Part III Optical Properties of Materials

Chap. 10 The optical constants

Chap. 11 Atomistic Theory of the Optical Properties

Chap. 12 Quantum Mechanical Treatment of the Optical Properties

Chap. 13 Applications

Quantum Mechanical Treatment of the Optical Properties

12.1 Introduction

- From the classical point of view, it is not evident why the electrons should behave freely at low frequencies and respond as if they would be bound at higher frequencies.

- An unconstrained interpretation for this is only possible by applying wave mechanics. This will be done in the present chapter.

12.2 Absorption of Light by Interband and Intraband Transitions

- For optical frequencies, the momentum of a photon, and thus its wave vector $k_{phot} = p/\hbar$ is much smaller than that of an electron: k_{phot} is much smaller than the diameter of the Brillouin zone (Fig.12.1)

Direct interband transition: electron transitions at which k remains constant (vertical transition)

Indirect interband transition: absorption of a light quantum under participation of a *phonon*; excess momentum is transferred to lattice.

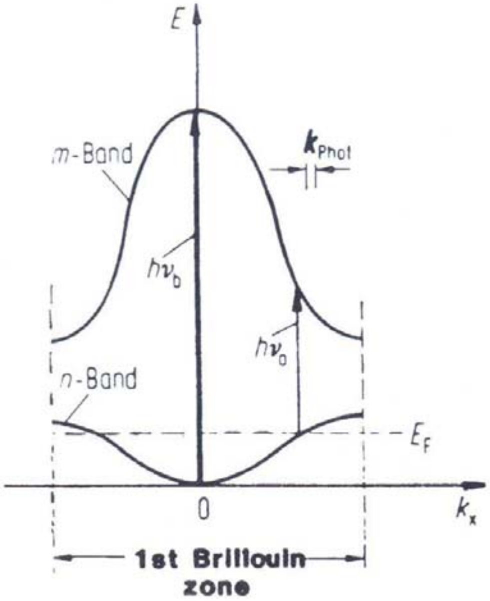

Figure 12.1. Electron bands and direct interband transitions in a reduced zone. (Compare with Fig. 5.4.)

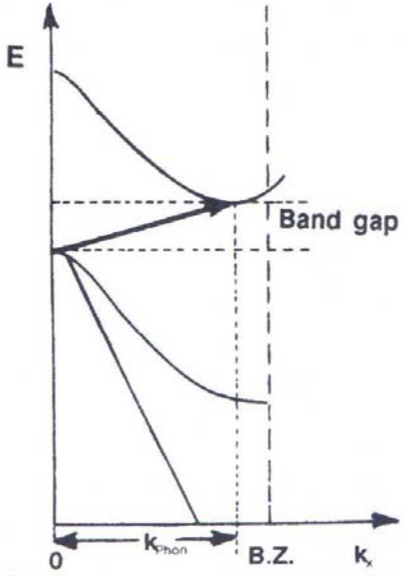

Figure 12.2. Indirect interband transition. (The properties of phonons are explained in Chapter 20.)

Quantum Mechanical Treatment of the Optical Properties

12.2 Absorption of Light by Interband and Intraband Transitions

An example for interband transition: Cu

The interband transition having the smallest possible energy difference is shown to occur between the upper d-band and the Fermi energy. This smallest energy is called, "**threshold energy for interband transition**" (or the **fundamental edge**" : marked in Fig 12.3 by a solid arrow.

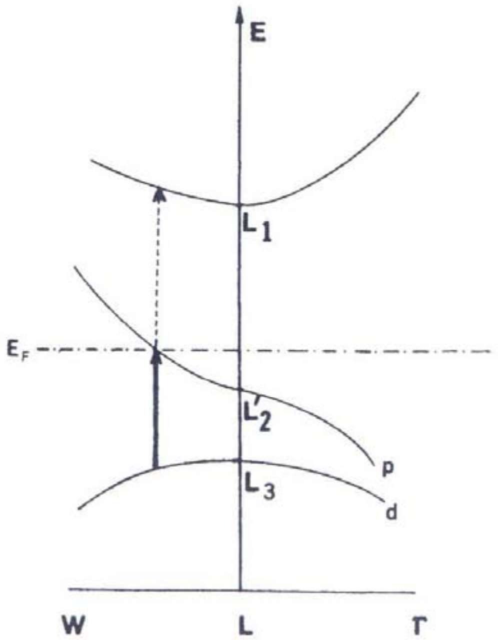

Figure 12.3. Section of the band diagram for copper (schematic). Two pertinent interband transitions are shown with arrows. The smallest possible interband transition occurs from a filled *d*-state to an unfilled state just above the Fermi energy.

Photon energy for this transition : 2.2 eV → the red color of Cu

At slightly higher photon energies, a second transition take place, which originates from the Fermi energy : marked a dashed line

Quantum Mechanical Treatment of the Optical Properties

12.2 Absorption of Light by Interband and Intraband Transitions

Interband transition: under certain conditions photons may excite electrons into a higher energy level *within the same band*. This occurs with participation of a phonon, i.e. a lattice vibration quantum (Fig 12.4)

Interband transitions are mainly observed in metals because metals have unfilled electron bands.

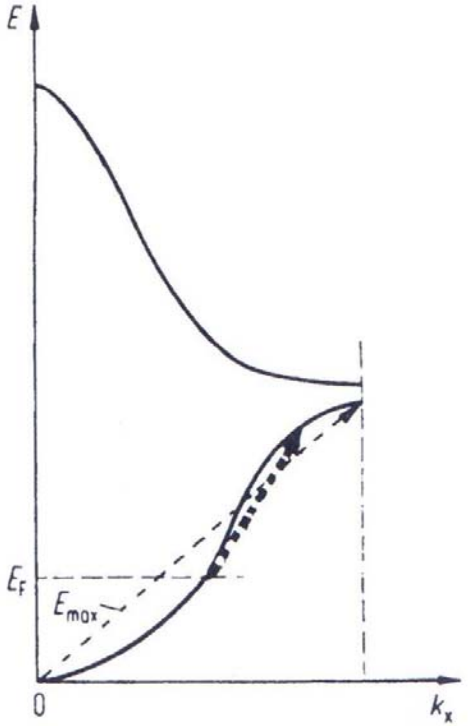

Figure 12.4. Intraband transitions. The largest energy that can be absorbed by intraband transitions is obtained by projecting the arrow marked "E_{max}" onto the energy axis.

12.3 Optical Spectra of Materials

- Optical spectra are the principal means to obtain experimentally the band gap and energies for interband transition.

- For isolated atoms and ions, the absorption and emission spectra are known to be extremely sharp.

- Plain reflection spectra of solids are not to useful for deduction of transition energies, mainly because *R* is a rather involved function of ε_1 and ε_2: Thus ε_2 (i.e. absorption) spectra are often utilized instead.

- Modulated optical spectra (Sec 13.1.3) separate the small contributions stemming from points of high symmetry (such as the centers and edges of the Brillouin zone) from the general much larger background.

Quantum Mechanical Treatment of the Optical Properties

*12.4 Dispersion

The alternating electric field of the light which impinges on the solid perturbs the potential field of the lattice periodically. Thus, we need to add to the potential energy a correction term, the so-called perturbation potential, *V'*

$$V = V_0 + V' \qquad E = A\cos\omega t$$

Then, $$V' = eEx = eA\cos(\omega t)\cdot x$$

Time dependent Schrödinger equation

$$\nabla^2\Psi - \frac{2m}{\hbar^2}V\Psi - \frac{2im}{\hbar}\frac{\partial\Psi}{\partial t} = 0$$

$$\nabla^2\Psi - \frac{2m}{\hbar^2}(V_0 + eAx\cos\omega t)\Psi - \frac{2im}{\hbar}\frac{\partial\Psi}{\partial t} = 0$$

Quantum Mechanical Treatment of the Optical Properties

*12.4 Dispersion

Our goal is to calculate the optical constant from the polarization

The classical polarization $P = Nex$ is replaced in wave mechanics by $P = Ne\int x\Psi\Psi^* d\tau$

As results, we obtain $\varepsilon_1 = n^2 - k^2 = 1 + \frac{Ne^2 A}{\varepsilon_0 \pi\hbar}\sum a_{ni}^2 \frac{\nu_{ni}}{\nu_{ni}^2 - \nu^2}$

This equation is the sought-after relation for the optical properties of solids, obtained by wave mechanics

Empirically introduced oscillator strength f_i: $f_i = \frac{4\pi m}{\hbar} a_{ni}^2 \nu_{ni}$

$h\nu_{ni}$ is that energy which an electron absorbs when it is exited from the *n*-band into the *i*-band. Thus, the resonance frequency, ν_{oi}, of the *i* th oscillator in Sec 11.17.4 is replaced in wave mechanics by a frequency ν_{ni}, that corresponds to an allowed electron transition from the *n*th into the *i*th band.