

Raman Scattering

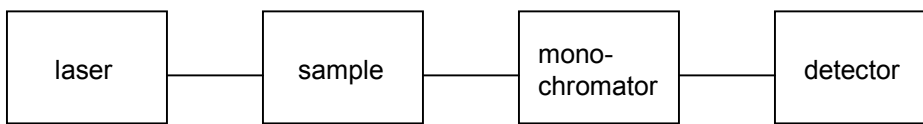
Most of the light incident on a solid is reflected, absorbed or transmitted. However, some fraction is also scattered into directions different from those described by the macroscopic Fresnel equations. One distinguishes two types of scattering:

elastic scattering (by defects/imperfections in the solid):
no frequency shift of the incoming radiation.

inelastic scattering (also called Raman scattering):
Frequency of incident light is shifted due to creation or absorption of excitations such as phonons or magnons. The discussion here will be mostly about phonons already familiar from previous sections.

Due to the weakness of the inelastic scattering intensity, an intense light source is required. Raman scattering from solids became practicable only after invention of the **laser**. Most Raman scattering experiments are carried out with visible laser light.

Basic setup:



$$\left. \begin{array}{l} \text{visible photon energy: } E \sim 1eV \\ \text{phonon/magnon excitation energy: } \Delta E \sim 10meV \end{array} \right\} \frac{\Delta E}{E} \sim 1\%$$

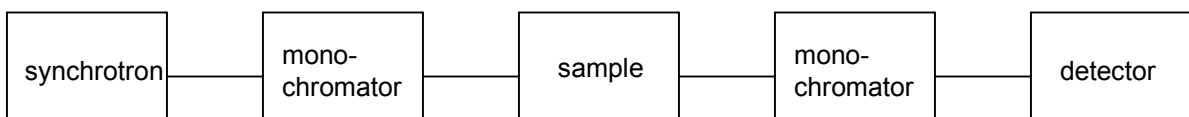
⇒ good resolution and stray light rejection is required for the spectrometer. One mostly uses double- or triple-grating monochromators.

General restriction of Raman spectroscopy with visible light: k -vector of photon $\sim 10^{-3} \text{ \AA}^{-1} \Rightarrow$ only phonons near Brillouin zone center can be detected.

Recently, it has become possible to do Raman scattering with X-rays:

$$E \sim 1-10keV, \frac{\Delta E}{E} \sim 10^{-6}.$$

Due to the very high resolution required, such experiments are only feasible with intense X-ray sources (synchrotrons). Since synchrotrons emit over a wide frequency range, another monochromator must be inserted:



As monochromators in the X-ray regime one often uses perfect single crystals of Si or Ge (lattice spacings comparable to X-ray wave length).

For X-rays, $k \sim 1\text{ \AA}^{-1}$, so it is possible to map out the phonon dispersion relation over the entire Brillouin zone.

Classical theory of Raman scattering

isotropic solid with electrical susceptibility χ

$$\begin{array}{lcl}
 P = \varepsilon_0 \chi E & D = \varepsilon_0 \varepsilon E \Rightarrow \varepsilon = 1 + \chi & \\
 \downarrow & \downarrow & \\
 & \text{electric displacement} & \\
 \text{polarization, electric dipole moment per unit volume} & &
 \end{array}$$

incident electromagnetic wave induces polarization:

$$\vec{E}(\vec{r}, t) = \vec{E}_i^0 \cos(\vec{k}_i \cdot \vec{r} - \omega_i t)$$

$$\vec{P}(\vec{r}, t) = \chi \vec{E}_i^0 \cos(\vec{k}_i \cdot \vec{r} - \omega_i t)$$

χ is modified by thermally excited phonons with atomic displacements

$$\vec{u}(\vec{r}, t) = \vec{u}_0 \cos(\vec{q} \cdot \vec{r} - \omega_0 t)$$

\vec{u}_0 small compared to lattice constant \Rightarrow expand

$$\chi = \chi_0 + \frac{\delta\chi}{\delta\vec{u}} \vec{u}(\vec{r}, t)$$

$$\vec{P}(\vec{r}, t) = \underbrace{\left[\chi_0 + \frac{\delta\chi}{\delta\vec{u}} \vec{u}(\vec{r}, t) \right]}_{\substack{(1) \\ (2)}} \vec{E}_i^0 \cos(\vec{k}_i \cdot \vec{r} - \omega_i t)$$

(1) in phase with incident radiation \Rightarrow elastic scattering
 (2) frequency shift due to phonon \Rightarrow inelastic scattering

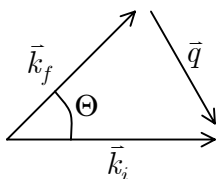
$$\begin{aligned}
 \vec{P}_{in}(\vec{r}, t) &= \frac{\delta\chi}{\delta\vec{u}} \vec{u}_0 \cos(\vec{q} \cdot \vec{r} - \omega_0 t) \vec{E}_i^0 \cos(\vec{k}_i \cdot \vec{r} - \omega_i t) \\
 &= \frac{1}{2} \frac{\delta\chi}{\delta\vec{u}} \vec{u}_0 \vec{E}_i^0 \left[\cos\left(\left(\vec{k}_i + \vec{q}\right) \cdot \vec{r} - \left(\omega_i + \omega_0\right)t\right) + \cos\left(\left(\vec{k}_i - \vec{q}\right) \cdot \vec{r} - \left(\omega_i - \omega_0\right)t\right) \right]
 \end{aligned}$$

inelastically scattered light contains two waves:

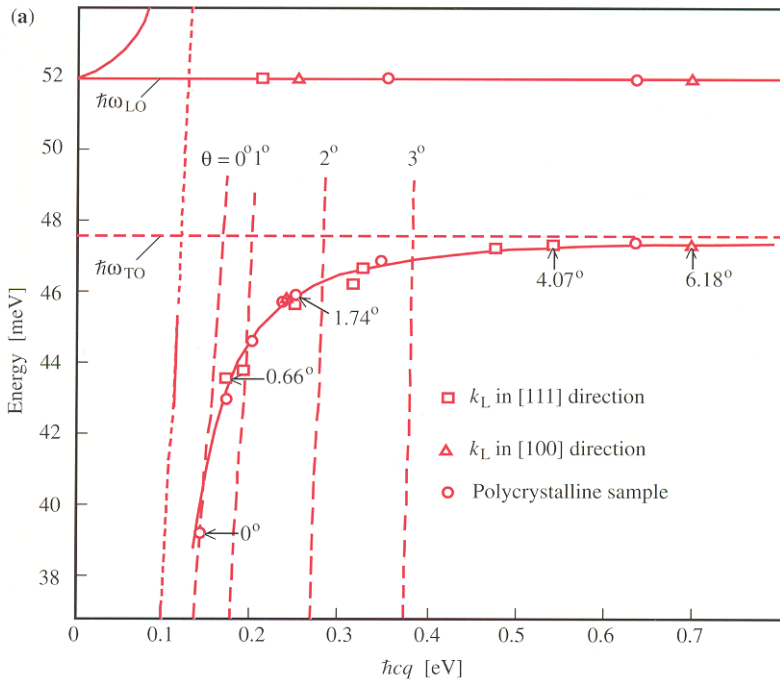
$$\vec{k}_f = \vec{k}_i - \vec{q}, \quad \omega_f = \omega_i - \omega_0 \quad \text{"Stokes" process, phonon creation}$$

$$\vec{k}_f = \vec{k}_i + \vec{q}, \quad \omega_f = \omega_i + \omega_0 \quad \text{"anti-Stokes" process, phonon absorption}$$

$\vec{k}_f, \vec{k}_i \ll$ Brillouin zone diameter \Rightarrow phonons can be probed only near the zone center, where their dispersion is negligible. This is a general restriction of optical spectroscopies. However, Raman scattering can be used to probe dispersion of **polaritons** (hybrid modes of transverse electromagnetic waves and transverse optical phonons) which show a strong dispersion near the zone center.



observe frequency shift as a function of scattering angle Θ



Aside:

Similar to absorption spectroscopies, **two-phonon** processes with $\bar{q}_1 + \bar{q}_2 \approx 0$ are also possible (from second-order terms in expansion of $\chi(\bar{u})$)

⇒ measure phonon density of states.

While the restriction to phonons near the Brillouin zone center is common to reflection / absorption spectroscopy and Raman scattering, some of the other restrictions of the former do not apply to the latter:

- inelastic light scattering can probe **acoustic** phonons. This is called Brillouin scattering. The only difference to Raman scattering is the dispersion of the acoustic phonons which is linear in q near the Brillouin zone center (see problem set).
- Raman scattering also probes **longitudinal** optical phonons directly (see figure).

Intensity of scattered radiation

This follows the intensity distribution of a radiating electric dipole (from classical electromagnetism):

$$I_s \sim \left(\frac{\omega_f}{c}\right)^4 (\bar{P}_{in} \cdot \bar{\epsilon}_f)^2 \sim \left(\frac{\omega_f}{c}\right)^4 \left| \bar{\epsilon}_i \cdot \frac{\delta\chi}{\delta\bar{u}} \bar{u} \cdot \bar{\epsilon}_f \right|^2$$

\uparrow \uparrow \uparrow
 polarization vectors of incident and scattered waves

\uparrow
 Rayleigh ω^4 law with $\bar{E}_i^0 = \bar{\epsilon}_i E_i^0$, $\bar{E}_f^0 = \bar{\epsilon}_f E_f^0$

The intensity depends on the polarization of incident and scattered light, and on the atomic displacements \bar{u} . By changing $\bar{\epsilon}_i$, $\bar{\epsilon}_f$ and observing the intensity variations, one can study not only the phonon energies, but also the displacement patterns.

Quantum Mechanical Theory of Raman Scattering

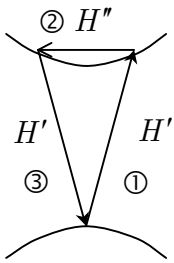
Complicated, because it requires third order time dependent perturbation theory, many possible intermediate states \Rightarrow only outline will be given.

For Raman scattering from phonons, need to consider two types of perturbation terms in Hamiltonian:

$H' = e\vec{r} \cdot \vec{E}$ as before: interaction between electron and photon in electric dipole approximation

H'' : electron-lattice interaction, specific form to be discussed below

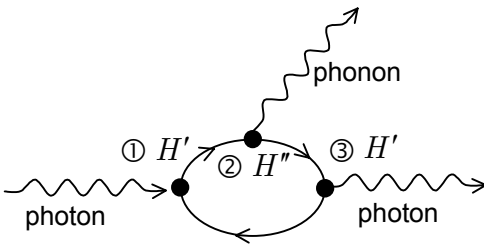
Example: semiconductor



Three steps:

- ① photon is excited across band gap
- ② phonon is created
- ③ electron falls back into ground state by emitting photon

Often this is described in terms of a "Feynman diagram":



The dots are called "interaction vertices"

Rules for translating these diagrams into expressions for transition rate: move from vertex to vertex, each introduces a term of the form

$$(1) \quad \sum_{\alpha} \frac{\langle \alpha | H' | i \rangle}{\hbar\omega_i - (E_{\alpha} - E_i)}$$

where $|i\rangle$ is the initial state, $|\alpha\rangle$ an intermediate state.

Proceed to second vertex:

$$(2) \quad \sum_{\alpha, \beta} \frac{\langle \beta | H'' | \alpha \rangle \langle \alpha | H' | i \rangle}{[\hbar\omega_i - (E_{\alpha} - E_i)] [\hbar\omega_i - (E_{\alpha} - E_i) - \hbar\omega_0 - (E_{\beta} - E_{\alpha})]}$$

where $|\beta\rangle$ is another intermediate state and $\hbar\omega_0$ is the phonon energy.

The last step adds another matrix element, but following the above procedure the energy denominator simply guarantees overall energy conservation:

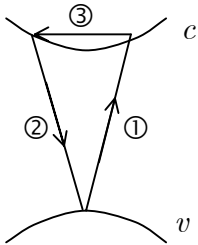
$$\hbar\omega_i - (E_\alpha - E_i) - \hbar\omega_0 - (E_\beta - E_\alpha) - \hbar\omega_f - (E_f - E_\beta) = \hbar\omega_i - \hbar\omega_0 - \hbar\omega_f - \underbrace{(E_f - E_i)}_{=0}$$

This term is incorporated as a delta function at the end (analogous to second-order perturbation theory), so that the total expression for the transition rate becomes

$$P = \frac{2\pi}{\hbar} \left| \sum_{\alpha, \beta} \frac{\langle i | H' | \beta \rangle \langle \beta | H'' | \alpha \rangle \langle \alpha | H' | i \rangle}{[\hbar\omega_i - (E_\alpha - E_i)] [\hbar\omega_i - \hbar\omega_0 - (E_\beta - E_i)]} \right|^2 \delta[\hbar\omega_i - \hbar\omega_f - \hbar\omega_0]$$

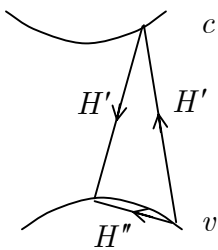
This seems only slightly more complicated than second-order perturbation theory, but there are a number of additional complications:

First, the time order of the three transitions can be different, for instance

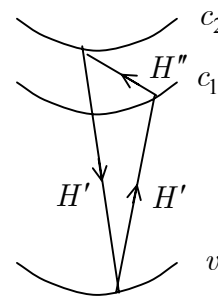


This results in a different term for the transition rate that adds coherently i.e. inside the $|\dots|$ to the first term. Altogether there are six permutations (see problem sheet).

Second, different processes may contribute to the scattering intensity of a given phonon, such as:



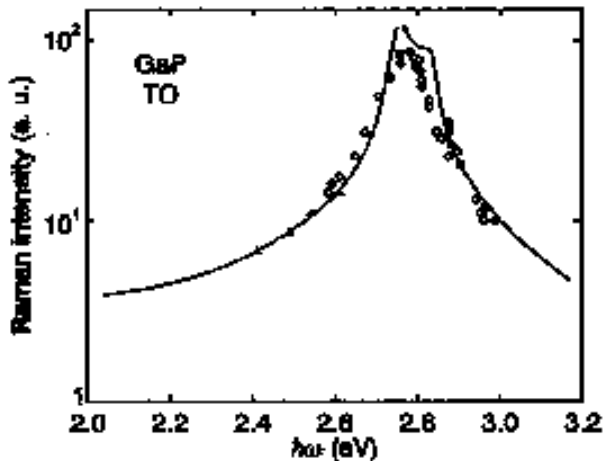
or, in a case with multiple bands:



Each of the processes (and others) contributes six additional terms to the transition rate. This shows you that it is in general very difficult to calculate Raman scattering intensities quantitatively. Sometimes, however, a small number of intermediate states dominate, e.g.

- photon energy near critical point in joint density of states (see section on interband transitions)
- intermediate state is exciton

In these cases the intensity can be sharply enhanced around particular photon energies, and one speaks of "resonant Raman scattering".



The two saddle points in the band structure are clearly seen

Resonant Raman scattering is one aspect that cannot be understood in terms of classical electromagnetism. Another aspect is the **temperature dependence** of the scattered intensity. To see this, consider the matrix element $\langle \beta | H'' | \alpha \rangle$ that appears in the transition rate. We follow our discussion of indirect interband transitions and write

$$H'' = \sum_{\nu} \left[V(\bar{r} - \bar{R}_{\nu} - \bar{u}_{\nu}) - V(\bar{r} - \bar{R}_{\nu}) \right]$$

$$\approx \sum_{\nu} \bar{u}_{\nu} \cdot \frac{\partial V(\bar{r} - \bar{R}_{\nu})}{\partial \bar{u}_{\nu}}$$

where \bar{R}_{ν} are the equilibrium positions of the nuclei, \bar{u}_{ν} their thermal displacements, and V is the electrostatic interaction of electrons and nuclei. Note that this becomes a **tensor** for more than one atom in the unit cell. Analogous to the one-dimensional harmonic oscillator treated in elementary quantum mechanics, we write

$$\bar{u}_{\nu} = \sqrt{\frac{\hbar}{2\mu\Omega}} \bar{\epsilon}_{\nu} [a^{+} + a]$$

where a^{+} and a are phonon creation and annihilation operators, respectively, μ is the nuclear mass, Ω the phonon energy and $\bar{\epsilon}_{\nu}$ the phonon polarization vector. (For simplicity, we have neglected the q -dependence of a and a^{+} , for details see section on interband transitions.)

a and a^{+} act on the nuclear part of the wave function, changing the occupation number n of a specific phonon such that

$$\underbrace{\langle n-1 |}_{\text{nuclear part of } |\beta\rangle} a \underbrace{|n\rangle}_{\text{nuclear part of } |\alpha\rangle} = \sqrt{n}$$

$$\langle n+1 | a^{+} |n\rangle = \sqrt{n+1}$$

where n is given by the Bose-Einstein distribution

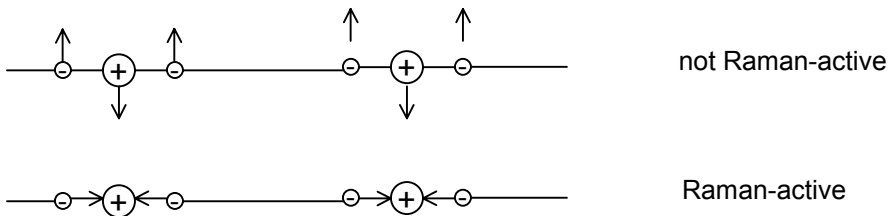
$$n = \frac{1}{e^{\hbar\Omega/k_B T} - 1}$$

The intensities of Stokes and anti-Stokes processes (proportional to the square of the matrix element) therefore become equal only for large temperatures (as in the classical case). As $T \rightarrow 0$, the anti-Stokes intensity goes to zero while the Stokes intensity remains nonzero (different from the classical prediction).

Another consequence of the functional form of H'' is the **Raman selection rules**. A general discussion of these rules can only be given in terms of group theory and must include the tensor properties of H'' , but an important qualitative aspect can be seen by inspection. Crudely speaking, it is clear that the derivative $\frac{\partial V}{\partial \bar{u}_\nu}$ follows the symmetry properties of the crystal lattice.

Specifically, it is inversion symmetric for lattices with inversion symmetry. For such lattices, the Raman intensity is therefore nonzero only for phonons whose displacement pattern is also inversion symmetric.

Example: triatomic chain



It is also easy to see that the upper phonon is IR-active (nonzero dipole moment) while the lower phonon is not.

Both techniques are therefore largely complementary, although a detailed analysis shows that some phonons can be detected by neither method (silent modes).