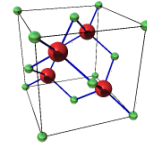


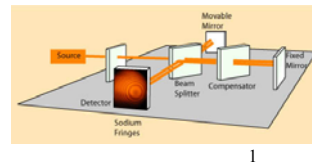
Phys 446:



Solid State Physics / Optical Properties

Lattice vibrations: optical properties and Raman scattering

Fall 2007



Lecture 6

Andrei Sirenko, NJIT

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Last week: (Ch. 3)

- Phonons, Einstein and Debye models, QZ1 results

• Today:

Optical Properties, Raman scattering, Thermal conductivity
Introduction to metals (Ch. 4)

Some Thermal Conductivities*	
Substance	k (W/m-K)
<i>Metals</i>	
Stainless steel	14
Lead	35
Aluminum	235
Copper	401
Silver	428
<i>Gases</i>	
Air (dry)	0.026
Helium	0.15
Hydrogen	0.18
<i>Building Materials</i>	
Polyurethane foam	0.024
Rock wool	0.043
Fiberglass	0.048
White paint	0.11
Window glass	1.0

*Conductivities change somewhat with temperature. The given values are at room temperature.

Thermal Conductivity

Temperature gradient in a material → heat flow from the hotter to the cooler end.

Heat current density j (amount of heat flowing across unit area per unit time) is proportional to the temperature gradient (dT/dx):

$$j_u = -K \frac{dT}{dx} \quad K - \text{thermal conductivity}$$

- In metals the heat is carried both by electrons and phonons; electron contribution is much larger
- In insulators, there are no mobile electrons ⇒ heat is transmitted entirely by phonons

Heat transfer by phonons

- *phonon gas*: in every region of space there are phonons traveling randomly in all directions, much like the molecules in an ordinary gas
- phonon concentration is larger at the hotter end → they move to the cooler end
- the advantage of using this gas model: can apply familiar concepts of the kinetic theory of gases

Elementary kinetic considerations:

if c is the heat capacity of the single particle, then moving from region with $T+\Delta T$ to a T , particle will give up energy $c\Delta T$

$$\Delta T \text{ between the ends of the free path length } l_x: \Delta T = \frac{dT}{dx} l_x = \frac{dT}{dx} v_x \tau$$

where τ is the average time between collisions

The net energy flux (n – concentration):

$$j_u = -n \langle v_x^2 \rangle \frac{dT}{dx} c \tau = -\frac{1}{3} n \langle v^2 \rangle c \tau \frac{dT}{dx}$$

for phonons, v is constant. $nc = C$; $l = v\tau$

$$\Rightarrow j_u = -\frac{1}{3} C v l \frac{dT}{dx} \quad \Rightarrow K = \frac{1}{3} C v l \quad - \text{phonon thermal conductivity}$$

Dependence of the thermal conductivity on temperature

- C_v dependence on temperature has already been discussed
- Sound velocity v essentially insensitive to temperature
- The mean free path l depends strongly on temperature

Three important mechanisms are to be considered:

- collision of a phonon with other phonons
- collision of a phonon with imperfections in the crystal
- collision of a phonon with the external boundaries of the crystal

The phonon-phonon scattering is due to the *anharmonic interaction*.
If interatomic forces are purely harmonic – no phonon-phonon interaction.

At high temperature atomic displacements are large \Rightarrow stronger anharmonism \Rightarrow phonon-phonon collisions become more important

At high T the mean free path $l \propto 1/T$: number of phonons $n \propto T$ at high T
collision frequency $\propto n \Rightarrow l \propto 1/n$

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Suppose that two phonons of vectors \mathbf{q}_1 and \mathbf{q}_2 collide, and produce a third phonon of vector \mathbf{q}_3 .

Momentum conservation: $\mathbf{q}_3 = \mathbf{q}_1 + \mathbf{q}_2$

\mathbf{q}_3 may lie inside the Brillouin zone, or not. If it's inside \rightarrow momentum of the system before and after collision is the same.

This is a *normal process*. It has no effect at all on thermal resistivity, since it has no effect on the flow of the phonon system as a whole.

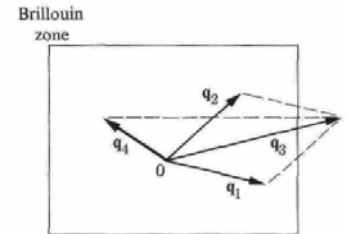
If \mathbf{q}_3 lies outside the BZ, we reduce it to equivalent \mathbf{q}_4 inside the first BZ: $\mathbf{q}_3 = \mathbf{q}_4 + \mathbf{G}$

Momentum conservation: $\mathbf{q}_1 + \mathbf{q}_2 = \mathbf{q}_4 + \mathbf{G}$

The difference in momentum is transferred to the center of mass of the lattice.

This type of process is known as the *umklapp process*

- highly efficient in changing the momentum of the phonon
- responsible for phonon scattering at high temperatures



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The second mechanism - phonon scattering results from defects.

Impurities and defects scatter phonons because they partially destroy the periodicity of the crystal.

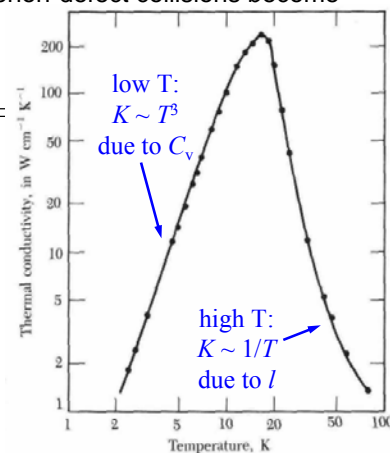
At very low T, both phonon-phonon and phonon-defect collisions become ineffective:

- there are only a few phonons present,
- the phonons are long-wavelength ones = not effectively scattered by defects, which are much smaller in size

In the low-temperature region, the primary scattering mechanism is the external boundary of the specimen - so-called *size* or *geometrical effects*.

Becomes effective because the phonon wavelengths are very long - comparable to the size of the sample L .

The mean free path here is $l \sim L$
 \Rightarrow independent of temperature.



Thermal conductivity of NaF (highly purified) 7

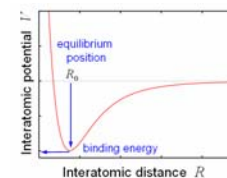
Anharmonism

So far, lattice vibrations were considered in harmonic approximation. Some consequences:

- Phonons do not interact; no decay
- No thermal expansion
- Elastic constants are independent of pressure and temperature
- Heat capacity is constant at high T ($T \gg \theta_D$).

Anharmonic terms in potential energy:

$$U(x) = cx^2 - gx^3 - fx^4 \quad x - \text{displacement from equilibrium separation at } T = 0$$



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Thermal expansion

Calculate average displacement using Boltzmann distribution function:

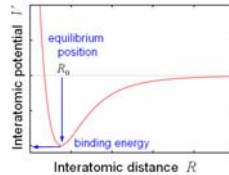
$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x e^{-U(x)/k_B T} dx}{\int_{-\infty}^{\infty} e^{-U(x)/k_B T} dx}$$

If anharmonic terms are small, can use Taylor expansion for exponent

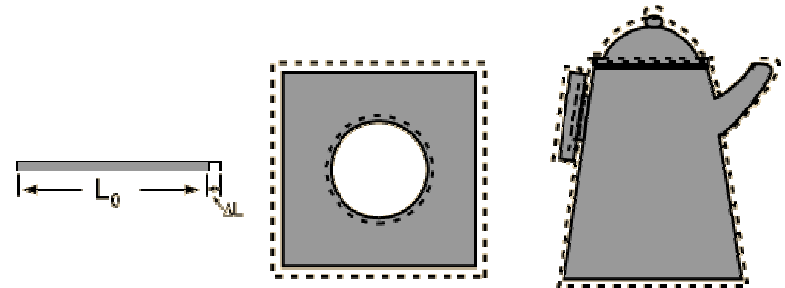
$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx e^{-cx^2/k_B T} \left(x + \frac{gx^4}{k_B T} + \frac{fx^5}{k_B T} \right)}{\int_{-\infty}^{\infty} dx e^{-cx^2/k_B T}} = \frac{3\pi^{1/2} g (k_B T)^{3/2}}{4 c^{5/2} (k_B T)^{1/2}} = \frac{3g}{4c^2} k_B T$$

thermal expansion

Origin of thermal expansion – asymmetric potential



Thermal expansion from Phys 103



Linear expansion
 $\frac{\Delta L}{L_0} = \alpha \Delta T$

Area expansion
 $\frac{\Delta A}{A_0} = 2\alpha \Delta T$

Volume expansion
 $\frac{\Delta V}{V_0} = 3\alpha \Delta T$

$$\langle x \rangle = \frac{3g}{4c^2} k_B T$$

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Techniques for probing lattice vibrations

- Inelastic X-ray scattering
- Neutron scattering
- Infrared spectroscopy
- Brillouin and Raman scattering

Inelastic X-ray scattering

$\mathbf{k} = \mathbf{k}_0 \pm \mathbf{q}$ $\hbar\omega = \hbar\omega_0 \pm \hbar\Omega(\mathbf{q})$ assumed $\Omega(\mathbf{q}) \ll \omega_0$
 - true for x-rays:
 $\hbar\Omega < 100 \text{ meV}$; $\hbar\omega_0 \sim 10^4 \text{ eV}$
 n – index of refraction
 $q = 2k_0 \sin \theta = 2n \frac{\omega_0}{c} \sin \theta$

measuring $\omega - \omega_0$ and $\theta \sin$ one can determine dispersion $\Omega(\mathbf{q})$

main disadvantage – difficult to measure $\omega - \omega_0$ accurately

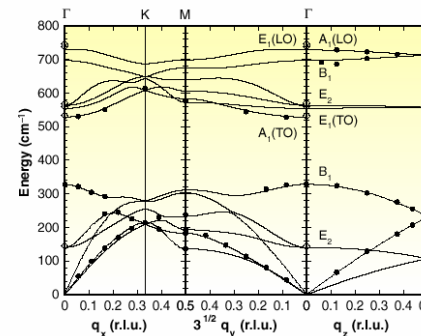
This difficulty can be overcome by use of **neutron scattering**

Energy of "thermal" neutrons is comparable with $\hbar\Omega$ (80 meV for $\lambda \approx 1 \text{ \AA}$)

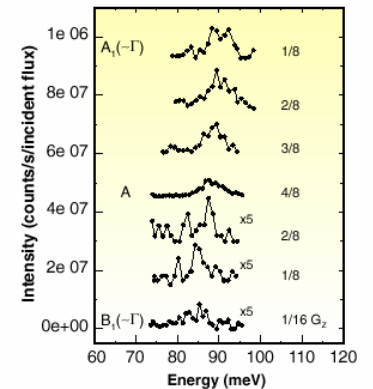
Techniques for probing lattice vibrations

- Inelastic X-ray scattering in GaN

$\mathbf{k} = \mathbf{k}_0 \pm \mathbf{q}$ $\hbar\omega = \hbar\omega_0 \pm \hbar\Omega(\mathbf{q})$
 $q = 2k_0 \sin \theta = 2n \frac{\omega_0}{c} \sin \theta$



Phonon dispersion of wurtzite GaN (filled circles: IXS data; solid lines: ab initio lattice-dynamical calculation).



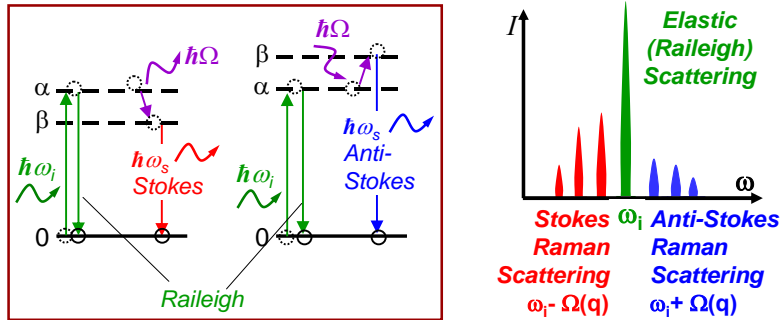
IXS spectra of wurtzite GaN along I-A. Values of q_2 (in units of $G_2 = 2\pi/c$) are given next to each spectrum.

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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^{1,3}

Raman scattering in crystalline solids

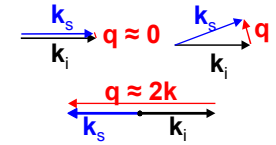
Not every crystal lattice vibration can be probed by Raman scattering. There are certain **Selection rules**:

1. Energy conservation:

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

2. Momentum conservation:

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



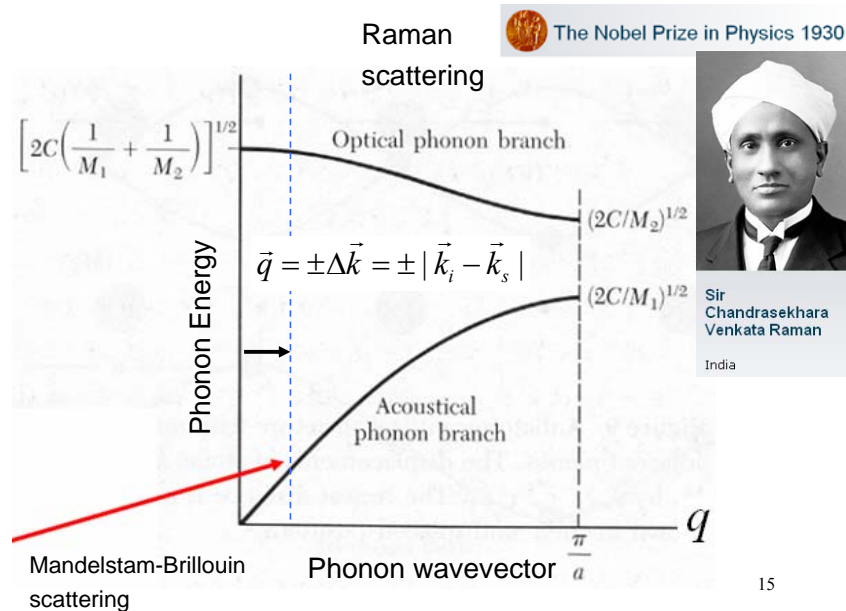
$$\lambda_i \sim 5000 \text{ \AA}, a_0 \sim 4-5 \text{ \AA} \Rightarrow \lambda_{\text{phonon}} \gg a_0$$

\Rightarrow only small wavevector (close to BZ center) phonons are seen in the 1st 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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Raman scattering in crystalline solids

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THE 1930 NOBEL PRIZE FOR PHYSICS: A CLOSE DECISION?

by

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SUMMARY

Raman scattering (in Russia called combination scattering) was discovered in 1928 by Indian and Russian scientists, at almost the same time. In 1930, the Nobel Prize for Physics was awarded to the Indian scientist Sir C.V. Raman, F.R.S., while the Russian scientists G.S. Landsberg and L.I. Mandelstam were rejected. The reasons for this are illustrated by analysing the nomination letters for the three scientists, as well as the report of the Nobel Committee for the year 1930.

INTRODUCTION

In 1930, the coveted Nobel Prize for Physics was awarded to Sir C.V. Raman (1888–1970) for his achievements in the field of light scattering and the discovery of the Raman effect. The effect deals with the scattering of monochromatic light from substances. The spectrum of the scattered light gives information about the molecular structure.

The discovery of the effect was hailed by an American physicist R.W. Wood (1868–1955) as ‘...one of the best convincing proofs of the quantum theory’. Due to the simplicity of the apparatus, the application of the discovery in the field of experimental and theoretical physics grew rapidly. Within two years and five months, 385 papers and five special monographs were published. The significance of the invention was so evident that the Nobel Committee decided to honour the discoverer within two years of the discovery.’

However, in the past, questions have been raised about the sharing of the prize between the Russian scientists and Raman. For example, the authors R.G.W. Brown and E.R. Pike write, ‘...in view of all the circumstances, however, it would be interesting to know why it was not shared with the Russians’. Similarly, Raman’s biographer, G.H. Keswani, asked, ‘Why did the Nobel Committee for physics not vote for the sharing of the prize: by the ... Russians?’ The famous Russian scientist L.L. Fabelinski pointed out: ‘In 1930 ... the Nobel Prize in physics was awarded to Raman alone for the discovery of combination scattering’, and ‘There remains the question why the Russian physicists were not awarded the Nobel Prize for physics

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Raman scattering



The Nobel Prize in Physics 1930



Sir Chandrasekhara Venkata Raman

India

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Example of Raman scattering in crystalline solids

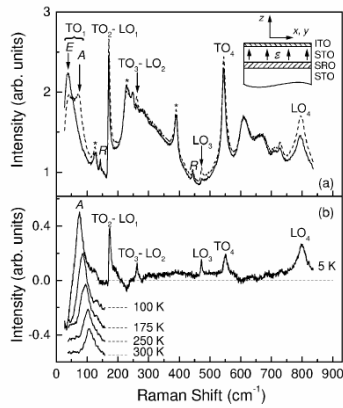
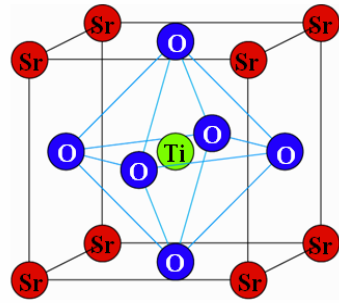


FIG. 1. (a) Solid and dotted lines show the Raman spectra of 1 μm STO film at $T = 5$ K without electric field and in the presence of an external electric field of 22×10^4 V/cm directed normal to the film plane, respectively. The soft-mode components are labeled A and E. Structural modes are denoted 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 $\mathcal{E} = 22 \times 10^4$ V/cm from that at $\mathcal{E} = 0$ 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

$$2 \times TO_1 + LO_1$$

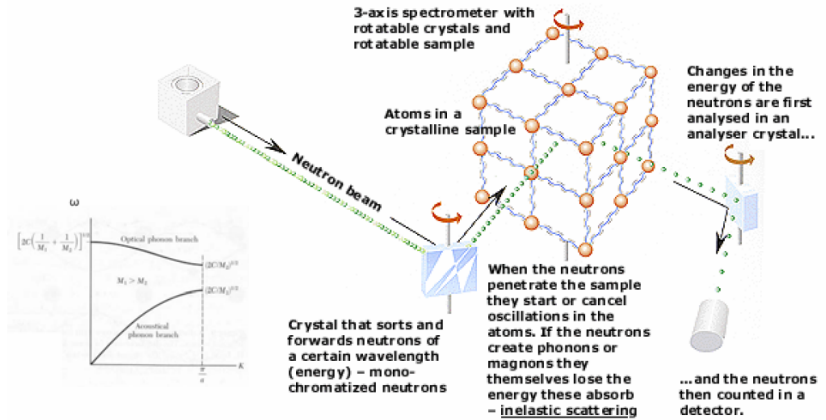
$$2 \times TO_2 + LO_2$$

$$2 \times TO_3 + LO_3$$

$$2 \times TO_4 + LO_4$$

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- How do we measure dispersion curves? Inelastic neutron scattering
- If you can measure the energy lost by the neutron (by causing a vibration in the solid), and you can measure which direction you created the wave (the wavevector), then you can construct a dispersion curve



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Summary

- ❖ Phonon thermal conductivity
$$K = \frac{1}{3} C v l$$
- ❖ Mechanisms of phonon scattering affecting thermal resistivity:
 - umklapp processes of phonon-phonons collision – important at high T
 - collision of a phonon with defects and impurities in the crystal
 - collision of a phonon with the external boundaries of the crystal – important at low T
- ❖ Anharmonicity of potential energy is responsible for such effects as:
 - phonon-phonon interaction
 - thermal expansion
- ❖ Techniques for probing lattice vibrations:
 - Inelastic X-ray scattering, Neutron scattering,
 - Infrared spectroscopy, Brillouin and Raman scattering
 - Electron energy loss spectroscopy

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Optical Properties of Solids

Dielectric function formalism

Phonon contribution to Dielectric function and

Light interaction with Phonons

(in this Lecture K is a wavevector of light)

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The interaction of radiation with matter

Name	Differential form	Integral form
Gauss's law:	$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0}$	$\oint_S \mathbf{E} \cdot d\mathbf{A} = \frac{Q_S}{\epsilon_0}$
Gauss' law for magnetism (absence of magnetic monopoles):	$\nabla \cdot \mathbf{B} = 0$	$\oint_S \mathbf{B} \cdot d\mathbf{A} = 0$
Faraday's law of induction:	$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$	$\oint_{\partial S} \mathbf{E} \cdot d\mathbf{l} = -\frac{d\Phi_{B,S}}{dt}$
Ampère's Circuital Law (with Maxwell's correction):	$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t}$	$\oint_{\partial S} \mathbf{B} \cdot d\mathbf{l} = \mu_0 I_S + \mu_0 \epsilon_0 \frac{d\Phi_{E,S}}{dt}$

$$\nabla = \mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z}$$

$\mathbf{P} = \chi_e \epsilon_0 \mathbf{E}$
 $\mathbf{M} = \chi_m \mathbf{H}$
 and the \mathbf{D} and \mathbf{B} fields are related to \mathbf{E} and \mathbf{H} by:

$$\mathbf{D} = \hat{\epsilon}(\omega) \mathbf{E}$$

$$c = \frac{c_0}{n} = \frac{1}{\sqrt{\mu \epsilon}}$$

where

$$n = \sqrt{\frac{\mu \epsilon}{\mu_0 \epsilon_0}}$$

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = (1 + \chi_e) \epsilon_0 \mathbf{E} = \epsilon \mathbf{E}$$

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) = (1 + \chi_m) \mu_0 \mathbf{H} = \mu \mathbf{H}$$

$$\mathbf{j} = \hat{\sigma}(\omega) \mathbf{E}$$

χ_e is the electrical susceptibility of the material,
 χ_m is the magnetic susceptibility of the material,
 ϵ is the electrical permittivity of the material, and
 μ is the magnetic permeability of the material

Symbol	Name	Numerical Value	SI Unit of Measure
c	Speed of light in vacuum	2.99792458×10^8	meters per second
ϵ_0	electric constant	8.85419×10^{-12}	farads per meter
μ_0	magnetic constant	$4\pi \times 10^{-7}$	henries per meter

For your references:

Symbol	Meaning (first term is the most common)	SI Unit of Measure
$\nabla \cdot$	the divergence operator	per meter (factor contributed by applying either operator)
$\nabla \times$	the curl operator	per second (factor contributed by applying the operator)
$\frac{\partial}{\partial t}$	partial derivative with respect to time	per second (factor contributed by applying the operator)
\mathbf{E}	electric field also called the electric flux density	volt per meter or, equivalently, newton per coulomb
\mathbf{B}	Magnetic field also called the magnetic induction also called the magnetic field density also called the magnetic flux density	tesla, or equivalently, weber per square meter
ρ	electric charge density	coulomb per cubic meter
ϵ_0	Permittivity of free space, a universal constant	farads per meter
$\oint_S \mathbf{E} \cdot d\mathbf{A}$	The flux of the electric field over any closed Gaussian surface S	joule-meter per coulomb
Q_S	net unbalanced electric charge enclosed by the Gaussian surface S, including so-called Bound charges	coulombs
$\oint_S \mathbf{B} \cdot d\mathbf{A}$	The flux of the magnetic field over any closed surface S	Tesla meter-squared or weber
$\int_{\partial S} \mathbf{E} \cdot d\mathbf{l}$	line integral of the electric field along the boundary (therefore necessarily a closed curve) of the surface S	Joule per coulomb
$\Phi_{B,S} = \int_S \mathbf{B} \cdot d\mathbf{A}$	magnetic flux over any surface S (not necessarily closed)	weber
μ_0	magnetic permeability of free space, a universal constant	henries per meter, or newtons per ampere squared
\mathbf{J}	current density	ampere per square meter
$\int_{\partial S} \mathbf{B} \cdot d\mathbf{l}$	line integral of the magnetic field over the closed boundary of the surface S	tesla-meter
$I_S = \int_S \mathbf{J} \cdot d\mathbf{A}$	net electrical current passing through the surface S	amperes
$\Phi_{E,S} = \int_S \mathbf{E} \cdot d\mathbf{A}$	Electric flux over any surface S, not necessarily closed	
$d\mathbf{A}$	differential vector element of surface area A, with infinitesimally small magnitude and direction normal to surface S	square meters
$d\mathbf{l}$	differential vector element of path length tangential to contour	meters

The interaction of radiation with matter

Decoupled form of MaxEq. in vacuum:

$$\frac{\partial^2 \mathbf{E}}{\partial t^2} - c^2 \cdot \nabla^2 \mathbf{E} = 0$$

$$\frac{\partial^2 \mathbf{B}}{\partial t^2} - c^2 \cdot \nabla^2 \mathbf{B} = 0$$

Same in material medium (solid state) [SI]

$$\nabla^2 \mathbf{E} = \epsilon \mu \frac{\partial^2 \mathbf{E}}{\partial t^2} + \sigma \mu \frac{\partial \mathbf{E}}{\partial t}$$

$$\nabla^2 \mathbf{H} = \epsilon \mu \frac{\partial^2 \mathbf{H}}{\partial t^2} + \sigma \mu \frac{\partial \mathbf{H}}{\partial t}$$

[CGS]

$$\nabla^2 \mathbf{E} = \frac{\epsilon \mu}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} + \frac{4\pi \sigma \mu}{c^2} \frac{\partial \mathbf{E}}{\partial t}$$

$$\nabla^2 \mathbf{H} = \frac{\epsilon \mu}{c^2} \frac{\partial^2 \mathbf{H}}{\partial t^2} + \frac{4\pi \sigma \mu}{c^2} \frac{\partial \mathbf{H}}{\partial t}$$

Solution:

Plane EM wave (light)

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

The interaction of radiation with matter

$$\nabla^2 \mathbf{E} = \epsilon \mu \frac{\partial^2 \mathbf{E}}{\partial t^2} + \sigma \mu \frac{\partial \mathbf{E}}{\partial t}$$

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

EM wave (light)

K-vector of light:

If K is real (no losses)

$$K^2_0 = \mu_0 \epsilon_0 \omega^2 = \frac{\omega^2}{c^2} \quad K_0 = \frac{2\pi}{\lambda} = \frac{\omega}{c}$$

$$K^2 = \mu \epsilon \omega^2 + i \omega \mu \sigma = \mu_0 \epsilon_0 \omega^2 \left(\frac{\mu \epsilon}{\mu_0 \epsilon_0} + i \frac{\mu \sigma}{\mu_0 \epsilon_0 \omega} \right)$$

Loss part of K-vector

for nonmagnetic media: $\mu = \mu_0$

$$K = K_0 \sqrt{\frac{\epsilon}{\epsilon_0} + i \frac{\sigma}{\epsilon_0 \omega}} = \tilde{n} K_0$$

complex refractive index: $\tilde{n} = \sqrt{\frac{\epsilon}{\epsilon_0} + i \frac{\sigma}{\epsilon_0 \omega}} = n_R + i n_I = n_R + i \frac{\alpha(\omega)}{2K_0}$

α - absorption coefficient (m^{-1}); $\mathbf{E}_0 = E_0 e^{-\alpha z/2}$ and $I(z) = I_0 e^{-\alpha(\omega)z}$

The interaction of radiation with matter

Complex Dielectric Function

$$\epsilon_{complex}(\omega) = \epsilon + \frac{i\sigma}{\omega} = \epsilon' + i \cdot \epsilon''$$

$$\tilde{n}_{complex}(\omega) = n_R + i \cdot n_I$$

$$\epsilon'_{real} = n_R^2 - n_I^2$$

$$\epsilon''_{imaginary} = 2 \cdot n_R \cdot n_I$$

Light along z-axis:

$$\vec{E}(z,t) = \vec{E}_0 e^{-i\omega t} \exp(iKz) = \vec{E}_0 e^{-i\omega t} \exp\left[izK_0 \sqrt{\frac{\epsilon}{\epsilon_0} + i \frac{\sigma}{\epsilon_0 \omega}}\right]$$

for $\lambda \gg a$, $K_0 \approx 0$

$$\vec{D} = \epsilon \vec{E}$$

$$\vec{B} = \mu \vec{H}$$

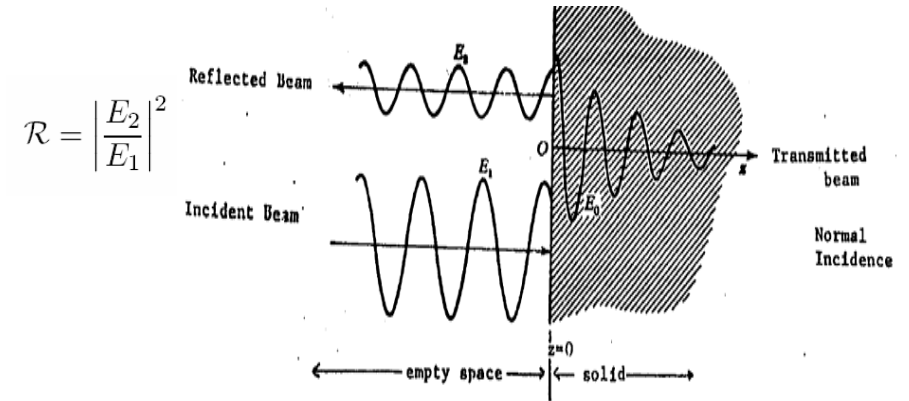
$$\vec{j} = \sigma \vec{E}$$

conductivity $\sigma_{complex}$, we will relate these quantities in two ways:

1. to observables such as the reflectivity which we measure in the laboratory,
2. to properties of the solid such as the carrier density, relaxation time, effective masses, energy band gaps, etc.

Linear spectroscopy

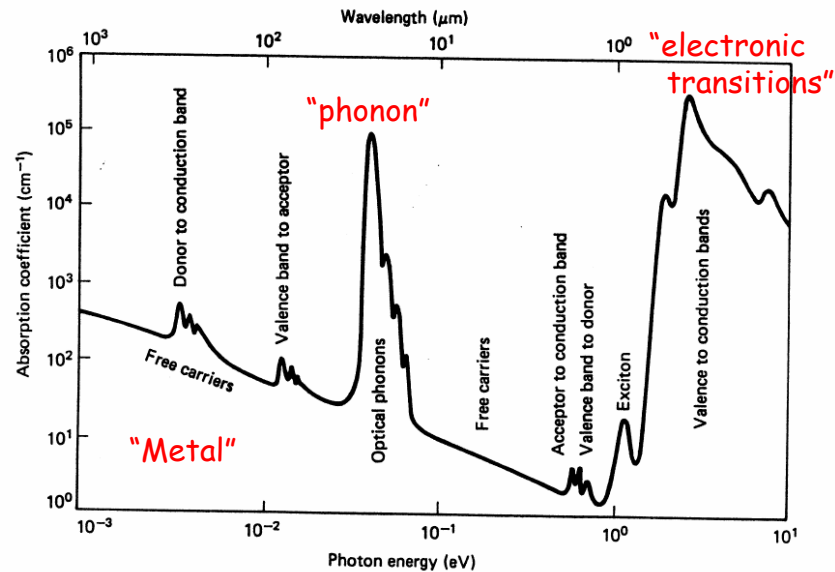
Schematic diagram for normal incidence reflectivity



$$R = \left| \frac{E_2}{E_1} \right|^2$$

$$R = \left| \frac{1 - \tilde{n}}{1 + \tilde{n}} \right|^2 = \frac{(1 - n_R)^2 + n_I^2}{(1 + n_R)^2 + n_I^2}$$

$$1 = R + A + T$$



Hypothetical absorption spectrum for a typical III-V semiconductor as a function of phonon energy.

Electric field and Displacement vector in a material medium

In general situation:

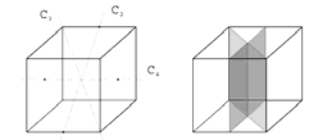
$$\vec{E}(r,t) = \vec{E}_0 \exp[i(\vec{K}\vec{r} - \omega t)] = \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

$$\hat{\epsilon} = \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix} = \begin{bmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{yy} & 0 \\ 0 & 0 & \epsilon_{zz} \end{bmatrix}$$

$$\vec{D} = \hat{\epsilon} \vec{E}$$

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

In crystals the number of independent components decreases according to the symmetry



In isotropic media:

$$\hat{\epsilon} = \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix} = \begin{bmatrix} \epsilon & 0 & 0 \\ 0 & \epsilon & 0 \\ 0 & 0 & \epsilon \end{bmatrix} = \epsilon$$

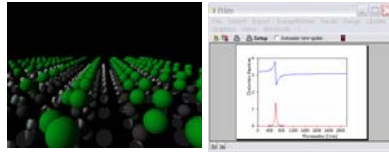
$$\hat{\epsilon}(\omega) = \epsilon_0 [1 + \hat{\chi}(\omega)]$$

6 independent components

Dielectric function contributions

$$\epsilon_r(\omega) = \epsilon(\omega) / \epsilon_0 = 1 + \chi_{ph}(\omega) + \chi_{FC}(\omega) + \chi_E(\omega)$$

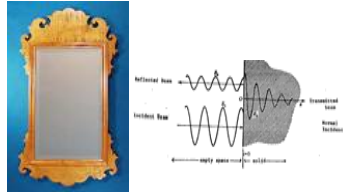
$$\chi_{ph}(\omega) = \sum_j \left(\frac{S_j^2}{\omega_{TOj}^2 - \omega^2 + i\omega\gamma_j} \right)$$



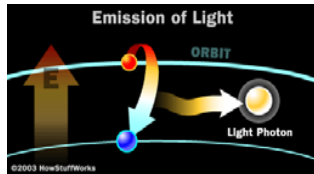
$$\chi_{FC}(\omega) = \frac{\Omega_p^2}{-\omega^2 + i\omega\gamma}$$

$$\Omega_p^2 = \frac{N_{FC} e^2}{\epsilon_{core} m^*}$$

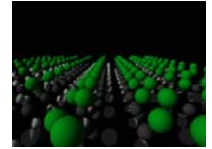
N_{FC} - carrier concentration



$$\chi_E(\omega) = \sum_j \frac{P_j^2}{\omega_{0j}^2 - \omega^2 + i\omega\gamma_j}$$



Ionic polarizability / Phonon contribution

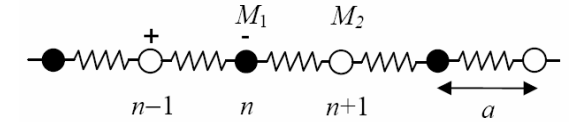


Evaluate the dielectric constant of an ionic crystal.

Ionic polarizability is related to the motion of ions.

Recall the linear chain model we used to describe lattice vibrations:

Equations of motion in the presence of external field:



$$M_1 \frac{d^2 u_n}{dt^2} = -C(2u_n - u_{n+1} - u_{n-1}) - e^* E$$

e^* - effective charge,

E - external field;

$$M_2 \frac{d^2 u_{n+1}}{dt^2} = -C(2u_{n+1} - u_{n+2} - u_n) + e^* E$$

assume $E = E_0 e^{i(qx - \omega t)}$

also assume long wavelength, $\lambda \gg a_0 \rightarrow q \approx 0 \Rightarrow$

$$u_n = u_{0-} e^{-i\omega t} \quad u_{n+1} = u_{0+} e^{-i\omega t}$$

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Substitute this solution into equations of motion, solve for u_{0+} , u_{0-} .

Get

$$u_{0-} = -\frac{e^*}{M_1(\omega_t^2 - \omega^2)} E_0 \quad u_{0+} = \frac{e^*}{M_2(\omega_t^2 - \omega^2)} E_0$$

where $\omega_t = \sqrt{2C \left(\frac{1}{M_1} + \frac{1}{M_2} \right)}$ - transverse optical phonon frequency at $q = 0$

The ionic polarization P_i is then $P_i = n_m e^* (u_{0+} - u_{0-})$

(n_m - number of dipoles per unit volume); $P = \epsilon_0 \chi E$

relative permittivity: $\epsilon_r = \epsilon / \epsilon_0 = 1 + \chi$; $\chi = \chi_{el} + \chi_i$

Get

$$\epsilon_r(\omega) = 1 + \chi_{el} + \frac{n_m e^{*2}}{M_R \epsilon_0 (\omega_t^2 - \omega^2)}$$

where $M_R = \left(\frac{1}{M_1} + \frac{1}{M_2} \right)^{-1} = \frac{M_1 M_2}{M_1 + M_2}$ - reduced mass

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At high frequencies, $\omega \gg \omega_t$, the ionic term vanishes: $\epsilon_{r\infty} = 1 + \chi_{el}$

at $\omega = 0$,

$$\epsilon_{r0} = 1 + \chi_{el} + \frac{n_m e^{*2}}{M_R \epsilon_0 \omega_t^2}$$

can rewrite

$$\epsilon_r(\omega) = 1 + \chi_{el} + \frac{n_m e^{*2}}{M_R \epsilon_0 \omega_t^2 (1 - \omega^2 / \omega_t^2)} = \epsilon_{r\infty} + \frac{\epsilon_{r0} - \epsilon_{r\infty}}{1 - \omega^2 / \omega_t^2}$$

Note that $\epsilon_r(\omega) \rightarrow \infty$. Also, $\epsilon_r(\omega) = 0$ at $\omega_l = \omega_t \cdot \sqrt{\frac{\epsilon_{r0}}{\epsilon_{r\infty}}}$

Between ω_t and ω_l $\epsilon_r(\omega) < 0 \Rightarrow$ index of refraction is imaginary:

$$N(\omega) = \sqrt{\epsilon_r} = i \cdot k(\omega) \quad \text{wave is reflected}$$

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Physical meaning of ω_l - the frequency of longitudinal optical phonon

$$\nabla \cdot \mathbf{D} = \varepsilon(\nabla \cdot \mathbf{E}) = 0$$

$$\nabla \times \mathbf{H} - \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} = \frac{4\pi}{c} \mathbf{j}$$

TO phonons:

LO phonons:

$$\nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = 0$$

no field in z direction;
from the symmetry of the
problem:

macroscopic field along z

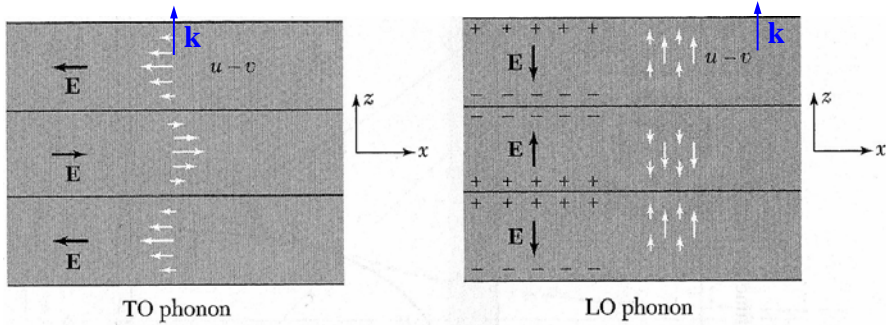
$$\nabla \cdot \mathbf{D} = 0$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\frac{\partial E_x}{\partial x} = 0 \Rightarrow \nabla \cdot \mathbf{E} = 0$$

$$\frac{\partial E_z}{\partial z} \neq 0 \Rightarrow \nabla \cdot \mathbf{D} = 0$$

only if $\varepsilon(\omega) = 0$



Lyddane-Sachs-Teller relation

We had $\varepsilon_r(\omega) = \varepsilon_{r\infty} + \frac{\varepsilon_{r0} - \varepsilon_{r\infty}}{1 - \omega^2/\omega_l^2}$ and $\omega_l^2 = \frac{\varepsilon_{r0}}{\varepsilon_{r\infty}} \omega_t^2$

combine, get

$$\varepsilon_r(\omega) = \varepsilon_{r\infty} \frac{\omega_l^2 - \omega^2}{\omega_t^2 - \omega^2} \quad \text{or} \quad \frac{\varepsilon_{r0}}{\varepsilon_{r\infty}} = \frac{\omega_l^2}{\omega_t^2}$$

If many phonon branches:

$$\varepsilon(\omega) = \varepsilon_{\infty} \prod_j \frac{\omega_{LOj}^2 - \omega^2}{\omega_{TOj}^2 - \omega^2}$$

If phonon decay is included:

$$\varepsilon(\omega) = \varepsilon_{\infty} \prod_j \frac{\omega_{LOj}^2 - \omega^2 - i\gamma_{LOj}\omega}{\omega_{TOj}^2 - \omega^2 - i\gamma_{TOj}\omega}$$

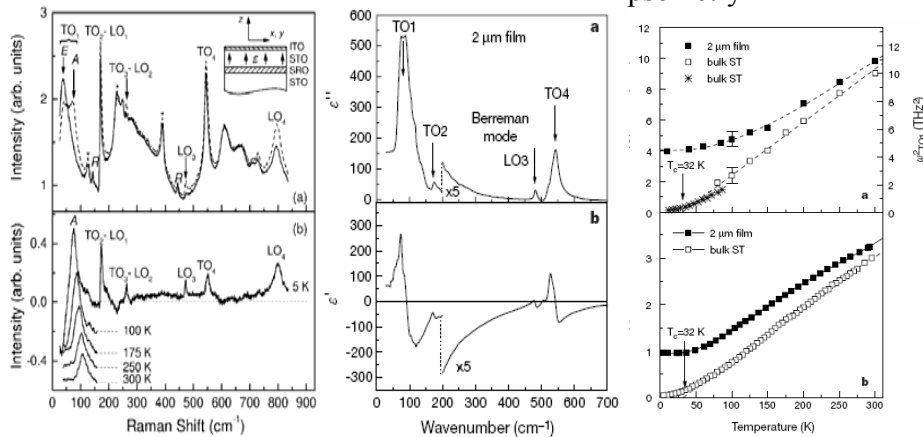
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Lyddane-Sachs-Teller relation

$$\frac{\varepsilon_{r0}}{\varepsilon_{r\infty}} = \frac{\omega_l^2}{\omega_t^2}$$

Raman

Ellipsometry



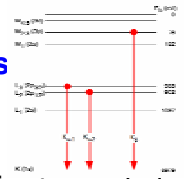
A.A. Sirenko, et al., *Nature* **404**, 373 (2000)

A.A. Sirenko, et al., *Phys. Rev. Lett.* **84**, 4625 (2000) and *Phys. Rev. Lett.* **82**, 44500 (1999)

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Electronic polarizability of solids (similar to electronic transitions in atoms)



For an accurate quantitative description, quantum mechanics is needed

But we can get some general ideas with classical approach

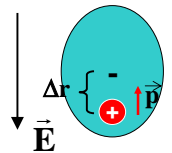
Recall our model of atom:

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

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

κ = spring constant

m = mass



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

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Without an external field:

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

Equation for harmonic oscillator. Solution: harmonic vibration

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

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) $eE_0 e^{-i\omega t} - m\omega_0^2 x = m \frac{d^2x}{dt^2}$

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

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

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

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

$$P = \frac{e^2ZN/m}{\omega_0^2 - \omega^2} E \quad \text{Recall } P = \epsilon_0 \chi E \text{ and } \epsilon = \epsilon_0(1 + \chi)$$

get
$$\chi = \frac{NZe^2}{\epsilon_0 m} \frac{1}{(\omega_0^2 - \omega^2)} \quad \text{or} \quad \epsilon = \epsilon_0 \left(1 + \frac{NZe^2}{\epsilon_0 m} \frac{1}{(\omega_0^2 - \omega^2)} \right)$$

and
$$n^2(\omega) = \frac{\epsilon}{\epsilon_0} = 1 + \frac{NZe^2}{\epsilon_0 m} \left(\frac{1}{\omega_0^2 - \omega^2} \right)$$

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Now, consider damping force proportional to speed :

$$F_{damp} = -m\gamma \frac{dx}{dt}$$

Equation of motion becomes (damped oscillator):

$$eE_0 e^{-i\omega t} - m\omega_0^2 x - m\gamma \frac{dx}{dt} = m \frac{d^2x}{dt^2}$$

Again, look for a solution $x(t) = x_0 e^{-i\omega t}$

get
$$x(t) = \frac{e}{m} E(t) \frac{1}{\omega_0^2 - \omega^2 + i\omega\gamma}$$
 Same form as before, just includes damping

Therefore

$$n^2(\omega) = \frac{\epsilon}{\epsilon_0} = 1 + \frac{NZe^2}{\epsilon_0 m} \left(\frac{1}{\omega_0^2 - \omega^2 + i\omega\gamma} \right)$$

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n is complex for nonzero damping: $\tilde{n} = n_R + in_I$

and $\vec{K} = \tilde{n}\vec{K}_0$, - complex wavenumber

What does it mean?

$$E = E_0 e^{i(Kx - \omega t)} = E_0 e^{i[n_R + in_I]K_0 x - i\omega t} = E_0 e^{-n_I K_0 x} e^{i(n_R K_0 x - \omega t)}$$

or $E = \tilde{E}_0 e^{i(n_R K_0 x - \omega t)}$ where $\tilde{E}_0 = E_0 e^{-n_I K_0 x}$

Amplitude decays as wave propagates – absorption; results from damping

Usually write $\tilde{n} \rightarrow n + i \frac{\alpha}{2k_0}$ Then $\tilde{E}_0 = E_0 e^{-\alpha x/2}$

instead of $n_R + in_I$ and intensity $I \propto \tilde{E}_0^2 = I_0 e^{-\alpha x}$

α - **absorption coefficient** (m^{-1})

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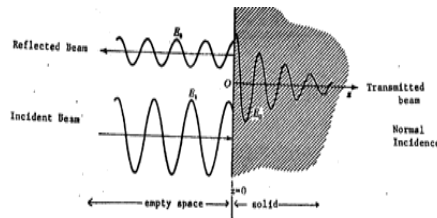
Reflectivity at normal incidence (in air)

Field amplitude: $r = \frac{n-1}{n+1}$ power (intensity): $R = |r|^2 = \frac{(n-1)^2}{(n+1)^2}$

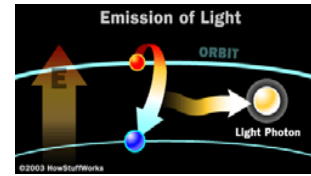
If $\tilde{n} = n_R + in_I$ then $R = |r|^2 = rr^* = \frac{(n_R - 1)^2 + n_I^2}{(n_R + 1)^2 + n_I^2}$

As we've seen, the dielectric function and refractive index are generally complex: $\epsilon_r = \epsilon_r' + i\epsilon_r''$ $\tilde{n} = n_R + in_I$

$\epsilon_r' = n_R^2 - n_I^2$; $\epsilon_r'' = 2n_R n_I$
 n_I is called *extinction coefficient*



We obtained



$$n^2(\omega) = \frac{\epsilon}{\epsilon_0} = 1 + \underbrace{\frac{NZe^2}{\epsilon_0 m} \left(\frac{1}{\omega_0^2 - \omega^2 + i\omega\gamma} \right)}_{\chi_e(\omega)}$$

Quantum mechanics gives similar result for Electronic polarizability:

$$\alpha_e(\omega) = \frac{e^2}{m} \sum_j \frac{f_j}{\omega_j^2 - \omega^2 + i\omega\gamma_j}$$

Many resonant frequencies ω_j correspond to energy transitions

Weighting factors f_j called oscillator strengths (related to transition matrix elements)

Optical properties of conductive solids (metals)



conductivity of a medium σ : $\mathbf{J} = \sigma\mathbf{E}$

Including conductivity in Maxwell's equations in the medium:

$$\nabla \times \mathbf{B} = \mu\mathbf{J} + \mu\epsilon \frac{\partial \mathbf{E}}{\partial t}$$

leads to wave equation: $\nabla^2 \vec{E} = \epsilon\mu \frac{\partial^2 \vec{E}}{\partial t^2} + \sigma\mu \frac{\partial \vec{E}}{\partial t}$

Differs from a "standard" wave equation by the first term in the right part

Still, look for plane wave solution: $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 e^{i(\vec{K} \cdot \vec{r} - \omega t)}$

Reflection from metals

Have complex refractive index n_i : $\tilde{n} = \left(\frac{\epsilon}{\epsilon_0} + i \frac{\sigma}{\epsilon_0 \omega} \right)^{1/2} = n_I + i \frac{\alpha}{2K_0}$
 $n_R, n_I = \alpha/2K_0$ are real

Reflectivity at normal incidence (in air) $R = |r|^2 = rr^* = \frac{(n_R - 1)^2 + n_I^2}{(n_R + 1)^2 + n_I^2}$

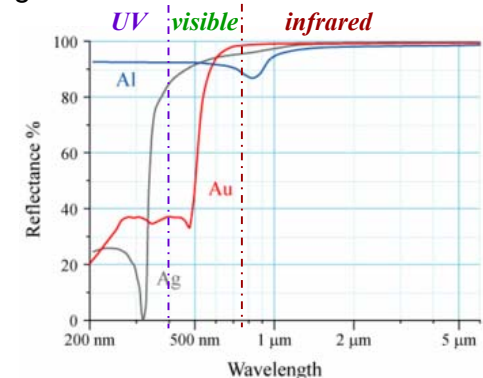
Consider a very good metal: large σ (e.g. silver: $\sigma \approx 6 \cdot 10^7 \Omega^{-1}m^{-1}$)

For $\lambda = 500 \text{ nm}$ and $\epsilon \approx \epsilon_0$

$$\frac{\sigma}{\epsilon_0 \omega} \approx 2000$$

then $\frac{\alpha}{2K_0} = n_I \gg n_R - 1$

$$\Rightarrow R \rightarrow 1$$



Dispersion equation in metals

The dispersion we got in a model of oscillating electrons:

$$n^2(\omega) = 1 + \frac{N_{FC}e^2}{\epsilon_0 m} \left(\frac{1}{\omega_0^2 - \omega^2 + i\omega\gamma} \right) \quad \omega_0 = \sqrt{k/m_e}$$

k - "spring constant"
 m_e - electron mass

in metal, there are free electrons - no restoring force $\Rightarrow \omega_0 = 0$

Still, there may be bound electrons, too.

So

$$n^2(\omega) = 1 + \underbrace{\frac{N_{FC}e^2}{\epsilon_0 m} \left(\frac{1}{-\omega^2 + i\omega\gamma_e} \right)}_{\text{free electrons}} + \underbrace{\sum_j \frac{f_j}{\omega_{0j}^2 - \omega^2 + i\omega\gamma_j}}_{\text{bound electrons (like in dielectric)}}$$

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If we neglect the contribution of bound electrons and also neglect free electron damping γ_e

Then
$$n^2(\omega) = 1 - \frac{N_{FC}e^2}{\epsilon_0 m \omega^2}$$

Introduce
$$\omega_p = \sqrt{\frac{N_{FC}e^2}{\epsilon_{core} m_e}} \quad \text{- plasma frequency}$$

$$\epsilon_{core} = \epsilon(\omega \rightarrow \infty)$$

Then
$$n^2(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \quad \epsilon'(\omega) = \epsilon_{core} \cdot \left[1 - \frac{\omega_p^2}{\omega^2} \right]$$

Below ω_p refractive index is complex - absorption;

above ω_p n is real, free electron absorption is small

For most metals ω_p lies in the UV range

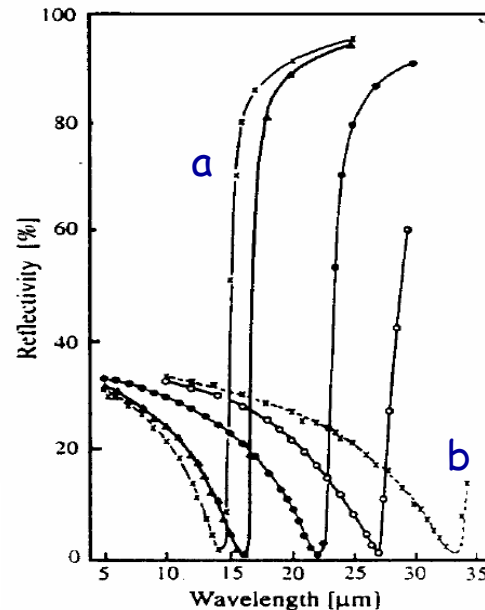
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The Free Carrier Contribution

Where carrier concentration is higher? Choose between *a* and *b*. Show work

Plasma edges observed in the room temperature reflectivity spectra of *n*-type InSb with carrier concentration n varying between $3.5 \times 10^{17} \text{ cm}^{-3}$ and $4.0 \times 10^{18} \text{ cm}^{-3}$.

$$\omega_p = \sqrt{\frac{N_{FC}e^2}{\epsilon_{core} m_e}}$$



Summary

- ❖ Ionic contribution to dielectric function is related to lattice vibrations and exhibits dispersion in infrared region, given by the Lyddane-Sachs-Teller relation:

$$\epsilon(\omega) = \epsilon_{\infty} \prod_j \frac{\omega_{LOj}^2 - \omega^2}{\omega_{TOj}^2 - \omega^2}$$

- ❖ Electronic polarizability is given by

$$\alpha_e(\omega) = \frac{e^2}{m} \left(\underbrace{\frac{1}{-\omega^2 + i\omega\gamma_e}}_{\text{free electrons}} + \underbrace{\sum_j \frac{f_j}{\omega_{0j}^2 - \omega^2 + i\omega\gamma_j}}_{\text{bound electrons}} \right)$$

- ❖ Dielectric function and refractive index are generally complex:

$$\epsilon_r = \epsilon_r' + i\epsilon_r''; \quad \tilde{n} = n_R + in_I; \quad \epsilon_r' = n_R^2 - n_I^2; \quad \epsilon_r'' = 2n_R n_I$$

absorption coefficient $\alpha = 2K_0 n_I$ n_I - extinction coefficient 48

For your references:

Symbol	Meaning (first term is the most common)	SI Unit of Measure
$\nabla \cdot$	the divergence operator	per meter (factor contributed by applying either operator)
$\nabla \times$	the curl operator	
$\frac{\partial}{\partial t}$	partial derivative with respect to time	per second (factor contributed by applying the operator)
E	electric field also called the electric flux density	volt per meter or, equivalently, newton per coulomb
B	Magnetic field also called the magnetic induction also called the magnetic field density also called the magnetic flux density	tesla , or equivalently, weber per square meter
ρ	electric charge density	coulomb per cubic meter
ϵ_0	Permittivity of free space , a universal constant	farads per meter
$\oint_S \mathbf{E} \cdot d\mathbf{A}$	The flux of the electric field over any closed Gaussian surface S	joule-meter per coulomb
Q_S	net unbalanced electric charge enclosed by the Gaussian surface S, including so-called <i>Bound charges</i>	coulombs
$\oint_S \mathbf{B} \cdot d\mathbf{A}$	The flux of the magnetic field over any closed surface S	Tesla meter-squared or webber
$\oint_{\partial S} \mathbf{E} \cdot d\mathbf{l}$	line integral of the electric field along the boundary (therefore necessarily a closed curve) of the surface S	Joule per coulomb
$\Phi_{B,S} = \int_S \mathbf{B} \cdot d\mathbf{A}$	magnetic flux over any surface S (not necessarily closed)	webber
μ_0	magnetic permeability of free space, a universal constant	henries per meter , or newtons per ampere squared
J	current density	ampere per square meter
$\oint_{\partial S} \mathbf{B} \cdot d\mathbf{l}$	line integral of the magnetic field over the closed boundary of the surface S	tesla-meter
$\mathbf{I}_S = \int_S \mathbf{J} \cdot d\mathbf{A}$	net electrical current passing through the surface S	amperes
$\Phi_{E,S} = \int_S \mathbf{E} \cdot d\mathbf{A}$	Electric flux over any surface S, not necessarily closed	
dA	differential vector element of surface area A, with infinitesimally small magnitude and direction normal to surface S	square meters
dl	differential vector element of <i>path length</i> tangential to contour	meters