

Section 13: Optical properties of solids

Optical methods are very useful for the quantitative determination of the electronic band structure of solids. Experiments on optical reflectivity, transmission and refraction provide the way to determine the dielectric constant of the solid, which is related to the band structure. The dielectric constant is related to the optical conductivity. The term “optical conductivity” means the electrical conductivity in the presence of an alternating electric field. The term “optical” here covers the entire frequency range, and is not restricted only to the visible region of the spectrum. In order to derive the relation between the dielectric constant and the optical conductivity, we assume that electric field is oscillating with angular frequency ω :

$$\mathbf{E}(t) = \mathbf{E}(\omega)e^{-i\omega t}. \quad (1)$$

This wave propagates through the medium with conductivity $\sigma(\omega)$ and the dielectric constant $\varepsilon_L(\omega)$, both being the function of ω . Index L for the dielectric constant here reflects the fact that this is the dielectric constant of the lattice and does not include the conduction electrons. This implies the polarization of the medium occurs only due to the bound charges (polarization due to ions). The *electric current* and the *electrical displacement* are related to the electric field by

$$\mathbf{j}(\omega) = \sigma(\omega)\mathbf{E}(\omega), \quad (2)$$

$$\mathbf{D}(\omega) = \varepsilon_L(\omega)\mathbf{E}(\omega). \quad (3)$$

In general the conductivity and the dielectric function are tensors. Here we assume for simplicity that the medium is isotropic, so that $\sigma(\omega)$ and $\varepsilon_L(\omega)$ are scalars, and therefore \mathbf{D} and \mathbf{j} are parallel to \mathbf{E} .

Now let me show that the dielectric constant and conductivity enter into a determination of the optical properties of a solid only in the combination. This can be seen from the Maxwell equation (CGS units)

$$\nabla \times \mathbf{H} = \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} + \frac{4\pi}{c} \mathbf{j}. \quad (4)$$

The first term on the right hand side of this equation corresponds to the *displacement* current associated with the polarization of the ion cores. The second term which is proportional to \mathbf{j} is the *convective* current of the conduction electrons. Using Eq.(1) this formula can be rewritten in the following form:

$$\nabla \times \mathbf{H} = \frac{1}{c} \varepsilon_L \frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c} \sigma \mathbf{E} = \frac{1}{c} \left(\varepsilon_L + \frac{4\pi i \sigma}{\omega} \right) \frac{\partial \mathbf{E}}{\partial t} = \frac{1}{c} \varepsilon \frac{\partial \mathbf{E}}{\partial t}, \quad (5)$$

where ε is a complex dielectric function,

$$\varepsilon = \varepsilon_L + \frac{4\pi i \sigma}{\omega}. \quad (6)$$

In this representation the conduction electrons are considered as a part of the dielectric medium. This consideration is plausible because in the presence of alternating electric field the conduction

electrons oscillate around their equilibrium positions without net translational motion. This is different from the DC conductivity when $\sigma(\omega)$ and $\varepsilon_L(\omega)$ describe distinguishable physical processes, where $\sigma(\omega)$ describes the "free charges" (those that can move freely over arbitrary distances in response to the DC field) and $\varepsilon_L(\omega)$ describes the "bound charges" (those that are bound to equilibrium positions).

The dielectric constant is directly related to the optical properties. The complex index of refraction of the medium N is defined as

$$N = \sqrt{\varepsilon} = n + ik, \quad (7)$$

where n is the usual refractive index and k is the extinction coefficient. In optical experiments, one does not usually measure n and k directly. The measurable quantities are the reflectivity R and the absorption coefficient α . It can be shown (see textbooks on electromagnetism) that these quantities are related to n and k by the expressions,

$$R = \frac{|1-N|^2}{|1+N|^2} = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2}, \quad (8)$$

$$\alpha = \frac{2\omega}{c}k. \quad (9)$$

Note that Eq.(8) gives the reflectivity at normal incidence. In general the formula becomes more complicated.

To determine n and k (and hence $\varepsilon = (n+ik)^2$) from the reflectivity (8), more information is required. Two approaches are followed:

1. One can exploit the fact that the real and imaginary part of the dielectric function are related by the Kramers-Kronig relations. These equations, plus a knowledge of R at *all* frequencies, permits one, in principle, to find the separate values of n and k . In practice the numerical analysis can be quite complicated, and the method has the disadvantage of requiring measurements to be made at enough frequencies to give reliable extrapolations to the entire frequency range.
2. One can use the generalization of (8) to non-normal angles of incidence. One then obtains a second expression for the reflectivity at a different angle of incidence, involving n , k , and the polarization of the incident radiation. By comparing this expression with the measured reflectivity, one obtains a second equation involving n and k , and the two can then be extracted.

Optical properties of free electrons

We use the equation of motion for the momentum we derived within the free electron model earlier in the presence of scattering:

$$\frac{d\mathbf{p}}{dt} = -e\mathbf{E} - \frac{\mathbf{p}}{\tau}. \quad (10)$$

We are looking for the steady-state solution in the form

$$\mathbf{p}(t) = \mathbf{p}(\omega)e^{-i\omega t}. \quad (11)$$

Substituting this equation into (10) yields the solution:

$$-i\omega\mathbf{p}(\omega) = -e\mathbf{E}(\omega) - \frac{\mathbf{p}(\omega)}{\tau}. \quad (12)$$

The current density $\mathbf{j} = -en\mathbf{p}/m$, we find

$$\mathbf{j}(\omega) = \frac{ne\mathbf{p}(\omega)}{m} = \frac{ne^2\tau}{m} \frac{\mathbf{E}(\omega)}{1-i\omega\tau}. \quad (13)$$

The frequency dependent conductivity is therefore given by

$$\sigma(\omega) = \frac{\sigma_0}{1-i\omega\tau}, \quad (14)$$

where $\sigma_0 = \frac{ne^2\tau}{m}$ is the Drude dc conductivity. The conductivity is now a complex quantity:

$$\text{Re } \sigma = \frac{\sigma_0}{1+\omega^2\tau^2}; \quad \text{Im } \sigma = \frac{\sigma_0\omega\tau}{1+\omega^2\tau^2}, \quad (15)$$

The real part represents the in-phase current which produces the resistive joule heating, while the imaginary part represents the $\pi/2$ out-of-phase inductive current. An examination of $\text{Re}\sigma$ and $\text{Im}\sigma$ as functions of the frequency shows that in the low-frequency region, $\omega\tau \ll 1$, $\text{Im}\sigma \ll \text{Re}\sigma$. That is, the electrons exhibit an essentially resistive character. Since $\tau \sim 10^{-14}$ s, this spans the entire familiar frequency range up to the far infrared. In the high-frequency region, $\omega\tau \gg 1$, however, which corresponds to the visible and ultraviolet regimes, $\text{Re}\sigma \ll \text{Im}\sigma$ and the electrons display an essentially inductive character. No energy is absorbed from the field in this range, and no joule heat appears.

The dielectric function is then given by

$$\epsilon = \left(\epsilon_L - \frac{4\pi\sigma_0\tau}{1+\omega^2\tau^2} \right) + \frac{4\pi i\sigma_0}{\omega(1+\omega^2\tau^2)}. \quad (16)$$

This equation and equations (7), (8), (9) determine the optical properties of a free electron gas. We consider now two frequency regions.

a) *The low-frequency region* $\omega\tau \ll 1$. In this frequency range we can neglect the real part of the dielectric constant and find that

$$\epsilon \approx i \frac{4\pi\sigma_0}{\omega}. \quad (17)$$

Using Eq (7) we obtain,

$$n \approx k = \sqrt{\frac{\text{Im } \epsilon}{2}} = \sqrt{\frac{2\pi\sigma_0}{\omega}}. \quad (18)$$

The inverse of the absorption coefficient $\delta = 2/\alpha = c/\omega k$ is known as the *skin depth*. The intensity $I = I_0 e^{-x/\delta}$, and hence δ , is a measure of the distance of penetration of the optical beam into the medium before the beam is dissipated. We can now evaluate the skin depth

$$\delta = \frac{c}{\sqrt{2\pi\sigma_0\omega}}. \quad (19)$$

In practice, δ has a very small value (for Cu at $\omega \sim 10^7 \text{ s}^{-1}$, $\delta = 100\mu\text{m}$), indicating that an optical beam incident on a metallic specimen penetrates only a short distance below the surface.

b) *The high-frequency region* $\omega\tau \gg 1$. This region covers the visible and ultraviolet ranges. Equation (16) shows that the dielectric constant is real

$$\varepsilon = \varepsilon_L - \frac{4\pi\sigma_0}{\omega^2\tau} = \varepsilon_L - \frac{4\pi ne^2}{\omega^2 m} = \varepsilon_L \left(1 - \frac{\omega_p^2}{\omega^2} \right), \quad (20)$$

where

$$\omega_p^2 = \frac{4\pi ne^2}{\varepsilon_L m}. \quad (21)$$

The frequency ω_p is known as the *plasma frequency*.

We can see from Eq.(20) that the high-frequency region can now be divided into two subregions: In the subregion $\omega < \omega_p$, $\varepsilon < 0$, and consequently, from (7), $n = 0$. In view of (8), this leads to $R = 1$. That is, the metal exhibits *perfect reflectivity*. In the higher subregion $\omega > \omega_p$, and $\varepsilon > 0$, and hence, by similar reasoning, $k = 0$. In this range, therefore, $\alpha = 0$, $0 < R < 1$, and the metallic medium acts like a nonabsorbing transparent dielectric, e.g., glass.

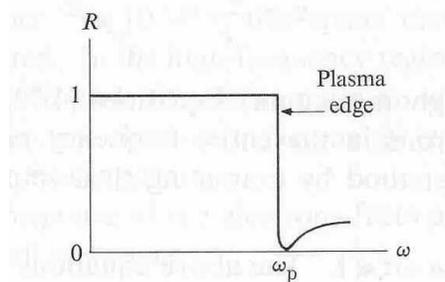


Fig. 1 The plasma reflection edge.

Figure 4.12 illustrates the dependence of reflectivity on frequency, exhibiting the dramatic *discontinuous* drop in R at $\omega = \omega_p$, which has come to be known as the *plasma reflection edge*. The frequency ω_p as seen from (21) is proportional to the electron density n . In metals, the densities are such that ω_p falls into the high visible or ultraviolet range (Table 1).

Table 1: Reflection Edges (Plasma Frequencies) and Corresponding Wavelengths for Some Metals

	Li	Na	K	Rb
ω_p (10^{16}s^{-1})	1.22	0.89	0.593	0.55
λ_p (\AA)	1550	2100	3150	3400

The nature of this charge density wave, known as a plasma oscillation, can be understood in terms of a very simple model. Imagine displacing the entire electron gas, as a whole, through a distance u with respect to the fixed positive background of the ions (Figure 2). The resulting surface charge gives rise to an electric field of magnitude $E=4\pi\sigma$, where $\sigma=neu$ is the charge per unit area at either end of the slab. This field tends to restore the electron distribution to equilibrium.

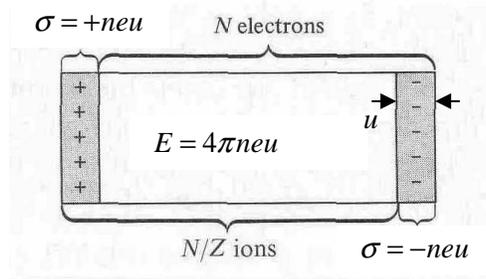


Fig. 2 Simple model of a plasma oscillation.

The equation of motion of the electron gas as a whole is

$$Nm \frac{d^2u}{dt^2} = -Ne4\pi neu = -4\pi ne^2 Nu \quad (22)$$

which lead to oscillation at the plasma frequency $\omega_p^2 = \frac{4\pi ne^2}{m}$.

Optical properties of the monovalent metals

Now we summarize the results. Within the free electron theory a reflectivity of the specific metal depends only on the plasma frequency and the relaxation time. Incident radiation simply accelerates free electrons, and if there were no collisions the electrons would radiate back all the acquired energy in the form of transmitted and reflected radiation. Since there is no transmission below the plasma frequency, all radiation would be perfectly reflected in the absence of collisions. Above the plasma frequency, transmission is possible, and the reflectivity declines.

At high frequencies ($\omega\tau \gg 1$ - optical and ultra violet range) the only effect of collisions is to round the sharp transition from perfect to partial reflection. Because of collisions some of the energy acquired by the electrons from the incident radiation is degraded into thermal energy, thereby diminishing the amount of reflected energy both above and below the plasma frequency. Because collisions have this effect at all frequencies, they introduce no striking frequency-dependent structure into the reflectivity. This is contrary to what we would expect for real metals, which have

different colors. The color of a metal is determined by the frequency dependence of its reflectivity: Some frequencies are reflected more strongly than others. The very different colors of copper, gold, and aluminum indicate that this frequency dependence can vary strikingly from one metal to another. This free electron reflectivity lacks the structure necessary to account for the characteristic striking variations from one metal to another.

At low frequencies $\omega\tau \ll 1$, according to the Drude theory, the real part of the optical conductivity and consequently the imaginary part of the dielectric function has a peak. This peak is known as Drude peak. At zero frequency we arrive at the result for the dc conductivity. The width of the peak is equal to the inverse relaxation time of electrons. The Drude peak near zero frequency is indeed observed for all metals. Fig.3 shows an example for the optical conductivity deduced from reflectivity measurements in three alkali metals. We see the appearance of the peak near a zero frequency. However, at higher frequencies the spectrum deviates significantly from the prediction of the Drude theory, according to which the optical conductivity should drop down to zero as $1/\omega^2$.

The origin of this difference comes from the fact that the Drude theory does not take into account *interband transitions*.

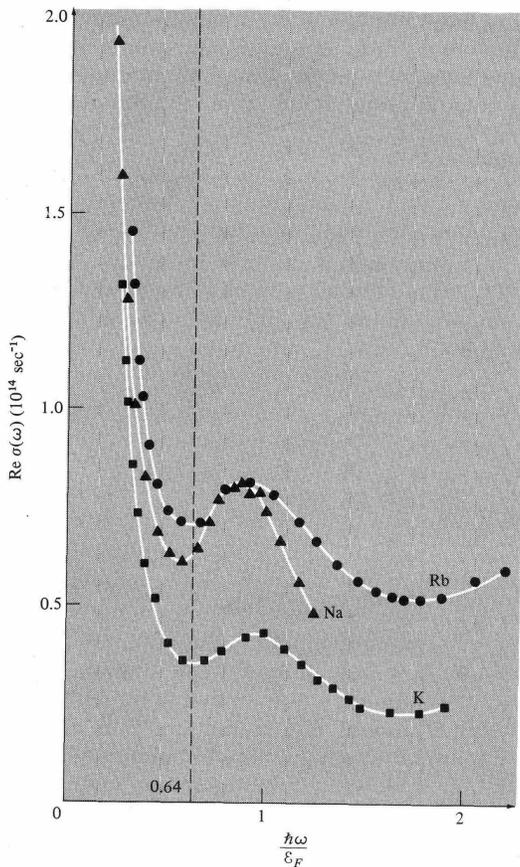


Fig.3. $\text{Re}\sigma(\omega)$, deduced from reflectivity measurements in three alkali metals. The interband threshold is evident, and occurs quite close to $0.64E_F$, where E_F is the free electron Fermi energy.

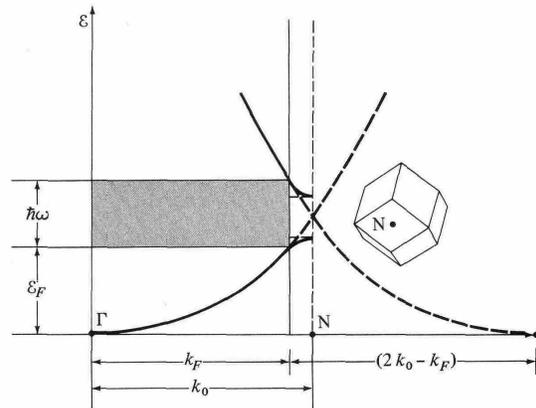


Fig.4. Free electron determination of the threshold energy for interband absorption in the alkali metals. Numerically, $\hbar\omega = 0.64E_F$.

Unlike free electrons, for Bloch electrons a strongly frequency-dependent mechanism for absorbing incident energy is possible. This can be understood by regarding the incident radiation as a beam of photons of energy $\hbar\omega$ and momentum $\hbar\mathbf{q}$. A photon may lose energy by exciting an electron from a level with energy E to one with energy $E' = E + \hbar\omega$. In the free electron case momentum conservation imposes the additional constraint $\mathbf{p}' = \mathbf{p} + \hbar\mathbf{q}$, which proves impossible to satisfy, thereby prohibiting this type of energy loss. In the presence of a periodic potential, however, the translational symmetry of free space is broken, and momentum conservation does not hold. Nevertheless, a weaker conservation law is still in force because of the remaining translational symmetry of the periodic potential. This restricts the change in electron wave vector in a following manner :

$$\mathbf{k}' = \mathbf{k} + \mathbf{q} + \mathbf{G}, \quad (23)$$

where \mathbf{G} is a vector of the reciprocal lattice. Equation (23) is a special case of "crystal momentum conservation," which has been already discussed before.

Since a photon of visible light has a wavelength of order 5000 \AA , the photon wave vector \mathbf{q} is typically of order 10^5 cm^{-1} . Typical Brillouin zone dimensions, on the other hand, are of order $k_F \sim 10^8 \text{ cm}^{-1}$. Thus the term \mathbf{q} in (23) can shift the wave vector \mathbf{k} by only a fraction of a percent of the dimensions of the Brillouin zone. Because two levels whose wave vectors differ by a reciprocal lattice vector are, in fact, belong to two different bands in the reduced zone scheme, the shift by \mathbf{G} can be ignored altogether, which implies that the wave vector of a Bloch electron is essentially unchanged when it absorbs a photon.

For the electron's energy to change by $\hbar\omega$, typically a few electron volts, the electron must move from one band to another without appreciable change in wave vector. Such processes are known as *interband transitions*. They can occur between the two electronic states for which the energy is conserved so that $E_{n'}(\mathbf{k}) = E_n(\mathbf{k}) + \hbar\omega$ for some \mathbf{k} and for two bands n and n' . $E_n(\mathbf{k})$ must lie below the Fermi level so that such an electron is available for excitation. $E_{n'}(\mathbf{k})$ must be above the Fermi level so that the final electronic level is not made unavailable by the Pauli principle. This critical energy or frequency is called the *interband threshold*.

The interband threshold may be due either to the excitation of electrons from the conduction band (highest band containing some electrons) into higher unoccupied levels, or to the excitation of electrons from filled bands into unoccupied levels in the conduction band (lowest band containing some unoccupied levels).

In the alkali metals the filled bands lie far below the conduction band, and the excitation of conduction band electrons to higher levels gives the interband threshold. Since the Fermi surface in the alkali metals is so close to a free electron sphere, the bands above the conduction band are also quite close to free electron bands, especially for values of \mathbf{k} within the Fermi "sphere," which does not reach all the way to the zone faces. A free electron estimate of the threshold energy $\hbar\omega$ follows from observing that the occupied conduction band levels with energies closest to the next highest free electron levels at the same k occur at points on the Fermi sphere nearest to a Bragg plane; i.e., at points (Figure 4) where the Fermi sphere meets the lines FN. As a result, the interband threshold is at $\hbar\omega = 0.64E_F$.

Figure 3 shows $\text{Re}\sigma(\omega)$, as deduced from the measured reflectivities of sodium, potassium, and rubidium. At lower frequencies the sharp decrease with increasing frequency characteristic of the free electron model is observed. In the neighborhood of $0.64E_F$, however, there is a noticeable rise in $\text{Re}\sigma(\omega)$, a striking confirmation of the nearly free electron estimate of the interband threshold.

The situation is quite different in the noble metals, due to the d -bands. Figure 5 shows the computed band structure of Cu, including the lowest-lying completely empty bands. The threshold for exciting an electron up from the conduction band occurs at point B (which is where the Fermi surface "neck" meets the hexagonal zone face (Figure 5) with an energy proportional to the length of the upper vertical arrow - about 4 eV. However, d -band electrons can be excited into unoccupied conduction band levels with considerably less energy than this. Such a transition occurs at the same point B , with an energy difference proportional to the length of the lower vertical arrow - about 2 eV. Another, somewhat lower, transition occurs at point A .

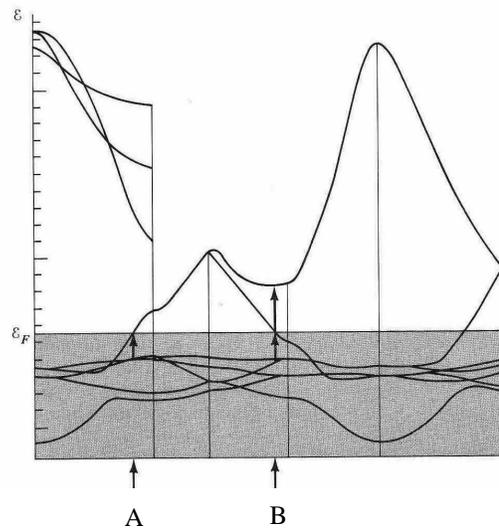


Fig.5 Calculated bands for copper, illustrating that the absorption threshold for transitions up from the conduction band is about 4 eV, while the threshold for transitions from the d -band to the conduction band is only about 2 eV. The energy scale is in tenths of a rydberg ($0.1 \text{ Ry} = 1.36 \text{ eV}$).

The measured absorption in copper (see Figure 6) does increase sharply at about 2 eV. Thus its reddish color is a direct manifestation of the rather low threshold for the excitation of d -band electrons into the conduction band, 2eV lying somewhere in the orange part of the visible spectrum. A threshold at about the same energy also produces the yellowish color of gold. Silver, however is more complicated: the threshold for the d -band excitation and plasmon-like threshold merge at about 4eV, resulting in a more uniform reflectivity throughout the visible range of spectrum (from about 2eV to 4eV).

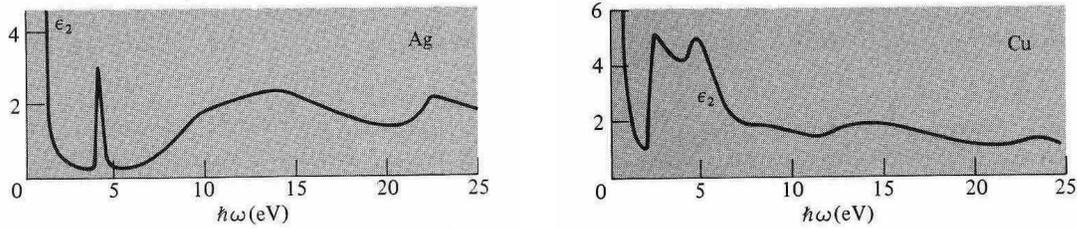


Fig.6 The imaginary part of the dielectric constants deduced from reflectivity measurements. (H. Ehrenreich and H. R. Phillip, *Phys. Rev.* 128, 1622 (1962).) Note the characteristic free electron behavior ($1/\omega^3$) below about 2 eV in copper and below about 4 eV in silver. The onset of interband absorption is quite apparent.

Finally we consider an example of the optical properties of a semiconductor and illustrate an important feature of the optical spectra. The feature is that the largest contribution to the dielectric functions comes from those points in the Brillouin zone at which $E_{n'}(\mathbf{k})$ and $E_n(\mathbf{k})$ have the same slope. At these points transitions accumulate to produce a peak in the absorption spectrum. Mathematically this condition can be written as

$$\nabla[E_{n'}(\mathbf{k}) - E_n(\mathbf{k})] = 0. \quad (24)$$

These points are known as the *critical points*.

Figure 7 shows the imaginary part of the dielectric function for Ge, and correlates the peaks in the curve with the critical points responsible for the high absorption values. One can see that studies of optical absorption can be highly useful in the determination of band structure, and particularly in delineating the various critical points in the zone.

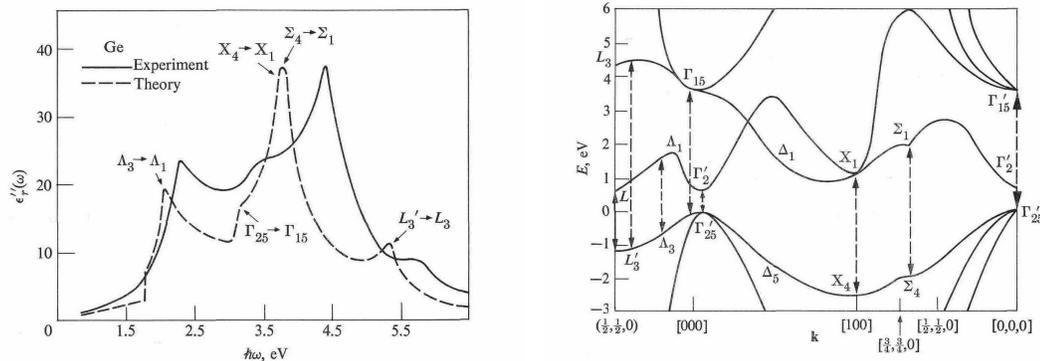


Fig. 7 (a) Imaginary dielectric constant versus photon energy for Ge. (b) The band structure of Ge. Dashed arrows indicate various critical points. [After Phillips, 1966]

As pointed out, the critical points assume a particularly significant role in the interpretation of interband-transition spectroscopic data. Since these points usually occur at symmetry points or along symmetry direction in the BZ a knowledge of the interband energy difference $E_{n'}(\mathbf{k}) - E_n(\mathbf{k})$ and the symmetry character (i.e., the location in the zone) of these points are highly useful in elucidating the band structure of the solid.