OPTICAL PROPERTIES OF SOLIDS

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optical properties of crystals

↳ very important per se

as a tool for materials characterization

as a source of technologies

We will start with some general considerations, describing the optical constants of homogeneous materials.

Macroscopic theory in Homogeneous Materials

We follow Grosso & Parravicini Solid State Physics 2nd edition

The propagation of e-m waves through a material is described by the Maxwell's equations. Here, we will summarize the optical constants - introduced in a phenomenological way.

assumptions

Let us restrict ourselves to non-magnetic media

$B = H$, $\mu = 1$ in the absence of external charges and currents

$\rho_{ext} = 0 \qquad J_{ext} = 0$

The Maxwell's eqs. for e-m waves are in such case:

in Gauss units

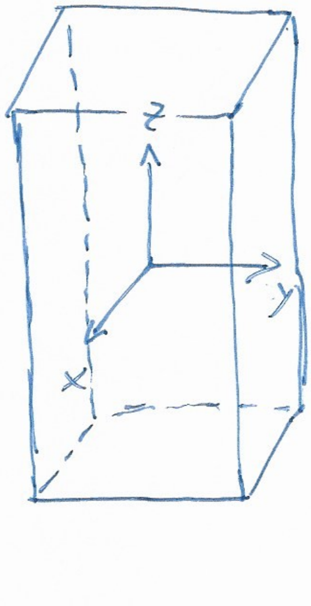
$$\operatorname{div} \vec{E} = 4\pi\rho \qquad \operatorname{curl} \vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t}$$

$$\operatorname{div} \vec{B} = 0 \qquad \operatorname{curl} \vec{B} = \frac{1}{c}\frac{\partial \vec{E}}{\partial t} + \frac{4\pi}{c}\vec{J}$$

the medium has charge density $\rho(\vec{r},t)$ and internal current density $\vec{J}(\vec{r},t)$.

but we will elaborate several quantities in dimensionless notation so that they are independent on the units used in the Maxwell's eqs.

Let us consider the propagation of a transverse e-m wave along z. Specifying the MEs in the geometry of the figure we have



$\vec{E} \parallel \hat{e}_x$

$\vec{B} \parallel \hat{e}_y$

$\vec{J} \parallel \hat{e}_x$

(i) $\vec{E}(\vec{r},t) = E(z)\, e^{-i\omega t}\, \hat{e}_x$

(ii) $\vec{B}(\vec{r},t) = B(z)\, e^{-i\omega t}\, \hat{e}_y$

(iii) $\vec{J}(\vec{r},t) = J(z)\, e^{-i\omega t}\, \hat{e}_x$

(i) $\Rightarrow$ $\mathrm{div}\,\vec{E} = 0$ and if we combine this with with the 1st ME $\Rightarrow$ $\rho = 0$.

(ii) $\Rightarrow$ $\mathrm{div}\,\vec{B} = 0$ so that the ME is satisfied.

The two remaining MEs give

$$\frac{dE(z)}{dz} = \frac{i\omega}{c} B(z)$$

$$-\frac{dB(z)}{dz} = -\frac{i\omega}{c} E(z) + \frac{4\pi}{c} J(z)$$

$$\Rightarrow \boxed{\frac{d^2E(z)}{dz^2} = -\frac{\omega^2}{c^2} E(z) - \frac{4\pi i\omega}{c^2} J(z)}$$

↳ relation derived from the MEs between the electric field and the current density

To proceed beyond this we need to establish a phenomenological (or microscopic constitutive relation) between $E(z)$ and $J(z)$.

Constitutive relation for the conductivity

$$J_\alpha(\vec{r},t) = \sum_\beta \int d\vec{r}\,' \int_{-\infty}^{t} \underbrace{\sigma_{\alpha\beta}(\vec{r},\vec{r}\,',t,t')}_{} E_\beta(\vec{r}\,',t')\,dt'$$

$\alpha, \beta = x, y, z$

is the so-called conductivity tensor which is generally a function of two times and two coords.

If the media is isotropic, the conductivity tensor has the form

$$\sigma_{\alpha\beta} = \sigma\,\delta_{\alpha\beta}$$

so it's essentially a scalar quantity.

We assume that the scalar conductivity σ is an homogeneous function of both space and time.

although this might seem at odds with the microscopic structure of a crystal (which is certainly not homogeneous) this simplification which essentially neglects local field effects originated by the inhomog. gives reasonable results in many relevant situations.

in a general case thus σ will depend on two space coordinates rather than their difference

Carrying these assumptions of space and time homogeneity to the constitutive relation gives:

relation in space-time domain

$$\boxed{\vec{J}(\vec{r},t) = \int_{-\infty}^{+\infty} d\vec{r}\,' \int_{-\infty}^{+\infty} dt'\, \sigma(\vec{r}-\vec{r}\,', t-t')\, \vec{E}(\vec{r}\,', t')}$$

is allowed cause we demand

$$\sigma(\vec{r}-\vec{r}\,', t-t') \equiv 0 \quad \text{for } t' > t$$

[causality]

The Fourier transform of the conductivity is defined as:

$$\sigma(\vec{q},\omega) = \int_{-\infty}^{+\infty} e^{i(\vec{q}\cdot\vec{r}-\omega t)}\, \sigma(\vec{r},t)\, d\vec{r}\, dt$$

and similarly for $\vec{E}(\vec{q},\omega)$ and $\vec{J}(\vec{q},\omega)$.

$$\boxed{J(\vec{q},\omega) = \sigma(\vec{q},\omega)\, \vec{E}(\vec{q},\omega)}$$

property of the FT

relation in momentum-frequency domain

Notice that in general the response at a given point $\vec{r}$ $(J(\vec{r},t))$ will depend on the electric field at all other points $E(\vec{r}\,',t')$

→ the response is most generally non-local.

In the <u>local response approximation</u>

$J(\vec{r},t)$ depends only on $E(\vec{r},t')$ $t'<t$

This means that the conductivity function takes the form:

$$\sigma(\vec{r}-\vec{r}',t-t') = \delta(\vec{r}-\vec{r}')\,\sigma(t-t')$$

Thus, the FT is wave-vector independent

$$\sigma(\vec{q},\omega) = \sigma(\vec{q}=0,\omega) = \sigma(\omega)$$

where $\sigma(\omega)$ is the so-called <u>complex conductivity</u> of the medium.

$\boxed{\text{local-response regime (or approx.)}}$

$\nearrow$ neglect the wave-vector dependence of the response function

$\searrow$ $J(\vec{r}) = \sigma(\omega)\,\vec{E}(\vec{r})$

encodes the time dependence of $\vec{J}$ and $\vec{E}$

$\downarrow$

What justifies this approximation?
or <u>When</u> it can be justified?

$\hookrightarrow$ "when the average distance traveled by the carriers is small with respect to the length of spatial variation of the electric field"

Grosso & Parravicini

Optical constants based on the Local-response Approx.

$$\frac{d^2E(z)}{dz^2} = -\frac{\omega^2}{c^2}E(z) - \frac{4\pi i\omega}{c^2}J(z)\,; \qquad \vec{J}(\vec{r}) = \sigma(\omega)\,\vec{E}(\vec{r})$$

$$\boxed{\frac{d^2E}{dz^2} = -\frac{\omega^2}{c^2}\left[1 + \frac{4\pi i\,\sigma(\omega)}{\omega}\right]E(z)}$$

The solution is a damped or undamped wave

$$E(z) = E_0\, e^{i\frac{\omega}{c}Nz}$$

where $N(\omega)$ is the complex refractive index

$$\boxed{N^2 = 1 + \frac{4\pi i\,\sigma(\omega)}{\omega}}\,.$$

Besides, by using the relations obtained earlier, one gets:

$$B(z) = N\,E(z)$$

Usually one writes

$$\boxed{N = n + ik}$$

n: ordinary refractive index

k: extinction coefficient

$$\boxed{E(z) = E_0\, e^{i\frac{\omega}{c}nz}\; e^{-\frac{\omega}{c}kz}}$$

From the previous eq. we see that

$\boxed{\frac{c}{n}}$ velocity of the e-m wave in the medium

$$\boxed{\delta(\omega) = \frac{c}{\omega k(\omega)}}$$

is the penetration depth (skin depth)

$\Downarrow$

the distance at which the field amplitude drops to $1/e$.

The intensity of the e-m wave is prop. to $|E(z)|^2$

$$I(z) = I_0 \exp(-2\omega k z/c)$$

Thus, the attenuation coefficient of the wave is

$$\boxed{\alpha(\omega) = \frac{2\omega k(\omega)}{c} = \frac{2}{\delta(\omega)}}$$

also known as absorption coefficient

The eq. $N^2 = 1 + \frac{4\pi i \sigma(\omega)}{\omega}$ can also be written as $N^2 = \varepsilon$ where ε is the complex dielectric function.

$$\varepsilon \equiv \varepsilon_1 + i\,\varepsilon_2 \implies \varepsilon_1 = n^2 - k^2 \;\wedge\; \varepsilon_2 = 2nk$$

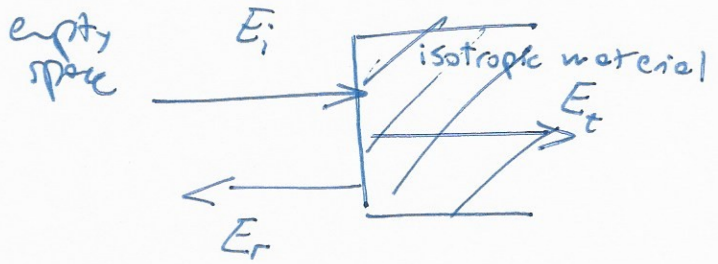
$$n^2 = \frac{1}{2}\left(\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}\right) \;\wedge\; k^2 = \frac{1}{2}\left(-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}\right)$$

One can verify that the conductivity and the dielectric function satisfy:

$$\varepsilon(\omega) = 1 + \frac{4\pi i \sigma(\omega)}{\omega}$$

p. 488

Reflectivity



e-m wave incident on a material (normal incidence)

$$E(z) = \begin{cases} E_t \, e^{i\frac{\omega}{c}Nz}, & z>0 \\ E_i \, e^{i\frac{\omega}{c}z} + E_r \, e^{-i\frac{\omega}{c}z}, & z<0 \end{cases}$$

at the interface we request continuity of the electric field parallel to the surface $E(z)$, this gives

$$E_i + E_r = E_t \, .$$

On the other hand, a similar reasoning for the y component of the magnetic field yields

$$N E_t = E_i - E_r$$

$$\Rightarrow \frac{E_r}{E_i} = \frac{1-N}{1+N}$$

Thus

$$\boxed{R = \left|\frac{E_r}{E_i}\right|^2 = \left|\frac{1-N}{1+N}\right|^2 = \frac{(n-1)^2+k^2}{(n+1)^2+k^2}}.$$

Kramers-Kronig relations

Source:

Marder

Condensed Matter Physics
2nd edition

20.3

Earlier we discussed magnitudes such as the complex dielectric function or the conductivity.

There is a constraint not considered up to now: causality.

The electric displacement D is related to the electric field by

$$\vec{D}(\omega) = \varepsilon(\omega)\,\vec{E}(\omega)$$

$$\vec{D}(t) = \int dt'\,\varepsilon(t')\,\vec{E}(t-t')$$

Since the electric displacement is produced in response to external fields, if the electric field is turned on at $t=0$ one can be sure that for $t<0$ the displacement must vanish too.

Let us assume that

$$\vec{E}(t) = t_0\,\vec{E}_0\,\delta(t)$$

t_0: constant with dimension of time characterizing the duration of the pulse

delta pulse at $t=0$

Then,

$$\vec{D}(t) = \varepsilon(t)\, t_0 \vec{E}_0$$

But since $\vec{D}(t) = 0$ for $t < 0$,

$$\boxed{\varepsilon(t) = 0 \quad \text{for } t < 0}$$

Notice that this still holds if ε is a tensor, or if the wave-vector dependence that we neglected is retained.

The only assumption is that ε relates $\vec{D}$ and $\vec{E}$ in a linear way.

$$\boxed{\varepsilon(\omega) = \int_0^\infty dt\, e^{i\omega t}\, \varepsilon(t)}$$

If we allow ω to move in the complex plane, Im ω needs to be positive, otherwise the exponential function in the integrand grows. This follows because ε vanishes for $t < 0$ and we expect it not to grow exponentially for $t > 0$.

↳ Therefore, $\varepsilon(\omega)$ cannot have any poles on the upper half of the complex ω plane.

Cauchy's theorem

From complex analysis, it follows that: $\lim_{\omega\to\infty} \varepsilon = \varepsilon^{\infty}$

$$\boxed{\varepsilon(\omega) - \varepsilon^{\infty} = \oint \frac{d\omega'}{2\pi i} \frac{\varepsilon(\omega') - \varepsilon^{\infty}}{\omega' - \omega - i\eta}}$$

closed contour in the upper half plane

This eq. contains essentially what is known as Kramers-Kronig relations. But to appreciate them one needs to separate it onto real and imaginary parts.

Now we deform the contour to take ω to the real axis

↳ this is $\eta \to 0^{+}$

$$(*) \quad \varepsilon(\omega) - \varepsilon^{\infty} = \lim_{\eta\to 0^{+}} \left\{ \int_{-\infty}^{\omega-\eta} \frac{d\omega'}{2\pi i} \frac{\varepsilon(\omega') - \varepsilon^{\infty}}{\omega' - \omega - i\eta} + \int_{\omega-\eta}^{+\infty} \frac{d\omega'}{2\pi i} \frac{\varepsilon(\omega') - \varepsilon^{\infty}}{\omega' - \omega - i\eta} + \right.$$

$+$ integral over the half circle around the pole $\}$

playing a bit with Cauchy's theorem we get

$$\varepsilon(\omega) - \varepsilon^{\infty} = P \int \frac{d\omega'}{\pi i} \frac{\varepsilon(\omega') - \varepsilon^{\infty}}{\omega' - \omega}$$

this is the

the factor 2 is not there

so-called Cauchy's ppal. value which is defined as the sum of the first two terms in the rhs of eq. *.

Now we can take the real and imaginary parts of the last eq.

$$\mathrm{Re}\left[\varepsilon(\omega)-\varepsilon^{\infty}\right] = \mathcal{P}\int \frac{d\omega'}{\pi}\,\frac{\mathrm{Im}\left[\varepsilon(\omega')-\varepsilon^{\infty}\right]}{\omega'-\omega}$$

$$\mathrm{Im}\left[\varepsilon(\omega)-\varepsilon^{\infty}\right] = -\mathcal{P}\int \frac{d\omega'}{\pi}\,\frac{\mathrm{Re}\left[\varepsilon(\omega')-\varepsilon^{\infty}\right]}{\omega'-\omega}$$

Since $\varepsilon(t)$ is real, $\varepsilon(\omega)=\varepsilon^{*}(-\omega)$

$\Rightarrow$ $\mathrm{Re}[\varepsilon(\omega)]$ is an even function

$\wedge$

$\mathrm{Im}[\varepsilon(\omega)]$ is an odd function

Therefore, using the notation $\varepsilon(\omega)=\underbrace{\varepsilon_1(\omega)+i\,\varepsilon_2(\omega)}_{\text{real}}$

we get

$$\boxed{\begin{aligned}\varepsilon_1(\omega)-\varepsilon^{\infty} &= \mathcal{P}\int_0^{\infty}\frac{2\omega' d\omega'}{\pi}\,\frac{\varepsilon_2(\omega')}{\omega'^2-\omega^2}\\ \varepsilon_2(\omega) &= -\mathcal{P}\int_0^{\infty}\frac{2\omega d\omega'}{\pi}\,\frac{\varepsilon_1(\omega')-\varepsilon^{\infty}}{\omega'^2-\omega^2}\end{aligned}}$$

which are the Kramers-Kronig relations

linking the real and the imaginary parts of the response function $\varepsilon(\omega)$.