

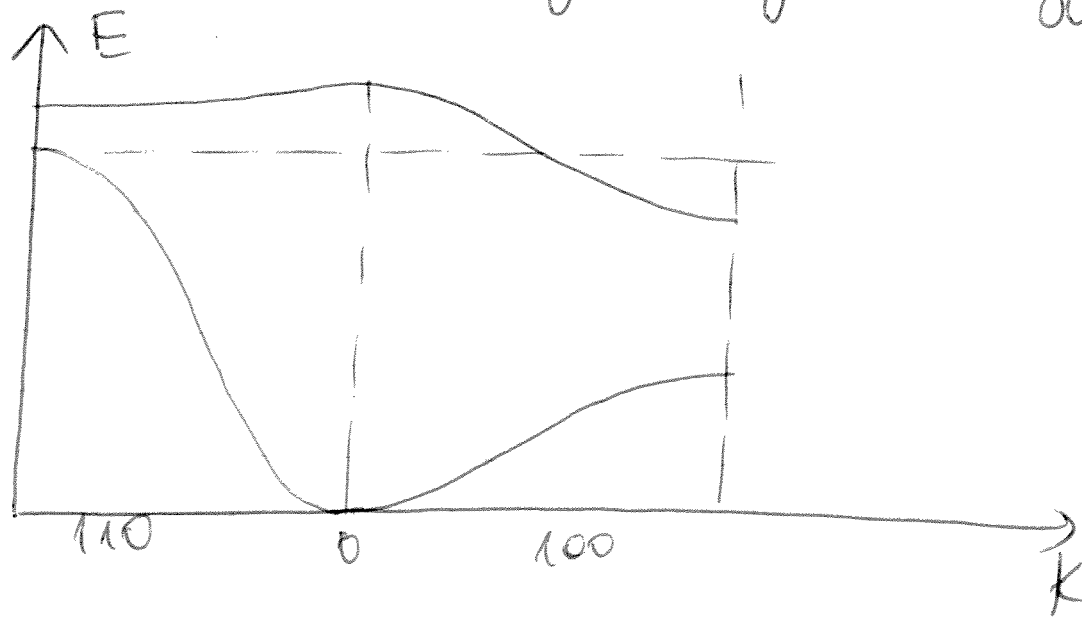
Lecture 11

Continue classification of solids from band theory.

Number of states per unit cell per band = 2.

Odd # of electrons per unit cell \Rightarrow always some unfilled bands \Rightarrow metal (neglecting electron-electron interactions).

Even # of electrons per unit cell : often insulators but not always. The reason that in dimensions higher than one bands may overlap in energy.



Then electrons may occupy states at the same energy in different bands and several bands may end up not completely filled.

Examples

1. Monovalent elements - one electron in the outer shell of the atom - crystal structure with one atom per unit cell \Rightarrow one electron per unit cell.
Alkali metals:

Li, Na, K, Rb, Cs - all metals.

Noble metals: Cu, Ag, Au.

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

3. Divalent elements (two electrons per unit cell):

Be, Mg, Ca, Sr, Ba - metals due to band overlap.

4. Tetravalent elements (4 electrons per unit cell):

C, Si, Ge - semiconductors.

Pb - 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 unfilled d-shell.

Start the tight-binding method.

We have obtained a description of bands in solids starting from free electrons and adding periodic crystal potential as weak perturbation.

It is useful and illuminating to consider the opposite limit: consider solid as a collection of atoms with the atomic wavefunctions of valence electrons barely overlapping.



Assume that every atom has 1 valence electron in an s-orbital.

Let $\psi(\vec{r} - \vec{R})$ be the atomic wavefunction of the valence electron for an atom at position \vec{R} .

We can construct Bloch functions directly out of $\psi(\vec{r} - \vec{R})$ in the following way:

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N} V(\vec{k})} \sum_{\vec{R}} \psi(\vec{r} - \vec{R}) e^{i\vec{k} \cdot \vec{R}}$$

Here N is the total number of atoms in the crystal, \vec{k} - momentum in the first BZ, and $V(\vec{k})$ is a normalization factor.

How do we see that this is a Bloch function?

The general form of a Bloch function is:

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

$$\text{Here } U_{\vec{k}}(\vec{r} + \vec{R}) = U_{\vec{k}}(\vec{r}).$$

Rewrite our Bloch function in this form:

$$\Psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{NV(\vec{k})}} \sum_{\vec{R}} \psi(\vec{r} - \vec{R}) e^{-i\vec{k} \cdot (\vec{r} - \vec{R})} e^{i\vec{k} \cdot \vec{r}}$$

$$U_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{NV(\vec{k})}} \sum_{\vec{R}} \psi(\vec{r} - \vec{R}) e^{-i\vec{k} \cdot (\vec{r} - \vec{R})}$$

Check that this is a periodic function.

$$U_{\vec{k}}(\vec{r} + \vec{R}) = \frac{1}{\sqrt{NV(\vec{k})}} \sum_{\vec{R}_1} \psi(\vec{r} - \vec{R}_1 + \vec{R}) \cdot e^{-i\vec{k} \cdot (\vec{r} - \vec{R}_1 + \vec{R})} =$$

change summation variable $\vec{R}_1 \rightarrow \vec{R}_1 + \vec{R}$

$$= \frac{1}{\sqrt{NV(\vec{k})}} \sum_{\vec{R}_1} \psi(\vec{r} - \vec{R}_1) e^{-i\vec{k} \cdot (\vec{r} - \vec{R}_1)} = U_{\vec{k}}(\vec{r})$$

Calculate normalisation of the ~~Block~~ Bloch function:

$$\int d\vec{r} |\Psi_k(\vec{r})|^2 = \frac{1}{NV(\vec{k})} \int d\vec{r} \sum_{\vec{R}, \vec{R}_1} \Psi^*(\vec{r}-\vec{R}) \cdot$$

$$\Psi(\vec{r}-\vec{R}_1) e^{-i\vec{k} \cdot (\vec{R}-\vec{R}_1)}$$

Assume that the overlap between the atomic wavefunctions is only nonzero when $\vec{R} = \vec{R}_1$ and when \vec{R} and \vec{R}_1 are nearest-neighbors in the crystal lattice:

$\vec{R}_1 = \vec{R} + \vec{\lambda}$, where $\vec{\lambda}$ is a nearest-neighbor vector.

~~Then we obtain:~~

Then we obtain:

$$\int d\vec{r} |\Psi_k(\vec{r})|^2 = \frac{1}{NV(\vec{k})} \left[\sum_{\vec{R}} \int d\vec{r} |\Psi^*(\vec{r}-\vec{R})|^2 + \right.$$

$$\left. + \sum_{\vec{R}, \vec{\lambda}} \int d\vec{r} \Psi^*(\vec{r}-\vec{R}) \Psi(\vec{r}-\vec{R}-\vec{\lambda}) e^{i\vec{k} \cdot \vec{\lambda}} \right]$$

$\int d\vec{r} |\Psi(\vec{r}-\vec{R})|^2 = 1$ - atomic wavefunctions are normalized.

$\int d\vec{r} \Psi^*(\vec{r}-\vec{R}) \Psi(\vec{r}-\vec{R}-\vec{\lambda})$ is independent of \vec{R}

due to translational invariance of the crystal
and is also independent of $\vec{\lambda}$ if ~~the crystal is~~
 $\psi(\vec{r}-\vec{R})$ is an s-orbital state.

$$\text{let } \int d\vec{r} \psi^*(\vec{r}-\vec{R}) \psi(\vec{r}-\vec{R}-\vec{\lambda}) = \alpha$$

$$\int d\vec{r} |\psi_{\vec{k}}(\vec{r})|^2 = \frac{1}{N V(\vec{k})} \left[N + \alpha N \sum_{\vec{\lambda}} e^{i\vec{k} \cdot \vec{\lambda}} \right] =$$

~~$$\frac{1}{V(\vec{k})} \left[1 + \alpha \sum_{\vec{\lambda}} (e^{i\vec{k} \cdot \vec{\lambda}} + e^{-i\vec{k} \cdot \vec{\lambda}}) \right] =$$~~

$$= \frac{1}{V(\vec{k})} \left[1 + \frac{\alpha}{2} \sum_{\vec{\lambda}} (e^{i\vec{k} \cdot \vec{\lambda}} + e^{-i\vec{k} \cdot \vec{\lambda}}) \right] =$$

$$= \frac{1}{V(\vec{k})} \left[1 + \alpha \sum_{\vec{\lambda}} \cos(\vec{k} \cdot \vec{\lambda}) \right] = 1$$

$$V(\vec{k}) = 1 + \alpha \sum_{\vec{\lambda}} \cos(\vec{k} \cdot \vec{\lambda})$$

when α is small $V(\vec{k})$ is almost 1.