

Practical course M

2.8 Raman spectroscopy

Tutor:
Reinhard Rückamp (Tel. 0221-470-7944)

August 29, 2012

1 Introduction

The Raman effect was first experimentally discovered by Sir C. V. Raman in 1928, what fore he owned the Nobel prize in 1930. The effect has been already predicted earlier by A. Smekal in 1923 as an analogue to the Compton effect. In principle the Raman effect is the inelastic scattering of light on interaction with matter.

The goal of this experiment is to measure the Raman spectra of single crystalline samples in different polarization directions of the incoming and scattered light. From this data the Raman tensors of the observed excitations will be obtained and their symmetries will be determined. Moreover the dependence of the Raman spectrum on experimental parameters will be explored.

2 Physical background

In this section the physical principles relevant for the Raman effect are discussed. However, this tutorial is not sufficient and further reading is necessary for preparation.

There are three subjects that are discussed in the following: First lattice vibrations and phonons as their quantum counterpart are considered. Second an overview of the Raman effect is provided and finally the Raman tensor is introduced.

2.1 Phonons

In a crystal the ions have fixed positions that are repeated within a periodical lattice. For those positions the potential energy of the crystal is minimized therefore deviations of these equilibrium positions will raise the total energy. From a quantum mechanical point of view one thinks of excited states separated from the ground state by one (or several) energy quantum (also called phonons) analogous to the discrete energy levels of the harmonic oscillator.

For these excited states, the displacement of the ions will not have an arbitrary pattern since the elongation of one single ion would in general cause other ions to be displaced via interactions between them. However, there are patterns of

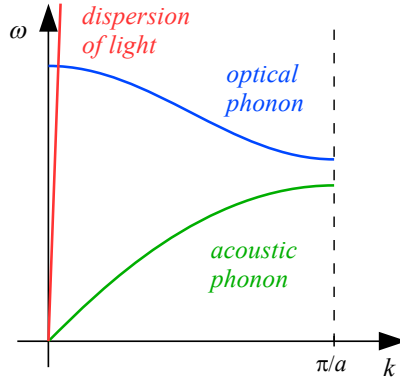


Figure 1: The frequency ω of an optical (blue) and an acoustic (green) phonon are shown as function of k . The dispersion of light (red) $\omega = ck$ with c the speed of light is shown to point out that momentum conservation $p = \hbar k$ leads to the assumption $k \approx 0$.

displacements that are independent of each other in the sense that if one pattern is excited it does not involve other patterns.

The vibrations that correspond to these patterns are called Eigenmodes of the crystal. These modes exhibit characteristic frequencies ω_i (with energies $\hbar\omega_i$). The frequency depends on the particular pattern of elongations as well as the wavelength λ or the wave vector $k = \frac{2\pi}{\lambda}$, respectively, i.e. the spatial periodicity. The number of independent patterns can be easily obtained by considering the case of infinite wavelength ($k = 0$) since one has only to count the displacement patterns within the unit cell. Assuming N ions within the unit cell each of them provides one degree of freedom for a displacement in x - y - and z -direction hence the total number turns out to be $3N$. The 3 acoustic modes become for $k = 0$ merely translations of the whole crystal that do not change the internal energy so that they have to be subtracted from this number. Therefore $3N - 3$ is the number of optical phonons. The assumption of $k = 0$ is reasonable for the visible range which provides only a tiny k due to the steep dispersion of light (Fig. 1).

2.2 Raman effect

If light of a certain frequency ω (energy $\hbar\omega$) interacts with matter¹ most of the scattered light has the same frequency ω , but there is also a small part that is shifted in frequency. This contribution, that provides information about the probed sample, is analyzed in Raman spectroscopy. For a comprehensive understanding of the Raman effect the use of quantum theory is unavoidable, but it is possible to gain insight into the effect purely based on a classical ground. In the following this approach is presented first, before the quantum description is discussed.

¹We will think in the following of crystals, however Raman spectroscopy is also applicable to liquids or gases.

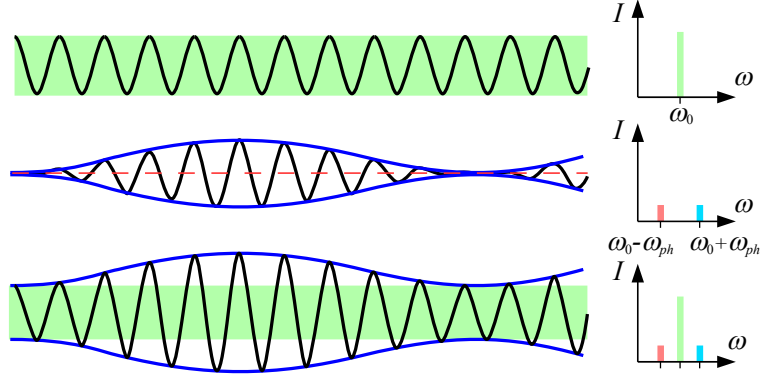


Figure 2: Top: Incident wave (solid line) of constant amplitude and frequency ω_0 . Middle: Contribution modulated via changes in the polarizability by the phonon (blue). The resulting beat consists of two frequencies $\omega_0 - \omega_{ph}$ and $\omega_0 + \omega_{ph}$. Bottom: In the resulting spectrum all contributions are present. Note that the changes in amplitude by the modulation of the phonon frequency are tiny compared to the amplitude. Here they are shown overestimated for clarity.

2.2.1 Classical interpretation

If an electromagnetic wave encounters a crystal it gives rise to an oscillating polarization $\vec{P}(t)$ within the crystal. The amplitude of such a polarization wave can be assumed to depend linear on the amplitude of the electrical field \vec{E} since the latter can be treated as small perturbation. Due to interaction between the ions within the crystal they cannot follow the electric field freely, but experience forces different to the direction of the electric field. Hence the polarization \vec{P} induced by an external electric field \vec{E} implies components perpendicular to \vec{E} and is thus given by a tensor quantity α_{ij} :

$$P_i = \sum_j \alpha_{ij} \cdot E_j$$

The tensor α_{ij} is called polarizability. The polarizability may change according to lattice vibrations² present in the crystal. Hence each component of α can be expanded into a series with respect to the elongation of the lattice vibration q :

$$\alpha = \alpha_0 + \frac{\partial \alpha}{\partial q} \cdot q + \text{h.c.}$$

α_0 is the contribution that is independent of the amplitude. There is an additional contribution of varying amplitude due to the presence of a phonon if $\frac{\partial \alpha}{\partial q} \neq 0$ as shown in Fig. 2. Assuming the vibrational frequency to be ω_1 , the elongation q turns out to be $q(t) = q_0 \cos(\omega_1 t)$. With an electromagnetic wave given by $E(t) = E_0 \cos(\omega_0 t)$ it follows that the polarization P is given by:

²In principle any excitations will be seen in the Raman spectrum as long as it changes the polarizability. Here we will think of phonons (i.e. lattice vibrations) for simplicity and since they are observed in most experiments.

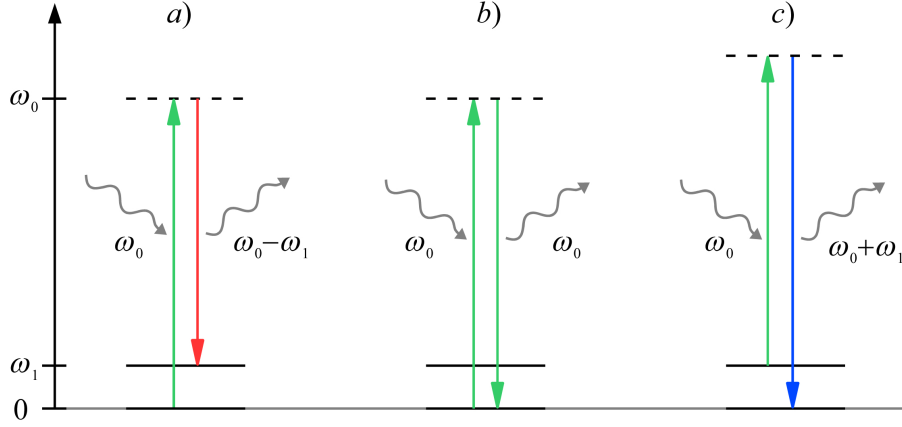


Figure 3: Quantum mechanical picture of the different scattering processes *a)* Inelastic Stokes scattering, the incoming photon of frequency ω_0 transfers the crystal in a first transition to a virtual state (broken line). In a second transition to a state where a phonon of energy ω_1 is excited an photon of the frequency $\omega_0 - \omega_1$ is emitted. *b)* Elastic Rayleigh scattering, the in and out going light is of the same frequency. *c)* Anti-Stokes scattering starts in a state where excitations are already present and ends via a virtual intermediate state in the ground state. The frequency of the emitted photon is hence raised to $\omega_0 + \omega_1$.

$$P(t) = \alpha_0 E_0 \cos(\omega_0 t) + \frac{\partial \alpha}{\partial q} E_0 \cos(\omega_0 t) q_0 \cos(\omega_1 t)$$

Using the equality $\cos(\phi) \cdot \cos(\psi) = \frac{1}{2} (\cos(\phi - \psi) + \cos(\phi + \psi))$ the right side can be rewritten as:

$$\alpha_0 E_0 \cos(\omega_0 t) + \frac{1}{2} \frac{\partial \alpha}{\partial q} E_0 q_0 (\cos((\omega_0 - \omega_1)t) + \cos((\omega_0 + \omega_1)t))$$

This shows that the response of the crystal contains in addition to the initial frequency ω_0 also contributions that are shifted upwards $\omega_0 + \omega_1$ and downwards $\omega_0 - \omega_1$ by the phonon frequency. The origin of these different contributions are elucidated in Fig2. The part lowered in frequency is called Stokes spectrum the one raised is called Anti-Stokes spectrum.

2.2.2 Quantum mechanical interpretation

The classical picture predicts equal intensities for the Stokes and the Anti-Stokes spectrum. In contrast to this prediction it is experimentally observed that the intensity of the Anti-Stokes spectrum is vanishing for temperature $T \rightarrow 0$. This behavior is only understood in a microscopic quantum picture. In Fig. 3 the three different types of scattering processes are shown in their quantum mechanical interpretation. In this picture it is evident that for low temperatures the number of excitations present within the crystal is small. Therefore the probability of the Anti-Stokes processes decreases whereas the intensity of the Stokes spectrum is not affected. The matrix element for Raman process is given as:

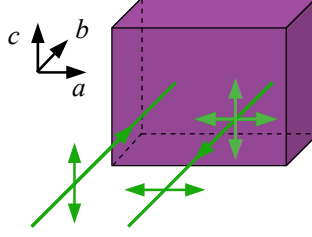


Figure 4: Example of a backscattering geometry: The incident laser beam is parallel to the b -axis of the crystal and its polarization is parallel to the crystallographic c -axis. The scattered light in direction of b is analyzed in polarization along a . The Porto notation for this process is then given by $b(ca)b$.

$$\sum_{\psi_v} \langle \psi_f | \vec{p} | \psi_v \rangle \langle \psi_v | \vec{p} | \psi_i \rangle$$

Where ψ_i/ψ_f denotes the initial/final state, ψ_v the virtual intermediate state, and \vec{p} the dipole operator. The sum runs over all intermediate states. By making using of the equality $\sum_n |\psi_n\rangle \langle \psi_n| = 1$ this can be rewritten as:

$$\langle \psi_f | \vec{p}^2 | \psi_i \rangle$$

For a certain choice of laser energy the intermediate state is not virtual anymore but an excited state of the crystal. In this case, so called resonant Raman scattering, the intensity of the Raman signal is usually strongly enhanced.

2.3 Raman activity and Raman tensor

The Raman spectrum for a certain sample depends on the geometry of the Raman experiment. Four parameters are relevant to characterize this geometry with respect to the crystallographic axes a, b, c :

- The direction of the incoming laser beam.
- The polarization of the laser.
- The direction of analyzer (polarizer). The analyzer discriminates between the different polarization direction of the scattered light.
- The direction of the stray light that is analyzed by the spectrometer.

These four parameters are brought into a compact form by the so called Porto notation. An example for the Porto notation is given in fig.4.

From section 2.2.1 it is obvious that a phonon mode will occur in the Raman spectrum only if it changes the polarizability α . This implies that the derivative of α with respect to the phonon coordinate q is non vanishing: $\frac{\partial \alpha}{\partial q} \neq 0$. Since α is a tensor this requirement depends on the direction of the electrical field with respect to the orientation of the crystal. The information whether a phonon mode is Raman allowed by symmetry reasons or not is given in compact form

by the so called Raman tensor. It is a 3×3 tensor with entries that correspond to the two directions given in the brackets of the Porto notation.

$$\begin{pmatrix} aa & ab & ac \\ ba & bb & bc \\ ca & cb & cc \end{pmatrix}$$

Two examples: point group C_{6v} , A_1 symmetry and point group C_{2v} , B_1 symmetry.

$$\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & f \\ 0 & 0 & 0 \\ g & 0 & 0 \end{pmatrix}$$

Note that the zeros of the Raman tensor are always symmetric, but not necessarily the entries. A zero stands for not allowed and the same letter in two components means that the phonon modes in these directions are degenerated by symmetry. The Raman tensor depends on the point group of the crystal and on the symmetry species (corresponding to one of its irreducible representation). The Raman tensors are tabled for instance in [1].

3 Preparation

As preparation for the experiment you should read up on following subjects:

Raman effect, phonon modes, polarization of light, experimental setup of a Raman spectrometer

3.1 Questions

- What order of magnitude is the proportion between the inelastic scattered light and the elastic scattered light?
- What are the typical length scales of the unit cell, the wavelength of the incident laser (visible light), and the wavelength of a phonon?
- How does the width of the entrance slit influences the resolution of the spectrometer?
Which other parameters are relevant for determination of the resolution?
- Which property of the Anti-Stokes Spectrum cannot be explained by a classical approach?
- Why is it not possible to measure a Stokes and Anti-Stokes spectrum using an Edge-filter?
- Why should the beam that is direct (specular) reflected by the sample surface not enter the spectrometer?
- Why can the dispersion of the incident photons be neglected?
- Why is a phonon mode of a crystal with a center of inversion either Raman active or infrared active but never both?

4 Experimental procedure

The experiment consists of three parts. First you check the alignment of the spectrometer and realign it if necessary. In the second part you investigate the correlation of the width of the entrance slit with the line width by measuring a rather sharp Raman line. In the last part you will determine the Raman spectra of different compounds provided by your tutor.

4.1 Alignment

Verify that the edge filter is mounted and all attenuators are used to block the laser. The full brightness of the laser would otherwise harm the CCD. In order to check the alignment you move the spectrometer to position 0 cm^{-1} in relative wavenumbers, i.e. the frequency of the incident laser. Collect a spectrum for only a few seconds. Remove successively the attenuator until you observe a pronounced peak in the vicinity of 0 cm^{-1} . Note that the maximum number of counts that can be processed by the CCD is 65000. If the peak center is shifted off 0 cm^{-1} , relocate it by adjusting the laser wavelength.

Si (111) sample

For the following alignment procedure make sure that at least the attenuator no. 3 is mounted. In order to adjust the sample position and the laser spot on the sample move the spectrometer to the absolute position 0 nm. Therefore switch first the calibration mode to absolute nm. In this position the grating is acting as a mirror. Select the alignment camera instead of the CCD, switch on the monitor, and open the entrance slit. Remove the edge filter from the optical path in order to observe the laser spot. A good alignment is achieved when the sample surface is in the focus of the objective and the laser spot is focused on the sample as well as positioned in the center of the entrance slit. The latter is observed by closing the entrance slit to the desired width for measurement.

After the alignment of sample and laser mount the edge-filter again and move the spectrometer at least to position 280 cm^{-1} relative to the laser line (for grating 2400). Switch the mirror from the alignment camera to the CCD (option side to option front).

Measure a silicon 111 surface. Zoom into the peak at 520 cm^{-1} . It should be in the range of $520\text{-}521\text{ cm}^{-1}$. If this is not the case, calibrate the spectrometer with assistance of your tutor.

4.2 Variation of the entrance slit

In principle you can use any sharp Raman line for task in this part. Below the case of a rotational line of the nitrogen molecule is described. Remove the Si sample and measure at 100 mW, i.e. remove all the attenuators. Below 200 cm^{-1} sharp peaks of rotational excitations of the nitrogen molecules appear in the spectrum. Measure this spectrum for at least 10 different width of the entrance slit. Where is the sample and why is a new alignment not necessary?

4.3 Raman spectra of single crystals

Measure the Raman spectra of the samples for all polarizations that are accessible by the sample geometry. In one surface of the sample you can observe Raman spectra for two polarization directions (horizontal h / vertical v). In combination with two polarizations of the laser (h/v) this yields four spectra: hh, vv, hv, vh where the latter two are equal. In order to align the single crystalline samples use the alignment procedure as described for the Si sample.

5 Analysis

5.1 Documentation of the spectrometer calibration

Plot the spectrum obtained at the laser line and for the silicon 111 sample. Fit the Si peak at 520 cm^{-1} using a Lorentz profile and compare the values of position and width of the peak to the literature.

5.2 Resolution of the spectrometer

Determine the full width at half maximum of one particular N_2 Raman line for spectra at different width of the entrance slit. Plot these values over the width of the entrance slit and discuss the effect on the line width and its intensity. Fit all peaks using both a Lorentz and a Gauss profile. What fits best? Try also a combination of a Gauss and a Lorentz fit: $\alpha \times \text{Lorentz} + \beta \times \text{Gauss}$, where $\alpha + \beta = 1$.

5.3 Determination of Raman tensors

Plot for each sample the measured Raman spectra and determine the peak position. Compare the peak positions of the different spectra (peaks of equal frequency can be assigned to the same phonon mode). Establish the Raman tensor for each phonon mode. A small contribution due to a slightly misaligned polarizer or leakage of the polarizer must be neglected. Determine the symmetry of the Phonon mode on basis of the Raman tensor.

5.4 Isostructural samples

If you measure isostructural sample, you can find a correspondence of the phonon modes by their symmetry. Check for the corresponding phonon frequencies which site is involved in the mode. In order to do so you must compare the ratio of the phonon frequencies to the square root of the ratio of the appropriate ion masses. If only this particular site would be involved in the vibration one would expect the ratio to be $\omega_1/\omega_2 = \sqrt{m_1/m_2}$. Deviations from this value indicate that other ions are involved, too.

References

- [1] R. L. W. Hayes, *Scattering of Light by Crystals*, John Wiley & Sons Ltd (Import), 1978.

Questionnaire for the M-practical course

Raman spectroscopy

Please fill in the form after you finished the experiment and discuss the criticism with your tutor wherever applicable.

The valuation is based on the german school mark system (1:best – 6:worst)

Semester: Winter 20__/_/ Summer 20__/_

Query 1:

How much did you learn from the experiment in terms of concepts in physics as well as technical skills?

[illegible]

Query 2:

How do you rate the quality of the experimental equipment?

[illegible]

Query 3:

Is the experiment up-to-date with recent topics in physics?

[illegible]

Query 4:

What is the advance in your experimental skills?

[illegible]

Query 5:

Did you have fun carrying out the experiment?

[illegible]

Query 6:

Is the tutorial of the experiment explicit?

[illegible]

Query 7:

How much time did you invest in the preparation?

h

Query 8:

How do you assess the experiment in total?

[illegible]

study course:	Master <input type="checkbox"/>	Teacher <input type="checkbox"/>
----------------------	--	---

Comments and suggestions

Overall mark for your tutor

Name of your tutor: _____

[illegible]