Optical Properties of Solids

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Macroscopic Properties

Studies of the dielectric function $\epsilon(\mathbf{K}, \omega)$ by optical spectroscopy are very useful in the determination of the overall band structure of a crystal, and optical spectroscopy has developed into the most important experimental tool for band structure determination. In the infrared, visible, and ultraviolet spectral regions the wavevector of the radiation is very small ($\mathbf{K} \simeq 0$) compared with the shortest reciprocal lattice vector, and therefore it may usually be taken as zero. We are concerned then with the real ϵ' and imaginary parts ϵ'' of the dielectric function at zero wavevector; $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$. However, the directly accessible functions from optical measurements are the reflectance $R(\omega)$, the refractive index $n(\omega)$, and the extinction coefficient $K(\omega)$. Our first objective is to relate the experimentally observable quantities to the real and imaginary parts of the dielectric function.

The **reflectivity coefficient** $r(\omega)$ is a complex function defined at the crystal surface as the ratio of the reflected electric field E(refl) to the incident electric field E(inc):

$$E(\text{refl})/E(\text{inc}) \equiv r(\omega) \equiv \rho(\omega) \exp[i\theta(\omega)]$$

Here, $\rho(\omega)$ and $\theta(\omega)$ are the amplitude and phase components of the reflectivity coefficient, respectively.

At normal incidence, the reflectivity *r* and reflectance *R* in the crystal can be expressed as

$$r(\omega) = \frac{n + iK - 1}{n + iK + 1} \quad \text{and} \quad R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} = r^* r = \rho^2$$

By definition, $n(\omega)$ and $K(\omega)$ are related to the dielectric function $\epsilon(\omega)$ by

$\sqrt{\epsilon(\omega)} \equiv n(\omega) + iK(\omega) \equiv N(\omega)$, where $N(\omega)$ is the complex refractive index.

$$\epsilon'(\omega) = n^2 - K^2 \; ; \qquad \epsilon''(\omega) = 2nK$$

The transmitted wave in the medium is attenuated because, by the dispersion relation for electromagnetic waves, the wavevector in the medium is related to the incident wavevector *k* in vacuum by $(n + iK)k$:

$$E_y(\text{trans}) \propto \exp\{[i[(n + iK)kx - wt]\} = \exp(-Kkx)\exp[i(nkx - \omega t)]$$

From the experimental we can measure the intensity of the reflected wave, which is termed the *reflectance* $R(\omega) = r^*(\omega)r(\omega)$. We also need to know the phase $\theta(\omega)$ of the reflected wave in order to obtain $n(\omega)$ and $K(\omega)$, but It is difficult to measure $\theta(\omega)$. We show below that it can be calculated from the measured reflectance $R(\omega)$ if this is known at all frequencies.

Kramers-Kronig Relations

The Kramers–Kronig relations are bidirectional mathematical relations, connecting the real and imaginary parts of any complex function that is analytic in the upper half-plane. The relations are often used to compute the real part from the imaginary part (or vice versa) of response functions in physical systems. The response of any linear passive system can be represented as the superposition of the responses of a collection of *j* damped harmonic oscillators with masses M_j. Let the response function $\alpha(\omega) = \alpha'(\omega) + i\alpha''(\omega)$ of the collection of oscillators be defined by $x_\omega = \alpha(\omega) F_\omega e^{-i\omega t}$, F_ω is the applied force and x_ω the displacement.

From the equation of motion, $M_j(d^2/dt^2 + \rho_j d/dt + \omega_j^2)x_j = F$

The complex response function of the oscillator system is

$$\alpha(\omega) = \sum_j \frac{f_j}{\omega_j^2 - \omega^2 - i\omega\rho_j} = \sum f_j \frac{\omega_j^2 - \omega^2 + i\omega\rho_j}{(\omega_j^2 - \omega^2)^2 + \omega^2\rho_j^2}$$

(a) The poles of $\alpha(\omega)$ are all below the real axis.

(b) The integral of $\alpha(\omega)/\omega$ vanishes when taken around an infinite semicircle in the upper half of the complex ω-plane. It suffices that $\alpha(\omega) \to 0$ uniformly as $|\omega| \to \infty$.

(c) The function $\alpha'(\omega)$ is even and $\alpha''(\omega)$ is odd with respect to real ω.

Consider the Cauchy integral in the form

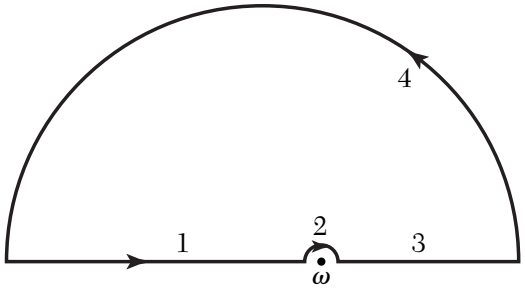
$$\alpha(\omega) = \frac{1}{\pi i}\ \mathrm{P}\int_{-\infty}^{\infty} \frac{\alpha(s)}{s-\omega}\,ds$$

where P denotes the principal part of the integral and the right-hand side is to integrate over the semicircle at infinity in the upper half-plane. We equate the real parts of the equation to obtain

$$\alpha'(\omega) = \frac{1}{\pi}\,\mathrm{P}\int_{-\infty}^{\infty} \frac{\alpha''(s)}{s-\omega}\,ds = \frac{1}{\pi}\,\mathrm{P}\left[\int_{0}^{\infty} \frac{\alpha''(s)}{s-\omega}\,ds + \int_{-\infty}^{0} \frac{\alpha''(p)}{p-\omega}\,dp\right]$$

Substitute *p* for −*s* and use property (c) that $\alpha''(-s) = -\alpha''(s)$, then

$$\int_{-\infty}^{0} \frac{\alpha''(p)}{p-\omega}\,dp = \int_{0}^{\infty} \frac{\alpha''(s)}{s+\omega}\,ds$$



$$s = \omega + u\,e^{i\theta}$$

in the limit as $u \to 0$

The segments (1) and (3) are by definition the principal part of the integral between −∞ and ∞. Because the integral over (1) + (2) + (3) + (4) must vanish,

$$\int_{(2)} \frac{\alpha(s)}{s-\omega}\,ds \to \alpha(\omega)\int_{\pi}^{0} \frac{iu\,e^{i\theta}d\theta}{u\,e^{i\theta}} = -\pi i\alpha(\omega)$$

$$\int_{(1)} + \int_{(3)} \equiv \mathrm{P}\int_{-\infty}^{\infty} \frac{\alpha(s)}{s-\omega}\,ds = -\int_{(2)} = \pi i\alpha(\omega)$$

We have the Kramers-Kronig relations:

$$\alpha'(\omega) = \frac{2}{\pi} \mathrm{P} \int_0^\infty \frac{s\alpha''(s)}{s^2 - \omega^2} ds$$

and

$$\alpha''(\omega) = -\frac{2\omega}{\pi} \mathrm{P} \int_0^\infty \frac{\alpha'(s)}{s^2 - \omega^2} ds$$

We can apply the Kramers-Kronig relations to $r(\omega)$ viewed as a response function between the incident and reflected waves.

$$E(\mathrm{refl})/E(\mathrm{inc}) \equiv r(\omega) \equiv \rho(\omega) \exp[i\theta(\omega)] = R^{1/2}\exp[i\theta(\omega)]$$

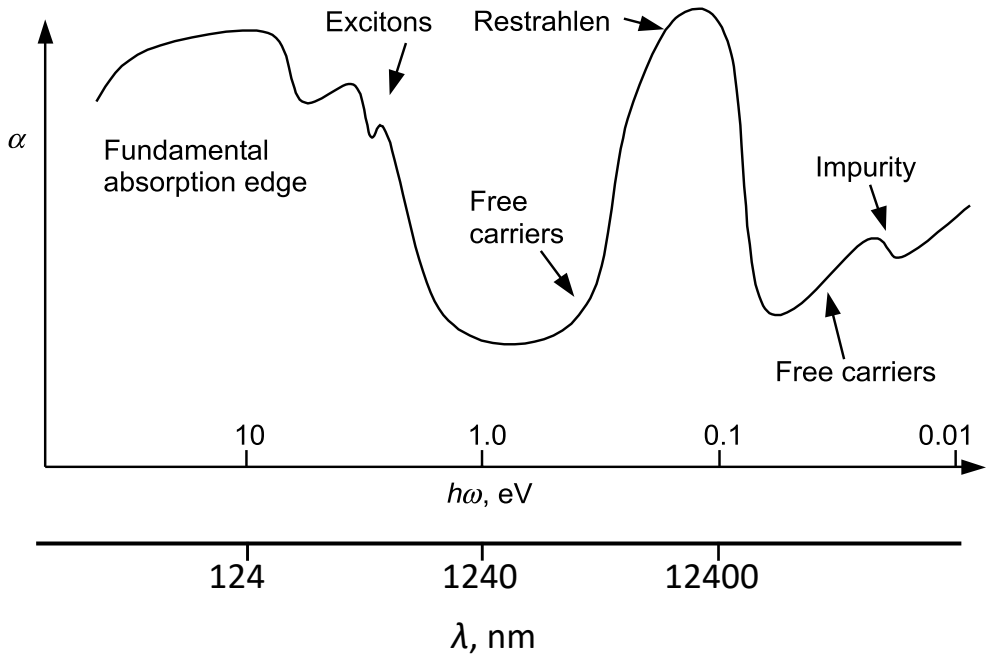
$$\Rightarrow \quad \ln r(\omega) = \ln R^{1/2}(\omega) + i\theta(\omega)$$

We apply the second Kramers-Kronig relations, then

$$\theta(\omega) = -\frac{\omega}{\pi} \mathrm{P} \int_0^\infty \frac{\ln R(s)}{s^2 - \omega^2} ds = -\frac{1}{2\pi} \int_0^\infty \ln \left| \frac{s + \omega}{s - \omega} \right| \frac{d \ln R(s)}{ds} ds$$

Spectral regions in which the reflectance is constant do not contribute to the integral; further, spectral regions $s >> \omega$ and $s << \omega$ do not contribute much because the function $\ln |(s + \omega)/(s - \omega)|$ is small in these regions.

Absorption Spectrum of a Semiconductor



There are several processes involved in absorption, but the main five are:

1. Absorption due to electronic transitions between bands that involve wavelengths typically less than ten micrometers;
2. Absorption by excitons at wavelengths with energies just below the absorption edge due to valence conduction band transitions;
3. Excitation and ionization of impurities that involve wavelengths ranging from about one micrometer to one thousand micrometers;
4. Excitation of lattice vibrations (optical phonons) in polar solids for which the usual wavelengths are ten to fifty micrometers;
5. Free-carrier absorption for frequencies up to the plasma edge, which is particularly important in metals.

Fermi Golden Rule

The Fermi golden rule can be used for calculating the transition probability rate for an electron that is excited by a photon from the valence band to the conduction band in a direct band-gap semiconductor. Consider an EM wave of frequency ω and wavevector **q**, its electric field is

$\mathbf{E} = -\partial\mathbf{A}/\partial t = i\omega A_0 \vec{\epsilon} e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}$, **A** is the vector potential of the EM wave.

For a charged particle in the valence band, the Hamiltonian is

$$H = \frac{(\mathbf{p} - Q\mathbf{A})^2}{2m_0} + V(\mathbf{r}) = H_0 + H' = \left[\frac{\mathbf{p}^2}{2m_0} + V(\mathbf{r})\right] + \left[\frac{e}{2m_0}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p})\right]$$

where *H'* is the perturbation of the EM wave. From here on we have transition probability based on time-dependent perturbation theory that

$$\Gamma_{if} = \frac{2\pi}{\hbar}|\langle f|H'|i\rangle|^2\delta(E_f - E_i \pm \hbar\omega) \quad \text{and} \quad H' \approx \frac{eA_0}{m_0}\vec{\epsilon}\cdot\vec{p}$$

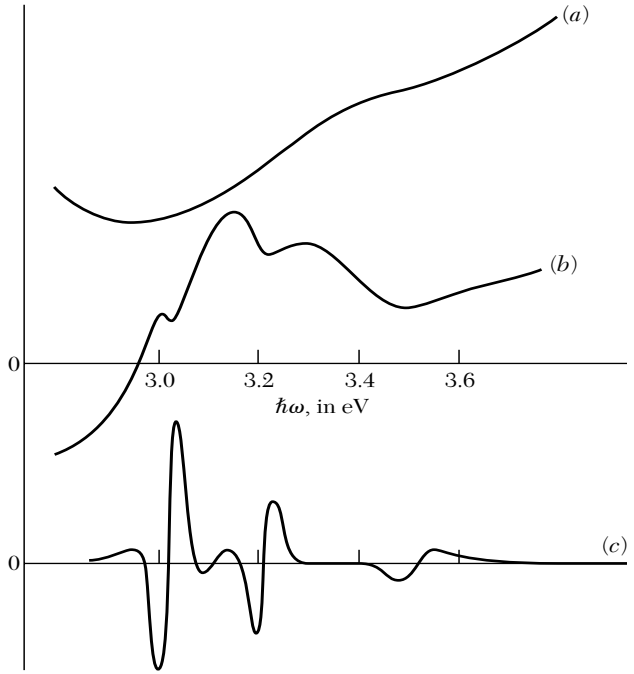
$$\Gamma_{cv} = \frac{2\pi}{\hbar}\left(\frac{eA_0}{m_0}\right)^2 |\vec{\epsilon}\cdot\boldsymbol{\mu}_{cv}(\mathbf{k})|^2\delta(E_c - E_v - \hbar\omega) \qquad \boldsymbol{\mu}_{cv} = -\frac{i\hbar}{\Omega_0}\int_{\Omega_0} d\mathbf{r}' u^*_{n_c,\mathbf{k}}(\mathbf{r}')\nabla u_{n_v,\mathbf{k}}(\mathbf{r}')$$

μ_{cv} is the *transition dipole moment matrix element* with the expectation value of $\langle c|(\text{charge}) \times (\text{distance})|v\rangle$

Electronic Interband Transitions

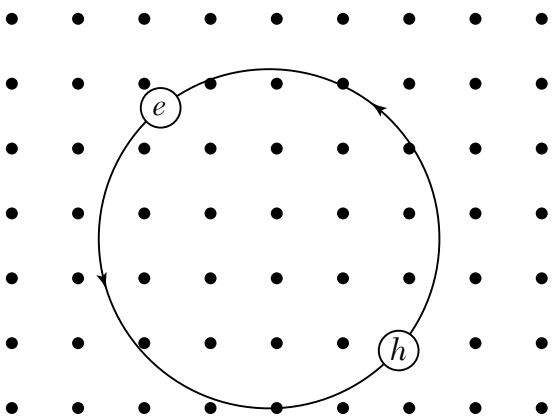
Direct interband absorption of a photon $\hbar\omega$ will occur at all points in the Brillouin zone for which energy is conserved: $\hbar\omega = \epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k})$. The total absorption at given ω is an integral over all transitions in the zone that satisfy the energy conservation and usually is broad and featureless. However, the energy-conservation relation does not exclude spectral structure in a crystal, because transitions accumulate at frequencies for which the bands *c, v* are parallel — that is, at frequencies where $\nabla_{\mathbf{k}}[\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k})] = 0$. At these critical points in **k** space the joint density of states $D_c(\epsilon_v+\hbar\omega)D_v(\epsilon_v)$ is singular.

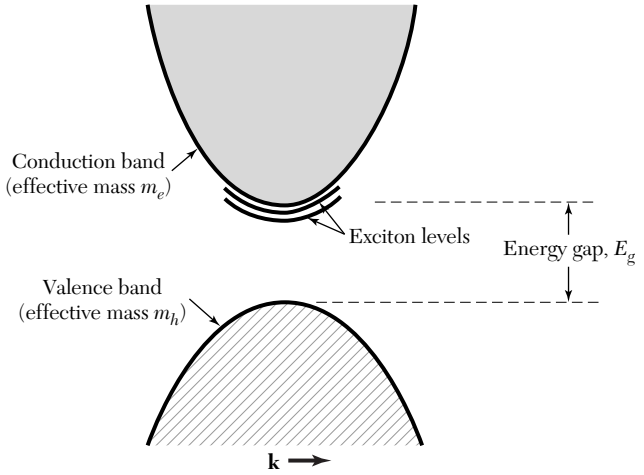
The broad bands convey much intelligence which emerges when derivatives are taken of the reflectance derivatives with respect to wavelength, electric field, temperature, pressure, or uniaxial stress, etc. One example is shown in the right figure the spectral region in germanium between 3.0 and 3.6 eV.



Excitons

Reflectance and absorption spectra often show structure for photon energies just below the energy gap, where we might expect the crystal to be transparent. This structure is caused by the absorption of a photon with the creation of a bound electron-hole pair.



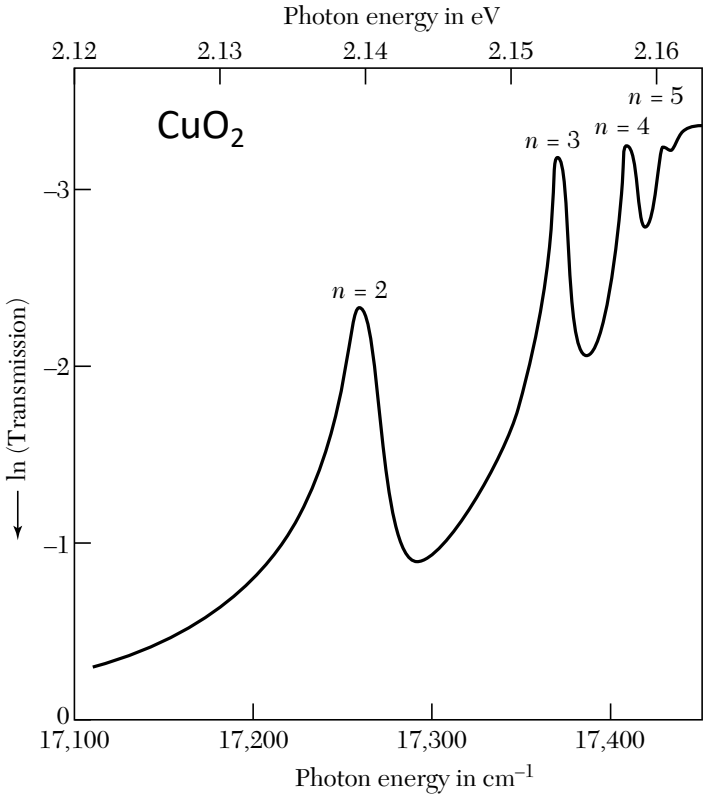


The lowest frequency absorption line of the crystal at absolute zero is not E_g, but is $E_g - E_{ex}$. E_{ex} is the binding energy of the exciton. An exciton can have translational kinetic energy. Excitons are unstable with respect to radiative recombination in which the electron drops into the hole in the valence band, accompanied by the emission of a **photon** or **phonons**.

Mott-Wannier Excitons

Consider an electron in the conduction band and a hole in the valence band. The pair is weakly bound and attracts each other by the coulomb potential

$U(r) = -e^2/\epsilon r$, where r is the distance between the particles and ϵ is the appropriate dielectric constant.



This is similar to the hydrogen atom problem and the energy levels referred to the top of the valence band are given by

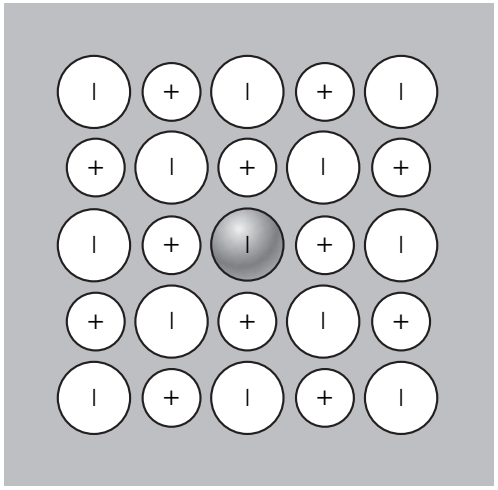
$$E_n = E_g - \frac{\mu e^4}{2\hbar^2 \epsilon^2 n^2}$$

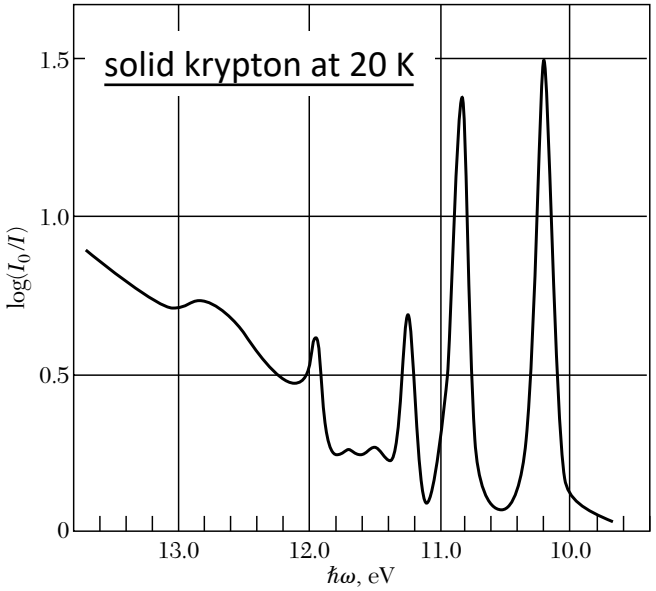
Here n is the principal quantum number and μ is the reduced mass:

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$$

Frenkel Excitons

In a tightly bound exciton, the excitation is localized on or near a single atom: the hole is usually on the same atom as the electron although the pair may be anywhere in the crystal. A Frenkel exciton is essentially an excited state of a single atom, but the excitation can hop from one atom to another by virtue of the coupling between neighbors.





Atomic krypton has its lowest strong atomic transition at 9.99 eV. The corresponding transition in the crystal is closely equal and is at 10.17 eV. The energy gap in the crystal is 11.7 eV, so the exciton ground state energy is $11.7 - 10.17 \simeq 1.5$ eV, referred to a free electron and free hole separated and at rest in the crystal.

Intraband Transition

Free-carrier absorption can be viewed as intraband absorption – the electron absorbing the photon remains in the same band. Free-carrier absorption is obviously important for metals, and is often of importance for semiconductors. Free electronic systems can be treated classically when their de Broglie wavelengths are small compared to the average interparticle separations. For many purposes, the process can be viewed classically by Drude theory with a relaxation time of $\tau \equiv 1/\omega_0$.

Assuming a sinusoidal electric field $E = E_0\exp(-i\omega t)$ and using an effective mass m^* rather than m:

$$m^*\ddot{x} + \frac{m^*}{\tau}\dot{x} = -eE_0\exp(-i\omega\tau)$$

Seeking a steady-state solution of the form $x = x_0\exp(-i\omega t)$, we find

$$x = (eE/m^*)(\omega^2 + i\omega/\tau)^{-1} = (eE/m^*)(\omega^2 + i\omega\omega_0)^{-1}$$

The polarization P due to the free carriers with density N is

$$P = -nex = \chi_n E = -(NeE/m^*)(\omega^2 + i\omega\omega_0)^{-1} = -\omega_p^2\,(\omega^2 + i\omega\omega_0)^{-1}E$$

Here $\omega_p^2 = Ne/m^*$, and ω_p is the *plasma frequency*.

$$\epsilon(\omega) = 1 + \chi(\omega) = 1 - \omega_p^2\,(\omega^2 + i\omega\omega_0)^{-1}$$

The complex dielectric constant ϵ_n is related to the refraction index n, and its real part $\epsilon'(\omega)$ as well as imaginary part $\epsilon''(\omega)$ are

$$\epsilon'(\omega) = n^2 - K^2 = 1 - \omega_p^2 (\omega^2 + \omega_0^2)^{-1}$$

$$\epsilon''(\omega) = 2nK = \omega_p^2 (\omega_0/\omega)(\omega^2 + \omega_0^2)^{-1}$$

The plasma frequency ω_p is proportional to the free-carrier concentration, ω_0 measures the electron–phonon coupling and ω is the frequency of light.

(i) Low frequency region: $\omega << \omega_0$ or $\omega/\omega_0 << 1$. We obtain

$$\epsilon'(\omega) = n^2 - K^2 \simeq 1 - \omega_p^2/\omega_0^2 \; ; \quad \epsilon''(\omega) = 2nK \simeq (\omega_0/\omega) >> 1$$

Here the imaginary part (of the dielectric constant) is much greater than the real part and we have high reflection because $R = \dfrac{(n-1)^2 + K^2}{(n+1)^2 + K^2}$.

(ii) Relaxation region: $\omega_0 << \omega << \omega_p$. We obtain

$$\epsilon'(\omega) = n^2 - K^2 \simeq 1 - \omega_p^2/\omega^2 \; ; \quad \epsilon''(\omega) = 2nK \simeq (\omega_p/\omega)^2(\omega_0/\omega) < \epsilon'(\omega)$$

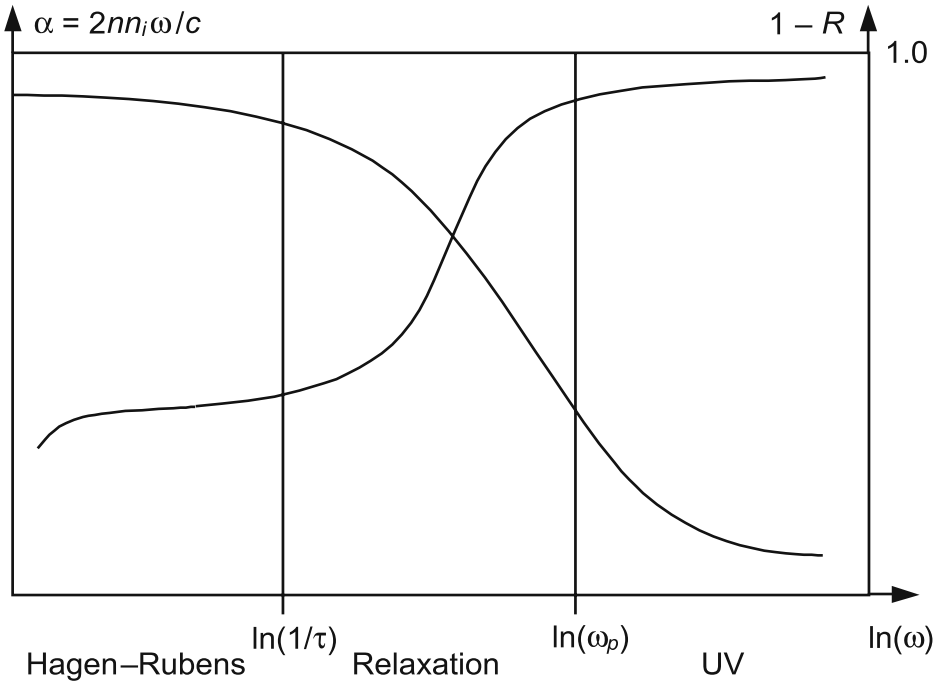
From these two relations, the imaginary part of the refractive index K is much greater than its real part n, so the metal is still strongly reflecting.

(iii) Ultraviolet region: $\omega >> \omega_p$, or $\omega/\omega_p >> 1$. We obtain

$$\epsilon'(\omega) = n^2 - K^2 \simeq 1 \; ; \quad \epsilon''(\omega) = 2nK \simeq (\omega_p/\omega)^3 << \epsilon'(\omega)$$

The imaginary part of the refractive index K is much smaller than its real part n, and there is little reflectance since this is the ultraviolet transparency region.

Absorption and reflection of metals



$$1 = \alpha + R + T$$

Plasmons

A plasmon is a quantum of plasma oscillation. The plasmon can be considered as a quasiparticle since it arises from the quantization of plasma oscillations, just like phonons are quantizations of mechanical vibrations. Thus, plasmons are collective (a discrete number) oscillations of the free electron gas density. For example, at optical frequencies, plasmons can couple with a photon to create another quasiparticle called a plasmon polariton. For a free-electron in an electric field *E* we have

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = -eE = -eE_0\exp(-\mathrm{i}\omega t) \quad \Rightarrow \quad x = \frac{eE}{m\omega^2}\,.$$

Then,

$$P = -Nex = -\frac{Ne^2}{m\omega^2}E\,, \qquad \text{and} \qquad \varepsilon(\omega) = 1 + \frac{P(\omega)}{\varepsilon_0 E(\omega)} = 1 - \frac{Ne^2}{\varepsilon_0 m\omega^2}$$

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \qquad \text{and} \qquad \omega_p^2 = \frac{Ne^2}{\varepsilon_0 m} \quad : \textit{Plasmon frequency}$$

If the positive ion core background has a dielectric constant of ε(∞) that is about constant, then

$$\varepsilon(\omega) = \varepsilon(\infty)\left[1 - \frac{\tilde{\omega}_p^2}{\omega^2}\right], \qquad \text{where} \qquad \tilde{\omega}_p = \frac{\omega_p}{\sqrt{\varepsilon(\infty)}}\,.$$

Polaritons

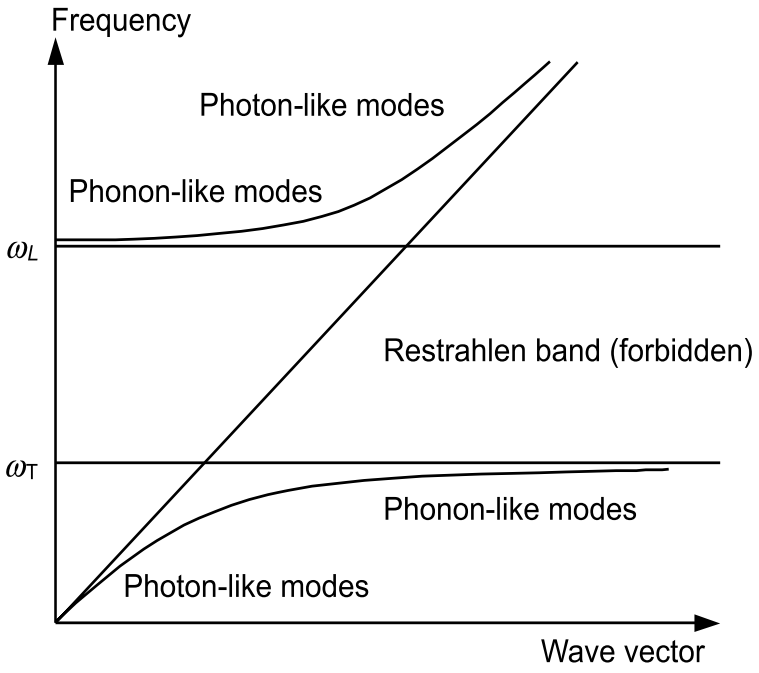
Polaritons are quasiparticles resulting from strong coupling of electromagnetic waves with an electric or magnetic dipole-carrying excitation. The polariton is a bosonic quasiparticle, which has a major feature of a strong dependency of the propagation speed of light through the crystal on the frequency of the photon.

A polariton is the result of the combination of a photon with a polar excitation in a material. The following are types of polaritons:

- ***Phonon polaritons*** result from coupling of an infrared photon with an optical phonon;
- ***Exciton polaritons*** result from coupling of visible light with an exciton;
- ***Intersubband polaritons*** result from coupling of an infrared or terahertz photon with an intersubband excitation;
- ***Surface plasmon polaritons*** result from coupling of surface plasmons with light.

Phonon Polaritons

Polar solids carry lattice polarization waves and hence can interact with electromagnetic waves, but by selection rules and conservation laws, only *transverse* optical phonons couple to electromagnetic waves. The dispersion relations for photons and the phonons of the polarization waves can cross. When these dispersion relations cross, the resulting quanta turn out to be neither photons nor phonons but mixtures called polaritons.



Since $n = \varepsilon^{1/2}$ with $\sigma = 0$, if $\varepsilon < 0$, one gets high reflectivity with n pure imaginary. Since

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

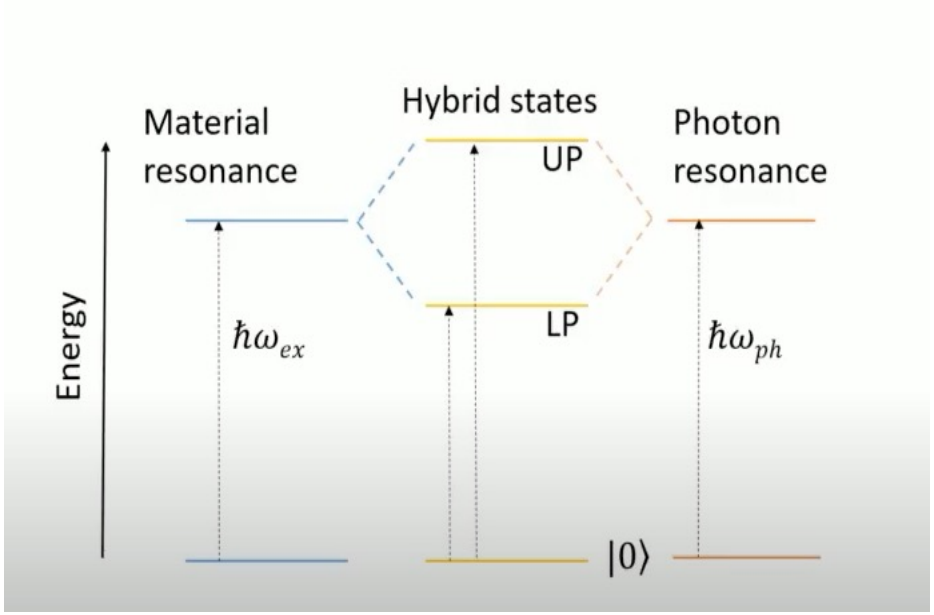
If

$$\omega_T^2 < \omega^2 < \omega_T^2 + \frac{c\varepsilon_0}{\varepsilon(\infty)}, \quad \text{then } \varepsilon < 0.$$

A band of forbidden non-propagating EM waves extends from ω_T to ω_L. ω_T is called the Restrahl frequency.

Exciton Polaritons

Exciton polariton is a type of polariton, a hybrid light and matter quasiparticle arising from the strong coupling of the electromagnetic dipolar oscillations of excitons and photons. The coupling of the two oscillators, photons modes in the semiconductor optical microcavity and excitons of the quantum wells, results in the energy anti-crossing of the bare oscillators, giving rise to the two new normal modes for the system, known as the upper and lower polariton resonances (or branches). The energy shift is proportional to the coupling strength.



The higher energy or upper mode (UPB, upper polariton branch) is characterized by the photonic and exciton fields oscillating in-phase, while the LPB (lower polariton branch) mode is characterized by them oscillating with phase-opposition.

Surface Plasma Polaritons

Surface plasmons are those plasmons that are confined to surfaces and that interact strongly with light resulting in a polariton. They occur at the interface of a material exhibiting positive real part of their relative permittivity, i.e. dielectric constant, (e.g. vacuum, air, glass and other dielectrics) and a material whose real part of permittivity is negative at the given frequency of light, typically a metal or heavily doped semiconductors. In addition to opposite sign of the real part of the permittivity, the magnitude of the real part of the permittivity in the negative permittivity region should typically be larger than the magnitude of the permittivity in the positive permittivity region, otherwise the light is not bound to the surface. With the light of 632.8 nm wavelength provided by a He-Ne laser, interfaces supporting surface plasmons are often formed by metals like silver or gold (negative real part permittivity) in contact with dielectrics such as air or silicon dioxide. Many geometric structures have been explored due to the capability of surface plasmons to confine light below the diffraction limit of light.

SPPs can be used to channel light efficiently into nanometer scale volumes, leading to direct modification of resonate frequency dispersion properties, as well as field enhancements suitable for enabling strong interactions with nonlinear materials.

Nonlinear Optical Process

Nonlinear optics is related to the analysis of the nonlinear interaction between light and matter when the light-induced changes of the medium optical properties occur. The nonlinear optical effects are weak, and typically observed only at very high light intensities (values of atomic electric fields, typically 10^8 V/m) such as those provided by lasers. A typical nonlinear optical process consists of two stages. First, the intense coherent light induces a nonlinear response of the medium, and then the modified medium influences the optical radiation in a nonlinear way. The nonlinear medium is described by a system of the dynamic equations including the optical field.

Nonlinear optical phenomena, in which the optical fields are not too large, can be described by a Taylor series expansion of the dielectric polarization density **P**(*t*) at time *t* in terms of the electric field **E**(*t*):

$$\mathbf{P}(t) = \varepsilon_0 \left(\chi^{(1)} \mathbf{E}(t) + \chi^{(2)} \mathbf{E}^2(t) + \chi^{(3)} \mathbf{E}^3(t) + \dots \right),$$

where the coefficients $\chi^{(n)}$ are the *n*-th-order susceptibilities of the medium, and the presence of such a term is generally referred to as an *n*-th-order nonlinearity. In general, $\chi^{(n)}$ is an (n + 1)-th-rank tensor representing both the polarization dependent nature of the interaction and the symmetries of the nonlinear material.

Wave Equation in a Nonlinear Material

Central to the study of electromagnetic waves is the wave equation. Starting with Maxwell's equations in an isotropic space, containing no free charge, it can be shown that

$$\nabla \times \nabla \times \mathbf{E} + \frac{n^2}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{E} = -\frac{1}{\varepsilon_0 c^2}\frac{\partial^2}{\partial t^2}\mathbf{P}^{\mathrm{NL}}, \quad \text{or} \quad \nabla^2\mathbf{E} - \frac{n^2}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{E} = \frac{1}{\varepsilon_0 c^2}\frac{\partial^2}{\partial t^2}\mathbf{P}^{\mathrm{NL}}$$

where $\mathbf{P}^{\mathrm{NL}}$ is the nonlinear part of the polarization density, and n is the refractive index, which comes from the linear term in **P**.

In general, an n-th order nonlinearity will lead to (n + 1)-wave mixing. As an example, if we consider only a second-order nonlinearity (three-wave mixing), then the polarization **P** takes the form $\mathbf{P}^{\mathrm{NL}} = \varepsilon_0 \chi^{(2)} \mathbf{E}^2(t)$.

If $E(t)$ is made up of two components at frequencies ω_1 and ω_2, then

$$\mathbf{E}(t) = \frac{1}{2}E_1 e^{-i\omega_1 t} + \frac{1}{2}E_2 e^{-i\omega_2 t} + \text{c.c.},$$

$$\mathbf{P}^{\mathrm{NL}} = \frac{\varepsilon_0}{4}\chi^{(2)}\left[{E_1}^2 e^{-i2\omega_1 t} + {E_2}^2 e^{-i2\omega_2 t} + 2E_1E_2 e^{-i(\omega_1+\omega_2)t} + 2E_1{E_2}^* e^{-i(\omega_1-\omega_2)t} + \left(|E_1|^2 + |E_2|^2\right)e^0 + \text{c.c.}\right]$$

which has frequency components at $2\omega_1$, $2\omega_2$, $\omega_1+\omega_2$, $\omega_1-\omega_2$, and 0, corresponding to the nonlinear effects known as second harmonic, sum frequency, difference frequency generations and optical rectification, respectively.

Phase Matching

In a typical situation, the electrical fields are traveling waves described by

$$E_j(\mathbf{x},t) = E_{j,0}e^{i(\mathbf{k}_j\cdot\mathbf{x}-\omega_j t)} + \text{c.c.}$$

at position **x**, with the wave vector $\|\mathbf{k}_j\| = \mathbf{n}(\omega_j)\omega_j/c,$ where *c* is the velocity of light in vacuum, and **n**(ω_j) is the index of refraction of the medium at angular frequency ω_j. Thus, the second-order polarization at angular frequency $\omega_3 = \omega_1 + \omega_2$ is

$$P^{(2)}(\mathbf{x},t) \propto E_1^{n_1} E_2^{n_2} e^{i[(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{x}-\omega_3 t]} + \text{c.c.}$$

At each position **x** within the medium, the oscillating second-order polarization radiates at angular frequency ω_3 and a corresponding wave vector $\|\mathbf{k}_3\| = \mathbf{n}(\omega_3)\omega_3/c.$

Constructive interference, and therefore a high-intensity ω_3 field, will occur only if

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

The above equation is known as the phase-matching condition. Typically, three-wave mixing is done in a birefringent crystalline material, where the refractive index depends on the polarization and direction of the light that passes through. The polarizations of the fields and the orientation of the crystal are chosen such that the phase-matching condition is fulfilled. This technique is called angle tuning.

Frequency Doubling

One of the most commonly used frequency-mixing processes is frequency doubling, or second-harmonic generation. Practically, frequency doubling is carried out by placing a nonlinear medium in a laser beam. While there are many types of nonlinear media, the most common media are crystals. These crystals have the necessary properties of being strongly birefringent, having a specific crystal symmetry, being transparent for both the impinging laser light and the frequency-doubled wavelength, and having high damage thresholds, which makes them resistant against the high-intensity laser light.

Common second-harmonic-generating (SHG) materials:

800 nm: barium borate (BBO)
806 nm: lithium iodate ($LiIO_3$)
860 nm: potassium niobate ($KNbO_3$)
980 nm: $KNbO_3$
1064 nm: monopotassium phosphate (KDP), lithium triborate (LBO) and β-BBO
1300 nm: gallium selenide (GaSe)
1319 nm: $KNbO_3$, BBO, KDP, potassium titanyl phosphate (KTP), lithium niobate ($LiNbO_3$), $LiIO_3$, and ammonium dihydrogen phosphate (ADP)
1550 nm: potassium titanyl phosphate (KTP), lithium niobate ($LiNbO_3$)

Problems

1. ***Hagen-Rubens relation for infrared reflectivity of metals.*** The complex refractive index $n + iK$ of a metal for $\omega\tau << 1$ is given by

$$\epsilon(\omega) \equiv (n + iK)^2 = 1 + 4\pi i\sigma_0/\omega \ ,$$

where σ_0 is the conductivity for static fields. We assume here that intraband currents are dominant; interband transitions are neglected. For the reflection coefficient at normal incidence, show that

$$R \simeq 1 - (2\omega/\pi\sigma_0)^{1/2} \ ,$$

provided that $\sigma_0 >> \omega$. This is the Hagen-Rubens relation. For sodium at room temperature, $\sigma_0 \simeq 2.1 \times 10^{17}$ s^{-1} in CGS and $\tau = 3.1 \times 10^{-14}$ s, as deduced from $\tau = \sigma_0 m/ne^2$. Radiation of 10 μm has $\omega = 1.88 \times 10^{14}$ s^{-1} , so that the Hagen-Rubens result should apply: $R = 0.976$. The result calculated from experimental values of n and K is 0.987. Hint: If $\sigma_0 >> \omega$, then $n^2 \simeq K^2$. This simplifies the algebra.

2. For intermediate frequencies $\omega_T < \omega < \omega_L$, given

$$\frac{\varepsilon(\omega)}{\varepsilon_0} - \frac{\varepsilon(\infty)}{\varepsilon_0} = \frac{3B_{\text{ion}}(\omega)}{[1 - B_{\text{el}} - B_{\text{ion}}(\omega)](1 - B_{\text{el}})},$$

and the equation of motion

$$\mu\ddot{v} + Gv = \frac{1}{3\varepsilon_0}\frac{Ne^2}{1 - B_{\text{el}}}v + eE,$$

derive the equation

$$\omega_T^2 + \frac{c\varepsilon_0}{\varepsilon(\infty)} = \omega_L^2,$$

where c is a defined as constant within the derivation. In this process, show intermediate derivations for the following equations defining constants as necessary:

$$\mu(\omega_T^2 - \omega^2)v = eE,$$

$$\frac{E}{E_{\text{loc}}} = \frac{1}{1 + F},$$

$$\varepsilon(\omega) = \varepsilon(\infty) + \frac{c\varepsilon_0}{\omega_T^2 - \omega^2}.$$