

Band Theory and Electronic Properties of Solids

Phys 674

Physics & Astronomy

King Saud University

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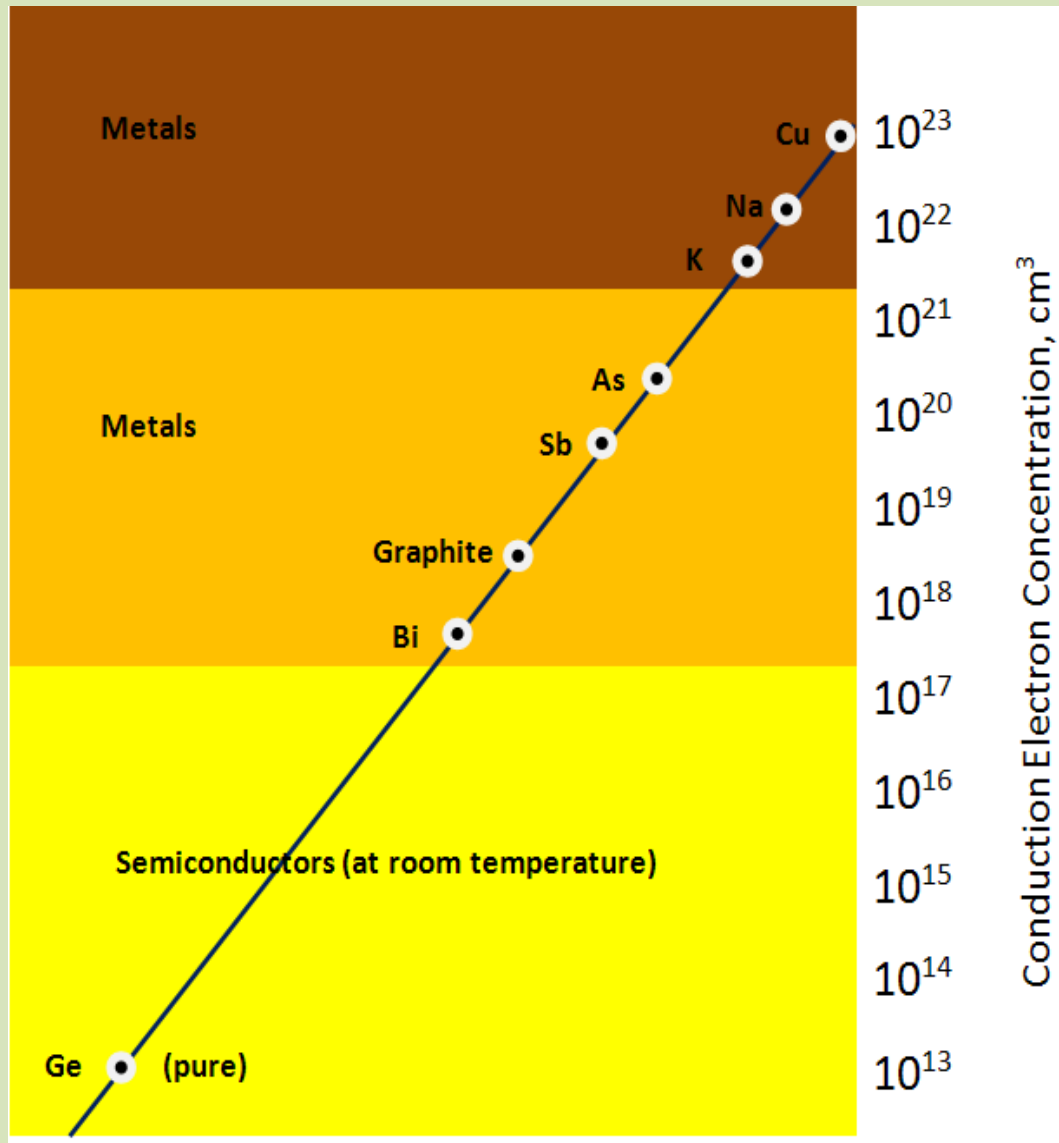
Lecture No. 09

Semiconductor Crystals

Prof. Nasser S. Alzayed

Semiconductor Crystals

Introduction



Carrier concentrations for different Conductors: Carrier concentrations for metals, semimetals, and semiconductors. The semiconductor range may be extended upward by increasing the impurity concentration, and the range can be extended downward to merge eventually with the insulator range.

Semiconductor Crystals

Introduction

- ❑ Conductors are classified based on electron concentration.
- ❑ Semiconductors are generally classified by their electrical resistivity at room temperature, with values in the range of 10^{-2} to $10^9 \Omega\text{-cm}$, and strongly dependent on temperature.
- ❑ *At 0 K, a pure, semiconductor will be an insulator.*
- ❑ Devices based on semiconductors include:
 - ✓ transistors
 - ✓ Switches
 - ✓ Diodes
 - ✓ photovoltaic cells
 - ✓ Detectors
 - ✓ Thermistors
- ❑ Popular semiconductors are: *silicon, germanium, and gallium arsenide.*

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Semiconductor Classes

Semiconductors are classified into 3 main types:

- ❑ III-V (three-five) compounds. Examples are indium antimonide (InSb) and gallium arsenide.
- ❑ II -VI compound; examples are zinc sulfide and cadmium sulfide.
- ❑ IV-IV compound like: Silicon carbide SiC .

	Silicon	GaAs	In _{0.50} Ga _{0.47} As	InAs	InSb	units
Energy gap	1.12	1.43	0.75	0.356	0.175	eV
Electron effective mass	0.19	0.072	0.041	0.027	0.013	
Electron mobility in pure material	1,500	8,500	14,000	30,000	78,000	cm ² V ⁻¹ s ⁻¹
Electron mobility at 1x10 ¹² cm ⁻²	600	4,600	7,800	20,000	30,000	"
Electron saturation vel ^y	1.0 x 10 ⁷	1.2 x 10 ⁷	8 x 10 ⁶	3 x 10 ⁷	5 x 10 ⁷	cm s ⁻¹
Electron mean free path length	28	80	106	194	226	nm
Intrinsic carrier conc ⁿ	1.6 x 10 ¹⁰	1.1 x 10 ⁷	5 x 10 ¹¹	1.3 x 10 ¹⁵	1.9 x 10 ¹⁶	cm ⁻³

Table 1 Summary of properties of silicon and several III-V

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Semiconductor Classes

Comparison Table

Type	Elements	Example	Bandgap	Key Applications
III-V	Group III + V	GaAs, InP	Direct	LEDs, Lasers, RF Transistors
II-VI	Group II + VI	ZnSe, CdTe	Direct	Solar Cells, IR Sensors
IV-IV	Group IV	Si, SiC	Indirect (mostly)	Microchips, Power Devices

The classification helps engineers choose the right semiconductor for specific applications based on ***bandgap, carrier mobility, and optical properties***.

- **III-V:** Best for optoelectronics and high-speed electronics.
- **II-VI:** Useful for light-emitting and detecting applications.
- **IV-IV (Si, SiC):** Dominates traditional electronics and power devices.

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Semiconductor Classes

① III - V

Group III : B, Al, Ga, In
 + " V : N, P, As, Sb } GaAs

② II - VI :

Group II : Zn, Cd, Hg } ZnSe or ZnO
 + " VI : O, S, Se, Te } CdTe

③ IV - IV

Group IV : Si, Ge, C
 + " IV :

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Semiconductor Classes

Semiconductors are also classified in different way:

❑ ***Intrinsic***: (pure semiconductor = undoped semiconductor)

Or: i-type semiconductor ($n = p$)

- ✓ the electrical properties of a semiconductor are not essentially modified by impurities in the crystal.
- ✓ An electronic band scheme leading to intrinsic conductivity is indicated in Fig. 2.
- ✓ The conduction band is vacant at absolute zero and is separated by an energy gap E_g from the filled valence band.
- ✓ Example: $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$

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Intrinsic Semiconductor

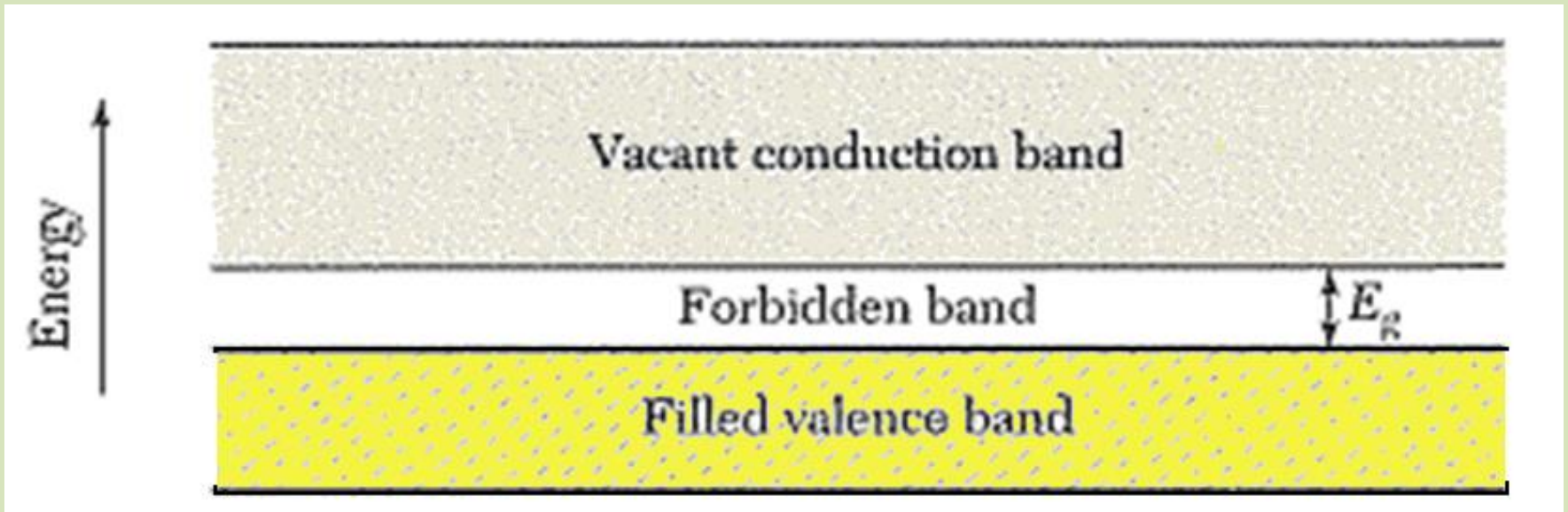
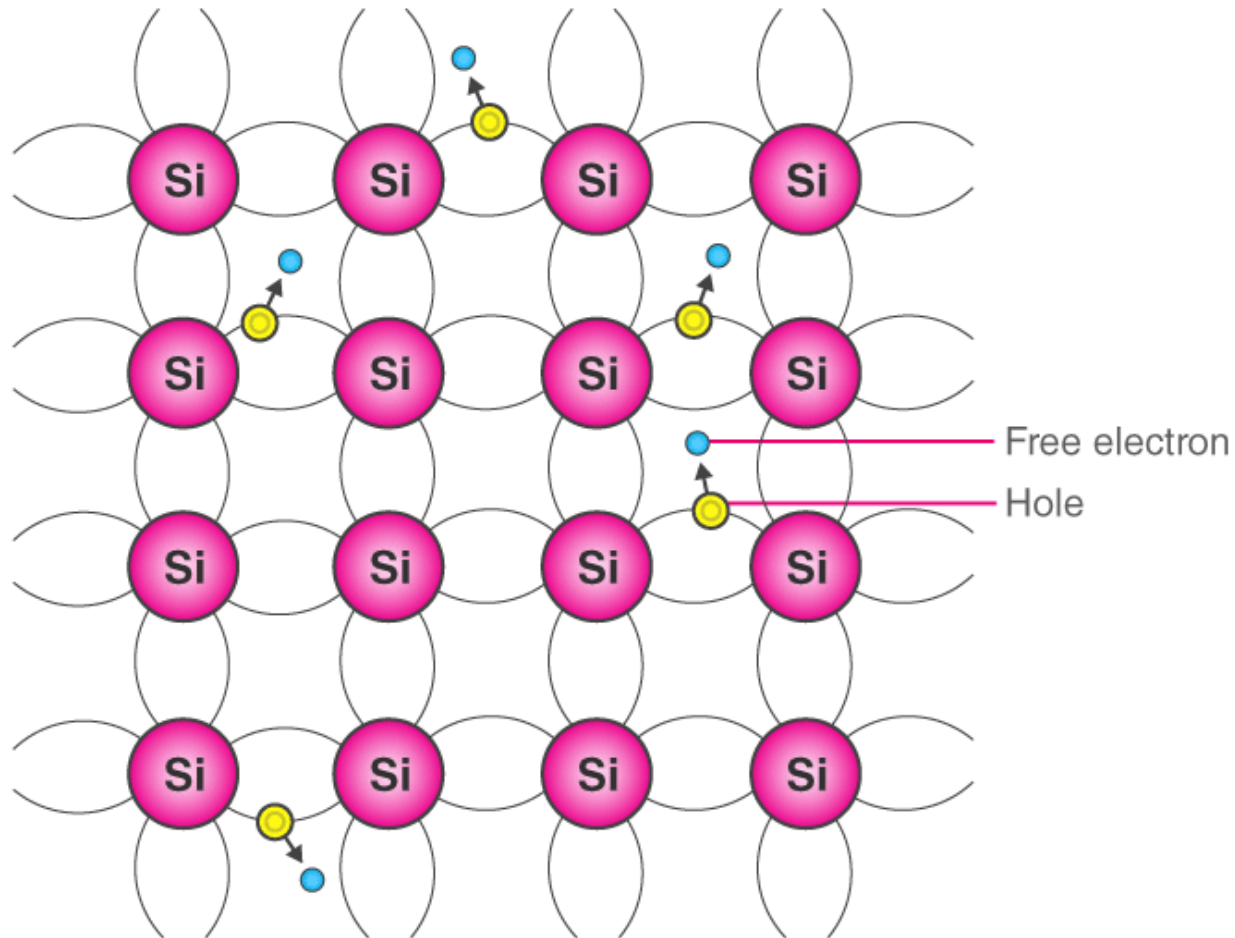


Figure 2 Band scheme for intrinsic conductivity in a semiconductor. At 0 K the conductivity is zero because all states in the valence band are filled and all states in the conduction band are vacant. As the temperature is increased, electrons are thermally excited from the valence band to the conduction band, where they become mobile. Such carriers are called "intrinsic."

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Intrinsic Semiconductor

INTRINSIC SEMICONDUCTORS



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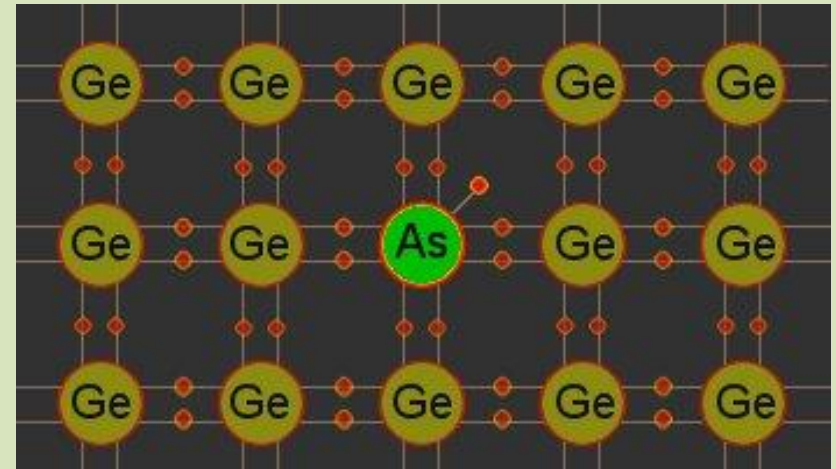
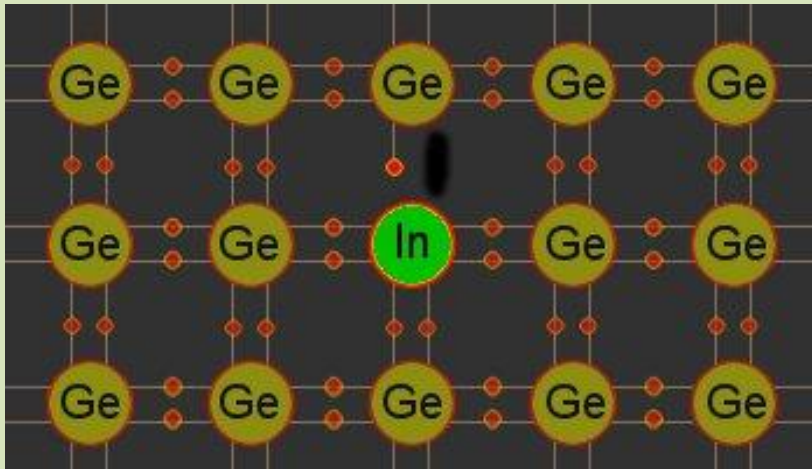
Extrinsic Semiconductors

Extrinsic: (doped semiconductor)

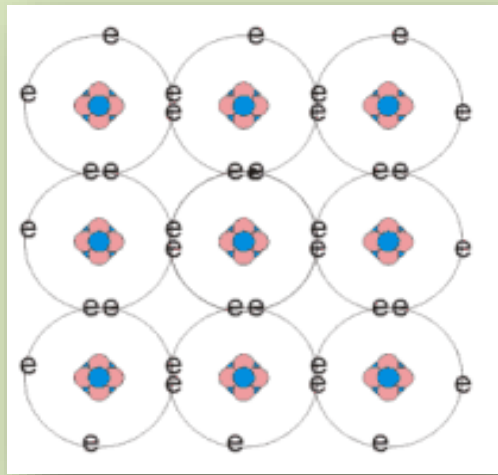
- ❑ This type is not pure. Its conductivity depends on doping.
- ❑ An extrinsic semiconductor can be formed from an intrinsic semiconductor by adding impurity atoms to the crystal in a process known as doping.
- ❑ For instance, Since Silicon belongs to group IV of the periodic table, it has 4 valence electrons. Each atom shares an electron with a neighboring atom. In this state it is an ***intrinsic*** semiconductor. B, Al, In, Ga all have three electrons in the valence band. When a small proportion of these atoms, (less than 1 in 10^6), is doped into the crystal the dopant atom has an insufficient number of bonds to share bonds with the surrounding Silicon atoms. ***One of the Silicon atoms has a vacancy for an electron.*** It creates a hole that contributes to the conduction process **at all temperatures**. Dopants that create holes in this manner are known as acceptors. This type of extrinsic semiconductor is known as ***p-type***. Elements that belong to group V of the periodic table such as As, P, Sb have an extra electron in the valence band. When added as a dopant to intrinsic Silicon, the dopant atom contributes an additional electron to the crystal. Dopants that add electrons to the crystal are known as donors and the semiconductor material is said to be ***n-type***.

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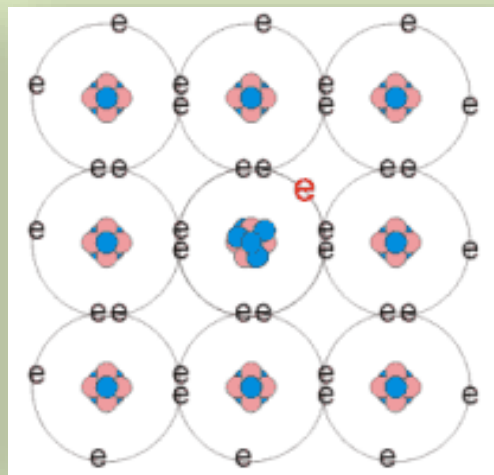
Intrinsic and Extrinsic Semiconductors



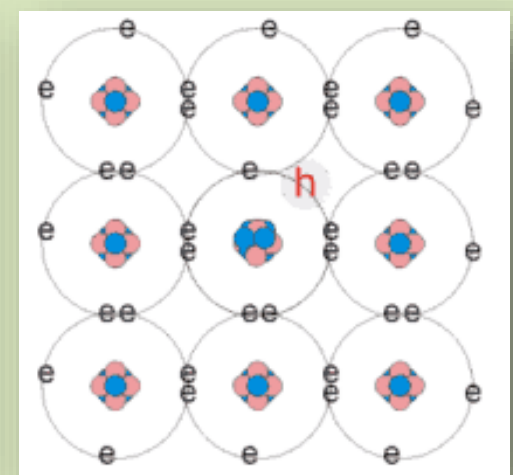
P-type (left) and n-type (right) of extrinsic semiconductors



Intrinsic



n-type



P-type

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Definition of Band gap

- ❑ *The band gap is the difference in energy between the lowest point of the conduction band and the highest point of the valence band.*
- ❑ The lowest point in the conduction band is called the *conduction band edge*
- ❑ the highest point in the valence band is called the *valence band edge*.
- ❑ As the temperature is increased, electrons are thermally excited from the valence band to the conduction band (Fig. 3).
- ❑ Both the electrons in the conduction band and the vacant orbitals or holes left behind in the valence band contribute to the electrical conductivity.

Semiconductor Crystals

Definition of Band gap

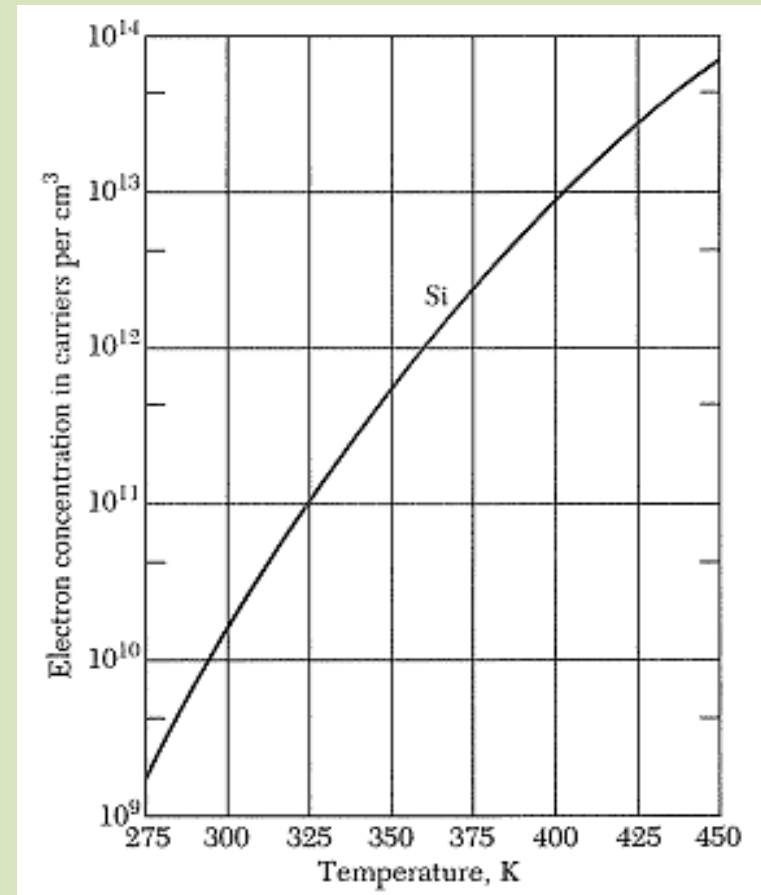
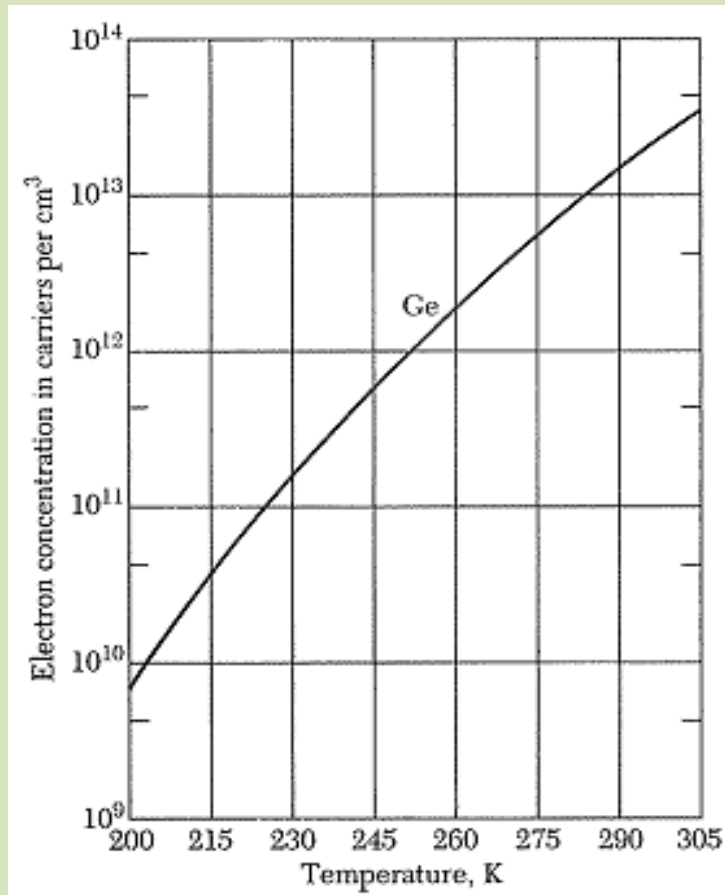


Figure 3: Intrinsic electron concentration as a function of temp. for (a) germanium and (b) silicon. Under intrinsic conditions the hole concentration is equal to the electron concentration.

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Direct and Indirect absorption

- ❑ The intrinsic conductivity and intrinsic carrier concentrations are largely controlled by $E_g/K_B T$
- ❑ When this ratio is large, the concentration of intrinsic carriers will be low and the conductivity will be low.
- ❑ The best values of the band gap are obtained by optical absorption. There are 2 different methods:

1- direct absorption process

2- indirect absorption process

- ❑ **For Direct absorption Process:**

the threshold of continuous optical absorption at frequency ω_g measures the band gap $E_g = \hbar\omega_g$ as shown in Figs. 4a and 5a. A photon is absorbed by the crystal with the creation of an electron and a hole.

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Direct and Indirect absorption

methods to measure E_g :

- ① optical absorption
- ② photoluminescence (PL) spectroscopy
 - excite e^- 's by laser
 - measure hw as they recombine
 - Emission peak \rightarrow band gap
- ③ Electroluminescence (EL)
same as PL But electric current is used instead of laser

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Direct and Indirect absorption

④ photoconductivity measurements.

① apply light

② measure I

⑤ scanning tunneling spectroscopy (STS)

- measure local density of states

⑥ Temp.-dependent resistivity

→ R changes with T as $T \rightarrow T_H$ E_F is crossed.

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Direct and Indirect absorption

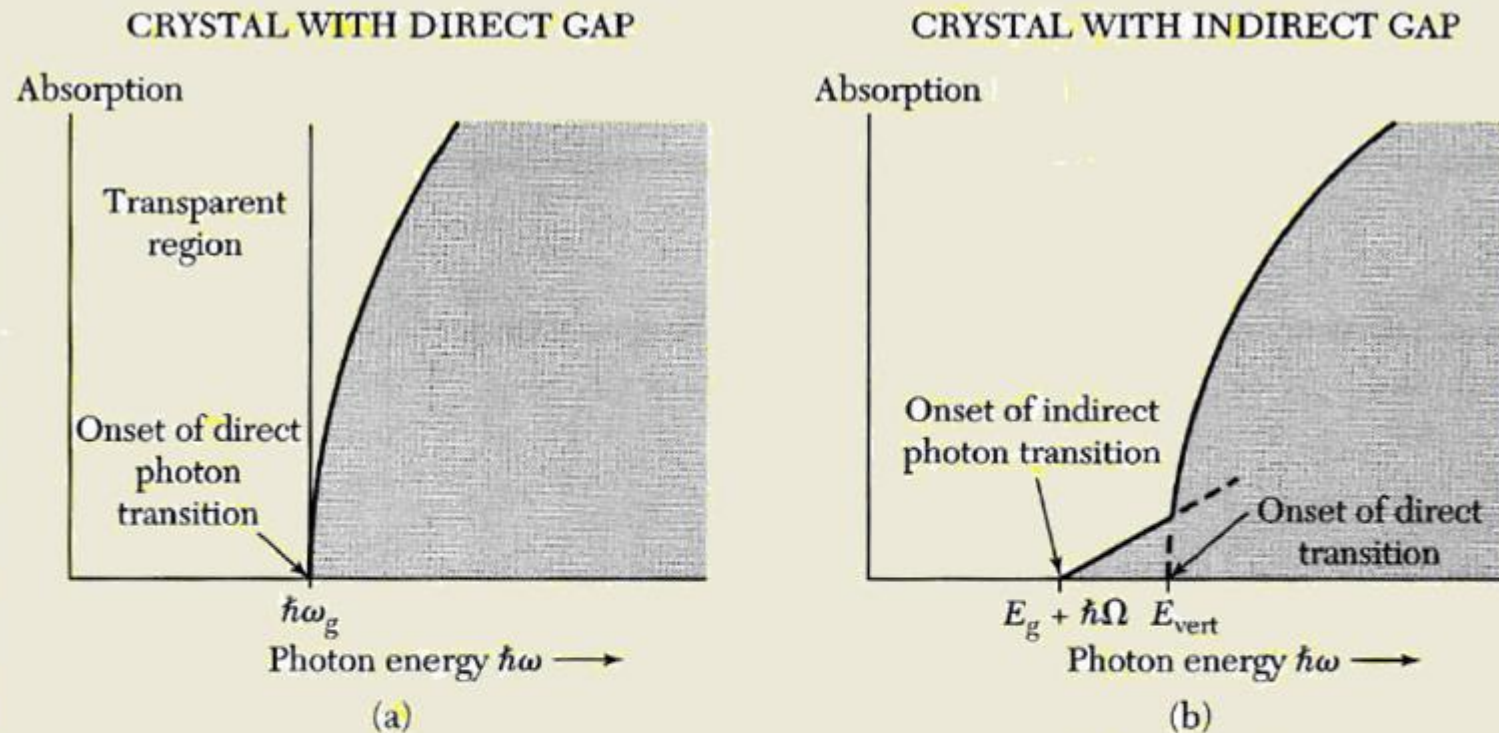


Figure 4 Optical absorption in pure insulators at absolute zero. In (a) the threshold determines the energy gap as $E_g = \hbar\omega_g$. In (b) the optical absorption is weaker near the threshold: at $\hbar\omega = E_g + \hbar\Omega$ a photon is absorbed with the creation of three particles: a free electron, a free hole, and a phonon of energy $\hbar\Omega$. In (b) the energy E_{vert} marks the threshold for the creation of a free electron and a free hole, with no phonon involved. Such a transition is called vertical; it is similar to the direct transition in (a). These plots do not show absorption lines that sometimes are seen lying just to the low energy side of the threshold. Such lines are due to the creation of a bound electron-hole pair, called an exciton.

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Direct and Indirect absorption

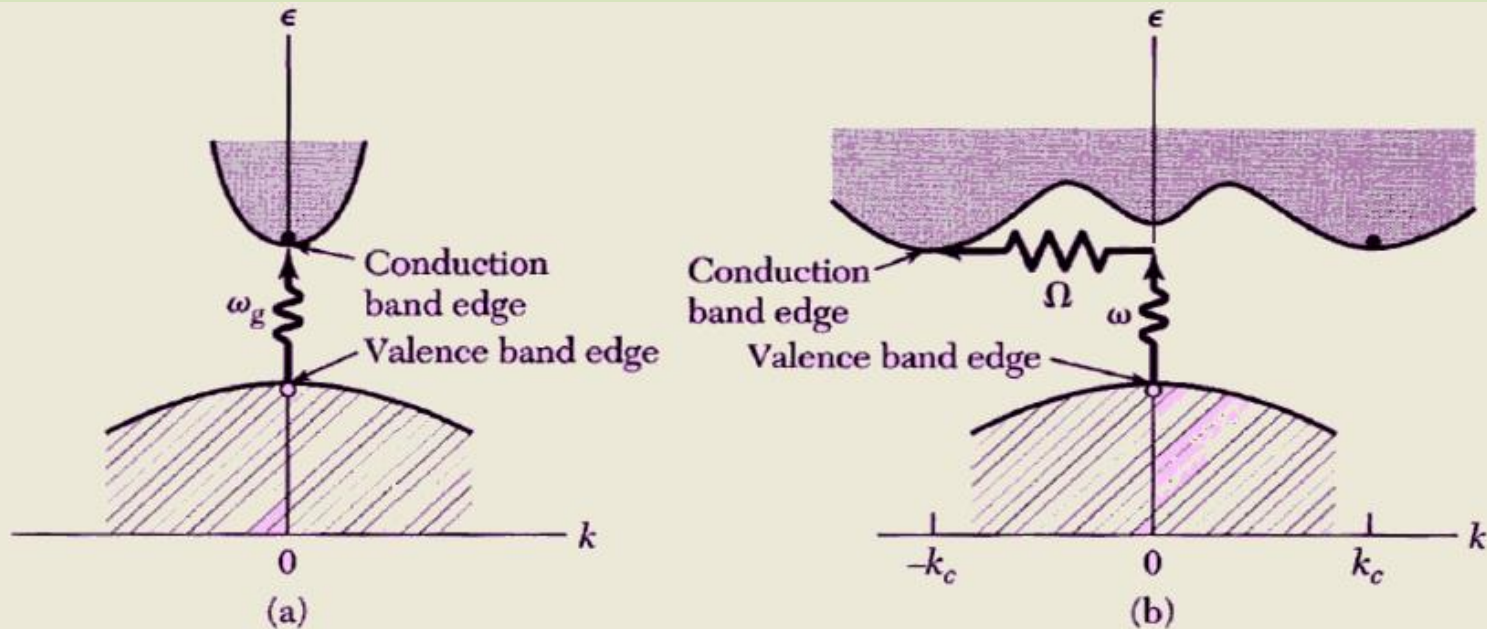


Figure 5 In (a) the lowest point of the conduction band occurs at the same value of k as the highest point of the valence band. A direct optical transition is drawn vertically with no significant change of k , because the absorbed photon has a very small wavevector. The threshold frequency ω_g for absorption by the direct transition determines the energy gap $E_g = \hbar\omega_g$. The indirect transition in (b) involves both a photon and a phonon because the band edges of the conduction and valence bands are widely separated in k space. The threshold energy for the indirect process in (b) is greater than the true band gap. The absorption threshold for the indirect transition between the band edges is at $\hbar\omega = E_g + \hbar\Omega$, where Ω is the frequency of an emitted *phonon* of wavevector $K \cong -k_g$. At higher temperatures phonons are already present; if a phonon is absorbed along with a photon, the threshold energy is $\hbar\omega = E_g - \hbar\Omega$. *Note:* The figure shows only the threshold transitions. Transitions occur generally between almost all points of the two bands for which the wavevectors and energy can be conserved.

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Indirect Absorption Process

❑ For Indirect absorption Process:

- ✓ in Figs. 4b and 5b the minimum energy gap of the band structure involves electrons and holes separated by a substantial wavevector k_c .
- ✓ Here a direct photon transition at the energy of the minimum gap cannot satisfy the requirement of conservation of wavevector.
- ✓ But if a phonon of wave vector K and frequency Ω is created in the process, then we can have:

$$k(\text{photon}) = k_c + k \cong 0$$

$$\text{and } \hbar\omega = E_g + \hbar\Omega$$

as required by the conservation laws.

phonon energy $\hbar\Omega$ is usually much less than E_g

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Energy Gap Experimental

Table 1 Energy gap between the valence and conduction bands
(*i* = indirect gap; *d* = direct gap)

Crystal	Gap	E_g , eV		Crystal	Gap	E_g , eV	
		0 K	300 K			0 K	300 K
Diamond	<i>i</i>	5.4		SiC(hex)	<i>i</i>	3.0	—
Si	<i>i</i>	1.17	1.11	Te	<i>d</i>	0.33	—
Ge	<i>i</i>	0.744	0.66	HgTe ^a	<i>d</i>	−0.30	
α Sn	<i>d</i>	0.00	0.00	PbS	<i>d</i>	0.286	0.34–0.37
InSb	<i>d</i>	0.23	0.17	PbSe	<i>i</i>	0.165	0.27
InAs	<i>d</i>	0.43	0.36	PbTe	<i>i</i>	0.190	0.29
InP	<i>d</i>	1.42	1.27	CdS	<i>d</i>	2.582	2.42
GaP	<i>i</i>	2.32	2.25	CdSe	<i>d</i>	1.840	1.74
GaAs	<i>d</i>	1.52	1.43	CdTe	<i>d</i>	1.607	1.44
GaSb	<i>d</i>	0.81	0.68	SnTe	<i>d</i>	0.3	0.18
AlSb	<i>i</i>	1.65	1.6	Cu ₂ O	<i>d</i>	2.172	—

^aHgTe is a semimetal; the bands overlap.

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Direct and indirect Absorption schematically

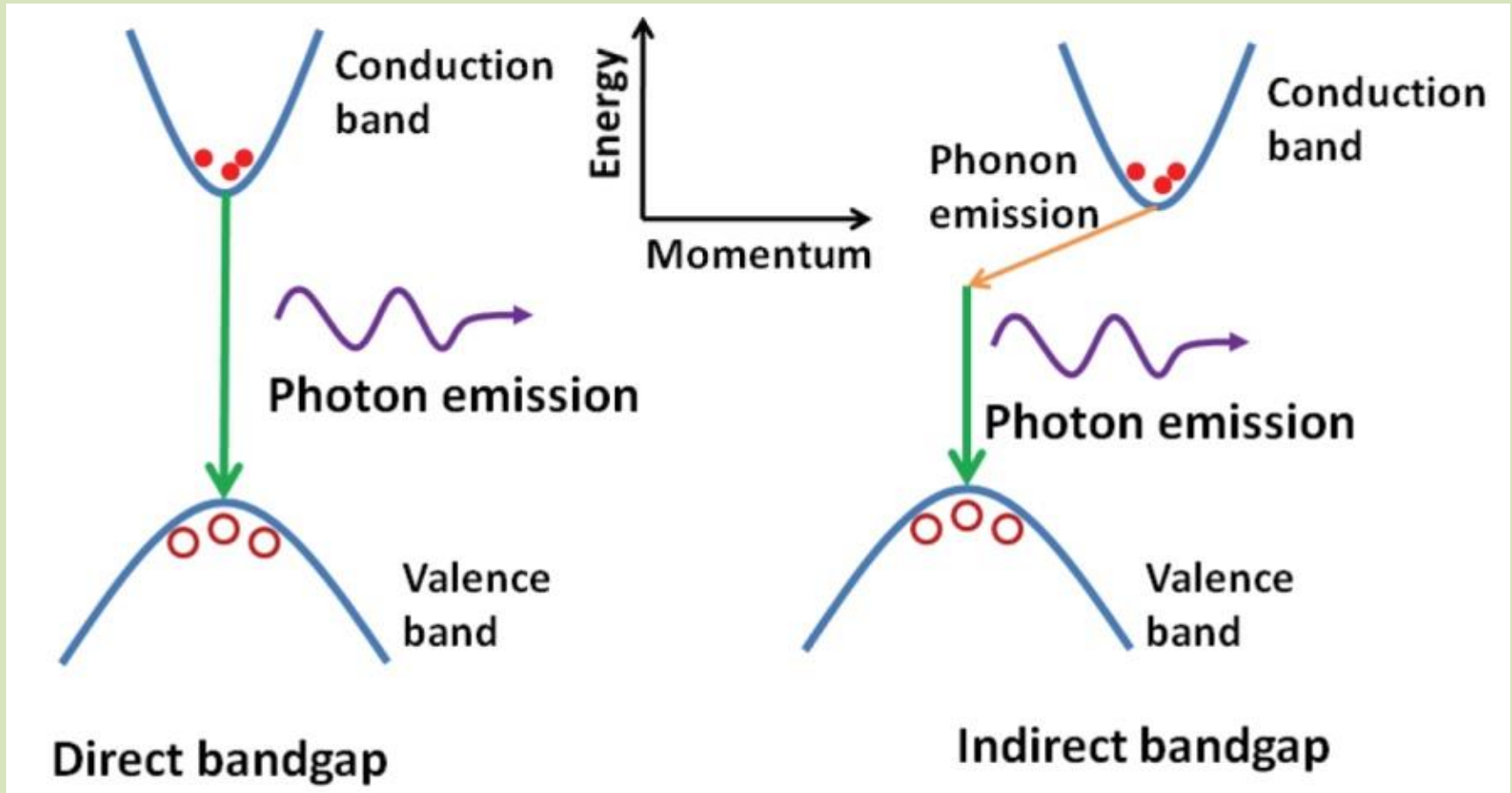


Illustration of a photon emission process in (a) the direct and (b) the indirect band gap semiconductors

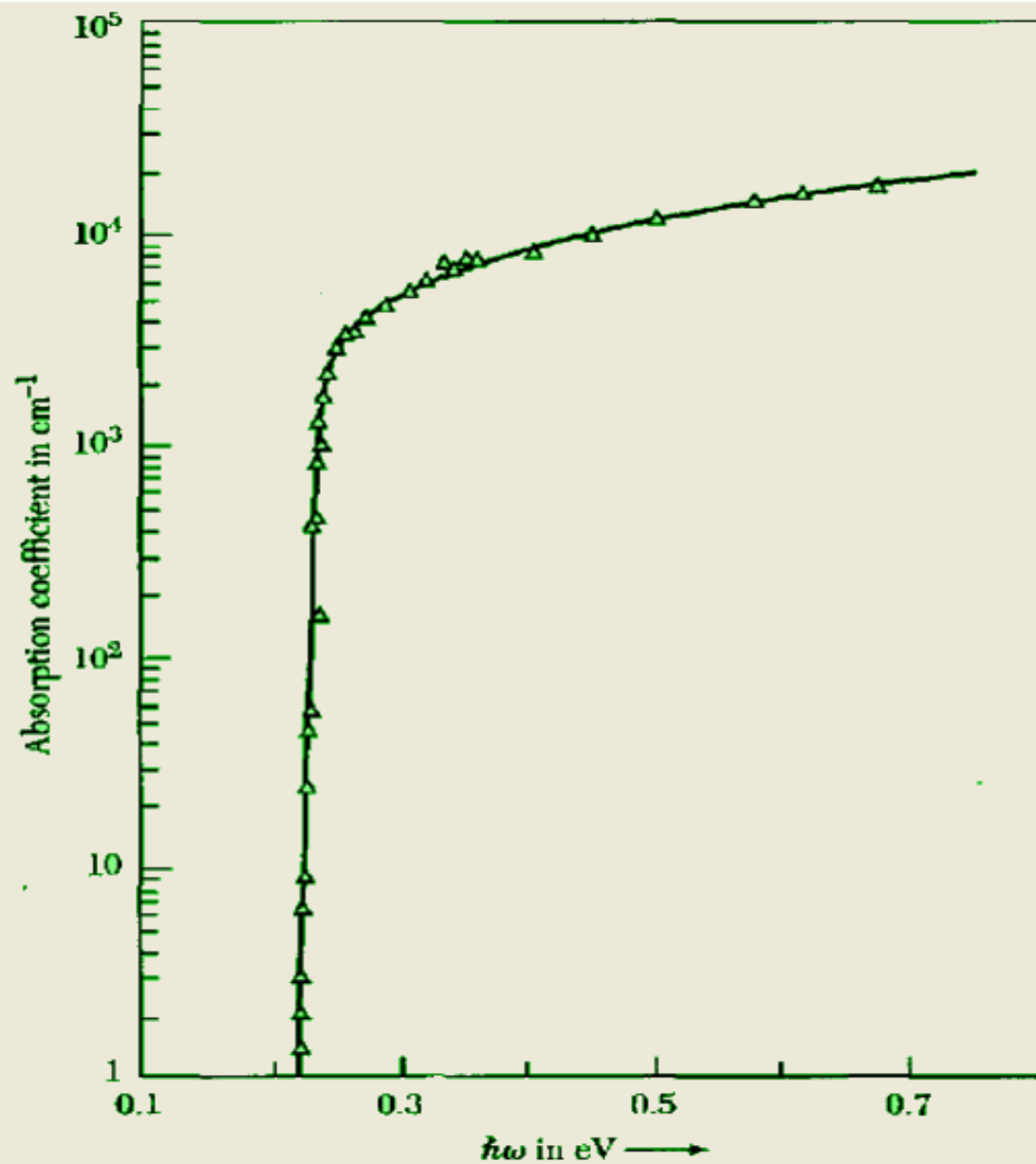
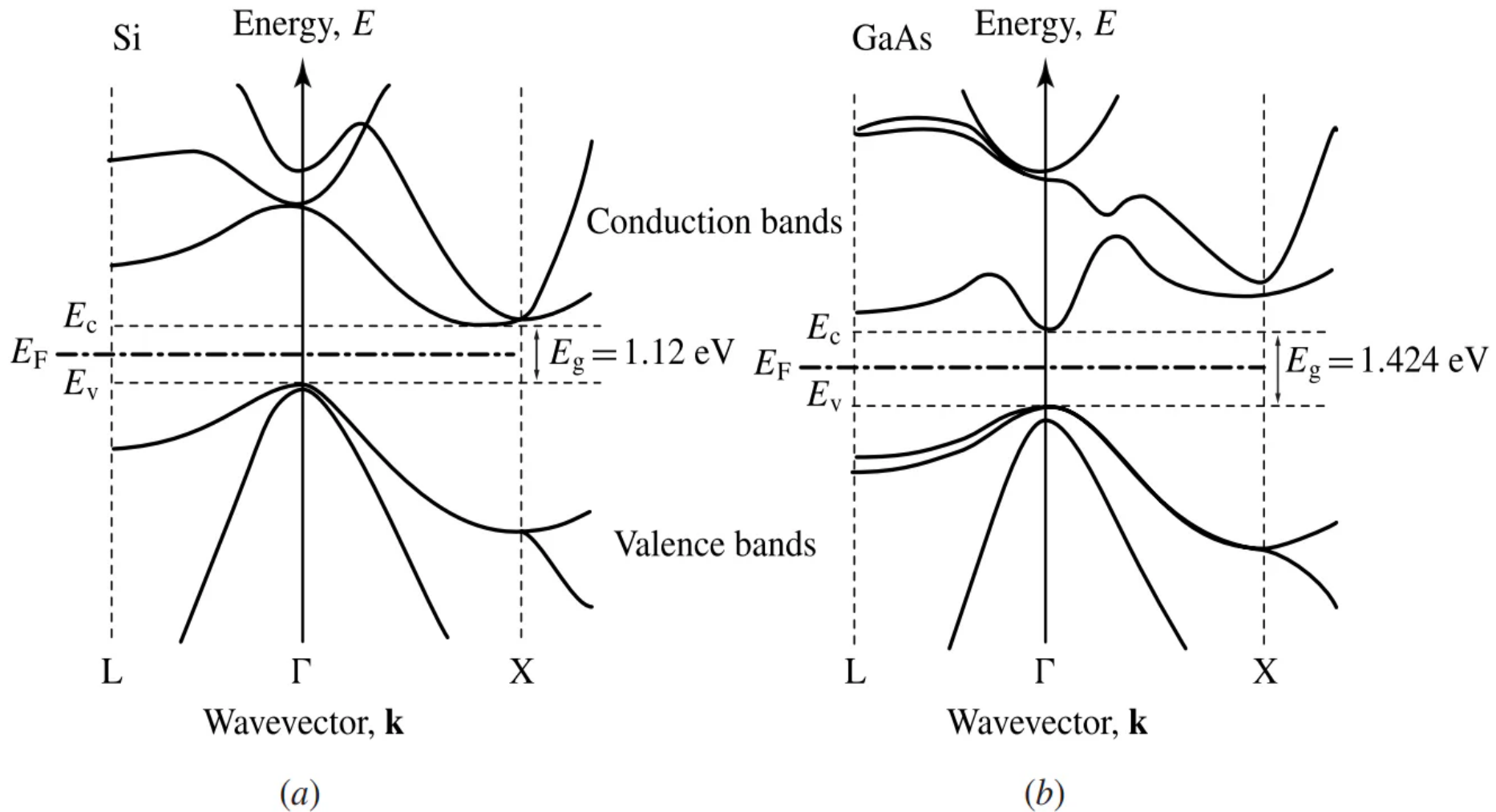


Figure 6 Optical absorption in pure indium antimonide, InSb. The transition is direct because both conduction and valence band edges are at the center of the Brillouin zone, $\mathbf{k} = 0$. Notice the sharp threshold. (After G. W. Gobeli and H. Y. Fan.)



Energy band structures of (a) Si, which is an indirect-gap semiconductor, and (b) GaAs, which is a direct-gap semiconductor. In each semiconductor, the Fermi level lies in the bandgap that separates the conduction and valence bands.

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Direct and indirect Absorption schematically

- ❑ The band gap may also be deduced from the temperature dependence of the conductivity or of the carrier concentration in the intrinsic range.
- ❑ The carrier concentration is obtained from measurements of the Hall voltage.
- ❑ Optical measurements determine whether the gap is direct or indirect.

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EQUATIONS OF MOTION

□ We derive the equation of motion of an electron in an energy band. We look at the motion of a wave packet in an applied electric field .

Group velocity is defined as : $v_g = \frac{d\omega}{dk}$

$$\because \varepsilon = \hbar\omega \rightarrow \omega = \varepsilon / \hbar$$

$$\therefore v_g = \frac{1}{\hbar} \frac{d\varepsilon}{dk} \quad \text{or : } \vec{v} = \frac{1}{\hbar} \vec{\nabla}_k \varepsilon(\vec{k}) \quad (1)$$

The work $\delta\varepsilon$ done on the electron by the electric field E in the time interval δt is:

$$\delta\varepsilon = -eE v_g \delta t \quad (2)$$

We used the normal work eq. $-eE = \text{force}$, $v_g \delta t = \text{Displacement}$

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EQUATIONS OF MOTION

From eq. (1) we notice that;

$$\delta\varepsilon = \frac{d\varepsilon}{d\kappa} \delta\kappa = \hbar v_g \delta\kappa \quad (3)$$

(2) and (3) give:

$$\delta\kappa = -(eE / \hbar) \delta t \quad (4)$$

$$\Rightarrow \hbar dk / dt = -eE$$

$$\Rightarrow \hbar \frac{dk}{dt} = F \quad (5)$$

- ❑ This is an important relation: in a crystal $\hbar dk/dt$ is equal to the external force on the electron.
- ❑ In free space $m dv/dt$ is equal to the force.
- ❑ the electron in the crystal is subject to forces from the crystal lattice as well as from external sources.

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EQUATIONS OF MOTION

- Eq. (5) Also includes forces from electric field (**E**) and from Lorentz force for a moving electron in Mag . Field (**B**).
- Hence, we can write the eq. of motion of the electron in the existence of **B** as:

$$\hbar \frac{d\mathbf{k}}{dt} = -e \vec{v} \times \vec{B} \quad (6)$$

using: $\vec{v} = \frac{1}{\hbar} \vec{\nabla}_k \mathcal{E}(\vec{k})$, we get:

$$\frac{d\mathbf{k}}{dt} = -\frac{e}{\hbar^2} \vec{\nabla}_k \mathcal{E} \times \vec{B} \quad (7)$$

Now LHS and RHS use **k** space.

- (7) means that in **B**, an electron moves in **k** space in a direction normal to the direction of the gradient of the energy \mathcal{E} , so that the electron moves on a surface of constant energy.

Thanks