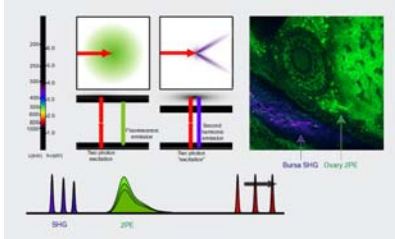


Phys 402:

# Nonlinear Spectroscopy: SHG and Raman Scattering



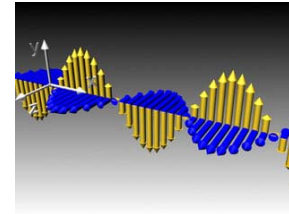
Spring 2008

Andrei Sirenko, NJIT Lecture 2

## Requirements: Polarization of Electromagnetic Waves

- ❖ General consideration of polarization
- ❖ How Polarizers work
- ❖ Representation of Polarization: Jones Formalism

*Polarization of light and materials properties are important to understand nonlinear effects!*



Common SHG materials

- 806 nm light : lithium iodate (LiIO<sub>3</sub>)
- 860 nm light : potassium niobate (K<sub>2</sub>NbO<sub>6</sub>)
- 960 nm light : KNbO<sub>3</sub>
- 1064 nm light : monopotassium phosphate (KH<sub>2</sub>PO<sub>4</sub>, KDP), lithium triborate (LBO) and β-barium borate (BBO).
- 1300 nm light : GaSe
- 1319 nm light : KNbO<sub>3</sub>, BBO, KDP, potassium titanyl phosphate (KTP), lithium niobate (LiNbO<sub>3</sub>), LiIO<sub>3</sub>, and Ammonium Dihydrogen Phosphate (ADP)

## Broad field of nonlinear effects

- Optical Kerr effect, intensity dependent refractive index;
  - Self-focusing;
  - Kerr-lens modelocking (KLM).
  - Self-phase modulation (SPM), a  $\chi^{(3)}$  effect.
  - Optical solitons.
  - Cross-phase modulation (XPM);
  - Four-wave mixing (FWM), can also arise from other nonlinearities.
  - Raman amplification,
  - Optical phase conjugation.
- Brillouin scattering, interaction of photons with acoustic phonons;
  - Optical phase conjugation.
- Two-photon absorption, simultaneous absorption of two photons, transferring the energy to a single electron;
- Multiple photoionisation, near-simultaneous removal of many bound electrons by one photon.
- Chaos in Optical Systems

We will consider in details only SHG and Raman Scattering

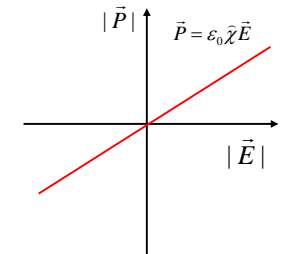
## Linear vs. Nonlinear Spectroscopy

- ❖ Linear spectroscopy:

$$\vec{D} = \epsilon_0 \hat{\epsilon} \vec{E} = \epsilon_0 (1 + \hat{\chi}) \vec{E} = \epsilon_0 \vec{E} + \epsilon_0 \vec{P}$$

$$\vec{P} = \epsilon_0 \hat{\chi} \vec{E}$$

$$\begin{bmatrix} D_x \\ D_y \\ D_z \end{bmatrix} = \epsilon_0 \cdot \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix} \cdot \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

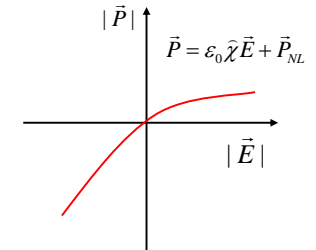


- ❖ Nonlinear effects:

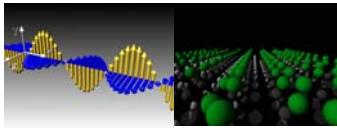
$$\vec{P} = \epsilon_0 \hat{\chi} \vec{E} + \vec{P}_{NL}$$

$$P_{NL} = \chi^{(2)} E^2$$

$$(\vec{P}_{NL})_i = 2d_{ijk} E_j E_k$$

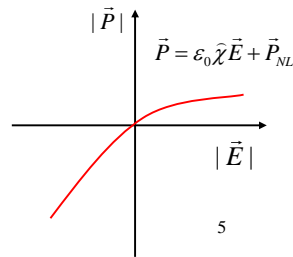
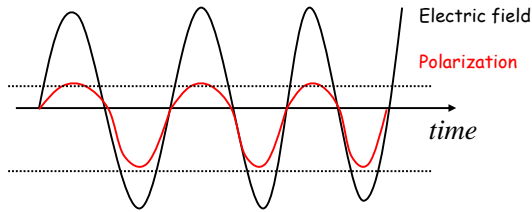
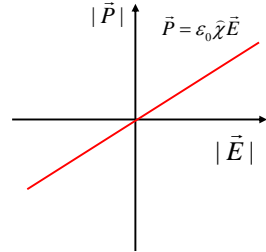
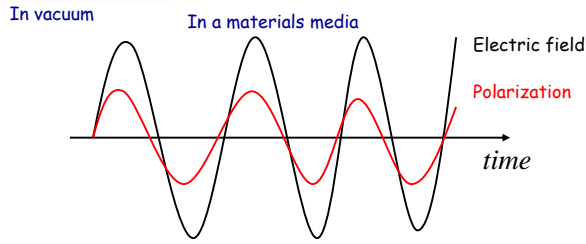


Induced polarization vs. electric field in linear dielectric and in a crystal without center of inversion, where electrons move in asymmetric potential.



## Electric field and Polarization

$$\vec{E}(r, t) = \vec{E}_0 \exp[i(\vec{k}\vec{r} - \omega t)]$$



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## Microscopic understanding of nonlinearity

### ❖ Electronic contribution to susceptibility (linear response)

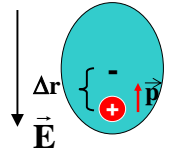
For simplicity consider one-dimensional case ( $\Delta r$  parallel to  $x$ )

Displaced electronic cloud feels a restoring force, which is linear (for small displacements)

$$\text{Total force } \mathbf{F} = e\mathbf{E} - \kappa\Delta\mathbf{r} = m \frac{d^2}{dt^2} \Delta\mathbf{r}$$

$\kappa$  = spring constant

$m$  = mass

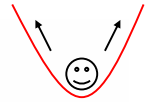


Without an external field:

$$-kx = m \frac{d^2 x}{dt^2}$$

Equation for harmonic oscillator. Solution: harmonic vibration

$$x(t) = x_0 e^{-i\omega_0 t} \quad \text{with frequency} \quad \omega_0 = \sqrt{k/m}$$



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Now, have electromagnetic wave with field  $E(t) = E_0 e^{-i\omega t}$

Force  $F(t) = eE_0 e^{-i\omega t}$

Equation of motion becomes (forced oscillator)  $eE_0 e^{-i\omega t} - m\omega_0^2 x = m \frac{d^2 x}{dt^2}$

Look for a solution  $x(t) = x_0 e^{-i\omega t}$  and get

$$x(t) = \frac{e/m}{\omega_0^2 - \omega^2} E_0 e^{-i\omega t} = \frac{e/m}{\omega_0^2 - \omega^2} E(t)$$

Expect strong response (large  $x$ ),  $\Rightarrow$  large susceptibility  $\chi \Rightarrow$  large refractive index  $n$  at  $\omega \approx \omega_0$

Dipole moment  $p = qx$ , so polarization  $P = eNZx$   
( $N$  atoms per unit volume,  $Z$  electrons per atom)  $\Rightarrow$

$$P = \frac{e^2 Z N / m}{\omega_0^2 - \omega^2} E \quad \text{Recall } P = \epsilon_0 \chi E \quad \text{and get} \quad \chi(\omega) = \frac{NZe^2}{\epsilon_0 m} \frac{1}{(\omega_0^2 - \omega^2)}$$

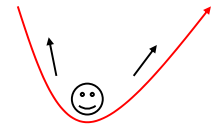
**Linear response:**

## Microscopic understanding of nonlinearity

### ❖ Electronic contribution to susceptibility (nonlinear response)

Electron is moving in an asymmetric potential with damping

$$\frac{\partial^2 x(t)}{\partial t^2} + \gamma \frac{\partial x(t)}{\partial t} + \omega_0^2 x(t) + Dx^2(t) = \frac{e}{2m} E_0 e^{-i\omega t}$$



$x$  – deviation from potential minimum

$mDx^2(t)$  Anharmonic restoring force

$\gamma \frac{\partial x(t)}{\partial t}$  Damping

**Linear response:**

Solution:  $x(\omega, t) = (q_1 e^{-i\omega t} + q_2 e^{-i2\omega t})$

$$q_1 = \frac{eE_0}{m} \frac{1}{\omega_0^2 - \omega^2 + i\gamma \cdot \omega}$$

$$q_2 = \frac{-De^2 E_0^2}{2m^2 [\omega_0^2 - \omega^2 + i\gamma \cdot \omega]^2 [\omega_0^2 - (2\omega)^2 + i\gamma \cdot 2\omega]}$$

**NonLinear response:**  
(second harmonic generation)

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For NL polarization at the second harmonic frequency:

$$P^{2\omega} = Neq_2 e^{-i2\omega t} = \chi_{NL}^{(2)} \cdot E_0^2 e^{-i2\omega t}$$

For correct power consideration we need to take the complex conjugate part of the electromagnetic wave

$$P^{2\omega} = \frac{1}{2} Neq_2 (e^{-i2\omega t} + e^{+i2\omega t}) = \frac{1}{2} d_{NL} \cdot E_0^2 (e^{-i2\omega t} + e^{+i2\omega t})$$

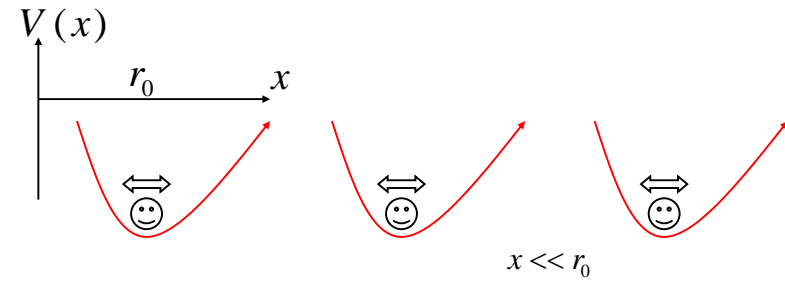
For nonlinear susceptibility we have:

$$\chi_{NL}^{(2)} = \frac{mD(\chi_L(\omega))^2 \cdot \chi_L(2\omega) \cdot \epsilon_0^3}{2N^2 |e^3|} \quad D \approx \frac{-3e^2}{\epsilon_0 m r_0^4}; \quad r_0 \approx 0.5 \text{ nm}$$

Why nonlinear effects are weaker than linear effects?

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Why nonlinear effects are usually weaker than linear ones?



$$V(x) = \frac{m}{2} x^2 + \frac{m}{3} D x^3 = \frac{e^2}{4\pi\epsilon_0} \left( \frac{-5.83}{r_0} + 24.1 \frac{x^2}{r_0^2} - 13.3 \frac{x^3}{r_0^3} + \dots \right)$$

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### Symmetry of nonlinear susceptibility tensor

$$|\vec{P}_{NL}| = \hat{\chi}^{(2)} \cdot |\vec{E}_1 \cdot \vec{E}_2|$$

$$(\vec{P}_{NL})_i = 2d_{ijk} E_j E_k$$

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \cdot \begin{bmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_z E_y \\ 2E_z E_x \\ 2E_x E_y \end{bmatrix}$$

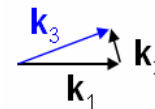
For cubic, tetragonal, and orthorhombic crystals:

$$\begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & d' & 0 & 0 \\ 0 & 0 & 0 & 0 & d' & 0 \\ 0 & 0 & 0 & 0 & 0 & d'' \end{bmatrix}$$

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### Two-wave mixing

General case of two-wave mixing:  $\omega_1 + \omega_2 = \omega_3$



$$(\omega_3 = \omega_1 + \omega_2)$$

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3$$

Wave equation for linear process  $\nabla^2 \vec{E} = \epsilon\mu \frac{\partial^2 \vec{E}}{\partial t^2} + \sigma\mu \frac{\partial \vec{E}}{\partial t}$

Using Laplace operator:

Wave equation for nonlinear process:  $\nabla^2 \vec{E} = \epsilon\mu \frac{\partial^2 \vec{E}}{\partial t^2} + \sigma\mu \frac{\partial \vec{E}}{\partial t} + \mu \frac{\partial^2 \vec{P}_{NL}}{\partial t^2}$

Wave propagation along z;

i, j, k index are permutations of x and y coordinates

$$\frac{dE_{1i}}{dz} = -\frac{\sigma_1}{2} \sqrt{\frac{\mu}{\epsilon_1}} E_{1i} - i\omega_1 \sqrt{\frac{\mu}{\epsilon_1}} d'_{ijk} E_{3j} E_{2k} e^{-i(k_3 - k_2 - k_1)z}$$

$$\frac{dE_{2k}^*}{dz} = -\frac{\sigma_2}{2} \sqrt{\frac{\mu}{\epsilon_2}} E_{2k}^* - i\omega_2 \sqrt{\frac{\mu}{\epsilon_2}} d'_{ijk} E_{1i} E_{3j} e^{-i(-k_3 + k_2 + k_1)z}$$

$$\frac{dE_{3j}}{dz} = -\frac{\sigma_3}{2} \sqrt{\frac{\mu}{\epsilon_3}} E_{3j} - i\omega_3 \sqrt{\frac{\mu}{\epsilon_3}} d'_{ijk} E_{1i} E_{2k} e^{-i(-k_3 + k_2 + k_1)z}$$

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## Second-harmonic generation

SHG:  $\omega + \omega = 2\omega$  ( $\omega_3 = 2\omega_1$ )  $\frac{dE_{1i}}{dz} \approx 0$  Small loss of power in the primary beam  
 $2\vec{k}_\omega = \vec{k}_{2\omega}$

$$\frac{dE_{3j}}{dz} = -i2\omega \sqrt{\frac{\mu}{\varepsilon}} d'_{ijk} E_{1i} E_{1k} e^{-i\Delta kz}$$

$$E_{3j}(z) = -i2\omega \sqrt{\frac{\mu}{\varepsilon}} d'_{ijk} E_{1i} E_{1k} \frac{e^{-i\Delta kz} - 1}{i\Delta k}$$

$$\text{Power}(2\omega) = E_{3j}(L) E_{3j}^*(L) = 4 \frac{\mu}{\varepsilon_3} \omega^2 (d'_{ijk})^2 E_{1i}^2 E_{1k}^2 \frac{\sin^2(\Delta kL/2)}{(\Delta kL/2)^2}$$

Coherence length:  $l = \frac{2\pi}{\Delta k}$

Phase matching requirement:  $2 \cdot |\vec{k}_\omega| = 2\tilde{n}(\omega) \frac{\omega}{c} = \tilde{n}(\omega) \frac{2\omega}{c}$

$$\Delta n = n_e - n_o$$

$$\hat{\varepsilon} = \begin{bmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{bmatrix} = \begin{bmatrix} n_e^2 & 0 & 0 \\ 0 & n_o^2 & 0 \\ 0 & 0 & n_o^2 \end{bmatrix}$$

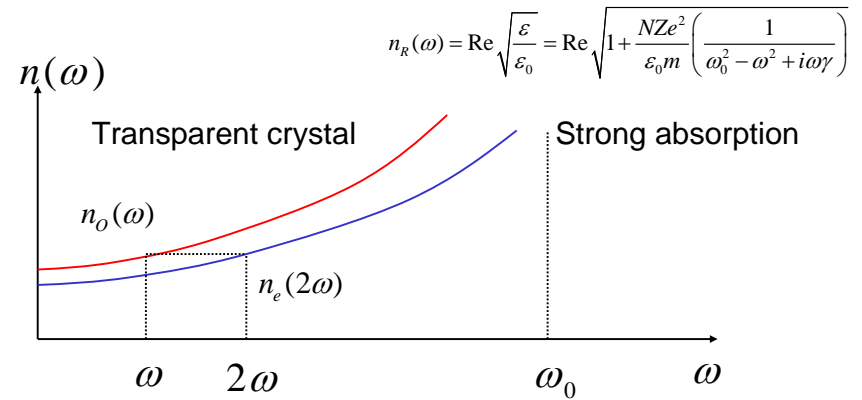
$$|\vec{k}_{2\omega}| = \tilde{n}(2\omega) \frac{2\omega}{c}$$

$$\tilde{n}(\omega) \neq \tilde{n}(2\omega) !$$

If in birefringent crystal  $n_e(2\omega) = n_o(\omega) \Rightarrow 2\vec{k}_\omega = \vec{k}_{2\omega}$  13

## Second-harmonic generation

If in birefringent crystal  $n_e(2\omega) = n_o(\omega) \Rightarrow 2\vec{k}_\omega = \vec{k}_{2\omega}$



Blue waves propagate with the same velocity in the crystal

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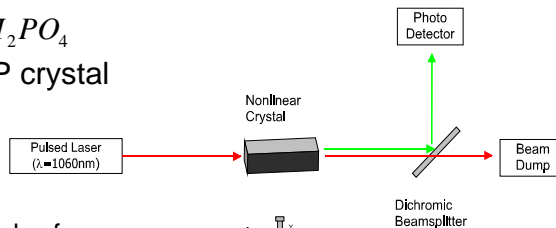
## Experimental setup for Second-harmonic generation

$$\omega + \omega = 2\omega$$

$$2\vec{k}_\omega = \vec{k}_{2\omega}$$

$$n_e(2\omega) = n_o(\omega)$$

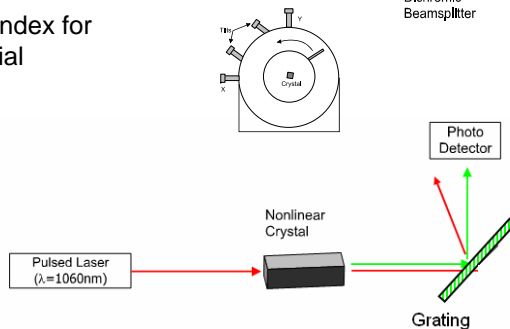
$KH_2PO_4$   
KDP crystal



Fine tuning of refractive index for Phase matching in uniaxial Nonlinear crystals:

$$\frac{1}{n(\theta)^2} = \frac{\cos^2 \theta}{n_o^2} + \frac{\sin^2 \theta}{n_e^2}$$

$$\hat{\varepsilon} = \begin{bmatrix} n_e^2 & 0 & 0 \\ 0 & n_o^2 & 0 \\ 0 & 0 & n_o^2 \end{bmatrix}$$



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## Applications of Second-harmonic generation

- ❖ Lasers (Nd:YAG, second harmonic)
- ❖ Coherent anti-Stokes Raman scattering
- ❖ Bio-imaging
- ❖ Materials Physics
- ❖ Solar Physics
- ❖ Quantum cryptography (two-wave mixing)

### Common SHG materials

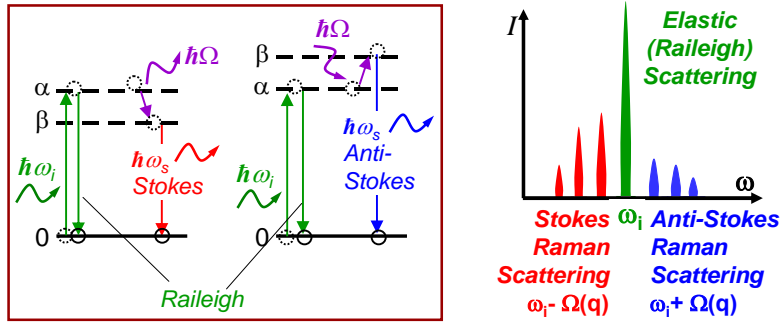
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- 1319 nm light :  $KNbO_3$ , BBO, KDP, potassium titanyl phosphate (KTP), lithium niobate ( $LiNbO_3$ ),  $LiIO_3$ , and Ammonium Dihydrogen Phosphate (ADP)

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## 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<sup>17</sup>

## Raman scattering in crystalline solids

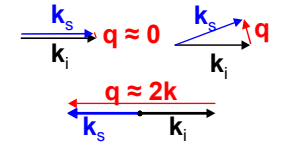
Not every crystal lattice vibration can be probed by Raman scattering. There are certain **Selection rules**:

### 1. Energy conservation:

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

### 2. Momentum conservation:

$$\mathbf{k}_i = \mathbf{k}_s \pm \mathbf{q} \Rightarrow 0 \leq |\mathbf{q}| \leq 2|\mathbf{k}| \Rightarrow 0 \leq |q| \leq \frac{4\pi m}{\lambda_i}$$



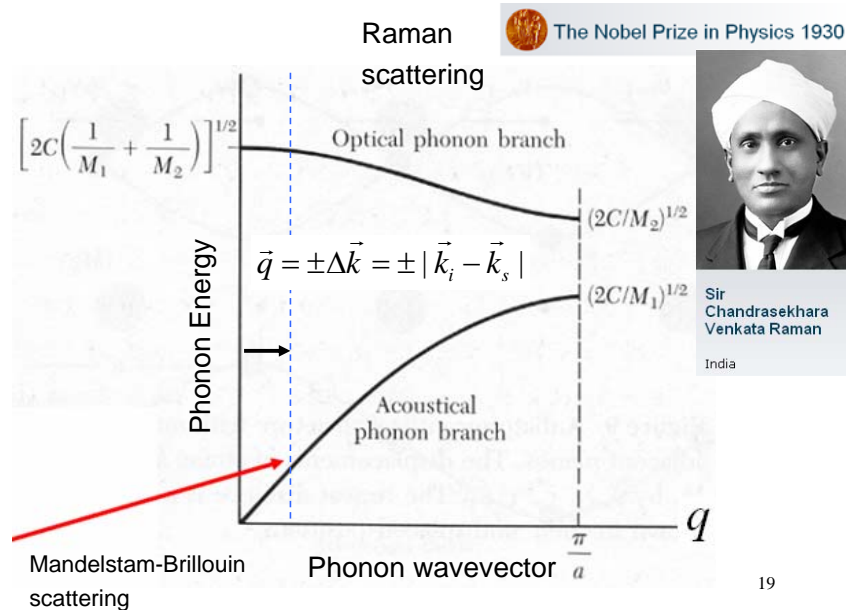
$$\lambda_i \sim 5000 \text{ \AA}, a_0 \sim 4-5 \text{ \AA} \Rightarrow \lambda_{\text{phonon}} \gg a_0$$

$\Rightarrow$  only small wavevector (close to BZ center) phonons are seen in the 1<sup>st</sup> order (single phonon) Raman spectra of bulk crystals

### 3. Selection rules determined by crystal symmetry

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## Raman scattering in crystalline solids



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## Example of Raman scattering in crystalline solids

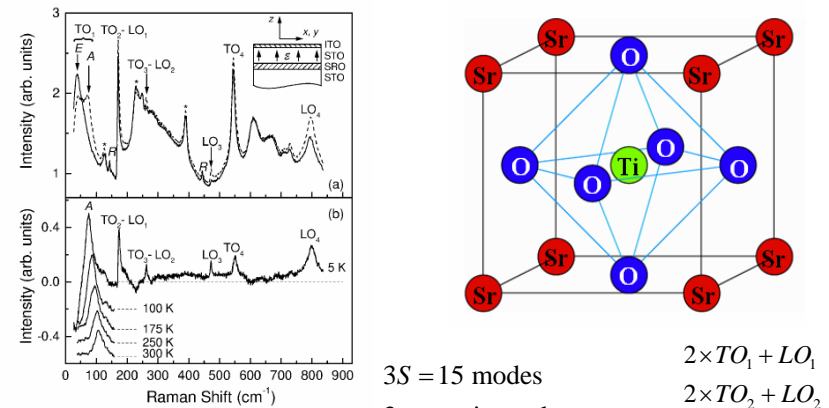


FIG. 1. (a) Solid and dotted lines show the Raman spectra of  $1 \mu\text{m}$  STO film at  $T = 5 \text{ K}$  without electric field and in the presence of an external electric field of  $22 \times 10^4 \text{ V/cm}$  directed normal to the film plane, respectively. The soft-mode components are labeled A and E. Structural modes are denoted by K. 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  $\ell = 22 \times 10^4 \text{ V/cm}$  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;  $3 \times 4$

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

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