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Reflection spectroscopy for anisotropic materials: Direct determination of phase differences; validity of Fresnel formulas

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The reflectance of an anisotropic crystal is generally a tensor quantity even at normal incidence. Phase differences among the tensor components can be obtained from polarized reflectance measurements. A simple method for doing so is described and tested here. Possible applications of phase-difference information range from checking Kramers-Kronig evaluations of absolute phases to substituting for the Kramers-Kronig procedure. In addition, the following is proved, subject to some simple assumptions: If reflection extinction directions exist, the standard Fresnel equations may be used to derive optical constants (n's and k's), regardless of the anisotropy of the crystal. Moreover, extinction directions come in perpendicular pairs.

I. INTRODUCTION

The optical properties of a solid, such as its complex dielectric constant, are frequently determined by reflection spectroscopy at normal incidence. The amplitude of reflection is measured directly, and the phase is inferred from the amplitude *spectrum* by means of an integral (Kramers-Kronig) transformation.[1] Phase information obtained more directly, even for just a few frequencies, could be useful in a number of ways. Section III of this paper elaborates on this point.

The phase of reflected light can be measured directly by interferometric procedures,[2,3] though with a microcrystalline sample of interest in this laboratory, we have been unable to obtain satisfactory precision with one such procedure. For an anisotropic material, the reflectivity even at normal incidence is generally a tensor with four components, each of which has its own magnitude and phase. In the absence of absolute phase measurements, a direct determination of the difference between the phases of two reflectivity components could be useful. Such information can be extracted from the state of polarization of the light reflected from an appropriately polarized incident beam.

The state of polarization of a normally reflected beam may be investigated by a number of methods,[4,5] e.g., the analogs of methods used for oblique incidence on isotropic materials.[6] Several methods have, in fact, been introduced.[7-9] A very simple method for thus obtaining quantitative phase-difference information at normal incidence is described in Sec. IV, along with an experimental test on a highly anisotropic dye crystal.

Even for highly anisotropic absorbing crystals, there usually are directions of polarization for the incident beam ("extinction directions") such that the reflected beam has the same polarization. It is common practice to extract optical properties by application of the Fresnel formula to the amplitude and phase of reflection for such polarizations. It is not obvious *a priori* that this procedure is always justified. Justification is given in Sec. V on the basis of mild assumptions about the dielectric tensor and the not-so-mild assumption that the parallelism between incident and reflected polarizations is mathematically exact. It is also shown that the existence of one extinction direction implies the existence of another at right angles to the first. The reader who is interested only in Sec. V may skip Secs. III and IV with impunity.

Section II collects some necessary preliminaries for the rest of this paper.

II. PRELIMINARIES

Consider reflection of monochromatic light, at normal incidence, from a crystal surface lying in the x, y plane. (See Fig. 1.) Let the electric vectors of the incident and reflected beams have complex amplitudes $\vec{E}_i$ and $\vec{E}_r$, which are parallel to the surface. They are related by

$$\vec{E}_r = \begin{pmatrix} E_{rx} \\ E_{ry} \end{pmatrix} = \left[-\begin{pmatrix} r_{xx}e^{i\phi_{xx}} & r_{xy}e^{i\phi_{xy}} \\ r_{yx}e^{i\phi_{yx}} & r_{yy}e^{i\phi_{yy}} \end{pmatrix} \right] \begin{pmatrix} E_{ix} \\ E_{iy} \end{pmatrix} = -\underline{R}\,\vec{E}_i\,, \tag{1}$$

where $\underline{R}$ is the reflection amplitude tensor, and the minus sign ensures that the ϕ's are zero for reflection from an isotropic, transparent medium with refractive index >1.

Polarization of the incident and reflected beams will be construed as the polarization of $\vec{E}_i$ and $\vec{E}_r$. If the incident beam is polarized along an extinction direction, then $\vec{E}_r \parallel \vec{E}_i$. If the reflecting surface has two perpendicular extinction directions, these may be used as x and y axes, and $\underline{R}$ be-

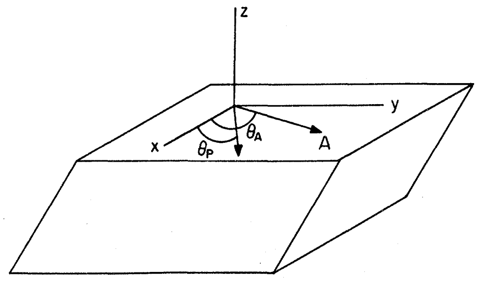

FIG. 1. Coordinate frame, polarizer angle θ_P, analyzer angle θ_A, and analyzer vector $\vec{A}$.

comes diagonal: $r_{xy}=r_{yx}=0$. Then two phase data, ϕ_{xx} and ϕ_{yy}, characterize $\underline{R}$. The method described in Sec. IV concentrates on the determination of the phase difference

$$\Delta\phi=\phi_{yy}-\phi_{xx}\,. \qquad (2)$$

For an isotropic medium, one may replace $\underline{R}$ in (1) by a scalar, $re^{i\phi}$. The Fresnel formula gives[1]

$$re^{i\phi}=(n+ik-1)/(n+ik+1)\,, \qquad (3)$$

where n is the real part of the complex index of refraction and k is the imaginary part (i.e., extinction coefficient). This formula can be solved for n and k, e.g.,

$$k=2r\sin\phi/(1+r^2-2r\cos\phi)\,. \qquad (4)$$

For an anisotropic material, it is commonly assumed that (3) or (4) can be applied to r_{xx} and ϕ_{xx} to obtain the optical constants pertaining to x-polarized light, $n_x(\omega)$ and $k_x(\omega)$, and similarly for y polarization (see Sec. V).

In the Kramers-Kronig procedure, the phases are computed from the amplitude spectra according to[1]

$$\phi(\omega)=\frac{2\omega}{\pi}\,\mathrm{P}\int_0^\infty \frac{\ln[r(\omega')]}{\omega^2-\omega'^2}\,d\omega'\,, \qquad (5)$$

where P stands for the "principal part"[10] ω and ω' are circular frequencies, and to ϕ and r one may attach any of the pairs of subscripts xx, yy, xy, or yx.

III. USES OF DIRECT PHASE INFORMATION

The value of directly measured phase-difference information does not seem to be generally appreciated. The method described in Sec. IV should make it rather easy to obtain phase-difference information, but, of course, the uses for the information are not tied to this method. Here are a number of possible uses for such information.

A. Test of Kramers-Kronig phase calculations

It is always desirable to check an indirect calculation against more direct measurements. In the present case, such a check may come from comparison with independent phase data or comparison of the derived optical constants with those obtained from oblique incidence reflection measurements or from transmission spectra. Each approach has been used occasionally.[8,11-15] Transmission data are hard to obtain at wavelengths of strong absorption.[13,16] In particular, for some strongly absorbing organic materials, crystals thin enough for transmission spectroscopy grow in a different form (possibly a different crystal structure) from that of larger crystals[15] so that a direct comparison of results from transmission and reflection spectroscopy is not possible.

There are several specific motivations for checking a Kramers-Kronig phase computation. An empirically based motivation is the reported gross failure of the procedure in a case where the phase has been measured directly[11] together with the significant discrepancies that are sometimes found between the computed optical constants and those obtained by more direct methods.[12] An *a priori* motivation is the number of possible sources of error in applying the standard Kramers-Kronig procedure such as the necessity of relying on a guessed model of the reflection behavior outside the experimental data range[1,12,13,17,18] and the sensitivity of the method to errors in the measured reflectance.[19] Although the resulting uncertainties are usually not too large, additional assurance may be welcome in specific cases. Finally, the expression for the phase as an integral over the reflectivity spectrum may itself not always be correct. It is recognized that the presence of a surface layer structure may invalidate this expression.[11,20] Even for reflection from a simple interface between vacuum and bulk material, the Kramers-Kronig formula (5) is less than securely founded.[21]

B. Absolute phase determination

Often, a crystal is opaque to y-polarized light, but is transparent enough to x-polarized light to allow the corresponding extinction coefficient k_x to be measured by transmission. Then the Fresnel formula (4) (with $k\rightarrow k_x$, $r\rightarrow r_{xx}$, and $\phi\rightarrow\phi_{xx}$) can be solved for ϕ_{xx}, and ϕ_{yy} itself can be obtained from a measurement of $\Delta\phi=\phi_{yy}-\phi_{xx}$. Then one can test the Kramers-Kronig results for the absolute phases as well as for their difference. If this procedure can be applied over the whole spectral region of interest, the Kramers-Kronig procedure may be avoided altogether, a fact of some value in cases[22] where the Kramers-Kronig procedure cannot be applied. Materials to which the present treatment is applicable include the present cyanine dye, tetracyanoquinodimethane (TCNQ)[18,23] and its complex with tetrathiafulvalene (TTF-TCNQ),[24] the mixed-valence compound $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$,[14] quinhydrone,[25] and xenon difluoride.[22]

If the material is nearly transparent to x-polarized light, one can take $\phi_{xx}=0$ without really measuring k_x. A procedure of this sort has been used previously on CdS,[11] ZnO,[11] and stressed ZnTe.[8] A criterion for $\phi_{xx}\approx 0$ is obtained from (4),

$$\sin\phi_{xx} \leqslant k_x(1+r_{xx})^2/2r_{xx}\,. \tag{6}$$

If the reflectance $r_{xx}{}^2 \sim 0.05$, it suffices to have $k_x \lesssim 10^{-2}$. Now, $k_x = 10^{-2}$ still represents absorption strong enough that crystal thicknesses of tens of microns are necessary for transmittance measurements. If, for this or some other reason, it is not possible to check that k_x is small enough, frequently a good indication is that r_{xx} is small (e.g., 5–10% for organic materials) and slowly varying through the spectral region of interest.

It is not hard to find the explicit solution of (4),

$$\phi_{xx} = \phi' - \phi'' \tag{7a}$$

or

$$\phi_{xx} = \pi - \phi' - \phi''\,, \tag{7b}$$

$$\phi' = \arcsin\left(\frac{k_x(1+r_{xx}{}^2)}{2r_{xx}(1+k_x^2)^{1/2}}\right)\,,\qquad \phi'' = \arcsin\left(\frac{k_x}{(1+k_x^2)^{1/2}}\right)\,. \tag{8}$$

One must judge between the two roots (7a) and 7(b) on further physical grounds. Typically, both ϕ' and ϕ'' will be small, and root (7b) will give ϕ_{xx} in the second quadrant ($\pi/2 \leqslant \phi_{xx} \leqslant \pi$). If $n_x \geqslant 1$, one can refer to the Fresnel formula (3) to show that ϕ_{xx} lies in the first quadrant and therefore, to select the root $\phi_{xx} = \phi' - \phi''$. Similar remarks apply to the use of (6). [Equations (7) and (8) naturally apply to isotropic materials as well.]

C. Introduction of measured phase information into the Kramers-Kronig procedure

The contribution of frequencies outside the experimental data range to the Kramers-Kronig integral is usually estimated by use of a model or extrapolation of the reflectance to those frequencies. Directly measured phase data can be added to the set of constraints used to adjust the model or extrapolation. Absolute phase values can be used to estimate this contribution to the integral directly.[26] (It should vary slowly, so few phase determinations should be required.) A variant of the Kramers-Kronig procedure can be used to reduce the sensitivity of the integral transformation to the unknown portion of the reflection spectrum by incorporating a known phase value at one frequency into the computation.[27]

If the Kramers-Kronig procedure is reliable for x polarization but not y (say), perhaps because of structure in the y reflectance continuing to the highest frequencies accessible, one could obtain ϕ_{yy} from the Kramers-Kronig computation of ϕ_{xx} plus a direct measurements of $\Delta\phi$.

IV. SIMPLE METHOD FOR MEASURING $\Delta\phi$

A. Principle

If the incident beam is linearly polarized obliquely to the two extinction directions, the reflected beam is in general elliptically polarized. Information about its state of polarization is obtained from the intensity passed through a linear analyzer as a function of analyzer position. The oblique incidence precursor of this method is the infrared work of Conn and Eaton, of Beattie, and of Hodgson.[28] More recently, Yamamoto and Miyauchi have used a phase-difference spectrum observed at normal incidence with crossed polarizer and analyzer to observe optical band gaps in the anisotropic semiconductor $CuGaS_2$.[9] The present study appears to be the first attempt to extract quantitative phase information in this way for normal incidence on anisotropic materials.

Suppose the incident beam is linearly polarized at an angle θ_P and the reflected beam is analyzed for linear polarization at an angle θ_A, where both angles are measured from the x axis towards the y axis. (See Fig. 1.) The intensity passed by the analyzer is $I(\theta_P,\theta_A) = (c/8\pi)\,|\vec{A}\cdot\vec{E}_r|^2$, where $\vec{A}$ is a unit vector in the analyzer direction and c is the speed of light. By expanding this expression according to (1), one can see how it expresses phase-difference information about $\underline{R}$. If the x and y axes are extinction directions,

$$I(\theta_P,\theta_A)/I_i = B^2 + C^2 + 2BC\cos\Delta\phi\,, \tag{9}$$

$$B = r_{xx}\cos\theta_P\cos\theta_A\,,\qquad C = r_{yy}\sin\theta_P\sin\theta_A\,,\qquad \Delta\phi = \phi_{xx} - \phi_{yy}\,, \tag{10}$$

where I_i is the intensity in the incident beam.

Measurements at three angles suffice to determine $\cos\Delta\phi$. These might be $\theta_A = 0$ and $\theta_A = \pi/2$, to obtain r_{xx} and r_{yy}, and θ_A equal to something else to obtain $\cos\Delta\phi$. Since r_{xx} and r_{yy} are generally required anyway, the cost of obtaining $\cos\Delta\phi$ is measurement at one additional angle. If one wishes to avoid measuring absolute reflectances, one may normalize the reflected intensity to unity at, say, $\theta_A=0°$. That is, one may measure an intensity ratio,

$$\frac{I(\theta_P,\theta_A)}{I(\theta_P,0)} = 1 + (D^2-1)\sin^2\theta_A + D\sin(2\theta_A)\cos\Delta\phi\,,$$

$$D=(r_{yy}/r_{xx})\tan\theta_P\,. \qquad (11)$$

From $\cos\Delta\phi$, one can determine $\Delta\phi$ except for its quadrant (1 or 4, 2 or 3); i.e., one can determine $|\Delta\phi|$ modulo 2π. For some purposes, this information may be enough. Or one may be able to guess the quadrant from physical considerations. If not, the proper quadrant can be determined by measuring $\sin\Delta\phi$ just accurately enough to determine its algebraic sign. One can do so by putting a fractional-wave plate (not necessarily a quarter-wave plate[4,5]) in the reflected beam ahead of the analyzer, with the axes of the plate parallel to the extinction directions of the reflecting surface (x and y axes). The effect is to replace $\Delta\phi$ in (9)–(11) by $\Delta\phi+\delta$, where δ is the phase difference caused by the fractional-wave plate. From (9) or (11), one now evaluates $\cos(\Delta\phi+\delta)=\cos\Delta\phi\cos\delta-\sin\Delta\phi\sin\delta$, from which $\sin\Delta\phi$ and $\Delta\phi$ modulo 2π may be extracted. Several variant procedures are obviously possible. Note also that few determinations of quadrant should ever be necessary on a given sample, since if the quadrant is known at one wavelength, it is known at neighboring wavelengths by continuity. Even if $\Delta\phi$ should equal 0 or π at some wavelength, the quadrant at shorter wavelengths can be identified from that at longer wavelengths, or *vice versa*, if $d(\Delta\phi)/d\omega\neq 0$ when $\Delta\phi=0$ or π.

B. Experimental test

We have investigated the quantitative reliability of the present method on microcrystals of the dye 1,1′-diethyl-2,2′-cyanine iodide, for which polarized reflection and transmission spectra are discussed elsewhere.[15] The crystals were grown on a glass slide by evaporation of a drop of methanolic solution of the dye (Eastman Organic Chemicals). Crystal surface areas suitable for reflectance measurements (no visible defects or dirt spots) were of the order of $2\times 2\ \mu m^2$.

A Leitz Ortholux petrographic microscope, described elsewhere,[29] was used with its built-in analyzer. With an isotropic reflection standard, the signals with polarizer and analyzer "crossed" and "parallel" were in a ratio ~1:2000. At each analyzer angle, the reflectance measurement was calibrated by comparison with the standard (Al mirror). The polarization of the incident light relative to the extinction directions of the crystal face was adjusted by rotating the microscope stage. The magnification required here necessitated a cone of incidence extending 15° from the surface normal.

The measurements reported here were performed on an unidentified[15] face of a crystal ~1000 Å thick. At 500-nm wavelength, the crystal was nearly transparent to x-polarized light, and its reflectance was highly anisotropic ($r_{yy}\sim 3r_{xx}$). A polarizer angle of $\theta_P=15°$ was chosen to make the x- and y-polarized components of the reflected light roughly equal in magnitude.

Figure 2 shows a plot of the reflectance ratios $I(\theta_P,\theta_A)/I(\theta_P,0)$ obtained from two separate series of measurements. The relatively large differences between run 1 and run 2 at large analyzer angles and the discrepancy between results at 15° and −165° are probably due to difficulties in obtaining identical focus settings for the crystal and the standard. Results at smaller angles appear to be more reliable. No data are reported at $\theta_A=-75°$ because it was not possible to calibrate the reflectance there.

The normalized reflection intensity should be given by (11). Data at −90° gave $D=0.80$ and 0.81

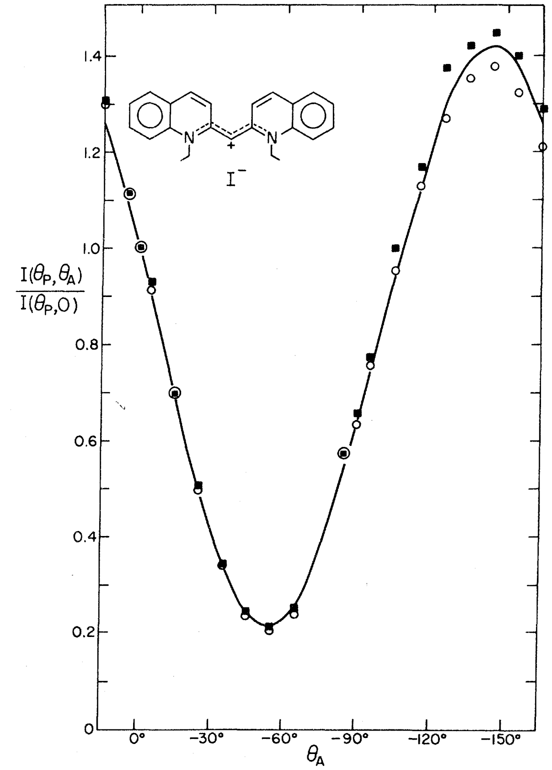

FIG. 2. Normalized reflection intensity as a function of analyzer angle θ_A with polarizer at $\theta_P=15°$. Experimental points from two runs are ○ and ■. Solid line is the theoretical result for $r_{yy}/r_{xx}=3.0$ and $|\Delta\phi|=44°$.

for the two runs. The data at analyzer angles between $-35°$ and $-55°$ all conformed to $0.71 \leqslant \cos \Delta\phi \leqslant 0.74$ and $43° \leqslant |\Delta\phi| \leqslant 45°$. This should be the best range of θ_A for obtaining $\cos\Delta\phi$, because its coefficient in (11) is large and the discrepancies noted at larger angles (e.g., near $-135°$) are avoided. A plot of (11) with $D=0.80$ and $|\Delta\phi|=44°$ is included in Fig. 2 to show the degree to which the dependence on θ_A has the theoretical form. The agreement with the experimental points is satisfactory.

The present material is transparent enough to light polarized along one extinction direction that the procedure described in subsection B can be applied to obtain absolute phase values as well as phase differences. Transmission and reflection measurements on a different crystal (~400 Å thick) gave, for the weakly absorbed polarization, $k_x = 0.022$, $r_{xx}=0.226$, and thus $\phi_{xx}=2°$ [see Eqs. (7) and (8)]. Combining this value with the estimate $43° \leqslant |\Delta\phi| \leqslant 45°$ and the assumption that $\phi_{yy} \geqslant 0$ gives $45° \leqslant \phi_{yy} \leqslant 47°$. This evaluation agrees reasonably well with the 53° obtained from a subtractive Kramers-Kronig transformation[27] applied to the 1000-Å crystal that used one assumed phase value, $\phi_{yy}(755\ \text{nm})=0$. The Kramers-Kronig results themselves had an element of uncertainty because of interference oscillations in the low-frequency transparent region[15] that were averaged manually before submitting the data to Kramers-Kronig analysis. The agreement between directly measured and Kramers-Kronig phase values is regarded as confirmation of the latter. Using $\phi_{yy} = 46°$ at 500 nm in the subtractive Kramers-Kronig procedure produced a phase spectrum and optical constants in substantial agreement with the results of the previous transformation.

C. Conclusion

We believe that the method investigated here does work satisfactorily. The experimental difficulties encountered, particularly that concerning the reproducibility of focus, seem to be more a result of the very small crystal studied than an inherent characteristic of the method. The method should be easy to automate for application throughout a spectrum, and it demands only the same equipment as is required anyway for reflection spectroscopy on anisotropic materials.

V. VALIDITY OF FRESNEL EQUATIONS

It is common practice to use the Fresnel equation (4) to extract a polarized absorption spectrum $k_x(\omega)$, say, from a reflection spectrum for light polarized along an extinction direction.[13-15,18,29,30] Two premises are involved: that, for this polarization, only one wave propagates inside the crystal, and that its complex refractive index governs the amplitude reflection coefficient in the same way as for an isotropic medium. Both premises are *almost* obvious. The difficulty with the first is that, in an absorbing anisotropic material, the propagated waves are in general elliptically polarized.[31] One must be convinced that an extinction direction cannot represent simultaneous coupling of the incident and reflected beams to two elliptically polarized waves in the crystal such that the boundary conditions are satisfied with $\vec{E}_i \parallel \vec{E}_r$. The second premise must be examined explicitly on the basis of the boundary conditions.

In this section, it is shown that both premises are indeed justified—that is, that the Fresnel formula may indeed be used to derive an absorption (and refractive index) spectrum—given the existence of an exact extinction direction and some mild assumptions about the dielectric tensor of the crystal. In addition, it is shown that the presence of one extinction direction implies the presence of another at 90° to the first, provided that the dielectric tensor is symmetric. The discussion could probably be based on existing treatments of reflection from anisotropic crystals,[32] but it seems easier and more instructive to give an elementary and fairly self-contained derivation.

The present discussion fails to connect with experiment in a significant way. Experiment can establish the existence, not of a mathematically exact extinction direction, but only of a direction in which crossed polarizer and analyzer yield a signal that is smaller than noise or experimental error. What is called for is, ideally, a set of error bounds on the extinction coefficient, refractive index, and degree of ellipticity of the major wave propagated in the crystal at an "extinction" setting, in terms of an experimental upper bound to the signal that may exist, undetected, at this setting. It is hoped that the following discussion can provide a basis for such further development, should the need arise.

Consider reflection from a crystal surface lying in the x, y plane, with crystal below ($z<0$) and vacuum above ($z>0$). (See Fig. 1.) Represent the normally incident and reflected beams by complex electric vectors $\vec{\mathcal{E}}_i = \vec{E}_i \exp[-i\omega(t+z/c)]$ and $\vec{\mathcal{E}}_r = \vec{E}_r \exp[-i\omega(t-z/c)]$. Assume that only normal transmitted waves $\vec{\mathcal{E}}_j = \vec{E}_j \exp[-i\omega(t+\hat{n}_j z/c)]$ need be considered inside the crystal ($j=1,2,\ldots$). Here $\vec{E}_i$, $\vec{E}_r$, and $\vec{E}_j$ are complex vectors ($\vec{E}_i$ and $\vec{E}_r$ parallel to the surface), ω is circular frequency, t is time, c is the speed of light in vacuo, and $\hat{n}_j = n_j + ik_j$ is the complex refractive index for the jth transmitted wave with real and imaginary parts n_j and k_j. It is assumed that $n_j > 0$ and $k_j \geqslant 0$.

The corresponding magnetic fields have the same form as the electric fields, with complex amplitudes $\vec{H}_i, \vec{H}_r, \vec{H}_j$ $(j=1,2,\ldots)$. The necessary Maxwell equations are[31,33]

$$\hat{n}_j \vec{e}_z \times \vec{H}_j = \underline{\hat{\epsilon}}\,\vec{E}_j, \quad \hat{n}_j \vec{e}_z \times \vec{E}_j = -\vec{H}_j, \qquad (12)$$

where $\underline{\hat{\epsilon}}$ is the complex dielectric tensor, $\vec{e}_z$ is a unit vector in the positive z direction, and the magnetic permeability has been equated with 1. Combining Eq. (12) gives

$$\hat{n}_j^2 \vec{E}_{j\perp} = \underline{\hat{\epsilon}}\,\vec{E}_j, \quad \vec{E}_{j\perp} = \begin{pmatrix} E_{jx} \\ E_{jy} \\ 0 \end{pmatrix}. \qquad (13)$$

Assume that $\underline{\hat{\epsilon}}$ has an inverse $\underline{\hat{\epsilon}}^{-1}$. Then no more than two transmitted waves $\vec{\mathcal{E}}_j$ can be linearly independent. The key fact is that any set of $\vec{E}_j$'s is linearly dependent if and only if the $\vec{E}_{j\perp}$'s are, as is readily seen by writing (13) in the form $\vec{E}_j = \hat{n}_j^2 \underline{\hat{\epsilon}}^{-1} \vec{E}_{j\perp}$. Since the $\vec{E}_{j\perp}$'s lie in the x, y plane, there are at most two $\vec{E}_{j\perp}$'s, or two $\vec{E}_j$'s, that are linearly independent. Suppose there is only one, $\vec{E}_1$. Then all $\vec{E}_j$'s are parallel and correspond to the same value of $\hat{n}_j$ because of (13) and the assumption that each $\hat{n}_j$ lies in the first quadrant (whereby $\hat{n}_j^2 = \hat{n}_1^2$ implies $\hat{n}_j = \hat{n}_1$). Then every $\vec{\mathcal{E}}_j$ is a multiple of $\vec{\mathcal{E}}_1$, and there is only one independent transmitted wave. Suppose, instead, there are two independent amplitudes, $\vec{E}_1$ and $\vec{E}_2$. If there is a transmitted wave $\vec{\mathcal{E}}_3$ that is linearly independent of $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$, its amplitude can be written as $\vec{E}_3 = a\vec{E}_1 + b\vec{E}_2$ with nonzero coefficients a and b. From (13) one obtains

$$\hat{n}_3^2 \vec{E}_{3\perp} = a\hat{n}_1^2 \vec{E}_{1\perp} + b\hat{n}_2^2 \vec{E}_{2\perp}. \qquad (14)$$

Since each $\hat{n}_j \neq 0$ and the expansion of $\vec{E}_3$ is unique, $\hat{n}_1^2 = \hat{n}_2^2 = \hat{n}_3^2$ and $\hat{n}_1 = \hat{n}_2 = \hat{n}_3$. Thus the propagating wave $\vec{\mathcal{E}}_3$ is a linear combination of $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$, contrary to assumption; only $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$ are linearly independent. Assume, henceforth, that there are two possible independent transmitted waves, $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$.

Now suppose that an extinction direction exists—say, parallel to the x axis—and that the incident beam is polarized along it. It will be shown that only a single transmitted wave is present in the crystal. *A priori*, the transmitted field could be $a_1\vec{\mathcal{E}}_1 + a_2\vec{\mathcal{E}}_2$ with a_1 and a_2 constants. The necessary boundary conditions are continuity of the electric and magnetic field components parallel to the reflecting surface, plus the specifications $\vec{E}_i \parallel \vec{E}_r \parallel x$ axis and $\vec{H}_i \parallel \vec{H}_r \parallel y$ axis. The $\vec{H}$'s may be expressed in terms of $\vec{E}$'s by (12) and its analog in vacuo. Two of the resulting equations are

$$a_1 E_{1y} + a_2 E_{2y} = 0, \quad \hat{n}_1 a_1 E_{1y} + \hat{n}_2 a_2 E_{2y} = 0. \qquad (15)$$

If $\hat{n}_1 \neq \hat{n}_2$, it follows that $a_1 E_{1y} = a_2 E_{2y} = 0$. Thus, either a_1 or a_2 vanishes, or else $E_{1y} = E_{2y} = 0$ and $\vec{E}_{1\perp} \parallel \vec{E}_{2\perp}$. The latter condition would imply $\vec{E}_1 \parallel \vec{E}_2$ and $\hat{n}_1 = \hat{n}_2$, a contradiction. Thus, if $\hat{n}_1 \neq \hat{n}_2$, either $a_1 = 0$ or $a_2 = 0$, and only one wave is present in the crystal. On the other hand, if $\hat{n}_1 = \hat{n}_2$, any linear combination of $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$ is itself a plane wave with the same complex refractive index, which one is free to identify as $\vec{\mathcal{E}}_1$ or $\vec{\mathcal{E}}_2$ by rechoosing $\vec{E}_1$ and $\vec{E}_2$ appropriately.

Name the one wave in the crystal $\vec{\mathcal{E}}_1$. (Thus, $a_2 = 0$.) For it, $\hat{n}_1$, n_1, and k_1 have the same significance as for the transmitted wave in an isotropic absorbing medium. According to (15), $E_{1y} = 0$, i.e., the x, y projection of $\vec{E}_1$ is parallel to the extinction direction. A second pair of equations resulting from the boundary conditions

$$\begin{aligned} E_{ix} + E_{rx} &= a_1 E_{1x} + a_2 E_{2x}, \\ E_{ix} - E_{rx} &= a_1 \hat{n}_1 E_{1x} + a_2 \hat{n}_2 E_{2x} \end{aligned} \qquad (16)$$

immediately gives the Fresnel equation equivalent to (3),

$$\frac{E_{rx}}{E_{ix}} = \frac{1-\hat{n}_1}{1+\hat{n}_1}. \qquad (17)$$

The polarization of the wave in the crystal is that of $\vec{D}_1$,[31] where $\vec{D}_1 = \underline{\hat{\epsilon}}\,\vec{E}_1 = \hat{n}_1^2 \vec{E}_{1\perp}$, and is parallel to the x axis. Thus polarization along an (exact) extinction direction excites a linearly polarized wave in the crystal.

Finally, suppose $\underline{\hat{\epsilon}}$ is a symmetric tensor,[34,35] though complex. Then the presence of one extinction direction implies another at 90° to the first. The projected amplitude of the second complex wave $\vec{E}_{2\perp}$ is (or can be chosen to be) perpendicular to $\vec{E}_{1\perp}$: If $\hat{n}_1 = \hat{n}_2$, one may construct $\vec{E}_{2\perp} \perp \vec{E}_{1\perp}$; and if $\hat{n}_1 \neq \hat{n}_2$, from (13) one has

$$\vec{E}_{2\perp} \cdot \vec{E}_{1\perp} = \vec{E}_2 \cdot \vec{E}_{1\perp} = \hat{n}_1^{-2} \vec{E}_2 \cdot (\underline{\hat{\epsilon}}\,\vec{E}_1) \qquad (18)$$

$$= \vec{E}_1 \cdot \vec{E}_{2\perp} = \hat{n}_2^{-2} \vec{E}_1 \cdot (\underline{\hat{\epsilon}}\,\vec{E}_2). \qquad (19)$$

But $\vec{E}_2 \cdot (\underline{\hat{\epsilon}}\,\vec{E}_1) = \vec{E}_1 \cdot (\underline{\hat{\epsilon}}\,\vec{E}_2)$, so the equality of the right-most members of (18) and (19) implies that both are zero, i.e., that $\vec{E}_{2\perp} \cdot \vec{E}_{1\perp} = 0$. Thus, $\vec{E}_{2\perp}$ is parallel to the y axis, and $E_{2x} = 0$. This time, suppose the incident beam is y polarized. Equations (16) now give $a_1 = 0$ and $E_{rx} = 0$, so $\vec{E}_r$ is also y polarized, and the y axis is a second extinction direction.

Most of the assumptions built into the preceding derivation should be evident. One that bears mention is the assumption that only normal waves,[33] and two of them, need be considered. Such need not always be the case.[33,36] It may also be worth indicating an example of a crystal surface that has no extinction directions.[37]

Note added in proof. The value of ellipsometry performed at normal incidence on anisotropic materials has recently been pointed out.[38]

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