DETERMINATION OF DEGREE OF ANISOTROPY OF KTP CRYSTAL USING ROTATING POLARIZER-ANALYZER RAS METHOD

By

Joseph Kassa

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The undersigned hereby certify that they have read and recommend to the Faculty of Science for acceptance a thesis entitled "**Determination of Degree of Anisotropy of KTP Crystal Using Rotating Polarizer-Analyzer RAS Method**" by **Joseph Kassa** in partial fulfillment of the requirements for the degree of **Master of Science**.

Dated: April 2007

Supervisors: ______________________
Dr. Araya Asfaw

____
Dr.Mesfin Redi

Examiner: ______________________
Prof. A.V. Gholap

____
Dr. Gizaw Mengistu

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Signature of Author

to my parents

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Abstract

Reflectance Anisotropy spectroscopy (RAS) is a non-destructive optical probe of surfaces that is capable of operating with in a wide range of environment. In this thesis, by applying this optical technique attempt was made to determine the degree of anisotropy of a biaxial Potassium Titanyl phosphate (KTP) crystal. Furthermore, by using rotating polarizer-analyzer method, we have tried to develop a more accurate and easy to use approach. The method used in this work can be used *in situ* real-time measurements.The degree of Anisotropy is determined to be $7.4 \times 10^{-3} \pm .0001$.

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Introduction

When an electromagnetic wave interacts with a crystal, a number of important optical properties can be observed. Crystal is a three dimensional representation of some unit of atoms or molecules whose microscopic structure is characterized by a periodic representation in three dimensions of a motif composed of atoms.

Anisotropic crystalline structure has a number of properties, which are dependent on the direction of observation. Thus, electrical conductivity may depend on the orientation of the electrical potential applied to the crystal; Young's modulus which describes the linear strain of a material resulting from a linear stress is equally a function of direction. Anisotropy is also a source of characteristic properties that are lacking in isotropic materials. As an example, one may consider piezoelectricity and birefringence. With the longitudinal effects, additional transverse effects may occur. In a crystal, an electric current does not necessarily flow parallel to the applied electric field. In general, a crystal under a longitudinal stress will undergo not only a longitudinal dimension change but also shear [1].

In most cases, anisotropic materials exhibit non-linear effects; that is the phase velocity of light waves in non-linear materials varies with the direction of propagation and the polarization of the wave. Thus, the phenomena which will now be described, are derived from non-linear polarization of material media. The effects depend on the crystal structure and are absent in isotropic media and centro-symmetric crystals. In this thesis I have attempted to determine the degree of anisotropy of the KTP crystal which has many optical importance.

Potassium titanyl phosphate ($KTiOPO_4$) is a non-linear optical crystal, which possesses excellent non-linear and electro-optic properties. A combination of high non-linear coefficient, wide transparency range and broad angular as well as thermal acceptances make KTP very attractive for different non-linear optical and wave guide applications. Its electro-optic wave-guide modulator figure of merit is nearly double of that of any other inorganic material. Furthermore, it is known as a quasi-one dimensional super ionic conductor of K^+ ions and at room temperature it is a ferro-electric material having a phase transition temperature at 934 ± 2^0C [2].

Transparency band edges of KTP crystal are at 0.35μm in the UV and 4.4μ m in the IR region. Due to very high effective non-linearity and excellent optical properties of KTP the effective transparency of the crystal lies in the $0.99 - 3.3\mu$m region [2]. This allows the use of the KTP crystal as an interactive and extractive frequency doubler for most commonly used lasers, such as Nd:YAG laser. The very large temperature band width of KTP is particularly advantageous for maintaining pulsed energy stability of the converted laser beam. Due to this feature and good thermal properties, KTP has exceptional figure of merit for frequency doubling of high average power in CW or quasi-CW lasers. Thus relatively high bulk damage threshold combined with a low absorptions loss at 1μ m, renders this material a prime choice for all interactive frequency doubling applications.

KTP belongs to the family of isomorphic compounds with the general composition of MTiOX, where X=P or As and M=K, Rb, NH_4, Ti or Cs (for X=As only) [3]. Solid solutions exist among the various members of the family, with only slight changes in lattice parameters. All members are orthorhombic and belong to the centric point group mm2 and space group $Pna2_1$ at room temperature. For KTP, the lattice constants are $a = 12.814\mathring{A}$, $b = 6.404\mathring{A}$ and $c = 10.616\mathring{A}$ and each unit cell contains eight formula units. Its complicated structure is characterized by chains of TiO_6 octahedraly linked at two corners by alternating long and short Ti-O bonds [3]. The analysis of Zumsteg et al indicates that it is primarily this short Ti-O bonds that give rise to the large non-linear effect observed in KTP [4].

RAS method for crystal structure determination has been done before, however, the experimental method used was very sensitive to alignment. Thus, the need for a reliable method arouse. Therefore the objectives of this work are to standardize the RAS for determining crystal structure and to modify the experimental setup so that it will be easy to carry out *in situ* real time measurements.

This thesis is organized in Five chapters. The first chapter generally deals with the interaction of matter with light. The optical properties of matter are interpreted on the basis of the electromagnetic theory of light by using Maxwell's equations. Then the propagation of electromagnetic wave through isotropic and anisotropic media is discussed. After that, Fresnel's coefficients are derived and explained. In the second chapter, the phenomena of polarization is thoroughly discussed. And moreover, the state of polarization is expressed mathematically by applying Jone's calculus and Stoke's vectors. The basic principles of RAS are introduced in the third chapter. The fourth chapter explains the experimental results along with the interpretation. The final chapter consists of brief summary and conclusion based on the experimental results.

Chapter 1

Theory of Light

1.1 Historical Background

Before the 17th century, knowledge about light was truly in the "Dark Ages". Although the Greeks had made significant progress with geometrical models in their time, this information, along with their other contributions, was suppressed in the years following the decline of Greek influence.

Further development of optical theory took place by virtue of the ideas of three prominent individuals: René du Perron Descartes, Pierre de Fermat, and Isaac Newton. There are fundamental differences in the philosophies of natural phenomena espoused by these early physicists. Most notable among the contrasts are the Cartesian (geometrically-oriented) versus the Newtonian (force-oriented) points of view. These early physicists are grouped together here because particle dynamics played an important role in their explanations of light. Mechanical models are inadequate; however, Descartes and Newton had such dominating influence in their day that any study of optics is incomplete without their ideas. Among their lasting contributions; Descartes was the first to publish the correct form of the law of refraction, and Newton first explained refraction's chromatic character. Fermat developed the principle of least time, which was similar to Hero's shortest path principle. This is a fundamental concept that is reinforced by modern theory.

The issues involving the nature of light were then and are now:

- its speed of propagation,
- the cause of sensation we call color,
- its tendency to travel in straight lines (rectilinear propagation),
- the law of reflection, and
- the phenomena of refraction, whose "law" was not discovered until later.

Any theory of light must deal with all of these characteristics. In addition, a comprehensive theory must deal with the phenomena of interference and diffraction, which were not known at the time. It must also be able to explain the subtleties of relativistic effects and the details of light/matter interactions, which were not revealed until the 19th and 20th centuries [5].

Although it has been determined that light behaved like a wave by the middle of the 19th century, there was still a question about what it was "waving". Most physicists at the time believed in the existence of ethereal medium in which the optical disturbance propagated. This medium had to posses some unusual characteristics. It had to pervade all space, thus being exceedingly rare. Yet young had shown, following experiments with the phenomenon of polarization by Fresnel and Arago, that light wave must also be transverse. It was difficult to imagine a medium as rare as the ether that was stiff enough such that it could support the shear restoring force necessary in a transverse mechanical wave.

In 1856, Wilhelm Weber and Rudolph Kohlrausch experimentally determined that the constant of proportionality between electric quantities and magnetic quantities was, within experimental error, the same as the speed of light. That this constant must bear the units of velocity is revealed from the fundamental definitions. This was recognized a short time later as much more than a coincidence. But it was not until the Scots physicist James Clerk Maxwell(1831-1879) collected electromagnetic theory into a correlated set of mathematical relationships that the hypothesis that light behaved like an electromagnetic wave was justified [6].

Maxwell's theory, developed during 1861-1862, dealt with the ether as the medium in which electromagnetic phenomena existed. He proposed that the electric field was a "displacement" or distortion of charged ether particles from their equilibria, where as the magnetic field was associated with rotating regions or "vortices" of charged ether particles. A change in the vortex structure of the ether (magnetic field) would produce displacement in the medium (electric field). This interrelationship is required in order that waves consisting of simultaneous fluctuations in the electric and magnetic field be possible.

The mechanical character of Maxwell's original formalism was a natural product of the times. Since Maxwell's proposal, we have learned that electric and magnetic field are more properly thought of as characteristics of space and relativity (the relative motion of one reference frame with respect to another). Maxwell's equations for the fields, however, remain valid even in the absence of an ether, since they describe how these characteristics are related to each other and to static and dynamic material charges. We need not invent an ether whose condition of strain or rotation is connected with the action of electric and magnetic forces. To do so is only to further complicate the issue. Experimentally observed classical electromagnetic phenomena, including the propagation of light, are entirely explained in terms of the fields themselves. In addition, if the ether were to exist then there was no reason to expect that the ether was at rest with respect to the earth, or, for that matter, with respect to the sun either. In 19th century model, the speed of light was linked to the ether reference frame. This requires that the speed of light as measured on earth should depend on the direction of the measurement.

To detect this anisotropy was the object of the experiments by A.A. Michelson in 1881 and with E.W. Morley in 1887. Michelson constructed a devise for this purpose, the Michelson interferometer. The experiment showed that light has a constant speed, independent of the motion of the measuring apparatus related to the hypothesized ether. Because the ether exerts no influence on the light, it is best to abandon the concept all together [5].

1.2 Maxwell's Equations

The study of the propagation of light through matter, particularly solid matter, comprises one of the important and interesting branches of optics. The many and varied optical phenomena exhibited by solids include such things as selective absorption, dispersion and double refraction, polarization effects, and electro-optical and magneto-optical effects. Many of the optical properties of solids can be understood on the basis of classical electromagnetic theory. This section applies the macroscopic Maxwell theory to the propagation of light through solids. The way in which the phenomena are described by the classical theory of light gives considerable physical insight and helps to provide the fundamental background [7].

1.2.1 Macroscopic Fields and Maxwell's Equations

The electromagnetic state of matter at a given point is described by four quantities:

1. The volume density of electric charge ρ
2. The volume density of electric dipoles, called the polarization **P**
3. The volume density of magnetic dipoles, called magnetization **M**
4. the electric current per unit area, called the current density **J**.

All of these quantities are considered to be macroscopically averaged in order to smooth out the microscopic vibrations due to atomic make up of the matter. They are related to the macroscopically averaged fields **E** and **H** by the following Maxwell's equations:

$$\nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t} - \mu_0 \frac{\partial \mathbf{M}}{\partial t} \tag{1.2.1}$$

$$\nabla \times \mathbf{H} = \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t} + \mathbf{J} \tag{1.2.2}$$

$$\nabla \cdot \mathbf{E} = -\frac{1}{\epsilon_0} \nabla \cdot \mathbf{P} + \frac{\rho}{\epsilon_0} \tag{1.2.3}$$

$$\nabla \cdot \mathbf{H} = -\nabla \cdot \mathbf{M} \tag{1.2.4}$$

If one introduces the abbreviation **D** for some quantity $\epsilon_0\mathbf{E}+\mathbf{P}$, known as the dielectric displacement, and the abbreviation **B** for $\mu_0(\mathbf{H}+\mathbf{M})$ called the magnetic induction, then the Maxwell's equations assume more compact form:

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{1.2.5}$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J} \tag{1.2.6}$$

$$\nabla \cdot \mathbf{D} = \rho \tag{1.2.7}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{1.2.8}$$

The response of the condition of the electrons to the electric field is given by the current equation (Ohm's law) $J = \sigma\mathbf{E}$ where σ is the conductivity. The constitutive relation $\mathbf{D} = \epsilon\mathbf{E}$ describes the aggregate response of the bound charges to the electric field. The corresponding magnetic relation is $\mathbf{B} = \mu\mathbf{H}$. An alterative way to express the response of the bound charge is $\mathbf{P} = (\epsilon - \epsilon_0)\mathbf{E} = \chi\epsilon_0\mathbf{E}$ which gives the proportionality between the polarization and the impressed electric field. The proportionality factor $\chi = \frac{\epsilon}{\epsilon_0} - 1$ is known as the electric susceptibility. In the study of the optics of matter, χ is the most important parameter.

In the case of isotropic media, for example, glass, χ is a scalar quantity having the same value for any direction of the applied electric field. For non isotropic media, such as most crystals, the magnitude of polarization varies with the direction of the applied field and consequently, χ must be expressed as a tensor. We shall find that the χ tensor of a crystal summarizes most of the optical properties [6, 7].

1.2.2 The General Wave Equation

In our study of solid state optics we shall be concerned only with nonmagnetic, electrically neutral media. Hence $\mathbf{M}$ and ρ are both zero. Maxwell's equations, in the form expressed by Equations (1.2.1 to 1.2.4), then reduces to the following.

$$\nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t} \tag{1.2.9}$$

$$\nabla \times \mathbf{H} = \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t} + \mathbf{J} \tag{1.2.10}$$

$$\nabla \cdot \mathbf{E} = -\frac{1}{\epsilon_0} \nabla \cdot \mathbf{P} \tag{1.2.11}$$

$$\nabla \cdot \mathbf{H} = 0 \tag{1.2.12}$$

The general wave equation for the **E** field is obtained by taking the curl of 1.2.9 and the time derivative of Equation(1.2.10 and eliminating **H**. The result is

$$\nabla \times (\nabla \times \mathbf{E}) + \frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} = -\mu_0 \frac{\partial^2 \mathbf{P}}{\partial t^2} - \mu_0 \frac{\partial \mathbf{J}}{\partial t} \tag{1.2.13}$$

The two terms on the right-hand side of the above equation are called source terms. They stem from the presence of polarization charges and conductive charges, respectively, with in the medium. The way in which the propagation of light is affected by the source is revealed by the solution of the wave equation when the source terms are included. In the case of nonconducting media the polarization term $-\mu_0 \partial^2 \mathbf{P}/\partial t^2$ is of importance. It turns out that this term leads to an explanation of many optical effects, including dispersion, absorption, double refraction, and optical activity to mention only a few [7].

1.3 Propagation of light in Isotropic Dielectric

In a nonconducting, isotropic medium, the electrons are permanently bound to the atoms comprising the medium and there is no preferential direction. This is what is meant by a simple isotropic dielectric such as glass. Suppose that each electron, of charge e^-, in a dielectric is displaced a distance $\mathbf{r}$ from its equilibrium position. The resulting macroscopic polarization $\mathbf{P}$ of the medium is given by

$$\mathbf{P} = -Ne\mathbf{r} \tag{1.3.1}$$

where N is the number of electrons per unit volume. If the displacement of the electron is the result of the application of a static electric field $\mathbf{E}$, and if the electron is elastically bound to its equilibrium position with a force constant K, then the force equation is

$$-e\mathbf{E} = K\mathbf{r} \tag{1.3.2}$$

The static polarization is therefore given by

$$\mathbf{P} = \frac{Ne^2}{K}\mathbf{E} \tag{1.3.3}$$

However, if the impressed field **E** varies with time, the above equation is incorrect. In order to find the true polarization in this case, we must take the actual motion of the electrons into account. To do this we consider the bound electrons as classical damped harmonic oscillators. The differential equation of motion is

$$m\frac{d^2\mathbf{r}}{dt^2} + m\gamma\frac{d\mathbf{r}}{dt} + K\mathbf{r} = -e\mathbf{E} \tag{1.3.4}$$

The term $m\gamma\ (d\mathbf{r}/dt)$ represents a frictional damping force that is proportional to the velocity of the electron, the proportionality constant being written as $m\gamma$.

Now suppose that the applied electric field varies harmonically with time according to the usual factor $e^{-(iwt)}$. Assuming that the motion of the electron has the same harmonic time dependence, we find that Equation 1.3.4 becomes

$$(-m\omega^2 - i\omega m\gamma + K)\mathbf{r} = -e\mathbf{E} \tag{1.3.5}$$

Consequently, the polarization, from equation 1.3.1, is given by

$$\mathbf{P} = \frac{Ne^2}{-m\omega^2 - i\omega m\gamma + K}\mathbf{E} \tag{1.3.6}$$

It reduces to the static value, Equation (1.3.3), when $\omega = 0$. Thus for a given amplitude of the impressed electric field, the amount of polarization varies with frequency. The phase of **P**, relative to that of the electric field, also depends on the frequency.

This is shown by the presence of the imaginary term in the denominator.

A more significant way of writing equation 1.3.6 is

$$\mathbf{P} = \frac{Ne^2/m}{\omega_0^2 - \omega^2 - i\omega\gamma}\mathbf{E} \tag{1.3.7}$$

in which we have introduced the abbreviation ω_0 given by

$$\omega_0 = \sqrt{\frac{K}{m}} \tag{1.3.8}$$

This is the effective resonance frequency of the bound electrons [5, 7].

The polarization Formula (1.3.7) is similar to the amplitude formula for a driven harmonic oscillator, as indeed it should be, since it is the displacement of the elastically bound electrons that actually constitutes the polarization. We should therefore expect to find an optical resonance phenomenon of some kind occurring for light frequencies in the neighborhood of the resonance frequency ω_0. As we shall presently see, the resonance phenomenon is manifest as a large change in the index of refraction of the medium and also by the strong absorption at or near the resonance frequency. To show how the polarization affects the propagation of light, we return to the general wave equation Equation(1.2.13). For a dielectric there is no conduction term. The polarization is given by Equation(1.3.7). Hence we have

$$\nabla \times (\nabla \times \mathbf{E}) + \frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} = -\frac{\mu_0 N e^2}{m}\left(\frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}\right)\frac{\partial^2 \mathbf{E}}{\partial t^2} \tag{1.3.9}$$

Also, from the linear relationship between $\mathbf{P}$ and $\mathbf{E}$, it follows from 1.2.11 that $\nabla \cdot \mathbf{E} = 0$. Consequently, $\nabla \times (\nabla \times \mathbf{E}) = -\nabla^2 \mathbf{E}$, and the above wave equation reduces to the somewhat simpler one

$$\nabla^2 \mathbf{E} = \frac{1}{c^2}\left(1 + \frac{Ne^2}{m\epsilon_0} \cdot \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}\right)\frac{\partial^2 \mathbf{E}}{\partial t^2} \tag{1.3.10}$$

after rearranging terms and using the relation $1/c^2 = \mu_0\epsilon_0$.

Let us seek a solution of the form

$$\mathbf{E} = \mathbf{E}_0 e^{i(\Bbbk z-\omega t)} \tag{1.3.11}$$

This trial solution represents what are called homogeneous plane harmonic waves. Direct substitution shows that this is a possible solution provided that

$$\Bbbk^2 = \frac{\omega^2}{c^2}\left(1 + \frac{Ne^2}{m\epsilon_0} \cdot \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}\right) \tag{1.3.12}$$

The presence of the imaginary term in the denominator implies that the wave number $\Bbbk$ must be a complex number. Let us inquire as to the physical significance of this. We express $\Bbbk$ in terms of its real and imaginary parts as $\Bbbk = k + i\alpha$

This amounts to the same thing as introducing a complex index of refraction $\aleph = n + i\kappa$ where

$$\Bbbk = \frac{\omega}{c}\aleph \tag{1.3.13}$$

Our solution in Equation (1.3.11) can then be written as

$$\mathbf{E} = \mathbf{E}_0 e^{-\alpha z} e^{i(kz-\omega t)} \tag{1.3.14}$$

The factor $e^{-\alpha z}$ indicates that the amplitude of the wave decreases exponentially with distance. This means that as the wave progresses, the energy of the wave is absorbed by the media. Since the energy in the wave at a given point is proportional to $\|\mathbf{E}\|^2$, then the energy varies with distance as $e^{-2\alpha z}$. Hence 2α is the *coefficient of absorption* of the medium. The imaginary part κ of the complex index of refraction is known as the *extinction index.* The two numbers α and κ are related by the equation

$$\alpha = \frac{\omega}{c}\kappa \tag{1.3.15}$$

The phase factor $e^{i(\kappa z-\omega t)}$ indicates that we have a harmonic wave in which the phase velocity is

$$u = \frac{\omega}{k} = \frac{c}{n} \tag{1.3.16}$$

From Equations (1.3.12) and (1.3.13) we have

$$\aleph^2 = (n + i\kappa)^2 = 1 + \frac{Ne^2}{m\epsilon_0} \cdot \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega} \tag{1.3.17}$$

Equating real and imaginary parts yields the following equations:

$$n^2 - \kappa^2 = 1 + \frac{Ne^2}{m\epsilon_0}\left(\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}\right) \tag{1.3.18}$$

$$2n\kappa = \frac{Ne^2}{m\epsilon_0}\left(\frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}\right) \tag{1.3.19}$$

from which the optical parameters n and κ may be found [7].

1.4 Propagation of Light in Crystals

The distinguishing basic future of the crystalline state, as far as optical properties are concerned, is the fact that crystals are generally electrically anisotropic; this means that the polarization produced in the crystal by a given electric field is not just a simple scalar constant times the field, but varies in a manner that depends on the direction of the applied field in relation to the crystal lattice. One of the consequences is that the speed of propagation of a light wave in a crystal is a function of the direction of propagation and the polarization of light.

It turns out that there are generally two possible values of the phase velocity for a given direction of propagation. These two values are associated with mutually orthogonal polarization of light waves. Crystals are said to be *doubly refracting* or *birefringent*. Actually not all crystals exhibit double refraction. Whether the do or do not depends on their symmetry. Crystals of the cubic class of symmetry, such as sodium chloride, never exhibit double refraction, but are optically isotropic. All crystals, other than cubic crystals, do show double refraction however [7].

A model to illustrate the isotropic polarizabilty of a crystal is shown in Figure (1.1). A bound electron is pictured here as attached to a set of fictitious elastic springs. The springs have different stiffnesses for different directions of the electron's displacement from its equilibrium position with in the crystal lattice. Consequently, the displacement of the electron under the action of an external field **E** depends on the direction of the field as well as its magnitude. This is also true of the resulting polarization **P**. The dependence of **P** on **E** is expressible as a tensor relation in the form

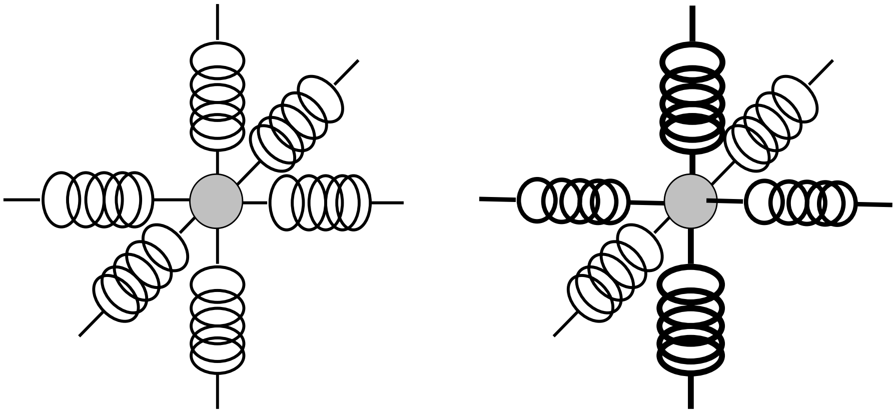


Figure 1.1: Model to show isotropic and anisotropic binding of an electron in a crystal.

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \epsilon_0 \begin{bmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{21} & \chi_{22} & \chi_{23} \\ \chi_{31} & \chi_{32} & \chi_{33} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \tag{1.4.1}$$

This is customarily abbreviated as

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E} \tag{1.4.2}$$

where χ is the susceptibility tensor:

$$\chi = \begin{pmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{21} & \chi_{22} & \chi_{23} \\ \chi_{31} & \chi_{32} & \chi_{33} \end{pmatrix}$$

The corresponding dielectric displacement $\mathbf{D}$ is given by $\mathbf{D} = \epsilon_0(1+\chi)\mathbf{E} = \epsilon\mathbf{E}$, where 1 is the unit matrix, and $\epsilon = \epsilon_0(1+\chi)$ which is known as the dielectric tensor.

For ordinary non absorbing crystals the χ-tensor is symmetric so there always exists a set of coordinate axes, called *principal axes*, such that the χ-tensor assumes the diagonal form

$$\chi = \begin{pmatrix} \chi_{11} & 0 & 0 \\ 0 & \chi_{22} & 0 \\ 0 & 0 & \chi_{33} \end{pmatrix}$$

The three χs are known as the *principal susceptibilities.* Corresponding to these, the quantities $K_{11} = 1 + \chi_{11}...$, and so forth, are called principal *dielectric constants.*

In view of Equation (1.4.2), the general wave equation Equation (1.2.13) can be written in the following form:

$$\nabla \times (\nabla \times \mathbf{E}) + \frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} = -\frac{1}{c^2}\chi\frac{\partial^2 \mathbf{E}}{\partial t^2} \tag{1.4.3}$$

It then follows that the crystal can sustain monochromatic plane waves of the usual form $e^{i(k\cdot r-\omega t)}$ provided the propagation vector $\mathbf{k}$ satisfies the equation

$$\mathbf{k} \times (\mathbf{k} \times \mathbf{E}) + \frac{\omega^2}{c^2}\mathbf{E} = -\frac{\omega^2}{c^2}\chi\mathbf{E} \tag{1.4.4}$$

Written out in terms of components, the above equation is equivalent to the following three equations:

$$\begin{aligned}
(-k_y^2 - k_z^2 + \frac{\omega^2}{c^2})E_x + k_x k_y E_y + k_x k_z E_z &= -\frac{\omega^2}{c^2 \chi_{11}} E_x \\
k_y k_x E_x + (-k_x^2 - k_z^2 + \frac{\omega^2}{c^2})E_y + k_y k_z E_z &= -\frac{\omega^2}{c^2 \chi_{22}} E_y \\
(-k_y^2 - k_z^2 + \frac{\omega^2}{c^2})E_x + k_x k_y E_y + k_x k_z E_z &= -\frac{\omega^2}{c^2 \chi_{33}} E_z
\end{aligned} \tag{1.4.5}$$

In order to interpret the physical meaning of these equations, suppose we have a particular case of a wave propagating in the direction of one of the principal axes, say the x-axis. In this case, $k_x = k, k_y = k_z = 0$, and the three equations reduce to

$$\begin{aligned}
\frac{\omega^2}{c^2} E_x &= -\frac{\omega^2}{c^2} \chi_{11} E_x \\
(-k^2 + \frac{\omega^2}{c^2})E_y &= -\frac{\omega^2}{c^2} \chi_{22} E_y \\
(-k^2 + \frac{\omega^2}{c^2})E_z &= -\frac{\omega^2}{c^2} \chi_{33} E_z
\end{aligned} \tag{1.4.6}$$

The first equation implies that $E_x = 0$ because neither ω nor χ_{11} is zero. This means that **E** field is transverse to the x-axis, which is the direction of propagation. Consider next the second equation. If $E_y \neq 0$, then

$$k = \frac{\omega}{c}\sqrt{1 + \chi_{22}} = \frac{\omega}{c}\sqrt{K_{22}} \tag{1.4.7}$$

The third equation, like wise, implies that if $E_z \neq 0$, then

$$k = \frac{\omega}{c}\sqrt{1 + \chi_{33}} = \frac{\omega}{c}\sqrt{K_{33}} \tag{1.4.8}$$

Now ω/k is the phase velocity of the wave. Thus we have two possible phase velocities, namely, $c/\sqrt{K_{22}}$ if the **E** points in the y direction, and $c/\sqrt{K_{33}}$ if the **E** vector is the z direction.

More generally we can show that for any direction of the propagation vector $\mathbf{k}$, there are two possible values of the magnitude k and hence two possible values of the phase velocity. To do this, let us introduce the three *principal indices of refraction* n_1, n_2 and n_3, defined by

$$\begin{aligned} n_1 &= \sqrt{1+\chi_{11}} = \sqrt{K_{11}} \\ n_2 &= \sqrt{1+\chi_{22}} = \sqrt{K_{22}} \\ n_3 &= \sqrt{1+\chi_{33}} = \sqrt{K_{33}} \end{aligned} \tag{1.4.9}$$

Now in Equation (1.4.5), in order for the nontrivial solution for E_x, E_y and E_z to exist, the determinant of the coefficients must vanish, namely

$$\begin{vmatrix} (n_1\omega/c^2) - k_y^2 - k_z^2 & k_x k_y & k_x k_z \\ k_y k_x & (n_2\omega/c^2) - k_y^2 - k_z^2 & k_y k_z \\ k_z k_x & k_z k_y & (n_3\omega/c^2) - k_x^2 - k_y^2 \end{vmatrix} = 0 \tag{1.4.10}$$

where we have used Equation(1.4.9). The above equation can be represented by a three-dimensional surface in $\mathbf{k}$ space. The form of this surface, or wave-vector surface, is shown in Figure (1.2).

To see how the surface is constructed, consider any one of the coordinate planes, say the xy plane. In the plane $k_z = 0$, and the determinant reduces to the product of the two factors

$$\left[\left(\frac{n_3\omega}{c}\right)^2 - k_x^2 - k_y^2\right]\left\{\left[\left(\frac{n_1\omega}{c}\right)^2 - k_y^2\right]\left[\left(\frac{n_2\omega}{c}\right)^2 - k_y^2\right] - k_x^2 k_y^2\right\} = 0 \tag{1.4.11}$$

Since the product must vanish, either or both of the factors must be equal to zero. Setting the first factor equal to zero gives the equation of a circle

$$k_x^2 + k_y^2 = \left(\frac{n_3\omega}{c}\right)^2 \tag{1.4.12}$$

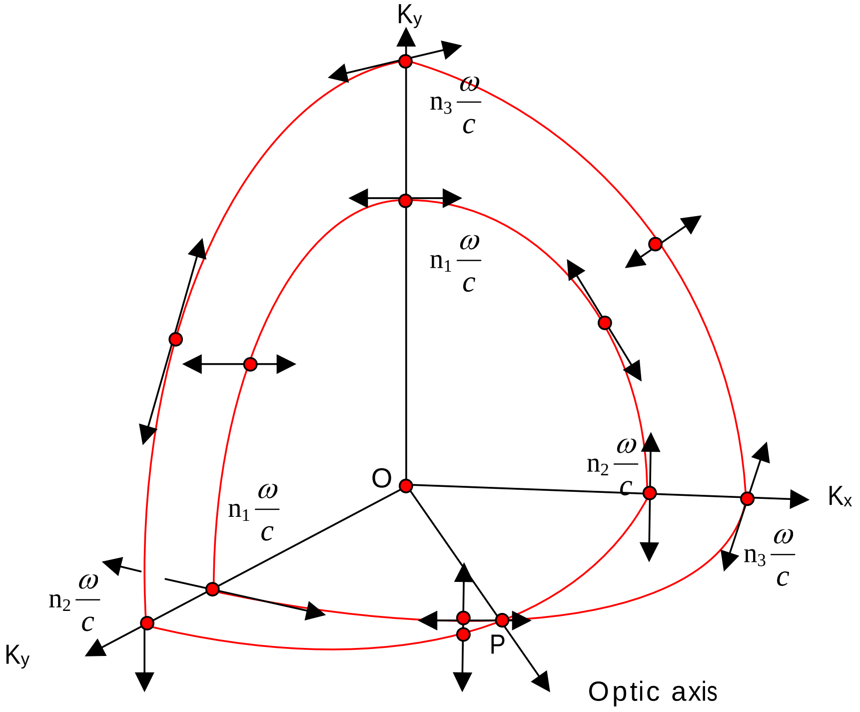


Figure 1.2: The wave-vector surface.

The second factor gives the equation of an ellipse

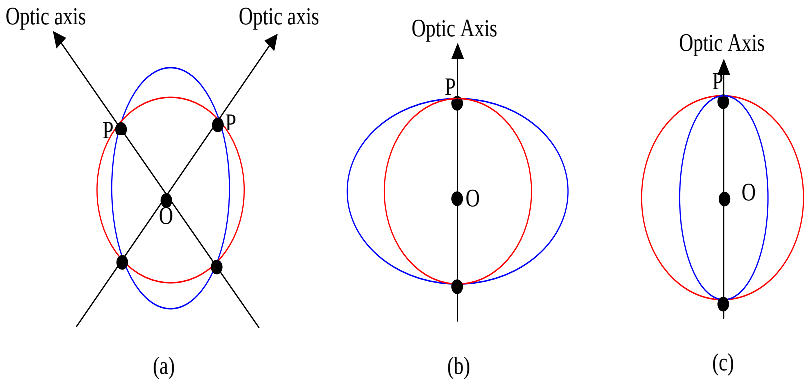
$$\frac{k_x^2}{(n_2\omega/c)^2} + \frac{k_y^2}{(n_1\omega/c)^2} = 1 \tag{1.4.13}$$

Similar equations are obtained for the xz and the yz planes. The intercept of the **k** surface with each coordinate plane therefore consists of one circle and one ellipse as shown. The complete **k** surface is double; that is, it consists of an inner sheet and an outer sheet. This implies that for any given direction of the wave vector **k**, there are two possible values for the wavenumber k. It follows that there are also two values of the phase velocity. Now we just showed that for a wave propagating in the x direction, the two phases velocities correspond to two mutually orthogonal directions of polarization. It turns out that the same is true for any directions of polarization; that is, the two phase velocities always correspond to two mutually orthogonal polarizations. Now, as we know, a light wave of arbitrary polarization can always be resolved into two orthogonally polarized waves. Hence, when unpolarized light or light of arbitrary polarization propagates through a crystal, it can be considered to consist of two independent waves that are polarized orthogonally with respect to each other and traveling with different phase velocities.

The nature of **k** surface is such that the inner and outer sheets touch at a certain point P as shown in Figure (1.2). This point defines a direction for which the two values of k are equal. The direction so defined is called an *optic axis*, the phase velocities of the two orthogonally polarized waves reduce to the same value.

The general case is shown in Figure (1.2 and 1.3a). Here the three principal indices n_1, n_2 and n_3 are all different. It is easy to see from the intercept that there are two optic axes. In this case the crystal is said to be *biaxial.* In many crystals it happens that two of the principal indices are equal, in which case there is only one optic axis and the crystal is called *uniaxial.* The **k** surface for a uniaxial crystal consists of a sphere and an ellipsoid of revolution, the axis of which is the optic axis of the crystal [Figure 1.3 (b and c)]. If all three indices are equal, then the **k** surface degenerates to a single sphere, and the crystal is not doubly refracting at all but is optically isotropic.

In view of the fact that the principal indices are related to the components of the χ tensor by Equation (1.4.9), we can conveniently classify crystals according to the χ tensor as in Table (1.1) [7].



(a) (b) (c)

Figure 1.3: intercepts of the wave-vector surfaces in the xz plane for (a)biaxial crystal; (b)uniaxial negative crystals;(c) uniaxial positive crystals

In a uniaxial crystal the index of refraction that corresponds to the two equal elements, $\chi_{11} = \chi_{22}$, is called the ordinary index n_0, and the other index, corresponding to χ_{33}, is called the *extraordinary index* n_E, it is called a negative crystal [6].

1.4.1 Phase-Velocity Surface

Knowing that the wave number k is related the magnitude v of the phase velocity by $k = \omega/v$, we can write the relation vectorially as

$$\mathbf{k} = \mathbf{v}\frac{\omega}{v^2} \tag{1.4.14}$$

In terms of components the above vector equation is equivalent to the three scalar equations

$$k_x = v_x\frac{\omega}{v^2} \qquad k_y = v_y\frac{\omega}{v^2} \qquad k_z = v_z\frac{\omega}{v^2} \tag{1.4.15}$$

Isotropic	*cubic*	$\chi = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}$	$\chi_{11} = \chi_{22} = \chi_{33} = a$ $n = \sqrt{1+a}$
Uniaxial	*trigonal* *tetragonal* *hexagonal*	$\chi = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$	$\chi_{11} = \chi_{22} = a, \chi_{33} = b$ $n_o = \sqrt{1+a}$ $n_E = \sqrt{1+b}$
Biaxial	*triclinic* *monoclinic* *orthorhombic*	$\chi = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$	$\chi_{11} = a, \chi_{22} = b, \chi_{33} = c$ $n_1 = \sqrt{1+a}$ $n_2 = \sqrt{1+b}$ $n_3 = \sqrt{1+c}$

Table 1.1: $\chi - tensor$ classification of crystals

Let us substitute the above values into the equation of the **k** surface in Equation (1.4.10). The result is

$$\begin{vmatrix} \frac{n_1^2 v^4}{c^2} - v_y^2 - v_z^2 & v_x v_y & v_x v_z \\ v_y v_x & \frac{n_2^2 v^4}{c^2} - v_y^2 - v_z^2 & v_y v_z \\ v_z v_x & v_z v_y & \frac{n_3^2 v^4}{c^2} - v_x^2 - v_y^2 \end{vmatrix} = 0 \tag{1.4.16}$$

after cancelation of ω^2 and division by v^4. This equation defines a three-dimensional surface that can be considered as the *reciprocal surface* to the **k** surface. It is called the *phase-velocity surface.* It is a double sheeted surface and gives directly the two possible values of the phase velocity for a given direction of plane wave propagation in the crystal. The general form of phase-velocity surface is shown in Figure(1.4). The intercepts with the coordinate planes consists of circles and *fourth-degree ovals*[7, 6, 5]. Thus for xy plane the two equations for the intercepts are

$$\begin{aligned} v^2 = v_x^2 + v_y^2 &= \frac{c^2}{n_3^2} \\ \frac{v_x^2}{n_2^2} + \frac{v_y^2}{n_1^2} &= \frac{v^4}{c^2} \end{aligned} \tag{1.4.17}$$

Similar relations hold for the other coordinate planes.

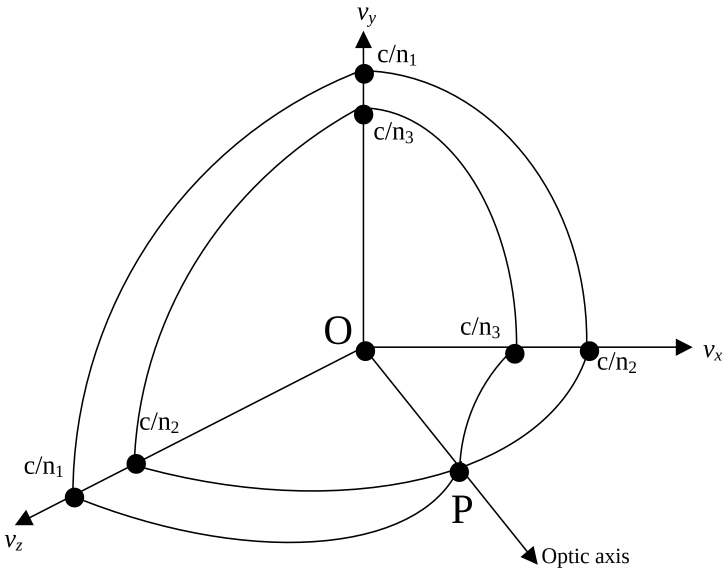


Figure 1.4: The phase-velocity surface

1.5 Maxwell Equations and Boundary Conditions

Suppose that an incident wave is monochromatic and planar, so that it has the form

$$\mathbf{E} = \mathbf{E}_{oi} \cos(k_r \cdot r - \omega_i t) \tag{1.5.1}$$

Assume that $\mathbf{E}_{oi}$ is constant in time; that is, the wave is linearly or plane polarized. Note that just as the origin of time, $t = 0$, is arbitrary, so too is the origin O in space, where $r = 0$. Without making any assumptions about their directions, frequencies, wavelengths, phases or amplitudes, we can write the reflected and transmitted waves as

$$\mathbf{E}_r = \mathbf{E}_{or} \cos(k_r \cdot r - \omega_r t + \epsilon_r) \tag{1.5.2}$$

and

$$\mathbf{E}_t = \mathbf{E}_{ot} \cos(k_t \cdot r - \omega_t t + \epsilon_t) \tag{1.5.3}$$

Here ϵ_r and ϵ_t are phase constants relative to $\mathbf{E}_i$ and are introduced here because the position of the origin in not unique.

The laws of electromagnetic theory lead to certain requirements that must be met by the fields, and these are referred to as the boundary conditions. Specifically, one of these is that the component of electric field intensity $\mathbf{E}$ that is the tangent to the interface must be continuous across it. Thus since $\hat{u}_n$ is the unit vector normal to the interface, regardless of the direction of the electric field with in the wavefront, the cross product of the electric field with the unit vector will be at right angles to the unit vector and therefore tangent to the interface. Thus,

$$\hat{u}_n \times \mathbf{E}_i + \hat{u}_n \times \mathbf{E}_r = \hat{u}_n \times \mathbf{E}_t \tag{1.5.4}$$

$$\hat{u}_n \times \mathbf{E}_{oi} \cos(k_i \cdot r - \omega_i t) + \hat{u}_n \times \mathbf{E}_{or} \cos(k_r \cdot r - \omega_r t + \epsilon_r) = \hat{u}_n \times \mathbf{E}_{ot} \cos(k_t \cdot r - \omega_t t + \epsilon_t) \tag{1.5.5}$$

This relationship must be true at any instant in time and at any point on the surface. Consequently, $\mathbf{E}_i$, $\mathbf{E}_r$ and $\mathbf{E}_t$ must have precisely the same functional dependence on the variables t and r.

$$(k_i \cdot r - \omega_i t)|_{y=\delta} = (k_r \cdot r - \omega_r t)|_{y=\delta} = (k_t \cdot r - \omega_t t)|_{y=\delta} \tag{1.5.6}$$

With this as the case, the cosines in Equation (1.5.4), cancel, leaving an expression independent of t and r. Since this must be true for the values of time, the coefficients of t must be equal. So $\omega_i = \omega_r = \omega_t$.

Recall that the electrons with in the media are undergoing forced linear vibrations at the frequency of the incident wave. Clearly, whatever light is scattered has that same frequency. Furthermore,

$$(k_i \cdot r)|_{y=\delta} = (k_r \cdot r + \epsilon_r)|_{y=\delta} = (k_t \cdot r + \epsilon_t)|_{y=\delta} \tag{1.5.7}$$

where r terminates on the interface. The values of ϵ_r and ϵ_t correspond to a given position of O, and thus they allow the relation to be valid regardless of that location. From the first two terms we obtain

$$[(k_i - k_r) \cdot r]|_{y=\delta} = \epsilon_r \tag{1.5.8}$$

This expression simply says that the endpoint of r sweeps out a plane perpendicular to the vector $(k_i - k_r)$. Thus $(k_i - k_r)$ is parallel to $\hat{u}_n$. Notice that since the incident and reflected waves are in the same medium, $k_i = k_r$. From the fact that $\hat{u}_n \times (k_i - k_r) = 0$, we get that

$$k_i \sin\theta_i = k_r \sin\theta_r \tag{1.5.9}$$

and hence the law of reflection $\theta_i = \theta_r$

Further, we see that all three vectors k_i, k_r and $\hat{u}_n$ are in the same plane of incidence. Equation (1.5.8) also shows that

$$[(k_i - k_t) \cdot r]|_{y=\delta} = \epsilon_t \tag{1.5.10}$$

so that k_t is also normal to the interface. Thus k_i, k_r, k_t, and $\hat{u}_n$ are all coplanar. As before, the tangential components of k_i and k_t must be equal, so

$$k_i sin\theta_i = k_t sin\theta_t \tag{1.5.11}$$

But because $\omega_i = \omega_t$, we can multiply both sides by c/ω_i to get

$$n_i sin\theta_i = n_t sin\theta_t \tag{1.5.12}$$

which is snell's law.

Notice that we could have chosen the origin **O** to be in the interface. In this case ϵ_r and ϵ_t would both have been zero. this is a simpler arrangement, so we will assume it from now on.

Suppose that a plane monochromatic wave is incident on the planar surface separating two isotropic media. Whatever the polarization of the wave, we can resolve the electric and magnetic fields into components parallel and perpendicular to the plane of incidence and treat these constituents separately.

1.6 Fresnel's Equations

1.6.1 Derivation of Fresnel's equation using the perpendicular component

Let assume that **E** is perpendicular to the plane of incidence and that **B** is parallel to it. Recall that $E = vB$, so that

$$\mathbf{k} \times \mathbf{E} = v\mathbf{B} \tag{1.6.1}$$

and

$$\mathbf{k} \cdot \mathbf{E} = 0 \tag{1.6.2}$$

since the tangential part of the electric field must be continuous across the boundary, We immediately get that

$$\mathbf{E}_{0i} + \mathbf{E}_{0r} = \mathbf{E}_{0t} \tag{1.6.3}$$

Note that although $\mathbf{E}_r$ and $\mathbf{E}_t$ must be normal to the plane of incidence by symmetry, we are guessing that they outward at the interface when $\mathbf{E}_i$ does. The directions of the magnetic fields follow from Equation (1.6.1).

We need to look at the boundary condition on the normal component of the field. Here we find that, instead of being continuous across the boundary like the tangential component, it is discontinuous. The important quantity turns out not to be **E**, but rather $\epsilon\mathbf{E}$. In other words, we require that the normal component of the product $\epsilon\mathbf{E}$ be continuous across the interface. Similarly, the normal component of $\mathbf{B}$ is continuous, as is the tangential component of $\mathbf{B}/\mu$. This later continuity condition requires that

$$-\frac{\mathbf{B}_i}{\mu_i}cos\theta_i + \frac{\mathbf{B}_r}{\mu_r}cos\theta_r = \frac{\mathbf{B}_t}{\mu_t}cos\theta_t \tag{1.6.4}$$

From equation 1.6.1 we get

$$\mathbf{B}_i = \frac{\mathbf{E}_i}{v_i} \qquad \mathbf{B}_r = \frac{\mathbf{E}_r}{v_r} \qquad \mathbf{B}_t = \frac{\mathbf{E}_t}{v_t} \tag{1.6.5}$$

Thus, since $v_i = v_r$, $\mathbf{B}_i = \mathbf{B}_r$ and using the definitions of the electric fields and remembering that the cosines are equal at the interface, this becomes

$$\frac{n_i}{\mu_i}(\mathbf{E}_{0i} - \mathbf{E}_{0r})cos\theta_i = \frac{n_t}{\mu_t}\mathbf{E}_{0t}cos\theta_t \tag{1.6.6}$$

combining this with equation 1.6.3 yields

$$\left(\frac{\mathbf{E}_{0r}}{\mathbf{E}_{0i}}\right)_\perp = \frac{\frac{n_i}{\mu_i}cos\theta_i - \frac{n_t}{\mu_t}cos\theta_t}{\frac{n_i}{\mu_i}cos\theta_i + \frac{n_t}{\mu_t}cos\theta_t} \tag{1.6.7}$$

and

$$\left(\frac{\mathbf{E}_{0t}}{\mathbf{E}_{0i}}\right)_\perp = \frac{2\frac{n_i}{\mu_i}cos\theta_i}{\frac{n_i}{\mu_i}cos\theta_i + \frac{n_t}{\mu_t}cos\theta_t} \tag{1.6.8}$$

The perpendicular subscript serves as a reminder that we are dealing with the case in which $\mathbf{E}$ is perpendicular to the plane of incidence. These two expressions, which are completely general statements applying to any linear, isotropic, homogeneous media, are two of the Fresnel equations. They can be simplified when the dielectrics satisfy $\mu_i \approx \mu_t \approx \mu_o$. This is a fairly common occurrence, so we can recast Equations(1.6.7) and (1.6.8) into their common forms

$$r_\perp \equiv \left(\frac{\mathbf{E}_{0r}}{\mathbf{E}_{0i}}\right)_\perp = \frac{n_icos\theta_i - n_tcos\theta_t}{n_icos\theta_i + n_tcos\theta_t} \tag{1.6.9}$$

and

$$t_\perp \equiv \left(\frac{\mathbf{E}_{0t}}{\mathbf{E}_{0i}}\right)_\perp = \frac{2n_i cos\theta_i}{n_i cos\theta_i + n_t cos\theta_t} \tag{1.6.10}$$

Here $r_\perp$ is the **amplitude reflection coefficient**, and $t_\perp$is the **amplitude transmission coefficient**.

1.6.2 Derivation of Fresnel's Equations using the parallel component

A similar pair of equations can be derived when the incoming **E** field lies in the plane of incidence. Continuity of tangential components of **E** on either side of the interface leads to

$$\mathbf{E}_{oi} cos\theta_i - \mathbf{E}_{or} cos\theta_r = \mathbf{E}_{ot} cos\theta_t \tag{1.6.11}$$

As before, continuity of the tangential components of B_μ yields

$$\frac{1}{\mu_i v_i}\mathbf{E}_{oi} + \frac{1}{\mu_r v_r} = \frac{1}{\mu_t v_t}\mathbf{E}_{ot} \tag{1.6.12}$$

Using the fact that $\mu_i = \mu_r$ and $\theta_i = \theta_r$ we can combine these to obtain two more Fresnel equations,

$$r_\parallel \equiv \left(\frac{\mathbf{E}_{0r}}{\mathbf{E}_{0i}}\right)_\parallel = \frac{\frac{n_t}{\mu_t} cos\theta_i - \frac{n_i}{\mu_i} cos\theta_t}{\frac{n_i}{\mu_i} cos\theta_t + \frac{n_t}{\mu_t} cos\theta_i} \tag{1.6.13}$$

and

$$t_\parallel \equiv \left(\frac{\mathbf{E}_{0t}}{\mathbf{E}_{0i}}\right)_\perp = \frac{2\frac{n_i}{\mu_i} cos\theta_i}{\frac{n_i}{\mu_i} cos\theta_t + \frac{n_t}{\mu_t} cos\theta_i} \tag{1.6.14}$$

When both media forming the interface are dielectrics, the amplitude coefficients become

$$r_\parallel \equiv \left(\frac{\mathbf{E}_{0r}}{\mathbf{E}_{0i}}\right)_\parallel = \frac{n_t cos\theta_i - n_i cos\theta_t}{n_i cos\theta_t + n_t cos\theta_i} \tag{1.6.15}$$

and

$$t_\parallel \equiv \left(\frac{\mathbf{E}_{0t}}{\mathbf{E}_{0i}}\right)_\parallel = \frac{2n_i cos\theta_i}{n_i cos\theta_t + n_t cos\theta_i} \tag{1.6.16}$$

If we use Snell's law, Equations (1.6.9, 1.6.10, 1.6.15 and 1.6.16) can be simplified more to yield

$$r_\perp = -\frac{sin(\theta_i - \theta_t)}{sin(\theta_i + \theta_t)} \tag{1.6.17}$$

$$r_\parallel = \frac{tan(\theta_i - \theta_t)}{tan(\theta_i + \theta_t)} \tag{1.6.18}$$

$$t_\perp = \frac{2sin\theta_t cos\theta_i}{sin(\theta_i + \theta_t)} \tag{1.6.19}$$

$$t_\parallel = \frac{2sin\theta_t cos\theta_i}{sin(\theta_i + \theta_t)cos(\theta_i - \theta_t)} \tag{1.6.20}$$

1.6.3 Amplitude Coefficients

Let's look first at the form of the amplitude coefficients over the range of θ_i values. At nearly normal incidence ($\theta_i \approx 0$) the tangent is essentially equal to sine. In this case, the amplitude reflection coefficients become

$$[r_\parallel]_{\theta_i=0} = [-r_\perp]_{\theta_i=0} = \left[\frac{sin(\theta_i - \theta_t)}{sin(\theta_i + \theta_t)}\right]_{\theta_i=0} \tag{1.6.21}$$

After explaining the sines and using Snell's law, this expression becomes

$$[r_\parallel]_{\theta_i=0} = [-r_\perp]_{\theta_i=0} = \left[\frac{n_t cos\theta_i - n_i cos\theta_t}{n_i cos\theta_t + n_t cos\theta_i}\right]_{\theta_i=0} \tag{1.6.22}$$

In the limit as θ_i goes to zero, $cos\theta_i$ and $cos\theta_t$ both approach one, and so

$$[r_\parallel]_{\theta_i=0} = [-r_\perp]_{\theta_i=0} = \left[\frac{n_t - n_i}{n_t + n_i}\right] \tag{1.6.23}$$

When $n_t > n_i$, we have external reflection. It follows from Snell's law that $\theta_i > \theta_t$ and $r_\perp$ is negative for all values of θ_i. In contrast, $r_\parallel$ starts out positive at $\theta_i = 0$ and decreases gradually until it equals zero when $(\theta_i + \theta_t) = 90^0$, since $tan 90^0$ is infinite. The particular value of the incident angle for which this occurs is denoted by θ_p and is referred as the Polarization angle. As θ_i increases beyond θ_p, $r_\parallel$ becomes progressively more negative, reaching -1 at 90^0. This has the effect that even a poor surface, such as the surface of a book, will become mirror like at a glancing angle of incidence.

At normal incidence, we see that

$$[t_{\|}]_{\theta_i=0} = [t_{\perp}]_{\theta_i=0} = \frac{2n_i}{n_i + n_t} \tag{1.6.24}$$

in addition, we find that

$$t_{\perp} - r_{\perp} = 1 \tag{1.6.25}$$

holds for all θ_i while

$$t_{\|} + r_{\|} = 1 \tag{1.6.26}$$

is true at normal incidence.

For internal reflection, $n_i > n_r$ in this case $\theta_t > \theta_i$ and $r_{\perp}$ will always be positive. In particular, $r_{\perp}$ will reach +1 at the critical angle, θ_c. Specifically, θ_c is the particular value for the incident angle such that $\theta_t = 90^0$. Similarly, $r_{\|}$ starts off negative, passes through zero at θ_p and increases to 1 at θ_c.

1.6.4 Phase shifts

Perpendicular components:

Recall that we saw that the negative sign associated with $r_{\perp}$ came about due to the perpendicular orientation that we chose for the normal component of the electric field. Had we chosen differently, we could have eliminated the negative sign. Thus the sign of $r_{\perp}$ is associated with the relative directions of $[\mathbf{E}_{oi}]_{\perp}$and $[\mathbf{E}_{or}]_{\perp}$. Also recall that a reversal of $[\mathbf{E}_{or}]_{\perp}$ is equivalent to introducing a phase shift, $\triangle\varphi_{\perp}$, of π radians into

$[\mathbf{E}_r]_\perp$. Hence, at the boundary $[\mathbf{E}_i]_\perp$ and $[\mathbf{E}_r]_\perp$ will be antiparallel and therefore π radians out of phase with each other. When we consider components normal to the plane of incidence, there is no confusion as to whether the two fields are in phase or π radians out of phase: if parallel, they are in phase; if antiparallel, they are π radians out of phase. We can summarize this by stating that "the component of the electric field normal to the plane of incidence undergoes a phase shift of π radians upon reflection when the incident medium has a lower index of refraction than the transmitting medium. When $n_i > n_t$, no phase shift in the normal component results on reflection, that is $\triangle\varphi_\perp = 0$ so long as $\theta_i < \theta_c$".

Parallel Components:

When we consider $[\mathbf{E}_i]_\parallel$, $[\mathbf{E}r]_\parallel$ and $[\mathbf{E}_t]_\parallel$ we need to define more explicitly what it means when we say in phase, since the field vectors are coplanar but not generally collinear. we can define two fields in the incident plane as being in phase if their y-components are parallel and are out of phase if the components are antiparallel. When the two electric fields are out of phase so too are their associated magnetic fields and vice versa. With this definition we need only look at the vectors normal to the plane of incidence. Recall that the amplitude reflection coefficient for the parallel component is given by Equation (1.6.10) which is positive ($\triangle\varphi_\parallel = 0$) as long as

$$n_t \cos\theta_i - n_i \cos\theta_t > 0 \tag{1.6.27}$$

that is, if

$$\sin(\theta_i - \theta_t)\cos(\theta_i + \theta_t) > 0 \tag{1.6.28}$$

This will be the case for $n_i < n_t$ if

$$(\theta_i + \theta_t) < \frac{\pi}{2} \tag{1.6.29}$$

and for $n_i > n_t$ when

$$(\theta_i + \theta_t) > \frac{\pi}{2} \tag{1.6.30}$$

Thus when $n_i < n_t$, $[\mathbf{E}_{or}]$ and $[\mathbf{E}]_{oi}$ will be in phase until $\theta_i = \theta_p$ and out of phase by π radians thereafter. In contrast, for internal reflection $r_{\parallel}$ is negative until $\theta_p^{'}$, which means that $\triangle\varphi_{\parallel} = \pi$. $\theta_p^{'}$ to θ_c, $r_{\parallel}$ is positive and $\triangle\varphi_{\parallel} = 0$. Beyond θ_c, $r_{\parallel}$ becomes complex and $\triangle\varphi_{\parallel}$ gradually increases to π at $\theta_i = 90^0$[7, 16, 18, 17]

Chapter 2

Polarization

An oscillating vector field must instantaneously have a unique direction. For the plane electromagnetic wave in an isotropic medium this direction must be perpendicular to the wave normal; if it remains constantly in the same direction, the wave is said to be Plane polarized. On the other hand, if the direction changes randomly, the wave is said to be unpolarized or randomly polarized.

Depending on the phase difference between two oscillating electric field vectors, we can have a linear, circular or elliptical polarization. Two plane polarized waves have combined to produce another wave which is also plane polarized.

If the phase difference is a multiple of $\pi/2$, the resultant oscillating vector now rotates following a circle or ellipse depending on the amplitudes of the two vectors. Linearly polarized light is a surprisingly common phenomenon in everyday circumstances. Light reflected from any smooth surfaces such as a wet road or a polished table top, partially linearly polarized; this is easily demonstrated by turning the polaroid glass which gives a change in brightness according to the change in angle between the plane of polarization and the transmission axis of the polaroid. The maximum effect is found for reflection at a particular angle of incidence, the Brewster angle.

2.1 Formal Description of Polarized Light

When light interacts with matter, the force exerted on the electron by the electric field of the light wave is much greater than the magnetic field. That is why the polarization is determined by the direction of electric field.

Let us consider an electromagnetic wave propagating along $\hat{x}$ direction. The orthogonal electric fields are along $\hat{y}$ and $\hat{z}$ axes. These components are the two plane polarized waves. There is a phase difference ϕ between the two components.

$$\mathbf{E}_y = E_{0y} \exp i(\omega t - kx)\hat{y} \tag{2.1.1}$$

$$\mathbf{E}_z = E_{0z} \exp i(\omega t - kx + \phi)\hat{z} \tag{2.1.2}$$

If we take the real component of the above equations, and taking the

electric field at a fixed space $x = 0$

$$\mathbf{E}_y = E_{0y} \cos{(\omega t)}\hat{y}$$

$$\mathbf{E}_z = E_{0z} \cos{(\omega t + \phi)}\hat{z}$$

Taking the magnitude of $\mathbf{E}_y$ and $\mathbf{E}_z$

$$\tfrac{|\mathbf{E}_y|}{E_{oy}} = \cos(\omega t)$$

$$\tfrac{|\mathbf{E}_z|}{E_{oz}} = \tfrac{|\mathbf{E}_y|}{E_{oy}} \cos(\phi) - \sin(\omega t)\sin(\phi)$$

Squaring both side and simplifying,

$$\frac{\mid \mathbf{E}_z \mid^2}{E_{oz}^2} + \frac{\mid \mathbf{E}_y \mid^2}{E_{oy}^2} - 2\frac{\mid \mathbf{E}_y \mid\mid \mathbf{E}_z \mid}{E_{oy}E_{oz}} cos(\phi) = \sin^2(\phi). \tag{2.1.3}$$

This is the general equation of ellipse. Depending on the values of ϕ, the equation can represent line, circle or ellipse. The sign of ϕ determines the sense of rotation.

Case I. When the phase difference is an integral multiple of π, equation(2.1.3) becomes

$$E_y = \pm\tfrac{A_y}{A_z}E_z$$

The wave is linearly polarized. The negative sign is when it is an odd multiple of π and the positive sign is when it is an even multiple of π.

Case II. When phase difference is an odd multiple of $\pi/2$ and $E_{oy} = E_{oz}$, equation(2.1.3) represents an equation of a circle.

$$E_y^2 + E_z^2 = A^2$$

This is a circularly polarized light, a given vector precess with a constant angular speed with constant magnitude. When z-component electric field leads y-component, we have clockwise rotation which is called right handed polarization.

Case III. When the phase difference is an odd multiple of $\pi/2$ and $E_{oz} \neq E_{oy}$, the polarization becomes elliptic whose major axis lies either on y or x axis.

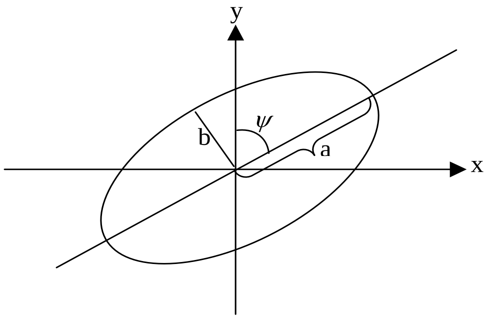


Figure 2.1: *Elliptically polarized light for arbitrary phase shift.*

Case IV. For a general case, when ϕ is not an integral multiple of $\pi/2$, elliptical polarization whose major axis does not lie along z or y will result. The tilting angle ψ is defined as

$$[\tan(2\psi) = \frac{2ab\cos(\phi)}{a^2-b^2}]$$

Ellipticity e is the ratio of the length of the semi-minor axis of the ellipse b to the length of semi- major axis a. The right-handed and left-handed circularly polarized states correspond to $e = 1$ and $e = -1$ respectively. Linearly polarized light has ellipticity of zero magnitude.

2.2 Modern Description of Polarized and Unpolarized Light

2.2.1 Poincarè Sphere

The Poincarè sphere is a unit radius spherical surface each point of which signifies a different polarization form [10]. It is a polarization space in the form of a spherical surface whose points are a one to one correspondence with different states of polarizations of light. The state of polarization of light can be described by using different kinds of polarization space. The complex plane representation of polarized light gives another space whose points are in one to one correspondence with different possibilities of polarization.

Consider a sphere of radius S_0. Any point on the sphere is represented by longitude 2θ and latitude 2ϵ. The following properties of polarized light can be associated with a point P on a sphere.

1. The north and the south pole stands for the left and right circular polarization respectively.
2. Every point on the equator represents a linear polarization form; each point implies different oscillation direction.

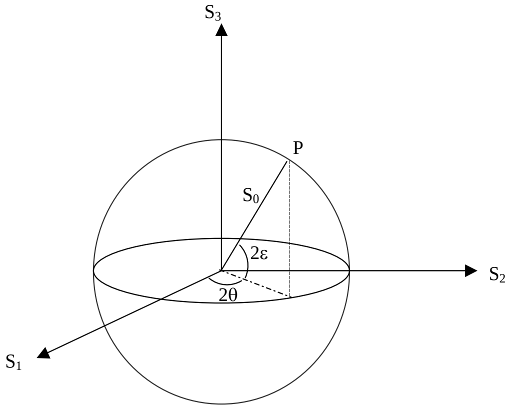


Figure 2.2: *Poincarè sphere.*

3. The northern hemisphere excluding the north pole represents right handed elliptical polarization and the southern hemisphere excluding the south pole represents left handed elliptical polarization.
4. The latitude whose common axis is polar axis from south to north pole represents an equiellipticity contour.

In general, the state of polarization is described by azimuthal ψ and ellipticity angle as described in the previous section. These two quantities represent a point on the Poincarè sphere with a coordinate of latitude 2ϵ and the longitude 2θ. A bilinear transformation can be produced form the Poincarè sphere representation to a cartesian coordinate system. A given point P is represented with a spherical coordinate $(S_0, \pi/2 - 2\epsilon, 2\theta)$. This can be expressed in a new cartesian coordinate system (see figure 2.2).

$$S_0^2 = S_1^2 + S_2^2 + S_3^2 = E_x^2 + E_y^2, \tag{2.2.1}$$

$$S_1 = S_0 \cos(2\epsilon)\cos(2\theta) = {E_x}^2 - {E_y}^2, \tag{2.2.2}$$

$$S_2 = S_0 \cos(2\epsilon)\sin(2\theta) = 2E_xE_y\cos\phi, \tag{2.2.3}$$

$$S_3 = S_0 \sin(2\epsilon) = 2E_xE_y\sin\phi, \tag{2.2.4}$$

where ϕ is the phase shift between the horizontal and the vertical components of the electric field **E** propagating in z direction .

If the radius of the Poincarè sphere is unity, the above equations represent Stokes parameters.

2.3 Stokes Vectors

In 1852 G.G. Stokes introduced four quantities, Stokes parameters, which are functions of the observable electromagnetic waves. It equally applies well to polarized light, partially polarized light and unpolarized light. Stokes vector is a 4 × 1 column of vector consisting of Stokes parameters. In order to exploit the use of compact matrix formalism to investigate the interaction between the light wave and the optical components, Stokes vectors is preferred to Poincarè sphere representation. It is often written horizontally to save space. Stokes parameters are a set of four real quantities with dimension of intensity given by equations(2.2.1-2.2.4)

The first parameter S_0 is the total intensity of the light waves. S_1 gives the difference between x and y components and can be either positive, negative or zero. It reduces to positive when the vibration is horizontal and reduces to negative when the vibration is vertical. It becomes zero when the beam is circularly polarized, elliptically polarized with major axis is at $\pm\pi/4$ or unpolarized. Thus it does indicate preference of x polarization to y polarizations. Stokes parameter S_3 represents the preference of the wave to either right or left handed circularly polarized component. The third component S_2 represents a preference for $\pm\pi/4$ linear polarization.

When a given light is completely polarized, the following relation holds.

$$S_0^2 = S_1^2 + S_2^2 + S_3^2.$$

For partially polarized light, the relation becomes,

$$S_0^2 > S_1^2 + S_2^2 + S_3^2.$$

The degree of polarization is the ratio of the intensity of totally polarized light to the total intensity of the light. Mathematically, it is given as,

$$P = \frac{S_1^2+S_2^2+S_3^2}{S_0^2}.$$

It is important to remember that Stokes vectors may be added only when the beams concerned are incoherent [12].

2.4 Jones Vectors and Matrices

Jones vector is an abstract mathematical space formed by all vectors that are obtained by considering all possible pairs of complex numbers for $\mathbf{E}_x$ and $\mathbf{E}_y$. It is a two elements column vector. Each element describes one component of electric field $\mathbf{E}$. It is superior to the Stokes vector in some ways and inferior in others. It is superior in that, it is applicable to the addition of coherent beams; also it is more compact. But it can not handle unpolarized or partially polarized light.

Consider a uniform transverse electric elliptically polarized plane wave. If such a wave is assumed to propagate in z-direction, $\mathbf{E}$ is given by

$$\mathbf{E}(z,t) = \tilde{E}_x cos(wt - 2\pi z/\lambda + \delta_x)\hat{x} + \tilde{E}_y cos(wt - 2\pi z/\lambda + \delta_y)\hat{y}, \qquad (2.4.1)$$

where $\tilde{E}_x$ and $\tilde{E}_y$ represent amplitudes of the linear, simple harmonic oscillation of the electric field components along the x and y axes, and σ_x and σ_y represent the respective phases of the oscillation.

A more compact mathematical description of the wave can be obtained from equation(2.4.1). This compact description is sufficient enough to fully explain the wave polarization and its modification after interacting with optical devices. The concise description is the Jones vector of a wave represented by the following matrix.

$$\mathbf{E} \;=\begin{pmatrix} \tilde{E}_x e^{(i\sigma_x)} \\ \tilde{E}_y e^{(i\sigma_y)} \end{pmatrix} \tag{2.4.2}$$

From the above equation, the Jones vectors for different polarization can be obtained.

1. For linearly polarized light wave, the normalized Jones vector is

   $$\mathbf{E} \;=\begin{pmatrix} \cos\theta \\ \sin\theta \end{pmatrix}$$

   where θ is the angle the vector makes with the x-axis.

   Particularly for x-polarization and y-polarization, the Jones vectors become $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$, and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$

2. For left and right circularly polarized light, the normalized Jones vectors are respectively

   $$\mathbf{E}_l = \tfrac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}$$

   $$\mathbf{E}_r = \tfrac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}$$

The main use of Jones vector is in computing the effect of inserting optical devices like polarizer, analyzer and retarder in a given system. This effect is easily computed by multiplying Jones vectors of incident beam by the respective Jones matrices of the optical devices [**?**]. The optical elements are represented by 2 × 2 Jones matrix. Consider an incident wave on a non depolarizing optical system that consists of a single optical device. Due to the interaction, a modified wave will emerge from the system. This is shown in following schematic diagram. The incident and the out going plane waves can be described by their appropriate Jones vectors $\mathbf{E}_1$ and $\mathbf{E}_0$. These two plane waves are related by a linear relation,

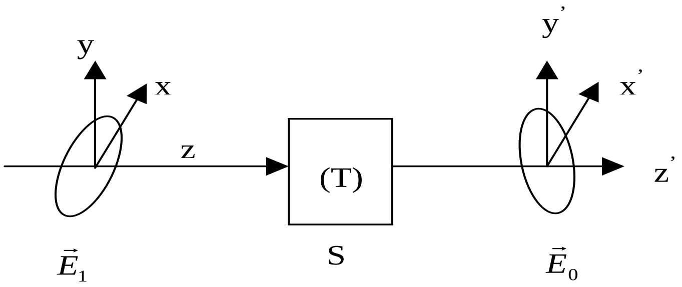


Figure 2.3: *Schematic diagram for incident and output plane waves of Jones vectors*

$$E_{0x} = T_{11}E_{1x} + T_{12}E_{1y}. \tag{2.4.3}$$

$$E_{0y} = T_{21}E_{1x} + T_{22}E_{1y}. \tag{2.4.4}$$

This can be written in a more compact form by matrix,

$$E_0 = TE_1, \text{ where } T = \begin{pmatrix} T_{11} & T12 \\ T_{21} & T_{22} \end{pmatrix}$$

The 2 × 2 transformation matrix T is called Jones matrix of the optical device. [12] It includes the overall effect of optical devices on the incident wave.

This result can be generalized for a series of successive optical devices. The out going light is given for such system simply as,

$$E_0 = T_n T_{n-1} ... T_1 T_0 E_1,$$

where T_n represents Jones matrix of the n^{th} optical device.

Chapter 3

Theory of RAS

Reflection anisotropy spectroscopy (RAS) is a non-destructive optical probe of surfaces that is capable of operation within a wide range of environments. RAS measures the difference in reflectance $\triangle r$ of normal incidence plane-polarization light between two orthogonal directions in the surface plane (x, y) normalization to the mean reflectance (r):

$$\frac{\triangle r}{r} = \frac{2(r_x - r_y)}{r_x + r_y}, \tag{3.0.1}$$

where the reflectance r are complex Fresnel reflectance amplitudes. In general , optical probes are not surface sensitive due to the fact that, with the possible exception of some high conductivity metals, the probe light penetrates many atomic layers into the bulk of 'opaque' materials. However, if the material being probed has a cubic crystal structure the bulk linear optical response to normal incidence light will be isotropic. In such materials and with such geometry, anisotropic reflectance can only arise from anisotropy in the surface region or from non-linear effects. Usually the later can be neglected in RAS measurements, and the observed reflectance anisotropy of cubic materials can be attributed to the surface.

Experimentally, RAS may be regarded as a development of spectroscopic ellipsometry (SE), a technique that enables the direct experimental determination of the dielectric function of materials with out the need of undertaking a Krammers-Kronig analysis of spectral reflectivity. In SE, particularly as applied to semiconductors, linearly polarized light is incident on the sample close to the Brewster angle [13]. In contrast, RAS uses linearly polarized light directed at near normal incidence to the sample surface.

The interpretation of RA spectra form a single crystal surface in non-trivial since the response of the surface under investigation depends upon the complex dielectric function of both the surface region and the bulk. The dielectric function is a different quantity to calculate from first principles even for the bulk of a crystalline solid. The translational symmetry of a crystal is broken by the introduction of a surface, and theoretical difficulties are increased by the introduction of intrinsic surface states and changes in character of the continuum states at the surface. The difficulty of theoretical work has led to the development of empirical approach that offer some insight into the surface electronic transitions that give rise to features in RA spectra.

3.1 Principles and instrumentation of RAS

The measurement of reflection anisotropy requires an accurate method of determining the polarization state of light reflected from a surface. Thus RAS a form of 'polarimetry' and shares a common heritage with techniques such as SE, circular dichroism (CD), optical rotary dispersion (ORD) and linearly birefringence (LB). The scientific communities using this techniques share methods and a good deal of instrumentation. For all these techniques improvement in accuracy and signal to noise can be archived by using 'polarization modulation' [19].

3.1.1 Intensity modulation

The Jones matrix formalism, discussed in chapter two, allows straight forward evaluation of the net effect of a succession of optical components simply by successive multiplication of their individual matrices. This process requires that all component matrices have been expressed in a common reference frame. To illustrate this point, consider the effect of an optical element with Jones matrix M upon polarization vector $\underline{u}$. In the $'xy'$ reference frame the change in polarization vector to $\underline{v}^{xy}$ can be expressed as

$$\underline{v} = M^{xy}\underline{u}^{xy} \tag{3.1.1}$$

The use of a different coordinate system, x'y', is equivalent to operating on $\underline{u}^{xy}$ and $\underline{v}^{xy}$ with the $xy \rightarrow x'y'$ transformation matrix T. It then follows that M in the dashed reference frame is given by

$$M^{x'y'} = T^{-1}M^{xy}T \tag{3.1.2}$$

A potential source of confusion arises in the formulation of the Jones Matrices for reflection devices. While it is eminently sensible, though not necessary, for x and y (or x' and y') to have the same definitions for input and output waves when considering transmission devices, the choice is not so obvious for reflecting devices. Most modern optics texts prefer coordinate systems in which light polarized in the plane of incidence, p polarized light, suffers a phase change of π upon reflection. This choice amounts to reversing the definition of either x or y for the reflected beam so that right-handed coordinate systems are used for both incident and reflected waves. In the context of RAS, however, one is considering cases of small anisotropy, and it is natural to choose coordinate system that most clearly shows this. Accordingly we adopt a convention in which x and y each have the sign for incident and reflected waves. A perfect isotropic mirror then has a normal incidence Jones reflection matrix given by the identity matrix. For a system with small and linear optical anisotropy in the plane of the surface there exist two orthogonal linear eigen polarizations with approximately equal eigen values (reflection amplitudes): $r_x \approx r_y$. In this diagonal reference frame the Jones reflection matrix has the form

$$\begin{pmatrix} r_x & 0 \\ 0 & r_y \end{pmatrix} \tag{3.1.3}$$

The original and simplest RA spectrometer was designed by Aspnes [8], and a schematic representation is shown in Figure (3.1).

Linearly polarized light is incident on a sample rotating with angular frequency ω. In the diagonal frame of the sample, the time dependent polarization vector of the input light has the form $\begin{pmatrix} sin\omega t \\ cos\omega t \end{pmatrix}$. The intensity of the light reflected by the sample is therefore

$$I \propto R - \frac{\triangle R}{2} cos 2\omega t, \tag{3.1.4}$$

where R and $\triangle R$ represent, respectively, the average and the anisotropy of the reflected intensities:

$$R = \frac{|r_x|^2 + |r_y|^2}{2}, \qquad \triangle R = |r_x|^2 - |r_y|^2. \tag{3.1.5}$$

The ratio of the oscillatory ($I_{2\omega}$) and time-independent (I_0) contributions to the reflected intensities is a direct measure of $\triangle R/R$:

$$\frac{I_{2\omega}}{I_0} = \frac{1}{2\sqrt{2}} \frac{\triangle R}{R} \tag{3.1.6}$$

The main disadvantage of the rotating sample spectrometer is simply that it is not always convenient or even possible to rotate the sample, particularly for *in situ* studies.

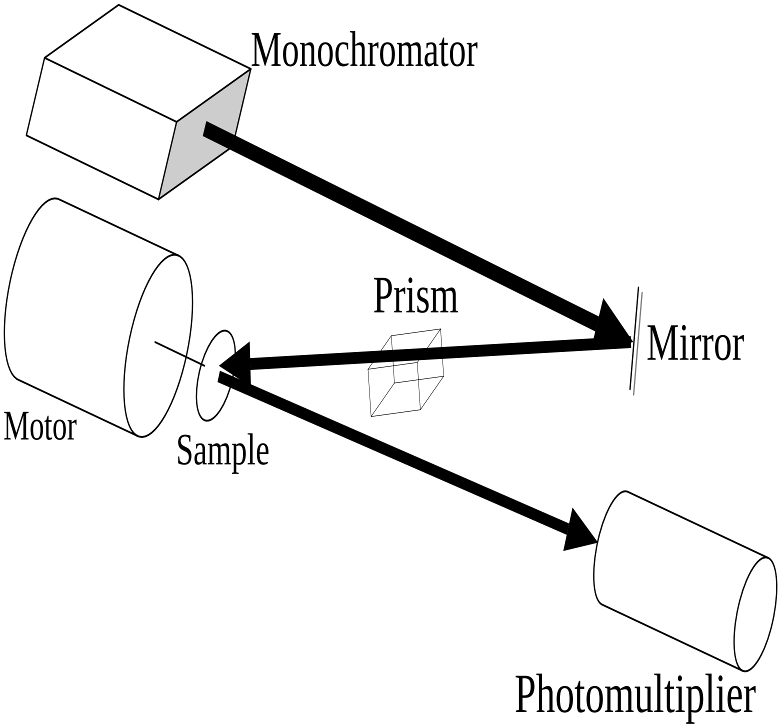


Figure 3.1: Schematic of an early RA spectrometer design with rotating sample

The remedy would appear to be trivial: rotate the polarizer instead of the sample. Unfortunately, slight polarization in the light source and a polarization dependence of the detector introduce false signals, preventing RAS measurements on an absolute scale. Nonetheless, the rotating analyzer configuration is well suited to *in situ* real-time measurements where *changes* in RAS signals are of primary importance.

An inherent drawback with mechanically rotating components is the difficulty of maintaining precise alignment. In addition, mechanical modulation techniques are relatively slow since a single modulation cycle is usually of the order $\geq 10^{-2}$s. Electro-optic modulation can be driven much faster- in Megahertz range- to greatly increase the potential time resolution for real-time studies.

3.1.2 Phase modulation

As in a related fields, photoelastic modulation has become popular in RAS community. The photoelastic modulation (PEM) is essentially a dynamic waveplate. In effect, one linear polarization, perpendicular to the modulation axis, is unaffected by the PEM while light polarized along the modulation axis undergoes retardation, Γ. This is achieved by applying an electric field to piezoelectric crystal coupled to a suitable transparent material such as fused silica. The electrically induced mechanical stress in the silica gives rise to birefringence, which is proportional to the stress. Thus a sinusoidal electric field introduces an oscillatory retardation:

$$\Gamma = \Gamma_0 \sin \omega t \tag{3.1.7}$$

To achieve significant retardation the crystal must be driven at its resonant frequency. Since the speed of sound in crystals is of the order of $10^3 m/s$, resonant frequencies are of the order of 10^5Hz for devices with physical dimensions of the order of 10^{-2}m. Such modulation frequencies are well beyond any mechanical resonance and promise temporal resolution approaching the microsecond regime. In addition to high speed and low noise, PEM modulation offers greater information content that the intensity modulation techniques discussed above. The RA is most fully expressed as $\triangle r/r$, a complex quantity while $\triangle R/R$ is real and, for small anisotropies, approximately equal to $2Re(\triangle r/r)$. By modulating phase rather than intensity, measurement of both the real and imaginary parts of $\triangle r/r$ becomes possible.

The spectral range of interest in most RAS studies ranges form the near infrared (NIR) through the visible to the near UV (1-6eV) and this places constraints on the materials that can be used. Because the difference in r_x and r_y is often small, the polarizer and analyzer should have high extinction ratio, typically greater than

10^5. Consequently, prism type polarizers are used. Prism polarizers fit into two broad categories: the beam splitting type, such as Rochon and Wollaston prisms, and the various Glan prisms that separate the two polarized beams by total internal reflection. Glan prisms may be regarded as preferable insofar that only one beam emerges, where as in the beam splitting type both linearly polarized beams emerge with polarizations at 90^0 to each other. The single beam poses no restrictions on location of the components in the optical layout and as such very compact layouts are possible. With two beams it is important to avoid any overlap, and this often requires longer distances between components.

Chapter 4

The RAS Technique, Data analysis and Interpretation

4.1 The rotating polarizer-analyzer RAS

In the previous chapter we have seen the general idea and setup of RAS. In a conventional RAS technique, the sample rotates trough 360^0s while the polarizer and analyzer remain fixed as shown in Figure (4.1). Light form the laser is chopped and then passes through a polarizer and onto the sample, mounted on a precision-motor driven rotator. The reflected light then passes through an analyzer fixed at 45^0 and reaches the detector which is connected to a Lock-in amplifier. The shortcoming of this technique is that it is not always easy, if not impossible, to rotate the sample keeping the sample to light interaction point fixed. Moreover, it cannot be used for *in situ* real-time measurements as discussed in chapter three of this paper.

In the second technique, which is a modification of the RAS technique and the focus of this paper, the polarizer-analyzer combination rotates instead of the sample, making it very suitable for *in situ* real-time measurements. The other advantage is that, it is a lot easier to work with once the polarizer-analyzer combination is set. That is to say, the sample can be changed or the face or point of observation of the

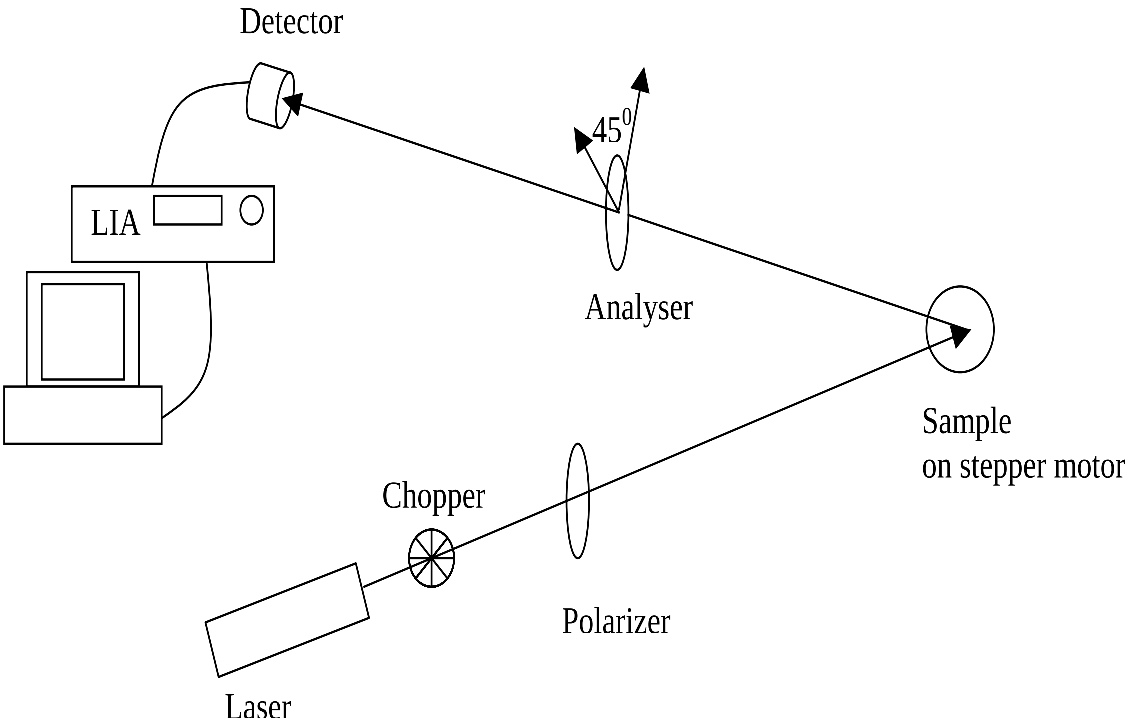


Figure 4.1: Rotating-sample RAS setup

same sample can be altered without having to worry about whether or not the point of observation is at the center of the rotator, which is an essential and very tedious task if one is using the rotating-sample technique, which makes this method very powerful. Figure (4.2) shows the complete setup.

Light from a 5mW He-Ne laser (PHYWE) passes through a half-wave mica retarder ($\lambda/2$) (MELLES GRIOT, Model: 02WRM02104102365) which is mounted on a precision motor (MELLES GRIOT, Model: 17BSC002) controlled nano-rotator (MELLES GRIOT, Model 17AMR101), after being chopped by an optical copper (Stanford Research Systems, Model: SR540). The half-wave retarder changes the direction of polarization of the laser and thus, if the axis of the retarder is rotated we find light of constantly rotating plane of polarization. Then this light is made to fall on the sample and is reflected to a rotating analyzer, which is 45 degrees phase shifted relative to the half-wave retarder, and finally, directed to the detector. The signal form the detector is fed to the Lock-in amplifier (Stanford Research Systems, Model: SR830). The Lock-in Amplifier is interfaced with a PC, and is controlled by a LabVIEW (National Instruments) program written in our working group.

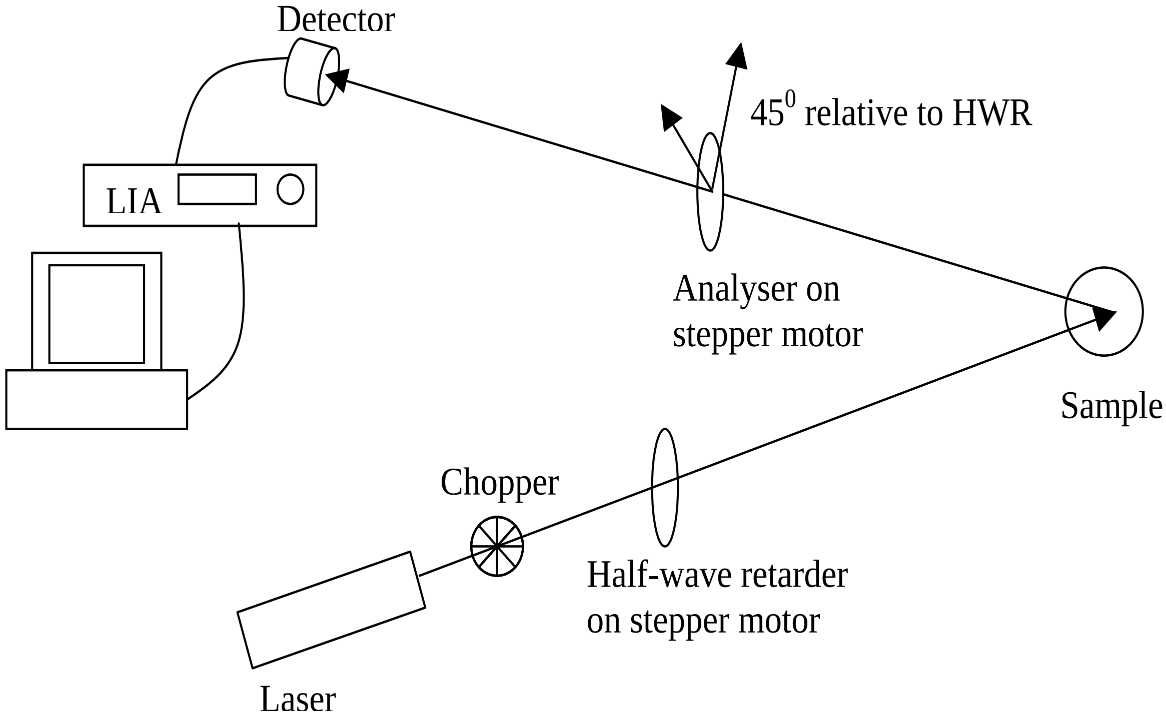


Figure 4.2: Rotating polarizer-analyzer setup

4.2 Determination of the optical axis of the KTP crystal

The next step in applying RAS is to determine the optical axis of the sample, in our case, the KTP crystal. To do so, we have to use ideas discussed in chapter one.

When light of arbitrary polarization propagates through an anisotropic crystal, it can be considered to consist of two independent waves that are polarized orthogonally with one another and traveling with two different phase velocities. But those two phase velocities have the same value if the light is passing through the optical axis. Due to this characteristic the transmitted and reflected light exhibit peculiar characters at the optical axes.

To apply this fact it is worthful to by review some properties of the sample. KTP is a biaxial anisotropic crystal and has a 2-fold C_2 symmetry (i.e. the crystal structure remains unchanged under 180^0 rotation). The crystal structure is orthorhombic and therefore has three refractive indices, n_1, n_2 and n_3, which are all different in magnitude.

When a linearly polarized light, with the polarization direction lying on the optical axis of an anisotropic crystal, the crystal behaves as though it is an isotropic crystal and passes through with a single speed. However, when light enters with a different polarization direction with that of the optical axis, it is refracted into two rays which are each polarized with vibration directions oriented at right angles to each other and have two different velocities. From these facts it is obvious that the intensity of the transmitted light is maximum when the direction of polarization of the incoming light is the same as the optical axis of the sample. Therefore the reflected light in the above situation should be minimum.

The KTP crystal, because of the existence of 2-fold C_2 symmetry and biaxial nature, is expected to have two optical axes. The measurement taken using the polarizer-analyzer RAS is as shown in the Figure 4.3. The polarization direction of light emerging from the retarder makes a 2 θ angle from the optical axis of the retarder if the incoming laser is making a θ degree with the optical axis. That means if we rotate the half-wave retarder through 360^0 then the emerging light will have its polarization direction rotated through 720^0. The graph is plotted for a 360^0 rotation for the retarder, which is equivalent to "rotating the laser" through 720^0 degrees.

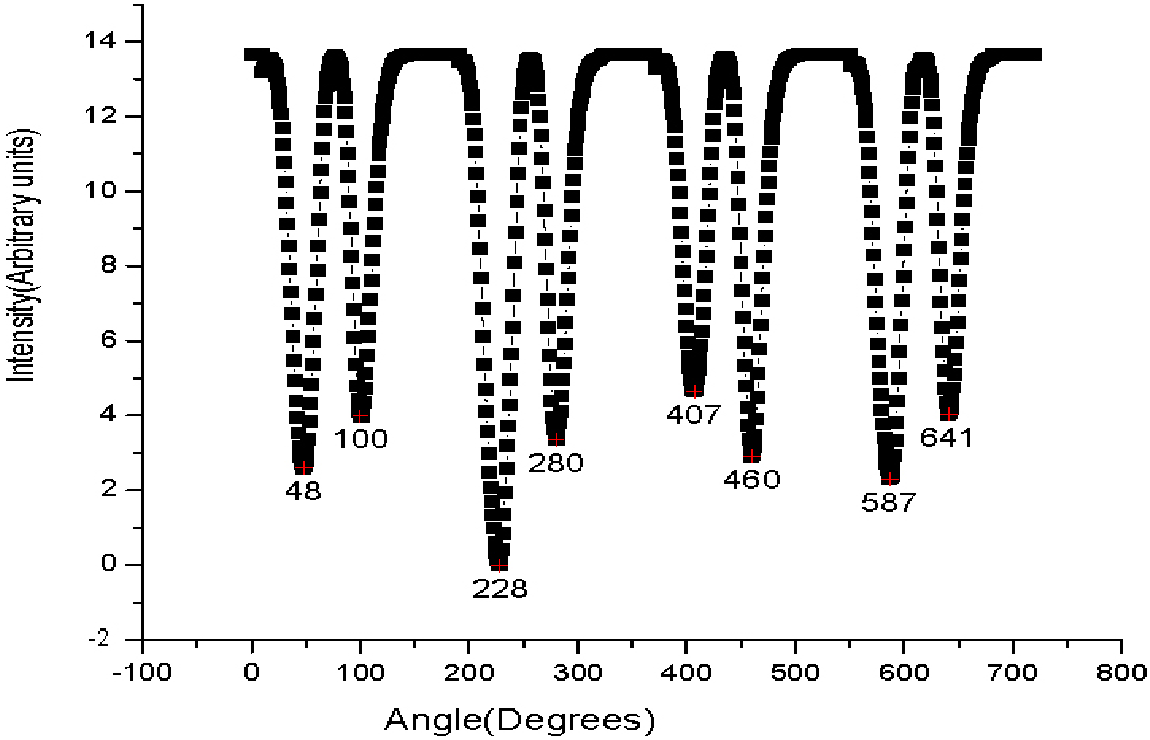


Figure 4.3: reflected light as a function of the angle of rotation using fixed sample RAS.

Figure (4.4) shows the measurement taken using rotating sample RAS. We know

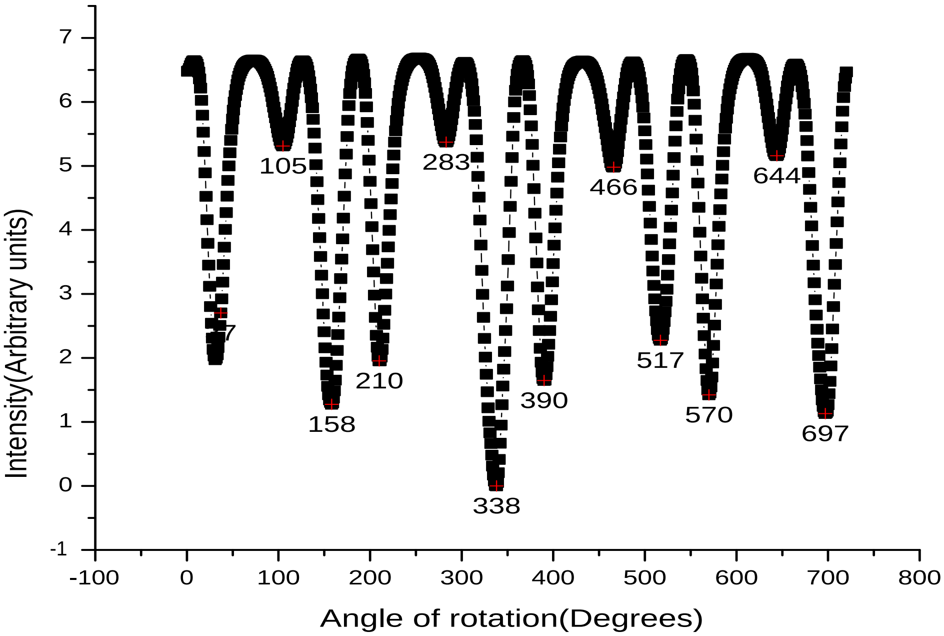


Figure 4.4: reflected light as a function of angle of rotation by using rotating sample RAS.

that the crystal has two optical axes and therefore we expect the spectra to have four minima, but because we have plotted the reflection through 720^0 we have eight minima.

These minima are at, taking only the first four, 48^0, 100^0, 228^0 and 280 degrees. These minima show that there are two 2-fold C_2 symmetries (the difference between 48^0 and 228^0, and 100^0 and 280^0 is 180 degrees, this shows repetition in every 180 degrees). In Figure 4.5, the data obtained for the angle of rotation from 180^0 to 360^0 is plotted along with the data obtained for 0^0 to 180^0. The nearly perfect overlap of these two data justifies the existence of C_2-symmetry.

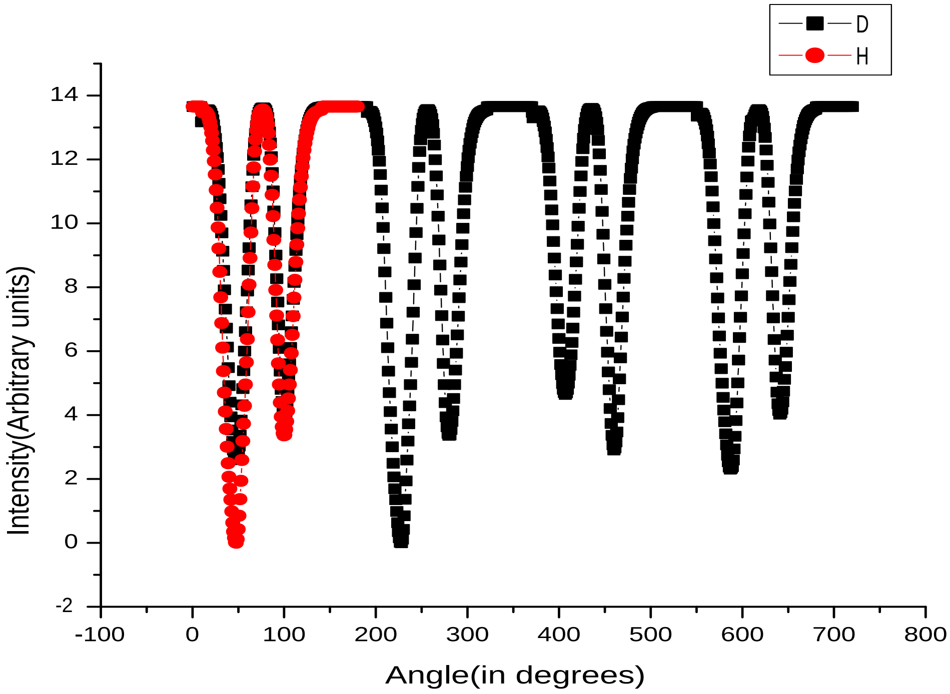


Figure 4.5: reflection intensity versus angle showing C_2.

4.3 Data analysis and interpretation

Since the optical axes the crystal have been determined, it is now possible to calculate the degree of anisotropy by using intensity modulation method. Rotating the polarizer starting from one of the optical axes a measurement was done (using rotating polarizer-analyzer method) and the data obtained is presented in Figure 4.6. The

Degree	$\|r_x\|^2 \times 10^{-5}$	Degree	$\|r_y\|^2 \times 10^{-5}$
44	1.346	314	1.355
45	1.344	315	1.354
46	1.344	316	1.355

Table 4.1: Values of r_x and r_y

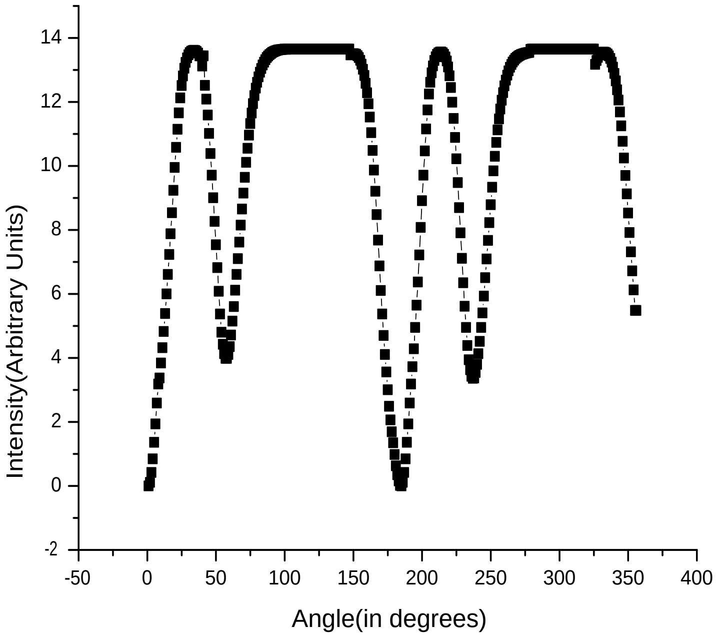


Figure 4.6: 360^0 rotation from an optical axis

reflected intensity r_x is the intensity at 45^0 and r_y is the intensity at 315^0. The values obtained for r_x and r_y are summarized as in table 4.1.

For 44^0 and 314^0 the change in reflectance Δ R and the average reflectance R are 9×10^{-8} and 1.350×10^{-5} respectively. The degree of anisotropy, which is the ratio of the two, is 6.7×10^{-3}. For the other two pairs of angles the degree of anisotropy is 7.4×10^{-3} and 8.1×10^{-3}. The average degree of anisotropy is $7.4 \times 10^{-3} \pm 0.0001$. In addition, from Figure 4.3 we can find the difference in angles between the optical axes. There are two optical axes and thus $\Delta\theta_3$ should be equal to $\Delta\theta_1$, and also $\Delta\theta_4$ should be equal to $\Delta\theta_2$. Thus

$$\Delta\theta_3 = \Delta\theta_1 = 100^0 - 48^0 = 52^0, \Delta\theta_4 = \Delta\theta_2 = 228^0 - 100^0 = 128^0 \tag{4.3.1}$$

Figure 4.7 shows the separation between the axes as calculated in Equation(4.3.1). The above results are found using rotating polarizer-analyzer setup. To compare the results with that of the result found by using the rotating sample setup, Figure (4.4) was shifted to the right and together with Figure (4.3) below. From the figure one can see that the results are in agreement. The angle difference between the optical axis are, using both methods, are alternating 52^0 and 128^0.

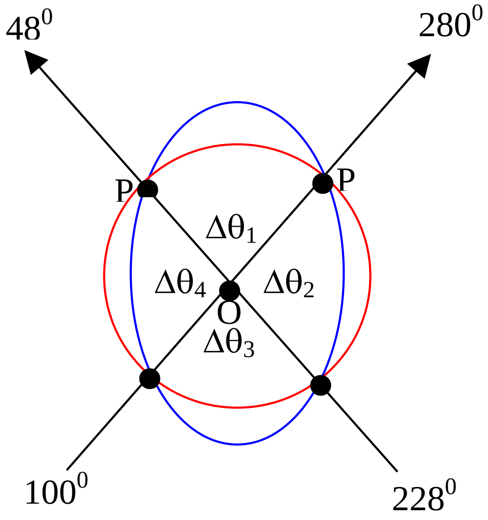


Figure 4.7: optical axes of KTP crystal

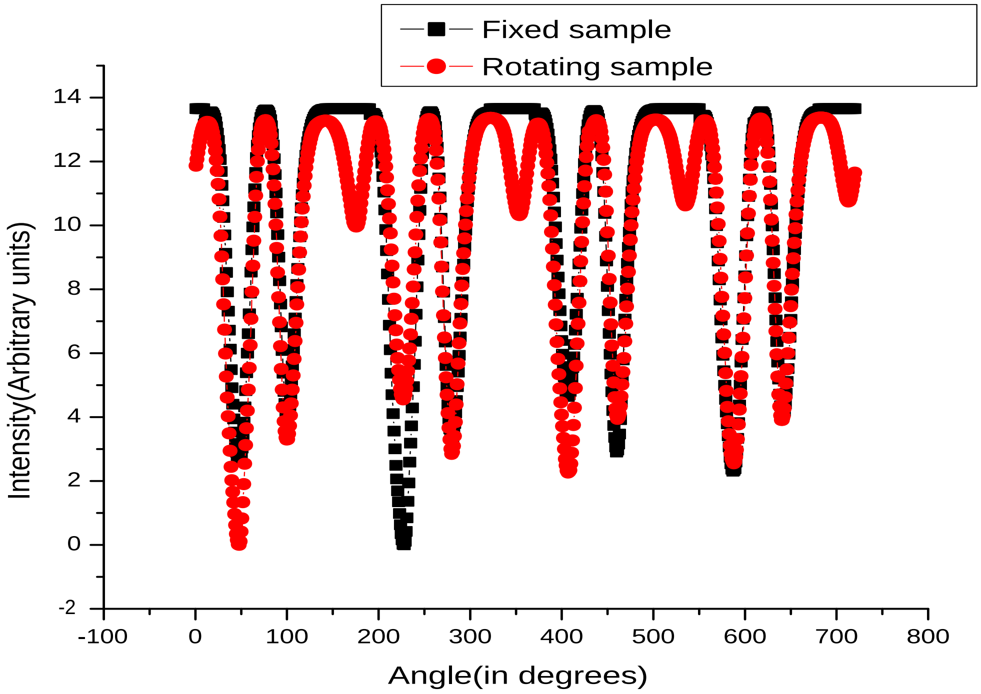


Figure 4.8: Results from the conventional and modified methods.

Chapter 5

Conclusion and Recommendations

In this work Reflectance Anisotropy spectroscopy (RAS) is applied to a KTP crystal and its degree of anisotropy is determined to be $7.4 \times 10^{-3} \pm .0001$. In the process it has been shown that the crystal is biaxial and has C_2 2-fold symmetry. In RAS the degree of anisotroppy is in the order of 10^{-3} which is in agreement with the result found from the experiment.

Furthermore, we have modified the RAS Technique for simplified handling and *in situ* real time measurement. Once the polarizer-analyzer combination is set one can use this method for real-time measurements with out much effort.

The method can also be applied for surface scanning measurements.

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