

Introduction to Solid State Physics

(C. Kittel)

Chapter 8

Semiconductor crystals

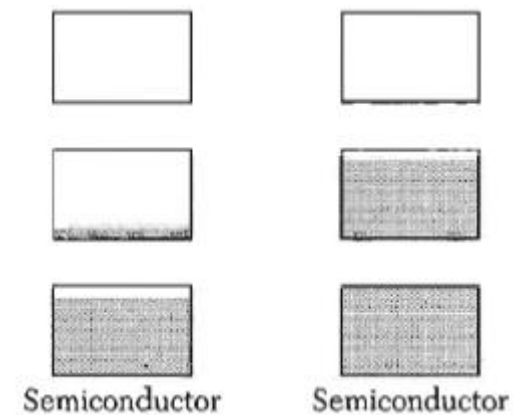
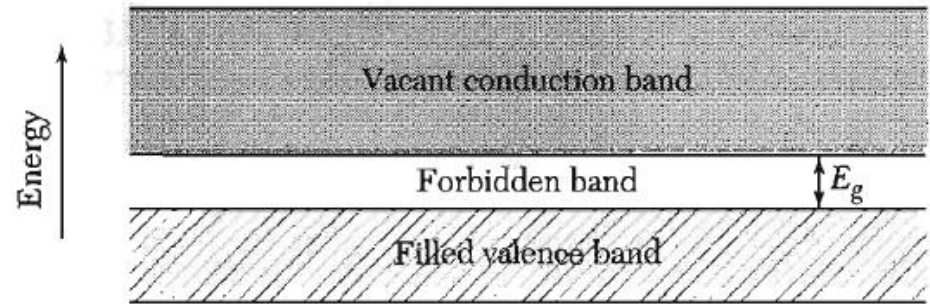
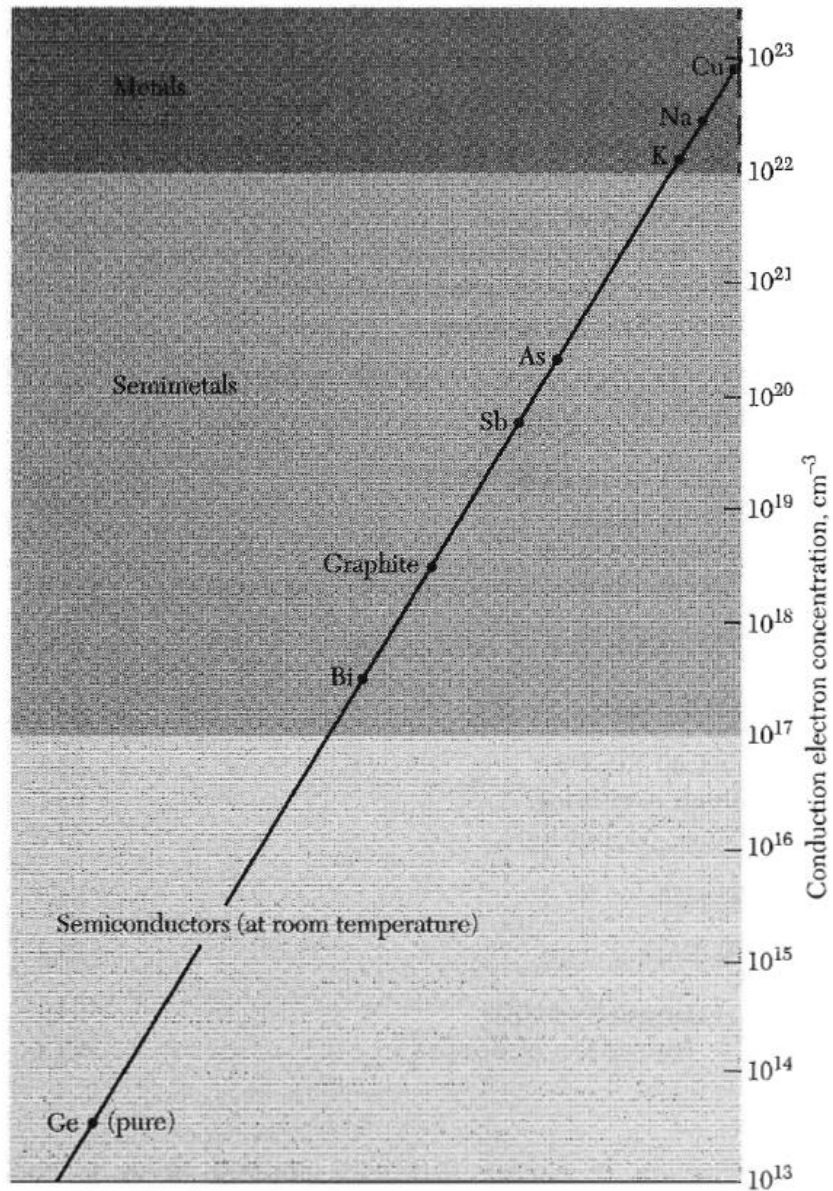
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Semiconductor Crystals

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Semiconductors

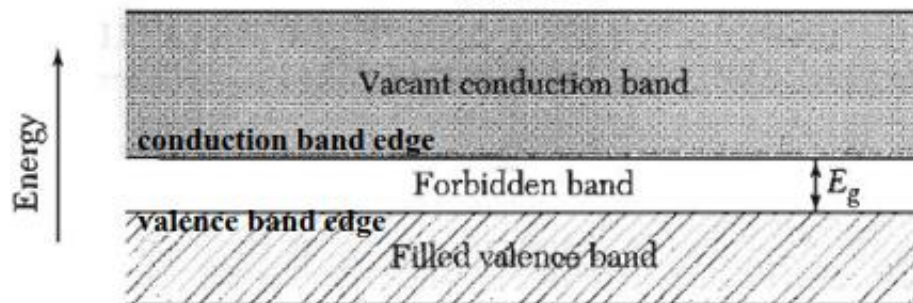


Semiconductors:

- electrical resistivity at room temperature
 $\sim 10^{-2}$ to 10^9 ohm-cm,
Strongly dependent on temperature
- Used for transistors, switches, diodes,
photovoltaic cells, detectors, and thermistors
- semiconductor compounds: III-V, II-VI

intrinsic semiconductor

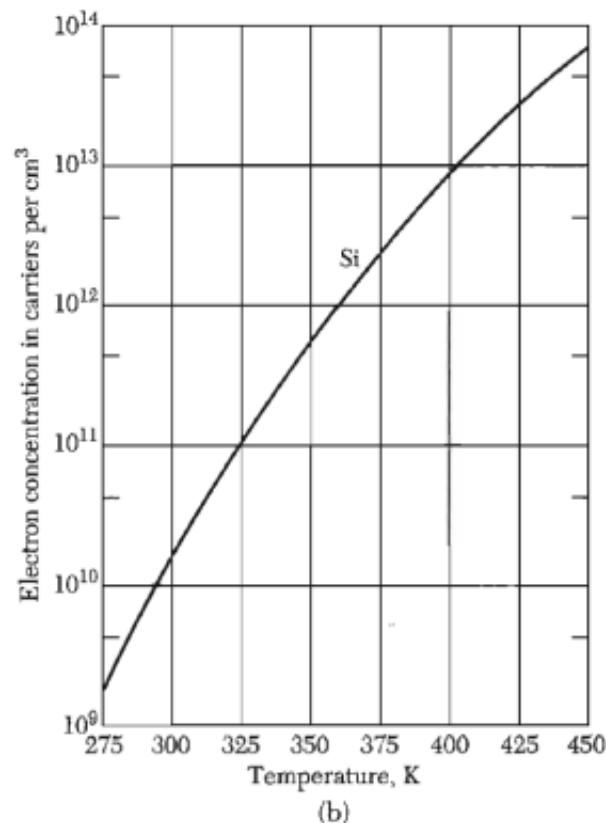
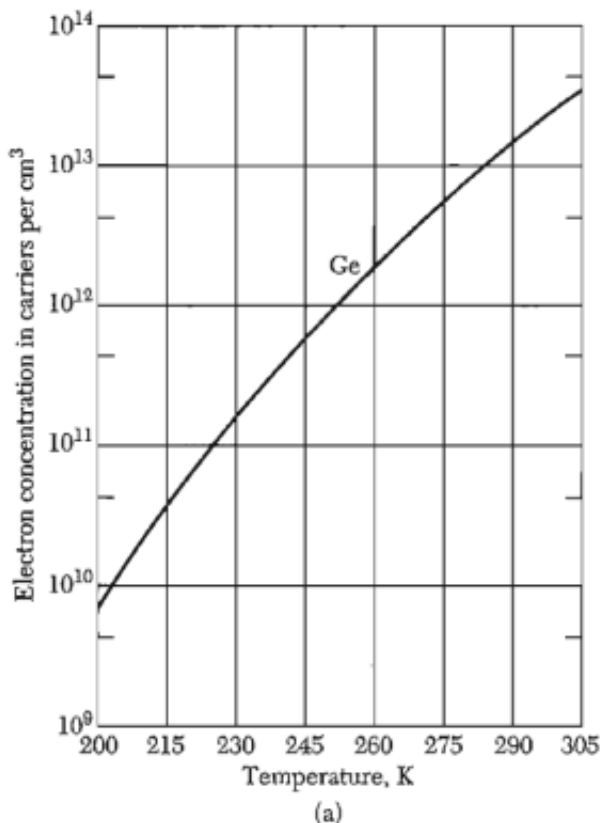
at zero T



Semiconductors

As the temperature is increased, electrons are thermally excited from the valence band to the conduction band. Both the **electrons** in the conduction band and the vacant orbitals or **holes** left behind in the valence band contribute to the electrical conductivity.

intrinsic carrier concentrations are largely controlled by $E_g/k_B T$



intrinsic
semiconductor
at room T



Semiconductor

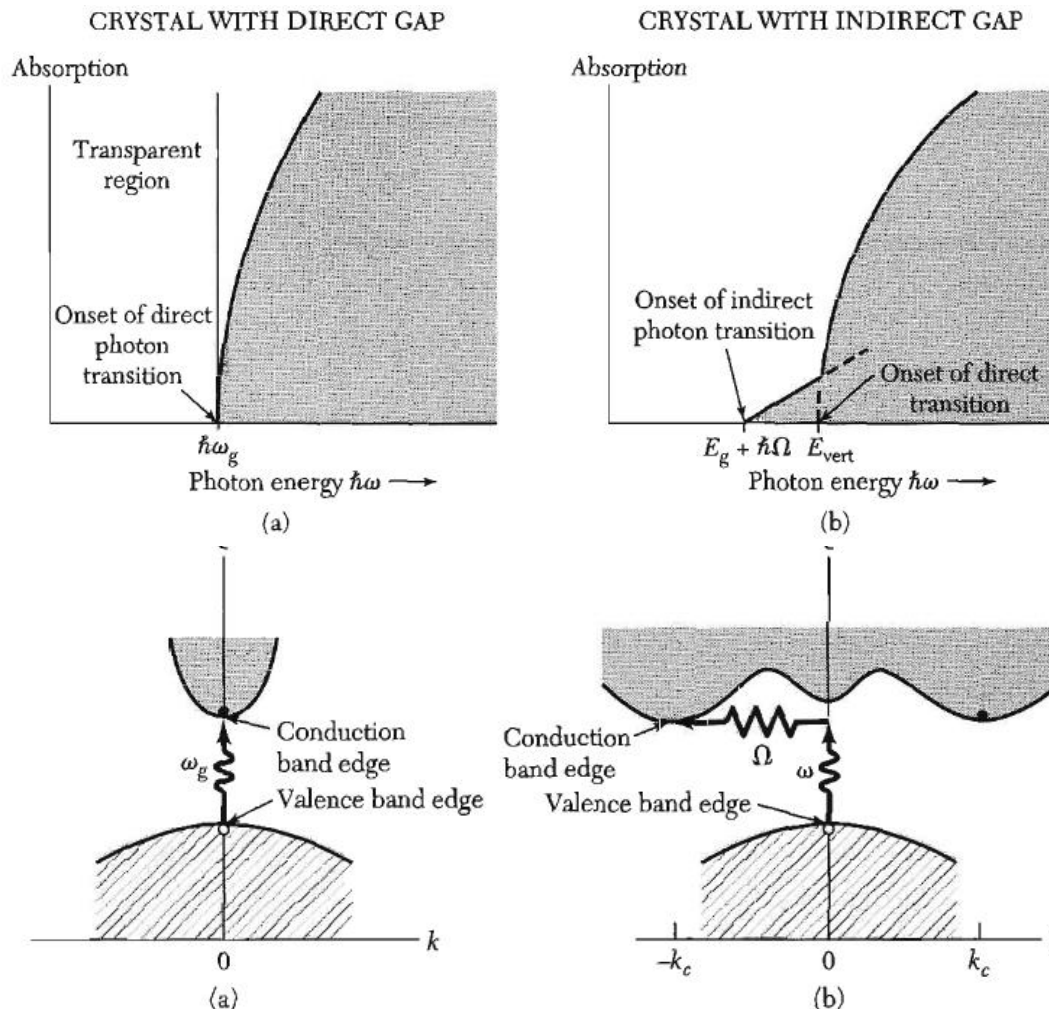
hole doped
semiconductor



Semiconductor

Semiconductors

Direct & Indirect Gap



Crystal	Gap	$E_g, \text{ eV}$	
		0 K	300 K
Si	<i>i</i>	1.17	1.11
Ge	<i>i</i>	0.744	0.66
GaAs	<i>d</i>	1.52	1.43

<indirect absorption process>

- photon \rightarrow electron+hole \pm phonon of energy $\hbar\Omega$
(phonon wavevector \mathbf{K} , phonon frequency Ω)
- $\hbar\Omega$ (~ 0.01 to 0.03 eV) $\ll E_g$
 $\hbar\omega = E_g \pm \hbar\Omega$
- $\mathbf{k}(\text{photon}) = \mathbf{k}_c + \mathbf{K} \cong \mathbf{0}$
- photon wavevectors are negligible at the energy range of interest.

Semiconductors

Holes: vacant orbitals in an otherwise filled band

A hole acts in applied electric and magnetic fields as if it has a **positive charge +e**.

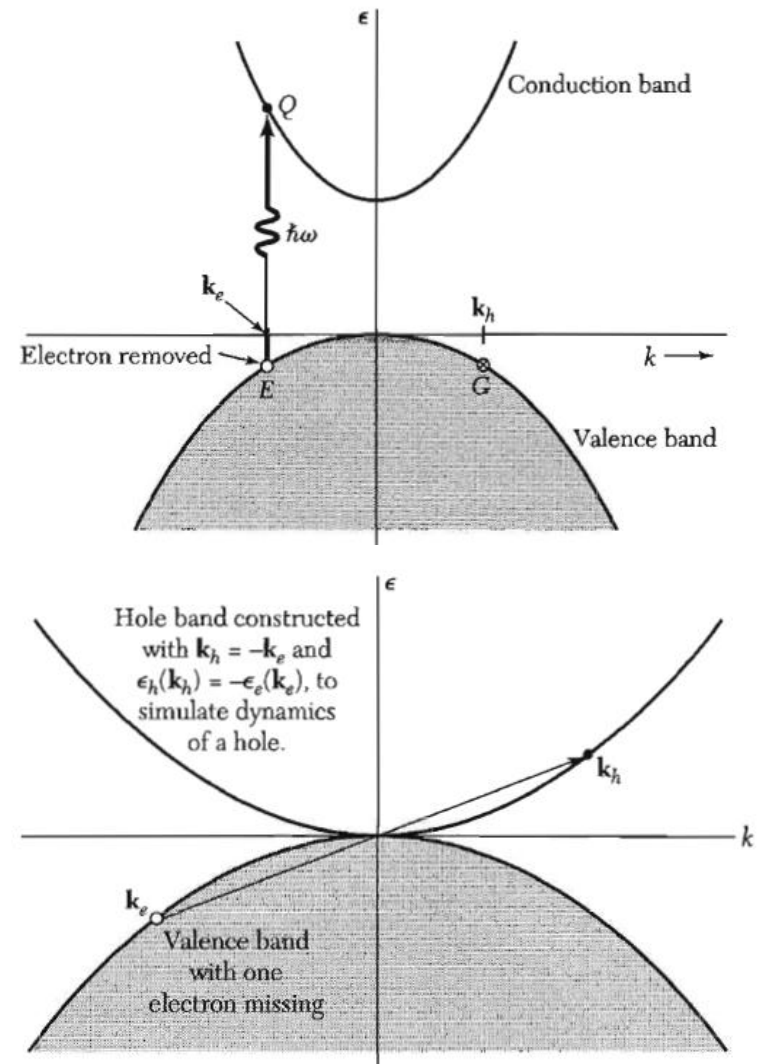
1. $\mathbf{k}_h = -\mathbf{k}_e$.
2. $\epsilon_h(\mathbf{k}_h) = -\epsilon_e(\mathbf{k}_e)$.
3. $\mathbf{v}_h = \mathbf{v}_e$. $\leftarrow \nabla \epsilon_h(\mathbf{k}_h) = \nabla \epsilon_e(\mathbf{k}_e)$

4. $m_h = -m_e$.

5. $\hbar \frac{d\mathbf{k}_h}{dt} = e(\mathbf{E} + \frac{1}{c} \mathbf{v}_h \times \mathbf{B})$.

(CGS)

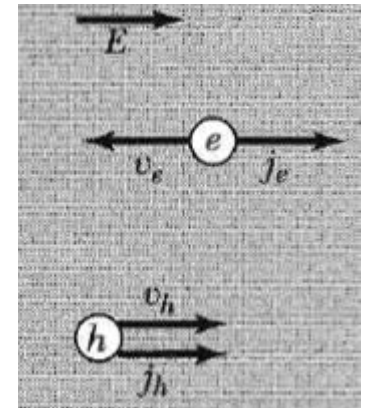
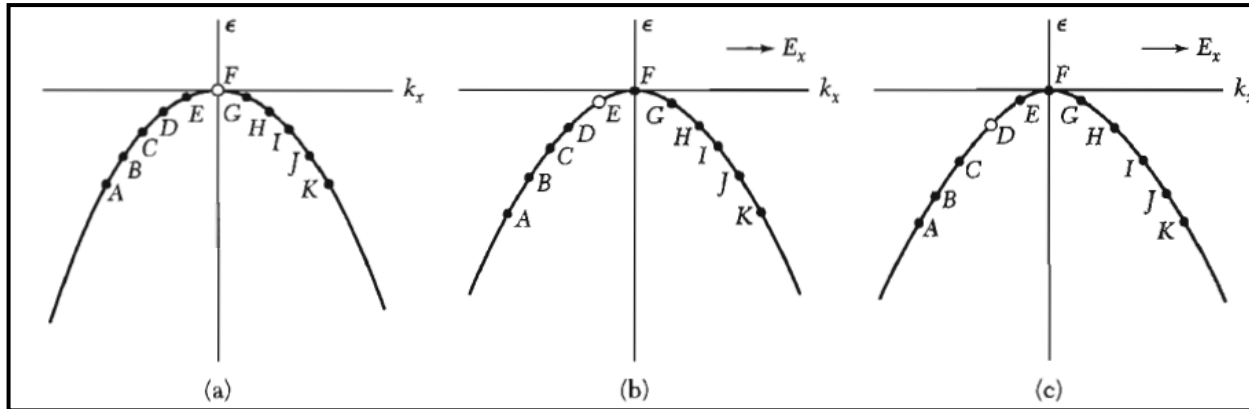
$$\hbar \frac{d\mathbf{k}_e}{dt} = -e(\mathbf{E} + \frac{1}{c} \mathbf{v}_e \times \mathbf{B})$$



Semiconductors

$$\mathbf{j} = \langle -e \rangle \mathbf{v}(G) = \langle -e \rangle [-\mathbf{v}(E)] = e \mathbf{v}(E)$$

Holes: vacant orbitals in an otherwise filled band



Effective mass

$$\epsilon(K) = \epsilon_c + (\hbar^2/2m_e)K^2 ; \quad m_e/m = 1/[(2\lambda/U)-1]$$

$$\frac{dv_g}{dt} = \hbar^{-1} \frac{d^2\epsilon}{dk^2} \frac{dk}{dt} = \hbar^{-1} \left(\frac{d^2\epsilon}{dk^2} \frac{dk}{dt} \right) \quad dk/dt = F/\hbar,$$

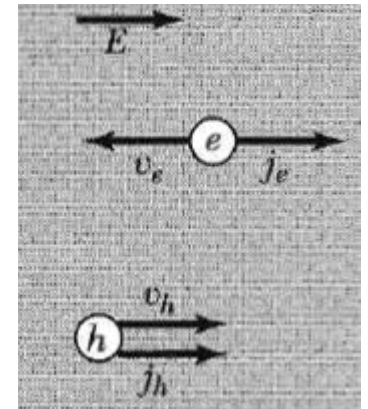
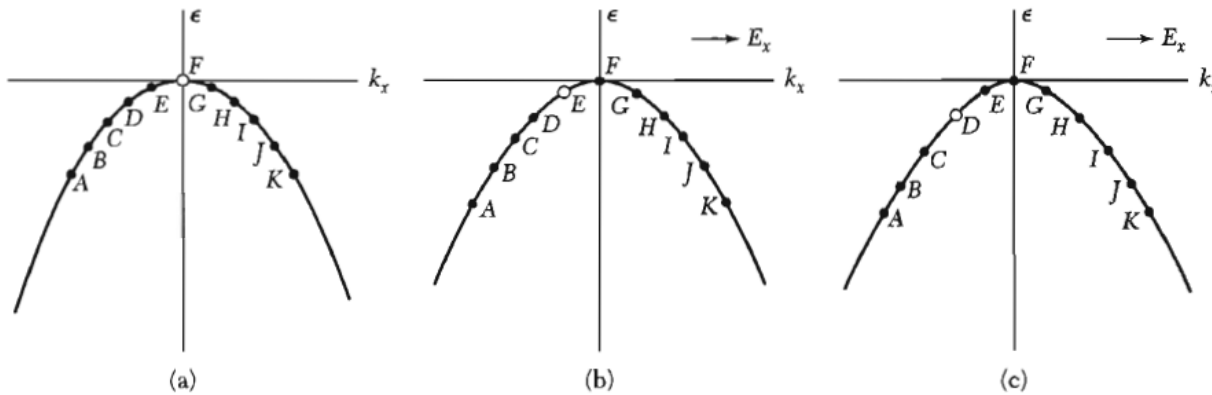
$$\frac{dv_g}{dt} = \left(\frac{1}{\hbar^2} \frac{d^2\epsilon}{dk^2} \right) F ; \quad \text{or} \quad F = \frac{\hbar^2}{d^2\epsilon/dk^2} \frac{dv_g}{dt} .$$

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2\epsilon}{dk^2} .$$

$$\left(\frac{1}{m^*} \right)_{\mu\nu} = \frac{1}{\hbar^2} \frac{d^2\epsilon_k}{dk_\mu dk_\nu} ; \quad \frac{dv_\mu}{dt} = \left(\frac{1}{m^*} \right)_{\mu\nu} F_\nu$$

Semiconductors

Holes: vacant orbitals in an otherwise filled band



Effective mass

$$\epsilon(K) = \epsilon_c + (\hbar^2/2m_e)K^2 ; \quad m_e/m = 1/[(2\lambda/U) - 1]$$

$$\frac{dv_g}{dt} = \hbar^{-1} \frac{d^2\epsilon}{dk dt} = \hbar^{-1} \left(\frac{d^2\epsilon}{dk^2} \frac{dk}{dt} \right) \quad dk/dt = F/\hbar,$$

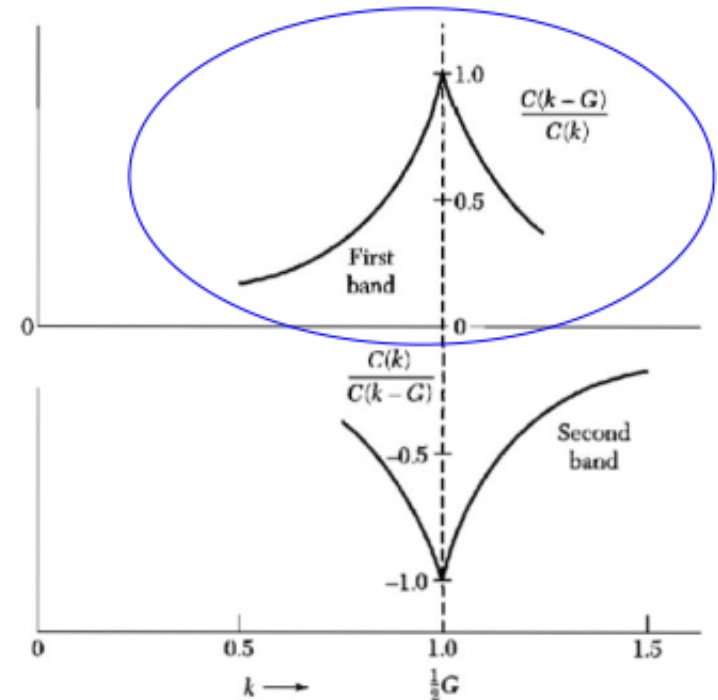
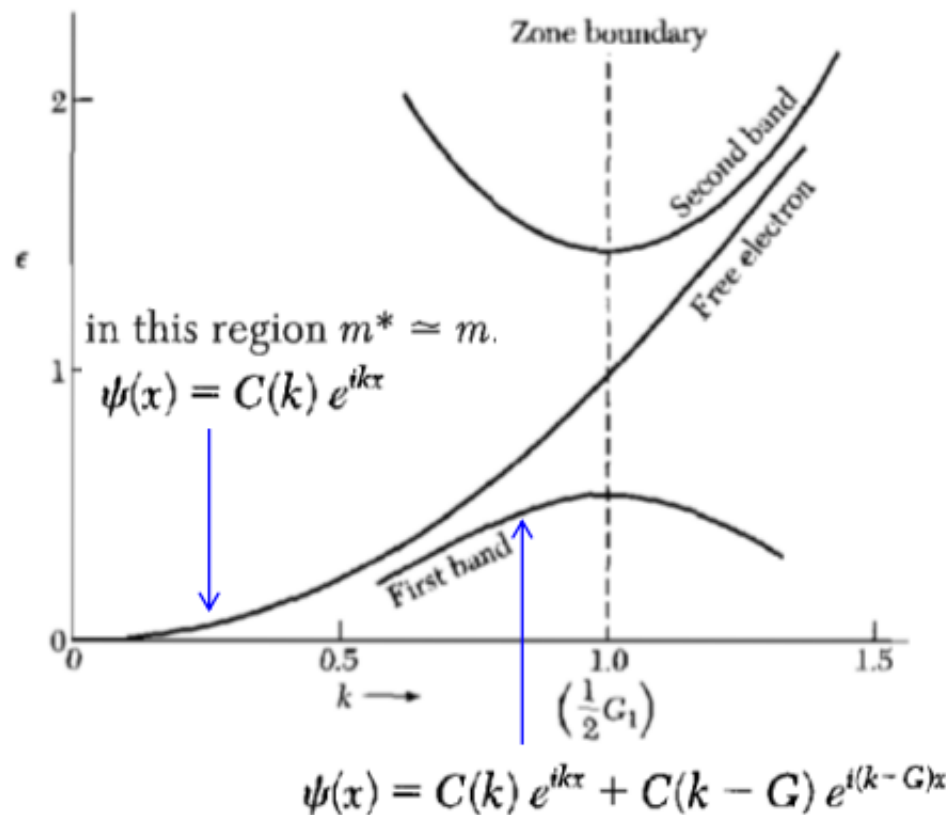
$$\frac{dv_g}{dt} = \left(\frac{1}{\hbar^2} \frac{d^2\epsilon}{dk^2} \right) F ; \quad \text{or} \quad F = \frac{\hbar^2}{d^2\epsilon/dk^2} \frac{dv_g}{dt} .$$

$$\boxed{\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2\epsilon}{dk^2} .}$$

$$\boxed{\left(\frac{1}{m^*} \right)_{\mu\nu} = \frac{1}{\hbar^2} \frac{d^2\epsilon_k}{dk_\mu dk_\nu} ; \quad \frac{dv_\mu}{dt} = \left(\frac{1}{m^*} \right)_{\mu\nu} F_\nu}$$

Equation of motion

Physical Interpretation of the Effective Mass



An increase in the reflected component as k is increased represents momentum transfer to the electron from the lattice.

- **A negative effective mass:** on going from state k to state $k + \Delta k$, the momentum transfer to the lattice from the electron is larger than the momentum transfer from the applied force to the electron. Although k is increased by Δk by the applied electric field, the approach to Bragg reflection can give an overall decrease in the forward momentum of the electron.

Semiconductors

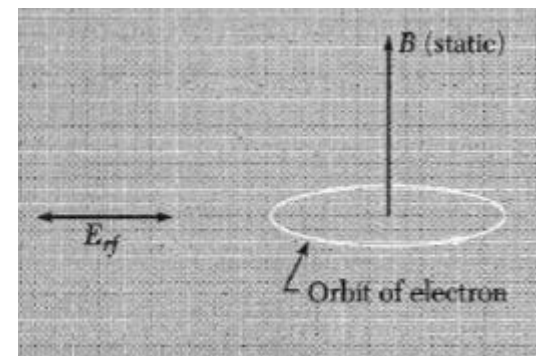
Measurement of Effective masses → Cyclotron resonance

Resonance absorption of energy from **rf E-field** \perp **B**

$$(\text{CGS}) \quad \omega_c = \frac{eB}{m^*c},$$

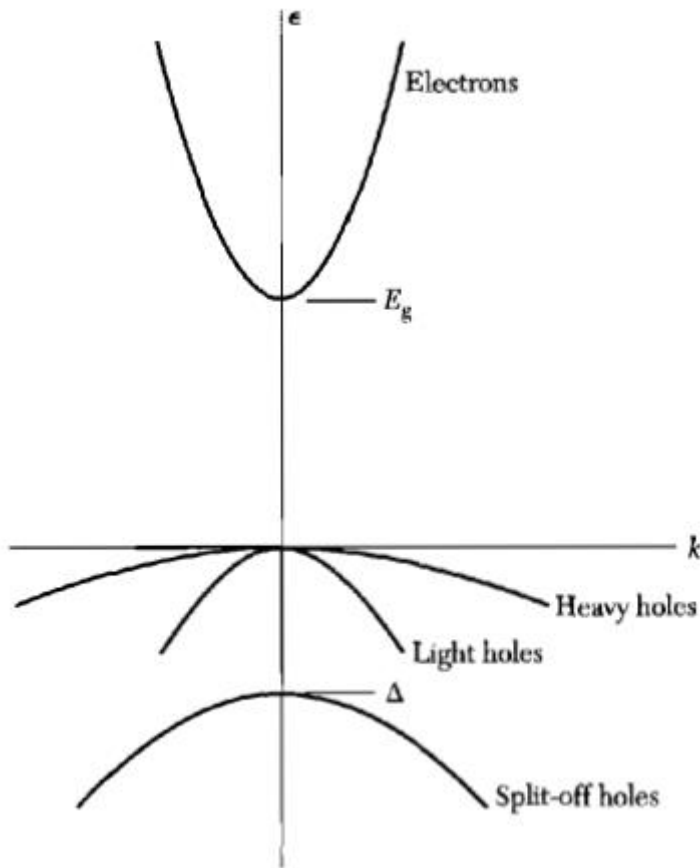
$$(\text{SI}) \quad \omega_c = \frac{eB}{m^*}$$

$$\omega_{\text{rf}} = \omega_c$$



$$\omega_c \tau \geq 1.$$

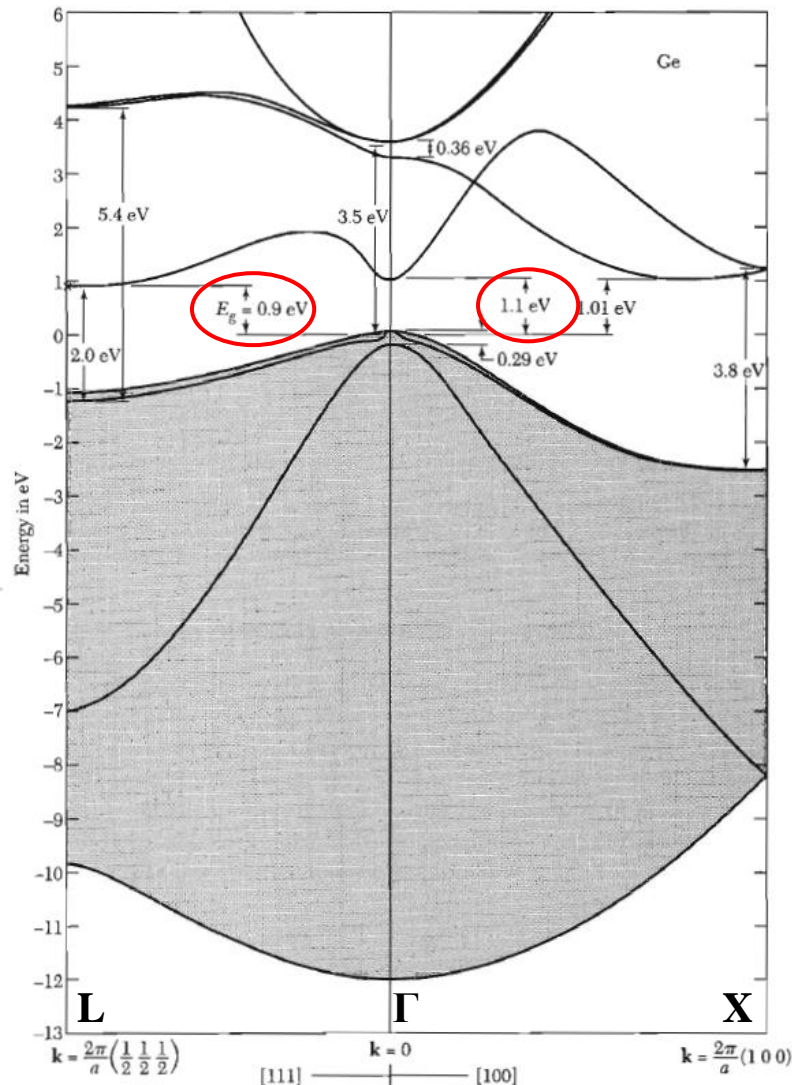
use of higher frequency radiation and higher magnetic fields, with high purity crystals in liquid helium.



Roughly, the light and heavy holes in germanium have masses $0.043 m$ and $0.34 m$; in silicon $0.16 m$ and $0.52 m$ in diamond $0.7 m$ and $2.12 m$.

Semiconductors

Band Structure – Si & Ge (indirect-gap semiconductors)

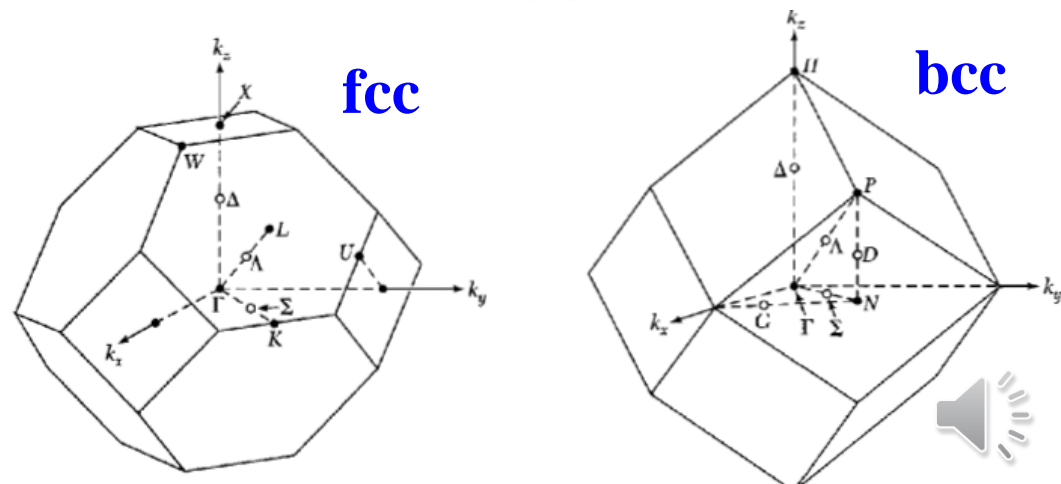


$$\epsilon(\mathbf{k}) = A k^2 \pm [B^2 k^4 + C^2 (k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)]^{1/2} \leftarrow p_{3/2}$$

$$\epsilon(k) = -\Delta + A k^2. \quad \text{split-off band} \leftarrow p_{1/2}$$

Si:	$A = -4.29$;	$ B = 0.68$;
	$ C = 4.87$;	$\Delta = 0.044 \text{ eV}$
Ge:	$A = -13.38$;	$ B = 8.48$;
	$ C = 13.15$;	$\Delta = 0.29 \text{ eV}$

Figure 15 Standard labels of the symmetry points and axes of the Brillouin zones



Semiconductors

Band Structure – GaAs (direct-gap semiconductors)

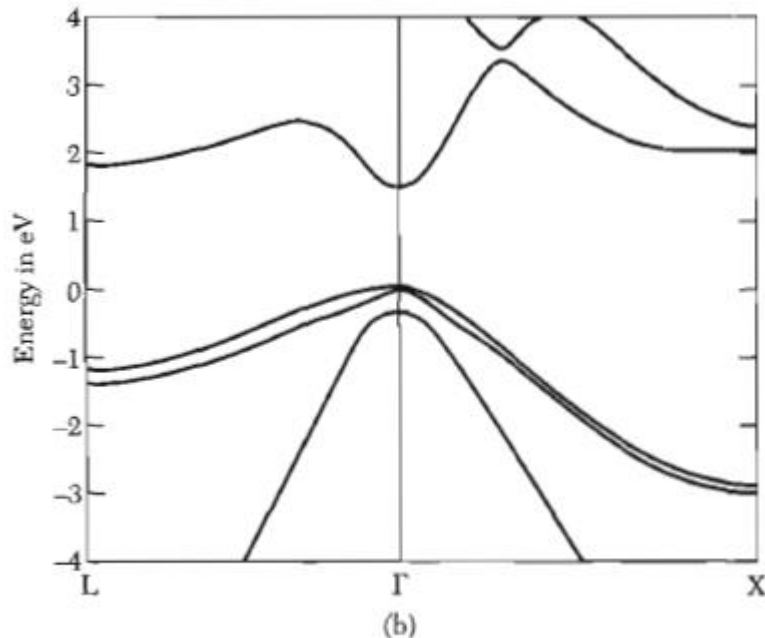


Figure 17b Band structure of GaAs, after S. G. Louie.

$$\epsilon(\mathbf{k}) = Ak^2 \pm [B^2k^4 + C^2(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)]^{1/2}$$

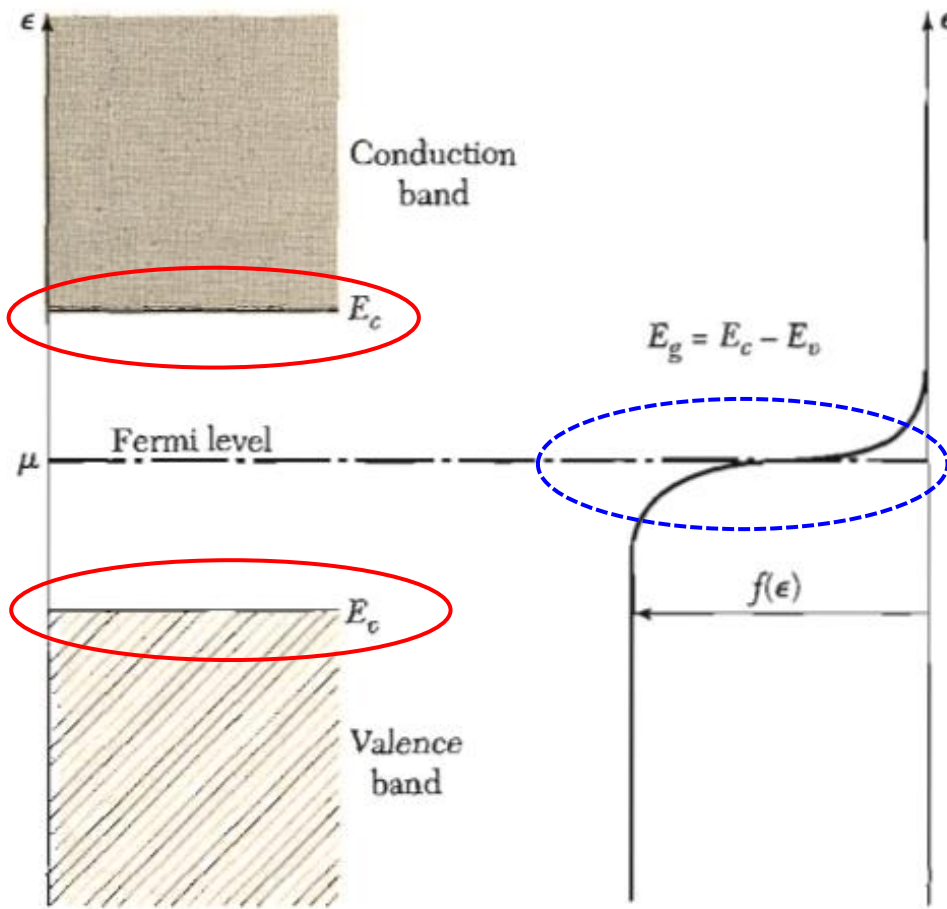
$$\epsilon(k) = -\Delta + Ak^2. \quad \text{split-off band}$$

$$A = -6.98, B = -4.5,$$

$$|C| = 6.2, \Delta = 0.341 \text{ eV.}$$

conduction electron mass of $0.067 m$.

Semiconductors



Fermi-Dirac distribution

$$f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1}.$$

the chemical potential μ
 μ is called the Fermi level.

Figure 18 Energy scale for statistical calculations. The Fermi distribution function is shown on the same scale, for a temperature $k_B T \ll E_g$. The Fermi level μ is taken to lie well within the band gap, as for an intrinsic semiconductor. If $\epsilon = \mu$, then $f = \frac{1}{2}$.



Properties of Semiconductors

INTRINSIC CARRIER CONCENTRATION

In the conduction band

$$\epsilon - \mu \gg k_B T, \quad f_e \approx \exp[(\mu - \epsilon)/k_B T]$$

$$\epsilon_k = E_c + \hbar^2 k^2 / 2m_e \quad D_e(\epsilon) = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} (\epsilon - E_c)^{1/2}$$

- Electron concentration in the conduction band

$$\begin{aligned} n &= \int_{E_c}^{\infty} D_e(\epsilon) f_e(\epsilon) d\epsilon = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} \exp(\mu/k_B T) \times \\ &\quad \int_{E_c}^{\infty} (\epsilon - E_c)^{1/2} \exp(-\epsilon/k_B T) d\epsilon, \\ &= 2 \left(\frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} \exp[(\mu - E_{c})/k_B T] \end{aligned}$$

In the valence band

$$f_h = 1 - f_e \approx \exp[(\epsilon - \mu)/k_B T]$$

$$D_h(\epsilon) = \frac{1}{2\pi^2} \left(\frac{2m_h}{\hbar^2} \right)^{3/2} (E_v - \epsilon)^{1/2}$$

- Hole concentration in the valence band

$$\begin{aligned} p &= \int_{-\infty}^{E_v} D_h(\epsilon) f_h(\epsilon) d\epsilon \\ &= 2 \left(\frac{m_h k_B T}{2\pi \hbar^2} \right)^{3/2} \exp[(E_{v} - \mu)/k_B T] \\ np &= 4 \left(\frac{k_B T}{2\pi \hbar^2} \right)^3 (m_e m_h)^{3/2} \exp(-E_g/k_B T) \end{aligned}$$

Si This useful result does not involve the Fermi level μ . At 300 K the value of np is $2.10 \times 10^{19} \text{ cm}^{-6}$, $2.89 \times 10^{26} \text{ cm}^{-6}$, and $6.55 \times 10^{12} \text{ cm}^{-6}$, for the actual band structures of Si, Ge, and GaAs, respectively.

$$np = 4 \left(\frac{k_B T}{2\pi\hbar^2} \right)^3 (m_e m_h)^{3/2} \exp(-E_g/k_B T)$$

constant at a given T ,
independent of impurity concentration

$A(T)$: e - h pair generation rate

$B(T)$: recombination rate

$$dn/dt = A(T) - B(T)np = dp/dt$$

In equilibrium $dn/dt = 0$, $dp/dt = 0$,
whence $np = A(T)/B(T)$.

Intrinsic semiconductors

$$n_i = p_i = 2 \left(\frac{k_B T}{2\pi\hbar^2} \right)^{3/2} (m_e m_h)^{3/4} \exp(-E_g/2k_B T) \quad \sim 10^{10} \text{ cm}^{-3}$$

$$\mu = \frac{1}{2} E_g + \frac{3}{4} k_B T \ln(m_h/m_e)$$

$$4.6 \times 10^9 \text{ cm}^{-3} \text{ in silicon}$$

VBM 기준 \rightarrow “midgap”
position

Extrinsic semiconductors (with impurity doping)

$n \sim N_d$ (or $p \sim N_a$) @ RT (~ complete ionization)

: $\sim 10^{14} \sim 10^{17} \text{ cm}^{-3}$ for typical doping (\rightarrow “non-degenerate” doping)

\rightarrow majority carrier (vs. minority carrier)

Intrinsic mobility

$$\mu = |v|/E .$$

$v = q\tau E/m$, drift velocity under E -field

$$\mu_e = e\tau_e/m_e ; \quad \mu_h = e\tau_h/m_h ,$$

$$\sigma = (ne\mu_e + pe\mu_h) ,$$

The mobilities depend on temperature as a modest power law. The temperature dependence of the conductivity in the intrinsic region will be dominated by the exponential dependence $\exp(-E_g/2k_B T)$ of the carrier concentration, Eq. (45).

See Table 3 Carrier mobilities at room temperature, in $\text{cm}^2/\text{V-s}$

$$\mu \sim 1000 \text{ cm}^2/\text{Vs}$$

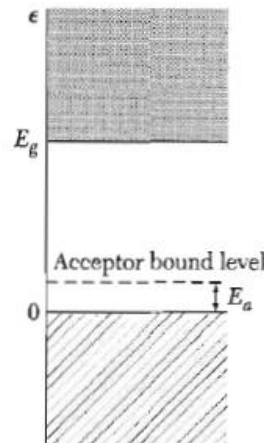
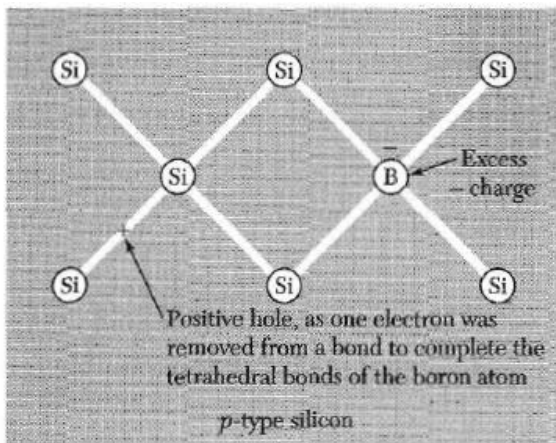
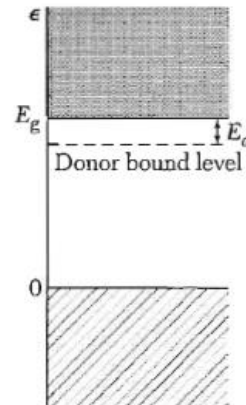
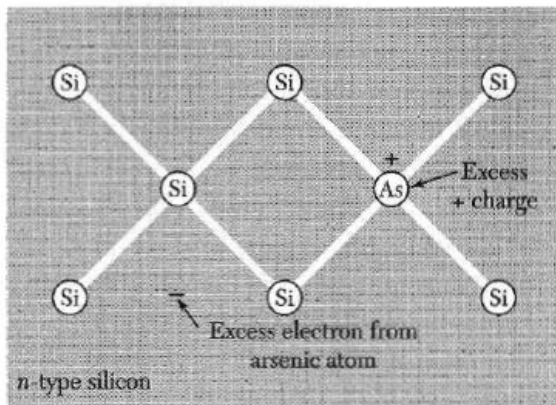
There is a tendency for crystals with small energy gaps at direct band edges to have high values of the electron mobility. Small gaps lead to small effective masses, which favor high mobilities. The highest mobility observed in a bulk semiconductor is $5 \times 10^6 \text{ cm}^2/\text{V-s}$ in PbTe at 4 K, where the gap is 0.19 eV.

small gap ~ little influence of potential ~ small effective mass ~ high mobility

the degeneracy at the top of the valence band complicates the effective mass problem.

Semiconductors

Doped Semiconductors



	n type	p type
doping.	donors.	acceptors
	Donor States.	Acceptor States.
	$(CGS) \quad E_d = \frac{e^4 m_e}{2\epsilon^2 \hbar^2} = \left(\frac{13.6 m_e}{\epsilon^2 m} \right) eV ; \sim 20 \text{ meV}$	
	$(CGS) \quad a_d = \frac{\epsilon \hbar^2}{m_e e^2} = \left(\frac{0.53 \epsilon}{m_e/m} \right) \text{\AA} ;$	
	$(60)(0.53) \approx 30 \text{ \AA in silicon.}$	

Thermal Ionization of Donors and Acceptors

$$n \sim N_d @ RT (\sim 10^{14} \sim 10^{17})$$

→ ~ complete ionization → ~ 1 Ω·cm

@ LT

$$n \cong (n_0 N_d)^{1/2} \exp(-E_d/2k_B T) , \quad k_B T \ll E_d$$

$$\text{with } n_0 \equiv 2(m_e k_B T / 2\pi \hbar^2)^{3/2} ;$$

N_d is the concentration of donors.

Thermoelectric Power

The **Peltier coefficient Π** is defined by $j_U = \Pi j_q$

(Ex. with electron only)

charge flux $j_q = n(-e)(-\mu_e)E = ne\mu_e E$

energy flux $j_U = n(E_c - \mu + \frac{3}{2}k_B T)(-\mu_e)E$

$$\Pi_e = -(E_c - \mu + \frac{3}{2}k_B T)/e$$

$$v_d = (-\mu_e)E$$

v_d : drift velocity

μ_e : electron mobility

μ : chemical potential

E_c : conduction band edge

The **absolute thermoelectric power Q** is defined from the open circuit electric field created by a temperature gradient:

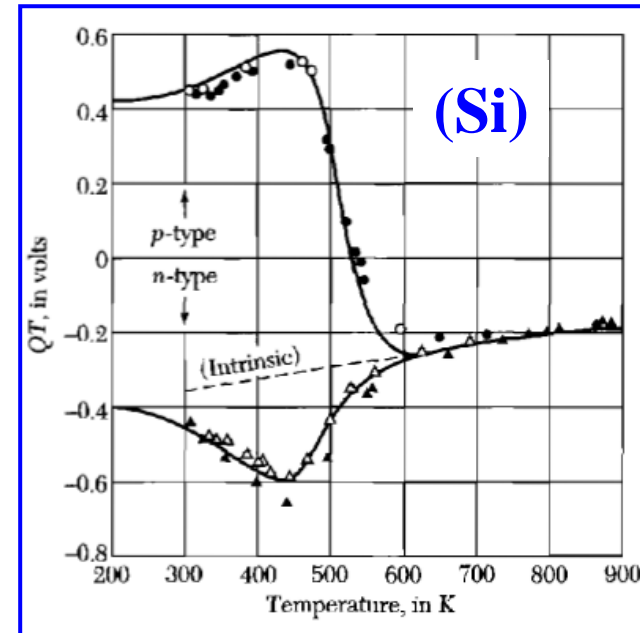
$$E = Q \text{ grad } T$$

The Peltier coefficient Π is related to the thermoelectric power Q by

$$\Pi = QT$$

Kelvin relation of irreversible thermodynamics.

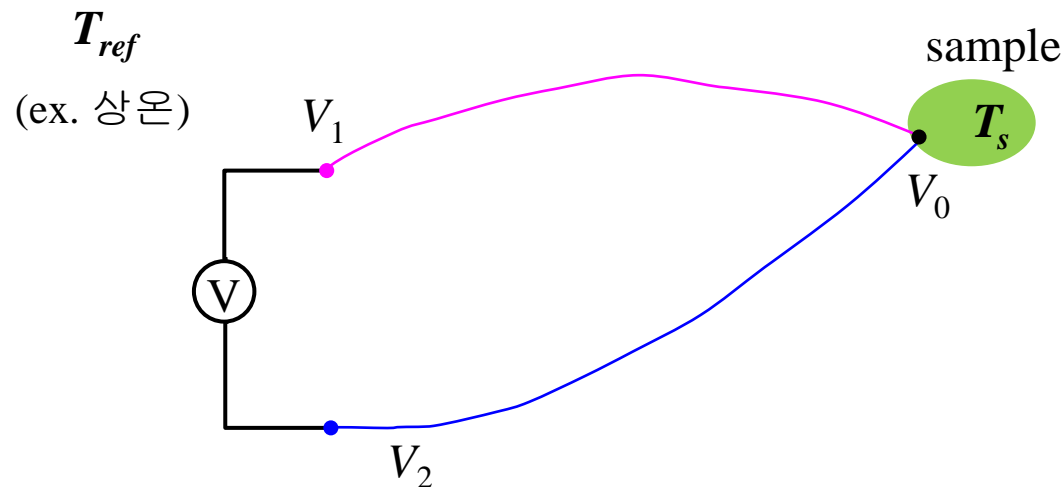
a rough and ready way to tell if the specimen is n type or p type



Thermoelectric Power

$$E = Q \operatorname{grad} T \rightarrow \Delta V = Q \Delta T$$

Measurement of a sample temperature



Q. Can you measure T_s with respect to 0 °C (\rightarrow absolute temperature)?

Semimetals

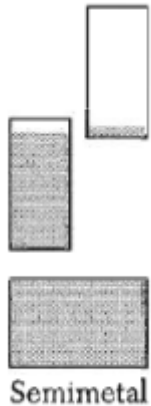


Table 7 Electron and hole concentrations in semimetals

Semimetal	n_e , in cm^{-3}	n_h , in cm^{-3}
Arsenic	$(2.12 \pm 0.01) \times 10^{20}$	$(2.12 \pm 0.01) \times 10^{20}$
Antimony	$(5.54 \pm 0.05) \times 10^{19}$	$(5.49 \pm 0.03) \times 10^{19}$
Bismuth	2.88×10^{17}	3.00×10^{17}
Graphite	2.72×10^{18}	2.04×10^{18}

Like semiconductors, the semimetals may be doped with suitable impurities to vary the relative numbers of holes and electrons. Their concentrations may also be varied with pressure, for the band edge overlap varies with pressure.

Summary & Homework

SUMMARY

- The smaller the energy gap, the smaller is the effective mass $|m^*|$ near the gap.
- A crystal with one hole has one empty electron state in an otherwise filled band. The properties of the hole are those of the $N - 1$ electrons in this band.
 - (a) If the electron is missing from the state of wavevector \mathbf{k}_e , then the wavevector of the hole is $\mathbf{k}_h = -\mathbf{k}_e$.
 - (b) The rate of change of \mathbf{k}_h in an applied field requires the assignment of a positive charge to the hole: $e_h = e = -e_e$.
 - (c) If \mathbf{v}_e is the velocity an electron would have in the state \mathbf{k}_e , then the velocity to be ascribed to the hole of wavevector $\mathbf{k}_h = -\mathbf{k}_e$ is $\mathbf{v}_h = \mathbf{v}_e$.
 - (d) The energy of the hole referred to zero for a filled band is positive and is $\epsilon_h(\mathbf{k}_h) = -\epsilon(\mathbf{k}_e)$.
 - (e) The effective mass of a hole is opposite to the effective mass of an electron at the same point on the energy band: $m_h = -m_e$.

Problems 8.1-8.3