$

$$T_A=\frac{A_t}{A_i}=\frac{1-\tilde{r}_{12}^2}{e^{i\tilde{\phi}h}-\tilde{r}_{12}^2e^{i\tilde{\phi}h}} \quad . \tag{40b}$$

The corresponding reflectance (R) and transmittance (T) are given by $R=|R_A|^2$ and $T=|T_A|^2$.

Replacing into Eqs. (40) the values for $\tilde{r}_{12}$ [see Eqs. (29)], $\tilde{r}_{23}$ [Eqs. (33a) and (34a)], and $\tilde{\phi}$ [Eqs. (38)], we obtain for the amplitude reflectance of absorbing crystal plates deposited on thick isotropic substrates:

$$(R_A)_s=\frac{E_y^{(r)}}{E_y^{(i)}}=\frac{\cos(\delta\tilde{\mathbf{J}}_y)(1-\tilde{\mathbf{J}}_b/\cos\theta_i)-i\sin(\delta\tilde{\mathbf{J}}_y)(\tilde{\mathbf{J}}_b/\tilde{\mathbf{J}}_y-\tilde{\mathbf{J}}_y/\cos\theta_i)}{\cos(\delta\tilde{\mathbf{J}}_y)(1+\tilde{\mathbf{J}}_b/\cos\theta_i)-i\sin(\delta\tilde{\mathbf{J}}_y)(\tilde{\mathbf{J}}_b/\tilde{\mathbf{J}}_y+\tilde{\mathbf{J}}_y/\cos\theta_i)} \quad , \tag{41a}$$

$$(R_A)_p=\frac{H_y^{(r)}}{H_y^{(i)}}=\frac{\cos\left[\delta\left[\frac{\tilde{\epsilon}_x}{\tilde{\epsilon}_z}\right]^{1/2}\tilde{\mathbf{J}}_z\right]\left[1-\frac{\tilde{\mathbf{J}}_b}{\tilde{\epsilon}_b\cos\theta_i}\right]-i\sin\left[\delta\left[\frac{\tilde{\epsilon}_x}{\tilde{\epsilon}_z}\right]^{1/2}\tilde{\mathbf{J}}_z\right]\left[\frac{\tilde{\epsilon}\tilde{J}_b}{\tilde{\epsilon}_b\tilde{\mathbf{J}}_z}-\frac{\tilde{\mathbf{J}}_z}{\tilde{\epsilon}\cos\theta_i}\right]}{\cos\left[\delta\left[\frac{\tilde{\epsilon}_x}{\tilde{\epsilon}_z}\right]^{1/2}\tilde{\mathbf{J}}_z\right]\left[1+\frac{\tilde{\mathbf{J}}_b}{\tilde{\epsilon}_b\cos\theta_i}\right]-i\sin\left[\delta\left[\frac{\tilde{\epsilon}_x}{\tilde{\epsilon}_z}\right]^{1/2}\tilde{\mathbf{J}}_z\right]\left[\frac{\tilde{\epsilon}\tilde{\mathbf{J}}_b}{\tilde{\epsilon}_b\tilde{\mathbf{J}}_z}+\frac{\tilde{\mathbf{J}}_z}{\tilde{\epsilon}\cos\theta_i}\right]} \quad , \tag{41b}$$

and for the amplitude transmittance of a crystal layer in air:

$$(T_A)_s=\frac{E_y^{(t)}}{E_y^{(i)}}=\left[\cos(\delta\tilde{\mathbf{J}}_y)-\frac{i}{2}\left[\frac{\tilde{\mathbf{J}}_y}{\cos\theta_i}+\frac{\cos\theta_i}{\tilde{\mathbf{J}}_y}\right]\sin(\delta\tilde{\mathbf{J}}_y)\right]^{-1} \quad , \tag{42a}$$

$$(T_A)_p=\frac{H_y^{(t)}}{H_y^{(i)}}=\left\{\cos\left[\delta\left[\frac{\tilde{\epsilon}_x}{\tilde{\epsilon}_z}\right]^{1/2}\tilde{\mathbf{J}}_z\right]-\frac{i}{2}\left[\frac{\tilde{\mathbf{J}}_z}{\tilde{\epsilon}\cos\theta_i}+\frac{\tilde{\epsilon}\cos\theta_i}{\tilde{\mathbf{J}}_z}\right]\sin\left[\delta\left[\frac{\tilde{\epsilon}_x}{\tilde{\epsilon}_z}\right]^{1/2}\tilde{\mathbf{J}}_z\right]\right\}^{-1} \quad . \tag{42b}$$

In Eqs. (41) and (42) $\delta=h\omega/c=2\pi h/\lambda_0$ is 2π times the thickness of the layer measured in vacuum wavelengths of the incident radiation.

The amplitude reflectance and transmittance formulas (41) and (42) are generalizations to the case of anisotropic crystal plates of the corresponding formulas for films of isotropic media.[4,5]

For layers thin enough such that $|\delta\tilde{\mathbf{J}}_y|\ll 1$ for TE waves, or $|\delta(\tilde{\epsilon}_x/\tilde{\epsilon}_z)^{1/2}\tilde{\mathbf{J}}_z|\ll 1$ for TM modes, there results from Eqs. (41) the following approximate expressions for the reflectivity of very thin crystal films deposited on a transparent substrate of $|\epsilon_b|>1$:

$$R_s=|(R_A)_s|^2\cong\left[\frac{J_b-\cos\theta_i}{J_b+\cos\theta_i}\right]^2\left[1+4\delta\epsilon_y''\left[\frac{\cos\theta_i}{\epsilon_b-1}\right]\right] \quad , \tag{43a}$$

$$R_p=|(R_A)_p|^2\cong\left[\frac{J_b-\epsilon_b\cos\theta_i}{J_b+\epsilon_b\cos\theta_i}\right]^2\left\{1+\frac{4\delta\cos\theta_i}{(\epsilon_b-1)(\epsilon_b\cos^2\theta_i-\sin^2\theta_i)}\left[J_b\epsilon_x''-\epsilon_b\left[\frac{\epsilon_z''}{\epsilon_z'^2+\epsilon_z''^2}\right]\sin^2\theta_i\right]\right\} \quad . \tag{43b}$$

In these and other expressions that follow, the principal components of the complex dielectric tensor are given by $\tilde{\epsilon}_\alpha=\epsilon_\alpha'+i\epsilon_\alpha''$; $\alpha=x,y,z$. The TE-polarized reflectance R_s, as in the similar case of very thin cubic crystal films discussed by Berreman,[5] shows peaks at the maxima of $\epsilon_y''(\omega)$, that is for the transversal frequencies of optic modes polarized along the y axis. On the other hand, the TM reflectance[19] R_p will exhibit maxima at the transversal frequencies of optic modes polarized along the x axis and, for off-axis incidence, minima at the frequencies where

$$|\mathrm{Im}(1/\tilde{\epsilon}_z)|=\epsilon_z''/[(\epsilon_z')^2+(\epsilon_z'')^2]$$

is maximum, i.e., at the longitudinal frequencies of optic modes polarized along the z axis.

If the substrate is a good conductor, so that $|\epsilon_b|$ is very large, Eqs. (43) reduce to

$$R_s\cong 1 \quad , \tag{44a}$$

$$R_p\cong 1-4\delta\left[\frac{\epsilon_z''}{(\epsilon_z')^2+(\epsilon_z'')^2}\right]\frac{\sin^2\theta_i}{\cos\theta_i} \quad . \tag{44b}$$

As discussed in Ref. 5 for the case of very thin cubic crystal films deposited on a metal substrate, because of the large value of $|\epsilon_b|$ almost no electric field can exist parallel and adjacent to the crystal-metal interface (which now constitutes a nodal plane of the electromagnetic wave). Hence transverse modes polarized along the plane cannot be stimulated in a very thin crystal film on a metal and absorption peaks only appear at the longitudinal frequency of optic modes polarized perpendicularly to the crystal plate in the TM-polarized component at nonzero angle of incidence.

From a first-order expansion of Eqs. (42) in powers of δ, we obtain the following approximate expressions for the transmittance of very thin crystal films in air:

$$T_s=|(T_A)_s|^2=1-\delta\epsilon_y''/\cos\theta_i \quad , \tag{45a}$$

$$T_p = |(T_A)_p|^2 = 1-\delta\left[\epsilon_x''\cos\theta_i + \left[\frac{\epsilon_z''}{\epsilon_z'^2+\epsilon_z''^2}\right]\frac{\sin^2\theta_i}{\cos\theta_i}\right] . \quad (45b)$$

We note that T_s will exhibit minima at the transverse frequencies of optic modes polarized along the y axis. For off-axis transmission, T_p will present minima at both the transversal frequency of x-polarized optic modes and at the longitudinal frequency of active modes polarized perpendicularly to the crystal plate.

We now turn to the case when the crystal sample is rough, i.e., the reflection-transmission processes at both surfaces of the sample add incoherently (see Fig. 2). In this case, the multiple-beam interference effects disappear and are the intensities of the various reflected and transmitted beams rather than their amplitudes which should be added. The intensity I_r of the wave reflected by a crystal plate deposited on a thick substrate when illuminated with a beam of intensity I_i is

$$I_r = I_i[\,|\tilde{r}_{12}|^2 + |\tilde{r}_{23}|^2(1-|\tilde{r}_{12}|^2)^2 e^{-4\phi''h}(1+|\tilde{r}_{23}|^2|\tilde{r}_{12}|^2 e^{-4\phi''h} + |\tilde{r}_{23}|^4|\tilde{r}_{12}|^4 e^{-8\phi''h} + \cdots)] . \quad (46)$$

where the relationship (35) has been used and ϕ'', which is one-half of the linear-absorption coefficient, is the imaginary part of $\tilde{\phi}$ given by Eqs. (38):

$$\phi'' = \phi_s'' = \mathrm{Im}(\tilde{\phi}_s) = \frac{\omega}{c}\,\mathrm{Im}(\tilde{\jmath}_y) \quad \text{(TE mode)} , \quad (47a)$$

$$\phi'' = \phi_p'' = \mathrm{Im}(\tilde{\phi}_p) = \frac{\omega}{c}\,\mathrm{Im}[(\tilde{\epsilon}_x/\tilde{\epsilon}_z)^{1/2}\tilde{\jmath}_z] \quad \text{(TM mode)} . \quad (47b)$$

The intensity I_t of the wave transmitted by the sample in air is

$$I_t = I_i(1-|\tilde{r}_{12}|^2)^2 e^{-2\phi''h} \times [1+|\tilde{r}_{12}|^4 e^{-4\phi''h} + |\tilde{r}_{12}|^8 e^{-8\phi''h} + \cdots] . \quad (48)$$

The corresponding reflectance R and transmittance T are

$$R = \frac{I_r}{I_i} = \frac{|\tilde{r}_{12}|^2 + |\tilde{r}_{23}|^2(1-2|\tilde{r}_{12}|^2)e^{-4\phi''h}}{1-|\tilde{r}_{23}|^2|\tilde{r}_{12}|^2 e^{-4\phi''h}} , \quad (49a)$$

$$T = \frac{I_t}{I_i} = \frac{(1-|\tilde{r}_{12}|^2)^2 e^{-2\phi''h}}{1-|\tilde{r}_{12}|^4 e^{-4\phi''h}} = \frac{(1-\mathcal{R})^2 e^{-2\phi''h}}{1-\mathcal{R}^2 e^{-4\phi''h}} , \quad (49b)$$

where in the last equation we have introduced the reflectance $\mathcal{R} = |\tilde{r}_{12}|^2$ of a thick absorbing crystal [Eqs. (29)]. For a crystal sample in air ($|\tilde{r}_{23}|^2 = |\tilde{r}_{12}|^2$), the reflectance (49a) becomes

$$R = \frac{\mathcal{R}[1+(1-2\mathcal{R})e^{-4\phi''h}]}{1-\mathcal{R}^2 e^{-4\phi''h}} . \quad (50)$$

If the crystal plate is deposited on a very good conductor, then $|\tilde{r}_{23}|^2 \cong 1$ and Eq. (49a) adopts the form:

$$R = \frac{\mathcal{R}+(1-2\mathcal{R})e^{-4\phi''h}}{1-\mathcal{R}e^{-4\phi''h}} , \quad (51)$$

which, as expected, takes the value $R \cong 1$ for transparent crystals ($\phi'' \cong 0$).

For TE waves, the transmittance (49b) becomes

$$T_s = \frac{(1-\mathcal{R}_s)^2 e^{-2\phi_s''h}}{1-\mathcal{R}_s^2 e^{-4\phi_s''h}} , \quad (52)$$

where $\mathcal{R}_s$ is given by Eq. (29a) and ϕ_s'' by Eq. (47a). Equation (52) is a generalization of the well-known formula for the transmittance of a layer of isotropic material at normal incidence:

$$T = \frac{(1-\mathcal{R})^2 e^{-\alpha h}}{1-\mathcal{R}^2 e^{-2\alpha h}} , \quad (53)$$

where α is the isotropic linear-absorption coefficient, to the case of absorbing crystal plates and arbitrary angle of incidence. For TM waves, we obtain the result

$$T_p = \frac{(1-\mathcal{R}_p)^2 e^{-2\phi_p''h}}{1-\mathcal{R}_p^2 e^{-4\phi_p''h}} , \quad (54)$$

where $\mathcal{R}_p$ is given by Eq. (30) and ϕ_p'' by Eq. (47b). Rewriting this latter equation, we can express the anisotropic absorption coefficient $2\phi_p''(\omega)$ in the form:

$$2\phi_p''(\omega) = \frac{2\omega}{c}\,\mathrm{Im}\left\{\left[\left[1-\frac{\sin^2\theta_i}{\tilde{\epsilon}_z(\omega)}\right]\tilde{\epsilon}_x(\omega)\right]^{1/2}\right\} . \quad (55)$$

Equation (55) shows that for resonances of $\tilde{\epsilon}_z(\omega)$ separated enough from the strong resonances of $\tilde{\epsilon}_x(\omega)$ in the spectrum and for radiation not incident normal to the crystal slab, the absorption coefficient will exhibit a maximum in the spectral range where $\tilde{\epsilon}_z(\omega)$ is small, i.e., for longitudinal frequencies of optic modes polarized along the z axis. We have already commented at the end of Sec. V that because the same dependence with the function $[1-\sin^2\theta_i/\tilde{\epsilon}_z(\omega)]$ which appears in Eq. (55), the off-axis reflectance $\mathcal{R}_p(\omega)$ on a thick crystal [Eq. (30)] will present a maximum at the same longitudinal frequencies as above. These will appear as minima in the transmittance spectrum of the crystal plate. As can be appreciated from Eqs. (54) and (55) the intensity of these peaks will be enhanced by the resonant absorption of the sample at the same frequencies. As expected, this effect is also present in the limiting case of crystal layers with smooth surfaces. In this case, however, the analysis has to be carried out numerically on the more complex expression that results from the absolute square of the TM amplitude transmittance (42b).

VII. SUMMARY AND CONCLUDING REMARKS

The main results of the present work are the derivation of the expressions for the amplitude reflection coefficients [Eqs. (41)] and amplitude transmission coefficients [Eqs.

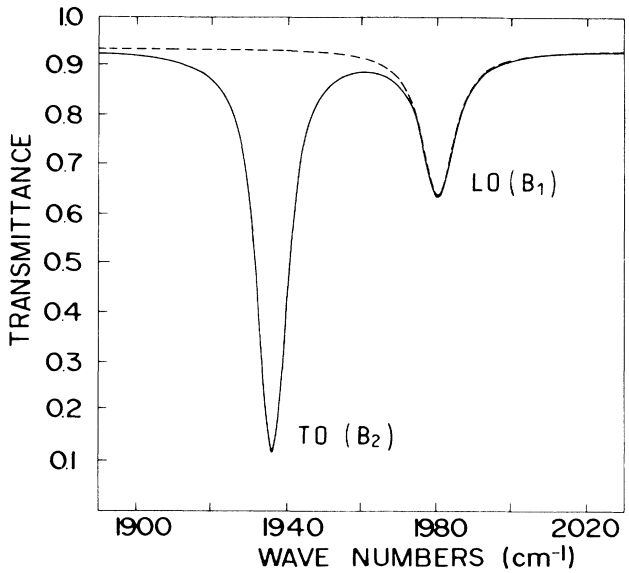

FIG. 3. Computed TM transmittance of a 15-μm-thick $Ba[Fe(CN)_5NO]\cdot 3H_2O$ crystal plate parallel to (100) in the NO stretching region for an incident ir beam subtending and angle of 5° with the **a** axis and with **E** parallel either to the (a,b) plane, solid line, or to the (a,c) plane, dashed line.

(42)] of orthorhombic (and higher symmetric) crystal plates with smooth surfaces and for the reflectance [Eq. (49a)] and transmittance [Eqs. (52) and (54)] of samples with rough surfaces.

The situation corresponding to the limiting reflectance of very thin anisotropic crystal films deposited on transparent dielectric [Eqs. (43)] or metallic [Eqs. (44)] substrates could not be easy to realize in practice because the difficulties in obtaining samples of very small thickness. In particular, however, Eq. (44b) still provides a qualitative explanation for the observation of peaks at only the LO-mode frequencies in the TM-polarized, off-axis ir reflectance spectrum from layers of anisotropic polycrystalline substances evaporated or mechanically deposited on a metallic substrate.[20] On the other hand, very thin films of isotropic materials are often obtained in multiphase stratified systems of physical interest. Studies on the reflection spectroscopy of these systems based upon the counterparts of Eqs. (43) and (44) that apply to the case of isotropic media can be found in Refs. 5 and 21.

Similar considerations as above apply to the limiting values of Eqs. (45) for the transmittance of very thin crystal films. In particular, the simple expressions (45) can be used to describe qualitatively the absorptions due to TO and LO vibrations in the transmittance spectrum of anisotropic crystal plates. For a full quantitative account of these absorptions we must recourse to the complete expressions (42), (52), and (54).

It is an usual practice in polarized ir spectroscopy of solids to measure LO mode frequencies by TM, off-axis transmittance of thin crystal plates (see, for example, Ref. 22). Berreman[5] has given a complete discussion regarding the coupling of LO modes to ir radiation in the case of very thin cubic crystal films. As discussed at the end of Sec. VI of the present work, the expressions (42b), (54), and (55) provide a quantitative description of the phenomenon in anisotropic crystal plates. These expressions have been employed to study the vibrational behavior of barium nitroprusside trihydrate (BNP), $Ba[Fe(CN)_5NO]\cdot 3H_2O$ [orthorhombic, space group C_{2v}^5 $(Pca2_1)$] in an spectral region including the strongly polar NO stretching mode. Figure 3 shows the computed polarized transmission spectra of a BNP crystal plate bounded by rough surfaces parallel to the (bc) plane in the range 1890–2030 cm^{-1}, calculated using Eqs. (54) and (55). The components of the dielectric tensor $\tilde{\epsilon}(\omega)$ of BNP in the above range were derived from reflection experiments and crystallographic information. The theoretical spectra are in good agreement with spectroscopic data (reported in Ref. 23) and show a sharp absorption band at about 1980 cm^{-1} (misassigned in Ref. 23) which is due to the NO longitudinal optic mode of factor-group symmetry species B_1 (polarized along the crystal **a** axis). The peak at about 1936 cm^{-1} corresponds to the NO transversal optic mode B_2 (polarized along **b**). A fuller account of these results will be published elsewhere.[24]

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