Slide 1

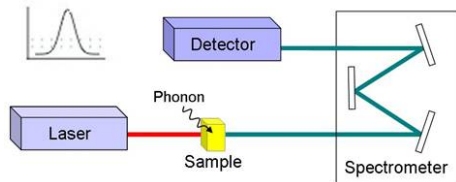# Phys 774:
Raman Scattering

Fall 2007

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Slide 2
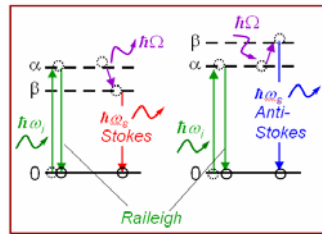
Introduction: Brillouin and Raman spectroscopy

Inelastic light scattering mediated by the *electronic polarizability* of the medium

- a material or a molecule scatters irradiant light from a source
- Most of the scattered light is at the same wavelength as the laser source (elastic, or *Raileigh scattering*)
- but a small amount of light is scattered at different wavelengths (inelastic, or **Raman scattering**)
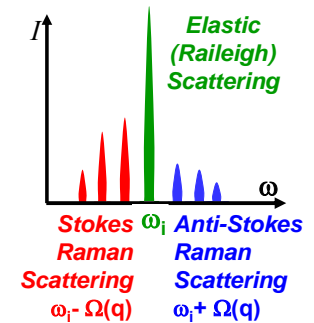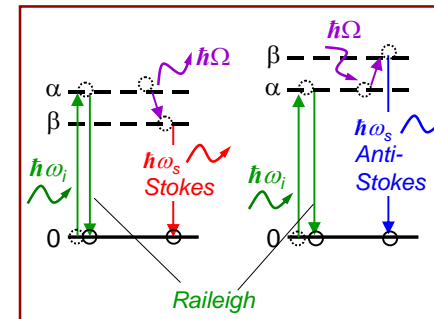
Analysis of scattered light energy, polarization, relative intensity provides information on lattice vibrations or other excitations 2

Slide 3

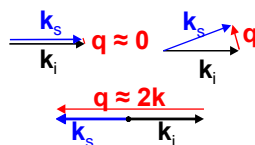### Raman scattering in crystalline solids

Not every crystal lattice vibration can be probed by Raman scattering. There are certain *Selection rules*:

1. Energy conservation:

$$\hbar\omega_i = \hbar\omega_s \pm \hbar\Omega$$

$\hbar\Omega$ Excitation energy

2. Momentum conservation in crystals:

$$\mathbf{k}_i = \mathbf{k}_s \pm \mathbf{q} \implies 0 \le |\mathbf{q}| \le 2|\mathbf{k}| \implies 0 \le |q| \le \frac{4\pi n}{\lambda_i}$$

$\lambda_i \sim 5000$ Å, $a_0 \sim 4\text{-}5$ Å $\implies \lambda_{phonon} \gg a_0$

Phonons

$\implies$ *only small wavevector (cloze to BZ center) phonons are seen in the 1st order (single phonon) Raman spectra of bulk crystals*
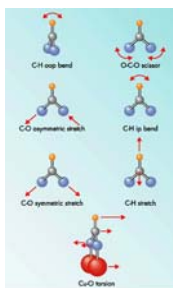
3. Selection rules determined by crystal symmetry and by symmetry of excitations

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Slide 4

### Raman scattering: how does it look like?

4
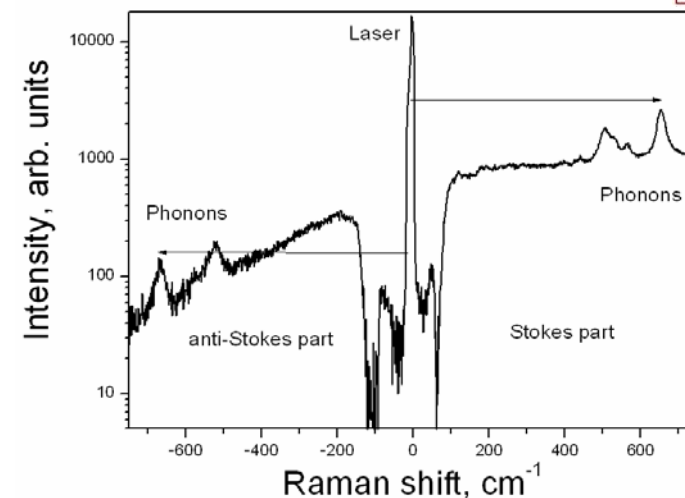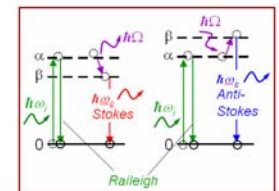
Excitations

1. Molecular vibrations
2. Phonons: acoustic and optical
3. Magnons
4. Collective excitations: Electrons+phonons = Plasmons
5. Resonant excitations: Spin-flip excitations
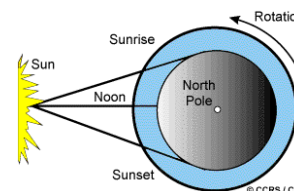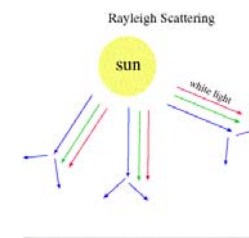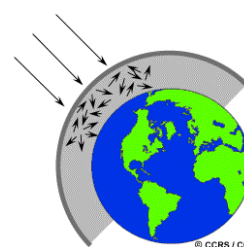
Experimental setups

1. Excitation source: Lasers or Synchrotron radiation
2. Sample: optical cryostats, magnets, pressure cells, etc
3. Polarizers for selection rules analysis
4. Spectrometers
5. Detectors
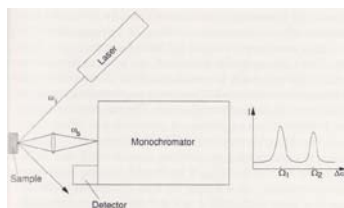
History of Raman scattering

Before Raman … : Rayleigh and Mie

$$\hbar\omega_i = \hbar\omega_s$$

Rayleigh Scattering

Scattered intensity

$$I = I_0 \frac{1+\cos^2\theta}{2R^2}\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2-1}{n^2+2}\right)^2\left(\frac{d}{2}\right)^6$$

Cross section

$$\sigma_s = \frac{2\pi^5}{3}\frac{d^6}{\lambda^4}\left(\frac{n^2-1}{n^2+2}\right)^2$$

History of Raman scattering
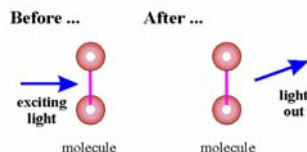
The Nobel Prize in Physics 1930

$$\hbar\omega_i = \hbar\omega_s \qquad \hbar\omega_i = \hbar\omega_s \pm \hbar\Omega$$

Rayleigh scattering
Elastic scattering dominates:

Before …   After …

exciting light   molecule   light out   molecule

emission at detector not at incidence

$\omega_{excitation}$
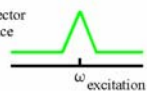
Raman scattering
1 part in 10^8 inelastic scattered:

exciting light   molecule   light out   molecule vibrates

emission

$\omega_{excitation}$ $\omega_{excit.}$ - $\omega_{vib.}$

Sir Chandrasekhara Venkata Raman
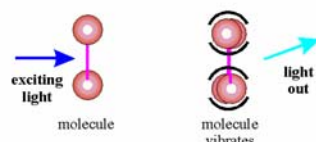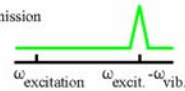
India

History of Raman scattering

The Nobel Prize in Physics 1930

Mandelstam-Brillouin scattering, 1928

~~The Nobel Prize in Physics 1930~~

Hg lamp

$$\begin{array}{c} H \quad\quad H \\ C = C \\ H \quad\quad H \end{array}$$

- Stretching: a change in the length of a bond, such as C-H or C-C
- Bending: a change in the angle between two bonds, such as the HCH angle in a methylene group
- Rocking: a change in angle between a group of atoms, such as a methylene group and the rest of the molecule.
- Wagging: a change in angle between the plane of a group of atoms, such as a methylene group and a plane through the rest of the molecule.
- Twisting: a change in the angle between the planes of two groups of atoms, such as a change in the angle between the two methylene groups.

Molecular vibrations:

Photo plate

Sir Chandrasekhara Venkata Raman

India

What is Raman shift ?

$$\hbar\omega_i = \hbar\omega_s \pm \hbar\Omega$$

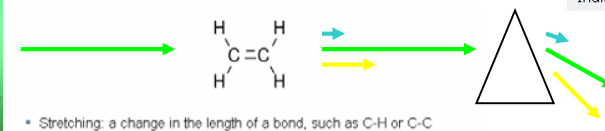$$Raman\ Shift = \hbar\omega_s - \hbar\omega_i = \pm\hbar\Omega$$

Hg lamp

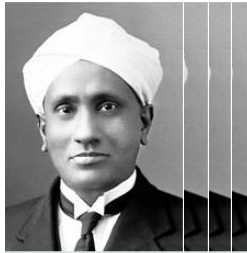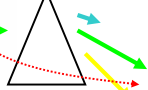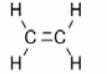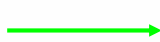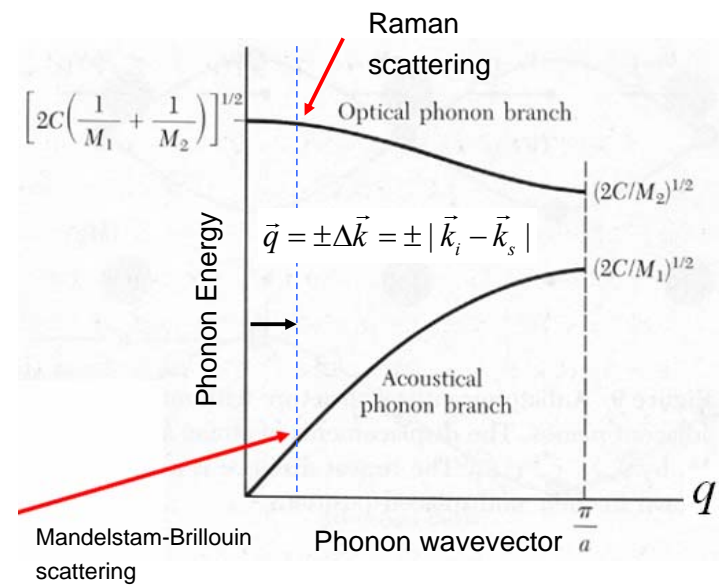Sir Chandrasekhara Venkata Raman

India

Molecular vibrations:

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Photo plate

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Mandelstam-Brillouin vs. Raman scattering
Examples of Phonons in Crystals

Raman scattering

$$\left[2C\left(\frac{1}{M_1} + \frac{1}{M_2}\right)\right]^{1/2}$$

Optical phonon branch

$(2C/M_2)^{1/2}$

$$\vec{q} = \pm\Delta\vec{k} = \pm\,|\,\vec{k}_i - \vec{k}_s\,|$$

$(2C/M_1)^{1/2}$

Acoustical phonon branch

Phonon Energy

Mandelstam-Brillouin scattering

Phonon wavevector $\frac{\pi}{a}$

q

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Phonons

- Quantum mechanics: energy levels of the harmonic oscillator are quantized
- Similarly the energy levels of lattice vibrations are quantized.
- The quantum of vibration is called a *phonon*
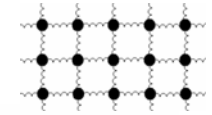 (in analogy with the photon - the quantum of the electromagnetic wave)

Allowed energy levels of the harmonic oscillator: $E = (n + \frac{1}{2})\hbar\omega$

where *n* is the quantum number

A normal vibration mode of frequency ω is given by $\mathbf{u} = \mathbf{A}e^{i(\mathbf{q}\cdot\mathbf{r} - \omega t)}$

mode is occupied by *n phonons* of energy $\hbar\omega$; momentum $\mathbf{p} = \hbar\mathbf{q}$
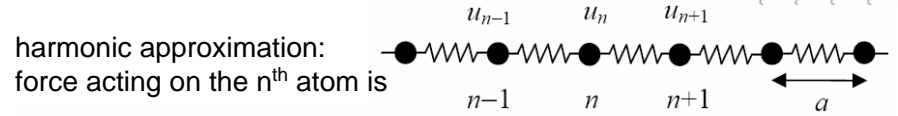
Number of phonons is given by :
(*T* – temperature)

$$n = \frac{1}{e^{\hbar\omega/kT} - 1}$$

The total vibrational energy of the crystal is the sum of the energies of the individual phonons:
(*p* denotes particular phonon branch)

$$E = \sum_{\mathbf{q}p} E_{\mathbf{q}p} = \sum_{\mathbf{q}p}(n_{\mathbf{q}p} + \frac{1}{2})\hbar\omega_p(\mathbf{q})$$

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1D Model of lattice vibrations

one-dimensional lattice: linear chain of atoms

harmonic approximation:
force acting on the nth atom is

u_{n-1} u_n u_{n+1}

$n-1$ n $n+1$ a

$$F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n)$$

equation of motion (nearest neighbors interaction only):

$$M\frac{\partial^2 u}{\partial t^2} = F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n) = -C(2u_n - u_{n+1} - u_{n-1})$$

M is the atomic mass, *C* – force constant

Now look for a solution of the form $u(x,t) = Ae^{i(qx_n - \omega t)}$

where x_n is the equilibrium position of the *n*-th atom $\to x_n = na$

obtain $M(-\omega^2)e^{iqna} = -C\left[2e^{iqna} - e^{iq(n+1)a} - e^{iq(n-1)a}\right]$

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$$M(-\omega^2)e^{iqna} = -C\left[2e^{iqna} - e^{iq(n+1)a} - e^{iq(n-1)a}\right] \quad \rightarrow$$

$$M\omega^2 = C\left(2 - e^{iqa} - e^{-iqa}\right) = 2C(1 - \cos qa) = 4C\sin^2\frac{qa}{2}$$

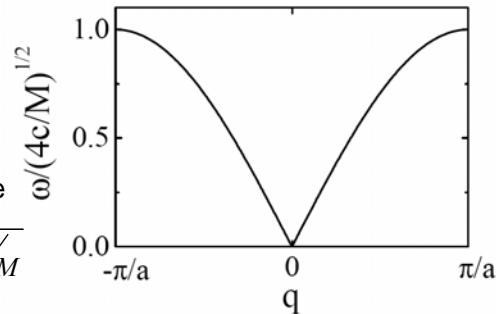$\Rightarrow$ the dispersion relation is $\quad \omega = \sqrt{\dfrac{4C}{M}}\left|\sin\dfrac{qa}{2}\right|$

Note: we change $q \rightarrow q + 2\pi/a$ *the atomic displacements and*
frequency ω do not change $\Rightarrow$ these solutions are physically identical

$\Rightarrow$ can consider only
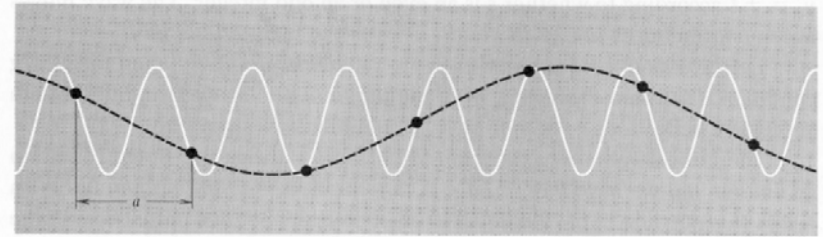
$$-\frac{\pi}{a} \le q \le \frac{\pi}{a}$$

i.e. q within the first Brillouin zone

The maximum frequency is $2\sqrt{C/M}$
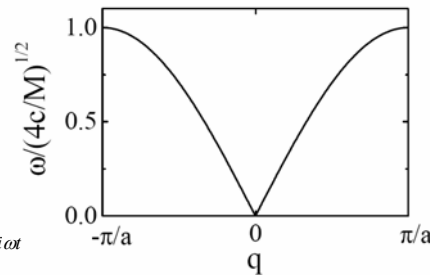
Dispersion relation

- Another way of showing this, physically, is by looking at the wavelengths of vibration:

- The wave represented by the solid curve conveys no new information not given by the dashed curve. Only wavelengths longer than 2a are needed to represent the motion. This means that K is limited by −π/a ≤ K ≤ π/a

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$$\omega = \sqrt{\frac{4C}{M}}\left|\sin\frac{qa}{2}\right|$$

At the boundaries of the Brillouin
zone $q = \pm\pi/a \rightarrow u_n = A(-1)^n e^{-i\omega t}$
standing wave

Phase and group velocity

phase velocity is defined as $\quad v_p = \dfrac{\omega}{q}$

group velocity $\quad v_g = \dfrac{d\omega}{dq} \qquad\qquad v_g = a\sqrt{\dfrac{C}{M}}\cos\dfrac{qa}{2}$

$v_g = 0$ at the boundaries of the Brillouin zone ($q = \pm\pi/a$) $\Rightarrow$
no energy transfer – standing wave

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Features of the Dispersion Relation

- Most of the waves described by the wavevector K are travelling waves (meaning that the waves propagate through the lattice).
- However, at the zone boundary, which is K = +/- π/a the wave becomes a standing wave. This means that the wave itself moves neither to the left or two the right.
- It is also a standing wave at K = 0 (the wavelength is infinite)
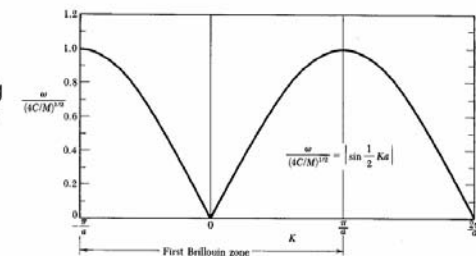
(at Ka = +/-π these are vibrating out of phase, and so the wave does not propagate)

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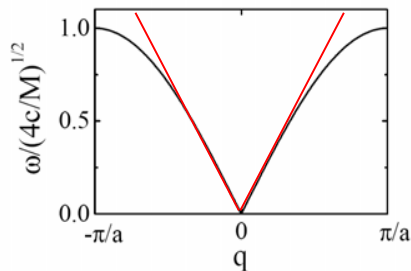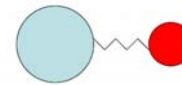*Long wavelength limit:* $\lambda >> a$; $q = 2\pi/\lambda << 2\pi/a \Rightarrow qa << 1$

small q - close to the center of Brillouin zone

$$\omega = \sqrt{\frac{4C}{M}}\left|\sin\frac{qa}{2}\right| \approx \sqrt{\frac{C}{M}}qa \quad \text{- linear dispersion}$$

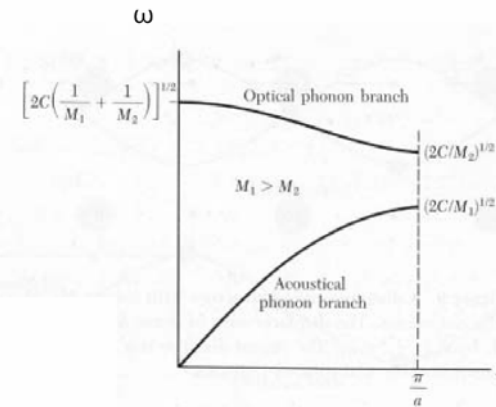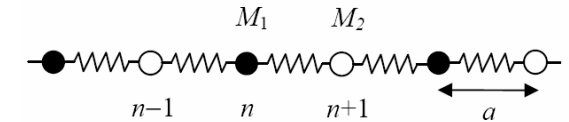$$v_p = v_g = a\sqrt{\frac{C}{M}} \quad \text{- sound velocity for the one dimensional lattice}$$

Diatomic lattice

one-dimensional linear chain, atoms of two types: M_1 and M_2

Optical Phonons

can interact with light

For diamond

Optical phonon frequency is $\approx$ 1300 cm^{-1}

$\lambda \approx$ 7700 nm

(far-IR)

$$\omega^2 = C\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4\sin^2 qa}{M_1 M_2}}$$

Note: the first Brillouin zone is now
  from $-\pi/2a$ to $+\pi/2a$

The lower curve - *acoustic branch*, the upper curve - *optical branch*.

at $q = 0$ for acoustic branch $\omega_0 = 0$; $A_1 = A_2$

$\Rightarrow$ the two atoms in the cell have the same amplitude and the phase dispersion is linear for small q
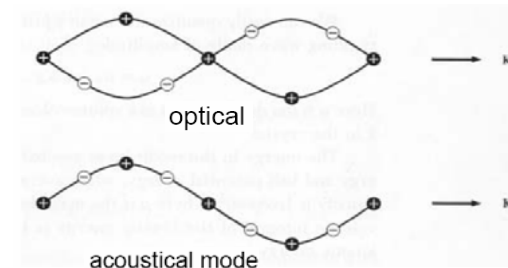
for optical branch at $q = 0$ $\quad \omega_0 = \sqrt{2C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)} \quad M_1A_1 + M_2A_2 = 0$

$\Rightarrow$ the center of mass of the atoms remains fixed. The two atoms move out of phase. Frequency is in infrared – that's why called optical

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Transverse optical and acoustical modes

optical

acoustical mode

- The <u>acoustic</u> branch has this name because it gives rise to long wavelength vibrations – speed of sound

- The <u>optical</u> branch is a higher energy vibration (the frequency is higher, and you need a certain amount of energy to excite this mode). The term "optical" comes from how these were discovered – notice that if atom 1 is +ve and atom 2 is –ve, that the charges are moving in opposite directions. You can excite these modes with electromagnetic radiation (ie. The oscillating electric fields generated by EM radiation)

Two Atoms/Primitive Basis

- If there are p atoms in the unit cell, there has to be 3p branches in the dispersion relation: 3 acoustical branches, and 3p-3 optical branches (there are more ways for the atoms to move for the optical modes)
- So, for Germanium, which has 2 atoms/unit cell (diamond structure: 000 and ¼ ¼ ¼), there has to be 6 branches: one longitudinal acoustic (LA), 2 transverse acoustic (TA), one longitudinal optical (LO), 2 transverse optical (TO)
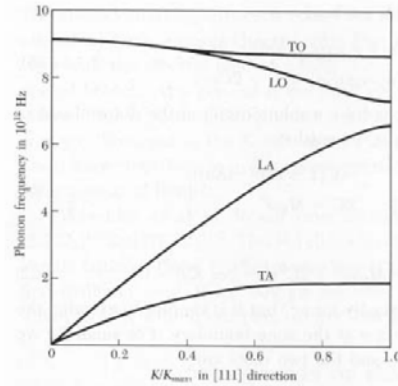
(phonon dispersion curve in the [111] direction for Germanium at 80 K, as determined by inelastic neutron scattering)

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Quasi-Classical Theory of Raman Scattering

$$\hbar\omega_i = \hbar\omega_s \pm \hbar\Omega$$

$$\vec{k}_i = \vec{k}_s \pm \vec{q}$$

$$\mathbf{P}(\omega_s) = \epsilon_0 \tilde{\chi}(\omega_i, \omega_s)\mathbf{E}(\omega_i)$$

$$\vec{Q} = \vec{Q}_0 \cdot e^{i(\vec{k}\cdot\vec{r} - \omega_0 t)}$$

$$I_s = I_i \frac{\omega_s^4 V}{(4\pi\epsilon\epsilon_0)^2 c^4} \left| e_s \tilde{\chi}(\omega_i, \omega_s) e_i \right|^2$$

$$\frac{\partial\chi}{\partial Q} = \frac{\partial\chi(E_C)}{\partial E} \cdot \frac{\partial E_C}{\partial Q}$$
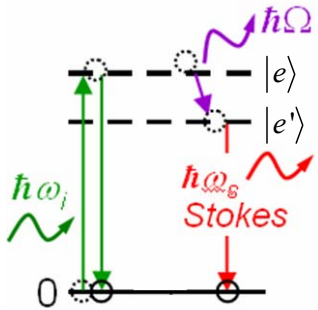
$$
\begin{aligned}
\chi_{\alpha,\beta}(\omega_i, \omega_s) =\ & \chi^0_{\alpha,\beta}(\omega_i) && \text{Elastic scatt.}\\
& + \sum_j Q_j \cdot \left(\frac{\partial\chi_{\alpha,\beta}(\omega_i)}{\partial Q_j}\right) && \text{Lattice Deformation}\\
& + \sum_j i\, Q_j \cdot q_j \left(\frac{\partial\chi_{\alpha,\beta}(\omega_i)}{\partial\nabla Q_j}\right) && \text{Deformation gradient}\\
& + \sum_{j,\gamma} Q_j \cdot E_\gamma \cdot \left(\frac{\partial^2\chi_{\alpha,\beta}(\omega_i)}{\partial Q_j \partial E_\gamma}\right) && \text{External E-field}\\
& + \sum_{j,j'} Q_j Q_{j'} \cdot \frac{1}{2}\left(\frac{\partial^2\chi_{\alpha,\beta}(\omega_i)}{\partial Q_j\, \partial Q_{j'}}\right) && \text{2-phonon process}\\
& + \dots
\end{aligned}
$$

Quantum Theory of Raman Scattering

$$\hbar\omega_i = \hbar\omega_s \pm \hbar\Omega$$

$$\vec{k}_i = \vec{k}_s \pm \vec{q}$$

- the electronic transition from the ground state $|0\rangle$ to an excited state $|e\rangle$: creation of an electron-hole pair due to the absorption of a photon with the energy $\hbar\omega_i$.
- the electron-lattice interaction, i.e. the electronic transition from $|e\rangle$ to $|e'\rangle$ under creation or annihilation of a phonon with $\hbar\Omega$.
- the transition from $|e'\rangle$ to the ground state $|0\rangle$: recombination of the electron-hole pair under emission of a photon $\hbar\omega_s$.

$$\chi_{\alpha,\beta}(\omega_i, \omega_s) = \frac{e^2}{m_0^2 \cdot \omega_s^2 \cdot V} \sum_{e,e'} \frac{\langle 0|p_\alpha|e'\rangle \langle e'|H_{E-L}|e\rangle \langle e|p_\beta|0\rangle}{(E_{e'} - \hbar\omega_s)(E_e - \hbar\omega_i)}$$
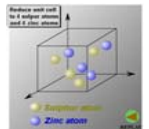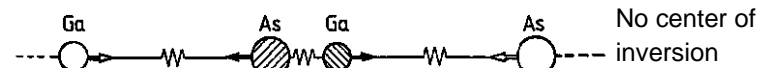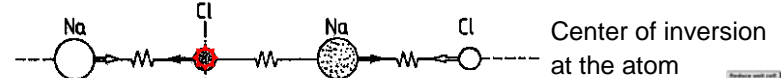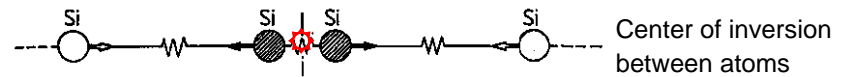
Here m_0 is the electron mass and V the scattering volume, p_α and p_β are vector components of the dipole operators of the scattered and incident light, and H_{E-L} is the electron-phonon interaction Hamiltonian. E_e and $E_{e'}$ are the energies of the excited electronic states.

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Selection rules for Raman Scattering by phonons

$$\vec{Q} = \vec{Q}_0 \cdot e^{i(\vec{k}\cdot\vec{r} - \omega_0 t)}$$

$$\hat{I}^- \cdot (\vec{Q}) = -\vec{Q} \quad \text{"odd"}$$
$$\hat{I}^- \cdot (\vec{Q}) = \vec{Q} \quad \text{"even"}$$

$A_{1g} \quad B_{2g}$ Symmetry of Raman-active modes, "g" – gerade (de.) = even

$A_{2u} \quad F_u$ Symmetry of IR-active modes, "u" – ungerade (de.) = odd

Center of inversion between atoms

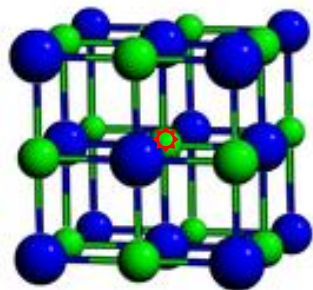Center of inversion at the atom

No center of inversion

Phonon symmetry for different crystal lattices: The dashed circles are the diatomic base of an elementary cell, open circles are atoms of neighbouring cells. The dash-dotted vertical lines mark the centre of inversion. (a) Si (O_h^7-structure) has a g-mode (even symmetry), which is Raman-active. (b) NaCl (O_h^5-structure) has a u-mode (odd symmetry), which is IR-active. (c) GaAs (T_d-structure) shows both Raman and IR-activity
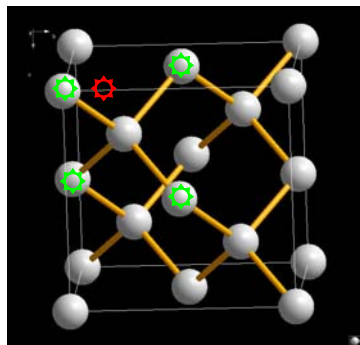
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Slide 25

Atomic displacement and Raman / IR-activity of optical phonons in crystals with the center of inversion

$$\vec{Q} = \vec{Q}_0 \cdot e^{i(\vec{k}\cdot\vec{r} - \omega_0 t)}$$

$$\vec{E} = \vec{E}_0 \cdot e^{i(\vec{k}\cdot\vec{r} - \omega t)}$$

$x \to -x$

$y \to -y$

$z \to -z$

$\hat{I}^- \cdot (\vec{Q}) = -\vec{Q}$

$\hat{I}^- \cdot (\vec{E}) = -\vec{E}$

$\hat{I}^- \cdot (\vec{Q}) = \vec{Q}$

$\hat{I}^- \cdot (\vec{E}) = -\vec{E}$

No IR-active phonons in Ge, Si, Diamond

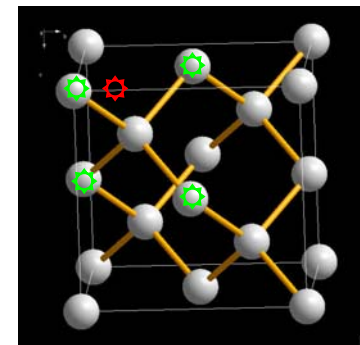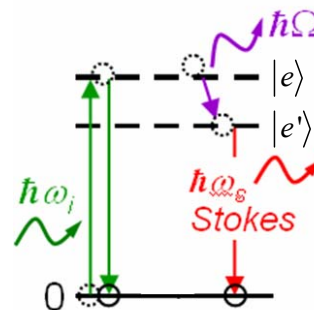No Raman-active phonons in NaCl, MgO, SrTiO$_3$

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Slide 26

Atomic displacement and Raman / IR-activity of optical phonons in crystals with the center of inversion

Phonons in Ge, Si, Diamond are Raman active

$$\vec{Q} = \vec{Q}_0 \cdot e^{i(\vec{k}\cdot\vec{r} - \omega_0 t)}$$

$$\vec{E} = \vec{E}_0 \cdot e^{i(\vec{k}\cdot\vec{r} - \omega t)}$$

$\hat{I}^- \cdot (\vec{Q}) = \vec{Q}$

$\hat{I}^- \cdot (\vec{E}) = -\vec{E}$

$$\chi_{\alpha,\beta}(\omega_i, \omega_s) = \frac{e^2}{m_0^2 \cdot \omega_s^2 \cdot V} \sum_{e,e'} \frac{\langle 0|p_\alpha|e'\rangle \langle e'|H_{E-L}|e\rangle \langle e|p_\beta|0\rangle}{(E_{e'} - \hbar\omega_s)(E_e - \hbar\omega_i)}$$
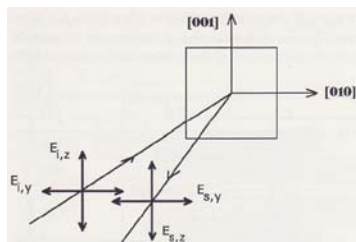

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Slide 27

Polarization Selection rules for Raman Scattering by phonons

$$I_s = I_i \frac{\omega_s^4 V}{(4\pi\epsilon\epsilon_0)^2 c^4} |e_s \tilde{\chi}(\omega_i, \omega_s) e_i|^2$$
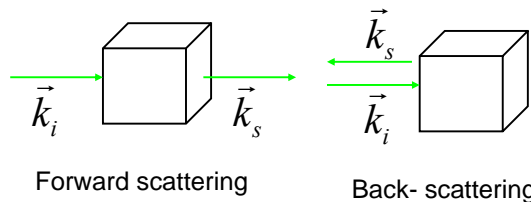
$$\vec{k}_i (\vec{E}_i, \vec{E}_s) \vec{k}_s$$

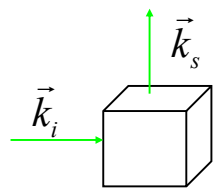$$\left(\frac{\partial \chi_{\alpha,\beta}(\omega_i)}{\partial Q_j} \right)$$

Raman tensor

Polarization configuration of experiment

Forward scattering

Back- scattering

90 deg scattering
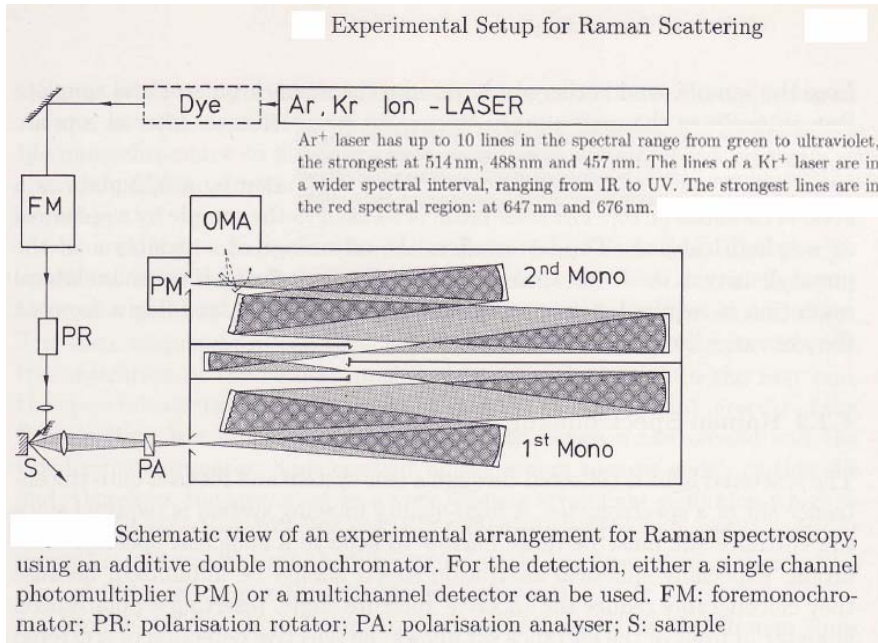
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Slide 28

Example of selection rules for Raman scattering by optical phonons in III-V semiconductor crystals (no center of inversion)

Observation of TO and LO phonons from Deformation Potential scattering (DP) or Fröhlich scattering (F) on materials with T$_d$ symmetry for various crystal-face directions and polarisation directions of the incident and scattered light E$_i$ and E$_s$

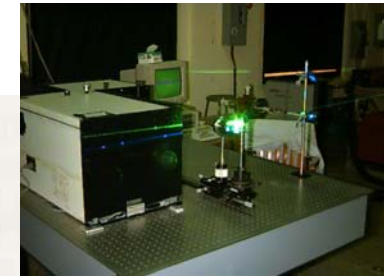| surface	E$_i$	E$_s$	TO	LO
(100)	[010]	[001]	-	DP $\frac{\partial\chi}{\partial Q} = \frac{\partial\chi(E_C)}{\partial E} \cdot \frac{\partial E_C}{\partial Q}$
	[010]	[010]	-	F
	[001]	[001]	-	F
	[011]	[011]	-	DP + F
	[011]	[0$\bar{1}$1]	-	-
(110)	[1$\bar{1}$0]	[1$\bar{1}$0]	DP	F
	[1$\bar{1}$0]	[001]	DP	-
	[001]	[001]	-	F
(111)	[1$\bar{1}$0]	[1$\bar{1}$0]	DP	DP + F
	[1$\bar{1}$0]	[11$\bar{2}$]	DP	-
	[11$\bar{2}$]	[11$\bar{2}$]	DP	DP + F

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Experimental setups for Raman scattering

Experimental Setup for Raman Scattering

Dye → Ar, Kr Ion - LASER

Ar+ laser has up to 10 lines in the spectral range from green to ultraviolet, the strongest at 514 nm, 488 nm and 457 nm. The lines of a Kr+ laser are in a wider spectral interval, ranging from IR to UV. The strongest lines are in the red spectral region: at 647 nm and 676 nm.

Schematic view of an experimental arrangement for Raman spectroscopy, using an additive double monochromator. For the detection, either a single channel photomultiplier (PM) or a multichannel detector can be used. FM: foremonochromator; PR: polarisation rotator; PA: polarisation analyser; S: sample

## Experimental setups for Raman scattering

SPEX – "Triplemate"
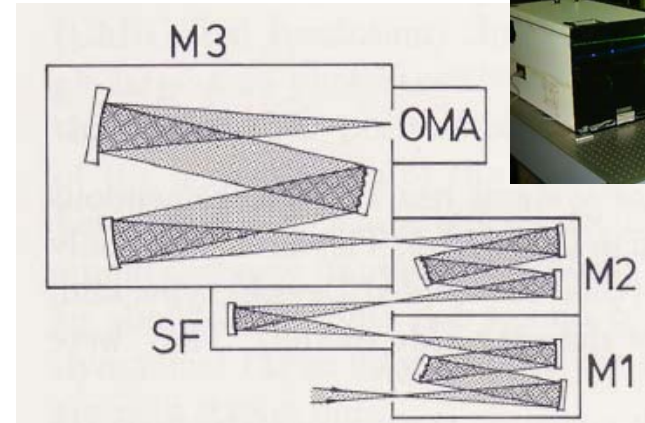
Triple monochromator setup for Raman spectroscopy, consisting of a subtractive double monochromator (M1; M2) with spatial filter (SF) for stray light reduction, followed by a third monochromator (M3) to project the spectrum onto the multichannel detector (OMA)

Stress analysis in microstructures using Raman scattering
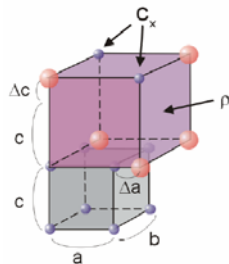
Development of the strain-induced shift of the Raman frequencies vs the layer thickness for Si_xGe_{1-x} on GaAs. The distinct shift of the phonon frequencies at 40 nm is due to the relaxation of the epilayer strain
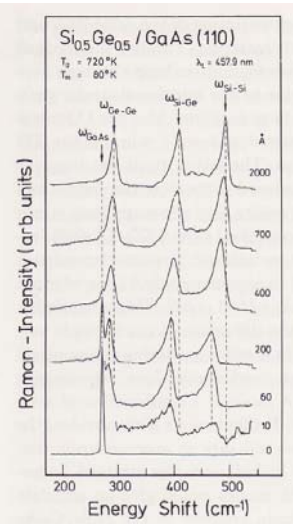
$$\varepsilon_L^{\parallel} = \varepsilon_{xx} = \varepsilon_{yy} = (a_0^S - a_0^L)/a_0^L \qquad \varepsilon_L^{\perp} = \frac{2 \cdot S_{12}}{S_{11} + S_{12}}\varepsilon_L^{\parallel}$$

The strain-induced shift of the phonon frequencies

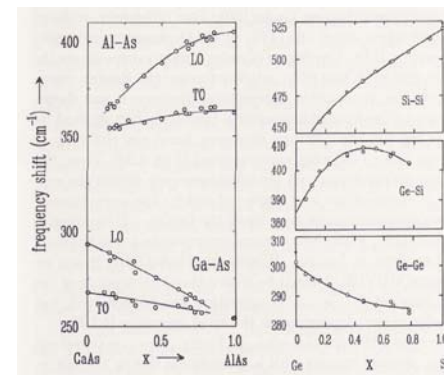$$\Delta\omega_{LO} = \left(\frac{p+2q}{3\omega_0^2} \cdot \frac{(S_{11} + 2S_{12})}{(S_{11} + S_{12})} + \frac{2}{3}\frac{q-p}{2\omega_0^2} \cdot \frac{(S_{11} - S_{12})}{(S_{11} + S_{12})}\right) \cdot \omega_0 \cdot \varepsilon_L^{\parallel}$$

$$\Delta\omega_{TO} = \left(\frac{p+2q}{3\omega_0^2} \cdot \frac{(S_{11} + 2S_{12})}{(S_{11} + S_{12})} - \frac{1}{3}\frac{q-p}{2\omega_0^2} \cdot \frac{(S_{11} - S_{12})}{(S_{11} + S_{12})}\right) \cdot \omega_0 \cdot \varepsilon_L^{\parallel}$$

phonon deformation potential values p and q are $-\omega_0^2$ and $-2\omega_0^2$
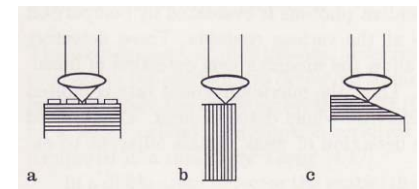
Composition analysis in microstructures

Multi-mode phonon behaviour in mixed crystals. Two-mode phonon behaviour in $Al_xGa_{1-x}As$: Ga-As and Al-As TO and LO modes (a)   three-mode phonon behaviour in Si_xGe_{1-x}: Si-Si, Si-Ge, and Ge-Ge mode (b)
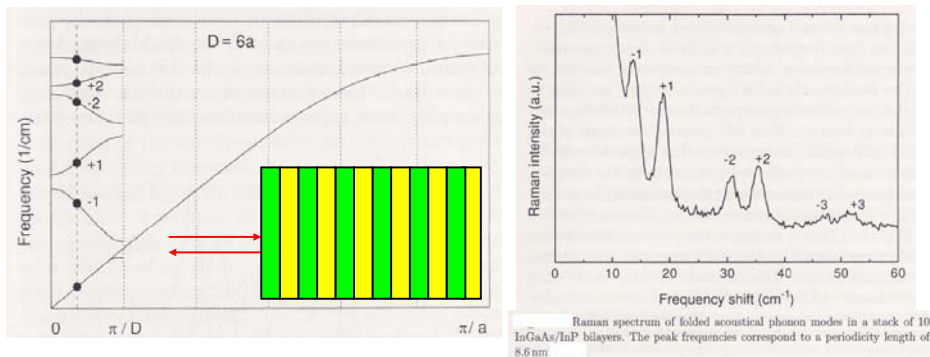
Micro-Raman scattering

$$I_s = I_i \frac{\omega_s^4 V}{(4\pi\epsilon\epsilon_0)^2 c^4}|e_s\tilde{\chi}(\omega_i, \omega_s)e_i|^2$$

Possible realisations of micro-Raman spectroscopy from heterostructures. a Locally resolved analysis of structured surfaces, b scan on a cleaved side-face, c scan on surface after bevel etching
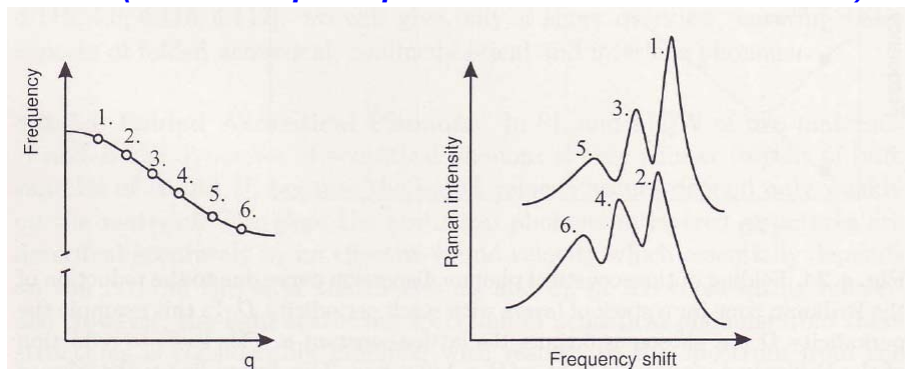
Folding of the acoustical phonon dispersion curve due to the reduction of the Brillouin zone for a stack of layers with stack periodicity D. In this example the periodicity D was chosen as 6 times the lattice constant a. This leads to reduction of the Brillouin zone from π/a to $\pi/D = 1/6 \times \pi/a$. The dotted line is the edge of the new Brillouin zone. The dashed vertical line symbolises the q-transfer in Raman scattering. The circles denote the frequency and wavevector values of the observed folded phonon modes.

Raman spectrum of folded acoustical phonon modes in a stack of 10 InGaAs/InP bilayers. The peak frequencies correspond to a periodicity length of 8.6 nm.
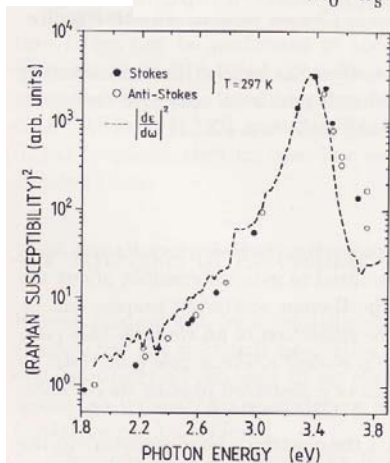
Optical phonon dispersion curve Ω with allowed q-values 1...6. and corresponding Raman spectra. The odd-index modes appear in off-diagonal polarisation configuration, while the even-index modes require the diagonal configuration

Resonant Raman scattering

$$\chi_{\alpha,\beta}(\omega_i, \omega_s) = \frac{e^2}{m_0^2 \cdot \omega_s^2 \cdot V} \sum_{e,e'} \frac{\langle 0|p_\alpha|e'\rangle \langle e'|H_{E-L}|e\rangle \langle e|p_\beta|0\rangle}{(E_{e'} - \hbar\omega_s)(E_e - \hbar\omega_i)}$$
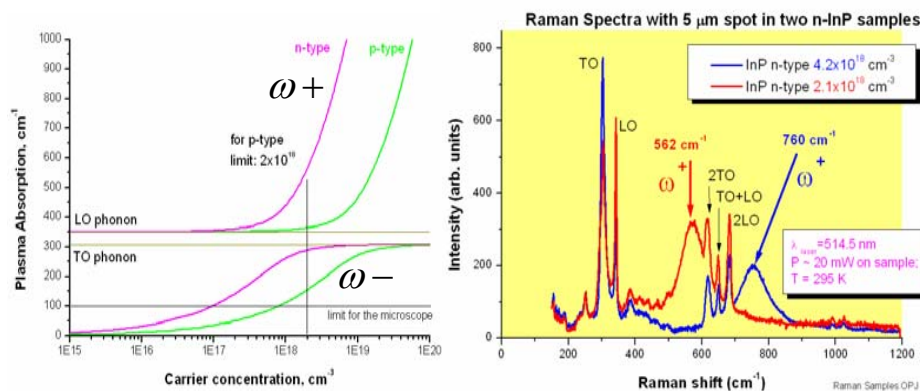

Squared Raman susceptibility of Si at room temperature for both Stokes and anti-Stokes data. The straight line represents the squared derivative of the dielectric function determined by spectroscopic ellipsometry

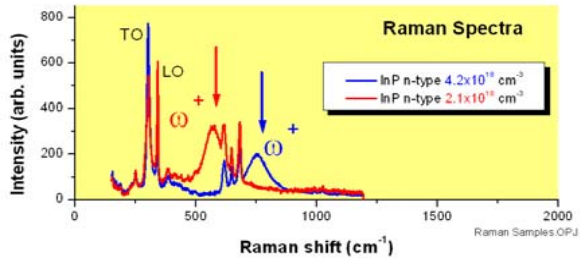## Raman scattering by coupled Plasmons: plasmon+LOph

$$\epsilon(\omega, q) = \epsilon_\infty + \frac{\omega_{TO}^2 \cdot (\epsilon_s - \epsilon_\infty)}{\omega_{TO}^2 - \omega^2 - i\omega\Gamma} - \frac{\omega_p^2}{\omega^2 - 3/5 \cdot v_F^2 \cdot q^2}$$

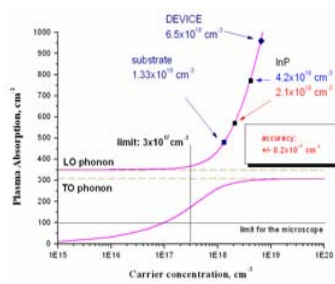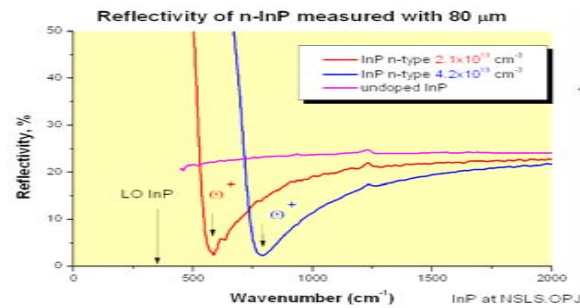$$\omega_p = \sqrt{\frac{n \cdot e^2}{\epsilon_0 \cdot \epsilon_\infty \cdot m^*}}$$

Eigenfrequencies of the coupled plasmon- LO-phonon modes Ω^- and Ω^+

Panel 1 (slide 37)

Raman scattering and IR reflectivity by Plasmons: e+ph

$$\omega_p = \sqrt{\frac{n \cdot e^2}{\epsilon_0 \cdot \epsilon_\infty \cdot m^*}}$$

Raman Spectra
- InP n-type 4.2×10^{18} cm^{-3}
- InP n-type 2.1×10^{18} cm^{-3}

Raman Samples.OPJ

Reflectivity of n-InP measured with 80 µm
- InP n-type 2.1×10^{18} cm^{-3}
- InP n-type 4.2×10^{18} cm^{-3}
- undoped InP

InP at NSLS.OPJ

Panel 2 (slide 38)

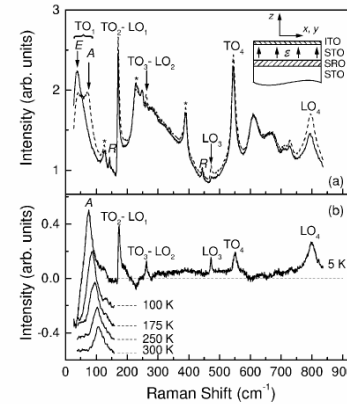### Example of E-field induced Raman scattering in crystalline solids

FIG. 1. (a) Solid and dotted lines show the Raman spectra of 1 µm STO film at $T = 5$ K without electric field and in the presence of an external electric field of 22×10^4 V/cm directed normal to the film plane, respectively. The soft-mode components are labeled A and E. Structural modes are denoted by R. Optical phonons from the SRO buffer layer are marked with stars. The inset shows the schematics of the investigated trilayer ITO/STO/SRO structure grown on an STO substrate. (b) Electric-field-induced modification of the Raman intensity obtain by subtracting spectrum at $\ell = 22 \times 10^4$ V/cm from that at $\ell = 0$ for different temperatures shown next to the spectra. Spectra are shifted vertically for clarity.
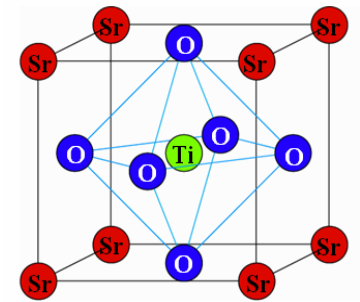
$3S = 15$ modes

3 acoustic modes

12 optical modes; 3×4

$2 \times TO_1 + LO_1$
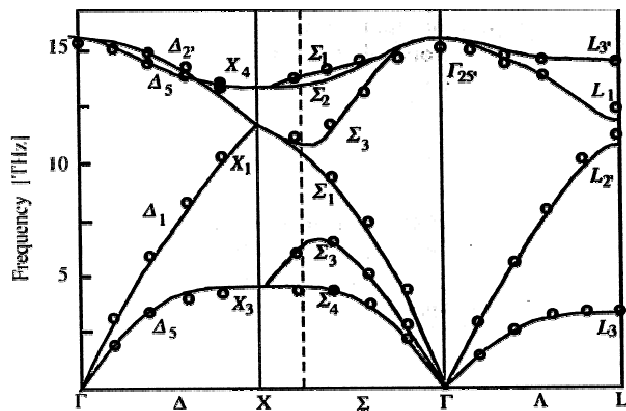$2 \times TO_2 + LO_2$
$2 \times TO_3 + LO_3$
$2 \times TO_4 + LO_4$

$$+ \sum_{j,\gamma} Q_j \cdot E_\gamma \cdot \left(\frac{\partial^2 \chi_{\alpha,\beta}(\omega_i)}{\partial Q_j \partial E_\gamma} \right)$$

Panel 3 (slide 39)

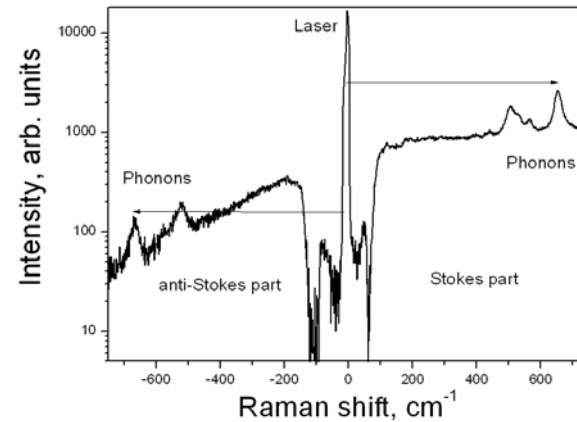HW: Which crystal has this phonon dispersion diagram ?

Panel 4

Raman thermometer

$$I_s = I_i \frac{\omega_s^4 V}{(4\pi\epsilon\epsilon_0)^2 c^4} |e_s \tilde{\chi}(\omega_i, \omega_s) e_i|^2$$

Classical formula is not complete!

You need to take Planck's statistics for phonons into account to calculate the scattering intensity

HW:

What is St/aSt ratio ???

Number of phonons is given by :
(T – temperature)

$$n = \frac{1}{e^{\hbar\omega/kT} - 1}$$

$Stokes \sim n+1$

$anti-Stokes \sim n$