Reflection ellipsometry of uniaxial crystals

John Lekner

Department of Physics, Victoria University of Wellington, Wellington, New Zealand

Received May 17, 1996; accepted January 10, 1997; revised manuscript received January 16, 1997

A method is proposed to determine the optical constants of uniaxial crystals by ellipsometry. The same scheme works for absorbing and nonabsorbing crystals. The quantities measured are ratios of the four reflection amplitudes r_{ss}, r_{sp}, r_{ps}, and r_{pp}, and angles. The common zeros of r_{sp} and r_{ps} determine the symmetry direction (optic axis in the plane of incidence) at which r_{pp}/r_{ss} is measured to obtain one equation linking the ordinary and extraordinary dielectric constants ϵ_o and ϵ_e, and the inclination χ of the optic axis to the normal to the reflecting plane. Measurement of r_{pp}/r_{ss} at right angles to the symmetry direction, and of r_{sp}/r_{ps} away from the symmetry direction gives two more equations for the unknowns. The method can be used on microscopic crystal faces. © 1997 Optical Society of America [S0740-3232(97)02006-1]

1. INTRODUCTION

The purpose of this paper is to propose a simple scheme for determining the dielectric constants and the orientation of the optic axis of a uniaxial crystal by reflection ellipsometry. The optic axis direction is specified by two angles χ and ϕ relative to the laboratory frame (defined in Section 2); χ, ϕ and the ordinary and extraordinary dielectric constants ϵ_o and ϵ_e are the four unknowns to be found, and I shall show how these can be determined from ratios of the four reflection amplitudes r_{ss}, r_{sp}, r_{ps}, and r_{pp}. If the crystal is nonabsorbing, the reflection amplitudes are all real and four real numbers are determined by the measurement of four real quantities (three reflection amplitude ratios and one angle). When the crystal is absorbing, the dielectric constants $\epsilon_o = {n_o}^2$ and $\epsilon_o = {n_e}^2$ are complex, the reflection amplitudes are also complex, and both real and imaginary parts are needed. The same method will, however, work for both absorbing and nonabsorbing crystals.

Biaxial crystals are not covered by the proposed scheme, which begins by setting an experimental criterion in terms of the sp and ps reflection amplitudes for whether the crystal is uniaxial or not.

2. REFLECTION BY A UNIAXIAL CRYSTAL

The reflection geometry is shown in Fig. 1. The medium of incidence, of refractive index $n_1 = \sqrt{\epsilon_1}$, occupies $z > 0$. The reflecting face of the crystal is the xy plane, the z axis is the inward normal, the zx plane is the plane of incidence, and θ is the angle of incidence. The optic axis, along the unit vector

$$\mathbf{c} = (\alpha, \beta, \gamma) \qquad \alpha^2 + \beta^2 + \gamma^2 = 1, \tag{1}$$

may be equivalently expressed in terms of the polar and azimuthal angles χ and ϕ relative to the laboratory xyz frame:

$$\mathbf{c} = (\sin\chi\cos\phi, \sin\chi\sin\phi, \cos\chi). \tag{2}$$

The reflection amplitudes r_{ss}, r_{sp}, r_{ps}, and r_{pp} determine the reflection properties completely. (The subscripts s and p refer to electric field components normal and parallel to the plane of incidence: r_{sp}, for example, gives the reflected electric field amplitude in the plane of incidence when the incident light wave is polarized normal to the plane of incidence.) Ellipsometry of anisotropic media is discussed in Refs. 1 and 2; the latter shows that each of the four usual ellipsometric arrangements measures one of the ellipsometric ratios

$$\rho_P = \frac{r_{pp} + r_{sp}\tan P}{r_{ps} + r_{ss}\tan P}, \qquad \rho_A = \frac{r_{pp} + r_{ps}\tan A}{r_{sp} + r_{ss}\tan A}, \tag{3}$$

where P is the angle between the polarizer easy axis and the incident p direction, and A is the angle between the analyzer easy axis and the reflected p direction. The angles P and A are measured from the p toward the s directions, with the vectors $\mathbf{p}$, $\mathbf{s}$, and $\mathbf{k}$ (the wave vector) forming a right-handed triplet.

For uniaxial crystals the reflection amplitudes are known analytically.[3,4] We shall not need the full formulas here, only the following results: r_{sp} and r_{ps} are identically zero for isotropic reflectors, and for uniaxial crystals they have the form (F is the same for r_{sp} and r_{ps})

$$r_{sp} = \beta(\alpha q_o + \gamma K)F \qquad r_{ps} = \beta(\alpha q_o - \gamma K)F \tag{4}$$

where $K = n_1(\omega/c)\sin\theta$ is the x component of the wave vector of the incident, the reflected, and the transmitted waves, and $q_o = [\epsilon_o(\omega/c)^2 - K^2]^{1/2}$ is the normal component of the ordinary wave vector in the crystal. For the ss and pp amplitudes, we shall need the values taken when the optic axis lies in the plane of incidence, where $\beta = 0$, $\sin\phi = 0$. These are[3–5]

$$r_{ss}(\beta = 0) = \frac{q_1 - q_o}{q_1 + q_o} \qquad r_{pp}(\beta = 0) = \frac{Q - Q_1}{Q + Q_1} \tag{5}$$

where ${q_1}^2 = \epsilon_1(\omega/c)^2 - K^2$, and $Q_1 = q_1/\epsilon_1$, and $Q = q_\gamma/n_o n_e$ with

$${q_\gamma}^2 = \epsilon_\gamma(\omega/c)^2 - K^2, \qquad \epsilon_\gamma = \epsilon_o + \gamma^2(\epsilon_e - \epsilon_o). \tag{6}$$

From Eq. (5) we obtain the quantity

0740-3232/97/0601359-04$10.00

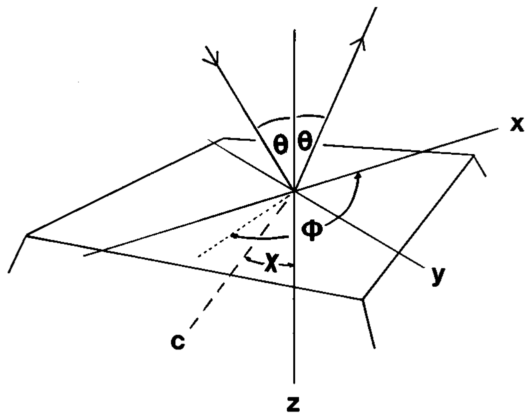

Fig. 1. Reflection by a uniaxial crystal: xy is the reflecting face and zx is the plane of incidence, with the inward normal along the z-axis. The optic axis **c** (long-dashed line) is at angle χ to the normal, and the plane containing **c** and the z-axis cuts the xy plane at angle ϕ to the x axis.

$$r_1 \equiv \left(\frac{r_{ss} - r_{pp}}{r_{ss} + r_{pp}}\right)_{\beta=0} = \frac{\epsilon_1 q_o Q - q_1{}^2}{q_1(q_o - \epsilon_1 Q)}. \tag{7}$$

We shall also use the value of the same ratio when $\cos\phi = 0$ ($\alpha = 0$):

$$r_2 \equiv \left(\frac{r_{ss} - r_{pp}}{r_{ss} + r_{pp}}\right)_{\alpha=0} = \frac{[(1-\gamma^2)\epsilon_o + \gamma^2\epsilon_1 \sin^2\theta][\epsilon_1 q_o q_e - \epsilon_o q_1{}^2]}{q_1[(1-\gamma^2)\epsilon_o(\epsilon_o q_e - \epsilon_1 q_o) + \gamma^2\epsilon_1(\epsilon_o q_o - \epsilon_1 q_e)\sin^2\theta]} \tag{8}$$

where (when $\alpha = 0$)

$$q_e^2 = \frac{\epsilon_o}{\epsilon_\gamma}[\epsilon_e(\omega/c)^2 - K^2]. \tag{9}$$

3. DETERMINATION OF THE CRYSTAL PARAMETERS

The crystal is mounted on a support stage which can be rotated about the z-axis (the normal to the reflecting face). It is important that the stage can be adjusted so that the angle of incidence does not change on rotation. The reflection amplitudes r_{sp} and r_{ps} are determined first. (Actually the ratios r_{sp}/r_{ss} and r_{ps}/r_{ss} are found: see Appendix A.)

1. If the ratios are zero at all values of the azimuthal angle ϕ, the crystal is isotropic (in which case the known inversion[6] of r_p/r_s obtained from ellipsometry can be used), or reflection is from the basal face (the one perpendicular to the optic axis). For reflection from the basal plane, with the optic axis coinciding with surface normal, $\chi = 0$ and $\gamma = 1$, and the formulas (5) apply, with

$$Q^2 = \frac{\epsilon_e(\omega/c)^2 - K^2}{\epsilon_o\epsilon_e}. \tag{10}$$

Measurement of the ratios r_1 and r_2 then gives two equations in the two remaining unknowns, ϵ_o and ϵ_e. (If the crystal is absorbing, r_{ss} and r_{pp} will be complex and so will r_1 and r_2, which then determine the complex dielectric constants ϵ_o and ϵ_e.)

2. If the reflection amplitudes r_{sp} and r_{ps} are not identically zero, from Eq. (4) they will have two common zeros as the uniaxial crystal is rotated through 360°. These zeros occur at $\beta = 0$, i.e., at $\phi = 0$ and π. (If r_{sp} and r_{ps} are not zero together twice in a full rotation, the crystal is not uniaxial.) When the crystal is aligned so that r_{sp} and r_{ps} are both zero, the optic axis lies in the plane of incidence, and Eq. (7) (with $Q = q_\gamma/n_o n_e$) gives the experimental value r_1 of $(\epsilon_1 q_o Q - q_1^2)/q_1(q_o - \epsilon_1 Q)$, while Eq. (8) relates the experimental value r_2 to the same unknown quantities ϵ_o, ϵ_e and $\gamma = \cos\chi$.

If the crystal is now rotated away from the $\beta = 0$ ($\phi = 0$ or π) direction, the ratio r_{sp}/r_{ps} can be measured. From Eq. (4),

$$r_3 \equiv \frac{r_{sp} + r_{ps}}{r_{sp} - r_{ps}} = \frac{\alpha q_o}{\gamma K} = \tan\chi\cos\phi\,\frac{q_o}{K}. \tag{11}$$

In the final expression of Eq. (11), $K = n_1(\omega/c)\sin\theta$ is given by the angle of incidence, and ϕ is a known rotation angle. (Since χ lies between 0 and $\pi/2$, $\tan\chi$ is positive, and the sign of r_3 removes the 0, π ambiguity in ϕ.) We thus have three relations, arising from the equations for the theoretical values of the experimentally determined ratios r_1, r_2, and r_3, so that the unknowns ϵ_o, ϵ_e and $\gamma = \cos\chi$ can be found numerically. We can solve Eq. (11) for $\cos^2\chi = \gamma^2$ in terms of q_o and r_3:

$$\gamma^2 = \frac{(q_o\cos\phi)^2}{(q_o\cos\phi)^2 + K^2 r_3{}^2}, \tag{12}$$

substitute into r_1 and r_2 (which do not depend on the sign of γ), and then solve for ϵ_o and ϵ_e.

I have not been able to obtain analytic solutions for ϵ_o and ϵ_e in terms of the measured ratios r_1, r_2, and r_3, which enter into Eqs. (7) and (8) after the substitution in Eq. (12) is made. It is possible to eliminate one of the unknowns and obtain a polynomial equation for the other, however: We solve Eq. (7) for Q and square and solve r_2 for q_e and square. Using Eq. (9) and $q_\gamma^2 = q_o{}^2 + \gamma^2(\epsilon_e - \epsilon_o)(\omega/c)^2$, respectively, we obtain two equations, $z_1 = 0$ and $z_2 = 0$. Both are linear in ϵ_e. We solve these for ϵ_e and equate the two values. This gives an equation $Z = 0$. Z reduces to a polynomial of the tenth degree in q_o on substituting $q_o{}^2 + K^2$ for $\epsilon_o(\omega/c)^2$. I have not been able to factor this polynomial to isolate the physical root, but it is useful in the estimation of inversion errors, to be discussed in Section 4.

4. EXAMPLE AND DISCUSSION

We have seen how the dielectric constants and the optic axis orientation of a uniaxial crystal may be determined by ellipsometry. If the crystal is absorbing, the complex reflection amplitudes must be measured. If the crystal is not absorbing, there will be a Brewster angle θ_{pp} at which $r_{pp}(\beta = 0)$ is zero. This angle is given by[4]

$$\tan^2\theta_{pp}(\beta = 0) = \frac{\epsilon_o\epsilon_e - \epsilon_1\epsilon_\gamma}{\epsilon_1(\epsilon_\gamma - \epsilon_1)}, \tag{13}$$

and at this angle of incidence $r_1 = 1$ for all transparent uniaxial crystals. The equation $r_1 = 1$ does contain information, however, so there is no need to avoid measurement at the Brewster angle. Angles to be avoided are those at which r_1 and r_2 give the same information, for example normal incidence, since there r_3 becomes infinite and r_1 and $-r_2$ tend to the same quantity, namely, $n_1 n_o(n_\gamma - n_e)/(n_o{}^2 n_e - n_1{}^2 n_\gamma)$. Highly oblique incidence is likewise not recommended, since at glancing incidence r_{sp} and r_{ps} go to zero, while $r_{ss} \to -1$ and $r_{pp} \to 1$. Finally, ϕ should not be a multiple of $\pi/2$ in the measurements of r_{sp} and r_{ps} [cos $\phi = \pm 1$ makes both amplitudes zero, while cos $\phi = 0$ annihilates r_3.

Figure 2 shows the reflection amplitudes for reflection from a cleavage face of calcite, as a function of the azimuthal angle ϕ, at 45° angle of incidence. The calcite cleavage faces are parallelograms with angles $A = 101°55'$ and $180° - A = 78°5'$. The optic axis makes equal angles with all faces at a blunt corner.[7] Thus the optic axis is at angle χ to each face normal, where

$$\gamma = \cos \chi = \frac{1}{\sqrt{3}} \tan(A/2), \tag{14}$$

which gives $\gamma = 0.7119$ and $\chi = 44.61° = 44°37'$. The $\phi = 0$, π direction lies along the bisector of A at the blunt corners of each face. The direction cosines of the optic axis are α, β, and γ, where

$$\alpha = N \cos \phi, \qquad \beta = N \sin \phi, \qquad N = \frac{\sqrt{1 + 2\cos A}}{\sqrt{3}\cos(A/2)} \tag{15}$$

($N = 0.7023$ for calcite). The refractive indices at the He–Ne wavelength of 633 nm are $n_o = 1.655$ and $n_e = 1.485$.

We note that $r_{ps}(\phi + \pi) = r_{sp}(\phi)$. This holds for reflection from all uniaxial crystals and follows from the general formulas derived in Ref. 3. Expressed in terms of the direction cosines α, β, and γ of the optic axis, the relation reads

$$r_{ps}(-\alpha, -\beta, \gamma) = r_{sp}(\alpha, \beta, \gamma). \tag{16}$$

(This relation is consistent with Eqs. (4) but does not follow from them, since it must also be shown that the function F is independent of the signs of the direction cosines. The latter result follows by methods similar to those used in Ref. 4.)

We also note that r_{ss} and r_{pp} repeat twice as ϕ ranges through 2π, in accord with the fact that r_{ss} and r_{pp} are invariant with respect to the change of sign of any of the direction cosines.[4] Thus $r_{ss}(\phi + \pi) = r_{ss}(\phi)$, $r_{pp}(\phi + \pi) = r_{pp}(\phi)$, in contrast to r_{sp} and r_{ps}, which have a period of 2π in ϕ.

Finally, we note the magnitudes of the reflection amplitudes. Bounds on the reflection amplitudes have been discussed in Ref. 5; in general, the sp and ps amplitudes are small, and hence an accurate value of the ratio $(r_{sp} + r_{ps})/(r_{sp} - r_{ps})$ in Eq. (11) may be difficult to determine. Thus the angle χ between the optic axis and the normal to the reflecting surface may be difficult to determine accurately by this method.

Sensitivity to experimental error is explored in Figs. 3 and 4, for calcite and for strongly absorbing selenium. In both cases the inversion is robust, with 10% errors leading to errors of the same magnitude or smaller, except that the deduced values of ϵ_o for selenium are very sensitive to errors in r_2.

It is concluded that the method proposed here is suitable for rapid but not highly accurate determination of uniaxial crystal parameters, with the advantages over orthodox[8–10] methods and recently proposed[11] methods that measurements can be made on crystals of microscopic size, that the same technique is applicable to absorbing as well as to transparent crystals, and that im-

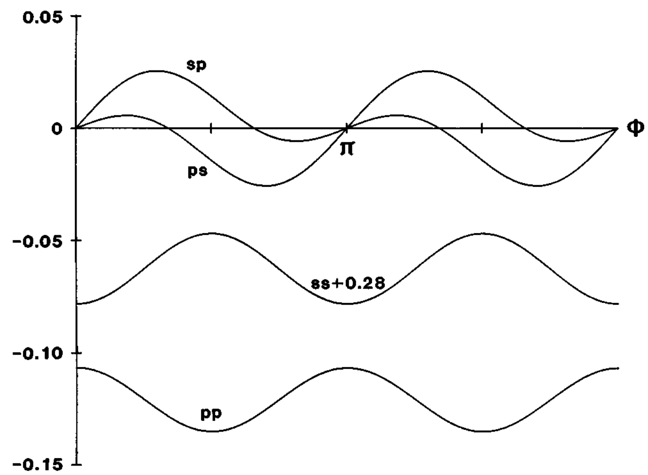

Fig. 2. Theoretical reflection amplitudes for the cleavage faces of calcite, as a function of the azimuthal angle ϕ, at 45° angle of incidence. The azimuthal angle goes from 0 to 2π as the crystal is rotated a full revolution. The angle between the normal to a cleavage plane and the optic axis is 44.61°. The refractive indices at 633 nm are $n_o = 1.655$, $n_e = 1.485$. Note the common zeros of r_{sp} and r_{ps} at $\phi = 0$ and π and also that the largest amplitude r_{ss} has been brought into the figure by adding 0.28.

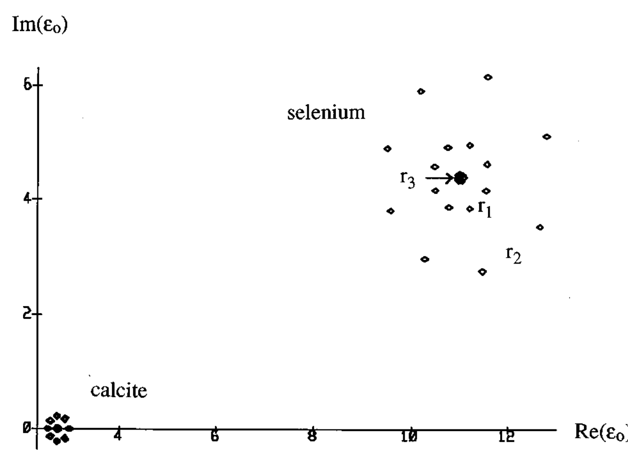

Fig. 3. Deduced ϵ_o values for calcite and selenium at $\phi = 45°$ and $\theta = 45°$, assuming 10% errors in the measured values of r_1, r_2, and r_3. The plotted values are obtained by varying r_1, r_2, and r_3 by 10% in magnitude away from their exact values, with eight different phases equally spaced around the unit circle, so that $|r - r^{\text{exact}}| = |r^{\text{exact}}|/10$. The true values of ϵ_o are $(1.655)^2 \approx 2.739$ for calcite at 633 nm and $(3.38 + 0.65i)^2 \approx 11.0 + 4.4i$ for selenium at 620 nm.

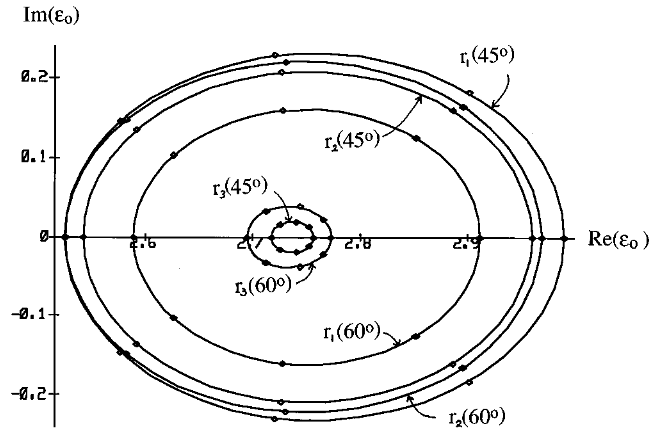

Fig. 4. Detail of the calcite error ovals, at $\phi = 45°$ and $\theta = 45°$ and 60°. The deduced ϵ_o values are obtained by taking 10% magnitude errors in r_1, r_2, and r_3, as in Fig. 3. The curves are ellipses fitted to the two points on the real axis, one focus being at the exact value $\epsilon_o = (1.655)^2 \approx 2.739$. The ellipses all have small ellipticities, ranging from 0.037 for the r_2 (60°) ellipse to 0.137 for the r_3 (60°) ellipse. The r_3 errors orbit about the right focus, the others about the left focus.

mersion in liquids of similar refractive index is not required.

APPENDIX A: EXTRACTION OF REFLECTION AMPLITUDE RATIOS

Ellipsometry can determine the relative phases of reflected waves of orthogonal polarizations, since the components of these polarizations along the analyzer easy axis are superposed and brought into interference. Of the two ellipsometric ratios given in Eqs. (3), the polarizer-sample-compensator-analyzer and polarizer-sample-modulator-analyzer configurations measure[2]

$$\rho_P = \frac{r_{pp} + r_{sp} \tan P}{r_{ps} + r_{ss} \tan P}. \tag{A1}$$

(The configurations with compensator or modulator before the sample measure ρ_A, which has the form of Eq. (A1) with r_{sp} and r_{ps} interchanged and A replacing P.)

Measurement of ρ_P at N different values of the polarizer angle P gives N linear homogeneous equations for the unknowns r_{ss}, r_{sp}, r_{ps}, and r_{pp}. Only the ratios of the reflection amplitudes can be found from these experimental values. Three measurements are thus sufficient to determine the three independent ratios. For example, we can set $P = 0$, $\pi/4$, and $\pi/2$, so $\tan P$ takes the values 0, 1, and ∞, and measure the corresponding complex numbers ρ_0, ρ_1 and ρ_∞. Solving for r_{sp}, r_{ps}, and r_{pp} in terms of r_{ss} then gives

$$r_{sp} = \rho_\infty r_{ss} \qquad r_{ps} = \frac{\rho_1 - \rho_\infty}{\rho_0 - \rho_1} r_{ss}$$

$$r_{pp} = \frac{\rho_0(\rho_1 - \rho_\infty)}{\rho_0 - \rho_1} r_{ss}. \tag{A2}$$

Extra measurements provide a check on the accuracy of the data. For example, if P is set to $-\pi/4$ (so $\tan P = -1$), the resulting measurement ρ_{-1} will be consistent with the previous measurements ρ_0, ρ_1, and ρ_∞ if

$$\rho_{-1} = \frac{\rho_0\rho_1 - 2\rho_0\rho_\infty + \rho_1\rho_\infty}{2\rho_1 - \rho_0 - \rho_\infty}. \tag{A3}$$

In practice this consistency relation will not be satisfied exactly, because of experimental error. In addition to the solutions in Eqs. (A2) in terms of $\{\rho_0, \rho_1, \rho_\infty\}$, there are solutions sets for r_{sp}/r_{ss}, r_{ps}/r_{ss}, and r_{pp}/r_{ss} in terms of $\{\rho_{-1}, \rho_1, \rho_\infty\}$, $\{\rho_{-1}, \rho_0, \rho_\infty\}$, and $\{\rho_{-1}, \rho_0, \rho_1\}$. For measurements of ρ_P at $N \geqslant 3$ values of P, there will be $N!/(N-3)!3!$ solution sets, which can be averaged to give the reflection amplitude ratios. A simpler approach is to measure repeatedly at three fixed values of the polarizer angle P and to average the ρ_P values obtained at each P, with occasional measurement at a fourth angle to provide a consistency check.

ACKNOWLEDGMENT

I am grateful to David Beaglehole for suggesting this problem and for stimulating conversations.

REFERENCES

1. R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1977).
2. J. Lekner, "Ellipsometry of anisotropic media," J. Opt. Soc. Am. A **10**, 1579–1581 (1993).
3. J. Lekner, "Reflection and refraction by uniaxial crystals," J. Phys., Condens. Matter **3**, 6121–6133 (1991).
4. J. Lekner, "Brewster angles in reflection by uniaxial crystals," J. Opt. Soc. Am. A **10**, 2059–2064 (1993).
5. J. Lekner, "Bounds and zeros in reflection by uniaxial crystals," J. Phys., Condens. Matter **4**, 9459–9468 (1992).
6. See, for example, Sec. 9-1 of J. Lekner, *Theory of Reflection* (Nijhoff/Kluwer, Dordrecht, The Netherlands, 1987).
7. F. A. Jenkins and H. E. White, *Fundamentals of Optics* (McGraw–Hill, New York, 1950), Sec. 24.7.
8. See, for example, the articles and references in E. D. Palik ed., *Handbook of Optical Constants of Solids* (Academic, Orlando, Fla., 1985).
9. N. H. Hartshorne and A. Stuart, *Crystals and the Polarising Microscope*, 4th ed. (Edward Arnold, London, 1970).
10. E. E. Wahlstrom, *Optical Crystallography*, 4th ed. (Wiley, New York, 1969).
11. F. Yang, G. W. Bradberry, and J. R. Sambles, "A method for the optical characterization of thin uniaxial samples," J. Mod. Opt. **42**, 763–774, 1241–1252, 1447–1458 (1995).