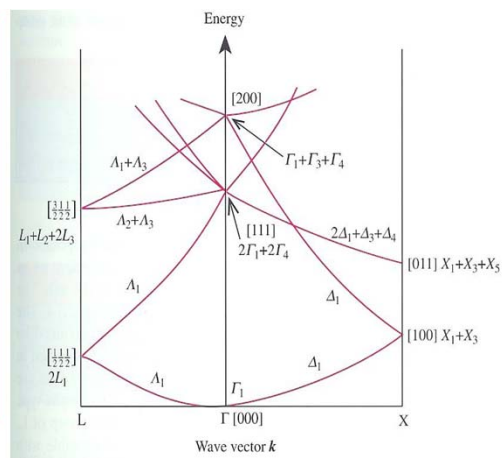
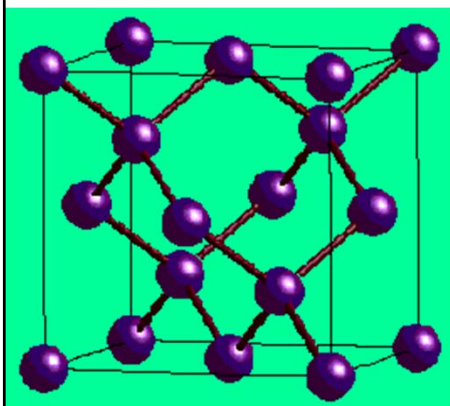


Chem 253B

Crystal Structure

Chem 253C

Electronic Structure



Electronic Structures of Solid

References

Ashcroft/Mermin: Chapter 1-3, 8-10

Kittel: chapter 6-9

Gersten: Chapter 7, 11

Burdett: chapter 1-3

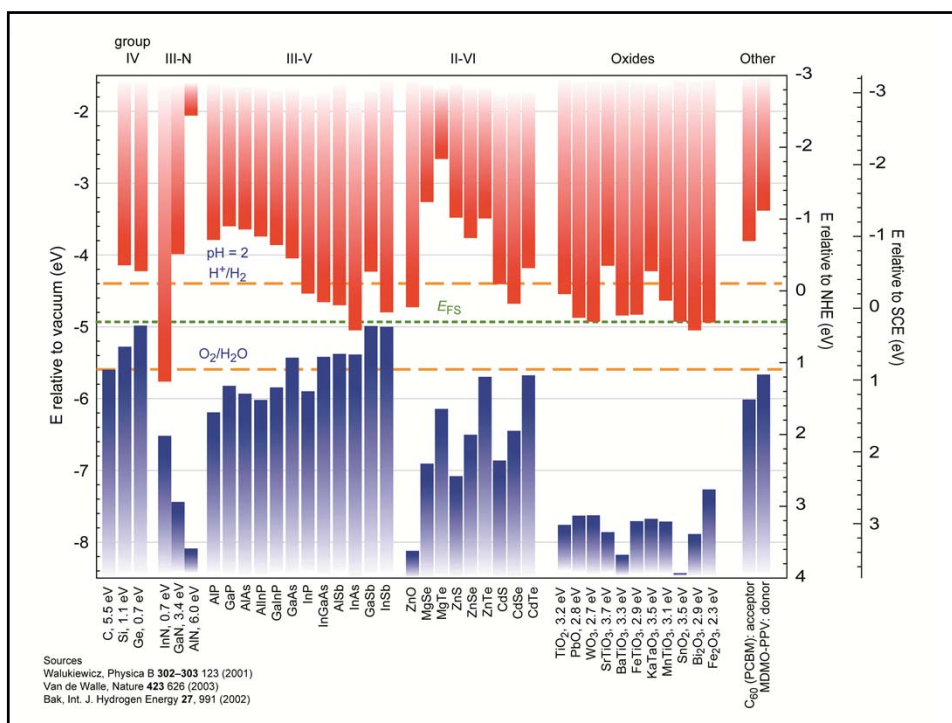
Hoffman: p1-20

Resistivities of Real Materials

Compound	Resistivity ($\Omega\text{-cm}$)	Compound	Resistivity ($\Omega\text{-cm}$)
Ca	3.9×10^{-6}	Si	~ 0.1
Ti	42×10^{-6}	Ge	~ 0.05
Mn	185×10^{-6}	ReO ₃	36×10^{-6}
Zn	5.9×10^{-6}	Fe ₃ O ₄	52×10^{-6}
Cu	1.7×10^{-6}	TiO ₂	9×10^4
Ag	1.6×10^{-6}	ZrO ₂	1×10^9
Pb	21×10^{-6}	Al ₂ O ₃	1×10^{19}

Most semiconductors in their pure form are not good conductors, they need to be doped to become conducting.

Not all so called "ionic" materials like oxides are insulators.



Properties of Semiconductors

Compound	Structure	Bandgap (eV)	e ⁻ mobility (cm ² /V-s)	h ⁺ mobility (cm ² /V-s)
Si	Diamond	1.11 (I)	1,350	480
Ge	Diamond	0.67 (I)	3,900	1,900
AlP	Sphalerite	2.43 (I)	80	---
GaAs	Sphalerite	1.43 (D)	8,500	400
InSb	Sphalerite	0.18 (D)	100,000	1,700
AlAs	Sphalerite	2.16 (I)	1,000	180
GaN	Wurtzite	3.4 (D)	300	---

Microscopic Conductivity

We can relate the conductivity, σ , of a material to microscopic parameters that describe the motion of the electrons (or other charge carrying particles such as holes or ions).

$$\sigma = ne(e\tau/m^*)$$

$$\mu = e\tau/m^*$$

$$\sigma = ne\mu$$

where

n = the carrier concentration (cm^{-3})

e = the charge of an electron = $1.602 \times 10^{-19} \text{ C}$

τ = the relaxation time (s) {the time between collisions}

m^* = the effective mass of the electron (kg)

μ = the electron mobility ($\text{cm}^2/\text{V-s}$)

Chem 253, UC, Berkeley ● ● ●

Carrier Mobility

Momentum gained
during the mean free flight

Momentum lost in a collision

$$eE\tau = m^* v_d$$

Drift velocity

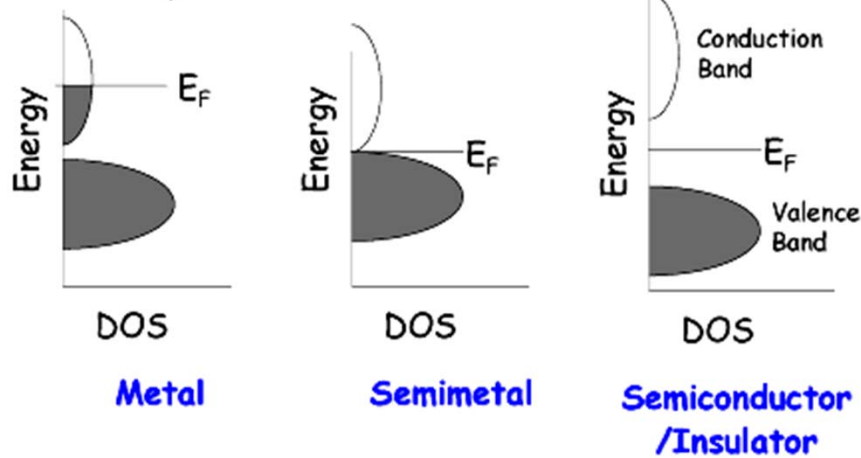
$$v_d = \frac{eE\tau}{m^*}$$

Mobility: the ratio of the drift velocity over the applied electric field

$$\mu = \frac{v_d}{E} = \frac{e\tau}{m^*}$$

$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$

Metals, Semiconductors & Insulators



In a metal the Fermi level cuts through a band to produce a partially filled band. In a semiconductor/insulator there is an energy gap between the filled bands and the empty bands. The distinction between a semiconductor and an insulator is artificial, but as the gap becomes large the material usually becomes a poor conductor of electricity. A semimetal results when the band gap goes to zero.

Simple metals

Electrons are considered as “**electron gas**” (Drude model), i.e. the application of an electric field accelerates them in the field direction.

Basic assumptions

no interaction between electrons; **Independent Electrons**
 constant potential background, **no periodic potential** of the lattice;
 electrons in a box have only kinetic energy, i.e. $E = \frac{1}{2} mv^2$

Schrödinger equation

$$\hat{H}\psi = E\psi$$

E : eigenvalue of \hat{H}
 \hat{H} : Hamilton operator
 $\hat{H} = -\hbar^2/(2m) \nabla^2 + V$

$\hbar = h/(2\pi)$; h : Planck's constant
 m : electron mass
 ∇^2 : $\text{nabla}^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$
 V : potential energy [here: $V = 0$]

ψ : wavefunction,
 contains information of movement of
 the electron (e^-) and its position

E : energy

Solutions for ψ ?

Free Electron Approximation

Simple metals: Quantum Theory

Boundary conditions

The electron is confined to the solid (a box of length L):

$$\psi(0) = 0 \text{ and } \psi(L) = 0$$

$$\hat{H}\psi = E\psi = -\hbar^2/(2m) d^2\psi/dx^2 + V$$

with $V = 0$:

$$0 = \hbar^2/(8\pi^2m) d^2\psi/dx^2 + E\psi$$

$$0 = d^2\psi/dx^2 + 8\pi^2m/\hbar^2 E\psi$$

We define for simplification

$$k^2 = 8\pi^2mE/\hbar^2, \text{ which gives:}$$

$$d^2\psi/dx^2 + k^2\psi = 0$$

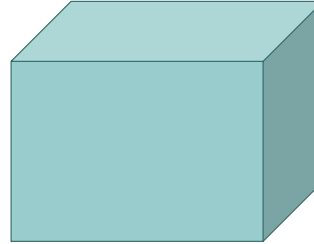
Thus, ψ is a function that is proportional to its second derivative:

$$\psi \propto d^2\psi/dx^2$$

Possible solution: $\psi = \exp(-ikx)$, or, if real:

$$\psi = \sin(kx) \Rightarrow d\psi/dx = k\cos(kx) \Rightarrow d^2\psi/dx^2 = -k^2\sin(kx)$$

General solution includes a constant A : $\psi = A\sin(kx)$



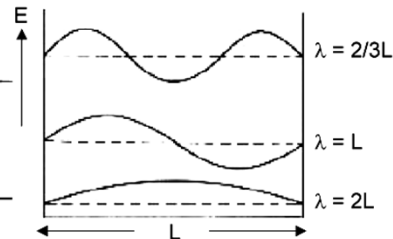
Simple metals: Quantum Theory

Are the boundary conditions [$\psi(0) = 0$ and $\psi(L) = 0$] fulfilled?

$$\psi = \sin(kx)$$

$$\psi(0) = \sin(k0) = 0$$

$$\psi(L) = \sin(kL) \text{ is } 0 \text{ if } kL = n\pi$$



What are k and E ?

With the definition $k^2 = 8\pi^2mE/\hbar^2$, and $kL = n\pi$:

$$k^2 = n^2\pi^2/L^2 = 8\pi^2mE/\hbar^2$$

$$\Rightarrow E = n^2\hbar^2/(8mL^2)$$

$$E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L} \right)^2$$

$$k = \frac{2\pi}{\lambda} = \frac{n\pi}{L}$$

We also know $E = \frac{1}{2}mv^2$ and $p = mv$,

and considering the particle-wave dualism:

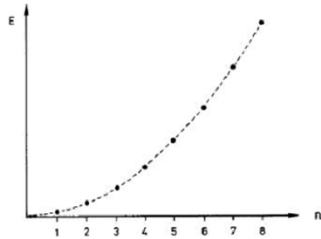
de Broglie: $p = h\nu = h/\lambda \Rightarrow p/h = 1/\lambda$

$$\Rightarrow k^2 = 8\pi^2mE/\hbar^2 = 8\pi^2m/\hbar^2 \cdot \frac{1}{2}mv^2 = 4\pi^2/\hbar^2 p^2 = 4\pi^2/\lambda^2$$

$$k = 2\pi/\lambda \quad \text{wavevector}$$

$$\psi = \sin(kx) = \sin(2\pi/\lambda x)$$

Simple metals



Allowed electron energies in a 1D box

For each allowed energy state

\Rightarrow 2 electrons

In a typical metal ($L \approx 1\text{cm} \Leftrightarrow 10^8$ unit cells)

ΔE between individual levels is very small,
i.e. energies are quasi-continuous.

$$E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L} \right)^2$$

From 1D to 3D:

$$\psi(r) = A \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z}$$

$$E(k) = \frac{\hbar^2}{2m} \left[\left(\frac{n_x \pi}{L_x} \right)^2 + \left(\frac{n_y \pi}{L_y} \right)^2 + \left(\frac{n_z \pi}{L_z} \right)^2 \right]$$

Chem 253, UC, Berkeley

Periodic Boundary Condition

L : **periodicity**, lattice constant

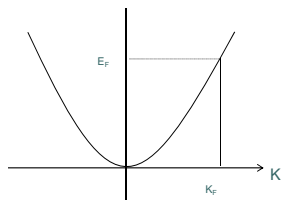
$$-\frac{\hbar^2}{2m} \nabla^2 \cdot \psi(r) = \varepsilon \psi(r)$$

$$\psi(x) = \psi(x + L)$$

Solution: traveling plane wave

$$\psi_n = A \exp(ik \cdot x)$$

Where: $k \cdot L = 2\pi n$



$$E(k) = \frac{\hbar^2 k_x^2}{2m}$$

3D Periodic Boundary Condition

$$\psi_n = A \exp(i\vec{k} \cdot \vec{r})$$

Normalization:

$$1 = \int \psi_n^* \psi_n dr = A^2 \int \exp(-i\vec{k} \cdot \vec{r}) \exp(i\vec{k} \cdot \vec{r}) dr = A^2 V$$

V: unit cell volume

$$\psi_n = V^{-1/2} \exp(i\vec{k} \cdot \vec{r})$$

$$k = \frac{2\pi}{\lambda}$$

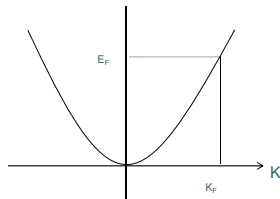
de Broglie wavelength

Energy Eigenvalue:

$$E(k) = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

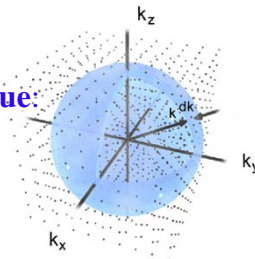
Moment Operator: $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial r}$ $\psi_n = A \exp(i\vec{k} \cdot \vec{r})$

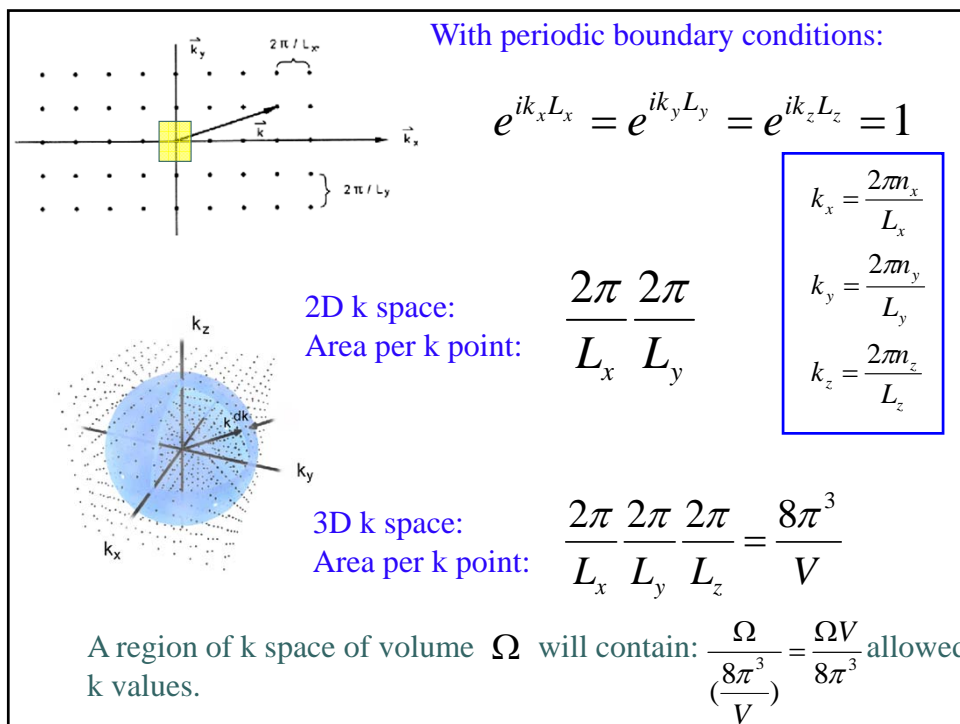
$$\hat{p} \psi(r) = \frac{\hbar}{i} \frac{\partial}{\partial r} \psi(r) = \hbar k \psi(r)$$



Momentum Eigenvalue:

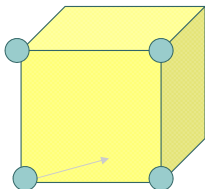
$$p = \hbar k$$





Reciprocal Lattice

Reciprocal lattice is always one of 14 Bravais Lattice.



$$\vec{a}^* = 2\pi \frac{b \times c}{a \cdot (b \times c)}$$

$$\vec{b}^* = 2\pi \frac{c \times a}{a \cdot (b \times c)}$$

$$\vec{c}^* = 2\pi \frac{a \times b}{a \cdot (b \times c)}$$

k space density of level: $\frac{V}{8\pi^3}$

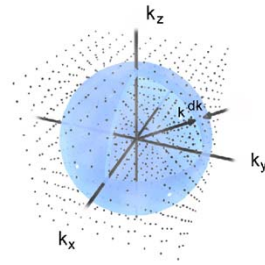
Non-interacting electrons: **Pauli exclusion principle**

Each wave vector $\mathbf{k} \rightarrow$ two electronic level (spin up/down)

Fermi wave vector: k_F

Volume enclosed by the Fermi surface:

$$\frac{4\pi}{3} k_F^3$$



of allowed states within: $\frac{4\pi}{3} k_F^3 \frac{V}{8\pi^3} = \frac{k_F^3}{6\pi^2} V$

of electrons N: $N = \frac{k_F^3}{3\pi^2} V$

Electronic density: $n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}$

$$k_F = (3\pi^2 n)^{1/3}$$

Free & independent electron ground state:

Fermi wave vector $k_F = (3\pi^2 n)^{1/3}$

Enclosed Fermi sphere

Fermi Surface

Fermi Momentum $p_F = \hbar k_F$

Fermi energy $E_F = \frac{\hbar^2 k_F^2}{2m}$

Fermi velocity $v_F = p_F / m^*$

Estimation based on conduction electron density:

$$\frac{V}{N} = \frac{1}{n} = \frac{4}{3} \pi r_s^3 = \frac{3\pi^2}{k_F^3}$$

$$k_F = \frac{(9\pi/4)^{1/3}}{r_s} = \frac{1.92}{r_s}$$

Radius of sphere where volume equals to the volume per conduction electron

$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

$$E_F = \frac{50.1 \text{ eV}}{(r_s / a_0)^2}$$

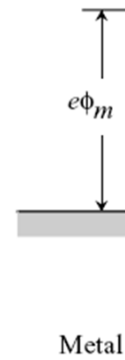
2-3, for many metal

Fermi energy for metallic elements: 1.5 –15 eV

Fermi temperature:

$$T_F = \frac{E_F}{k_B} = \frac{58.2}{(r_s / a_0)^2} \times 10^4 \text{ K}$$

Element	Work function, ϕ_m (volt)
Ag, silver	4.26
Al, aluminum	4.28
Au, gold	5.1
Cr, chromium	4.5
Mo, molybdenum	4.6
Ni, nickel	5.15
Pd, palladium	5.12
Pt, platinum	5.65
Ti, titanium	4.33
W, tungsten	4.55



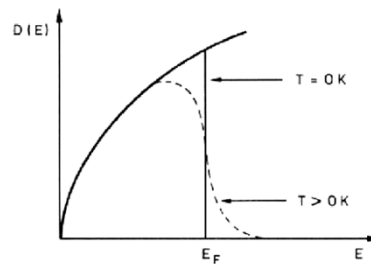
Density of States

The number of orbitals/states per unit energy range

$$D(E) = \frac{dN}{dE}$$

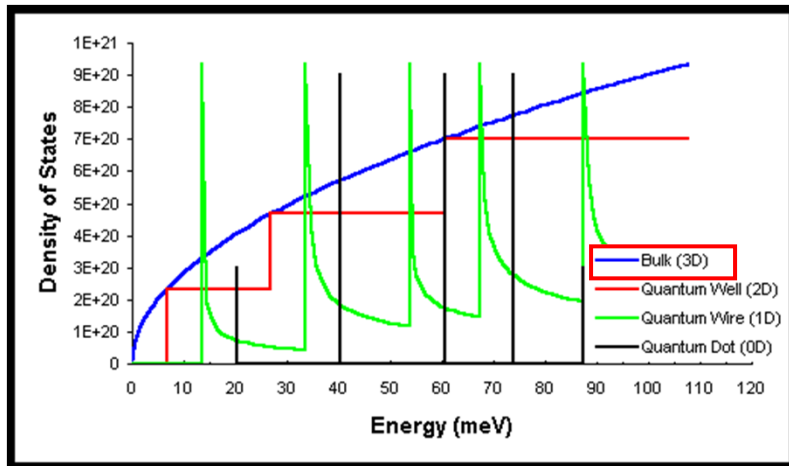
$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

$$N = \frac{V}{3\pi^2} \left(\frac{2\pi E}{\hbar^2} \right)^{3/2}$$



$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$

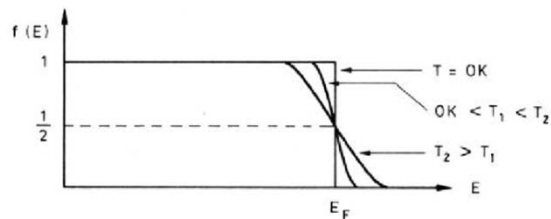
Quantum Confinement and Dimensionality



Fermi-Dirac distribution:

$$f(E) = \frac{1}{\exp[(E - E_F) / k_B T] + 1}$$

Energy distribution of electrons



Fermi-Dirac Function

The Fermi-Dirac function gives the fraction of allowed states, $f(E)$, at an energy level E , that are populated at a given temperature.

$$f(E) = 1/[1 + \exp\{(E-E_F)/kT\}]$$

where the Fermi Energy, E_F , is defined as the energy where $f(E) = 1/2$. That is to say one half of the available states are occupied. T is the temperature (in K) and k is the Boltzman constant ($k = 8.62 \times 10^{-5}$ eV/K)

As an example consider $f(E)$ for $T = 300$ K and a state 0.1 eV above E_F :

$$f(E) = 1/[1 + \exp\{(0.1 \text{ eV})/((300\text{K})(8.62 \times 10^{-5} \text{ eV/K}))\}]$$

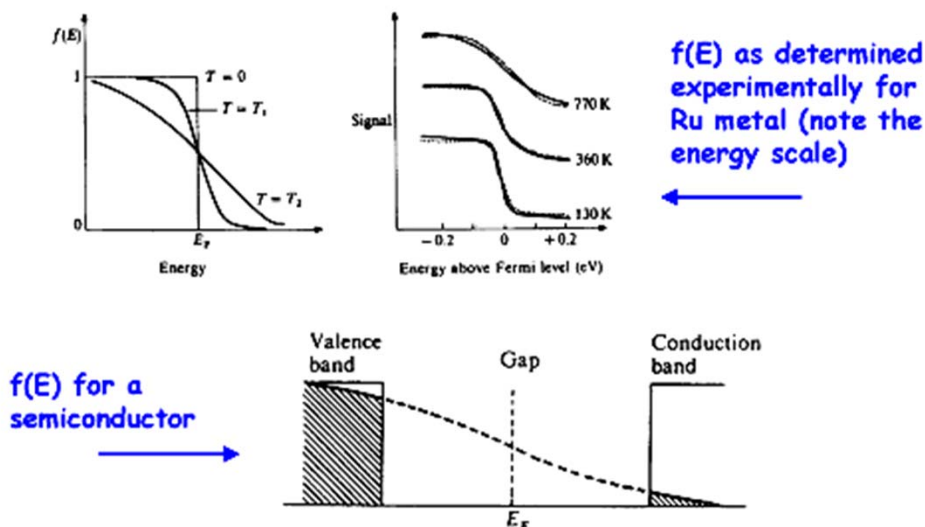
$$f(E) = 0.02 = 2\%$$

Consider a band gap of 1 eV.

$$f(1 \text{ eV}) = 1.6 \times 10^{-17}$$

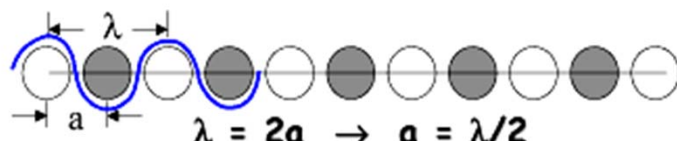
See that for even a moderate band gap (Silicon has a band gap of 1.1 eV) the intrinsic concentration of electrons that can be thermally excited to move about the crystal is tiny. Thus pure Silicon (if you could make it) would be quite insulating.

Fermi Dirac Function Metals and Semiconductors



Crystal Momentum

To better understand the meaning of k , consider an electron at the outer edge of the Brillouin zone, where $k = \pi/a$. The phase of the electronic wavefunction changes sign every unit cell (similar to a p-orbital changing phase at its nodal plane)



$$\lambda = 2a \rightarrow a = \lambda/2$$

$$k = \pi/a \rightarrow a = \pi/k$$

Combining these two relationships gives:

$$\lambda/2 = \pi/k$$

$$k = 2\pi/\lambda \quad \lambda = 2\pi/k$$

The wavelength of the wavefunction is inversely proportional to k .

Crystal Momentum

Now consider the DeBroglie relationship (wave-particle duality of matter)

$$\lambda = h/p$$

$$p = h/\lambda$$

$$p = \hbar k/2\pi$$

where.,

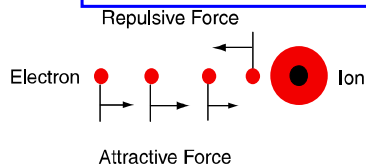
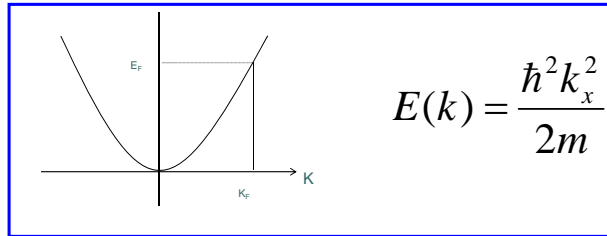
- p is the momentum of the wavepacket,
- h is Planck's constant, 6.626×10^{-34} J-s

The momentum of an electron is directly proportional to k .

k is a measure of the "crystal" momentum of an electron in the ψ_k wavefunction.

Nearly Free Electron Model

Adding small perturbation by the periodic potential of the ionic cores



Periodic Boundary Condition

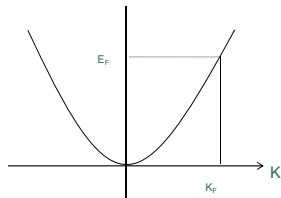
$$-\frac{\hbar^2}{2m} \nabla^2 \cdot \psi(r) = \varepsilon \psi(r)$$

$$\psi(x) = \psi(x + L)$$

Solution: traveling plane wave

$$\psi_n = A \exp(ik \cdot x)$$

Where: $k \cdot L = 2\pi n$



$$E(k) = \frac{\hbar^2 k_x^2}{2m}$$

Dispersion Curve

3D Periodic Boundary Condition

$$\psi_n = A \exp(i\vec{k} \cdot \vec{r})$$

Normalization:

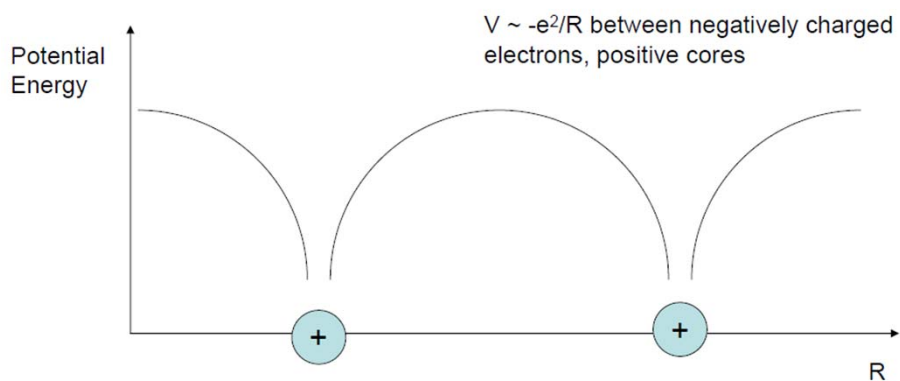
$$1 = \int \psi_n^* \psi_n dr = A^2 \int \exp(-i\vec{k} \cdot \vec{r}) \exp(i\vec{k} \cdot \vec{r}) dr = A^2 V$$

V: unit cell volume

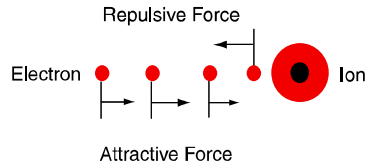
$$\psi_n = V^{-1/2} \exp(i\vec{k} \cdot \vec{r})$$

$$k = \frac{2\pi}{\lambda}$$

de Broglie wavelength



Periodic Potentials and Bloch's Theorem



$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_L \right] \phi = E \phi$$



$$V_L(r) = V(r + \vec{R})$$

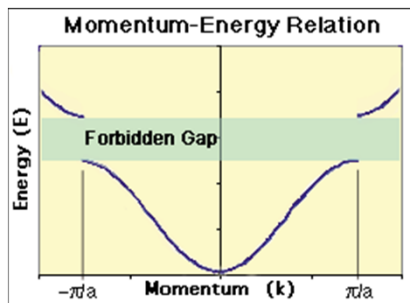
\vec{R} Lattice vector

Bloch's theorem: the eigenstates of the Hamiltonian above can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais Lattice.

Bloch Wavefunction:
$$\phi(r) = \frac{e^{ik \cdot r}}{\sqrt{V}} u(r)$$

$$u(r) = u(r + \vec{R}) \text{ periodic part of Bloch function}$$

Bragg reflection of electron waves in crystal is the cause of the energy gap.

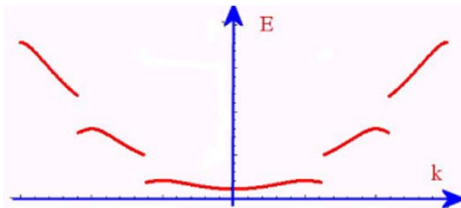


First Bragg reflection:

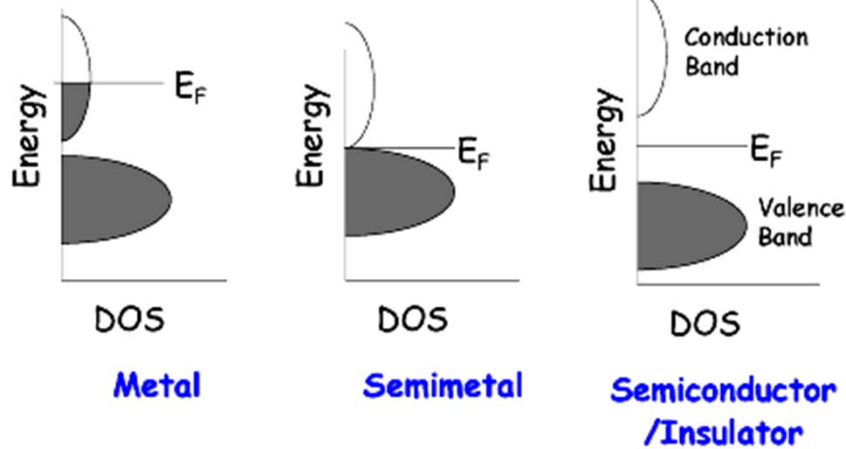
$$\pm \frac{\pi}{a}$$

Other gap:

$$\pm \frac{n\pi}{a}$$



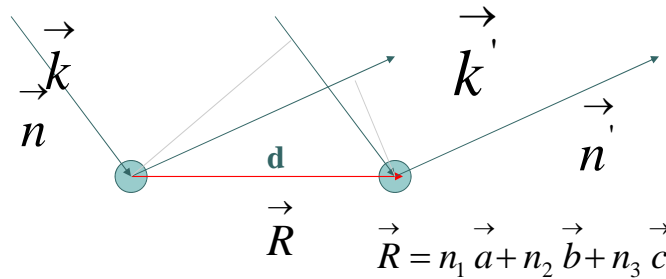
Metals, Semiconductors & Insulators



In a metal the Fermi level cuts through a band to produce a partially filled band. In a semiconductor/insulator there is an energy gap between the filled bands and the empty bands. The distinction between a semiconductor and an insulator is artificial, but as the gap becomes large the material usually becomes a poor conductor of electricity. A semimetal results when the band gap goes to zero.

Chem 253, UC, Berkeley

Reciprocal Lattice



$$e^{i\vec{R} \cdot (\vec{k} - \vec{k}')} = 1$$

Laue Condition

$$\vec{K} = \vec{k}' - \vec{k}$$

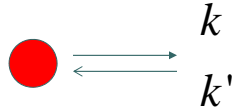
Reciprocal lattice vector

$$e^{-i\vec{K} \cdot \vec{R}} = 1$$

For all \vec{R} in the Bravais Lattice

For 1D Lattice:
Reciprocal lattice vector:

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

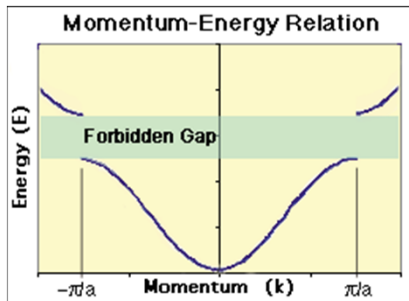


$$\vec{K} = \vec{k} - \vec{k}'$$

Diffraction Condition: $k = \pm \frac{1}{2} K = \pm \frac{\pi}{a} n$

Can be extended to 3D

*Bragg reflection of electron waves
in crystal is the cause of the energy gap.*



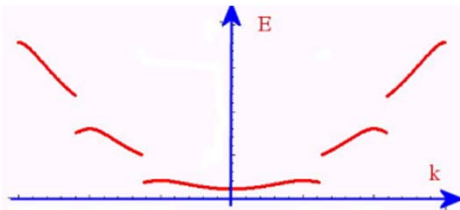
First Bragg reflection:

$$\pm \frac{\pi}{a}$$

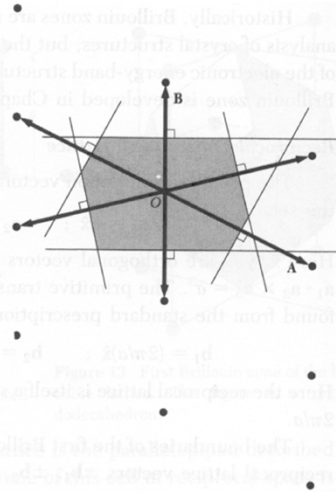
First Brillouin Zone

Other gap:

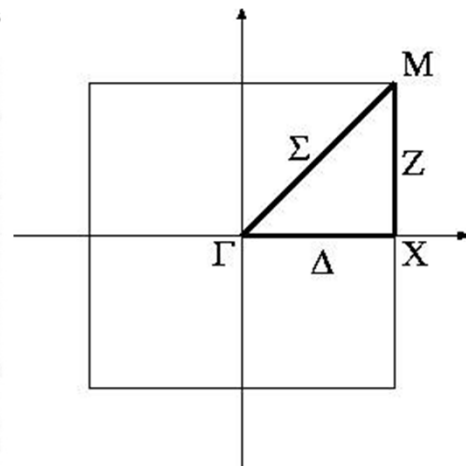
$$\pm \frac{n\pi}{a}$$



Examples for Brillouin zones

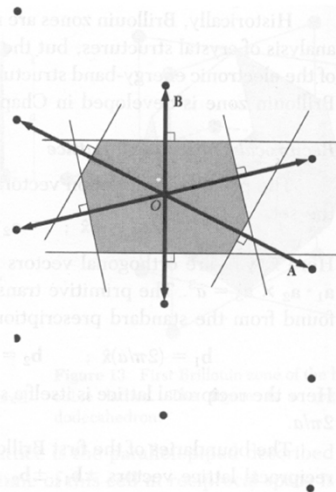


2-D, general

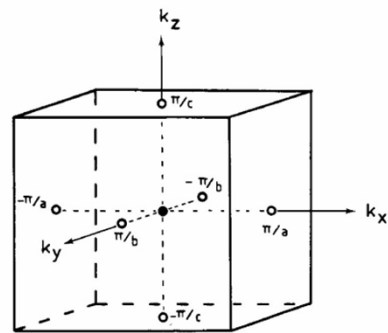


1st Brillouin Zone

Examples for Brillouin zones



2-D, general



cubic primitive

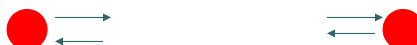
Wigner-Seitz cell

The wavefunction at $\pm \frac{\pi}{a}$ are not traveling wave of free electrons:

$$\exp(\pm ikx) = \exp(\pm i \frac{\pi}{a} x)$$

Instead: equal parts of the waves traveling to the left and right

A wave travels neither to the left nor to the right is a standing wave.



Two different standing waves:

$$\psi(+) = \exp(i \frac{\pi}{a} x) + \exp(-i \frac{\pi}{a} x) = 2 \cos \frac{\pi}{a} x$$

$$\psi(-) = \exp(i \frac{\pi}{a} x) - \exp(-i \frac{\pi}{a} x) = 2 \sin \frac{\pi}{a} x$$

Probability density:

$$\propto |\psi|^2$$

