Practical course M
2.7 Fourier spectroscopy

April 20, 2016

1 Introduction

In this experiment Fourier spectroscopy will be used to measure the reflectance of BeO in the infrared range. The signature of phonon modes can be observed within this spectral range. As a single crystal is used, the measurement can be performed for different directions of the polarization of the incident light. In addition the influence of parameters used in the Fourier transformation will be studied. Fourier spectroscopy provides a powerful tool for the investigation of the optical properties in the far infra-red(FIR) and mid infra-red(MID).

2 Preparation

2.1 Theory

- Fourier spectroscopy [1] (part 1)
- Zerofilling factor [1] (part 1)
- Apodization function [1] (part 2: 2.1 and 2.2)
- Drude-Lorentz model
- Phonons
- Drude model of the electrical conductivity [5]
- Beryllium Oxide structure
- Linearly polarized light

2.2 Software

- ReFit, read the user manual sections: 1.2; 2.2.1; 2.2.2; 2.2.3
- Do the tutorial 3.1 (keep in mind that in your experiment you will need just one oscillator while in the tutorial you are using 2 oscillators and a Drude peak)

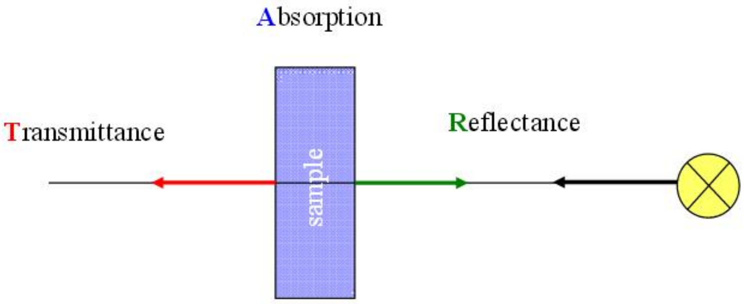

Figure 1: Light can be reflected, transmitted or absorbed by a sample.

2.3 Questions

- Once you obtained the dielectric constant ($\epsilon = \epsilon_1 + i\epsilon_2$) from the measured reflectivity, how can you calculate complex conductivity ($\sigma = \sigma_1 + i\sigma_2$) and refractive index ($N = n + ik$)?
  What is the relationship between ϵ, σ and N? [5]
- Assume to shine linearly polarized light on a dipole, with light propagation parallel to dipole axis (electromagnetic field of light and dipole are oscillating at the same frequency).
  Dipole and plane of polarization form an angle. How does the coupling of light with dipole depend on this angle?

3 Physical background

3.1 Fourier spectroscopy

The importance of optical properties for understanding the physics of the solid state has motivated the experimentalists to measure them accurately. The dielectric function ϵ or the optical conductivity σ are hard to measure directly. The quantities one is able to observe in experiment are the transmittance T and the reflectance R.[1]

In order to obtain the reflectance and the transmittance of the sample, it is necessary to compare the reflectivity spectrum and the transmission spectrum , respectively to a reference spectrum. For the reflectivity reference, the reflectivity spectrum of a gold mirror is used. For the transmission reference, the transmission of an empty sample holder is used. The actual setup of switching between the reference and the sample is shown in Fig.2

A straightforward experimental setup, which used to be used for decades, for measuring T and R is shown in Fig. 3. Light coming from a source with a continuous spectrum is split up into its frequency components by a grid. A light with a narrow frequency range is picked up by a slit, passes the sample and is measured by a detector. By repeating the measurement without the sample,

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[1] In sophisticated experiments also other quantities are observed, e.g. by ellipsometry the ratio R_p/R_s (R_p reflectance of light polarized parallel to the plane of incidence, R_s reflectance of light polarized perpendicular to the plane of incidence) and the phase shift θ of the reflected light are measured. From these two quantities other optical properties are obtained.

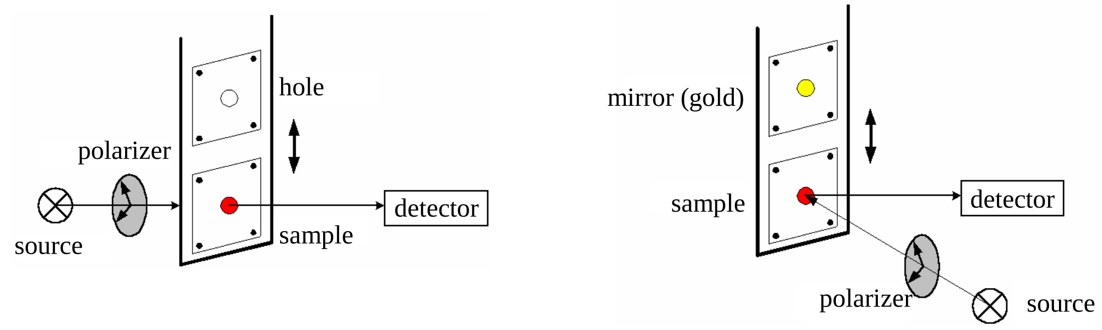

Figure 2: The position of the sample and of the reference can be switched rapidly at any temperature. Both are mounted on the same copper plate. The picture is taken from [**?**].

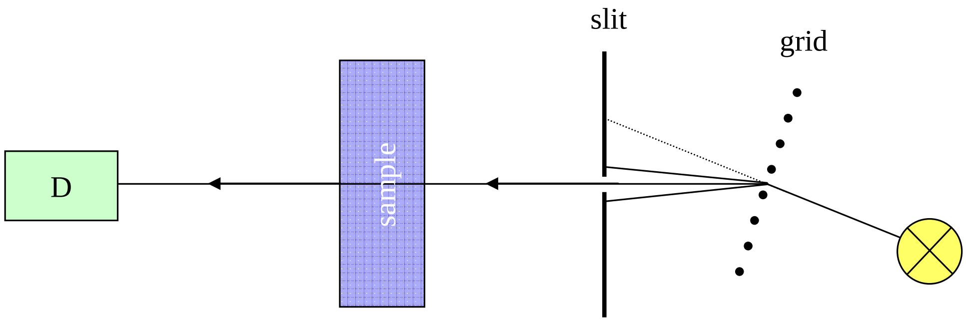

Figure 3: The principle setup of a spectrometer using a monochromator. The light from the source is passing a grid first. Under a certain diffraction angle, a narrow frequency band with its maximum at that angle is selected by a slit. The beam is passing the sample and is detected by a detector D.

the reference is obtained. The quotient of the transmission with sample and transmission without sample is the transmittance at that frequency. However it is replaced by Fourier spectroscopy, since the range can be measured at once. The principle experimental setup of a Fourier spectrometer is shown in Figs. 4 and 5. The light passes through a Michelson interferometer before hitting the sample. The striking difference to the conventional setup is the absence of a monochromator. So there is no elimination of frequencies before hitting the sample. Also the detector is not sensitive to the wavelength of the incident light (in contrast to the human eye). It measures only intensities, as function 0of time. Actually the frequency dependent spectrum is calculated after the measurement. The trick is that during a measurement one of the mirrors of the interferometer is moving. Hence the length of the path for the bundle of light reflected at the moving mirror is varying with time in comparison to the one coming from the fixed mirror. Therefore this the intensity of light of one wavelength is oscillating between constructive and destructive interference with a period that is determined by the mirror velocity and the wavelength of the

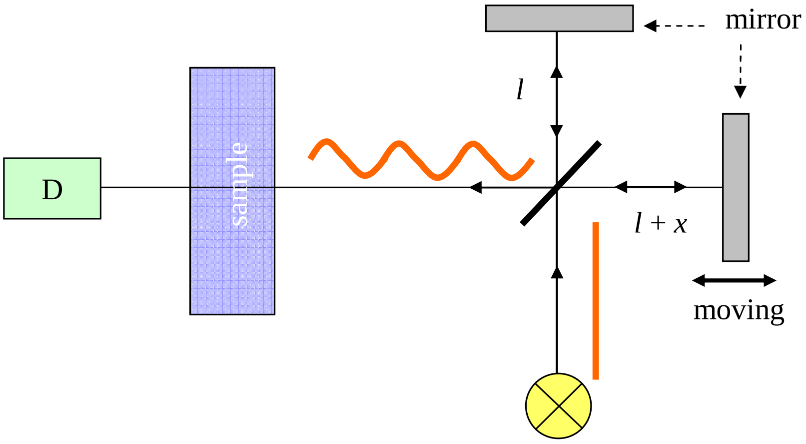

Figure 4: The principle components of a Fourier spectrometer. On the time scale relevant for the detector, the light from the source has constant amplitude, indicated by the orange line. After passing the interferometer, the amplitude depends on the difference x (relative to the wavelength) of the paths the two beams have traveled before interfering. Upon moving one of the mirrors, the amplitude oscillates in time between constructive and destructive interference as indicated by the oscillating orange line. After passing the sample the intensity is measured by a detector D.

light. As the velocity of the mirror is the same for all wavelengths, the period of the oscillations is characteristic for the wavelength of the light. The intensity oscillations can be detected by a detector. For a constant mirror velocity the resulting intensity for light of one single wavelength will be a cosine measured as function of the mirror position.

In one scan of the mirror all wavelengths from the source are measured simultaneously, giving a superposition of all cosine terms from all frequencies contained in the spectrum of the source. The intensity as a function of the position of the mirror is called interferogram. An example of an interferogram is given in Fig. 6. The original spectrum is obtained by decomposing the interferogram into cosine terms. This decomposition is actually a Fourier transformation, from which the name of the method is derived from.

So far we have discussed the basic mode of operation of a Fourier spectrometer. However, there are more components which are essential for receiving the spectrum of the sample. At first it is important to determine the position of the mirror as a function of time. This is done by measuring additionally the interferogram of a laser which is detected by a diode after passing the interferometer. The laser gives a well-defined cosine signal. Since the laser intensity is orders of magnitude stronger than the intensity of the light coming from the source, the signal obtained by the diode is not influenced by the light of the source. The signal detected by the diode is used to trigger the detector, in a way that a data point is collected whenever the mirror has moved by one laser wavelength.[2] The

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[2] In between two minima of the diode signal the detector is triggered electronically, giving a higher density of data points. This is needed to measure a broader range of frequencies. With the density of data points acquired for a laser frequency ω_L, only a frequency interval of width $\omega_L/2$ can be measured.

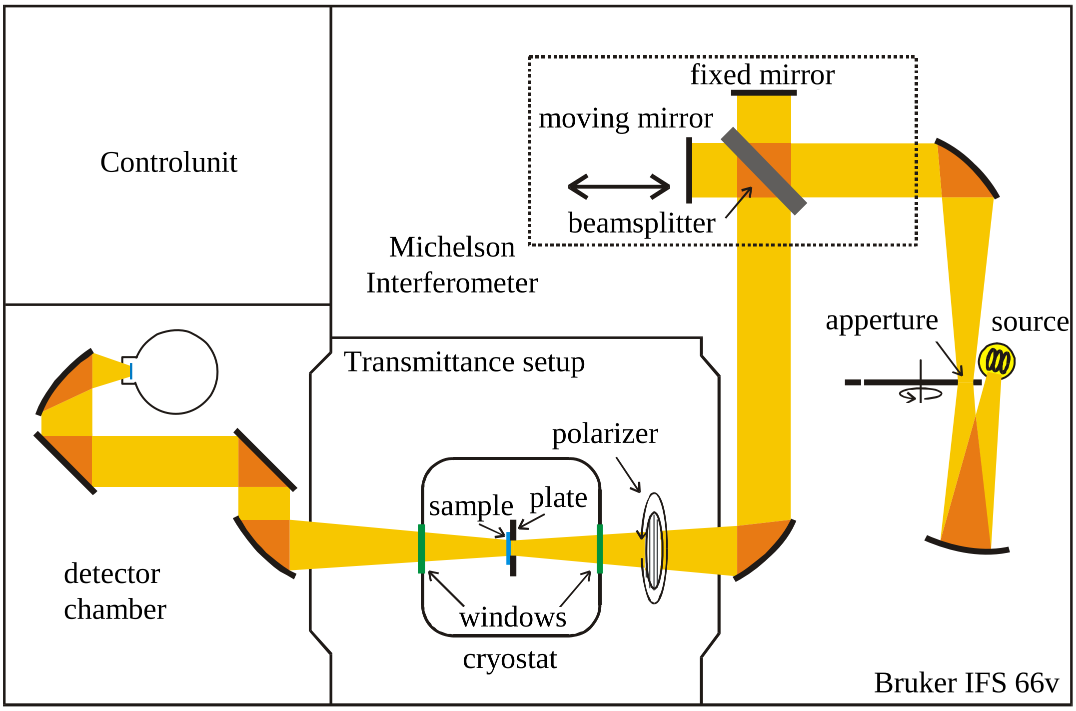


Figure 5: Sketch of the Bruker IFS 66 v/S. All results within this work were obtained with this spectrometer.

laser wavelength is known with high accuracy of 1 to 10^6. Compared to the use of a momochromator, the advantages of Fourier spectroscopy in the infrared range are

- due to the precise knowledge of the laser wavelength, Fourier spectroscopy has a very high accuracy in frequency.
- short measuring times due to the measurement of all frequencies simultaneously. for the short measuring times all other parameters like for instance the temperature stay constant between measuring the sample and the reference.
- the resolution depends only on the length of the interferogram. It can be increased by increasing the distance the mirror moves. Therefore no intensity of the signal is lost, i.e. the signal-to-noise ratio is independent of the resolution.
- due to the precise knowledge of the laser wavelength, Fourier spectroscopy has a very high accuracy in frequency.

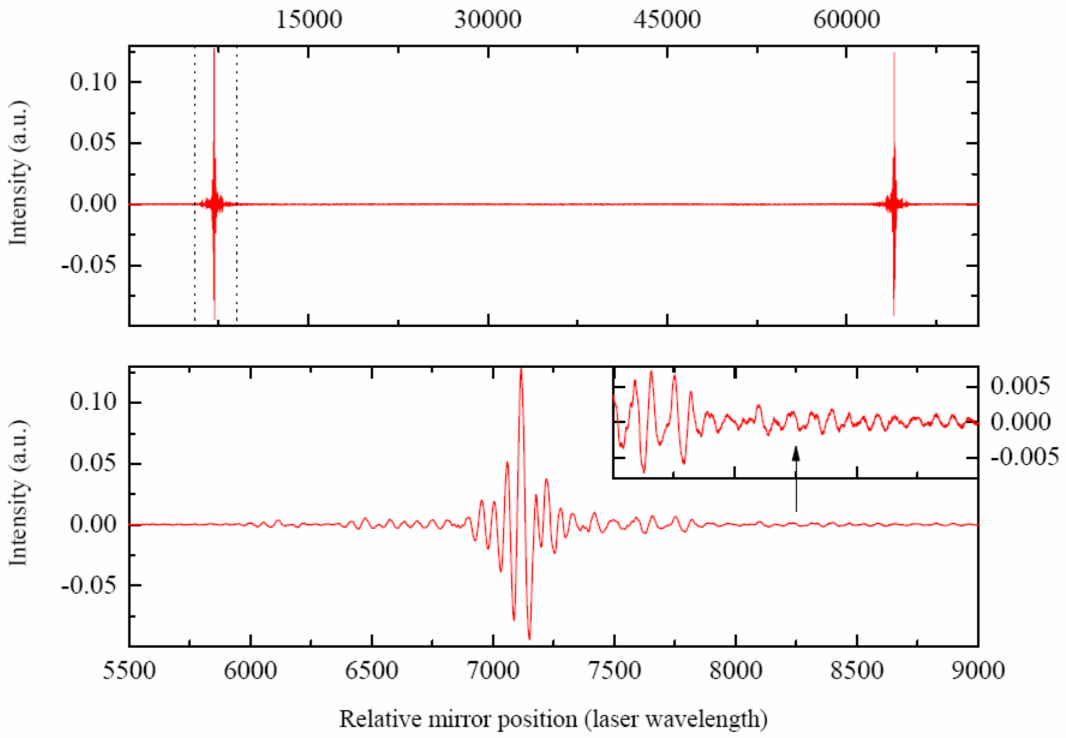


Figure 6: In the upper panel an interferogram is shown. The peaks (white-light position) correspond to the position for which both mirrors have equal distance to the beamsplitter. Two peaks occur because the mirror has been moved forward and backward, crossing the white-light position twice in one scan. In the lower panel the part between the dashed lines (in the upper panel) is plotted on an enlarged scale in order to show the detailed structure of the interferogram. The inset displays the fine structure of the interferogram away from the white-light peak. It has the same x axis as the whole panel but is enlarged in y direction.

The spectrum consists of discrete data points. Therefore a discrete form of the Fourier transformation has to be used.

$$S(k \cdot \triangle\nu) = \sum_{m=0}^{N-1} I(m \cdot \triangle x) \exp(i\, 2\pi k m/N)$$

with S intensity function of frequency (spectrum); $k \cdot \triangle\nu$ discrete frequency; I intensity function of mirrors position (interferogram); $m \cdot \triangle x$ descrete mirror position; N number of measured points; m integer number in the range $[0, N-1]$ In comparison with the continuous transformation

$$S(\nu) = \int I(x) \cdot \exp(i\, 2\pi\nu) dx$$

with $\nu \equiv k \cdot \Delta\nu$ continuous frequency; $x \equiv m \cdot \Delta x$ continuous mirror position. The resulting spectrum of the Fourier transformation depends on varies parameters. The wrong choice of these parameters can lead to non physically results.

One mistake is due to the finite length of the interferogram, whereas the cosine function extends from $-\infty$ to ∞. The finite interferogram may therefore be regarded as an infinite interferogram times a function (apodisation function) that is equal to zero beyond the range of the measured interferogram. The Fourier transformation is also sensitive to this function, i.e. the result of the Fourier transformation is a convolution of the infinite interferogram (which would give the unaltered spectrum) and the apodisation function. Different Apodisation functions can be chosen. They are basically equal to one in the measurement range but the transition between zero and one is chosen differently. However, this effect gets important only for rapid variation of the intensity within the spectrum, i.e. for very sharp lines (compared to the frequency resolution). Such features occur in spectra of for instance molecules.

When applying the Fourier transformation it is important that the frequency range under investigation is at least as wide as the spectrum of the light source. Otherwise frequencies higher than the cut-off frequency are folded back, falsifying the resulting spectrum. It is also worth to note that the resolution of the *spectrum* corresponds to the length of the interferogram, and that the resolution of the *interferogram* determines the width of the spectral range obtained. This correspondence opens the opportunity to increase the density of points in the spectrum by adding zeros to the interferogram. However, this is not increasing the information but corresponds to a smoothing through the discrete spectrum.

The final remark is about the occurrence of a phase $\neq 0$ of the cosine terms due to a deviation of the mirror symmetry of the measured interferogram at the white-light position. The asymmetry results form the discrete structure that is in general not centered exactly at the white-light position. This phase shift is corrected by taking the absolute value of the amplitude.

In conclusion, Fourier spectroscopy is an excellent tool for the investigation of optical properties of matter. It is fast and provides a very high accuracy. The commercially available spectrometer comes along with a software which makes the measuring procedure rather convenient and the results very satisfying.

3.2 Interaction of light and matter

3.3 IR absorption

In crystals vibrations can be excited via two physical mechanisms: the absorption of light quanta (IR absorption/spectroscopy) and the inelastic scattering of photons (Raman spectroscopy). Based on selection rules, not all vibrational modes present in a crystal can be observed via IR Spectroscopy or Raman spectroscopy. Modes observable with IR spectroscopy are called "IR active"; modes observable by Raman spectroscopy are called "Raman active".

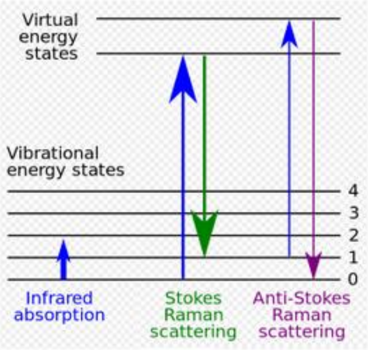
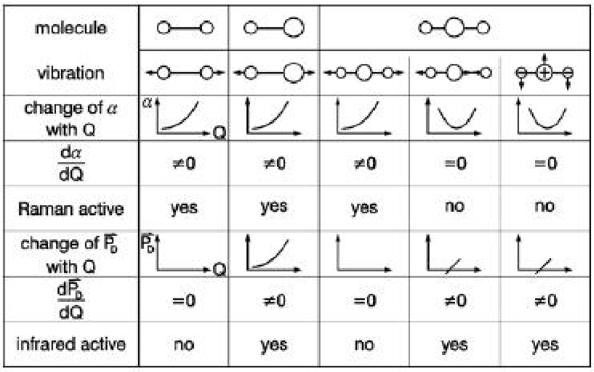


Figure 7

In order for a vibrational mode to be "Raman active", it must be associated with changes in the polarizability.
In order for a vibrational mode to be "IR active", it must be associated with changes in the dipole. A permanent dipole is not necessary, as the rule requires only a change in dipole moment, for instance antiphase vibrations (optical phonons). In order to observe a direct absorption, the oscillating electromagnetic field of the incident photon has to couples with the dipole oscillating at the same frequency.



molecule					
vibration					
change of α with Q					
$\frac{d\alpha}{dQ}$	≠0	≠0	≠0	=0	=0
Raman active	yes	yes	yes	no	no
change of $\vec{P}_D$ with Q					
$\frac{d\vec{P}_D}{dQ}$	=0	≠0	=0	≠0	≠0
infrared active	no	yes	no	yes	yes

Figure 8: Selection rules for Raman and for infrared activity of vibration.
Q represent the deformation due to vibration, α is the polarizability and P_D is the dipole moment.

3.3.1 Drude-Lorentz model for dielectric function in insulators

In this section a microscope model for interaction between light and matter will be discussed. Fourier spectroscopy is measuring the linear response of the matter. This means the photons excites states out of the equilibrium and the equilibrium is regained before the next interaction. In the classical picture the interaction between the charged atoms and the electrons can be described by Coulomb interaction. The oscillating electromagnetic field of the light will displace charges from their equilibrium position. For a ionic crystal (like BeO) the displacement of charges can be separated into different contributions shown in Fig. 9.

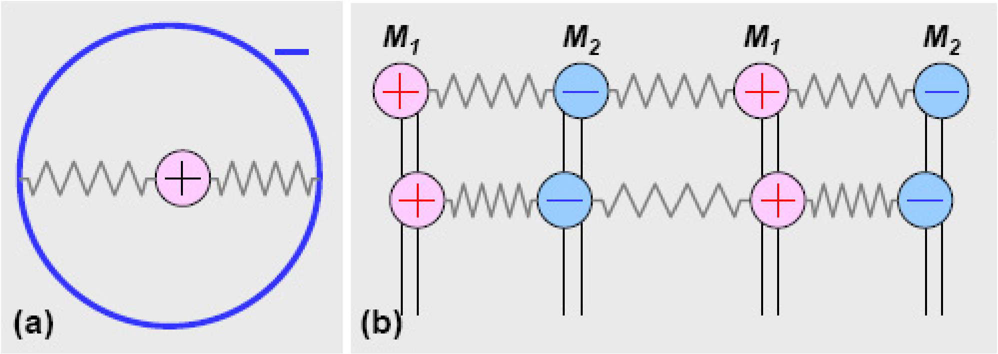


Figure 9: Two different mechanisms leading to a dipole moment of an insulating ionic crystal. (a) Shift of the negative electron against the positive nucleus. (b) Shift of negatively charged ions M_2 against the positively charged ions M_1.

One way the dipole moment present itself is shifting the negatively charged electron against the positively charged nucleus. The second possibility is to displace the negatively charged ions against the positive ones (ionic polarization). Its resonance frequencies lies in the far-infrared region. This is the coupling of the photons to phonons (lattice vibrations).
On this microscopic oscillators the Drude Lorentz is based. The displacement of the charges by an external electric magnetic field can be translated into the macroscopic quantity epsilon, the dielectric function. The relation between the resonance frequency ω_0, the scattering rate γ and the dielectric constant as a function of frequency is derived below.

Known from classical mechanics, for external electromagnetic wave $Ee^{-i\omega t}$.
Forced harmonic oscillator:

$$m\ddot{x} + m\gamma\dot{x} + m\omega_o^2 x = qEe^{-i\omega t} \tag{1}$$

Using Ansatz: $x(t) = x_o e^{-i\omega t}$
With polarization: $P = \epsilon_o(\epsilon - 1)E = Nqx$
N density of dipoles, x displacement
The resultant dielectric function is:

$$\epsilon = 1 + \frac{\omega_p^2}{\omega_o^2 - \omega^2 - i\omega\gamma} \tag{2}$$

Where $\omega_p^2 = \frac{Ne^2}{\epsilon_o m}$

If we consider different contributions to polarization P from different modes, the resultant dielectric function is a sum over all modes (j).

$$\epsilon = 1 + \sum_j \frac{\omega_{p,j}^2}{\omega_{o,j}^2 - \omega^2 - i\omega\gamma_j} \tag{3}$$

Each mode/oscillator is characterized by:

	Classically	Q.M.
$\omega_{o,j}$	Resonant frequency	Energy difference between ground and excited state
γ_j	Damping	Scattering rate
$\omega_{p,j}^2$	Plasma frequency	Square of the dipole matrix element

3.3.2 Approximation for optical and IR region

All solid material have a number of strong excitations for high frequencies associated with electronic transitions in the material. Their frequencies are usually located in the far UV to X-ray wavelength region. Crystals have additional strong oscillators with resonant frequencies in the IR region, associated with vibrational modes in the lattice. Since we want to measure and study BeO behavior in IR region, there is no need to characterize modes at high frequencies. The only relevant parameter is the total contribution in the IR range coming from all modes at frequencies above the IR range (ϵ_∞).

For frequencies lower than the resonant frequency $\omega << \omega_o$

$$\epsilon(\omega << \omega_o) = \epsilon_\infty = 1 + \sum_j \frac{\omega_{p,j}^2}{\omega_o^2} \tag{4}$$

So the final dielectric function in the IR range is:

$$\epsilon = \epsilon_\infty + \sum_j \frac{\omega_{p,j}^2}{\omega_{o,j}^2 - \omega^2 - i\omega\gamma_j} \tag{5}$$

3.3.3 Drude-Lorentz method for metals

Here we apply the formalisms developed in the previous sections to the electrodynamics of metals, i.e. materials with a partially filled electron band. Optical transitions between electron states in the partially filled band, the so-called intraband transitions, together with transitions between different bands, the interband transitions, are responsible for the electrodynamics. Here the focus will be on intraband excitations.

The model due to Drude regards metals as a classical gas of electrons executing a diffusive motion. The central assumption of the model is the existence of an average relaxation time $\tau = 1/\gamma$ which governs the relaxation of the system to equilibrium.

As we did previously we describe the system with Harmonic oscillator model but this time without restoration force (since the free electrons are not bonded)

$$m\ddot{x} + m\gamma\dot{x} = -qEe^{-i\omega t} \tag{6}$$

Solving the differential equation we find the dielectric function:

$$\epsilon = 1 - \frac{\omega_p^2}{\omega^2 - i\omega\gamma} \tag{7}$$

Where $\omega_p^2 = \frac{4\pi N e^2}{\epsilon_0 m_e}$
The current density is defined: $\mathbf{J} = -Ne^2\mathbf{v}$
with N the density of charge carriers; $\mathbf{v}$ is the carrier velocity, and $-e$ is the electronic charge
Assuming respectively applied electric field and conduction current density:

$\mathbf{E} = Ee^{-i\omega t}$ $\mathbf{J} = Je^{-i\omega t}$

Substituting into the equation of motion we obtain:

$$\mathbf{J} = \frac{Ne^2}{m_e}\frac{1}{-i\omega + \gamma}\mathbf{E} \tag{8}$$

For static field ($\omega = 0$ or $\frac{d\mathbf{J}}{dt} = 0$) the value the conductivity reduces to the known formula of the dc conductivity σ_{dc} $[\Omega^{-1}cm^{-1}]$

$$\sigma_{dc} = \frac{Ne^2}{m_e\gamma} \tag{9}$$

4 Experimental procedure

- Measure gold mirror with different zerofilling factors
- Measure gold mirror with different apodization functions
- Measure Reflectivity of BeO
- Measure Reflectivity of Stainless steel

5 Analysis

5.1 Zerofilling

Plot the three reference measurements (with different zerofillings) for one of the negative peaks at around 1500 cm^{-1} Discuss which zerofilling factor describes the peak better. Explain which factor you chose for the next measurement and why. What does this negative peak represent?

5.2 Apodization function

Plot the three reference measurements (with different apodization functions) for the same peak chosen in the previous section. Discuss which factor describes the peak better.

5.3 Phonon measurement in BeO

Using "RefFit" fit with Drude Lorentz model the measured reflectivity (R) for the measurement with polarizer at 0^o and 90^o. The range to fit should be about 500-1300 cm^{-1}, but you should choose it (explain why you have to cut part of your data before fitting it). Plot:

- Reflectivity vs freq. (both 0^o,90^o) with fitted curves.
- Refractive index vs freq. given by the model (both 0^o,90^o).
- Extinction coeff. vs freq. (both 0^o,90^o).
- Real dielectric function vs freq. (both 0^o,90^o).
- Imaginary dielectric function vs freq. (both 0^o,90^o).

Compare and discuss your results with the paper: *"Optical Phonons in BeO Crystals"*[2]
Plot reflectivity at 45^o (same range you have used for the fit), without fitting it. Discuss what can you see and how you could eventually fit it.

5.4 Stainless steel measurement

Here the aim is to calculate the charge carrier density of the two stainless steel samples.
Using "RefFit" fit the reflectivity up to about $5000 cm^{-1}$ (you are free to choose

even a wider range but be sure to neglect the data range where noise is overcoming the actual signal).
As expected the measured reflectivity should be fit by a Drude-Loretz oscillator for free electrons ($\omega_0 = 0$). But even if you are interested in characterising the sample‘s behaviour for frequencies above $500cm^{-1}$ contribution coming from phonons at lower frequencies have to be taken into account.
Therefore an additional oscillator is necessary with following parameters: $\omega_0 = 200cm^{-1}$, $\omega_p = 8000cm^{-1}$, $\gamma = 200$ (ω_p and γ are allowed to change, while ω_0 should be fix during the fit). Plot:

- Reflectivity vs freq. both: data and fit.
- Real conductivity σ_1 vs freq. Just the free electrons component without the one coming from phonons at low freq. (remove the oscillator at low freq. before plotting σ_1).

Calculate the charge carrier density using eq.(9) and reading σ_{dc} from the plotted σ_1 vs freq. In eq.(9) γ is in s^{-1} units while in RefFit is given in cm^{-1}.
$2\pi c * \gamma[cm^{-1}] = \gamma[s^{-1}]$.

References

[1] Werner Herres and Joern Gronholz *Understanding FT-IR Data Processing.*

[2] Eugene Loh *Optical Phonons in BeO Crystals* Phys. Rev. 166, 673.

[3] Charles Kittel *Introduction to Solid State Physics.*

[4] Neil W. Ashcroft *Solid State Physics.*

[5] Martin Dressel *Electrodynamics of Solids: Optical Properties of Electrons in Matter.*

[6] Kuzmani *Solid state spectroscopy.*