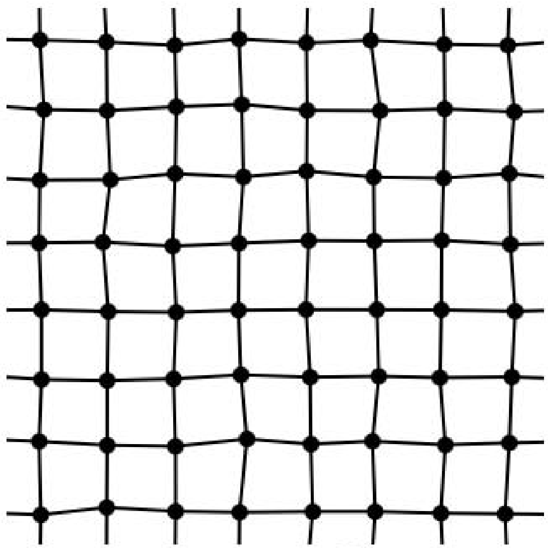
Quasiparticles

Phonons

N_{atom} atoms in crystal
$3N_{atom}$ normal modes
p atoms in the basis
N_{atom}/p unit cells
N_{atom}/p translational symmetries
N_{atom}/p k-vectors
$3p$ modes for every k vector
3 acoustic branches and $3p$-3 optical branches

Normal Modes and Phonons

At finite temperatures, the atoms in a crystal vibrate. In the simulation below, the atoms move randomly around their equilibrium positions.



T = 300 K - +

Normal modes are eigenfunctions of T

$$u_{lmn}^{x} = u_{\vec{k}}^{x} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3 - \omega t\right)\right)$$

$$u_{lmn}^{y} = u_{\vec{k}}^{y} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3 - \omega t\right)\right)$$

$$u_{lmn}^{z} = u_{\vec{k}}^{z} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3 - \omega t\right)\right)$$

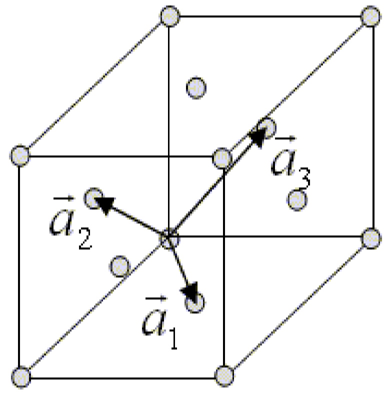
These are eigenfunctions of T.

$$T_{pqr}u_{lmn}^{x} = u_{\vec{k}}^{x} \exp\left(i\left(l\vec{k}\cdot\left(\vec{a}_1 + p\vec{a}_1\right) + m\vec{k}\cdot\left(\vec{a}_2 + q\vec{a}_2\right) + n\vec{k}\cdot\left(\vec{a}_3 + r\vec{a}_3\right) - \omega t\right)\right)$$

$$= \exp\left(i\left(lp\vec{k}\cdot\vec{a}_1 + qm\vec{k}\cdot\vec{a}_2 + rn\vec{k}\cdot\vec{a}_3\right)\right)u_{\vec{k}}^{x} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3 - \omega t\right)\right)$$

$$= \exp\left(i\left(lp\vec{k}\cdot\vec{a}_1 + qm\vec{k}\cdot\vec{a}_2 + rn\vec{k}\cdot\vec{a}_3\right)\right)u_{lmn}^{x}$$

fcc



$$\vec{a}_1 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y} \qquad \vec{b}_1 = \frac{2\pi}{a}\left(\hat{k}_x + \hat{k}_y - \hat{k}_z\right)$$

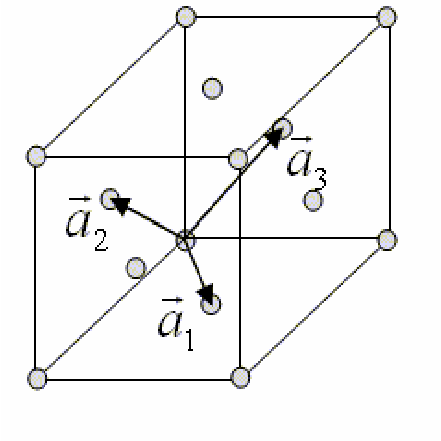
$$\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z} \qquad \vec{b}_2 = \frac{2\pi}{a}\left(\hat{k}_x - \hat{k}_y + \hat{k}_z\right)$$

$$\vec{a}_3 = \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z} \qquad \vec{b}_3 = \frac{2\pi}{a}\left(-\hat{k}_x + \hat{k}_y + \hat{k}_z\right)$$

$$\begin{aligned} m\frac{d^2u^x_{lmn}}{dt^2} = \frac{C}{2}\Big[& \left(u^x_{l+1mn} - u^x_{lmn}\right) + \left(u^x_{l-1mn} - u^x_{lmn}\right) + \left(u^x_{lm+1n} - u^x_{lmn}\right) + \left(u^x_{lm-1n} - u^x_{lmn}\right) \\ & + \left(u^x_{l+1mn-1} - u^x_{lmn}\right) + \left(u^x_{l-1mn+1} - u^x_{lmn}\right) + \left(u^x_{lm+1n-1} - u^x_{lmn}\right) + \left(u^x_{lm-1n+1} - u^x_{lmn}\right) \\ & + \left(u^y_{l+1mn} - u^y_{lmn}\right) + \left(u^y_{l-1mn} - u^y_{lmn}\right) - \left(u^y_{lm+1n-1} - u^y_{lmn}\right) - \left(u^y_{lm-1n+1} - u^y_{lmn}\right) \\ & + \left(u^z_{lm+1n} - u^z_{lmn}\right) + \left(u^z_{lm-1n} - u^z_{lmn}\right) - \left(u^z_{l+1mn-1} - u^z_{lmn}\right) - \left(u^z_{l-1mn+1} - u^z_{lmn}\right)\Big] \end{aligned}$$

and similar expressions for the *y* and *z* motion

fcc



$$\vec{a}_1 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y}$$

$$\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z}$$

$$\vec{a}_3 = \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z}$$

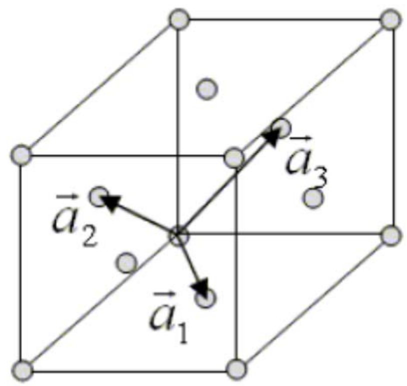
Substitute the eigenfunctions of T into Newton's laws.

$$u_{lmn}^{x} = u_{\vec{k}}^{x}\exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3\right)\right) = u_{\vec{k}}^{x}\exp\left(i\left(\frac{(l+m)k_x a}{2} + \frac{(l+n)k_y a}{2} + \frac{(m+n)k_z a}{2}\right)\right).$$

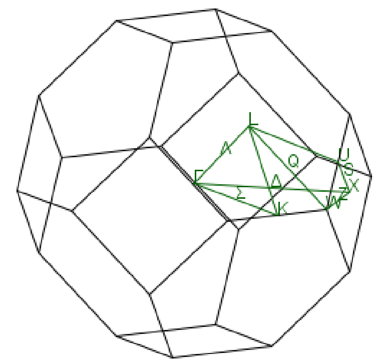
$$\begin{vmatrix}
4-\cos\left(\frac{k_xa}{2}+\frac{k_ya}{2}\right)-\cos\left(\frac{k_xa}{2}+\frac{k_za}{2}\right)-\cos\left(\frac{k_xa}{2}-\frac{k_ya}{2}\right)-\cos\left(\frac{k_xa}{2}-\frac{k_za}{2}\right)-\frac{m\omega^2}{\sqrt{2}C} & -\cos\left(\frac{k_xa}{2}+\frac{k_ya}{2}\right)+\cos\left(\frac{k_xa}{2}-\frac{k_ya}{2}\right) & -\cos\left(\frac{k_xa}{2}+\frac{k_za}{2}\right)+\cos\left(\frac{k_xa}{2}-\frac{k_za}{2}\right) \\
-\cos\left(\frac{k_xa}{2}+\frac{k_ya}{2}\right)+\cos\left(\frac{k_xa}{2}-\frac{k_ya}{2}\right) & 4-\cos\left(\frac{k_ya}{2}+\frac{k_xa}{2}\right)-\cos\left(\frac{k_ya}{2}+\frac{k_za}{2}\right)-\cos\left(\frac{k_ya}{2}-\frac{k_xa}{2}\right)-\cos\left(\frac{k_ya}{2}-\frac{k_za}{2}\right)-\frac{m\omega^2}{\sqrt{2}C} & -\cos\left(\frac{k_ya}{2}+\frac{k_za}{2}\right)+\cos\left(\frac{k_ya}{2}-\frac{k_za}{2}\right) \\
-\cos\left(\frac{k_xa}{2}+\frac{k_za}{2}\right)+\cos\left(\frac{k_xa}{2}-\frac{k_za}{2}\right) & -\cos\left(\frac{k_ya}{2}+\frac{k_za}{2}\right)+\cos\left(\frac{k_ya}{2}-\frac{k_za}{2}\right) & 4-\cos\left(\frac{k_za}{2}+\frac{k_xa}{2}\right)-\cos\left(\frac{k_za}{2}+\frac{k_ya}{2}\right)-\cos\left(\frac{k_za}{2}-\frac{k_xa}{2}\right)-\cos\left(\frac{k_za}{2}-\frac{k_ya}{2}\right)-\frac{m\omega^2}{\sqrt{2}C}
\end{vmatrix} = 0$$

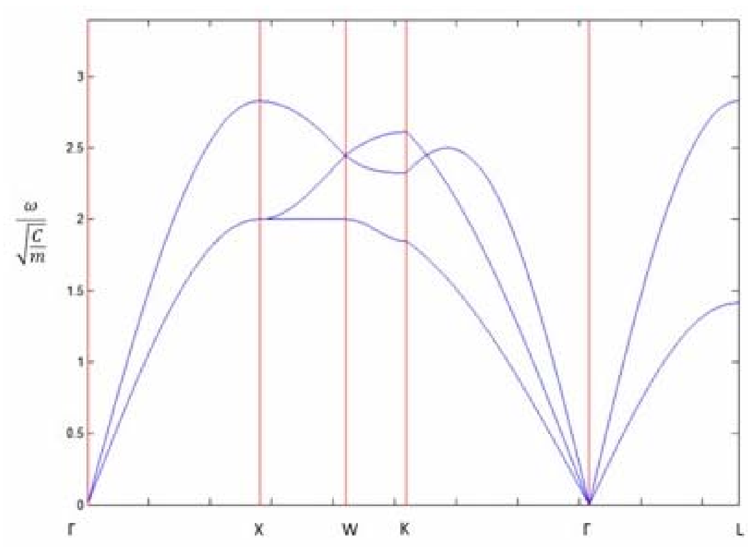
http://lamp.tu-graz.ac.at/~hadley/ss1/phonons/fcc/fcc.html

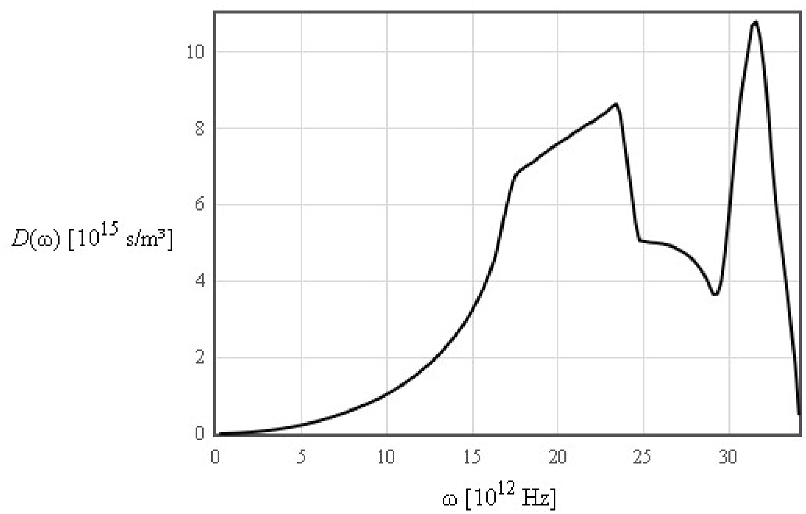
fcc phonons



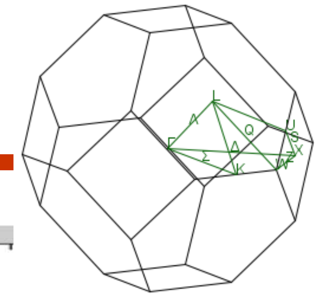
3N degrees of freedom

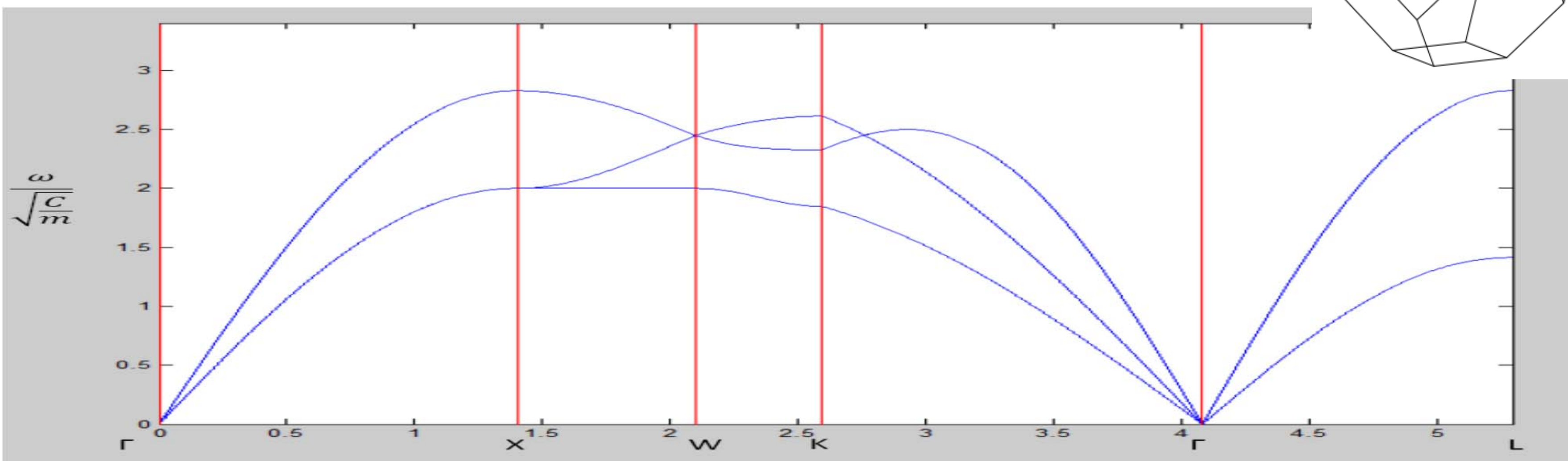






Phonon dispersion Au





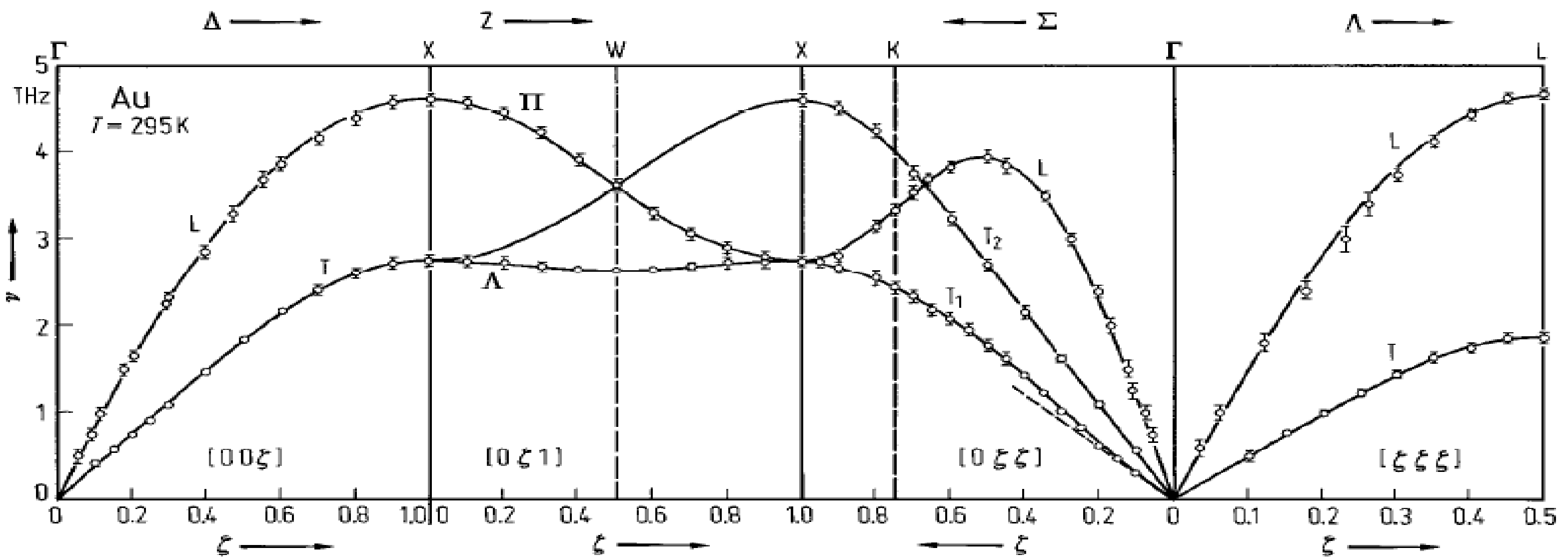
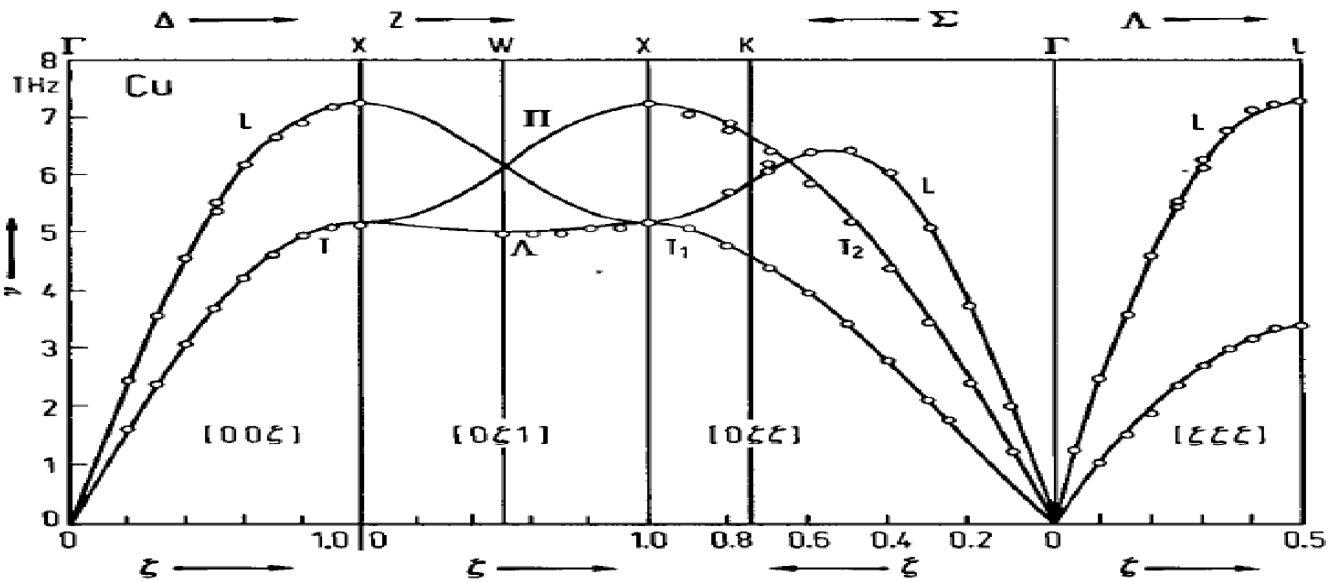


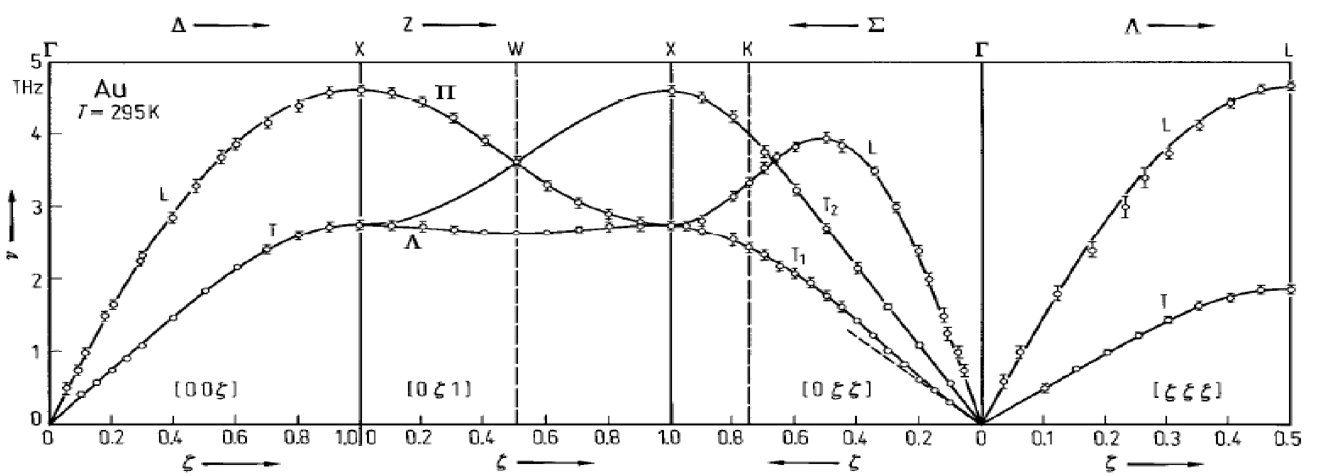
Fig. 1. Au. Phonon dispersion relations in the principal symmetry directions according to [73Ly1]. The solid curves represent both the fourth neighbour general force model (M1) and the fifth neighbour axially symmetric model (M2) of Table 3 Au. The dotted line in the Σ direction is corresponding to the velocity of sound appropriate to the [0ζζ] T_1 branch.

From Springer Materials: Landholt Boernstein Database

Materials with the same crystal structure will have similar phonon dispersion relations



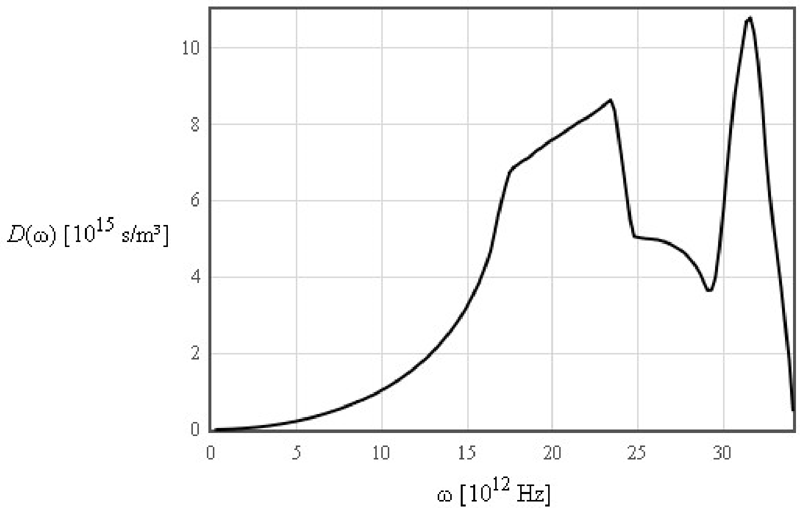
Cu



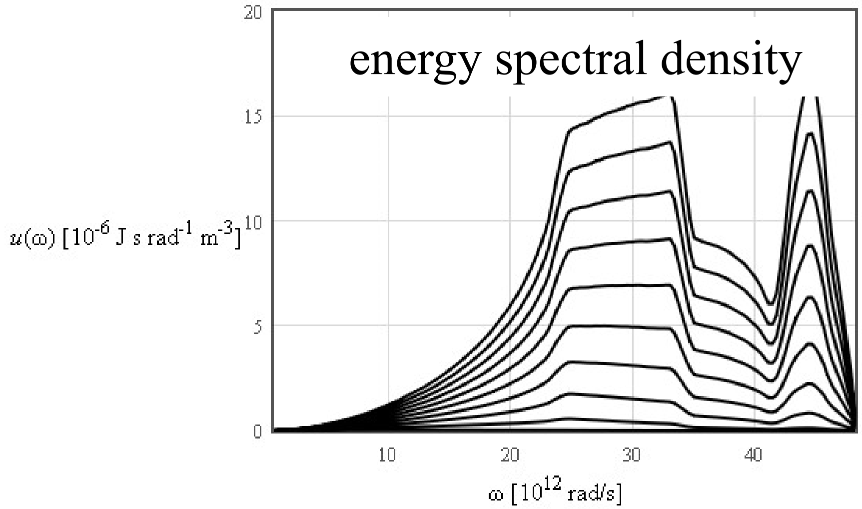
Au

Fig. 1. Au. Phonon dispersion relations in the principal symmetry directions according to [73Ly1]. The solid curves represent both the fourth neighbour general force model (M1) and the fifth neighbour axially symmetric model (M2) of Table 3 Au. The dotted line in the Σ direction is corresponding to the velocity of sound appropriate to the [0ζζ] T_1 branch.

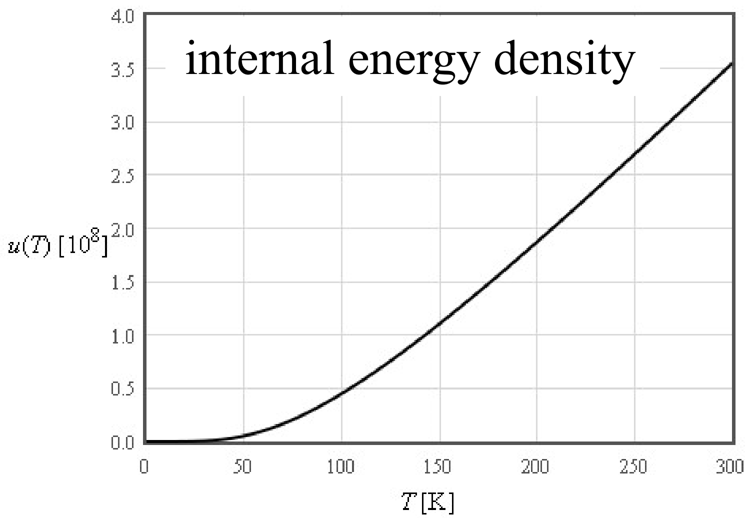
fcc phonons



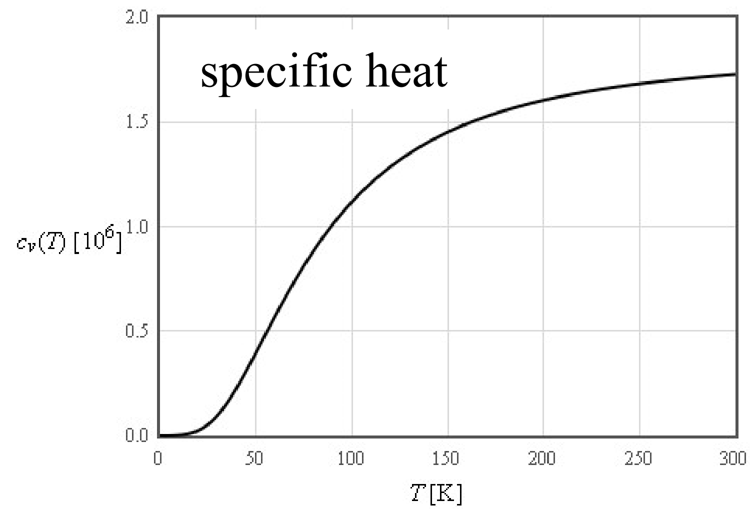
D(ω) [10^15 s/m³]
ω [10^12 Hz]



energy spectral density
u(ω) [10^-6 J s rad^-1 m^-3]
ω [10^12 rad/s]

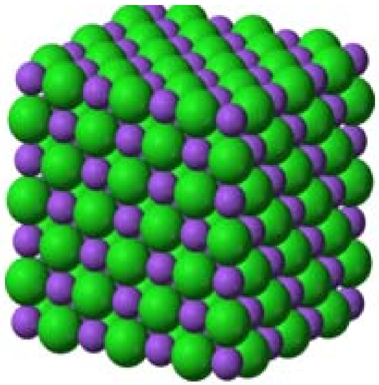


internal energy density
u(T) [10^8]
T [K]



specific heat
c_V(T) [10^6]
T [K]

NaCl



2 atoms/unit cell

6 equations

3 acoustic and
3 optical branches

x - Richtung:

$$M_1 \frac{d^2 u^x_{nml}}{dt^2} = C\left(-2u^x_{nml} + v^x_{(n-1)m(l-1)} + v^x_{n(m-1)l}\right)$$

$$M_2 \frac{d^2 v^x_{nml}}{dt^2} = C\left(-2v^x_{nml} + u^x_{(n+1)m(l+1)} + u^x_{n(m+1)l}\right)$$

y - Richtung:

$$M_1 \frac{d^2 u^y_{nml}}{dt^2} = C\left(-2u^y_{nml} + v^y_{(n-1)(m-1)l} + v^y_{nm(l-1)}\right)$$

$$M_2 \frac{d^2 v^y_{nml}}{dt^2} = C\left(-2v^y_{nml} + u^y_{(n+1)(m+1)l} + u^y_{nm(l+1)}\right)$$

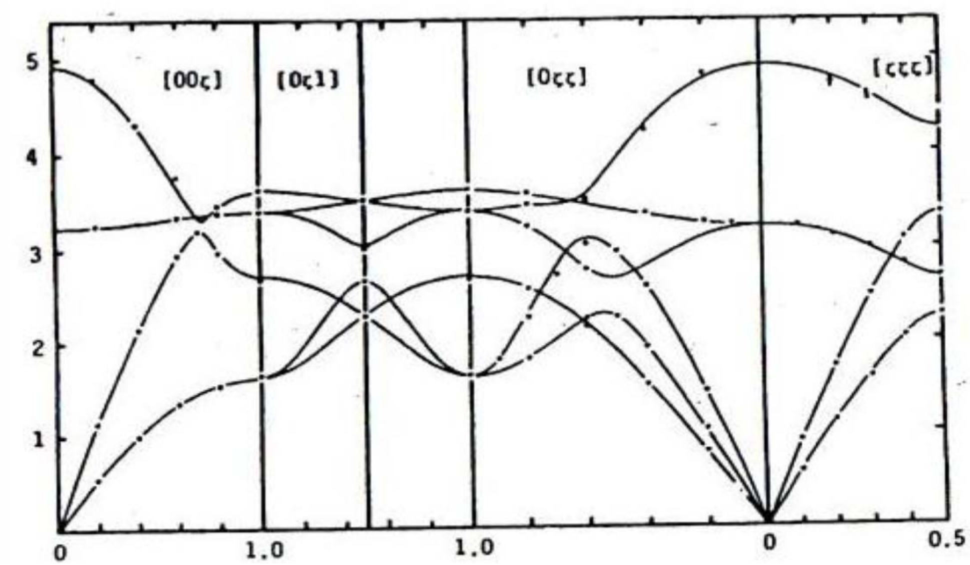
z - Richtung:

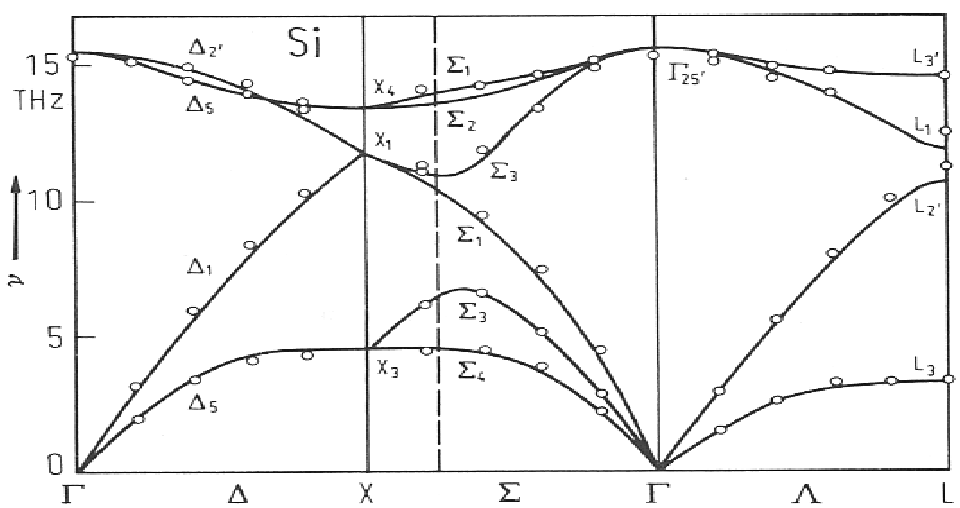
$$M_1 \frac{d^2 u^z_{nml}}{dt^2} = C\left(-2u^z_{nml} + v^z_{n(m-1)(l-1)} + v^z_{(n-1)ml}\right)$$

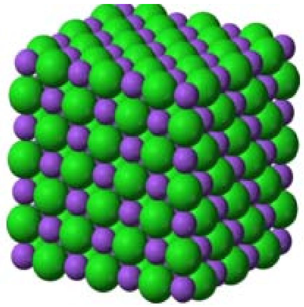
$$M_2 \frac{d^2 v^z_{nml}}{dt^2} = C\left(-2v^z_{nml} + u^z_{n(m+1)(l+1)} + u^z_{(n+1)ml}\right)$$

$$u^x_{nml} = u^x_{\vec{k}} \exp\left(i\left(\vec{k}\cdot\vec{a}_1 + \vec{k}\cdot\vec{a}_2 + \vec{k}\cdot\vec{a}_3 - \omega t\right)\right) \qquad v^x_{nml} = v^x_{\vec{k}} \exp\left(i\left(\vec{k}\cdot\vec{a}_1 + \vec{k}\cdot\vec{a}_2 + \vec{k}\cdot\vec{a}_3 - \omega t\right)\right)$$

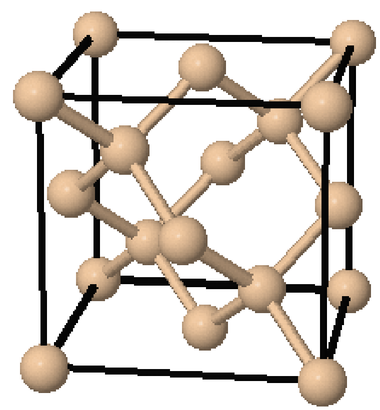
Two atoms per primitive unit cell







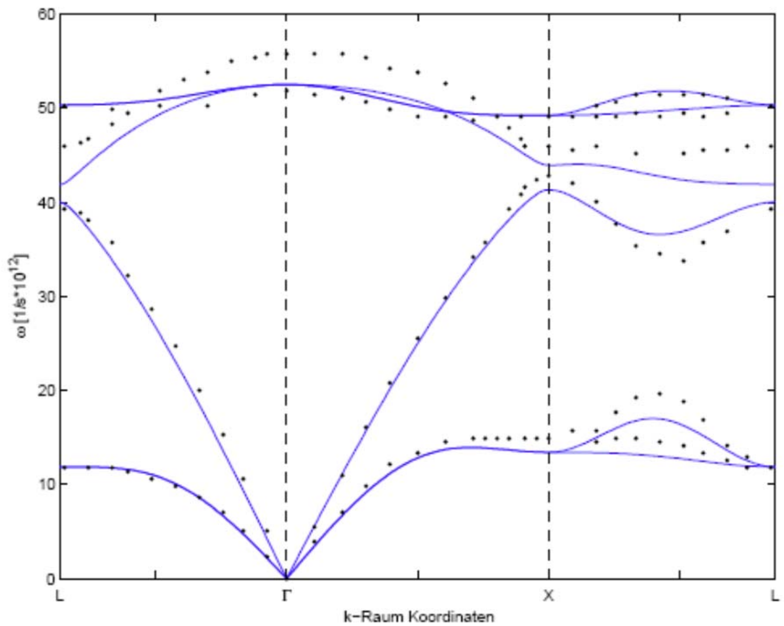
NaCl

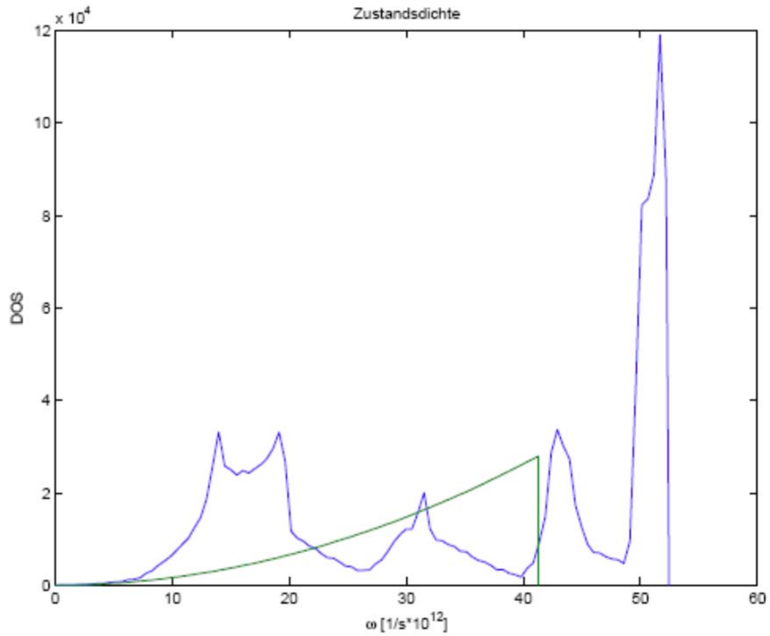


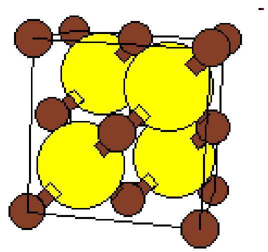
Si

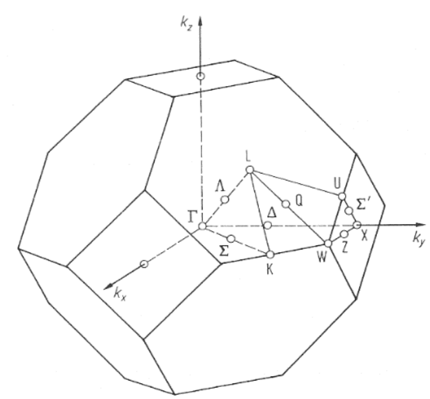
GaAs

Hannes Brandner

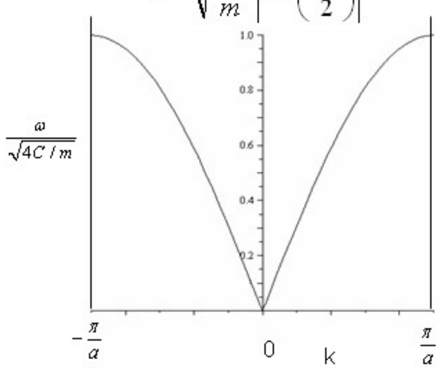
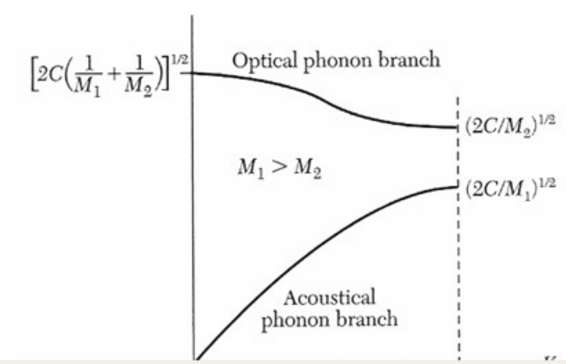








http://lamp.tu-graz.ac.at/~hadley/ss1/phonons/phonontable.html

	Linear Chain $m\frac{d^2u_s}{dt^2} = C(u_{s+1} - 2u_s + u_{s-1})$	**Linear chain 2 masses** $M_1\frac{d^2u_s}{dt^2} = C(v_{s-1} - 2u_s + v_s)$ $M_2\frac{d^2v_s}{dt^2} = C(u_s - 2v_s + u_{s+1})$	**Linear chain 2 spring constants** $M\frac{d^2u_s}{dt^2} = C_1(v_{s-1} - 2u_s + v_s)$ $M\frac{d^2v_s}{dt^2} = C_2(u_s - 2v_s + u_{s+1})$
Eigenfunction solutions	$u_s = A_k e^{i(ksa-\omega t)}$	$u_s = ue^{i(ksa-\omega t)}$ $v_s = ve^{i(ksa-\omega t)}$	$u_s = ue^{i(ksa-\omega t)}$ $v_s = ve^{i(ksa-\omega t)}$
Dispersion relation	$\omega = \sqrt{\frac{4C}{m}}\left\lvert\sin\left(\frac{ka}{2}\right)\right\rvert$ 	$\omega^2 = C\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4\sin^2 ka}{M_1M_2}}$ 	

Phonon quasiparticle lifetime

Phonons are the eigenstates of the linearized equations, not the full equations.

Phonons have a finite lifetime that can be calculated by Fermi's golden rule.

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} \left| \langle f | H_{ph-ph} | i \rangle \right|^2 \delta\left(E_f - E_i\right)$$

Occupation is determined by a master equation (not the Bose-Einstein function).

$$\begin{bmatrix} \frac{dP_0}{dt} \\ \frac{dP_1}{dt} \\ \vdots \\ \frac{dP_N}{dt} \end{bmatrix} = \begin{bmatrix} -\sum_{i \neq 0} \Gamma_{0 \to i} & \Gamma_{1 \to 0} & \cdots & \Gamma_{N \to 0} \\ \Gamma_{0 \to 1} & -\sum_{i \neq 1} \Gamma_{1 \to i} & \cdots & \Gamma_{N \to 1} \\ \vdots & \vdots & \ddots & \vdots \\ \Gamma_{0 \to N} & \Gamma_{1 \to N} & \cdots & -\sum_{i \neq N} \Gamma_{N \to i} \end{bmatrix} \begin{bmatrix} P_0 \\ P_1 \\ \vdots \\ P_N \end{bmatrix}$$

Acoustic attenuation

The amplitude of a monocromatic sound wave decreases as the wave propagates through the crystal as the phonon quasiparticles decay into phonons with other frequencies and directions.

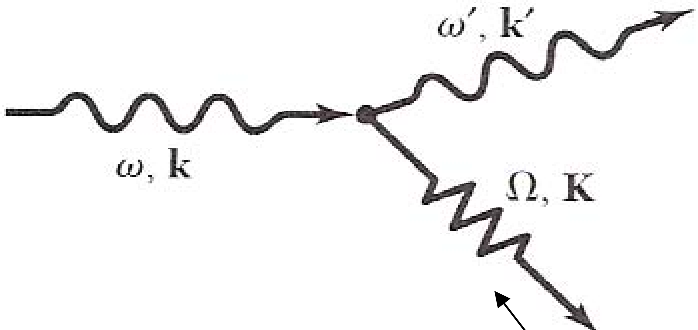
Raman Spectroscopy

C. V. Raman

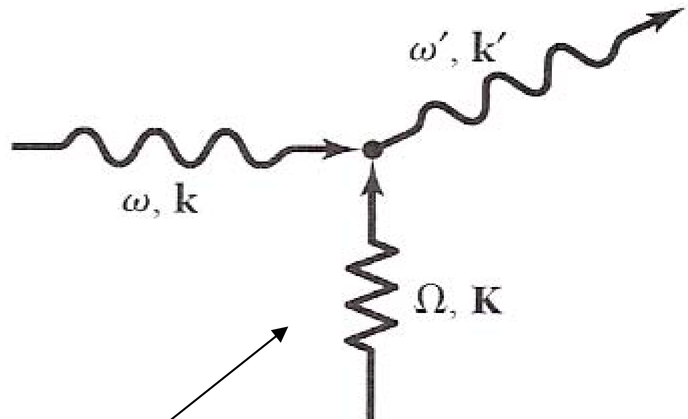
Inelastic light scattering

$$\omega = \omega' \pm \Omega$$

$$\vec{k} = \vec{k}' \pm \vec{K} \pm \vec{G}$$



Stokes



Anti-Stokes

Phonons, magnons, plasmons, polaritons, excitons

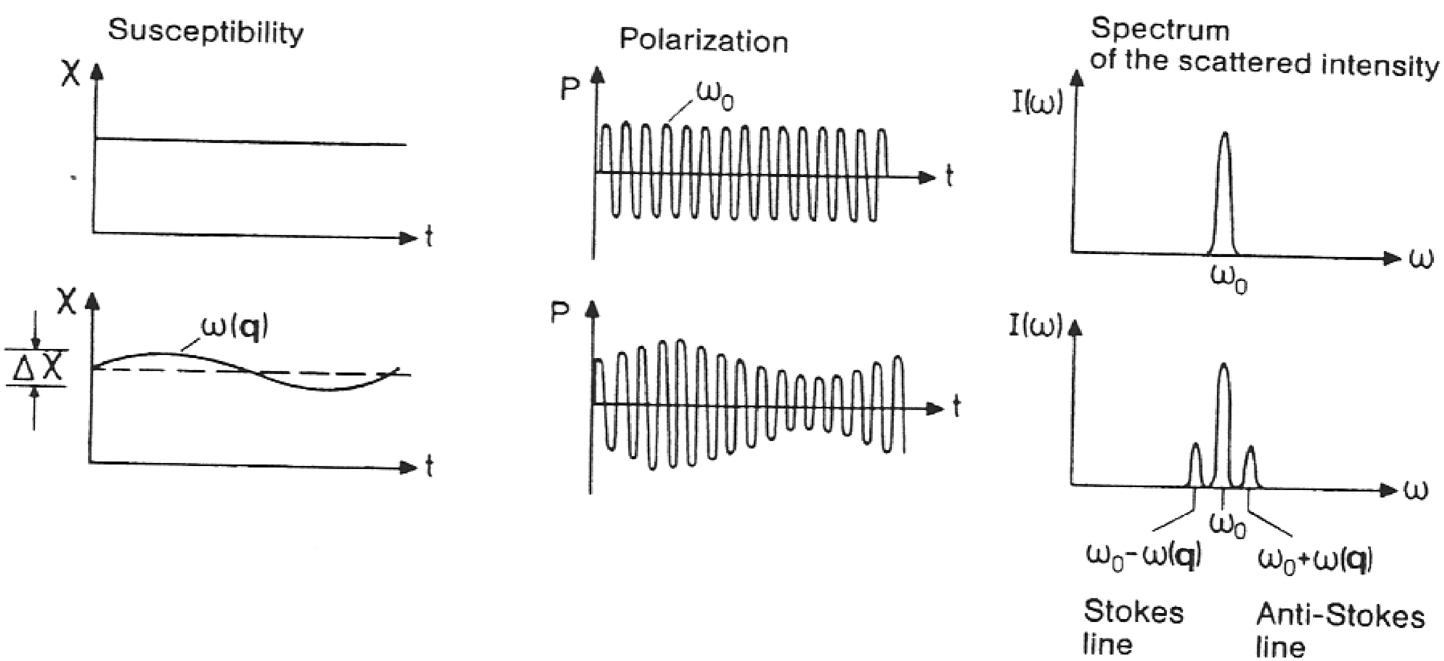
$$\vec{K} \approx 0$$

Raman Spectroscopy

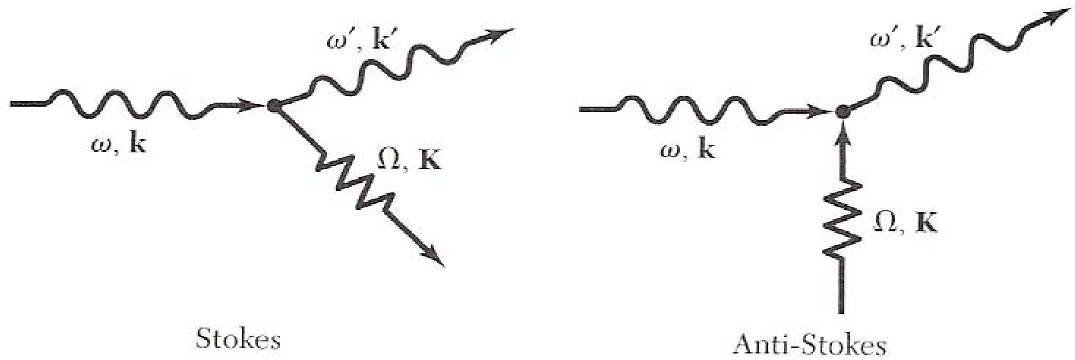
$$\chi = \chi_0 + \frac{\partial \chi}{\partial X} X \cos(\Omega t)$$

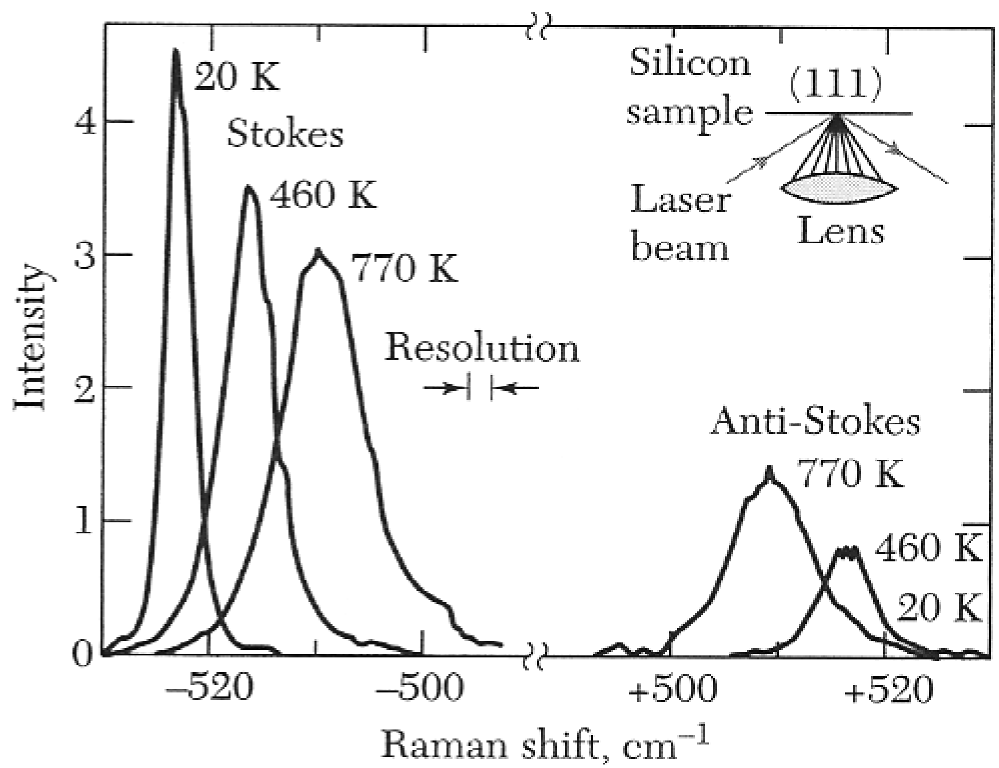
$$\vec{P} = \varepsilon_0 \chi \vec{E} \cos(\omega t) + \varepsilon_0 \frac{\partial \chi}{\partial X} X \cos(\Omega t) \vec{E} \cos(\omega t)$$

There are components of the polarization that oscillate at $\omega \pm \Omega$.



Raman Spectroscopy





Stokes:

$$I(\omega - \Omega) \propto n_k + 1$$

anti-Stokes:

$$I(\omega + \Omega) \propto n_k$$

PHYSICAL REVIEW B, VOLUME 64, 035204

Vacancy-hydrogen defects in silicon studied by Raman spectroscopy

E. V. Lavrov* and J. Weber

Raman spectroscopy

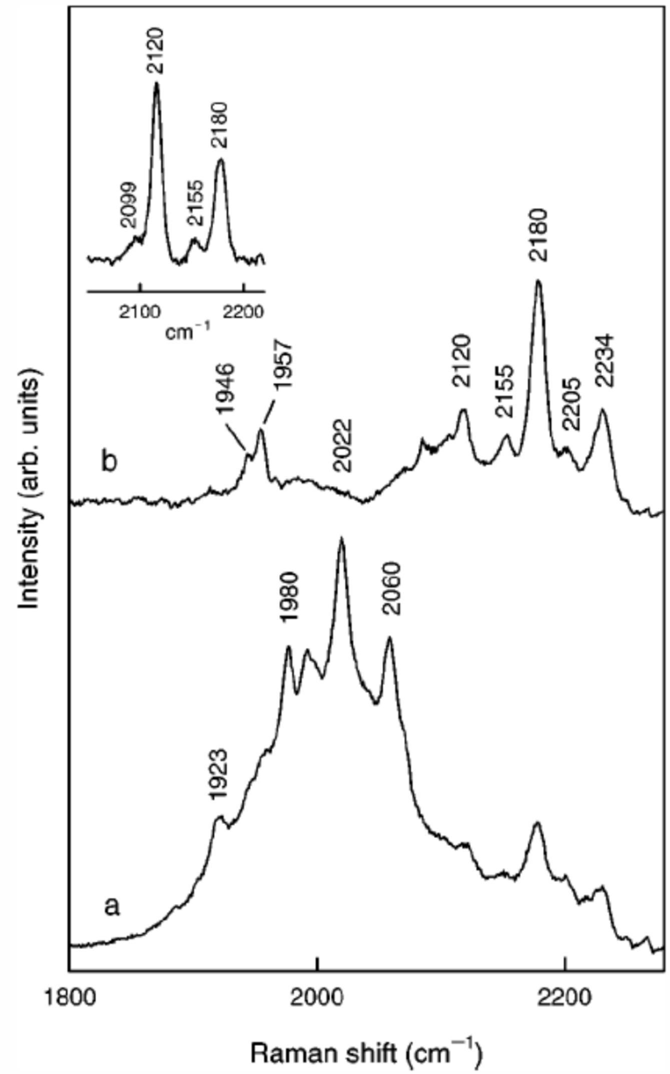
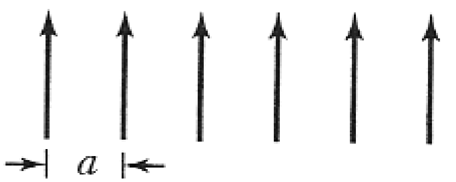
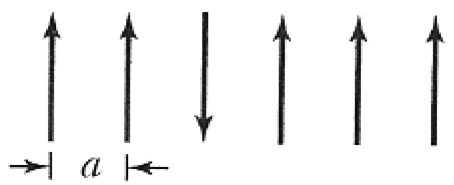
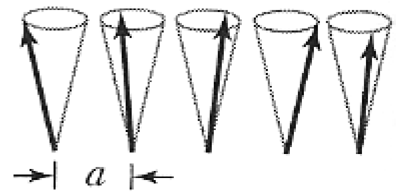


FIG. 1. Raman spectra measured at room temperature on the H_2-implanted sample: (a) as-implanted sample, (b) after annealing at 400 °C for 2 min. Spectra are offset vertically for clarity.

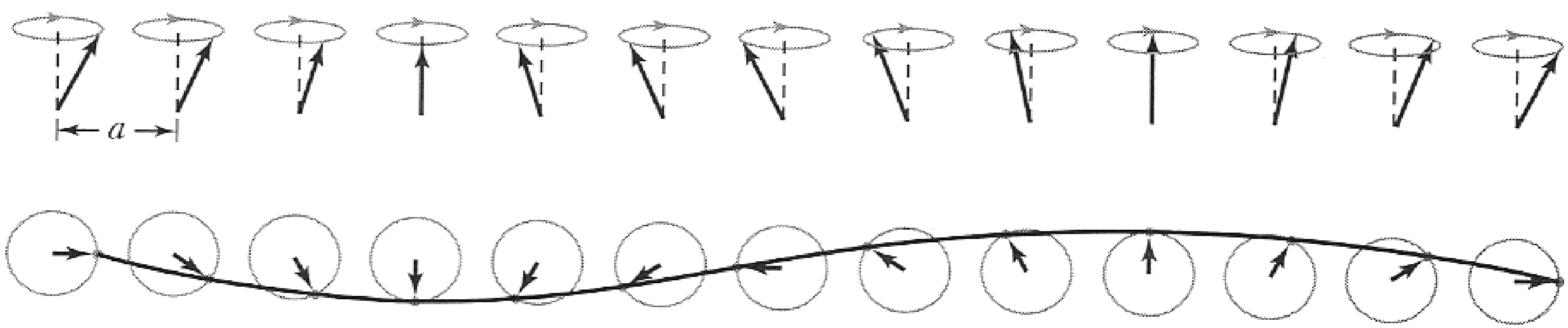
Magnons







Magnons are excitations of the ordered ferromagnetic state



Longitudinal plasma waves

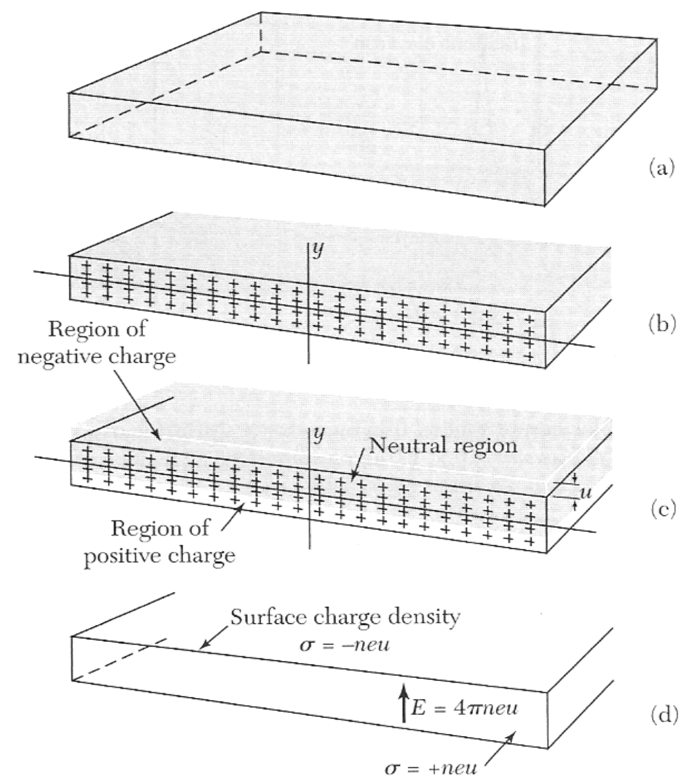
$$nm\frac{d^2y}{dt^2} = -neE$$

$$E = \frac{ney}{\varepsilon_0}$$

$$nm\frac{d^2y}{dt^2} = -\frac{n^2e^2y}{\varepsilon_0}$$

$$\frac{d^2y}{dt^2} + \omega_p^2 y = 0$$

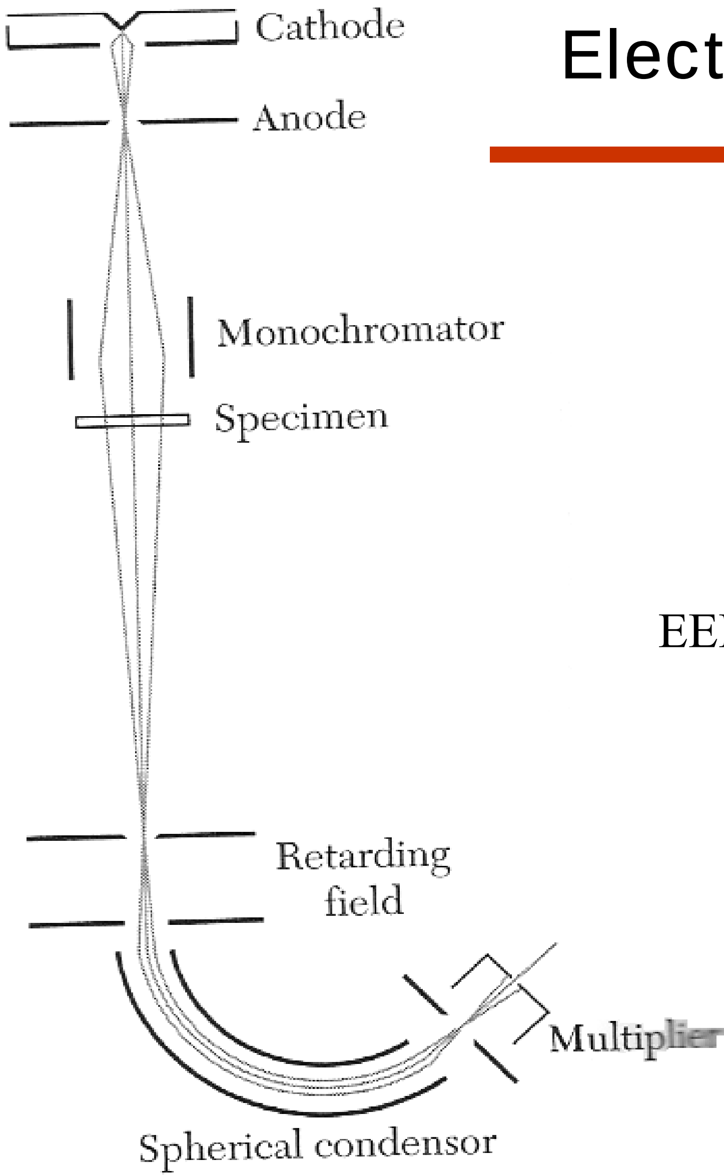
Plasma frequency $$\omega_p = \sqrt{\frac{ne^2}{m\varepsilon_0}}$$



Kittel

There is no magnetic component of the wave.

Plasma waves can be quantized like any other wave

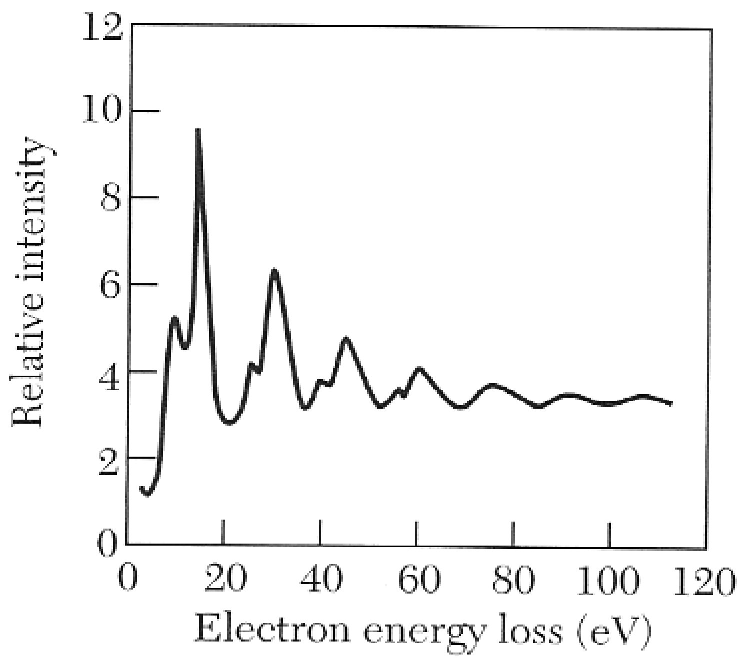


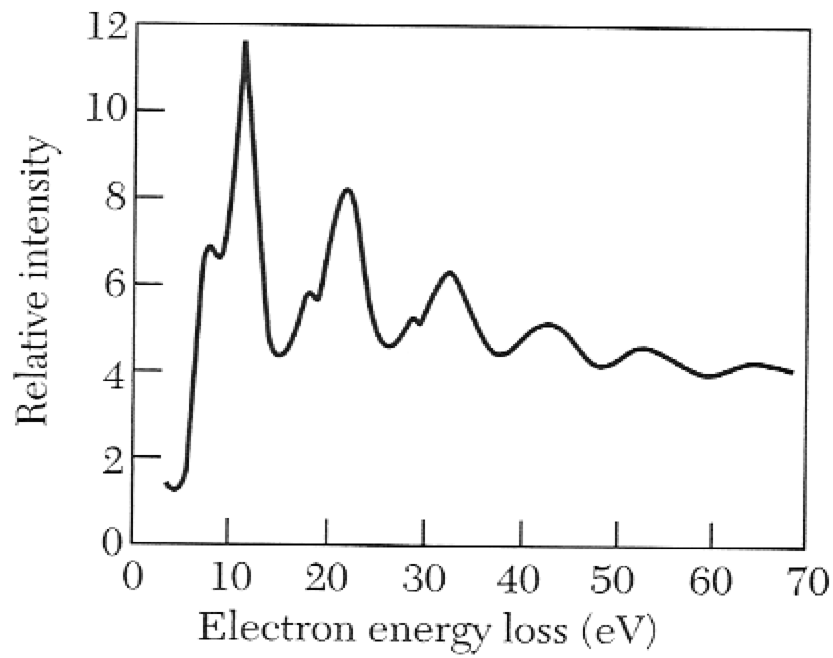
Electron energy loss spectroscopy

$$\Delta E = n\hbar\omega_p$$

EELS is often used to measure phonons

Electron energy loss spectroscopy





Aluminum

Plasmons 15.3 eV

Surface plasmons 10.3 eV

Magnesium

Plasmons 10.6 eV

Surface plasmons 7.1 eV

Transverse optical plasma waves

The dispersion relation for light

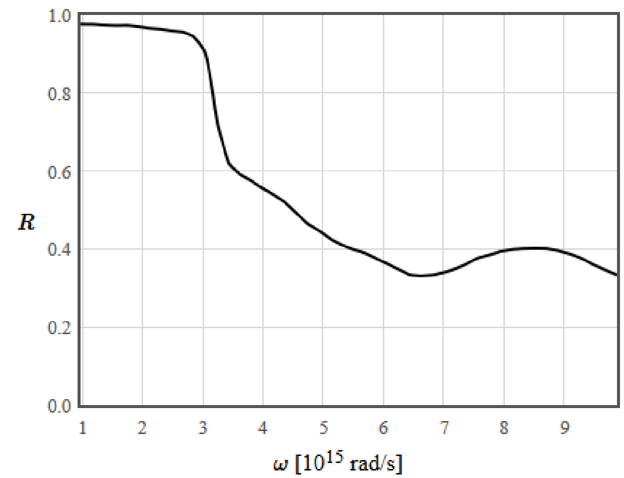
$$\varepsilon\varepsilon_0\mu_0\omega^2 = \frac{\varepsilon\omega^2}{c^2} = k^2$$

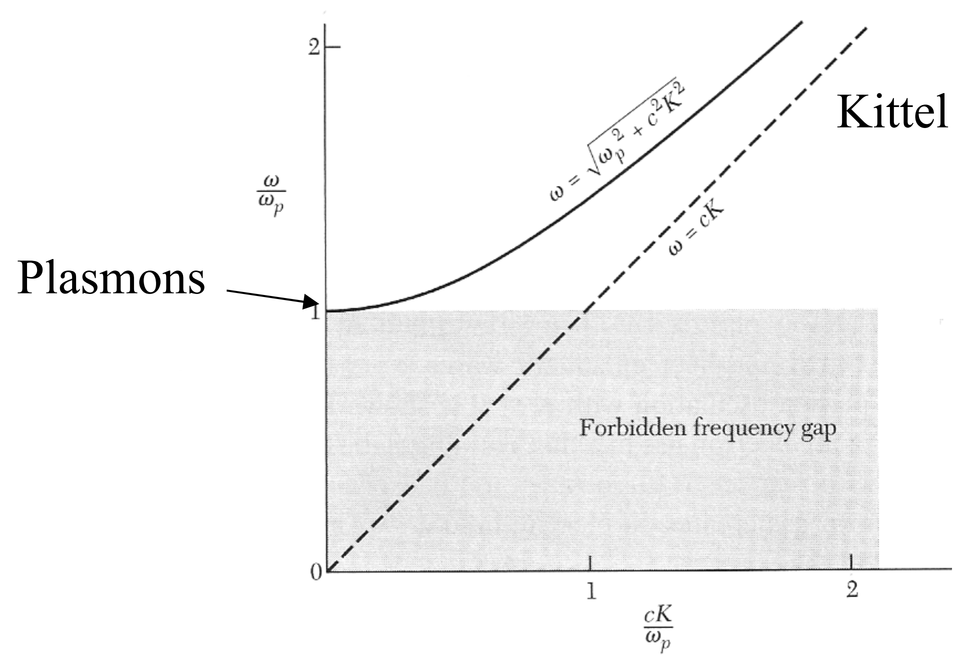
For a free electron gas

$$\varepsilon = 1 - \frac{\omega_p^2}{\omega^2}$$

$$\left(1 - \frac{\omega_p^2}{\omega^2}\right)\omega^2 = c^2k^2$$

$$\omega^2 = \omega_p^2 + c^2k^2$$

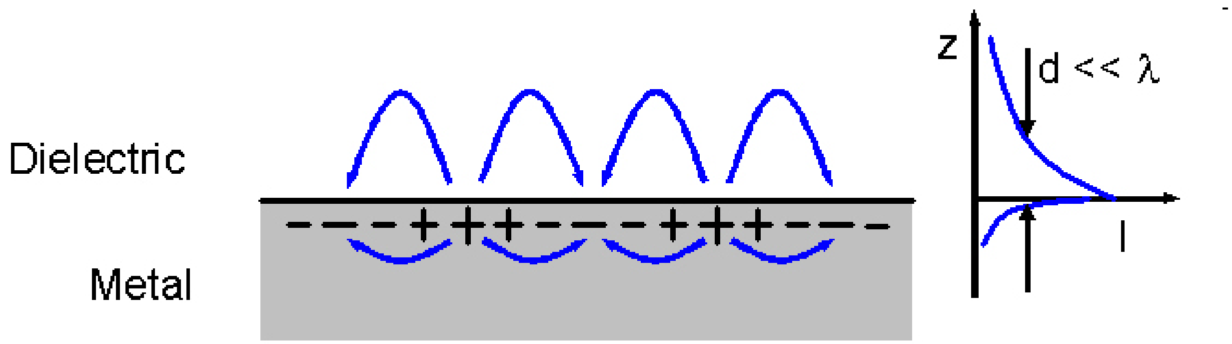




Surface Plasmons

Waves in the electron density at the boundary of two materials.

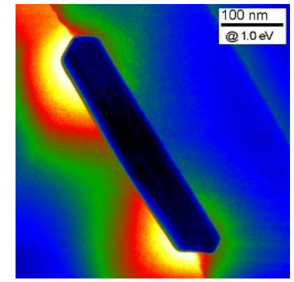
Surface plasmons have a lower frequency that bulk plasmons. This confines them to the interface.



Surface Plasmons

High-resolution surface plasmon imaging of gold nanoparticles by energy-filtered transmission electron microscopy

PHYSICAL REVIEW B 79, 041401 R 2009



Surface plasmons on nanoparticles are efficient at scattering light.

Green and blue require different sized particles.

Nature Photonics

LETTERS

Organic plasmon-emitting diode

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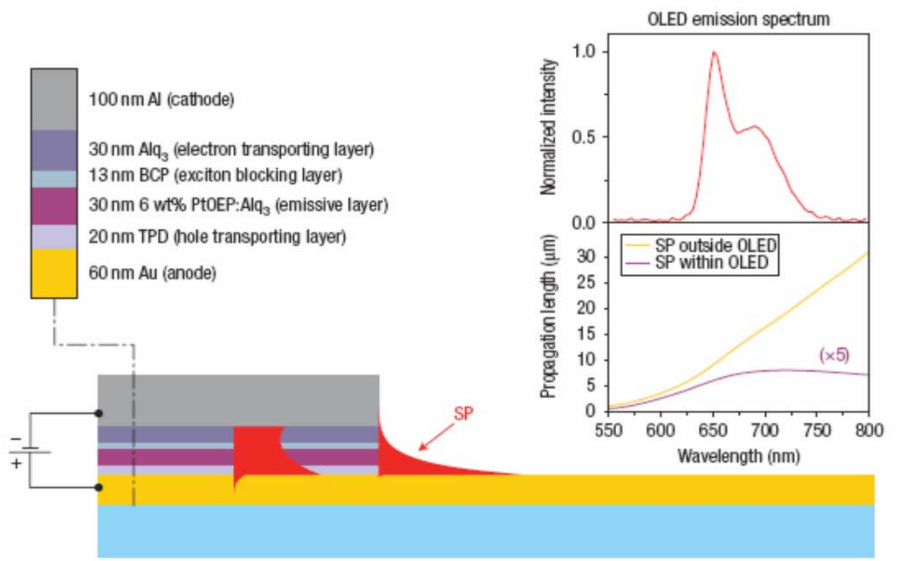
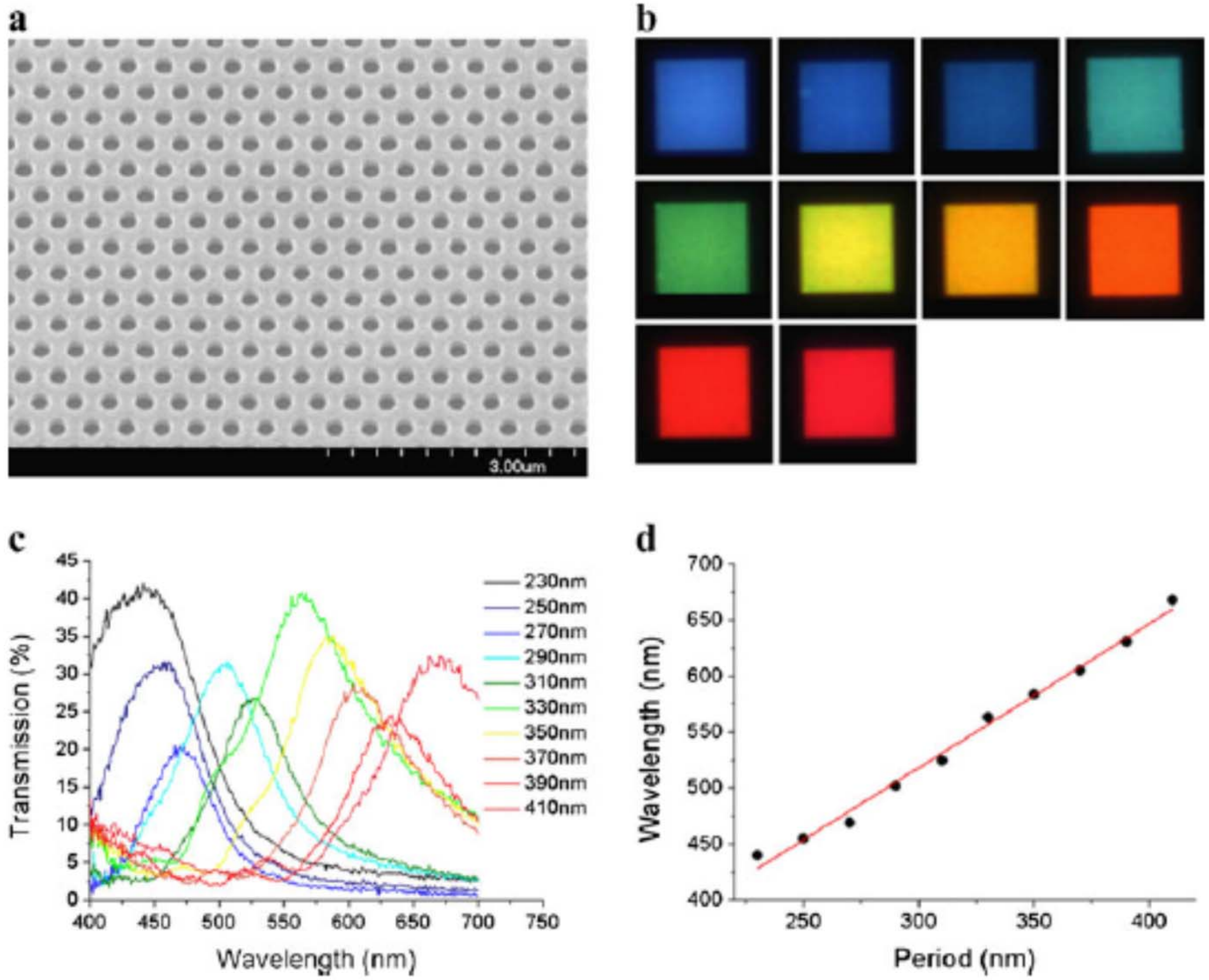
Surface plasmons are hybrid modes of longitudinal electron oscillations and light fields at the interface of a metal and a dielectric[1,2]. Driven by advances in nanofabrication, imaging and numerical methods[3,4], a wide range of plasmonic elements such as waveguides[5,6], Bragg mirrors[7], beamsplitters[8], optical modulators[9] and surface plasmon detectors[10] have recently been reported. For introducing dynamic functionality to plasmonics, the rapidly growing field of organic optoelectronics[11] holds strong promise due to its ease of fabrication and integration opportunities. Here, we introduce an electrically switchable



Surface plasmons are used for biosensors.

Plasmon filter

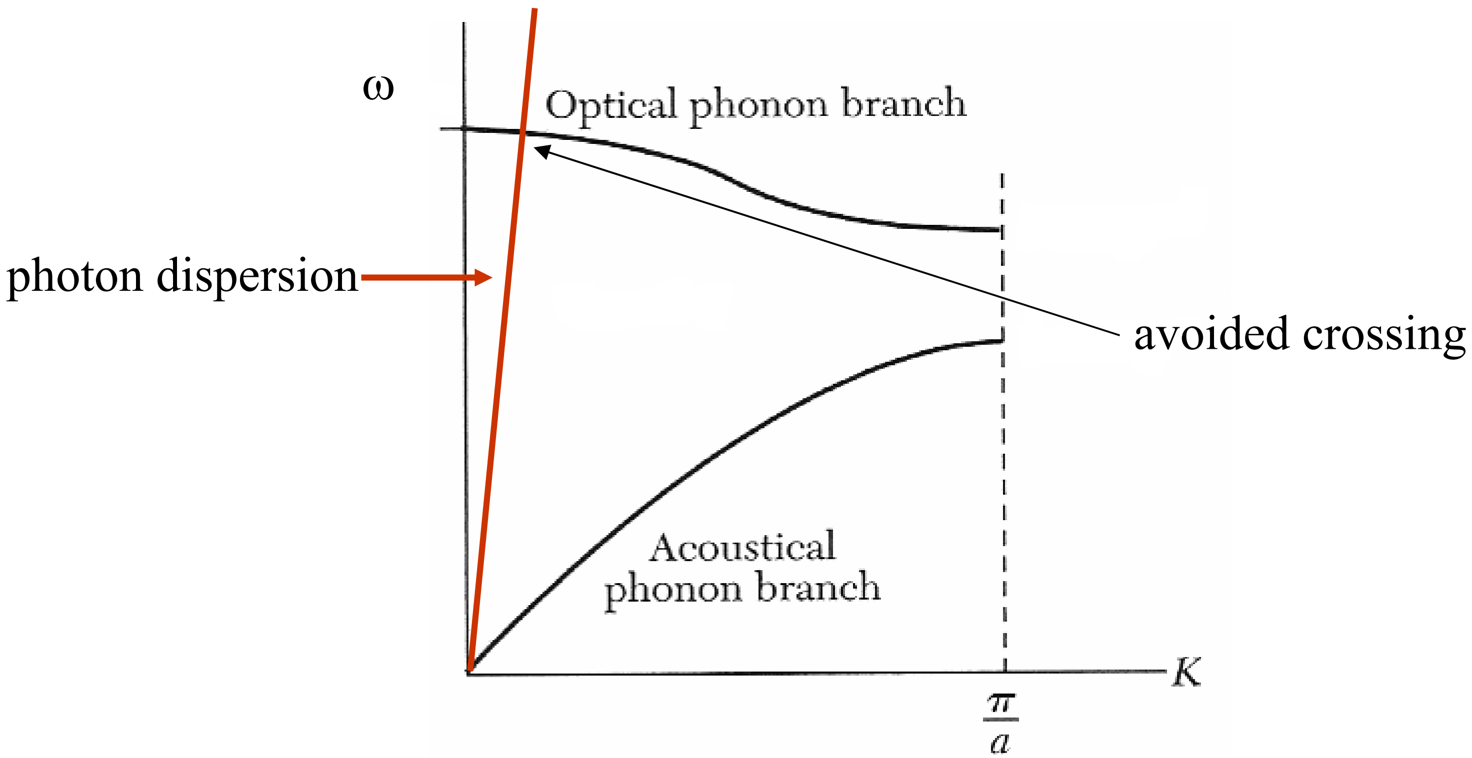


Plasmon modes on the other side of the metal films are excited.

http://web.pdx.edu/~larosaa/Applied_Optics_464-564/Lecture_Notes_Posted/2010_Lecture-7_
SURFACE%20PLASMON%20POLARITONS%20AT%20%20METALINSULATOR%20INTERFACES/Lecture_on_the_Web_SURFACE-PLASMONS-POLARITONS.pdf

Polaritons

Transverse optical phonons will couple to photons with the same ω and *k*.



Light Bragg reflects off the sound wave; sound Bragg reflects off the light wave.

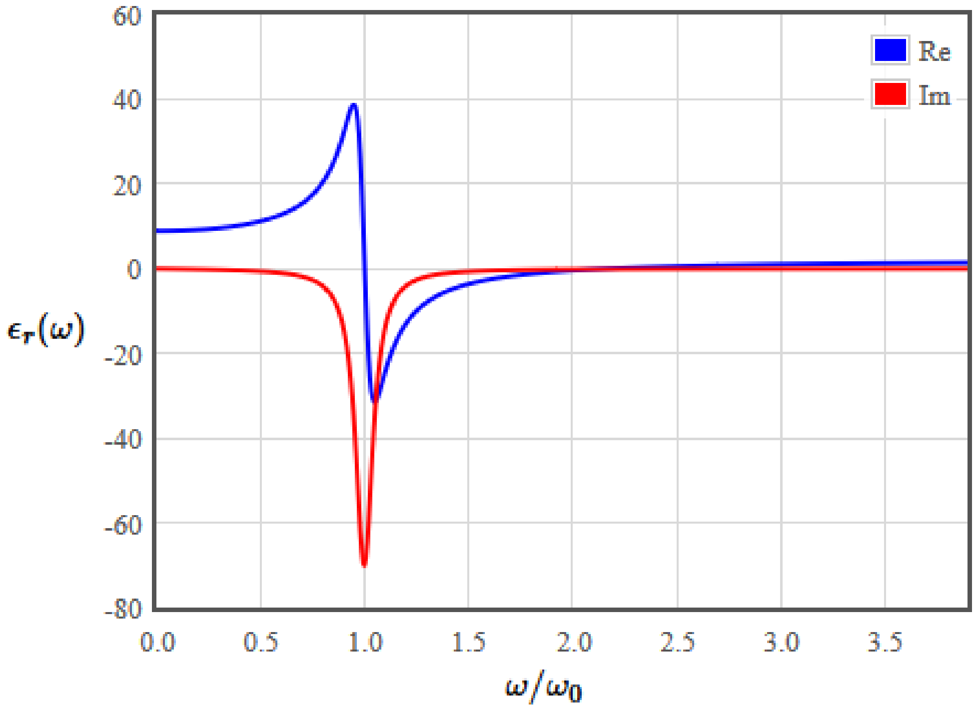
Polaritons

The dispersion relation for light

$$\varepsilon\varepsilon_0\mu_0\omega^2 = \frac{\varepsilon\omega^2}{c^2} = k^2$$

For an insulator

$$\epsilon_r(\omega) = \epsilon(\infty) + \frac{\omega_0^2(\epsilon(0)-\epsilon(\infty))}{\omega_0^2-\omega^2+i\gamma\omega}$$



The description of polaritons is already built into the dielectric function.

Polaritons

Ignore the loss term $i\gamma\omega$

$$\varepsilon(\omega) = \varepsilon(\infty) + \frac{\omega_0^2\left(\varepsilon(0) - \varepsilon(\infty)\right)}{\omega_0^2 - \omega^2}$$

Use a common denominator

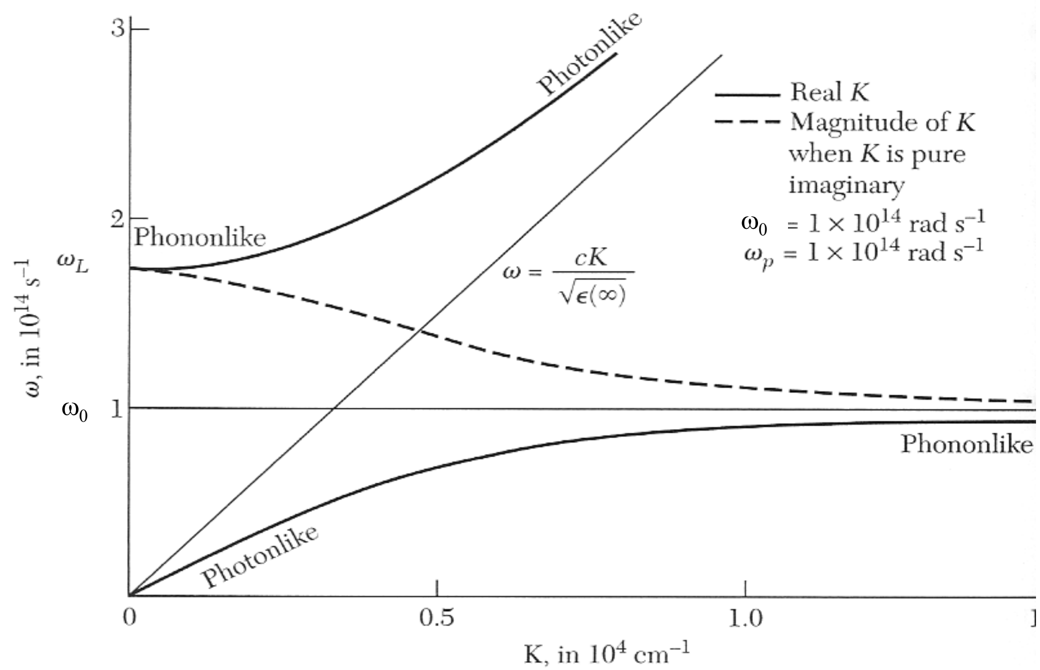
$$\varepsilon(\omega) = \frac{\varepsilon(\infty)\left(\omega_0^2 - \omega^2\right) + \omega_0^2\left(\varepsilon(0) - \varepsilon(\infty)\right)}{\omega_0^2 - \omega^2}$$

Define ω_L $\quad \omega_0^2\varepsilon(0) = \varepsilon(\infty)\omega_L^2$

$$\varepsilon(\omega) = \varepsilon(\infty)\frac{\omega_L^2 - \omega^2}{\omega_0^2 - \omega^2}$$

Polaritons

$$\varepsilon(\infty)\frac{\omega_L^2-\omega^2}{\omega_0^2-\omega^2}\frac{\omega^2}{c^2}=k^2$$

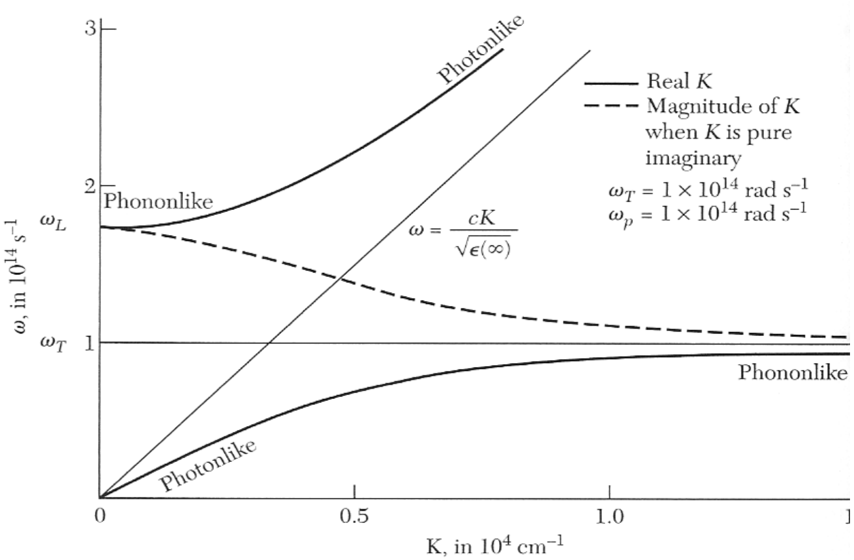


There are two solutions for every k, one for the upper branch and one for the lower branch.

A gap exists in frequency.

Polaritons are the normal modes near the avoided crossing.

Polaritons allow us to study the properties of phonons using optical measurements



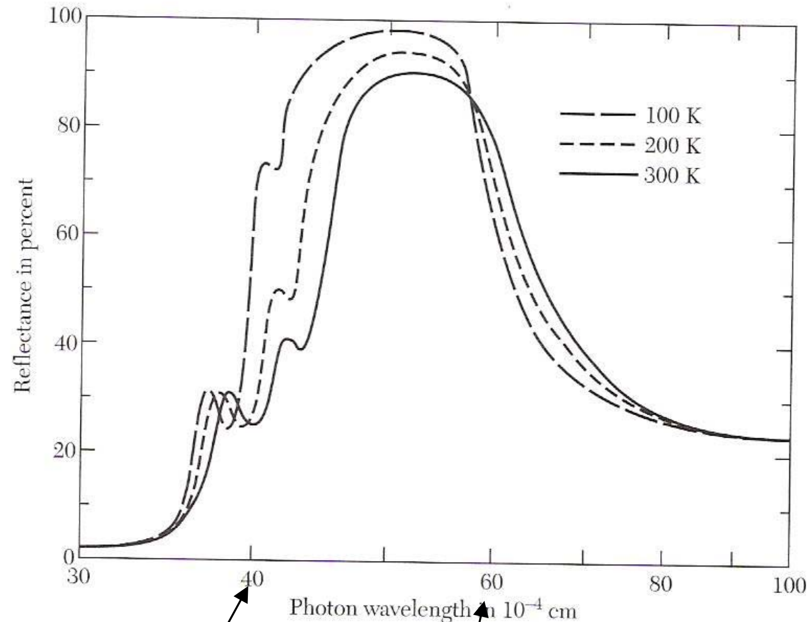


Figure 15 Reflectance of a crystal of NaCl at several temperatures, versus wavelength. The nominal values of ω_L and ω_T at room temperature correspond to wavelengths of 38 and 61 × 10^{-4} cm, respectively. (After A. Mitsuishi et al.)

ω = 4.7E13

ω = 3.1E13

Kittel

By looking at the reflectance in different crystal directions, you can determine the frequencies of the transverse optical phonons.

Polaritons and optical properties

Print version

Advanced Solid State Physics

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- Linear response
- Transport
- Crystal Physics
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- Quasiparticles
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Optical properties of insulators and semiconductors

In an insulator, all charges are bound. By applying an electric field, the electrons and ions can be pulled out of their equilibrium positions. When this electric field is turned off, the charges oscillate as they return to their equilibrium positions. A simple model for an insulator can be constructed by describing the motion of the charge as a damped mass-spring system. The differential equation that describes the motion of a charge is,

$$m\frac{d^2x}{dt^2}+b\frac{dx}{dt}+kx=-qE.$$

Rewriting above equation using $\omega_0=\sqrt{\frac{k}{m}}$ and the damping constant $\gamma=\frac{b}{m}$ yields,

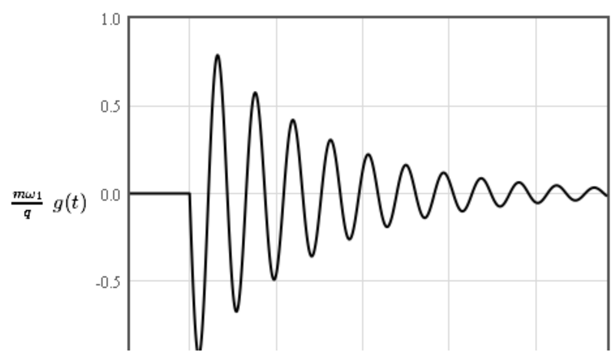
$$\frac{d^2x}{dt^2}+\gamma\frac{dx}{dt}+\omega_0^2x=-\frac{qE}{m}.$$

If the electric field is pulsed on, the response of the charges is described by the **impulse response function** $g(t)$. The impulse response function satisfies the equation,

$$\frac{d^2g}{dt^2}+\gamma\frac{dg}{dt}+\omega_0^2g=-\frac{q}{m}\delta(t).$$

The solution to this equation is zero before the electric field is pulsed on and at the time of the pulse the charges suddenly start oscillating with the frequency $\omega_1=\sqrt{\omega_0^2-\frac{\gamma^2}{4}}$. The amplitude of the oscillation decays exponentially to zero in a characteristic time $\frac{2}{\gamma}$.

$$g(t)=-\frac{q}{m\omega_1}\exp\left(-\frac{\gamma}{2}t\right)\sin(\omega_1 t).$$

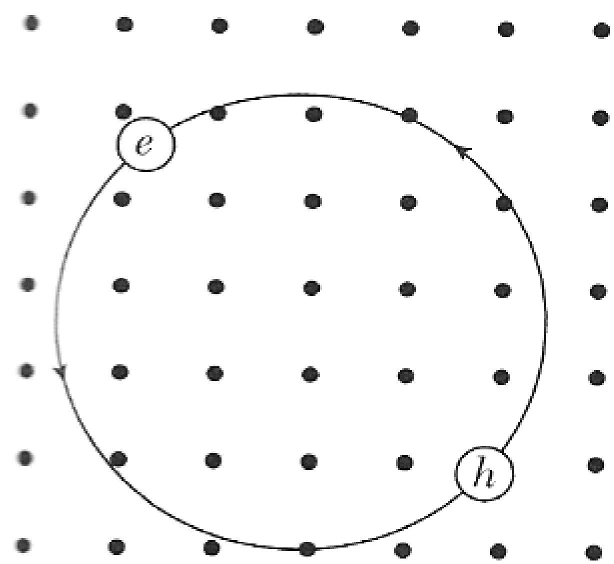


Excitons

Bound state of an electron and a hole in a semiconductor or insulator

Mott Wannier excitons

(like positronium)



Mott-Wannier Excitons

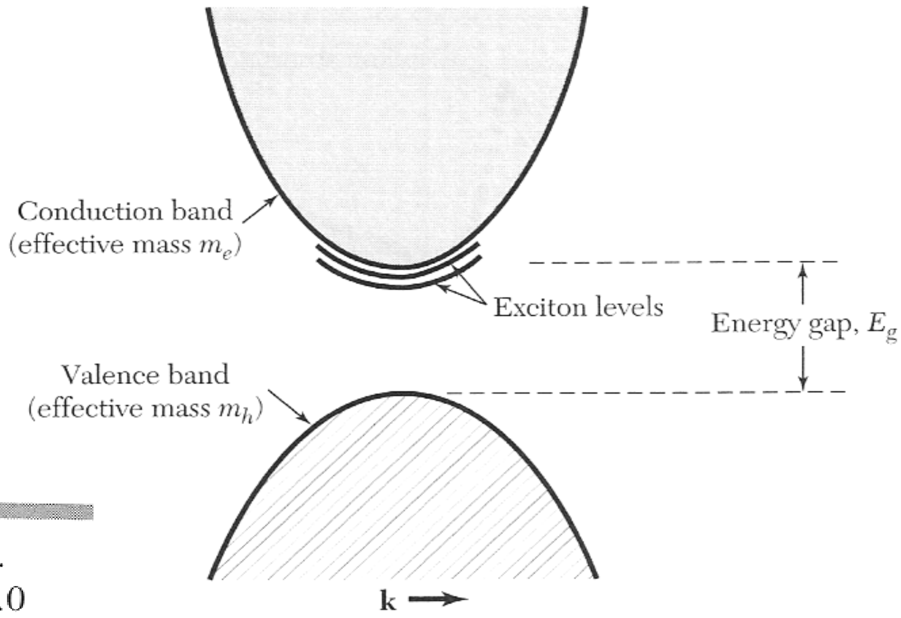
Bound state of an electron and a hole in a semiconductor or insulator (like positronium)

Hydrogenic model

$$E_{n,K} = E_g - \frac{\mu^* e^4}{32\pi^2\hbar^2\varepsilon^2\varepsilon_0^2 n^2} + \frac{\hbar^2 K^2}{2\left(m_h^* + m_e^*\right)}$$

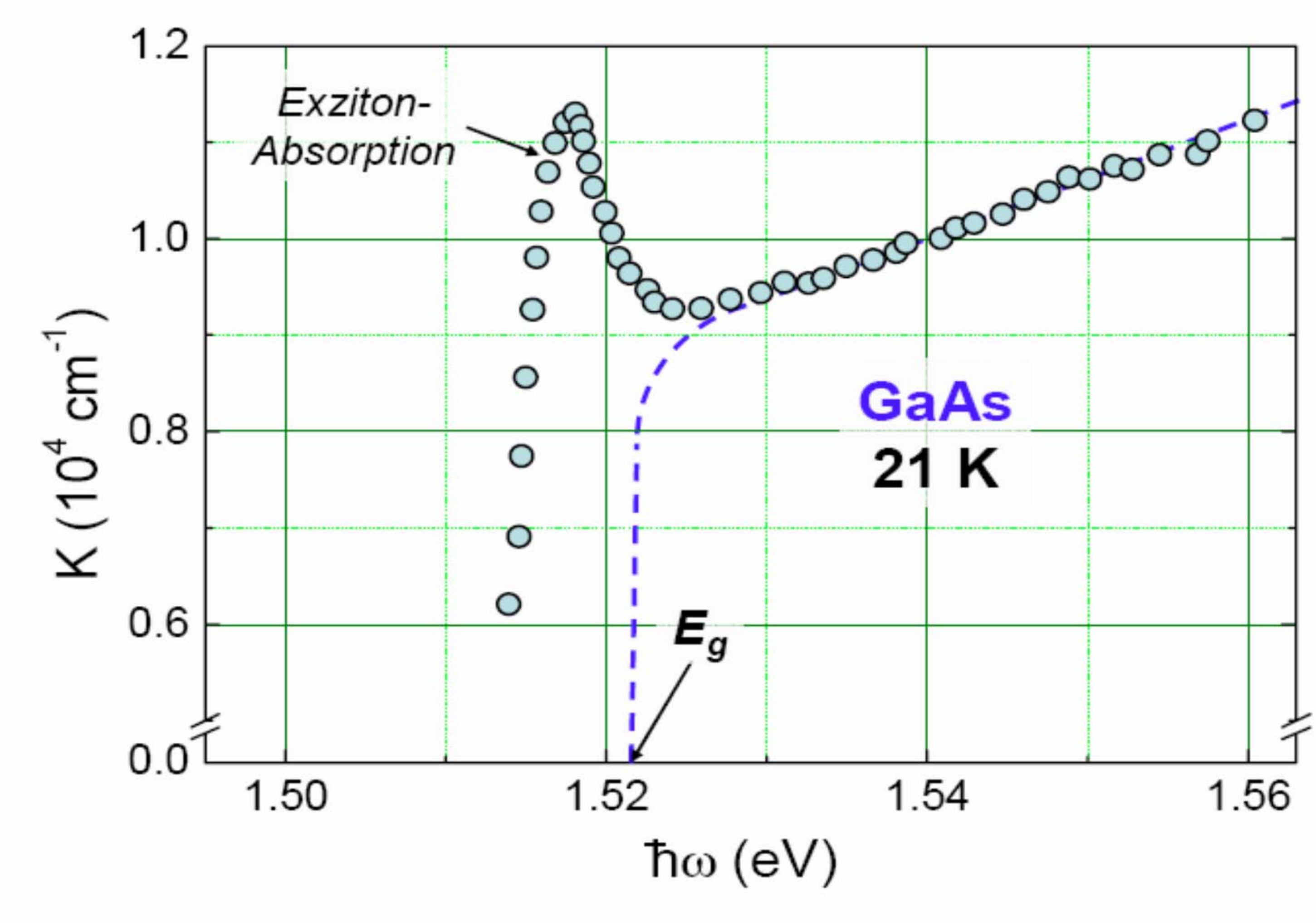
Table 1 Binding energy of excitons, in meV

Si	14.7	BaO	56.
Ge	4.15	InP	4.0
GaAs	4.2	InSb	(0.4)
GaP	3.5	KI	480.
CdS	29.	KCl	400.
CdSe	15.	KBr	400.



Kittel

Excitons



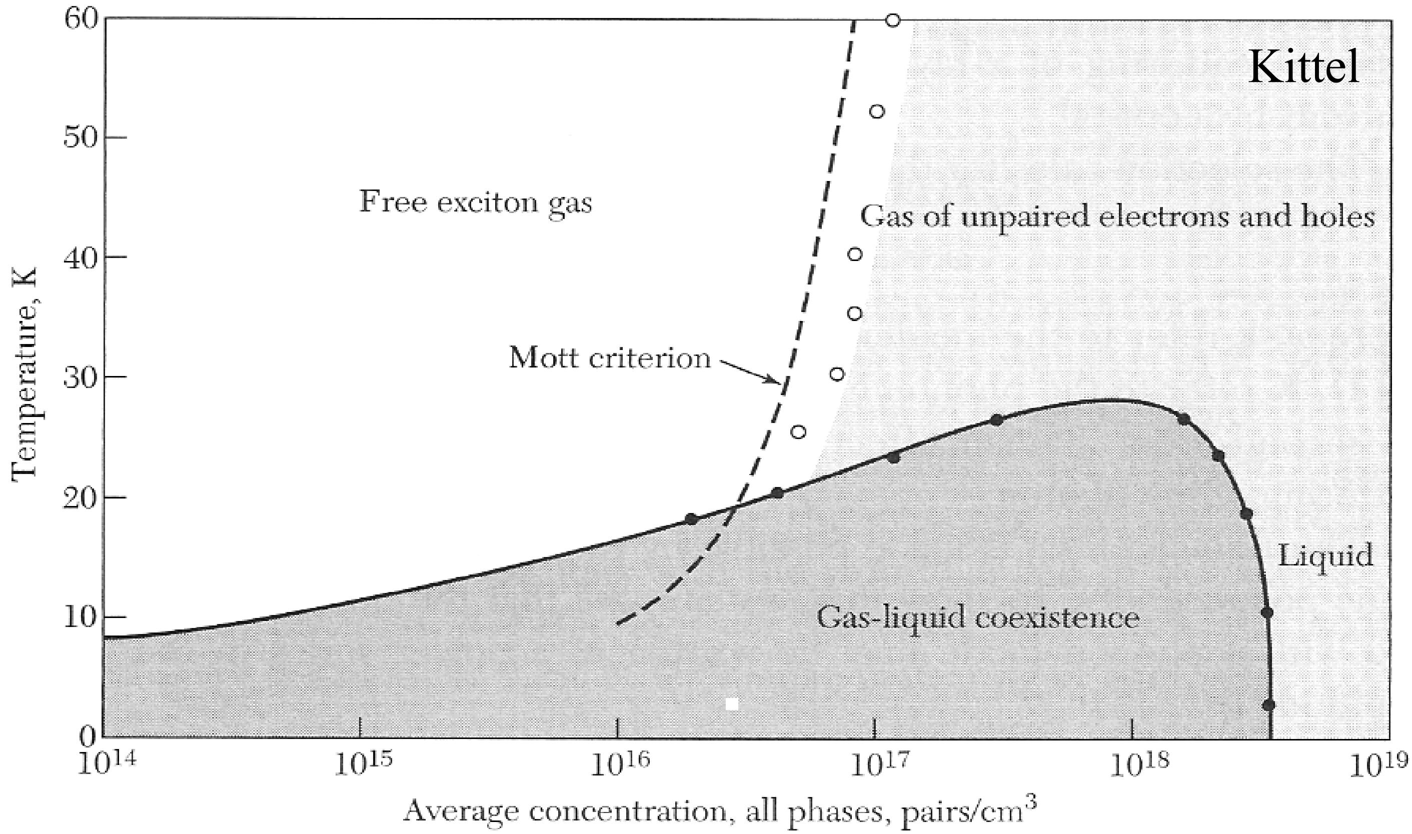
Gross & Marx

Excitons

Biexcitons H_2?

Metallic plasma droplets

Observe with an infrared camera



Phase diagram for photoexcited electrons and holes in unstressed silicon.

See: C. D. Jeffries, Electron-Hole Condensation in Semiconductors, Science 189 p. 955 (1975).