Fall Semester, 2008

재료의 전자기적 성질

Electronic Properties of Materials

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Grading

Midterm Exam 30%

Final Exam 40%

Homework & Attendance 30%

(# absence more than 4 lectures = F)

Overall Contents

Part I Fundamentals

Electron Theory : Matter Waves

Electromagnetic Theory : Maxwell Equations

Part II Electrical Properties of Materials

Part III Optical Properties of Materials

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Part V Thermal Properties of Materials

Lattice Waves

Part I Fundamentals

Electron Theory : Matter Waves

Chap. 1 Introduction

Chap. 2 The Wave-Particle Duality

Chap. 3 The Schördinger Equation

Chap. 4 Solution of the Schördinger Equation for Four Specific Problems

Chap. 5 Energy Bands in Crystals

Chap. 6 Electrons in a Crystal

Electromagnetic Theory : Maxwell Equations

Chap. 4 Light Waves

(Electrons in Solids, 3rd Ed., R. H. Bube)

1. Introduction

Three approaches to understand electronic properties of materials

- **Continuum theory** : consider only macroscopic quantities, interrelate experimental data
  ex) Ohm's law, Maxwell equations, Newton's law, and Hagen-Rubens equation

- **Classical electron theory** : postulate that free electrons in metals drift as a response to an external force and interact with certain lattice atoms
  ex) Drude equations

- **Quantum theory** : explain important experimental observations which could not be readily interpreted by classical means
  ex) Schrödinger Equation

1. Introduction

Basic equations

$$Newton's\ law\ : F = ma$$

$$Kinetic\ \ energy : E_{kin} = \frac{1}{2} m\upsilon^2$$

$$Momentum : p = m\upsilon$$

$$E_{kin} = \frac{p^2}{2m}$$

$$Speed\ \ \text{of}\ \ \text{light} : c = \nu\lambda$$

$$\text{Velocity}\ \ \text{of}\ \ \text{wave} : \upsilon = \nu\lambda \quad \text{Angular}\ \ \text{frequency} : \omega = 2\pi\nu$$

$$\text{Einstein's mass-energy equivalence} : E = mc^2$$

2. The Wave-Particle Duality

- **Light : electromagnetic wave**

  light quantum (called a photon)

Energy $E = \nu h = \omega \hbar$

Planck constant $\hbar = \dfrac{h}{2\pi}$

1924 yr de Broglie $\lambda p = h$

"Wave nature of electrons" "Matter wave"

For a general wave $\upsilon = \nu \lambda$

"Wave number" $k = \dfrac{2\pi}{\lambda} \longrightarrow \upsilon = \dfrac{\omega}{k}$

2. The Wave-Particle Duality

- **Description of electron wave**

- The simplest waveform : harmonic wave

- A wave function (time- and space-dependent)

$$\Psi = \sin(kx - \omega t)$$

Electron wave : a combination of several wave trains

Assuming two waves,

$$\Psi_1 = \sin[kx - \omega t]$$

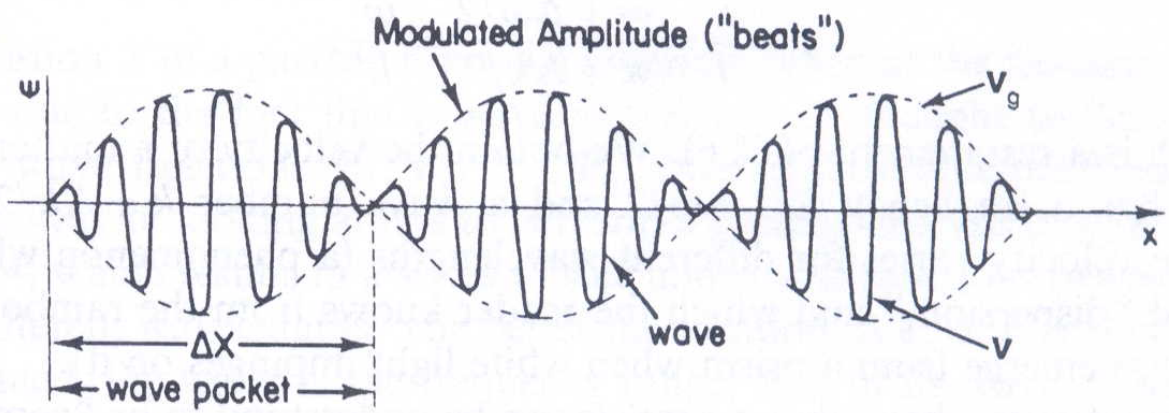
$$\Psi_2 = \sin[(k + \Delta k)x - (\omega + \Delta\omega)t]$$

2. The Wave-Particle Duality

➢ Description of electron wave

Supposition of two waves:

$$\Psi_1 + \Psi_2 = \Psi = \underbrace{2\cos\left(\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x\right)}_{\text{Modulated amplitude}} \cdot \underbrace{\sin\left[\left(k + \frac{\Delta k}{2}\right)x - \left(\omega + \frac{\Delta\omega}{2}\right)t\right]}_{\text{sine wave}}$$



"Wave Packet"

Figure 2.1. Combination of two waves of slightly different frequencies. ΔX is the distance over which the particle can be found.

2. The Wave-Particle Duality

The extreme conditions

(a) No variation in angular frequency and wave number : monochromatic wave

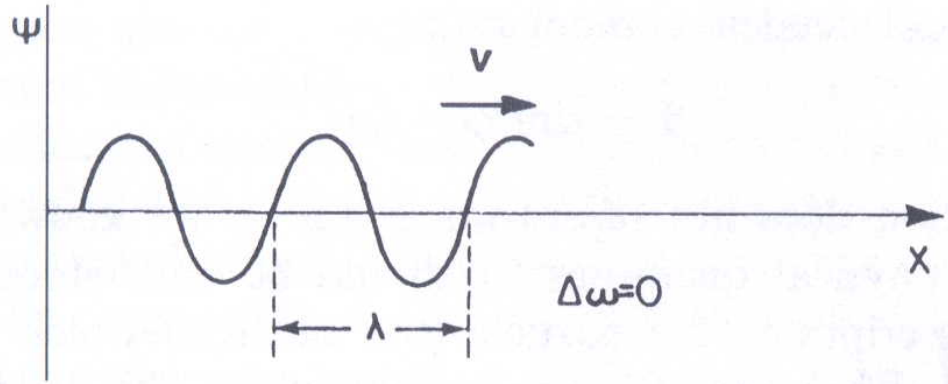


Figure 2.2. Monochromatic matter wave ($\Delta\omega$ and $\Delta k = 0$). The wave has constant amplitude. The matter wave travels with the phase velocity, v.

2. The Wave-Particle Duality

The extreme conditions

(b) Very large variation in angular frequency and wave number

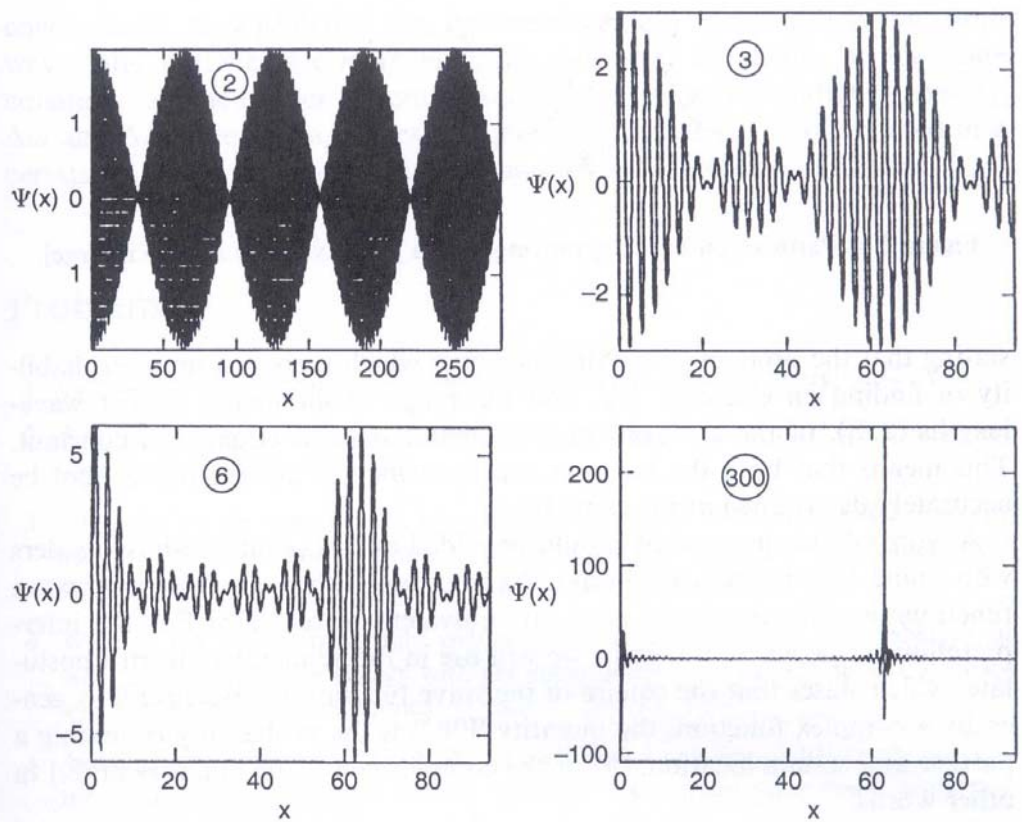


Figure 2.3. Superposition of Ψ-waves. The number of Ψ-waves is given in the graphs. (See also Fig. 2.1 and Problem 2.8.)

Phase velocity :

velocity of a matter wave

$$\upsilon = \frac{x}{t} = \frac{\omega + \Delta\omega/2}{k + \Delta k/2} = \frac{\omega'}{k'}$$

Group velocity:

velocity of a pulse wave

(i.e., a moving particle)

$$\upsilon_g = \frac{x}{t} = \frac{\Delta\omega}{\Delta k} = \frac{d\omega}{dk}$$

2. The Wave-Particle Duality

The extreme conditions

(b) Very large variation in angular frequency and wave number

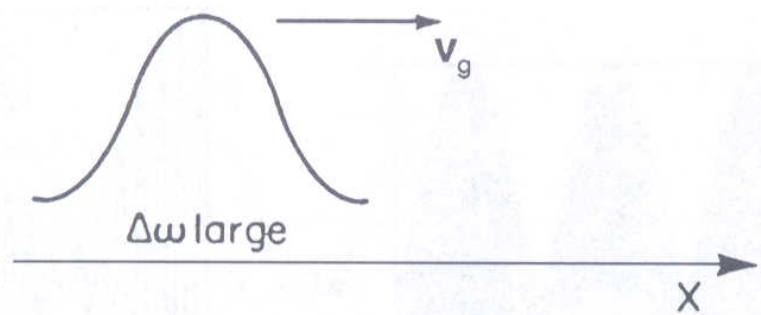


Figure 2.4. Particle (pulse wave) moving with a group velocity v_g ($\Delta\omega$ is large).

Heisenberg's Uncertainty principle $\Delta p \cdot \Delta x \geq h$

Probability of finding a particle at a certain location

$$\Psi\Psi^* dxdydz = \Psi\Psi^* d\tau$$

Q&A

1. Plank constant $h = 6.63 \times 10^{-34}$ J·sec
2. Traveling wave $\Psi(x,t) = \sin 2\pi(\frac{x}{\lambda} - vt)$

$$\Psi = \sin(kx - \omega t)$$

3. Phase velocity versus Group velocity

$$\upsilon = \frac{x}{t} = \frac{\omega + \Delta\omega/2}{k + \Delta k/2} = \frac{\omega'}{k'} \qquad \upsilon_g = \frac{x}{t} = \frac{\Delta\omega/2}{\Delta k/2} = \frac{d\omega}{dk}$$

4. Prove $\upsilon_g = \upsilon$ (velocity of particle)?

$E = h\nu = \hbar\omega$ and $k = p/\hbar \rightarrow d\omega = dE/\hbar$ and $dk = dp/\hbar$

$\upsilon_g = d\omega/dk = dE/dp$

Since $E = m\upsilon^2/2$ and $p = m\upsilon$, $dE/dp = \upsilon$

Relativistic expressions: $E = mc^2$, $E = h\nu$ and $p = m\upsilon$

$\upsilon_g = d\omega/dk = d\omega/d\upsilon/dk/ /d\upsilon = \upsilon$

Q&A

- Why is the wave nature of matter not more apparent to us in our daily observation?

- Can the de Bloglie wavelength of a particle be smaller than a linear dimension of the particle? Larger? Is there necessarily any relation between such quantities?

- Is the frequency of a de Broglie wave given by E/h? Is the velocity given by v? Is the velocity equal to c? Explain

Q&A

Mathematical description of traveling waves

Consider a string stretched along the x axis whose vibrations are in the y direction

Assuming simple harmonic motion,

At $t = 0$, $y = A\sin 2\pi vt$

where A is the amplitude of the vibrations

If t is replaced by $\frac{x}{\upsilon} - t$, then $y = A\sin 2\pi v(\frac{x}{\upsilon} - t)$: Wave Formula

where υ is the wave speed

Since the wave speed is given by $\upsilon = v\lambda$, we have $y = A\sin 2\pi(\frac{x}{\lambda} - vt)$

Part I Fundamentals

Electron Theory : Matter Waves

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3. The Schrödinger Equation

3.1 The Time-Independent Schrödinger Equation

- Time-independent Schrödinger equation: *a vibration equation*

$$\boxed{\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0}$$

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$$

where, m = the (rest) mass of the electron,

E = the total energy of the system,

E_{kin} = kinetic energy,

V = the potential energy (or potential barrier)

$$E = E_{kin} + V$$

- Applicable to the calculation of the properties of atomic systems in *stationary* conditions

3. The Schrödinger Equation

3.2 The Time-Dependent Schrödinger Equation

Time-dependent Schrödinger equation: ***a wave equation***

$$\boxed{\nabla^2\Psi - \frac{2mV}{\hbar^2}\Psi - \frac{2mi}{\hbar}\frac{\partial\Psi}{\partial t} = 0}$$

Since $\Psi(x,y,z,t) = \psi(x,y,z)\cdot e^{i\omega t}$

$$\frac{\partial\Psi}{\partial t} = \psi i\omega e^{i\omega t} = \Psi i\omega \longrightarrow$$

and $E = \nu h = \omega\hbar \longrightarrow$

Then $\nabla^2\psi + \frac{2m}{\hbar^2}(E-V)\psi = 0 \longrightarrow \nabla^2\Psi - \frac{2mV}{\hbar^2}\Psi - \frac{2mi}{\hbar}\frac{\partial\Psi}{\partial t} = 0$

Applying differential operators to the wave function $E = -\hbar i\frac{\partial}{\partial t}$ $\quad \mathbf{p} = -\hbar i\nabla$

(**Hamiltonian operators**)

$$E_{total} = E_{kin} + E_{pot} = \frac{p^2}{2m} + V \longrightarrow -\hbar i\frac{\partial\Psi}{\partial t} = \frac{\hbar^2 i^2}{2m}\nabla^2\Psi + V\Psi$$

3.3 Special Properties of Vibrational Problems

- When boundary conditions are imposed, only certain vibrational forms are possible. ex) a vibrating string

- Vibration problems determined by boundary conditions :

  Boundary (or eigenvalue) problems

  A pecularity of these problems : not all frequency values are possible and therefore, not all values for the energy are allowed because of $E = \nu h$

The allowed values : ***eigenvalues***

The function belonging to the eigenvalues as a solution of the vibration equation : ***eigenfunctions***

The ***normalized eigenfunction***: $\int \psi \psi^* d\tau = \int |\psi|^2 d\tau = 1$

4. Solution of Schrödinger Equation

4.1 Free Electrons

Suppose electrons propagating freely (i.e., in a potential-free space) to the positive x-direction.

Then $V = 0$ and thus

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \longrightarrow$$

The solution for the above differential equation for an undamped vibration with spatial periodicity, (see Appendix 1)

$$\psi(x) = Ae^{i\alpha x}$$

where $\alpha = \sqrt{\frac{2m}{\hbar^2}E} \longrightarrow \alpha = \sqrt{\frac{2m}{\hbar^2}E} = \frac{p}{\hbar} = \frac{2\pi}{\lambda} = k \qquad |\mathbf{k}| = \frac{2\pi}{\lambda}$

Thus $\Psi(x) = Ae^{i\alpha x} \cdot e^{i\omega t}$

$$E = \frac{\hbar^2}{2m}\alpha^2 \longrightarrow E = \frac{\hbar^2}{2m}k^2$$

"energy continuum"

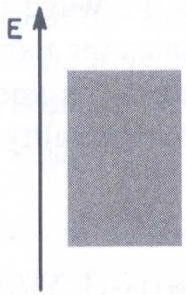


Figure 4.1. Energy continuum of a free electron (compare with Fig. 4.3).

4.2 Electron in a Potential Well (Bound Electron)

Consider an electron bound to its atomic nucleus.

Suppose the electron can move freely between two infinitely high potential barriers

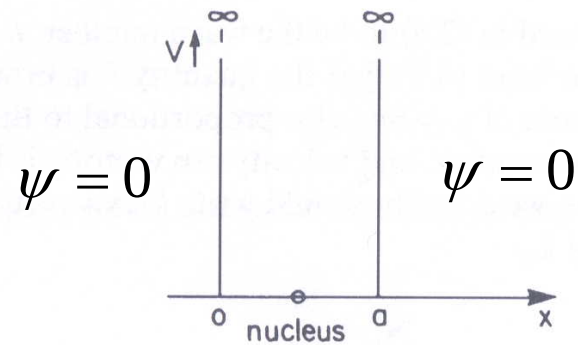


Figure 4.2. One-dimensional potential well. The walls consist of infinitely high potential barriers.

At first, treat 1-dim propagation along the x-axis inside the potential well

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0$$

The solution $\psi = Ae^{i\alpha x} + Be^{-i\alpha x}$ where $\alpha = \sqrt{\frac{2m}{\hbar^2} E}$

4.2 Electron in a Potential Well (Bound Electron)

Applying boundary conditions,

$$x = 0, \qquad \psi = 0 \longrightarrow$$

$$x = a \qquad \psi = 0 \longrightarrow$$

With Euler equation, $\sin\rho = \frac{1}{2i}(e^{i\rho} - e^{-i\rho})$

$$A[e^{i\alpha a} - e^{-i\alpha a}] = 2Ai \cdot \sin\alpha a = 0$$

$$\alpha a = n\pi, \qquad n = 0,1,2,3,....$$

"energy levels"

Finally, $E_n = \frac{\hbar^2}{2m}\alpha^2 = \frac{\hbar^2\pi^2}{2ma^2}n^2$

$$n = 1,2,3,....$$

"energy quantization"

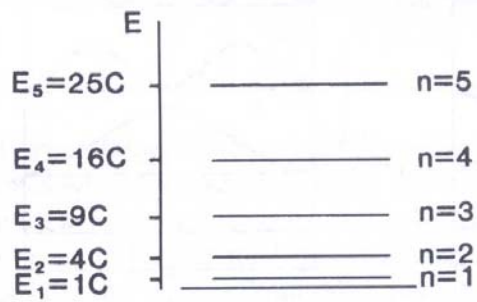


Figure 4.3. Allowed energy values of an electron that is bound to its atomic nucleus. E is the excitation energy in the present case. $C = \hbar^2\pi^2/2ma^2$, see (4.18). (E_1 is the zero-point energy.)

4.2 Electron in a Potential Well (Bound Electron)

Now discuss the wave function

$$\psi = 2Ai \cdot \sin \alpha x \quad \psi^* = 2Ai \cdot \sin \alpha x$$

$$\psi\psi^* = 4A^2 \sin^2 \alpha x \quad \int_0^a \psi\psi^* d\tau = 4A^2 \int_0^a \sin^2(\alpha x) dx = \frac{4A^2}{\alpha}[-\frac{1}{2}\sin \alpha x \cos \alpha x + \frac{\alpha x}{x}]_0^a = 1$$

$$A = \sqrt{\frac{1}{2a}}$$

$$2\pi r = n\lambda$$

$$r = \frac{\lambda}{2\pi} n$$

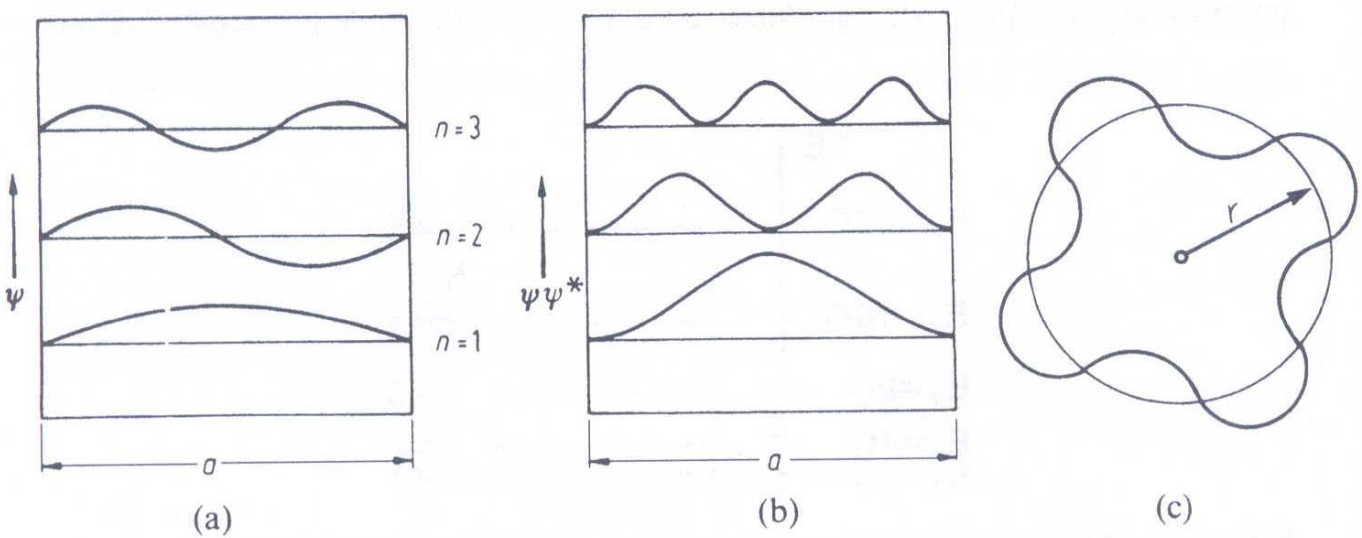


Figure 4.4. (a) ψ function and (b) probability function $\psi\psi^*$ for an electron in a potential well for different n-values. (c) Allowed electron orbit of an atom.

4.2 Electron in a Potential Well (Bound Electron)

For a hydrogen atom,
Coulombic potential

$$E = \frac{me^4}{2(4\pi\varepsilon_0\hbar)^2}\frac{1}{n^2} = -13.6\cdot\frac{1}{n^2}(eV)$$

$$V = -\frac{e^2}{4\pi\varepsilon_0 r}$$

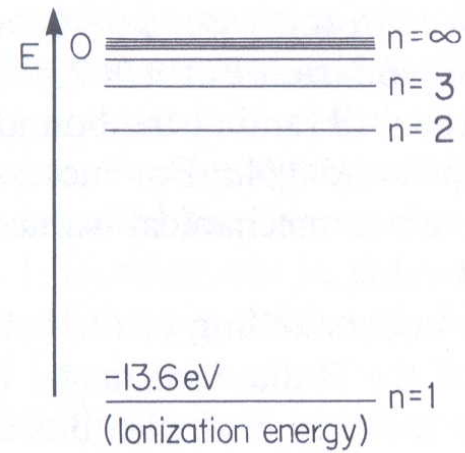


Figure 4.5. Energy levels of atomic hydrogen. E is the binding energy.

In 3-dim potential

$$E_n = \frac{\hbar^2\pi^2}{2ma^2}(n_x^{\ 2} + n_y^{\ 2} + n_z^{\ 2})$$

The same energy but different quantum numbers: "degenerate" states

4.3 Finite Potential Barrier (Tunnel Effect)

Suppose electrons propagating in the positive *x*-direction encounter a potential barrier V_0 (> total energy of electron, *E*)

- Region (I) $x < 0$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0$$

- Region (II) $x > 0$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0$$

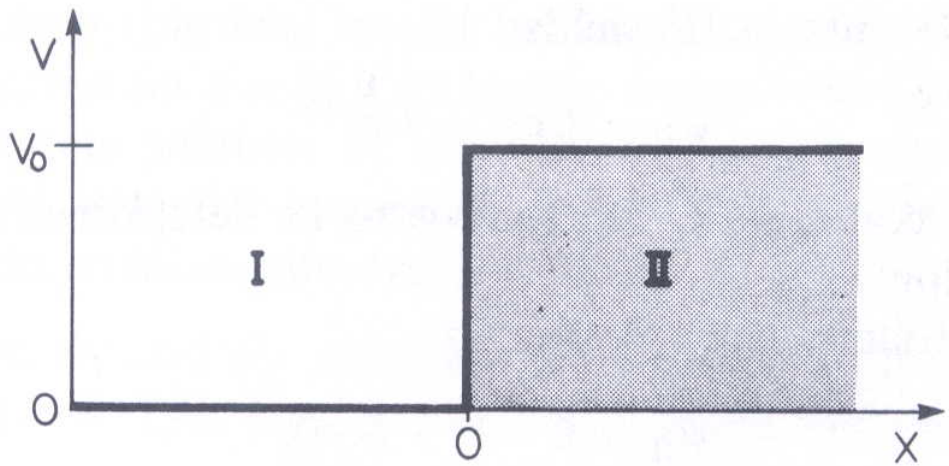


Figure 4.6. Finite potential barrier.

The solutions (see Appendix 1)

$$\psi_I = Ae^{i\alpha x} + Be^{-i\alpha x} \qquad \alpha = \sqrt{\frac{2m}{\hbar^2}E}$$

$$\psi_{II} = Ce^{i\beta x} + De^{-i\beta x} \qquad \beta = \sqrt{\frac{2m}{\hbar^2}(E - V_0)}$$

4.3 Finite Potential Barrier (Tunnel Effect)

Since $E - V_0$ is negative, $\beta = \sqrt{\frac{2m}{\hbar^2}(E - V_0)}$ becomes imaginary.

To prevent this, define a new parameter, $\gamma = i\beta$

Thus, $\gamma = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$, and $\psi_{II} = Ce^{i\beta x} + De^{-i\beta x} \longrightarrow$

Determination of C or D by B.C. For $x \to \infty$ $\psi_{II} = C \cdot \infty + D \cdot 0$

Since $\Psi\,\Psi^*$ can never be lager than 1, $\psi_{II} \to \infty$ is no solution, and thus $C \to 0$,
which reveals Ψ-function decreases in Region II

$$\psi_{II} = De^{-\gamma x}$$

Using (A.27) + (4.39) in textbook, the damped wave becomes

$$\Psi = De^{-\gamma x} \cdot e^{i(\omega t - kx)}$$

4.3 Finite Potential Barrier (Tunnel Effect)

As shown by the dashed curve in Fig 4.7, a potential barrier is penetrated by electron wave : ***Tunneling***

* For the complete solution,

(1) At $x = 0$ $\quad \psi_I = \psi_{II}$: continuity of the function

$$Ae^{i\alpha x} + Be^{-i\alpha x} = De^{i\gamma x} \longrightarrow$$

(2) At $x = 0$ $\quad \dfrac{d\psi_I}{dx} \equiv \dfrac{d\psi_{II}}{dx}$: continuity of the slope of the function

$$Ai\alpha e^{i\alpha x} - Bi\alpha e^{-i\alpha x} = -\gamma De^{-\gamma x}$$

With $x = 0$ $\quad Ai\alpha - Bi\alpha = -\gamma D$

Consequently, $\quad A = \dfrac{D}{2}(a + i\dfrac{\gamma}{\alpha})$

$$B = \frac{D}{2}(1 - i\frac{\gamma}{\alpha})$$

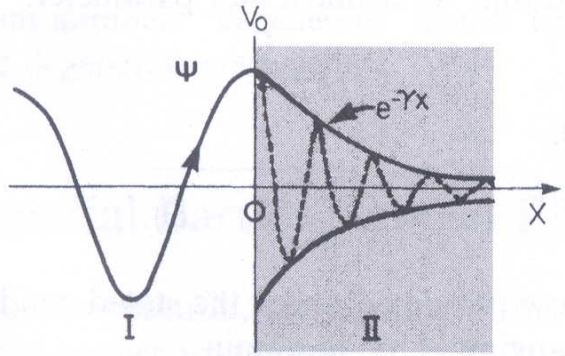


Figure 4.7. ψ-function (solid line) and electron wave (dashed line) meeting a finite potential barrier.

4.3 Finite Potential Barrier (Tunnel Effect)

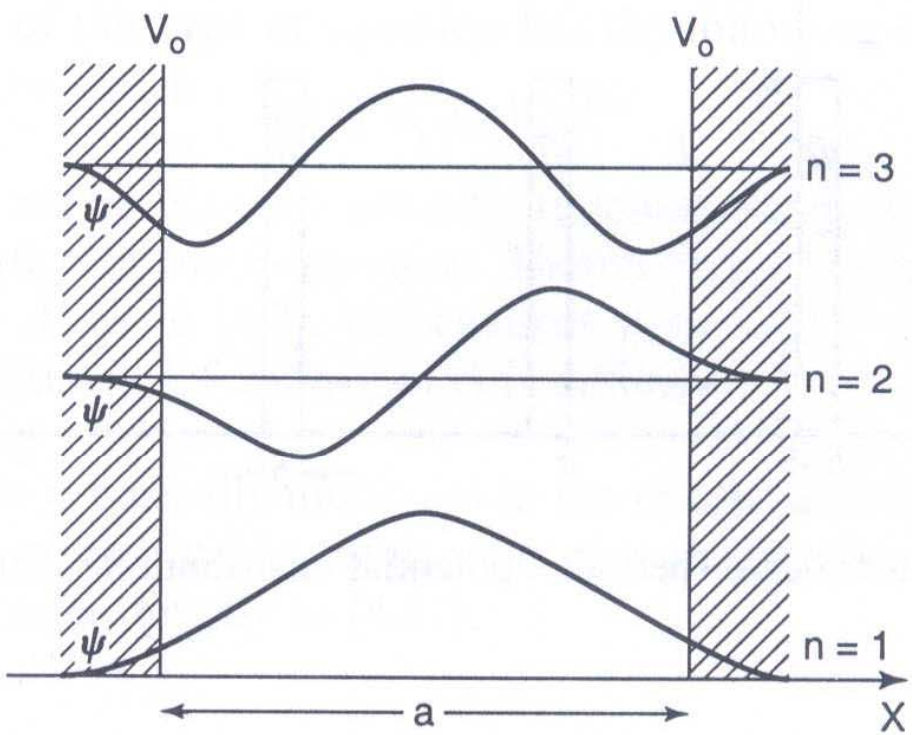


Figure 4.8. Square well with finite potential barriers. (The zero points on the vertical axis have been shifted for clarity.)

4.4 Electron in a Periodic Field of Crystal (the Solid State)

The behavior of an electron in a crystal → A motion through periodic repetition of potential well

well length : a

barrier height : V_0

barrier width : b

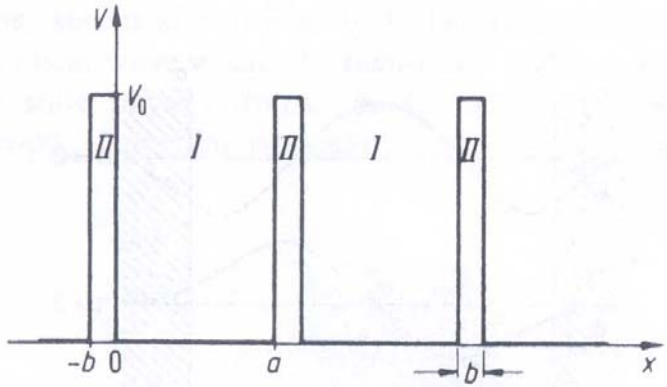


Figure 4.9. One-dimensional periodic potential distribution (simplified) (**Kronig-Penney model**).

Region (I)

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0$$

Region (II)

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V_0)\psi = 0$$

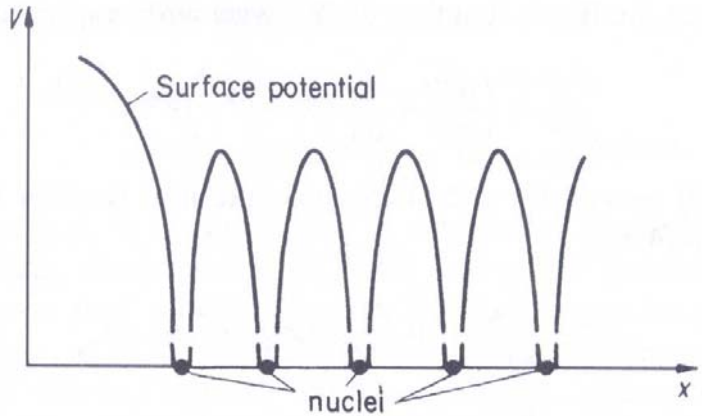


Figure 4.10. One-dimensional periodic potential distribution for a crystal (**muffin tin potential**).

4.4 Electron in a Periodic Field of Crystal (the Solid State)

(Continued) For abbreviation

$$\alpha^2 = \frac{2m}{\hbar^2}E \qquad \gamma^2 = \frac{2m}{\hbar^2}(V_0 - E)$$

The solution of this type equation (not simple but complicate)

$$\psi(x) = u(x)\cdot e^{ikx}$$ **(*Bloch function*)**

Where, u(x) is a periodic function which possesses the periodicity of the lattice in the x-direction

The final solution of the Schrödinger equations;

$$P\frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka \qquad \text{where} \quad P = \frac{maV_0 b}{\hbar^2}$$

4.4 Electron in a Periodic Field of Crystal (the Solid State)

Mathematical treatment for the solution : ***Bloch function***

$$\psi(x) = u(x) \cdot e^{ikx}$$

Differentiating the Bloch function twice with respect to x

$$\frac{d^2\psi}{dx^2} = \left(\frac{d^2u}{dx^2} + \frac{du}{dx}2ik - k^2u\right)e^{ikx}$$

Insert 4.49 into 4.44 and 4.45 and take into account the abbreviation

$$\frac{d^2u}{dx^2} + 2ik\frac{du}{dx} - (k^2 - \alpha^2)u = 0 \quad \textbf{(I)} \qquad \frac{d^2u}{dx^2} + 2ik\frac{du}{dx} - (k^2 + \gamma^2)u = 0 \quad \textbf{(II)}$$

The solutions of (I) and (II)

$$u = e^{-ikx}(Ae^{i\alpha x} + Be^{-i\alpha x}) \quad \textbf{(I)} \qquad u = e^{-ikx}(Ce^{-\gamma x} + De^{\gamma x}) \quad \textbf{(II)}$$

4.4 Electron in a Periodic Field of Crystal (the Solid State)

(Continued) From continuity of the function ψ *and* $\frac{d\psi}{dx}$

$$A + B = C + D$$

du/dx values for equations (I) & (II) are identical at $x = 0$

$$A(i\alpha - ik) + B(-i\alpha - ik) = C(\gamma - ik) + D(\gamma - ik)$$

Further, ψ and u is continuous at $x = a + b \rightarrow$ Eq. (I) at $x = 0$ must be equal to Eq. (II) at $x = a + b$, Similarly, Eq. (I) at $x = a$ is equal to Eq. (II) at $x = b$

$$Ae^{(i\alpha - ik)a} + Be^{(-i\alpha - ik)a} = Ce^{(ik+\gamma)b} + De^{(ik-\gamma)b}$$

Finally, *du/dx* is periodic in $a + b$

$$Ai(\alpha - k)e^{ia(\alpha - k)} - Bi(\alpha + k)e^{-ia(\alpha + k)} = -C(\gamma + ik)e^{(ik+\gamma)b} + D(\gamma - ik)e^{(ik-\gamma)b}$$

limiting conditions : using 4.57- 4.60 in text and eliminating the four constant A-D, and using some Euler eq.(see Appendix 2)

$$\frac{\gamma^2 - \alpha^2}{2\alpha\gamma}\sin(\gamma b)\cdot\sin(\alpha a) + \cos(\gamma b)\cdot\cos(\alpha a) = \cos k(a + b)$$

4.4 Electron in a Periodic Field of Crystal (the Solid State)

If V_0 is very large, then E in 4.47 is very small compared to V_0 so that

$$\gamma = \sqrt{\frac{2m}{\hbar^2}}\sqrt{V_0} \times b \quad \rightarrow$$

Since $V_0 b$ has to remain finite and $b \rightarrow 0$, γb becomes very small.

For a small γb, we obtain (see tables of the hyperbolic function)

$$\cosh(\gamma b) \approx 1 \quad and \quad \sinh(\gamma b) \approx \gamma b$$

Finally, neglect α^2 compared to γ^2 and, b compared to a so that 4.61 reads as follow

$$\frac{m}{\alpha\hbar^2} V_0 b \sin\alpha a + \cos\alpha a = \cos ka$$

Let $P = \dfrac{maV_0 b}{\hbar^2}$, then $P\dfrac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka$

4.4 Electron in a Periodic Field of Crystal (the Solid State)

"Electron that moves in a periodically varying potential field can only occupy certain allowed energy zone"

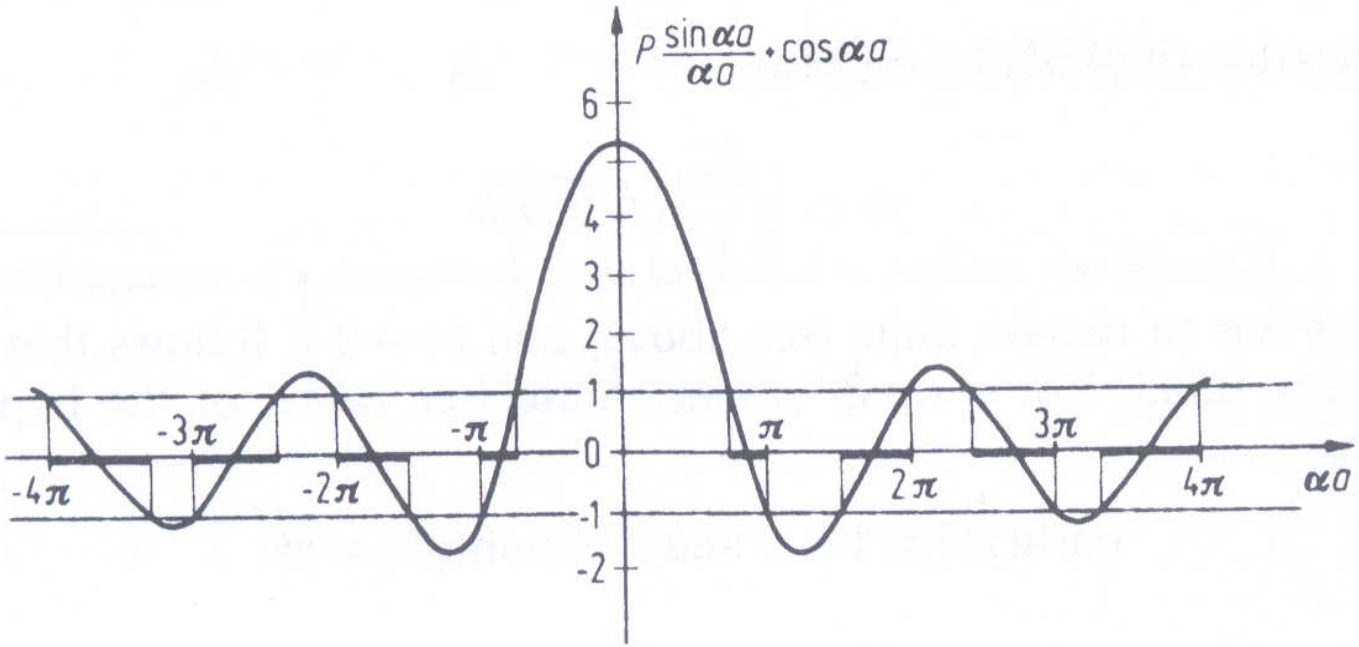


Figure 4.11. Function $P(\sin\alpha a/\alpha a)+\cos\alpha a$ versus αa. P was arbitrarily set to be $(3/2)\pi$.

4.4 Electron in a Periodic Field of Crystal (the Solid State)

The size of the allowed and forbidden energy bands varies with P.

For special cases

(a) If the potential barrier strength, $V_0 b$ is large, P is also large and the curve on Fig 4.11 steeper. The allowed band are narrow.

(b) $V_0 b$ and P are small, the allowed band becomes wider.

(c) If $V_0 b$ goes 0, thus, $P \to 0$

From 4.67, $\cos \alpha a = \cos ka$

$$E = \frac{\hbar^2 k^2}{2m}$$

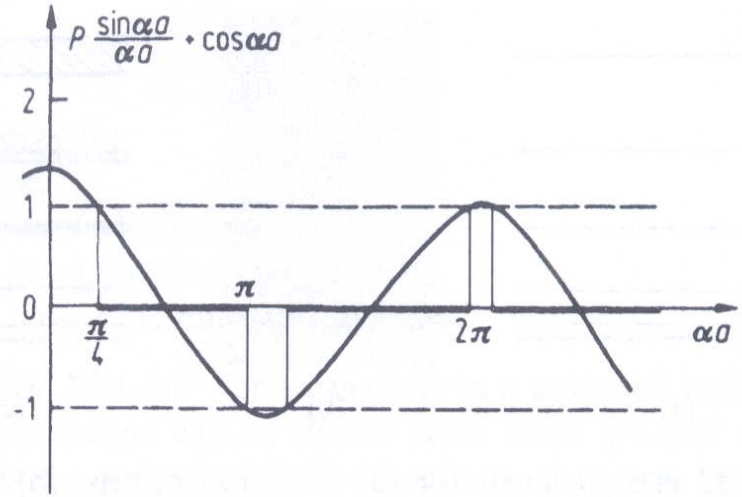


Figure 4.12. Function $P(\sin \alpha a/\alpha a) + \cos \alpha a$ with $P = \pi/10$.

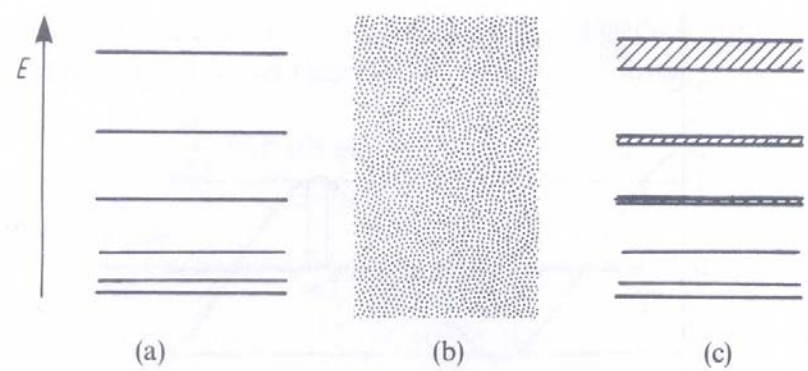


Figure 4.13. Allowed energy levels for (a) bound electrons, (b) free electrons, and (c) electrons in a solid.

4.4 Electron in a Periodic Field of Crystal (the Solid State)

(d) If the $V_0 b$ is very large, $P \to \infty$

$$\frac{\sin \alpha a}{\alpha a} \to 0$$

$$\sin \alpha a \to 0 \qquad \alpha a = n\pi$$

$$\alpha^2 = \frac{n^2 \pi^2}{a^2} \quad \text{for} \quad n = 1,2,3,....$$

Combining 4.46 and 4.69

$$E = \frac{\pi^2 \hbar^2}{2ma^2} \cdot n^2$$

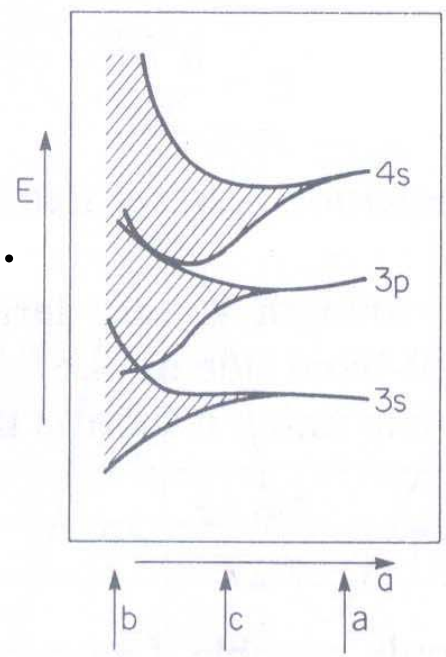


Figure 4.14. Widening of the sharp energy levels into bands and finally into a quasi-continuous energy region with decreasing interatomic distance, *a*, for a metal (after calculations of Slater). The quantum numbers are explained in Appendix 3.

Part I Fundamentals

Electron Theory : Matter Waves

Chap. 1 Introduction

Chap. 2 The Wave-Particle Duality

Chap. 3 The Schördinger Equation

Chap. 4 Solution of the Schördinger Equation for Four Specific Problems

Chap. 5 Energy Bands in Crystals

Chap. 6 Electrons in a Crystal

Electromagnetic Theory : Maxwell Equations

Chap. 4 Light Waves

(Electrons in Solids, 3rd Ed., R. H. Bube)

5. Energy Bands in Crystals

5.1 One-Dimensional Zone Schemes

For free electrons, the wave number in 1-dim

$$E = \frac{\hbar^2}{2m} k^2 \longrightarrow k_x = const.E^{1/2}$$

Figure 5.1. Electron energy E versus the wave vector k_x for free electrons.

In a crystal

$$P\frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \qquad \text{If } P = 0, \quad \cos \alpha a = \cos ka$$

$$\cos \alpha a = \cos k_x a \equiv \cos(k_x a + n2\pi)$$: more general form in 1-dim

$$n = 0,\ \pm 1,\ \pm 2, \ldots.$$

$$\left.\begin{aligned} \alpha a &= k_x a + n2\pi \\ \alpha &= \sqrt{\frac{2m}{\hbar^2}} E^{1/2} \end{aligned}\right\} \quad k_x + n\frac{2\pi}{a} = \sqrt{\frac{2m}{\hbar^2}} E^{1/2}$$

5. Energy Bands in Crystals

5.1 One-Dimensional Zone Schemes

$$k_x + n\frac{2\pi}{a} = \sqrt{\frac{2m}{\hbar^2}}E^{1/2}$$

***E* is a periodic function of k_x with the periodicity of $2\pi / a$**

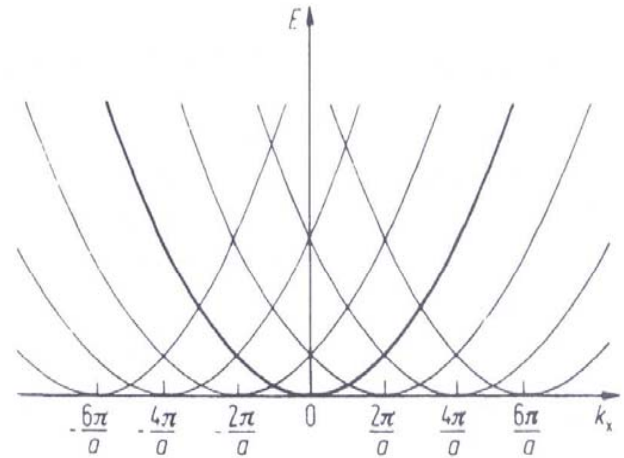


Figure 5.2. Periodic repetition of Fig. 5.1 at the points $k_x = n \cdot 2\pi/a$. The figure depicts a family of free electron parabolas having a periodicity of $\pm 2\pi/a$.

If an electron propagates in *a periodic potential*, discontinuities of the electron energies are observed when $\cos k_x a$ has a maximum or a minimum, i.e., when $\cos k_x a = \pm 1$

$$k_x a = n\pi, \qquad n = \pm 1, \pm 2, \pm 3, \ldots, \qquad \text{or} \qquad k_x = n \cdot \frac{\pi}{a}$$

At these singularities, a deviation from the parabolic E *vs* k_x occurs and the branches of the individual parabolas merge into the neighboring ones (see Fig.5.3)

5. Energy Bands in Crystals

5.1 One-Dimensional Zone Schemes

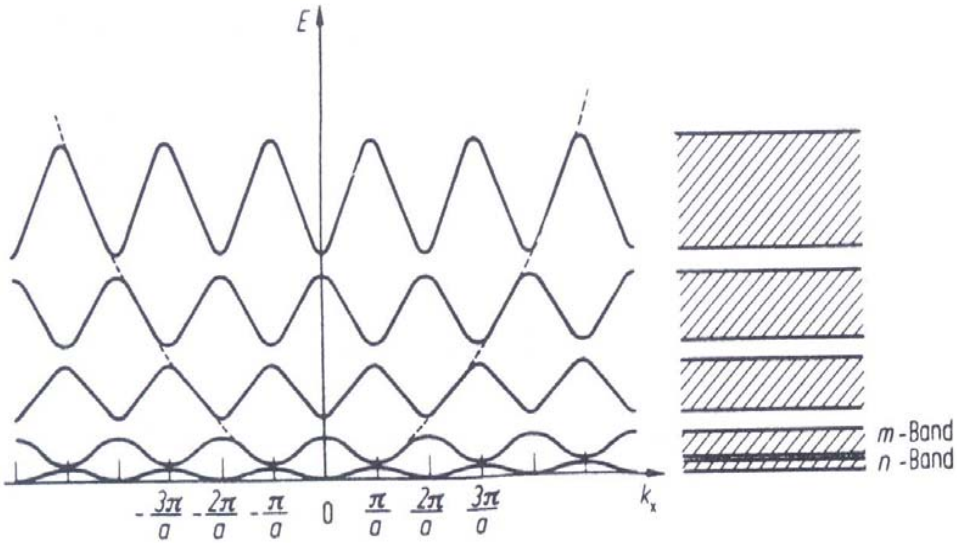


Figure 5.3. Periodic zone scheme.

The electrons in a crystal behave like free electrons for most k_x value except $k_x \rightarrow n\pi/a$

periodic zone scheme (see Fig 5.3)

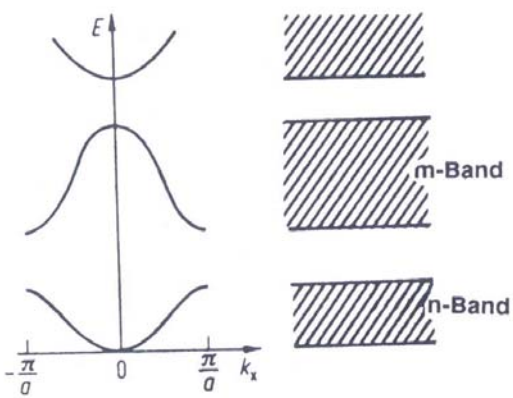


Figure 5.4. Reduced zone scheme. (This is a section of Fig. 5.3 between $-\pi/a$ and $+\pi/a$.)

reduced zone scheme (see Fig 5.4)

$$\pi/a \leq k_x \leq \pi/a$$

5. Energy Bands in Crystals

5.1 One-Dimensional Zone Schemes

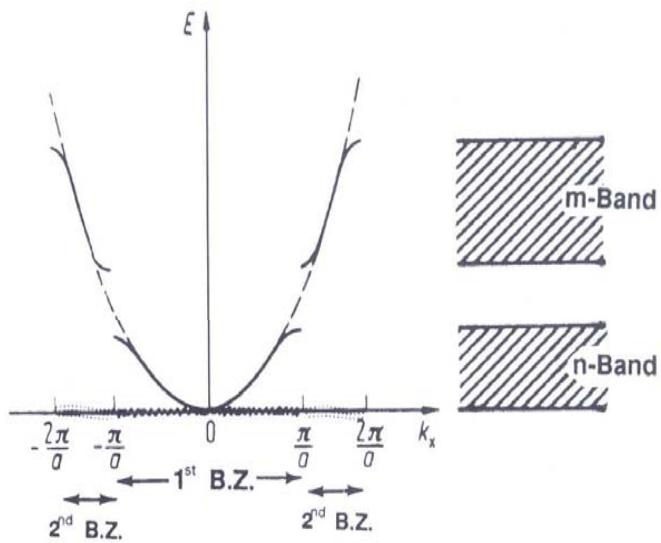


Figure 5.5. Extended zone scheme. The first and second Brillouin zones (BZ) are shown, see Section 5.2.

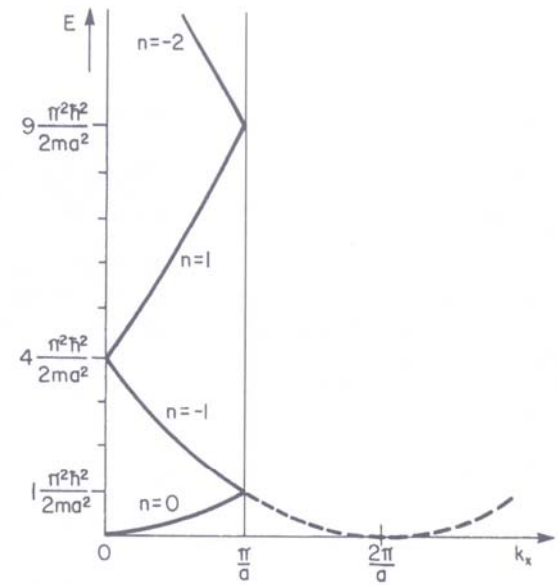


Figure 5.6. "Free electron bands" plotted in the reduced zone scheme (cubic primitive crystal structure). Compare this figure with the central portion of Fig. 5.2, that is, with the region from zero to π/a. Note the sameness of the individual bands.

extended zone scheme (see Fig 5.5)

Deviations from the free electron parabola at the critical points $k_x = n\,\pi/a$ are particularly easy to identify.

free electron bands (see Fig 5.6)

Free electrons in a reduced zone scheme from

$$k_x + n\frac{2\pi}{a} = \sqrt{\frac{2m}{\hbar^2}}E^{1/2}$$

$$E = \frac{\hbar^2}{2m}\left(k_x + n\frac{2\pi}{a}\right)^2, \quad n = \pm 0, \pm 1, \pm 2, \ldots.$$

5. Energy Bands in Crystals

5.1 One-Dimensional Zone Schemes

$$E = \frac{\hbar^2}{2m}(k_x + n\frac{2\pi}{a})^2, \quad n = \pm 0, \pm 1, \pm 2, ...$$

By inserting different *n*-values, one can calculate the shape of branches of the free electron bands

$$n = 0, \quad E = \frac{\hbar^2}{2m}k_x^2 \quad (parabola \;\; with \;\; 0 \;\; \text{as origin})$$

$$n = -1, \quad E = \frac{\hbar^2}{2m}(k_x - \frac{2\pi}{a})^2 \quad (parabola \;\; with \;\; \frac{2\pi}{a} \;\; \text{as origin})$$

$$\text{For } k_x = 0, \quad E = 4\frac{\pi^2\hbar^2}{2ma^2}$$

$$\text{For } k_x = \frac{\pi}{a}, \quad E = 1\frac{\pi^2\hbar^2}{2ma^2}$$

5.2 One- and Two-Dimensional Brillouin Zones

1-d Brillouin Zone

The first Brillouin Zone (BZ) :

$\pi/a \leq k_x \leq \pi/a$: n-Band

The second Brillouin Zone (BZ):

$\pi/a \leq k_x \leq 2\pi/a$, $-\pi/a \leq k_x \leq -2\pi/a$: m-band

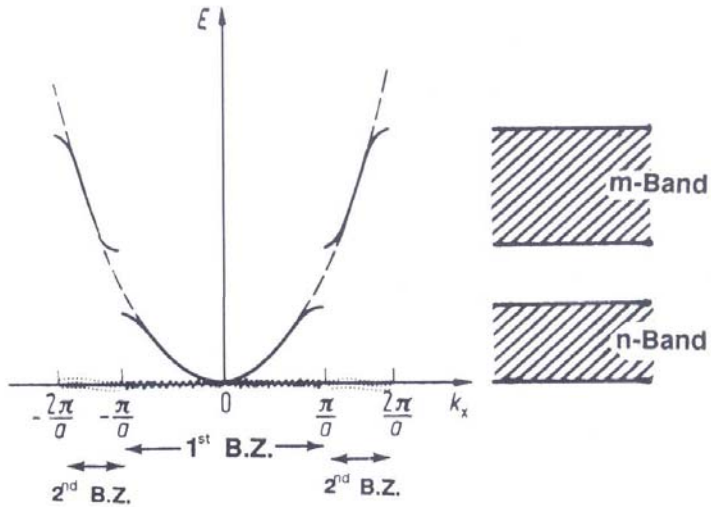


Figure 5.5. Extended zone scheme. The first and second Brillouin zones (BZ) are shown, see Section 5.2.

- Individual branches in an extended zone scheme (Fig. 5.5) can be shifted by $2\pi/a$ to left or to right.

Shift the branches of 2nd BZ to the positive side of E- k_x diagram by $2\pi/a$ to the left, and likewise the left band by $2\pi/a$ to the right → The result is shown in Fig. 5.4 (a reduced zone scheme)

- The same can be done in 3rd BZ and all BZ (because of the $2\pi/a$ periodicity) → relevant information of all BZ can be contained in the 1st BZ (a reduced zone scheme)

5.2 One- and Two-Dimensional Brillouin Zones

2-d Brillouin Zone

Description for the movement of an electron in the potential of 2-d lattice

- Wave vector $\boldsymbol{k} = (k_x, k_y)$: 2-d reciprocal lattice (Fig 5.7)
- A 2-d field of allowed energy regions which correspond to the allowed energy band → 2-d BZ
- 1st zone in 2-d: the area enclosed by four "Bragg planes" having four shortest lattice vectors, $\mathbf{G_1}$: bisectors on the lattice vectors
- For the following zone, construct the bisectors of the next shortest lattice vectors, $\mathbf{G_2}$, $\mathbf{G_3}$…
- For the zone of higher order the extended limiting lines of the zones of lower order are used as additional limiting lines.

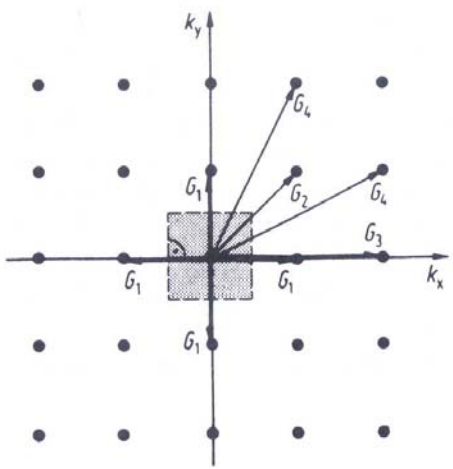


Figure 5.7. Four shortest lattice vectors in a $k_x - k_y$ coordinate system and the first Brillouin zone in a two-dimensional reciprocal lattice. (Cubic primitive crystal structure.)

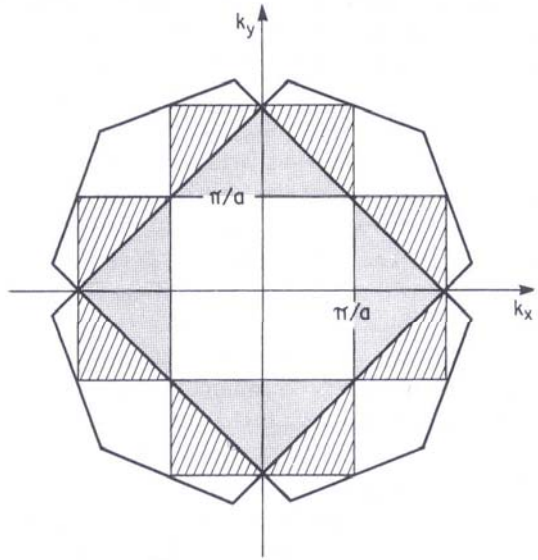


Figure 5.8. The first four Brillouin zones of a two-dimensional, cubic primitive reciprocal lattice.

5.2 One- and Two-Dimensional Brillouin Zones

"Usefulness of BZ"

- energy bands of solids (discussed in later section)
- the behavior of electrons which travel in a specific direction in reciprocal space

Example: in 2-d lattice, an electron travels at 45° to k_x-axis, then the boundary of the BZ is reached, according to Fig 5.8, for $k_{crit} = \frac{\pi}{a}\sqrt{2}$

this yields with (4.8) a maximal attainable energy of $E_{\max} = \frac{\pi^2\hbar^2}{a^2 m}$

If the boundary of a BZ is reached at $k_{crit} = \frac{\pi}{a}$

the largest energy of electrons moving parallel to k_x or k_y axis $E_{\max} = \frac{1}{2}\left(\frac{\pi^2\hbar^2}{a^2 m}\right)$

5.2 One- and Two-Dimensional Brillouin Zones

- Once the maximal energy has been reached, the electron waves (those of the incident and the Bragg-reflected electrons) form standing waves (the electrons are reflected back into the BZ.)

- Overlapping of energy bands: bands are drawn in different directions in *k*-space (Fig 5.9) :

the consequence of

$$k_{crit} = \frac{\pi}{a} \quad \text{and} \quad k_{crit} = \frac{\pi}{a}\sqrt{2}$$

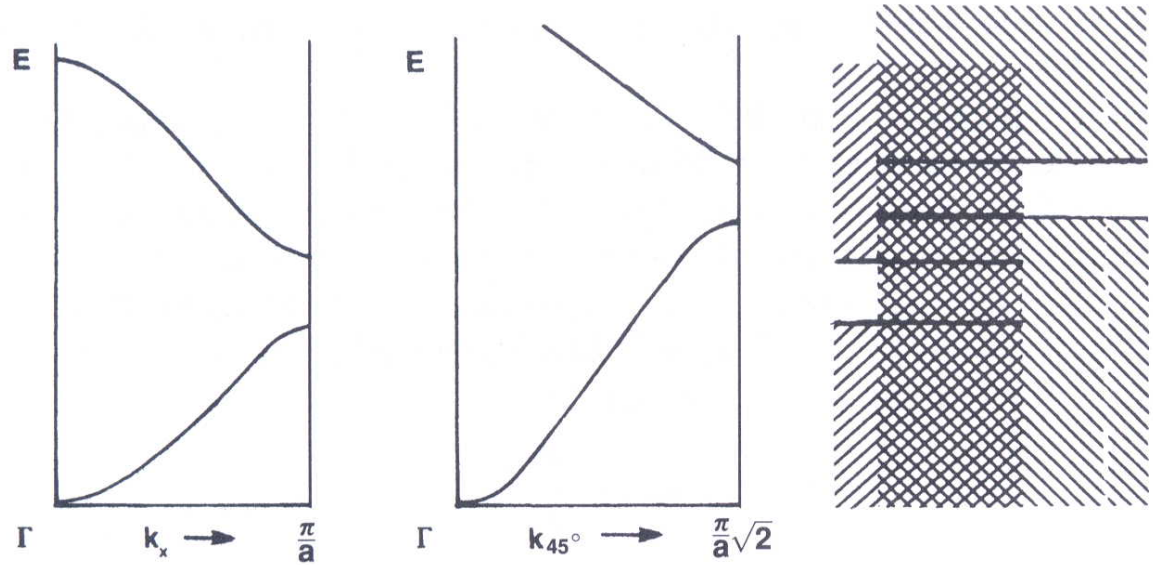


Figure 5.9. Overlapping of allowed energy bands.

5.2 One- and Two-Dimensional Brillouin Zones

A different illustration of the occurrence of critical energies at which a reflection of the electron wave takes place :

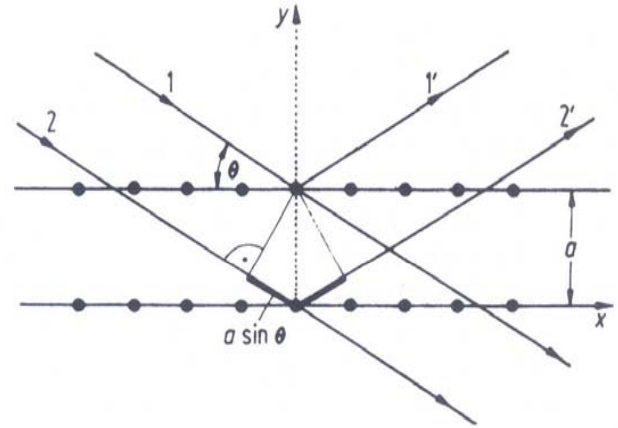


Figure 5.10. Bragg reflection of an electron wave in a lattice. The angle of incidence is θ.

Bragg relation

$$2a\sin\theta = n\lambda, \qquad n = 1,2,3,...$$

Since $\lambda = 2\pi/k$

$$2a\sin\theta = n\frac{2\pi}{k} \longrightarrow k_{crit} = n\frac{\pi}{a\sin\theta}$$

For a perpendicular incidence, $\theta = 90^o$, $\quad k_{crit} = \dfrac{\pi}{a}$

If $\theta = 45^o$, $\quad k_{crit} = \dfrac{\pi}{a}\sqrt{2}$

For increasing electron energies, a critical k-value is finally reached for which "reflection" of the electron wave at the lattice plane occurs.
At k_{crit}, the transmission of electron beam through the lattice is prevented.

5.3 Three-Dimensional Brillouin Zones

- In previous section, it was shown that at the boundaries of the zones the electron waves are Bragg-reflected by the crystal.

- The wave vector, $|\boldsymbol{k}| = 2\pi/\lambda$, was seen to have the unit of reciprocal length and thus is defined in the reciprocal lattice.

- The construction of 3-d Brillouin zones for two important crystal structures of face centered cubic (FCC) and body centered cubic (BCC) : important features in common with "**Wigner- Seitz cells**"

5.4 Wigner - Seitz Cells

Crystals have symmetrical properties

- An accumulation of "**unit cell**"
- Smallest possible cell "**primitive cell**" (consist of 1 atom)
- BCC, FCC : conventional non-primitive unit cells

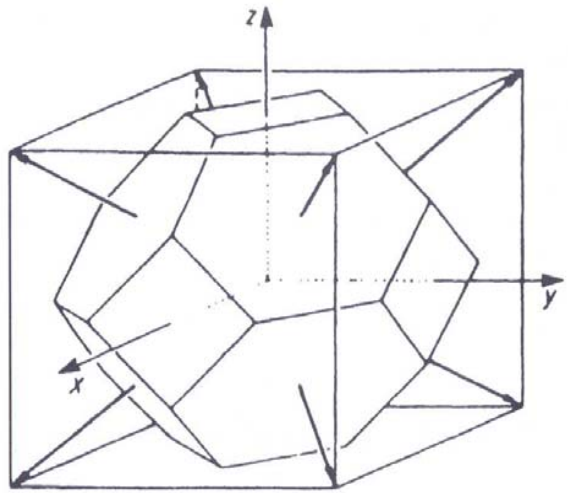


Figure 5.11. Wigner–Seitz cell for the body-centered cubic (bcc) structure.

- **Wigner-Seitz cell** : a special type of primitive unit cell that shows the cubic symmetry of cubic cells

- W-S cell construction: bisects the vectors from a given atom to its nearest neighbors and place a plane perpendicular to these vectors at the bisecting points. For BCC (Fig 5.11) & FCC (Fig. 5. 13)

5.4 Wigner - Seitz Cells

- The atomic arrangement of FCC: corners and faces of cube, or center points of the edges and the center of the cell (Fig 5.12)

-The W-S cell for FCC shown in Fig 5.13

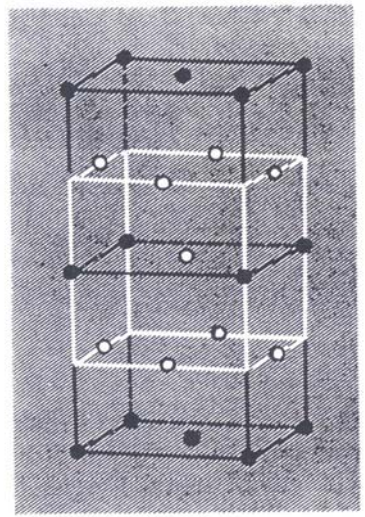


Figure 5.12. Conventional unit cell of the fcc structure. In the cell which is marked black, the atoms are situated on the corners and faces of the cubes. In the white cell, the atoms are at the centers of the edges and the center of the cell.

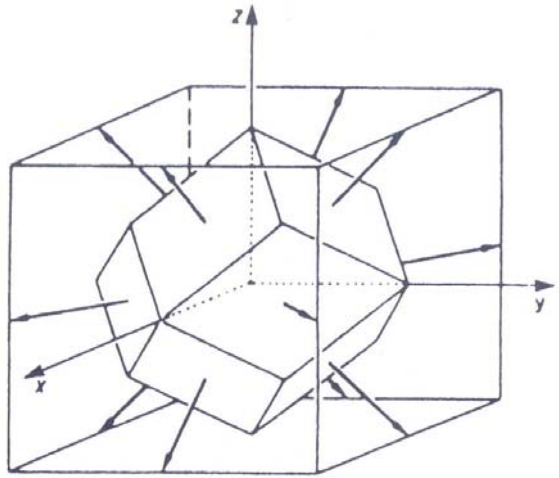


Figure 5.13. Wigner–Seitz cell for the fcc structure. It is constructed from the white cell which is marked in Fig. 5.12.

5.5 Translation Vectors and the Reciprocal Lattice

Fundamental vectors or primitive vectors : $\mathbf{t}_1, \mathbf{t}_2, \mathbf{t}_3$

Translation vectors, **R** : combination of primitive vectors

$$\mathbf{R} = n_1\mathbf{t}_1 + n_2\mathbf{t}_2 + n_3\mathbf{t}_3$$

where n_1, n_2, and n_3 are integers.

Three vectors for the reciprocal lattice: $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$

a translation vector for the reciprocal lattice, **G**

$$\mathbf{G} = 2\pi(h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3)$$

where h_1,h_2, and h_3 is integer

$$\mathbf{t}_1 = \frac{a}{2}(-\mathbf{i} + \mathbf{j} + \mathbf{l})$$

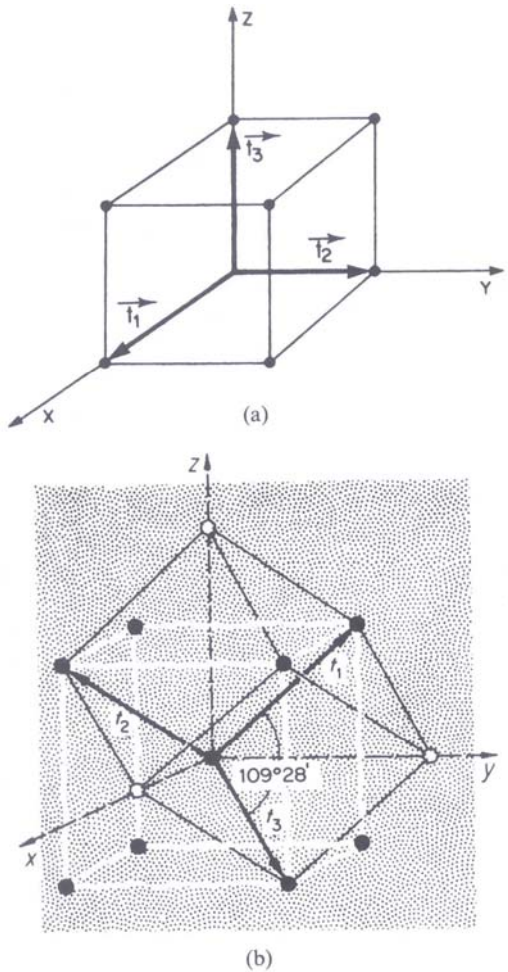


Figure 5.14. (a) Fundamental lattice vectors $\mathbf{t}_1, \mathbf{t}_2, \mathbf{t}_3$ in a cubic primitive lattice. (b) Fundamental lattice vectors in a conventional (white) and primitive, noncubic unit cell (black) of a bcc lattice. The axes of the primitive (noncubic) unit cell form angles of 109° 28′.

5.5 Translation Vectors and the Reciprocal Lattice

The relation between real and reciprocal lattices

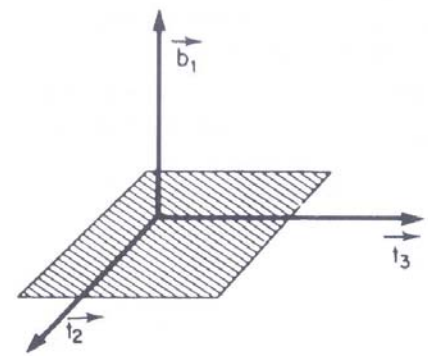


Figure 5.15. Plane formed by $\mathbf{t}_2$ and $\mathbf{t}_3$ with perpendicular vector $\mathbf{b}_1$.

By definition,

$$\left.\begin{aligned} \mathbf{b_1} \bullet \mathbf{t_1} &= 1, \\ \mathbf{b_1} \bullet \mathbf{t}_2 &= 0, \\ \mathbf{b_1} \bullet \mathbf{t}_3 &= 0. \end{aligned}\right\}$$

Kronecker-Delta symbol

$$\mathbf{b}_n \mathbf{t}_m = \delta_{nm},$$

where $\delta_{nm} = 1$ for $n = m$ and $\delta_{nm} = 0$ for $n \neq m$

$$\mathbf{b}_1 = const.\ \mathbf{t}_2 \times \mathbf{t}_3 \longrightarrow \mathbf{b}_1 \bullet \mathbf{t}_1 = const.\ \mathbf{t}_1 \bullet \mathbf{t}_2 \times \mathbf{t}_3 = 1 \longrightarrow const = \frac{1}{\mathbf{t}_1 \bullet \mathbf{t}_2 \times \mathbf{t}_3}$$

$$\mathbf{b}_1 = \frac{\mathbf{t}_2 \times \mathbf{t}_3}{\mathbf{t}_1 \bullet \mathbf{t}_2 \times \mathbf{t}_3} \qquad \mathbf{b}_2 = \frac{\mathbf{t}_3 \times \mathbf{t}_1}{\mathbf{t}_1 \bullet \mathbf{t}_2 \times \mathbf{t}_3} \qquad \mathbf{b}_3 = \frac{\mathbf{t}_1 \times \mathbf{t}_2}{\mathbf{t}_1 \bullet \mathbf{t}_2 \times \mathbf{t}_3}$$

5.5 Translation Vectors and the Reciprocal Lattice

Calculation for the reciprocal lattice of a BCC crystal

Real crystal

a: lattice constant , **t_1, t_2, t_3 :** primitive lattice vectors,

i, j, l : unit vectors in the x, y, z coordinate system (see Fig. 5.14(b))

$$\mathbf{t}_1 = \frac{a}{2}(-\mathbf{i}+\mathbf{j}+\mathbf{l})$$

Abbreviated, $\mathbf{t}_1 = \frac{a}{2}(\bar{1}\,1\,1)$ $\mathbf{t}_2 = \frac{a}{2}(1\,\bar{1}\,1)$ $\mathbf{t}_3 = \frac{a}{2}(1\,1\,\bar{1})$

$$\mathbf{t}_2 \times \mathbf{t}_3 = \frac{a^2}{4}\begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{vmatrix} = \frac{a^2}{4}(\mathbf{i}+\mathbf{j}+\mathbf{l}+\mathbf{l}-\mathbf{i}+\mathbf{j})$$

$$= \frac{a^2}{4}(2\mathbf{j}+2\mathbf{l}) = \frac{a^2}{2}(\mathbf{j}+\mathbf{l})$$

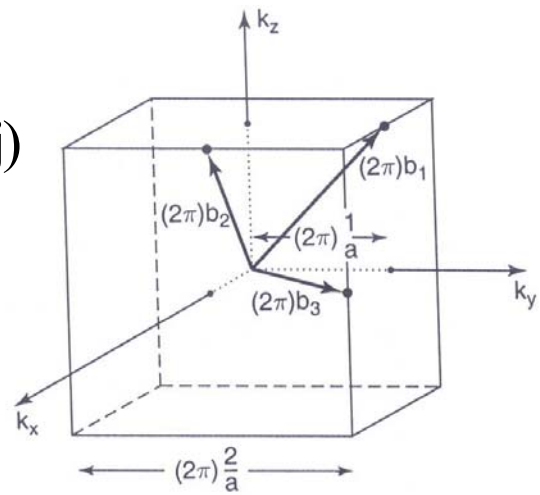


Figure 5.16. Lattice vectors in reciprocal space of a bcc crystal. The primitive vectors in the reciprocal lattice are (because of (5.13)) larger by a factor of 2π. The lattice constant of the cube then becomes $2\pi \cdot 2/a$.

5.5 Translation Vectors and the Reciprocal Lattice

(continued)

$$\mathbf{t}_1 \bullet \mathbf{t}_2 \times \mathbf{t}_3 = \frac{a^3}{4}(-\mathbf{i}+\mathbf{j}+\mathbf{l}) \bullet (0+\mathbf{j}+\mathbf{l}) = \frac{a^3}{4}(0+1+1) = \frac{a^3}{2}$$

$$\mathbf{b}_1 = \frac{\mathbf{t}_2 \times \mathbf{t}_3}{\mathbf{t}_1 \bullet \mathbf{t}_2 \times \mathbf{t}_3} \longrightarrow \mathbf{b}_1 = \frac{\frac{a^2}{2}(\mathbf{j}+\mathbf{l})}{\frac{a^3}{2}} = \frac{1}{a}(\mathbf{j}+\mathbf{l}),$$

$$\mathbf{b}_1 = \frac{1}{a}(011) \quad \mathbf{b}_2 = \frac{1}{a}(101) \quad \mathbf{b}_3 = \frac{1}{a}(110)$$

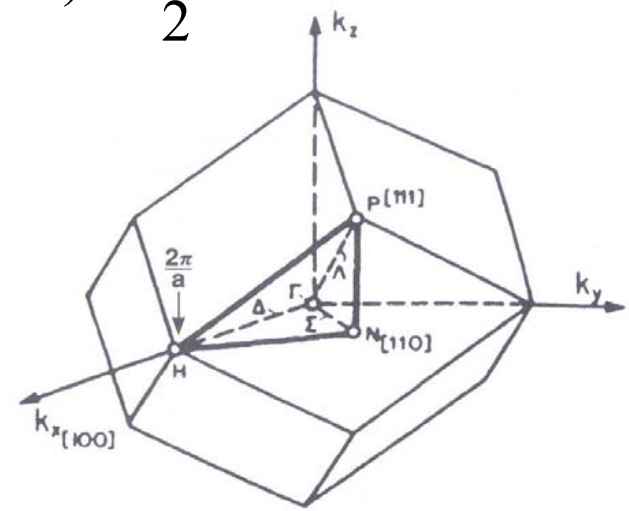


Figure 5.17. First Brillouin zone of the bcc crystal structure.

BCC (reciprocal lattice) $\longrightarrow$ **FCC (real lattice)**

1st Brillouin zone for BCC $\longrightarrow$ **Wigner-Seitz cell for FCC**

$\longleftarrow$

Vice versa

5.6 Free electron Bands

Periodicity of $E(\mathbf{k})$ → all information of electron contained in the 1st Brillouin Zone (BZ)

$E_{\mathbf{k}'}$ for **k'** for outside 1st BZ → $E_{\mathbf{k}}$ with in 1st BZ with a suitable translation vector **G**

$$\mathbf{k}' = \mathbf{k} + \mathbf{G}$$

"Energy bands are not alike in different directions in **k**-space"

for the demonstration, "free electron band" is used (Fig 5.6 **).**

In 3-D, from (5.7)

$$E_{k'} = \frac{\hbar^2}{2m}(\mathbf{k} + \mathbf{G})^2$$

$$E = \frac{\hbar^2}{2m}(k_x + n\frac{2\pi}{a})^2, \quad n = \pm 0, \pm 1, \pm 2, ... \qquad \textbf{(5.7)}$$

5. Energy Bands in Crystals

5.6 Free electron Bands

In Fig 5.17, three important directions

[100] from Γ(origin) to point H : Δ

[110] from Γ to N : Σ

[111] from Γ to P : Λ

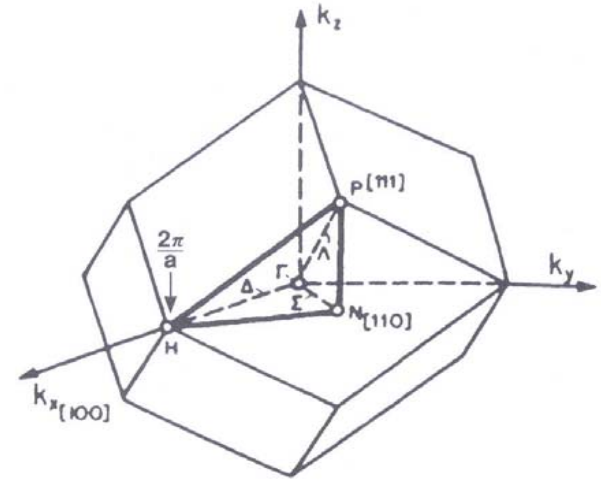


Figure 5.17. First Brillouin zone of the bcc crystal structure.

Fig 5.18 calculated by using the following eqn.

$$E_{k'} = \frac{\hbar^2}{2m}(\mathbf{k} + \mathbf{G})^2$$

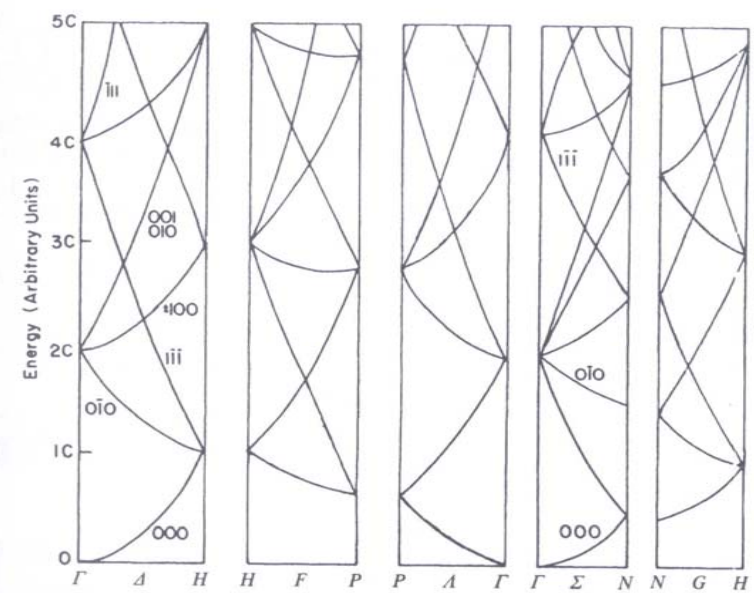


Figure 5.18. Energy bands of the free electrons for the bcc structure. The numbers given on the branches are the respective h_i values (see the calculation in the text). Compare to Fig. 5.6. $C = \hbar^2 2\pi^2/ma^2$, see (5.38).

5.6 Free electron Bands

band calculation for BCC $\Gamma - H \quad [100]$ direction

$\mathbf{k}_{\Gamma-\mathrm{H}} \equiv \mathbf{k}_{\mathbf{x}}$ between 0 and $2\pi/a$ (boundary of BZ)

For this direction (5.35) becomes

$$E = \frac{\hbar^2}{2m}\left(\frac{2\pi}{a}x\mathbf{i} + \mathbf{G}\right)^2$$

Where x may take values between 0 and 1. to start with, let $\mathbf{G} = 0$, then

$$E = \frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right)^2 (x\mathbf{i})^2 \equiv Cx^2$$

where $C = \frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right) = \frac{2\hbar^2\pi^2}{ma^2}$

this curve is labeled (000) in Fig 5. 18 since $h_1,h_2,h_3 = 0,0,0$ for $\mathbf{G}=0$

5.6 Free electron Bands

For the case of $h_1,h_2,h_3 = 0,-1,0$

$$\mathbf{G} = -\frac{2\pi}{a}(\mathbf{i}+\mathbf{l})$$

combined (5.36) and (5.38)

$$E = \frac{\hbar^2}{2m}\left[\frac{2\pi x}{a}\mathbf{i} - \frac{2\pi}{a}(\mathbf{i}+\mathbf{l})\right]^2 = C[\mathbf{i}(x-1)-\mathbf{l}]^2$$

$$C = [(x-1)^2+1] = C(x^2-2x+2)$$

For $x=0 \rightarrow E=2C$

and for $x=1 \rightarrow E=1C$

The band labeled $(0\,\bar{1}\,0)$

in Fig 5.18 obtained.

Similarly, For FCC, see

Figs. 5.19 & 5. 20

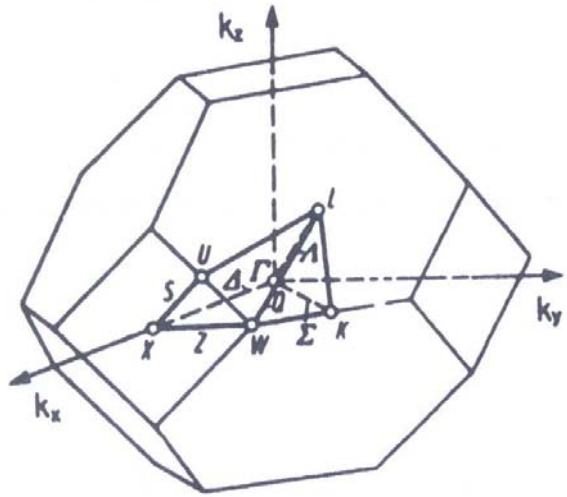


Figure 5.19. First Brillouin zone of the fcc structure.

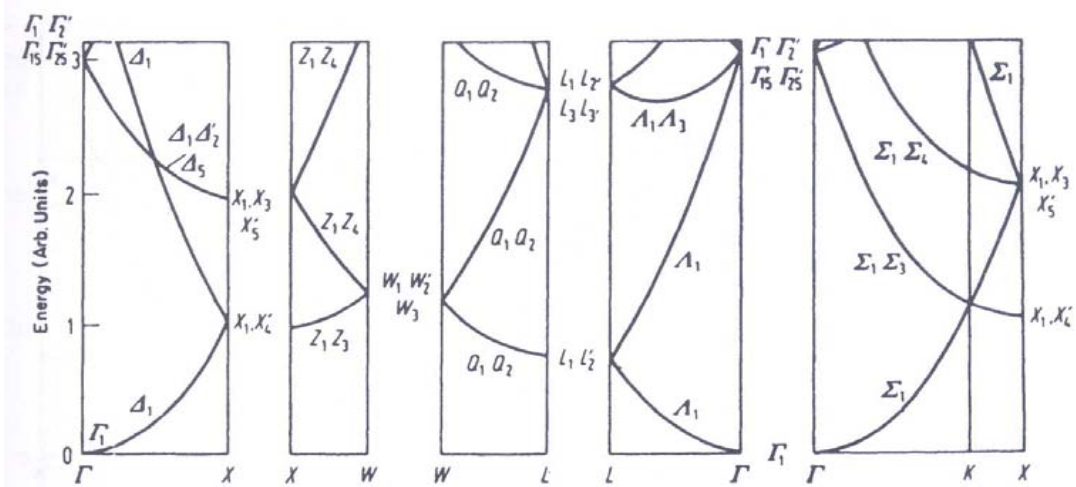


Figure 5.20. Free electron bands of the fcc structure. The letters on the bottom of the graphs correspond to letters in Fig. 5.19 and indicate specific symmetry points in k-space.

5.7 Band Structures for Some Metals and Semiconductors

Band structure of actual solids:

Figs. 5.21-24

(results of extensive, computer-aided calculations)

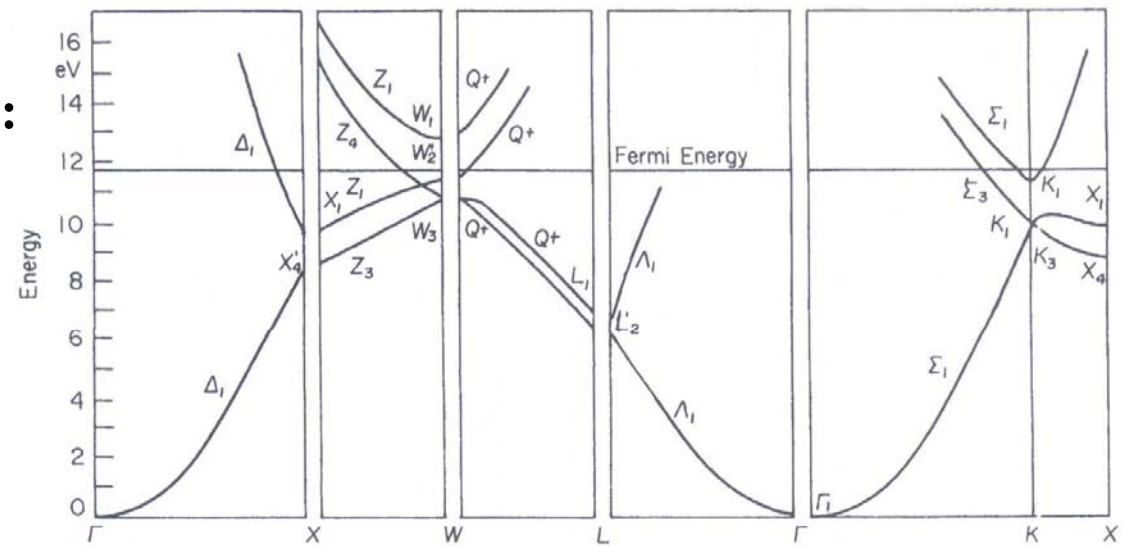


Figure 5.21. Energy bands for aluminum. Adapted from B. Segal, *Phys. Rev.* **124**, 1797 (1961). (The meaning of the Fermi energy will be explained in Section 6.1.)

Directions in *k*-space

[100] : $\Gamma - X$

[110] : $\Gamma - K$

[111]: $\Gamma - L$

Band diagram for aluminum

- parabola-shaped band: free- electron like

5. Energy Bands in Crystals

5.7 Band Structures for Some Metals and Semiconductors

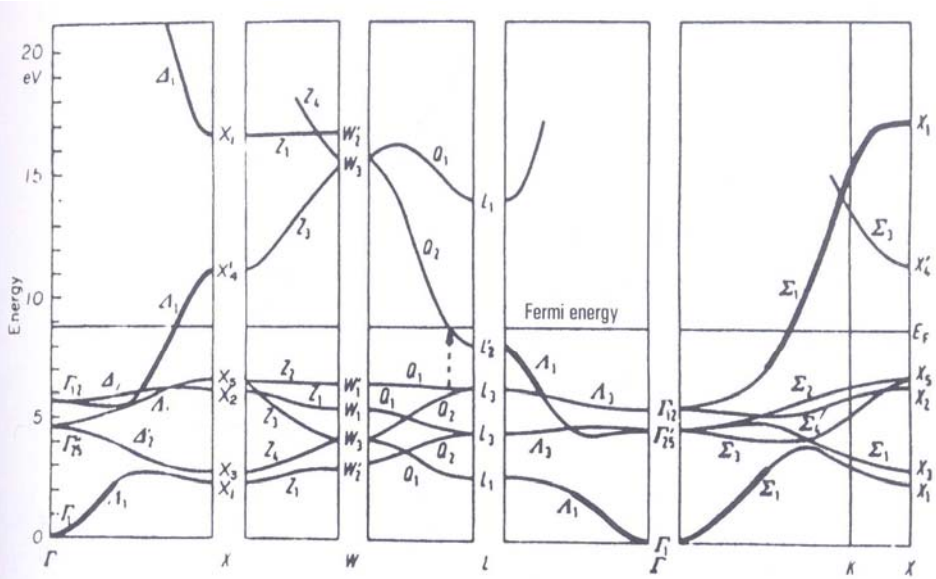


Figure 5.22. Band structure of copper (fcc). Adapted from B. Segal, *Phys. Rev.* **125**, 109 (1962). The calculation was made using the *l*-dependent potential. (For the definition of the Fermi energy, see Section 6.1.)

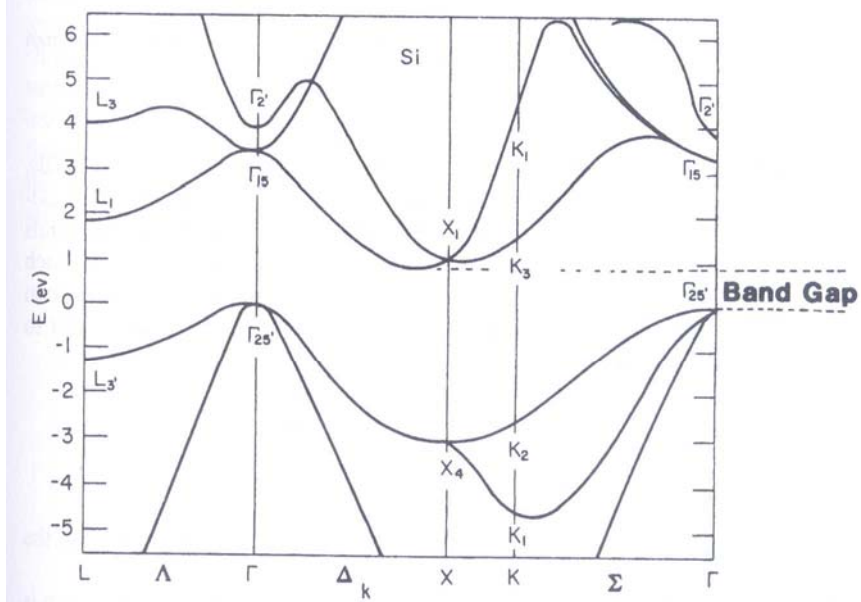


Figure 5.23. Calculated energy band structure of silicon (diamond-cubic crystal structure). Adapted from M.L. Cohen and T.K. Bergstresser, *Phys. Rev.* **14**, 789 (1966). See also J.R. Chelikowsky and M.L. Cohen, *Phys. Rev.* **B14**, 556 (1976).

Band diagram for copper

- Lower half of the diagram closely spaced and flat running bands (due to 3d-bands of Cu)

Band diagram for silicon

- Band gap : near 0~ 1eV → "semiconductor properties"

5.7 Band Structures for Some Metals and Semiconductors

Band diagram gallium arsenide:

so called III – IV semiconductor

Important for “optoelectronic devices”

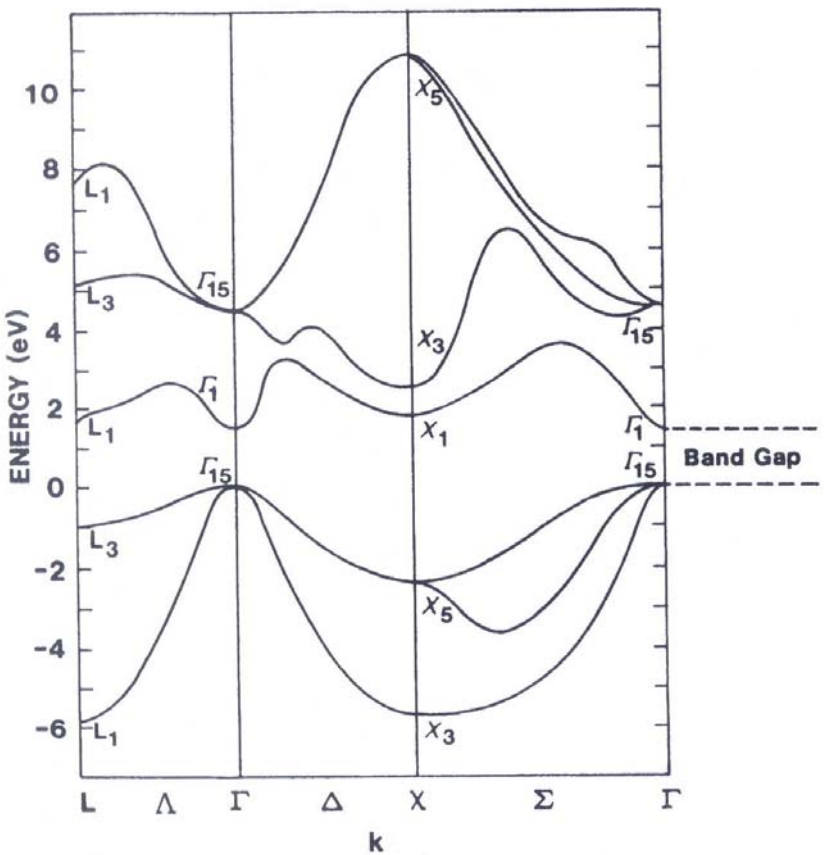


Figure 5.24. Calculated energy band structure of GaAs. Adapted from F. Herman and W.E. Spicer, *Phys. Rev.* **174**, 906 (1968).

5.8 Curves and Planes of Equal Energy

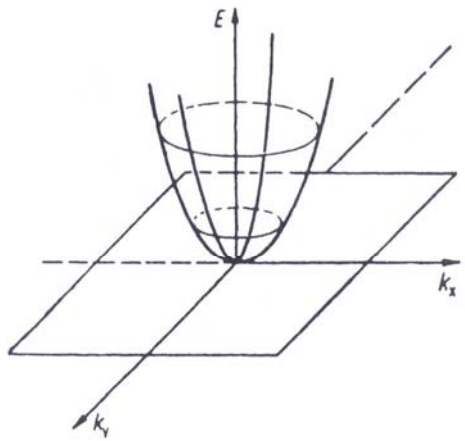


Figure 5.25. Electron energy E versus wave vector **k** (two-dimensional). This figure demonstrates various curves of equal energy for free electrons.

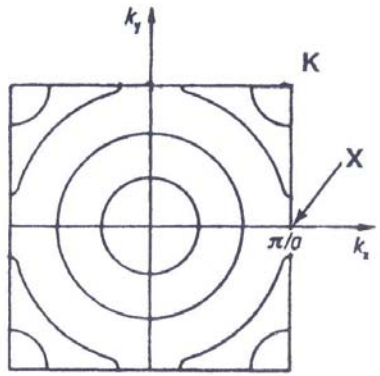


Figure 5.26. Curves of equal energy inserted into the first Brillouin zone for a two-dimensional square lattice.

Energy vs. wave vector, *k*

Fig 5.25: curves of equal energy for free electrons

Fig 5.26: near boundary of BZ- deviation from a circular form (2-d)

Fig 5.27: 3-d BZ for Cu

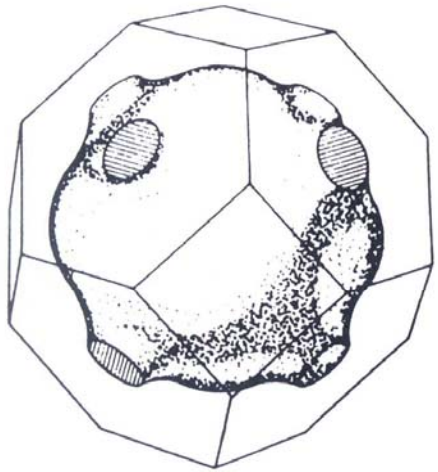
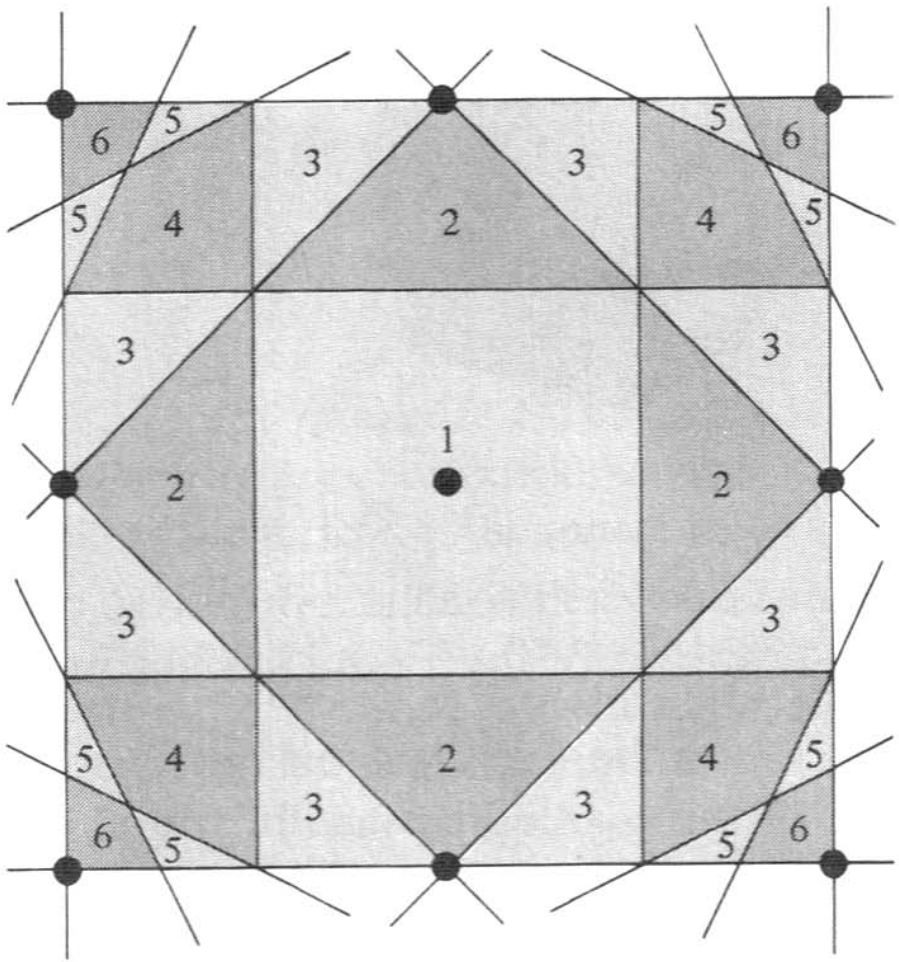


Figure 5.27. A particular surface of equal energy (Fermi surface, see Section 6.1) and the first Brillouin zone for copper. Adapted from A.B. Pippard, *Phil. Trans. Roy. Soc. London*, **A 250**, 325 (1957).

Q&A2

Brillouin Zone in 2-d

Figure 9.7
Illustration of the definition of the Brillouin zones for a two-dimensional square Bravais lattice. The reciprocal lattice is also a square lattice of side b. The figure shows all Bragg planes (lines, in two dimensions) that lie within the square of side $2b$ centered on the origin. These Bragg planes divide that square into regions belonging to zones 1 to 6. (Only zones 1, 2, and 3 are entirely contained within the square, however.)



From Solid State Physics, N.W. Aschcroft & N. D. Mermin, Holt, Rinehart and Winston

Brillouin Zone in 3-d

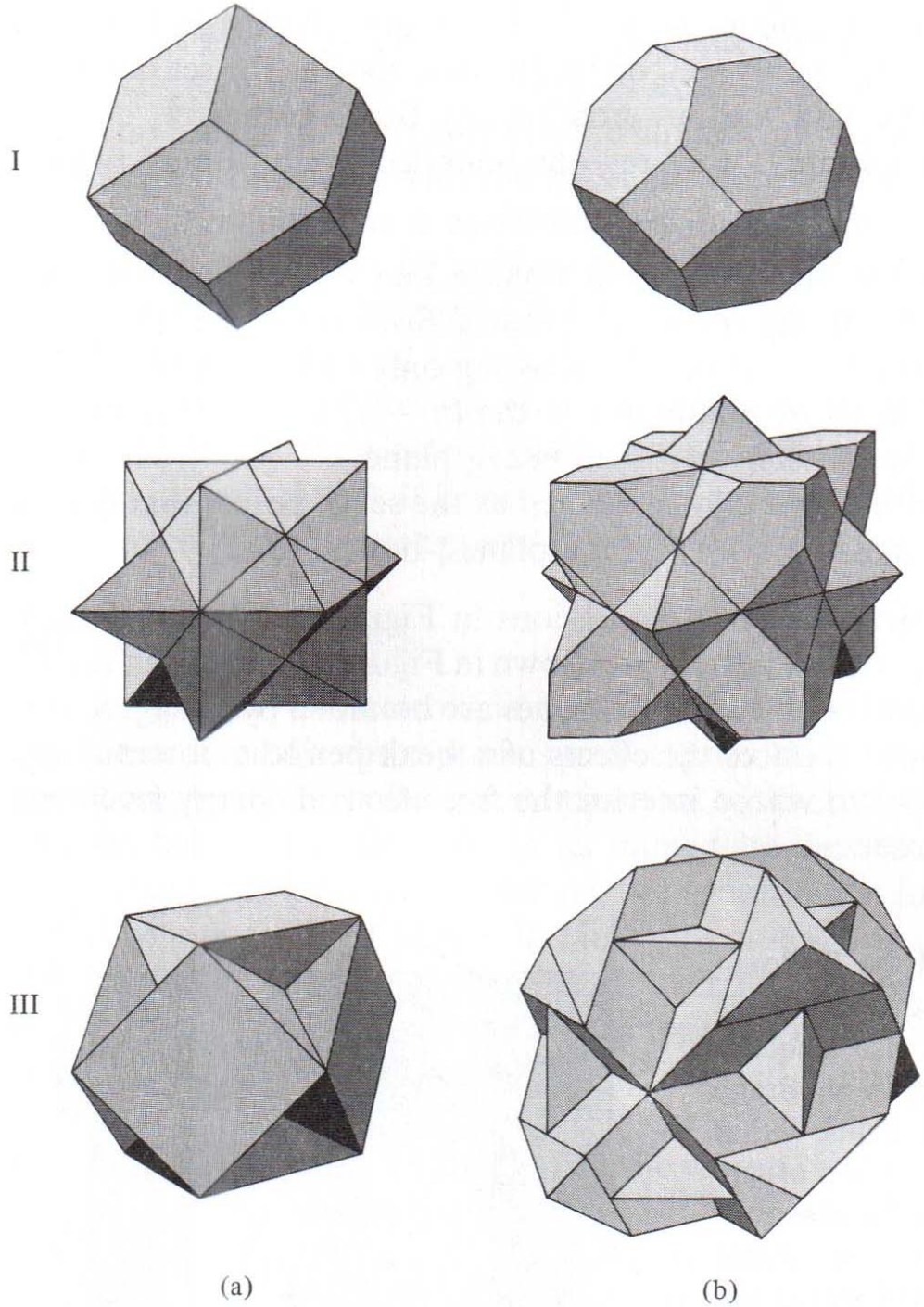


Figure 9.8

Surfaces of the first, second, and third Brillouin zones for (a) body-centered cubic and (b) face-centered cubic crystals. (Only the *exterior* surfaces are shown. It follows from the definition on page 163 that the *interior* surface of the *n*th zone is identical to the exterior surface of the $(n-1)$th zone.) Evidently the surfaces bounding the zones become increasingly complex as the zone number increases. In practice it is often simplest to construct free electron Fermi surfaces by procedures (such as those described in Problem 4) that avoid making use of the explicit form of the Brillouin zones. (After R. Lück, doctoral dissertation, Technische Hochschule, Stuttgart, 1965.)

Part I Fundamentals

Electron Theory : Matter Waves

Chap. 1 Introduction

Chap. 2 The Wave-Particle Duality

Chap. 3 The Schördinger Equation

Chap. 4 Solution of the Schördinger Equation for Four Specific Problems

Chap. 5 Energy Bands in Crystals

Chap. 6 Electrons in a Crystal

Electromagnetic Theory : Maxwell Equations

Chap. 4 Light Waves

(Electrons in Solids, 3rd Ed., R. H. Bube)

6.1 Fermi Energy and Fermi Surface

The Fermi energy, E_F:

- An important part of an electron band diagram
- Defined as **"the highest energy that the electrons assume at T = 0 K"**
- Fermi energy for Al and Cu : see Fig 5.21, 5.22

Fermi energy for semiconductor:

- The above definition can occasionally be misleading, particularly when dealing with semiconductors
- Fermi function at E_F, $F(E_F) = ½$: see Section 6.2 for more accurate definition

Fermi surface (in 3-d *k*-space) for Cu : see Fig 5.27

6.2 Fermi Distribution Function

Fermi function, $F(E)$: The probability that a certain energy level is occupied by electrons

$$F(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}$$

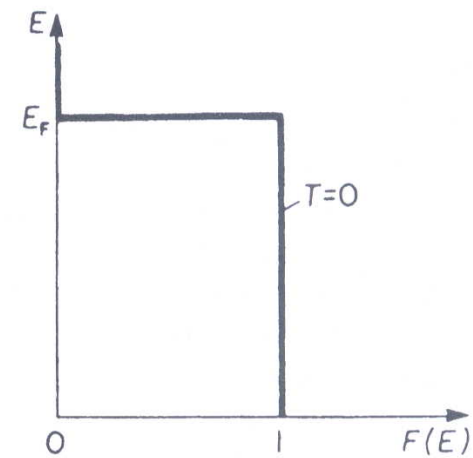


Figure 6.1. Fermi distribution function, F(E), versus energy, E, for $T = 0$.

Fermi distribution for $T = 0$ K (Fig 6.1)

and for higher T ($T \neq 0$ K) (Fig 6.2)

At high energy ($E >> E_F$), $F(E)$ is approximated by classical Boltzmann distribution

$$F(E) \approx \exp\left[-\left(\frac{E - E_F}{k_B T}\right)\right]$$

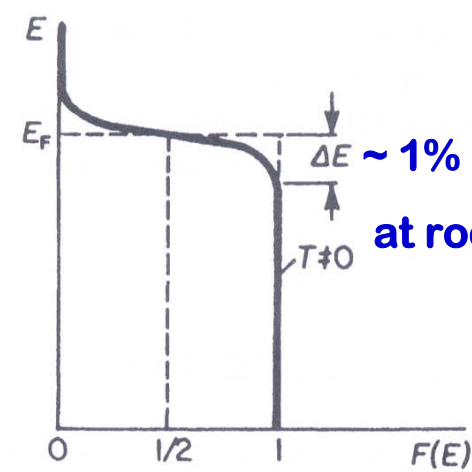


Figure 6.2. Fermi distribution function for $T \neq 0$.

6.3 Density of States

"How energy levels are distributed over a band?"

Assume free electrons are confined in a square potential well of crystal.

Similar to the case in Sec. 4.2, by using B.C., the solution of the Schrödinger equation

$$E_n = \frac{\pi^2 \hbar^2}{2ma^2}(n_x^{\ 2} + n_y^{\ 2} + n_z^{\ 2})$$

$$n^2 = n_x^{\ 2} + n_y^{\ 2} + n_z^{\ 2}$$

where n_x, n_y, n_z are principal quantum numbers,

a is the length of the crystal

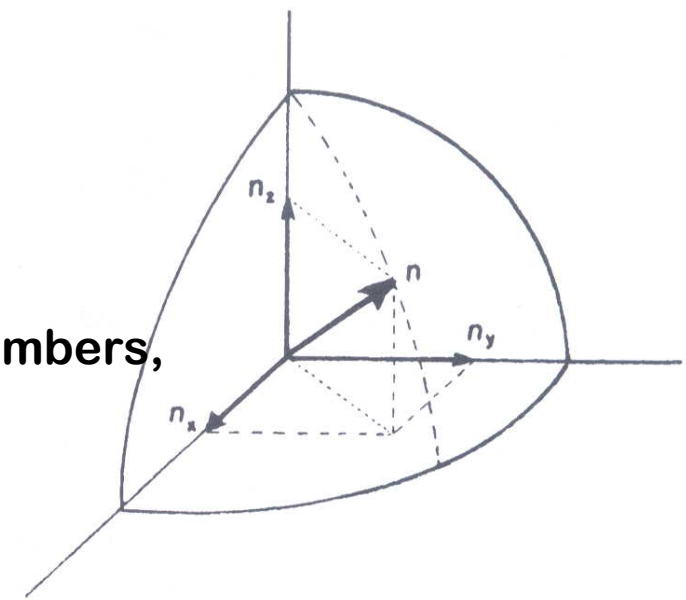


Figure 6.3. Representation of an energy state in quantum number space.

6.3 Density of States

A specific energy level, E_n for each set of $n_x.n_y,n_z$, called "**energy state**"

- Equal values of the energy, E_n lie on the surface of sphere with radius n

- All points within the sphere represent quantum states with energy smaller than E_n

- The **# of quantum state, η**, with an energy equal to or smaller than E_n, is proportional to the volume of the sphere

(n values can be defined in positive octant of the n-space)

In a one-eighth of the volume of the sphere with radius n

(# of energy state η),

$$\eta = \frac{1}{8}\cdot\frac{4}{3}\pi n^3 = \frac{\pi}{6}\left(\frac{2\pi a^2}{\pi^2\hbar^2}\right)^{3/2} E^{3/2}$$

6.3 Density of States

Density of state, *Z(E)* : # of energy states per unit energy in the energy interval *dE*

(a^3 = volume that the electrons can occupy)

Z(E)* : differentiation of η with respect to the energy, *E

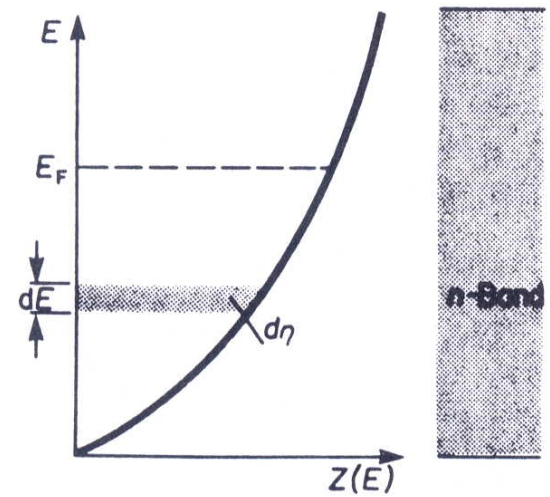


Figure 6.4. Density of states $Z(E)$ within a band. The electrons in this band are considered to be free.

$$\frac{d\eta}{dE} = Z(E) = \frac{\pi}{4}\left(\frac{2ma^2}{\pi^2\hbar^2}\right)^{3/2} E^{1/2} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

$$d\eta = Z(E)\cdot dE$$

6.4 Population Density

Pauli principle : each energy state can be occupied by one electron of positive spin and one of negative spin

Population density $N(E) = 2 \cdot Z(E) \cdot F(E)$

$$N(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}$$

For $T \to 0$ and $E < E_F \to N(E) = 2 \cdot Z(E)$, $F(E) = 1$

For $T \neq 0$, $E \approx E_F$, $\to$ the Fermi distribution function causes a smearing out of $N(E)$

(Fig 6.5)

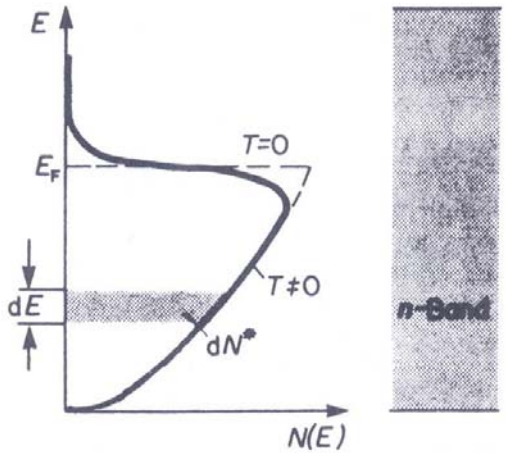


Figure 6.5. Population density $N(E)$ within a band for free electrons. dN^* is the number of electrons in the energy interval dE.

6.4 Population Density

# of electrons *N, that have an energy equal to or smaller than the energy *E_n* (The area within the curve in Fig 6.5) For an energy interval between *E* and *E + dE***

$$dN^* = N(E)dE$$

From (6.8) and (6.9) and consider simple case *T→ 0 and E < E_F ,F(E) = 1*

$$N^* = \int_0^{E_F} N(E)dE = \int_0^{E_F} \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}dE = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{\ 3/2}$$

$$E_F = \left(3\pi^2 \frac{N^*}{V}\right)^{2/3} \frac{\hbar^2}{2m}$$

If we define #of electrons per unit volume as *N' = N*/V,*

$$E_F = (3\pi^2 N')^{2/3} \frac{\hbar^2}{2m}$$

6.5 Complete Density of States Function Within a Band

E **vs. Z(*E*) in actual crystals**

- Low energy : free-electronlike

- Higher energy : fewer energy state available (Fig 5.26)

→ Z(*E*) decrease with increasing *E*

- The corners of the BZ : Z(*E*) dropped to zero

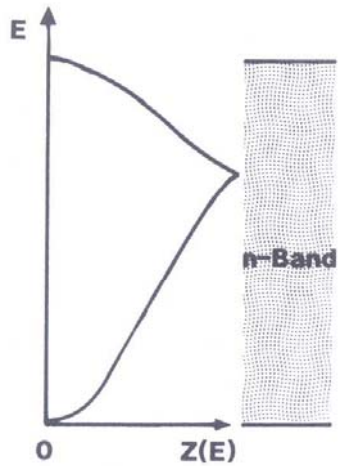


Figure 6.6. Schematic representation of the complete density of states function within a band.

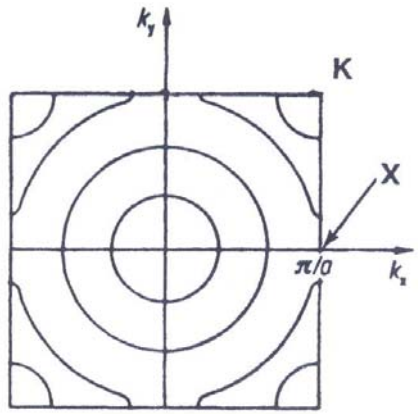


Figure 5.26. Curves of equal energy inserted into the first Brillouin zone for a two-dimensional square lattice.

6.6 Consequences of the Band Model

Insulators : solids in which the highest filled band is completely occupied by electron

Alkali metal: the valence band is essentially half-filled, electrons can drift under external field

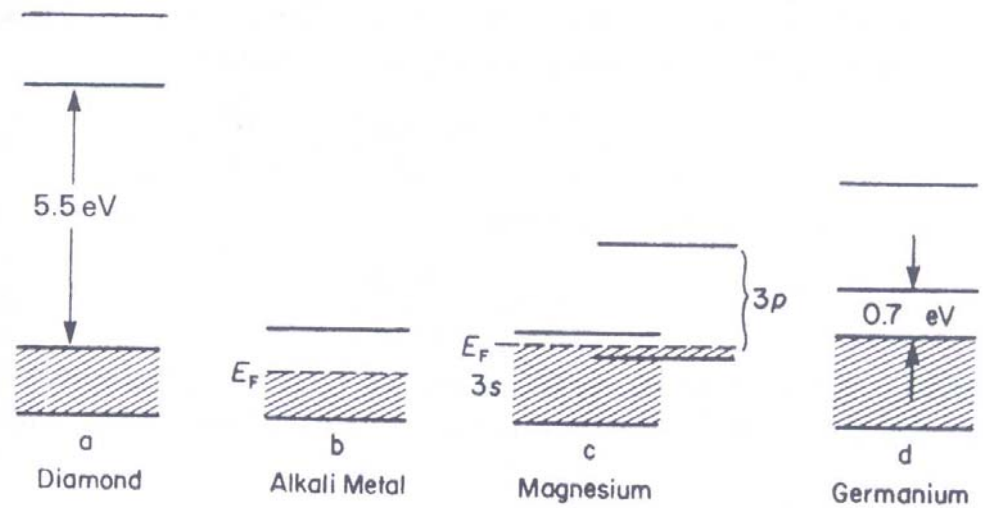


Figure 6.7. Simplified representation for energy bands for (a) insulators, (b) alkali metals, (c) bivalent metals, and (d) intrinsic semiconductors.

Bivalent metals: upper band partially overlapped ; weak binding forces of the valence electrons on atom

Semiconductors: valence band is completely filled with electron; relatively narrow band gap (intrinsic semiconductors); a sufficiently large energy can excite electron from valence band to conduction band → some electron conduction

6.7 Effective Mass

Effective mass (of electron), m^*

experimentally determined electron mass

- Deviation of m^* from free electron mass m_0: usually attributed to interaction between drifting electrons and atoms in a crystal

- For example,

Electron accelerated in an electric field might be slowed down slightly due to "collisions" with some atom → ratio m^*/m_0 >1

The electron wave in another crystal might have just the right phase in order that the response to an external electric field is enhanced→ m^*/m_0 <1

- Derivation of effective mass

group velocity (2.10)

$$\upsilon_g = \frac{d\omega}{dk} = \frac{d(2\pi\nu)}{dk} = \frac{d(2\pi E/h)}{dk} = \frac{1}{\hbar}\frac{dE}{dk}$$

6.7 Effective Mass

(continued) $$a = \frac{d\upsilon_g}{dt} = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt}$$

(4.7) $$p = \hbar k \quad \rightarrow \quad \frac{dp}{dt} = \hbar\frac{dk}{dt}$$

$$a = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}\frac{dp}{dt} = \frac{1}{\hbar^2}\cdot\frac{d^2E}{dk^2}\cdot\frac{d(m\upsilon)}{dt} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}F$$

$$a = \frac{F}{m} \qquad m^* = \hbar^2\left(\frac{d^2E}{dk^2}\right)^{-1}$$

6.7 Effective Mass

$$m^* = \hbar^2 \left(\frac{d^2 E}{dk^2} \right)^{-1}$$

Effective mass is inversely proportional to the curvature of and electron band.

In Fig 6.8, m^* is small and positive near the center of BZ

Negative m^* (upper part of the band in Fig 6.8) : "particle travels in the opposite direction to an applied electric force (and opposite to an electron"; called "**electron hole**"

cf) exciton : an electron/hole pair

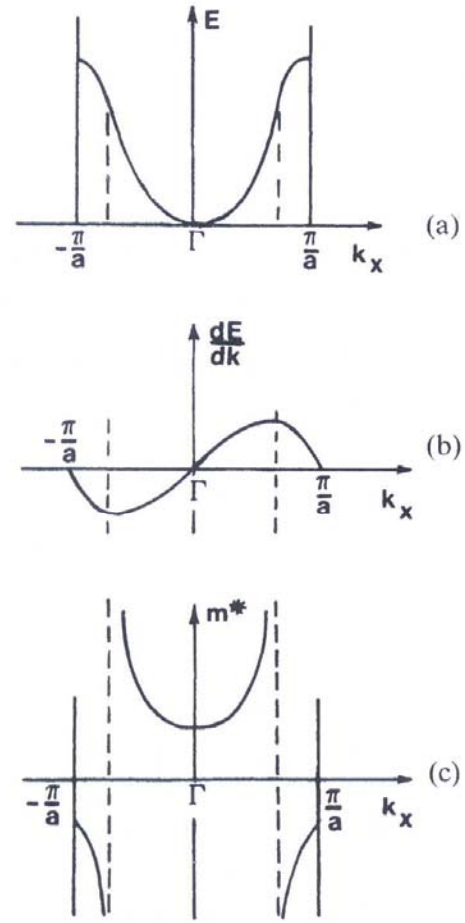


Figure 6.8. (a) Simple band structure, as shown in Fig. 5.4. (b) First derivative and (c) inverse function of the second derivative of the curve shown in (a).

Part II Electrical Properties of Materials

Chap. 7 Electrical Conduction in Metals and Alloys

Chap. 8 Semiconductors

Chap. 9 Electrical Properties of Polymers, Ceramics, Dielectrics, and Amorphous Materials

7.1 Introduction

Observations of electrical phenomena

- BC 600 : **Thales** discovered "a piece of amber, having been rubbed with a piece of cloth, attracted feathers and other light particles"

Electricity was from the Greek word *elektron* meaning amber

- In early 1700s : **Stephen Gray** found "some substances conduct electricity whereas others do not"

- In 1733 : **DuFray** postulated "the existence of two types of electricity – *glass electricity* and *amber electricity* dependent on which material was rubbed"

- From then on, scientists contributed to our knowledge of electrical phenomena: **Coulomb, Galvani, Volta, Oersted, Ampère, Ohm, Seebeck, Faraday, Henry, Maxwell, Thomson,**

- At the turn of 20th century: **Drude** achieved "a satisfactory understanding of electrical phenomena on an atomistic basis"

7.2 Survey

Conductivity, σ : ability to conduct electrical current

span over 25 orders of magnitude (see Fig. 7.1)

over 40 orders of magnitude if a superconductor is included

Classification of materials by their electrical properties :

conductors, semiconductors, nonconductors (insulators, dielectrics)

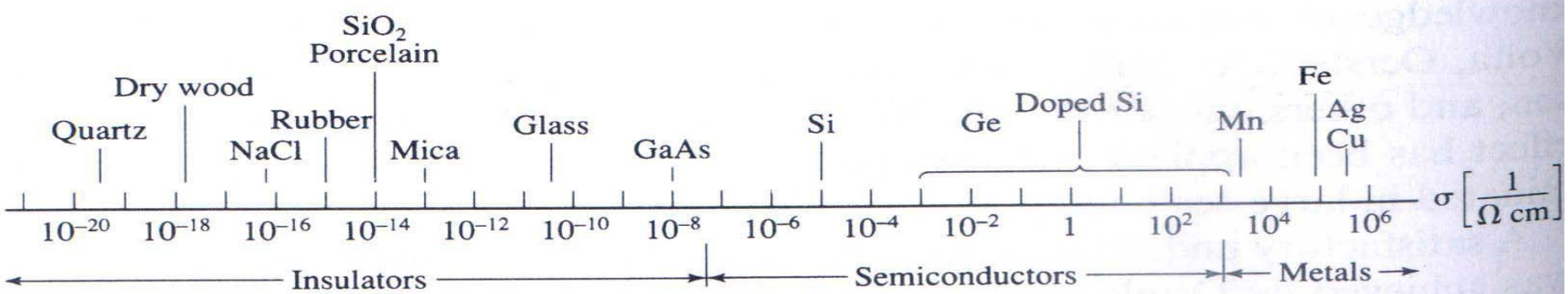


Figure 7.1. Room-temperature conductivity of various materials. (Superconductors, having conductivities many orders of magnitude larger than copper, near 0 K, are not shown. The conductivity of semiconductors varies substantially with temperature and purity.) It is customary in engineering to use the centimeter as unit of length rather than the meter. We follow this practice.

7.2 Survey

Ohm's law $V = RI$ **or** $j = \sigma E$

potential difference , *V* (in volt), electrical current, *I* (in amp), and electrical resistance, *R* (in ohms, *i.e.* Ω)

$j = \dfrac{I}{A}$ **: current density (A/cm²), σ : conductivity (1/Ωcm)**

$E = \dfrac{V}{L}$ **: electrical field strength (V/cm)**

$j = N\upsilon e$ ***N*: number of electrons per unit volume, *v*: velocity, *e*: charge**

$R = \dfrac{L\rho}{A}$ ***L* : length of conductor, *A* : cross-sectional area**

$\rho = \dfrac{1}{\sigma}$ **: specific resistance, or resistivity (Ωcm)**

7.3 Conductivity – Classical Electron Theory

Drude's postulation : a free "electron gas" or "plasma", consisting of valence electrons of the individual atoms in a crystal

$$N_a = \frac{N_0 \delta}{M}$$

number of atoms per cubic centimeter for a monovalent metal such as N_a, where, N_0 is Avogadro constant, δ the density, M the atomic mass of the element, assuming one electron from each atom

($N_a =$ 10^{22} to 10^{23} free electrons per cm^3)

$$m\frac{d\upsilon}{dt} = eE$$

Equation of electron motion, where ***e*** is charge, ***m*** mass

An electron, accelerated by an electric field, increase its **drift velocity** until it encounters a collision. Electron motion counteracted by **a friction force** $\gamma\upsilon$ which opposes electric force eE.

Suppose the resistance in metals is due to interactions of the drifting electrons with lattice atoms (i.e., essentially with imperfections in the crystal lattice)

$$m\frac{d\upsilon}{dt} + \gamma\upsilon = eE$$

where γ is constant

7.3 Conductivity – Classical Electron Theory

At $\upsilon = \upsilon_F$ (a final drift velocity), $d\upsilon/dt = 0$ (steady state)

$$\gamma \upsilon_F = eE \quad \longrightarrow \quad \gamma = \frac{eE}{\upsilon_F}$$

To obtain complete equation for the drifting elections under electric filed force and friction (or damping) force

$$m\frac{d\upsilon}{dt} + \frac{eE}{\upsilon_F}\upsilon = eE$$

The solution,

$$\upsilon = \upsilon_F\left[1 - \exp\left(-\left(\frac{eE}{m\upsilon_F}t\right)\right)\right]$$

A relaxation time is defined b

$$\tau = \frac{m\upsilon_F}{eE}$$

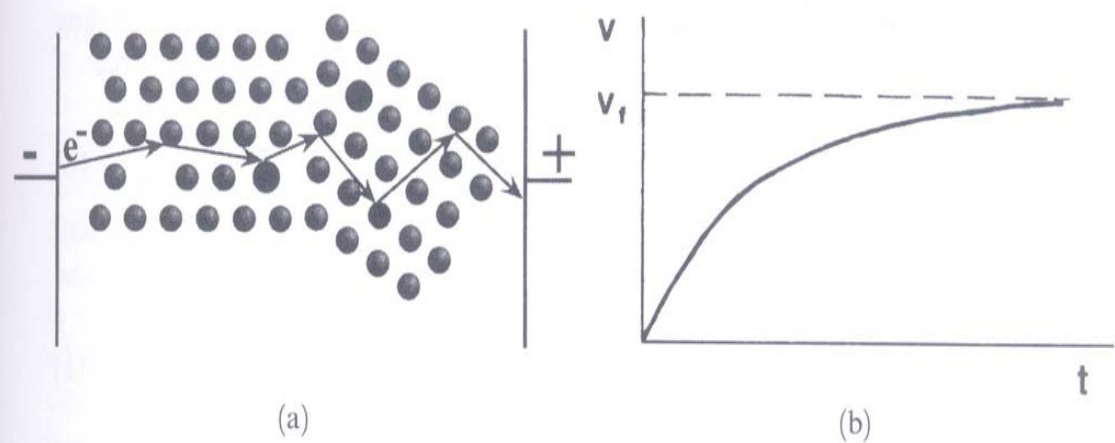


Figure 7.2. (a) Schematic representation of an electron path through a conductor (containing vacancies, impurity atoms, and a grain boundary) under the influence of an electric field. This classical model does not completely describe the resistance in materials. (b) Velocity distribution of electrons due to an electrostatic force and a counteracting friction force. The electron eventually reaches the final velocity v_f.

7.3 Conductivity – Classical Electron Theory

Current density *j* is proportional to the velocity of the drifting electrons and number of free electrons, N_f

$$j = N_{\mathrm{f}} \upsilon_{\mathrm{f}} e = \sigma E$$

Combining the above equation with $\tau = \dfrac{m\upsilon_F}{eE}$

$$\boxed{\sigma = \frac{N_{\mathrm{f}} e^2 \tau}{m}}$$

mean free path is defined by $l = \upsilon\tau$

7.4 Quantum Mechanical Consideration

- Visualize the velocity of electrons in a velocity space (Fig 7.3) with and without electric field

- The maximum velocity that electrons are able to assume is the Fermi velocity v_F

- Only specific electrons participate in conduction : these electrons drift with a high velocity which is approximately the Fermi velocity v_F

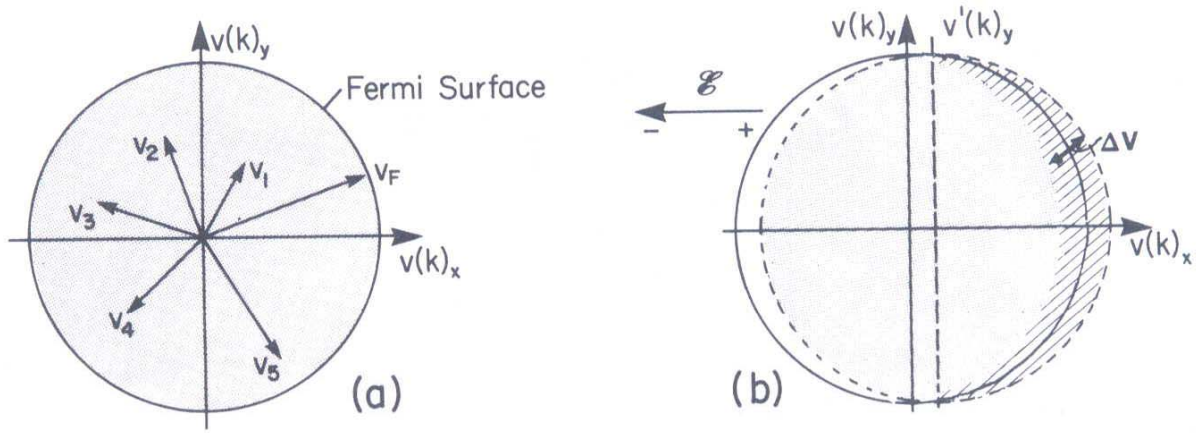


Figure 7.3. Velocity of electrons in two-dimensional velocity space. (a) Equilibrium and (b) when an electric field is applied. The shaded areas to the left and right of the $v(k)_y$-axis are of equal size. They cancel each other. The cross-hatched area remains uncompensated.

7.4 Quantum Mechanical Consideration

A large number of electrons possess E_F energy since the density of states and thus the population density is highest around E_F (Fig 7.4)

ΔE : a little extra energy needed to raise a substantial number of electrons from the Fermi level into slightly higher states

Consequently, energy (or velocity) of electrons accelerated by the electric field E is only slightly larger than E_F (or V_F) so that mean velocity ~ V_F

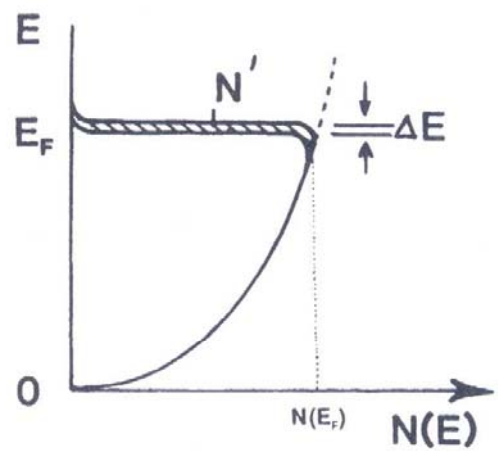


Figure 7.4. Population density $N(E)$ versus energy for free electrons (see Fig. 6.5) and displacement ΔE by an electric field (see Fig. 7.3(b)). N' is the number of displaced electrons per unit volume (see (6.11a)) in the energy interval ΔE. $N(E)$ is defined per unit energy and, in the present case, also per unit volume, see (6.8).

7.4 Quantum Mechanical Consideration

Calculation of the conductivity by quantum mechanics

The velocity of electron responsible for electron conduction: V_F

The number of electrons displaced by electric field E: N'

$$j = \upsilon_F e N' \qquad N' = N(E_F)\Delta E$$

Then $$j = \upsilon_F e N(E_F)\Delta E = \upsilon_F e N(E_F)\frac{dE}{dk}\Delta k$$

Since $$E = \frac{\hbar^2}{2m}k^2 \longrightarrow \frac{dE}{dk} = \frac{\hbar^2}{m}k = \frac{\hbar^2 p}{m\hbar} = \frac{\hbar m \upsilon_F}{m} = \hbar \upsilon_F$$

$$j = \upsilon_F{}^2 e N(E_F)\hbar\Delta k$$

7.4 Quantum Mechanical Consideration

(continued) $p = \hbar k$ and $F = m\frac{d\upsilon}{dt} = \frac{d(m\upsilon)}{dt} = \frac{dp}{dt} = \hbar\frac{dk}{dt} = eE$

$$dk = \frac{eE}{\hbar}dt \quad \text{or} \quad \Delta k = \frac{eE}{\hbar}\Delta t = \frac{eE}{\hbar}\tau$$

$$j = \upsilon_F{}^2 eN(E_F)\hbar\Delta k \longrightarrow j = \upsilon_F{}^2 e^2 N(E_F)E\tau$$

(***E_F*** **: Fermi energy ,** ***E*****: electric field)**

If electric field vector points negative *v(k)*$_x$ direction, only the projections of *V*$_F$ on the positive *v(k)*$_x$ –axis contribute to the current (see Fig. 7.5)

7.4 Quantum Mechanical Consideration

Thus, sum up all contribution of the velocities in the 1st and 4th quadrants in Fig 7.5

$$j = e^2 N(E_F) E\tau \int_{-\pi/2}^{+\pi/2} (\upsilon_F \cos\theta)^2 \frac{d\theta}{\pi} = e^2 N(E_F) E\tau \frac{\upsilon_F^2}{\pi} \int_{-\pi/2}^{+\pi/2} \cos^2\theta d\theta$$

$$= e^2 N(E_F) E\tau \frac{\upsilon_F^2}{\pi} \left[\frac{1}{4}\sin 2\theta + \frac{\theta}{2} \right]_{-\pi/2}^{+\pi/2}$$

$$j = \frac{1}{2} e^2 N(E_F) E\tau \upsilon_F^2$$

(E_F:Fermi energy , E: electric field)

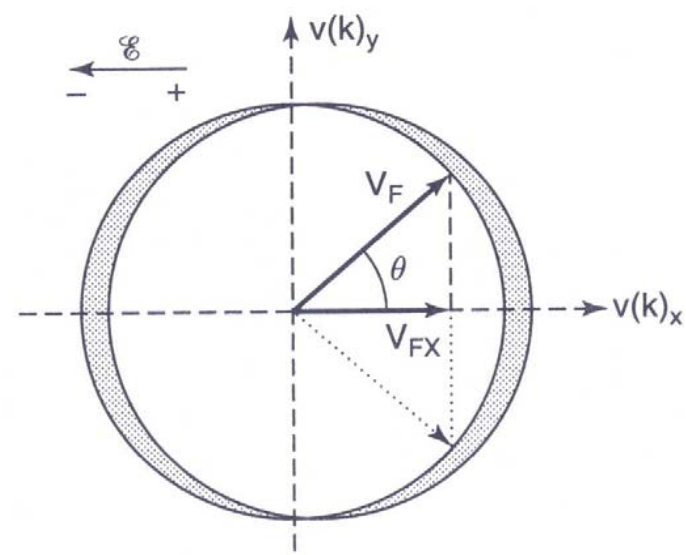


Figure 7.5. Two-dimensional velocity space.

7.4 Quantum Mechanical Consideration

(continued) Similar calculation for a spherical Fermi surface

$$j = \frac{1}{3} e^2 N(E_F) E \tau \upsilon_F^2$$

Thus, the conductivity, with $\sigma = j / E$

$$\sigma = \frac{1}{3} e^2 \upsilon_F^2 \tau N(E_F)$$

Conductivity depends on

Fermi velocity, the relaxation time,

And population density

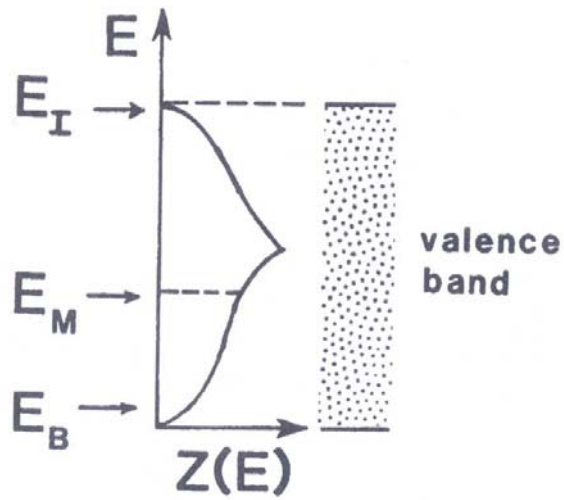


Figure 7.6. Schematic representation of the density of states (Fig. 6.6) and thus, with minor modifications, also the population density (6.7). Examples for highest electron energies for a monovalent metal (E_M), for a bivalent metal (E_B), and for an insulator (E_I) are indicated.

7.5 Experimental Results and Their Interpretation

7.5.1 Pure metals

- Resistivity of a metal decreases linearly with decreasing temperature until it reaches a finite value (Fig 7.7)

- The empirical equation $\rho_2 = \rho_1[1+\alpha(T_2 - T_1)]$

α is the linear temperature coefficient of resistivity

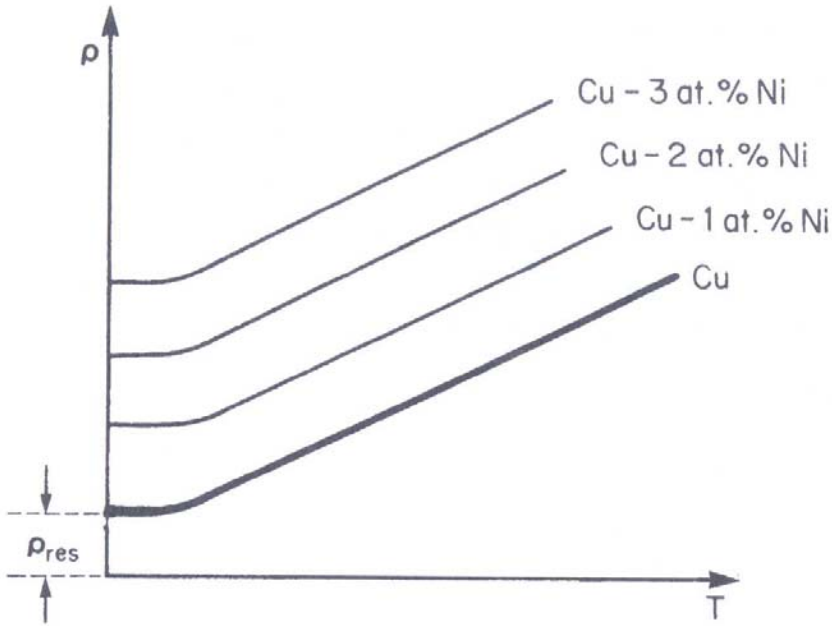


Figure 7.7. Schematic representation of the temperature dependence of the resistivity of copper and various copper–nickel alloys. ρ_{res} is the residual resistivity.

7.5 Experimental Results and Their Interpretation

7.5.1 Pure metals

- Matthiessen's rule: the resistivity arises from independent scattering processes which are additive

$$\rho = \rho_{\text{th}} + \rho_{\text{imp}} + \rho_{\text{def}} = \rho_{\text{th}} + \rho_{\text{res}}$$

Thermally induced part of the resistivity ρ_{th} : ideal resistivity

Resistivity by impurities ρ_{imp} and defects ρ_{def} : residual resistivity

- Compare thermally induced change in conductivity in the light of the quantum mechanical and classical model

$$\sigma = \frac{N_{\text{f}} e^2 \tau}{m} \qquad \sigma = \frac{1}{3} e^2 \upsilon_F^2 \tau N(E_F)$$

Consider the temperature dependence of each parameters of these equations

7.5.2 Alloys

The resistivity of alloys increases with increasing amount of solute content. However, the slope of ρ vs. *T* lines remain constant.

Several mechanisms for the resistivity increase following Matthiessen's rule

- atoms of different size cause electron scattering
- atoms having different valences introduce a local charge difference →increase scattering probability
- different electron concentration alter position of Fermi energy →changes the population density *N*(*E*) (eqn. (6.8)) and conductivity (eqn. (7.26))

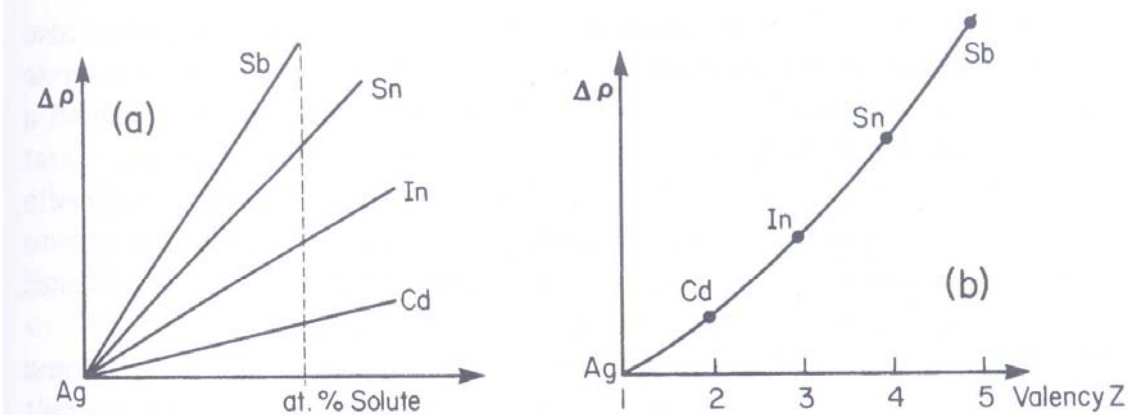


Figure 7.8. Resistivity change of various dilute silver alloys (schematic). Solvent and solute are all from the fifth period. (a) Resistivity change versus atomic % solute and (b) resistivity change due to 1 atomic % of solute.

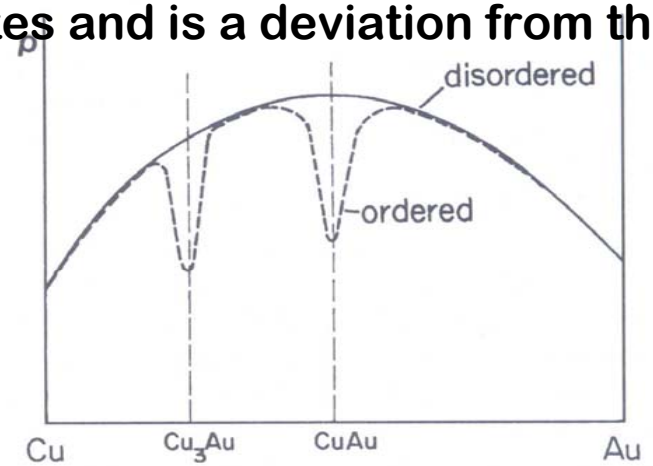
7.5.2 Alloys

Linde's rules : the resistivity of dilute single-phase alloys increase with the square of the valence differences solute and solvent constitutions (Fig. 7.8)

Nordheim's rule : true for alloys containing a transition metal (Fig. 7.9)

$$\rho = X_A \rho_A + X_B \rho_B + C X_A X_B$$ C: materials constant

Kondo effect : some alloys show a minimum in the resistivity at low temperature. It is due to additional scattering of electrons by magnetic moments of the solutes and is a deviation from the Matthiessen rule



Max. at ρ ~ 50% solute content

Figure 7.9. Schematic representation of the resistivity of ordered and disordered copper–gold alloys.

7.5.3 ordering

Long range ordering

- the solute atoms are periodically arranged in the matrix
- for example, in a 50/50 alloy the A and B atoms alternately occupy successive lattice sites, then electron waves are coherently scattered, which causes a decrease in resistivity (Fig. 7.9)
- Cu_3Au, CuAu Au_3Mn

Short range ordering

- small domains in which the atoms are arranged in an ordered fashion
- α copper-aluminum : much smaller resistance decrease

7.6 Superconductivity

Superconductors are materials whose resistivites become immeasurably small or actually zero below a critical temperature, T_C

Table 7.1. Critical Temperatures of Some Superconducting Materials.

Materials	T_c [K]	Remarks
Tungsten	0.01	—
Mercury	4.15	H.K. Onnes (1911)
Sulfur-based organic superconductor	8	S.S.P. Parkin et al. (1983)
Nb_3Sn and Nb–Ti	9	Bell Labs (1961), Type II
V_3Si	17.1	J.K. Hulm (1953)
Nb_3Ge	23.2	(1973)
La–Ba–Cu–O	40	Bednorz and Müller (1986)
$YBa_2Cu_3O_{7-x}$[a]	92	Wu, Chu, and others (1987)
$RBa_2Cu_3O_{7-x}$[a]	~92	R = Gd, Dy, Ho, Er, Tm, Yb, Lu
$Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$	113	Maeda et al. (1988)
$Tl_2CaBa_2Cu_2O_{10+\delta}$	125	Hermann et al. (1988)
$HgBa_2Ca_2Cu_3O_{8+\delta}$	134	R. Ott et al. (1995)

[a]The designation "1-2-3 compound" refers to the molar ratios of rare earth to alkaline earth to copper. (See chemical formula.)

7.6 Superconductivity

As T decrease below $T_c \rightarrow$ transition into the superconducting state

for pure and structurally perfect elements : sharp transition

Transition temperature, T_c often varies with the atomic mass, m_a

$$m_a^{\alpha} \cdot T_c = const.$$

where α is materials constant

: Isotope effect

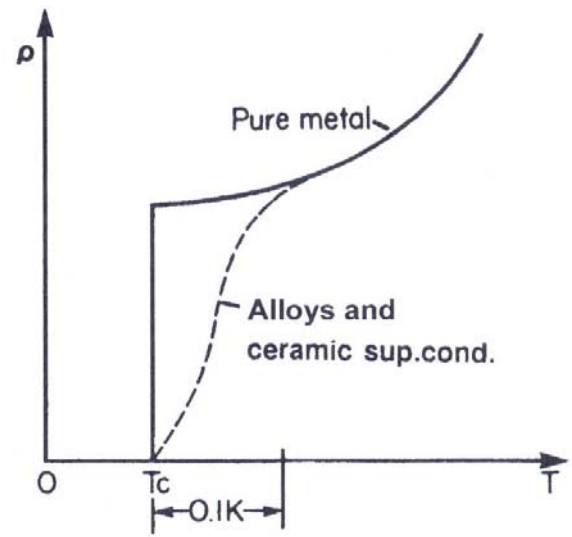


Figure 7.10. Schematic representation of the resistivity of pure and impure superconducting elements. T_c is the transition or critical temperature.

7.6 Superconductivity

The critical magnetic field strength H_c :a magnetic field above which superconductivity is destroyed

$$H_c = H_0\left(1-\frac{T^2}{T_c^2}\right)$$

Similar way, another limiting parameter exist:
The critical current I_c, above which superconductivity is destroyed

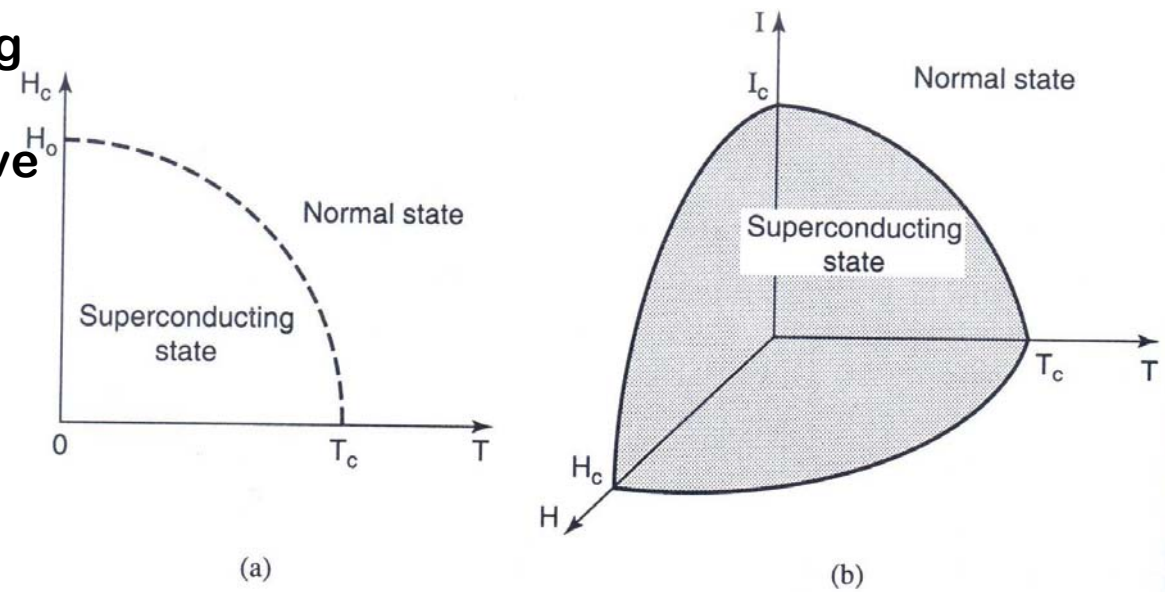


Figure 7.11. (a) Dependence of critical field strength, H_c, at which superconductivity is destroyed, in relation to the temperature of the specimen. (b) The limits of superconductivity are defined in a critical T-H-I-diagram.

7.6 Superconductivity

Two classes of superconducting materials

- **Type I** : transition between superconducting and normal state (destruction of superconducting state by magnetic field) occurs sharply; H_C is relatively low.

- **Type II** : the elimination superconducting state by magnetic field is gradual ; H_{C1} and H_{C2} exist

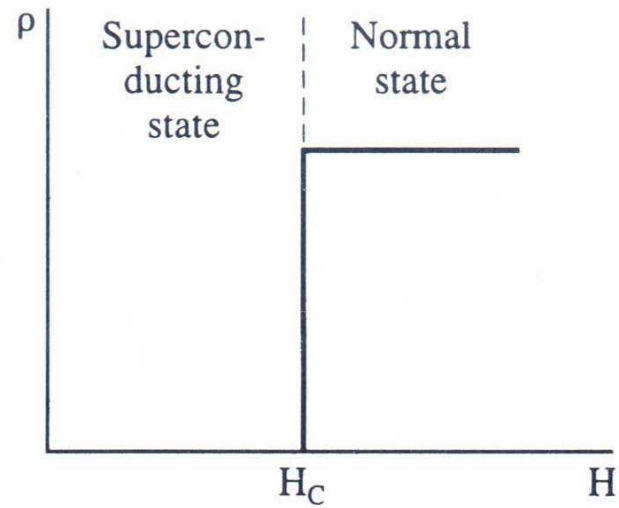


Figure 7.12. Schematic representation of the resistivity of a *type I* (or soft) superconductor when a magnetic field of field strength H is applied. These solids behave like normal conductors above H_c.

7.6 Superconductivity

Type II superconductor : the interval between H_{C1} and H_{C2}, superconducting and normal conducting areas are mixed in the solid, called vortex state

Vortices, or fluxoids : small circular regions in the normal state, which carry the smallest possible unit of a magnetic flux, called a **flux quantum**

$$\phi_0 = \frac{h}{2e} = 2.07\times10^{-15}(T\cdot m^2)$$

- current flows perpendicular to these fluxoids → "**Lorentz force** on the fluxoids"

- moving fluxoids become obstacles for drifting electrons

"**Fluxoid pinning**" by microstructural inhomogeneities in the matrix

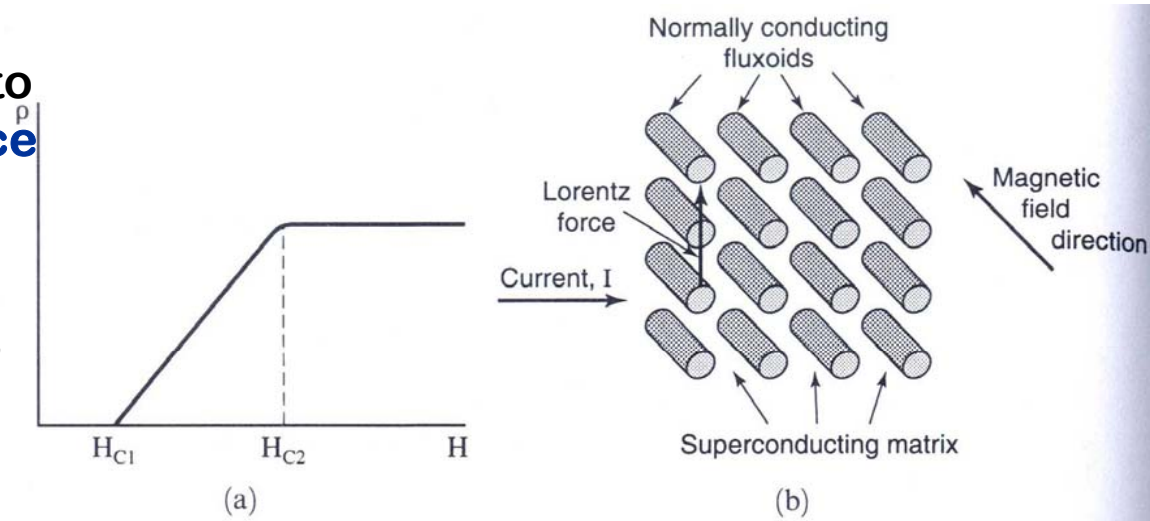


Figure 7.13. (a) Schematic representation of the resistivity of a *type II* (or hard) superconductor. The region between H_{c1} and H_{c2} is called the *vortex state*. Above H_{c2}, the solid behaves like a normal conductor. (b) Schematic representation of fluxoids in a superconducting matrix.

7.6 Superconductivity

High-temperature Superconductor

(or High-Tc Superconductor)

Ceramic superconductor : $RBa_2Cu_3O_{7-x}$

Characterized by two-dimensional sheets of atoms : Cu-O

Tetragonal : oxygen deficient, non-superconducting

Orthorhombic : superconducting

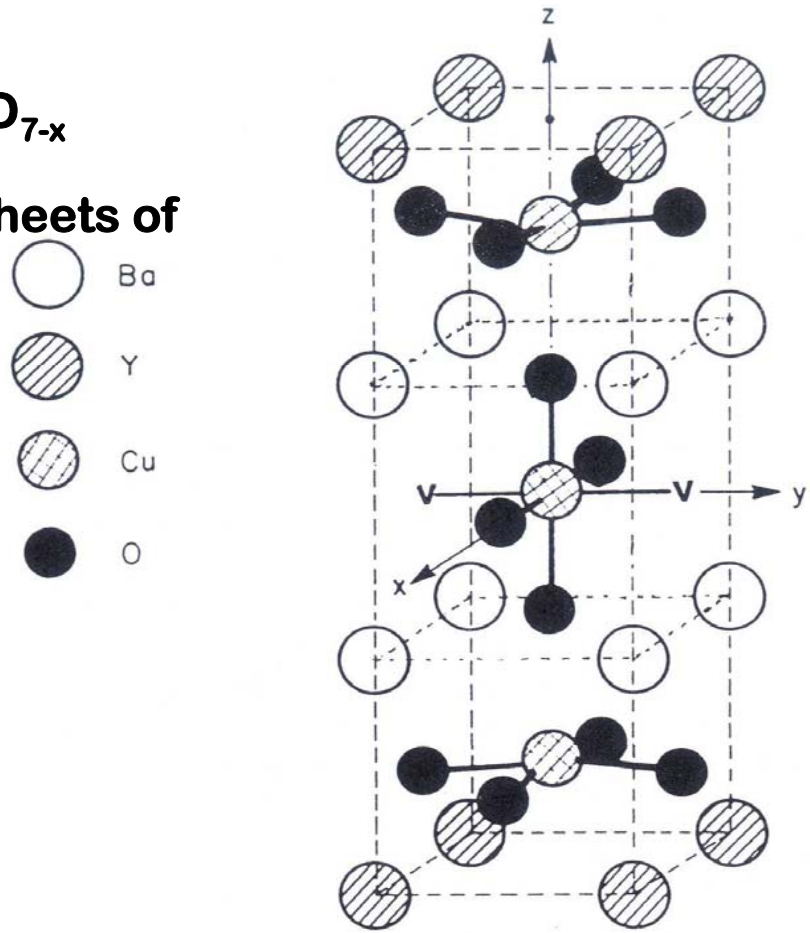


Figure 7.14. Room-temperature unit cell of $YBa_2Cu_3O_{7-x}$. The structure is an orthorhombic layered perovskite ($BaTiO_3$) containing periodic oxygen vacancies. Two examples for oxygen vacancies are indicated by a "V." Adapted from M. Stavola, *Phys. Rev. B*, **36**, 850 (1987).

7.7 Thermoelectric Phenomena

Fig. 7.19, Potential difference, ΔV, between two thermocouple is observed, which is essentially proportional to the temperature difference, Δ*T*: thermoelectric power, or Seebeck coefficient

$$\frac{\Delta V}{\Delta T} = S$$

Cu - 45%Ni : 43 μV/K

For higher temperature

- **90% Ni-10% Cr**
- **95%Ni-2% Mn-2%Al**
- **Pt-13%Rh**

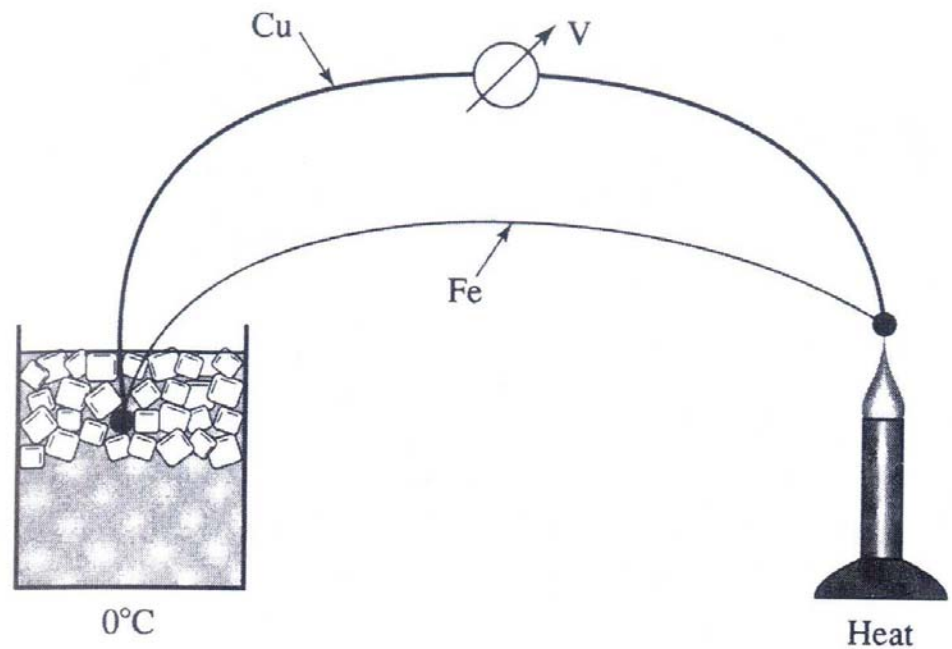


Figure 7.19. Schematic representation of two thermocouples made of copper and iron which are brought in contact with each other (Seebeck effect).

7.7 Thermoelectric Phenomena

Peltier effect : **A reverse of the Seebeck effect, A direct electric current that flows through junctions made of different materials causes one junction to be cooled and the other to heat up (depending on the direction of the current)**

"Thermoelectric refrigerators"

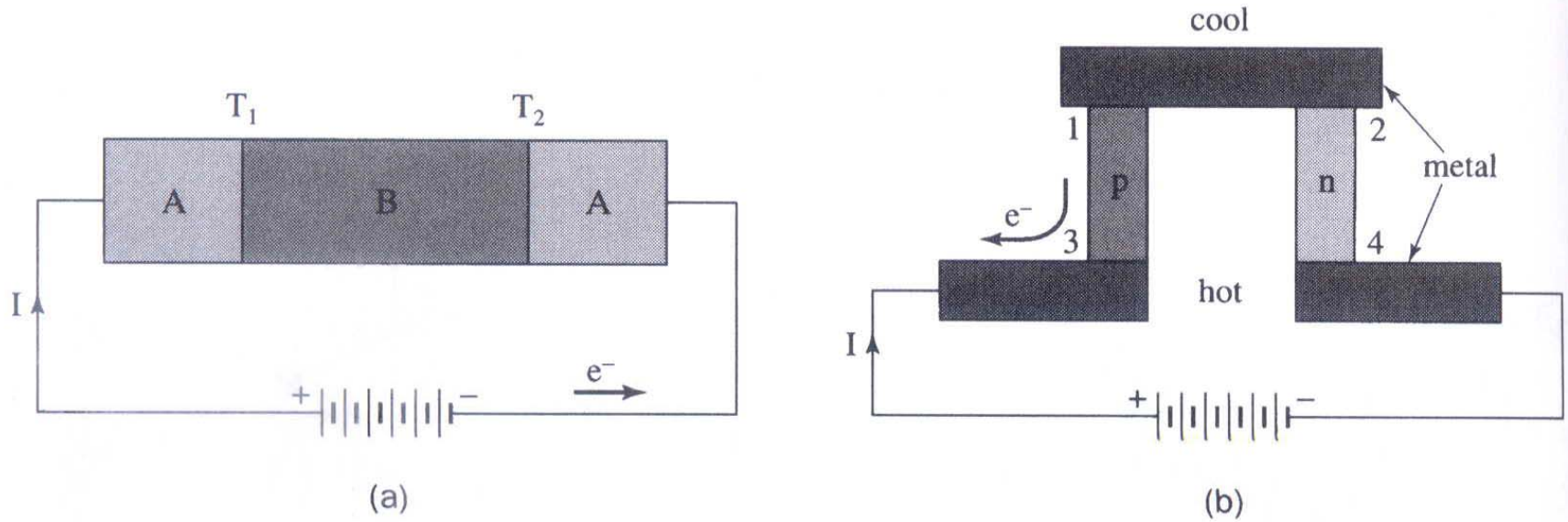


Figure 7.20. Thermoelectric refrigeration devices which make use of the Peltier effect. (a) Principle arrangement. (b) Efficient device utilizing p- and n-type semiconductors (see Section 8.3) in conjunction with metals.

Part II Electrical Properties of Materials

Chap. 7 Electrical Conduction in Metals and Alloys

Chap. 8 Semiconductors

Chap. 9 Electrical Properties of Polymers, Ceramics, Dielectrics, and Amorphous Materials

8.1 band Structure

Material characterization by band structure

- **Metal:** partially filled valence bands with electrons

- **Insulator:** completely filled valence bands and a large energy gap up to unfilled conduction band

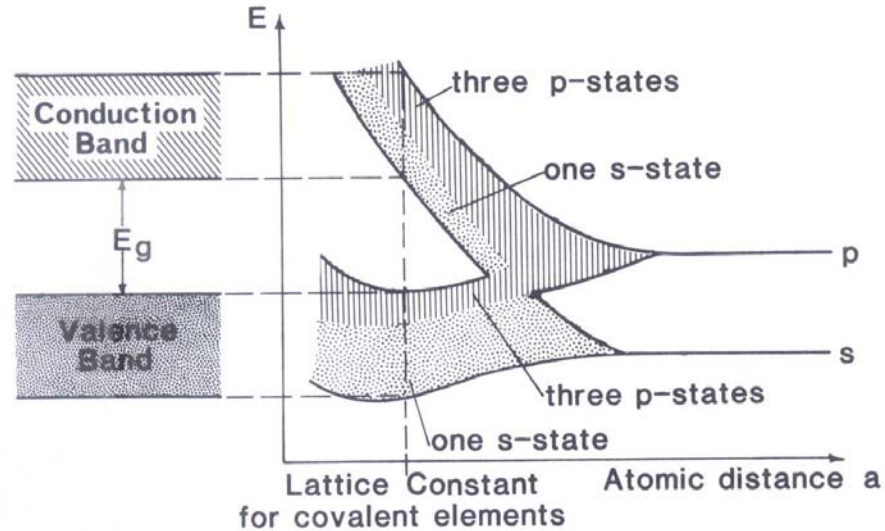


Figure 8.1. Sharp energy levels, widening into bands, and band overlapping with decreasing atomic distance for covalent elements. (Compare with Fig. 4.14.)

- **Semiconductor:** in low temperature, completely filled valence band and a narrow gap between this and the next higher, unfilled conduction band

Because of band overlapping, the valence band as well as the conduction band consist of *hybrid (mixed) s*- and *p*-state → the eight highest *s* + *p* states(2 *s*- and 6 *p*- states split into two separate (*s* + *p*) bands) (Fig. 8.1)

8.1 band Structure

Fig. 8.2: calculated band structure of Si

The valence band can accommodate $4N_a$ electrons: one lowest *s*-state and three *p*-states (4 *sp*- hybrids) and empty conduction band of 4 *sp*-hybrids

Gap energy, E_g for group IV elements (Table 8.1)

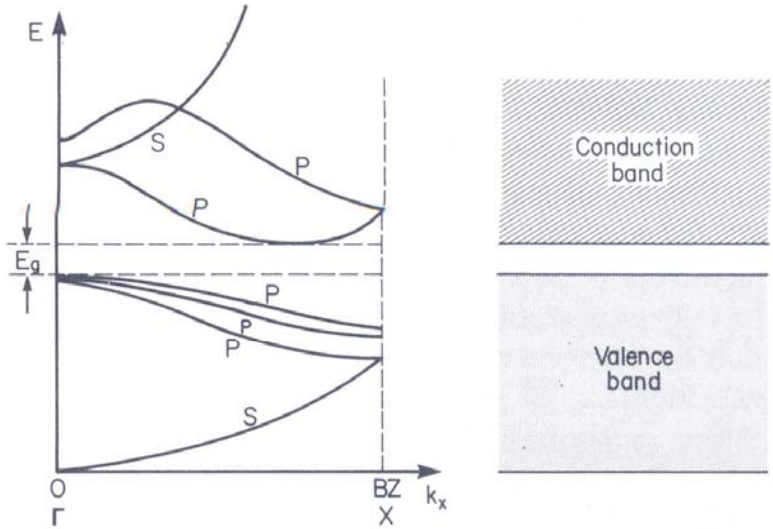


Figure 8.2. Schematic band structure of silicon in the k_x (or X) direction (plotted in the reduced zone scheme). The separation of the two highest p-states in the valence band is strongly exaggerated. Compare with the complete band structure of Fig. 5.23.

Temperature dependence of gap energy

(empirical equation)

$$E_{gT} = E_{g0} - \frac{\xi T^2}{T + \theta_D}$$

E_{g0} is the band gap energy at T = 0 K,

$$\xi \approx 5 \times 10^{-4} eV / K \quad \theta_D : \text{Debye temperature}$$

Table 8.1. Gap Energies for Some Group IV Elements at 0 K (see also Appendix 4).

Element	E_g [eV]
C (diamond)	5.48
Si	1.17
Ge	0.74
Sn (gray)	0.08

8.2 Intrinsic Semiconductors

The conduction mechanism is predominated by the properties of the pure crystal

(i) Electron excitation from the valence band into conduction band, usually by thermal energy (interband transition)

(ii) Electron holes left behind in the valence band can also contribute to the conduction

- Fermi energy in semiconductor:

Energy for which the Fermi distribution function, $F(E) = 1/2$

$$E_F = -E_g/2$$

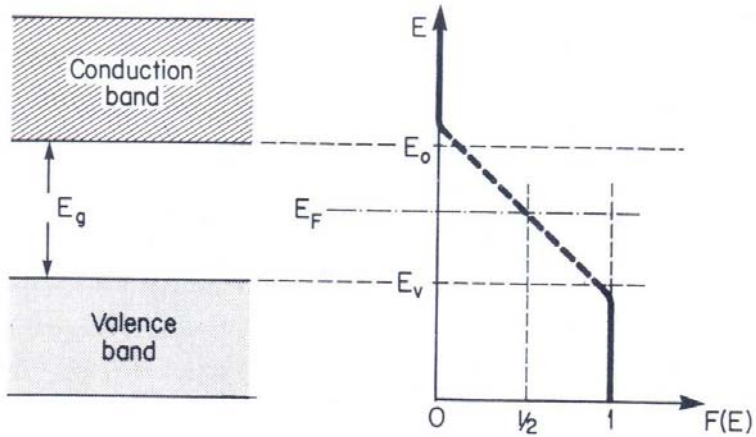


Figure 8.3. Schematic Fermi distribution function and Fermi energy for an intrinsic semiconductor for $T > 0$ K. The "smearing out" of the Fermi distribution function at E_0 and E_V is exaggerated. For reasons of convenience, the zero point of the energy scale is placed at the bottom of the conduction band.

8.2 Intrinsic Semiconductors

Number of electrons in the conduction band

N* : number of electrons that have an energy equal to or smaller than a given energy E_n

For an energy interval between *E* and *E + dE,*

$$dN^* = N(E)dE$$

Where the population density $N(E) = 2 \cdot Z(E) \cdot F(E)$

Density of state *Z(E)* (see eqn. (6.5))

$$Z(E) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \qquad F(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} \approx \exp\left[-\left(\frac{E - E_F}{k_B T}\right)\right]$$

Because $E - E_F$ is about 0.5eV and $k_B T$ at *R.T.* is of the order of 10^{-2}eV, the exponential factor is large compared to 1

8.2 Intrinsic Semiconductors

Integration over all available electrons that have energies larger than the energy at the bottom of the conduction band (*E = 0*)

$$N^* = \frac{V}{2\pi^2} \cdot \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty E^{1/2} \cdot \exp\left[-\left(\frac{E - E_F}{k_B T}\right)\right] dE$$

$$N^* = \frac{V}{2\pi^2} \cdot \left(\frac{2m}{\hbar^2}\right)^{3/2} \exp\left(\frac{E_F}{k_B T}\right) \int_0^\infty \cdot E^{1/2} \cdot \exp\left[-\left(\frac{E}{k_B T}\right)\right] dE$$

$$N^* = \frac{V}{2\pi^2} \cdot \left(\frac{2m}{\hbar^2}\right)^{3/2} \exp\left(\frac{E_F}{k_B T}\right) \frac{k_B T}{2} (\pi k_B T)^{1/2}$$

$$= \frac{V}{4} \left(\frac{2mk_B T}{\pi\hbar^2}\right)^{3/2} \exp\left(\frac{E_F}{k_B T}\right)$$

8.2 Intrinsic Semiconductors

Introducing $E_F = -E_g/2$ and effective mass ratio m^*_e/m_0

$N_e = N^*/V$: number of conduction band electrons per unit volume

$$N_e = \frac{1}{4}\left(\frac{2mk_B}{\pi\hbar^2}\right)^{3/2}\left(\frac{m_e^*}{m_0}\right)^{3/2} T^{3/2}\exp\left[-\left(\frac{E_g}{2k_BT}\right)\right]$$

where the constant factor $\frac{1}{4}\left(\frac{2mk_B}{\pi\hbar^2}\right)^{3/2}$ has the value $4.84\times10^{15}\,(cm^{-3}K^{-3/2})$

$$N_e = 4.84\times10^{15}\left(\frac{m_e^*}{m_0}\right)^{3/2} T^{3/2}\exp\left[-\left(\frac{E_g}{2k_BT}\right)\right]$$

- The number of electrons in the conduction band per cm^3 is a function of E_g and T. A numerical evaluation of N_e per cm^3 in Si at RT ~ 10^9 : only one in 10^{13} atoms contributes an electron to the conduction

- "The number of electrons in the conduction band" = "the number of holes in the valence band". Thus equation for N_e can be written for the holes by assuming $m^*_e = m^*_h$

8.2 Intrinsic Semiconductors

- Conductivity of an intrinsic semiconductor is determined by number of current carriers (electrons and holes) and also by their mobility

The mobility of the current carriers μ :

$$\mu = \frac{\upsilon}{E}$$ drift velocity per unit ***E***

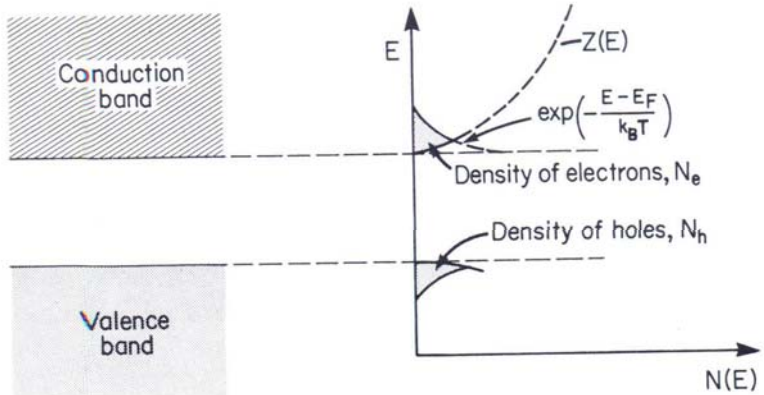


Figure 8.4. Density of electrons (N_e) and holes (N_h) for an intrinsic semiconducto

From $j = \sigma E$ & $j = N\upsilon e$

$$\sigma = N\frac{\upsilon}{E}e = N\mu e$$

$$\sigma = N_e e\mu_e + N_h e\mu_h,$$

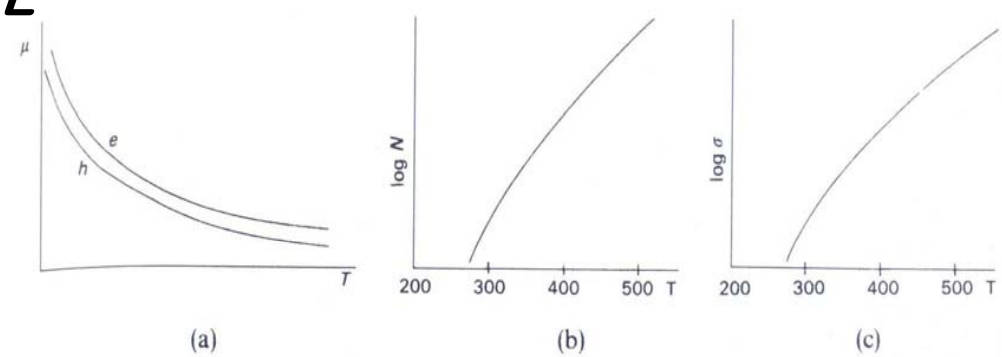


Figure 8.5. Schematic representation of the temperature dependence of (a) electron and hole mobilities, (b) number of carriers in an intrinsic semiconductor, and (c) conductivity for an intrinsic semiconductor. (T is given in Kelvin.)

$$\sigma = 4.84\times10^{15}\left(\frac{m^*}{m_0}\right)^{3/2} T^{3/2} e(\mu_e + \mu_h)\exp\left[-\left(\frac{E_g}{2k_BT}\right)\right]$$

8.3 Extrinsic Semiconductors

8.3.1 Donors and Acceptors

Extrinsic semicondutors: in most semiconductor devices, a considerably higher number of charge carriers are introduced by doping,i.e., by adding small amount of impurities (**dopants**) to the semiconductor materials

- n-type semiconductor: dopants (donor, element of group V : P,As,Sb)

  → major carrier :donor electrons (negative carrier)

- p-type semiconductor: dopants (acceptor, elements of group III : B,Al,Ga,In)

  → major carrier: holes (positive carriers)

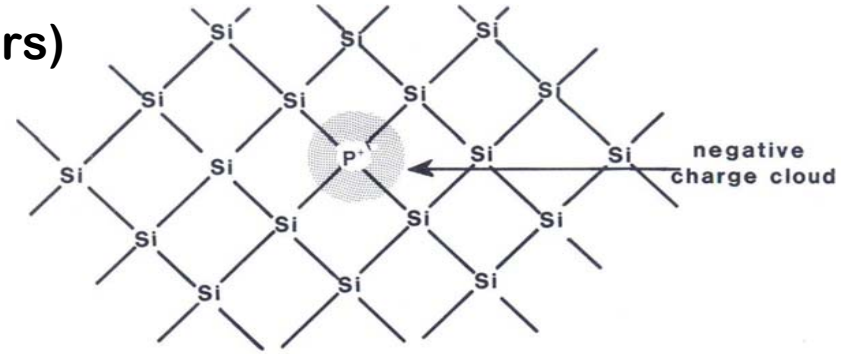


Figure 8.6. Two-dimensional representation of the silicon lattice. An impurity atom of group V of the periodic table (P) is shown to replace a silicon atom. The charge cloud around the phosphorus atom stems from the extra phosphorus electron. Each electron pair between two silicon atoms constitutes a covalent bond (electron sharing). The two electrons of such a pair are indistinguishable, but must have opposite spin to satisfy the Pauli principle.

8.3 Extrinsic Semiconductors

8.3.2 Band Structure

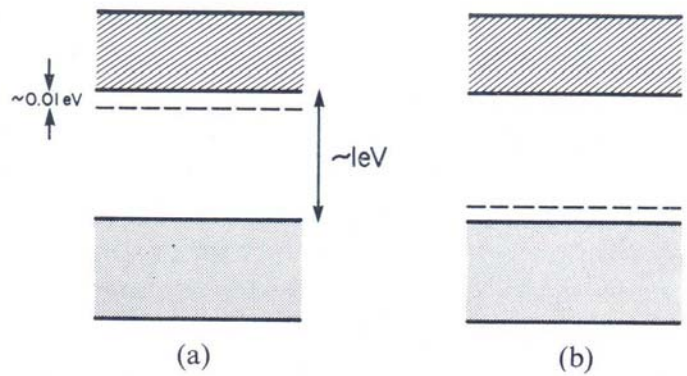


Figure 8.7. (a) Donor and (b) acceptor levels in extrinsic semiconductors.

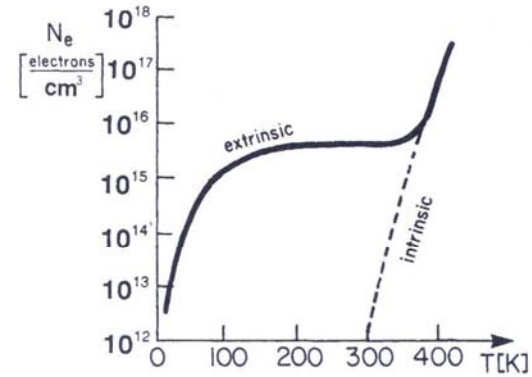


Figure 8.8. Schematic representation of the number of electrons per cubic centimeter in the conduction band versus temperature for an extrinsic semiconductor with low doping.

8.3.3 Temperature Dependence of the Number of Carriers

With increasing temperature,

- n-type: the donor electrons overcome small potential barrier (Fig 8.7) : excite from the donor levels into the conduction band. → N_e deviation from intrinsic way. Once all electron in donor levels have been excited into conduction band, further temperature increase does not create additional electron (Fig8.8)

- p-type : electrons excite from valence band into the acceptor levels, creating positive charge carriers (holes).

8.3 Extrinsic Semiconductors

8.3.4 Conductivity

$$\sigma = N_{de} e \mu_e$$

where N_{de}: number of donor electrons

μ_e : mobility of the donor electrons

N_{de}, μ_e : two competing effects on conductivity of semiconductors

- For low doping and at low temperature, the conductivity decreases with increasing temperature : lattice vibration → decrease mobility

At higher temperature: conductivity increase : intrinsic effects → increase number of carriers

- For high doping : temperature dependence on conductivity is less pronounced due to the already higher number of carrier

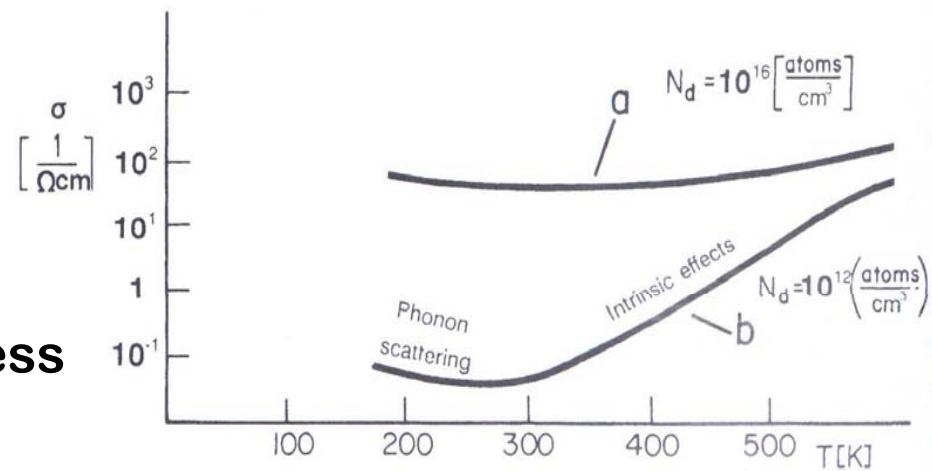


Figure 8.9. Conductivity of two extrinsic semiconductors, (a) high doping and (b) low doping. N_d = number of donor atoms per cubic centimeter.

8.3.5 Fermi Energy

***E_F* level position**

- n-type semiconductor

: between donor level and

conduction band

- p-type semiconductor

: between acceptor level

and valence band

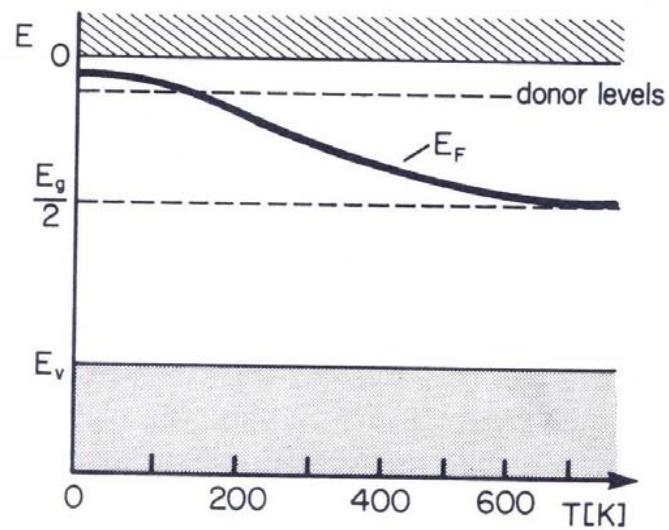


Figure 8.10. Fermi level of an *n*-type semiconductor as a function of temperature. $N_d \approx 10^{16}$ (atoms per cubic centimeter).

With increasing temperature, *E_F* of both type semiconductors approach the value for intrinsic semiconductors, i.e., - *E_g*/2

8.4 Effective Mass, *m* *

Evaluation of the effective mass of the charge carriers in semiconductors

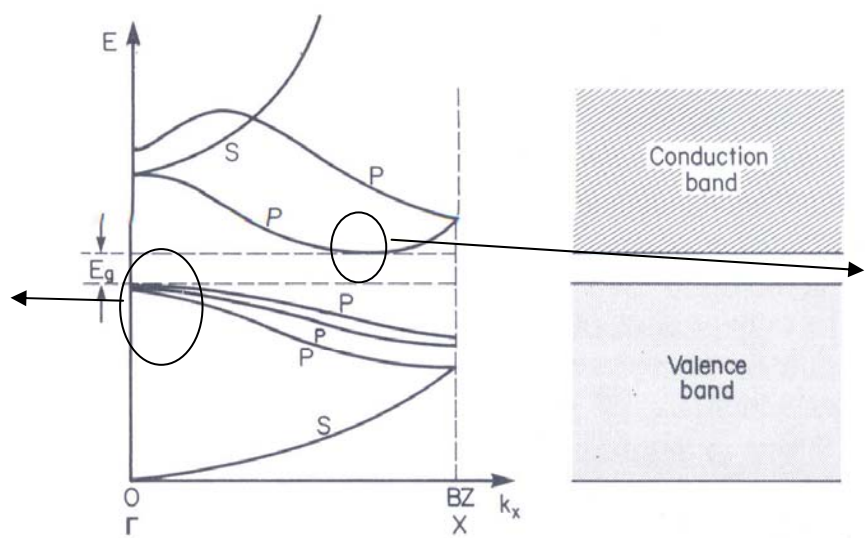
m* **is inversely proportional to the curvature of an electron band.**

Consider the upper portion of the valence bands and the lower portion of the conduction bands for Si

Curvature: convex downward -> a negative effective mass, implying this band is populated by electron holes.

2 heavy holes : smaller curvature

1 light hole : larger curvature



Curvature : convex upward -> populated by electrons

In 3-d, a spheroid shape:

Longitudinal mass m_l^*

Transverse mass m_t^*

Figure 8.2. Schematic band structure of silicon in the k_x (or X) direction (plotted in the reduced zone scheme). The separation of the two highest p-states in the valence band is strongly exaggerated. Compare with the complete band structure of Fig. 5.23.

8.5 Hall Effect

"Number and type of charge carriers can be measured by making use of Hall effect"

Consider n-type semiconductor

Suppose electric current density j flow in the positive *x* direction and magnetic field is applied *z* direction

Lorentz force, F_L on electrons:

$$F_L = \upsilon_x B_z e$$

The electron accumulate on one side of the slap → cause Hall field F_H, thus Hall force

$$F_H = eE_y$$

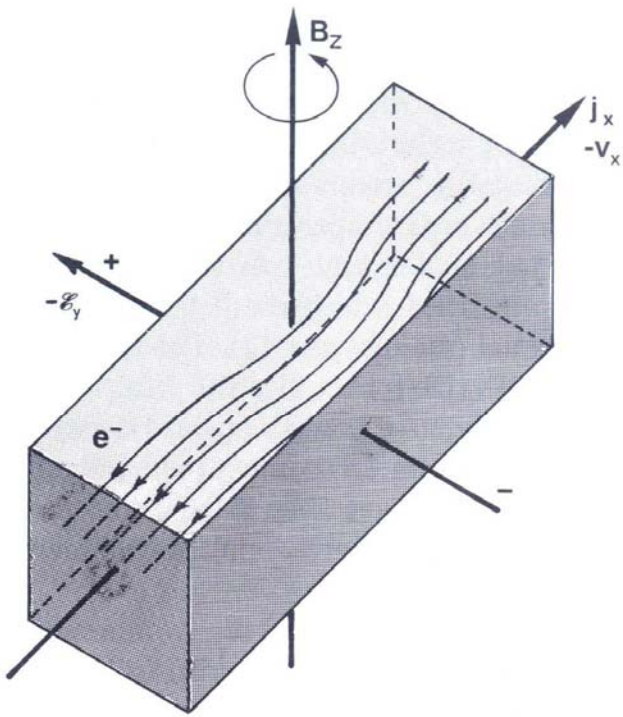


Figure 8.11. Schematic representation of the Hall effect in an *n*-type semiconductor (or a metal in which electrons are the predominant current carriers).

8.5 Hall Effect

(continued) In equilibrium $F_L + F_H = 0$ $\upsilon_x B_z e = eE_y$

$$E_y = \upsilon_x B_z$$

$$j_x = -N\upsilon_x e$$

Combining the two, yields for the number of conduction electrons per unit volume

$$N = -\frac{j_x B_z}{eE_y}$$

variables on the right side of this equation can be measured and thus N can be obtained.

- **Hall constant** is defined as $R_H = -\frac{1}{Ne}$

which is inversely proportional to the density of charge carriers, N.

- negative (positive) R_H : major charge carrier are electrons (holes)

Additional Materials

(Chap. 19 in Materials Science & Engineering, An Introduction, 4th Ed., W.D. Callister Jr.)

Intrinsic Semiconductor

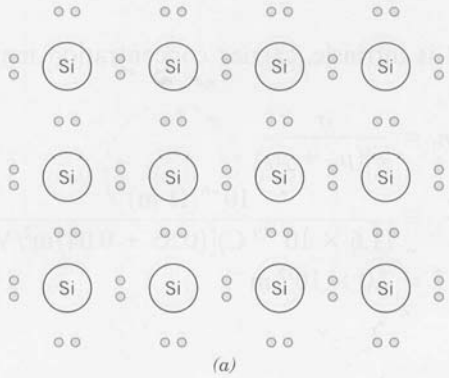


FIGURE 18.10 Electron bonding model of electrical conduction in intrinsic silicon: (*a*) before excitation, (*b*) and (*c*) after excitation (the subsequent free-electron and hole motions in response to an external electric field).

Atomic bonding model

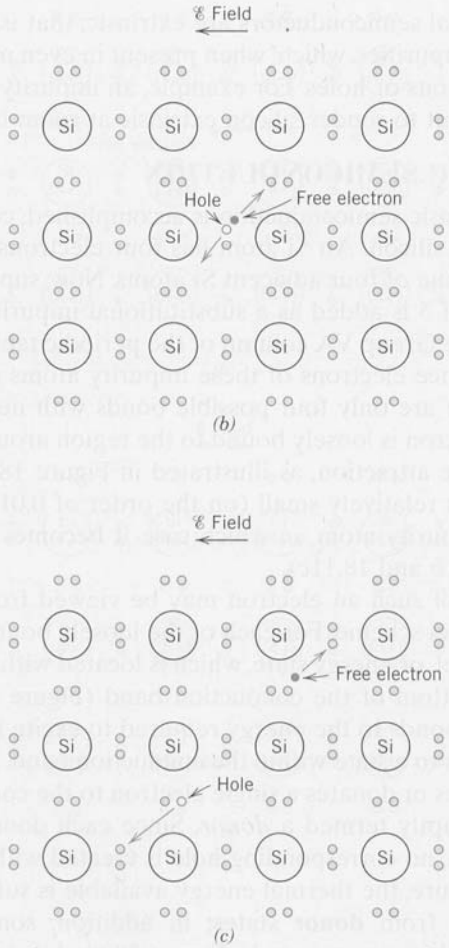
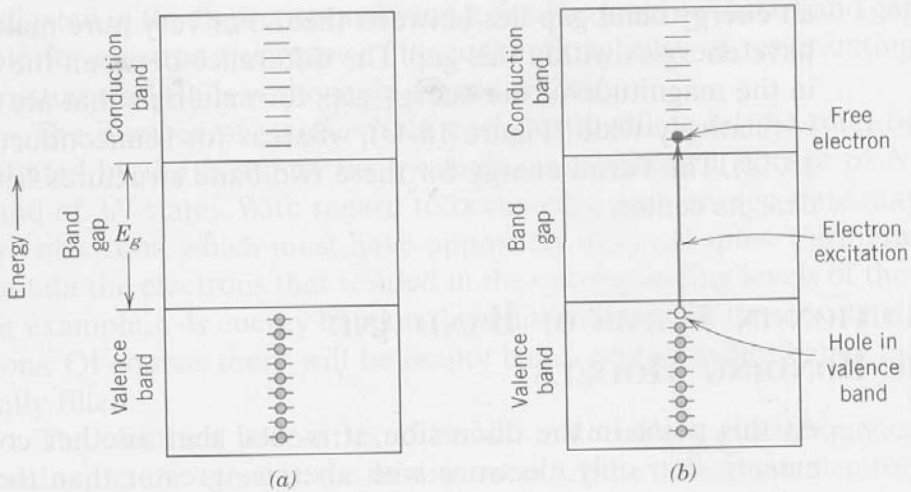


FIGURE 18.6 For an insulator or semiconductor, occupancy of electron states (*a*) before and (*b*) after an electron excitation from the valence band into the conduction band, in which both a free electron and a hole are generated.



Band model

n-type semiconduction

- Addition of 5 valence electrons to Si:
  P, As, Sb
  (group VA in periodic table)

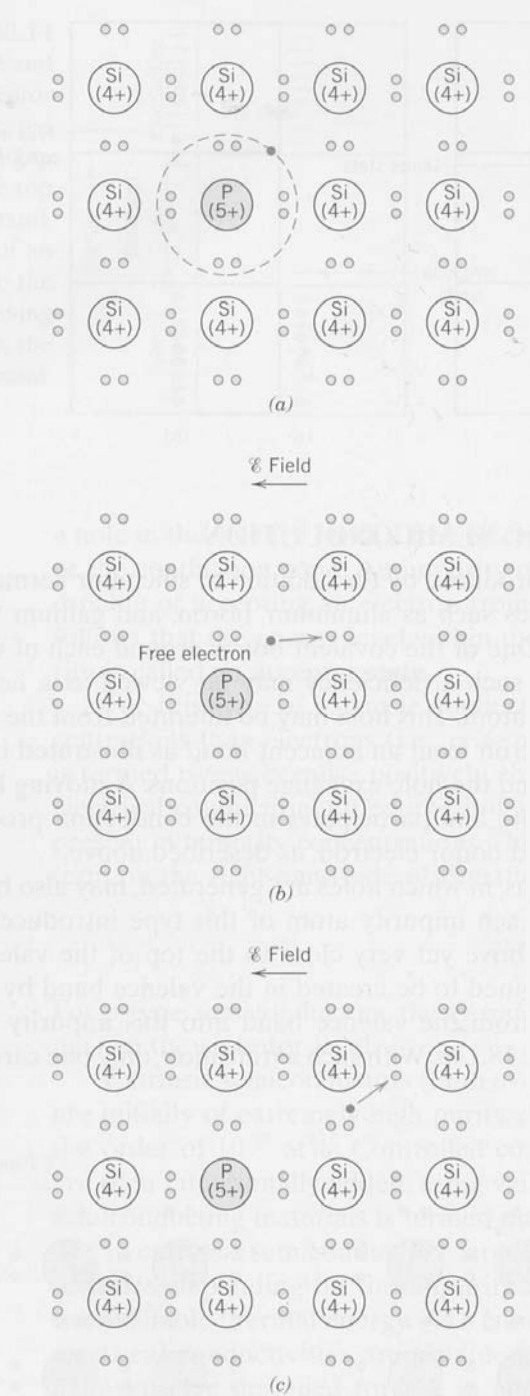


FIGURE 18.11 Extrinsic n-type semiconduction model (electron bonding). (a) An impurity atom such as phosphorus, having five valence electrons, may substitute for a silicon atom. This results in an extra bonding electron, which is bound to the impurity atom and orbits it. (b) Excitation to form a free electron. (c) The motion of this free electron in response to an electric field.

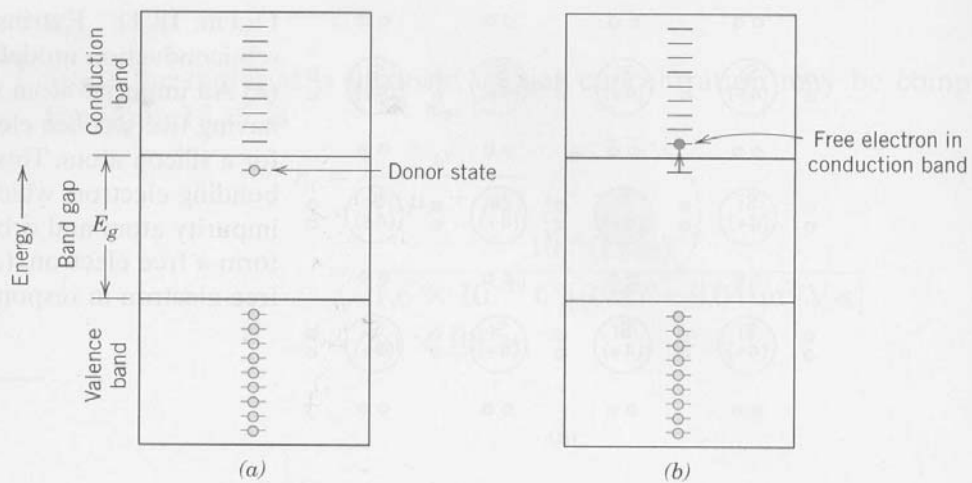


FIGURE 18.12 (a) Electron energy band scheme for a donor impurity level located within the band gap and just below the bottom of the conduction band. (b) Excitation from a donor state in which a free electron is generated in the conduction band.

p-type semiconduction

-Addition of 3 valence electrons to Si, Ge: B, Al (group IIIA in periodic table)

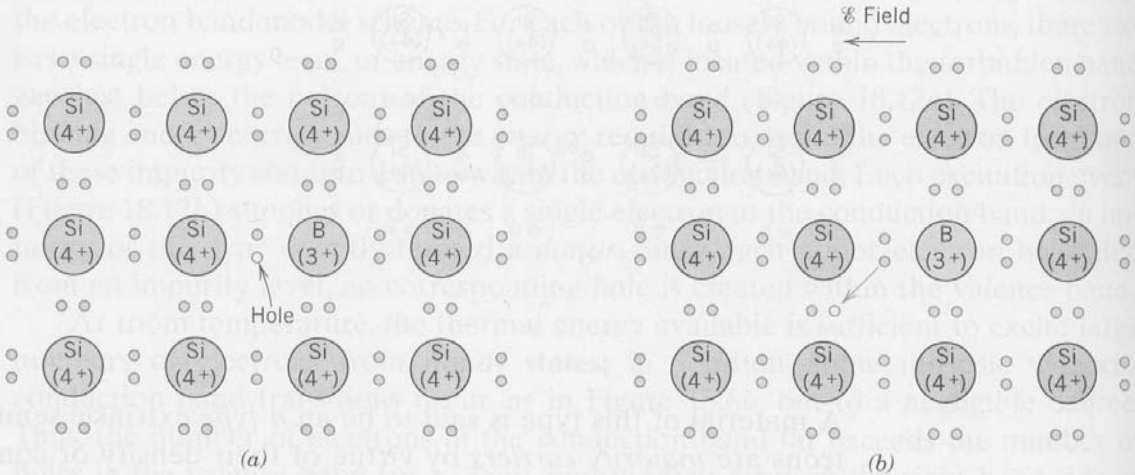


FIGURE 18.13 Extrinsic *p*-type semiconduction model (electron bonding). (*a*) An impurity atom such as boron, having three valence electrons, may substitute for a silicon atom. This results in a deficiency of one valence electron, or a hole associated with the impurity atom. (*b*) The motion of this hole in response to an electric field.

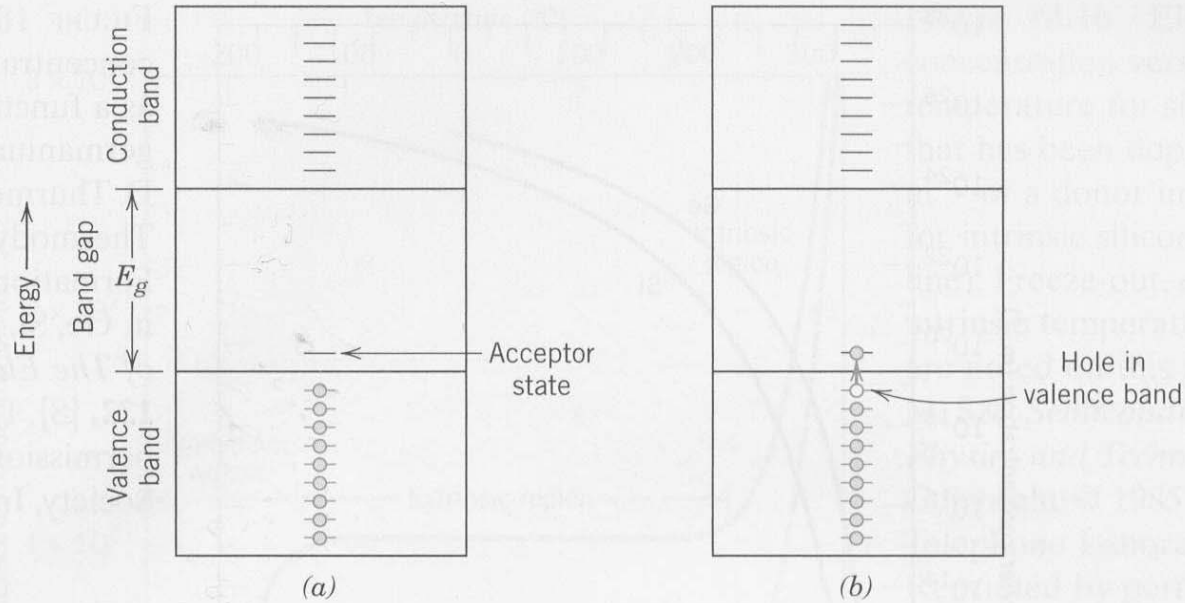


FIGURE 18.14 (*a*) Energy band scheme for an acceptor impurity level located within the band gap and just above the top of the valence band. (*b*) Excitation of an electron into the acceptor level, leaving behind a hole in the valence band.

Part II Electrical Properties of Materials

Chap. 7 Electrical Conduction in Metals and Alloys

Chap. 8 Semiconductors

Chap. 9 Electrical Properties of Polymers, Ceramics, Dielectrics, and Amorphous Materials

8.6 Compound Semiconductors

GaAs (III-V compound)

- larger band gap compared to Si
- larger electron mobility due to smaller electron effective mass (Fig 5.24)
- direct band gap (chap 12) : optical properties

Applications

- High-frequency devices
- Laser / light-emitting diodes (LED)

8.6 Compound Semiconductors

Other compound semiconductors
(applications: optoelectronic devices)

Group III-V elements
- GaP, GaN, InP, InAs, InSb, AlSb

Group II-VI elements
- ZnO, ZnS, ZnSe, CdS, CdTe, HgS

Group IV-VI
- PbS, PbSe, and PbTe

Ternary or quaternary alloys
- $Al_xGa_{1-x}As$, $Al_xGa_{1-x}As_ySb_{1-y}$, $GaAs_{1-x}P_x$: LEDs
$GaAs_{1-x}As$ also used in modulation-doped field-effect transistors (MODFET)

Silicon carbide: Group IV-IV
- band gap 3eV, very high temperature(700°C) device
- Emit light in the blue end of the visible spectrum

8.7 Semiconductor Devices

8.7.1 Metal-Semiconductor Contacts

Types of contacts in semiconductor/metal

rectifying contact (8.7.2)

widely utilized in electronic devices to convert alternating current into direct current

ohmic contact

electron can flow in both ways and obeys Ohm's law

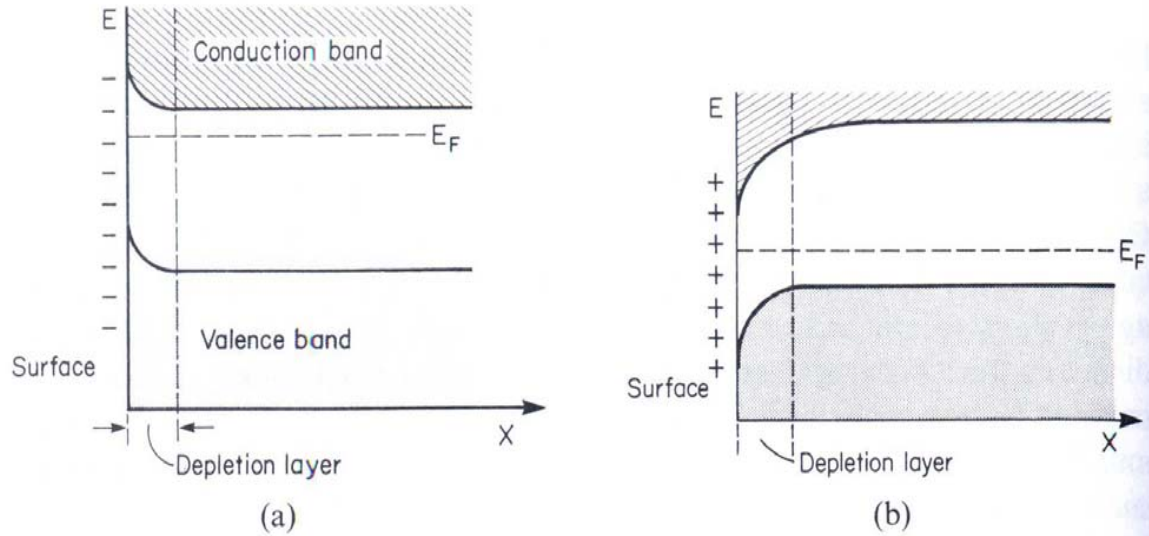


Figure 8.12. (a) Band diagram for an *n*-type semiconductor whose surface has been negatively charged. (b) Band diagram for a *p*-type semiconductor, the surface of which is positively charged. *X* is the distance from the surface.

Band diagram for n-type and p-type semiconductors (Fig 8.12)

n- type : surface negatively charged → repelling force on electron band edge → bent upward , **depletion layer** (*space-charge region*)

p-type: band edge bent downward

8.7.2 Rectifying Contacts (Schottky Barrier Contacts)

Work function, ϕ : the energy difference between the Fermi energy and the ionization energy which is necessary to transport an electron from E_F to infinity

Metal / n-type semiconductor, $\phi_M > \phi_S$: After contact (Fig 8.13b), electrons flow from semiconductor "down" to metal until Fermi energies of both solids are equal → the metal will be charged negatively and potential barrier is formed just as shown in Fig 8.12

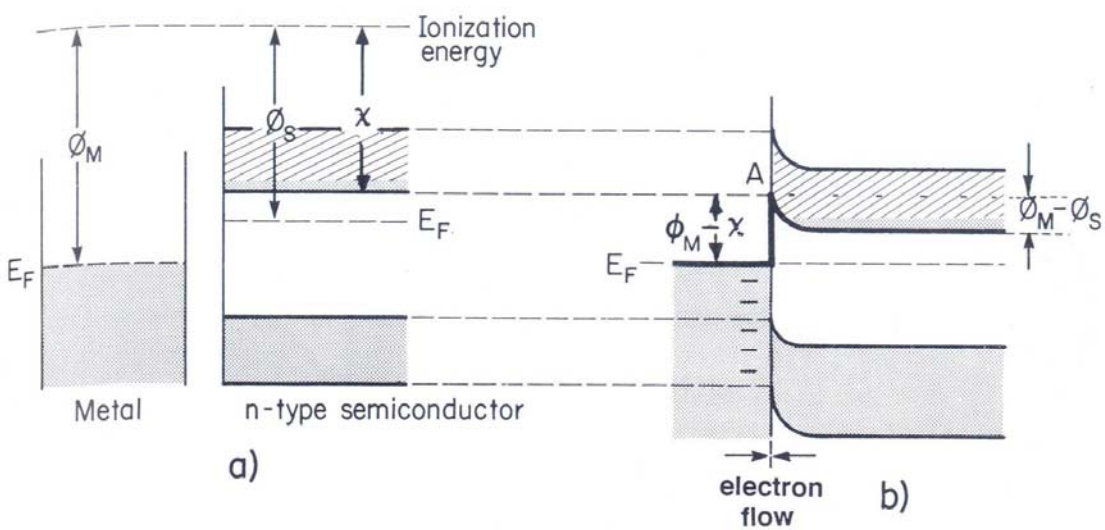


Figure 8.13. Energy bands for a metal and an *n*-type semiconductor (a) before and (b) after contact. $\phi_M > \phi_S$. The potential barrier is marked with heavy lines. χ is the *electron affinity*.

In equilibrium state, electrons from both sides cross the potential barrier. This electron flow constitutes the so-called **diffusion current**

8.7.2 Rectifying Contacts (Schottky Barrier Contacts)

Metal / p-type semiconductor, $\phi_M < \phi_S$

Electrons diffuse from metal into the semiconductor, thus charging the metal and, therefore, the surface of the semiconductor positively. Consequently a downward potential barrier is formed.

Contact potential:

the potential height for an electron diffusing from the semiconductor into metal: $\phi_M - \phi_S$ height of the potential barrier from metal side : $\phi_M - \chi$, where χ electron affinity

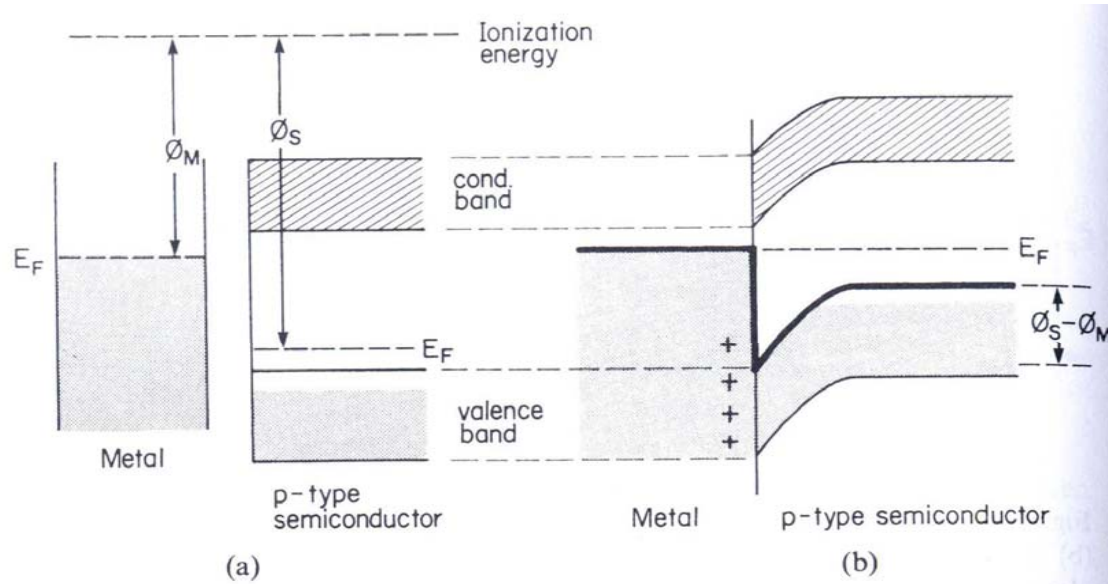


Figure 8.14. Energy bands for a metal and a *p*-type semiconductor (a) before and (b) after contact. $\phi_M < \phi_S$.

8.7.2 Rectifying Contacts (Schottky Barrier Contacts)

Net current flow in metal / n-type semiconductor by d.c biasing

- **Reverse bias** (when metal is connected to the negative terminal) : metal is charged even more negatively → the electron in the semiconductor are repelled even more → the potential barrier is increased and depletion layer becomes wider (Fig 8.15a)

Both barrier are relatively high, the diffusion currents in both directions are negligible, voltage independent small drift current from metal into the semiconductor

- **Forward Bias** (semiconductor is connected to negative terminal)

The potential barrier reduced. the depletion layer is narrow

: a large electron flow from semiconductor into metal

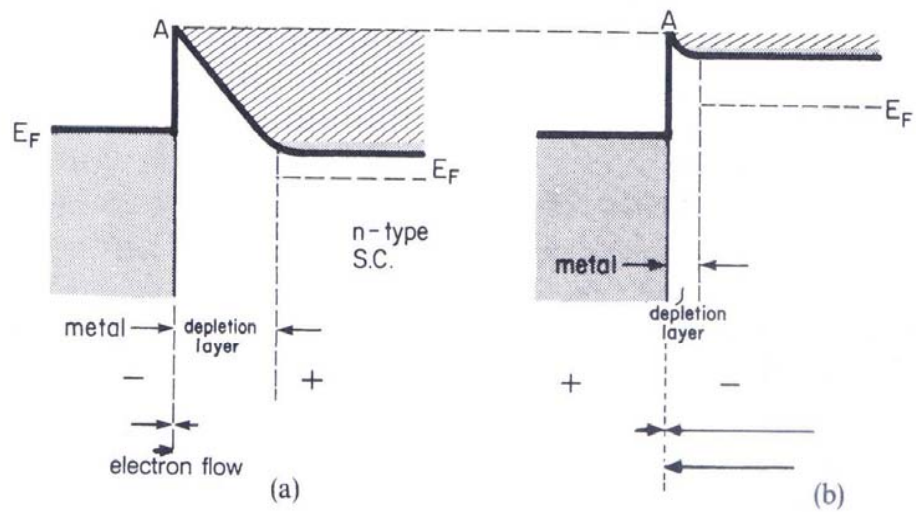


Figure 8.15. Metal–semiconductor contact with two polarities: (a) reverse bias and (b) forward bias. The number of electrons that flow in both directions and the net current is indicated by the length of the arrows. The potential barriers are marked by heavy lines.

8.7.2 Rectifying Contacts (Schottky Barrier Contacts)

The voltage current characteristic (Fig 8.16a)

Rectifier : convert alternating current into direct current (Fig 8.16b)

The current that flows from the metal into semiconductor

$$I_{\mathrm{MS}} = ACT^2 \exp\left[-\left(\frac{\phi_{\mathrm{M}} - \chi}{k_{\mathrm{B}}T}\right)\right]$$

where, *A* is the area of contact (see Fig. 8.13) and *C* is a constant

The current flowing from semiconductor into the metal

$$I_{\mathrm{SM}} = ACT^2 \exp\left[-\left(\frac{\phi_{\mathrm{M}} - \phi_{\mathrm{S}} - eV}{k_{\mathrm{B}}T}\right)\right]$$

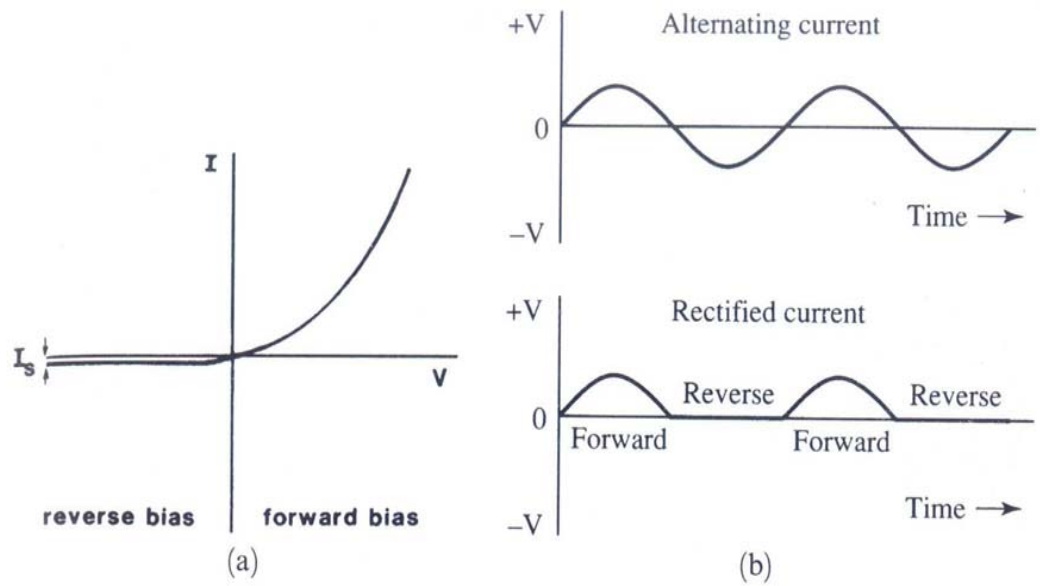


Figure 8.16. (a) Characteristic of a rectifier. The reverse current is grossly exaggerated! (b) Voltage versus time curves to demonstrate the behavior of an alternating current and a current for which the negative voltage has been eliminated.

8.7.2 Rectifying Contacts (Schottky Barrier Contacts)

The net current $I_{net} = I_{SM} - I_{MS}$ consists of namely, the saturation current

$$\mathrm{I_S} = ACT^2 \exp\left[-\left(\frac{\phi_\mathrm{M} - \phi_\mathrm{S}}{k_\mathrm{B}T}\right)\right]$$

and voltage-dependent term. The net current is obtained by combining the last two equation

$$\mathrm{I_{net}} = I_\mathrm{S}\left[\exp\left(\frac{eV}{k_\mathrm{B}T}\right) - 1\right]$$

Forward bias (positive V) the net current increase exponentially with V

8.7.3 Ohmic Contacts (Metallization)

Ohmic contact: no barrier exists for the flow of electrons in either diction (Fig 8.17c)

For the case of metal / n-type semiconductor contact, and $\phi_M < \phi_S$, electron flow from metal to semiconductor, charging metal positively.(cf, another case : metal / n-type semiconductor contact, and $\phi_M > \phi_S$)

The band of semiconductor bend "downward" and no barrier

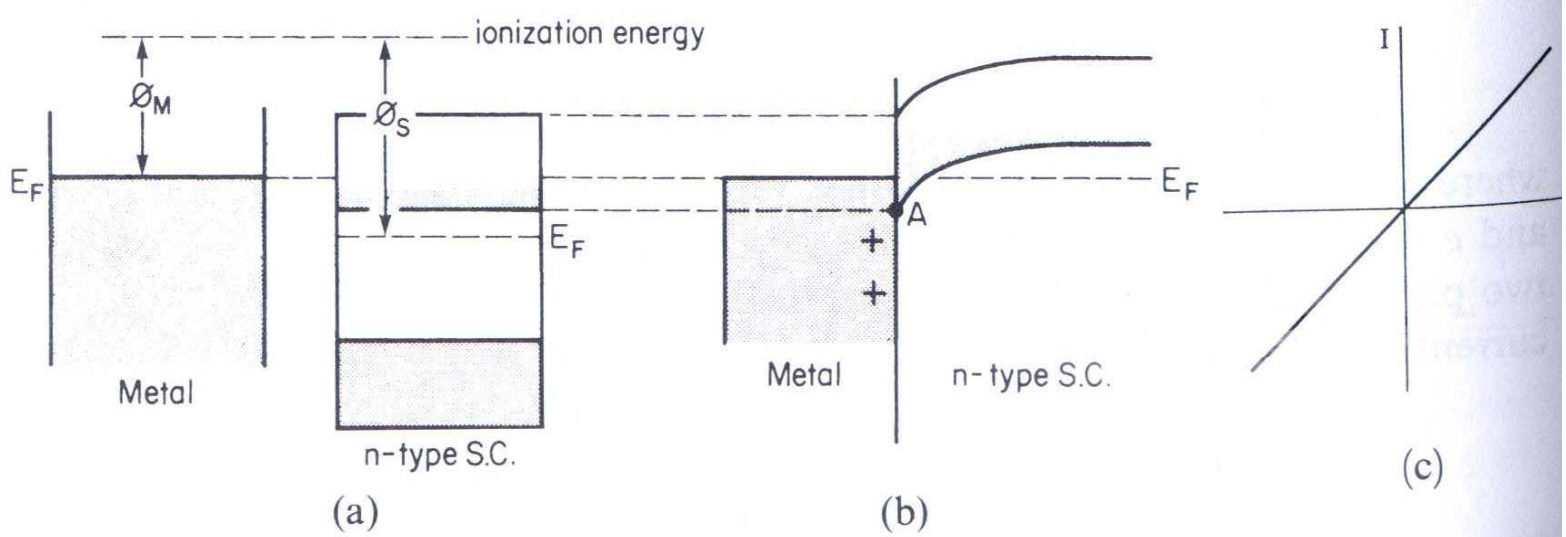


Figure 8.17. Ohmic contact between metal and n-type semiconductor ($\phi_M < \phi_S$). (a) Metal and semiconductor are separate. (b) Metal and semiconductor are in contact. (c) Current–voltage characteristic.

8.7.4 *p-n* Rectifier (Diode)

After p-n contact : electron flow from higher level (*n*-type) "down" into p-type so that p-slide is negatively charged

Conduction band: electron in the p-region diffuse "down" into *n* -region, in equilibrium state the number of electrons crossing the junction in both directions is identical

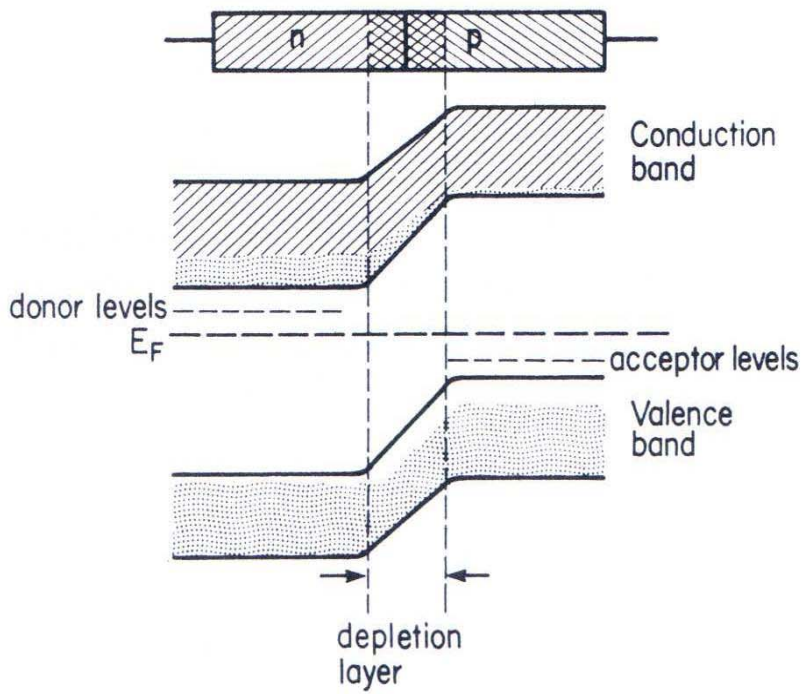


Figure 8.18. Schematic band diagram for a *p–n* junction (diode) in equilibrium.

8.7 Semiconductor Devices

8.7.4 *p-n* Rectifier (Diode)

" **quasi-Fermi levels**" (Fig 8.19a)

Electron density varies in the junction from the *n*-side to the *p*-side by many orders of magnitude, while electron current is almost constant. Consequently, the E_F is almost constant over depletion layer

External potential applied (Fig 8.19)

- Reverse bias (connecting positive terminal to n-side): depletion layer becomes wider and potential barrier grows higher

- Forward bias: barrier decreases in height, a large net electron flow occurs from *n*-type to *p*-type region

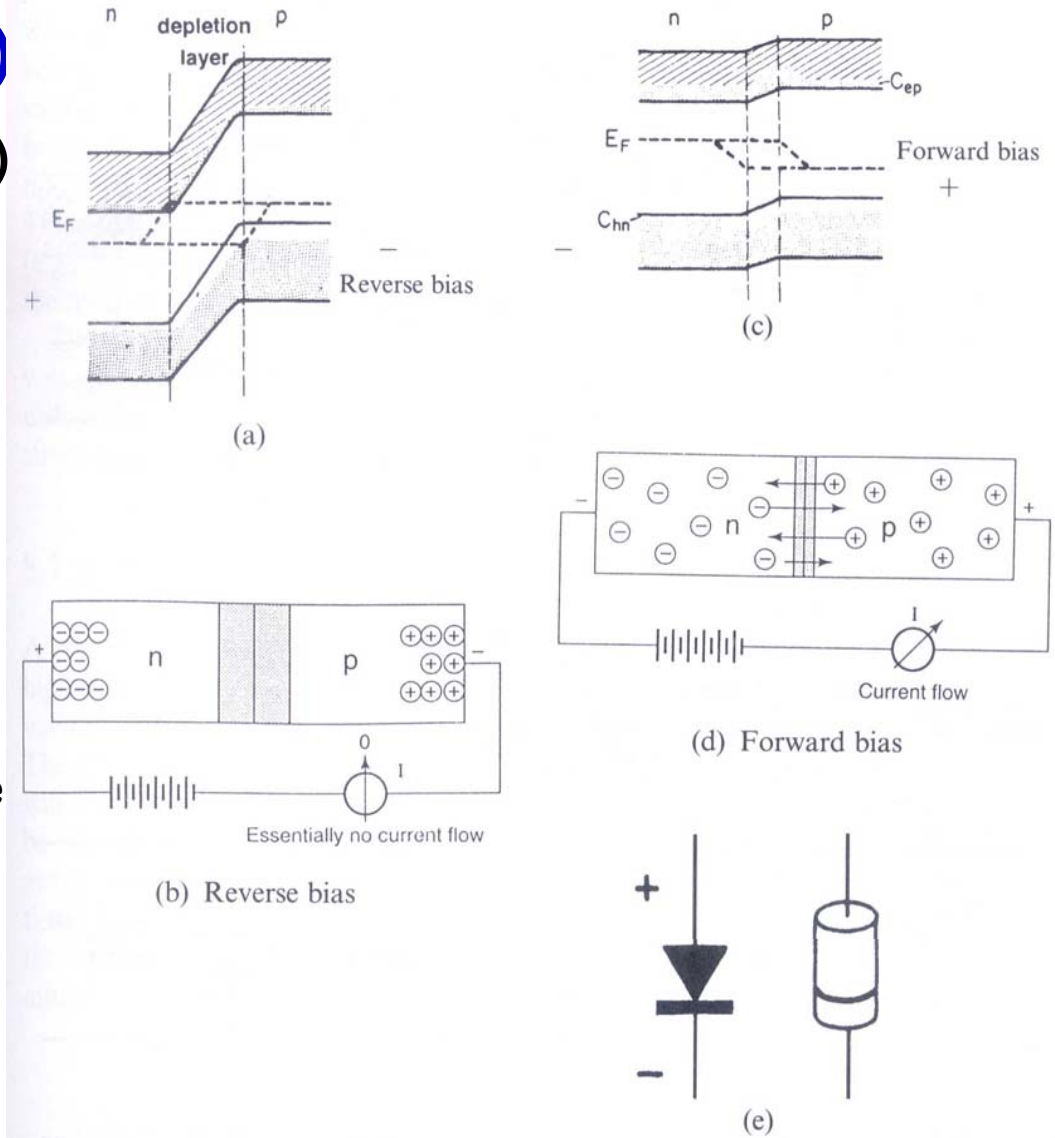


Figure 8.19. (a) + (b) Reverse and (c) + (d) forward biasing of a *p–n* junction (diode). (e) Symbol of a *p–n* rectifier in a circuit and designation of polarity in an actual rectifier.

8.7.4 *p-n* Rectifier (Diode)

The diffusion constant is connected with the mobility (Einstein relation)

$$D_{\mathrm{ep}} = \frac{\mu_{\mathrm{ep}} k_{\mathrm{B}} T}{e}$$

The saturation current, I_S in reverse bias, Shockley equation (ideal diode law)

$$I_{\mathrm{S}} = Ae\left(\frac{C_{\mathrm{ep}} D_{\mathrm{ep}}}{L_{\mathrm{ep}}} + \frac{C_{\mathrm{hn}} D_{\mathrm{hn}}}{L_{\mathrm{hn}}}\right)$$

C_{hn}: equilibrium concentration of the holes in *n*-region, C_{ep} :concentration of electron in the *p*-region, D: diffusion constant, L: diffusion length

The minority carrier diffusion length is given by a reinterpretation of a well known equation of thermodynamics,

$$L_{\mathrm{ep}} = \sqrt{D_{\mathrm{ep}} \cdot \tau_{\mathrm{ep}}}$$

while τ_{ep} is the lifetime of electrons in the p-type region before these electrons are annihilated by recombination with holes

8.7.5 Zener Diode

- **Breakdown:** when the reverse voltage is increased above a critical value, high electric filed causes some electrons to become accelerated with a velocity at which **impact ionization** occurs → **avalanching** process

- **Zener breakdown (Tunneling):** another breakdown process; when the doping is heavy and thus the barrier width becomes very thin (< 10nm), applying high enough reverse voltage causes the bands to shift to the degree that some electron in the valence band of *p*-side are apposite to empty states in the conduction band of *n*-side and these electron can tunnel through the depletion layer (Fig 8.20b) ; a circuit protection device (Fig 8.20d)

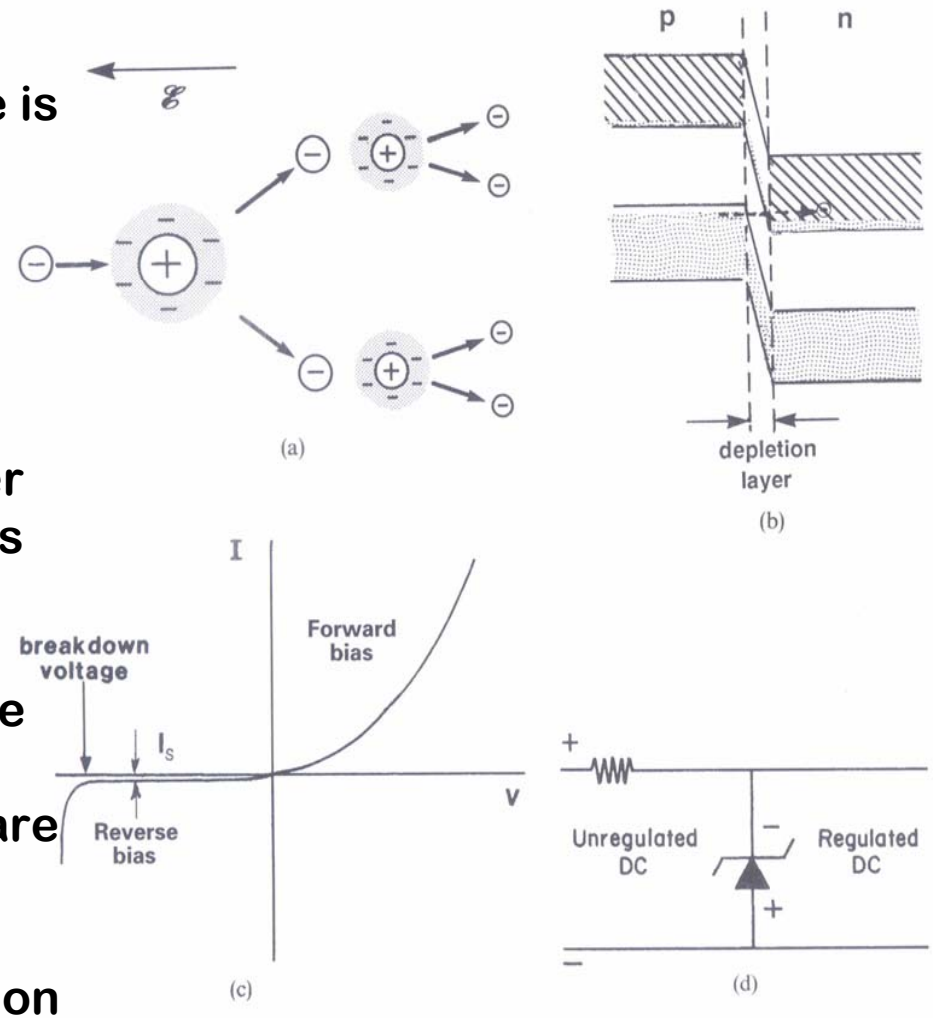


Figure 8.20. (a) Electron avalanche created at breakdown voltage. (b) Tunneling (Zener breakdown). (c) Voltage–current characteristic of a *p–n* diode exhibiting a breakdown voltage at a large reverse voltage. As in Fig. 8.16(a), I_s is shown grossly exaggerated. (d) Zener diode in a circuit for voltage regulation.

8.7.6 Solar Cell (Photodiode)

: a *p-n* junction diode

1. Light of high energy fall on or near the depleted area

2. Electron are lifted from the valence band into the conduction band, leaving holes in the valence band

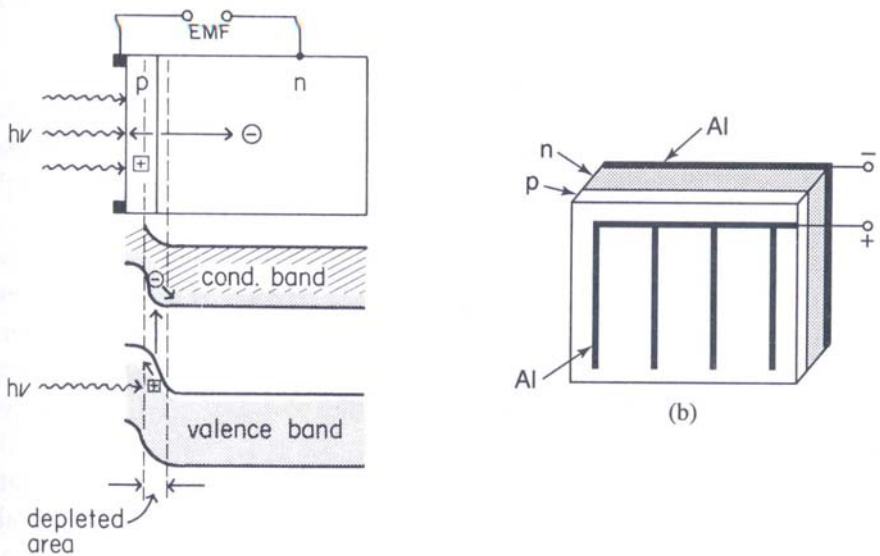


Figure 8.21. Solar cell; the *p*-region is only about 1 μm thick. (a) side view; (b) Front view.

3. The electron in the depleted area immediately "roll down" into the *n*-region, whereas the holes are swept into the *p*-region

→ The carriers can be measured in an external circuit (photographic exposure meter) or used to generate electrical energy

In order to increase the effective area of the junction (Fig 8.21)

- extremely thin *p*-type region (1 μm) :light radiation through *p*-region
- narrow metal electrode (in the form of strips)

8.7 Semiconductor Devices

8.7.6 Solar Cell (Photodiode)

- The closer a carrier was created to the *p-n* boundary, the larger is its change of contributing to the current. (the electron - hole created some distance away from the depleted region, do not separated by junction field and eventually recombine; do not contribute to the electric current) : see Fig 8.22

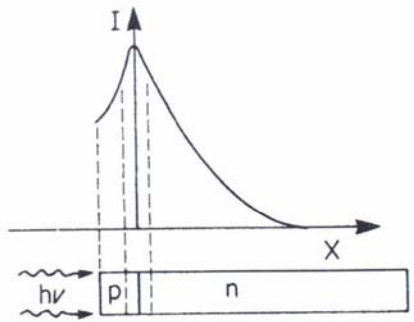


Figure 8.22. Schematic representation of the contribution of electrons and holes to the photocurrent (I) with respect to the distance x from the p–n junction.

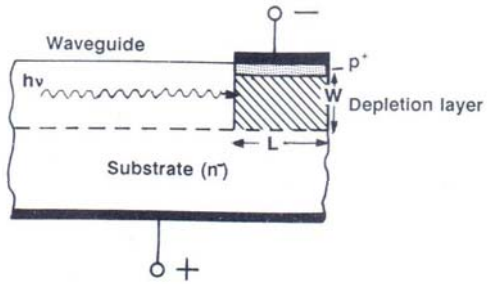


Figure 8.23. Schematic of a transverse-type photodiode that is connected to a light-carrying medium such as an optical fiber or a waveguide ($L \approx 100$ nm).

- Quantum efficiency

$$\eta = 1 - \frac{\exp(-\alpha W)}{1 + \alpha L}$$

W, L: the width and length of depletion region

α : a parameter that determines the degree of photon absorption by the electrons

8.7 Semiconductor Devices

*8.7.7 Avalanche Photodiode

- A *p-n* photodiode that is operated in a high reverse bias mode, i.e. at near-breakdown voltage

1. Electron and holes created by transition from the valence band into the conduction band by the incident light, are accelerated through the depleted area with high velocity → which, in turn, ionize the lattice atom and generate secondary hole-electron pairs, thus generate even more hole-electron pairs → photo current gain
2. Low light-level application, detectors in long-distance, fiber optics telecommunication system

8.7 Semiconductor Devices

*8.7.8 Tunnel Diode

A *p-n* junction diode - depleted area is very narrow ; → heavy doping Fermi energy extends into the valence band of *p*-type semiconductor

energy band diagram and I-V characteristic : Fig 8.24

- The voltage is increase to 100mV (in Fig 8.24d), the potential barrier might be decreased do much that, opposite to the filled *n*-conduction state, no tunneling take place; current decreases with increasing forward voltage: "**negative current-voltage characteristic**" : c-d region

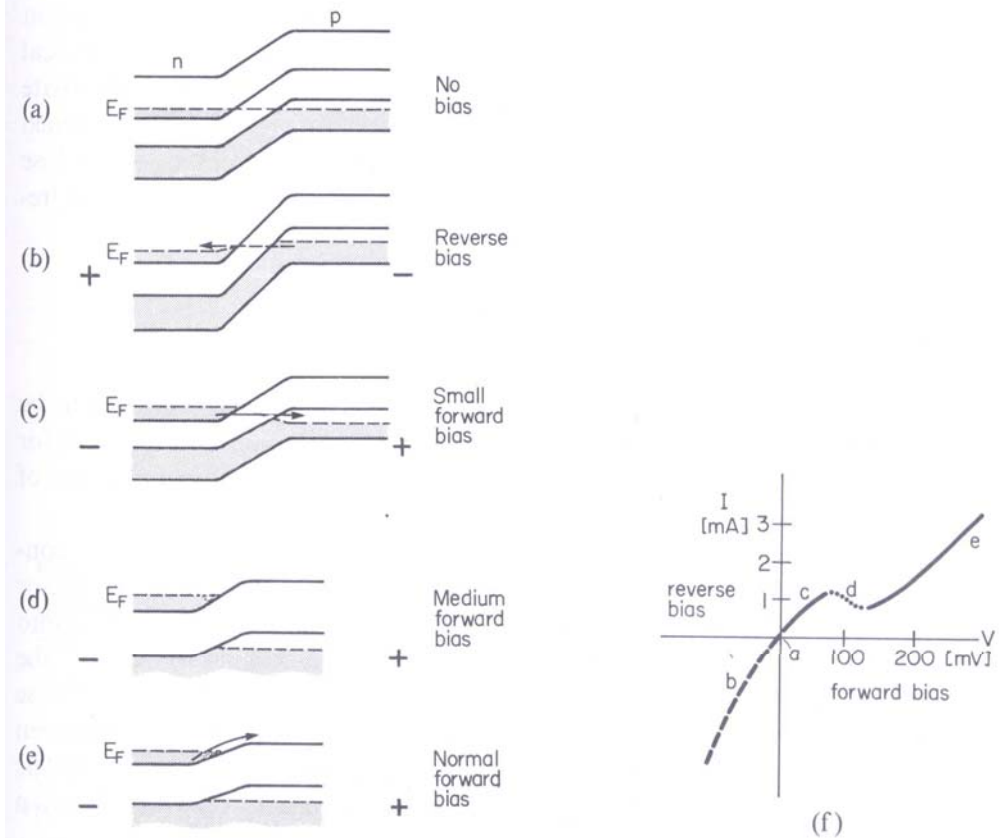


Figure 8.24. (a)–(e) Schematic energy band diagrams for highly doped *n*- and *p*-type semiconductors (tunnel diode). (a) No bias. (b) Reverse bias. (c) Small forward bias. (d) Medium forward bias. (e) "Normal" forward bias. (f) Voltage–current characteristic for a tunnel diode.

8.7 Semiconductor Devices

8.7.9 Transistors

Bipolar Junction Transistor

n-p-n transistor (*n-p* diode back to back with *p-n* diode) ; three connections of the transistor are called emitter(E), base(B), and collector(C)

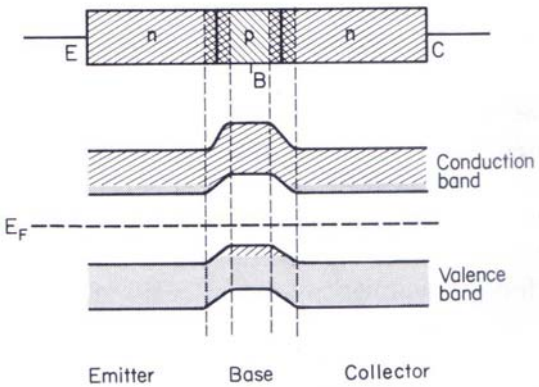


Figure 8.25. Schematic band diagram of an unbiased *n–p–n* bipolar junction transistor.

- For the amplification of a signal, the "diode" consisting of emitter and base is forward biased, whereas the base-collector "diode" is strongly reverse biased (Fig 8.26a)

1. The electrons injected into the emitter needed to have enough energy to be able to "climb" the potential barrier into the base region.

2. The electron diffuse through the base area until they heave reached the depletion region between base and collector.

3. The electrons are accelerated in the strong electric field produced by the collector voltage → this acceleration case amplification of the input a.c signal

8.7 Semiconductor Devices

8.7.9 Transistors

Bipolar Junction Transistor

The electron flow from emitter to collector can be controlled by the bias voltage on the base

- A large positive (forward) bias decreases the potential barrier and the width of the depleted region between emit

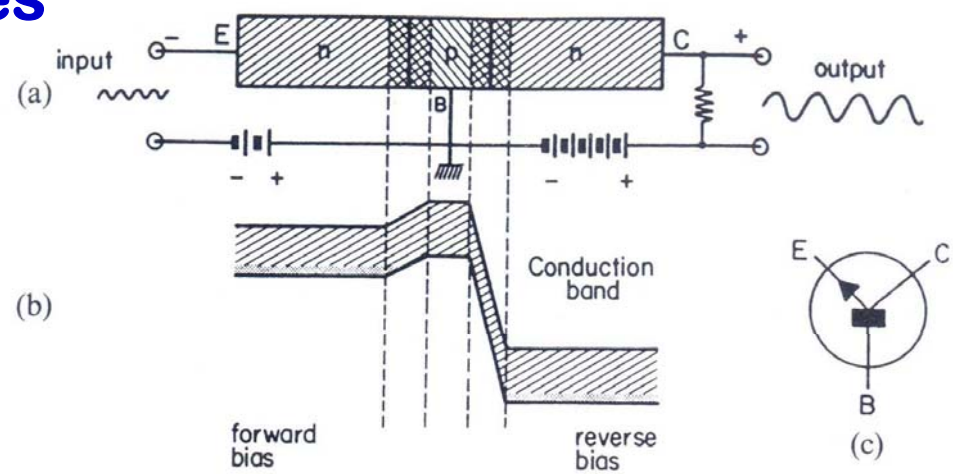


Figure 8.26. (a) Biasing of an n–p–n bipolar transistor. (b) Schematic band diagram (partial) of a biased n–p–n bipolar transistor. (c) Symbol used for a bipolar n–p–n transistor.

→ The electron injection into the *p*-area is relatively high

- A small, but still positive base voltage results in a comparatively larger barrier height and in a wider depletion area, which causes a smaller electron injection from the emitter into the base area.

- the strong collector signal mimics the waveform of the input signal

: this feature is utilized for the amplification of music or voice, etc

8.7 Semiconductor Devices

8.7.9 Transistors

Metal-Oxide-Semiconductor Field-Effect Transistor

- A field-effect transistor consists of a channel through which the charge carriers need to pass on their way from a *source* (S) to the *drain* (D)

- The electrons that flow from the source to the drain can be controlled by an electric field which is established by applying a voltage to the so-called *gate* (G)

- The gate electrode is electrically insulated from the channel by a thin oxide layer which prevent a d.c current to flow from gate to channel

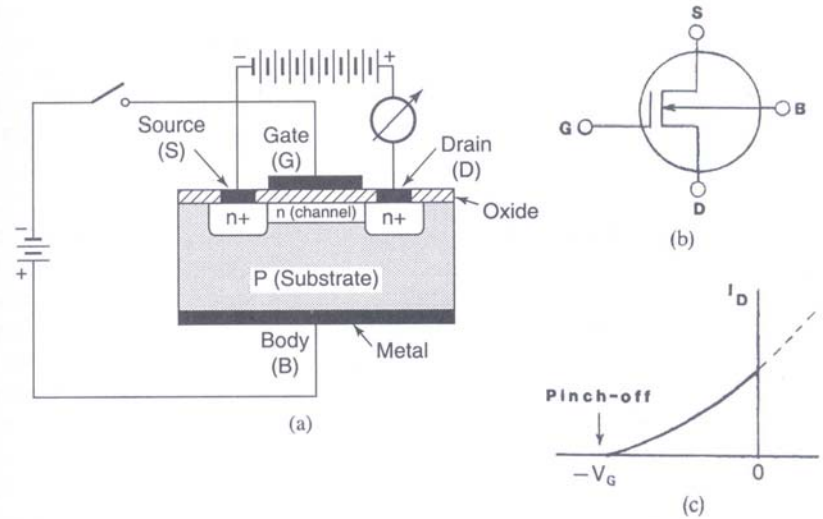


Figure 8.28. (a) Schematic representation of an *n*-channel depletion- (normally on) type MOSFET. The dark areas symbolize the (aluminum) metallizations. The "oxide" layer may consist of SiO_2, nitrides (Si_3N_4), oxinitrides (Si_3N_4–SiO_2), or multilayers of these substances. This layer is about 10 nm thick. The gate voltage is applied between terminals G and B. Quite often the B and S terminals are interconnected. (b) Circuit symbol for *n*-channel depletion-type MOSFET. (c) Gate voltage/Drain current characteristic ("Transfer" characteristic). For positive gate voltages (dashed portion of the curve) the device can operate in the "enhancement mode" (see Fig. 8.29(c)).

8.7 Semiconductor Devices

8.7.9 Transistors

Metal-Oxide-Semiconductor Field-Effect Transistor

Two types of MOSFETs are common:

1. **Depletion-type MOSFET** or **"normally on" MOSFET**

- Consists of high-doped source and drain regions and a low doped channel, all of the same polarity (e.g. *n*-type): Fig8.28a
- The channel width is controlled by the voltage between gate and body
- A negative charge on the gate drives the channel electrons away from the gate and towards the substrate; the conductive region of the channel becomes narrowed by a negative gate voltage.
- The more negative voltage (V_G), the smaller the current through the channel from source to drain until eventually the current is pinched off (Fig 8.28c)

8.7 Semiconductor Devices

8.7.9 Transistors

Metal-Oxide-Semiconductor Field-Effect Transistor

2. Enhancement-type MOSFET or "normally-off" MOSFET

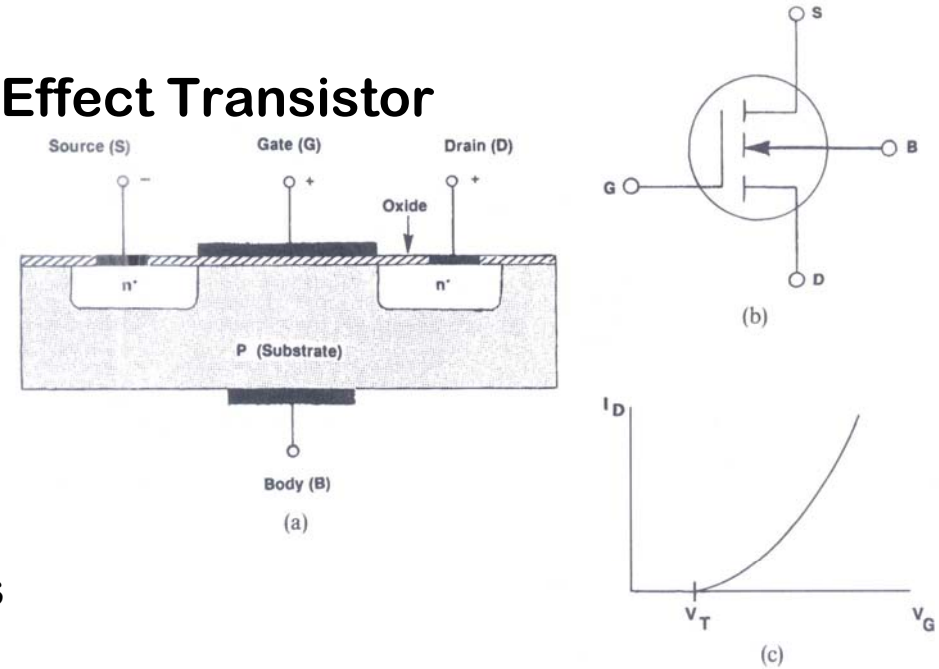


Figure 8.29. (a) Enhancement (normally-off)-type *n*-channel MOSFET. For details, see the caption of Fig. 8.28. (b) Circuit symbol. (The broken line indicates that the path between S and D is normally interrupted.) (c) Gate voltage (V_G)/drain current (I_D) characteristic. V_T is the threshold gate voltage above which a drain current sets in.

- No built-in channel for electron conduction at least as long as no gate voltage is applied.
- If large enough positive voltage is applied to the gate, most of the holes immediately below the gate oxide are repelled, i.e., they are driven into the substrate, thus removing possible recombination sites and negative charge carriers are attracted into this channel; a path for the electrons between source and drain can be created by a positive gate voltage
- Usages: memories, microcomputers, logic circuits, amplifiers, analog switches and operational amplifiers

8.7 Semiconductor Devices

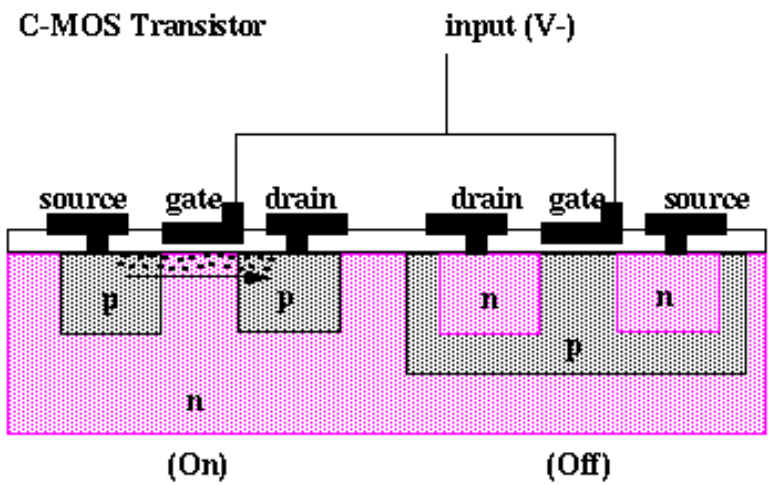
8.7.9 Transistors

Metal-Oxide-Semiconductor Field-Effect Transistor

CMOSFET: *complementary* MOSFET

- Both an n-channel and a p-channel device are integrated on one chip and wired in series

- This tandem device has become the dominant technology for information processing, because of its low operating voltage (0.1V), low powder consumption, and short channel length with accompanying high speed



http://www.plexoft.com/SBF/images/tokuyasu-mirror/cmos-trans.gif

8.7 Semiconductor Devices

8.7.10. Quantum Semiconductor Devices

-To explain the nature of a quantum device: recall "the behavior of one electron in a potential well (Sec 4.2)"

- *Size quantization* : dimensions of the crystalline solid are reduced to the size of the wavelength of electron (e.g., 20nm for GaAs ; → density of state, Z(E) is quantized

- A small-band gap material is sandwiched between two layers of a "wide-band gap material (Fig 8.33a,b): the configuration for which all three dimensions of the center materials have values near the electron wavelength, is called **quantum dot** (**quantum wire** for 2-d, **quantum well** for 1-d confinement) → potential barrier between two GaAs region

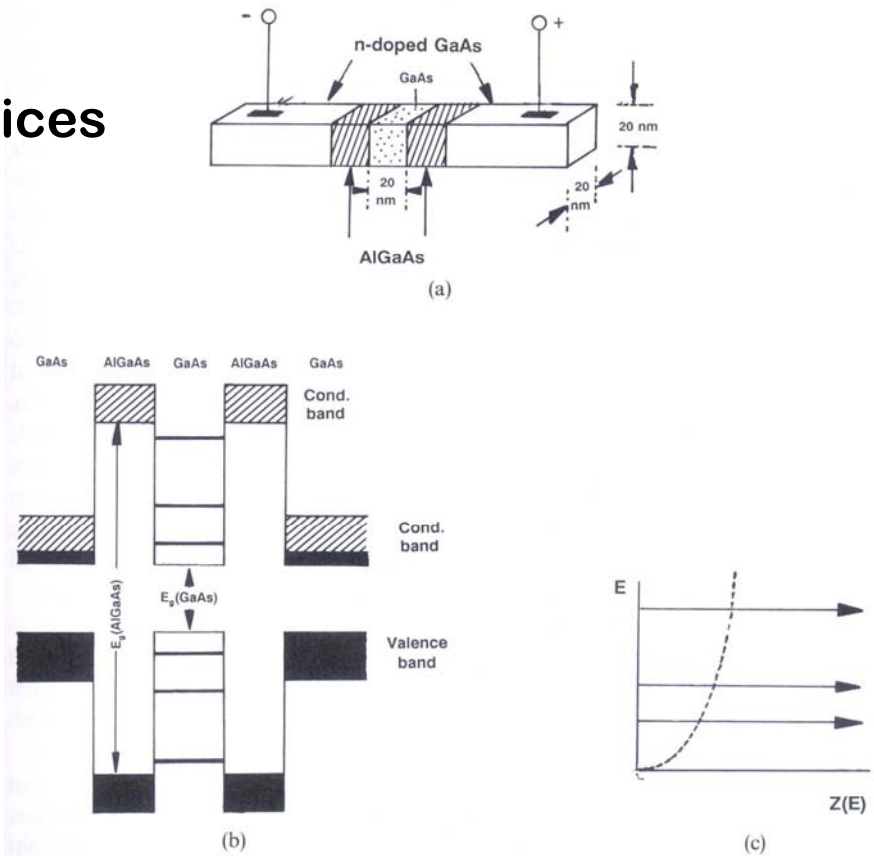


Figure 8.33. (a) Schematic representation of a quantum dot structure. (b) Energy levels for GaAs for the quantum dot structure depicted in (a). (*Note*: The gap energy difference between GaAs ($E_g = 1.42$ eV) and AlGaAs is greatly exaggerated. This difference may be as small as 0.2 eV.) (c) Discontinuous density of energy states for a quantum dot structure. The dashed parabola indicates the density of states for a bulk crystal, as is known from Fig. 6.4.

8.7 Semiconductor Devices

8.7.10. Quantum Semiconductor Devices

- Fig 8.34: If a large voltage is applied to the device, the conduction band of the *n*-doped GaAs is raised to a level at which its conduction electrons are at the same height as an empty energy state of the center GaAs region.

→ At this point, the electrons are capable of tunneling though the potential barrier formed by the AlGaAs region and thus reach one of these discrete energy state

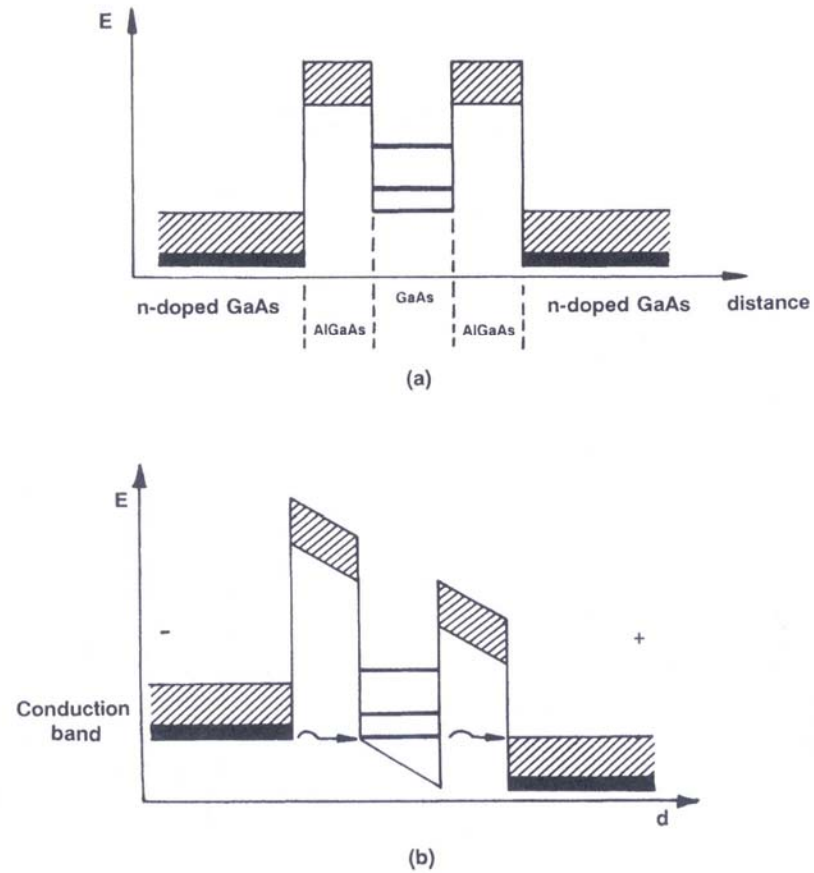


Figure 8.34. Parts of two energy band structures for the quantum device shown in Fig. 8.33. For simplicity, only the conduction bands are shown. (a) No applied voltage. (b) With applied voltage, which facilitates electron tunneling from the conduction band of the *n*-doped GaAs into an empty energy level of the center GaAs region.

8.7 Semiconductor Devices

8.7.10. Quantum Semiconductor Devices

- If a slightly higher voltage is applied, the electrons of the n-doped GaAs are no longer at par with an empty energy level and tunneling comes to a near standstill a I-V characteristic with negative differential resistance (Fig 8.35)

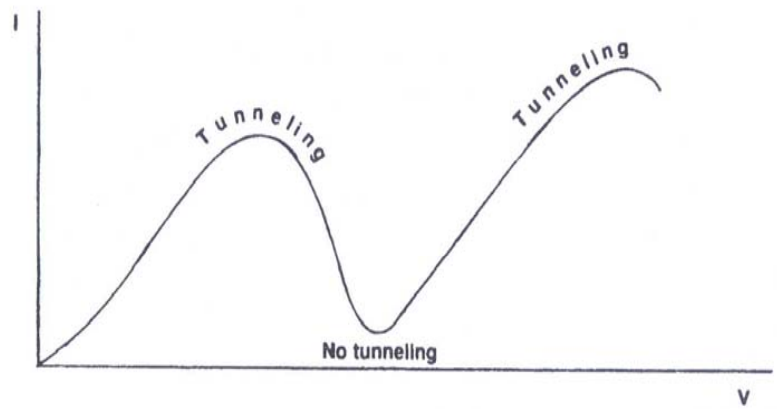


Figure 8.35. Current–voltage characteristic of a quantum dot device as depicted in Figs. 8.33 and 8.34.

- An array of a multitude of quantum wells stacked on top of each other : The periodic arrangement of wide-band gap and narrow band gap materials is called *supperlattice*

- Quantum devices are about one-hundredth of the size of presently known FETs

- The major problems have still to be overcome concerning interconnections, device architecture, and fabrication of three-terminal devices

8.7 Semiconductor Devices

8.7.11. Semiconductor Device Fabrication

(Text reading p.146-155)

Techniques for single-crystal growth

1.Czochralski

2. Float-zone technique

3. Bridgman tech

Once the rods have been obtained, They are sliced, lapped, etched, and polished to obtain 0.3-0.4mm thick wafers

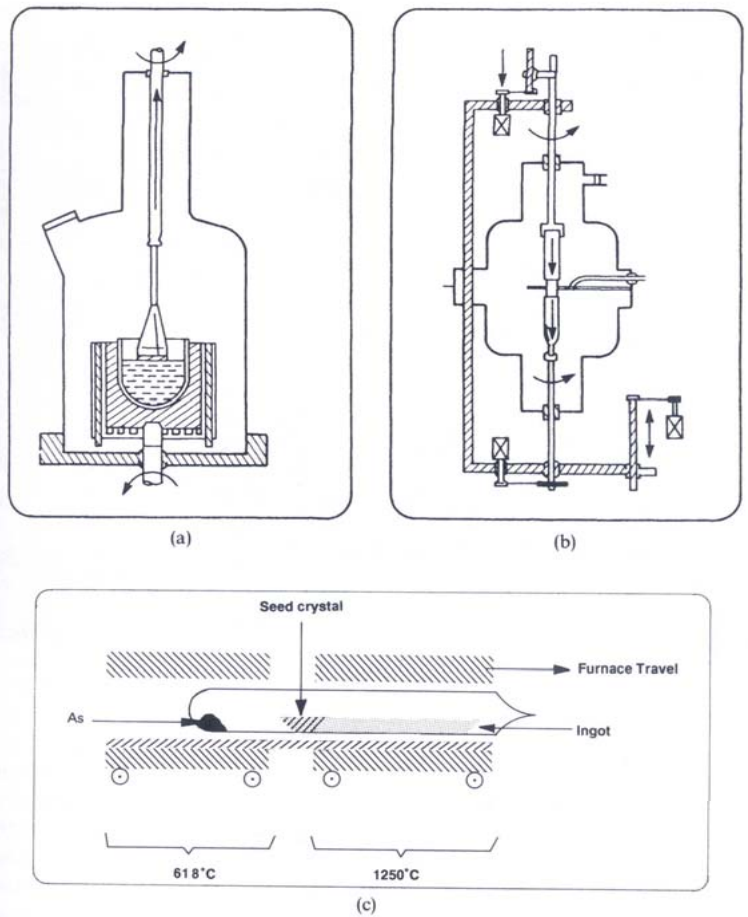


Figure 8.36. Techniques for single-crystal growth. (a) Czochralski method. Heating is performed by radio frequency coils or (for big crucibles) by resistance heating. (b) Float zone method. (c) Bridgman method (demonstrated for GaAs). (d) A 300 mm (12 inch) silicon single crystal is removed from the crucible. (Courtesy Wacker Siltronic AG)

8.7 Semiconductor Devices

8.7.11. Semiconductor Device Fabrication

Device fabrication on the wafers

- Surface oxidation,
- Photolithography
- Oxide Etch
- Photoresist Strip
- Doping
- Metallization
- Packaging

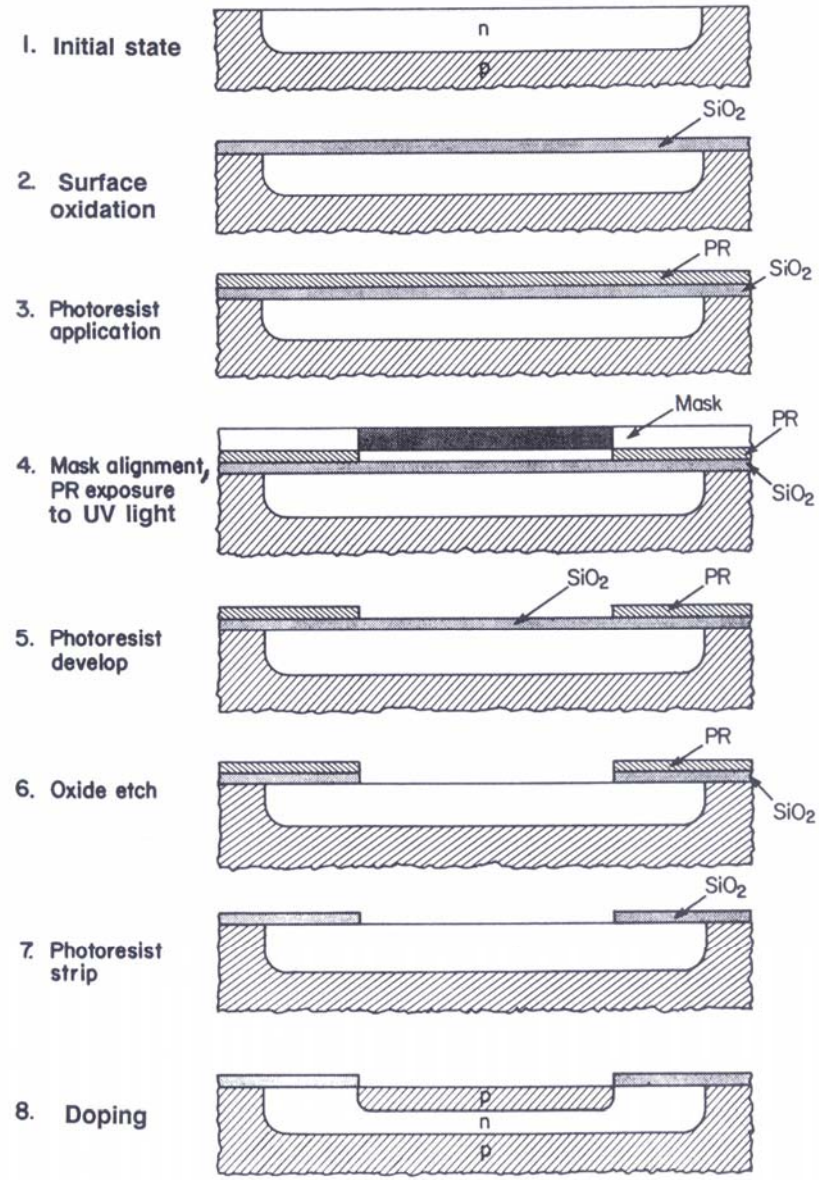


Figure 8.37. Photoresist (PR) masking sequence to obtain a *p–n–p* bipolar transistor

Part II Electrical Properties of Materials

Chap. 7 Electrical Conduction in Metals and Alloys

Chap. 8 Semiconductors

Chap. 9 Electrical Properties of Polymers, Ceramics, Dielectrics, and Amorphous Materials

9.1 Conducting Polymers and Organic Metals

Polymers consist of (macro)molecules which are long and chainlike. Several atoms combine and form a specific building block, called a **monomer**, and thousands of monomer combine to a polymer. (see Fig. 9.1)

Figure 9.1. (a) Polyethylene. (b) Polyvinylchloride. (The dashed enclosures mark the repeat unit. Polyethylene is frequently depicted as two CH_2 repeat units for historical reasons.

The binding force between individual atoms within a chain: usually covalent and sometimes ionic in nature

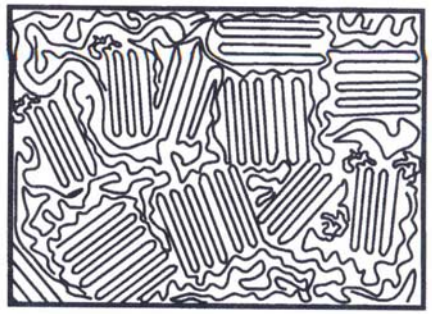


Figure 9.2. Simplified representation of a semicrystalline polymer (folded-chain model).

The binding force between macromolecules: a weak Van der Walls type

Degree of order or degree of periodicity of the atoms in polymers: dependent on the length of the molecules and on the regularity of molecular structure. Certain heat treatment affects some structural parameters; e.g. slow cooling yield, for certain polymer, a crystalline structure (Fig. 9.2)

9.1 Conducting Polymers and Organic Metals

A high degree of crystallinity and a relatively high conductivity have been found in polyacetylene, a simplest conjugated organic polymer; the prototype of a conducting polymer

A conjugated polymer has alternating single and double bonds between the carbons (see Fig. 9.3)

Two principle isomers: *trans, cis*

trans : the hydrogen atoms are alternately bound to opposite sides of the carbon

cis : the hydrogen atoms are situated on the same side of the double-bond carbons

Trans-polyacetylene is obtained as silvery flexible film that has a conductivity comparable to that of silicon (Fig. 9.4)

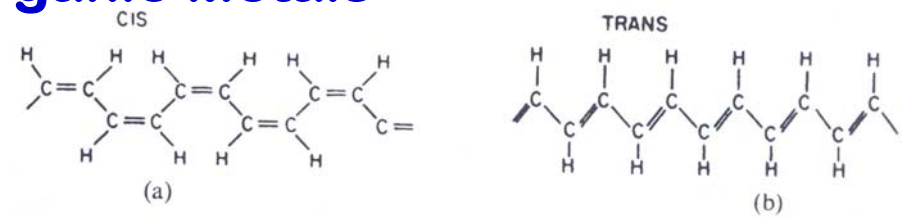


Figure 9.3. Theoretical isomers of polyacetylene (a) *cis*-transoidal isomer, (b) *trans*-transoidal isomer. Polyacetylene is synthesized as *cis*-$(CH)_x$ and is then isomerized into the *trans*-configuration by heating it at 150°C for a few minutes.

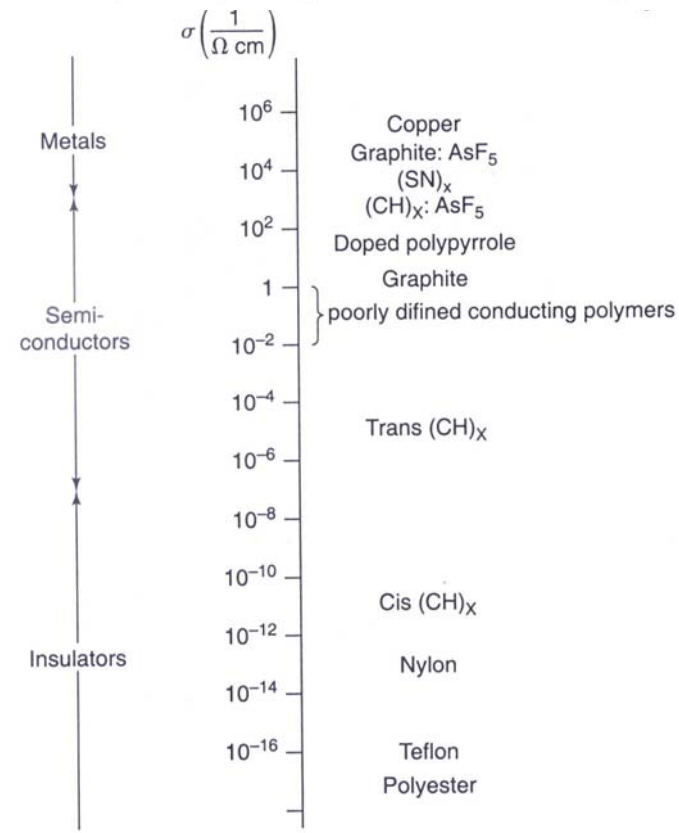


Figure 9.4. Conductivities of polymers in Ω^{-1} cm^{-1}. (Compare with Fig. 7.1.)

9.1 Conducting Polymers and Organic Metals

Calculated band structure for *trans*-(CH)x

assuming different distances between the carbon atoms

- Fig 9.5(a) all carbon length are equal, the resulting band in the highest is partially filled : metal behavior ; the electrons in the double bond of a conjugated polymer (called π-electron) are loosely bound to the neighboring carbon atoms, thus one of these electron is easily dissociated from carbon atom by a small energy → contribute to electrical conduction

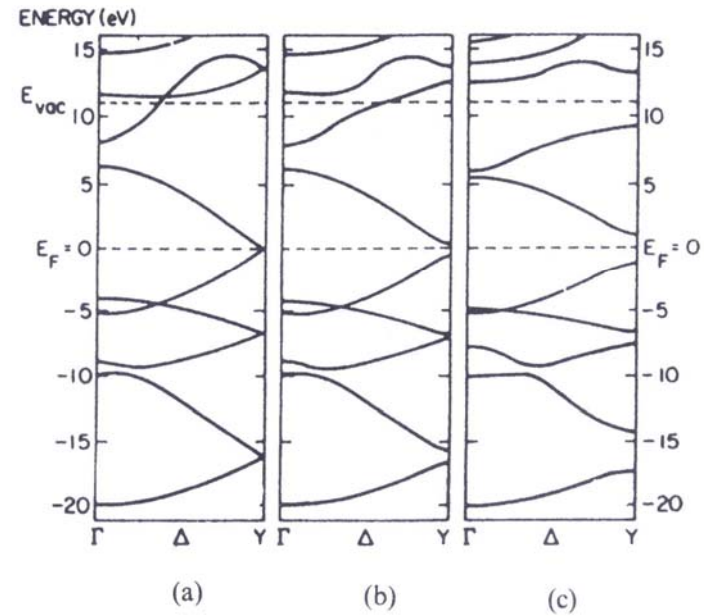


Figure 9.5. Calculated band structure of *trans*-$(CH)_x$ for different carbon–carbon bond lengths: (a) uniform (1.39 Å); (b) weakly alternating (C=C, 1.36 Å; C—C, 1.43 Å); and (c) strongly alternating (C=C, 1.34 Å; C—C, 1.54 Å). Note the band gaps at *Y* as bond alternation occurs. Reprinted with permission from P.M. Grant and I.P. Batra, *Solid State Comm.* **29**, 225 (1979).

- Fig 9.5(b),(c) : Real case; the distance between the carbon atoms alternate because of single and double bonds. The width of band gap near the Fermi level depends mainly on the extent of alternating bond lengths : semiconductor or insulator. In order to improve the conductivity of $(CH)_x$: decrease the disparity in the carbon-carbon bond lengths, thus approaching uniform bond length.

9.1 Conducting Polymers and Organic Metals

Conductivity increase by doping in polymer-based semiconductor : Fig 9.4 and Fig 9.6

- The dopant molecules diffuse between the $(CH)_x$ chains and provide a charge transfer between the polymer and the dopant

- Doping level in polymer "20 ~ 40 %"

Conduction mechanism in polyacetylene :

"**soliton**" is a structural distortion in a conjugated polymer and is generated when a single bond meets another single bond as shown in Fig 9.7.

At the distortion point a localized nonbonding electron state is generated in the center of forbidden band.

Near the center of a soliton, the bond lengths are equal : uniform bond length constitute a metal.

When many solitons have been formed and their sphere of influence overlap, a metal-like conductor would result.

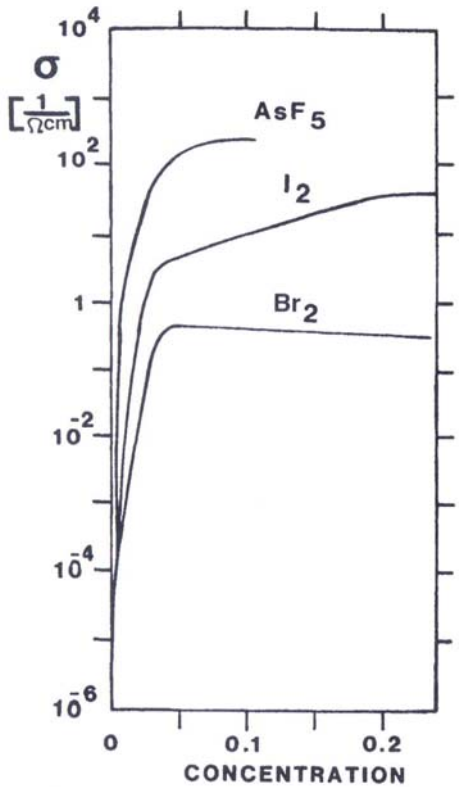


Figure 9.6. Conductivity change of polyacetylene as a result of doping.

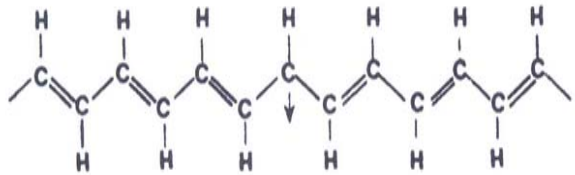


Figure 9.7. A broken symmetry in polyacetylene creates a *soliton*. (An *antisoliton* is the mirror image of a soliton.)

9.1 Conducting Polymers and Organic Metals

Other conductive polymers: polyanilines, polypyrroles, polythiophenes, polyphenylenes, polypphenylene vinylene, and their derivatives

Charge-transfer complexes : the conduction is increased by producing a mixture of easily ionized electron donors and electron acceptors, The charge is shared between the donors and acceptors: graphite, AsF_5-doped graphite (higher conductivity)

Charge-transfer salts :a donor molecule, such as tetrathiafulvalene (TTF), transfer electrons to an acceptor molecule, like tetracyanoquinodimethane (TCNQ) : the planar molecules stack on top of each other in sheets, thus allowing an overlap of wave functions and a formation of conduction bands that are partially filled with electron due to the charge transfer ; doped complexes of C60 (so called Buckyball) which exhibits superconductivity at low temperature.

9.2 Ionic Conduction

The ionic conduction is caused by the movement of some charged ions which hop from lattice site to lattice site under the influence of electric field.

This ionic conductivity,

$$\sigma_{\text{ion}} = N_{\text{ion}} e \mu_{\text{ion}}$$

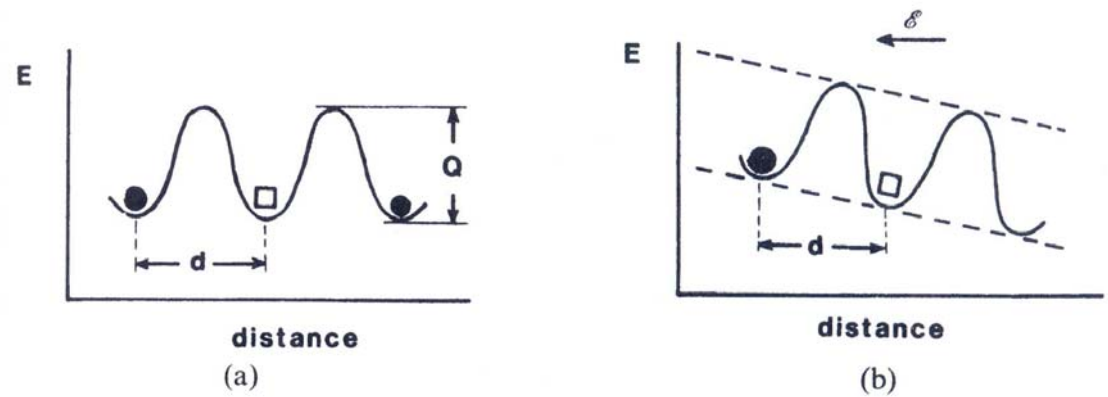


Figure 9.8. Schematic representation of a potential barrier, which an ion (●) has to overcome to exchange its site with a vacancy (□). (a) Without an external electric field; (b) with an external electric field. d = distance between two adjacent, equivalent lattice sites; Q = activation energy.

N_{ion}: number of ions per unit volume that can change their position under the influence of an electric filed

μ_{ion} : the mobility of ions

The conditions for ions to move in a crystalline solid

1. They must have sufficient energy to pass over an *energy barrier.* (Fig. 9.8)

2. The lattice site next to a conducting ion must be empty. → ***N_{ion}*** depends on the vacancy concentration in the crystal (i.e., on the number of *Schotty defects*)

9.2 Ionic Conduction

Diffusion theory links the mobility of ions with the diffusion coefficient, ***D*** through Einstein relation

$$\mu_{\text{ion}} = \frac{De}{k_B T} \quad , \qquad D = D_0 \exp\left[-\left(\frac{Q}{k_B T}\right)\right]$$

Arrhenius equation

Q is the activation energy, D_0 is a pre-exponential factor that depends on the vibrational frequency of atoms and some structural parameter.

Combining with $\sigma_{\text{ion}} = N_{\text{ion}} e \mu_{\text{ion}}$ yields

$$\sigma_{\text{ion}} = \frac{N_{\text{ion}} e^2 D_0}{k_B T} \exp\left[-\left(\frac{Q}{k_B T}\right)\right] \qquad \sigma_{\text{ion}} = \sigma_0 \exp\left[-\left(\frac{Q}{k_B T}\right)\right]$$

$$\ln \sigma_{\text{ion}} = \ln \sigma_0 - \left(\frac{Q}{k_B}\right)\frac{1}{T}$$

9.2 Ionic Conduction

$$\ln \sigma_{\text{ion}} = \ln \sigma_0 - \left(\frac{Q}{k_B}\right)\frac{1}{T}$$

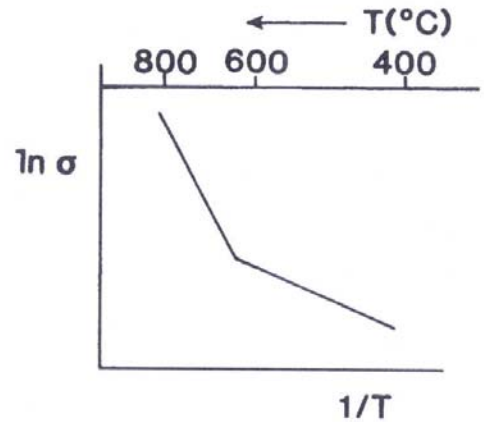


Figure 9.9. Schematic representation of $\ln \sigma$ versus $1/T$ for Na^+ ions in sodium chloride. (Arrhenius plot.)

- From the slopes of the straight lines in Arrhenius plots, the activation energy ***Q*** is calculated.

- In Fig. 9.9, two different activation barriers.

  - *Extrinsic region at low temperature*:
    Activation energy is small.
    The thermal energy is just sufficient to allow the hopping of ions already existing vacancy

  - *Intrinsic region at higher temperature:*
    The thermal energy is large enough to create additional vacancies.
    The related activation energy is thus the sum of the activation energies for vacancy creation and ion movement.

9.2 Ionic Conduction

Whenever vacant lattice site is created, an overall charge neutrality needs to be maintained.

- Both a cation and anion are removed from a lattice (**Schottky defect**)

- Formation of vacancy- interstitial pair (**Frenkel defect**)

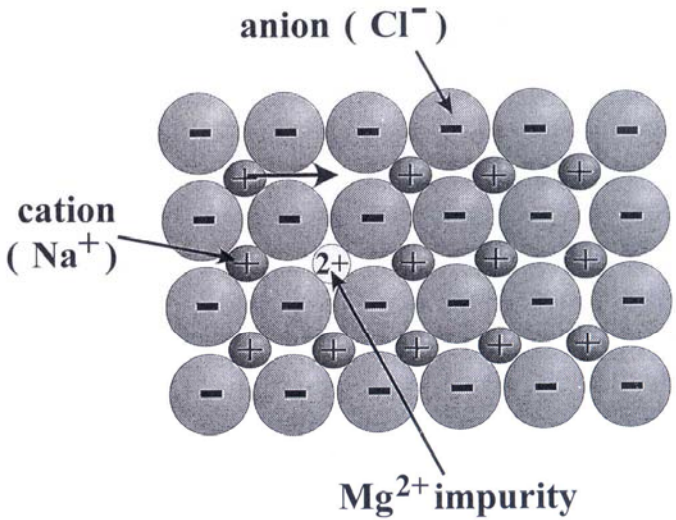


Figure 9.10. Schematic representation of a {100} plane of an ionic crystal having the NaCl structure. The diffusion of a cation into a cation vacancy is shown. Also depicted is the creation of a cation vacancy when replacing a Na^+ ion with a Mg^{2+} ion.

- Vacancies creation by differently charged impurities : By replacing a monovalent metal atom with a divalent atom a positively charged vacancy needs to be introduced.

(Examples)

1. Mg^{2+} ion substitutitution for a monovalent Na^+ ion: extra Na^+ ion has to be removed to restore charge neutrality (Fig.9.10).
2. Calcia(CaO)-stabilized Zirconia(ZrO_2): Ca^{2+} ions substitute for Zr^{4+} ions, and then an anion vacancy needs to be created to maintain charge neutrality.

9.3 Conduction in Metal Oxides

Metal oxide can be insulating, have metallic conduction properties, or be semiconducting : For understanding the mechanisms involved in metal oxides, their electronic configuration in the orbital (or band structure) should be considered. (Appendix 3. p.409)

1. TiO_2 (O : $1s^2\ 2s^2 2p^4$, Ti: $3d^2 4s^2$)

- Noble gas configuration, insulator

- Oxygen have four 2*p*-electrons in its outermost shell. Two more electrons will bring O^{2-} into the closed-shell configuration and four electrons are obviously needed to accomplish the same for two oxygen ions: 4 electrons are provided from Ti 3*d*- and 4*s*-shells.

- Since ionic bonds are involved, any attempted removal of electrons would require a considerable amount of thermal energy : insulator with wide band gap.

9.3 Conduction in Metal Oxides

2. TiO (O : $1s^2\ 2s^2 2p^4$, Ti: $3d^2 4s^2$)

- Metallic

- Only two titanium valence electrons are needed to fill the 2*p*-shell of one oxygen ion, two more titanium electrons are free to serve as conduction electron

3. ZnO (O : $1s^2\ 2s^2 2p^4$, Zn: $3p^{10} 4s^2$)

- Insulator for stoichiometric : a filled *2p*-band and an empty zinc 4*s*-band employing a gap energy of 3.3 eV

- *n*-type semiconductor for non-stoichiometric : if interstitial Zn atoms (or oxygen vacancy) are introduced into the lattice, then the valence electrons of these Zn interstitials are loosely bound to their nuclei ; first ionization energy is 0.05 eV (act as a donor)

9.3 Conduction in Metal Oxides

4. SnO_2 (some times doped with In_2O_3)

- Transparent in the visible region and a reasonable conductor in the 1 $\Omega^{-1}cm^{-1}$ range

- Optoelectronics to provide electrical contacts without blocking the light from reaching a device: **indium-tin-oxide (ITO)**

5. NiO (O : $1s^2\ 2s^2 2p^4$,Ni: $3p^8 4s^2$)

- Insulator for stoichiometric : a filled oxygen 2*p*-band and empty nickel 4*s*-band ; deep-lying localized electron states in the forbidden band close to the upper edge of the valence band are observed

- *p*-type semiconductor for nonstoichiometric; obtained by removing some nickel atoms, thus creating vacancies.

9.4 Amorphous Materials (Metallic Glasses)

Structural features of amorphous materials

- Random arrangement of atoms
- Short range order
- Diffraction patterns consist of diffuse rings
- Positional disorder (in case of pure materials), compositional disorder (more than one element): the individual species are randomly distributed

Many elements and compounds that are generally known to be crystalline under equilibrium conditions can also be obtained in the nonequilibrium amorphous state by applying rapid solidification techniques: fast quenching, melt spinning, vapor deposition, sputtering, radiation damage, filamentary casting in continuous operation, spark-processing, etc.

The degree of amorphousness (or, the degree of short range order) can be varied by the severity of quench

ex) **metallic glasses** or *glassy metals*, amorphous semiconductor

9.4 Amorphous Materials (Metallic Glasses)

Atomic structure of amorphous metals and alloy

- Dense random packing of hard spheres model (Fig. 9.11) (Bernal model) : ideal
- In transition metal-metalloid compounds (such as Ni-P) it is thought that the small metalloid atoms occupy the holes which occur as a consequence of this packing (Bern-Polk model)

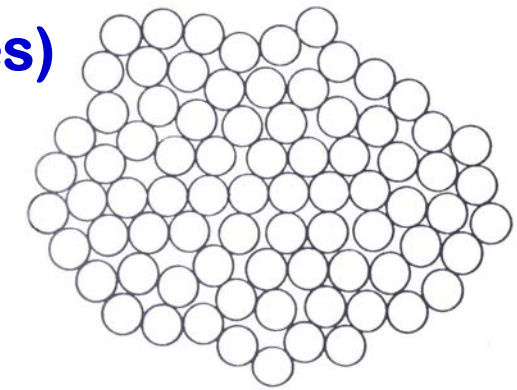


Figure 9.11. Two-dimensional schematic representation of a dense random packing of hard spheres (Bernal model).

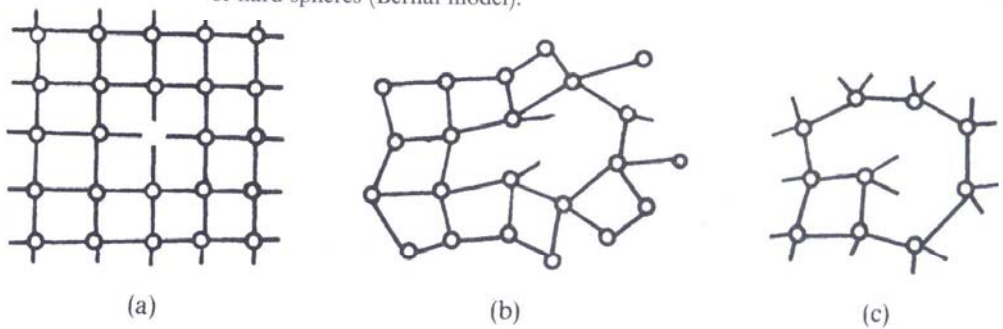


Figure 9.12. Defects in crystalline and amorphous silicon. (a) Monovacancy in a crystalline semiconductor; (b) one and (c) two dangling bonds in a continuous random network of an amorphous semiconductor. (Note the deviations in the interatomic distances and bond angles.)

The atoms in amorphous semiconductors : no close packing

- Atoms of group IV elements (covalent bond): Often arranged in a continuous random network with ordering up to the third or fourth nearest neighbors (Fig 9.12b,c)
- Amorphous pure silicon contains numerous dangling bonds similar to those found in the crystalline silicon in the presence of vacancies (Fig 9.12a)

9.4 Amorphous Materials (Metallic Glasses)

The calculation of electronic structure for amorphous metals and alloys: **cluster model approach**

e.g.) Fig 9.13 : the electronic structure of amorphous Zr-Cu

- A series of clusters were assumed which exhibit the symmetry of closed-packed lattice fcc (as Cu) and hcp (as for Zr)

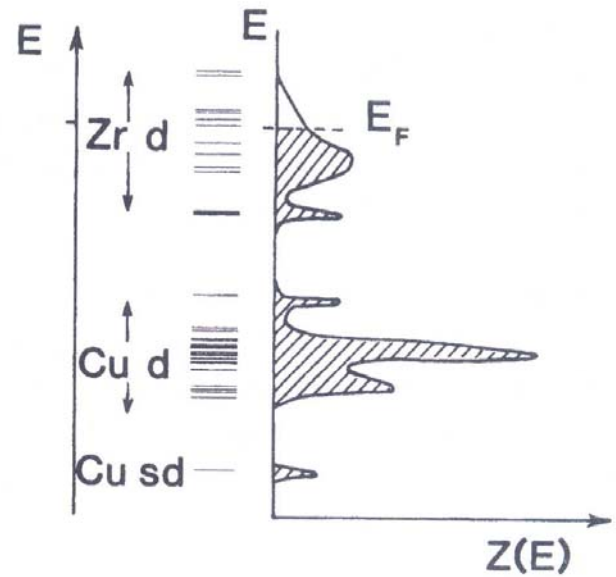


Figure 9.13. Schematic representation of the molecular orbital energy level diagram and the density of states curves for Zr–Cu clusters. The calculated density of states curves agree reasonably well with photoemission experiments.

- Partially filled electron states: *metal-like* conduction, $Z(E)$ near E_F is small, which suggest relatively small values for conductivity. (σ for Cu-Zr = 5×10^3 / Ω *cm*)

- The electrical resistivity of many metallic glasses (such as $Pd_{80}Si_{20}$ or $Fe_{32}Ni_{36}Cr_{14}P_{12}B_{16}$) stays constant over a wide temperature range : resistance standards

9.4 Amorphous Materials (Metallic Glasses)

The energy level diagram and density of states curves for amorphous semiconductors

- stronger binding forces between the atoms in covalently bound materials, the valence electrons are tightly bound, or localized → the density of state for localized state extends into the "band gap" (Fig 9.14)

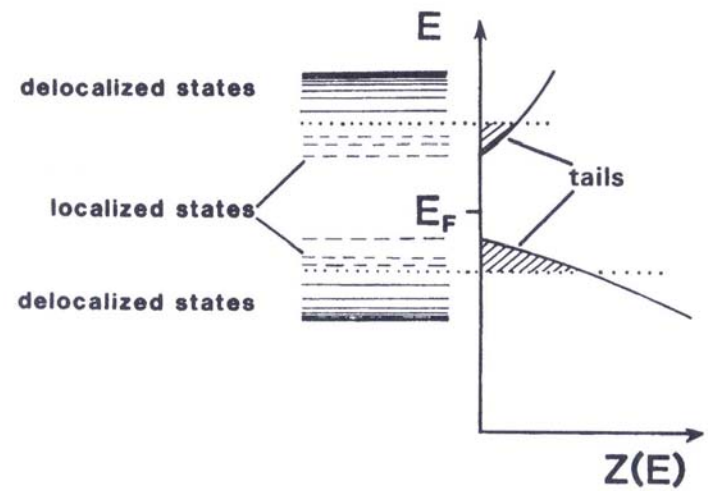


Figure 9.14. Localized and delocalized states and density of states $Z(E)$ for amorphous semiconductors. Note the band tails, which are caused by the localized states.

Electrical conductivity for amorphous semiconductors

$$\sigma_A = N_A e \mu_A$$

Density of carriers (N_A) in amorphous semiconductor is extremely small ; electrons are localized, mobility of charge carriers is small – incoherent scattering (absence of periodic lattice)

$$\sigma_A = \sigma_0 \exp\left[-\left(\frac{Q_A(T)}{k_B T}\right)\right]$$

Temperature-dependent activation process; activation energy Q_A

9.4. Amorphous Materials (Amorphous Semiconductor)

9.4.1. Xerography or electrophotography

- An important application of amorphous semiconductor : selenium, silicon

- When deposited on a cylindrically shaped metallic substrate, constitutes the photoreceptor drum (Fig. 9.15)

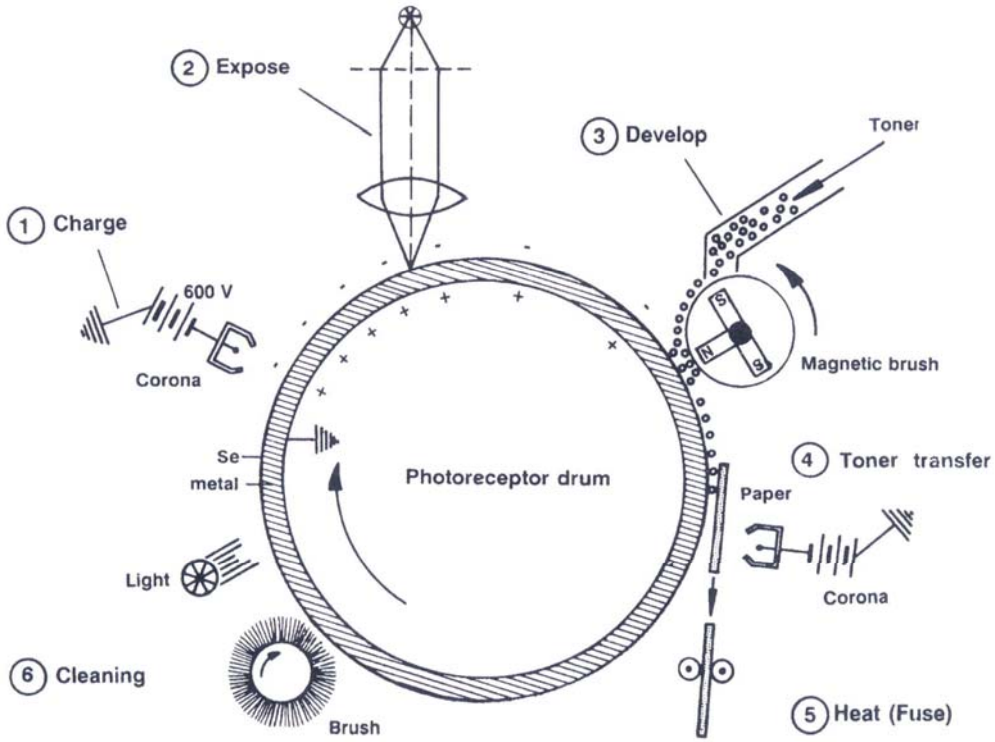


Figure 9.15. Schematic representation of the electrophotography process. The individual steps are explained in the text.

Before copying, the photoreceptor is charged by corona wire to which a high voltage is applied. 2. Light which have been reflected from the document to be copied fall on the photoreceptor, electron hall pair formed causing photoreceptor to become conducting. This step discharge the affected parts on the drum, creating a latent image on the photoreceptor. 3. Toner develop ; 4. Toner transfer to papers ; 5. Heat (toner is fused)

9.5 Dielectric Properties

Capacitance, *C*: the ability to store an electric charge, *q* per unit applied voltage, *V*.

$$C = \frac{q}{V} \quad \text{and} \quad C = \varepsilon\, \varepsilon_0 \frac{A}{L}$$

where $$\varepsilon = \frac{C}{C_{vac}}$$

Area, *A* of the plate, the distance, *L* between electrodes

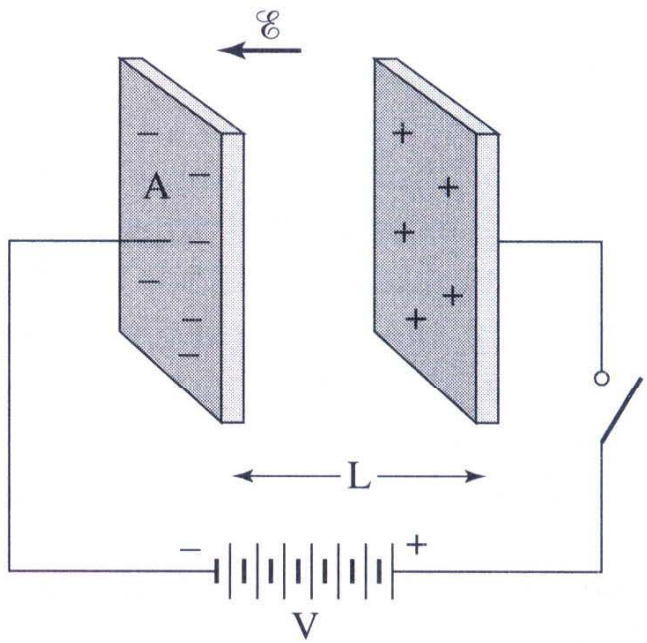


Figure 9.16. Two metal plates, separated by a distance, *L*, can store electric energy after having been charged momentarily by a battery.

Determine the magnitude of the added storage capability;

ε : dielectric constant (unitless), or *relative permittivity,* ε_r

ε_0 : permittivity of empty space , 8.85 $\times$ 10^{-12} F/m

9.5 Dielectric Properties

Table 9.1. DC dielectric constants of some materials

Potassium tantalate niobate	6000	
Barium titanate ($BaTiO_3$)	4000	Ferroelectric
Potassium Niobate ($KNbO_3$)	700	
Rochelle salt ($NaKC_4H_4O_6 \cdot 4H_2O$)	170	
Water	81.1	
Acetone	20	
Silicon	11.8	
GaAs	10.9	
Marble	8.5	
Soda-lime-glass	6.9	
Porcelain	6.0	
Epoxy	4.0	
Fused silica	4.0	Dielectric
Nylon 6,6	4.0	
PVC	3.5	
Ice	3.0	
Amber	2.8	
Polyethylene	2.3	
Paraffin	2.0	
Air	1.000576	

9.5 Dielectric Properties

Electric dipole moment

$$p = q \cdot x$$

x **is the separation between the positive and negative charge (Fig 9.17c)**

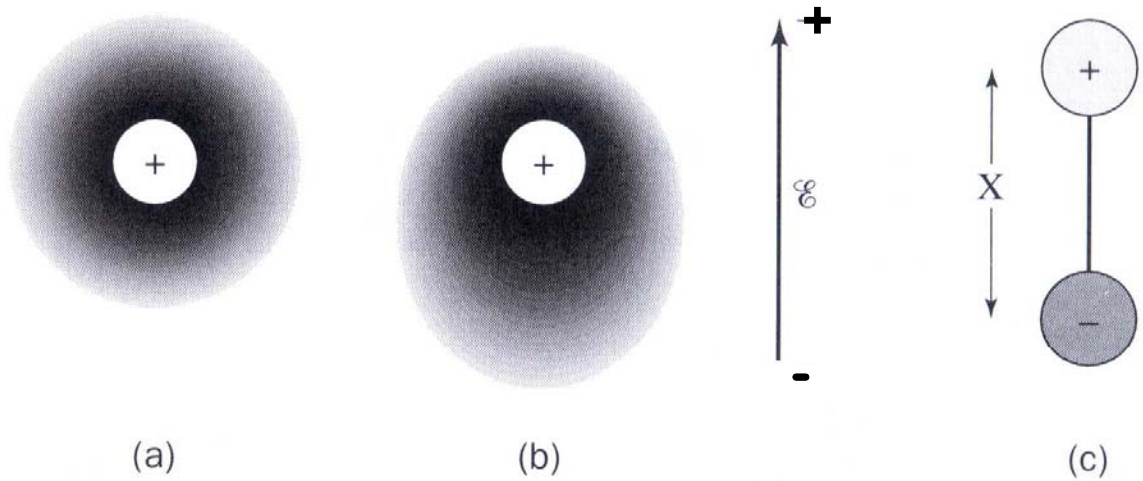


Figure 9.17. An atom is represented by a positively charged core and a surrounding, negatively charged, electron cloud (a) in equilibrium and (b) in an external electric field. (c) Schematic representation of an electric dipole as, for example, created by separation of the negative and positive charges by an electric field, as seen in (b).

- The dipole moment is a vector pointing from the negative to charge.

Polarization : the process of dipole formation (or alignment of already existing dipoles) under the influence of an external electric field that has an electric field strength, *E*

9.5 Dielectric Properties

- Dipole formation of all involved atoms within a dielectric material cause a charge redistribution so that the surface nearest to the positive capacitor plate is negatively charge (and vice versa): Fig. 9.18a

- Electric field lines within a dielectric material are weakened due to polarization: Fig 9.18b

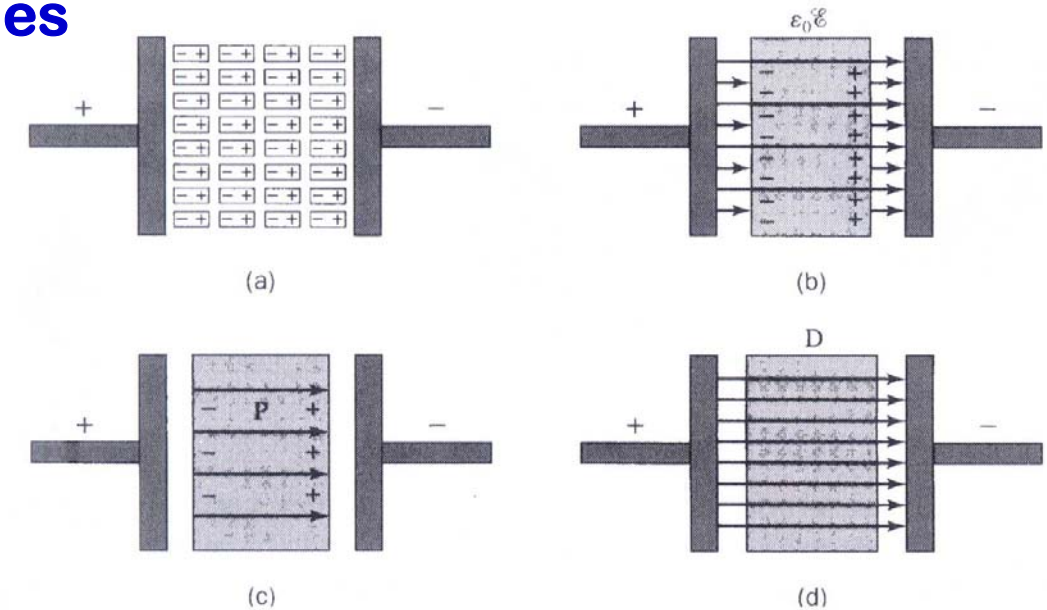


Figure 9.18. Schematic representation of two capacitor plates between which a dielectric material is inserted. (a) Induction of electric dipoles of opposite charge. (b) Weakening of the electric field *within* the dielectric material [Eq. (9.13)]. (c) The direction of the polarization vector is from the negative induced charge to the positive induced charge see Fig. 9.17(b). (d) The dielectric displacement, D, within the dielectric material is the sum of $\varepsilon_0\mathscr{E}$ and P [Eq. (9.15)].

$$E = \frac{E_{\text{vac}}}{\varepsilon}$$

$$D = \varepsilon\varepsilon_0 E = \frac{q}{A}$$

$$D = \varepsilon_0 E + P$$

Dielectric displacement, *D* or surface charge density

Dielectric polarization *P*, the induced electric dipole moment per unit volume (Fig 9.18 c and d)

Units for *D* and *P* are C m^{-2}

9.5 Dielectric Properties

The mechanism of polarization

- **Electric polarization** (Fig 9.17)

- **Ionic polarization**: cations and anions are somewhat displaced from the equilibrium positions under the influence of an external field and thus give rise to a net dipole moment

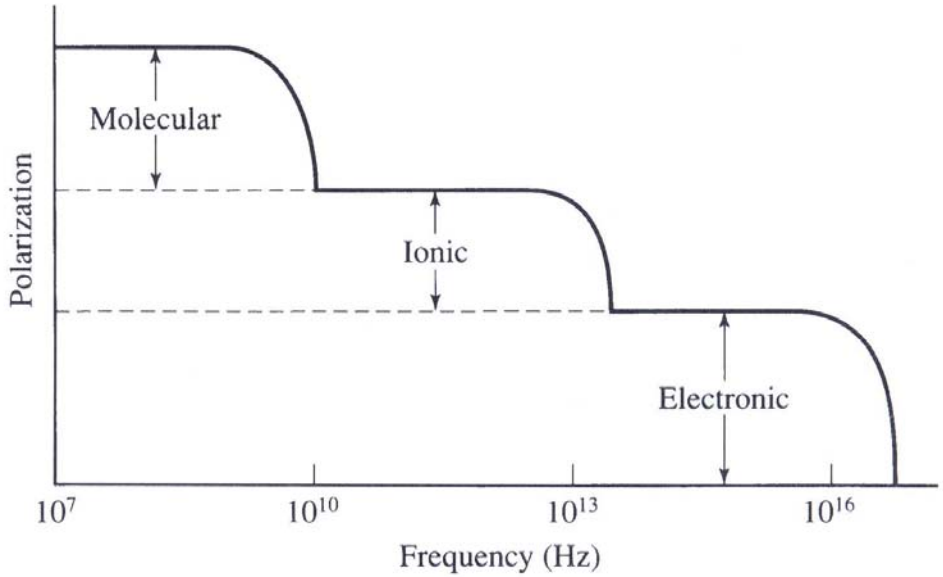


Figure 9.19. Schematic representation of the polarization as a function of excitation frequency for different polarization mechanisms.

- **Orientation polarization**: permanent dipole align to the external electric filed; *molecular polarization*

How quickly do the dipoles to reorient or to align under a rapidly changing electric filed (in alternating circuit)

Polarization mechanisms which can respond equally quick to an alternating electric field (Fig. 9.19)

9.5 Ferroelectricity, Piezoelectricity, and Electrostriction

Ferroelectric materials

- A spontaneous polarization without the presence of an external electric field : suitable for the manufacturing of small sized, highly efficient capacitors

- Hysteresis loop (Fig. 9.20)

  P_s: saturation polarization

  P_r : remanent polarization

  E_c : coercive filed

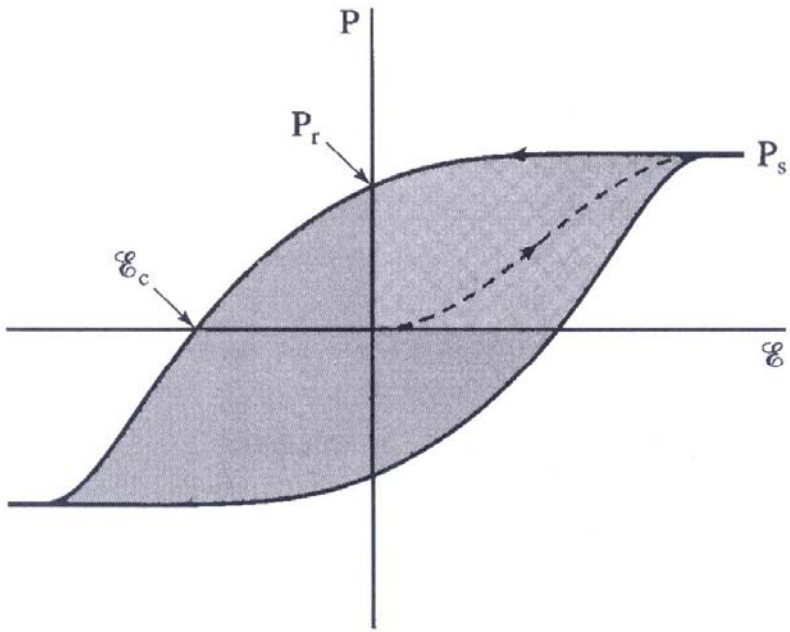


Figure 9.20. Schematic representation of a hysteresis loop for a *ferroelectric* material in an electric field. Compare to Figure 15.6.

- A critical temperature (called, Curie temperature) exists, above which the ferroelectric effect are destroyed and the material becomes paraelectric (a kind of dielectric)

9.5 Ferroelectricity, Piezoelectricity, and Electrostriction

Why do certain material possess spontaneous polarization?

- Tetragonal $BaTiO_3$: the negatively charged oxygen ions and the positively charged Ti^{4+} ion are slightly displaced from their symmetrical position (Fig 9.21)

- A large number of such dipole moment line up in a clusters (also called *domains*)

- In virgin state, the polarization directions of the individual domains are randomly oriented: no net polarization

- An external field orients the dipoles of favorably oriented domains parallel to *E*: those domains in which the dipoles are already nearly parallel to *E* at the expense of unfavorably oriented domains

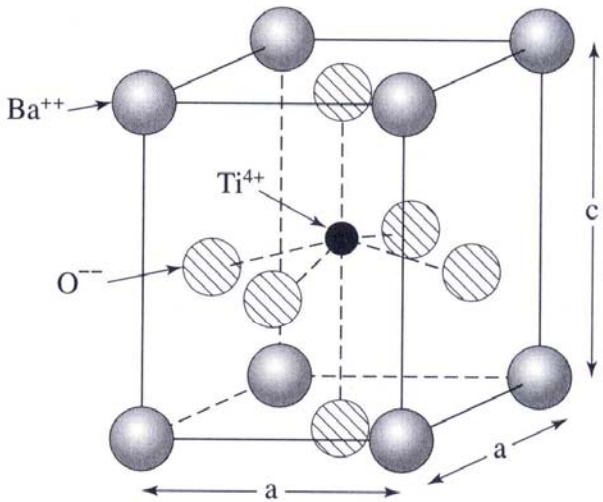


Figure 9.21. Tetragonal crystal structure of barium titanate at room temperature. Note the upward displacement of the Ti^{4+} ion in the center compared to the downward displacement of all surrounding O^{2-} ions. $a = 0.398$ nm; $c = 0.403$ nm.

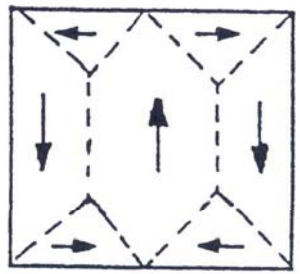


Figure 9.22. Schematic representation of spontaneous alignments of electric dipoles within a domain and random alignment of the dipole moments of several domains in a ferroelectric material such as $BaTiO_3$. Compare to Figure 15.9.

9.5 Ferroelectricity, Piezoelectricity, and Electrostriction

- **Piezoelectricity** : If pressure is applied to a ferroelectric material, such as $BaTiO_3$, a change in the polarization occur, which results in a small voltage across the sample

Transducers : convert mechanical strain onto electricity ; strain gages, microphones, sonar detectors, and phonograph pickups

- **Electrostriction** : inverse mechanism of piezoelectricity; an electric field produce a change on dimensions in a ferroelectric material

An earphone, quartz crystal resonator (which is used in electronic devices as a *frequency selective element*)

Polarization P

Definition

▶ P **is defined by the electric dipole moment per unit volume of material :** $P = Np$

where N **= number of dipoles/unit volume,** p **= avg. dipole moment.**

▶ P **also represents the surface charge density of the** ***bound charge***

The total charge Q

$$Q = C_o V \ (= Q_f : \textit{free charge})$$
$$+ \ (C - C_o)V \ (= Q_b : \textit{bound charge})$$

The total charge density D

$$D = Q/A = Q_f/A + Q_b/A = \varepsilon E$$

where $Q_f/A = \varepsilon_o E$ (Gauss Law)

and $P = Q_b d/\textit{volume of the dielectric material}$

$(\because p = Q_b d) \quad = Q_b/A$

Then $D = \varepsilon_o E + P = \varepsilon E = \varepsilon_r \varepsilon_o E$ **since** $\varepsilon_r = C/C_o = \varepsilon/\varepsilon_o$

$$\boxed{P = \varepsilon E - \varepsilon_o E}$$

Dielectric Constant ε

material property determining the capacitance C

The charge on a capacitor,

$$Q = CV$$

where C [Farad (F)] , Q [Coulomb (C)], V [Volt (V)].

Since $Q = AD = A\varepsilon E$, $C = A\varepsilon E/V = \frac{A}{d}\varepsilon$

$$\boxed{C = \frac{\epsilon}{\epsilon_o} C_o = \varepsilon_r C_o}$$

C_o (capacitance in vacuum) = $\frac{A}{d}\varepsilon_o$

ε_o : permittivity (dielectric constant) of a vacuum,

ε_r : relative permittivity (dielectric constant)

$$\varepsilon_r = C/C_o = \varepsilon/\varepsilon_o$$

Also

$$P = (\varepsilon - \varepsilon_o)E = \varepsilon_o(\varepsilon_r - 1)E$$

$$\chi = \varepsilon_r - 1 = \frac{P}{\epsilon_o E}$$

$$Q_f = \frac{Q}{\epsilon_r} \quad \textbf{(free charge)}$$

$$Q_f = Q(1 - \frac{1}{\epsilon_r}) \quad \textbf{(bound charge)}$$

Dielectric Loss Factor $tan\delta$

represents the relative expenditure of energy to obtain a given amount of charge storage

With a sinusoidal voltage $V = V_o \exp i\omega t$, since $Q = \int I dt$,

$$I = dQ/dt = C\frac{dV}{dt}.$$

Then, a charging current I_c is given by

$$I_c = i\omega CV = \omega CV_o exp\ [i(\omega t + \pi/2)]$$

∴ 90° advanced in phase compared with V in the ideal dielectric.

For real dielectrics, (90° − δ) advanced in phase occurs due to a loss.

$E = V/d$, $E = E_o \exp(i\omega t)$ **and** $D = D_o \exp(i\omega t - \delta)$

Since $D = \varepsilon E = \varepsilon E_o \exp(i\omega t)$

$$\varepsilon = (D_o/E_o)\exp(-\delta) = \varepsilon_s \exp(-\delta) = \varepsilon_s(\cos\delta - i\sin\delta)$$

where ε_s is the static dielectric constant. In terms of a complex dielectric constant

$$\varepsilon_r = \varepsilon_r' - i\varepsilon_r'' = (\varepsilon' - i\varepsilon'')/\varepsilon_o$$

$$\varepsilon_r' = \varepsilon_s \cos\delta,\ \varepsilon_r'' = \varepsilon_s \sin\delta$$

The loss tangent, $tan\delta = \varepsilon_r'/\varepsilon_r'' = \varepsilon'/\varepsilon''$

Then the total current I in terms of ε_r,

$$I = dQ/dt = C\frac{dV}{dt} = i\omega CV = \varepsilon_r C_0 i\omega V$$

$$= (\varepsilon_r' - i\varepsilon_r'')C_0 i\omega V$$

$$= i\omega\varepsilon_r' C_0 V + \omega\varepsilon_r'' C_0 V$$

I_c**(charging current)** $= i\omega\varepsilon_r' C_0 V = i\omega CV = i\omega\varepsilon' E$

I_l**(loss current)** $= \omega\varepsilon_r'' C_0 V = \omega\varepsilon'' CV$

$$= \omega\varepsilon'' E = I_c \tan\delta = \sigma E$$

where σ is the dielectric conductivity

The corresponding energy loss W at the max. voltage V_0

$$W = 2\pi\varepsilon' \frac{V_o^2}{2} \tan\delta \quad \text{per cycle}$$

$$= 2\pi f\varepsilon' \frac{V_o^2}{2} \tan\delta \quad \text{per second}$$

- Dielectric Strength: ***The ability to withstand large field strengths without electrical breakdown.***

Ferroelectricity

The spontaneous alignment of electrical dipoles by their mutual interaction (spontaneous polarization P_s)

Since the average dipole moment *p* of the charged particles is proportional to the local electric field *E'*,

$$p = \alpha E'$$

Then $$P = N\alpha E' = \frac{N\alpha E}{1 - N\alpha/3\epsilon_o}$$

since $E' = E + \frac{P}{3\epsilon_o}$ **(Mosotti field)**

$$\chi = \varepsilon_r - 1 = \frac{P}{\epsilon_o E} = \frac{N\alpha/\epsilon_o}{1 - N\alpha/3\epsilon_o}$$

(Clausius-Mosotti equation)

Therefore, when $N\alpha/3\varepsilon_o \rightarrow 1$, the *P*, χ and ε_r must go to infinity.

As the local fields *E'* is proportional to the polarization *P*, spontaneous polarization is expected at some low temperature at which the randomizing effect of thermal energy is overcome and all the electric dipoles line up in parallel arrays.

If the orientation polarizability is much larger than that

for the electronic and ionic portions,

$\alpha_o = C/k_B T$ **where C is Curie constant.**

At T_c (Curie temp),

$$T_c = NC/3k_B\varepsilon_0 = N\alpha_o T/3\varepsilon_0$$

Consequently,

Below T_c, spontaneous polarization occurs

Above T_c, $\chi = \varepsilon_r - 1 = \frac{P}{\varepsilon_o E} = \frac{3T_c}{T - T_c}$

Curie-Weiss Law

Characteristics of Ferroelectrics

- **Appearance of very high dielectric constants**
- **A hysteresis loop for polarization**
- **The existence of ferroelectric domains**

Electromagnetic Theory : Maxwell Equations

Light Waves

(Electrons in Solids, 3rd Ed., R. H. Bube)

Light Waves

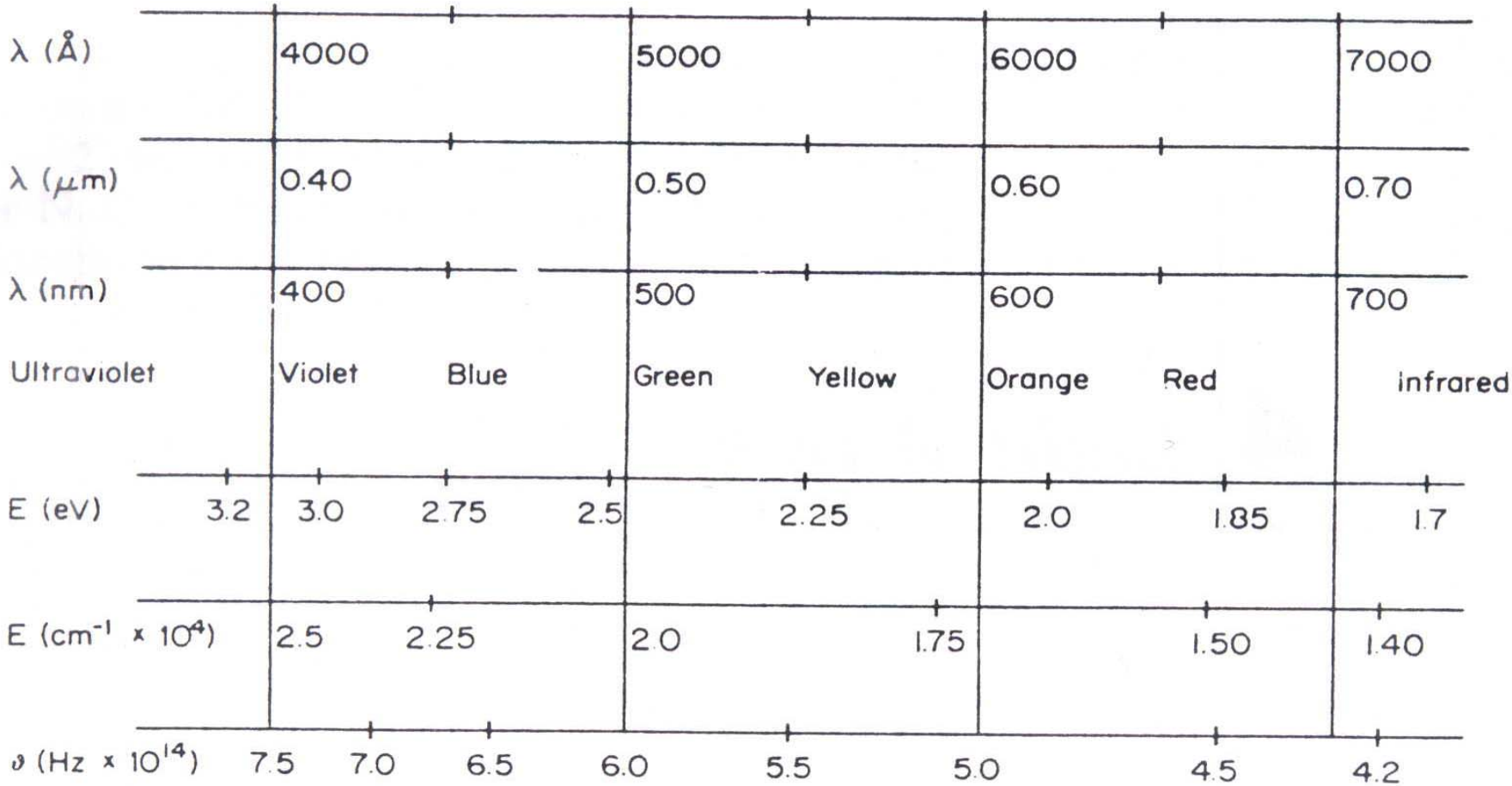


FIG. 4.1 The near-visible region of the electromagnetic spectrum with a variety of wavelenth, energy, wave-number, and frequency scales.

Light Waves

Properties of electric and magnetic fields

Wave equations for EM waves:

Maxwell's equations

TABLE 4.1 Maxwell's Equations

	Gaussian Units	SI Units
1.	$\nabla \cdot \mathbf{D} = 4\pi\rho$	$\nabla \cdot \mathbf{D} = \rho$
2.	$\nabla \cdot \mathbf{B} = 0$	$\nabla \cdot \mathbf{B} = 0$
3.	$\nabla \times \mathcal{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}$	$\nabla \times \mathcal{E} = -\frac{\partial \mathbf{B}}{\partial t}$
4.	$\nabla \times \mathbf{H} = \frac{1}{c}\frac{\partial \mathcal{E}}{\partial t} + \frac{4\pi \mathbf{J}}{c}$	$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J}$

D—electric displacement

$\mathbf{D} = \varepsilon_r \mathcal{E}$ $\qquad$ $\mathbf{D} = \varepsilon_r \varepsilon_o \mathcal{E}$

ε_r—dielectric constant; $\varepsilon_o = (36\pi \times 10^9)^{-1}$ F/m—permittivity of free space

$\mathcal{E}$—electric field

ρ—charge density

B—magnetic induction

$\mathbf{B} = \mu_r \mathbf{H}$ $\qquad$ $\mathbf{B} = \mu_r \mu_o \mathbf{H}$

μ_r—permeability; $\mu_0 = 4\pi \times 10^{-7}$ H/m—permeability of free space

H—magnetic field

$\mathbf{J} = \sigma\mathcal{E}$—current density; σ—electrical conductivity

The First Maxwell Equation : $\nabla \bullet \mathbf{D} = \rho$ in SI unit

From coulomb's Law: the force on a charge *q* due to another charge *q'* separated by distance *r*

$$F = \frac{qq'}{4\pi\varepsilon_0 r^2}$$

If we define the electric field generated from *q* is E_q, the force on a charge *q'* in *free space* is given by $F = q' E_q$

$$E_q = \frac{q}{4\pi\varepsilon_0 r^2}$$

Electric field due to charge *q* in the dielectric material with dielectric constant ε_r

$$E_q = \frac{q}{4\pi\varepsilon_r \varepsilon_0 r^2}$$

Light Waves

Polarization, P : dielectric dipole moment per unit volume induced by the electric field

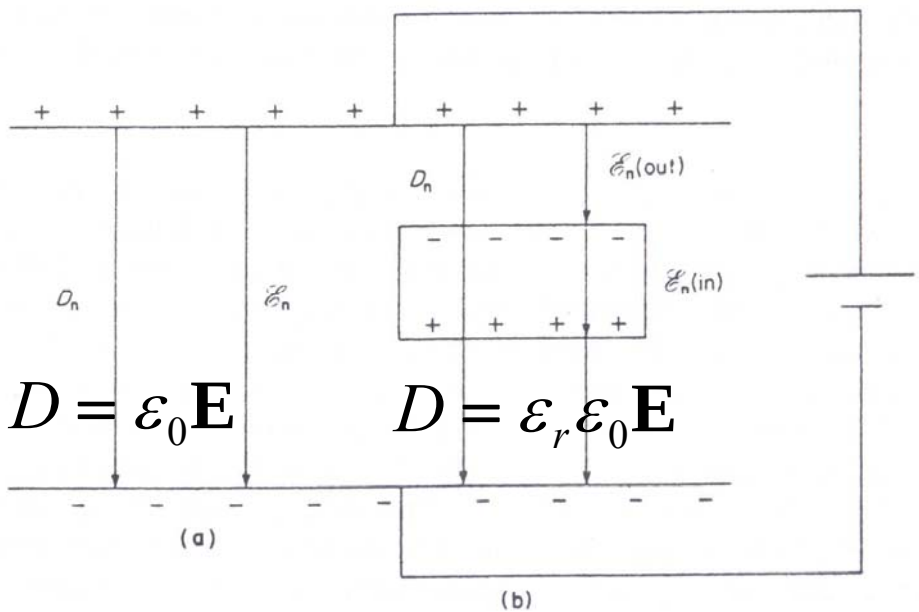


FIG. 4.2 Illustration of relationship between displacement **D** and electric field $\mathcal{E}$ with the simple case of a material between two condenser plates. (a) With no material between the plates the normal components are related $D_n = \varepsilon_0 \mathcal{E}_n$. (b) With polarizable material between the plates $D_n = \varepsilon_r \varepsilon_0 \mathcal{E}_n$ is the same both in free space and in the material, since it is conserved upon crossing the boundary. Because of the polarizability of the material, however, the electric field in the material is reduced so that $\mathcal{E}_n(\text{in}) = \mathcal{E}_n(\text{out})/\varepsilon_r$. Note that in this simple example, the tangential component of $\mathcal{E}$ that is conserved on crossing the boundary between the two materials is zero in all cases.

$$\mathbf{P} = N\mathbf{p} = Nq^*\mathbf{d}$$

Where *N* is the volume density of dipoles, p is the dipole moment, and *q is the charge involved in the dipole moment, with positive and negative charges separated by distance *d***

Light Waves

The polarization is proportional to electric field $\mathbf{P} = \varepsilon_0 \chi \mathbf{E}$

Proportional constant, χ: dielectric susceptibility

Since the electric displacement, **D** is defined by

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 \varepsilon_r \mathbf{E}$$

Thus $\varepsilon_r = 1 + \chi$

Since there are a number of possible mechanism contributing the dielectric susceptibility (depending on frequency of EM waves)

$$\varepsilon_r = 1 + \sum_i \chi_i$$

For the displacement of atoms in the lattice χ_L and that of electrons in an atom, χ_e $\varepsilon_{r(lo)} = 1 + \chi_L + \chi_e$ $\varepsilon_{r(hi)} = 1 + \chi_e$

The following relation is a good indication of the relative degree of ionic binding for materials

$$\{[1/\varepsilon_{r(hi)}] - [1/\varepsilon_{r(lo)}]\} = \chi_L / [\varepsilon_{r(hi)} \varepsilon_{r(lo)}]$$

Light Waves

Consider charge *q* with spherical symmetry and $E_q(r)$ at a distance *r*

$$E_q = \frac{q}{4\pi\varepsilon_r\varepsilon_0 r^2}$$

Divergence theorem

$$\oiint_A \mathbf{F}\cdot dS = \iiint_V \nabla\cdot\mathbf{F}\,dV$$

$$4\pi r^2 E_q = \frac{q}{\varepsilon_r\varepsilon_0} \longrightarrow \int \mathbf{E}\cdot dS = \frac{q}{\varepsilon_r\varepsilon_0} \longrightarrow \int \nabla\cdot\mathbf{E}\,dV = \int \frac{\rho}{\varepsilon_r\varepsilon_0}\,dV$$

By writing $\mathbf{D} = \varepsilon_0\varepsilon_r\mathbf{E}$, $\nabla \bullet \mathbf{D} = \rho$

The first Maxwell Equation for an isotropic and homogeneous material.

$\mathbf{E} = -\nabla\phi$ where ϕ the is called electrostatic potential

$$\frac{\partial^2\phi}{\partial x^2} = -\frac{\rho}{\varepsilon_r\varepsilon_0}$$

Poisson's Equation

The Second Maxwell Equation

$$\nabla \bullet \mathbf{B} = 0$$

"Isolated magnetic poles do not exist"

Only magnetic dipoles exist. A line of force starting on a "North" pole is terminated on a "South pole". No divergence of magnetic field line.

When we apply a magnetic field to a material, the magnetization M

$$\mathbf{M} = \kappa \mathbf{H}$$

Where κ is the magnetic susceptibility

A quantity B is conserved at an interface even when magnetization is present

$$\mathbf{B} = \mu_0 \mathbf{H} + \mu_0 \mathbf{M} \quad \text{(in SI unit)}$$

$$\mu_r = 1 + \kappa$$

$$\mathbf{B} = \mathbf{H} + 4\pi \mathbf{M} \quad \text{(in cgs unit)}$$

$$\mu_r = 1 + 4\pi\kappa$$

Light Waves

The Third Maxwell Equation $\nabla \times \mathbf{E} = -\dfrac{\partial \mathbf{B}}{\partial t}$

When a wire is moved into or out of the pole of magnet. The wire will be subjected to a changing magnetic flux $\partial\Phi / \partial t$, with $\Phi = \int \mathbf{B} \bullet \mathrm{d}\mathbf{S}$

A potential difference ϕ has been induced in the wire with a value which can be given simply by

$$\phi = -\frac{\partial \Phi}{\partial t}$$

ϕ : a line integral of electric field **E**

$$\int \mathbf{E} \cdot \mathbf{dl} = -\int \frac{\partial \mathrm{B}}{\partial t} \cdot \mathbf{dS} \longrightarrow \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

By Stoke's Theorem

$$\oint_C \mathbf{F} \cdot d\mathbf{l} = \iint_A \nabla \times \mathbf{F} \cdot d\mathbf{S}$$

The Fourth Maxwell Equation

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J}$$

" A continuous electrical current I or a displacement current ($\frac{\partial \mathbf{D}}{\partial t}$) gives rise to a magnetic field"

Consider the attempt to measure a magnetic field around a wire carrying a current. At distance *r* from a wire direct current I

$$\mathbf{H} = \frac{\mathbf{I}}{2\pi r}$$

$$\int \mathbf{H} \cdot \mathbf{dl} = \int \frac{\partial \mathbf{D}}{\partial t} \cdot \mathbf{dS} + \mathbf{I}$$

$\frac{\partial \mathbf{D}}{\partial t}$ **displacement current**

By Stoke's Theorem and $\mathbf{I} = \int \mathbf{J} \bullet d\mathbf{S}$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J}$$

where J is electrical current density

$$\mathbf{J} = \sigma \mathbf{E}$$

Dielectric Relaxation Time

Suppose that a charge is placed on a neutral material. The length of time it takes for this charge to relax either to a uniform charge density if the material is electrically isolated, or to zero, restoring the neutral state, by the excess charge leaking off to ground: dielectric relaxation time, τ_{dr}

$$\nabla \bullet \nabla \times \mathbf{A} = 0$$

A is any vector: applied to the 4th Maxwell Equation

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J}$$

$$\nabla \bullet \nabla \times \mathbf{H} = 0, \quad \mathbf{J} = \sigma \mathbf{E} \qquad \mathbf{D} = \varepsilon_0 \varepsilon_r \mathbf{E}$$

$$0 = \frac{\partial (\nabla \bullet \mathbf{D})}{\partial t} + \nabla \bullet \mathbf{J}$$

1st Maxwell equation

$$\frac{\partial \rho}{\partial t} = -\frac{\sigma \rho}{\varepsilon_r \varepsilon_0} \xrightarrow{\text{solution}} \rho = \rho_0 \exp\left(-\frac{t}{\tau_{dr}}\right) \qquad \tau_{dr} = \frac{\varepsilon_r \varepsilon_0}{\sigma}$$

Electromagnetic wave equation

Deviation of wave equation from Maxwell Equation

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$ (3rd Maxwell equation)

$$\nabla \times \nabla \times \mathbf{E} = \nabla(\nabla \bullet \mathbf{E}) - \nabla^2 \mathbf{E} \quad , \quad \mathbf{B} = \mu_0 \mu_r \mathbf{H} \quad , \quad \nabla \bullet E = \frac{\rho}{\varepsilon_r \varepsilon_0}$$

$$-\mu_{\mathrm{r}} \mu_0 \frac{\partial}{\partial t}(\nabla \times \mathbf{H}) = \frac{\nabla \rho}{\varepsilon_r \varepsilon_0} - \nabla^2 \mathbf{E}$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J} \quad , \quad \mathbf{D} = \varepsilon_0 \varepsilon_r \mathbf{E} \quad , \quad \mathbf{J} = \sigma \mathbf{E}$$

$$-\varepsilon_{\mathrm{r}} \varepsilon_0 \mu_{\mathrm{r}} \mu_0 \frac{\partial^2 \mathbf{E}}{\partial t^2} - \mu_{\mathrm{r}} \mu_0 \sigma \frac{\partial \mathbf{E}}{\partial t} = \frac{\nabla \rho}{\varepsilon_r \varepsilon_0} - \nabla^2 \mathbf{E}$$

Electromagnetic wave equation (continued)

We can neglect the first term on the right of the equation if we are interested in the steady-state condition after the decay of any such space charge

$$\nabla^2 \mathbf{E} = \varepsilon_r \varepsilon_0 \mu_r \mu_0 \frac{\partial^2 \mathbf{E}}{\partial t^2} + \mu_r \mu_0 \sigma \frac{\partial \mathbf{E}}{\partial t}$$

If we calculate $\nabla \times \nabla \times \mathbf{H}$, rather than $\nabla \times \nabla \times \mathbf{E}$

We obtain the same form of equations for the magnetic field **H**

$$\nabla^2 \mathbf{H} = \varepsilon_r \varepsilon_0 \mu_r \mu_0 \frac{\partial^2 \mathbf{H}}{\partial t^2} + \mu_r \mu_0 \sigma \frac{\partial \mathbf{H}}{\partial t}$$

Electromagnetic wave equation: the case of no absorption

In the absence of all absorption processes: a first time derivative term of the EM equation equal to zero: then EM equation → "Harmonic wave"

$$\nabla^2 \mathbf{E} = \varepsilon_r \varepsilon_0 \mu_r \mu_0 \frac{\partial^2 \mathbf{E}}{\partial t^2} \qquad \nabla^2 \mathbf{H} = \varepsilon_r \varepsilon_0 \mu_r \mu_0 \frac{\partial^2 \mathbf{H}}{\partial t^2}$$

Solution of these equations have the form

$$\mathbf{E} = \mathbf{E_0} \exp\left[i(\mathbf{k} \cdot \mathbf{r} - \omega t)\right] \qquad \mathbf{H} = \mathbf{H_0} \exp\left[i(\mathbf{k} \cdot \mathbf{r} - \omega t)\right]$$

In the form of EM wave equation, we can conclude immediately the phase velocity of the electromagnetic waves is given by

$$\upsilon = \frac{1}{\left(\varepsilon_r \varepsilon_0 \mu_r \mu_0\right)^{1/2}} = c, \quad \text{in vacuum} \quad c = \left(\varepsilon_0 \mu_0\right)^{-1/2}$$

Appendix: The Divergence Theorem and Stoke's Theorem

The Divergence Theorem: Because of the definition of the divergence, it can be shown that

$$\int_V \nabla \bullet \mathbf{A} dV = \int_V \mathbf{A} \bullet \mathbf{n} dS$$

Thus converting a volume integral of the divergence of **A** into surface integral of the scalar product of **A** with the vector **n**, the outward drawn unit vector normal to ***dS***

Stoke's Theorem: It follows from the properties of the curl that

$$\int_s \mathbf{n} \bullet (\nabla \times \mathbf{F}) dS = \oint \mathbf{F} \bullet \mathrm{d}\mathbf{s}$$

thus converting a surface integral of the curl **F** to a line integral of **F** over a closed path on the surface

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

Introduction

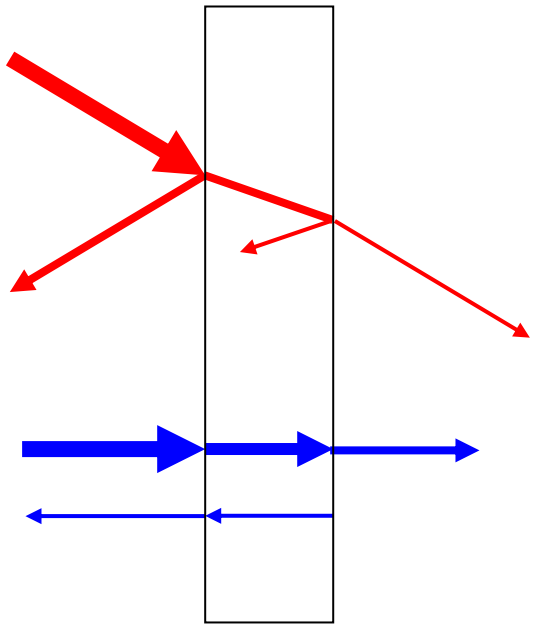
- ✓ The interactions of light with the valence electrons of a material is postulated to be responsible for the optical properties.
- ✓ Light comprises only extremely small segment of the entire electromagnetic spectrum (Fig 10.1)
- ✓ Optical methods are among the most important tools for elucidating the electron structure of matter
- ✓ Optical devices : lasers, photodetectors, waveguides, light-emitting diodes, flat-panel displays
- ✓ Applications for communication : fiber optics, medical diagnostics, night viewing, solar applications, optical computing and etc..
- ✓ Traditional utilizations: widows, antireflection coating; lenses, mirrors, etc..

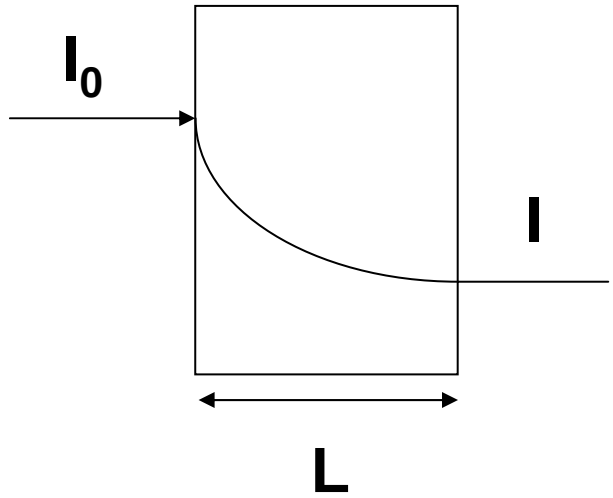
cf) BBR (black body radiation)

Introduction

Interactions between light and matter

- Refraction
- Reflection
- Transmission
- Absorption
- Luminescence





$I/I_0 = ?$

What is light?

Light

- Speed: c~$3x10^{10}$ cm/s in vacuum
- Ray: geometric optics such as lens, mirror
- Electromagnetic wave: refraction, reflection, interference, diffraction, hologram, etc.
- A stream of photons: absorption and emission

Spectrum (wavelength) of light

γ-ray (10^{-2} Å) ~ X-ray (1 Å) ~ UV(100 nm)
~ visible (400nm (blue) ~ 700nm (red))
~ IR (~10 μm) ~ microwave (GHz) ~ radio (MHz-KHz)

Introduction

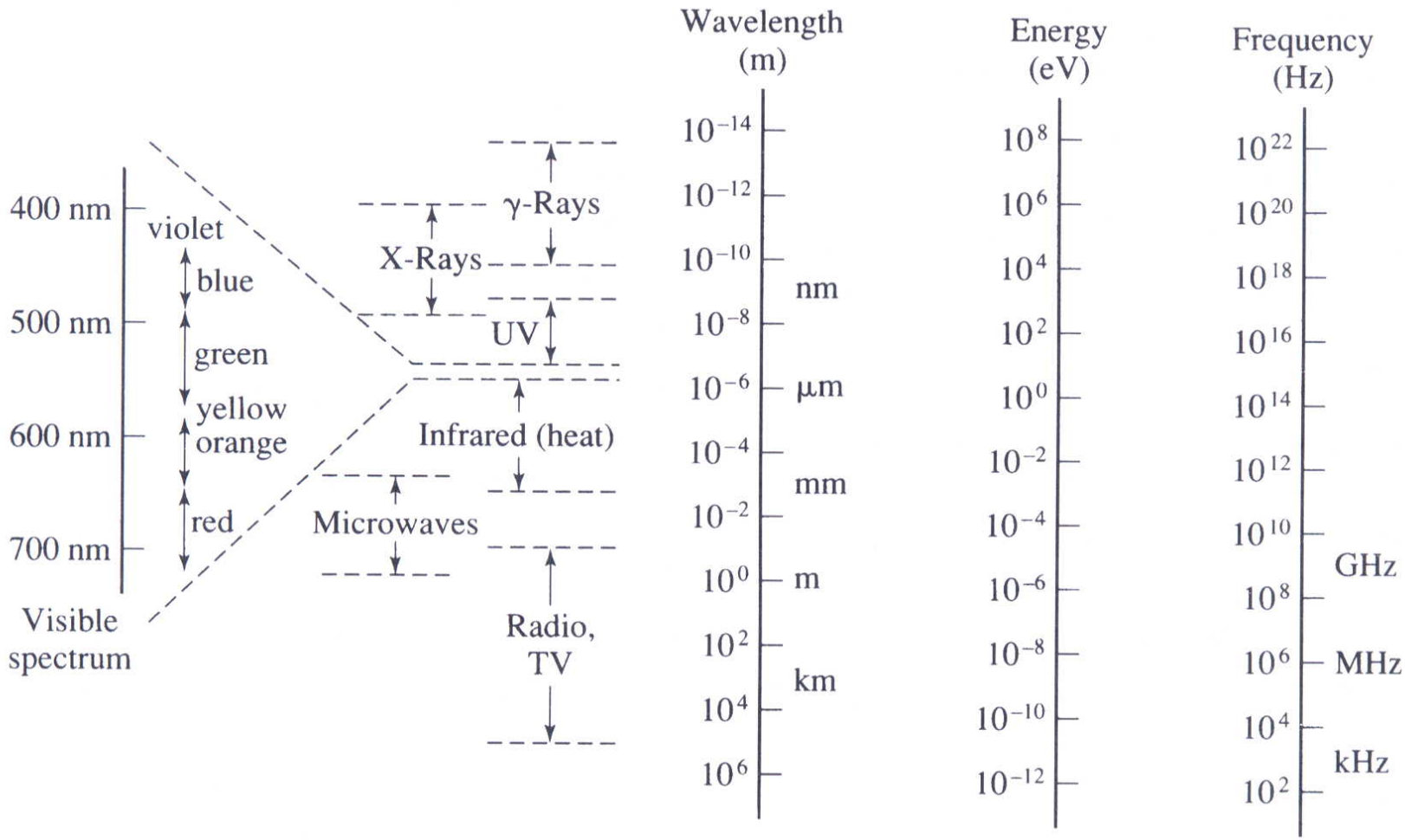
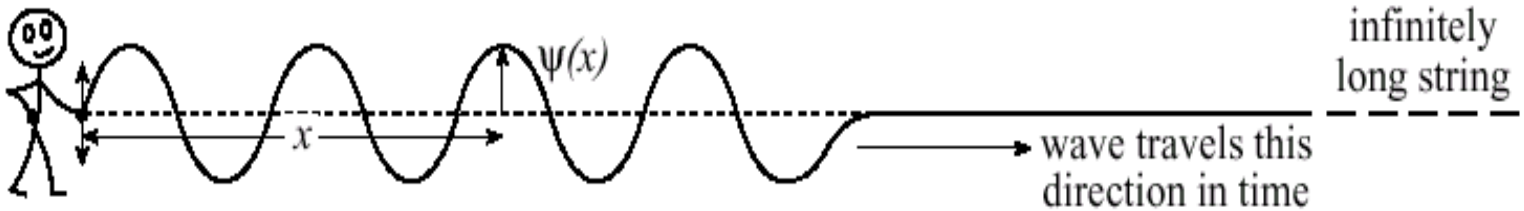
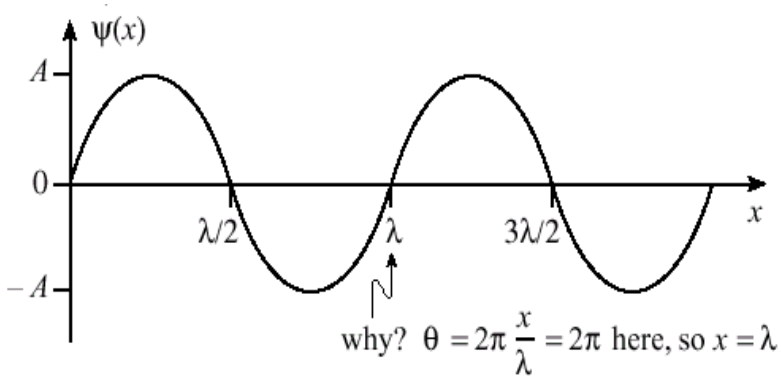


Figure 10.1. The spectrum of electromagnetic radiation. Note the small segment of this spectrum that is visible to human eyes.

Electromagnetic Wave

Periodic displacement in time and position



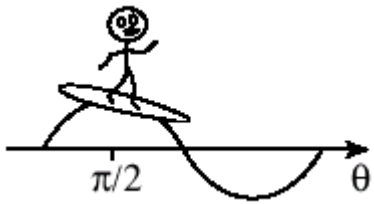


$$\psi(x,t) = A\sin\left(2\pi\frac{x}{\lambda} \pm 2\pi\nu t\right) = A\sin\left(2\pi\left[\frac{x}{\lambda} \pm \nu t\right]\right).$$

$$\boxed{k \equiv \frac{2\pi}{\lambda}} \text{ and } \boxed{\omega \equiv 2\pi\nu}.$$

$$\boxed{\psi(x,t) = A\sin(kx \pm \omega t)}.$$

$$\boxed{\psi(x,t) = A\cos(kx \pm \omega t)},$$



$$\psi(x,t) = A\sin(kx - \omega t)$$

$$\psi(x,t) = A\sin(kx + \omega t)$$

Electromagnetic Wave

- **E** = **A** cos(kx - ωt + ϕ),
- **E** = **A / 2** [exp{i(kx - ωt+ ϕ)} + cc],
- **E** = Re [**A** exp{i(kx - ωt+ ϕ)}],
- **E** = **A**exp{i(kx - ωt + ϕ)} for convenience:

  - This, of course, is not strictly correct; when it happens, it is always understood that what is meant by this equation is the real part of Aexp{i(kx-wt)}. This representation is OK for linear mathematical operations, such as differentiation, integration, and summation, are concerned. The exception is the product or power.

  - **E**: electric field
  - **A**: amplitude, I=**E**•**E***
  - k: wavenumber, wavevector (=$2\pi/\lambda$)
  - ω: angular frequency (=$2\pi\nu$)
  - ϕ: phase

Intensity of a Light Wave, *I*: *the quantity which determines the amount of energy per unit time per unit cross-sectional area that is carried by a wave:*

$$I = \psi^2 = \frac{Energy}{Time \cdot Area} = \frac{Power}{Area}\left(\frac{\text{Watts}}{\text{meters}^2}\right).$$

Electromagnetic Wave

- Polarization state specified by the electric field vector, **E**(**r**,t)
- Assuming propagation in the z-direction
  - Transverse wave lies in xy-plane
  - Two mutually independent components are

$$E_x = A_x \cos(\omega t - kz + \delta_x)$$

$$E_y = A_y \cos(\omega t - kz + \delta_y)$$

  - A_x, A_y are independent positive amplitudes
  - δ_x, δ_y are independent phases
- These correspond to elliptic polarization with relative phase $\delta=\delta_y-\delta_x$.

Electromagnetic Wave

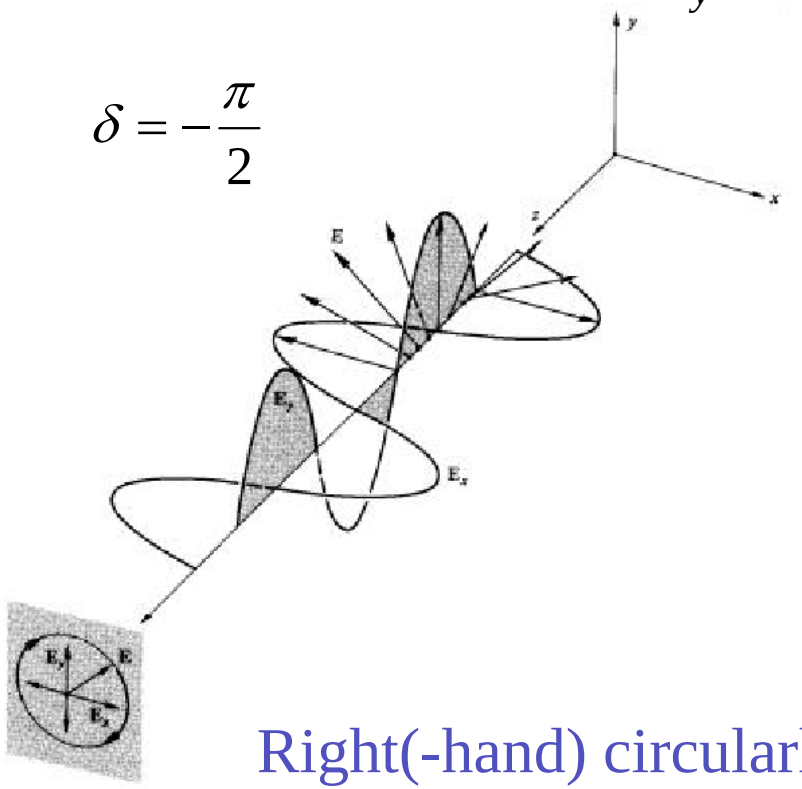
Polarization of light-circular polarization

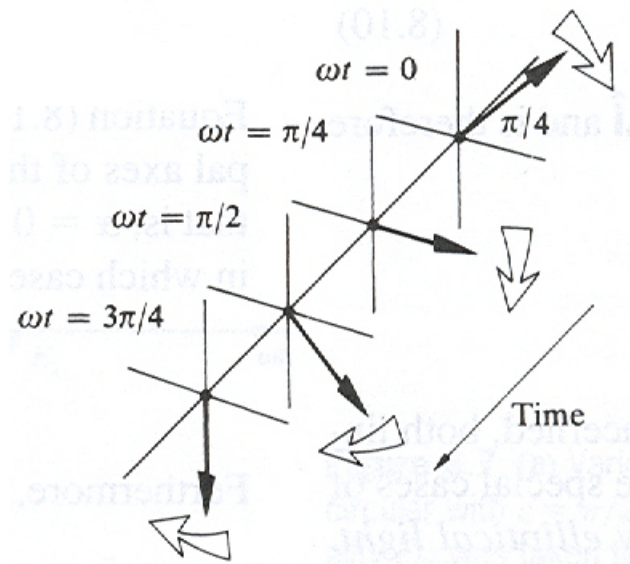
$\delta=\delta_y-\delta_x=\pm\pi/2,\ A_y = A_x$

$$E_x = A_x \cos(\omega t - kz + \delta_x)$$

$$E_y = A_y \cos(\omega t - kz + \delta_y)$$

$$\delta = -\frac{\pi}{2}$$





Right(-hand) circularly polarized

(look back at the source)

Electromagnetic Wave

Polarization of light-circular polarization

Beam of light is circularly polarized if the electric field vector undergoes uniform rotation in the xy-plane

$$\delta = \delta_y - \delta_x = \pm\pi/2$$

$$A_y = A_x$$

Beam of light is right-hand circularly polarized when $\delta = -\pi/2$ which corresponds to counter-clockwise rotation of the E field vector in xy-plane

Beam of light is left-hand circularly polarized when $\delta = +\pi/2$ which corresponds to clockwise rotation of the E field vector in xy-plane.

A linear polarized wave can be synthesized from two oppositely polarized circular or elliptic waves of equal amplitude.

Contents

10 The optical Constants

10.2 Index of Refraction, *n*

Snell's law : refractive power of a material

$$\frac{\sin\alpha}{\sin\beta} = \frac{n_{\text{med}}}{n_{\text{vac}}} = n$$

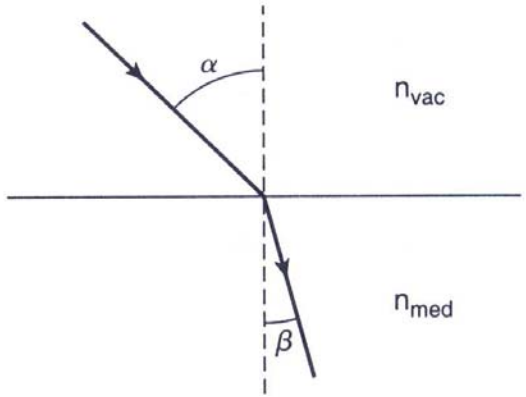


Figure 10.2. Refraction of a light beam when traversing the boundary from an optically thin medium into an optically denser medium.

The index of refraction of vacuum, n_{vac} is arbitrarily set to be unity

$$\frac{\sin\alpha}{\sin\beta} = \frac{c_{\text{vac}}}{c_{\text{med}}} \quad \text{thus} \quad n = \frac{c_{\text{vac}}}{c_{\text{med}}} = \frac{c}{\upsilon}$$

light passes from vacuum into a medium

Dispersion: the property that the magnitude of the refractive index, *n* depends on the wavelength of the incident light. In metals, *n* also varies with α

When light passes from vacuum into a medium, its velocity as well as its wavelength decreases in order to keep the frequency constant.

10.3 Damping Constant, *k*

Consider a plane-polarized wave propagating along the positive *z*-axis and which vibrates in the *x*-direction. (Fig.10.3) We neglect possible magnetic effects. The electromagnetic wave equation may be written as

$$c^2 \frac{\partial^2 E_x}{\partial z^2} = \varepsilon \frac{\partial^2 E_x}{\partial t^2} + \frac{\sigma}{\varepsilon_0} \frac{\partial E_x}{\partial t}$$

See (A. 26) in Appendix 1

Where E_x is the *x*-component of the electric field strength, ε is the dielectric constant, σ is the (a.c.) conductivity and ε_0 is a constant, called permittivity of empty space

The solution to the above wave equation

$$E_x = E_0 \exp\left[i\omega \left(t - \frac{zn}{c} \right) \right]$$

E_0 is the maximal value of the electric field strength and $\omega = 2\pi\nu$ is the angular frequency

10.3 Damping Constant, *k*

Differentiating the above equation once with respect to time and twice with respect to time and *z*, and inserting these values into the wave equation yields

$$\hat{n}^2 = \varepsilon - \frac{\sigma}{\varepsilon_0 \omega} i = \varepsilon - \frac{\sigma}{2\pi\varepsilon_0 \nu} i \quad \text{and} \quad \hat{n} = n_1 - i n_2$$

n_2 is often denoted by k and then (10.7) written as $\hat{n} = n - ik$

n_2 or k is the damping constant (sometimes called, *absorption constant*, *attenuation index*, or *extinction coefficient*).

$$\hat{n}^2 = n^2 - k^2 - 2nki = \varepsilon - \frac{\sigma}{2\pi\varepsilon_0 \nu} i$$

Then $\varepsilon = n^2 - k^2 \qquad \sigma = 4\pi\varepsilon_0 nk\nu$

And $\hat{n}^2 = n^2 - k^2 - 2nik \equiv \hat{\varepsilon} = \varepsilon_1 - i\varepsilon_2$

$$\varepsilon_1 = n^2 - k^2 \qquad \varepsilon_2 = 2nk = \frac{\sigma}{2\pi\varepsilon_0 \nu}$$

10.3 Damping Constant, *k*

ε_1, ε_2: The real and the imaginary parts of the complex dielectric constant

ε_2: *absorption* (*product*)

For insulator ($\sigma \approx 0$) it follows from (10.11) that $k \approx 0$. then (10.10) reduces to $\varepsilon = n^2$ (Maxwell relation).

$$n^2 = \frac{1}{2}\left(\sqrt{\varepsilon^2 + \left(\frac{\sigma}{2\pi\varepsilon_0\nu}\right)^2} + \varepsilon\right) = \frac{1}{2}(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1)$$

$$k^2 = \frac{1}{2}\left(\sqrt{\varepsilon^2 + \left(\frac{\sigma}{2\pi\varepsilon_0\nu}\right)^2} - \varepsilon\right) = \frac{1}{2}(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1)$$

Table 10.1. Characteristic Penetration Depth, W, and Damping Constant, k, for Some Materials ($\lambda = 589.3$ nm).

Material	Water	Flint glass	Graphite	Gold
W(cm)	32	29	6×10^{-6}	1.5×10^{-6}
k	1.4×10^{-7}	1.5×10^{-7}	0.8	3.2

The Optical Constants

10.3 Damping Constant, *k*

Return to (10.5) $$E_x = E_0 \exp\left[i\omega\left(t - \frac{zn}{c}\right)\right]$$

Replace the index of refraction by complex index of refraction (10.8)

$$E_x = E_0 \exp\left[i\omega\left(t - \frac{z(n-ik)}{c}\right)\right]$$

$$E_x = E_0 \underbrace{\exp\left[-\frac{\omega k}{c} z\right]}_{\text{damped}} \cdot \underbrace{\exp\left[i\omega\left(t - \frac{zn}{c}\right)\right]}_{\text{undamped}}$$

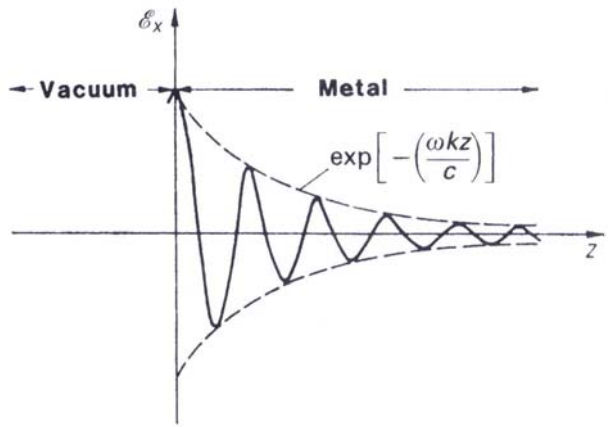


Figure 10.4. Modulated light wave. The amplitude decreases exponentially in an optically dense material. The decrease is particularly strong in metals, but less intense in dielectric materials, such as glass.

Damping constant, *k* determines how much the amplitude decreases : the degree of damping of the light wave

At high frequencies the electromagnetic wave are conducted only on the outer surface of wire : ***skin effect***

10.4 Characteristic Penetration Depth, *W*, and Absorbance, α

The damping term in (10.18)

$$I = E^2 = I_0 \exp\left(-\frac{2\omega k}{c} z\right)$$

$$\frac{I}{I_0} = \frac{1}{e} = e^{-1}$$

We define *a characteristic penetration depth*, *W*, as that distance at which the intensity of the light wave, which travels through a material, has decreased to 1/e of its original value

in conjunction with (10.19)

$$z = W = \frac{c}{2\omega k} = \frac{c}{4\pi\nu k} = \frac{\lambda}{4\pi k}$$

The inverse of W is called *attenuation* or the *absorbance*

By making use of (10.21), (10.14), and (10,11)

$$\alpha = \frac{4\pi k}{\lambda} = \frac{2\pi\varepsilon_2}{\lambda n} = \frac{\sigma}{nc\varepsilon_0} = \frac{2\omega k}{c}$$

10.5 Reflectivity, *R*, and Transmittance *T*

reflectivity $$R = \frac{I_R}{I_0}$$

I_R reflected intensity

I_0 incoming intensity

I_T transmitted intensity

transmissivity, or *transmittance* $$T = \frac{I_T}{I_0}$$

Experiments have shown that for insulators, *R* depends solely on the index of refraction. For perpendicular incidence one finds.

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

Also, can be derived from Maxwell equations

n is generally a complex quantity. *R* should be real. Thus, *R* becomes

$$R = \left|\frac{\hat{n}-1}{\hat{n}+1}\right|^2 = \frac{(n-ik-1)}{(n-ik+1)} \cdot \frac{(n+ik-1)}{(n+ik+1)} = \frac{(n-1)^2+k^2}{(n+1)^2+k^2}$$

10.5 Reflectivity, *R*, and Transmittance *T*

The reflectivity is also a function of ε_1, ε_2

$$R = \frac{n^2 + k^2 + 1 - 2n}{n^2 + k^2 + 1 + 2n}$$

(1) $$n^2 + k^2 = \sqrt{(n^2 + k^2)^2} = \sqrt{n^4 + 2n^2k^2 + k^2}$$

$$= \sqrt{n^4 - 2n^2k^2 + k^4 + 4n^2k^2} = \sqrt{(n^2 - k^2)^2 + 4n^2k^2}$$

$$= \sqrt{\varepsilon_1^2 + \varepsilon_2^2}$$

(2) $$2n = \sqrt{4n^2} = \sqrt{2(n^2 + k^2 + n^2 - k^2)} = \sqrt{2(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1)}$$

Inserting (1) and (2) into (10.26)

$$R = \frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + 1 - \sqrt{2(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1)}}{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + 1 + \sqrt{2(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1)}}$$

10.6 Hagen-Ruben Relation

To find relationship between reflectivity and conductivity

For small frequency (i.e $\nu < 10^{13} s^{-1}$), the ratio $\sigma / 2\pi\varepsilon_0\nu$ for metals is very large $\sigma / 2\pi\varepsilon_0\nu \approx 10^{17}\ s^{-1}$. with $\varepsilon \approx 10$ we obtain

$$\frac{\sigma}{2\pi\varepsilon_0\nu} \approx \frac{10^{17}}{10^{13}} \rangle\rangle \varepsilon \quad \longleftarrow \quad \varepsilon_2 = 2nk = \frac{\sigma}{2\pi\varepsilon_0\nu}$$

Then (10.15) and (10.16) reduce to $n^2 \approx \dfrac{\sigma}{4\pi\varepsilon_0\nu} \approx k^2$

By combing the slightly modified equation (10.26) with (10.31)

$$R = \frac{n^2 + 2n + k^2 + 1 - 4n}{n^2 + 2n + 1 + k^2} = 1 - \frac{4n}{2n^2 + 2n + 1}$$

10.6 Hagen-Ruben Relation

If $2n + 1$ is neglected as small compared to $2n^2$ (which can be done only for small frequencies for which n is much larger than 1), then (10.32) reduces by using (10.31) to

$$R = 1 - \frac{2}{n} = 1 - 4\sqrt{\frac{\nu}{\sigma}\pi\varepsilon_0}$$

Set $\sigma = \sigma_0$ (d.c. conductivity) which is again only permissible for small frequencies, i.e., in the infrared region of the spectrum . This yields the Hagen-Ruben equation,

$$R = 1 - 4\sqrt{\frac{\nu}{\sigma_0}\pi\varepsilon_0}$$

The Hagen-Ruben relation is only valid at frequencies below $10^{13}\ s^{-1}$, or equivalently, at wavelength larger than about 30 μm.

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

Introduction

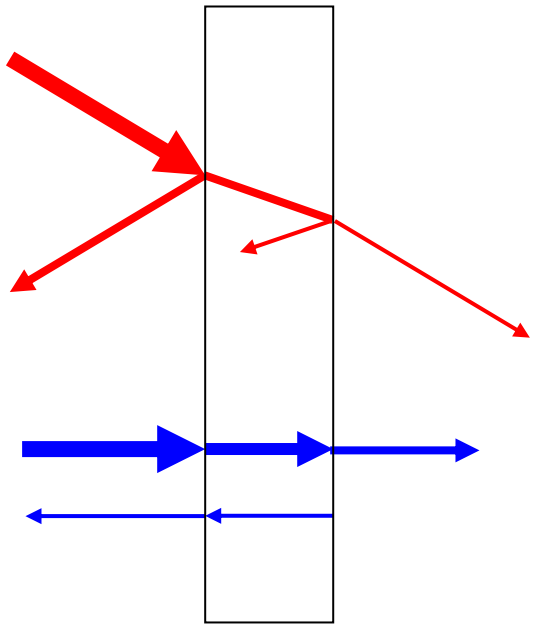
- ✓ The interactions of light with the valence electrons of a material is postulated to be responsible for the optical properties.
- ✓ Light comprises only extremely small segment of the entire electromagnetic spectrum (Fig 10.1)
- ✓ Optical methods are among the most important tools for elucidating the electron structure of matter
- ✓ Optical devices : lasers, photodetectors, waveguides, light-emitting diodes, flat-panel displays
- ✓ Applications for communication : fiber optics, medical diagnostics, night viewing, solar applications, optical computing and etc..
- ✓ Traditional utilizations: widows, antireflection coating; lenses, mirrors, etc..

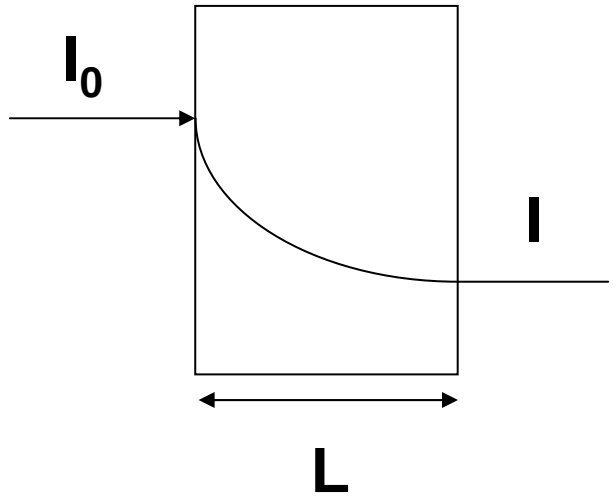
cf) BBR (black body radiation)

Introduction

Interactions between light and matter

- Refraction
- Reflection
- Transmission
- Absorption
- Luminescence





$I/I_0 = ?$

What is light?

Light

- Speed: c~$3x10^{10}$ cm/s in vacuum
- Ray: geometric optics such as lens, mirror
- Electromagnetic wave: refraction, reflection, interference, diffraction, hollogram, etc.
- A stream of photons: absorption and emission

Spectrum (wavelength) of light

γ-ray (10^{-2} Å) ~ X-ray (1 Å) ~ UV(100 nm)
~ visible (400nm (blue) ~ 700nm (red))
~ IR (~10 μm) ~ microwave (GHz) ~ radio (MHz-KHz)

Introduction

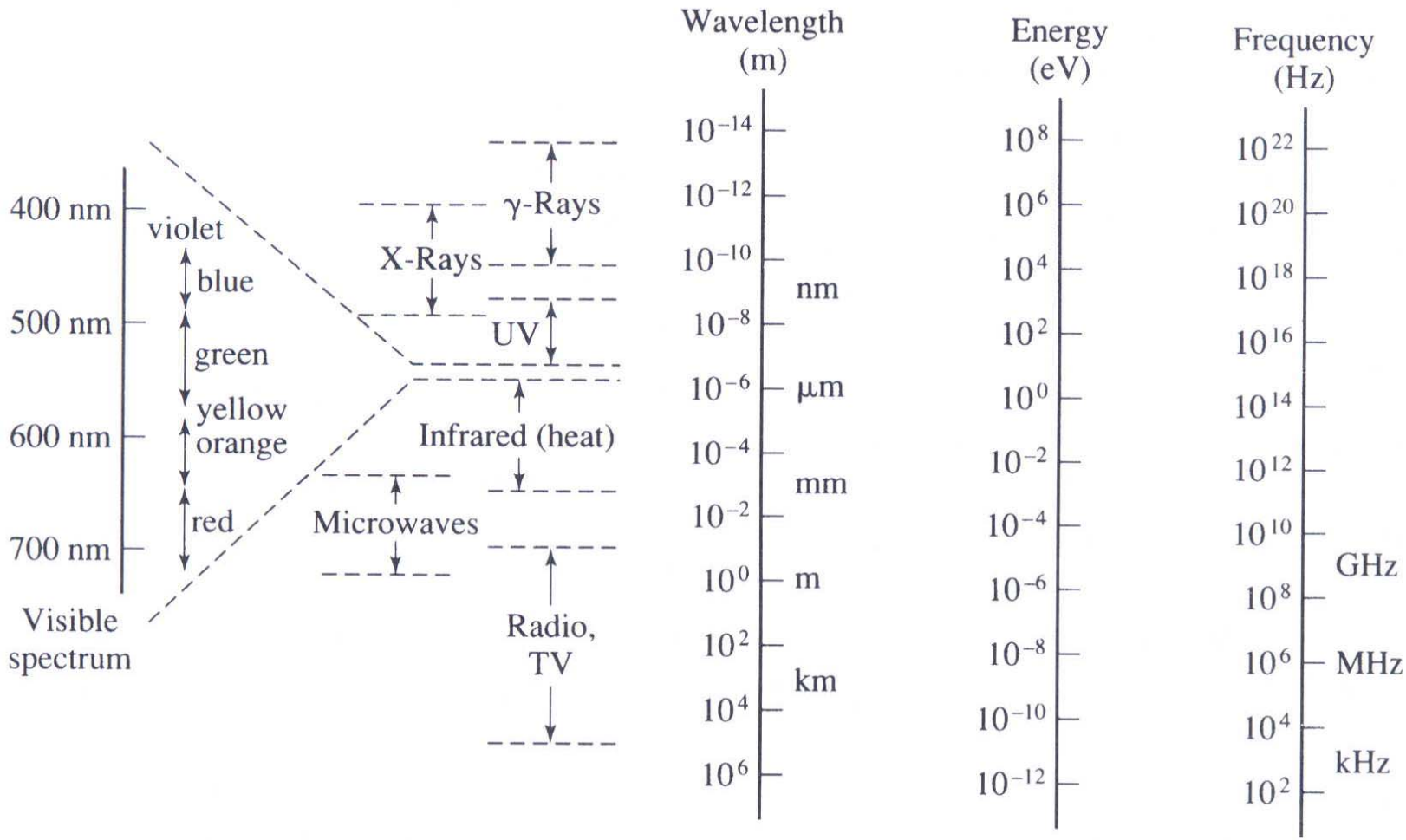
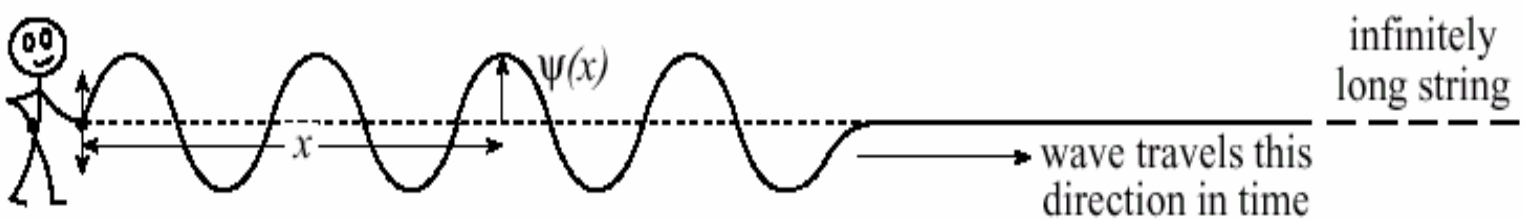
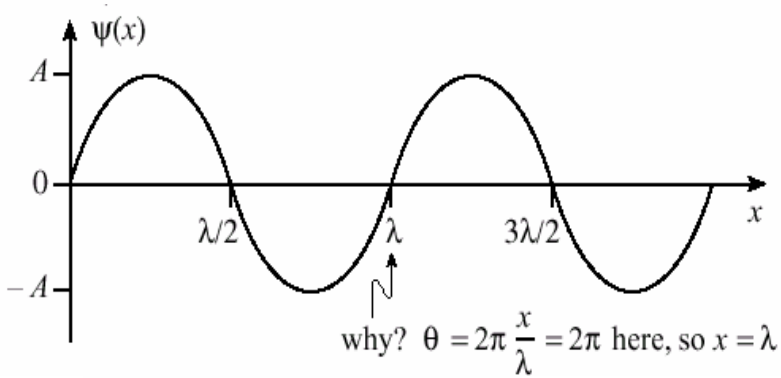


Figure 10.1. The spectrum of electromagnetic radiation. Note the small segment of this spectrum that is visible to human eyes.

Electromagnetic Wave

Periodic displacement in time and position



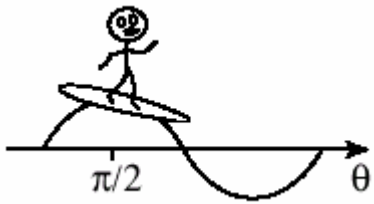


$$\psi(x,t) = A\sin\left(2\pi\frac{x}{\lambda} \pm 2\pi\nu t\right) = A\sin\left(2\pi\left[\frac{x}{\lambda} \pm \nu t\right]\right).$$

$$\boxed{k \equiv \frac{2\pi}{\lambda}} \text{ and } \boxed{\omega \equiv 2\pi\nu}.$$

$$\boxed{\psi(x,t) = A\sin(kx \pm \omega t)}.$$

$$\boxed{\psi(x,t) = A\cos(kx \pm \omega t)},$$



$$\psi(x,t) = A\sin(kx - \omega t)$$

$$\psi(x,t) = A\sin(kx + \omega t)$$

Electromagnetic Wave

- $\mathbf{E} = \mathbf{A}\cos(kx - \omega t + \phi)$,
- $\mathbf{E} = \mathbf{A}/2\,[\exp\{i(kx - \omega t + \phi)\} + cc]$,
- $\mathbf{E} = \mathrm{Re}\,[\mathbf{A}\exp\{i(kx - \omega t + \phi)\}]$,
- $\mathbf{E} = \mathbf{A}\exp\{i(kx - \omega t + \phi)\}$ for convienence:

  - This, of course, is not strictly correct; when it happens, it is always understood that what is meant by this equation is the real part of $A\exp\{i(kx-wt)\}$. This representation is OK for linear mathematical operations, such as differentiation, integration, and summation, are concerned. The exception is the product or power.

  - **E**: electric field
  - **A**: amplitude, $I = \mathbf{E} \bullet \mathbf{E}^*$
  - k: wavenumber, wavevector ($=2\pi/\lambda$)
  - ω: angular frequency ($=2\pi\nu$)
  - ϕ: phase

Intensity of a Light Wave, *I*: *the quantity which determines the amount of energy per unit time per unit cross-sectional area that is carried by a wave:*

$$I = \psi^2 = \frac{Energy}{Time \cdot Area} = \frac{Power}{Area}\left(\frac{\text{Watts}}{\text{meters}^2}\right).$$

Electromagnetic Wave

- Polarization state specified by the electric field vector, **E**(**r**,t)
- Assuming propagation in the z-direction
  - Transverse wave lies in xy-plane
  - Two mutually independent components are

$$E_x = A_x \cos(\omega t - kz + \delta_x)$$

$$E_y = A_y \cos(\omega t - kz + \delta_y)$$

  - A_x, A_y are independent positive amplitudes
  - δ_x, δ_y are independent phases
- These correspond to elliptic polarization with relative phase $\delta=\delta_y-\delta_x$.

Electromagnetic Wave

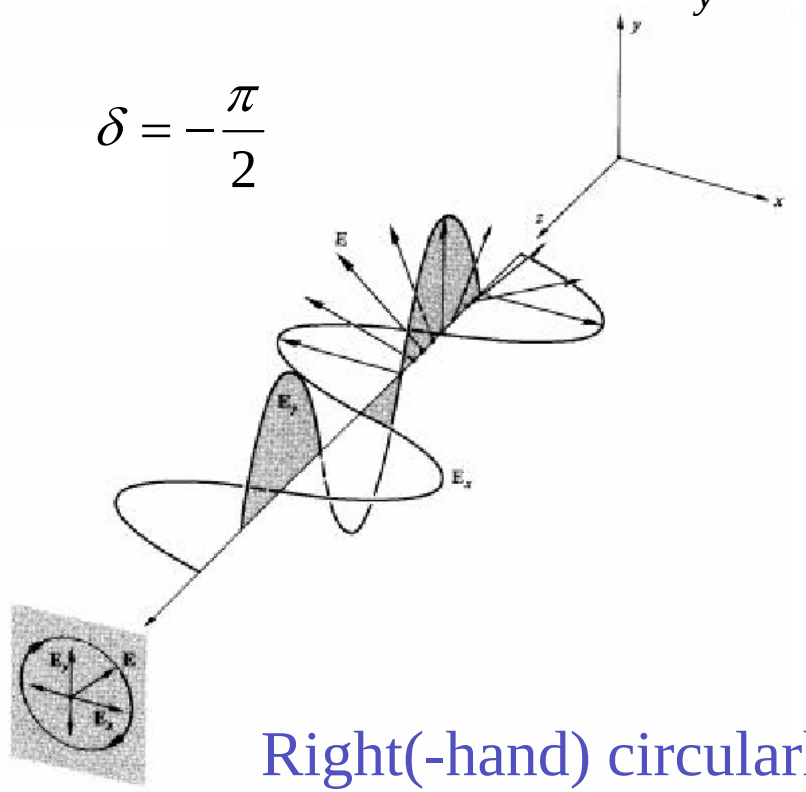
Polarization of light-circular polarization

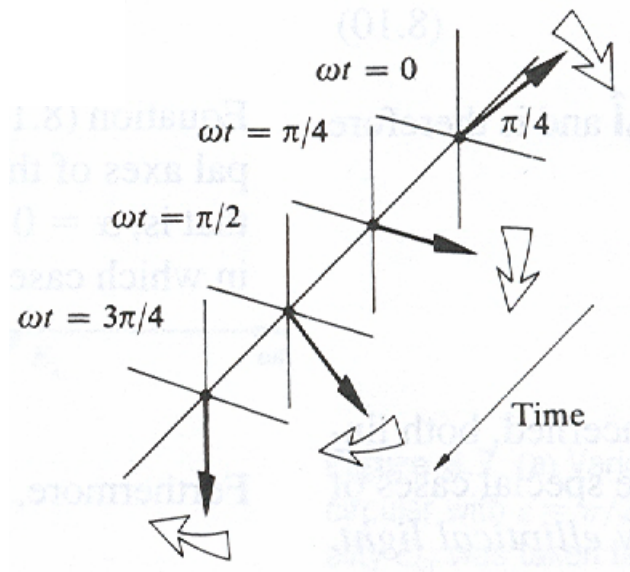
$\delta=\delta_y-\delta_x=\pm\pi/2,\ A_y = A_x$

$$E_x = A_x \cos(\omega t - kz + \delta_x)$$

$$E_y = A_y \cos(\omega t - kz + \delta_y)$$

$$\delta = -\frac{\pi}{2}$$





Right(-hand) circularly polarized

(look back at the source)

Electromagnetic Wave

Polarization of light-circular polarization

Beam of light is circularly polarized if the electric field vector undergoes uniform rotation in the xy-plane

$$\delta = \delta_y - \delta_x = \pm\pi/2$$

$$A_y = A_x$$

Beam of light is right-hand circularly polarized when $\delta = -\pi/2$ which corresponds to counter-clockwise rotation of the E field vector in xy-plane

Beam of light is left-hand circularly polarized when $\delta = +\pi/2$ which corresponds to clockwise rotation of the E field vector in xy-plane.

A linear polarized wave can be synthesized from two oppositely polarized circular or elliptic waves of equal amplitude.

Contents

10 The optical Constants

10.2 Index of Refraction, *n*

Snell's law : refractive power of a material

$$\frac{\sin\alpha}{\sin\beta} = \frac{n_{\text{med}}}{n_{\text{vac}}} = n$$

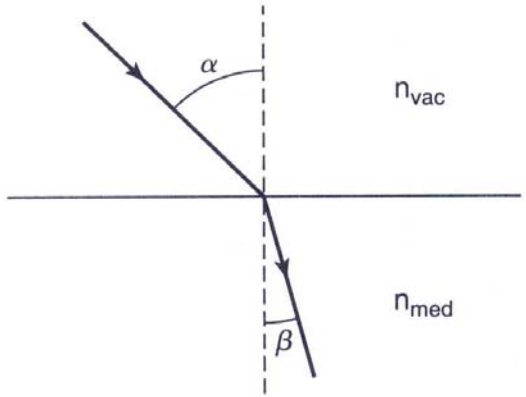


Figure 10.2. Refraction of a light beam when traversing the boundary from an optically thin medium into an optically denser medium.

The index of refraction of vacuum, n_{vac} is arbitrarily set to be unity

$$\frac{\sin\alpha}{\sin\beta} = \frac{c_{\text{vac}}}{c_{\text{med}}} \quad \text{thus} \quad n = \frac{c_{\text{vac}}}{c_{\text{med}}} = \frac{c}{\upsilon}$$

light passes from vacuum into a medium

Dispersion: the property that the magnitude of the refractive index, *n* depends on the wavelength of the incident light. In metals, *n* also varies with α

When light passes from vacuum into a medium, its velocity as well as its wavelength decreases in order to keep the frequency constant.

10.3 Damping Constant, *k*

Consider a plane-polarized wave propagating along the positive *z*-axis and which vibrates in the *x*-direction. (Fig.10.3) We neglect possible magnetic effects. The electromagnetic wave equation may be written as

$$c^2 \frac{\partial^2 E_x}{\partial z^2} = \varepsilon \frac{\partial^2 E_x}{\partial t^2} + \frac{\sigma}{\varepsilon_0} \frac{\partial E_x}{\partial t}$$

See (A. 26) in Appendix 1

Where E_x is the *x*-component of the electric field strength, ε is the dielectric constant, σ is the (a.c.) conductivity and ε_0 is a constant, called permittivity of empty space

The solution to the above wave equation

$$E_x = E_0 \exp\left[i\omega \left(t - \frac{zn}{c} \right) \right]$$

E_0 is the maximal value of the electric field strength and $\omega = 2\pi\nu$ is the angular frequency

10.3 Damping Constant, *k*

Differentiating the above equation once with respect to time and twice with respect to time and *z*, and inserting these values into the wave equation yields

$$\hat{n}^2 = \varepsilon - \frac{\sigma}{\varepsilon_0 \omega} i = \varepsilon - \frac{\sigma}{2\pi\varepsilon_0 \nu} i \quad \text{and} \quad \hat{n} = n_1 - i n_2$$

n_2 is often denoted by k and then (10.7) written as $\hat{n} = n - ik$

n_2 or k is the damping constant (sometimes called, *absorption constant*, attenuation index, or *extinction coefficient*).

$$\hat{n}^2 = n^2 - k^2 - 2nki = \varepsilon - \frac{\sigma}{2\pi\varepsilon_0 \nu} i$$

Then $\varepsilon = n^2 - k^2 \qquad \sigma = 4\pi\varepsilon_0 nk\nu$

And $\hat{n}^2 = n^2 - k^2 - 2nik \equiv \hat{\varepsilon} = \varepsilon_1 - i\varepsilon_2$

$$\varepsilon_1 = n^2 - k^2 \qquad \varepsilon_2 = 2nk = \frac{\sigma}{2\pi\varepsilon_0 \nu}$$

10.3 Damping Constant, *k*

ε_1, ε_2: The real and the imaginary parts of the complex dielectric constant

ε_2: absorption (product)

For insulator ($\sigma \approx 0$) it follows from (10.11) that $k \approx 0$. then (10.10) reduces to $\varepsilon = n^2$ (Maxwell relation).

$$n^2 = \frac{1}{2}\left(\sqrt{\varepsilon^2 + \left(\frac{\sigma}{2\pi\varepsilon_0\nu}\right)^2} + \varepsilon\right) = \frac{1}{2}(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1)$$

$$k^2 = \frac{1}{2}\left(\sqrt{\varepsilon^2 + \left(\frac{\sigma}{2\pi\varepsilon_0\nu}\right)^2} - \varepsilon\right) = \frac{1}{2}(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1)$$

Table 10.1. Characteristic Penetration Depth, W, and Damping Constant, k, for Some Materials ($\lambda = 589.3$ nm).

Material	Water	Flint glass	Graphite	Gold
W(cm)	32	29	6×10^{-6}	1.5×10^{-6}
k	1.4×10^{-7}	1.5×10^{-7}	0.8	3.2

10.3 Damping Constant, *k*

Return to (10.5) $$E_x = E_0 \exp\left[i\omega\left(t - \frac{zn}{c}\right)\right]$$

Replace the index of refraction by complex index of refraction (10.8)

$$E_x = E_0 \exp\left[i\omega\left(t - \frac{z(n-ik)}{c}\right)\right]$$

$$E_x = E_0 \underbrace{\exp\left[-\frac{\omega k}{c} z\right]}_{\text{damped}} \cdot \underbrace{\exp\left[i\omega\left(t - \frac{zn}{c}\right)\right]}_{\text{undamped}}$$

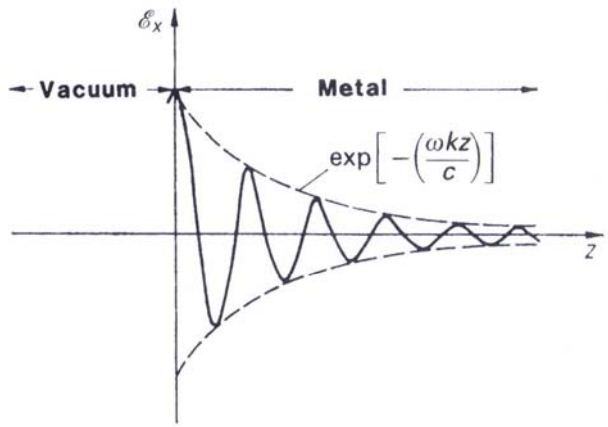


Figure 10.4. Modulated light wave. The amplitude decreases exponentially in an optically dense material. The decrease is particularly strong in metals, but less intense in dielectric materials, such as glass.

Damping constant, *k* determines how much the amplitude decreases : the degree of damping of the light wave

At high frequencies the electromagnetic wave are conducted only on the outer surface of wire : *skin effect*

10.4 Characteristic Penetration Depth, W, and Absorbance, α

The damping term in (10.18)

$$I = E^2 = I_0 \exp\left(-\frac{2\omega k}{c} z\right)$$

$$\frac{I}{I_0} = \frac{1}{e} = e^{-1}$$

We define a characteristic penetration depth, ***W***, as that distance at which the intensity of the light wave, which travels through a material, has decreased to 1/e of its original value

in conjunction with (10.19)

$$z = W = \frac{c}{2\omega k} = \frac{c}{4\pi \nu k} = \frac{\lambda}{4\pi k}$$

The inverse of W is called attenuation or the absorbance

By making use of (10.21), (10.14), and (10,11)

$$\alpha = \frac{4\pi k}{\lambda} = \frac{2\pi \varepsilon_2}{\lambda n} = \frac{\sigma}{nc\varepsilon_0} = \frac{2\omega k}{c}$$

10.5 Reflectivity, R, and Transmittance T

Determination for the reflectivity $R = \frac{I_R}{I_0}$

I_R the reflected intensity

I_0 incoming intensity

transmissivity, or transmittance $T = \frac{I_T}{I_0}$

Experiments have shown that for insulators, *R* depends solely on the index of refraction. For perpendicular incidence one finds.

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

Also, can be derived from Maxwell equations

n is generally a complex quantity. *R* should be real. Thus, *R* becomes

$$R = \left|\frac{\hat{n}-1}{\hat{n}+1}\right|^2 \qquad R = \frac{(n-ik-1)}{(n-ik+1)} \cdot \frac{(n+ik-1)}{(n+ik+1)} = \frac{(n-1)^2+k^2}{(n+1)^2+k^2}$$

10.5 Reflectivity, *R*, and Transmittance *T*

The reflectivity is also a function of ε_1, ε_2

$$R = \frac{n^2 + k^2 + 1 - 2n}{n^2 + k^2 + 1 + 2n}$$

(1) $$n^2 + k^2 = \sqrt{(n^2 + k^2)^2} = \sqrt{n^4 + 2n^2k^2 + k^2}$$

$$= \sqrt{n^4 - 2n^2k^2 + k^4 + 4n^2k^2} = \sqrt{(n^2 - k^2)^2 + 4n^2k^2}$$

$$= \sqrt{\varepsilon_1^2 + \varepsilon_2^2}$$

(2) $$2n = \sqrt{4n^2} = \sqrt{2(n^2 + k^2 + n^2 - k^2)} = \sqrt{2(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1)}$$

Inserting (1) and (2) into (10.26)

$$R = \frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + 1 - \sqrt{2(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1)}}{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + 1 + \sqrt{2(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1)}}$$

10.6 Hagen-Ruben Relation

To find relationship between reflectivity and conductivity

For small frequency (i.e $\nu < 10^{13} s^{-1}$) the ratio $\sigma / 2\pi\varepsilon_0\nu$ for metals is very large $\sigma / 2\pi\varepsilon_0\nu \approx 10^{17}\ s^{-1}$. with $\varepsilon \approx 10$ we obtain

$$\frac{\sigma}{2\pi\varepsilon_0\nu} \approx \frac{10^{17}}{10^{13}} \rangle\rangle \varepsilon$$

Then (10.15) and (10.16) reduce to $n^2 \approx \dfrac{\sigma}{2\pi\varepsilon_0\nu} \approx k^2$

By combing the slightly modified equation (10.26) with (10.31)

$$R = \frac{n^2 + 2n + k^2 + 1 - 4n}{n^2 + 2n + 1 + k^2} = 1 - \frac{4n}{2n^2 + 2n + 1}$$

10.6 Hagen-Ruben Relation

If $2n+1$ is neglected as small compared to $2n^2$ (which can be done only for small frequencies for which n is much larger than 1), then (10.32) reduces by using (10.31) to

$$R = 1 - \frac{2}{n} = 1 - 2\sqrt{\frac{\nu}{\sigma}\pi\varepsilon_0}$$

Set $\sigma = \sigma_0$ which is again only permissible for small frequencies, i.e., in the infrared region of the spectrum . This yields the Hagen-Ruben equation

$$R = 1 - 2\sqrt{\frac{\nu}{\sigma_0}\pi\varepsilon_0}$$

The Hagen-Ruben relation is only valid at frequencies below 10^{13} s^{-1}, or equivalently, at wavelength larger than about $30\mu m$

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

11.1 Survey

- **Hagen-Rubens equations** (Fig 11.1(a))

The validity of equations derived from continuum theory, considering only macroscopic quantities and interrelating experimental data, are often limited to frequencies for which the atomistic structure of solids does not play a major role.

- **Drude model** (Fig 11.1(a))

In the visible and near IR region, an atomistic model needs to be considered to explain the optical behavior of metals. Moving electrons collide with certain metal atoms in a nonideal lattice. Absorption band cannot be explained by the Drude theory.

- **Lorentz postulations** (Fig 11.1(a))

The electrons are considered to be bound to their nuclei, and an external electric field displaces the positive charge of an atomic nuleus against the negative charge of its electron cloud: "harmonic oscillator"

Atomistic Theory of the Optical Properties

11.1 Survey

An oscillator absorbs a maximal amount of energy when excited near its resonance frequency. (Fig 11.1b)

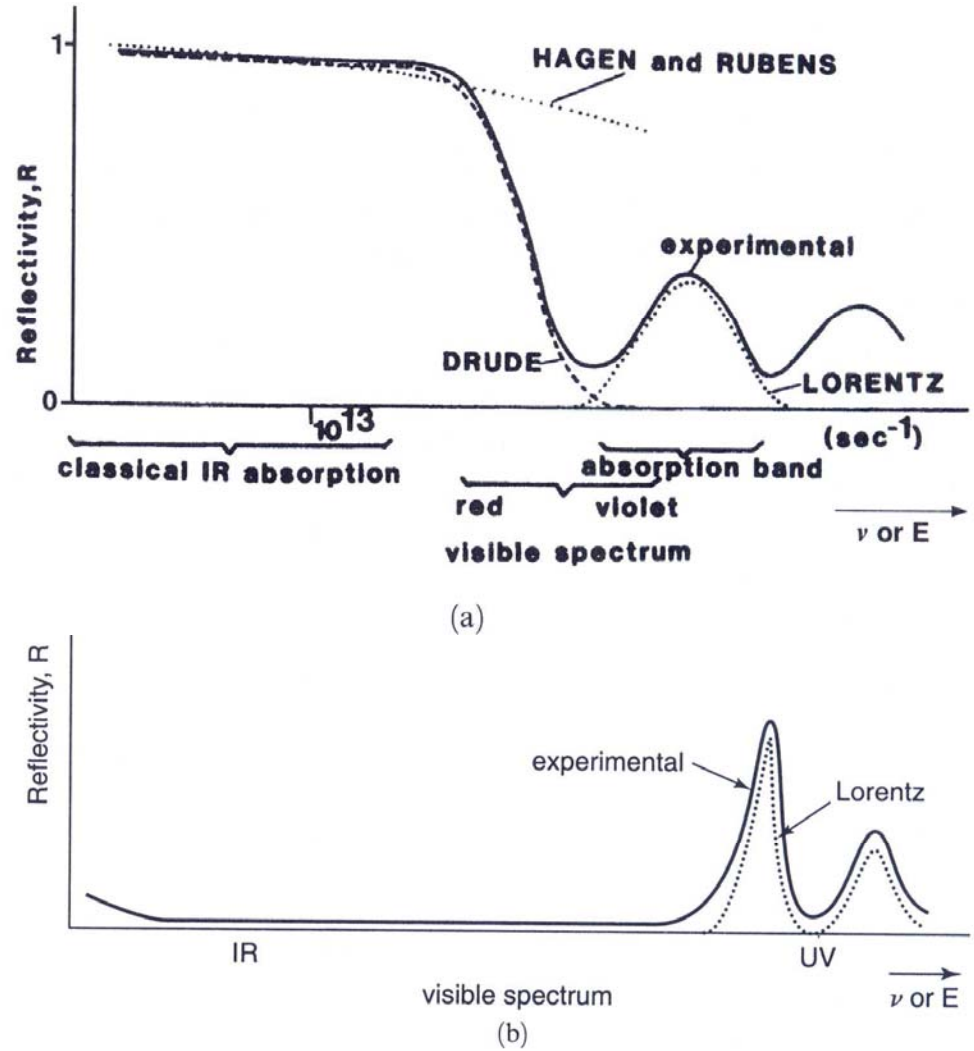


Figure 11.1. Schematic frequency dependence of the reflectivity of (a) metals, (b) dielectrics, experimentally (solid line) and according to three models.

11.2 Free Electrons Without Damping

Let's consider the interaction of a plane-polarized light with the electrons. The field strength of the plane-polarized light wave is given by

$$E = E_0 \exp(i\omega t)$$ where ω (= $2\pi\nu$) is the angular frequency

$$m\frac{d^2x}{dt^2} = eE = eE_0 \exp(i\omega t)$$

The stationary solution of this vibrational equation is obtained by forming the second derivative of the trial solution $x = x_0 \exp(i\omega t)$

This yields

$$x = -\frac{eE}{m4\pi^2\nu^2}$$

The vibrating electrons carries an electric dipole moment.

$$P = exN_f$$ where N_f is free electrons per cubic centimeter

11.2 Free Electrons Without Damping

The dielectric constant $\varepsilon = 1 + \dfrac{P}{\varepsilon_0 E}$

Inserting (11.3) and (11.4) into this equation $\hat{\varepsilon} = 1 - \dfrac{e^2 N_{\mathrm{f}}}{4\pi^2 \varepsilon_0 \mathrm{m} \nu^2}$

The dielectric constant equals the square of the index of refraction, *n*

$$\hat{n}^2 = 1 - \frac{e^2 N_f}{4\pi^2 \varepsilon_0 \mathrm{m} \nu^2}$$

We consider two special cases as follows,

(a) For small frequencies, the term $\dfrac{e^2 N_f}{4\pi^2 \varepsilon_0 \mathrm{m} \nu^2}$ is larger than one.

Then $\hat{n}^2$ is negative and imaginary. An imaginary $\hat{n}^2$ means that the real part of $\hat{n}$ disappears. Eq.(10.25) becomes, for $n = 0$

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

i.e., the reflectivity is 100 % (Fig 11.3)

11.2 Free Electrons Without Damping

(b) For large frequency (UV light), the term $\frac{e^2 N_f}{4\pi^2 \varepsilon_0 m \nu^2}$ becomes smaller than one. Thus $\hat{n}^2$ is positive and $\hat{n} = n$ real. The reflectivity for real values of $\hat{n}$, i.e., for $k = 0$, becomes

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

The material is essentially transparent for these wavelengths (Fig 11.3)

We define a characteristic frequency, ν_1 often called **plasma frequency**, which separates the reflective region from the transparent region. (Fig 11.3) The plasma frequency can also be deduced from (11.6) or (11.7). In these equations $\frac{e^2 N_f}{4\pi^2 \varepsilon_0 m \nu^2}$ must have the unity of the square of a frequency, which we define to be ν_1

$$\nu_1^2 = \frac{e^2 N_f}{4\pi^2 \varepsilon_0 m}$$

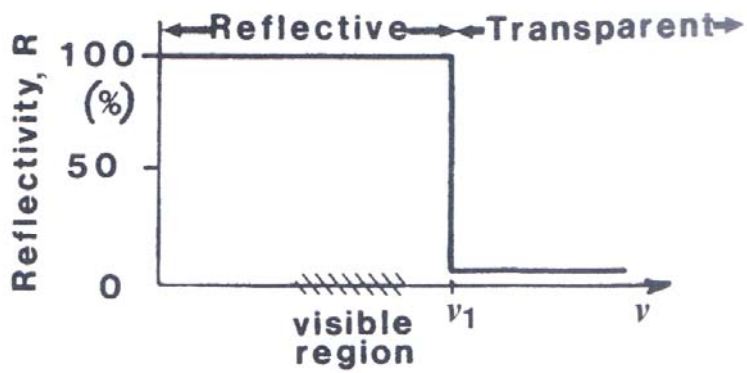


Figure 11.3. Schematic frequency dependence of an alkali metal according to the free electron theory without damping. ν_1 is the plasma frequency.

11.2 Free Electrons Without Damping

The alkali metals are transparent near UV and reflect the light in the visible region (Table 11.1) : the *s*-electrons of the outer shell of the alkali metals can be considered to be free.

Table 11.1. Plasma Frequencies and Effective Numbers of Free Electrons for Some Alkali Metals.

Metal	Li	Na	K	Rb	Cs
ν_1 (10^{14} s^{-1}), observed	14.6	14.3	9.52	8.33	6.81
ν_1 (10^{14} s^{-1}), calculated	19.4	14.3	10.34	9.37	8.33
λ_1 nm ($= c/\nu_1$), observed	150	210	290	320	360
N_{eff}[free electrons/atom]	0.57	1.0	0.8	0.79	0.67

In Table 11.1, the calculated and the observed values for ν_1 are only identical for sodium : sodium does exactly one free electron per atom contribute to the electron pas.

For other metals "effective number of free electrons" is commonly introduced, which is defined to be the ratio between the observed and calculated ν_1 values

$$\frac{\nu_1^2(\text{observed})}{\nu_1^2(\text{calculated})} = N_{eff}$$

$$N_{\text{eff}} = \frac{(1-n^2+k^2)\nu^2 4\pi^2\varepsilon_0 m}{e^2}$$

***N_{eff}* can be obtained by measuring *n* and *k* in the red or IR spectrum**

11.3 Free Electrons With Damping

To take account of the damping, we add to the vibration equation (11.2) a damping term $\gamma(dx/dt)$, which is proportional to the velocity

$$m\frac{d^2x}{dt^2}+\gamma\frac{dx}{dt}=eE=eE_0\exp(i\omega t) \qquad (11.11)$$

We determine first the damping factor, γ

The damping is depicted to be a friction force which counteracts the electron motion $\upsilon'=\text{const.}$

$$\frac{d^2x}{dt^2}=0 \longrightarrow \frac{eE}{\gamma}=\frac{dx}{dt}=\upsilon' \longrightarrow \upsilon'=\frac{j}{eN_f}, \quad j=\sigma_0 E$$

$$\longrightarrow \gamma=\frac{N_f e^2}{\sigma_0}$$

Thus (11.11) becomes, $$m\frac{d^2x}{dt^2}+\frac{N_f e^2}{\sigma_0}\frac{dx}{dt}=eE=eE_0\exp(i\omega t)$$

11.3 Free Electrons With Damping

The stationary solution of eqn. $m\frac{d^2x}{dt^2}+\frac{N_f e^2}{\sigma_0}\frac{dx}{dt}=eE=eE_0\exp(i\omega t)$

obtained by differentiating the trial solution $x=x_0\exp(i\omega t)$ by time and inserting the second derivatives into the equation, which yields

$$-m\omega^2 x+\frac{N_f e^2}{\sigma_0}x\omega\omega=eE$$

$$x=\frac{E}{\frac{N_f e\omega}{\sigma_0}-\frac{m\omega^2}{e}} \longrightarrow P=exN_f$$ then $$P=\frac{eN_f E}{\frac{N_f e\omega}{\sigma_0}i-\frac{m\omega^2}{e}}$$

$$\longrightarrow \varepsilon=1+\frac{P}{\varepsilon_0 E}$$ then $$\hat{\varepsilon}=1+\frac{P}{\varepsilon_0 E}=1+\frac{1}{\frac{2\pi\varepsilon_0\nu}{\sigma_0}i-\frac{m4\pi^2\varepsilon_0}{N_f e^2}\nu^2}$$

$$\hat{\varepsilon}=1+\frac{1}{\frac{2\pi\varepsilon_0\nu}{\sigma_0}i-\frac{\nu^2}{\nu_1^2}}=1+\frac{\nu_1^2}{i\nu\frac{2\pi\varepsilon_0\nu_1^2}{\sigma_0}-\nu^2}$$ the term $\frac{e^2N_f}{4\pi^2\varepsilon_0 m\nu^2}$ equal to ν_1^2

11.3 Free Electrons With Damping

The term $2\pi\varepsilon_0\nu_1^2/\sigma_0$ in (11.22) has the unity of a frequency. We define a damping frequency

$$\nu_2 = \frac{2\pi\varepsilon_0\nu_1^2}{\sigma_0} = 2\pi\varepsilon_0\nu_1^2\rho_0$$

Table 11.2. Resistivities and Damping Frequencies for Some Metals.

Metal	Li	Na	K	Rb	Cs	Cu	Ag	Au
ρ_0 ($\mu\Omega$ cm)[a]	8.55	4.2	6.15	12.5	20	1.67	1.59	2.35
ν_2 (10^{12} s^{-1})	10.1	4.8	3.1	4.82	5.15	4.7	4.35	5.9

[a] *Handbook of Chemistry and Physics*, 1977; room-temperature values.

Table 11.2 lists values for ν_2 which were calculated using experimental ρ_0 and ν_1 values. Now (11.22) becomes ,

$$\hat{\varepsilon} = 1 + \frac{\nu_1^2}{i\nu\nu_2 - \nu^2},$$

where $\hat{\varepsilon}$ is identical to $\hat{n}^2$

$$(\hat{n})^2 = n^2 - 2nki - k^2 = 1 - \frac{\nu_1^2}{\nu^2 - \nu\nu_2 i}$$

11.3 Free Electrons With Damping

Multiplying the numerator and denominator of the fraction in (11.25) by the complex conjugate of the denominator allows us to equate individually real and imaginary parts.

This provides the Drude equations for the optical constants

$$n^2 - k^2 = \varepsilon_1 = 1 - \frac{\nu_1^2}{\nu^2 + \nu_2^2}$$

$$2nk = \varepsilon_2 = \frac{2\sigma}{\nu} = \frac{\nu_2}{\nu}\frac{\nu_1^2}{\nu^2 + \nu_2^2}$$

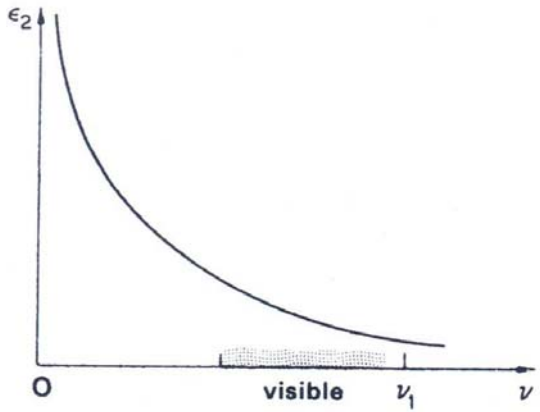


Figure 11.4. The absorption, $\varepsilon_2 = 2nk$, versus frequency, ν, according to the free electron theory (schematic).

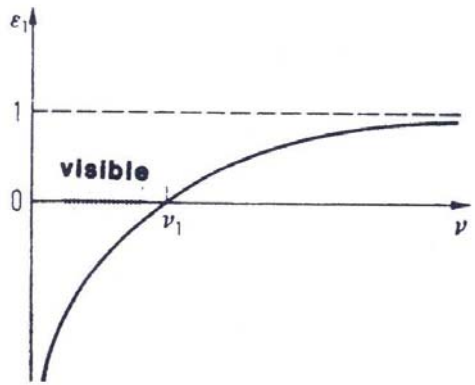


Figure 11.5. The polarization, $\varepsilon_1 = n^2 - k^2$, as a function of frequency according to the Drude theory (schematic).

with the characteristic frequencies $\nu_1 = \sqrt{\dfrac{e^2 N_f}{4\pi^2 \varepsilon_0 m}}$ and $\nu_2 = \dfrac{2\pi\varepsilon_0 \nu_1^2}{\sigma_0}$

11.4 Special Cases

For the *UV*, *visible*, and *near IR* regions, the frequency varies between 10^{14} and 10^{15} s^{-1}. The average damping frequency, ν_2 is 5×10^{12} s^{-1} (Table 11.2). Thus, $\nu^2 >> \nu_2^2$. Equation (11.27) then reduced to

$$\varepsilon_2 = \frac{\nu_2}{\nu}\frac{\nu_1^2}{\nu^2}$$

With $\nu \approx \nu_1$ (Table 11.1) We obtain $\varepsilon_2 \approx \dfrac{\nu_2}{\nu}$

For very small frequencies $\nu^2 << \nu_2^2$, we may neglect ν^2 in the denominator of (11.27). This yields, with (11.23)

$$nk\nu = \frac{\sigma}{4\pi\varepsilon_0} = \frac{1}{2}\frac{\nu_1^2}{\nu_2} = \frac{\sigma_0}{4\pi\varepsilon_0}$$

Thus, in the far *IR* the a.c. conductivity, σ and the d.c. conductivity σ_0 may be considered to be identical

11.5 Reflectivity

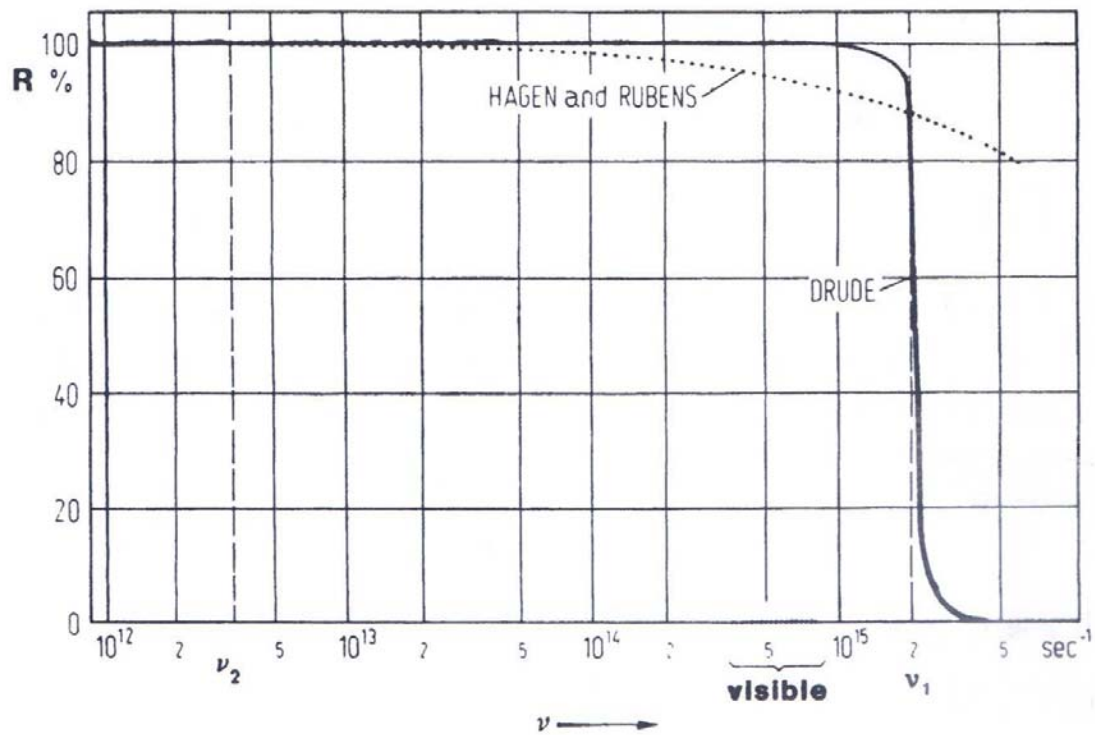


Figure 11.6. Calculated spectral reflectivity for a metal using the exact Drude equation (solid line), and the Hagen–Rubens equation (10.34) using $\nu_1 = 2 \times 10^{15}\ s^{-1}$ and $\nu_2 = 3.5 \times 10^{12}\ s^{-1}$.

The reflectivity of metal is calculated using (10.29) in conjunction with (11.26) and (11.27).

11.6 Bound Electrons (Classical Electron Theory of Dielectric Materials)

"At higher frequency, the light is absorbed and reflected by metal as well as by nonmetals in a narrow frequency band" →
It can be interpreted by Lorentz model: He assumed that under the influence of and external electric field, the positively charged electron cloud are displaced with respect to each other (Fig 11.7) →
"harmonic oscillator"

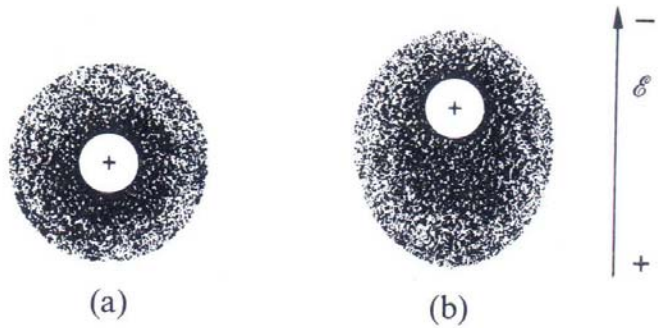


Figure 11.7. An atom is represented as a positively charged core and a surrounding, negatively charged electron cloud (a) in equilibrium and (b) in an external electric field.

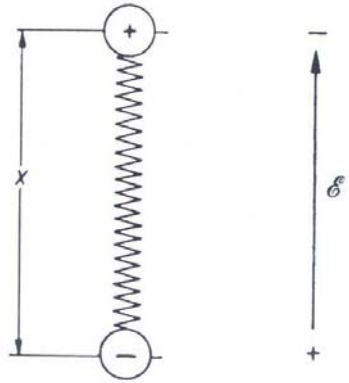


Figure 11.8. Quasi-elastic bound electron in an external electric field (harmonic oscillator).

11.6 Bound Electrons

Under the influence of and alternating electric field (i.e. by light), the electron is thought to perform forced vibrations

$$eE = eE_0 \exp(i\omega t)$$

The vibration equation: $m\frac{d^2x}{dt^2} + \gamma'\frac{dx}{dt} + kx = eE_0 \exp(i\omega t)$

kx: restoring force (***x*** is displacement, k is the spring constant), *γ'*: damping parameter

The stationary solution for week damping (see Appendix 1)

$$x = \frac{e\varepsilon_0}{\sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2\omega^2}} \exp[i(\omega t - \phi)]$$

where $\omega_0 = 2\pi\nu_0 = \sqrt{\frac{k}{m}}$ is resonance frequency of the oscillator, Φ is the phase

difference between forced vibration and the excitation force of the light wave (see Appendix 1)

$$\tan\phi = \frac{\gamma'\omega}{m(\omega_0^2 - \omega^2)} = \frac{\gamma'\nu}{2\pi m(\nu_0^2 - \nu^2)}$$

11.6 Bound Electrons

$P = exN_a$ **Inserting (11.33) yields** $P = \dfrac{e^2 N_a E_0 \exp[i(\omega t - \phi)]}{\sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2\omega^2}}$

with $\exp[i(\omega t - \phi)] = \exp(i\omega t)\cdot\exp(-i\phi)$

$$P = \frac{e^2 N_a E}{\sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2\omega^2}}\exp(-i\phi)$$

which yield (11.5) $\varepsilon = 1 + \dfrac{P}{\varepsilon_0 E}$ **and (10.12)** $\hat{n}^2 = n^2 - k^2 - 2nik \equiv \hat{\varepsilon} = \varepsilon_1 - i\varepsilon_2$

$$\hat{\varepsilon} = n^2 - k^2 - 2nki = 1 + \frac{e^2 N_a E}{\varepsilon_0\sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2\omega^2}}\exp(-i\phi)$$

with $\exp(-i\phi) = \cos\phi - i\sin\phi$

$$n^2 - k^2 - 2nki = 1 + \frac{e^2 N_a}{\varepsilon_0\sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2\omega^2}}\cos\phi$$

$$- i\frac{e^2 N_a}{\varepsilon_0\sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2\omega^2}}\sin\phi$$

11.6 Bound Electrons

The trigonometric terms in (11.42) are replaced, using (11.35), as follows

$$\cos\phi = \frac{1}{\sqrt{1+\tan^2\phi}} = \frac{m(\omega_0^2-\omega^2)}{\sqrt{m^2(\omega_0^2-\omega^2)^2+\gamma'^2\omega^2}}$$

$$\sin\phi = \frac{\tan\phi}{\sqrt{1+\tan^2\phi}} = \frac{\gamma'\omega}{\sqrt{m^2(\omega_0^2-\omega^2)^2+\gamma'^2\omega^2}}$$

separating the real and imaginary parts in (11.42) finally provides the optical constants

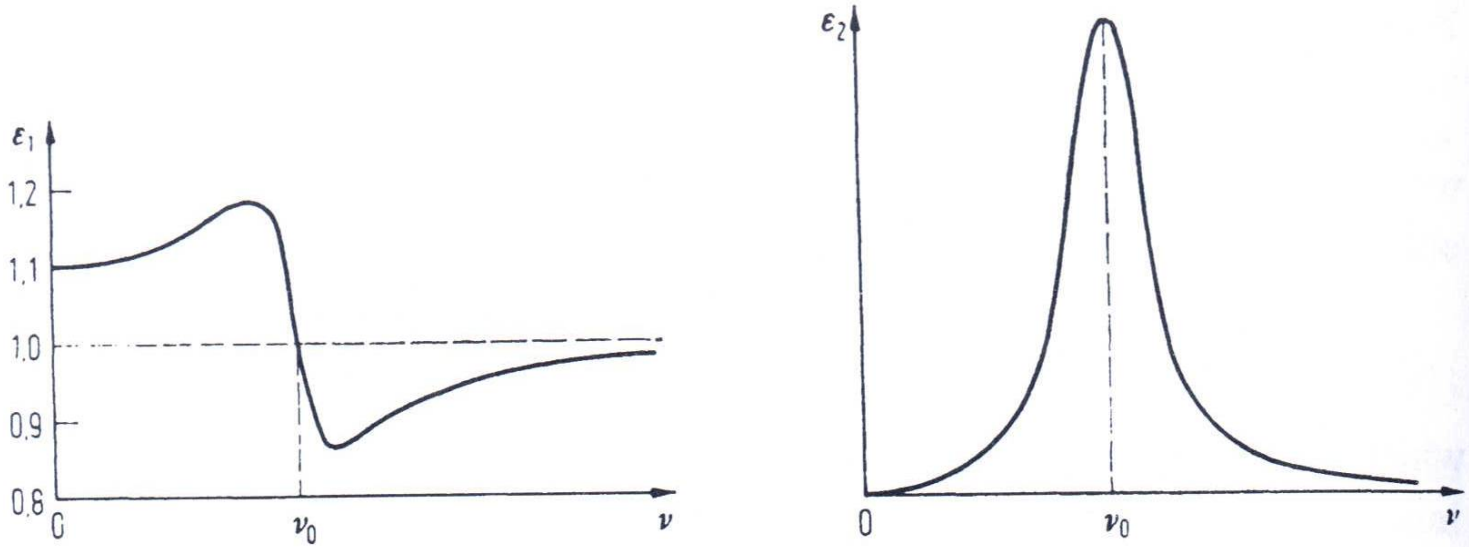
$$\varepsilon_1 = n^2 - k^2 = 1 + \frac{e^2 m N_a(\omega_0^2-\omega^2)}{\varepsilon_0[m^2(\omega_0^2-\omega^2)^2+\gamma'^2 v^2]}$$

$$\varepsilon_1 = 1 + \frac{e^2 m N_a(v_0^2-v^2)}{\varepsilon_0[4\pi^2 m^2(v_0^2-v^2)^2+\gamma'^2 v^2]}$$

that is,

$$\varepsilon_2 = 2nk = \frac{e^2 N_a \gamma'\omega}{\varepsilon_0[m^2(\omega_0^2-\omega^2)^2+\gamma'^2\omega^2]} \quad \text{or} \quad \varepsilon_2 = \frac{e^2 N_a \gamma' v}{2\pi\varepsilon_0[4\pi^2 m^2(v_0^2-v^2)^2+\gamma'^2 v^2]}$$

11.6 Bound Electrons

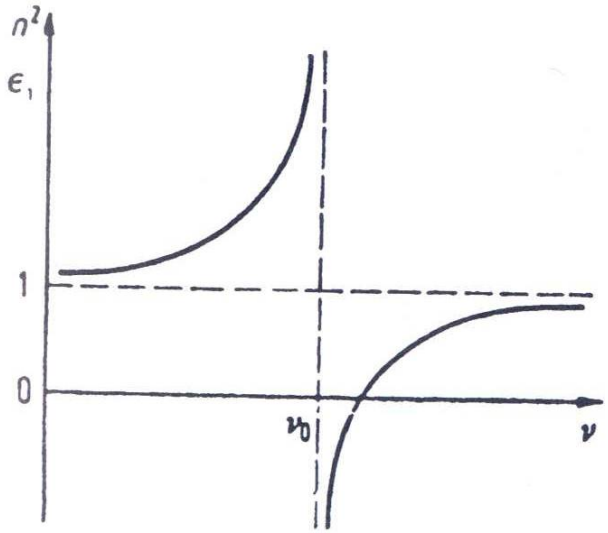


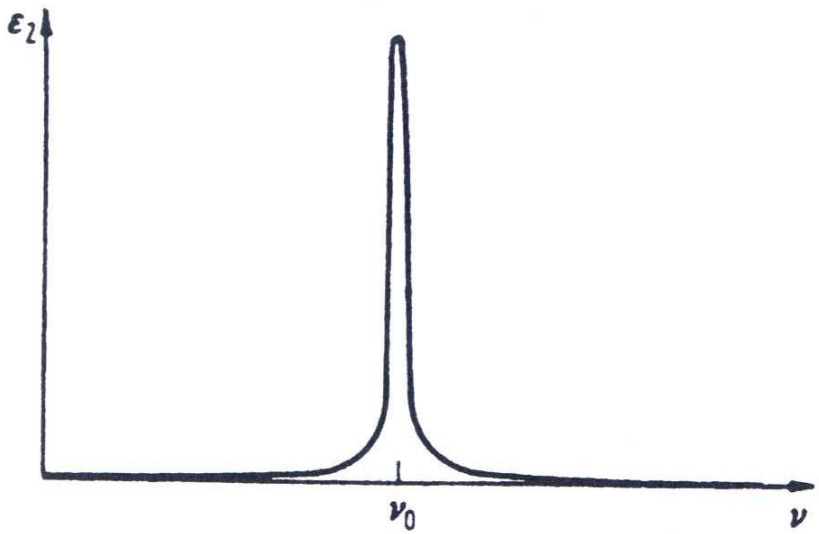
Figures 11.9 and 11.10. Frequency dependence of polarization, $\varepsilon_1 = n^2 - k^2$, and absorption, $\varepsilon_2 = 2nk$, as calculated with (11.45) and (11.46), respectively, using characteristic values for N_a and γ'.

11.7* Discussion of the Lorentz Equation for Special Cases

Small Damping : γ' is very small, equation (11.45) reduced to

$$\varepsilon_1 = n^2 - k^2 = 1 + \frac{e^2 N_a}{4\pi^2 \varepsilon_0 m (\nu_0^2 - \nu^2)}$$





Figures 11.11 and 11.12. The functions $\varepsilon_1(n^2)$ and ε_2, respectively, versus frequency according to the bound electron theory for the special case of small damping.

11.7* Discussion of the Lorentz Equation for Special Cases

Absorption near ν_0 : Electrons absorb most energy from light at the resonance frequency, i.e., ε_2 has a maximum near ν_0. For small damping, the absorption band becomes an absorption line (Fig 11.12)

$$\varepsilon_2 = \frac{e^2 N_a}{2\pi\varepsilon_0 \gamma' \nu_0}$$

More than One Oscillator

$$\varepsilon_1 = n^2 - k^2 = 1 + \frac{e^2 m N_a}{\varepsilon_0} \sum_i \frac{f(\nu_{0i}^2 - \nu^2)}{4\pi^2 m^2 (\nu_{0i}^2 - \nu^2)^2 + \gamma_i'^2 \nu^2}$$

$$\varepsilon_2 = 2nk = 1 + \frac{e^2 N_a}{2\pi\varepsilon_0} \sum_i \frac{f_i \nu \gamma_i'}{4\pi^2 m^2 (\nu_{0i}^2 - \nu^2)^2 + \gamma_i'^2 \nu^2}$$

11.8 Contribution of Free Electrons and Harmonic Oscillators to the Optical Constants

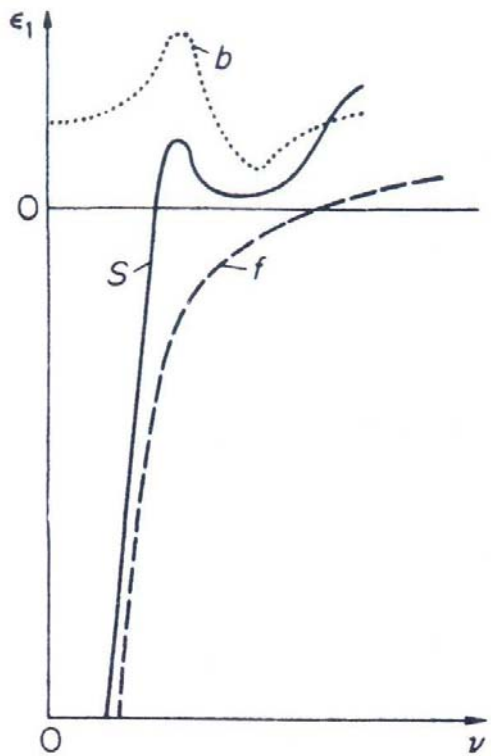
The optical properties of metals may be described by postulating a certain number of free electrons and a certain number of harmonic oscillators. Both the free electrons and the oscillators contribute to the polarization.

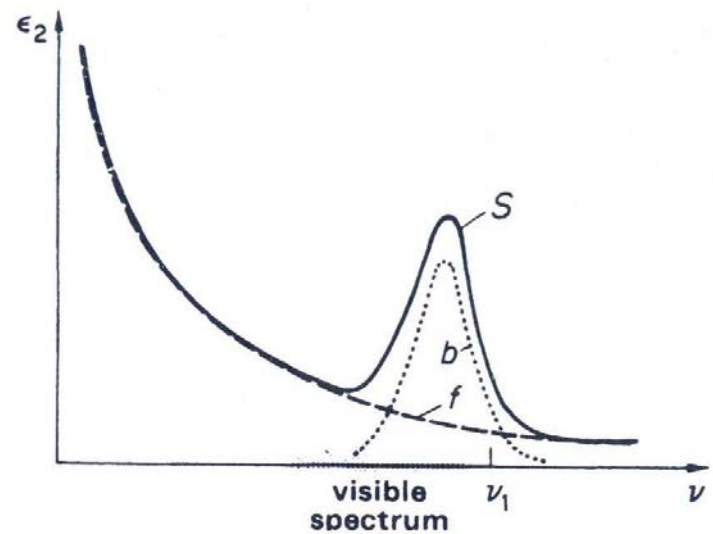
Thus, the equations for the optical constants may be rewritten, by combining (11.26), (11.27),(11.49), and(11.50)

$$\varepsilon_1 = 1 - \frac{v_1^2}{v^2 + v_2^2} + \frac{e^2 m N_a}{\varepsilon_0} \sum_i \frac{f(v_{0i}^2 - v^2)}{4\pi^2 m^2 (v_{0i}^2 - v^2)^2 + \gamma_i'^2 v^2}$$

$$\varepsilon_2 = 2nk = \frac{v_2}{v} \frac{v_1^2}{v^2 + v_2^2} + \frac{e^2 N_a}{2\pi\varepsilon_0} \sum_i \frac{f_i v \gamma_i'}{4\pi^2 m^2 (v_{0i}^2 - v^2)^2 + \gamma_i'^2 v^2}$$

11.8 Contribution of Free Electrons and Harmonic Oscillators to the Optical Constants





Figures 11.13 and 11.14. Frequency dependence of ε_1 and ε_2 according to (11.53) and (11.54). ($i = 1$). f = free electron theory; b = bound electron theory; S = summary curve (schematic).

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 $\boldsymbol{k}_{phot} = p/\hbar$ is much smaller than that of an electron: $\boldsymbol{k}_{phot}$ is much smaller than the diameter of the Brillouin zone (Fig.12.1)

Direct interband transition: electron transitions at which $\boldsymbol{k}$ remains constant (vertical transition)

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

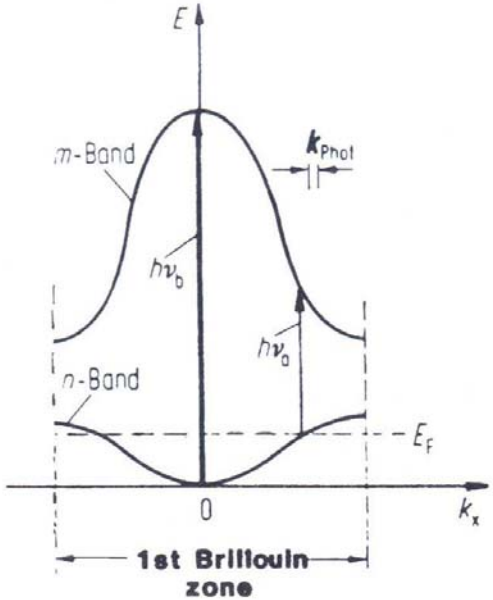


Figure 12.1. Electron bands and direct interband transitions in a reduced zone. (Compare with Fig. 5.4.)

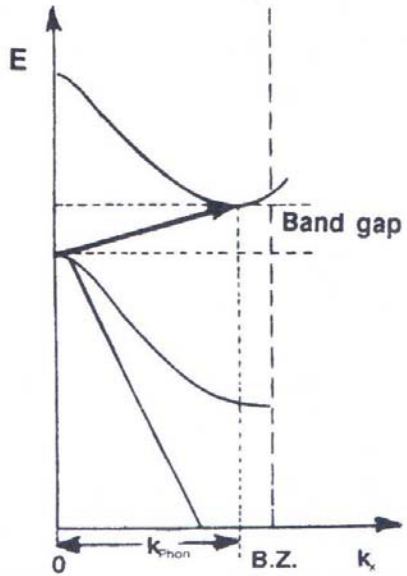


Figure 12.2. Indirect interband transition. (The properties of phonons are explained in Chapter 20.)

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.

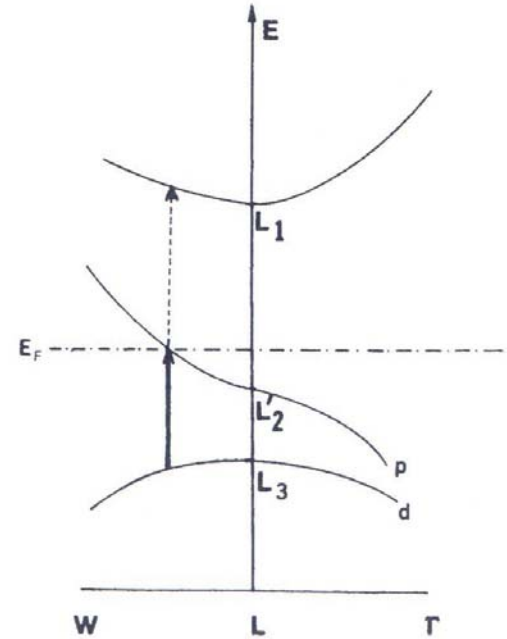


Figure 12.3. Section of the band diagram for copper (schematic). Two pertinent interband transitions are shown with arrows. The smallest possible interband transition occurs from a filled *d*-state to an unfilled state just above the Fermi energy.

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

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.

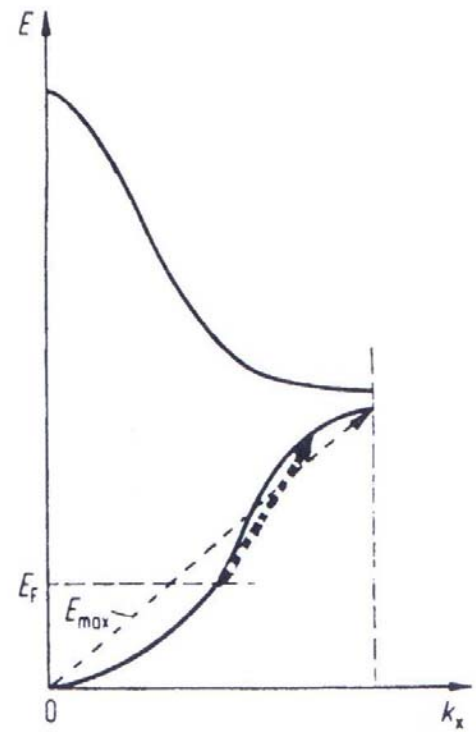


Figure 12.4. Intraband transitions. The largest energy that can be absorbed by intraband transitions is obtained by projecting the arrow marked "E_{max}" onto the energy axis.

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.

*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'***

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

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.

Part IV Magnetic Properties of Materials

Chap. 14. Foundations of Magnetism

Chap. 15. Magnetic Phenomena and Their Interpretation- Classical Approach

Chap. 16. Quantum Mechanical Considerations

Chap. 17. Applications

Magnetic Field, *H*

- ***H*** **represents a magnetic force generated in a volume of the space due to a change in magnetic energy of that of the space.**

  Examples of the magnetic force
  - A force on a current-carrying conductor
  - A torque on a magnetic dipole
  - A reorientation of spins on electrons within atoms

- ***H*** **is fundamentally generated by an electrical charge in motion.**
  Earth (~ 0.7Oe)
  Bulk magnets (~ 5,000Oe)
  Current-carrying conductors (~30,000Oe)
  Superconductors (>100,000Oe)
  (ref. Table 1.1 in David Jiles)

- **Unit**
  mks or SI(Systeme Interrnational): [A/m]
  cgs: [Oe]

$$1\ \text{Oe} = \frac{1000}{4\pi}\ \text{A/m}\ (\sim 79.6\ \text{A/m})$$

Basic Concepts in Magnetism

- (See Fig. 14.1) Diamagnetic materials are expelled from the field, whereas para-, ferro-, antiferro-, and ferrimagnetic materials are attracted in different degrees.

$$F = V\chi\mu_0 H \frac{dH}{dx} \quad (14.1)$$

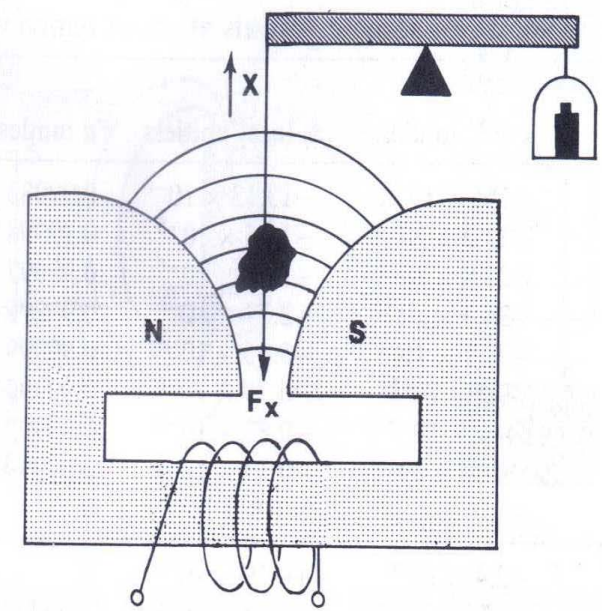


Figure 14.1. Measurement of the magnetic susceptibility in an inhomogeneous magnetic field. The electromagnet is driven by an electric current, which flows through the helical windings of a long insulated wire called a solenoid. The magnetic flux lines (dashed) follow the iron core.

F: force

V : the volume of the sample

χ : susceptibility

H : magnetic field

$\frac{dH}{dx}$: the change of the magnetic field strength ***H*** in the ***x***-direction

Magnetic Induction, *B*

- ***B*** **is the response of a medium to an applied magnetic field** ***H***
- ***B*** **is defined by** $B = \frac{\Phi}{A}$

B **is the magnetic flux, Φ [Wb] passing through a unit cross-sectional area.**

Magnetic flux, Φ?

- Generated by the presence of a magnetic field in a medium.

- By Lentz law, the voltage ***V*** **is induced as Φ changes**

$$V = -N\frac{d\Phi}{dt} = -NA\frac{dB}{dt}$$ **called, "electromagnetic induction"**

$$1\ volt = -(1)\frac{\Phi_f - \Phi_i}{dt}$$ **If $\Phi_f = 0$, $\Phi_i = 1$ Wb**

(1Wb = 1 volt•sec)

Maxwell's equation (Gauss's law)

$\nabla \cdot B = 0$: Always form a closed path!

- **Unit: [G], [T]**

1 Tesla = 1 Wb/m^2 (= 1 volt•sec/m^2)

A force of 1 N/m on a conductor carrying 1 A perpendicular to the direction of ***B***

Relation between *B* and *H*

$B = \mu H$, where μ is permeability(투자율)

$\mu = \mu_o$ in free space

$= 4\pi \times 10^{-7}$ H/m (or Wb/A)

Relative permeability $\mu_r = \mu/\mu_o$

$\mu_r = 1$ in a perfect vacuum(free space)

Basic Concepts in Magnetism

$$H = \frac{In}{L}(A/m) \quad (14.2)$$

H : the field strength

I : current

n : the number of the windings

L : the length of the solenoid

$$B = \mu\mu_0 H \quad (14.3)$$

B : magnetic induction or *magnetic flux density* (tesla; ***T***)

μ : permeability or relative permeability(μ_r)

(unitless)

Magnetic Moment, *m*

- **Definitions :**

  $m = pl$ in a bar magnet

  $m = iA$ in a conductor loop

- **Unit**

	SI	cgs
	[Am^2]	[emu]
	[Wbm]	[erg/Oe]

$$1 \text{ Wbm} = \frac{1}{4\pi} \quad 10^{10} \text{Gcm}^3$$

- **Measurements of *m***

  i) Torque measurement: $\tau = \mu_o m \times H = m \times B$

  $\tau = \tau_{max}$ if m is perpendicupar to H (or B), and then

  $m = \tau_{max}/\mu_o H$

  Since $m = pl$ and $p = \Phi/\mu_o$ in the Sommerfeld conversion

  $m = \Phi l/\mu_o$

  ii) Magnetization measurement

  $m = MV$

Magnetization, *M*

▶ ***M*** **is the total magnetic moment *m* per unit volume (*m* per unit mass = specific magnetization σ)**

$M = m/V$ (cf. $\sigma = M/\rho$ [emu/g]), where ρ is density

Since $m = \Phi l/\mu_o$, $V = Al$

$M = \Phi/\mu_o A = B/\mu_o$

Therefore, $B = \mu_o M$ when $H = 0$

▶ **Saturation Magnetization**

M_o : complete saturation, where all atomic moments are aligned parallel to H_a

M_s : technical saturation, where multiple-domains become single domain

▶ **Relation between *M* and *H***

$M = \chi H$, where χ is susceptibility(자화율) ↔ $B = \mu H$ (μ is permeability(투자율))

μ and χ are not useful for ferromagnets.

Need differential values: $\mu' = dB/dH$, $\chi' = dM/dH$

▶ **Relationship between *H*, *B*, and *M***

A universal relationship

$B = \mu_o(H + M)$: SI(Sommerfeld)

$= \mu_o H + I$: SI(Kennelly)

$= H + 4\pi M$: cgs(Gaussian)

$B = \mu_o(H + M) = \mu_o(H + \chi H) = \mu_o(1 + \chi)H$

Since $B = \mu H = \mu_o \mu_r H$, $\mu_r = 1 + \chi$

μ_r and χ are different ways of describing the response of a material to magnetic fields.

Basic Concepts in Magnetism

$$\mu = 1 + \chi \qquad (14.4)$$

(See Table 14.1)

- For empty space and, for all practical purpose, also for air,

  $\chi = 0$ and thus $\mu = 1$

- For diamagnetic materials,

  χ is small and negative. $\rightarrow$ μ is slightly less than 1

- For para- and antiferromagnetic materials,

  χ is small and positive. $\rightarrow$ μ is slightly larger than 1

- For ferro- and ferrimagnetic materials,

  χ and μ are large and positive.

$\Rightarrow$ The magnetic constants are temperature-dependent, expect diamagnetic materials. The susceptibility for ferromagnetic materials depends on the field strength, *H*.

Basic Concepts in Magnetism

Table 14.1. Magnetic constants of some materials at room temperature

Material	χ (SI) unitless	χ (cgs) unitless	μ unitless	Type of magnetism
Bi	-165×10^{-6}	-13.13×10^{-6}	0.99983	
Be	-23.2×10^{-6}	-1.85×10^{-6}	0.99998	
Ag	-23.8×10^{-6}	-1.90×10^{-6}	0.99997	
Au	-34.4×10^{-6}	-2.74×10^{-6}	0.99996	Diamagnetic
Ge	-71.1×10^{-6}	-5.66×10^{-6}	0.99999	
Cu	-9.7×10^{-6}	-0.77×10^{-6}	0.99999	
Si	-4.1×10^{-6}	-0.32×10^{-6}	0.99999	
Water	-9.14×10^{-6}	-0.73×10^{-6}	0.99999	
Superconductors[a]	-1.0	$\sim -8 \times 10^{-2}$	0	
β-Sn	$+2.4 \times 10^{-6}$	$+0.19 \times 10^{-6}$	1	
W	$+77.7 \times 10^{-6}$	$+6.18 \times 10^{-6}$	1.00008	
Al	$+20.7 \times 10^{-6}$	$+1.65 \times 10^{-6}$	1.00002	Paramagnetic
Pt	$+264.4 \times 10^{-6}$	$+21.04 \times 10^{-6}$	1.00026	
Low carbon steel	$\approx 5 \times 10^{3}$	3.98×10^{2}	5×10^{3}	
Fe–3%Si (grain-oriented)	4×10^{4}	3.18×10^{3}	4×10^{4}	Ferromagnetic
Ni–Fe–Mo (supermalloy)	10^{6}	7.96×10^{4}	10^{6}	

[a] See Section 7.6.

Note: The table lists the unitless susceptibility, χ, in SI and cgs units. (The difference is a factor of 4π, see Appendix 4.) Other sources may provide mass, atomic, molar, volume, or gram equivalent susceptibilities in cgs or SI units. μ has the same value in both unit systems, see Section 14.3.

Source: Landolt-Börnstein, *Zahlenwerte der Physik*, Vol. 11/9, 6th Edition, Springer-Verlag, Berlin (1962).

Basic Concepts in Magnetism

$$B = \mu_0 H + \mu_0 M$$ in free space (14.5)

$$M = \chi H$$ ***M***: magnetization (14.6)

$$\phi = BA$$ (14.7)

ϕ: magnetic flux
B: magnetic flux density

$$\phi = \mu_0 HA$$ (14.7a)

in free space (**M=0**)

$$M = \frac{\mu_m}{V}$$ (14.8)

μ_m : magnetic moment

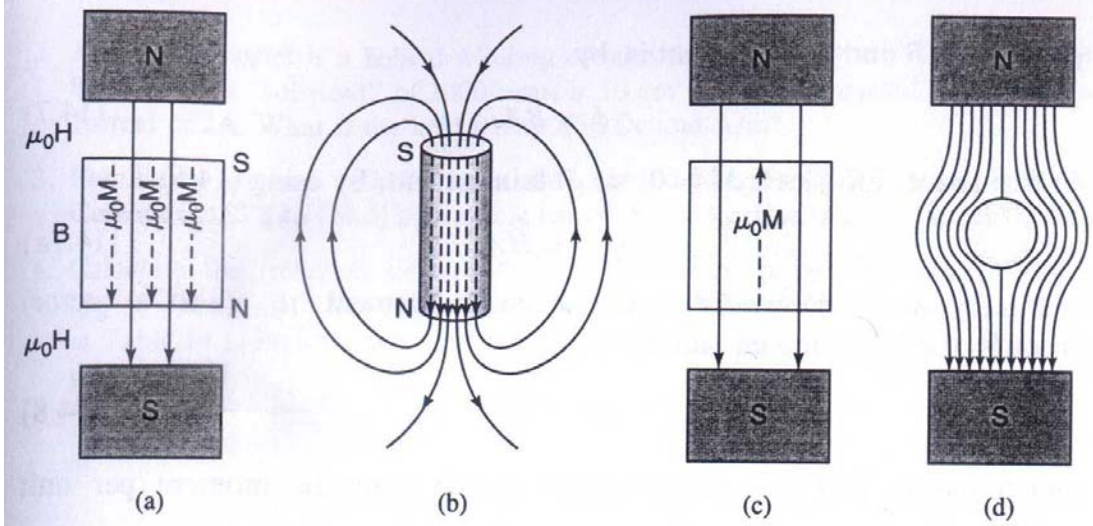


Figure 14.2. Schematic representation of magnetic field lines in and around different types of materials. (a) *Para- or ferromagnetics*. The magnetic induction **(B)** inside the material consists of the free-space component (μ_0**H**) plus a contribution by the material (μ_0**M**); see Eq. (14.5). (b) The magnetic field lines outside a material point from the north to the south poles, whereas inside of para- or ferromagnetics, **B** and μ_0**M** point from south to north in order to maintain continuity. (c) In *diamagnetics*, the response of the material counteracts (weakens) the external magnetic field. (d) In a thin surface layer of a *superconductor*, a supercurrent is created (below its transition temperature) which causes a magnetic field that opposes the external field. As a consequence, the magnetic flux lines are expelled from the interior of the material. Compare to Figure 9.18.

Units

- **SI unit** ***VS*** **cgs unit**

$$B = \mu_0 H + \mu_0 M \quad (14.5)$$

$$B = \mu\mu_0 H \quad (14.3)$$

$$\mu = 1 + \chi \quad (14.4)$$

magnetic field strength, *H* (Oersted)
magnetic induction, *B* (Gauss)

In some European countries, and in many international scientific journals

$$B = H + 4\pi M \quad (14.9)$$

$$B = \mu H \quad (14.10)$$

$$\mu = 1 + 4\pi\chi \quad (14.11)$$

magnetic field strength, *H* (A/m)
magnetic induction, *B* (Tesla)

The scientific and technical literature on magnetism, particularly in the USA

Overview –Types of Magnetism

➢ Diamagnetism

- ❑ **Lenz's Law** : a current is induced in a wire loop whenever a bar magnet is moved toward (or from) the loop. The current induces a magnetic moment opposite to the bar magnet (Fig.15.1(a)

- ❑ The external field (H_{ex}) accelerates or decelerates the orbiting electrons, in order that their magnetic moment is in opposite direction from H_{ex}

- ❑ **Lamor precession**: Precessions of electron orbits about the magnetic field direction (Fig.15 1(b))

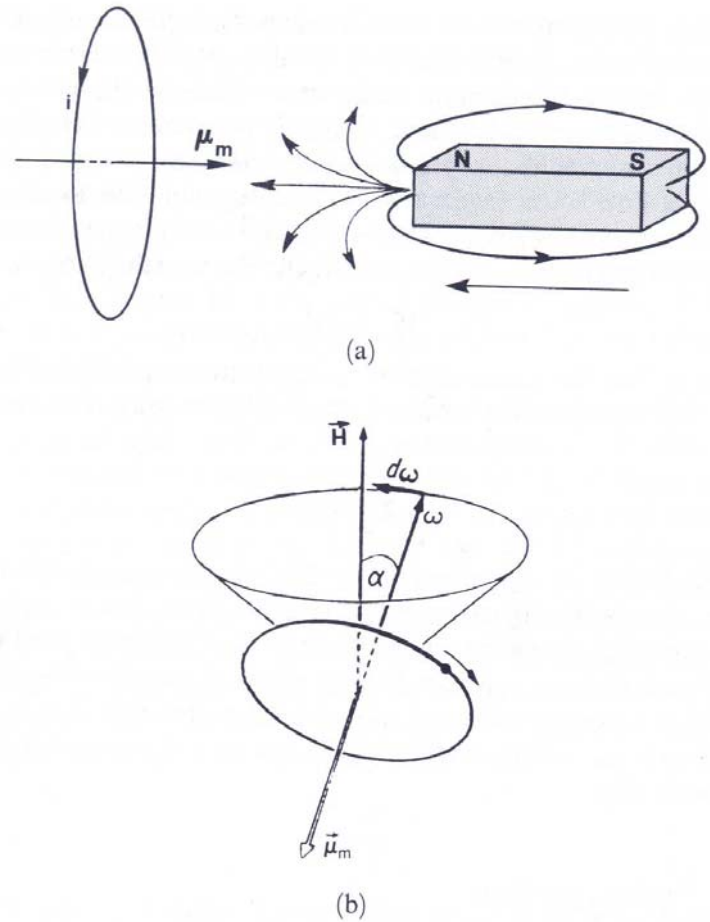


Figure 15.1. Explanation of diamagnetism. (a) Induction of a current in a loop-shaped piece of wire by moving a bar magnet toward the wire loop. The current in the loop causes a magnetic field that is directed opposite to the magnetic field of the bar magnet (Lenz's law). (b) Precession of an orbiting electron in an external magnetic field. Precession is the motion which arises as a result of external torque acting on a spinning body (such as a spinning top) or, as here, on an orbiting electron.

Overview –Types of Magnetism

➢ Diamagnetism

❑ Diamagnetism in superconducting materials (Sec. 7.6)

- **Meissner effect** : Superconductors expel the magnetic flux lines in the superconducting state. Inside superconductor ***B*** is zero. (Fig. 14.2(d))

$$H = -M$$

- Perfect diamagnetism: Magnetization is equal and opposite to the external magnetic field.

Susceptibility, $\chi = M/H = -1$

❑ Usage of strong diamagnetism of superconductor

- Frictionless bearing: support of loads by a repelling magnetic field
- Levitation: magnet hovers above a superconducting materials
- Suspension effect: a chip of superconducting material hangs beneath a magnet

Overview –Types of Magnetism

➢ Paramagnetism

Largely due to electron spin motion. An additional source stems from orbiting motion.

- An external field turns randomly oriented magnetic moments into the field direction

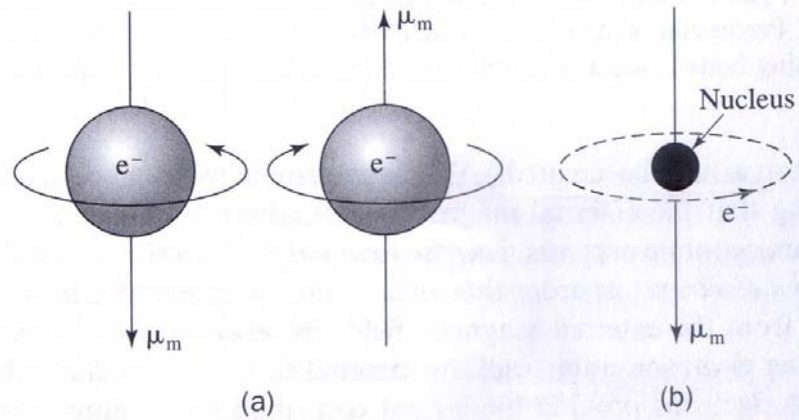


Figure 15.2. (a) Schematic representation of electrons which spin around their own axes. A (para)magnetic moment μ_m results; its direction depends on the mode of rotation. Only two spin directions are shown (called "spin up" and "spin down"). (b) An orbiting electron is the source of *electron-orbit paramagnetism*.

☐ **Spin paramagnetism** : net magnetic moment results from electrons which spin around their own axis (Fig.15.2(a))

- Observed in some metal and salts of transition elements

☐ **Electron-orbit paramagnetism** : net magnetic moment stems from magnetic moments of orbiting electrons (Fig.15.2(b))

- Free atoms (dilute gases), rare earth elements and their salts and oxides

Overview –Types of Magnetism

➢ Paramagnetism

Temperature dependence of paramagnetism

- **Curie law** : susceptibility, χ, is inversely proportional to the absolute temperature T

$$\chi = C/T \qquad (15.1)$$

where, C is Curie constant

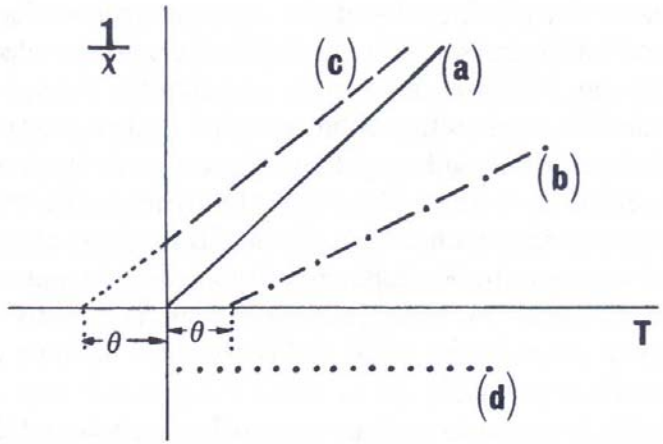


Figure 15.3. Schematic representation of (a) the Curie law and (b) and (c) the Curie–Weiss law. (d) The diamagnetic behavior is also shown for comparison.

- **Curie-Weiss law** : a more general relationship

$$\chi = C/(T-\theta) \qquad (15.2)$$

where θ is another constant that has same unit as the T

- Ni (above Curie temperature), Fe and β-Co, rare earth elements, salts of transition elements (e.g., the carbonate, chlorides, and sulfates of Fe, Co, Cr, Mn obey Curie-Weiss law)

Overview –Types of Magnetism

➢ Paramagnetism

Figure 15.4. Schematic representation of the spin alignment in a *d*-band which is partially filled with eight electrons (Hund's rule).

- Why only spin paramagnetism is observed in most solids?

In crystals, the electron orbits are essentially coupled to the lattice, which prevents the orbital magnetic moments from turning into the field direction *("orbital quenched")*.

- Exception of *"orbital quenched"* elements: Rear earth elements and their derivatives having "deep-lying 4*f*-electrons". The latter ones are shielded by the outer electrons from the crystalline field of the neighboring ions , and thus orbital magnetic moments of the *f*-electrons may turn into the external magnetic field and contributed to electron-orbit paramagnetism

- **The *g*-factor** : the friction of total magnetic moment contributed by orbital motion versus by spin motion
- **Hund's rule** and **Pauli principle**
- **Bohr magneton** : the smallest unit (or quantum) of the magnetic moment

$$\mu_B = e\hbar/(4\pi m) = 9.274 \times 10^{-24}\ J/T \equiv (A\cdot m^2) \qquad (15.3)$$

Overview –Types of Magnetism

➢ Ferromagnetism

- ❑ A ring shaped solenoid (Fig.15.5)

  By increasing current external field is increased, then the magnetization, ***M***, rises showing a hysteresis loop (Fig 15.6)

  - M_s : saturation magnetization
  - M_r : remanance
  - H_c : coercive field

- ❑ Hard (soft) magnetic materials:

  a large (small) M_r and H_C

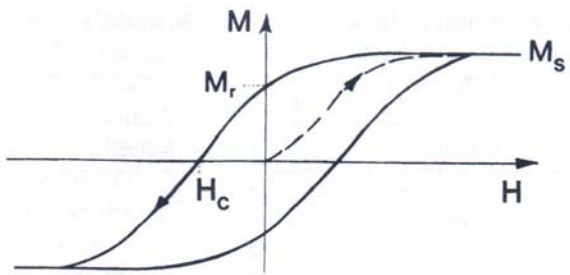


Figure 15.6. Schematic representation of a hysteresis loop of a ferromagnetic material. The dashed curve is for virgin material.

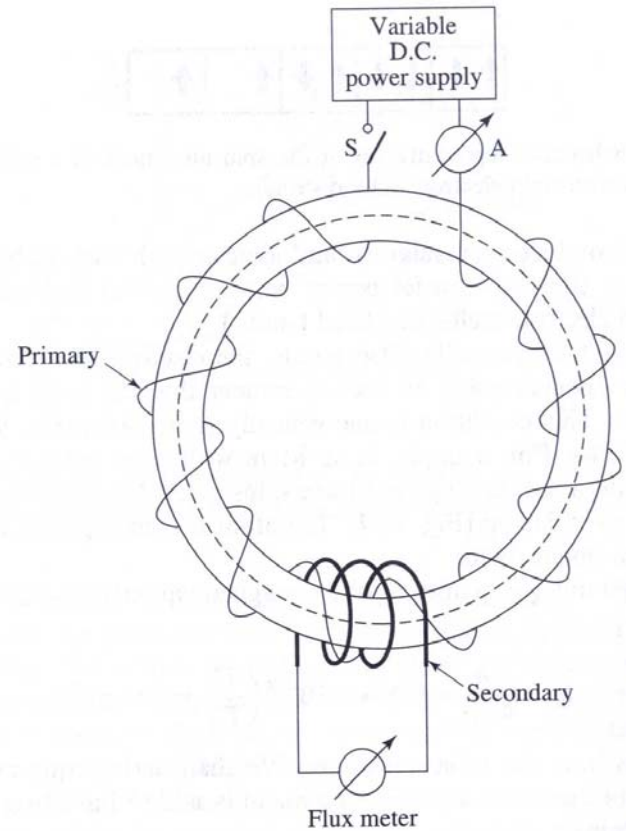


Figure 15.5. A ring-shaped solenoid with primary and secondary windings. The magnetic flux lines are indicated by a dashed circle. Note, that a current can flow in the secondary circuit only if the current (and therefore the magnetic flux) in the primary winding changes with time. An on–off switch in the primary circuit may serve for this purpose.

Overview –Types of Magnetism

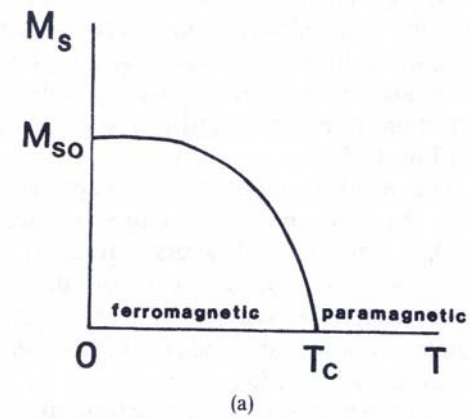
➢ Ferromagnetism

- ❑ *T* dependence of M_s (Fig.15.7(a))

  Above the Curie Temperature, T_C ferromagnetics become paramagnetic.

- ❑ A small difference between T_C and θ *(in Curie-Weiss law)* is due to a gradual transition from ferromagnetism to paramagnetism (Fig. 15.7(b))

  - Magnetic short-range transition: Small clusters of spins are still aligned slightly above $T_C \rightarrow$ gradual transition (Fig. 15.7(b))



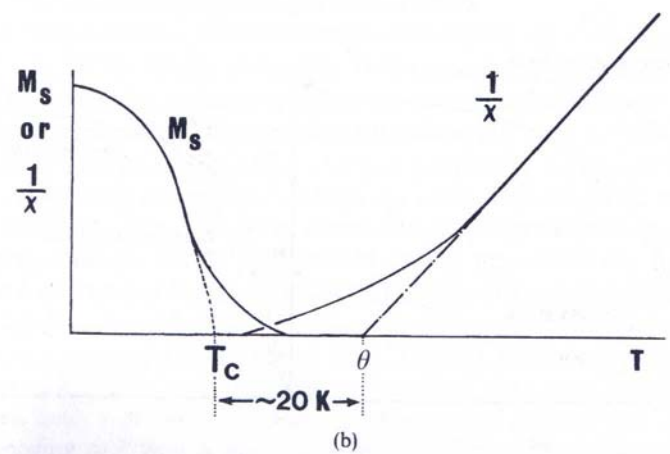


Figure 15.7. (a) Temperature dependence of the saturation magnetization of ferromagnetic materials. (b) Enlarged area near the Curie temperature showing the paramagnetic Curie point θ (see Fig. 15.3) and the ferromagnetic Curie temperature T_C.

Table 15.1. Saturation Magnetization at 0 K and Curie Temperature (T_C) for Some Ferromagnetic Materials.

Metal	M_{S0} (A/m)	M_{S0} (Maxwells/cm^2)	T_C (K)
Fe	1.75×10^6	2.20×10^4	1043
Co	1.45×10^6	1.82×10^4	1404
Ni	0.51×10^6	0.64×10^4	631
Gd	5.66×10^6	7.11×10^4	289

Overview –Types of Magnetism

➢ Ferromagnetism

- ❑ **Piezomagnetism :** the magnetization of ferromagnetics is stress dependent (Fig 15.8)

  Ex) a compressive stress increases *M* for Ni, while tensile stress reduces *M*.

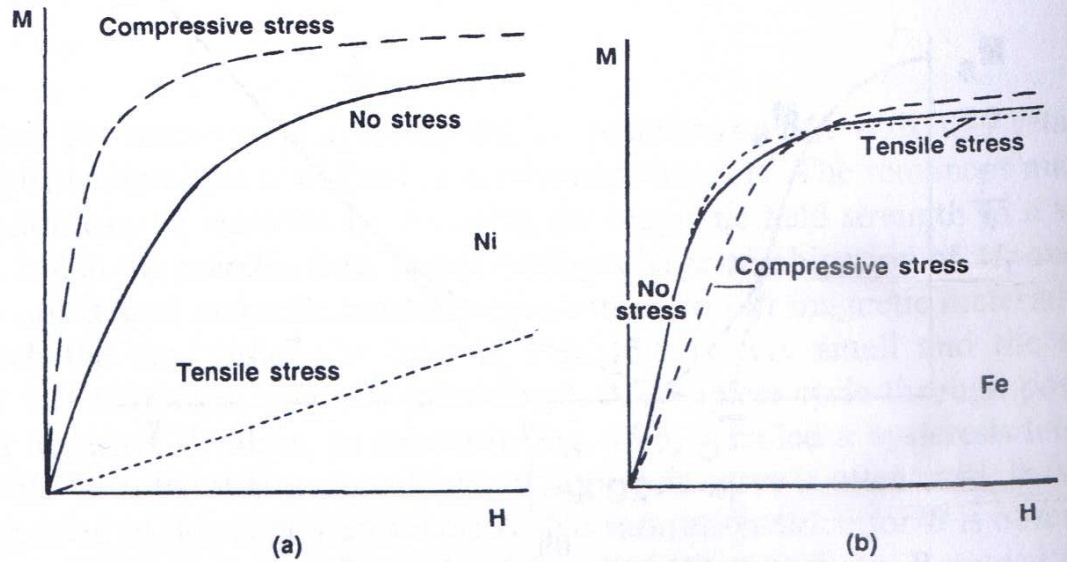


Figure 15.8. Schematic representation of the effect of tensile and compressive stresses on the magnetization behavior of (a) nickel and (b) iron. (Piezomagnetism.)

- ❑ **Magnetostriction :** inverse of piezomagnetism
  - magnetic field causes a change in dimension of a ferromagnetic substance
  - also observed in ferrimagnetic or antiferromagetic materials
  - terbium-dysprosium-iron display magnetostriction about 3 orders of magnitude larger than iron-nickel alloys

Overview –Types of Magnetism

➢ Ferromagnetism

❑ Explanation of Ferromagnetism

- **Spontaneous magnetization:**

  • the spins of unfilled *d*-band spontaneously aligned parallel to each other below T_C within magnetic domains without the presence of external magnetic field (Fig 15.9)

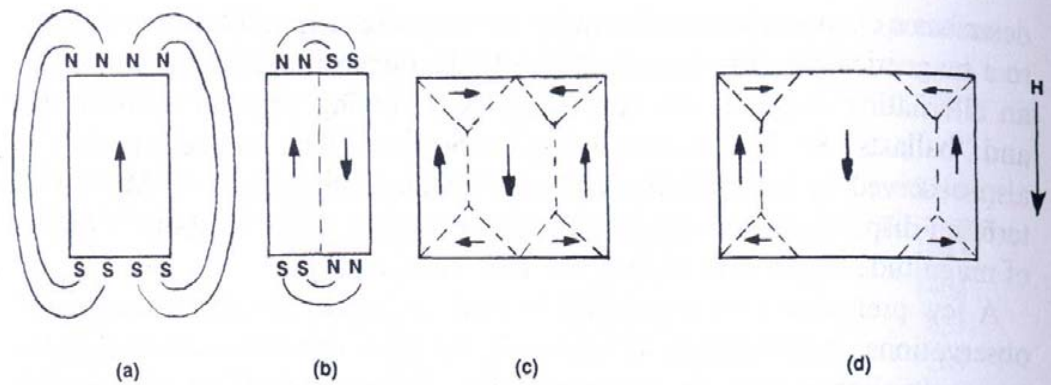


Figure 15.9. (a) Spontaneous alignment of all spins in a single direction. (b) Division into two magnetic domains having opposite spin directions. (c) Closure domains in a cubic crystal. (d) Growth of a domain whose spins are parallel to an external magnetic field. (The domain walls are *not* identical with the grain boundaries.)

• **exchange energy** causes adjacent spins to align parallel to each other

❑ Magnetic Domain structure

• Energetically favorable by a reduction in **magnetostatic energy**

→ Spontaneous division into many individual domains in which all spins are aligned in the same direction

• Closure domain structure: most favorable in the point of magnetostatic energy Fig. 15.9 (c)

Overview –Types of Magnetism

➢ Ferromagnetism

❑ Magnetic Domain

- The individual domains are magnetized to saturation.
- The spin direction in each domain is different so that as a whole it cancels each other and thus the net magnetization is zero.
- An external magnetic field causes to grow the domain whose spins are parallel or nearly parallel to the external field.
- At the technical saturation magnetization, M_S, the entire crystal contains one single domain, having all spins aligned parallel to external field.
- Domain wall: the region between individual domains in which the spins rotate from one direction into the next.
- Barkhausen effect : a discontinuous domain wall movement by external field

Overview –Types of Magnetism

➢ Antiferromagnetism

- Spontaneous alignment of moment below critical Temp. (Néel Temp.)
- Aligned in antiparallel (Fig 15.10)
- No net magnetism
- Néel Temperature, T_N
- Modified Curie-Weiss law for antiferromangtics

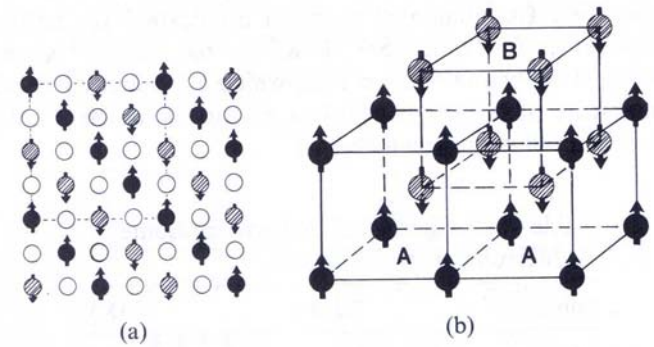


Figure 15.10. Schematic representation of spin alignments for antiferromagnetics at 0 K. (a) Display of a (100) plane of MnO. The gray (spin down) and black (spin up) circles represent the Mn ions. The oxygen ions (open circles) do not contribute to the antiferromagnetic behavior. MnO has a NaCl structure. (b) Three-dimensional representation of the spin alignment of manganese ions in MnF_2. (The fluorine ions are not shown.) This figure demonstrates the interpenetration of two manganese sublattices, A and B, having antiparallel aligned moments.

$$\chi = C/(T-(-\theta)) = C/(T+\theta) \quad (15.4)$$

the extrapolation of paramagetic (above T_N) line to $1/\chi = 0$ yield a negative θ

Table 15.2. Characteristic Data for Some Antiferromagnetic Materials.

Substance	T_N (K)	$-\theta$ (K)
MnO	116	610
MnF_2	67	82
α-Mn	100	?
FeO	198	570
NiO	523	~2000
CoO	293	330
Cr	310	?

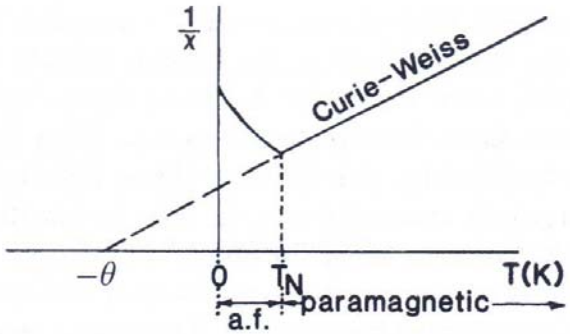


Figure 15.11. Schematic representation of the temperature dependence of a polycrystalline antiferromagnetic (a.f.) material.

Overview –Types of Magnetism

➢ Ferrimagnetism

- Exhibit spontaneous magnetic moment and hysteresis below a Curie temperature, similarly as ferromagntics
- Aligned in antiparallel, but magnetic moment remain uncanceled.
- Ceramic (oxide) materials, poor electrical conductor

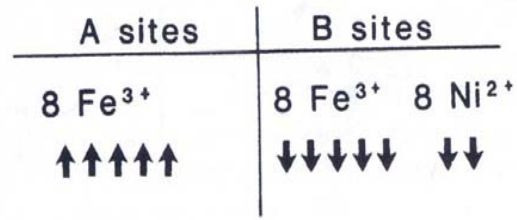


Figure 15.12. Distribution of spins upon A and B sites for the inverse spinel $NiO \cdot Fe_2O_3$. The spins within one site are arranged considering Hund's rule (Fig. 15.4). The iron ions are equally distributed among the A and B sites. The nickel ions are only situated on B sites. The relevance of the number of ions per unit cell is explained later on in the text.

Table 15.3. Calculated and Measured Number of Bohr Magnetons for Some Ferrites.

Ferrite	Mn	Fe	Co	Ni	Cu
Calculated μ_B	5	4	3	2	1
Measured μ_B	4.6	4.1	3.7	2.3	1.3

- Nickel ferrite $NiO \cdot Fe_2O_3$ (Fig 15.12)

  - Two uncanceled spins, $2\mu_B$ per formula unit

- The small discrepancy between experiment and calculation (Table 15.3) is caused by some contribution of orbital effects to the overall magnetic moment.

Overview –Types of Magnetism

➢ Ferrimagnetism

- ❑ Cubic ferrite (Spinel structure) (Fig.15.13)
  - $MO{\cdot}Fe_2O_3$, where M = Mn, Ni, Fe, Co, Mg, etc.
  - In the unit cell, total 56 ions (8 M^{2+} ions, 16 Fe^{3+} ions, 32 O_2^- ions)
    64 tetrahedral *A* site / 8 = 8
    32 octahedral *B* site / 2 = 16
  - Normal Spinel :
    8 M^{2+} in A, 16 Fe^{3+} in B
  - Inverse Spinel :
    8 Fe^{3+} in A, 8 M^{2+} + 8 Fe^{3+} in B
- ❑ Temperature dependence of ferrimagnetics (Fig.15.14)

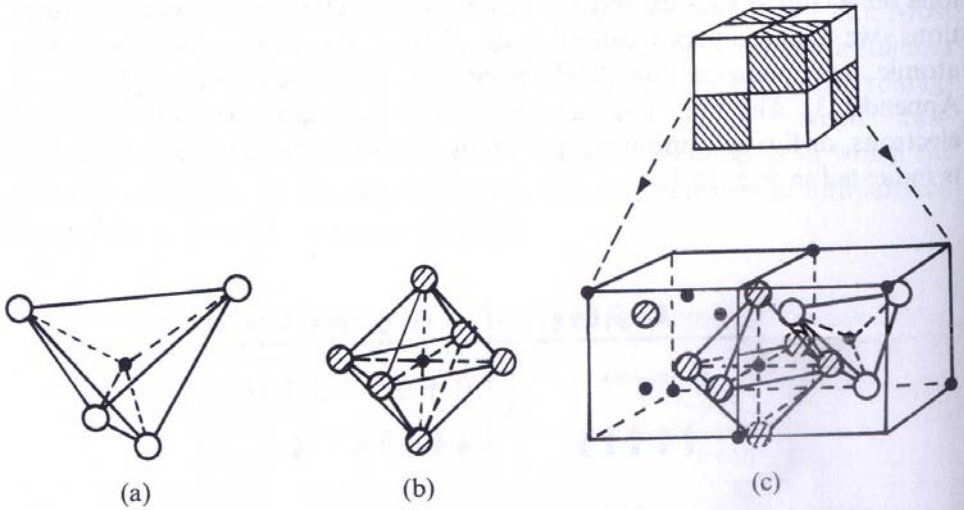


Figure 15.13. Crystal structure of cubic ferrites. The small filled circles represent metal ions, the large open or shaded circles represent oxygen ions: (a) tetrahedral or A sites; (b) octahedral or B sites; and (c) one-fourth of the unit cell of a cubic ferrite. A tetrahedron and an octahedron are marked. Adapted from J. Smit, and H.P.J. Wijn, *Ferrites*, Wiley, New York (1959).

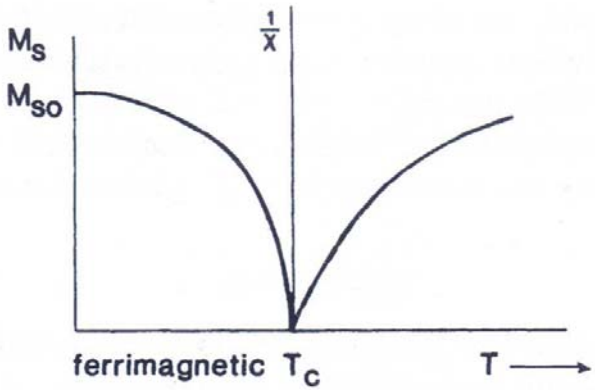


Figure 15.14. Schematic representation of the temperature dependence of the saturation magnetization, M_s, and the reciprocal susceptibility for ferrites.

Langevin Theory of Diamagnetism

Magnetic moment μ_m, created by a current *I*, passing through a loop-shaped wire of area *A*

$$\mu_m = I \cdot A = \frac{e}{t} A = \frac{e}{s/v} A = \frac{ev\pi r^2}{2\pi r} = \frac{evr}{2} \qquad (15.5)$$

Where, e = electron charge, r = radius of the orbit, $s = 2\pi r$ = length of orbit, v = velocity of the orbiting electron, t = orbiting time

Electrostatic force $|F|$ on the orbiting electron

$$F = ma = Ee \qquad (15.6)$$

where, E is the electric field and m is mass of the electron

Acceleration of the electron

$$a = dv/dt = Ee/m \qquad (15.7)$$

$$E = V_e/L$$

where, V_e = induced voltage(or emf), L= orbit length

Langevin Theory of Diamagnetism

A change in an external magnetic flux, ϕ, induces in loop-shaped wire an emf which opposes, according to Lentz's law, the change in flux:

$$V_e = -d\phi / dt = d(\mu_0 HA) / dt \qquad (15.9)$$

By, combining (15.7) – (15.9)

$$dv / dt = Ee / m = V_e e / Lm = -\frac{eA\mu_0}{Lm} dH / dt = -\frac{e\pi r^2 \mu_0}{2\pi rm} dH / dt = -\frac{er\mu_0}{2m} dH / dt \qquad (15.10)$$

A change in the magnetic field strength from 0 to *H* yields a change in the velocity of the electron

$$\int_{v_1}^{v_2} dv = -\frac{er\mu_0}{2m} \int_0^H dH \qquad (15.11)$$

$$\Delta v = -\frac{er\mu_0 H}{2m} \qquad (15.12)$$

Langevin Theory of Diamagnetism

This change in electron velocity yields in turn a change in magnetic moment as we see by combining (15.5) with (15.12):

$$\Delta\mu_m = \frac{e\Delta v r}{2} = -\frac{e^2 r^2 \mu_0 H}{4m} \qquad (15.13)$$

So far we assumed that magnetic field is perpendicular to the plane of the orbiting electron. In reality the orbit plane varies constantly in direction with respect to the external field. Thus we have to find a average value for $\Delta\mu_m$

$$\overline{\Delta\mu_m} = -\frac{e^2 r^2 \mu_0 H}{6m} \qquad (15.14)$$

If you take all Z electron, Z = atomic number , and $\bar{r}$ is the average radius of all electronic orbits,

$$\overline{\Delta\mu_m} = -\frac{e^2 Z \bar{r}^2 \mu_0 H}{6m} \qquad (15.15)$$

Langevin Theory of Diamagnetism

The magnetization caused by this change of magnetic moment:

$$M = \mu_m / V = -\frac{e^2 Z \overline{r^2} \mu_0 H}{6mV} \qquad (15.16)$$

This finally yields, together with (14.6), the diamagnetic susceptibility,

$$\chi_{dia} = M / H = -\frac{e^2 Z \overline{r^2} \mu_0}{6mV} = -\frac{e^2 Z \overline{r^2} \mu_0}{6m} \frac{N_0 \delta}{W} \qquad (15.17)$$

Where, $N_0\delta/W$ is the number of atoms per unit volume, N_0 = Avogadro constant, δ = density, W = atomic mass

The quantities in (15.17) are essentially temperature-independent.

Langevin Theory of (Electron Orbit) Paramagnetism

Langevin postulated that the magnetic moment of the orbiting electron are responsible for paramangetism.

When magnetic moment, μ_m is aligned by an external magnetic field, the potential energy is:

$$E_p = -\mu_m \mu_0 H \cos\alpha \qquad (15.18)$$

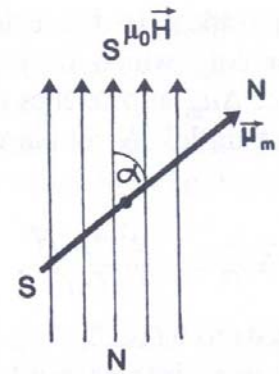


Figure 15.15. Schematic representation of the magnetic moment of an electron that has been partially aligned by an external magnetic field.

Where α is the angle between field direction and μ_m

The probability of an electron to have the energy E_p is proportional to $exp(-E_p/k_BT)$, where k_B is the Boltzmann constant, T is the absolute temperature.

Langevin Theory of (Electron Orbit) Paramagnetism

Assume the electrons to be situated at the center of a sphere. The vectors, representing their magnetic moment, may point in all possible direction (Fig 15.16)

This infinitesimal number *dn* of magnetic moments per unit vol. which have the energy E_p is:

$$dn = const.dA \exp(-E_p/k_B T) \qquad (15.19)$$

$$dA = 2\pi R^2 \sin\alpha d\alpha \qquad (15.20)$$

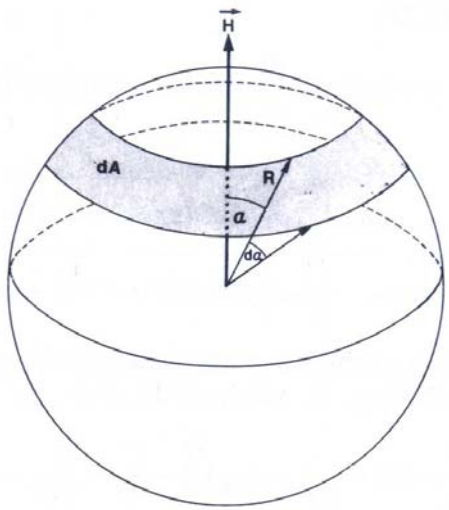


Figure 15.16. Schematic representation of a unit sphere in whose center the electrons are thought to be located.

where R=1 is the radius of the unit sphere. Combining (15.18) –(15.20)

$$dn = const.2\pi \sin\alpha d\alpha \cdot \exp\left(\frac{\mu_m \mu_0 H}{k_B T}\cos\alpha\right) \qquad (15.21)$$

For abbreviation $\zeta = \dfrac{\mu_m \mu_0 H}{k_B T}$ (15.22)

Langevin Theory of (Electron Orbit) Paramagnetism

Integrating (15.21)

$$n = 2\pi const.\int_0^{\pi} \sin\alpha \exp(\zeta \cos\alpha) d\alpha \qquad (15.23)$$

$$const. = \frac{n}{2\pi \int_0^{\pi} \sin\alpha \exp(\zeta \cos\alpha) d\alpha} \qquad (15.24)$$

Total magnetization is the sum of all individual magnetic moments

$$M = \int_0^{n} \mu_m \cos\alpha dn \qquad (15.25)$$

with (15.21)

$$M = const.2\pi\mu_m \int_0^{\pi} \cos\alpha \sin\alpha \exp(\zeta \cos\alpha) d\alpha \qquad (15.26)$$

with (15.24)

$$M = \frac{n\mu_m \int_0^{\pi} \cos\alpha \sin\alpha \exp(\zeta \cos\alpha) d\alpha}{\int_0^{\pi} \sin\alpha \exp(\zeta \cos\alpha) d\alpha} \qquad (15.27)$$

Langevin Theory of (Electron Orbit) Paramagnetism

This function can be brought into a standard form by setting ***x = cos*α**, and ***dx = - sin*α*d*α**

$$M = n\mu_m(\cos\zeta - \frac{1}{\zeta}) = n\mu_m(\frac{\zeta}{3} - \frac{\zeta^3}{45} + \frac{2\zeta^5}{945} - \cdots) \qquad \textbf{(15.28)}$$

Where the expression in parenthesis is called Langevin funtion ***L*(ζ)**.
The term $\zeta = \mu_m \mu_0 H / k_B T$ is usually much smaller than one, so that:

$$M = n\mu_m \frac{\zeta}{3} = \frac{n\mu_m^{\ 2}\mu_0 H}{3k_B T} \qquad \textbf{(15.29)}$$

Which yield, for the susceptibility (14.6) at not-too-high field strength,

$$\chi_{para}^{orbit} = \frac{M}{H} = \frac{n\mu_m^{\ 2}\mu_0}{3k_B}\frac{1}{T} \equiv C\frac{1}{T} \qquad \textbf{(15.30)}$$

This is Curie's law (15.1), which express that the susceptibility is inversely proportional to the temperature. The Curie constant is:

$$C = \frac{n\mu_m^{\ 2}\mu_0}{3k_B} \qquad \textbf{(15.31)}$$

Langevin Theory of (Electron Orbit) Paramagnetism

- **Discussion of the Langevin theory**

- The magnetization, *M* is a linear function of *H* for a given temperature and for small fields (Fig 15.17), (Eq.15.29)

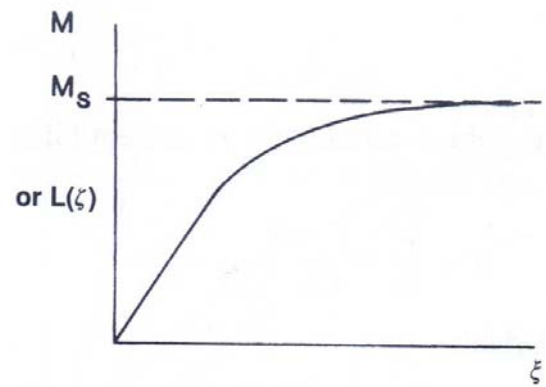


Figure 15.17. Schematic representation of the Langevin function $L(\zeta) = \coth\zeta - 1/\zeta$, where $\xi = \mu_m \mu_0 H / k_B T$.

- For large fields *H*, the magnetization reaches M_s at which all magnetic moment aligned to their maximum value.

- Langevin theory can explain the Curie law.

- Refinement of Langevin function by applying quantum theory
-> Brillouin function

Molecular Field Theory

Weiss postulation: Total magnetic moment H_t is thought to be composed of two parts, external field H_e and *molecular filed* H_m

$$H_t = H_e + H_m \qquad (15.32)$$

where, $H_m = \gamma M$ (γ = *molecular field constant*) (15.33)

$$\chi = M / H_t = \frac{M}{H_e + \gamma M} = C / T \qquad (15.34)$$

$$M = \frac{H_e C}{T - \gamma C} \qquad (15.35)$$

Finally, we obtain

$$\chi = \frac{M}{H_e} = \frac{C}{T - \gamma C} = \frac{C}{T - \theta} \qquad (15.36)$$

Weiss postulated that the above-introduced internal or molecular field is responsible for this parallel alignment of spins, and considered ferromagnetics to be essentially paramagnetics having a very large molecular field. In the quantum theory, the H_m is essentially the exchange force (Sec 16.2).

Molecular Field Theory

Let us consider the case for no external magnetic field. Then the spins are only subjected to the molecular filed H_m. This yields for the Langevin variable ζ (see (15.22)) with (15.33)

$$\zeta = \frac{\mu_m \mu_0 H}{k_B T} = \frac{\mu_m \mu_0 \gamma M}{k_B T} \qquad (15.37)$$

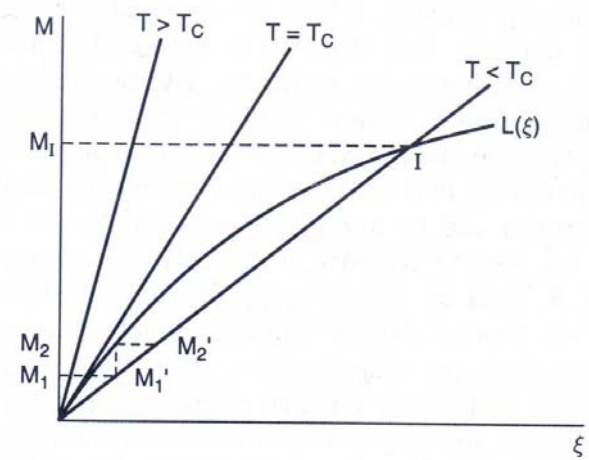


Figure 15.18. Langevin function $L(\zeta)$, i.e., (15.28) and plot of (15.38) for three temperatures.

And provides for the magnetization by rearranging (15.37):

$$M = \frac{k_B T}{\mu_m \mu_0 \gamma} \zeta \qquad (15.38)$$

The magnetization is linear function of ζ with the temperature as a proportionality factor (Fig.15.18)

The intersection *I* of a given temperature line with the Langevin function $L(\zeta)$ represents the finite spontaneous magnetization, M_I, at this temperature

Molecular Field Theory

- In Fig.15.18

  - $T < T_C$: With increasing temperature, slope is increased, the point of intercept, I, is decreased, and therefore the value for the spontaneous magnetization is decreased.

  - At Curie temperature, T_C: no intercept, and hence no spontaneous magnetization

The slope $k_B/(\mu_m \mu_0 \gamma)$ in (15.38) is identical to the slope of the $L(\zeta)$ near the origin, which is $n\mu_m/3 = M/3$. This yields, for T_C

$$\frac{k_B T}{\mu_m \mu_0 \gamma} = \frac{M}{3} \qquad (15.39)$$

Molecular filed constant, γ, calculated by measuring T_C and inserting T_C into Eq.(15.39)

$$\gamma = \frac{k_B T_C}{\mu_m \mu_0 M} \qquad (15.40)$$

This yield, for the molecular magnetic field strength (15.33)

$$H_m = \gamma M = \frac{3 k_B T_C}{\mu_m \mu_0} \qquad (15.41) \quad (\sim 10^7 \text{ Oe !!!})$$

Paramagnetism and Diamagnetism

1. Paramagnetism

- Magnetic moment of the spinning electrons: dominant contribution to paramagnetism

- Susceptibilities for paramagnetic metals based on the energy theory

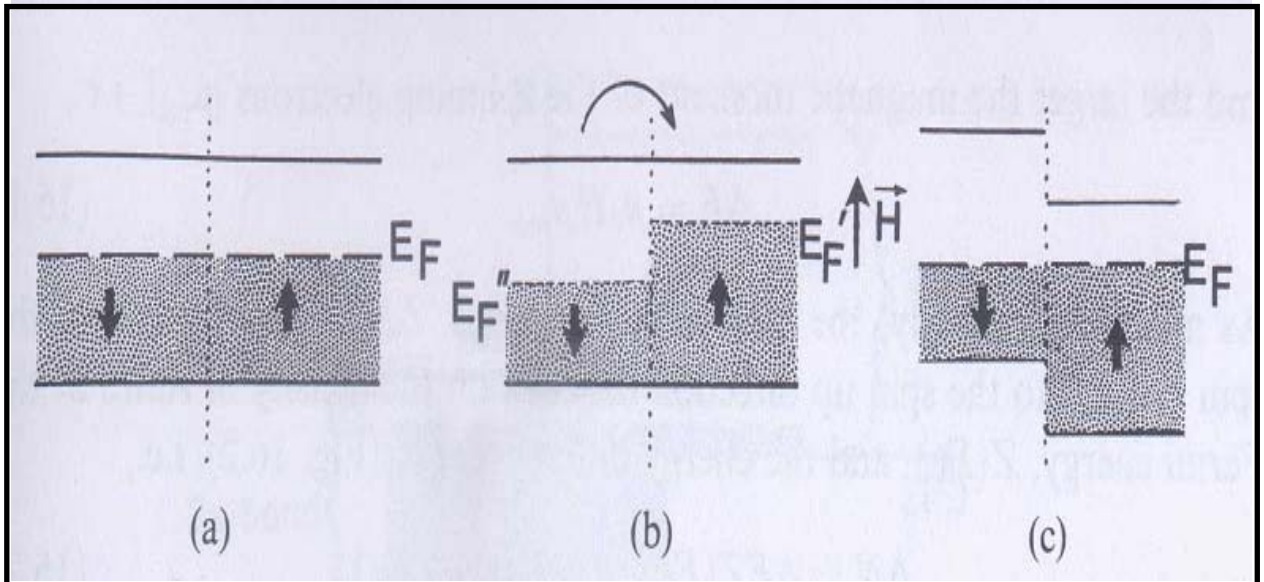


Fig16.1. Schematic representation of the effect of an external magnetic field on the electron distribution in a partially filled electron band (a) Without magnetic field (b) and (c) with magnetic field.

Paramagnetism and Diamagnetism

- The density of states of the two half-bands (Fig. 16.2). We can observe a relatively large *Z(E)* near E_F. Thus, a small change in energy may cause a large number of electrons to switch to the opposite spin direction.

- The susceptibility ($\chi_{spin,\ para}$) of paramagnetism

ΔE is larger - the larger the external magnetic field strength |H|,and the larger the magnetic moment of the spinning electrons $|\mu_{ms}|$

$$\Delta E = \mu_0 H \mu_{ms} \quad (16.1)$$

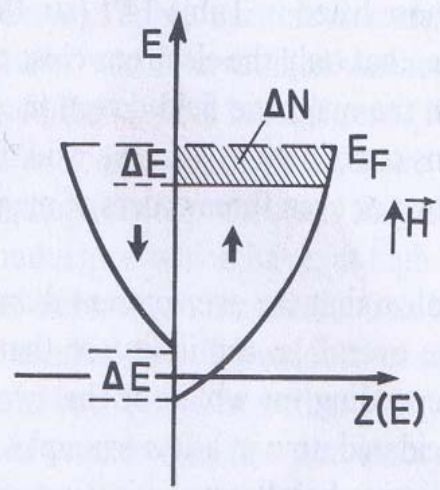


Figure 16.2. Schematic representation of the density of states $Z(E)$ in two half-bands. The shift of the two half-bands occurs as a result of an external magnetic field. Free electron case. (See also Fig. 16.1(c).) The area ΔN equals $\Delta E \cdot Z(E)$.

Paramagnetism and Diamagnetism

The number of electrons , ΔN (transferred from spin down to up) depends on the density of states at the Fermi energy, $Z(E_F)$

$$\Delta N = \Delta E Z(E_F) = \mu_0 H \mu_{ms} Z(E_F) \qquad (16.2)$$

The magnetization |M| is $$M = \frac{\mu_m}{V} \qquad (16.3)$$

The magnetization is larger, the more electrons are transferred from spin down into spin up states.

$$M = \frac{\mu_{ms}}{V}\Delta N = \frac{\mu^2{}_{ms}\,\mu_0 H Z(E_F)}{V} \qquad (16.4)$$

Thus, the susceptibility $$\chi = \frac{M}{H} = \frac{\mu^2{}_{ms}\mu_0 Z(E_F)}{V} \qquad (16.5)$$

The spin magnetic moment of one electron equals one Bohr magneton, μ_B

$$\boxed{\chi_{spin,para} = \frac{\mu_B{}^2 \mu_0 Z(E_F)}{V}} \qquad (16.6)$$

2. Diamagnetism

- Susceptibility (χ) of metals might be positive or negative depending on which of the two components (paramagnetism, diamagnetism) predominates.

- Example of diamagnetism 1(beryllium)

- Be is a bivalent metal having a filled *2s*-shell in its atomic state. However, in the crystalline state, band overlapping can be found, which causes some of the *2s*-electrons to spill over into the *2p*-band. *2s*-electrons populate the very bottom of *2p* band. (see Fig. 16.3)

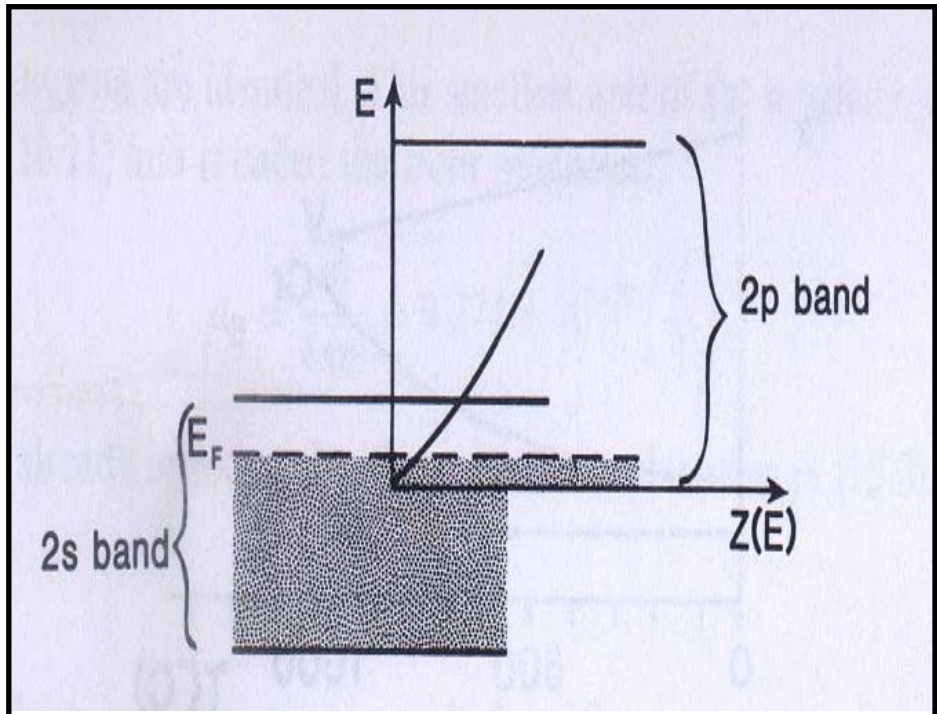


Fig16.3. Overlapping of 2s-and 2p-bands in Be and the density of states curve for the 2p-band.

Thus, the density of states at the Fermi level, and consequently, χ_{para}, is very small.→ Diamagnetic susceptibility predominates, which makes Be diamagnetic.

Paramagnetism and Diamagnetism

- Example of diamagnetism 2 (copper)

The Fermi energy of copper is close to the band edge. (see Fig. 5. 22). Thus, the density of states near E_F, and the paramagnetic susceptibility are relatively small compared with diamagnetic susceptibility.

- Diamagnetic susceptibility

$$\chi_{dia} = -\frac{e^2 Z r^2 \mu_0}{6mV} \qquad (16.7)$$

Copper has about ten 3*d*-electrons, which makes *Z*~10.

The radius of *d*-shells is fairly large.

→ Thus, for copper, χ_{dia} is large compared with χ_{para}

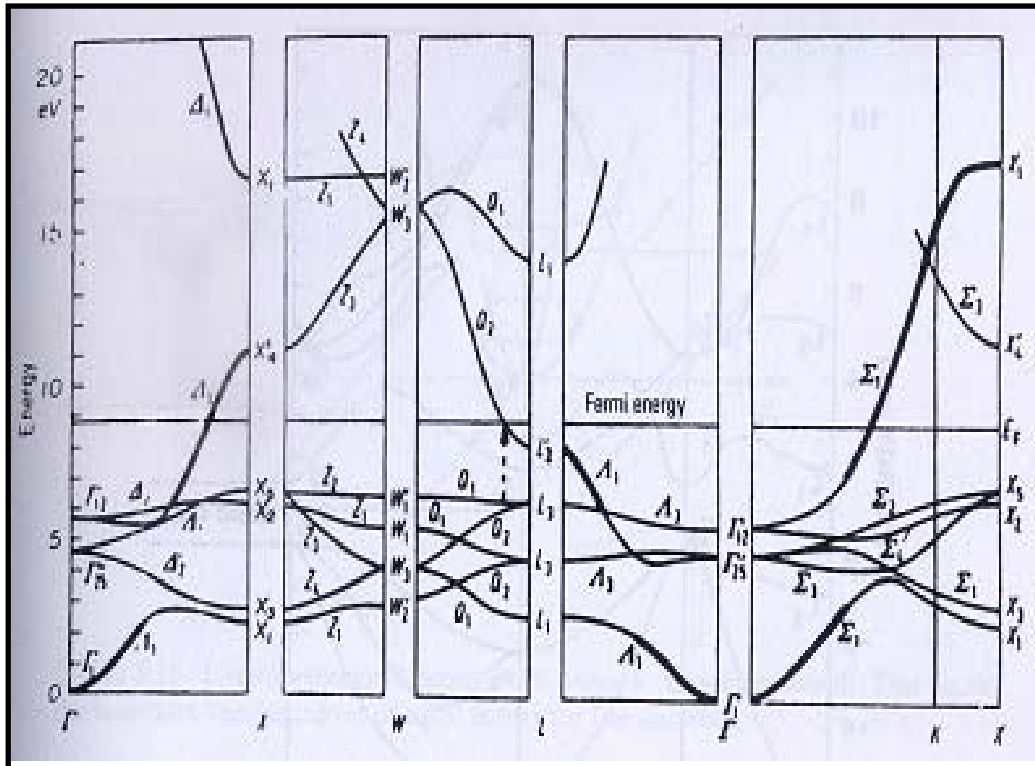


Fig 5. 22. Band structure of copper (fcc). Adapted from B.Segal, Phys. Rev. 125, 109 (1962). The calculation was made using the l-dependent potential.

3. Quantum-mechanical point of view of magnetic moment of an orbiting electron

- The orbital motion of an electron induces a magnetic moment, μ_m.

Recall μ_m from a current passing through a loop-shaped wire.

$$\mu_m = I \times A = \frac{e}{t} A = \frac{e}{s/v} A = \frac{ev\pi r^2}{2\pi r} = \frac{evr}{2}$$ (***A*** **= area of loop)** (16.8)

Electrons which have mass, ***m*** can make de Brogli wave.

$$2\pi r = n\lambda = n\frac{h}{p} \rightarrow rp = \frac{h}{2\pi} n = \hbar n,$$ (***mvr*** **= angular momentum)**

$$mvr = \hbar n = \frac{nh}{2\pi} \quad (16.9)$$

$$\mu_m = \frac{enh}{4\pi m} \quad (16.10)$$

For *n* =1, $$\mu_m = \frac{eh}{4\pi m} \quad (16.11)$$

Bohr magneton $$\mu_B = \frac{eh}{4\pi m} = 9.274 \times 10^{-24} \left(\frac{J}{T}\right) \quad (16.12)$$

Ferromagnetism and Antiferromagnetism

❑ Characterization of ferromagnet (unfilled d-bands): *d* - band diagram of Fe,Co,Ni (Fig 16.5)

- d-bands overlap the next higher s-band. d-band can accommodate up to ten electrons, so that the density of states for a d-band is relatively large

- For instance, the density of states of Ni near Fermi energy are comparatively large, one needs only a relatively small amount of energy to transfer a considerable number of electrons from spin down into spin up configurations.

- only minimum energy is needed to change spin direction in the ferromagnetic metals.

❑ Difference between para- and ferromagnet

- paramagnet: external magnetic field is needed for spin alignment, no magnetic domain

- ferromagnet: spontaneous spin alignment, magnetic domain formation

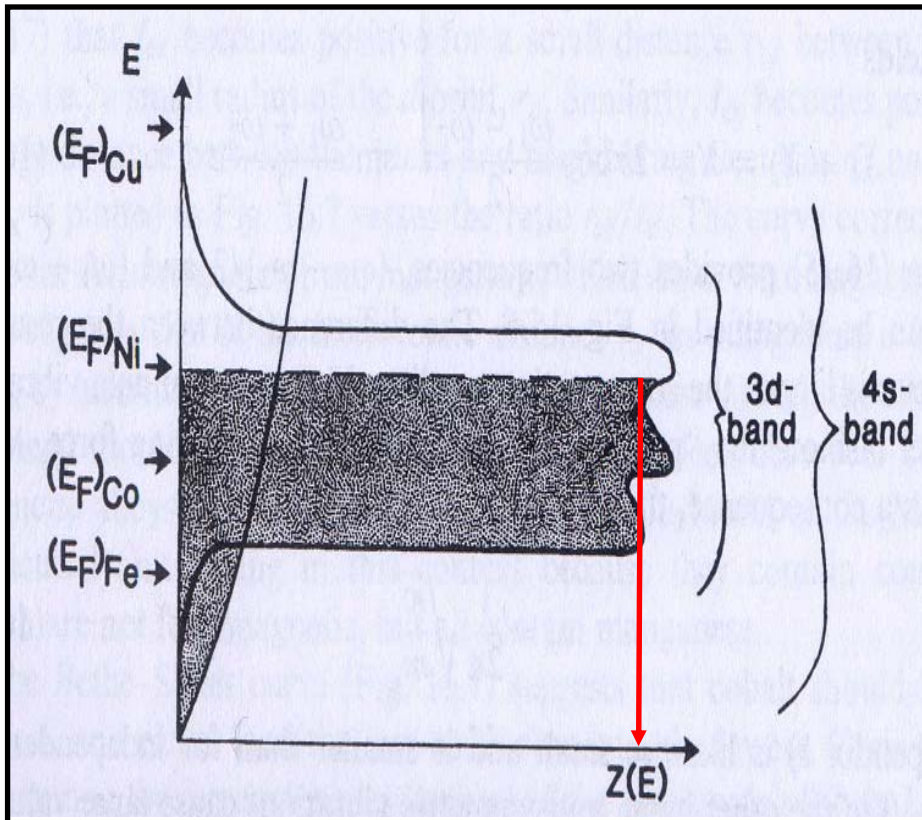


Fig 16.5. Schematic representation of the density of states for 4s-and 3d-bands the Fermi energies for iron, cobalt, nickel, and copper. The population of the bonds by the ten nickel (3d+4s)-electrons is indicated by the shaded area.

Ferromagnetism and Antiferromagnetism

❑ Exchange energy

"Set free" when equal atomic system are closely coupled, and in this way exchange their energy

❑ Explanation of exchange energy

- Two ferromagnetic atoms: two identical pendula interconnected by a spring.
- The spring represents the interactions of electrical and magnetic fields

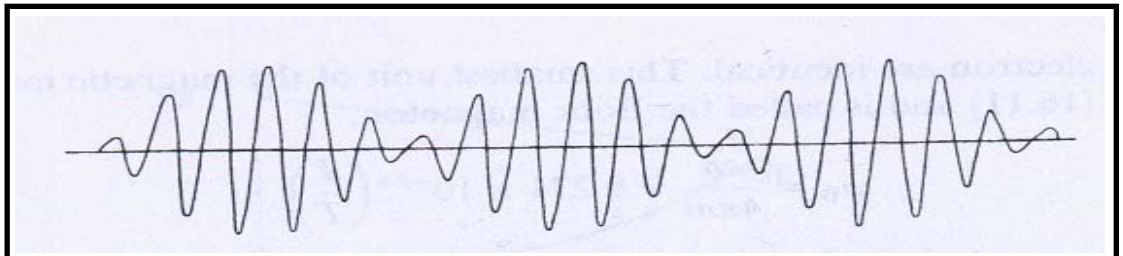


Fig16.6. Amplitude modulation resulting from the coupling of two pendula. The vibrational pattern shows beats, Similarly as known for two oscillators that have almost identical pitch.

- One pendulum deflect → its amplitude decrease, with energy transferring to 2nd pendulum, which in turn transfer its energy back to the 1st one.
- The amplitudes of two pendula decrease and increase periodically with time. (Fig16.6)

Ferromagnetism and Antiferromagnetism

The mathematical expression for two pendula pattern

$$X_1 = b \sin w_1 t \qquad (16.13)$$

$$X_2 = b \sin w_2 t \qquad (16.14)$$

which yields

$$X_1 + X_2 = X = 2b \cos \frac{w_1 - w_2}{2} t \sin \frac{w_1 + w_2}{2} t \qquad (16.15)$$

Equation (16.15) provides two frequencies, $\frac{(w_1 - w_2)}{2}$, $\frac{(w_1 + w_2)}{2}$

The difference of frequencies is larger, the stronger the coupling.

Ferromagnetism and Antiferromagnetism

If the two pendula vibrate in a parallel fashing, the restoring force, *kx*, is small. As a result, the frequency is smaller than for independent vibration

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad (16.16)$$

This equation shows that two coupled and systemically vibrating systems have a lower *E* two individual systems.

Ferromagnetism and Antiferromagnetism

- By solving the appropriate Schrodinger equation for two atoms only, ferromagnetism can be quantum mechanically explained.

$$I_{ex} = \int \psi_a(1)\psi_b(2)\psi_a(2)\psi_b(1)\left[\frac{1}{r_{ab}} - \frac{1}{r_{ab}} - \frac{1}{r_{b1}} + \frac{1}{r_{12}}\right] d\tau \quad (16.17)$$

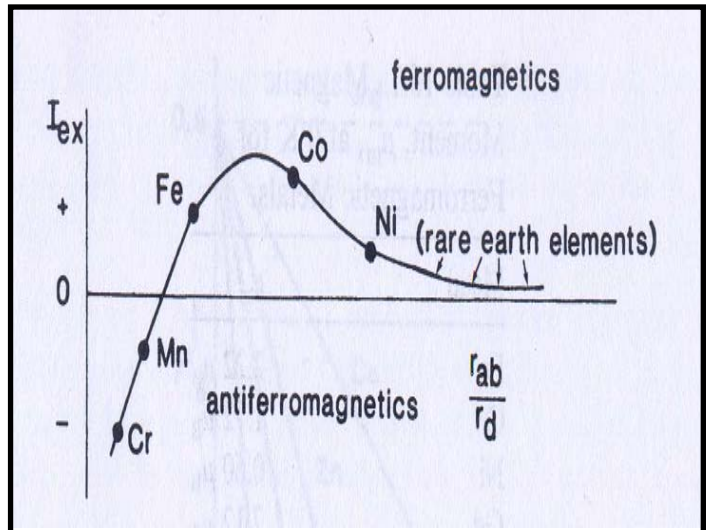


Fig 16.7. Exchange integral, I_{ex}, versus the ratio of inter atomic distance, r_{ab}, and the radius of an unfilled d-shell. The position of the rare earth elements (which have unfilled f-shells) are also shown for completeness.

- I_{ex} is positive → parallel spins are energetically more favorable than antiparallel spins. (vice versa)

- I_{ex} becomes positive for a small distance r_{12} between the electrons, i.e., a small radius of the d-orbit, r_d. Similarly, I_{ex} becomes positive for a large distance between the nuclei and neighboring electrons r_{a2} and r_{b1}.

- I_{ex} *vs.* r_{ab}/r_d (Fig 16.7)

Ferromagnetism and Antiferromagnetism

- Bohr magneton of Ni

- Band overlapping is found between 3*d* and 4*s* band, so that combined ten (3*d*+4*s*)-electrons occupy the lower *s*-band and fill, almost completely, the *3d*-band.

→ Nickel 3*d*-band : filled by 9.4 electrons (experimentally) .

- Hund's rule : the electrons in a solid occupy the available electron states in a manner which maximizes the imbalance of spin moments.

- For Ni : 5 electrons are spin up and an average of 4.4 electrons are spin down. As a result, we can obtain a spin imbalance of 0.6 μ_B per atom.

Table 16.1. Magnetic Moment, μ_m, at 0 K for Ferromagnetic Metals.

Metal	μ_m
Fe	2.22 μ_B
Co	1.72 μ_B
Ni	0.60 μ_B
Gd	7.12 μ_B

Ferromagnetism and Antiferromagnetism

- Magnetic behavior of Nickel-based alloys

  (Fig 16.8)

Ni : $1s^2$ $2s^2\ 2p^6$ $3s^2\ 3p^6\ 3d^8$ $4s^2$

Cu : $1s^2$ $2s^2\ 2p^6$ $3s^2\ 3p^6\ 3d^{10}$ $4s^1$

- For Cu, no "unfilled d- or f-band", the condition for ferromagnetism.

- If copper is alloyed to nickel, the extra copper electrons progressively fill the *d*-band and compensate some of the unsaturated spins of nickel → the magnetic moment per atom of this alloy is reduced.

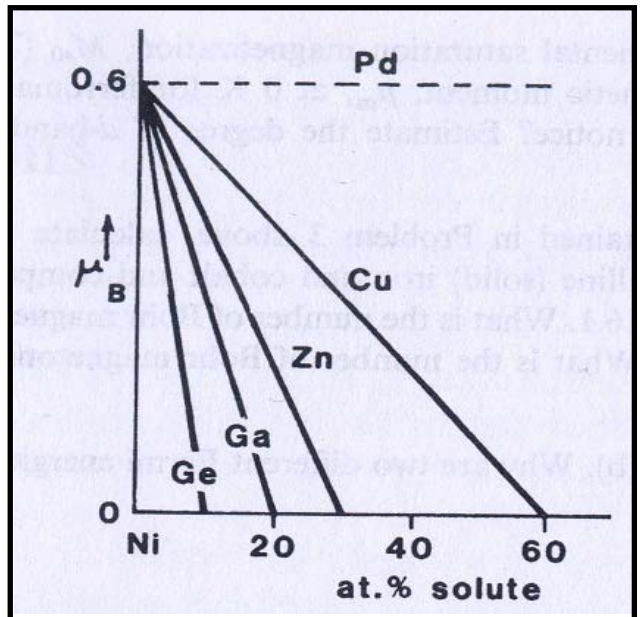


Fig16.8. Magnetic moment per nickel atom as a function of solute concentration

- The *3d* - band of Ni is filled by only 9.4 electrons (0.6 electron lacks per atom). Thus, about 60% copper atoms are needed until the magnetic moment of Ni has reached a zero value.

Part IV Magnetic Properties of Materials

Chap. 14. Foundations of Magnetism

Chap. 15. Magnetic Phenomena and Their Interpretation- Classical Approach

Chap. 16. Quantum Mechanical Considerations

Chap. 17 Applications

Introduction

- The production of ferro- and ferrimagnetic materials is large-scale operation:
  - The price of the material that goes into a chip is a minute fraction of the device fabrication cost.
  - The annual sales of electrical steel, used for electromotors and similar devices, reach the millions of tons

- Other large-scale production items
  - Permanent magnets for loudspeakers
  - Magnetic recording materials

Electrical steels
(Soft Magnetic Materials)

1.Core Losses

- The core loss is the energy that is dissipated in the form of heat within the core of electromagnetic devices
- Several types of losses : eddy current loss, hysteresis loss
- Typical core losses are between 0.3 and 3 W/kg (Table 17.1)

Table 17.1. Properties of Some Soft Magnetic Materials.

Name	Composition (mass %)	Permeability, μ_{max} (unitless)	Coercivity, H_c (Oe)	Coercivity, H_c (A/m)	Saturation induction[a], B_s (kG)	Saturation induction[a], B_s (T)	Resistivity, $\rho(\mu\Omega \cdot cm)$	Core loss at 1.5 T and 60 Hz (W/kg)
Low carbon steel	Fe–0.05% C	5×10^3	1.0	80	21.5	2.1	10	2.8
Nonoriented silicon iron	Fe–3% Si, 0.005% C, 0.15% Mn	7×10^3	0.5	40	19.7	2	60	0.9
Grain-oriented silicon iron	Fe–3% Si, 0.003% C, 0.07% Mn	4×10^4	0.1	8	20	2	47	0.3
78 Permalloy	Ni–22% Fe	10^5	0.05	4	10.8	1.1	16	≈2
Mumetal	77% Ni; 16% Fe, 5% Cu, 2% Cr	10^5	0.05	4	6.5	0.6	62	
Supermalloy	79% Ni; 16% Fe, 5% Mo	10^6	0.002	0.1	7.9	0.8	60	
Supermendur	49% Fe, 49% Co, 2% V	6×10^4	0.2	16	24	2.4	27	
Metglas #2605 annealed	$Fe_{80}B_{20}$	3×10^5	0.04	3.2	15	1.5	≈200	0.3

[a]Above B_s the magnetization is constant and $dB/d(\mu_0 H)$ is unity.

Electrical steels
(Soft Magnetic Materials)

- **Eddy current loss (Fig. 17.1)**
  - An current in the primary coil causes an alternating magnetic flux in core → induces in the secondary coil an alternating V_e, see (14.7) and (15.9)

$$V_e \propto -\frac{d\phi}{dt} = -A\frac{dB}{dt} \qquad (17.1)$$

  - This emf gives rise to the eddy current, I_e (Fig.17.1(a))
    Larger eddy current→ the larger μ ($B = \mu_0 \mu \cdot H$) → the larger conductivity σ of core material →the higher the applied frequency→ the larger the cross-section A

  - Skin effect
    At high frequency, the eddy current shields the interior of the core from the magnetic field, so that only a thin exterior layer of the core contributes to the flux multiplication.

Electrical steels
(Soft Magnetic Materials)

- To minimize eddy current
  - Decreasing σ
    - Ferrite core
    - Insulating coated Fe core

    -The decrease in σ is a large decrease in μ
  - Decreasing lamination thickness . (Fig. 17.1(b))
    - The cross-section (A) is reduced, Decrease V_e

      →additionally reduces losses (skin effect)
  - These losses, however, less than 1% of the total energy transferred.

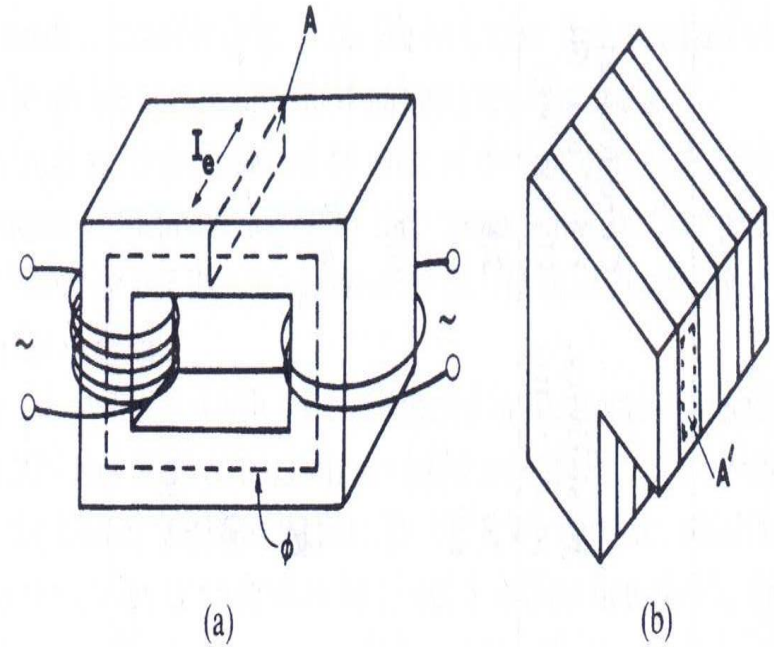


Figure 17.1. (a) Solid transformer core with eddy current, I_e, in a cross-sectional area A. Note the magnetic flux lines ϕ. (b) Cross section of a laminated transformer core. The area A' is smaller than area A in (a).

Electrical steels
(Soft Magnetic Materials)

- **Hysteresis loss**
  - Hysteresis losses are encountered when the magnetic core is subjected to a complete hysteresis cycle (Fig. 15.6)
  - The work thus dissipated into heat is proportional to the area enclosed by a B/H loop.
  - Proper materials selection and rolling of the materials with subsequent heat treatment greatly reduces the area of a hysteresis loop.

Electrical steels
(Soft Magnetic Materials)

2. Grain Orientation

- The permeability of electrical steel can be increased and hysteresis losses can be decreased by making use of favorable grain orientations in the material.

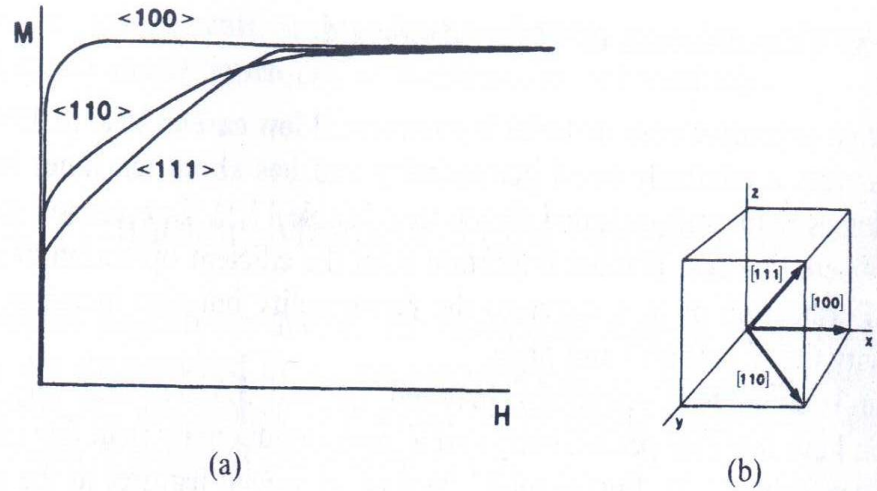


Figure 17.2. (a) Schematic magnetization curves for rod-shaped *iron single crystals* having different orientations (virgin curves). The magnetic field was applied in three different crystallographic directions. (Compare with Fig. 15.6, which refers to poly-crystalline material). (b) Reminder of the indices which identify directions in space. (See also Footnote 14 in Section 5.6).

- Magnetic anisotropy
  - Magnetic properties depend on the crystallographic direction in which an external field is applied.
  - Magnetization curves of iron (Fig.17.2(a))

▪ Easy direction : Saturated direction is achieved with the smallest possible field strength. (Nickel→ easy direction<111>, hard direction <100>)

▪ The spontaneous orientation of the spin magnetic moments in the demagnetized state.

▪ They are aligned in the easy directions.

Electrical steels
(Soft Magnetic Materials)

- **Grain-oriented electrical steel Process-Iron (Fig. 15.9)**

  ①In pure iron the spins are aligned along the <100> directions.

  ②External field is applied parallel to an easy direction.

  ③The domains already having favorable alignment grow.

  ④The crystal contains one single domain.

  ➔**The energy consumed during this process is used to move the domain walls through the crystal.**

  ⑤Metal sheets possess a texture. → a preferred orientation of the grain.

  ⑥In α-iron and α-iron alloys the <100> direction is parallel to the rolling direction.

  ⑦ Utilizing electrical steel.

  ⑧During the rolling, the grains are elongated and their orientation is altered.

  ⑨The sheets are recrystallized, whereby some crystals grow in size at the expense of others.

Summary

- The magnetic properties of grain-oriented steels are best in the direction parallel to the direction of rolling.

Electrical steels
(Soft Magnetic Materials)

3. Composition of Core Materials

- **Low carbon steel (0.05%C)**
  - Low μ, high core losses (Table 17.1)
  - Low cost
  - Purification of iron → $\mu \uparrow$, σ (eddy current)$\uparrow$, cost $\uparrow$

Electrical steels
(Soft Magnetic Materials)

3. Composition of Core Materials

- **Iron-silicon alloys (1.4-3.5%Si)**
  - Higher μ, lower σ (than low carbon steel)
  - γ- loop (phase diagram)
  - The core losses decrease with increasing silicon content
  - For silicon concentrations above 4 or 5 wt%, material becomes too brittle to allow rolling.
  - Other contents in Iron-silicon alloy
    - Al, Mn (less than 1%) →influence on the grain structure → reduce hysteresis losses.
  - Grain-oriented silicon "steel"
    - Highly efficient-high flux multiplying core applications.
- **Multi-component Ni-based alloys**
  - Highest permeability
  - **Permalloy, Supermalloy, Mumetal** (Table 17.1)
  - Shield electronic equipment

Electrical steels
(Soft Magnetic Materials)

4. Amorphous Ferromagnets

- **Amorphous metals**
  - Consisting of Fe, Ni, or Co with B, Si, or phosphorus metals.
  - A higher μ and a lower H_c than grain-oriented silicon-iron (Table 17.1)
  - A large electrical resistivity.
  - Small eddy current losses.
  - Low saturation induction.
  - Core losses increase rapidly at higher flux densities (above 1.4T).

- **The application of metallic glasses**
  - Small flux densities (low currents)
    - Transformers.
    - Magnetic sensors.
    - Magnetostrictive transducers.

Permanent Magnets
(Hard Magnetic Materials)

- **Hard magnetic materials**
  - A large remanence B_r (or M_r).
  - A relatively large coercivity H_c.
  - A large area within the hysteresis loop.

- **Demagnetization curve**
  - A part of a hysteresis loop.
  - B times H is zero at the intercepts of the demagnetization curve.

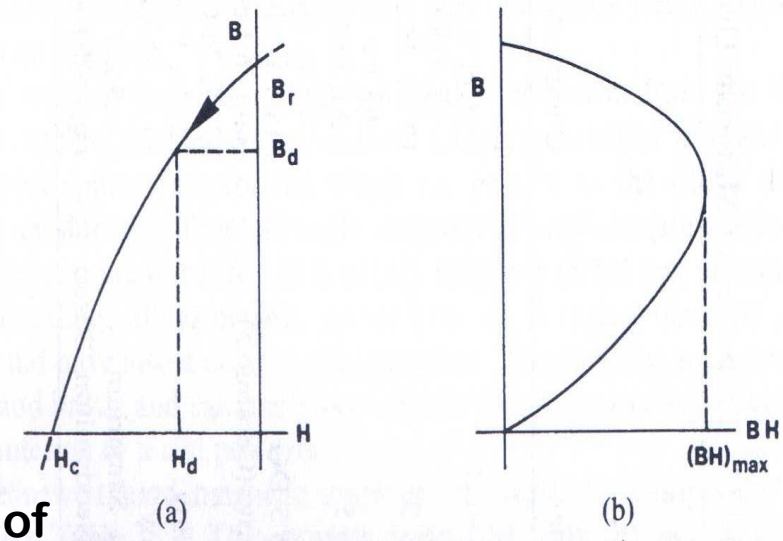


Figure 17.3. (a) Demagnetization curve for a ferromagnetic material. (Second quadrant in a B–H diagram.) (b) Energy product, BH, as a function of induction, B.

- **Maximum energy product $(BH)_{max}$**
  - the area within the hysteresis loop.
  - the energy product peaks somewhere between these extreme values.

Depending on the shape and size of the hysteresis curve (Fig. 17.3)

Permanent Magnets
(Hard Magnetic Materials)

- **Hard magnetic materials**

the values of B_r, H_c, and $(BH)_{max}$ for some materials which are used as permanent magnets are listed in Table 17.2

Table 17.2. Properties of Materials Used for Permanent Magnets.

Material	Composition (mass %)	Remanence B_r (kG)	Remanence B_r (T)	Coercivity H_c (Oe)	Coercivity H_c (A/m)	Maximum energy product $(BH)_{max}$ per Volume (MGOe)	Maximum energy product $(BH)_{max}$ per Volume (kJ/m^3)
Steel	Fe–1% C	9	0.9	51	4×10^3	0.2	1.6
36 Co steel	36 Co, 3.75 W, 5.75 Cr, 0.8 C	9.6	0.96	228	1.8×10^4	0.93	7.4
Alnico 2	12 Al, 26 Ni, 3 Cu, 63 Fe	7	0.7	650	5.2×10^4	1.7	13
Alnico 5	8 Al, 15 Ni, 24 Co, 3 Cu, 50 Fe	12	1.2	720	5.7×10^4	5.0	40
Alnico 5 DG	same as above	13.1	1.3	700	5.6×10^4	6.5	52
Ba-ferrite (Ceramic 5)	$BaO \cdot 6\ Fe_2O_3$	3.95	0.4	2,400	1.9×10^5	3.5	28
PtCo	77 Pt, 24 Co	6.45	0.6	4,300	3.4×10^5	9.5	76
Remalloy	12 Co, 17 Mo, 71 Fe	10	1	230	1.8×10^4	1.1	8.7
Vicalloy 2	13 V, 52 Co, 35 Fe	10	1	450	3.6×10^4	3.0	24
Cobalt–Samarium	Co_5Sm	9	0.9	8,700	6.9×10^5	20	159
Iron–Neodymium–Boron	$Fe_{14}Nd_2B_1$	13	1.3	14,000	1.1×10^6	40	318

Permanent Magnets
(Hard Magnetic Materials)

- **Hard magnetic materials**
  - The remanence B_r : the maximal residual induction.

- **Demagnetizing field**
  - All permanent magnets need to have exposed poles.
  - The exposed poles create a demagnetizing field, H_d→ reduces the B_r

➔ **The demagnetizing field depends on the shape, size, and gap length of magnet.**

  - A reduced value for the residual induction→ B_d (Fig. 17.3)

- **Fringing and leakage** (fig. 17.4)

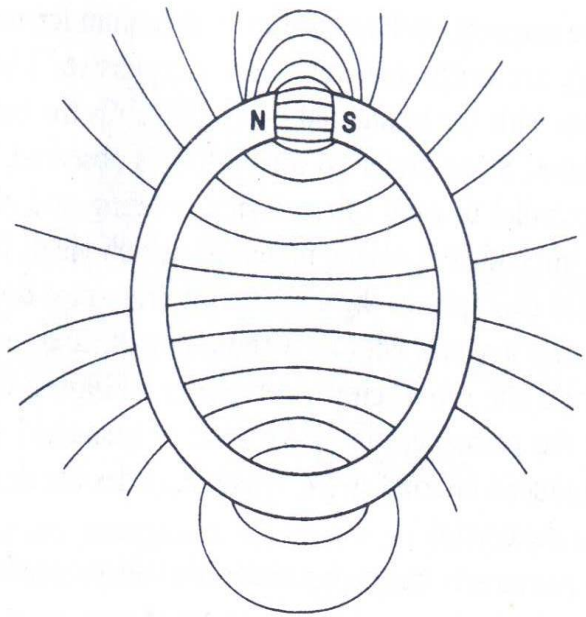


Figure 17.4. Fringing and leakage of a permanent magnet.

Permanent Magnets
(Hard Magnetic Materials)

- **Alnico alloys (Table 17.2)**
  - Based on Co-addition to Fe_2NiAl
    (minor constituents such as Cu and Ti).
  - **Improvement**
    - Alnico 2 : homogenization at 1250℃, fast cooling, and tempering at 600℃
    - Alnico 5 : cooling the alloys in a magnetic field.
    - Alnico 5-DG : A preferred orientation

      -long columnar grains with a preferred<100>axis (heat flow)

      -a magnetic field parallel to the <100> yields

      -shape anisotropy: parallel to the <100> directions
  - Neodymium-boron-iron
    - A superior coercivity, a larger $(BH)_{max}$
    - Disadvantage : low curie temperature of about 300 ℃

Permanent Magnets
(Hard Magnetic Materials)

- **Ceramic ferrite magnets**
  - $BaO \cdot 6Fe_2O_3$ or $SrO \cdot 6Fe_2O_3 (MO \cdot 6Fe_2O_3)$
  - Brittle and relatively inexpensive.
  - Crystallized plates of hexagonal *c*-axis (easy axis) perpendicular to the plates
  - The flat plates arrange parallel during pressing and sintering →Some preferred orientation
  - Application : in the gaskets of refrigerator doors

- **High carbon steel magnets**
  - With or without Co, W, or Cr are only of historic interest.
  - The permanent magnetization of quenched steel stems from the martensite-induced internal stress, which impedes the domain walls from moving through the crystal.

Permanent Magnets
(Hard Magnetic Materials)

- **The goal of research on permanent magnetic materials**
  - To improve corrosion resistance, price, remanence, corecivity, magnetic ordering temperature, and processing procedures.
  - Carbon and nitrogen are increasingly used as the metalloid in iron/rare earth magnets such as in Fe-Nd-C or in $Fe_{17}Sm_2N_x$.
  - Nitrogen treatment of sintered $Fe_{14}Nd_2B$ raises the T_c by more than 100K.
  - Corrosion of the Fe-Nd-B sintered magnets is a serious problem.
  - The corrosion resistance can be improved by utilizing inter-metallic compounds such as Fe-Nd-Al or Fe-Nd-Ga, or by applying a moisture-impervious coating.

Magnetic Recording and Magnetic Memories

- Magnetic recording tapes, disks, drums, or magnetic strips on credit cards consist of small, needlelike oxide particles about 0.1 X 0.5 μm.

- The particles are too small to sustain a domain wall
  →a single magnetic domain which is magnetized to saturation along the major axis (shape anisotropy).

- The elongated particles are aligned by field during manufacturing.
  - Ferrimagnetic γ-Fe_2O_3 : H_c= 20-28 kA/m(250-350Oe), T_c =600℃
  - Ferromagnetic CrO_2 : H_c =40-80kA/m(500-1000Oe), T_c =128 ℃

- High H_c and high B_r prevent self-demagnetization and accidental erasure.
  → provide strong signals, and permit thinner coatings.
  - A high H_c – tape duplication by "contact printing"

- Video tape (Co-doped γ -Fe_2O_3) : higher T_c and a H_c of 48kA/m(600 Oe).
- Most recently, iron particles have been utilized (H_c =120kA/m).

Magnetic Recording and Magnetic Memories

- **Recording head**
  - The recording head of a tape machine consist of a laminated electromagnet made of permalloy or soft ferrite (Table 17.1) which has air gap about 0.3μm wide (Fig. 17.5)
  - The tape is passed along this electromagnet, whose fringing field redirects the spin moments of the particles in a certain pattern proportional to the current.
  - This leaves permanent record of the signal.
  - the moving tape induces an alternating emf in the coil
  - The emf - amplified, filterd, and fed to a loudspeaker.

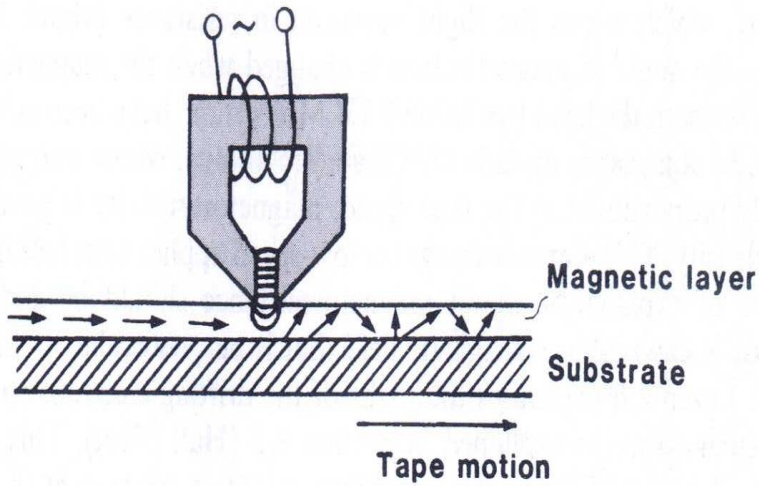


Figure 17.5. Schematic arrangement of a recording (playback) head and a magnetic tape. (Recording mode.) The gap width is exaggerated. The plastic substrate is about 25 μm thick.

Magnetic Recording and Magnetic Memories

- **Recording head**
  - Senust : gap surfaces are coated with a micrometer-thick metal layer composed of Al, Fe, and Si.
  - Metal-in-gap (M-I-G) technology
    →the superior high-frequency behavior and good wear properties of ferrites with the higher coercivity of ferromagnetic metals.
  - Thus, high fields are necessary to record efficiently on high density media.
  - For ultrahigh recording densities (extremely small bit sizes) the signal strength produced in the reading heads diminishes.
  - The lastest head technology→ a thin magneto-resistive element.
    →senses the slight variation in resistance (about 2%) that occurs as the angle of magnetization is changed when the magnetized data bits pass beneath the head.→1.8Mbits/mm^2
  - Inductive head : low-speed applications (credit cards)

Magnetic Recording and Magnetic Memories

- **Magneto-resistance**
  - In magnetic field a conductor is perpendicular to an electric field, the Lorentz force causes the paths of the drifting electrons to bend in near circular form. (Hall effect)
  - This bending leads to a decrease of the electron mobility, μ_e

$$\sigma_0 = N_e \cdot \mu_e \cdot e = \frac{1}{\rho_0} \qquad (17.2)$$

  - Conductivity, σ_0 , decreases and the resistivity, ρ_0, increases. (N_e is the free electron concentration and e is the charge of an electron). The relative change in resistivity,

$$\frac{\Delta \rho}{\rho_0} = (\mu_e \Delta B)^2 \qquad (17.3)$$

    is proportional to the square of the variation in magnetic field strength, ΔB
  - The magneto-resistive head senses this change in magnetic field strength and thus, yields a resistance change.

Magnetic Recording and Magnetic Memories

- GMR (MnFe, MnNi, NiO)
  - Giant magneto-resistive materials
  - A resistance response of about 20%
- CMR (lanthanum manganate , etc.)
  - Colossal magneto-resistive materials
  - 50% resistance changes, allowing a further increase in areal densities.
- Ferrite-core memories
  - The dominant devices for random-access storage in computers.
  - A nearly square-shaped hysteresis loop and a low coercivity, is threaded with a wire (Fig. 17.6(a))
  - A sufficiently high current pulse→ the core becomes magnetically saturated.
  - An opposite-directed current pulse→ magnetizes the ferrite core counterclockwise.

Magnetic Recording and Magnetic Memories

- **Ferrite-core memories**
  - Two magnetization directions constitute the two possible values (0 and 1) in the binary system.
  - Memory system (Fig.17.6(c))
    →switch the X_3/Y_2 core from 0 to 1.
    →a current $\propto H_s/2$
    →current is sent through each of the X1 and the Y2 wire (Fig.17.6(b)).
    →the X_3/Y_2 core with the necessary field for switching.
  - Requirement
    high weight / bit ratio

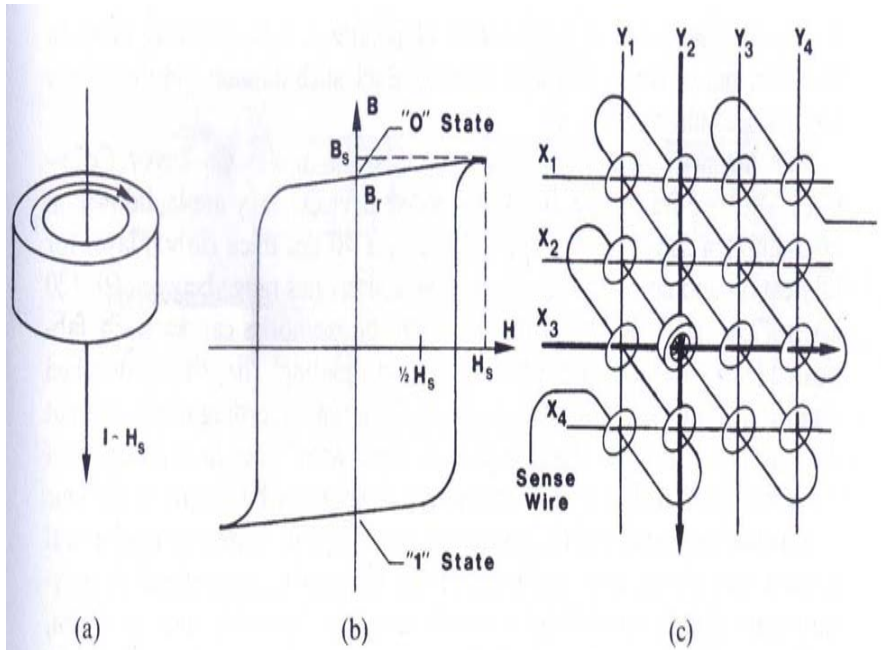


Figure 17.6. (a) Single ferrite core which is magnetized by a current-induced magnetic field; (b) square-shaped hysteresis loop of a soft ferrite memory core; and (c) one plane of a "coincident-current core memory device."

Magnetic Recording and Magnetic Memories

- **Bubble domain memory**
  - Form in thin crystals of "canted" anti-ferromagnetic oxides, amorphous alloyed films, or in ferri-magnetic materials.
  - The domains can be visibly observed and optically read by the way in which they rotate the plane of polarization of polarized light(Faraday effect, or Kerr effect).
  - Each such domain constitutes one bit of stored information.

- **Thin magnetic films**
  - Consisting of Co-Ni-Pt or Co-Cr-Ta or Co_{75}-Cr_{13}-Pt_{12} in hard-disk devices.
  - H_c : 60-120kA/m (750-1500Oe)
  - Easily fabricated –vapor deposition, sputtering, electroplating.
  - Switched rapidly, a small unit size.
  - A density of 1.8 Mbits/mm^2 with a track separation of 3 μm and a bit length of 150nm.

Magnetic Recording and Magnetic Memories

- **Magneto-optical memories**
  - No mechanical contact between medium and beam.
  - A polycarbonate disk is covered by a certain magnetic material.
  - Their spins are initially vertically aligned ,see Fig. 17.7(a).
  - Laser beam heat→ cooling in magnetic field→ delivers the information to be stored

→the spins in the magnetic domain re-orient according to the strength and direction of magnetic field.

  - The newly oriented magnetic domain has been rotated (Fig. 17.7(b))
  - Spin up is a “one” and spin down is a “zero”.

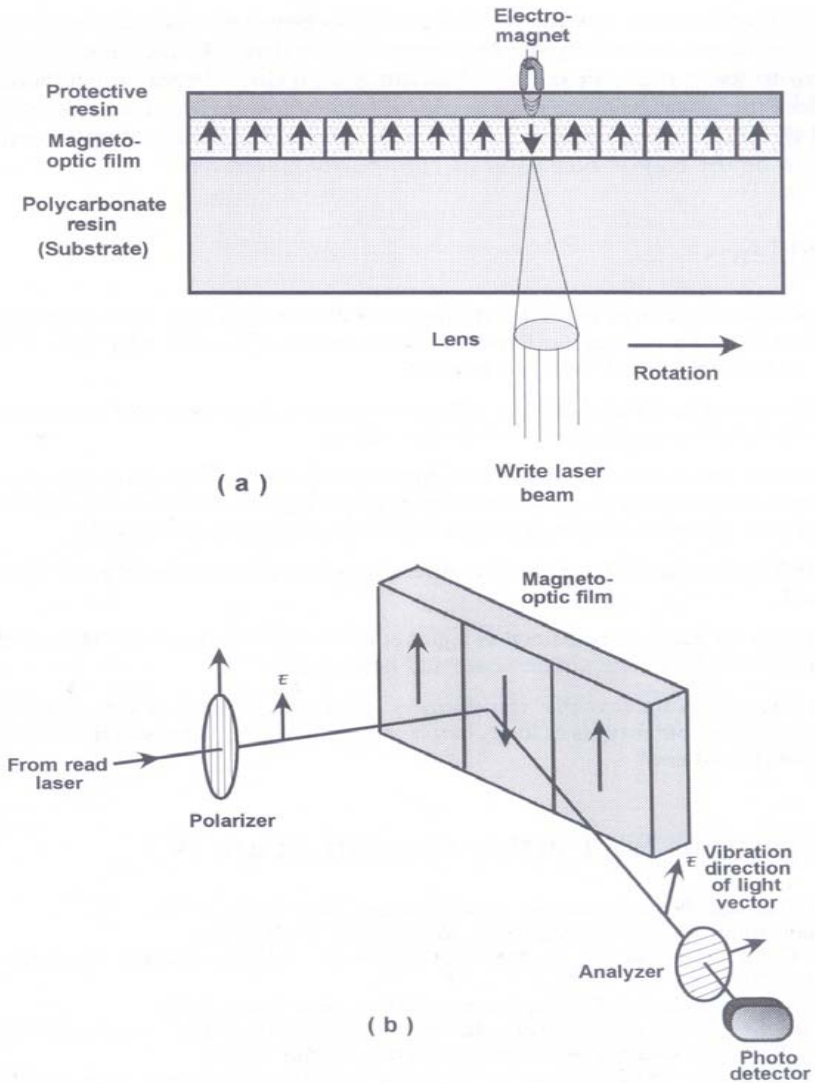


Figure 17.7. (a) Schematic representation of a magneto-optical disk in the writing mode (simplified). (b) Read-out mode of a magneto-optical device. (Polarizer and analyzer are identical devices.)

Magnetic Recording and Magnetic Memories

- **Magneto-optical memories**
  - Magneto-optical disks have a one thousand times larger storage density than common floppy disks and a ten times faster access time.

- Magnetic disks (for random access) or tapes (mainly for music recordings, etc.) are the choices for long-term, large-scale information storage, particularly since no electric energy is needed to retain the information.

- Tapes and floppy disks make direct contact with the recording (and playback) head.

- Hard drive system utilize a “flying head” that hovers a few micrometers or less above the recording medium on an air cushion, caused by the high speed of the disk.

Part V. Thermal Properties of Materials

Chap. 18. Introduction

Chap. 19. Fundamentals of Thermal Properties

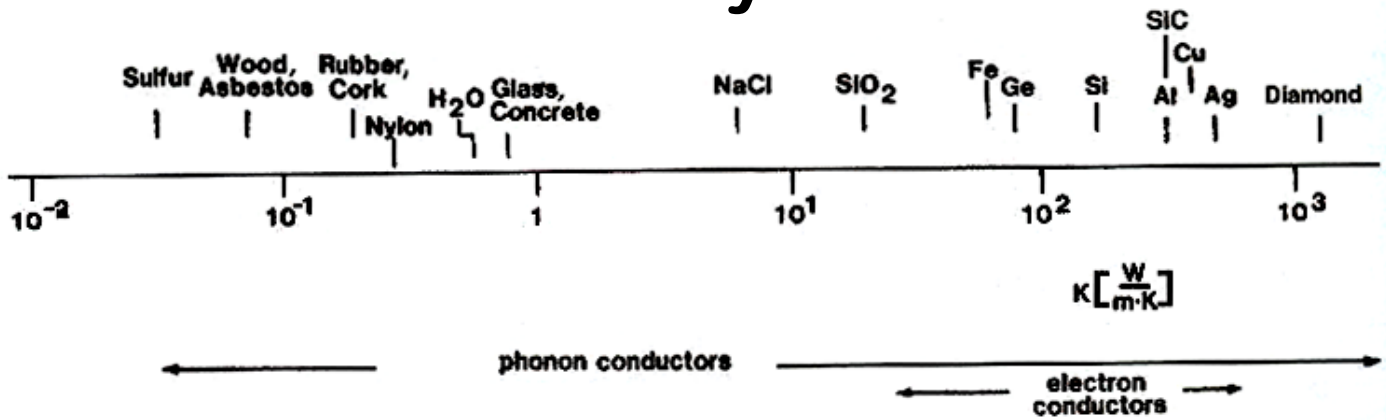
Chap. 20. Heat Capacity

Chap. 21. Thermal Conduction

Chap. 22. Thermal Expansion

Introduction

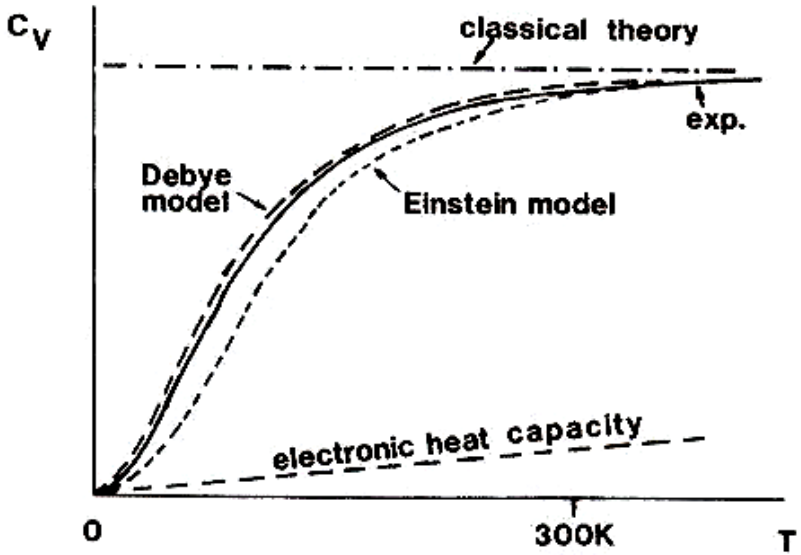
➢ Thermal conductivity



Phonons: lattice vibration quanta which are thought to be created in large numbers in the hot part of a solid and partially eliminated in the cold part

Specific heat capacity

Molar heat capacity



Heat Capacity

➢ Fundamental Concepts and Definitions

- heat, work, energy

1st law of thermodynamics $\Delta E = Q + W$

Unit: joule (J) in SI, 1 cal = 4.184 J (1J = 0.239 cal)

- heat capacity, *C'*, [J/K]:

The amount of heat, *dQ*, which needs to be transferred to a substance to raise its temperature by a certain temperature interval, *dT*

- heat capacity at constant volume, $C_V^{'}$

heat capacity at constant pressure, $C_P^{'}$

$$C_V^{'} = \left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \qquad C_P^{'} = \left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

H = E + PV

$$C_P^{'} - C_V^{'} = \frac{\alpha^2 VT}{\kappa}$$

small for solids

Heat Capacity

➢ Fundamental concepts and definitions

- specific heat capacity- materials constant

$$c = \frac{C'}{m} \; [\mathrm{J/g \cdot K}]$$

temperature dependent

- without work

$$\Delta E = Q = m \Delta T c_V$$

Table 19.1. Experimental Thermal Parameters of Various Substances at Room Temperature and Ambient Pressure.

Substance	Specific heat capacity (c_p) $\left(\frac{J}{g \cdot K}\right)$	Molar (atomic) mass $\left(\frac{g}{mol}\right)$	Molar heat capacity (C_p) $\left(\frac{J}{mol \cdot K}\right)$	Molar heat capacity (C_v) $\frac{J}{mol \cdot K}$
Al	0.897	27.0	24.25	23.01
Fe	0.449	55.8	25.15	24.68
Ni	0.456	58.7	26.8	24.68
Cu	0.385	63.5	24.48	23.43
Pb	0.129	207.2	26.85	24.68
Ag	0.235	107.9	25.36	24.27
C (graphite)	0.904	12.0	10.9	9.20
Water	4.184	18.0	75.3	

Heat Capacity

➢ Fundamental concepts and definitions

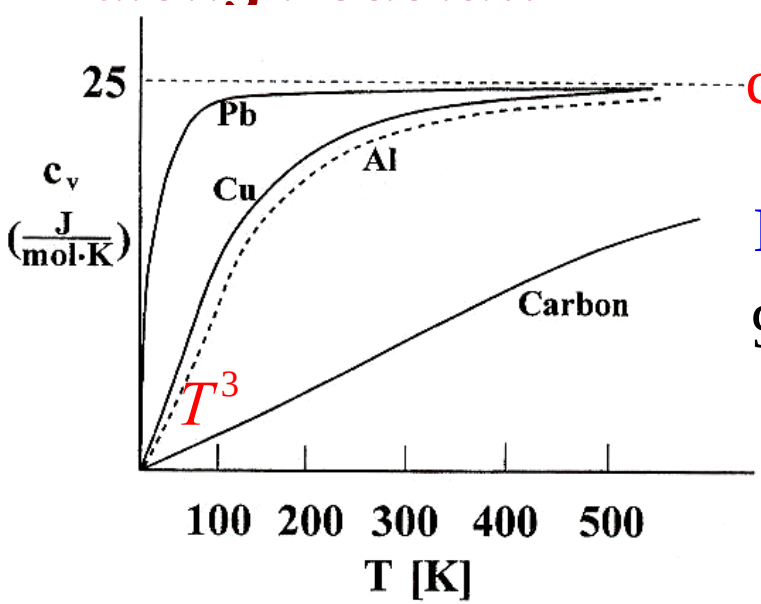
- molar heat capacity

$$C_V = \frac{C_V'}{n} = c_V \cdot M \quad [\mathrm{J/mol \cdot K}]$$

M: molar mass, $n = N / N_A$, N_A : Avogadro's number

- C_V ~ 25 J/mol K (6 cal/mol K) for most solids

→ Dulong Petit law



constant~3R

Debye temp, θ_D

96% of final value

Table 19.2. Debye Temperatures of Some Materials.

Substance	θ_D (K)
Pb	95
Au	170
Ag	230
W	270
Cu	340
Fe	360
Al	375
Si	650
C	1850
GaAs	204
InP	162

Heat Capacity

- **Classical theory of heat capacity**

- interpret Dulong and Petit law using atomistic concept

- atom- harmonic oscillator

average energy of the oscillator: $E = k_B T$

in 3-D, average energy per atom: $E = 3k_B T$

based on kinetic theory of gases

kinetic energy: $E_{kin} = \frac{3}{2} k_B T$ **potential energy:** $E_{pot} = \frac{3}{2} k_B T$

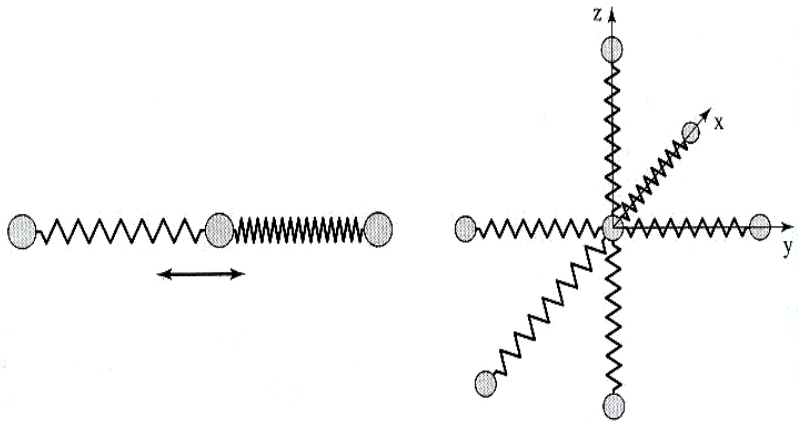
$$E = 2 \cdot \frac{3}{2} k_B T = 3k_B T$$

- total internal energy per mole

$$E = 3N_A k_B T$$

- molar heat capacity

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3N_A k_B = 3R$$



Heat Capacity

- **Quantum mechanical- Einstein model**

- overcome of shortcoming in Dulong and Petit law

- energies of classical oscillator quantized

only certain vibrational modes are allowed

lattice vibration quanta- phonons

- phonon- particle-wave duality

$$E = \hbar w, \quad \vec{\mathrm{p}} = \hbar \vec{k}$$

elastic wave (longitudinal and/or transverse)

acoustic and optical bands

density of vibrational modes, D(w)

Heat Capacity

➢ Phonon

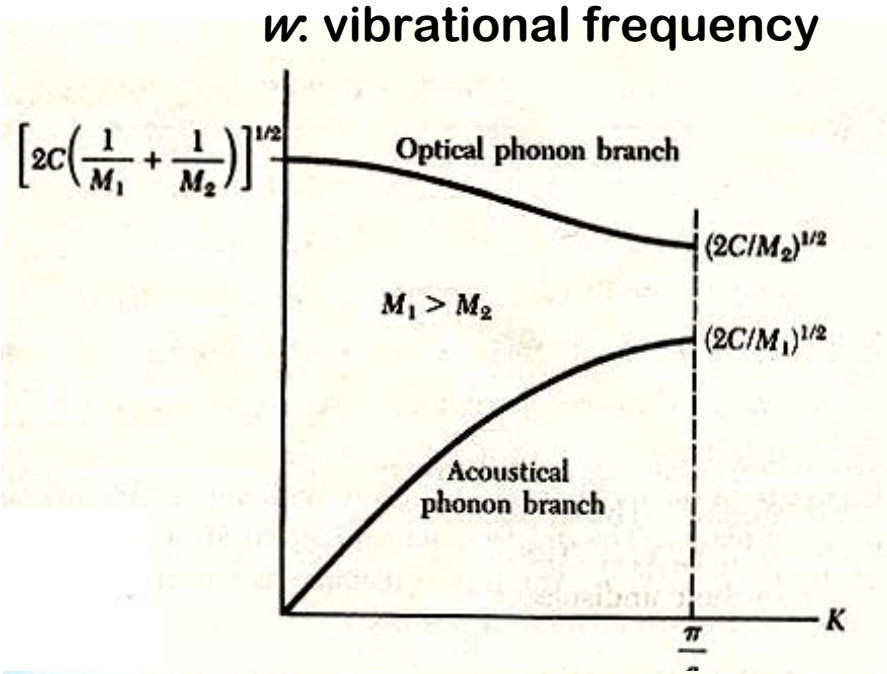


Figure 7 Optical and acoustical branches of the dispersion relation for a diatomic linear lattice, showing the limiting frequencies at $K = 0$ and $K = K_{max} = \pi/a$. The lattice constant is a.

Kittel, Introduction to Solid State Physics

density of vibration mode, $D(w)$

$$D(w) = \frac{3Vw^2}{2\pi^2 v_s^3}$$

v_s : sound velocity

Heat Capacity

- **Quantum mechanical- Einstein model**

- assumption: independent oscillator (one frequency)

allowed energies of a single oscillator

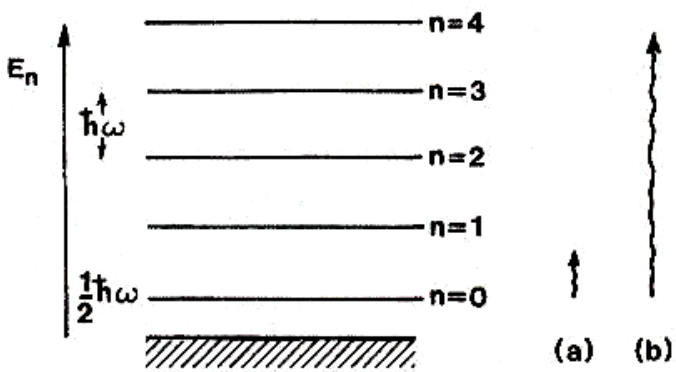
$$E_n = n\hbar w$$

- phonon- not conserved

follow Bose and Einstein statistics

average number of phonons,

$$\overline{N}_{ph} = \frac{1}{\exp(\frac{\hbar w}{kT}) - 1}$$

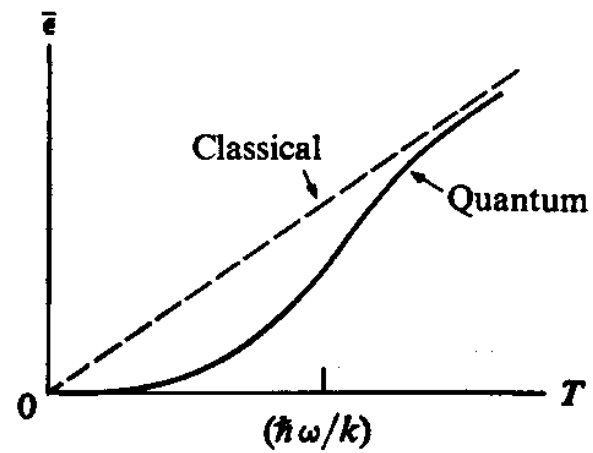


Heat Capacity

➢ Quantum mechanical- Einstein model

- average energy of an isolated oscillator

$$E_{osc} = \hbar w \overline{N}_{ph} = \frac{\hbar w}{\exp(\frac{\hbar w}{kT}) - 1}$$



Omar, Elementary Solid State Physics

- total energy of a solid

$$E = 3N_A \frac{\hbar w}{\exp(\frac{\hbar w}{kT}) - 1}$$

let $\hbar w = k_B \theta_E$

- molar heat capacity

$$E = \left(\frac{\partial E}{\partial T}\right)_V = 3N_A k_B \left(\frac{\hbar w}{k_B T}\right)^2 \frac{\exp(\frac{\hbar w}{kT})}{(\exp(\frac{\hbar w}{kT}) - 1)^2} = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{\exp(\frac{\theta_E}{T})}{(\exp(\frac{\theta_E}{T}) - 1)^2}$$

Heat Capacity

- **Quantum mechanical- Einstein model**

- in high temp limit

$$e^{\theta_E/T} = 1 + (\frac{\theta_E}{T}) + \frac{1}{2}(\frac{\theta_E}{T})^2 + \ldots$$

$$C_v = 3R(\frac{\theta_E}{T})^2 \frac{\frac{1+\theta_E}{T}}{(1+\frac{\theta_E}{T}-1)^2} = 3R$$

- in low temp range $T << \theta_E$

$$C_v = 3R(\frac{\theta_E}{T})^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2} = 3R(\frac{\theta_E}{T})^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T})^2}$$

$$= 3R(\frac{\theta_E}{T})^2 e^{-\theta_E/T} = B(T)e^{-\theta_E/T}$$

approaches zero exponentially

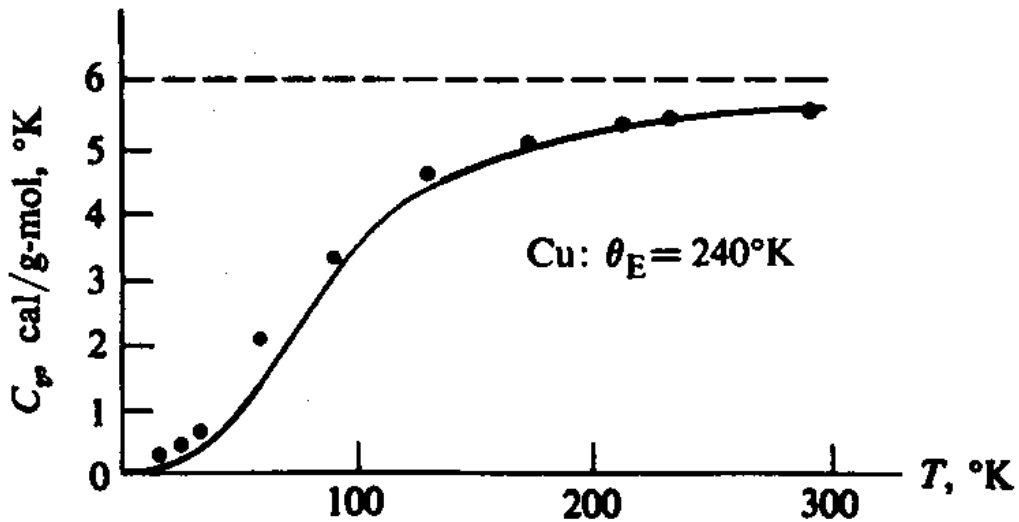
Heat Capacity

- **Quantum mechanical- Einstein model**

- one adjustable parameter: $\theta_E \ (or\ w_E)$

For Cu, $\theta_E = 240\text{K}$

$\omega_E = k\theta_E / \hbar = 2.5\times10^{13} s^{-1}$ infrared region



Omar, Elementary Solid State Physics

Heat Capacity

- **Quantum mechanical- Debye model**

- assumption

i) collective lattice modes (oscillate interdependently)

$$0 < \omega < \omega_D$$

ii) continuous medium

$$v_s = w/k: \text{ constant}$$

lower limit: $w = 0$

upper limit (Debye frequency, w_D) – total number of modes included are equal to the number of degrees of freedom for the entire solid ($3N_A$)

$$E = \int E_{osc}(\omega) D(\omega) d\omega = \frac{3V}{2\pi^2 v_s^3} \int_o^{\omega_D} \frac{\hbar\omega^3}{e^{\hbar\omega/kT} - 1} d\omega$$

Heat Capacity

- **Quantum mechanical- Debye model**

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3V}{2\pi^2 v_s^3}\frac{\hbar^2}{kT^2}\int_o^{\omega_D}\frac{\omega^4 e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}d\omega$$

$$= 9R\left(\frac{T}{\theta_D}\right)^3\int_o^{\theta_D/T}\frac{x^4 e^x}{(e^x-1)^2}dx \qquad x = \hbar\omega/kT \qquad k\theta_D = \hbar\omega$$

at low temp, $T << \theta_D$ $\qquad \int_o^{\infty}\frac{x^4 e^x}{(e^x-1)^2}d\omega = \frac{4\pi^4}{15}$

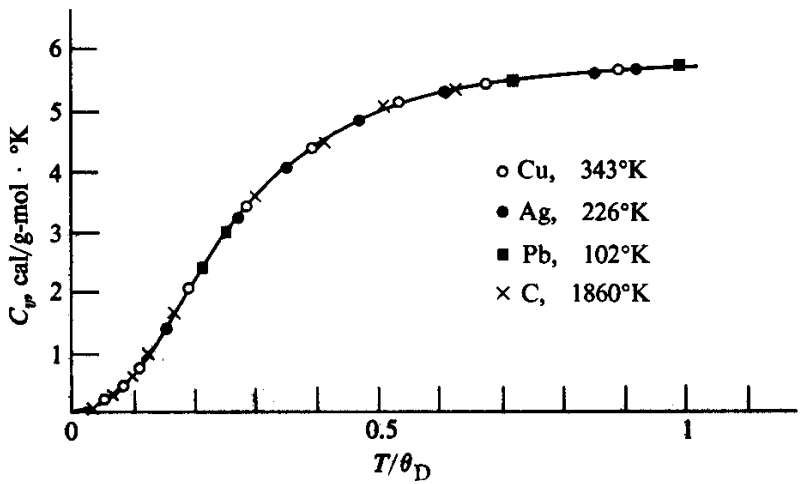
$$C_v = 9R\left(\frac{T}{\theta_D}\right)^3\frac{4\pi^4}{15} = \frac{12\pi^4 R}{5}\left(\frac{\mathrm{T}}{\theta_\mathrm{D}}\right)^3$$

at high temp, $T >> \theta_D$ $x \sim$ small $e^x \cong 1 + x$

$$C_v = 9R\left(\frac{T}{\theta_D}\right)^3\int_o^{\theta_D/T}x^2 d\omega = 9R\left(\frac{T}{\theta_D}\right)^3\frac{1}{3}\left(\frac{\theta_D}{T}\right)^2 = 3R$$

Heat Capacity

- Quantum mechanical- Debye model



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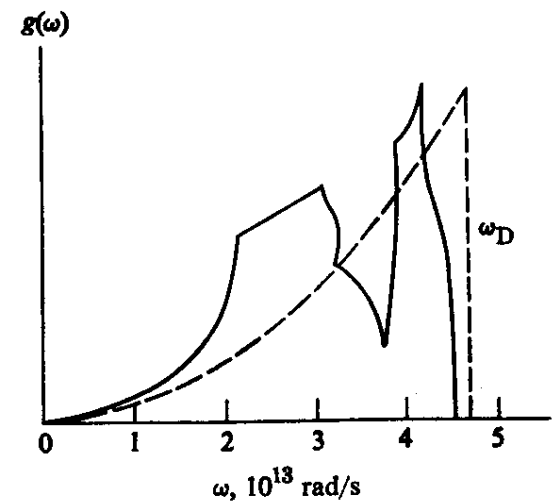


Omar, Elementary Solid State Physics

- Debye model's limitations
  - continuous medium-linear dispersion relation
  - optical mode
  - $\theta_D = \theta_D(T)$
  - actual density of states of the lattice

Heat Capacity

- **Electronic contribution to heat capacity**

- electron contribution - small compared to that of the phonons

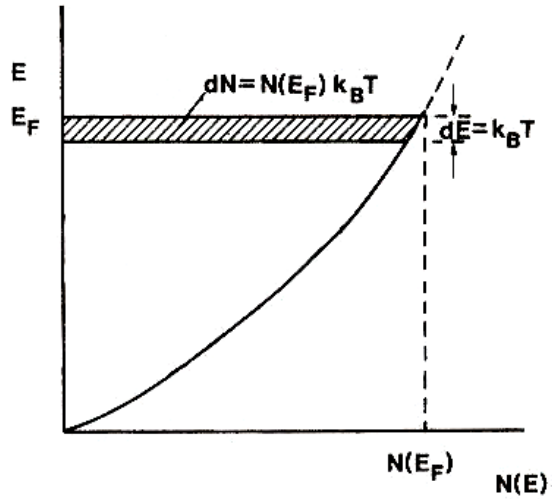
- metal and alloys- free electrons

only those electrons which lie within an energy interval k_BT of the Fermi energy contribute ($dN=N(E_F)k_BT$)

- excited electron behaves like a monoatomic gas

$$E_{kin} = \frac{3}{2}k_BTdN = \frac{3}{2}k_BTN(E_F)k_BT$$

$$C_V^{el} = \left(\frac{\partial E}{\partial T}\right)_V = 3k_B^2TN(E_F)$$



Heat Capacity

- **Electronic contribution to heat capacity**

$$N(E_F) = \frac{3N^*}{2E_F}$$

N^* : # of electron whose energy less than E_F

$$C_V^{el} = \frac{9}{2}\frac{N^* k_B^2 T}{E_F} \rightarrow C_V^{el} = \frac{\pi^2}{2}\frac{N^* k_B^2 T}{E_F} = \frac{\pi^2}{2} N^* k_B \frac{T}{T_F}$$

assume one free electron per atom

$$C_V^{el} = \frac{\pi^2}{2}\frac{N_A k_B^2 T}{E_F} = \frac{\pi^2}{2} R \frac{T}{T_F}$$

- C_V~T dependence
- at room temp: less than 1%
- appreciable contributions: at low temp
above Debye temp

Heat Capacity

➢ Electronic contribution to heat capacity

$$C_v^{total} = C_v^{el} + C_v^{ph} = \gamma T + \beta T^3 \qquad \gamma = 3k_B^2 N(E_F)$$

$$\frac{C_v^{total}}{T} = \gamma + \beta T^2$$

intercept $\gamma \rightarrow N(E_F)$

effective thermal mass

$$\frac{m_{th}^*}{m_o} = \frac{\gamma_{obe}}{\gamma_{cal}}$$

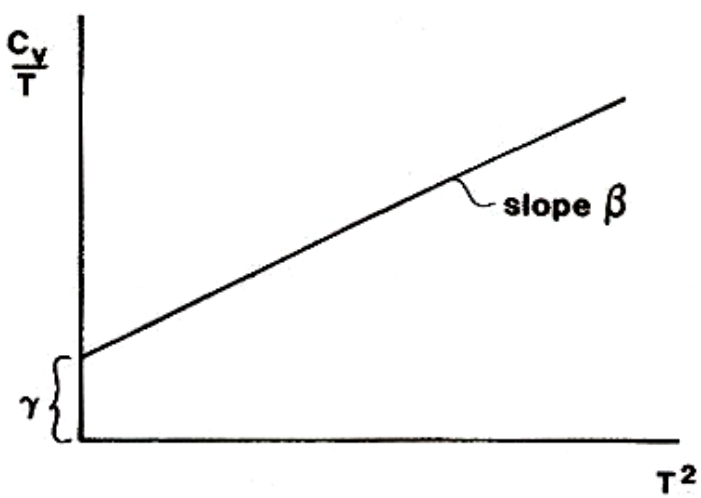


Table 20.1. Calculated and Observed Values for the Constant γ, see (20.31).

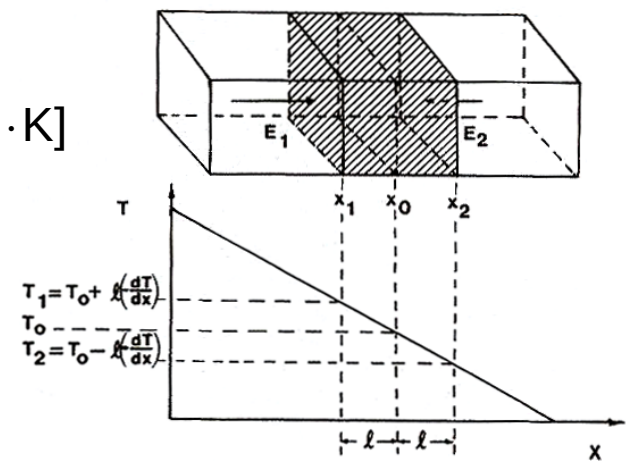
Substance	γ, observed $\left(\frac{J}{mol \cdot K^2}\right)$	γ, calculated $\left(\frac{J}{mol \cdot K^2}\right)$	$\frac{m_{th}^*}{m_0}$
Ag	0.646×10^{-3}	0.645×10^{-3}	1.0
Al	1.35×10^{-3}	0.912×10^{-3}	1.48
Au	0.729×10^{-3}	0.642×10^{-3}	1.14
Na	1.3×10^{-3}	0.992×10^{-3}	1.31
Fe	4.98×10^{-3}	—	—
Ni	7.02×10^{-3}	—	—

Thermal Conduction

➢ Thermal conductivity, K

- transfer of thermal energy
- heat flux ~ temp. gradient

$$J_Q = -K\frac{dT}{dx} \qquad k[J/s\cdot m\cdot K]$$



- the energy E_1, per unit time and unit area, of the electrons that dirft from the left into the sample volume
  = number of electrons, z, times the energy of the electrons

$$E_1 = z\cdot\frac{3}{2}k_B(T_o + l(-\frac{dT}{dx}) = \frac{n_V v}{6}\frac{3}{2}k_B(T - l\frac{dT}{dx})$$

$$(\because\ z = \frac{1}{6}n_V v,\ \ n_V = \frac{N}{V})$$

$$E_2 = \frac{n_V v}{6}\frac{3}{2}k_B(T + l\frac{dT}{dx})$$

heat flux J_Q

$$J_Q = E_2 - E_1 = -\frac{n_V v}{6}\frac{3}{2}k_B(2l\frac{dT}{dx}) = -\frac{n_V v}{2}k_B l\frac{dT}{dx}$$

$$J_Q = -\frac{n_V v}{2}k_B l\frac{dT}{dx}, \qquad J_Q = -K\frac{dT}{dx}$$

$$\therefore\ K = \frac{n_V v k_B l}{2}$$

- temperature gradient in x-direction, dT/dx
- consider the volume of unit area and length of $2l$
  l: mean free path between two consecutive collision

- the larger heat conductivity, K, the more electrons, n_V
  the larger their velocity, v, the larger mean free path, l
- relationship between K and C_V^{el}
  kinetic energy of all electrons per unit volume

$$E = n_V\,\tfrac{3}{2}k_B T, \qquad C_V^{el} = \left(\frac{dE}{dT}\right)_V = n_V\,\tfrac{3}{2}k_B$$

$$K = \frac{1}{3}C_V^{el} v l$$

Thermal Expansion

- **Coefficient of linear expansion, α_L**

- the amount by which each unit length of a material changes when the temperature of the material changes by one degree

$$\frac{\Delta L}{L} = \alpha_L \Delta T$$

volume expansion coefficient, α_V

$$\frac{\Delta V}{V_o} = \alpha_v \Delta T$$

$\alpha_v \approx 3\alpha_l$ for isotropic solid

- **Temperature dependence of α_L**

- similar to the temperature dependence of $C_V = f(T)$

- for dielectric materials

α_L approaches a constant value for T > θ_D
vanishes as T^3 for T → 0

- for metals,

α_L~T at very low temp
α_L~ depends on the sum of heat capacities of phonon and electron in other temperature regions