Chapter 3

Theory of Spectrometry on Layered Systems

In this chapter the theoretical background behind spectroscopy on stratified systems will be treated. Due to the vast variety of possible cases the treatment will be mainly restricted to those cases used later in the dissertation. Other treatments can be found in references [1-4].

In the first part of section 3.1 we will go through the mathematics to calculate the transmission and reflection coefficient for a two-layer system, taking into account the interference in both the film and the substrate. Furthermore some illustrative examples of special cases will be given. The second part studies the influence of film thickness on the temperature dependence of the transmissivity. We will demonstrate how the sensitivity to the real and imaginary part of the dielectric function changes for different thicknesses. The significance of this analysis will be demonstrated later in chapter 6 of this dissertation, where an experimental study of these concepts is presented.

In section 3.2 we will introduce the subject of reflection using a finite angle of incidence, and its experimental implications. Moreover, including the transmission coefficient we can calculate the absorptivity in a thin film, relevant to the experiments presented in chapter 7. Finally, in section 3.3 we will briefly discuss the possibility to obtain the complex dielectric function ($\epsilon = \epsilon' + i\epsilon''$) analytically, by measuring both reflection and transmission on the same sample.

3.1 Transmission

3.1.1 Transmission Through a Two-Layer System

In optical spectroscopy one is able to measure three macroscopic material properties directly, namely the transmissivity $T$, the reflectivity $R$ and the absorptivity $A$. Obviously, by virtue of the conservation of energy, it is always true that $T + R + A = 1$. Therefore it is sufficient to measure two properties in order to determine all three. However, since each property has its own requirements leading to quite distinct experimental considerations, it
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is often difficult to determine even two properties on the same sample. Furthermore, the measured quantities are often amplitudes, whereas the phase (as for instance in $\hat{R} = R e^{i\Phi}$) is undetermined. This inhibits the determination of the microscopic properties of the sample using merely $T$, $A$ or $R$. A common way to circumvent this problem is to make use of so-called Kramers-Kronig relations.

$$\Phi(\omega) = -\frac{2\omega}{\pi} \int_0^\infty \frac{\ln|\sqrt{R(\omega')}|}{(\omega')^2 - \omega^2} d\omega' \quad (3.1)$$

Since $T$, $R$ and $A$, under ordinary circumstances are causal functions, and therefore have their poles in the lower half of the complex plane, one can directly determine $\Phi$ using these relations. However, for the use of Kramers-Kronig relations the experimentally determined reflectivity coefficient has to be extrapolated to zero and infinite frequency. The final results are usually rather sensitive to the nature of the used extrapolations.

Knowing both the amplitude and the phase, the real and imaginary part of the dielectric function $\varepsilon$ or any other optical property, such as the conductivity $\sigma$, can be determined. These quantities contain the desired information about the interior of the material such as phonon frequencies, energy gaps, the free electron response etc. The use of Kramers-Kronig transformations is however not the only method to obtain both the real and imaginary part of the response functions. Other approaches, such as ellipsometry, focus on determining two independent quantities experimentally, thus allowing to determine the real and imaginary part analytically. Also, as we will show later in this chapter, using a thin film it is possible to measure both $R$ and $T$ on the same sample and obtain all the required information.

In this section we will focus on an alternative approach, using the interference pattern observed in optical spectra, when the wavelength of the applied radiation is comparable to the sample thickness. Starting point for this analysis are the Fresnel equations, which describe the reflection and transmission coefficients on an interface between two media, having a different refractive index.

$$r_p = \frac{n_1 \cos \phi_1 - n_2 \cos \phi_2}{n_1 \cos \phi_1 + n_2 \cos \phi_2}$$

$$t_p = \frac{2n_1 \cos \phi_1}{n_1 \cos \phi_1 + n_2 \cos \phi_2}$$

$$r_s = \frac{n_2 \cos \phi_1 - n_1 \cos \phi_2}{n_2 \cos \phi_1 + n_1 \cos \phi_2}$$

$$t_s = \frac{2n_1 \cos \phi_1}{n_2 \cos \phi_1 + n_1 \cos \phi_2} \quad (3.2)$$

Here $n_i = \sqrt{\varepsilon_i}$ are the refractive indices of both media, $\phi_i$ are the angles of propagation in the respective media and the suffixes $p$ and $s$ indicate the state of polarization of the incident light. The $p$-polarized light has its electric field vector parallel to the plane of incidence, while this is perpendicular for the $s$-polarized radiation. From this we can calculate the reflection and transmission coefficients at each interface of a stratified medium. At this
point we will concentrate on the transmission through a two-layer system although other examples will be given later. For clarity the two-layer system is drawn in fig. 3.1, together with the directions of the beam and the indices indicating the respective media. The angles between the directions of propagation of the waves in the respective media are interrelated via Snell’s law

\[
\sin \phi_0 = n \sin \phi_1 = p \sin \phi_2
\]  

(3.3)

From this it immediately follows that in the case of an absorbing medium, where the index of refraction is complex, the angle \( \phi_i \) will be complex as well. The physical reason for this can be easily understood if we consider the planes of equal phase and the planes of equal amplitude for the incident waves. For an isotropic, absorbing medium, the planes of equal phase will be perpendicular to the direction of propagation. However, since the reduction in amplitude of the wave in the medium depends on the distance travelled in the medium, the planes of equal amplitude will be parallel to the surface of separation, which is in most cases a plane boundary. Therefore, only in the case of normal incidence the planes of equal phase and equal amplitude will be parallel to one another. Also the distinction between the \( s \)- and \( p \)-polarized light vanishes at normal incidence.

Assuming for now that the light is incident normal to the surface, we obtain the fol-
Following Fresnel coefficients for the first interface

\[ r_{01} = -r_{10} = \frac{1 - n}{1 + n} \]  
\[ t_{01} = \frac{t_{10}}{n} = \frac{2}{1 + n} \]  

(3.4)

Following the incident beam we see that it first crosses the interface between medium 0 and medium 1, where a fraction \( t_{01} \) is transmitted. At the next interface, between medium 1 and 2, the radiation has acquired a phase shift equal to \( e^{i\phi} \) and a fraction \( t_{12} \) is transmitted. The phase angle \( \phi \) is equal to \( kd_1n \) where \( k \) is the wavevector of the incident light \( (k = 2\pi \nu/c) \) and \( d_1 \) is the thickness of the first layer. However, part of the beam reflected on the interface between medium 1 and 2 ends up in the second layer after being reflected from the interface \( 1 \rightarrow 0 \), in total having picked up a factor of \( r_{12}t_{10}e^{2i\phi} \). Summing over all contributions, the final transmission coefficient through the first layer will be:

\[ \tau_{02} = \frac{t_{01}t_{12}e^{i\phi}}{r_{12}r_{10}e^{2i\phi}} \]  

(3.5)

where we have used the well-known expression for a geometrical series to include all the contributions. A similar contribution will arise from the multiple reflections within the second layer so that the transmission through the entire system, \( t_{tr} \) is described by

\[ t_{tr} = \frac{\tau_{02}t_{30}e^{i\psi}}{1 - r_{20}r_{20}e^{2i\psi}} \]  
\[ \psi = kd_2p \]  

(3.6)

where the phase factor \( \psi \) indicates the phase shift acquired by the beam traversing the substrate once. Please note that also the part of the beam being reflected at the last interface will give rise to interferences within the film, which are included in \( \rho_{20} \).

\[ \rho_{20} = r_{21} + \frac{t_{21}r_{10}t_{12}e^{2i\phi}}{1 - r_{10}r_{12}e^{2i\phi}} \]  

(3.7)

Obviously, in order to calculate the experimentally obtained transmission coefficient, we have to take the absolute value of eq. (3.6), since we are dealing with intensities instead of field amplitudes, i.e. \( T_{tr} = |t_{tr}^2| \).

Using identical arguments as given above, the reflectivity coefficient, \( r_I \) can be calculated, including all interference factors.

\[ r_I = \rho_{02} + \frac{\tau_{02}r_{30}r_{20}e^{2i\psi}}{1 - r_{20}r_{20}e^{2i\psi}} \]  

(3.8)

where the summed contribution of the film is embodied in the phase factors \( \tau_{02}, \tau_{20}, \rho_{02} \) and \( \rho_{20} \).

\[ \rho_{02} = r_{01} + \frac{t_{01}r_{12}t_{10}e^{2i\phi}}{1 - r_{10}r_{12}e^{2i\phi}} \]  

(3.9)
The definitions for $\tau_{02}$ and $\rho_{20}$ were already given in the course of the derivation of the transmission coefficient, as were the phase angles $\phi$ and $\psi$.

Evident from the transmission and reflection coefficients formulated above, is that the thicknesses of the layers play an essential role in the determination of the interference pattern of the complete system. The phase of the pattern is thus mainly determined by the product $k_1d$. An example of the implications of this observation can be seen in chapter 6.

Relevant Examples

In the remainder of this section we will focus on the transmission coefficient, $t_{lr}$. During our experiments the first layer (1) will be a (superconducting) film, deposited on a substrate (2). Since the thickness of the film is much smaller than the wavelength, we are only sensitive to the period of the interference effects arising within of the substrate. Therefore usually also the transmission through an uncovered substrate is measured and modeled using eq. (3.6), simply by setting $d_1 = 0$. We thus experimentally obtain the values for both the real and the imaginary part of the refractive index of the substrate. These values are subsequently used in the analysis of the transmission through the two-layer system.

Before we proceed to discuss the two-layer system and the influence of the film and substrate properties in more detail, some illustrative examples will be given, making use of eq. (3.6), applying some reasonable assumptions and approximations.

Comparison $T_{\text{left} \rightarrow \text{right}}$ and $T_{\text{right} \rightarrow \text{left}}$

In a way completely analogous to the argument above we can formulate the transmission through the same sample for a beam incident on the interface on the right hand side. This yields:

$$t_{rl} = \frac{t_{02}\tau_{20}e^{i\psi}}{1 - \rho_{20}\tau_{20}e^{2i\psi}}, \quad \psi = kd_2p \quad (3.10)$$

From the expressions for $\tau_{02}$ and $\tau_{20}$ given in eqs. (3.5) and (3.9) we obtain

$$\tau_{20} = p\tau_{02} \quad (3.11)$$

while furthermore $t_{02} = t_{20}/p$. This implies that, as expected, the transmission for light traversing from right to left is equal to the transmission for light traversing from left to right. Most importantly, they will have an identical phase.

Bare Substrate

In the case that we are dealing with a simple, uncovered dielectric, we can state that $d_1 = 0$. Furthermore we are dealing with a frequency independent dielectric constant $p = \eta + i\kappa$ where both $\eta$ and $\kappa$ are real numbers. Then eq. (3.6) reduces to:

$$t_{\text{sub}} = \frac{4p}{2p^2\cos\psi - 2i\sin\psi} \quad (3.12)$$
In fig. 3.2 we show several calculated transmission spectra for different dielectric constants to illustrate the general behavior as a function of both $\eta$ and $\kappa$. We see that increasing the real part of the refractive index, $\eta$, reduces the distance between the peaks, as well as the absolute transmission in the minima. If the absorption coefficient, $\kappa$, is enhanced we see that the magnitude of the maxima is reduced and the overall transmission becomes "tilted".

**Wedged Substrate**

Another approximation one can make, starting from the two-layer system, is to neglect the interference effect within the substrate. This has large experimental relevance since a commonly used trick in transmission spectroscopy is to wedge the substrate, thereby destroying the phase coherence and thus the interference. In this way one measures directly the transmission through the thin film, except for a constant factor, and is therefore able
to obtain for instance its temperature dependence [5]. Equation 3.6 then reduces to:

\[ t_{\text{red}} = \frac{2p}{1 + p} \frac{2n}{n(1 + p) \cos \phi - i(p + n^2) \sin \phi} \]  

(3.13)

where \( n \) is the complex dielectric function of the film and \( p \) is the dielectric constant of the substrate.

**Free Standing Film**

We can go one step further, and omit the substrate completely. We then end up having a free standing film, which is an idealized case, but rather instructive as we will see later on. Starting from eq. (3.13) we can take \( p = 1 \) resulting in

\[ t_{\text{free}} = \frac{2n}{2n \cos \phi - i(1 + n^2) \sin \phi} \]  

(3.14)

In transmission experiments usually the studied films are optically thin, meaning that we are allowed to apply the so-called thin film limit. This means that we take \( \phi \ll 1 \), or equivalently \( k d_1 n \ll 1 \). Taking \( \cos \phi \approx 1 \) and \( \sin \phi \approx \phi \) yields

\[ t_{\text{free}} = \frac{1}{1 - \frac{ikd_1}{2}(1 + \epsilon)} \]  

(3.15)

where we replaced \( n^2 \) by \( \epsilon \). Since we are interested in the relative significance of the real and the imaginary part of the dielectric function we use \( \epsilon = \epsilon' + i\epsilon'' \). The transmission is then given by

\[ T_{\text{free}} = |t_{\text{free}}^2| = \left[ 1 + \left( \frac{\pi \nu d_1 \epsilon''}{c} \right)^2 + \left( \frac{2\pi \nu d_1 \epsilon''}{c} + \left( \frac{\pi \nu d_1 (\epsilon' + 1)}{c} \right)^2 \right]^{-1} \]  

(3.16)

Assuming furthermore that \( |\epsilon'| \gg 1 \) and \( (\pi \nu d_1 \epsilon'')/c \ll 1 \) this reduces further to:

\[ T_{\text{free}} = |t_{\text{free}}^2| = \left[ 1 + \left( \frac{2\pi \nu d_1 \epsilon''}{c} \right)^2 + \left( \frac{\pi \nu d_1 \epsilon'}{c} \right)^2 \right]^{-1} \]  

(3.17)

From this expression it is evident that the thickness plays an important role in determining the relative significance of the real and imaginary parts. For thin films the absorptive term \( \sim \epsilon'' \) on the right hand side of equation (3.17) will dominate, while for thicker films, the reactive term \( \sim \epsilon' \) will be most significant. From eq. (3.17) one can estimate a critical thickness \( (d_c) \), at which the real and imaginary part are equally important:

\[ d_c = \frac{2\epsilon''}{\pi \nu (\epsilon')^2} \]  

(3.18)

We will return to the critical thickness in section 3.1.2 and in chapter 6.
Maxima and Minima in the Interference Pattern

It is interesting to focus on the maxima in the Fabry-Perot interference pattern of the film-substrate system for several reasons. At these frequencies, it is relatively straightforward to determine the film properties analytically from the complete expression given in eq. (3.6). Moreover, at these frequencies the effect of the film on the transmission coefficient is most severe, allowing a very precise determination of the absolute magnitude of the conductivity of the film. To demonstrate this we return to equations (3.4) to (3.7). Substituting all Fresnel coefficients at the respective interfaces by their values in terms of the dielectric properties of the film and the substrate yields

\[
\tau_{02} = \frac{2n}{(p+1)n\cos \phi - i(\epsilon + p)\sin \phi}
\]

\[
\rho_{20} = \frac{p-n}{p+n} \left( 1 + \frac{p(n-1)e^{i\phi}}{p-n} \tau_{02} \right)
\]

By substitution of \(\tau_{02}\) the latter can be further reduced to

\[
\rho_{20} = \frac{(p-1)n\cos \phi + i(\epsilon - p)\sin \phi}{(p+1)n\cos \phi - i(\epsilon + p)\sin \phi}
\]

We are interested in the experimental transmission coefficient, involving transmitted intensities, therefore eq. (3.6) becomes

\[
T = |t_{tr}^2| = 4p^2 \left| \frac{\tau_{02}}{(1+p)e^{-i\psi} + (1-p)\rho_{20}e^{i\psi}} \right|^2
\]

Substituting eqs. (3.19) and (3.20) into (3.21) and assuming that the thin film limit is valid, we finally obtain

\[
T_{tr} = \frac{1}{\cos \psi \cos \phi} \left[ \frac{1}{1 - \left( \frac{n^2+p^2}{2np} \right) \tan \psi \tan \phi - i\left( \frac{1+p^2}{2p} \right) \tan \psi - i\left( \frac{1+n^2}{2n} \right) \tan \phi} \right]
\]

In case of a maximum in transmission through the bare substrate, we can state \(\sin \phi = 0\) and \(\cos \phi = 1\).

\[
T_{max} = \frac{1}{1 + kd_1\epsilon'' + \left( \frac{kd_1\epsilon''}{2} \right)^2 + \frac{k^2d_1^2}{4}(1 + \epsilon')^2}
\]

which is, as expected, completely equivalent to the result for the free standing film, given before in eq. (3.16). In case of a minimum the opposite is valid, \(\sin \phi = 1\) and \(\cos \phi = 0\), resulting in

\[
T_{min} = \frac{4p^2}{(1+p^2)^2 + (1+p^2)(kd_1\epsilon'')^2 + 2kd_1(1+p^2)\epsilon'' + (kd_1|p^2 + \epsilon'|)^2}
\]
Also in this case, taking $p = 1$ yields the free standing film results given in eq. (3.15), since we neglected the interference effects within the film, by assuming that the thin film limit is valid. Please note, that one has to be very careful in defining maxima and minima. In fact, for a superconducting film on a substrate, the maxima and minima in the transmission of the entire system will be interchanged in the superconducting state, as compared to the normal state. Therefore I will use the terms maximum and minimum strictly in relation to the transmission through a bare substrate.

### 3.1.2 Influence of the Thickness on the Temperature Dependence of the Transmission Coefficient

In order to get a feeling for the influence of specific material properties on the transmission coefficient we need to adopt a model to work with. There have been strong objections to the use of the Drude model, and especially at higher frequencies it is well established that the class of high $T_c$ superconductors does not follow the ordinary metallic description very well, as can be seen for instance in the linear frequency dependence of the scattering rate $\gamma$. However, at low frequencies this description still works sufficiently well, and therefore we will make use of this fairly straightforward model. We can henceforth describe the dielectric function of the film using the well-known two-fluid description [6, 7],

$$
\epsilon = 1 + \frac{2i\sigma}{\nu} - \frac{\nu^2_{pn}(T)}{\nu(\nu + i\gamma(T))} - \frac{\nu^2_{ps}(T)}{\nu^2}
$$

(3.25)

Here $\nu_{pn}(T)$ is the normal state plasma frequency, $\gamma(T)$ is the scattering rate, $\nu_{ps}(T)$ is the superfluid plasma frequency and $\nu$ is the measurement frequency. We recall that $\epsilon'' = 2\sigma_1/\nu$ above $T_c$, and $\sigma_1 \to 1/\rho_{dc}$ for low frequencies. Furthermore, $\epsilon' = -\epsilon^2/(2\pi\nu\lambda)^2$ at low temperatures and is therefore directly related to the penetration depth of the material. This enables us to obtain, in addition to its temperature dependence, an absolute value for $\lambda$ using $\nu_{ps}$ [cm$^{-1}$] $= 1/2\pi\lambda$.

For the measurements presented in this dissertation, the scattering rate $\gamma$ remains larger than the measurement frequency $\nu$, so that $\lambda$ and $\sigma_1$ have only a weak frequency dependence. Mm-wave experiments performed under conditions where $\nu > \gamma$ have been reported by Dähne et al. [8]. Even though in our case $\lambda$ and $\sigma_1$ show no frequency dependence, we would like to emphasize the importance of the fact that the available frequency range is as broad as possible. Therefore we calculated the frequency dependence of the dielectric properties in and around our frequency range (4 - 6 cm$^{-1}$) and plotted these in fig. 3.3. The values we used for these calculations are given in table 3.1. Next, we used the properties from fig. 3.3 to determine the transmission through a film deposited on a wedged substrate (eq. (3.13)), in order to concentrate on the phenomena directly correlated to the thin film. The result is shown in fig. 3.4, where again the part in between the two vertical dash-dotted lines is our available frequency. In fig. 3.3a we see that $\epsilon'$ is enhanced by about a factor of $10^4$ (note the logarithmic scale) upon entering the superconducting state. This is due to the presence of the superfluid density, i.e., the $\delta$-function at zero-frequency,
Figure 3.3: Frequency dependence of the real (a) and imaginary (b) part of $\varepsilon$, plotted for several different temperatures (270 K: solid line, 90 K: dotted line, 60 K: short dashed line, 4 K: long dashed line). The area in between the two vertical dash-dotted lines is our available frequency range.

Figure 3.4: Frequency dependence of the transmission through a thin film on a wedged substrate, plotted for several different temperatures (270 K: solid line, 90 K: dotted line, 60 K: short dashed line, 4 K: long dashed line). The area in between the two vertical dash-dotted lines is our available frequency range.
showing its typical $1/\nu^2$ frequency dependence. In fig. 3.3b we see that the magnitude of \( \varepsilon'' \) is in between the values of \( \varepsilon' \), being much larger in the normal state and much smaller in the superconducting state. \( \varepsilon'' \) has a $1/\nu$ dependence as expected for a frequency independent \( \sigma_1 \), since $\epsilon = 1 + 2i\sigma_1/\nu$. The transmission we obtain using these parameters shows a frequency independent behavior in the normal state, but attains a strong frequency dependence below $T_c$, which can be recognized if the available frequency range is sufficiently broad.

An additional advantage of having a broad frequency range can be inferred from fig. 3.2. We see that for typical values of $\eta = 3$ to $4$, the available frequency range from 4 to 6 cm$^{-1}$ covers approximately a single oscillatory period. The addition of a source at higher frequencies would allow the use of 2 or 3 periods for the analysis, facilitating this considerably. It is hence evident that the use of substrates having a high value for $\eta$ and/or a large thickness is advantageous.

Now that we adopted a model for the dielectric function of the film, we can return to eq. (3.18) and calculate the critical thickness as a function of the microscopic optical properties of the film. Since the magnitudes of both contributions \( \varepsilon' \) and \( \varepsilon'' \) is very different for a normal metal or a superconductor (due to the presence of the superfluid), $d_c$ can be calculated for two distinct cases. Assuming that $\nu^2 \ll \gamma^2$ we find that

\[
d_c \approx \frac{2c\gamma^3}{\pi \nu^2 \nu_{pm}^2} \quad \text{(metal)} \tag{3.26}
\]

\[
d_c \approx \frac{32\pi^3 \nu_{pm}^2 \nu^2 \chi^4}{c^3 \gamma} \quad \text{(superconductor)} \tag{3.27}
\]

Taking common values for 123-superconductors ($\gamma = 100$ cm$^{-1}$, $\nu = 5$ cm$^{-1}$, $\nu_{pm} = 10^4$ cm$^{-1}$ and $\lambda = 2000$ Å), we obtain that $d_c \sim 2.5 \mu$m in the normal state, while $d_c \sim 0.4$ Å for $T \ll T_c$. Consequently, for most thin films the transmission in the normal state will be determined by $\sigma_1$, while in the superconducting state it will be determined by $\lambda$.

However, an indication that this assumption may not be valid in all cases can be seen in fig. 3.5. In this figure the temperature dependence of the transmission coefficient is

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$\nu_{pm}$ (cm$^{-1}$)</th>
<th>$\gamma$ (cm$^{-1}$)</th>
<th>$\nu_{ps}$ (cm$^{-1}$)</th>
<th>$\sigma_1$ ($\Omega^{-1}$cm$^{-1}$)</th>
<th>$\lambda$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>$10^4$</td>
<td>300</td>
<td>0</td>
<td>5500</td>
<td>-</td>
</tr>
<tr>
<td>90</td>
<td>$10^4$</td>
<td>150</td>
<td>0</td>
<td>11000</td>
<td>-</td>
</tr>
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<td>75</td>
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<td>2000</td>
</tr>
<tr>
<td>4</td>
<td>2000</td>
<td>20</td>
<td>9800</td>
<td>3000</td>
<td>1620</td>
</tr>
</tbody>
</table>

Table 3.1: Parameters used for the calculation of the frequency dependence of $\varepsilon'$, $\varepsilon''$, and $T_{wed}$, presented in figs. 3.3 and 3.4.
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Figure 3.5: Temperature dependence of the transmission through a superconducting thin film, shown for two different thicknesses a: 24 Å and b: 1000 Å

shown for two different film thicknesses, 24 and 1000 Å. We used a BCS-like temperature dependence for the penetration depth, represented by the empirical Gorter-Casimir expression \[ \lambda(T) = \lambda(0) \left[ 1 - \left( \frac{T}{T_c} \right)^4 \right]^{-1/2} \]

and an idealized, linear temperature dependence for the resistivity ($\sim 1/\sigma_1$) down to 0 K. The parameters used for this calculation are summarized in table 3.2. It is evident from the shape of the curve around $T_c$ that $\sigma_1$, being continuous at $T_c$, plays a far more prominent role in the case of the thin film (a), whereas the distinct kink at $T_c$ for the thicker film is caused by the presence of the superfluid appearing in $\epsilon' (\sim 1/\lambda^2)$.

Equivalently to having a critical thickness for fixed dielectric properties, by fixing the thickness and accounting for the temperature dependence of the dielectric properties one can estimate the temperature range at which the real and imaginary contributions will be equally important. In fig. 3.6 the critical thickness, $d_c$, is presented as a function of temperature. For this calculation we used the penetration depth results obtained on a
3.1. Transmission

Figure 3.6: Temperature dependence of the critical thickness $d_c$.

Figure 3.7: (a) Temperature dependence of $\varepsilon'$ and $\varepsilon''$, used for the calculation of $d_c$ shown in fig. 3.6. In the insets the temperature dependence of $\lambda$ and $\sigma_1$ are shown in the upper and lower panel respectively.
Table 3.2: Parameters used for the calculation of the temperature dependence of the transmissivity for different film thicknesses, shown in fig. 3.5.

<table>
<thead>
<tr>
<th>property</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (Å)</td>
<td>24-2000</td>
</tr>
<tr>
<td>σ(300) (Ω⁻¹cm⁻¹)</td>
<td>4000</td>
</tr>
<tr>
<td>λ(0) (Å)</td>
<td>4000</td>
</tr>
<tr>
<td>γ (cm⁻¹)</td>
<td>300</td>
</tr>
<tr>
<td>η</td>
<td>4</td>
</tr>
<tr>
<td>ν (GHz)</td>
<td>150</td>
</tr>
<tr>
<td>Tc (K)</td>
<td>92</td>
</tr>
</tbody>
</table>

YBa₂Cu₃O₇₋δ single crystal, reported in reference [10] while for σ₁ we used results on a similar single crystal, presented in reference [11]. The temperature dependences of λ and σ₁ are shown in insets of fig. 3.7. The real and imaginary part of ε, calculated at our center frequency (ν = 5 cm⁻¹), are plotted in the upper and lower panel of fig. 3.7 respectively. The additional curvature at low temperatures is a result of the scattering rate γ becoming comparable or even smaller than ν. The critical thickness changes rapidly around Tc, indicating that for most thin films, the transmission is dominated by ε'' in the normal state, while it is governed by ε' in the superconducting state. For the single crystals used in this calculation, the crossover region around Tc is rather small. A more specific experimental analysis using the measured values for DyBa₂Cu₃O₇₋δ will be given in the chapter 6.

3.2 Reflection using an Oblique Angle of Incidence

Semi-infinite Medium

We return to eq. (3.2) where the Fresnel coefficients are given for an arbitrary interface and angle of incidence. During the entire analysis presented above we assumed to be working under normal incidence conditions, whereby the distinction between the p-polarized and s-polarized light disappears. However, the use of a non-zero angle of incidence in a polarized reflection measurement on an anisotropic medium, yields valuable information in all three directions of the crystal axes. Intuitively this can be easily understood by realizing that one polarization (p) will contain the planar response, having the axial response admixed, while the s-polarization is only sensitive to the planar response. This means that we can use the information known from the s-polarization to extract the information about the c-axis stored in the p-polarized reflectivity.

In this section we will briefly discuss some of the mathematics involved and also hint at the physical implications. In chapter 5 we will return to this topic and demonstrate
its strength by polarized reflectivity measurements performed on a Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ thin film at an incidence angle equal to 45°. A more detailed description and many experimental results obtained with the so-called Polarized Angle Resolved Infrared Spectrometry technique (PARIS), are described in reference [12].

The measurement configuration is depicted in fig. 3.8, where we have indicated the directions of the polarizations and the crystal axes. We assume that the crystal structure of the high T$_c$ superconductor under investigation is tetragonal, and hence there will be no anisotropy in the in-plane dielectric function. In order to describe the total response of the reflecting ab-plane and the c-axis direction perpendicular to this plane, we have to start with the complex Fresnel reflection coefficients for a uniaxial crystal. The optical axis is oriented perpendicular to the reflecting surface, hence we can write the reflection coefficients as [3]

\[
rs = \frac{\cos \theta - \sqrt{n_o^2 - \sin^2 \theta}}{\cos \theta + \sqrt{n_o^2 - \sin^2 \theta}} \\
rp = \frac{n_on_c \cos \theta - \sqrt{n_e^2 - \sin^2 \theta}}{n_on_c \cos \theta + \sqrt{n_e^2 - \sin^2 \theta}}
\]

(3.29)
Here $\theta$ is the incident angle and $n_o$ and $n_e$ are the ordinary and extraordinary refractive indices respectively. Since we are measuring reflected intensities, the phase $\Phi$, given by $\tilde{R} = Re^{i\Phi}$, has to be determined using Kramers-Kronig relations. In doing this for a non-zero angle of incidence one needs to be careful, since experimental uncertainties might lead to having negative values for $\Phi$. This would then lead to spurious negative values for the optical conductivity calculated using $R$ and $\Phi$. When both quantities $R$ and $\Phi$ are known and non-negative, we can proceed and determine $\epsilon_o$ and $\epsilon_e$ by solving eq. (3.29) in terms of $r_s$ and $r_p$:

$$
\epsilon_o = \sin^2 \theta + \left( \frac{1 - r_s}{1 + r_s} \right)^2 \cos^2 \theta 
$$

$$
\epsilon_e = \sin^2 \theta \left[ 1 - \epsilon_o \left( \frac{1 - r_p}{1 + r_p} \right)^2 \cos^2 \theta \right]^{-1}
$$

Given $\epsilon_o$ and $\epsilon_e$ we can calculate other interesting response functions such as the optical conductivity and the loss function.

The expressions stated above, can be applied directly to the reflectivity measurements on the high $T_c$ superconductors. The ordinary dielectric function $\epsilon_o$ then corresponds to the sample response within the ab-plane, while $\epsilon_e$ corresponds to the response in the c-axis direction, perpendicular to the plane.

Using the large anisotropy present in these materials, we can derive an approximate expression for the reflectivity, and thereby the absorptivity, of the $p$-polarized light, knowing that the sample surface corresponds to the ab-plane.

$$
A_p \approx 1 - R_p = 4 \frac{\text{Re}(x \cdot l^*)}{1 + x \cdot l^*}^2
$$

Here we have introduced

$$
x = \frac{1}{n_{ab}}
$$

$$
l = \frac{1}{\cos \theta} \sqrt{1 - \frac{1}{\epsilon_e} \sin^2 \theta}
$$

To get a physical feeling of the implications of eq. 3.31, we use that in the limit of metallic conductivity, $\text{Im}(n_{ab}) \gg 1$. This means that $1/\text{Im}(n_{ab})$ can be used as the expansion parameter of a Taylor series. Furthermore we assume that $|\sin^2 \theta/\epsilon_e| \ll 1$, so that the leading term of the series expansion becomes

$$
1 - R_p = \frac{2 \sin^2 \theta}{\text{Im}(n_{ab}) \cos \theta} \text{Im} \left( -\frac{1}{\epsilon_e} \right)
$$

Note that $\text{Im}(-\epsilon_e^{-1})$ is precisely the definition of the loss function in the c-axis direction, having peaks at the resonance frequencies, such as transverse optical phonons and
plasmons. Since $n_{ab}$ is featureless in the low frequency region in case of metallic planar behavior, this implies that the absorptivity of the $p$-polarized light measured in the $ab$-plane will have peaks at the resonant frequencies characteristic for the $c$-axis direction. This phenomenon is closely related to the physical mechanism leading to the well-known Berreman effect for dielectric overlayers on metallic substrates [13]. Due to for instance surface roughness, this effect can even be present in reflectivity measurements at smaller incidence angles, where the distinction between $\sigma$ and $p$-polarization becomes smaller [14]. The correspondence between the structure in the $ab$-plane reflectivity and the $c$-axis resonances might easily lead be misinterpreted as a correlation between the $c$-axis phonon modes and the $ab$-plane electronic degrees of freedom [15,16].

**Thin Film**

In the previous part of this section we have estimated the absorption for the case of a semi-infinite anisotropic superconducting film in order to get a physical feeling for the influence of the angle of incidence on the observed spectra. For the semi-infinite layer we could neglect transmission and calculate the absorption coefficient directly from the reflectivity. Using the same formalism we will now calculate the absorption coefficient within a thin film on a semi-infinite substrate. In this case both transmissivity and reflectivity need to be taken into account.

The physical interest is the comparison of the frequency dependence of the absorptivity of the film and the frequency dependence of the experimental data obtained by Photo Induced Activation of Mm-wave Absorption (PIAMA) presented in chapter 7. In this particular case therefore, we are merely interested in the absorption within the film, not the absorptivity of the entire sample. Hence we assume that the substrate is semi-infinite, thereby neglecting the interference within the substrate. This is reasonable since the transmission coefficient at the dielectric-air interface ($2 \to 0$) will be rather high, while the reflectivity coefficient for the beam at the dielectric-film interface ($2 \to 1$) will be large. Henceforth the secondary contribution to the absorption within the film will be very small and interference effects only give rise to a minor correction.

The complex transmission and reflection coefficients given in the beginning of this chapter (eqs. (3.6) and (3.8)) can also be used in this case, provided that the appropriate Fresnel coefficients are used. We can rewrite the coefficients for the sake of clarity as

\[
\begin{align*}
t^x_{br} &= \frac{t^x_{01} t^x_{12} e^{i\phi_x}}{1 - r^x_{01} r^x_{12} e^{2i\phi_x}} \\
r^x_l &= \frac{r^x_{01} + r^x_{12} e^{2i\phi_x}}{1 - r^x_{01} r^x_{12} e^{2i\phi_x}} \quad (3.34)
\end{align*}
\]

where we used that $r_{01} = -r_{10}$ and $t_{01} t_{10} = 1 - r^2_{01}$, while $x$ is the suffix indicating either $p$-polarized or $s$-polarized light. The Fresnel coefficients for both polarizations on the subsequent interfaces for the case of an anisotropic film on an isotropic substrate are
given by [3]

\[ r_{01}^p = \frac{n_{ab}n_c \cos \theta_0 - \sqrt{n_c^2 - \sin^2 \theta_0}}{n_{ab}n_c \cos \theta_0 + \sqrt{n_c^2 - \sin^2 \theta_0}} \]

\[ r_{12}^p = \frac{-n_{ab}n_c \cos \theta_2 + p\sqrt{n_c^2 - p^2 \sin^2 \theta_2}}{n_{ab}n_c \cos \theta_2 + p\sqrt{n_c^2 - p^2 \sin^2 \theta_2}} \]

\[ r_{01}^s = \frac{\cos \theta_0 - \sqrt{n_{ab}^2 - \sin^2 \theta_0}}{\cos \theta_0 + \sqrt{n_{ab}^2 - \sin^2 \theta_0}} \]

\[ r_{12}^s = \frac{-p \cos \theta_2 + \sqrt{n_{ab}^2 - p^2 \sin^2 \theta_2}}{p \cos \theta_0 + \sqrt{n_{ab}^2 - p^2 \sin^2 \theta_2}} \quad (3.35) \]

for the case that the optical axis of the uniaxial film is perpendicular to its boundaries. The transmission coefficients can be determined using

\[ t_{ij}^p = 1 + r_{ij}^p \]

\[ t_{ij}^s = 1 + r_{ij}^s \quad (3.36) \]

where i and j are the indices denoting the respective media. We have adopted the notation applicable to the high $T_c$ superconductors, i.e. $n_{ab}$ denotes the planar complex index of refraction and $n_c$ denotes the c-axis response. Furthermore, p is the substrate refractive index and $\theta_0$ and $\theta_2$ are the incident angle and the angle of propagation within the substrate respectively. These angles are related via Snell’s law

\[ \frac{\sin \theta_0}{\sin \theta_2} = p \quad (3.37) \]

The phase factors, $\phi^x$, appearing in eq. (3.34) are given by

\[ \phi^p = kd_1 \left( \frac{n_{ab}}{n_c} \right) \sqrt{n_c^2 - \sin^2 \theta_0} \]

\[ \phi^s = kd_1 \sqrt{n_{ab}^2 - \sin^2 \theta_0} \quad (3.38) \]

where $k$ is the wavevector and $d_1$ is the thickness of the film. The only phase factor appearing in the expressions above stems from the film, due to the approach to neglect the interference effects in the substrate for our purpose, i.e. to calculate the absorptivity within the film. The absorptivity can finally be calculated by

\[ A_{film}^x = 1 - |t_{ij}^x|^2 - |r_{ij}^x|^2 \quad (3.39) \]

where x indicates as before the two possible polarizations.

In chapter 7 it will be shown that the dielectric properties of the substrate, such as Reststrahlenbands in between the transverse and longitudinal phonon frequencies will severely
modify the absorptivity within the film due to the altered matching at the film-substrate interface. Physically speaking, a higher reflectivity at the interface enhances the effective average path length the rays traverse within the film, causing an enhanced absorption at these frequencies. This phenomenon is commonly referred to as the Berreman-effect [13].

3.3 Calculation of the Complex Dielectric Function From T and R

As explained earlier in this chapter, one of the main problems in infrared spectrometry is to acquire both the real and the imaginary part of the dielectric function from the available experimental information. Frequently Kramers-Kronig relations are used to obtain the phase information in addition to the measured reflection coefficient. The combination of phase and amplitude can then be used to determine the complex $\epsilon$. In this section we will discuss the possibility of measuring both the transmissivity, $T$, and the reflectivity, $R$, of the same thin film. Since these are two independent parameters, the full complex dielectric function $\epsilon$ can be obtained analytically. In Chapter 5 an experimental example using a NbN-film will be presented.

Common practice in FTIR-spectroscopy is to measure the transmission through the film+substrate system and a bare substrate. By division of these spectra the contribution of the substrate is eliminated and the transmission coefficient of the film throughout the measured frequency range is obtained. Please note that in order to do so, the thickness of the substrate used in the reference measurement has to be identical to the one on which the film is deposited, otherwise absorption contributions present in the substrate do not cancel completely.

The obtained transmission and reflection coefficients can hence be modeled using the expression for a single layer. Since also the thickness of the film is of the order of several tens of nm, i.e. much smaller than the wavelength, we can in addition neglect the interference effects within the film. At the first interface (air $\rightarrow$ film) the reflected intensity is defined as:

$$ R = \left( \frac{1 - n}{1 + n} \right)^2 = \frac{(\eta - 1)^2 + \kappa^2}{(\eta + 1)^2 + \kappa^2} $$

Although the sinusoidal contribution due to interference can be neglected in the film, the multiple reflections still have to be taken into account for the absorption in order to obtain the right formulation for the reflectivity and transmission coefficients. We can define the absorbed intensity for a single pass inside the film as:

$$ \Phi = e^{-4\pi kd/\lambda} $$
Applying as before the expression for the geometrical series one obtains

\[
T = \frac{(1 - R)^2 \phi}{1 - (R\phi)^2}
\]

\[
R_{\text{tot}} = R + \frac{R(1 - R)^2 \phi^2}{1 - (R\phi)^2} = R(1 + T\phi)
\]  

(3.42)

equivalent to eqns. (3.6) and (3.8). Using the first part of eq. (3.42) we obtain

\[
R = \frac{1}{1 + T\phi} \left( 1 \pm \sqrt{T^2 - T\phi + \frac{T}{\phi}} \right)
\]  

(3.43)

which yields, when substituted into the second part of eq. (3.42)

\[
R_{\text{tot}} = 1 \pm \sqrt{T^2 - T\phi + \frac{T}{\phi}}
\]  

(3.44)

Solving in terms of the extinction coefficient \( \kappa \) finally yields

\[
k = \frac{\lambda}{4\pi d} \ln \left( \frac{1}{\phi} \right)
\]  

(3.45)

where now \( \phi \) has been written in terms of the experimentally obtained reflection and transmission coefficients, \( R_{\text{tot}} \) and \( T \).

\[
\phi = -\frac{(1 - R_{\text{tot}})^2 - T^2}{2T} \pm \sqrt{\left( \frac{(1 - R_{\text{tot}})^2 - T^2}{2T} \right)^2 + 1}
\]  

(3.46)

Only the solution using the summation is physically relevant. The real part of the optical constant can be extracted from eq. (3.40)

\[
\eta = \frac{1 + R}{1 - R} \pm \sqrt{\left( \frac{1 + R}{1 - R} \right)^2 - \kappa^2 - 1}
\]  

(3.47)

where the reflection coefficient \( R \) can be written in terms of the experimentally observed variables by using eq. (3.42)

\[
R = \frac{R_{\text{tot}}}{1 + T\phi}
\]  

(3.48)

From the obtained complex refractive index, all desired optical constants can be determined analytically.

In case that interference effects are non-negligible, the derivation given above becomes rather cumbersome, and one needs to use numerical methods to obtain both the real and complex part of \( n \).
References


