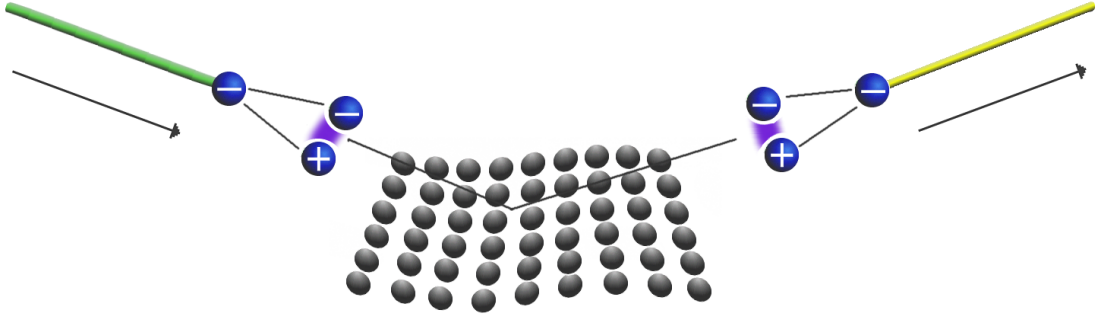


# Raman Scattering in Solids

## Introduction

Light can be scattered either elastically or inelastically. Raman scattering is an inelastic process. From the macroscopic point of view an incoming photon is scattered at the lattice. This process induces a phonon in the solid and reduces the energy of the photon by the energy lost in the scattering event. However, this description implies a direct interaction of the photon and the phonon. Such an interaction is very improbable and has not been experimentally verified yet. The Raman process as it occurs in solid states involves the excitation of an electron (Fig. 1).



**Fig. 1:** The Raman scattering event includes photon-electron and electron-lattice interaction. An incoming photon excites an electron. The excited electron-hole pair is scattered and falls back to the origin state by emission of a photon.

## The Raman Tensor - Macroscopic Theory

Electromagnetic radiation can induce microscopic polarizations of a material. A system's response to an electromagnetic field is known as the electric susceptibility  $\chi$ .  $\chi$  is a second rank tensor. An incoming electromagnetic field  $\mathbf{F}(\mathbf{r}, t) = \mathbf{F}(\mathbf{k}, \omega) \cos(\mathbf{k} \cdot \mathbf{r} - \omega t)$  leads to a local polarization

$$\mathbf{P}(\mathbf{r}, t) = \mathbf{P}(\mathbf{k}, \omega) \cos(\mathbf{k} \cdot \mathbf{r} - \omega t), \quad (1)$$

of the material due to the relation

$$\begin{aligned} \mathbf{P}(\mathbf{k}, \omega) \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) &= \chi(\mathbf{k}, \omega, \mathbf{Q}) \mathbf{F}(\mathbf{k}, \omega) \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) \\ \Leftrightarrow \mathbf{P}(\mathbf{k}, \omega) &= \chi(\mathbf{k}, \omega, \mathbf{Q}) \mathbf{F}(\mathbf{k}, \omega), \end{aligned} \quad (2)$$

where  $\mathbf{P}$  is the polarization.  $\mathbf{k}$  and  $\omega$  are the wave vector and frequency of the incoming electromagnetic field.  $\mathbf{Q}$  is the lattice displacement and can be expressed as a function of the

phonon wave vector  $\mathbf{q}$

$$\mathbf{Q}(\mathbf{r}, t) = \mathbf{Q}(\mathbf{q}, \omega_0) \cos(\mathbf{q} \cdot \mathbf{r} - \omega_0 t). \quad (3)$$

It is immediately clear on a qualitative basis that the system response to electromagnetic radiation depends on the atomic positions. Therefore,  $\chi$  can be expanded as a Taylor series in  $\mathbf{Q}$

$$\chi(\mathbf{k}, \omega, \mathbf{Q}) = \chi_0(\mathbf{k}, \omega) + (\partial\chi/\partial Q)_0 \mathbf{Q}(\mathbf{r}, t) + \dots \quad (4)$$

The electric susceptibility splits into a static and a dynamic  $\mathbf{Q}$ -dependent part. Applying this consideration to the material's polarization leads to a static polarization term  $\mathbf{P}_0$ , oscillating with the incoming field and a term  $\mathbf{P}_{ind}$  which is induced by the lattice displacement (phonon). Combining Eqs. (2) and (4) yields

$$\begin{aligned} \mathbf{P}(\mathbf{r}, t, \mathbf{Q}) &= \mathbf{P}_0(\mathbf{r}, t) + \mathbf{P}_{ind}(\mathbf{r}, t, \mathbf{Q}) \\ &= \chi_0(\mathbf{k}, \omega) \mathbf{F}(\mathbf{k}, \omega) \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) + (\partial\chi/\partial Q)_0 \mathbf{Q}(\mathbf{r}, t) \mathbf{F}(\mathbf{k}, \omega) \cos(\mathbf{k} \cdot \mathbf{r} - \omega t). \end{aligned} \quad (5)$$

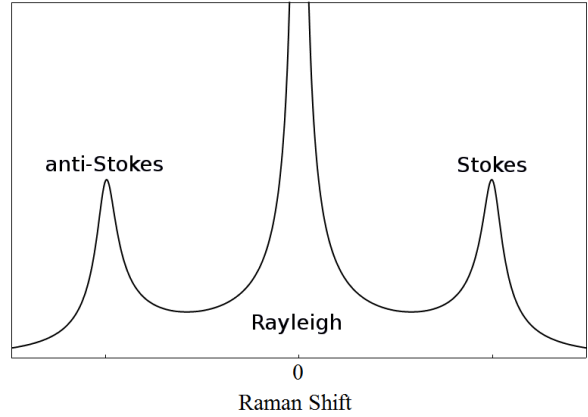
Inserting Eq. (3) leads to

$$\mathbf{P}_{ind}(\mathbf{r}, t, \mathbf{Q}) = (\partial\chi/\partial Q)_0 \mathbf{Q}(\mathbf{q}, \omega_0) \cos(\mathbf{q} \cdot \mathbf{r} - \omega_0 t) \mathbf{F}(\mathbf{k}, \omega) \cos(\mathbf{k} \cdot \mathbf{r} - \omega t). \quad (6)$$

Using an addition theorem Eq. (6) can be expanded to

$$\begin{aligned} \mathbf{P}_{ind}(\mathbf{r}, t, \mathbf{Q}) &= \frac{1}{2} (\partial\chi/\partial Q)_0 \mathbf{Q}(\mathbf{q}, \omega_0) \mathbf{F}(\mathbf{k}, \omega) \{ \cos[(\mathbf{k} + \mathbf{q}) \cdot \mathbf{r} - (\omega + \omega_0)t] \\ &\quad + \cos[(\mathbf{k} - \mathbf{q}) \cdot \mathbf{r} - (\omega - \omega_0)t] \}. \end{aligned} \quad (7)$$

Equation (7) contains two waves which have both shifted wave vectors and frequencies compared to the incoming photon. The so called *Stokes* wave has the wave vector  $k_{Stokes} = k - q$  and a frequency  $\omega_{Stokes} = \omega - \omega_0$ . The *anti-Stokes* wave is defined by  $k_{anti-Stokes} = k + q$  and  $\omega_{anti-Stokes} = \omega + \omega_0$ . In the Stokes process the occupation number of a phonon increases, while the incoming light transmits parts of its energy to the material. The anti-Stokes process resembles a stimulated emission. The occupation number of a phonon state decreases. The phonon energy is transmitted to the incoming light. Both processes are illustrated in Fig. 2.



**Fig. 2:** The Raman spectrum consists of a Stokes and an anti-Stokes line that are located symmetrically around the Rayleigh scattered component of the laser light.

The probabilities of the Stokes and the anti-Stokes process strongly depend on the initial occupation number of the phonon state. At room temperature the Stokes prevails the anti-Stokes process (See problem 1).

Equation (7) shows that the Stokes and the anti-Stokes lines have the same energetic distance from the incoming laser light. The positions of these Raman lines are located symmetrically around the Rayleigh scattered component. Hence a peak in a spectrum can always be verified as having a Raman origin by scanning the anti-Stokes side. Photoluminescence, artifacts from the substrate or stray light have no corresponding component in the anti-Stokes spectrum.

In summary, an incoming electromagnetic wave polarizes a material. As soon as the electric susceptibility is assumed to change locally with the lattice displacement,  $\chi$  can be expanded as a Taylor series in  $\mathbf{Q}$  and the new term  $(\partial\chi/\partial Q)_0 \mathbf{Q}(\mathbf{r}, t)$  predicts inelastic Raman scattering. A slightly modified term is known as the Raman tensor. Introducing a unit vector in direction of the lattice displacement  $\hat{\mathbf{Q}} = \mathbf{Q}/|\mathbf{Q}|$ , the Raman tensor can be expressed as

$$\mathbf{R} = (\partial\chi/\partial Q)_0 \hat{\mathbf{Q}}(\mathbf{r}, t). \quad (8)$$

Assuming  $\mathbf{e}_i$  and  $\mathbf{e}_s$  to be the unit vectors of the polarisation of the incoming and scattered light, respectively, the Raman scattering intensity is proportional to

$$I \propto |\mathbf{e}_i \cdot \mathbf{R} \cdot \mathbf{e}_s|^2. \quad (9)$$

The Raman tensor is a symmetric second rank tensor if we neglect the difference in frequency of the incoming and outgoing light. The Raman tensor has the same symmetry as the corresponding phonon. Whether a Raman-active phonon can be observed under certain experimental conditions regarding the incoming and scattered polarisation or not is determined by Eq. (9). Using these Raman selection rules the symmetry of the Raman tensor and hence the symmetry of the underlying phonon can be identified by Raman experiments with different scattering geometries.

## Microscopic Point of View

From the macroscopic point of view, a photon is scattered by a phonon and its energy is changed by a discrete value. The coupling of such an interaction is very weak. However, the coupling of photons and electrons is very strong.

The microscopic theory of the scattering process thus involves the excitation of an electron. In solids an electron can be excited to an uncorrelated electron-hole pair (in semiconductors), to a virtual state or to an exciton. In all cases an electron-hole pair is created which can interact with the lattice. We can separate the Raman process into three steps.

1. An incoming photon  $\omega_i$  creates an electron-hole pair. This state is referred to as the intermediate state  $|a\rangle$ . The process is mediated by the electron-radiation Hamiltonian  $H_{e-r}$ .
2. The electronic intermediate state  $|a\rangle$  is scattered by the lattice. A phonon is created and

the intermediate state is converted into another intermediate state  $|b\rangle$ . This is an electron-lattice interaction, hence related to  $H_{e-ion}$ .

3. The electron-hole pair of state  $|b\rangle$  decays radiatively. A photon  $\omega_s$  is emitted via  $H_{e-r}$ .

Due to Feynman's theory the Raman process can also be described by all possible permutations of the interactions described above. However, the order shown above gives the most important contribution to the scattering cross section. In the vicinity of electronic resonances the contributions of the other permutations are negligible. Fig. 3 shows one out of six Feynman diagrams of such a scattering event.  $\omega_i$  and  $\omega_s$  denote the incoming and outgoing photon.  $\Omega$  stands for the phonon and  $|a\rangle$ ,  $|b\rangle$  represent the intermediate electronic states.

The energy shift between incoming and outgoing light is called Raman shift. The dimension of the Raman shift is  $cm^{-1}$ . As a result from time reversal invariance the Feynman diagram in Fig. 3 can also be read from the right to the left. This order of time represents the anti-Stokes process. A phonon is annihilated and its energy is added to the energy of the incoming photon.

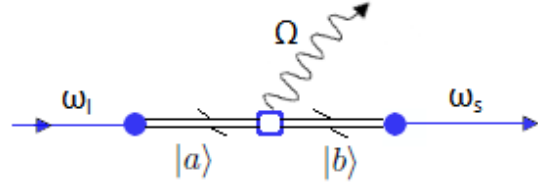


Fig. 3: Feynman diagram of the Raman process.

Each vertex in the Feynman diagram represents an interaction. The Raman process is usually described by third order perturbation theory. From Fermi's golden rule we can derive the scattering probability:

$$P \approx \frac{2\pi}{\hbar} \left| \frac{\langle 0 | H_{e-r} | a \rangle \langle a | H_{e-ion} | b \rangle \langle b | H_{e-r} | 0 \rangle}{(\hbar\omega_i - E_a + i\Gamma)(\hbar\omega_s - E_b + i\Gamma)} \right|^2. \quad (10)$$

The electronic state  $|a\rangle$  and  $|b\rangle$  can be real or virtual states. However, if one of the states involved is a real state and the incoming or outgoing photon meets the energy of the state, the scattering probability is in resonance.

With the same experimental method it is also possible to examine rotational spectra in molecules. However, in the present experiment we will focus on Raman scattering in solid states.

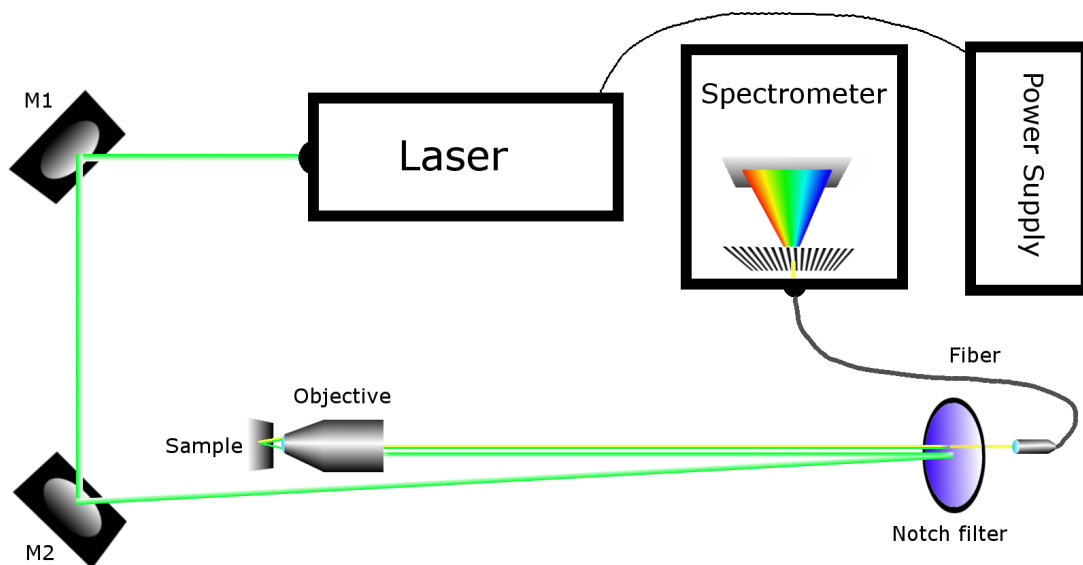
In this experiment you will use Raman scattering to determine the phonon energy of a Si, CaF2 and a graphite sample.

## Security Rules

Please follow the security rules:

- You are not allowed to wear watches and rings during the experiment. Reflections might be as dangerous as looking into the beam directly.
- Do not expose anything to the beam. Straylight might hurt your eyes.
- Do not bring your hands into the beam. It seriously hurts.
- Wear the laser protection glasses.

## Experimental Setup



**Fig. 4:** Experimental setup

Fig.4 shows the experimental setup of the Raman experiment. As light source we use a Nd:YAG laser with a wavelength of 532nm and a power of 200mW. Two mirrors guide the light to a notchfilter. Since the Raman light is orders of magnitude weaker than the elastically reflected laser light, a notchfilter is used to cut off the laser line. A dielectric coating reflects the light of only this particular wavelength. Therefore, the notchfilter can also be used as a mirror for this wave length. It reflects the light towards a 40x microscope objective. The objective focuses the light onto the sample. Therefore, this experimental setup is called a micro-Raman setup. The scattered light is collected by the objective and hits the notchfilter at the same position as the incident beam if the setup is calibrated correctly. The notchfilter then cuts off the laser light and only the inelastically scattered part hits the fiber behind the

notchfilter. The fiber guides the light into the spectrometer. The spectrometer consists of a fixed grating and a detector. The grating disperses the light onto the detector. Due to this process the spectral distribution of the light is converted into a spatial distribution and can be recorded by the detector. The data analysis is done by a computer program.

## The Experiment

First you have to choose the sample by turning the corresponding knob. For the beam alignment put the neutral density filter into the beam. If the beam is aligned correctly you should see an image of the scattered light on the notchfilter. By turning the focus knob the image on the notchfilter will sharpen and de-sharpen. Make sure that the image stays symmetric while changing the focus. If it is not symmetric use M2 to make it symmetric. If the beam is adjusted correctly you have to block the beam and record a darkframe image. This is done by left-clicking the dark bulb button. A right-click on the same button will release the darkframe. Note: The software cannot use the same darkframe for all integration times. Therefore, you have to record a new darkframe after changing the integration time. First you should use small integration times in the region of 3 seconds. This gives you the possibility to get an overview of the spectrum. Once you know which area is of interest concerning the Raman peak you should average over three integrations with 60 seconds.

## Problems

Please solve problems 1-3 as a preparation for the experiment.

1. A Raman peak of Si(111) is located at  $521\text{cm}^{-1}$ . Determine the energy of the corresponding phonon and compare the energy with the thermal energy at room temperature. What can be said about the intensity of the Stokes and anti-Stokes line? What happens if the experiment is done at higher/lower temperature?
2. Determine the momentum and wavenumber of a photon ( $532\text{nm}$ ) and compare it to the size of the Brillouin zone of silicon ( $a=0.357\text{nm}$ ). What is the conclusion for the position of the phonon in the Brillouin zone? Use a typical phonon dispersion relation for your explanation (e.g. from Kittel, Introduction to Solid States Physics).
3. Suppose the following Raman shifts: silicon  $521\text{cm}^{-1}$ ,  $\text{CaF}_2$   $321\text{cm}^{-1}$ , graphite G-peak  $1580\text{cm}^{-1}$ . Calculate the position (in nm) of the peaks in the spectrum for an excitation wave length of  $532\text{nm}$ .
4. Take Raman spectra (Stokes and anti-Stokes) of silicon, calcium fluoride and graphite. Determine the Raman shift and the resulting phonon energy.
5. Calculate the intensity ratio of Stokes/anti-Stokes and Stokes/laserline for each measurement. Suppose an optical density of 5-6 at  $532\text{nm}$  for the notchfilter. What can be

said about the intensity of the Raman scattered light compared to the intensity of the Rayleigh scattered component.

6. Suppose a semiconductor with a direct bandgap. What do you expect in case the incident laser energy is below/equal/above to the bandgap energy. Which step in the Feynman diagram is affected? What happens if the energy of the scattered photon is equal to the bandgap energy? Discuss the relevance of the  $\Gamma$  in Eq. (10).

## Literature

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- O. Madelung, Introduction to Solid-State Theory, Springer 1996
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- A. Yariv, Quantum Electronics, Wiley 1989