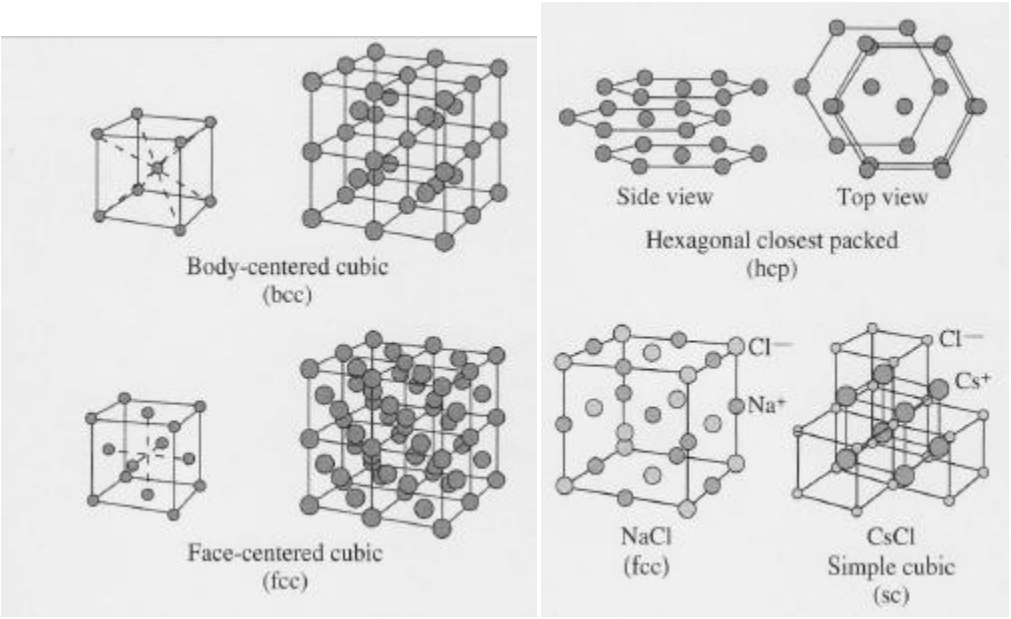
PH102, 2014W, Lecture Notes: February 13, Thurs, Class 12
Solid State: Crystals, Energy Bands, and Conduction

Crystalline Solids

- A large number of atoms are bonded together to create structures of macroscopic scale.
- Crystal lattice is defined as "a structural unit that repeats to fill space without gap and without overlap."
- To fill three dimensional space, there are only 14 possible lattice types, some of which are shown below.

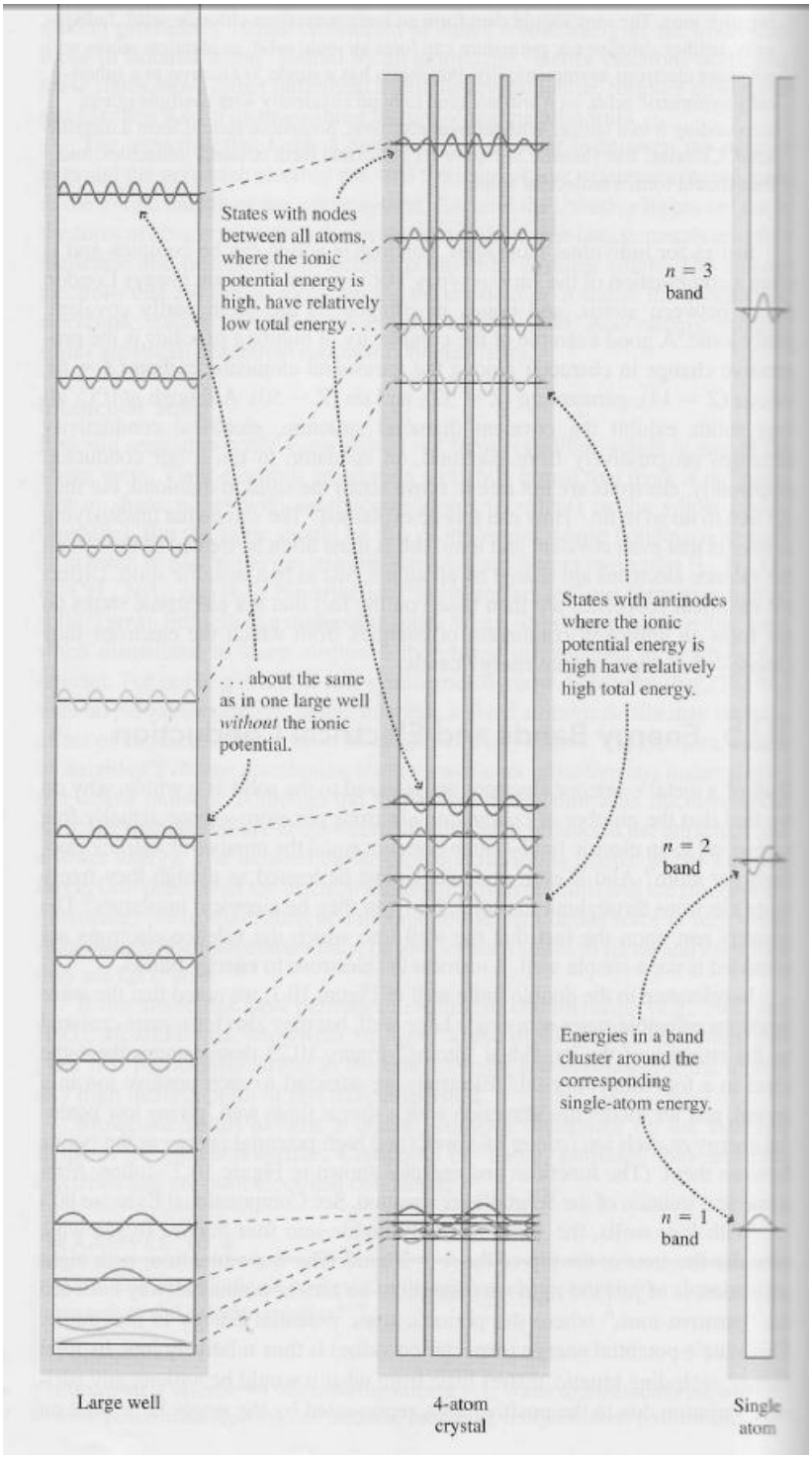


Another way of categorizing solids is to use what type of bonding is involved in solids:

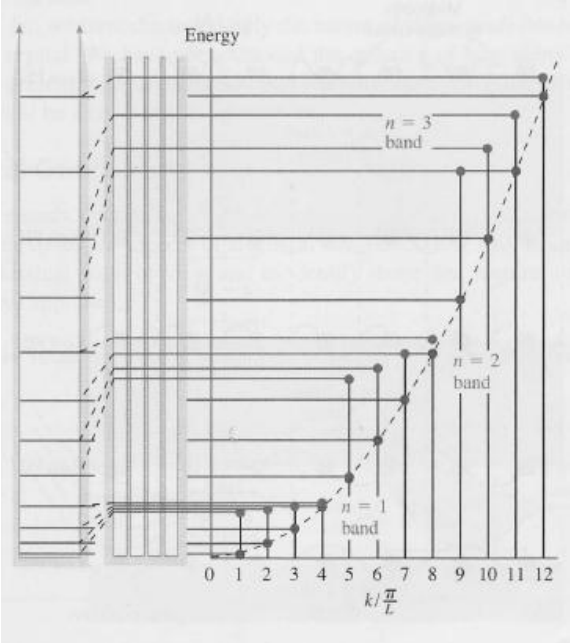
- **Molecular solid** is formed by the Van der Waals force between molecules due to fluctuations that create instantaneous dipole moments for molecules to form weak bonds. Molecules with permanent dipole moments such as water can form a stronger bond among molecules than those with no permanent dipole moments.
- **Ionic solid** is formed by the Coulomb force between positively and negatively charged ions. Ionic solid is relatively hard with high melting points. It is a poor conductor because electrons are not free. Ionic bond lacks directionality. Ionic solid does not form among elements.
- **Covalent solid** is formed by sharing electrons through covalent bonds. The crystalline lattice is strong, has high melting points, and assumes a geometry determined by the directionality of the covalent bonds. It is a poor conductor because all electrons are locked into the covalent bonds. It is not malleable.
- **Metallic solid** forms through sharing electrons by all ions and electrons are free to move around within the solid. Therefore, metallic solid is a good conductor and it is malleable. Metallic solid forms a lattice structure, but not as strong as a lattice structure formed by covalent bonds.

Energy Bands

- The shape of wave functions for a 4 atom crystal is similar to that of one single atom large well, but four energy states of the large single well are grouped into an energy band in a 4 atom crystal.
- Each band corresponds to one of the energy levels allowed in a single atom case. In each band, there are 4 possible energy states.
- Since the potential energy between positive ions and free electrons are electrostatic, the potential energy will be relatively lower when the electron and the ion are closer, that is nodes of the wave function appear between ions. Potential energy can be relatively higher when electrons are farther away from the ions, that is, where antinodes of the wave function appear between the ions. These create energy band gaps.



- If we plot this relationship in the $Energy\ (E)$ and wave number (k) space, we can draw the figure on the right. Since $E = \frac{\hbar^2}{2m}k^2$, the E plot over k looks like a parabolic curve, but k is quantized by the relationship: $k = \frac{n\pi}{L}$. The four energy levels are also grouped into an energy band.

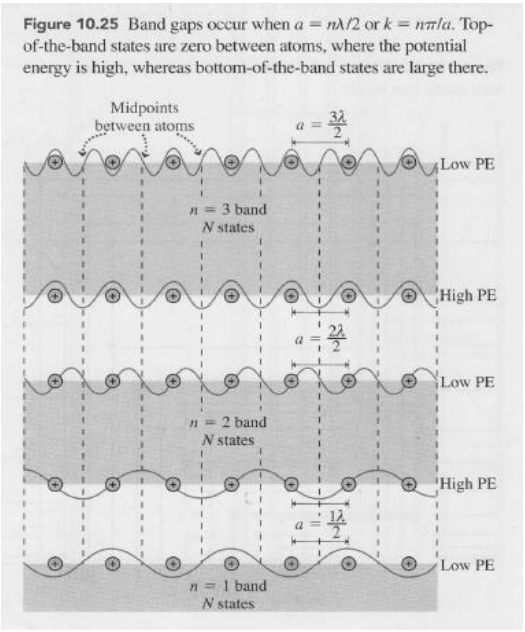


Expanding this analogy to an N-atom crystal of which spacing between two neighboring ions is a.

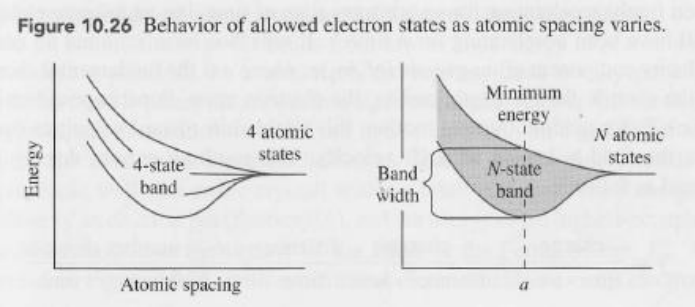
- There will be energy bands.
- Each energy band corresponds to one of the energy levels allowed in a single atom.
- Each energy band consists of N states.
- The energy gap occurs at $k = \frac{n\pi}{a}$. Since $k = \frac{2\pi}{\lambda}$, thus the energy gap occurs whenever

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

$$a = \frac{n}{2}\lambda$$



- If N is large, then the energy band can be considered as a continuum of energies as shown in the diagram below. The width of the band depends on the spacing between ions (thus depends on the crystal structure). As spacing, a, decreases, the band width increases. If two ions are getting closer than the most stable spacing, then the energy increases. Therefore, a crystal will form when the energy becomes minimum, see that the energy is minimum at spacing a in the diagram on the right.



- For an N-atom one dimensional crystal, energy bands over k are shown in the figure on the right.
- In all solids, electrons fill energy bands from low to high according to the Exclusion Principle.

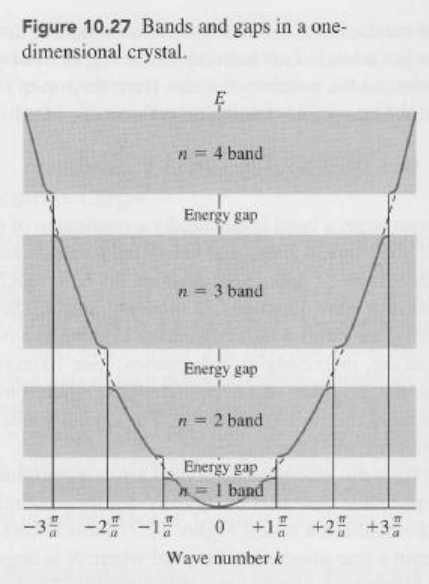
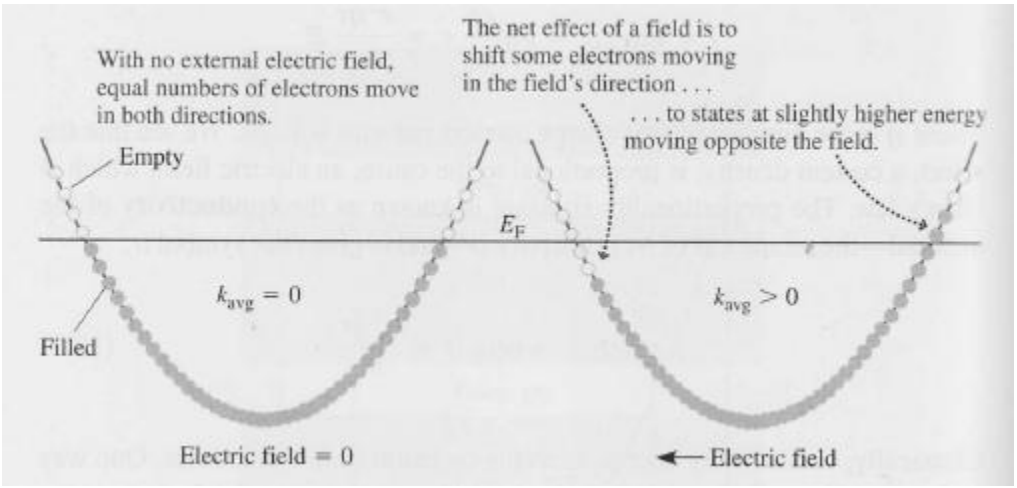


Figure 10.27 Bands and gaps in a one-dimensional crystal.

Conduction

- In a conductor, the top most band is only partially filled and this is where conduction electrons are. Lower full bands do not participate in conduction. Conduction electrons move freely inside the entire crystal with no ionic potential.
- Electrons in a conductor will fill up the energy levels upto Fermi Energy (E_F, the highest occupied energy state measured from the bottom of the band)
- When there is no external electric field, an equal amount of electrons move up and down the E_F state, creating no net momentum $k_{avg} = 0$. When there is an external electric field, electrons will move opposite to the direction of the electric field, therefore, increasing momentum, $k_{avg} > 0$. If all electrons in the conduction energy band move to the next available energy states, the net shift will occur among the highest-energy states.



A more realistic ionic potential features Coulomb potential as shown on the right. In this case, electrons in the low energy states do not combine to energy bands. Only valence electrons at higher energy states form energy bands.

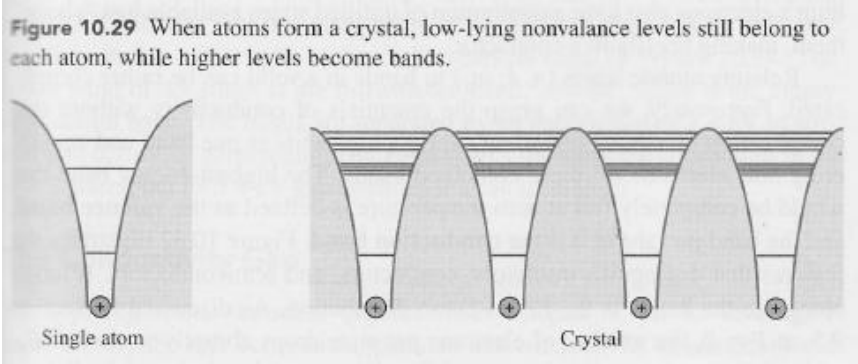


Figure 10.29 When atoms form a crystal, low-lying nonvalance levels still belong to each atom, while higher levels become bands.

Drift Velocity and Conductivity

- Classically, electrons in a conductor move freely until they collide with positive ions in a lattice. Collisions will slow down electrons, thus providing resistance to conduction. After collision the electron will change direction and continue to move in that direction until the next collision. As a result, when there is no electric field, the net velocity due to collisions will be zero.
- When an electric field is present, the electrons gain, between collisions, a component of velocity opposite to the field. An electron under an external electric field will accelerate for a time until the next collision, i.e. collision time, τ. The drift velocity refers to the velocity acquired by a charge carrier under an external electric field. In this case,

$$v_{drift} = \frac{eE}{m_e}\tau$$

- Current density j

$$j \equiv \frac{charge}{time \text{ x } area} = \frac{charge}{distance \text{ x } area}\frac{distance}{time} = \frac{e \text{ x } No.of\ electrons}{volume}v_{drift} = eNv_{drift}$$

$$j = eN\frac{eE}{m_e}\tau = e^2\frac{N\tau}{m_e}E = \sigma E$$

Where $\sigma\ (conductivity) = e^2\frac{N\tau}{m_e}$

Example:

The density of Silver = 10.5 x $10^3\ kg/m^3$

(1) Approximate atomic separation

$$density = \frac{mass\ (= N \text{ x } mass\ of\ one\ Silver\ atom)}{volume\ (= a^3)}$$

$$a = \left(\frac{N \text{ x } mass\ of\ one\ Silver\ atom}{density}\right)^{\frac{1}{3}} = 2.57 \text{ x } 10^{-10}\ m$$

(2) Velocity of electrons associated with E_F

$$E_F = \frac{1}{2}mv^2$$

$$v = \sqrt{\frac{2E_F}{m}} = 1.39\ x\ 10^6\ m/s$$

Collision time

$$\tau = \frac{a}{v} = 1.85 \text{ x } 10^{-16}\ sec$$

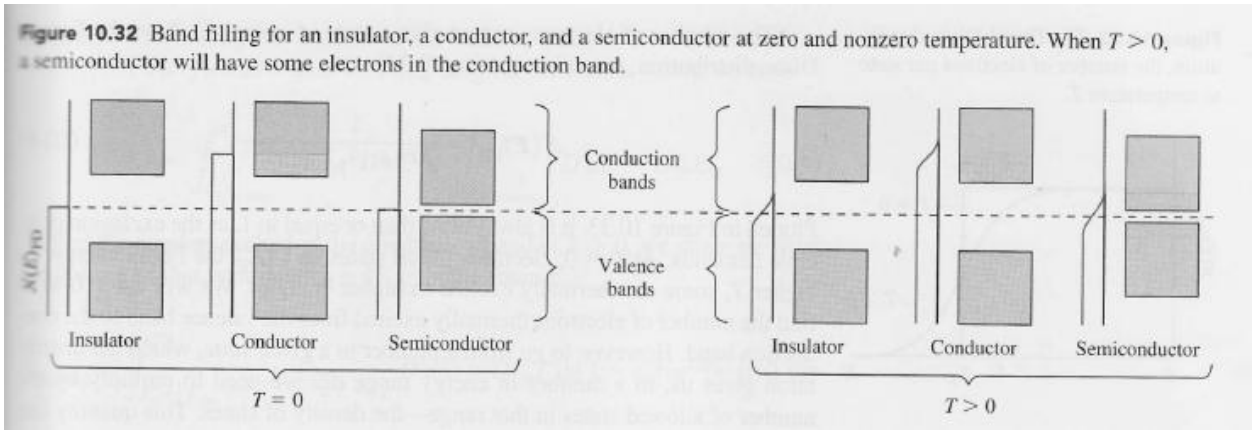
(3) Conductivity

$$\sigma = e^2\frac{N\tau}{m_e} = 3\ x\ 10^5\ \Omega^{-1}m^{-1}$$

This conductivity value is 1/100 of the actual value. This means that conduction electrons in silver passes more than a few silver ions before colliding with a silver ion.

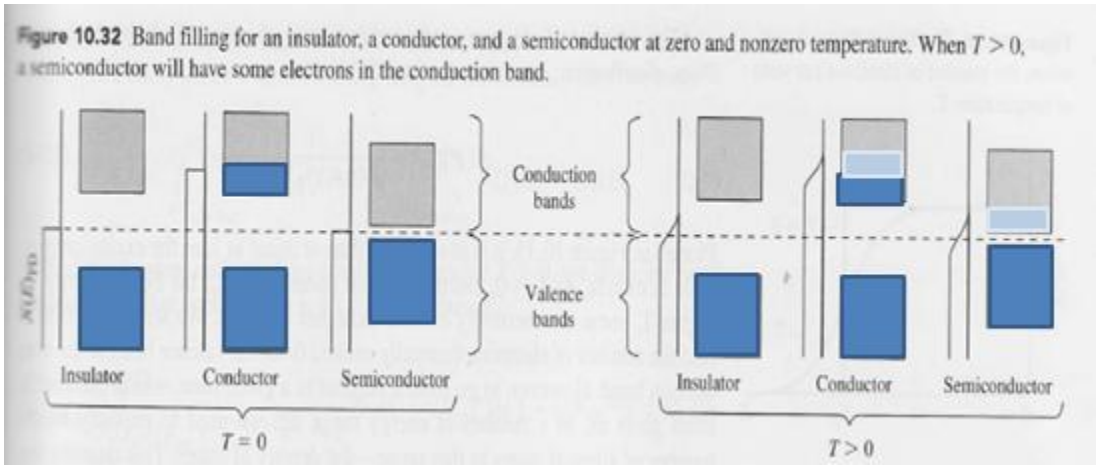
Band structures for conductor, insulator, and semiconductor

- Valence band: the highest-energy band that would be completely full at zero temperature
- Conduction band: the band that is above the valence band.
- For conductors, the conduction band is not completely filled, so that conduction electrons can freely move when an external electric field is present.
- For insulators, the valence band is completely full and the conduction band is empty. There is a large gap between the conduction and the valence bands, prohibiting electrons move from the valence band to the conduction band under an ordinary electric field.
- For semiconductors, the conduction band is empty and the valence band is full but the band gap is small so that electrons can move at ordinary temperatures. Conventionally, when the band gap is smaller than 2eV, the material is called semiconductor.



- Li is a conductor with one 2s electron per atom. The conduction band is half filled.
- Be is also a conductor despite having two 2S electrons per atom because the energy bands for 2s and 2p are overlapped.

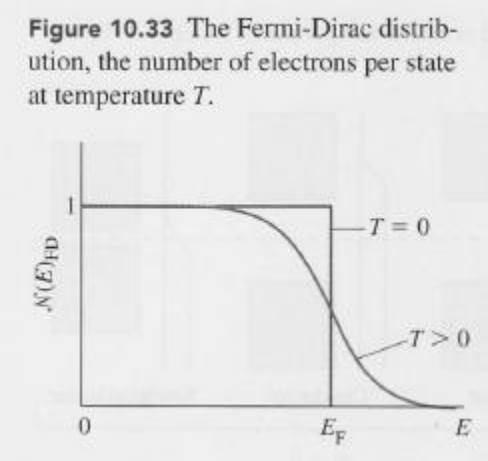
Conduction-Valence Band Gap



As shown in the Figure above, at T=0, there are no electrons in the conduction bands of insulators and semiconductors. The gap between conduction and valence band is much larger for insulators than for semiconductors. Substance with a conduction-valence band gap of lower than

2 eV is considered a semiconductor. The gap for an insulator is much bigger, for example, diamond, an insulator, is 5.4 eV.

At T>0, the occupation number for electrons in a solid changes from the T=0 distribution as shown in the diagram on the right.



$$\mathcal{N}(E) = \frac{1}{e^{(E-E_F)/k_BT} + 1}$$

Let's consider the proportion of electrons that will be excited to be in the conduction band at T>0.

- Consider Density of Energy states $D(E)$ = D (constant)
- The number of electrons in the valence band at T=0:

$$N_{Valence} = \int_{E_{valence-bottom}}^{E_{valence-top}} \mathcal{N}(E)D(E)dE = \int_{E_{valence-bottom}}^{E_{valence-top}} 1 \cdot DdE = D\Delta E_{Valence}$$

- At T>0, the number of electrons that will be excited to be in the conduction band:

$$N_{Excited} = \int_{E_F+\frac{1}{2}E_{gap}}^{\infty} \mathcal{N}(E)D(E)dE$$

$$= \int_{E_F+\frac{1}{2}E_{gap}}^{\infty} \frac{D}{e^{(E-E_F)/k_BT} + 1} dE = Dk_BT\ln(1 + e^{-E_{gap}/2k_BT}) \sim Dk_BTe^{-E_{gap}/2k_BT}$$

Since $e^{-E_F/2k_BT}$ is small and thus $\ln\left(1 + e^{-\frac{E_{gap}}{2k_BT}}\right) \sim e^{-\frac{E_{gap}}{2k_BT}}$

$$\frac{N_{Excited}}{N_{Valence}} = \frac{Dk_BTe^{-E_{gap}/2k_BT}}{D\Delta E_{Valence}} = \frac{k_BT}{\Delta E_{Valence}} e^{-E_{gap}/2k_BT}$$

➔ k_BT at room temperature ~ .026 eV
➔ $\Delta E_{Valence}$ ~ 10 eV
➔ $\frac{k_BT}{\Delta E_{Valence}}$ ~ .0026 eV
➔ Insulator (assuming 5eV): $e^{-E_{gap}/2k_BT} \sim e^{-5/2\cdot.026} \sim e^{-100} \sim 10^{-42}$ → no electrons in the conduction band at the room temperature
➔ Semiconductor (assuming 1 eV): $e^{-E_{gap}/2k_BT} \sim e^{-1/2\cdot.026} \sim e^{-20} \sim 10^{-8}$ → considering the number of electrons is at the order of 10^{23}, a significantly large amount of electrons can be expected in the conduction band of a semiconductor at the room temperature.