Chapter 2
Experimental Technique

2.1 General Introduction

The presence of the visible light coming from the sun was essential to the evolution of the present forms of life, not only because it was a source of energy. The sunlight, scattered from different objects, carries also an information about the objects themselves, for example their color, form or dimensions. This type of information was crucial in the species’s fight for survival. To receive this information, the species developed molecular receptors in the visible part of spectrum (which has energies of about 1eV). The intensity of this reaching the earth is high, and the energies of the first absorptions in molecules may be around 1eV, making them suitable as detectors. In that perspective, the present optical spectroscopy is just an improvement of the technique of receiving even more information about the objects themselves, with the use of better sources, detectors, etc.

The incoming sunlight has three main characteristics: wavelength, polarization and intensity. As known, there are three molecule receptors to “measure” the spectral distribution of the incoming light. The relative intensities given by the three sensors is measured, thus providing us with the colorful image of the world. This is basically the only thing which the human eye, and thus humans, can observe easily on some incoming light. The small wavelengths of the light (about 1µm, thousand time smaller than the usual observable value of 1mm) can be observed only via some type of experiments, like diffraction. The same happens with the quanta of light. It is interesting to note that the human eye responds to absorption of a single quanta [65, 66], that is a single molecular receptor is able to have a single absorption transition, and transmit further the information to the brain. The signal is however not allowed to reach the brain, by some neural filters, unless at least about 9 different photons are detected within less than 100 ms [65]. That is to avoid the “quantum noise” in the low intensity light!

The polarization of light was not very important to the evolution of humans, because the light coming from the sun is unpolarized, even though by reflection and refraction with air molecules or different objects it acquires a certain degree of polarization. The portion of the sky which is 90° away from the sun tends in this way to be partially polarized. This is important for some insects, like bees for example. They use the sun as a compass, being able to see the polarization pattern of the sky [67]. A Danish archaeologist, Thorkild Ramskou, suggested [68] that the Vikings might have used also the polarization of the
2.2 Introduction to visible light ellipsometry

There are many ways in which a measurement of the reflected polarized light can take place. All use however some components called polarizers, which linearly polarize the light when travelling through them, and possible quarter-wave plates. For example, the nulling ellipsometer technique uses one polarizer before the light touches the surface, and a quarter-wave plate together with another polarizer (the analyzer) after the light is reflected. The orientations of the quarter-wave plate and the analyzer are varied until no light passes through the analyzer. From these orientations one extracts the surface properties. Modern nulling ellipsometers use computers to rotate the elements and to automatically calculate the ellipsometry signal very quickly. However, the nulling technique is not ideal for automated instruments because it is based on measuring a zero signal. This was an advantage in the early ellipsometers because the human eye is very sensitive to small changes in the signal around the ‘null’. However, modern light detectors exhibit significantly higher noise at low intensities.

Another technique is Phase Modulated Ellipsometry, where the polarization of the light is modulated by a Photo-modulator. We encounter also Rotating Polarizer Ellipsometer and Rotating Analyzer Ellipsometer. We will deal in the course of this theses with an Rotating Polarizer Ellipsometer, and in Fig. 2.1 we detail its method.

As we can see from Fig. 2.1, the monochromatic light given by the monochromator passes through a fixed polarizer before touching the surface. This produces linearly polarized light that can be decomposed theoretically into two linearly polarized components, one in the plane of incidence ($E^i_p$) and one perpendicular to it ($E^i_s$), having the same phase. Because of the geometry, if the sample measured is a bulk isotropic sample, the two components are still linearly polarized after reflection on the sample, but the two phases and amplitudes are now different. We can quantify this by defining different reflectivity coefficients for the $p$ and $s$ components:

$$
\tilde{R}_p = \frac{\tilde{E}^r_p}{\tilde{E}^i_p}; \tilde{R}_s = \frac{\tilde{E}^r_s}{\tilde{E}^i_s};
$$

(2.1)
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where \( \sim \) denotes complex numbers, and \( i \) and \( r \) stand for incidence and reflected beams. In more general cases, when the sample is anisotropic, one should use the general Jones matrices formalism [69] to define a reflection matrix:

\[
\begin{pmatrix}
\tilde{E}_p^r \\
\tilde{E}_s^r
\end{pmatrix} =
\begin{pmatrix}
\tilde{R}_{pp} & \tilde{R}_{ps} \\
\tilde{R}_{sp} & \tilde{R}_{ss}
\end{pmatrix}
\begin{pmatrix}
\tilde{E}_p^i \\
\tilde{E}_s^i
\end{pmatrix}
\] (2.2)

In any of the two cases, anisotropic or isotropic, the recomposed light after reflection is elliptically polarized, because the relative amplitudes and phases of the two \( p \) and \( s \) components have changed. The light ellipse is described basically by two numbers, its orientation with respect to the plane of incidence, and the ratio of the two principal axes. These two real numbers are measured by the two remaining parts of the equipment (see Fig. 2.1), the rotating polarizer (the analyzer) and the detector.

By rotating the analyzer, we can measure the intensity on the detector as a function of the analyzer angle \( A \). Because of the ellipse of the light, it has a simple sinusoidal form:

\[
I_D = I_0[1 + \alpha \cos(2A) + \beta \sin(2A)]
\] (2.3)

By fitting the measured curve, we can obtain the values of \( \alpha \) and \( \beta \), and the only thing left is to correlate them to the properties of the sample, namely the dielectric function. A general anisotropic sample is described however by a three-dimensional complex tensor, and one measurement is not sufficient. If the sample is orthorhombic, this tensor can be reduced to 6 real numbers, provided the orientation of the sample is known, and thus, in principle, three measurements are sufficient to find the tensor.

The case of isotropic samples is the simplest, since the dielectric tensor reduces to a single complex number for each frequency. One measurement is thus sufficient. Here we can define the complex ratio:

\[
\tilde{\rho} = \tan \Psi e^{i\Delta} = \frac{\tilde{R}_{pp}}{\tilde{R}_{ss}}
\] (2.4)

and then the coefficients \( \alpha \) and \( \beta \) from 2.3 can be then expressed as:

![Figure 2.1: The principle of a Rotating Analyzer Ellipsometer, described in text](image-url)
Figure 2.2: Left panel: $\Psi$ and $\Delta$ for two angles of incidence, measured for CoSi. Right panel: The corresponding dielectric functions $\epsilon_1$ and $\epsilon_2$ calculated using Formula 2.9. Inset of right panel: the reflectivity at normal incidence.

\[
\alpha = \frac{\tan^2 \Psi - \tan^2 P}{\tan^2 \Psi + \tan^2 P}
\]

(2.5)

\[
\beta = \frac{2\tan \Psi \cos \Delta \tan P}{\tan^2 \Psi + \tan^2 P}
\]

(2.6)

where $P$ is the angle of the first polarizer, which is kept fixed during the measurements. Inverting these two equations, we obtain [69]:

\[
\tan(\Psi) = \sqrt{\frac{1 + \alpha}{1 - \alpha}} |\tan(P)|
\]

(2.7)

\[
\cos(\Delta) = \frac{\beta}{\sqrt{1 - \alpha^2}} |\tan(P)|
\]

(2.8)

From the equations above we can have access to the values $\Delta$ and $\Psi$, which are not only connected to the dielectric properties of the surface measured, but also geometry dependent. The relation between $\rho$ and the dielectric function $\tilde{\epsilon}$ is obtained with the use of Fresnel reflection laws [69], leading for an isotropic sample the following result:

\[
\tilde{\epsilon} = \sin^2 \theta \left[ 1 + \tan^2 \theta \left( \frac{1 - \rho}{1 + \rho} \right)^2 \right]
\]

(2.9)

where $\theta$ is the angle of incidence. Later in the thesis, we will use this relation for anisotropic samples as well. However, in that case, we will call the function $\tilde{\epsilon}$ the pseudo-dielectric function, to stress the fact that it does not describe the real dielectric tensor.
2.3. THE INFLUENCE OF WINDOWS

In Fig. 2.2 we present the measurements on an isotropic material, namely CoSi. The left panel shows the measured $\Psi$ and $\Delta$, for two angles of incidence. As we can see, there is a strong angular dependence of these two experimental quantities. The corresponding dielectric functions, calculated with formula 2.9 are presented in the right panel of Fig 2.2. The two angle of incidence measurements give the same dielectric functions, as expected, showing thus the precision of the experimental instrument.

A well known advantage of ellipsometry is that one can measure directly the two components of the complex dielectric function of an isotropic sample. This is opposed to reflectivity measurements, where one measures a single experimental function, namely the reflectivity, and one uses Kramer-Kronig relations to calculate the complex dielectric function[70]. A less obvious advantage is provided by the resolution of the instrument to measure frequency dependent changes. As we can see from the inset of Fig. 2.2, the reflectivity of CoSi is not strongly frequency dependent in the measured range (about 20%), but $\Psi$ and $\Delta$ are (about 50%). Other advantages of ellipsometry, as opposed to reflectivity, include the fact that it does not need a reference to measure the absolute values.

It is interesting to note that, since the instrument measures changes in polarization of light, it probably should have been named polarimeter. However, when the technique was well established to receive a name, the name polarimeter was already in use for a different instrument, which measures the specific rotation of optically active materials. Since the state of the light is elliptical after reflecting off the surface, as we have seen above, the term ellipsometer was chosen.

2.3 The influence of windows

Measuring at low temperatures implies the presence of a cryostat. Ellipsometry is a technique sensitive to thin layers, and one should use lower pressures than in the usual reflectivity measurements. That is because the layer which is formed by air condensing on the surface of the sample is easily detected in ellipsometry. We have used an Ultra High Vacuum cryostat, with a base pressure of $2 \times 10^{-8} \text{ mbar}$ at room temperature, before starting the cooling. After a rapid cooling process of about half hour to 4K, the pressure in the chamber reaches $2 \times 10^{-9} \text{ mbar}$ very quickly, due to the fact that the cold finger of the cryostat acts as a cryogenic pump. We have checked that a measurement time of few hours assures that no "ice" grows on the sample to values detectable by the ellipsometer.

A second problem introduced by the presence of windows is the change in the polarization state of the incoming and outgoing light. We used quartz windows, which preserve the polarization state if the incoming beam enters perpendicular on the windows. However, due to the particular construction geometry of the cryostat, the light enters at a slightly tilted angle. This misalignment leads to different values of the measured $\Psi$ and $\Delta$. However, the changes introduced by the windows are not temperature dependent, and thus one could correct for them, knowing the room temperature values of $\Psi$ and $\Delta$ in the presence and in the absence of the windows. This can be done, most easily if the windows have been aligned at least perpendicular to the plane of incidence.

If the windows are placed perpendicular to the plane of incidence, and for an isotropic
sample, each component of the light beam \( p \) and \( s \), see Fig. 2.1) preserves independently its orientation. In other words, the \( p \)-polarized light remains \( p \)-polarized after entering the first window of the cryostat, reflecting the surface, and passing through the exit window. However, every time the light beam hits the surface of a window, some part of the \( p \) and \( s \) components is reflected. Since the windows are tilted, one component is reflected more than the other. This modifies also the ratio of the transmitted components, so after the whole chain window-sample-window, the ratio of the \( p \) and \( s \) components are modified. We can write the following relation:

\[
\tilde{E}_e^e = \tilde{E}_i^p \ast \tilde{R}_{\text{wind}1}^p \ast \tilde{R}_{\text{sample}}^p \ast \tilde{R}_{\text{wind}2}^p \\
\tilde{E}_e^s = \tilde{E}_i^s \ast \tilde{R}_{\text{wind}1}^s \ast \tilde{R}_{\text{sample}}^s \ast \tilde{R}_{\text{wind}2}^s
\]  

(2.10)  

(2.11)

where \( \tilde{R} \) represents the complex reflectivity of different components, and \( \tilde{E} \) is the electric field (in the complex form) of the incoming \( (i) \) or exiting \( (e) \) light beam. The effect of the two windows can now be rewritten in a simpler relation, if we divide the upper relations, and use the definition 2.4:

\[
\tilde{\rho}_{wp} = \tilde{\rho}_{\text{wind}} \ast \tilde{\rho}_{\text{wa}}
\]  

(2.12)

where \( wp \) stands for the measurements with windows being present, and \( wa \) for the
measurements with windows absent. We see thus the way in which the corrections can be done for the measurements at low temperatures. One measures the room temperature sample with and without the windows, obtaining $\tilde{\rho}_{wp}$ and $\tilde{\rho}_{wa}$. Replacing this into 2.4 on gets $\tilde{\rho}_{\text{wind}}$, the window correction values. At low temperatures, one measures $\tilde{\rho}_{wp}^T$, and uses the previously found value $\tilde{\rho}_{\text{wind}}$ (which is temperature independent) and 2.4 to obtain the correct complex ratio of the sample $\tilde{\rho}_{wa}^T$.

In Fig. 2.3 we have checked this procedure, by two measurements on GaAs performed in the presence and absence of the windows. Prior to this, two other measurements were performed in the same configuration for FeSi, from which the influence of the windows was calculated using 2.12, namely $\tilde{\rho}_{\text{wind}}$. This was used to correct the values measured on GaAs in the presence of windows $\tilde{\rho}_{wp}$, to see if we obtain the same values as for the measurements done in absence of the windows. As we can see from figure 2.12, the corrected values (represented as symbols) are located closely to the values obtained from the measurements done in the absence of the windows, showing that the correction procedure is working.

2.4 Thin films

 Probably the widest industrial application of ellipsometry today is the monitoring of the thickness and properties of thin films. The sensitivity of an ellipsometer is such that a change in film thickness of a few Angstroms is usually easy to detect. If a film is thin enough to show an interference color pattern then it will probably be a good ellipsometric sample. This effect is a result of the interference which takes place between the first part
of the light beam reflected from the surface of the thin film, with the one reflected from
the surface of the film/substrate interface.

A proper description of the system gives a relation between the measured parameters
$\alpha$, $\beta$ and the intrinsic dielectric functions of both the substrate and thin film, and the
thickness of the latter [69]. Depending on the known dielectric properties and the thickness
of the thin film, a number of measurements may be necessary to extract the information.
For example, if the dielectric function of the substrate is known, two measurements would
be, in principle, sufficient to extract the dielectric function of an isotropic thin layer and
its thickness. It turns out however that, in practice, the pseudo-dielectric function of the
system is hardly angle dependent. Thus, most of the time, it is very difficult to determine
the exact thickness of the thin layer, if its dielectric function is not known, or at least
some information is supplied about its general behavior. To exemplify this effect, we
present here measurements on a $Cu_3N$ layer (see Fig. 2.4).

Copper nitrides have attracted considerable attention as a new material for optical
storage devices. In Fig. 2.4 we present optical measurements performed at room tem-
perature on a thin layer of $Cu_3N$ (about 18nm) grown at 150$^\circ$ on MgO [71], with the
incidence polarizer kept fixed at 45$^\circ$. The measurements have taken place for two angles
of incidence, 60$^\circ$ and 80$^\circ$. From the lefthand side panel of Fig. 2.4 we see a strong angle
dependence of the measured experimental values $\Psi$ and $\Delta$. As discussed previously, in
principle, this means that we have 4 measured real numbers for each frequency, and thus
we would be able to find out both the thickness and the complex dielectric function of
the film, that is three real numbers at one frequency.

However, correlations in the measured data prevent this from happening. A better
way to see this is to plot the pseudo-dielectric function defined in Formula 2.9. From
the righthand side panel of Fig. 2.4 we see that the two pseudo-dielectric functions $\epsilon_{1,2}^{ps}$
for the two angles of incidence come almost one on the top of the other, as mentioned
previously. That means that the the big changes in $\Psi$ and $\Delta$ were given only by the angle
of incidence. A trial to fit both $\tilde{\epsilon}$ and the thickness of the thin film, has given values from
2nm to 50nm for the thickness. We therefore had to use a different technique to measure
the thickness, namely X-Ray diffraction, and than use the resulting thickness to calculate
the intrinsic dielectric function of $Cu_3N$. The result is presented in the righthand panel
of Fig. 2.4.

2.5 Magnetic Kerr effect

As discussed previously, in general non-isotropic materials, the dielectric function
describing the optical properties is a complex tensor $\tilde{\epsilon}^T$. This tensor has three equal
diagonal terms $\tilde{\epsilon}$, and no off-diagonal terms for an isotropic sample. The presence of a
static magnetic field $B$ influences this tensor. For an isotropic sample it acquires off-
diagonal terms in the plane perpendicular to the magnetic field. If the magnetic field $B$
is oriented along the $x$-axis, there is a non-zero off-diagonal element which couples the $y$-
and $z$-components of the optical $E$-field. The dielectric tensor $\tilde{\epsilon}^T$ becomes:
2.5. MAGNETIC KERR EFFECT

Figure 2.5: Left panel: The influence of the magnetic field, oriented in the plane of the sample and in the plane of incidence, on a film of EuO. The opposite directions of the fields are designated by + and −. Right panel: The calculated diagonal ($\epsilon_1$, $\epsilon_2$) and non-diagonal ($q_1$, $q_2$) dielectric functions.

$$\tilde{\epsilon}^T = \begin{pmatrix} \tilde{\epsilon} & 0 & 0 \\ 0 & \tilde{\epsilon} & i\tilde{q}\tilde{\epsilon} \\ 0 & -i\tilde{q}\tilde{\epsilon} & \tilde{\epsilon} \end{pmatrix} \quad (2.13)$$

where $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$ and $\tilde{q} = q_1 + iq_2$.

The effect of a static magnetic field on the dielectric tensor leads thus to measurable magneto-optical effects. If these effects are observed in transmission, they are referred to as Faraday effects (discovered by Michael Faraday). If they are measured in the reflection configuration, they are referred to as the Kerr effects (by the name of its discoverer, the Reverend J. C. Kerr).

EuO is a material known to present Kerr rotations and colossal magneto-resistance [72]. We have measured the Kerr effect for a thin film of EuO (50 nm) grown on a Cr layer. The film was grown as described in Ref. [72], and later kept in air for more than two weeks, prior to the optical experiments described here. In Fig. 2.5 we present magneto-optical measurements done on EuO. The sample was measured at $T = 25K$. First, measurements in the absence of magnetic field were performed. Knowing the thickness of the sample, and the optical properties of the Cr layer on which the EuO thin film is grown, we determined the dielectric function $\tilde{\epsilon}$ of the isotropic EuO. The results are presented in the righthand panel of Fig. 2.5. The sample presents a broad absorption spectrum around 12000 cm$^{-1}$ and an onset of a stronger absorption at 25000 cm$^{-1}$.

We then applied a magnetic field of the order of 0.01 $T$, which was aligned at the intersection of the surface plane with the plane of incidence (along $x$), in two opposite directions. From the lefthand panel of Fig. 2.5 we see that changes are observed in $\Psi$ and $\Delta$. They are less than one degree, and cannot be explained only by the small value of the magnetic field. We believe that also the degradation of the layer kept in ambient pressure for a long time played a role.
A new model for the experiment was created, using the tensor 2.13, the known thickness of the layer, its previously calculated diagonal term $\tilde{\epsilon}$, geometry factors, and the known optical properties of Cr. The data measured in the presence of the field was then fitted with the new model, leading to the off-diagonal $\tilde{q}$ presented in the right panel of Fig. 2.5. The absolute value of $\tilde{q}$ is a result of the magnitude of the applied magnetic field $B$. The plots show that the imaginary part the off-diagonal term $\tilde{q}$ is larger also around 12000cm$^{-1}$ suggesting thus that the splitting induced by the magnetic field acts on the same energy levels responsible for the transition.

It also shows that one can use bare ellipsometry measurements to calculate the off-diagonal terms of magneto-optical media.

2.6 Normal incidence ellipsometry

Usual ellipsometry is done at the Brewster angle. This is defined as the angle where the reflection of the $p$-polarized component is minimal. It was shown that this minimum is zero in the case of isotropic transparent samples [69]. Measuring at this angle assures a large ratio between the $s$-polarized and $p$-polarized components, and thus an easier way to measure the parameters of the ellipse.

Normal incidence ellipsometry is useless thus for isotropic samples, since the incoming polarized light remains linearly polarized after the reflection. There are, however, cases in which ellipsometry at normal incidence may yield some information, and below we will present such an example.

CuO is a monoclinic crystal, which presents interest mainly in connection with the problem of high temperature superconductors [73]. It is an optical biaxial crystal, in the sense that its axis $b$ is perpendicular to the $ac$ plane, but the axes $a$ and $c$ are not perpendicular to each other, forming an angle of 99.5$^\circ$. In a system of orthogonal coordinates $xyz$ with $x \parallel a$, $y \parallel b$, and $z$ lying in the $ac$ plane, the axis $z$ is slightly tilted towards the axis $c$. The dielectric tensor can be written as:

$$
\tilde{\epsilon}^T = \begin{pmatrix}
\tilde{\epsilon}_{xx} & 0 & \tilde{\epsilon}_{xz} \\
0 & \tilde{\epsilon}_{yy} & 0 \\
\tilde{\epsilon}_{zx} & 0 & \tilde{\epsilon}_{zz}
\end{pmatrix}
$$

(2.14)

where $\tilde{\epsilon}_{xz} = \tilde{\epsilon}_{zx}$ in the absence of magnetic field.

In principle, if all terms from the above matrix would be real, the matrix can be diagonalized, meaning that one can choose a different orthogonal system of coordinates $x'y'z'$ for which the tensor $\tilde{\epsilon}^T$ would have only diagonal terms. The $y'$ axes of the new system may be chosen as the old one, but the new $x'z'$ system would be rotated in the $ac$ plane with respect to the old $xy$ system. The angle between the two systems would be given by [74]:

$$
tan 2\varphi = \frac{2\tilde{\epsilon}_{xx}}{\tilde{\epsilon}_{xx} - \tilde{\epsilon}_{zz}}
$$

(2.15)

This angle would describe the rotation of the principal axes within the $ac$ plane. Because the dielectric function $\epsilon$ is frequency dependent, the angle $\varphi$ is also frequency dependent.
In the general case however, the dielectric function is complex, and one usually diagonalizes the real part and imaginary part of the dielectric tensor $\tilde{\epsilon}^T$ separately. The formula 2.14 may still be used, but it will lead to a complex angle of rotation $\varphi$. We want to exemplify in this subchapter that, by doing normal incidence ellipsometry, one can have direct access to it.

Consider the dielectric tensor only in the $ac$ plane, given by

$$
\tilde{\epsilon}_{ac} = \begin{pmatrix} \tilde{\epsilon}_{xx} & \tilde{\epsilon}_{xz} \\ \tilde{\epsilon}_{xz} & \tilde{\epsilon}_{zz} \end{pmatrix}
$$

(2.16)

For normal incidence, this is related directly to the Jones matrix of the complex reflectivity tensor $\tilde{R}$ (defined in 2.1) by the following relation [74]:

$$
\tilde{\epsilon}_{ac} = \left[ (1 - \tilde{R})(1 + \tilde{R})^{-1} \right]^2
$$

(2.17)

A direct use of this formula in 2.15, yields the following relation:

$$
\tan 2\varphi = \frac{2\tilde{R}_{zz}}{\tilde{R}_{xx} - \tilde{R}_{zz}}
$$

(2.18)

We have aligned the sample close to normal incidence, with $x||p$ and $z||s$. Even if we discuss here normal incidence, we will refer to $p$ and $s$, where $p$ indicates now the direction $x$ on the sample surface and $s$ perpendicular to that. We may thus write:
\[
\tan 2\varphi = \frac{2\tilde{R}_{ps}/\tilde{R}_{pp}}{1 - \tilde{R}_{ss}/\tilde{R}_{pp}}
\] (2.19)

The values of the two complex ratios in 2.19 are directly available in a special type of ellipsometric measurement, called generalized ellipsometry. This differs from the usual type of ellipsometry measurements where the first polarizer is kept at 45° by choosing different angles. The idea of this type of measurements is that, for a general anisotropic sample, the coefficients \(\alpha\) and \(\beta\) are not given by the simple relations 2.6, but by a more complicated relation [75]:

\[
\alpha = \frac{(|\tilde{R}_{pp}|^2 - |\tilde{R}_{sp}|^2) + (|\tilde{R}_{ps}|^2 - |\tilde{R}_{ss}|^2) \tan^2 P + 2[Re(\tilde{R}_{pp} \tilde{R}_{ps}^*) - Re(\tilde{R}_{ss} \tilde{R}_{sp}^*)] \tan P}{(|\tilde{R}_{pp}|^2 + |\tilde{R}_{sp}|^2) + (|\tilde{R}_{ss}|^2 + |\tilde{R}_{ps}|^2) \tan^2 P + 2[Re(\tilde{R}_{pp} \tilde{R}_{ps}^*) + Re(\tilde{R}_{ss} \tilde{R}_{sp}^*)] \tan P}
\]

\[
\beta = \frac{2[Re(\tilde{R}_{pp} \tilde{R}_{sp}^*) + Re(\tilde{R}_{ss} \tilde{R}_{ps}^*)] \tan^2 P + [Re(\tilde{R}_{pp} \tilde{R}_{ps}^*) + Re(\tilde{R}_{sp} \tilde{R}_{sp}^*)] \tan P}{(|\tilde{R}_{pp}|^2 + |\tilde{R}_{sp}|^2) + (|\tilde{R}_{ss}|^2 + |\tilde{R}_{ps}|^2) \tan^2 P + 2[Re(\tilde{R}_{pp} \tilde{R}_{ps}^*) + Re(\tilde{R}_{sp} \tilde{R}_{sp}^*)] \tan P}
\]

If the sample is anisotropic, one can do measurements at the same angle of incidence for more angles of the fixed polarizer \(P\), and fit all the data together. One can thus obtain the "normal" ratio: \(\tilde{\rho}_{AnE} = \tilde{R}_{pp} / \tilde{R}_{ss}\), the anisotropic "p into s" ratio \(\tilde{\rho}_{Aps} = \tilde{R}_{ps} / \tilde{R}_{pp}\) and "s into p" \(\tilde{\rho}_{Asp} = \tilde{R}_{sp} / \tilde{R}_{ss}\). Equation 2.19 can be rewritten as:

\[
\tan 2\varphi = \frac{2\tilde{\rho}_{Aps}}{1 - 1/\tilde{\rho}_{AnE}}
\] (2.20)

We have done a generalized anisotropy measurement on the \(ac\) face of the CuO sample, aligned with the \(a\) axis in the plane of incidence(\(a||x||p\)). The configuration was close to normal incidence, with an angle of incidence of \(\theta=11^\circ\). The results of \(\tilde{\rho}_{AnE}\) and \(\tilde{\rho}_{Aps}\) are presented in the Fig. 2.6, using their corresponding values of \(\Psi\) and \(\Delta\), according to 2.4. Then, the real and imaginary parts of the complex angle \(\varphi\) where calculated using 2.20 and presented in the right-hand panel of Fig. 2.7. In the left-hand panel of the same figure, the \textit{pseudo-dielectric} function of CuO is presented for \(E||a\) and \(E \perp a\).

As we can see from Fig. 2.7, the values of \(Im[\varphi]\) and \(Re[\varphi]\) are quite small, on the order of few degrees. This is expected, since the angle between the \(a\) and \(c\) axes is close to 90°. The imaginary part of \(\varphi\) is positive and shows an absorption behavior, and \(Re[\varphi]\) a dispersive behavior. For the moment, it is not clear to us how the values of the complex \(\varphi\) can be related to the orientation of the eigenmodes of different transitions. It is interesting to note however, that \(Im[\varphi]\) has a similar behavior as the imaginary part of the pseudo-dielectric function for \(E \perp a\) (see Fig. 2.7), with a peak around 25000cm\(^{-1}\). The latter comes from a transition which takes place mainly along the \(c\) axis. It is thus expected that the eigenmodes of this transition are tilted with respect the ones of the \(a\) axis, giving the behavior of \(Im[\varphi]\).

### 2.7 Alignment of orthorhombic samples

An unusual use of the visible ellipsometer may be the alignment of orthorhombic samples. This may sound not very important, but it is practical when measuring the
samples themselves, since it reduces the time needed to align the samples in the X-Ray
diffactometer.

The principle of this alignment is simple. Usually we want to align the axes of the
orthorhombic sample with the axes of the equipment. If the sample is already cut along
one plane (and this was \( ab \) plane in the case of \( \alpha'\)-NaV\(_2\)O\(_5\)) we want then to align one
axis, \( a \) or \( b \), in the plane of incidence. This can be done by testing the polarization of the
outcoming light. The \( s \) polarized component must in this case remain \( s \) polarized after
reflection, due to symmetry, and the same must hold for the \( p \) polarized component.

Thus an easy check can be done directly by irradiating the sample with only \( s \) polarized
light (\( P=90^\circ \)), and rotate the surface of the sample, until the outcoming light presents
no \( p \) component. In this case the outcoming beam is again linearly polarized at 90\(^\circ\) with
respect to the plane of incidence if the orthorhombic sample is correctly aligned. The
electric field on the detector must have then the following angular dependence

\[
E \sim \sin(A)
\]

and thus the intensity on the detector can be written as:

\[
I_D \sim \sin^2(A) \sim 1 - \cos(2A)
\]

Comparing this with the intensity on the detector given by 2.3 we obtain \( \alpha = -1 \) and
\( \beta = 0 \). Thus, a linearly polarized light beam at 90\(^\circ\) with respect to the plane of incidence
gives \( \alpha = -1 \) and \( \beta = 0 \). The only thing left to do in order to align the sample, is to
rotate the surface of the sample until \( \alpha = -1 \) and \( \beta = 0 \).
Figure 2.8: The response of the ellipsometer as a function of the rotation of the sample around the normal of its measured plane, for an anisotropic material. The polarizer angle is $P=90^\circ$ the angle of incidence $\theta = 60^\circ$ frequency of the light $\omega=9800\text{cm}^{-1}$ and the surface measured is $ab$ of $\alpha'$-NaV$_2$O$_5$. Inset: a zoom in for $\beta$ crossing zero.

In Fig 2.8 we present such a measurement done on the $ab$ surface of $\alpha'$-NaV$_2$O$_5$. The polarizer angle is $P=90^\circ$ the angle of incidence $\theta=60^\circ$ and the frequency used is $\omega=9800\text{cm}^{-1}$. As we can see, the sensitivity of $\beta$ crossing zero is much larger than that of $\alpha$ reaching -1. From the inset of Fig 2.8 we estimate that the sensitivity of the equipment is in this case smaller than 0.4$^\circ$.

This does not represent however the error in the alignment of the sample, since systematic errors may appear. Thus, in our case, the crossing of $\beta$ to zero happens at 353$^\circ$ and 262$^\circ$. The difference between these two angles is 91$^\circ$ showing thus that a systematic error of 1$^\circ$ exists. However, we have checked using X-ray diffraction technique, that the $\beta$ crossing of the zero corresponds indeed to the sample having one axis in the plane of incidence, the error between these two techniques being less than 2$^\circ$. We want to stress however that this procedure may not work always, for example for the $ab$ plane of the high temperature superconductors, since they present usually a small in-plane anisotropy.