Infrared reflectivity of uniaxial microcrystalline powders

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The Fresnel reflection coefficients for an absorbing uniaxial crystal are derived in a convienient form for the case in which the optic axis has a general orientation with respect to the plane of incidence. In the region of a strongly absorbing vibrational mode the dominant reflection mechanism of a microcrystalline powder is assumed to be a composite regular (mirror) reflection from the properly aligned faces of crystalline fragments in which the orientations of the optic axes are random. The angle-of-incidence dependence of the transverse-magnetic reflectivity from the ν_3 mode in microcrystalline sodium nitrate is modeled and compared with experimental data.

INTRODUCTION

The determination of transverse and longitudinal frequencies in crystals by a study of the near-normal-incidence reflectivity spectra has been a fairly standard technique, particularly in its application to strongly absorbing internal and external modes. The analysis is usually accomplished by describing the complex dielectric constant in terms of a classical damped-harmonic-oscillator model. The crystals studied have usually been isotropic; if anisotropic systems are considered only special orientations of the crystallographic axes are permissible in order that the usual analysis be valid. In particular if the system is uniaxial the reflectivity must be measured from a face which is either perpendicular or parallel to the optic axis.

It has been pointed out in the literature that the polarized infrared reflectivity spectrum of a microcrystalline powder provides information about the frequencies of the transverse and longitudinal modes in the corresponding bulk single crystal.[1,2] The reflectivity in a microcrystalline sample exhibits a maximum in the vicinity of the longitudinal-mode frequency of the single crystal; however, the frequency of this reflectivity maximum increases with increasing angle of incidence. Furthermore the low-frequency reflectivity "wing" eventually exhibits a minimum at sufficiently large angle of incidence, while the minimum in the high-frequency reflectivity wing, although always present, becomes more pronounced as the angle of incidence is increased. It is therefore of interest to investigate the angle-of-incidence-dependent reflectivity of a microcrystalline powder.

REFLECTIVITY OF ABSORBING UNIAXIAL CRYSTALS

Before describing the infrared reflectivity of a microcrystalline powder in any detail it will be necessary to consider the reflectivity of a single absorbing uniaxial crystal whose optic axis has an arbitrary orientation with respect to the crystal face from which the reflectivity is occurring. The problem of the reflectivity of an absorbing uniaxial crystal has been treated by Mosteller and Wooten[3] as well as Flournoy and Schaffers,[4] for the case in which the optic axis is perpendicular to the reflecting crystal face. A calculation of the reflectivity in an absorbing uniaxial crystal in which the optic axis has a general orientation with respect to the plane of incidence and the reflecting face has been given by Berek[5] and later by Damany and Uzan.[6] The latter authors point out that the general solution is very tedious and give explicit equations for a few experimental geometries.

The reflectivity equations will be rederived here in a form which is particularly convenient for treating anisotropic media. Consider a reflection experiment as described by the coordinate system in Fig. 1(a). A plane, monochromatic, electromagnetic wave is incident on a crystal face defined by the xy plane; the plane of incidence is the xz plane, and the optic axis of the crystal is indicated by the vector $\vec{A}$. The orientation of the optic axis $\vec{A}$ with respect to the coordinate system $\{x, y, z\}$ is described by the two polar angles α and β as shown in Fig. 1(b).

It is well known that two types of waves, an ordinary wave and an extraordinary wave, can be propagated in a uniaxial crystal. The description of these has been given in sufficient detail[3,7] and will be only briefly summarized here. The ordinary wave behaves as if the medium were isotropic. The electric field $\vec{E}^o$ and the electric displacement $\vec{D}^o$ are collinear and are perpendicular both to the direction of propagation as given by wave vector $\vec{k}^o$ and the principal plane defined by the optic axis $\vec{A}$ and the wave vector $\vec{k}^o$. The direction of propagation is identical to the direction of energy flow and is governed by Snell's law. In an extraordinary wave the direction of energy flow as given by

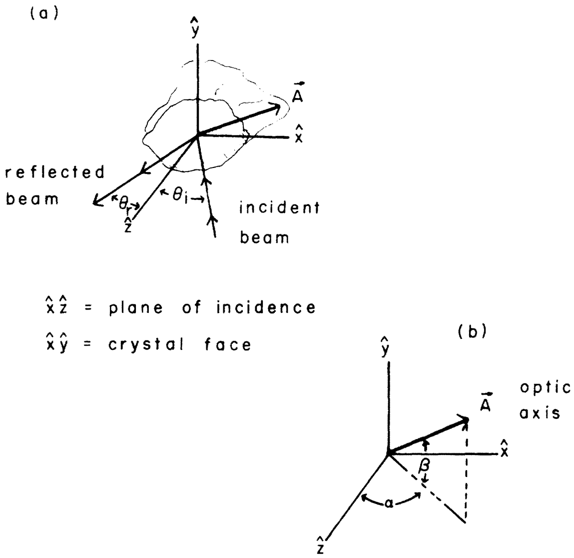

FIG. 1. (a) Coordinate system and experimental geometry of the reflection experiment. (b) Orientation of the optic axis with respect to the plane of incidence.

the Poynting vector $\vec{S}^e$ does not coincide with the direction of wave propagation $\vec{k}^e$; the electric field $\vec{E}^e$ and the electric displacement $\vec{D}^e$ are also not collinear but differ by the same angle as do $\vec{S}^e$ and $\vec{k}^e$. The vectors $\vec{S}^e$, $\vec{k}^e$, $\vec{D}^e$, and $\vec{E}^e$ all lie in the principal plane defined by $\vec{k}^e$ and the optic axis $\vec{A}$. The situation is shown in Figs. 2 and 3, in which a transverse electric (TE) wave is incident on the crystal face at an angle of incidence θ_i and is reflected at an angle θ_r. The incident wave excites both an ordinary transmitted wave (wave vector $\vec{k}^o$), Fig. 2, and an extraordinary transmitted wave (wave vector $\vec{k}^e$), Fig. 3. A similar

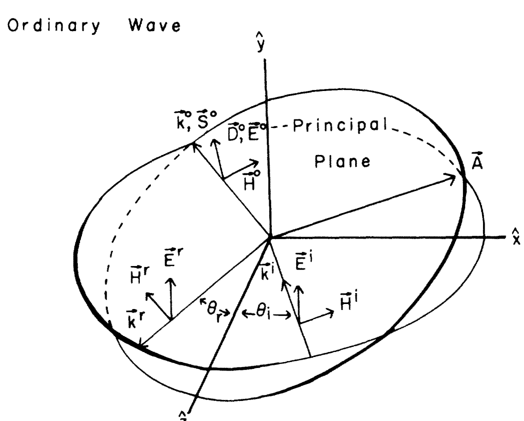

FIG. 2. Fields in an ordinary wave propagating in a uniaxial crystal as a result of incident TE electromagnetic radiation.

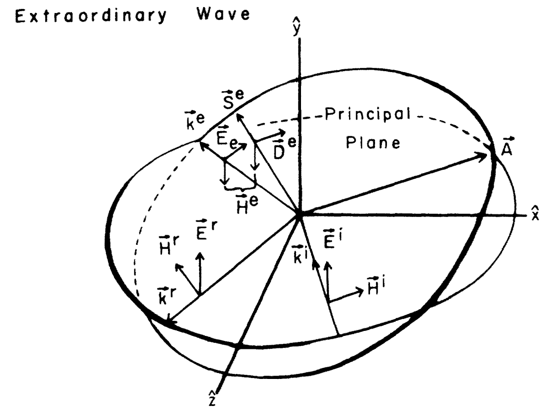

FIG. 3. Fields in an extraordinary wave propagating in a uniaxial crystal as a result of incident TE electromagnetic radiation.

figure could have also been drawn for the transverse magnetic (TM) case which is also treated here.

DIELECTRIC TENSOR FOR AN ABSORBING UNIAXIAL CRYSTAL

The optical and dielectric properties of a medium can be completely characterized by the dielectric tensor $\overleftrightarrow{\epsilon}$ and the conductivity tensor $\overleftrightarrow{\sigma}$, both of which are symmetric second rank tensors. It is assumed here that the medium is nonmagnetic so that the magnetic permeability $\mu = 1$. The dielectric tensor can be transformed to principal dielectric axes and has the principal values $\epsilon_X = \epsilon_0$, $\epsilon_Y = \epsilon_0$, and $\epsilon_Z = \epsilon_e$. It is further assumed that the principal axes of the conductivity tensor coincide with the principal axes of the dielectric tensor. The principal values of the conductivity tensor are then included in with the principal values of the dielectric tensor by writing the principal values of the dielectric tensor as complex quantities,

$$\epsilon_\alpha = \epsilon'_\alpha + i\epsilon''_\alpha = \epsilon'_\alpha + i4\pi\sigma_\alpha/\omega, \quad \alpha = X, Y, Z \qquad (1)$$

where ω is the circular frequency in rad/sec.

The various field vectors are proprotional to $e^{i(\vec{k}\cdot\vec{r}-\omega t)}$, where $\vec{k}$ is the complex wave vector. The complex-wave-vector surface can be decomposed into two surfaces with the complex Fresnel equation. The spherical wave surface

$$k^2/\epsilon_0 = (\omega/c)^2 \qquad (2a)$$

corresponds to the propagation of the ordinary wave and the ellipsoidal wave surface

$$(k_X^2 + k_Y^2)/\epsilon_e + k_Z^2/\epsilon_0 = (\omega/c)^2 \qquad (2b)$$

corresponds to the propagation of the extraordinary wave.

In general the principal dielectric axes of the crystal will not coincide with the set of laboratory fixed axes with respect to which a particular reflectivity measurement is being made. Therefore it is necessary to write down the transformation equations between these two sets of axes. Referring to Fig. 1(a) a vector $\vec{r}$ in the laboratory fixed system is related to a vector $\vec{R}$ in the crystal fixed system (principal dielectric axes) by $\vec{r}=\overleftrightarrow{M}\cdot\vec{R}$, where

$$\overleftrightarrow{M}=\begin{pmatrix} \cos\alpha & -\sin\alpha\sin\beta & \sin\alpha\cos\beta \\ 0 & \cos\beta & \sin\beta \\ -\sin\alpha & -\cos\alpha\sin\beta & \cos\alpha\cos\beta \end{pmatrix}. \quad (3)$$

The dielectric tensor in the principal-axes system is

$$\overleftrightarrow{\epsilon}^P=\begin{pmatrix} \epsilon_0 & 0 & 0 \\ 0 & \epsilon_0 & 0 \\ 0 & 0 & \epsilon_e \end{pmatrix}, \quad (4)$$

and in the laboratory fixed system is

$$\overleftrightarrow{\epsilon}^L=\overleftrightarrow{M}\cdot\overleftrightarrow{\epsilon}^P\cdot\overleftrightarrow{M}^{-1}=\epsilon_0\overleftrightarrow{I}+(\epsilon_e-\epsilon_0)\begin{pmatrix} \sin^2\alpha\cos^2\beta & \sin\alpha\cos\beta\sin\beta & \sin\alpha\cos\alpha\cos^2\beta \\ \sin\alpha\sin\beta\cos\beta & \sin^2\beta & \cos\alpha\cos\beta\sin\beta \\ \sin\alpha\cos\alpha\cos^2\beta & \cos\alpha\cos\beta\sin\beta & \cos^2\alpha\cos^2\beta \end{pmatrix}. \quad (5)$$

FIELDS IN THE TRANSMITTED WAVES

In order to describe the electric and magnetic fields in the transmitted waves it is necessary to invoke two of Maxwell's equations, which for the field vectors proportional to $e^{i(\vec{k}\cdot\vec{r}-\omega t)}$ can be written

$$\vec{D}=-(c/\omega)\vec{k}\times\vec{H}, \quad (6a)$$

$$\vec{H}=(c/\omega)\vec{k}\times\vec{E}\ , \quad (6b)$$

and two of the constitutive equations,

$$\vec{D}=\overleftrightarrow{\epsilon}\cdot\vec{E}, \quad (6c)$$

$$\vec{B}=\vec{H}. \quad (6d)$$

The latter follows since $\mu=1$. At this point it is useful to note that the right-hand sides of the two Maxwell equations are written in the form of vector cross products while the right-hand sides of the two constitutive equations are written as a tensor operating on a vector. In isotropic media this causes no problem in the application of boundary conditions across the interface of two media since the dielectric tensor in those cases is a constant diagonal tensor and Eq. (6c) resembles Eq. (6d) in that the right-hand side becomes a scalar times a vector. In anisotropic media considerable simplification may be achieved if the operator $\vec{k}\times$ is written as a tensor, i.e.,

$$\vec{k}\times\rightarrow\begin{pmatrix} 0 & -k_z & k_y \\ k_z & 0 & -k_x \\ -k_y & k_x & 0 \end{pmatrix}. \quad (7)$$

The two Maxwell Eqs. (6a) and (6b) now become

$$\vec{D}=-(c/\omega)\overleftrightarrow{k}\cdot\vec{H}, \quad (8a)$$

$$\vec{H}=(c/\omega)\overleftrightarrow{k}\cdot\vec{E}. \quad (8b)$$

Ordinary transmitted wave

A unit vector normal to the principal plane defined by $\vec{k}^o$ and $\vec{A}$ is

$$\hat{P}^o=(\vec{k}^o\times\vec{A})/|\vec{k}^o\times\vec{A}|=(\overleftrightarrow{k}^o\cdot\vec{A})/|\overleftrightarrow{k}^o\cdot\vec{A}|. \quad (9)$$

Since the electric field in the ordinary transmitted wave is perpendicular to the principal plane it may be written

$$\vec{E}^o=E^o\hat{P}^o=E^o(\overleftrightarrow{k}^o\cdot\vec{A})/|\overleftrightarrow{k}^o\cdot\vec{A}|. \quad (10)$$

The magnetic field $\vec{H}^o$ is in the principal plane and is orthogonal to both $\vec{k}^o$ and $\vec{E}^o$. As in the case of the electric field the magnetic field may also be written as the product of an amplitude H^o and a unit vector in the direction of $\vec{H}^o$,

$$\vec{H}^o=H^o(\overleftrightarrow{k}^o\cdot\hat{P}^o)/|\overleftrightarrow{k}^o\cdot\hat{P}^o|. \quad (11)$$

From Eq. (8b)

$$\vec{H}^o=(c/\omega)\overleftrightarrow{k}^o\cdot\vec{E}^o=(c/\omega)E^o\overleftrightarrow{k}^o\cdot\hat{P}^o. \quad (12)$$

Equations (11) and (12) may be equated to identify

$$E^o=(\omega/c)H^o/|\overleftrightarrow{k}^o\cdot\hat{P}^o|, \quad (13)$$

and from Eq. (9)

$$|\overleftrightarrow{k}^o\cdot\hat{P}^o|=|\overleftrightarrow{k}^o\cdot\overleftrightarrow{k}^o\cdot\vec{A}|/|\overleftrightarrow{k}^o\cdot\vec{A}|. \quad (14)$$

Finally the amplitude of E^o may be written as a function of the amplitude of H^o,

$$E^o=(\omega/c)H^o|\overleftrightarrow{k}^o\cdot\vec{A}|/|\overleftrightarrow{k}^o\cdot\overleftrightarrow{k}^o\cdot\vec{A}| \quad (15)$$

The electric and magnetic fields are now

$$\vec{E}^o = \frac{(\omega/c)H^o}{|\overleftrightarrow{k}^o\cdot\overleftrightarrow{k}^o\cdot\vec{A}|}\overleftrightarrow{k}^o\cdot\vec{A}, \tag{16a}$$

$$\vec{H}^o = \frac{H^o}{|\overleftrightarrow{k}^o\cdot\overleftrightarrow{k}^o\cdot\vec{A}|}\overleftrightarrow{k}^o\cdot\overleftrightarrow{k}^o\cdot\vec{A}\,. \tag{16b}$$

Extraordinary transmitted wave

A unit vector normal to the principal plane defined by $\vec{k}^e$ and $\vec{A}$ is

$$\hat{P}^e = (\vec{k}^e\times\vec{A})/|\vec{k}^e\times\vec{A}| = (\overleftrightarrow{k}^e\cdot\vec{A})/|\overleftrightarrow{k}^e\cdot\vec{A}|. \tag{17}$$

Since the magnetic field is normal to this plane it may be written

$$\vec{H}^e = H^e\hat{P}^e = \frac{H^e}{|\overleftrightarrow{k}^e\cdot\vec{A}|}\overleftrightarrow{k}^e\cdot\vec{A}. \tag{18}$$

Using one of the Maxwell equations [Eq. (8a)]

$$\vec{D}^e = -\frac{c}{\omega}\overleftrightarrow{k}^e\cdot\vec{H}^e = -\frac{(c/\omega)H^e}{|\overleftrightarrow{k}^e\cdot\vec{A}|}\overleftrightarrow{k}^e\cdot\overleftrightarrow{k}^e\cdot\vec{A}. \tag{19}$$

The electric field may be written with the aid of Eqs. (6c) and (19) as

$$\vec{E}^e = \overleftrightarrow{\epsilon}^{-1}\cdot\vec{D}^e = -\frac{(c/\omega)H^e}{|\overleftrightarrow{k}^e\cdot\vec{A}|}\overleftrightarrow{\epsilon}^{-1}\cdot\overleftrightarrow{k}^e\cdot\overleftrightarrow{k}^e\cdot\vec{A}. \tag{20}$$

FIELDS IN THE INCIDENT AND REFLECTED WAVES

The electric and magnetic fields are referred to the laboratory fixed set of axes specified by the unit basis vectors $\hat{x}$, $\hat{y}$, $\hat{z}$ in Fig. 2. It is necessary to distinguish two types of reflection measurements which can be made at a given angle of incidence. In one case the magnetic field is perpendicular to the plane of incidence (xz plane) while the electric field lies in this plane. The electromagnetic wave is then referred to as a transverse magnetic (TM) wave (also a p or parallel polarized wave). The other case occurs when the electric field is perpendicular to the plane of incidence and the magnetic field lies in the plane. This is a transverse electric (TE) wave (also an s or perpendicularly polarized wave). A generally oriented wave incident on the crystal may be considered as a linear superposition of a TE wave and a TM wave.

Transverse electric case

Referring to Figs. 1 and 2 the electric and magnetic fields in the incident wave are

$$\vec{E}^i = E^i\hat{y}, \tag{21a}$$

$$\vec{H}^i = H^i(\cos\theta_i\,\hat{x} - \sin\theta_i\,\hat{z}). \tag{21b}$$

It is well known that $E^i = H^i$ when the wave is incident on the crystal face through air. Again referring to Figs. 1 and 2 the electric and magnetic fields in the reflected wave are

$$\vec{E}^r = E^r\hat{y}, \tag{22a}$$

$$\vec{H}^r = H^r(-\cos\theta_r\,\hat{x} - \sin\theta_r\,\hat{z}), \tag{22b}$$

with $E^r = H^r$ and $\theta_i = \theta_r$ (law of reflection).

Transverse magnetic case

Although this experiment is not explicitly shown it can be easily visualized by interchanging the electric field vector and the magnetic field vector in the incident and reflected waves in Fig. 2. It follows that the magnetic and electric fields in the incident wave are

$$\vec{H}^i = H^i\hat{y}, \tag{23a}$$

$$\vec{E}^i = E^i(-\cos\theta_i\,\hat{x} + \sin\theta_i\,\hat{z}), \tag{23b}$$

with $H^i = E^i$. Analogously the magnetic and electric fields in the reflected wave are

$$\vec{H}^r = H^r\hat{y}, \tag{24a}$$

$$\vec{E}^r = E^r(\cos\theta_r\,\hat{x} + \sin\theta_r\,\hat{z}), \tag{24b}$$

with $E^r = H^r$ and $\theta_i = \theta_r$.

Reflection amplitudes

The reflectivity R as measured in a particular experiment is equal to the square of the modulus of the reflection amplitude,

$$R_{\mathrm{TE,TM}} = |r_{\mathrm{TE,TM}}|^2. \tag{25}$$

The reflection amplitudes are determined for the TE and TM cases by the application of the two boundary conditions that the tangential components of the electric field and the tangential components of the magnetic field be continuous across the interface between two media.

Transverse electric incident wave

The continuity of the y component of the electric field and Eqs. (16), (18) and (20)–(22) leads to

$$\frac{(\omega/c)H^o}{|\overleftrightarrow{k}^o\cdot\overleftrightarrow{k}^o\cdot\vec{A}|}(\overleftrightarrow{k}^o\cdot\vec{A})_y - \frac{(c/\omega)H^e}{|\overleftrightarrow{k}^e\cdot\vec{A}|}(\overleftrightarrow{\epsilon}^{-1}\cdot\overleftrightarrow{k}^e\cdot\overleftrightarrow{k}^e\cdot\vec{A})_y = H^i + H^r, \tag{26a}$$

recalling that $E^i = H^i$ and $E^r = H^r$. The continuity of the x component of the magnetic field gives

$$\frac{H^o}{|\overleftrightarrow{k}^o\cdot\overleftrightarrow{k}^o\cdot\vec{A}|}(\overleftrightarrow{k}^o\cdot\overleftrightarrow{k}^o\cdot\vec{A})_x + \frac{H^e}{|\overleftrightarrow{k}^e\cdot\vec{A}|}(\overleftrightarrow{k}^e\cdot\vec{A})_x = H^i\cos\theta_i - H^r\cos\theta_r\,, \tag{26b}$$

while the continuity of the y component gives

$$\frac{H^o}{|\overleftrightarrow{k}^o\cdot\overleftrightarrow{k}^o\cdot\vec{A}|}(\overleftrightarrow{k}^o\cdot\overleftrightarrow{k}^o\cdot\vec{A})_y + \frac{H^e}{|\overleftrightarrow{k}^e\cdot\vec{A}|}(\overleftrightarrow{k}^e\cdot\vec{A})_y = 0. \tag{26c}$$

These equations can be solved for the ratio of the magnetic field amplitudes H^r and H^i, which is the reflection amplitude r_{TE}:

$$r_{\mathrm{TE}}=\left(\frac{H^r}{H^i}\right)_{\mathrm{TE}}=\left[\left(\frac{(\omega/c)(\vec{k}^o\cdot\vec{A})_y}{(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_y}+\frac{(c/\omega)(\vec{\epsilon}^{-1}\cdot\vec{k}^e\cdot\vec{k}^e\cdot\vec{A})_y}{(\vec{k}^e\cdot\vec{A})_y}\right)\cos\theta_i-\left(\frac{(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_x}{(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_y}-\frac{(\vec{k}^e\cdot\vec{A})_x}{(\vec{k}^e\cdot\vec{A})_y}\right)\right]\Bigg/$$
$$\left[\left(\frac{(\omega/c)(\vec{k}^o\cdot\vec{A})_y}{(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_y}+\frac{(c/\omega)(\vec{\epsilon}^{-1}\cdot\vec{k}^e\cdot\vec{k}^e\cdot\vec{A})_y}{(\vec{k}^e\cdot\vec{A})_y}\right)\cos\theta_i\;\left(\frac{(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_x}{(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_y}-\frac{(\vec{k}^e\cdot\vec{A})_x}{(\vec{k}^e\cdot\vec{A})_y}\right)\right]. \qquad (27)$$

Transverse magnetic incident wave

The continuity of the x component of the electric field and Eqs. (16), (18), (20), (23), and (24) leads to

$$\frac{(\omega/c)H^o}{|\vec{k}^o\cdot\vec{k}^o\cdot\vec{A}|}(\vec{k}^o\cdot\vec{A})_x-\frac{(c/\omega)H^e}{|\vec{k}^e\cdot\vec{A}|}(\vec{\epsilon}^{-1}\cdot\vec{k}^e\cdot\vec{k}^e\cdot\vec{A})_x=H^r\cos\theta_r-H^i\cos\theta_i. \qquad (28a)$$

The continuity of the y component of the magnetic field gives

$$\frac{H^o}{|\vec{k}^o\cdot\vec{k}^o\cdot\vec{A}|}(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_y+\frac{H^e}{|\vec{k}^e\cdot\vec{A}|}(\vec{k}^e\cdot\vec{A})_y=H^i+H^r, \qquad (28b)$$

while the continuity of the x component yields

$$\frac{H^o}{|\vec{k}^o\cdot\vec{k}^o\cdot\vec{A}|}(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_x+\frac{H^e}{|\vec{k}^e\cdot\vec{A}|}(\vec{k}^e\cdot\vec{A})_x=0. \qquad (28c)$$

The solution for the reflection amplitude r_{TM} is

$$r_{\mathrm{TM}}=\left(\frac{H^r}{H^i}\right)_{\mathrm{TM}}=\left[\left(\frac{(\vec{k}^e\cdot\vec{A})_y}{(\vec{k}^e\cdot\vec{A})_x}-\frac{(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_y}{(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_x}\right)\cos\theta_i-\left(\frac{(\omega/c)(\vec{k}^o\cdot\vec{A})_x}{(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_x}+\frac{(c/\omega)(\vec{\epsilon}^{-1}\cdot\vec{k}^e\cdot\vec{k}^e\cdot\vec{A})_x}{(\vec{k}^e\cdot\vec{A})_x}\right)\right]\Bigg/$$
$$\left[\left(\frac{(\vec{k}^e\cdot\vec{A})_y}{(\vec{k}^e\cdot\vec{A})_x}-\frac{(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_y}{(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_x}\right)\cos\theta_i+\left(\frac{(\omega/c)(\vec{k}^o\cdot\vec{A})_x}{(\vec{k}^o\cdot\vec{k}^o\cdot\vec{A})_x}+\frac{(c/\omega)(\vec{\epsilon}^{-1}\cdot\vec{k}^e\cdot\vec{k}^e\cdot\vec{A})_x}{(\vec{k}^e\cdot\vec{A})_x}\right)\right]. \qquad (29)$$

Before Eqs. (27) and (29) can be used it is necessary that the components of the wave vector for both the ordinary wave and the extraordinary wave be obtained. The solutions for these are given by Eqs. (18), (19), and (22) of Ref. 6 and are directly applicable here since the coordinate system as defined here (Fig. 1) is identical to that of Ref. 6.

MICROCRYSTALLINE REFLECTIVITY

Electromagnetic radiation reflected by a particulate surface is usually considered to consist of contributions from regular reflection and diffuse reflection. Regular reflection refers to the reflection of an electromagnetic wave incident on the interface between two media and is completely described by the Fresnel reflection coefficients which depend on the properties of the electromagnetic wave and the optical constants of the two media. Diffuse reflection occurs when the incident radiation penetrates into the interior of a particulate sample and a portion returns to the surface after partial absorption and multiple scattering at the boundaries of the individual particles. There is no general theory which adequately describes diffuse reflection; however, an excellent review of reflectance spectroscopy has been given by Wendlandt and Hecht[8] in which various treatments of diffuse reflectance under different conditions are discussed. There is some evidence that for strong absorbers regular reflection is the dominant reflection mechanism.[9] Therefore as a first approximation the following somewhat naive model of reflectivity in a microcrystalline powder will be adopted. The size of the microcrystals is assumed to be sufficiently large such that their optical constants are similar to bulk-crystal optical constants. Regular reflection is assumed to be the dominant reflection mechanism and occurs from those faces of the microcrystals which are appropriately aligned with respect to the incident electromagnetic radiation. The optic axis of each microcrystal has some general orientation with respect to the reflecting face, hence the need for the general reflectivity solution previously given.

An additional problem concerns the proper orientation averaging of the microcrystals in the powder. The simplest assumption is that the fragments are randomly distributed with respect to the orientation of their optic axes to the plane of incidence. In this case the proper orientational averaging is a simple rotational averaging:

$$\bar{R}(\theta_i,\omega)=\frac{2}{\pi}\int_0^{\pi/2}\int_0^{\pi/2}R(\theta_i,\omega,\alpha,\beta)\cos\beta\,d\beta\,d\alpha. \qquad (30)$$

For a doubly degenerate mode the integration need only be over $\frac{1}{8}$ of the sphere. However, it might be expected that owing to preferential fracturing along cleavage planes a microcrystalline

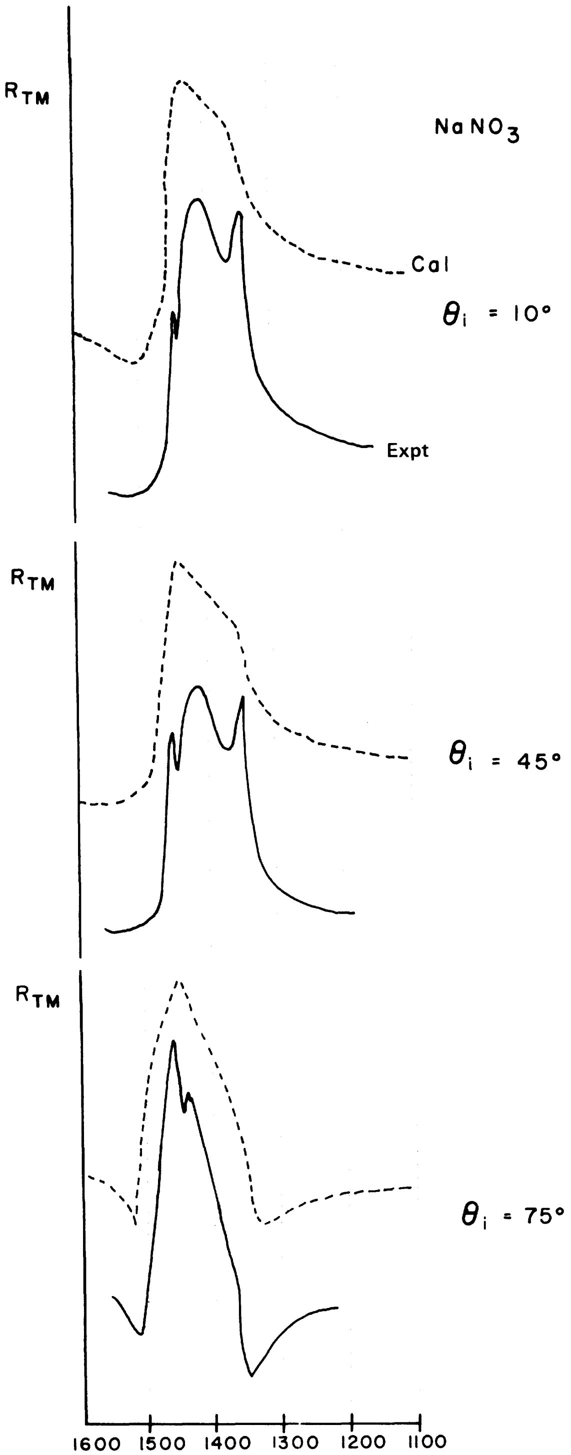

FIG. 4. Angle-of-incidence dependence of the TM reflectivity of a microcrystalline $NaNO_3$ sample.

powder produced by an abrasion process might well be composed of tiny crystals in which certain crystal faces are more probable than others. In that case Eq. (30) would have to be modified by the inclusion of a weighting factor favoring those values of α and β corresponding to the occurrence of preferred cleavage faces.

A comparison of the calculated angle-of-incidence dependence of the rotationally averaged reflectivity with the data obtained by Bates[2] for the ν_3 asymmetric stretching mode of sodium nitrate is shown in Fig. 4. The optical constants for sodium nitrate were generated from a damped-harmonic-oscillator model choosing a longitudinal frequency of 1455 cm^{-1}, a transverse frequency equal to 1353 cm^{-1}, and a damping constant of 10 cm^{-1}. The values selected were those chosen in conjunction with another study[10] involving the optical constants of bulk single-crystal sodium nitrate and no attempt was made to refine the values of those parameters to fit the data here. The ordinary and extraordinary refractive indices used here were those obtained by Tandon,[11] 1.587 and 1.336, respectively.

As the angle of incidence increased from 10° to 75° Bates found that the position of the largest TM reflectivity maximum increased from 1448 to 1460 cm^{-1}. The calculation here also predicts an increase in the maximum from 1434 to 1454 cm^{-1}. The existence of considerable TM reflectivity in the vicinity of the longitudinal frequency for particular experimental geometries has been observed and discussed.[11] Apparently the TM reflectivity maximum in a uniaxial microcrystalline sample can be explained in terms of sufficient numbers of crystalline fragments presenting the appropriate crystal faces to the incoming beam. The behavior of the high-and low-frequency reflectivity "wings" as discussed in the Introduction is also rather nicely described by these calculations. As is evident in Fig. 4, this rather crude model fails to describe the fine structure in the reflectivity band, particularly the existence of several reflectivity maxima which are especially evident in the spectra observed at lower angles of incidence. This is hardly surprising in view of the rather extreme simplifying assumptions made, especially the neglect of the diffuse reflectivity contribution to the observed reflectivity. Therefore the results of these calculations might best be viewed as providing rather satisfactory qualitative agreement with the experimental measurements of the reflectivity from a uniaxial microcrystalline powder.

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