XII. Optical Properties

- A very brief discussion (as we run out of time)

See related discussions on

- Lattice optical Properties in IR (Ch. X)
- Free-carrier absorption (Ch. XI Part 1)
  (metals, plasmonics)

A. (Too many) Optical Coefficients

- Called "optical constants", but they are hardly "constants"
- Too many of them!

$$\underset{\substack{\uparrow\\ \varepsilon_1+i\varepsilon_2}}{\tilde{\varepsilon}},\ \underset{\substack{\uparrow\\ n+i\underset{\nwarrow\ \text{extinction coefficient}}{\kappa}}}{\tilde{n}},\ \tilde{\sigma},\ \text{real } \varepsilon + \text{real } \sigma;\ \underset{\substack{\uparrow\\ \text{reflectivity}}}{R} = r^{*}\overset{\substack{\text{reflection amplitude}\\ \swarrow}}{r},\ \underset{\substack{\uparrow\\ \text{transmissivity}}}{T},\ \overset{\substack{\text{absorption coefficient}\\ \downarrow}}{\alpha}$$

- Don't take that you will get a curve from your apparatus, that is!
- Further complicated by the units (c.g.s, gaussian, SI)
- Further complicated by $\vec{D}$, $\vec{\mathcal{E}}$, $\vec{P}$ ($\vec{B}$, $\vec{M}$, $\vec{H}$) in EM and the separation of charges into "free" and "bound"

B. Complex $\tilde{n}$, $\tilde{\varepsilon}$ and Absorption

- For non-conductors, convenient to work with complex dielectric constant

$$\underset{\text{no units}}{\varepsilon_r}\,\overset{\text{with units}}{\varepsilon_0} = \varepsilon$$

work with this (call it ε for "simplicity") — now it is the relative dielectric constant

then
$$\underset{\substack{\text{Complex}\\ \text{dielectrix constant}}}{\tilde{\varepsilon}} = \underset{\text{real}}{\varepsilon_1} + i\underset{\substack{\text{imaginary}\\ \text{(dissipative)}}}{\varepsilon_2} = (\underset{\text{refractive index}}{n} + i\underset{\text{extinction}}{\kappa})^2 \qquad (1)$$

In such a medium,

$$\vec{\mathcal{E}} = \vec{\mathcal{E}}_0 \, e^{i(kz-\omega t)} \quad \text{becomes}$$

$ck=\omega$ → $k = \frac{\omega}{c}\tilde{n}$
(vacuum)

$$\vec{\mathcal{E}} = \vec{\mathcal{E}}_0 \, \underbrace{e^{-\frac{\omega}{c}\kappa z}}_{\text{decaying}} \, e^{i\left(\frac{\omega}{c} n z - \omega t\right)} \qquad (2)$$

defines the absorption coefficient

Then Intensity drops with z as $I(z) = I(0)\, e^{-\alpha z}$ (3) Beer's Law

$$\therefore \quad \alpha = \frac{2\omega}{c}\kappa = \frac{4\pi}{\lambda}\kappa \qquad (4)$$

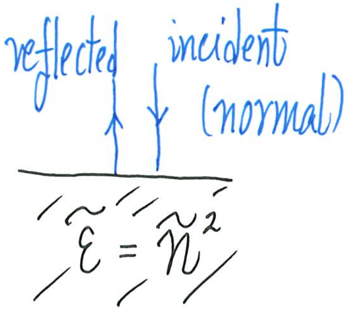
↖ wavelength in vacuum

We also have

$$\mathcal{E}_1 = n^2 - \kappa^2$$
$$\mathcal{E}_2 = 2n\kappa \qquad (5)$$

(non-magnetic materials)

because $\tilde{\mathcal{E}} = \tilde{n}^2$



$$\tilde{r} = \frac{1-\tilde{n}}{1+\tilde{n}} \quad (6) \; ; \quad R = \tilde{r}^*\tilde{r} = |\tilde{r}|^2 = \frac{(n-1)^2+K^2}{(n+1)^2+K^2} \quad (7)$$

Complex ($\tilde{r}$) real and positive (R)

C. Response Functions have real and imaginary parts connected by Kramers-Kronig Relations

- Causality (response only comes after stimulation)
- Physics concerns "real" stuff — Real input (stimulation) and real output (response)

Most relevant here is

$$\vec{P} = \varepsilon_0 \chi \vec{\mathcal{E}} \quad (8)$$

χ ← electric suspectivity

with which

$$\vec{D} = \varepsilon_0\vec{\mathcal{E}} + \vec{P} = \varepsilon_0\vec{\mathcal{E}} + \varepsilon_0\chi\vec{\mathcal{E}} = \varepsilon_0\underbrace{(1+\chi)}\vec{\mathcal{E}} = \varepsilon_0\underbrace{\varepsilon}\vec{\mathcal{E}} \quad (9)$$

related

Eq. (8) is an example of stimulation-response pairs

$$\underbrace{P(\vec{x},t)}_{\text{response at } \vec{x} \text{ and } t} = \iint \underbrace{\chi(\vec{x},\vec{x}\,';t,t')}_{\wr} \underbrace{\mathcal{E}(\vec{x}\,',t')}_{\text{may due to stimulations at } \vec{x}\,' \text{ and } t'} d^3x'\,dt' \qquad (10)$$

χ characterizes the response of system (c.f. Green's function)

- Most general, possibly non-local in space and non-local in time
- Keep non-local in time only (for simplicity)$^+$ $\qquad G = \delta(\vec{x}-\vec{x}\,')\,G(t-t')$

$$P(t) = \int_{-\infty}^{\infty} \chi(t-t')\,\mathcal{E}(t')\,dt'$$

Causality $\Rightarrow \chi(t-t') = 0$ for $t-t' < 0$ OR $t < t'$ (before stimulation acts)

$$P(t) = \int_{-\infty}^{\boxed{t}} \chi(t-t')\,\mathcal{E}(t')\,dt' \qquad (11)$$

"Make Sense"

$^+$ The consequence is $\mathcal{E}(\omega)$, otherwise $\mathcal{E}(\vec{q},\omega)$

Generally, $X(t) = \int_{-\infty}^{t} G(t-t')\, f(t')\, dt'$

a pair

Fourier Transformations:

$f(\omega) = \int_{-\infty}^{\infty} f(t)\, e^{i\omega t}\, dt$

etc.

complex in general

$X(\omega) = G(\omega)\, f(\omega)$ (12) "Convolution"

analytic in upper complex plane

[Convenience: For monochromatic stimulus $f(\omega)$, response $X(\omega)$ is obtained by $G(\omega) f(\omega)$]

Cauchy's Theorem as applied to response functions

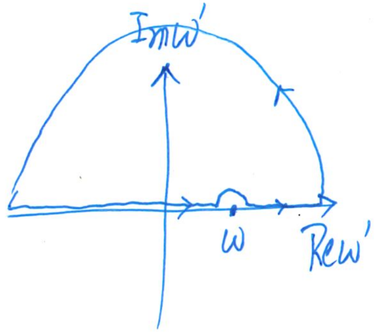
$$G(\omega) = \frac{1}{i\pi} P \int_{-\infty}^{\infty} \frac{G(\omega')\, d\omega'}{\omega' - \omega} \qquad (13)$$

Cauchy Principal value

the "i" gives the connections between real and imaginary parts

Related to:

- Analytic function
- Residual theorem



Writing $G(\omega) = \mathrm{Re}\, G(\omega) + i\, \mathrm{Im}\, G(\omega)$

$$\mathrm{Re}\, G(\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\mathrm{Im}\, G(\omega')\, d\omega'}{\omega' - \omega} \; ; \quad \mathrm{Im}\, G(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\mathrm{Re}\, G(\omega')\, d\omega'}{\omega' - \omega} \tag{14}$$

- Kramer-Kronig relations ("KK relations")
- It says, if we know the imaginary part $\mathrm{Im}\, G(\omega)$ for ALL ω (from $-\infty$ to $+\infty$), then we also know $\mathrm{Re}\, G(\omega)$ by doing an integral.

[Note: But the "negative ω" portion doesn't sound nice, stay tuned]

$\chi(\omega) = \chi_1(\omega) + i\chi_2(\omega)$ susceptibility connecting P and $\mathcal{E}$

KK relations: $$\chi_1(\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\chi_2(\omega')\, d\omega'}{\omega' - \omega} \; ; \quad \chi_2(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\chi_1(\omega')\, d\omega'}{\omega' - \omega} \tag{15}$$

In physical systems, we have a real-valued response $\chi(t)$. This gives the Fourier transformed $\chi(\omega)$ having $\underbrace{\chi^*(\omega) = \chi(-\omega)}$

$$\therefore \quad \chi_1(\omega) - i\chi_2(\omega) = \chi_1(-\omega) + i\chi_2(-\omega)$$

$$\Rightarrow \begin{cases} \text{Real part} & \chi_1(-\omega) = \chi_1(\omega) & \text{even function of } \omega \\ \text{Imaginary part} & \underbrace{\chi_2(-\omega)}_{\text{also know values for } \underline{\text{negative } \omega\text{'s}} \text{ (mathematical)}} = \underbrace{-\chi_2(\omega)}_{\text{experimentally assessible [positive } \omega\text{'s]}} & \text{odd function of } \omega \end{cases}$$

It then follows that a more useful form is:

$$\boxed{\chi_1(\omega) = \frac{2}{\pi} P\int_{\underset{\text{note lower limit}}{0}}^{\infty} \frac{\omega' \chi_2(\omega')}{\omega'^2 - \omega^2} d\omega' \; ; \quad \chi_2(\omega) = -\frac{2}{\pi}\omega P\int_{\underset{\text{note lower limit}}{0}}^{\infty} \frac{\chi_1(\omega') d\omega'}{\omega'^2 - \omega^2}} \qquad (16)$$

From Eq. (9), $\varepsilon = 1 + \chi \Rightarrow \begin{cases} \chi_1 = \varepsilon_1 - 1 \\ \chi_2 = \varepsilon_2 \end{cases}$, so

$$\varepsilon_1(\omega) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad ; \quad \varepsilon_2(\omega) = \frac{-2\omega}{\pi} P \int_0^\infty \frac{\varepsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega' \text{ (formally)}$$

$$= -\frac{2\omega}{\pi} P \int_0^\infty \frac{\varepsilon_1(\omega')\, d\omega'}{\omega'^2 - \omega^2} \quad \text{(equivalent)}^{+} \qquad (17)$$

Useful in getting $\varepsilon_1(\omega)$ if we know $\varepsilon_2(\omega)$ for ALL ω's.

[+] The second term can be shown to vanish, but the formal expression keeps the form of KK relations. For details of KK relations, see the "Calculus of Residues" in complex variables.

D. Experimentalists know KK relations well

- At the heart of experiments in studying optical properties

$$\underbrace{\frac{E_{\text{reflected}}}{E_{\text{incident}}}}_{\Downarrow} = \tilde{r} = \frac{1-\tilde{n}}{1+\tilde{n}}$$

$\tilde{r}$ is a response function! $\tilde{r} = \tilde{r}(\omega) =$ Complex Reflectivity Amplitude

Write $\tilde{r}(\omega) = \rho(\omega)\, e^{i\theta(\omega)}$ general expression for complex number

then

$$\underbrace{\ln \tilde{r}(\omega)}_{\text{a response function}} = \underbrace{\ln \rho(\omega)}_{\text{real part}} + i\, \underbrace{\theta(\omega)}_{\text{imaginary part}} \qquad (18)$$

$$\underset{\substack{\Uparrow \\ \text{from Eq. (16), KK relations}}}{\text{So,}}\ \theta(\omega) = -\frac{2\omega}{\pi} P\int_0^\infty \frac{\ln \rho(\omega')\, d\omega'}{\omega'^2-\omega^2} = -\frac{2\omega}{\pi} P\int_0^\infty \frac{\ln \rho(\omega')\, d\omega'}{\omega'^2-\omega^2} + \overbrace{\frac{2\omega}{\pi} P\int_0^\infty \frac{d\omega'}{\omega'^2-\omega^2} \ln \rho(\omega)}^{\text{just zero}}$$

$$\theta(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\ln\left[\frac{\rho(\omega')}{\rho(\omega)}\right]}{\omega'^2-\omega^2}\, d\omega' = \frac{2\omega}{\pi} P \int_0^\infty \frac{\ln\left[\frac{\rho(\omega')}{\rho(\omega)}\right] d\omega'}{\omega^2-\omega'^2} \qquad (19)$$

One can measure the Reflectivity $R = \tilde{r}^* r = \rho(\omega)^2$

$\therefore \quad \rho(\omega) = \sqrt{R}$

so $\rho(\omega)$ is an experimentally accessible value [need to measure $R(\omega)$ for as wide a range of ω as possible]

$$\therefore \boxed{\theta(\omega) = \frac{\omega}{\pi} \int_0^\infty \frac{\ln\left[\frac{R(\omega')}{R(\omega)}\right] d\omega'}{\omega^2-\omega'^2}} \qquad (20)$$

this is the most useful form of the Kramers-Kronig relation in experimental physics (learning functions of complex variables and contour integrations is useful!)

Eq. (20) suggests an approach

(i) Measure $R(\omega)$ for very wide range of ω (change apparatus, change source)

(ii) know $\rho(\omega)$, obtain $\theta(\omega)$ from KK relation

(iii) $\tilde{r}(\omega) = \rho(\omega)\, e^{i\theta(\omega)}$ is known $\Rightarrow$ $\dfrac{1-\tilde{n}}{1+\tilde{n}} = \tilde{r}$ is known

(iv) Solve for $\tilde{n}(\omega)$, so $n(\omega)$ and $K(\omega)$ are known!

(v) $\tilde{\varepsilon}(\omega) = \tilde{n}^2 = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ $\Rightarrow$ $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are known!

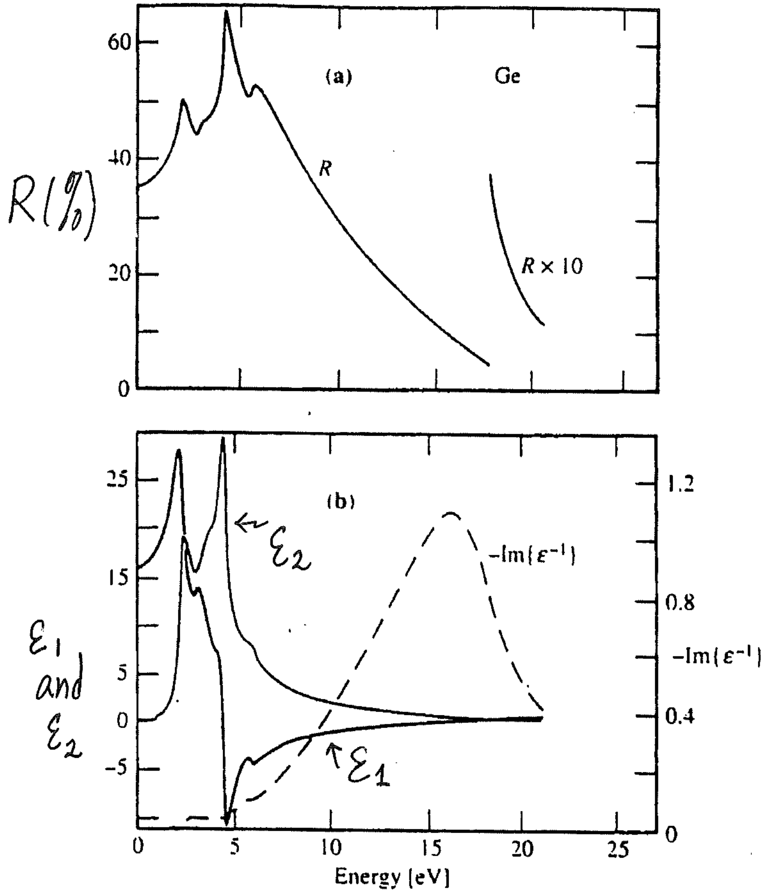
(vi) From K, get $\alpha(\omega)$

[Measure R doesn't need thin samples. Thin samples are needed for R and T measurements]

This approach is general[+], as it comes from general physical and mathematical considerations.

[+] For metals, the static conductivity gives a pole at $\omega = 0$ $\left(\varepsilon_2 = \dfrac{\sigma_0}{\varepsilon_0 \omega}\right)$ which needs extra care.

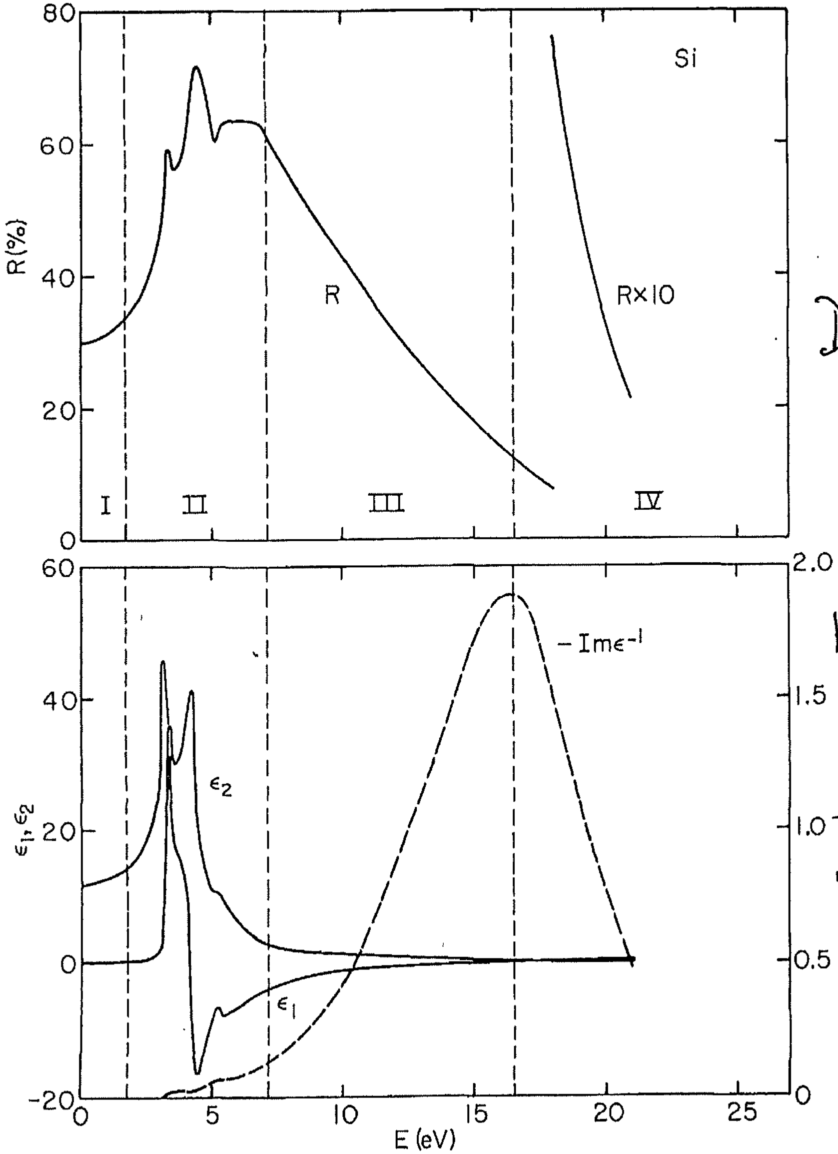
examples of application: Ge



(a) Frequency dependence of the reflectivity of Ge over a wide frequency range. (b) Plot of the real $[\varepsilon_1(\omega)]$ and imaginary $[\varepsilon_2(\omega)]$ parts of the dielectric functions for Ge obtained by a Kramers–Kronig analysis of the reflectivity data in part (a).

[H.R. Philipp and H. Ehrenreich, Phys. Rev. 129, 1550 (1963)]

Silicon



Data

$\downarrow$

KK relation

$\mathrm{Im}\left[\frac{-1}{\tilde{\varepsilon}(\omega)}\right]$ is called the energy loss function

The spectral dependence of the reflectance and dielectric functions of Si. Regions I, II, III, and IV correspond to the regions with the same designation shown in previous figures [H. R. Philipp and H. Ehrenreich, *Phys. Rev.* **129**. 1550 (1963).]

Classics in Optical Properties of Solids

- F. Wooten, "Optical Properties of Solids"
- M. Fox, "Optical Properties of Solids" (easier)
- H. Ehrenreich, in "Optical Properties of Solids", edited by J. Tauc (1966)
- F. Stern, "Elementary Optical Properties of Solids", in $\underbrace{\text{Solid State Physics}}_{\text{a series with review articles (publishes one volume per year)}}$, Vol. 15 (1963)

Remark

What was discussed here formed the basis of ellipsometry

E. Curve Fitting: A more practical approach

- Fit to what?

Lorentz oscillator(s): damped, forced oscillator

$$m\frac{d^2\vec{r}}{dt^2}+\Gamma m\frac{d\vec{r}}{dt}+m\omega_0^2\vec{r}=-e\vec{\mathcal{E}}_{local}$$

for an electron bound to nucleus under $\vec{\mathcal{E}}_{local}$

$$\tilde{\vec{p}}=\tilde{\alpha}(\omega)\vec{\mathcal{E}}_{local}$$

for $e^{-i\omega t}$ time variation

$$\tilde{\alpha}(\omega)=\frac{e^2}{m}\frac{1}{(\omega_0^2-\omega^2)-i\Gamma\omega}$$

$\Gamma \sim 1/\text{time}$

$$\tilde{\varepsilon}(\omega)=1+\frac{Ne^2}{m\varepsilon_0}\frac{1}{(\omega_0^2-\omega^2)-i\Gamma\omega} \qquad (21)$$

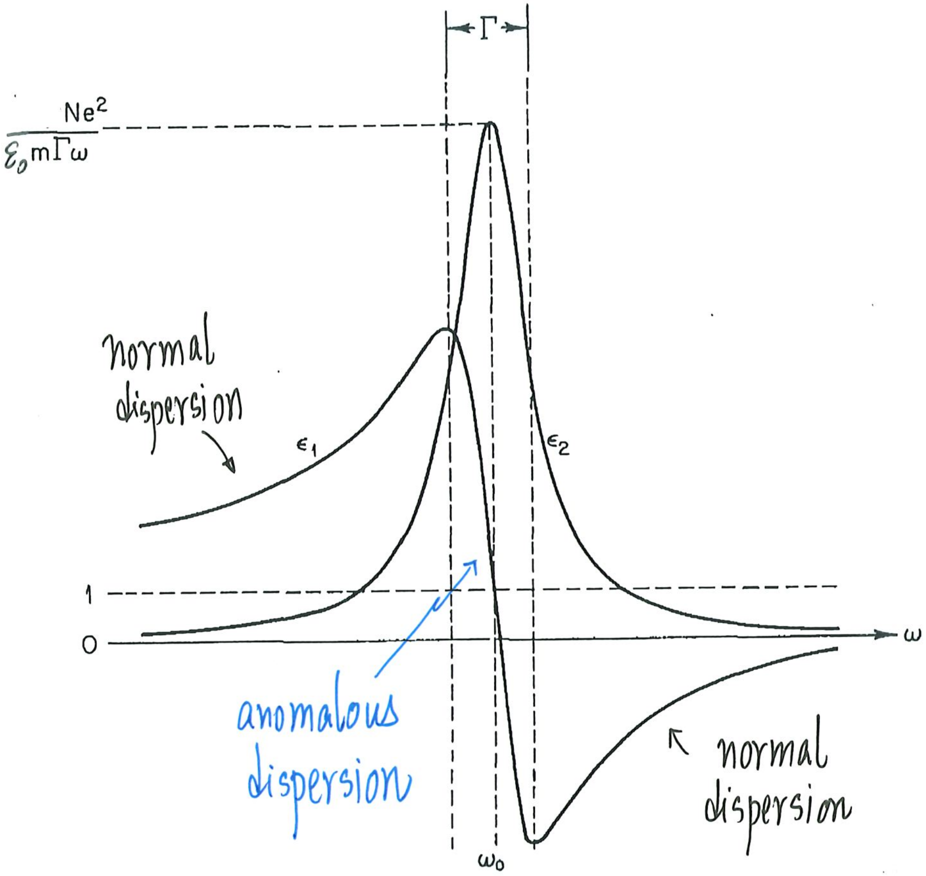
(not considering local field effect in a crystal, see Clausius-Mossotti relation)

Lorentz oscillator model of $\tilde{\varepsilon}(\omega)$

N atoms per unit volume (actually N is electron density that bound with frequency ω_0)

$$\varepsilon_1(\omega) = n^2 - K^2 = 1 + \frac{Ne^2}{m\varepsilon_0}\,\frac{\omega_0^2-\omega^2}{(\omega_0^2-\omega^2)^2+\Gamma^2\omega^2} \qquad (22a)$$

$$\varepsilon_2(\omega) = 2nK = \frac{Ne^2}{m\varepsilon_0}\,\frac{\omega\Gamma}{(\omega_0^2-\omega^2)^2+\Gamma^2\omega^2} \qquad (22b) \quad \propto \underbrace{\Gamma}_{\text{so damping term } \Gamma\frac{d\vec{r}}{dt} \text{ is dissipative}}$$

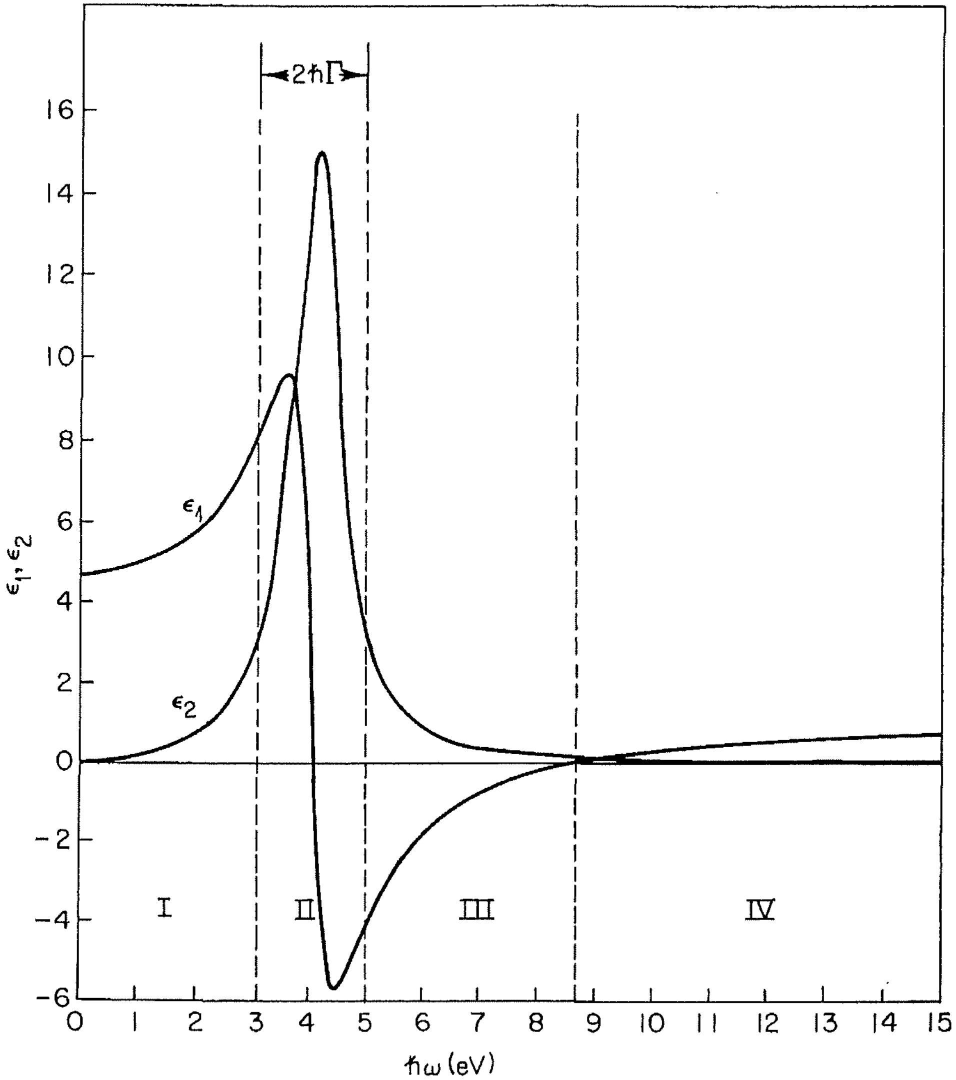


Frequency dependence of ε_1 and ε_2.

ε_1 can be positive and negative (no problem)

ε_2 cannot be negative (lossy material)

← Must-know common sense (the form of Lorentz oscillator)



Spectral dependence of ε_1 and ε_1. The curves are calculated for the case in which $\hbar\omega_0 = 4$ eV, $\hbar\Gamma = 1$ eV, and $Ne^2/m\varepsilon_0 = \underset{\uparrow}{\underbrace{60}}$. The onset of region IV is defined by $\varepsilon_1 = 0$.

$\left(\frac{eV}{\hbar}\right)^2$ in units

[Drawn for a particular set of parameters]

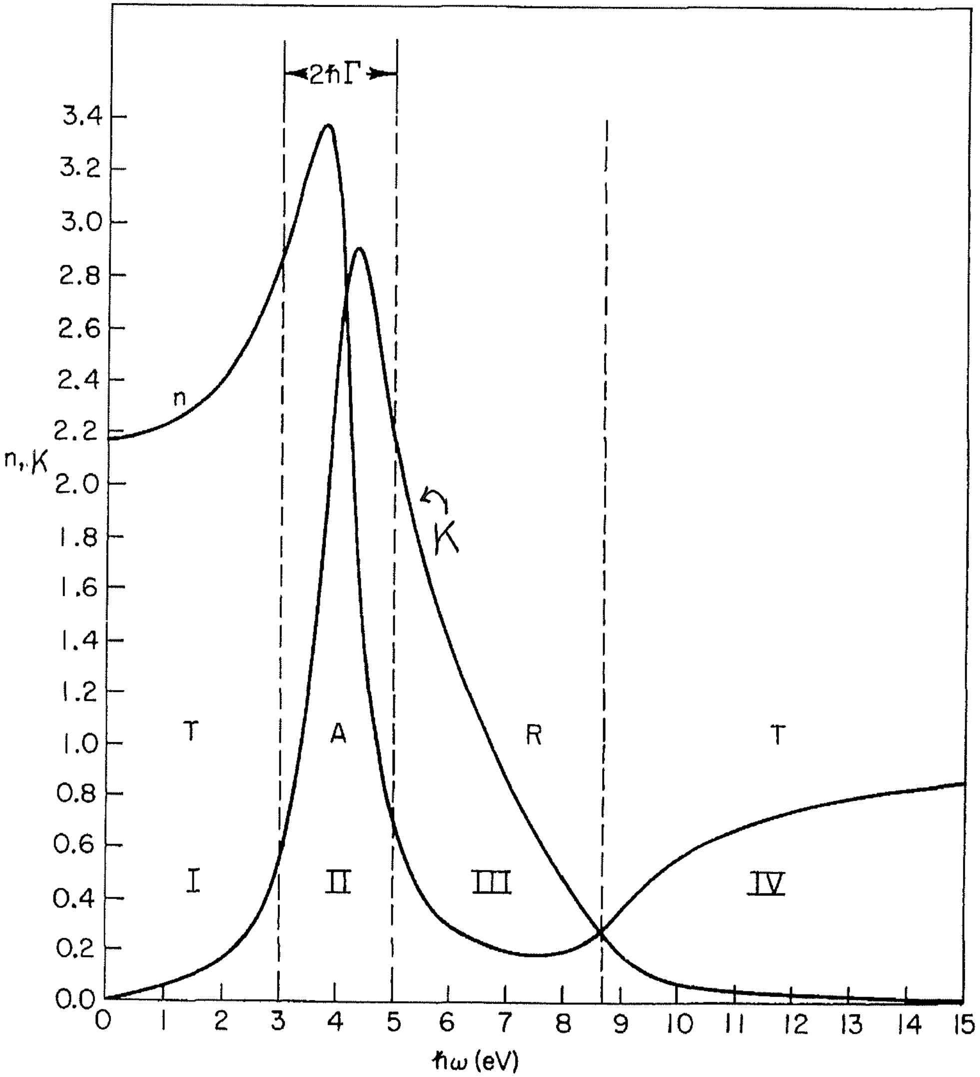
Let's look at
$\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$
of a Lorentz oscillator
and its associated
quantities

Regions I, II, III, IV
have different behavior

[Taken from Wooten, "Optical Properties of Solids"]

$$\tilde{\varepsilon} = \tilde{n}^2 \Rightarrow n = \sqrt{\frac{1}{2}\left((\varepsilon_1^2 + \varepsilon_2^2)^{1/2} + \varepsilon_1\right)} \, ; \quad K = \sqrt{\frac{1}{2}\left((\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1\right)} \qquad (23)$$

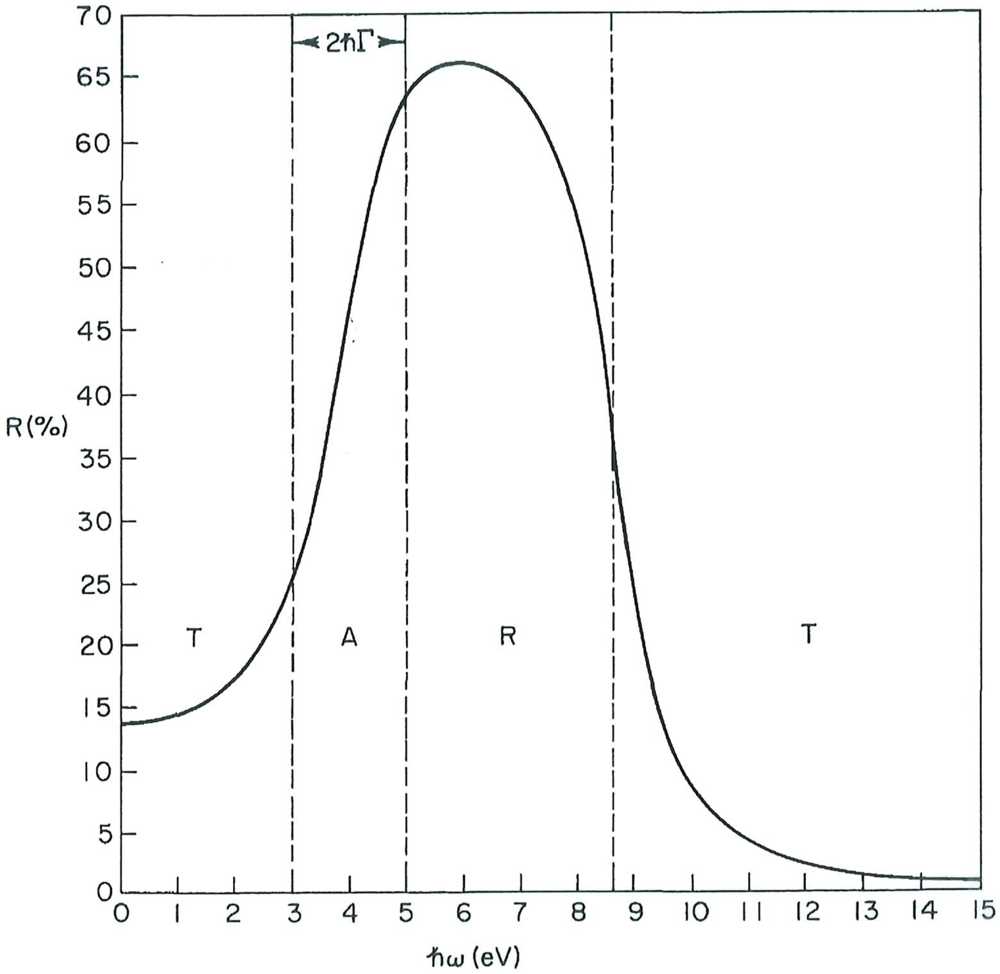
n = refractive index
K = extinction coefficient



Spectral dependence of n and k. The curves are calculated from the values of ε_1 and ε_2 given in last fig. The regions I, II, III, and IV can be seen to be primarily transmitting (T), absorbing (A), reflecting (R), and transmitting (T), respectively. These results follow from consideration of Eq. (23) and the realization that strong absorption takes place only in the neighborhood of a transition frequency.

[From Wooten, "Optical Properties of Solids]

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2}$$



Spectral dependence of R, using n and K in previous figure.

Recall: This could be the starting point of applying the KK relation to obtain $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ from measurement of $R(\omega)$.

(i) Could you see from $R(\omega)$ that $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are of a Lorentz oscillator form?

(ii) From $R(\omega)$ data to $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, then fit Lorentz oscillator, and ask what is $\underbrace{\text{the mechanism}}_{\text{what is that } \omega_0,\ \Gamma\text{?}}$?

Oscillator Strength : A phenomenological approach

- The $\varepsilon_2(\omega)$ and $\varepsilon_1(\omega)$ data may have several Lorentz oscillators (features) at different ω_j's

N_j = density of electrons bound with frequency ω_j $(j = \overset{\text{some \# oscillators}}{\overbrace{1, 2, 3, \text{say}}})$

$$\sum_j N_j = N \quad \text{or} \quad \sum_j \frac{N_j}{N} = 1 \Rightarrow \sum_j f_j = 1$$

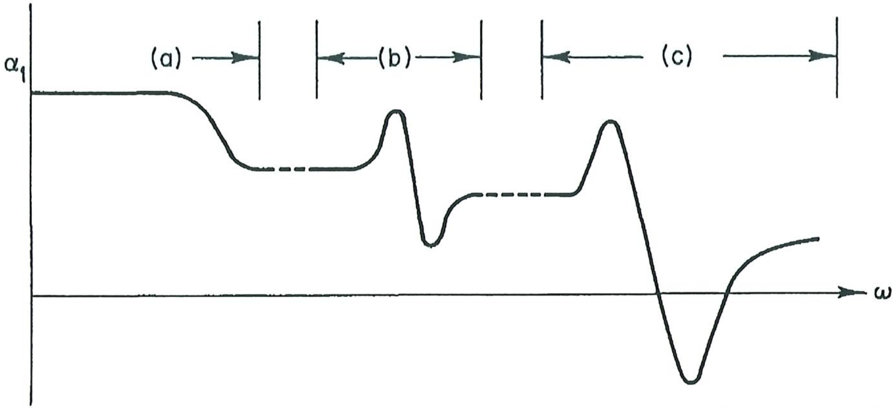
$$\tilde{\varepsilon} = 1 + \frac{e^2}{m\varepsilon_0} \sum_j \frac{N_j}{(\omega_j^2 - \omega^2) - i\Gamma_j \omega}$$

$$= 1 + \frac{e^2}{m\varepsilon_0} \sum_j \frac{N f_j}{(\omega_j^2 - \omega^2) - i\Gamma_j \omega}$$

$$\underbrace{N_j = N f_j,\ \omega_j,\ \Gamma_j}_{\text{parameters for each oscillator}}$$

- With $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ from data, fit Lorentz oscillator(s)
- Then ask what the characteristic frequencies correspond to? (some elementary excitations in the solid?)

It is common to have oscillators at different frequencies contributing to the polarization of a material

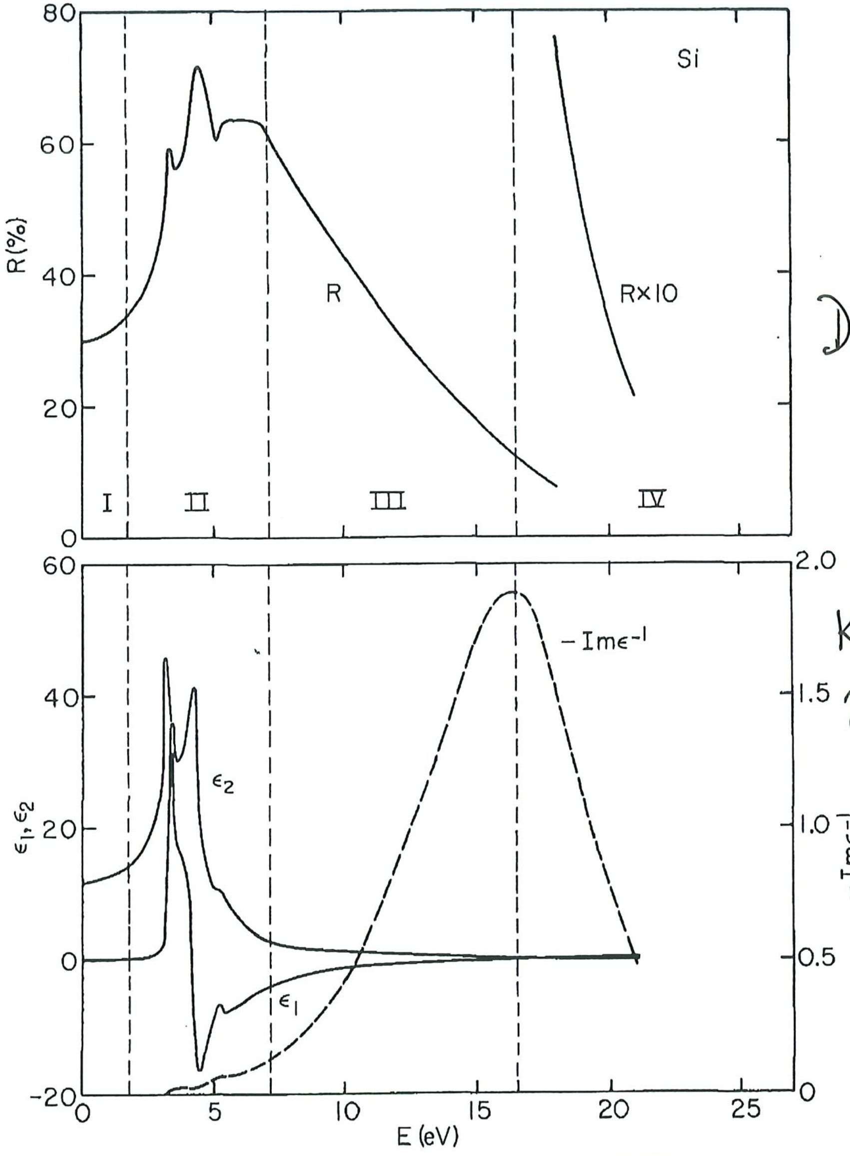


Frequency dependence of contributions to the polarizability arising from orientation of (a) permanent dipoles (microwave), (b) ionic lattice vibrations (infrared), and (c) displacement of electrons (visible and ultraviolet).

(c.f. molecular physics)

Oscillator strengths are integrals $|\langle f|\hat{H}'|i\rangle|^2$ in QM and therefore can be evaluated by perturbation theory.

Examples of Applications: Silicon



Data

↓

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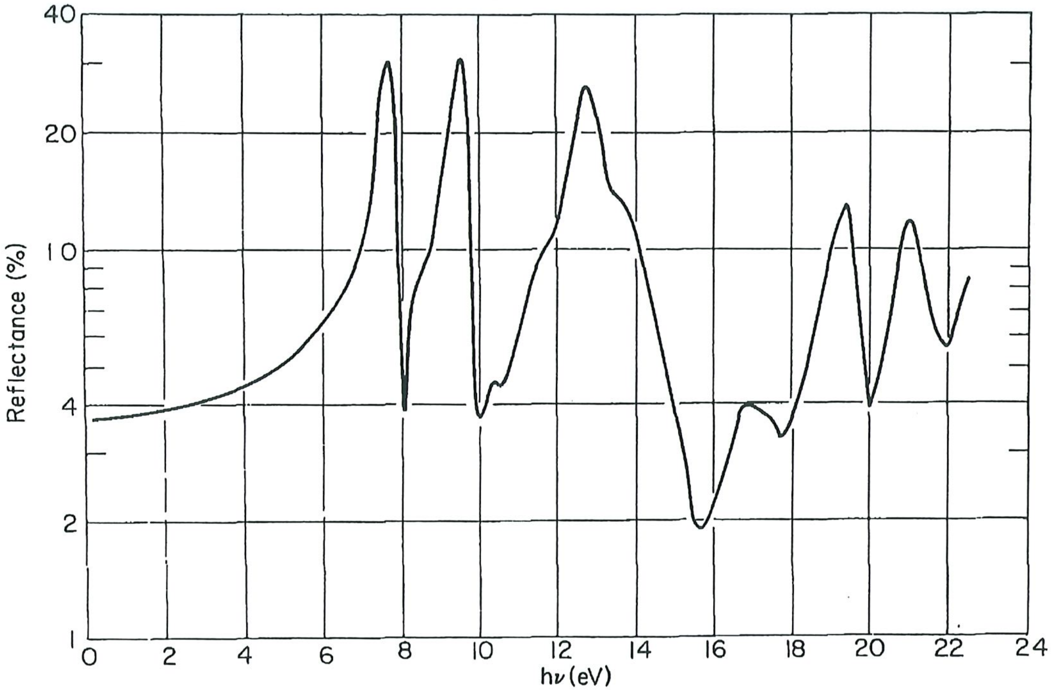

The spectral dependence of the reflectance of KCl. The region of transparency extends to about 7 eV. Above 7 eV, there are a number of sharp peaks related to narrow energy bands and excitons. [From H. R. Philipp and H. Ehrenreich, *Phys. Rev.* 131, 2016 (1963).]

$R(\omega)$ has many more structures $\Rightarrow$ $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ more complicated and more elementary excitations are involved