Lecture 8. Metals, Semiconductors, Insulators

- Classification of materials
- Monovalent metals
- Limitations of the Band Theory (Mott and Peierls insulators)
- Divalent metals
- Insulators
- Semiconductors
- Direct and indirect optical transitions in semiconductors
- Measuring $\varepsilon(k)$: PES, ARPES, and IPES

For the first midterm – please prepare two problems per student and email them to me by the end of this week.
The electronic properties of materials are determined by filling the electron energy bands with valent electrons. The Figure illustrates the band formation for a material with $ns$ and $np$ orbitals (e.g. typical semiconductors Si and Ge). Each cell contains two atoms, and these orbitals can form bonding and anti-bonding combinations. If each unit cell contains eight valence electrons from two atoms in it, four of these bands are occupied while the other four are empty.
Classification of Materials

**Metals**: both filled and empty states in the top (conduction) band, large DoS at $E_F$.

**Semimetals**: Fermi level is near an overlap between two higher-energy bands, $g_{3D}(E_F) \neq 0$ but small. Examples: $As$, $Sb$, $Bi$, $\alpha$-tin (gray tin), graphite.

**Band Insulators (incl. semiconductors)**: the highest completely filled band (the valence band) is separated from the lowest empty band (the conduction band) by the band gap. For semiconductors $E_g < 3.2 \text{ eV}$, for insulators $E_g > 3.2 \text{ eV}$ ($\hbar \omega \approx 3.2 \text{ eV}$ corresponds to the upper (violet) limit of visible light spectrum).

**Band Gap**: If some bands are completely filled and all others remain empty, the gap between the highest occupied level and the lowest unoccupied level is called the band gap, $E_g$. 

![Diagram of classification of materials](image)

**Diagram Notes**:
- $g_{3D}(\varepsilon)$: DOS function
- $\varepsilon$: Energy level
- $E_F$: Fermi level
- $E_g$: Band gap
- Metal, semi-metal, semiconductor, insulator
Charming Simplicity of 1D

Simplicity – deceptive, see below.
Is a 1D monovalent element always a metal? According to the band theory for non-interacting electrons, yes. But we neglected electron-electron interactions, electron-phonon interactions, etc.

When the kinetic energy and the Coulomb interaction energy of a system are comparable to each other, the electron behavior can be quite different. In the materials where electrons are strongly correlated, the independent-quasiparticle approximation, which is the basis of conventional band theory, breaks down.
The Hubbard Model (tight-binding approximation): competition between the kinetic term $t$ allowing for tunneling ('hopping') of particles between sites of the lattice and the potential term $U$ that describes the on-site repulsion.

The Mott Metal-Insulator Transition is driven by electron-electron correlations. Two electrons sitting on the same site would feel a large Coulomb repulsion, and this would split the band in two. With one electron per site, the lower band would be full, and the system would be an insulator.
Peierls Metal-Insulator Transition (electron-phonon coupling)

1D chain of atoms with half-filling: Peierls transition is driven by electron-phonon coupling. Dimerization causes small energy savings, based on the distortion of the bands in the vicinity of the BZ boundary. The effect occurs when the system is close to its ground state – hence, the Peierls transition from 1D band metal to 1D band insulator is observed with lowering $T$.

At $T < T_C$, periodic lattice distortion doubles the size of the unit cell (halves the Brillouin zone). The band gaps open at the position where the backfolded bands intersect the original bands (red lines). For a half filled band, these band gaps lie at the Fermi level and result in a MIT.

Peierls realized that a 1D equally spaced chain with one electron per ion is unstable (1930s). In the 1970s, various quasi-1D materials (e.g. NbSe$_3$, TTF-TCNQ) were synthesized in search for 1D high-$T_C$ superconductors. What was found is that these materials underwent an insulating transition rather than a superconducting one.

Z. Wang et al., PRB 40, 11589 (1989)
Imagine a monovalent element with a cubic lattice (such thing doesn’t exist). What would be the ratio \( \frac{\text{vol}_{\text{Fermi sphere}}}{\text{vol}_{\text{BZ}}} \)?

Thus, there would be many empty states in the BZ, and such an element would be a metal.

Monovalent alkali elements such as \( Na, K \) form BCC Bravais lattices. The unit cell of the BCC lattice is a cube of side \( a \) containing two lattice points (2 atoms).

The electron density - \( n = \frac{2}{a^3}, \quad k_F = (3\pi^2 n)^{1/3} \approx \frac{1.24\pi}{a} \) (the free-electron model).

The shortest distance to the BZ boundary for the BCC lattice is \( \frac{\sqrt{2\pi}}{a} \approx \frac{1.41\pi}{a} \).

Thus, plenty of empty states in the BZ – alkali elements are metals. The Fermi surface is almost spherical. The alkali metals have properties which are quite close to the predictions of the Sommerfeld model.
$\textbf{Cu}$ ($1s^22s^22p^63s^23p^63d^{10}4s^1$) is a monovalent element with FCC lattice. FCC lattice in real space corresponds to BCC lattice in $k$-space.

The isoenergetic curves are “attracted” to the BZ boundaries along the directions of the smallest $k_{\text{boundary}}$.

Reason for “necks”: 

Cu Fermi surface
color = inverse mass
Band Structure of Cu

\textbf{Cu} ([\textit{Ar}] 3d^{10} 4s^1 ) The electrons in the low-lying levels of the Ar configuration can be considered as part of the inert ion cores. To accommodate 11 additional electrons at least six bands are required: five \textit{d}-bands lying in a narrow energy range \(\sim 2 - 5\,\text{eV} \) below \(E_F\), and the \textit{s(p)}-band extended between 9\,\text{eV} below \(E_F\) and \(> 2\,\text{eV}\) above \(E_F\). \(E_F\) lies far enough above the \textit{d}-bands that for purposes of Fermi surface determination one can use a nearly free electron calculation for the \textit{s}-band.
Insulators with Even Numbers of Valence Electrons

The number of electrons \((2Np)\) is sufficient to completely fill an integer number of bands up to a band gap. **If the gap band is sufficiently large**, there won’t be partially filled bands. Such substances, called band insulators or semiconductors depending on the value of \(E_g\), should not conduct electricity at \(T = 0\). At non-zero \(T\), the electrical conduction can occur in semiconductors if thermal excitation is sufficient to excite electrons across the gap, leaving filled and empty states both above and below the gap. Insulators – Diamond et al., semiconductors - Ge and Si.

Fermi surface?
Metals with Even Numbers of Valence Electrons

However the divalent metals (e.g. Be, Mg, Ca) do exist! In 2D and 3D the highest states of the lower band can be at a higher energy than the lowest states of the upper band. Therefore both bands are partly filled, ensuring that such materials conduct electricity at $T = 0$.

All 1D divalent elements are insulators - e.g. (NbSe$_4$)$_3$I.

Overlap of two bands may occur in different $k$-directions for sufficiently small band gaps.
Metals with Even Numbers of Valence Electrons (cont’d)

2D

No periodic Potential
Divalent= Enough electrons
To fill 1st zone

with weak periodic potential

weak potential Lowest Band (in 1st BZ)

2nd band

with strong periodic potential – 1st BZ exactly filled (insulator)

Fermi surface

1st band

Calcium FCC (Divalent)

2nd band
Atomic energy levels are broadened into bands when the interatomic spacing is reduced.

Monovalent atoms have half-filled bands.

Divalent atoms have filled valence bands at large $a$ but become conductors when $a$ is small and the bands overlap.
Remember how to obtain these results?
Holes in the 2\textsuperscript{nd} BZ and electrons in the 3\textsuperscript{d} BZ shape the Hall effect in Aluminum: the Hall coefficient has a positive sign and yields an effective density of carriers a third of the free electron value (to be covered in L12).
Electron scattering “averages” the effective mass of conducting electrons at the time scales $> \tau$.

http://www.phys.ufl.edu/fermisurface/periodic.pdf
Semiconductors: at $T = 0$ the highest completely filled band (the valence band) is separated from the lowest empty band (the conduction band) by a not-too-wide band gap $E_g$. Therefore the material does not conduct electricity at $T = 0$. At $T \neq 0$ a small fraction of electrons is thermally excited into the conduction band and empty states occur in the valence band. This enables electrical conduction.

**Si**

- Direct band gap $- 3.4 \text{ eV}$
- Indirect band gap $- 1.1 \text{ eV}$

The shading indicates the lowest conduction band and the highest valence band, with the band gap in between.

Where Electrons and Holes Live in the $k$-space

Even with heavy doping, the carrier concentration rarely exceeds $10^{26} m^{-3}$. The atom concentration in $Si$ is $\sim 5 \times 10^{28} m^{-3}$. Thus, electrons occupy only a very small fraction of the conduction band where their energy is lowest (and holes occupy only a very small fraction of the valence band), and we should be mostly interested in the properties of the energy spectrum in the vicinity of the $\varepsilon(k)$ minimum for the conduction band and in the vicinity of its maximum for the valence band. The effective mass approximation applies, the effective mass is typically a tensor.

direct-band-gap semiconductor

indirect-band-gap semiconductor
Fermi Surface of n-doped Si

FIGURE 2.19. (a) Brillouin zone of Si with constant-energy surfaces for the six equivalent X-valleys. (b) Enlarged view of one of the valleys, showing the longitudinal and doubly degenerate transverse masses $m_L$ and $m_T$. Which mass is bigger?
The visible-light photons with energy $h\nu < 2 \ eV$ have $k_{ph} = \frac{\omega}{c} \sim 10^{-3} k_e \ (k_e \sim \frac{\pi}{a})$. Thus, the photon-induced excitations of electrons from the valence band to the conduction band are essentially **vertical in $k$-space**.

Direct optical transitions.

Indirect optical transitions – require electron-phonon interaction.

Radiative recombination is far slower in indirect band gap materials than direct band gap ones. This is why light-emitting and laser diodes are almost always made of direct band gap materials (GaAs, GaP, etc.), and not indirect band gap ones (e.g. Si).
Light with a photon energy close to the band gap can penetrate much farther before being absorbed in an indirect band gap material than a direct band gap one. This fact is very important for photovoltaics. *Si* is the most common solar-cell material, despite the fact that it is indirect-gap and therefore does not absorb light very well. Silicon solar cells cannot be much thinner than $\sim 0.1$ mm, otherwise much of the light (particularly in the infrared) would simply pass through. Thin-film solar cells made of direct band gap materials (such as *CaTe*) can be much thinner (often less than 1 micron thick).
Electron states near the edges tail into what would have been the forbidden gap of the crystal; deep in the tail, the DoS falls off exponentially.

Localized–delocalized transition in 3D (Anderson transition) (L11) occurs near either band edge. The borderline between the extended and localized states is called a “mobility edge”.
Short-range order is sufficient to create an optical gap!

Thus, the concept of “band gap” remains useful even in absence of energy bands. Still, significant differences exist between crystalline and amorphous electronic state densities. Van Hove singularities in the crystal DOS are replaced by a smooth DoS variations in amorphous semiconductors, with defect states within the gap and the “tail” states in the vicinity of the conduction and valence band edges.

Fermi surfaces in *metals* were mapped in the de Haas - van Alphen measurements (see L.12). Require big ultra-pure single crystals and low $T$.

- $\varepsilon(k)$ for *occupied* states – Photoelectron Spectroscopy (PES) and Angle-Resolved Photoemission Spectroscopy (ARPES).
- $\varepsilon(k)$ for *unoccupied* states – inverse PES.
- $DoS$ – Tunneling Spectroscopy.
Measuring DoS: UV and X-Ray Photoelectron Spectroscopy (PES)

The photoelectrons are collected, energy resolved, and counted - a spectrum of electron intensity as a function of the measured kinetic energy. The PES (UPS) instruments use broadband light sources (synchrotron radiation, helium gas sources of UV light).

\[ E_{e,\text{out}} = \hbar \omega - \Phi - (E_F - E_{e,\text{in}}) \]

PES probes occupied states!
soft x-ray photon
10-1000 eV

valence levels

core levels

Energy

Binding Energy, eV

Copper

Fermi Level

$d$

momentum, $k$

Experimental Spectrum

Count Rate
# electrons/sec at detector
Figure 12. Characterizing photoemission experiments for the determination of the energy resolution of a spectrometer. The main panel gives a Fermi edge of polycrystalline silver, measured at \( T = 8 \) K with He I (\( h\nu = 21.23 \) eV). Fitting the data with a Gaussian broadened FDD by using the least-squares method yields a Gaussian FWHM of 3 meV. The inset shows another measurement on xenon in the gaseous phase. The total line width, fitted by a Gaussian, is 4.3 meV, consisting of intrinsic and experimental broadenings.
(a) Typical 4th harmonic spectrum (open circles) and Gaussian fit (solid line). (b) Raw photoemission spectrum from polycrystalline gold at $T = 20K$ (open circles) and Fermi-Dirac function fit (solid line).

Angle Resolved Photoemission Spectroscopy (ARPES)

- direct experimental technique to measure the band dispersion $\varepsilon(k)$ and Fermi surface.

Requires properly aligned single crystal in order to perform angle or, equivalently, momentum-resolved measurements.

Light sources: synchrotron radiation at ~ 20-200 eV, plasma Helium discharge at ~ 20 eV, or more recently, lasers at 7 eV and 11 eV.

Energy conservation:

$$E = \frac{\hbar^2}{2m_e} (K_{\perp}^2 + K_{\parallel}^2) + \Phi = \hbar \omega + \varepsilon(k_{\perp}, k_{\parallel})$$

Photon momentum is neglected because it is small compared with electron momentum. The electron momentum in the plane of the sample is conserved ($K_{\parallel} = k_{\parallel} + G$), but no information on $k_{\perp}$

$$\varepsilon(k_{\perp}, k_{\parallel}) = \frac{\hbar^2}{2m_e} [K_{\perp}^2 + (k_{\parallel} + G)^2] + \Phi - \hbar \omega$$
ARPES data for Cu

Conventional (He Iα, left) and laser-ARPES (right) data from the Cu(111) surface. A. Tamai et al., PRB 87, 075113 (2013)

Electron binding energy

$|E_B| = E - E_F$

Fermi-Dirac cutoff

$F(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1}$

In-plane momentum

$\varepsilon(k) = \frac{\hbar^2 k^2}{2m^*}$
ARPES for 2D materials

ARPES is especially useful in the study of two-dimensional materials where the momentum directions of interest are parallel to the surface ($k_\perp$ does not exist).
The penetration depth of 20 eV photons into Cu is $\sim 10\, nm$.

The inelastic mean free path of electrons with $\varepsilon = 20\text{keV}$ in Cu is $\sim 0.6\, nm$.

For comparison, the size of the Cu unit cell is 0.36 $nm$.

Atomically clean surface by...
- Cleaving in-situ
- Growing material in-situ
- Sputter-and-anneal
The “universal curve” for surface sensitivity in photoemission. Electron inelastic mean free paths from a variety of materials are plotted versus kinetic energy relative to $E_F$ (the lowest kinetic energies shown will not be able to overcome the work function). Indicated on the plot are the kinetic energy ranges for standard ARPES and laser ARPES.

IPES: Spectroscopy of Unoccupied Electronic States

Analysis of the photons emitted by electrons hitting a sample.

UPS and IPES spectra of clean MoO$_3$

The Band Theory explains the difference between materials: metals, semiconductors, insulators.

The Band Theory ignores the electron-electron and electron-phonon interactions and overlooks Mott and Peierls insulators.

The Band Theory provides description of direct and indirect optical transitions in semiconductors.

Measuring $\varepsilon(k)$: PES, ARPES, IPES