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# SOLIDS

## PURPOSE / LEARNING OBJECTIVES:

Familiarize with **the solid structure**.

Understand differences between **bonding** in gaseous molecules and molecules belonging to a solid

Describe important **solid properties** from the band theory.

# OUTLINE

- ▶ Types of solids
- ▶ Band theory
- ▶ Free-electron model
- ▶ Electron motion in a periodic structure
- ▶ Conductors, Insulators and Semiconductors
- ▶ Quantum theory of electrical conductivity
- ▶ Radiative transition in solids



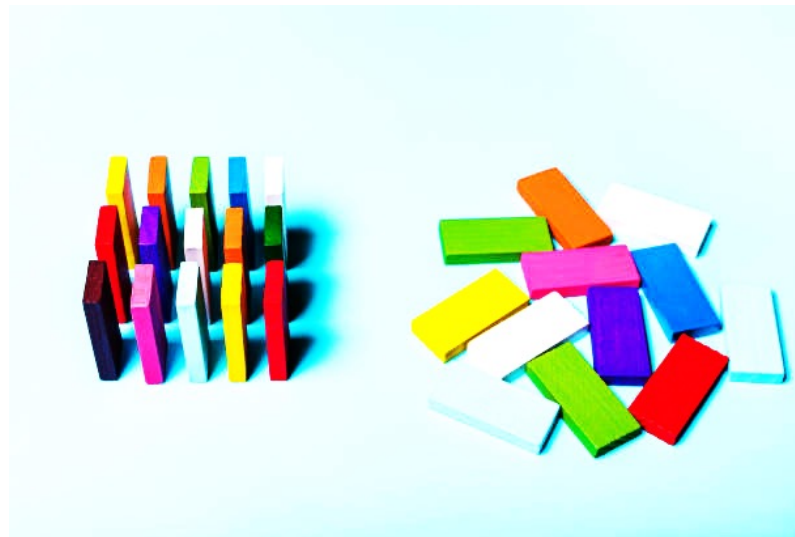
# Gases vs. Solids

- ▶ In gases the average distance between molecules is much greater than the size of the molecules and the intermolecular forces are much weaker than the forces which hold the atoms in the molecule together. Thus in gases the molecules retain their **individuality**.
- ▶ In a solid, the atoms (or molecules) are tightly packed and held in more or less fixed positions by forces, of electromagnetic origin, which are of the same order of magnitude as those involved in molecular binding. The properties of the molecules/atoms of the solids are modified by the nearby atoms
- ▶ From the quantum-mechanical point of view, determining the structure of a solid consists in finding a stable configuration of nuclei and electrons which are subject to their electronic interactions and which move according to the laws of quantum mechanics.
- ▶ The two main differences between the structure of a solid and that of a molecule are the large number of atoms involved and the regularity in their arrangement. Several types of approximations are used to study the structure of a solid, depending on the dominant factors involved in each solid.

# Periodicity

- ▶ Some solids, show a **regular arrangement** of the atoms or groups of atoms: the structure exhibits a periodicity constituting what is called a crystal lattice;
- ▶ Therefore, it is necessary to study only the basic unit or cell of the lattice, since all properties repeat from cell to cell.

**ORDER**

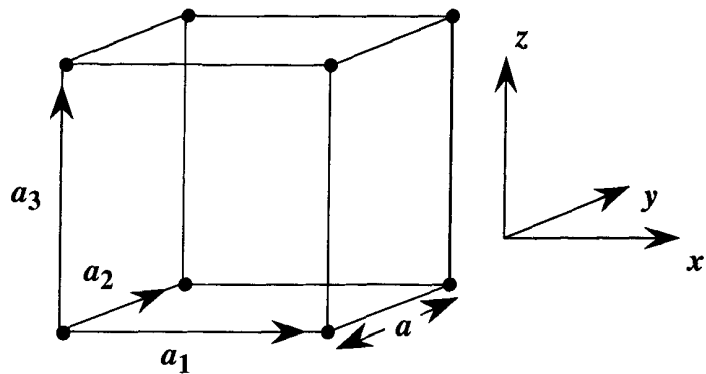


# Lattice

A lattice is defined by 3 vectors ( $a_1, a_2, a_3$ ) and each point in the lattice ( $R'$ ) can be obtained by translation from another point ( $R$ ):

$$R' = R + m_1 a_1 + m_2 a_2 + m_3 a_3$$

with  $m_1, m_2, m_3$  integers.

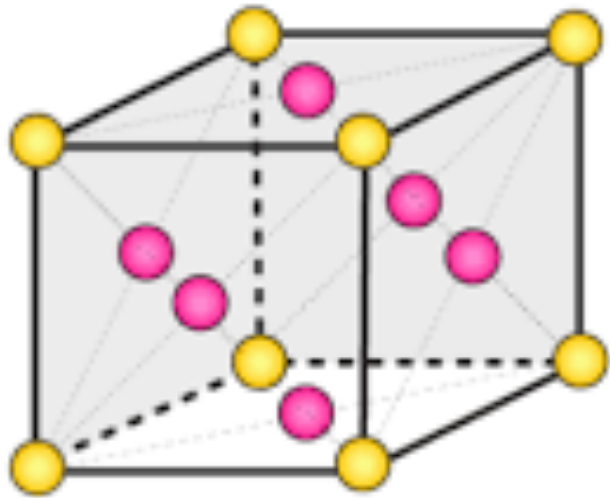


# Bravais lattices

System	Number of lattices	Restrictions on conventional cell axes and angles
Triclinic	1	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Cubic	3	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$
Trigonal	1	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
Hexagonal	1	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$



# Semiconductor lattice



Face-centred Cubic Unit Cell (FCC)

Most semiconductors have an underlying fcc lattice with **two atoms per basis** of coordinates

$$(000) \text{ and } \left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$$

Elemental semiconductors such as Si, Ge, C fall in this category but also many other like GaAs, AlAs, CdS...

# Types of solids

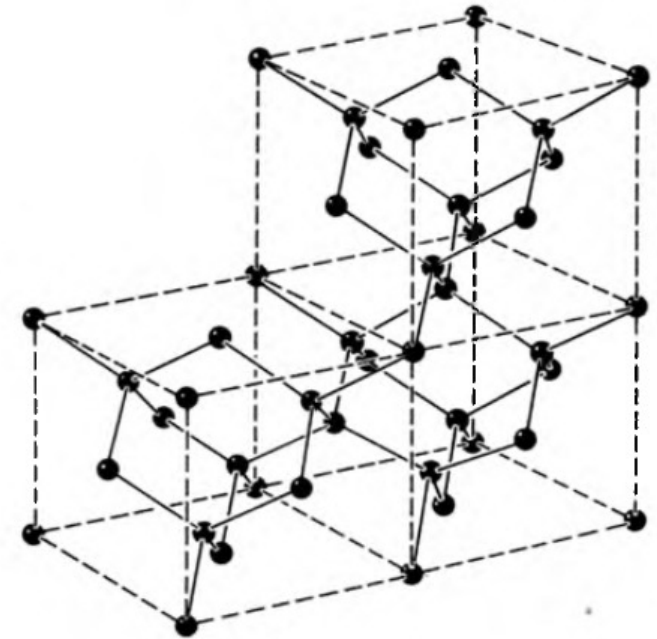
- ▶ Atoms and molecules are stuck together by chemical bonds. Solids may be classified according to the predominant type of binding.
  - ▶ Covalent solids (e.g., in semiconductors, e.g. Si, ZnO)
  - ▶ Ionic solids (in salts, e.g. NaCl)
  - ▶ Hydrogen solids (e.g. in ice)
  - ▶ Van der Waals or molecular solids (e.g. in physisorbed CO<sub>2</sub> condensed on solid surfaces)
  - ▶ Metallic solids (in metals, e.g. Cu)
- ▶ Characteristic distances that we will consider are **bond lengths**. E.g. in a solid

$$L \approx 3\text{\AA} \approx 3 \times 10^{-8} \text{cm}$$



# Covalent solids

- ▶ In a covalent solid the atoms are bound together by localized directional bonds similar to those found in our discussion of the  $H_2$  molecule.
- ▶ The crystal lattice is determined by the orientation and nature of the directional bonds.
- ▶ A typical case is diamond, in which the four bonding electrons of each carbon atom are oriented along the directions of  $sp^3$  hybrid wave functions



# Macroscopic features of covalent solids

- ▶ Extremely hard and difficult to deform
- ▶ Poor conductors of heat and electricity because there are no free electrons to carry energy or charge from one place to another
- ▶ High energy is required to excite whole-crystal vibrations in a covalent solid due to the rigidity of the bonds. Whole-crystal vibrations therefore have a high frequency.
- ▶ Electronic excitation energies of covalent solids are of the order of a few eV, large compared with the average thermal energy (of the order of  $kT$ ), which at room temperature (298 °K) is about  $2.4 \times 10^{-2}$  eV; hence covalent solids are normally in their electronic ground state
- ▶ Many covalent solids are transparent, because their first electronic state is higher than the photon energies in the visible spectrum

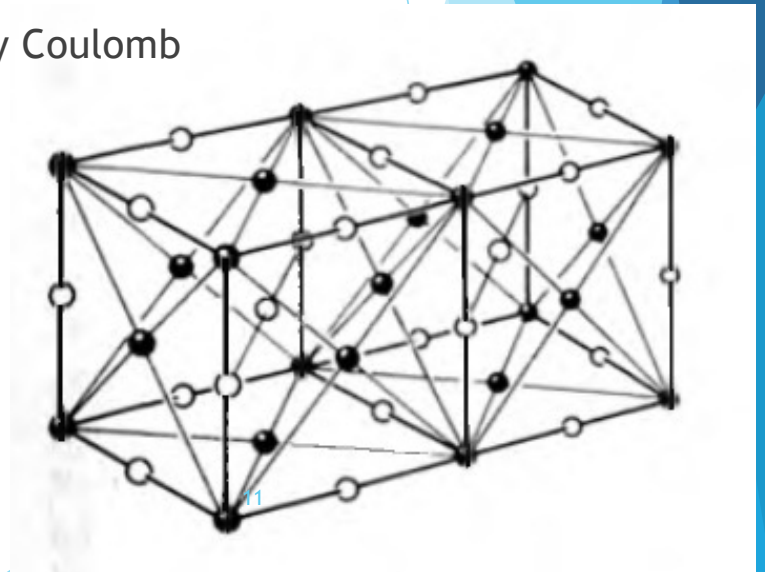
# Ionic crystals

- ▶ They consist of a regular array of positive and negative ions resulting from the transfer of one electron (or more) from one kind of atom to another.
- ▶ The ions are so arranged that a stable configuration is produced under their mutual electronic interactions.
- ▶ Strong forces due to the charges: the ions are bound together by Coulomb interaction

$$V(r) = Z \frac{q_1 q_2}{r}$$

- ▶ Strong forces means large melting points

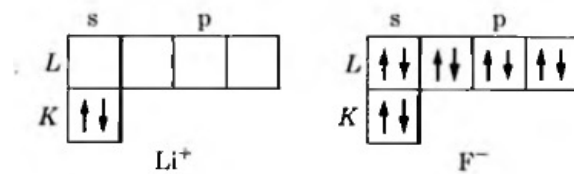
Na<sup>+</sup>Cl<sup>-</sup>



# Macroscopic properties of ionic crystals

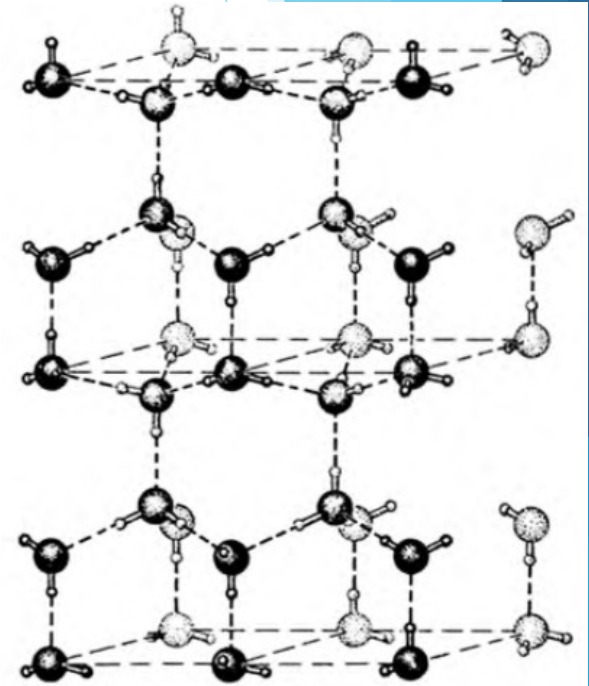
- ▶ Because they have no free electrons, ionic crystals are also poor conductors of heat and electricity
- ▶ However, at high temperatures the ions may gain some mobility, resulting in better electrical conductivity.
- ▶ Some ionic crystals strongly absorb electromagnetic radiation in the far infrared region of the spectrum: energy needed for exciting lattice vibrations. This energy is generally lower for ionic than for covalent crystals, due to their relatively weaker binding force.
- ▶ Most ionic crystals are diamagnetic because the ions, having a complete shell structure with all electrons paired, have no net magnetic moment.
- ▶ The ions are spherically symmetric\*, and thus their binding does not show directional preference, as do those of covalent solids.

\* Because in the ionic form they have a complete shell structure



# Hydrogen-bond solids

- ▶ They are characterized by strongly polar molecules having one or more hydrogen atoms, such as water,  $\text{H}_2\text{O}$ , and hydrofluoric acid,  $\text{HF}$
- ▶ E.g. ice, in which the water molecules have tetrahedral arrangement.
- ▶ The relatively open structure of ice accounts for the larger volume which ice has by comparison with water in the liquid phase.



*Arrangement of water molecules in ice.*

# Molecular solids

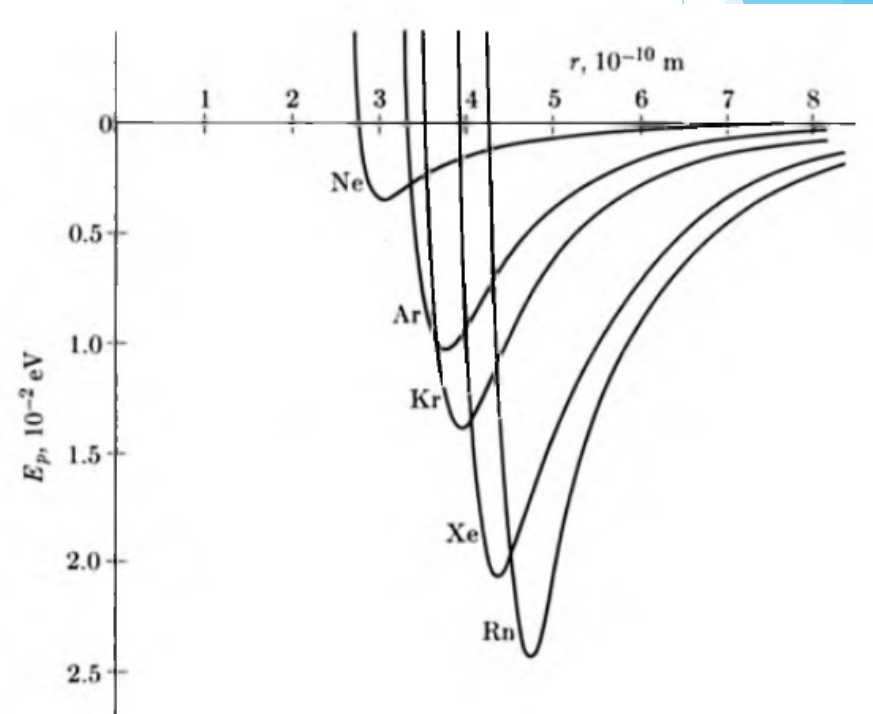
- ▶ These solids are made of substances whose molecules are not polar.
- ▶ No covalent bonds between atoms of two different molecules may be formed. Molecules in this type of solid retain their individuality.
- ▶ They are bound by the same intermolecular forces that exist between molecules in a gas or a liquid: Van der Waals' bonds
- ▶ Interaction between **fluctuating induced dipoles**.
- ▶ Potential energy of interaction between two neutral molecules at distance  $d$  and with electronic cloud of size  $r$ :

$$V(r) \sim -\frac{1}{r^6}$$

- ▶ It is the force that causes condensation of inert or non-interacting gases. Materials bound by this force have a very low melting point.

# Macroscopic properties of molecular solids

- ▶ Molecular solids are not conductors of heat and electricity
- ▶ They are very compressible and deformable
- ▶ Potential energy curves describing the interaction between two atoms of an inert gas in the solid state is shown in the figure



# Metals

- ▶ Metals are elements which have relatively small ionization energies, and whose atoms have only a few weakly bound electrons in their outermost incomplete shells.
- ▶ These outermost weakly bound electrons are easily set free using the energy released when the crystal is formed.
- ▶ A metal thus has a regular lattice of spherically symmetric positive ions that remain when the outermost electrons are set free, forming an electronic “gas”
- ▶ These electrons move, more or less freely, through the crystal lattice and therefore are not localized.



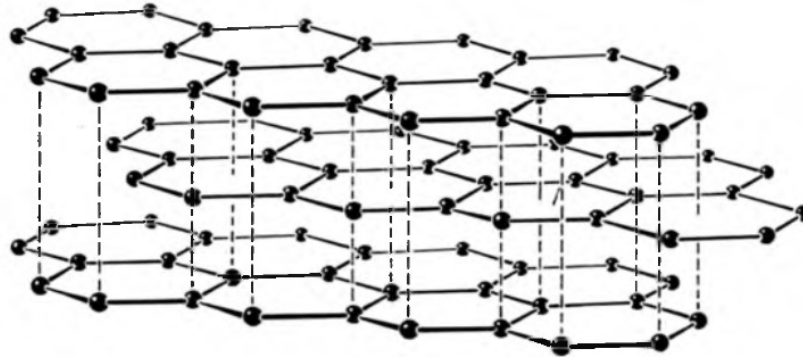


# Macroscopic properties of metals

- ▶ Excellent thermal and electrical conductivity, for which the free electrons are mainly responsible, the reason being that the free electrons easily absorb any energy from electromagnetic radiation or lattice vibrations and increase their kinetic energy and their mobility
- ▶ Metals are opaque, since the free electrons can absorb the photons in the visible region
- ▶ High reflection coefficient for electromagnetic waves, which gets scattered by the free electrons
- ▶ Forces holding the metal lattice together are spherically symmetric; therefore these lattices resemble the closely packed spheres discussed for ionic crystals.



# Solid with mixed properties



- ▶ E.g. graphite
- ▶ Layers of carbon atoms arranged in the form of a hexagon. The atoms in a layer are bonded by localized covalent  $\sigma$  -bonds which use  $sp^2$  hybrid wave functions and nonlocalized  $\pi$ -bonds, as in benzene
- ▶ The nonlocalized  $\pi$  -bonding electrons are free to move parallel to the layers, which explains the electrical conductivity of graphite parallel to the layers but not perpendicular to them.
- ▶ Successive layers of atoms are held together by weak van der Waals forces, which accounts for the flaky, slippery nature of graphite. In fact, it is used as a lubricant.

# Calculation of the internal potential energy of an ionic NaCl crystal.

- ▶ The attractive electric potential of  $\text{Na}^+$  with 6 nearest neighbors  $\text{Cl}^-$  is:

$$E_{p1} = 6 \left( -\frac{e^2}{4\pi\epsilon_0 R} \right)$$

- ▶ The repulsive potential energy between the 12  $\text{Na}^+$  ions at a distance  $\sqrt{2}R$  is

$$E_{p2} = 12 \left( \frac{e^2}{4\pi\epsilon_0 \sqrt{2}R} \right)$$

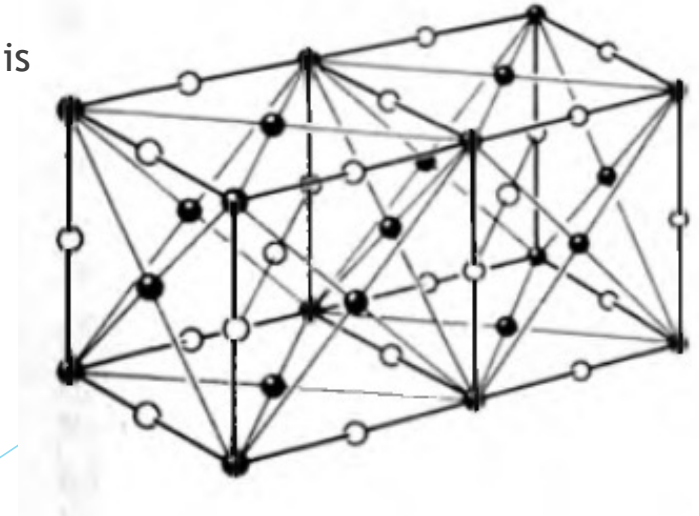
- ▶ The attractive electric potential of  $\text{Na}^+$  with 8  $\text{Cl}^-$  at distance  $\sqrt{3}R$  is

$$E_{p3} = 8 \left( -\frac{e^2}{4\pi\epsilon_0 \sqrt{3}R} \right)$$

- ▶ The repulsive potential energy with 6  $\text{Na}^+$  ions at a distance  $2R$  is

$$E_{p4} = 6 \left( \frac{e^2}{4\pi\epsilon_0 2R} \right)$$

R is the distance between nearest neighbors



# Internal potential energy of an ionic NaCl crystal

- ▶ The resultant potential energy is their sum:

$$E_p = -\frac{e^2}{4\pi\epsilon_0 R} \left( 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - 3 + \dots \right) = -\frac{\alpha e^2}{4\pi\epsilon_0 R}$$

- ▶  $\alpha$  is the sum inside the parentheses, and is called Madelung's constant.
- ▶ In the case of a face-centered-cubic lattice such as NaCl, the Madelung constant is 1.7476.
- ▶ In general,  $\alpha$  depends only on the geometry of the crystal; for a bodycentered lattice, such as CsCl, its value is 1.7627.
- ▶ Since  $\alpha$  is positive, the potential energy is negative and the interionic force is attractive at all distances, with no minimum.
- ▶ Therefore the crystal should coalesce into a closely packed structure with no stable configuration. However, we know that this is not the case.

# Internal potential energy of NaCl crystal

- ▶ The disagreement results from considering the ions as point charges.
- ▶ When two atoms come very close together the nuclear repulsion (partially screened by the electron shells) and the repulsion among the filled electron shells enter into effect.
- ▶ We should add a short-range repulsive term to the potential energy:

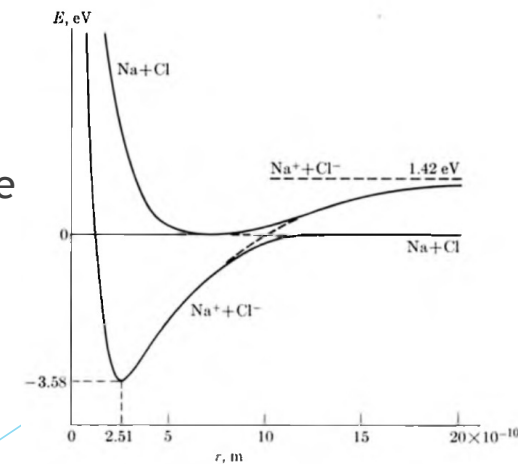
$$E_{p,repulsive} = \frac{\beta e^2}{4\pi\epsilon_0 R^n}$$

- ▶ Therefore the effective potential energy becomes:

$$E_p = -\frac{e^2}{4\pi\epsilon_0} \left( \frac{\alpha}{R} - \frac{\beta}{R^n} \right)$$

- ▶ The graph of this potential energy is similar to the molecular one

$\beta$  and  $n$  are two constants to be determined



# Calculation of eq potential energy

$$\left(\frac{dE_p}{dR}\right)_{R=R_0} = -\frac{e^2}{4\pi\epsilon_0 R_0} \left(-\frac{\alpha}{R_0^2} + \frac{n\beta}{R_0^{n+1}}\right) = 0 \rightarrow \beta = \alpha \frac{R_0^{n-1}}{n}$$

- ▶ We can include  $\beta$  in the eq of the potential energy:

$$E_p = -\frac{\alpha e^2}{4\pi\epsilon_0 R_0} \left(\frac{R_0}{R} - \frac{1}{n} \left(\frac{R_0}{R}\right)^2\right)$$

- ▶ The equilibrium potential energy of the  $\text{Na}^+$  ion, obtained by setting  $R = R_0$  is

$$E_p = -\frac{\alpha e^2}{4\pi\epsilon_0 R_0} \left(1 - \frac{1}{n}\right)$$

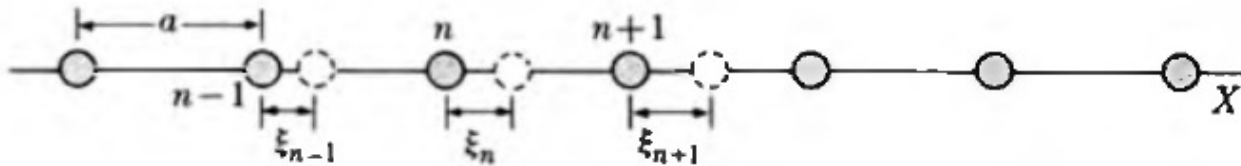
- ▶ We find a similar result if we start with a  $\text{Cl}^-$  ion. Given that  $N$  is the number of ion pairs in the crystal (which in our case is the same as the number of molecules), the internal potential energy of the crystal is

$$U = -\frac{N\alpha e^2}{4\pi\epsilon_0 R_0} \left(1 - \frac{1}{n}\right)$$

# Heat of formation of the crystal

- ▶ The experimental value of  $U$  for NaCl is  $-7.77 \cdot 10^5$  J mole<sup>-1</sup> or  $-185.7$  kcal mole<sup>-1</sup>.
- ▶ This result is obtained by measuring the heat of formation of the crystal.
- ▶ Substituting this value of  $U$  previous Eq., with  $N$  equal to Avogadro's number and  $R_0 = 2.81 \cdot 10^{-10}$  m, we obtain  $n = 9.4$ .
- ▶ For other cubic crystals the value of  $n$  is of the same order of magnitude. This value of  $n$  is consistent with other calculations.

# Lattice vibrations



- ▶ Let us consider a linear lattice; that is, a row of identical atoms separated the distance  $a$
- ▶ As a first approximation we shall assume that during the vibrations each atom interacts only with its two neighbors
- ▶ If  $\beta$  is the elastic constant of the bond, the force on the  $n^{\text{th}}$  atom to the right due to the  $(n+1)^{\text{th}}$  atom is  $\beta(\xi_{n+1} - \xi_n)$
- ▶ Thus the equation of motion is

$$M \frac{d^2 \xi_n}{dt^2} = \beta (\xi_{n+1} - \xi_n) - \beta (\xi_n - \xi_{n-1}) = \beta (\xi_{n+1} - 2\xi_n + \xi_{n-1})$$

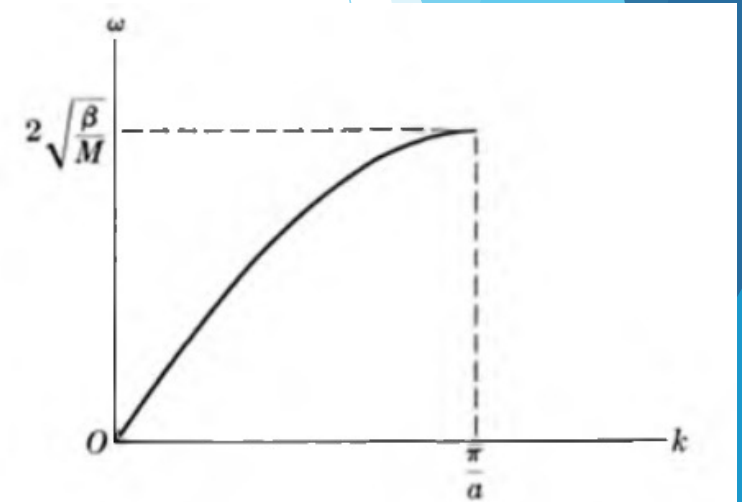


# Lattice vibrations

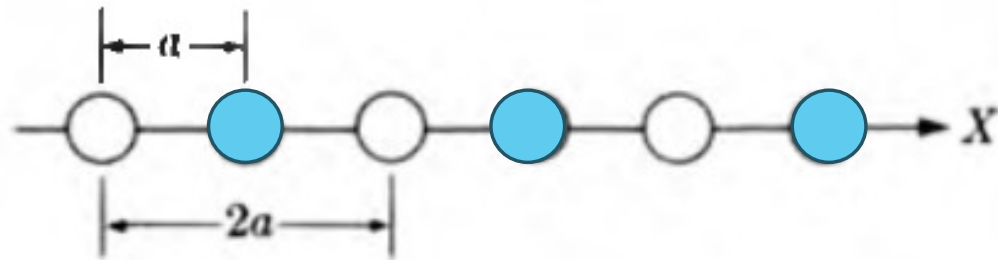
- ▶ We try a solution of the form  $\xi_n = \xi_0 e^{-i(\omega t + kna)}$
- ▶ The term  $kna$  gives the phase of each atom and resembles the phase term  $kx$  in a wave propagating through a continuous medium.
- ▶ Solving the differential equation we obtain:

$$-M\omega^2 = \beta(e^{ika} + e^{-ika} - 2) = -4\beta \sin^2 \frac{1}{2} ka \rightarrow \omega = 2 \sqrt{\frac{\beta}{M}} \sin \frac{1}{2} ka$$

- ▶ This equation gives the allowed frequencies in the lattice.
- ▶ The fact that there is a maximum frequency means that there is an upper limit or cutoff frequency for the elastic (i.e., acoustical) waves in a solid.



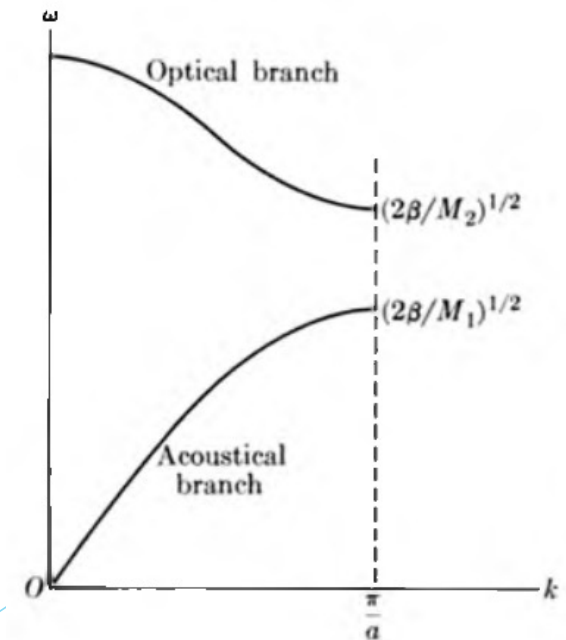
# Lattice vibrations



- ▶ Let us now consider a lattice composed of two kinds of atoms of masses  $M_1$  and  $M_2$ , arranged alternately so that the distance between neighboring atoms is  $a$  and the lattice space period is  $2a$
- ▶ In this case, the frequency varies with the wave vector as:

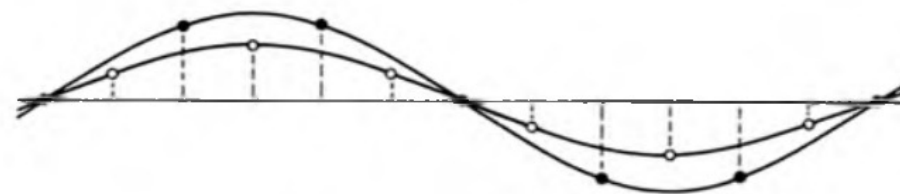
$$\omega^2 = \beta \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \pm \beta \left[ \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4 \sin^2 ka}{M_1 M_2} \right]^{1/2}.$$

- ▶ The upper values of  $\omega$  constitute the optical branch and the lower ones the acoustical branch of the frequency spectrum of the lattice.
- ▶ The reason for naming the branches “acoustical” and “optical” is that in the acoustical mode both classes of ions oscillate in phase, while in the optical mode they have a phase difference of  $\pi$ .

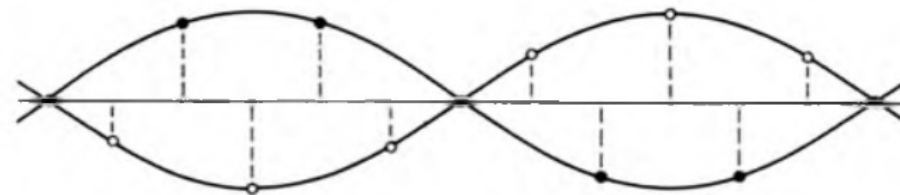


# Optical and acoustic modes

- ▶ The induced dipole moment in the optical mode is much larger than in the acoustical mode, and therefore the optical mode shows stronger emission and absorption of electromagnetic radiation than the acoustical mode.
- ▶ The optical frequencies fall in the infrared region of the spectrum, and hence ionic crystals display a strong response to infrared electromagnetic radiation.
- ▶ In a more refined analysis, the normal modes of vibration of a solid must be quantized
- ▶ The similarity to the absorption or emission of radiation suggests introduction of the concept of a **phonon**



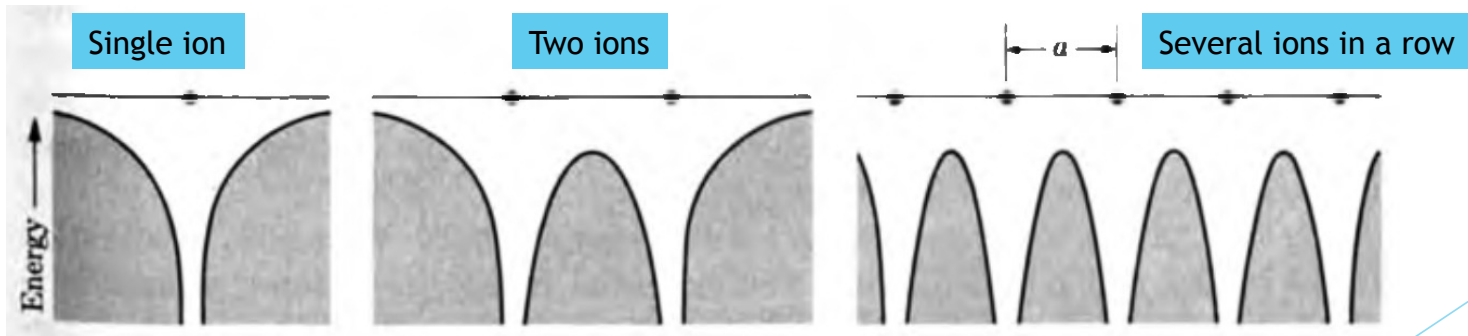
(a) Acoustical mode



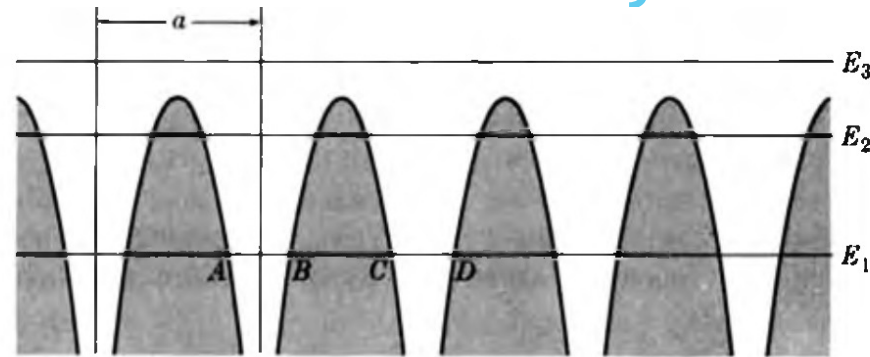
(b) Optical mode

# Electron motion in solids

- ▶ When an electron moves past an ion, the potential energy it feels is the coulomb potential energy, proportional to  $1/r$
- ▶ When there are several ions like in three-dimensional crystal the potential energy of an electron moving through the lattice also has a three-dimensional periodicity, repeating from one cell to the next.



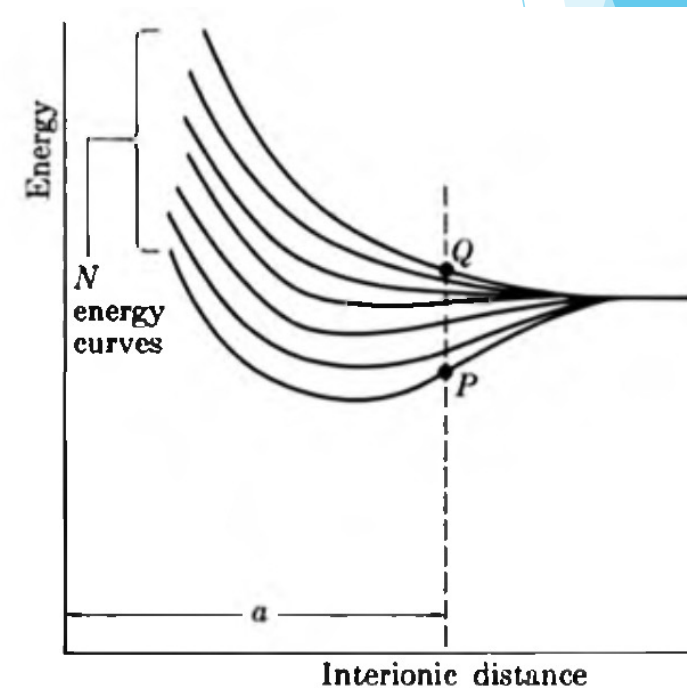
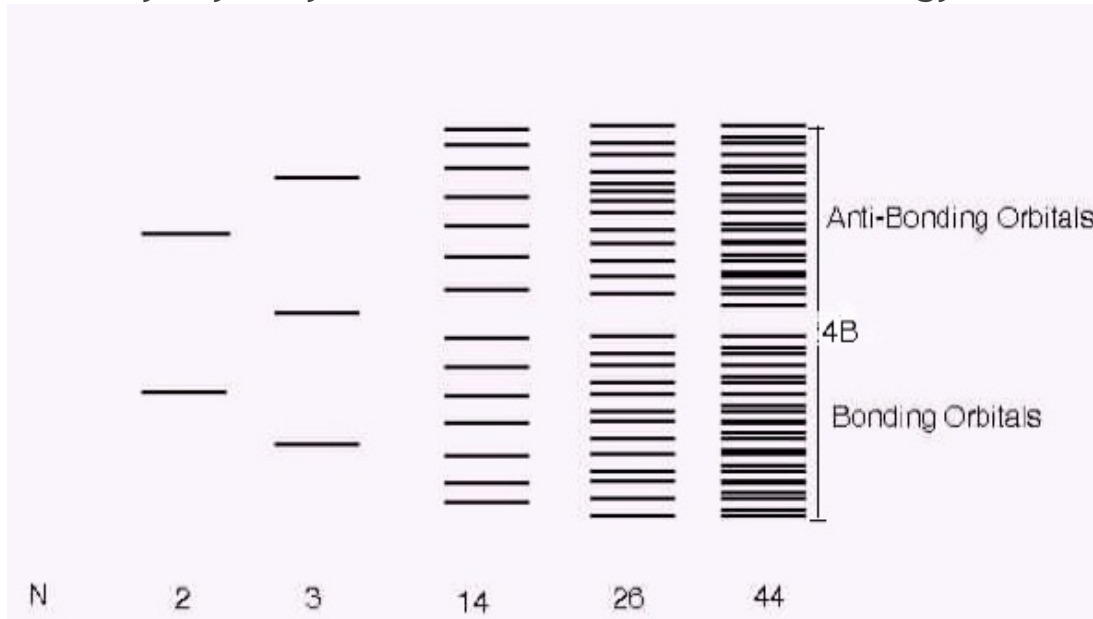
# Energy levels in a linear crystal lattice



- ▶ The innermost electrons (e.g. in  $E_1$ ) in a crystal are essentially localized and their energies and wave functions may be considered the same as in the isolated atoms.
- ▶ An electron with energy  $E_2$  is not bound so strongly to a particular ion and, by leaking through the potential barrier, it can move about in the lattice.
- ▶ An electron with energy  $E_3$  is not bound to any atom in particular; it has great freedom of movement throughout the lattice.
- ▶ These quasi-free electrons are not only responsible for most of the collective properties of the lattice (such as the electric and thermal conductivities), but they also provide for the binding of the atomic ions which form the crystal structure.

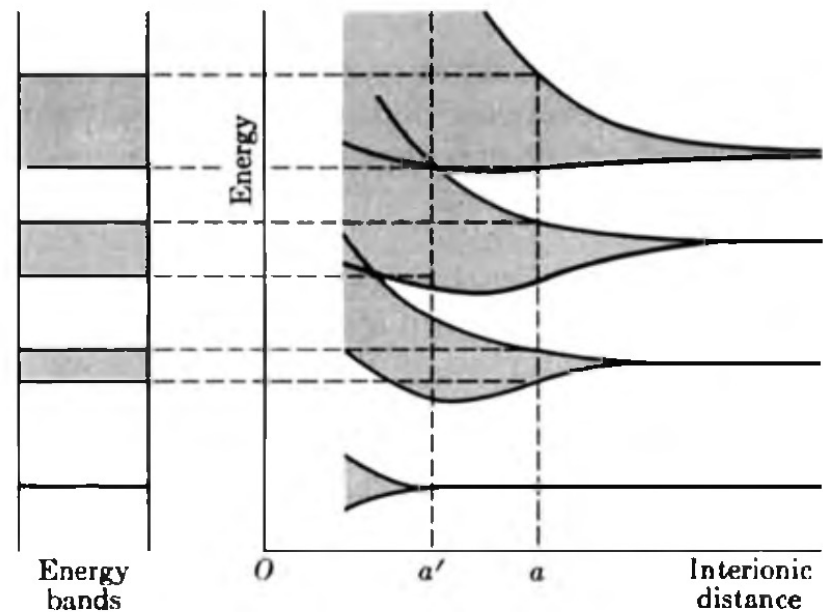
# Band formation

- ▶ In a molecule, each atomic energy level splits into a number of levels equal to the number of atoms.
- ▶ In a lattice, each atomic energy level gives rise to  $N$  closely spaced levels. Their spacing and position depend on the interionic separation
- ▶ When  $N$  is very large the different energy levels are so closely spaced that one may say they form a continuous band of energy



# Band theory

- ▶ An energy band corresponding to a given atomic state can accommodate a maximum of  $2N$  electrons, or two electrons per ion due to Pauli's exclusion principle
- ▶ The bands are designated as s-, p-, d-, etc., according to the value of the angular momentum of the atomic state to which they are related.
- ▶ From the energy curves at the right, we can see that the higher the atomic energy level, the larger the interionic distance at which the bands begin to be formed.
- ▶ As the interionic distance decreases the bands begin to overlap.



# Valence and conduction bands

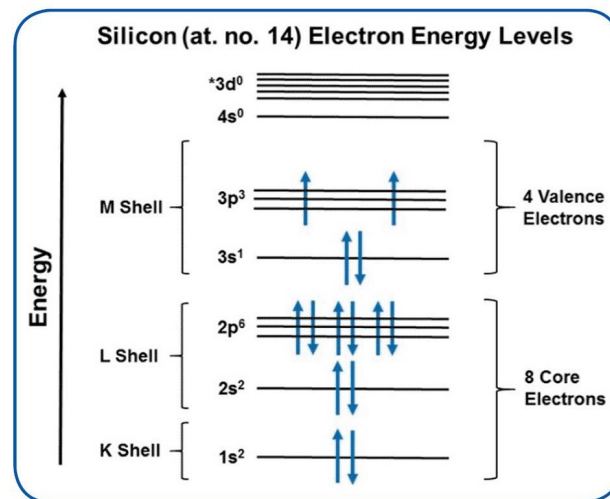
- ▶ Bands associated with the inner complete shells in the parent atoms have their full quota of electrons allowed by Pauli's principle. Electrons in these bands are also more or less localized.
- ▶ The band corresponding to the uppermost atomic shell, occupied by the valence electrons, is the most interesting in connection with the solid properties.
- ▶ If this uppermost band is not completely filled, it is called the **conduction band**.
- ▶ But if it is full, it is called the **valence band**, and the empty band just above it is then called the **conduction band**.





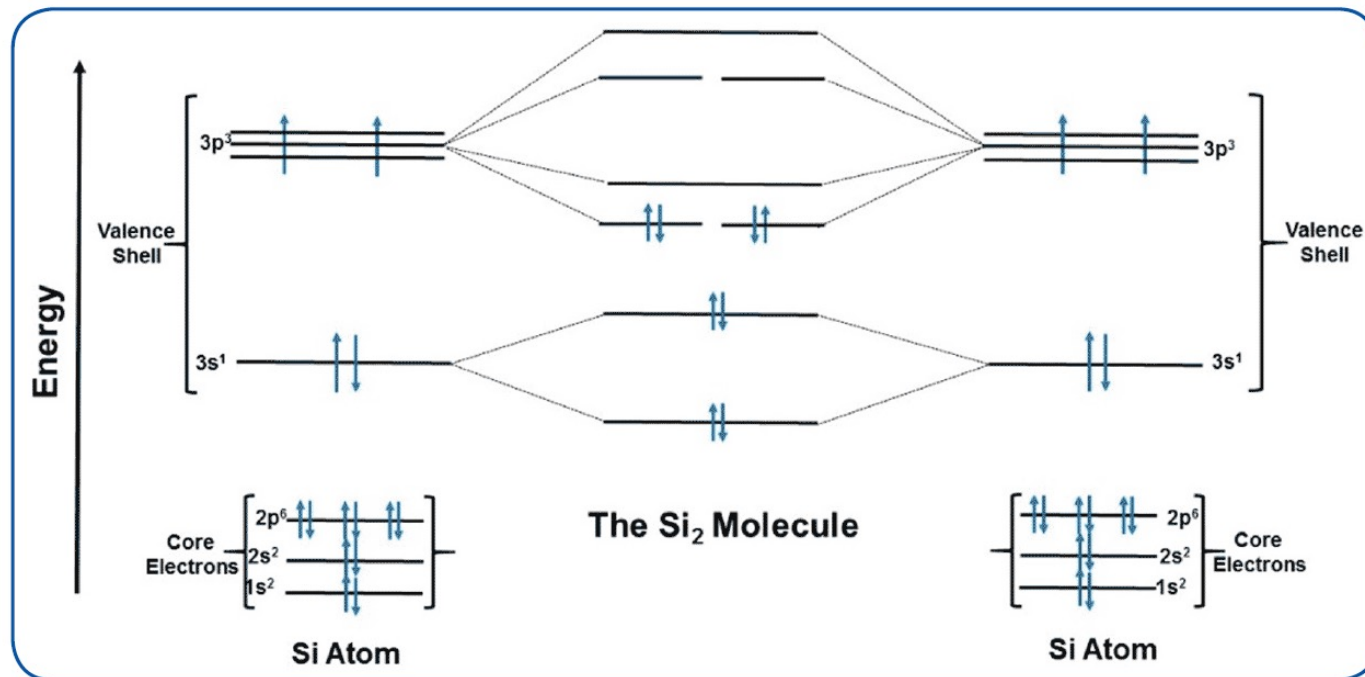
# Example - Single Si atom

- ▶ In Si, the M shell is only partially occupied with 4 electrons (compared to 18 possible)
- ▶ Therefore, M shell is not closed. 4 electrons are valence electrons. They determine the chemical bonding and the electronic properties.
- ▶ Excitation takes place by lifting a 3s<sup>1</sup> electron into a 3p<sup>3</sup> level creating an electron-hole pair.



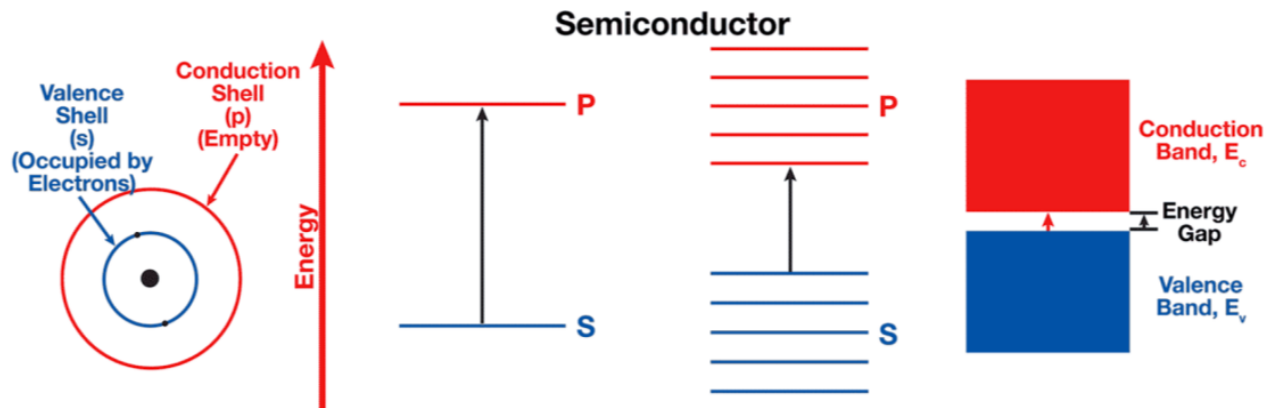
# Si<sub>2</sub> molecule

- ▶ When two Si atoms bind together, the 4 individual valence electrons interact and create new molecular sub-shells responsible for the chemical binding
- ▶ The new energy levels are above and below the related energies in single atoms: MORE energy levels with SMALLER excitation energies



# Si crystal

- ▶ When the number of Si atoms increases and turn into a crystal the energy level splitting proceeds leading to:
  - ▶ Formation of a quasi-continuous energy levels due to extremely small energy differences
  - ▶ With two, energy separated bands: VALENCE and CONDUCTION bands
- ▶ The energy in between defines the semiconductor energy gap, which is 1.12 eV for pure Si



# Free-electron model in a solid

- ▶ Analysis of the motion of electrons in the conduction band
- ▶ Assumption: we ignore the periodic fluctuation of the potential energy and assume that the electrons move freely in a region of constant average potential energy.
- ▶ The approximate wave function of an electron of momentum  $\mathbf{p} = \hbar\mathbf{k}$  will be:  
$$\psi = e^{i\mathbf{k}\mathbf{r}}$$
- ▶ For such wavefunction the condition  $|\psi|^2 = 1$  is fulfilled, meaning that we have the same probability of finding the electron anywhere in the lattice in other words the electron is free to move.

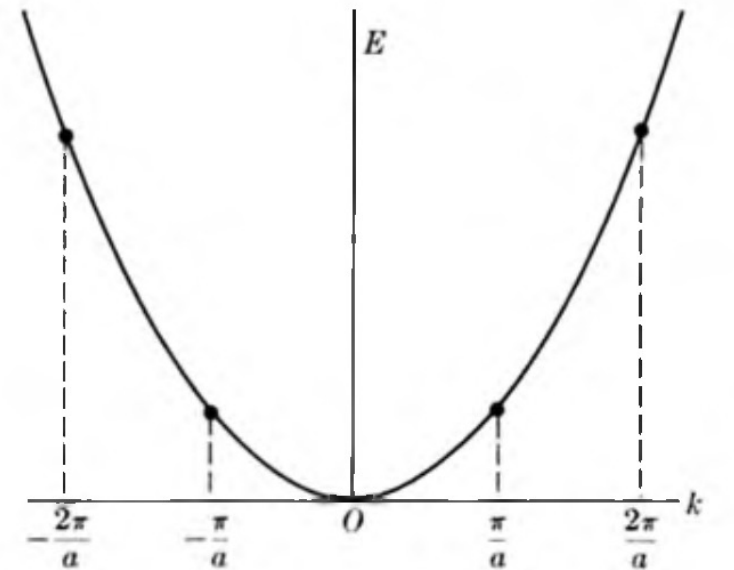
# Energy in the free-electron model

- ▶ The energy of the electron, disregarding the constant average potential energy, will have only a kinetic term:

$$E = \frac{p^2}{2m_e} = \frac{\hbar^2 k^2}{2m_e}$$

- ▶ This equation describes a parabola, meaning that the free-electron model allows all values of  $k$ , so it does not provide information about the width of a band
- ▶ Nevertheless, we can impose a quantization condition, considering that to sustain standing waves, the electron's wavelength  $\lambda$  must satisfy the requirement  $n\frac{\lambda}{2} = L$  where  $L$  is the length of a linear lattice of  $N$  ions spaced of  $a$ .

$$k = \frac{2\pi}{\lambda} = \frac{n\pi}{L} = \frac{n\pi}{Na} \quad \text{with } n=1,2,3,\dots,N$$



# Width of the band

- ▶ The difference between successive values of  $k$  is  $\frac{\pi}{Na}$ , which is very small if  $N$  is very large and justifies treating  $k$  as a continuous variable in spite of the quantization condition
- ▶ If  $n=N$  we find the max  $k$  allowed:  $k_{max} = \frac{\pi}{a}$ . Thus the range of  $k$ -values allowed within the band is between  $-\frac{\pi}{a}$  and  $\frac{\pi}{a}$ .
- ▶ The maximum energy in the band, which is also the width of the band, is then

$$E_{max} = \frac{\hbar^2 \pi^2}{2m_e a^2}$$

- ▶ Note that the width of the band is independent of the number of ions composing the lattice, a result to be expected, since adding more ions means more states but the periodicity of the lattice, which determines  $k_{max}$  remains the same

# Density of (energy) states of free electrons in a solid

- ▶ DOS tells us how the electrons may distribute themselves in a band among the energies from zero up to  $E_{\max}$

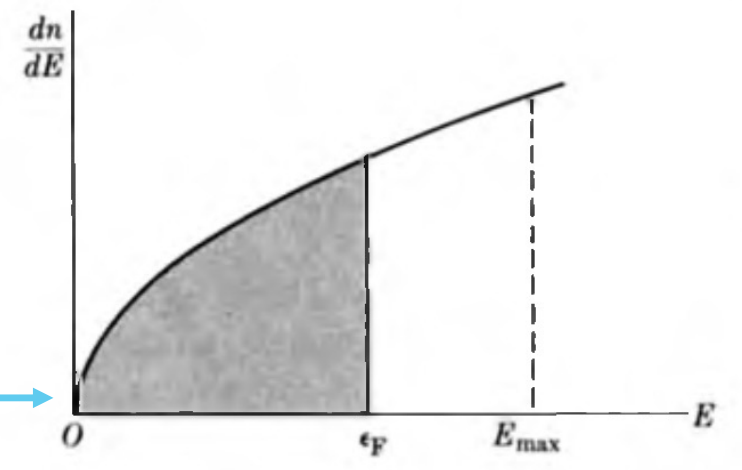
- ▶ The total number of electrons per unit volume with energy between  $E$  and  $E + dE$  in the band is

$$dn = \frac{8\pi(2m_e^3)^{1/2}}{h^3} E^{1/2} dE = g(E)dE$$

- ▶ If the metal is in its ground state (i.e., at absolute zero), all electrons occupy the lowest possible energy levels compatibly with the exclusion principle.

- ▶ The number of electrons per unit volume that can be accommodated up to an energy  $E$  is given by

$$n = \int_0^E g(E)dE = \frac{8\pi(2m_e^3)^{1/2}}{h^3} \int_0^E E^{1/2} dE = \frac{16\pi(2m_e^3)^{1/2}}{3h^3} E^{3/2}$$



# Fermi energy

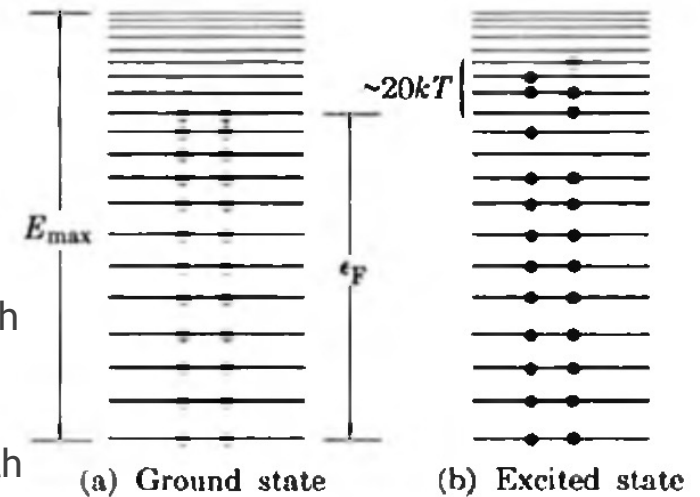
Metal	Li	Na	K	Rb	Cs	Cu	Ag	Au	Mg	Al
$\epsilon_F$ , eV	4.72	3.12	2.14	1.82	1.53	4.07	5.51	5.54	7.3	11.9

- ▶ If the total number of electrons per unit volume is less than the total number of energy levels available in the band, the electrons will then occupy all energy states up to a maximum energy, designated by  $\epsilon_F$ , and called the Fermi energy

- ▶ If  $E = \epsilon_F$ ,  $n$  should be  $n_0$ , therefore

$$\epsilon_F = \frac{h^2}{8m_e} \left( \frac{3n_0}{\pi} \right)^{2/3}$$

- ▶ When the Fermi energy is equal to the energy band width, the band is fully occupied.
- ▶ When a band is not completely full, a small amount of energy is enough to excite the uppermost electrons to nearby energy levels.
- ▶ Only the uppermost electrons can be thermally excited, since  $kT$  at room temperature is about 0.025 eV, which is very small compared with  $\epsilon_F$ , and the exclusion principle makes it impossible for the low-energy electrons to be excited into nearby occupied states.

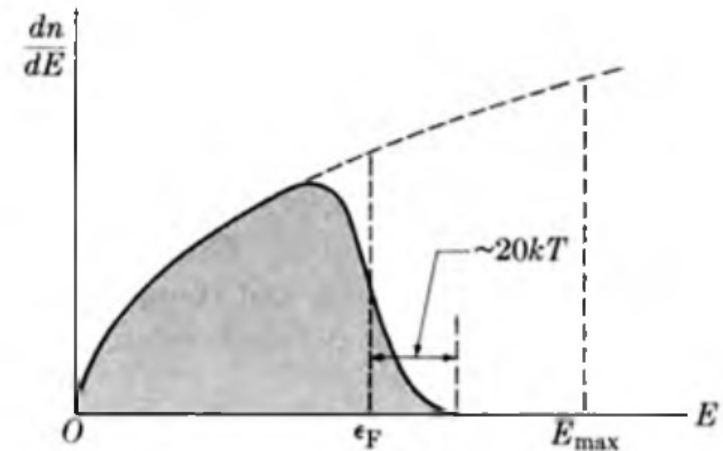




# Work function of a metal

- ▶ The electrons that can be thermally excited are those with an energy greater than  $\epsilon_F$ .
- ▶ The states occupied by the excited electrons fall in an energy region of the order of  $20 kT$  (0.5 eV) above  $\epsilon_F$ .
- ▶ The work function of a metal is the energy which is needed to extract an electron from the highest occupied level.
- ▶ At absolute zero the Fermi energy is the uppermost occupied level.
- ▶ Since thermal energies are very small compared with the Fermi energy, only a very few electrons are excited above the Fermi energy even at room temperatures.
- ▶ For this reason the work function is practically constant over a wide range of temperatures.

Distribution of electrons among the energy levels in a thermally excited state of the lattice



# Electron Motion in a Periodic Structure

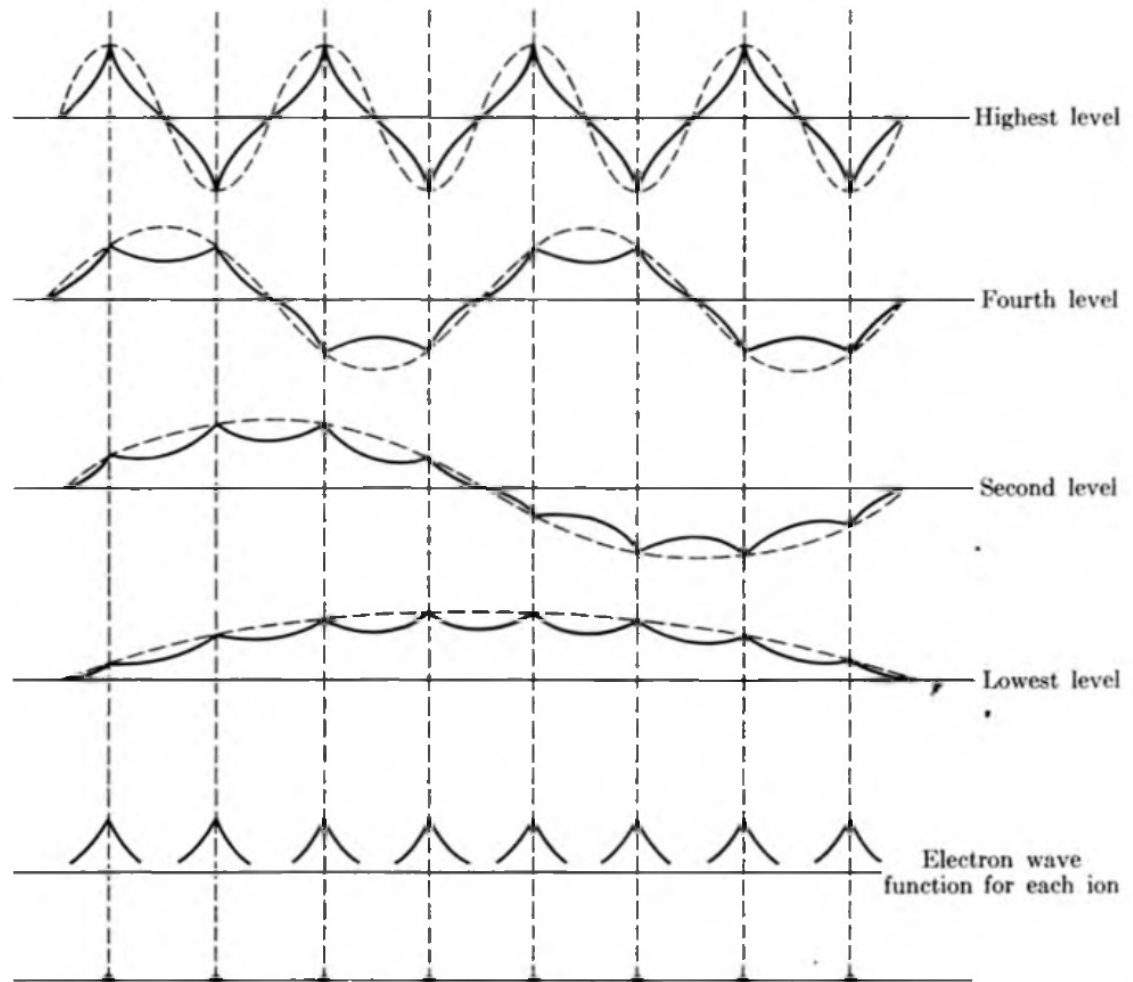
- ▶ To improve the free-electron model of a solid, we shall incorporate the effect of the periodic structure of the lattice.
- ▶ In the wavefunctions, we should include a term  $u(\mathbf{r})$  that imposes a change in the amplitude of the wavefunctions with the period of the lattice:

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r})$$

- ▶ In one dimension,  $u(x)=u(x+a)$  with  $a=$  lattice parameter:  $u$  is a modulating amplitude, repeating itself from one lattice cell to the next.
- ▶ Bloch theorem:  $u$  is a periodic function with the same period as the lattice spacing: the system can be completely characterized by their behavior in a primitive cell, also called single Brillouin zone.

# Wavefunctions in a periodic structure

We may obtain a picture of the wave functions by considering that  $u(x)$  resembles the wave function of the isolated atoms and replacing  $e^{ikx}$  by the wave functions of a free particle in a potential box.

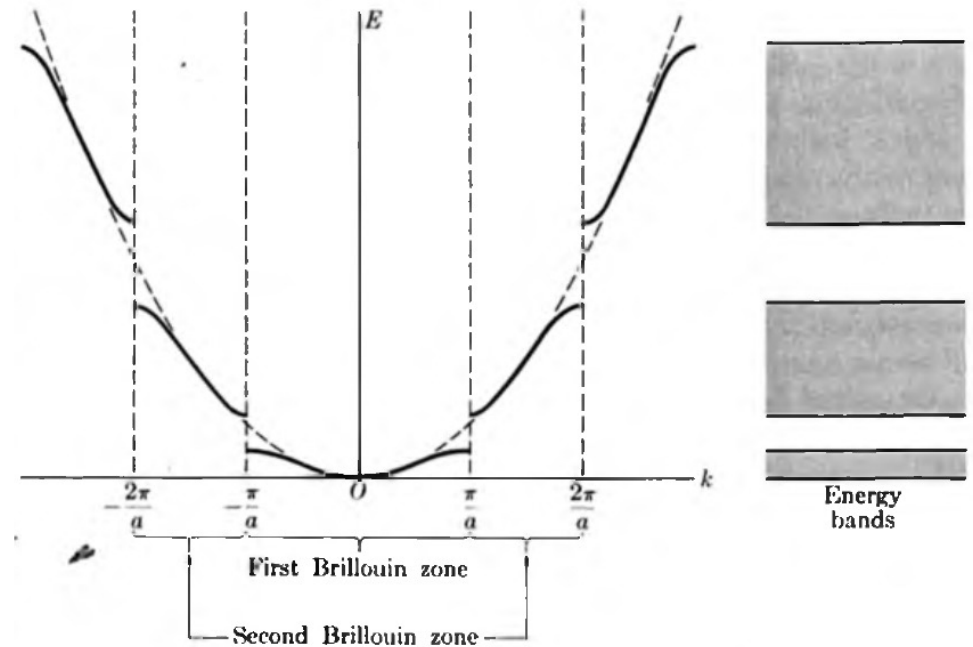


# Energy in a periodic structure

- ▶ The energy of the electron is not entirely kinetic, as it is in the case of the free electron model, because of the potential energy due to the lattice ions.
- ▶ The expression for the energy in terms of  $k$  is complicated and depends on the geometry of the lattice.
- ▶ The important result is that the energy has a discontinuity or gap at certain values of  $k$  which, for a linear lattice of spacing  $a$ , are given by

$$k = \frac{n\pi}{a}, \quad n = \pm 1, \pm 2, \dots$$

- ▶ For values of  $k$  not near the Brillouin zone boundaries, the energy follows the parabolic behaviour similar to that of a free particle.
- ▶ Therefore the lattice effect is to produce energy gaps: the values of  $k = \frac{n\pi}{a}$  are those at which the lattice blocks the motion of the electrons in a given direction by forcing them to move in the opposite direction.

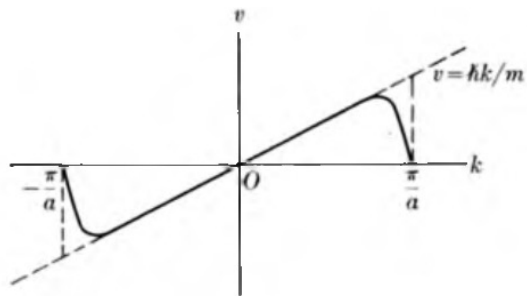


# Electron velocity

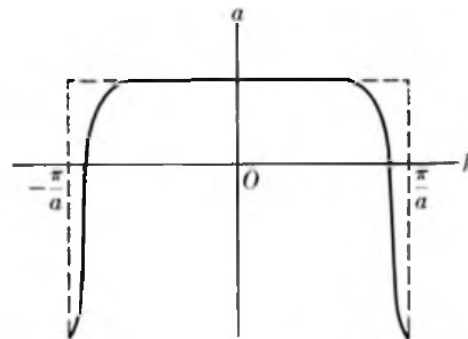
- ▶ The velocity of the electrons represented by a wave packet centered about the energy  $E$  and wave number  $k$  is

$$v = \frac{1}{\hbar} \frac{dE}{dk}$$

- ▶ The velocity is zero both at the bottom and at the top of the band. At intermediate regions in the band, it is very close to the free-electron velocity,  $\hbar k/m$



Velocity



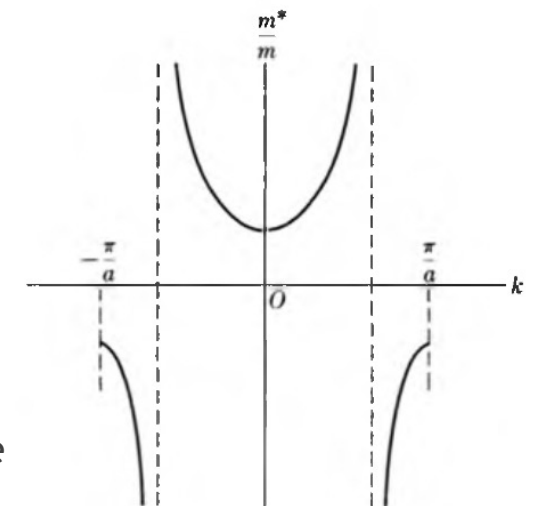
Acceleration

# Effective mass of the electron

- ▶ The effective mass  $m^*$  of the electron is given by  $m^* = F / a$ , where  $F$  is the external force applied to the electron (such as an electric field) and  $a$  is the actual acceleration due both to  $F$  and to the lattice interaction.
- ▶ Thus we cannot expect that  $m^*$  will be the same as the electron mass, nor should we expect it to be a constant.

$$m^* = \frac{\hbar^2}{d^2E/dk^2}$$

- ▶  $m^*$  is a function of the parameters of the lattice and of the electron's lattice momentum  $\hbar k$ .
- ▶  $m^*$  is positive at the bottom of an energy band and negative at the top. It becomes very large, actually infinite, at the inflection point of the energy curve

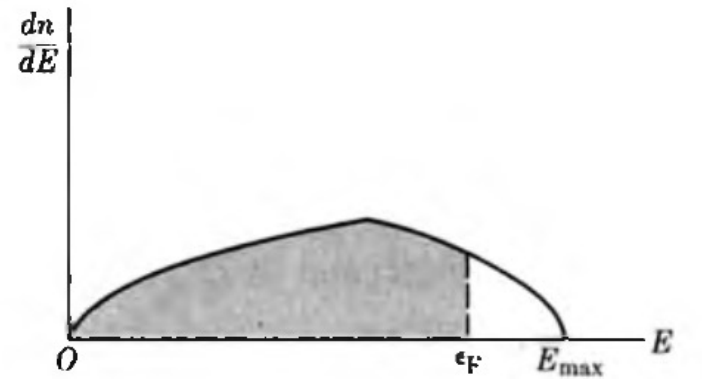


$m^*$  at  $k=0$

Metal	Li	Na	K	Rb	Cs
$m^*/m_e$	1.40	0.98	0.94	0.87	0.83

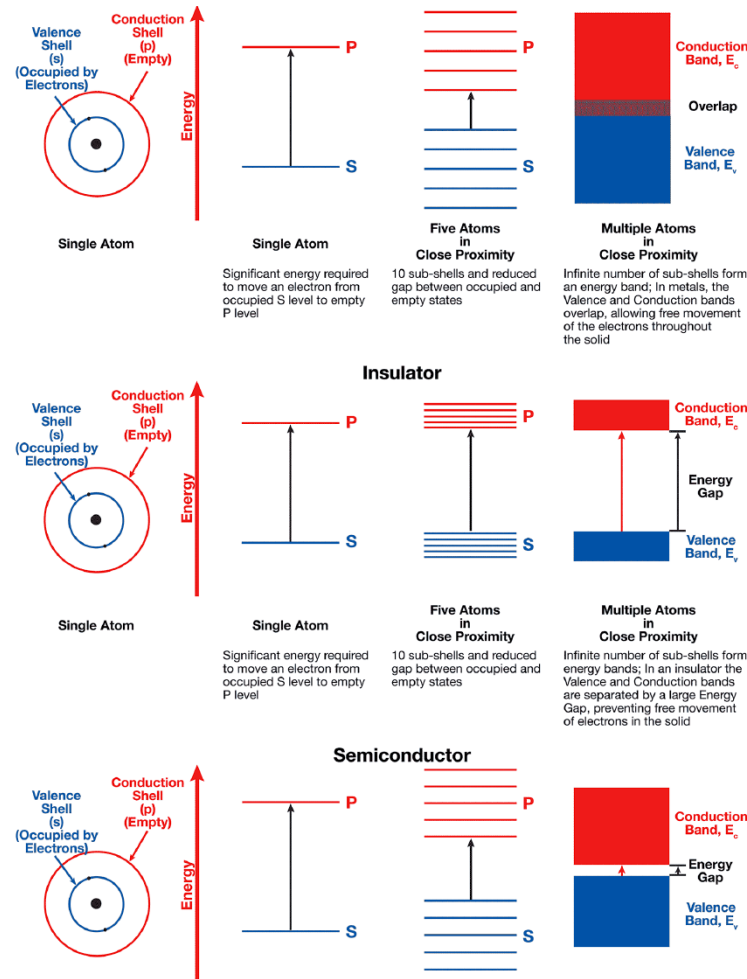
# Density of states in a periodic structure

- ▶ At the bottom of the band the density of states closely resembles the parabolic curve of the free-electron model, but instead of increasing steadily, the curve decreases almost parabolically at the top of the band.



# Metals, insulator and semiconductor

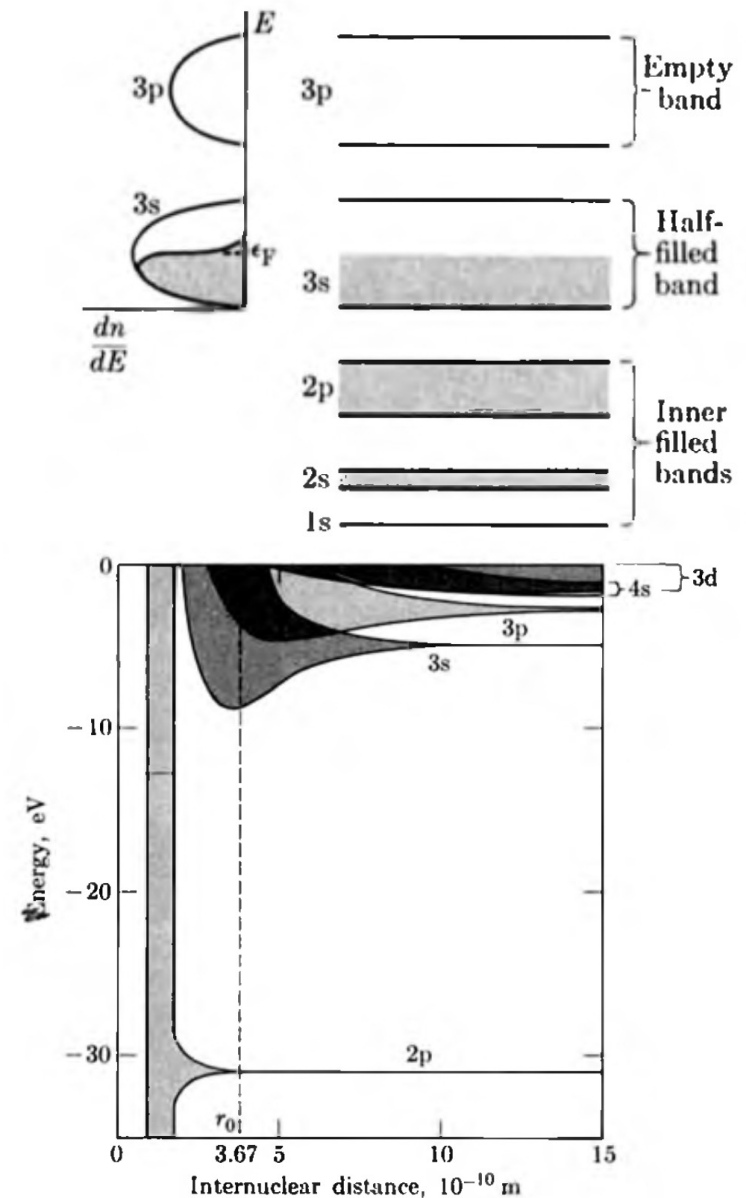
- ▶ Metals have NO bandgap: the conduction and valence band overlap (free movement in E-fields)
- ▶ Insulators have high bandgap (e.g. SiO<sub>2</sub> 9eV)
- ▶ Transport in semiconductor materials:
  - ▶ Excitation (electr.-hole formation)
  - ▶ External electric field (movement of carriers)





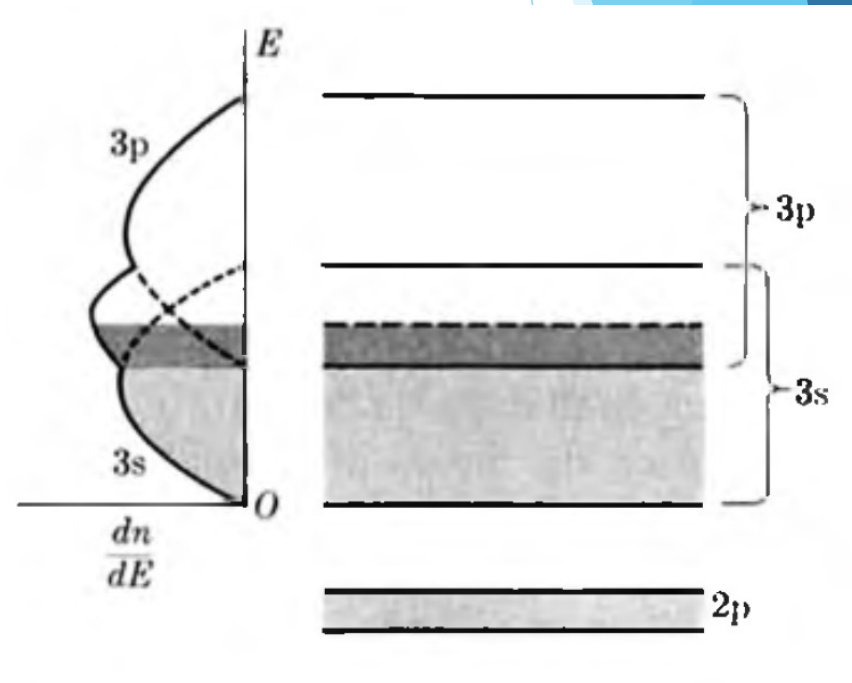
# Band structure of sodium

- ▶ Bands corresponding to the 1s, 2s, and 2p atomic levels are completely filled because the respective atomic shells are also complete.
- ▶ But the 3s band, which can accommodate up to two electrons per atom, is only half filled, since the 3s level in each sodium atom has only one electron.
- ▶ Actually the situation is slightly more complex because of the possible superposition of the bands (bottom fig).
- ▶ At the equilibrium distance  $r_0$  in the metal, about  $3.67 \cdot 10^{-10}$  m, the 2p level remains practically undisturbed, but the bands corresponding to the 3s and 3p atomic levels overlap.



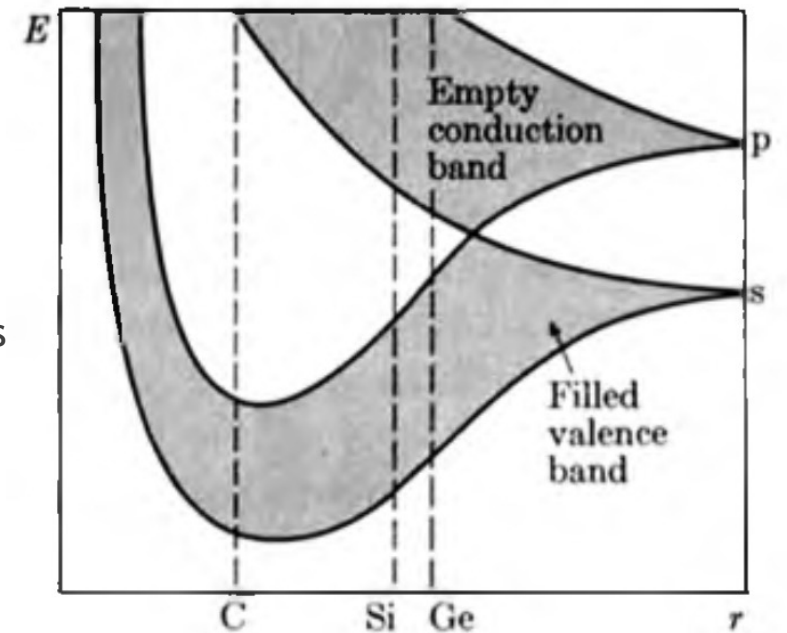
# Bann structure of Magnesium

- ▶ The magnesium atom has the configuration  $1s^2 2s^2 2p^6 3s^2$ , and therefore all the atomic shells are filled. However, the first excited level,  $3p$ , is rather close to  $3s$ .
- ▶ Normally, with no overlapping, the  $3s$  band should be filled and the  $3p$  band empty, and magnesium should be an insulator
- ▶ Those substances whose atoms have complete shells but which, in the solid state, are conductors because of the overlapping of a filled band and an empty band are often called semimetals.
- ▶ In the transition metals group, such as iron, the overlapping bands are  $3d$ ,  $4s$ , and  $4p$ , and the number of electrons is insufficient to fill these bands.
- ▶ Similarly, in the rare-earth group, the overlapping bands involved are  $4f$ ,  $5d$ ,  $6s$ , and  $6p$ . Hence these elements, when in the solid state, are conductors.



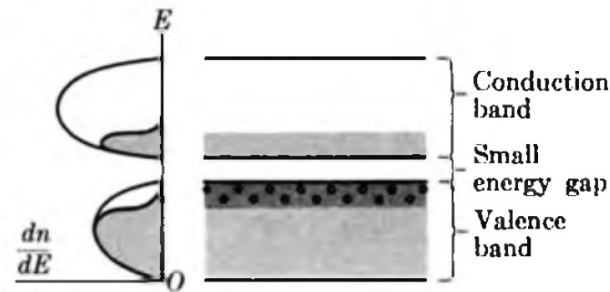
# Band Structure for diamond, Si and Ge

- ▶ The bands correspond to the atomic 2s and 2p levels in diamond, which can accommodate up to 8 electrons. However, the carbon atom has only 4 electrons available for these levels
- ▶ The 4 electrons are normally in the lower or valence band, while the upper band is empty. At the equilibrium distance in diamond, about  $1.5 \times 10^{-10}$  m, the gap is about 5 eV.
- ▶ This may be considered as a relatively large energy gap; it explains why diamond is such a good insulator.
- ▶ The same band scheme also applies to silicon and germanium: the gap between the valence and conduction bands at the equilibrium separation of the atoms is much smaller (1.1 eV in silicon and 0.7 eV in germanium), and this makes it much easier to excite the uppermost electrons in the valence band into the conduction band.



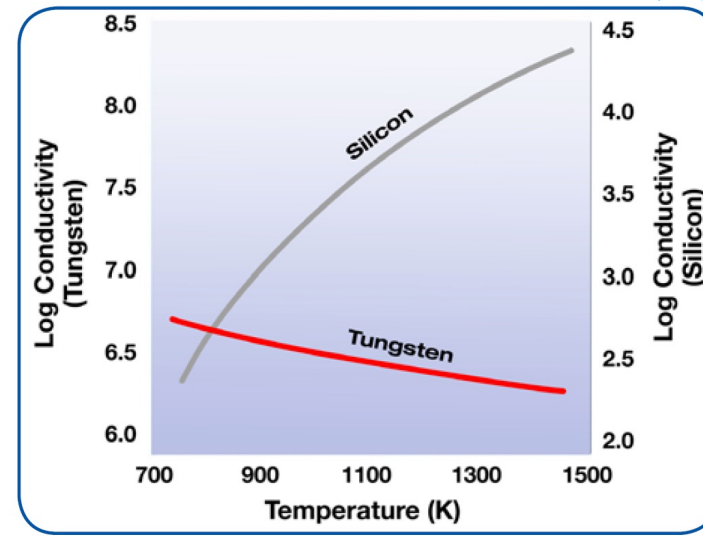
# Intrinsic conductivity in a semiconductor

- ▶ As the temperature increases, more electrons are able to jump into the next band.
- ▶ This has two results:
  - ▶ The few electrons in the upper or conduction band act as they would in a metal,
  - ▶ the empty states, or holes, left in the lower or valence band act in a similar way, but as if they were positive electrons
- ▶ Thus we have electric conduction from the excited electrons in the conduction band and from the holes in the valence band; the conductivity increases rapidly with the temperature because more electrons are excited to the conduction band.



# Effect of Temperature on electrical conductivity

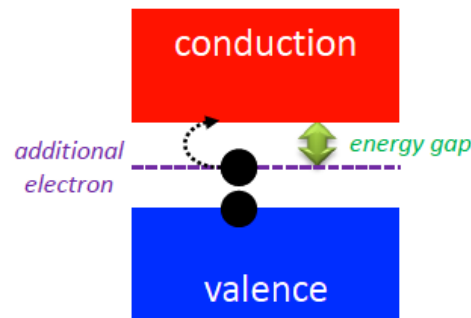
- ▶ In semiconductors at 0° C, the electrons are tightly bound in the valence band
- ▶ Increasing the temperature adds thermal energy, which increases the conductivity
- ▶ Hence, semiconductors have a negative temperature coefficient of resistance
- ▶ Metals have overlapping bands, which allows movement even at 0° C
- ▶ For increasing temperatures, the atomic lattices increase their vibration, which leads to increasing scattering probability of electrons, reducing the electric conductivity
- ▶ Hence metals have a positive temperature coefficient of resistance



# The energy gap

Class	Properties	Material	Resistivity	Conductivity
			( $\Omega.cm$ )	( $\Omega^{-1}.cm^{-1}$ )
Conductors	MANY free electrons which allow easy and fast electric "flow" Practically NO energy barrier	Silver	$1.63 \times 10^{-8}$	$6.17 \times 10^7$
		Copper	$1.72 \times 10^{-8}$	$5.95 \times 10^7$
		Aluminum	$2.65 \times 10^{-8}$	$2.65 \times 10^7$
Semiconductors	In BETWEEN insulators and conductors LOW and TUNABLE energy barrier	Carbon (Graphite)	$(3 - 60) \times 10^{-5}$	$(1.67 - 33.3) \times 10^3$
		Germanium	$(1 - 500) \times 10^{-3}$	$(2 - 1000) \times 10^0$
		Silicon	$(0.1 - 60) \times 10^0$	$(1.67 - 1000) \times 10^{-2}$
Insulators	VERY FEW free electrons which are barely moveable VERY HIGH energy barrier	Hard Rubber	$(1 - 100) \times 10^{13}$	$1 \times 10^{-15}$ to $1 \times 10^{-13}$
		Glass	$(1 - 1000) \times 10^9$	$1 \times 10^{-13}$ to $1 \times 10^{-9}$
		Quartz (fused)	$7.5 \times 10^{17}$	$1.33 \times 10^{-18}$

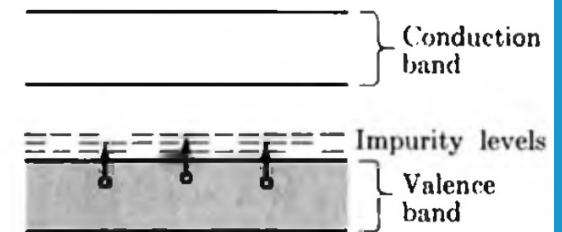
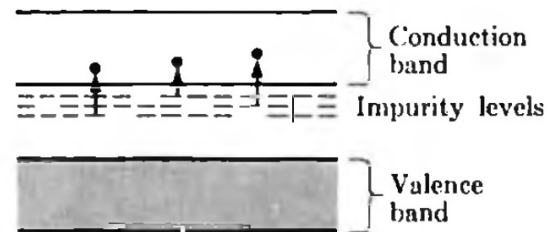
How to reduce the bandgap?



# Tuning the band gap

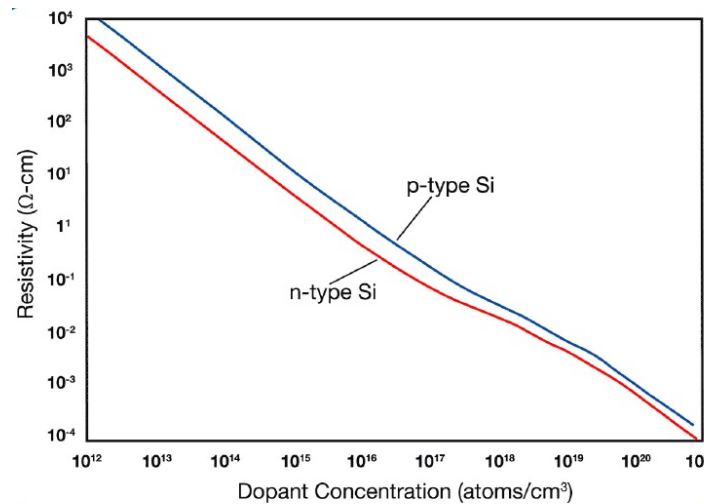
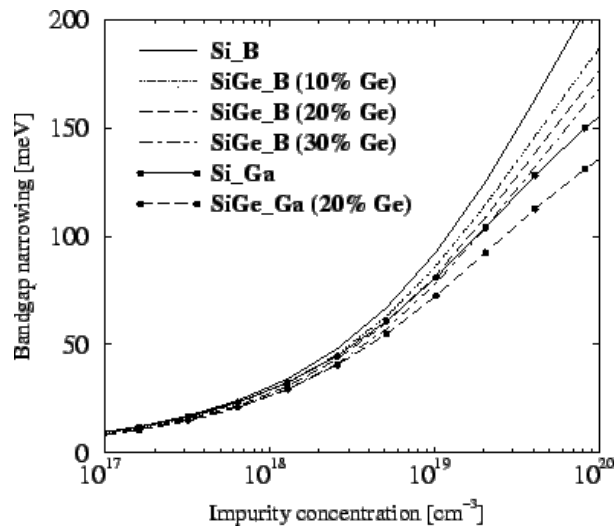
- ▶ The conductivity of a semiconductor can also be enhanced by the addition of certain impurities. Suppose that we replace some of the atoms of the semiconductor by atoms of a different substance
- ▶ Doping means replacing individual atoms, following a few rules:
  - ▶ The new atom should be similar in size to the one being replaced
  - ▶ The new atom should have an additional electron or an additional hole
- ▶ Elements to the immediate left/right/above or below the core material are used
  - ▶ SiP: additional electrons, increase negative charge carriers → n-type Si (electron transport, P is called donor)
  - ▶ SiB: additional holes, increase positive charge carriers → p-type Si (hole transport, B is called acceptor)

	IIIA	IVA	VA	
	Boron 5 <b>B</b> 10.811	Carbon 6 <b>C</b> 12.011	Nitrogen 7 <b>N</b> 14.007	
P-type Dopants	Aluminum 13 <b>Al</b> 26.982	Silicon 14 <b>Si</b> 28.086	Phosphorus 15 <b>P</b> 30.974	N-type Dopants
	Gallium 31 <b>Ga</b> 69.723	Germanium 32 <b>Ge</b> 72.64	Arsenic 33 <b>As</b> 74.922	
	Indium 49 <b>In</b> 114.82	Tin 50 <b>Sn</b> 118.71	Antimony 51 <b>Sb</b> 121.76	
	↑ <b>Elemental Semiconductors</b>			



# Doping

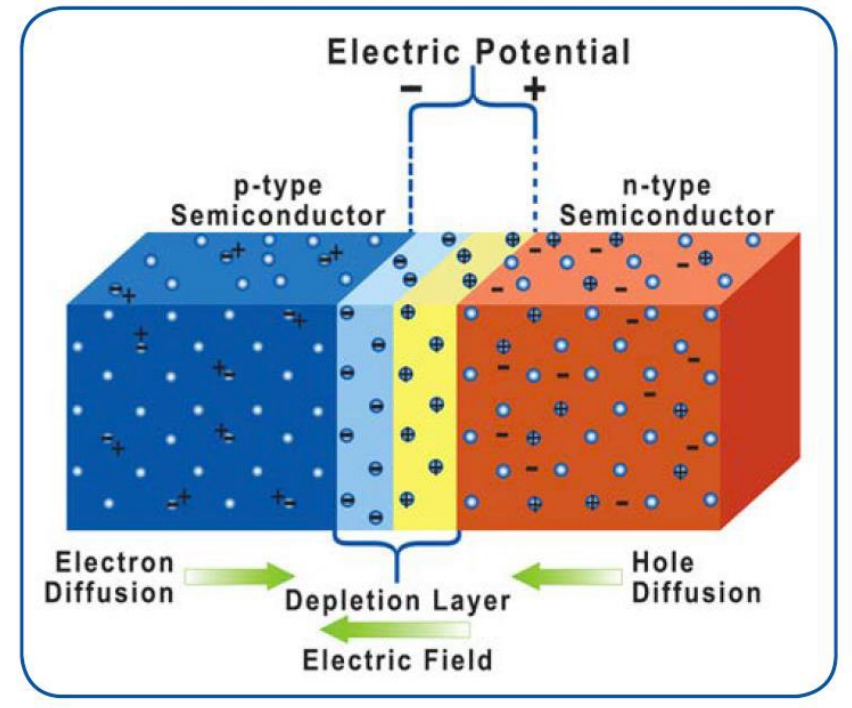
- ▶ By using different materials/combinations/dopants one can tune:
  - ▶ Bandgap energy
  - ▶ Transport type (n or p-types)
  - ▶ Overall resistivities
- ▶ To produce significant changes in the conductivity of a semiconductor, it is sufficient to have about one impurity atom per million semiconductor atoms.





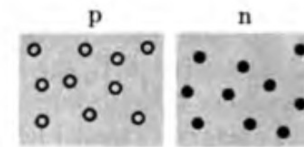
# The p-n Junction and its behavior

- ▶ When a p-type semiconductor and a n-type semiconductor are brought in contact a p-n junction forms:
  - ▶ The p-type region has many holes
  - ▶ The n-type region has many electrons
  - ▶ In the p-n boundary we have inter-diffusion ideally to have the same concentrations everywhere
- ▶ However, the migration of charged particles **BUILDS UP** an electric field around the junction → limiting the further migration
- ▶ Hence, there is an area around the junction which has no free electrons/holes, called **depletion layer**
- ▶ For **Si-based devices**, the potential difference at the junctions is around **0.7 V**



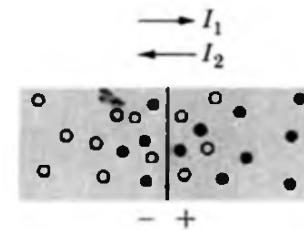
# p-n junction

- ▶ a: two samples placed in contact
- ▶ b: a diffusion or flow of holes from the left to the right and of electrons from the right to the left. This double flow produces a double layer of positive and negative charges on both sides of the junction, setting up a potential difference across the junction
- ▶ Due to the recombination of holes and electrons, the number of holes in the n-type semiconductor tends to decrease, which allows a small hole current  $I_1$  to flow continuously from the p-side to the n-side.
- ▶ At the same time, due to thermal excitation, hole-electron pairs are produced in the n-type semiconductor, and these excess holes can flow very readily across the junction into the p-side with a current  $I_2$ .
- ▶ At equilibrium both hole currents are identical; that is,  $I_1 = I_2$

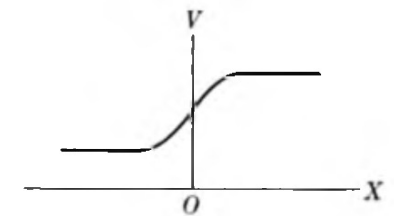


(a)

○ : holes (positive)  
● : electrons (negative)

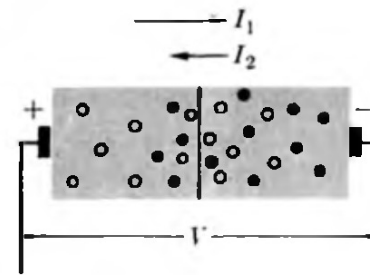


(b)

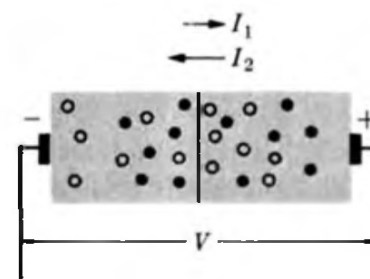
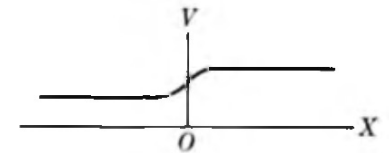


# P-n junction

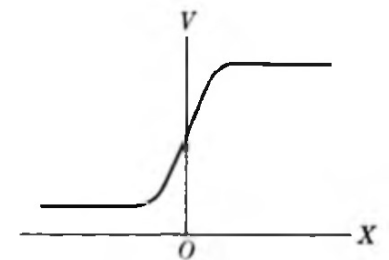
- ▶ c: If a potential difference  $V$  is applied, with the p-side joined to the positive terminal and the n-side to the negative terminal of the source of  $V$ , the height of the potential difference across the junction decreases.
- ▶ This allows a larger current  $I_1$  to the right, without actually changing the thermally generated current  $I_2$  to the left.
- ▶ Thus a net hole current  $I_1 - I_2$  results across the junction to the right, and this current increases very rapidly with  $V$ , due to the large supply of holes from the p-side.
- ▶ d: if the potential difference  $V$  is reversed, the potential difference across the junction increases. This reduces the value of  $I_1$ , without substantially affecting  $I_2$ , since the supply of holes from the n-side is temperature limited.
- ▶ Thus a net current to the left will exist across the junction which will approach the constant value  $I_2$  with increasing  $V$



(e)



(d)



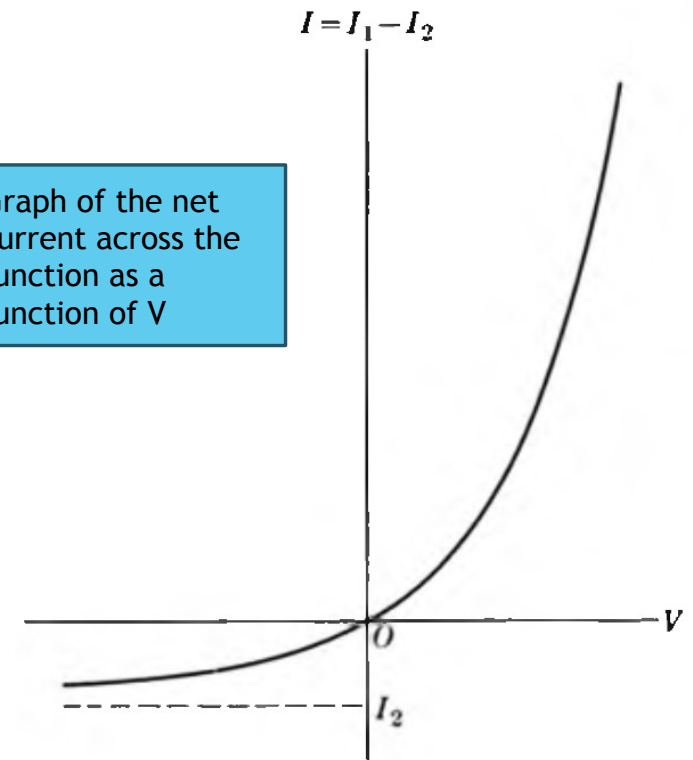
# Net current p-n junction

- ▶ The net current across the junction as a function of  $V$  is:

$$I = I_1 - I_2 = I_2 \left( e^{\frac{V}{kT}} - 1 \right)$$

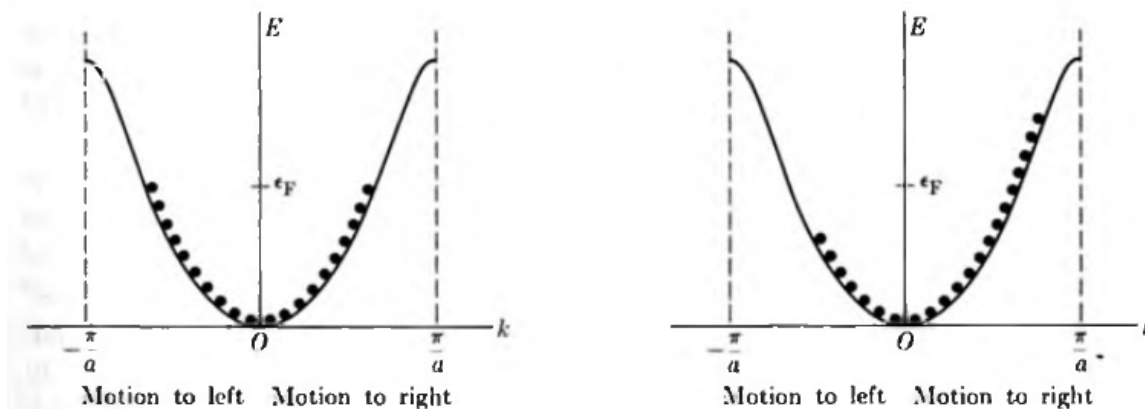
- ▶ We conclude that a p-n junction acts as a rectifier or a detector device favoring the passage of a current in the direction  $p \rightarrow n$ .

Graph of the net current across the junction as a function of  $V$



# Electrical Conductivity

- ▶ Let us consider the solid to be in its ground state with no electric field applied, and assume that the electrons are in the first Brillouin zone
- ▶ The electrons are occupying the lowest states within the band, in a symmetric form, so that no net current exists.
- ▶ If an electric field is applied, all electrons experience a force in a direction opposite to the field and, their  $k$ -values increase in the direction of the force.
- ▶ The result is an asymmetric distribution of the electrons within the metal. This gives rise to a net electric current in the metal, since more electrons move in one direction than in the opposite direction.



# Paradox

- ▶ As long as the electric field is applied, the occupation of states with  $k$  parallel to the force increases with time and the occupation of those states with  $k$  opposite decreases with time. In other words, the current increases continuously with time, even if the electric field is constant, due to the continuous acceleration of the electrons.
- ▶ This is in contrast with Ohm's law that states that a constant electric field produces a constant electric current; that is, when an electric field is applied, the conduction electrons in a metal acquire an average and constant drift velocity.
- ▶ Therefore we conclude that there must be some mechanism which prevents the electrons under the applied electric field from accelerating indefinitely up to the top of the conduction band.

# Drude and Lorentz theory

- ▶ Classical theory: frequent collisions of the electrons with the positive ions, which constitute the metal lattice, prevent the electron from being accelerated continuously because the collisions drift the electrons in the opposite direction of the electric field.
- ▶ Conductivity =  $\sigma = \frac{ne^2\tau}{m_e}$
- ▶ where  $n$  is the number of electrons per unit volume and  $\tau$  is a parameter called the relaxation time.
- ▶ The conductivity in this eq does not depend on temperature. Nevertheless, it was experimentally demonstrated that  $\sigma$  varies with  $1/T$
- ▶ Classical theory is not correct and we need quantum theory

# Quantum theory for electrical conductivity

- ▶ Electron = a wave packet.
- ▶ The motion of a wave packet may be hindered by scattering. Initially the wave packet is moving in a particular direction with the wave number  $k$ ; after the scattering it is moving with a different wave number, say  $k'$ , in a different direction.
- ▶ Scattering produces a transition  $k \rightarrow k'$ . In the transition, some momentum and energy are transferred to the scatterer.
- ▶ The effect of the applied electric field is to accelerate the electrons in a certain direction; the effect of the scattering is to disarray the electron motion, hindering the accelerating effect of the electric field.
- ▶ A steady state is produced when these two effects balance each other, in a statistical sense, resulting in a constant average velocity of the conduction electrons.
- ▶ Since scattering cannot violate the exclusion principle, the electrons must be scattered into vacant states.
- ▶ The electrons that are scattered are the most energetic ones.





# Electron scattering

- ▶ Any irregularity in the periodicity of a lattice disturbs the otherwise free motion of the electron, and the disturbance can be considered as a scattering.
- ▶ These lattice irregularities are due to two factors:
  - ▶ **Imperfections in the solid:** vacant spaces, interstitial and displaced atoms, dislocations, and impurities. The contribution to the conductivity due to scattering by imperfections in the lattice is essentially independent of temperature.
  - ▶ **Thermal oscillatory motion of the ions** which constitute the lattice. Since the ions do not all oscillate in phase, their vibrations give rise to small fluctuations in the lattice spacing. the lattice-vibration effect is temperature-dependent, since the amplitude of the vibrations depends on the vibrational energy and this in turn depends on the temperature.

# Electronic conductivity

- ▶ To account for the lattice vibrations effect on the conductivity we use again the effective mass  $m^*$  defined for the electron motion in a lattice, therefore

$$\sigma = \frac{ne^2\tau}{m^*}$$

- ▶ Also  $n$  is not the total number of electrons per unit volume in the conduction band; rather it is the effective number of electrons which participate in the conduction. This number is smaller than the total number of electrons in the conduction band, due to the restriction imposed by the exclusion principle.
- ▶ Given that  $P_s$ , is the probability of scattering of the electrons per unit time, the relaxation time is given by

$$\tau = \frac{1}{P_s}$$

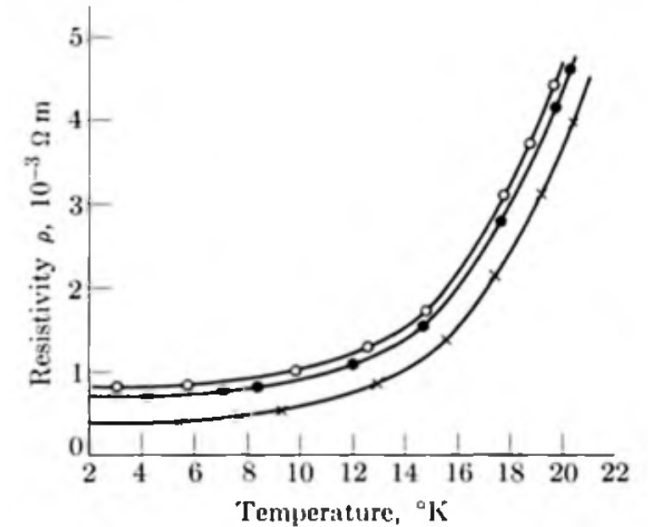
# Scattering probability

- ▶  $\Sigma_s$  = scattering probability per unit length, also called the macroscopic scattering cross section
- ▶ The conduction electrons move with a velocity very close to that corresponding to the Fermi energy. Designating this velocity by  $v_F$ , we have that  $P_s = v_F \Sigma_s$  and  $\tau = 1/v_F \Sigma_s$
- ▶  $\Sigma_s$  is given by the macroscopic cross section due to the impurities  $\Sigma_{s,i}$  and the one due to the lattice vibrations  $\Sigma_{s,v}$
- ▶ Therefore we can write the resistivity of the metal as

$$\rho = \frac{1}{\sigma} = \frac{m^* v_F}{n e^2} (\Sigma_{s,i} + \Sigma_{s,v}) = \rho_i + \rho_v$$

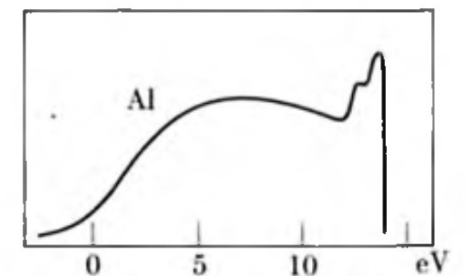
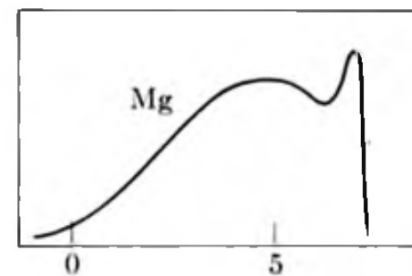
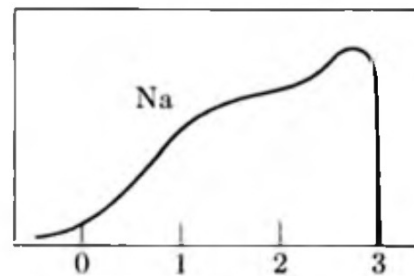
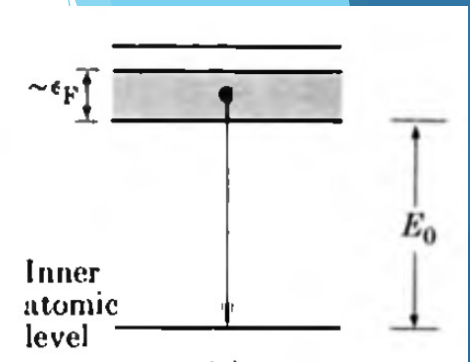
- ▶  $\rho_i$  is the resistivity of the metal due to the impurities and therefore is essentially temperature independent (but varies from one specimen to another), and
- ▶  $\rho_v$  is the resistivity due to thermal vibrations; increases with the temperature and is the same for all specimens of the same metal.

Resistivity of three specimens of sodium with different impurities



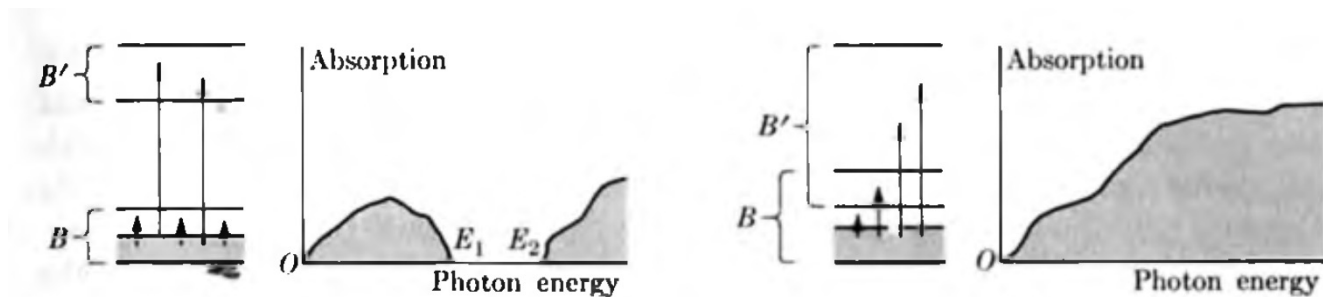
# Radiative Transition in solids

- ▶ X-ray emission in solids takes place when, for example, an electron in the uppermost band undergoes a transition into a lower-level band where a vacant state exists.
- ▶ These vacant states are produced by electron bombardment or by absorption of radiation.
- ▶ The electron making the transition can start from any of the possible energy levels in the uppermost band, and therefore the energy of the emitted photons has a spread of the order of  $E_F$  (that is, the photons have energies between  $E_0$  and about  $E_0 - E_F$ ).
- ▶ A sharp drop of the intensity obviously occurs for  $E_F$



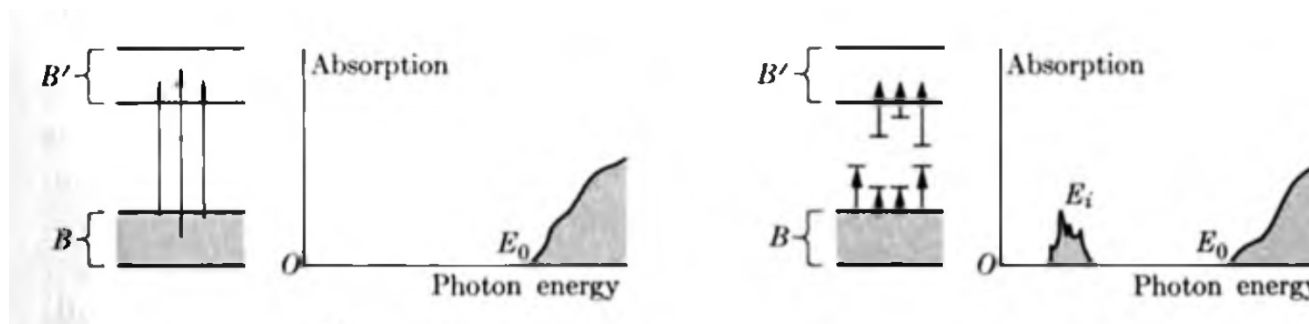
# Absorption

- ▶ Electrons in B can be excited into nearby empty states in the same band when they absorb photons with energies from zero up to the energy required to reach the top of the band.
- ▶ The other photons that can be absorbed are those that take an electron from B into B'.
- ▶ If the bands B and B' overlap, no energy gap exists and a continuous absorption spectrum results.



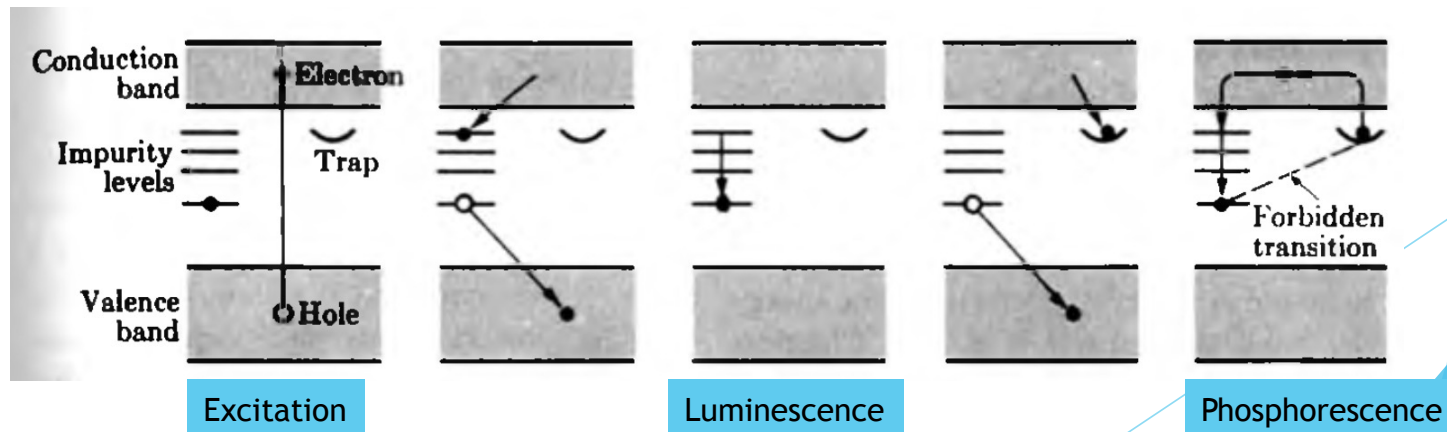
# Absorption

- ▶ In the case of an insulator, only transitions from the valence band  $B$  into the conduction band  $B'$  are possible. Therefore, to induce transitions, the photons must have a minimum energy of a few eV.
- ▶ This would also be the case for semiconductors, except that due to the smallness of their energy gap, some electrons occupy band  $B'$
- ▶ Lattice defects, mainly impurities, have important consequences. They introduce new energy levels, which may fall in the energy gap. Electron transitions into these energy levels allow absorption of photons of much lower energies than needed to go from  $B$  to  $B'$



# Luminescence

- ▶ When the electrons in atoms, molecules, or solids are excited by some means there are several processes which compete to bring about deexcitation
- ▶ In some instances the favored process is radiative transition and the substance glows when it is illuminated with radiation of the proper wavelength, or is excited by some other means.
- ▶ Substances having this property are called luminescent. Luminescence in solids is closely related to impurities and lattice defects.



# Questions

- What defines the type of solids?
- How are bands formed?
- What are the limitations of the free-electron model?
- What is the difference between conductors, semiconductors and insulators?
- How can we describe the electrical conductivity?
- How can the Fermi energy and the band width be measured experimentally?
- What are the phenomena of luminescence and phosphorescence?



# Reference

- ▶ Chapter 6 from Alonso-Finn “Fundamental University Physics. III Quantum and Statistical Physics”

