

Lecture 10

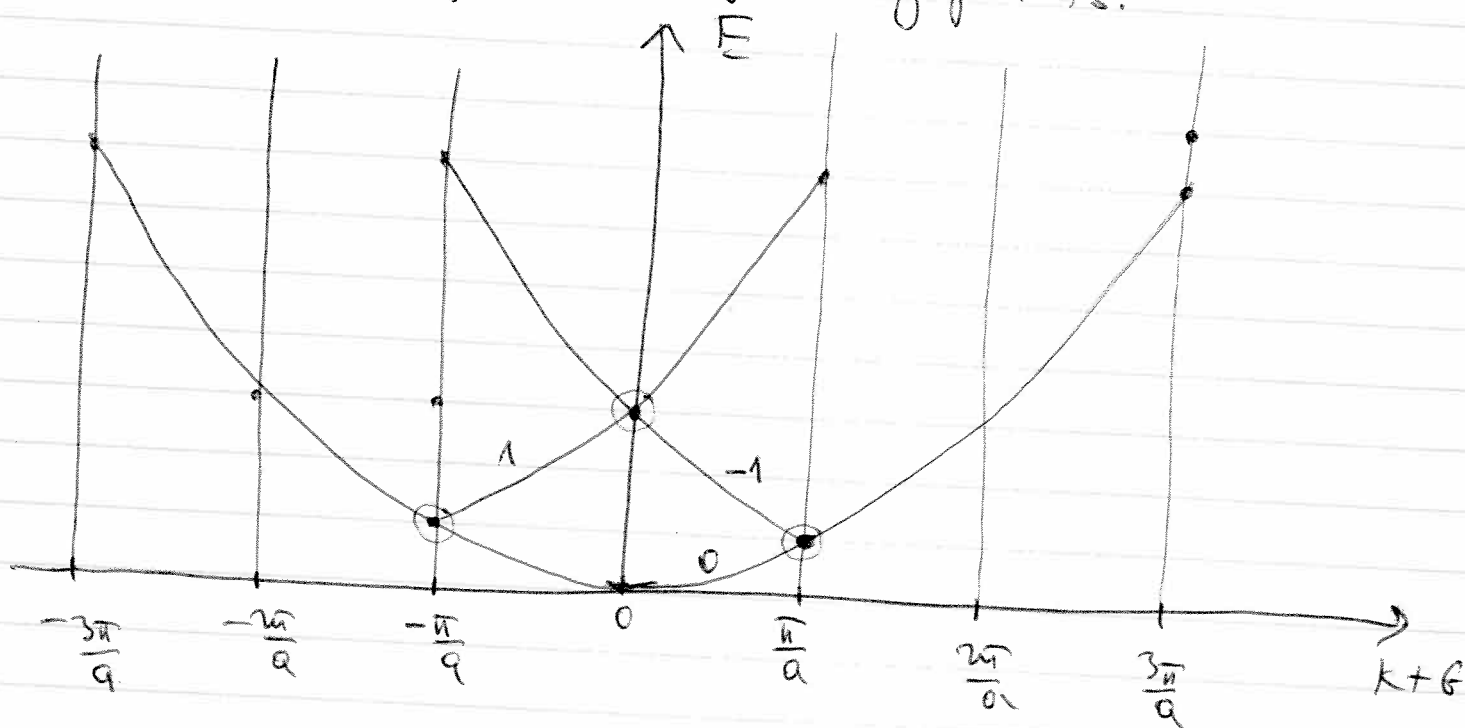
Considering electrons in weak periodic potential...

$$\sum_{G'} H_{GG'} U_k(G') = E U_k(G)$$

$$H_{GG'} = \epsilon_{k+G} \delta_{GG'} + U(G-G')$$

$$\epsilon_{k+G} = \frac{\hbar^2 (k+G)^2}{2m}$$

Weak periodic potential modifies free electron dispersion only near degeneracy points.



Consider the lowest in energy degeneracy point at $k = \frac{\pi}{a}$.

~~At this point~~ At this point the branch corresponding to $G=0$ is degenerate with the branch $G = -\frac{2\pi}{a}$. To see how the free electron dispersion near this point is modified, we need to consider the following

2x2 block of the matrix H_{EE} :

$$H = \begin{pmatrix} \epsilon_{k-\frac{\pi}{a}} & U^*\left(\frac{\pi}{a}\right) \\ U\left(\frac{\pi}{a}\right) & \epsilon_k \end{pmatrix}$$

The rest of the matrix involves other branches of the free-electron dispersion, which are far away in energy from ϵ_k (far away compared to U).

Diagonalize H :

$$\begin{aligned} \det(H - IE) &= \det \begin{pmatrix} \epsilon_{k-\frac{\pi}{a}} - E & U^*\left(\frac{\pi}{a}\right) \\ U\left(\frac{\pi}{a}\right) & \epsilon_k - E \end{pmatrix} = \\ &= \left(\epsilon_{k-\frac{\pi}{a}} - E \right) \left(\epsilon_k - E \right) - \left| U\left(\frac{\pi}{a}\right) \right|^2 = \\ &= E^2 - E \left(\epsilon_k + \epsilon_{k-\frac{\pi}{a}} \right) + \epsilon_k \epsilon_{k-\frac{\pi}{a}} - \left| U\left(\frac{\pi}{a}\right) \right|^2 = 0 \end{aligned}$$

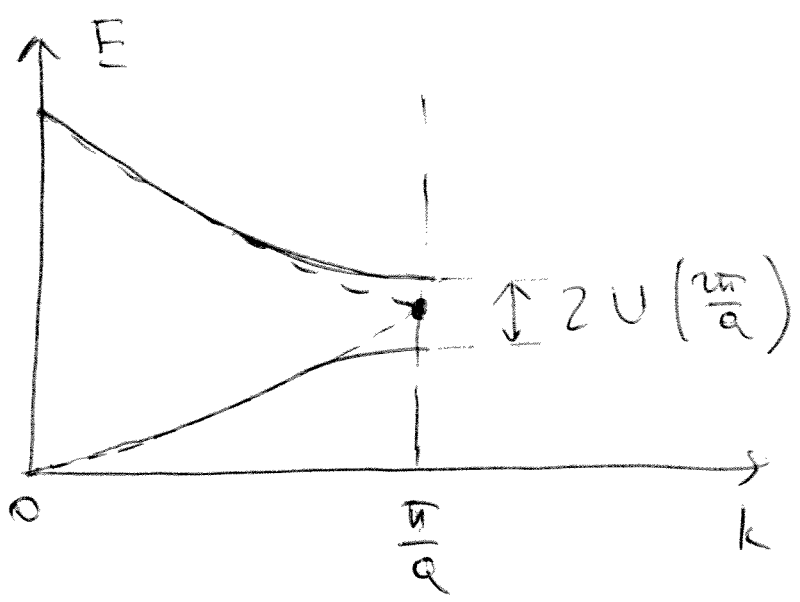
The solutions are:

$$E_{k\pm} = \frac{\epsilon_k + \epsilon_{k-\frac{\pi}{a}}}{2} \pm \sqrt{\left(\frac{\epsilon_k - \epsilon_{k-\frac{\pi}{a}}}{2} \right)^2 + \left| U\left(\frac{\pi}{a}\right) \right|^2}$$

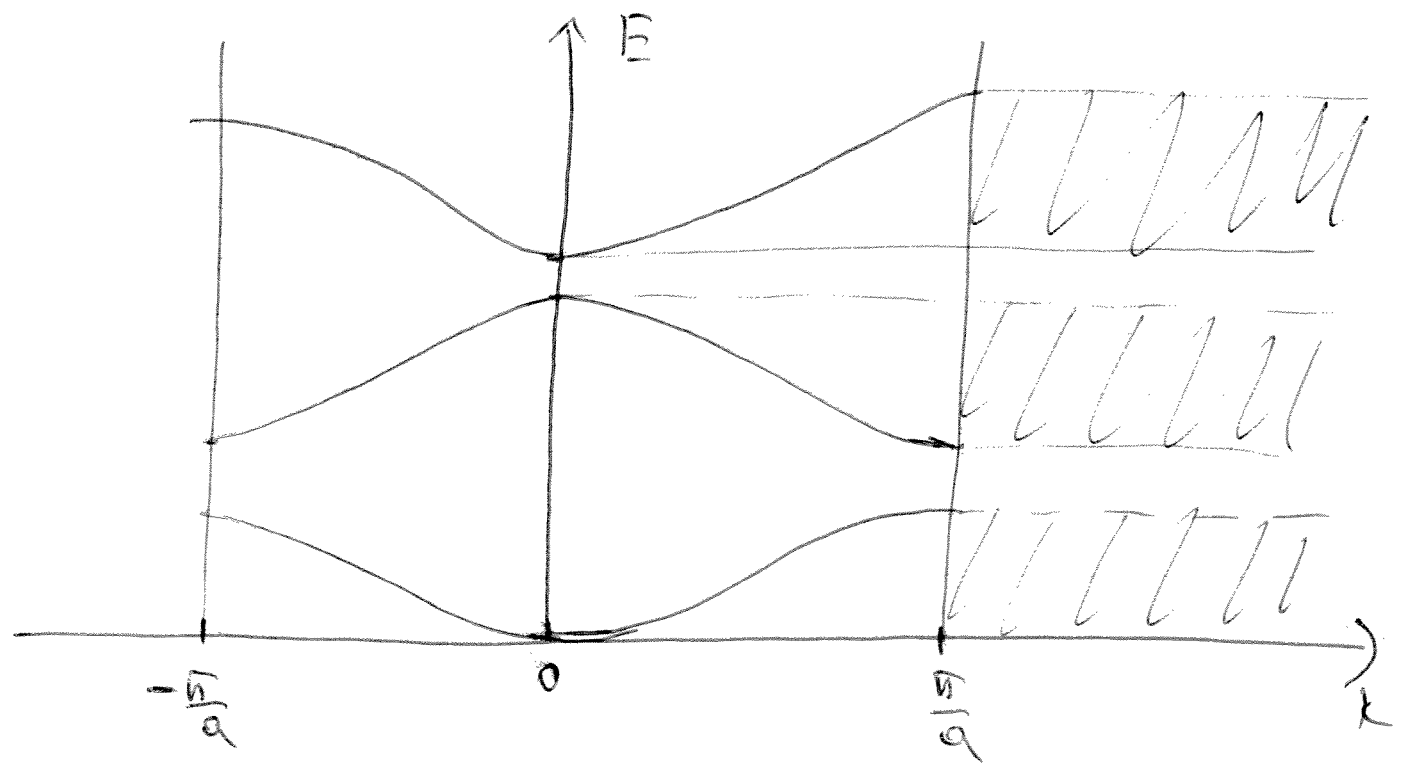
Exactly at the degeneracy point $k = \frac{\pi}{a}$ we have:

$$\epsilon_k = \epsilon_{\frac{\pi}{a}} = \epsilon_{\frac{\pi}{a} - \frac{\pi}{a}}$$

$$E_{\frac{\pi}{a} \pm} = E_{\frac{\pi}{a}} \pm |U(\frac{\pi}{a})| \text{ - the degeneracy is lifted.}$$



This lifting of degeneracy happens at every degeneracy point. Thus the dispersion of electron in periodic potential has the following general form:



Allowed values of E form bands.
Intervals of forbidden values form bandgaps.

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Thus the ~~spectrum~~ energy spectrum of the electrons is drastically modified by the periodic potential.

Instead of the continuous dispersion $E_k = \frac{\hbar^2 k^2}{2m}$ of free electrons, the dispersion has the form of bands E_{nk} , where the crystal momentum \vec{k} is restricted to the first BZ. Within a given band n , E_{nk} is a continuous function of \vec{k} . But different bands are generally separated by band gaps - intervals of forbidden values of the energy.

The eigenstates of the electrons have the form:

$$\Psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} U_{n\vec{k}}(\vec{r})$$

The similarity of these eigenstates to plane waves explains why electrons are (almost) not scattered by periodic potential. They are only scattered by imperfections in it - this is why metals have high ~~more~~ conductivities.

The appearance of bands in the spectrum of the electrons also explains the existence of insulators.

Generally, it is ^{often} convenient to represent the electronic energy spectrum by the density of states function, instead of drawing it as a function of the BZ momentum \vec{k} (can get very complicated in 3D).

I introduced the density of states function $g(\epsilon)$ as a way to convert Brillouin integrals over momentum to integrals over energy.

Suppose we want to calculate the electron density:

$$n = 2 \int \frac{d^3k}{(2\pi)^3} \sum_n n_F(E_{nk})$$

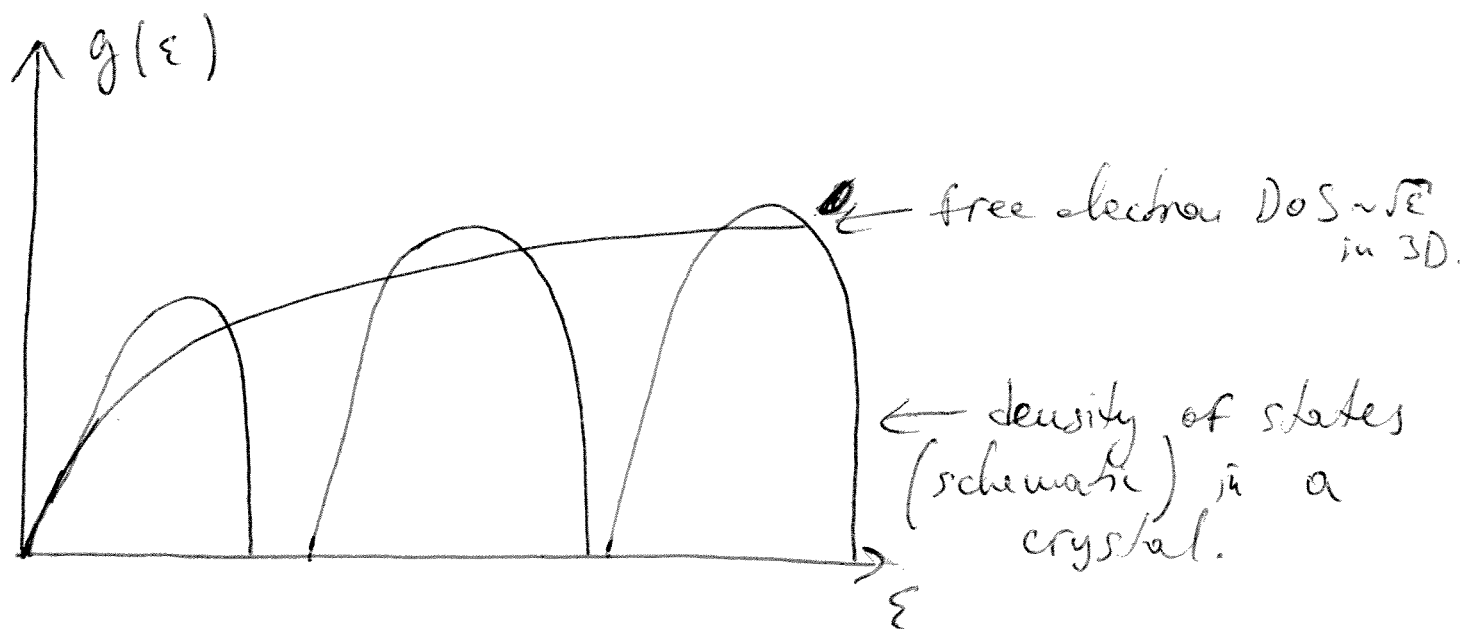
The integral over k is now restricted to the first BZ.

~~Introduce~~ Introduce density of states $g(\epsilon)$ as:

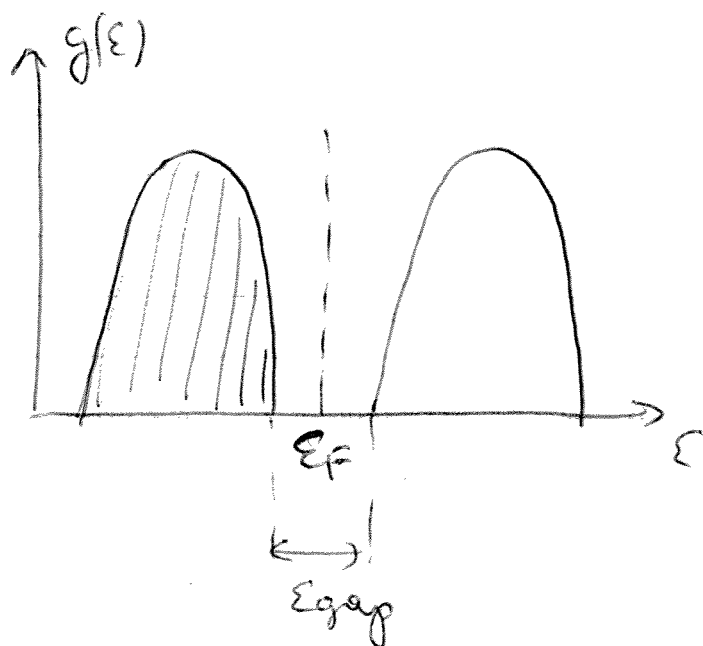
$$g(\epsilon) = 2 \int \frac{d^3k}{(2\pi)^3} \sum_n \delta(\epsilon - E_{nk})$$

Then we have:

$$n = \int d\epsilon g(\epsilon) n_F(\epsilon)$$



Assume we have some number of bands completely filled, while the rest are completely empty;

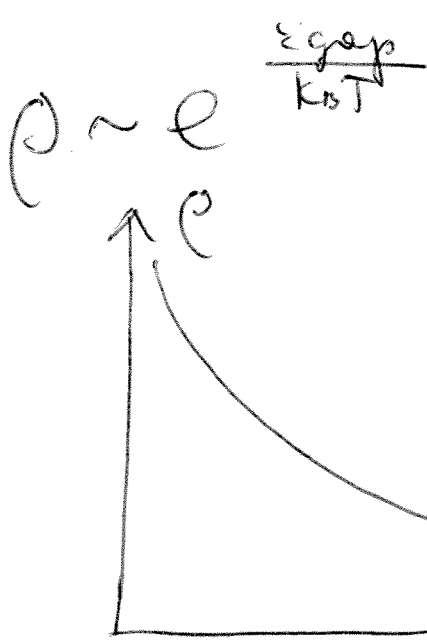


This means that the Fermi level is somewhere in the gap between the highest filled and lowest unfilled band. How would such a solid respond to electromagnetic field?

To have any response, ~~we~~ we need to change the occupation of the energy levels (accelerate the electrons). But in the above situation this is impossible ~~because~~ due to Pauli principle, unless electrons are transferred to unfilled band. This can only happen if the electromagnetic field is strong enough to overcome the bandgap. Thus such materials, which have some number of completely filled bands, while the rest are completely empty, are insulators.

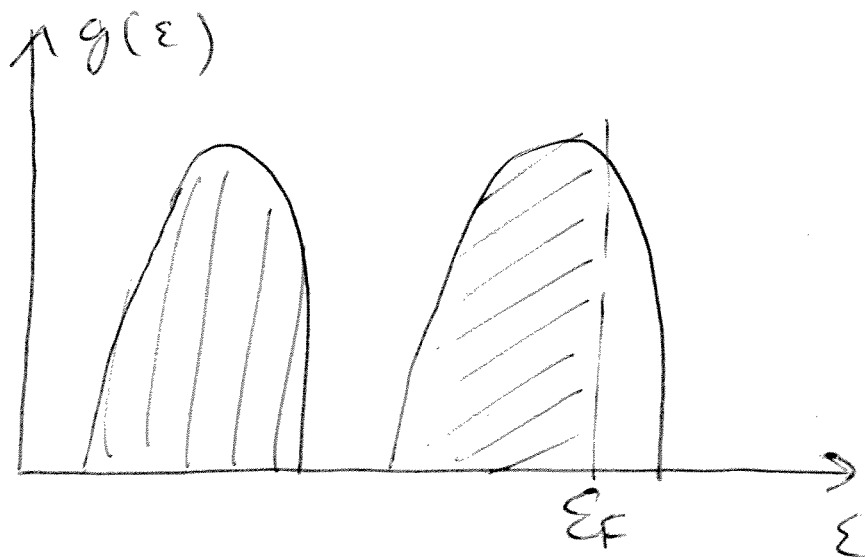
At finite temperature, there will always be some $\frac{\epsilon_{\text{gap}}}{k_B T}$ occupation in the ~~the~~ 'upper band', proportional to $e^{-\frac{\epsilon_{\text{gap}}}{k_B T}}$.

Correspondingly insulator will always have a finite resistivity at nonzero temperature:



Characteristic feature of any insulator is a ~~the~~ divergence of the resistivity as $T \rightarrow 0$.

Now consider a situation when ~~there~~ there is a number of filled bands, but ~~the~~ one band is not completely filled - Fermi level is within the band:



Now an arbitrarily weak electric field will be able to change occupation of different crystal momentum states and thus accelerate the electrons.

Thus the materials with incompletely filled band are

generally metals (but can be insulators due to electron-electron interactions - Mott insulators).

~~Can we tell just by looking at the~~

How can we tell from the crystal structure whether a given material is a metal or an insulator?

Consider a particular band $E_{\vec{k}}$. The number of ~~allowed~~ states in a band is equal to twice (due to spin) the number of wavevectors in the first Brillouin zone.

$$\vec{k} = k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3$$

$$k_i = \frac{2\pi n_i}{N_i}, \quad N_i - \text{number of unit cells in the basis direction } \vec{a}_i.$$

First BZ: $-\frac{N_i}{2} \leq n_i < \frac{N_i}{2} \Rightarrow$ the number of ~~allowed~~ different n_i 's in the first BZ is N_i .

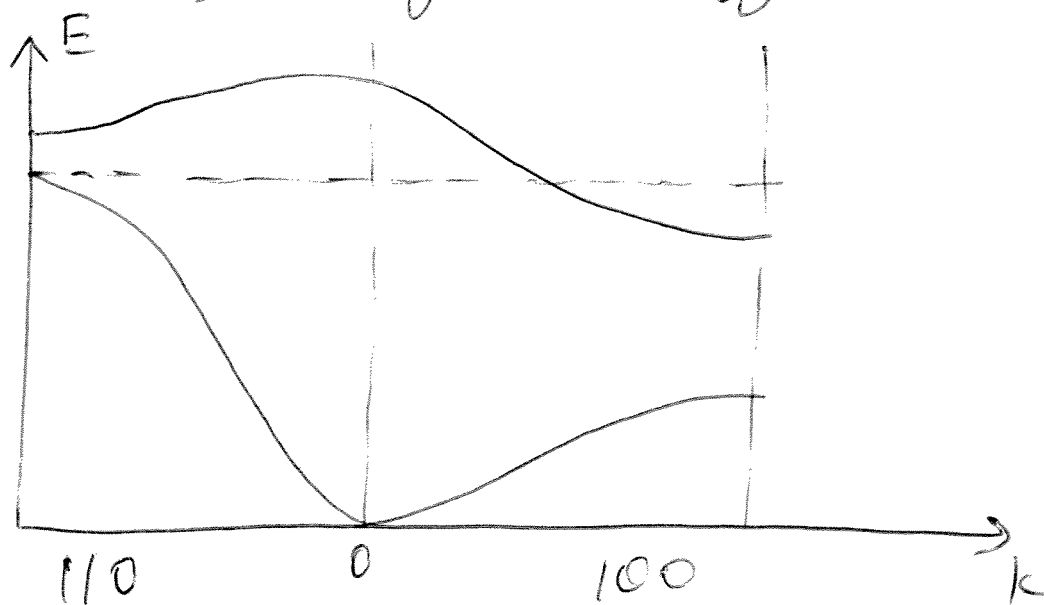
The total number of ~~all~~ states in a single band is: $2N_1 N_2 N_3 = 2N$, where N is the total number of unit cells in the sample. Thus the total number of states per unit cell per band is:

$$\frac{2N}{N} = 2$$

This solid with an odd number of electrons per unit cell is always (aslectry electron-electron interactions) a metal. Since one band will always end up not completely filled.

Solids with even number of electrons per unit cell are often insulators, but not always.

The reason is that in dimensions higher than one, bands may overlap in energy:



Then electrons may ~~occupy~~ ^{occupy} ~~several~~ states of the same energy in different bands and ~~both~~ ^{several} bands may end up not completely filled.

Examples:

1. Monovalent elements - one electron in the outer shell of the atom: Li, Na, K, Rb, Cs - all metals.

Noble metals: Cu, Ag, Au - also one electron in the outer ~~and~~ shell.

2. Solids with 3 electrons per unit cell: Al, Ga, In, Tl - all metals.

3. Most divalent elements (two valence electrons per unit cell): Sr, Ba are not insulators due to band overlap.

4. Trivalent elements (4 valence electrons per unit cell) can be either metals or semiconductors.

C, Si, Ge are semiconductors.

Pb is a metal.

Sn (Pb) can be either metal or semiconductor - can exist in 2 different phases with different crystal structure.

5. Transition elements: Cr, Mn, Fe, Co, Ni -

all metals, although may have either even or odd # of valence electrons per unit cell - this is due to an unfilled d-shell, which results in s-d band mixing.