Lecture 22: Metals (Review and Kittel Ch. 9) and Superconductivity I (Kittel Ch. 10)

Leiden, Netherlands - 1911

Hg sample

Resistance $\Omega$

$< 10^{-5} \Omega$

$4.6 \text{ K}$
Outline

• Normal metals
  Recall properties
  (From lectures 12, 13; Kittel ch. 6)

• Superconductivity - Experimental Facts
  ZERO resistance at nonzero temperature
  Exclusion of magnetic fields
  Heat Capacity shows there is a gap
  Isotope effect

• (Kittel Ch 10)
What is special about electrons?

- Fermions - obey exclusion principle
- Fermions have spin $s = 1/2$ - two electrons (spin up and spin down) can occupy each state

**Electron Gas**

- Kinetic energy $= \left( \frac{p^2}{2m} \right) = \left( \frac{\hbar^2}{2m} \right) k^2$
- Fermi Surface is the surface in reciprocal space that is the boundary between the filled and empty states
- For the electron gas this is a sphere of radius $k_F$

where

\[ N_{\text{elec}} / V = \left( \frac{1}{3\pi^2} \right) k_F^3 \]

The Fermi energy is

\[ E_F = \left( \frac{\hbar^2}{2m} \right) k_F^2 \]
Recall - Electron Gas

Density of States 3 dimensions

- \( D(E) = \frac{1}{2\pi^2} E^{1/2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sim E^{1/2} \)
Fermi Distribution

- At finite temperature, electrons are not all in the lowest energy states

- Applying the fundamental law of statistics to this case (occupation of any state and spin only can be 0 or 1) leads to the Fermi Distribution (Kittel appendix)

  \[ f(E) = \frac{1}{\exp\left(\frac{E - \mu}{k_B T}\right) + 1} \]

Chemical potential for electrons = Fermi energy at T=0

\[ \mu \]

\[ k_B T \]
### Typical values for electrons

- Here we count only valence electrons (see Kittel table)

<table>
<thead>
<tr>
<th>Element</th>
<th>$N_{\text{elec}}$/atom</th>
<th>$E_F$</th>
<th>$T_F = E_F/k_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1</td>
<td>4.7 eV</td>
<td>5.5 x10^4 K</td>
</tr>
<tr>
<td>Na</td>
<td>1</td>
<td>3.23eV</td>
<td>3.75 x10^4 K</td>
</tr>
<tr>
<td>Al</td>
<td>3</td>
<td>11.6 eV</td>
<td>13.5 x10^4 K</td>
</tr>
</tbody>
</table>

- Conclusion: For typical metals the Fermi energy (or the Fermi temperature) is much greater than ordinary temperatures
Heat Capacity for Electrons

• Just as for phonons the definition of heat capacity is \( C = \frac{dU}{dT} \) where \( U = \) total internal energy.

• For \( T \ll T_F = E_F / k_B \) it is easy to see that roughly \( U \sim U_0 + N_{\text{elec}} \frac{T}{T_F} k_B T \) so that
  \[
  C = \frac{dU}{dT} \sim N_{\text{elec}} k_B \left( \frac{T}{T_F} \right)
  \]
Heat capacity

- Comparison of electrons in a metal with phonons

\[ \text{Electrons have } C \sim N_{\text{elec}} k_B \left( \frac{T}{T_F} \right) \]

\[ \text{Phonons approach classical limit } C \sim 3 N_{\text{atom}} k_B \]

Electrons dominate at low T in a metal

Phonons dominate at high T because of reduction factor \( \left( \frac{T}{T_F} \right) \)
What about a real metal?

- In a crystal the energies are not $E = \left( \frac{h^2}{2m} \right) k^2$

- Instead the energy is $E_n(k)$, where $k$ is the wavevector in the Brillouin Zone, and $n = 1, 2, 3, \ldots$ labels the bands.

- The energy $E_n(k)$ is different for $k$ in different directions.

- The concepts still apply
  - The states are filled for $E_n(k) < E_{\text{Fermi}}$
  - The states are empty for $E_n(k) > E_{\text{Fermi}}$

- This defines the Fermi surface: the surface in $k$-space where $E_n(k) < E_{\text{Fermi}}$ – the boundary between filled and empty states.
The Fermi surface in copper

Cu has the fcc crystal structure

The figure shows the Brillouin Zone and the Fermi Surface

Note that the Fermi surface is nearly spherical!

The Fermi surface is very different from a sphere in many crystals – but the idea is still the same!

See Kittel ch. 9, Fig 29 for the same figure

Figure from Nara Women’s University
www.phys.nara-wu.ac.jp
Heat capacity

- Experimental results for metals
  \[ \frac{C}{T} = \gamma + A T^2 + \ldots. \]

- It is most informative to find the ratio \( \frac{\gamma}{\gamma_{\text{free}}} \) where \( \gamma_{\text{free}} = \left( \frac{\pi^2}{2} \right) \left( \frac{N_{\text{elec}}}{E_F} \right) k_B^2 \) is the free electron gas result. Equivalently since \( E_F \propto 1/m \), we can consider the ratio \( \frac{\gamma}{\gamma_{\text{free}}} = \frac{m_{\text{free}}}{m_{\text{th}^*}} \), where \( m_{\text{th}^*} \) is an thermal effective mass for electrons in the metal.

<table>
<thead>
<tr>
<th>Metal</th>
<th>( m_{\text{th}^*}/m_{\text{free}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>2.18</td>
</tr>
<tr>
<td>Na</td>
<td>1.26</td>
</tr>
<tr>
<td>K</td>
<td>1.25</td>
</tr>
<tr>
<td>Al</td>
<td>1.48</td>
</tr>
<tr>
<td>Cu</td>
<td>1.38</td>
</tr>
</tbody>
</table>

- \( m_{\text{th}^*} \) close to \( m_{\text{free}} \) is the “good”, “simple metals”!
Electrical Conductivity & Ohm’s Law

• Consider electrons in an external field $E$. They experience a force $F = -eE$

• Now $F = dp/dt = \hbar \frac{dk}{dt}$, since $p = \hbar k$

• Thus in the presence of an electric field all the electrons accelerate and the $k$ points shift, i.e., the entire Fermi surface shifts.

The same ideas apply to real metals with non-spherical Fermi surfaces
Electrical Conductivity & Ohm’s Law

- What limits the acceleration of the electrons?
- **Scattering** increases as the electrons deviate more from equilibrium
- After field is applied a new equilibrium results as a balance between acceleration by field and scattering

![Equilibrium - no field](image1)

![With applied field](image2)
Electrical Conductivity and Resistivity

• The conductivity $\sigma$ is defined by $j = \sigma E$, where $j =$ current density

• How to find $\sigma$?

• From before $F = dp/dt = m dv/dt = \hbar dk/dt$

• Equilibrium is established when the rate that $k$ increases due to $E$ equals the rate of decrease due to scattering, then $dk/dt = 0$

• If we define a scattering time $\tau$ and scattering rate $1/\tau$
  $\hbar (dk/dt + k/\tau) = F = q E$ ($q =$ charge)

• Now $j = n q v$ (where $n =$ density) so that
  $j = n q (\hbar k/m) = (n q^2/m) \tau E$
  $\Rightarrow \sigma = (n q^2/m) \tau$

• Resistance: $\rho = 1/\sigma \propto m/(n q^2 \tau)$
Scattering mechanisms

• Impurities - wrong atoms, missing atoms, extra atoms, 
  ....

  Proportional to concentration

• Lattice vibrations - atoms out of their ideal places

  Proportional to mean square displacement

• (Really these conclusions depend upon ideas from the next section that there is no scattering in a perfect crystal.)
Electrical Resistivity

• Resistivity $\rho$ is due to scattering: Scattering rate inversely proportional to scattering time $\tau$

$$\rho \propto \text{scattering rate} \propto 1/\tau$$

• Matthiessen’s rule - scattering rates add

$$\rho = \rho_{\text{vibration}} + \rho_{\text{impurity}} \propto 1/\tau_{\text{vibration}} + 1/\tau_{\text{impurity}}$$

- Temperature dependent
  $\propto \langle u^2 \rangle$

- Temperature independent
  - Sample dependent
Electrical Resistivity

- Consider relative resistance $R(T)/R(T=300\text{K})$
- Typical behavior (here for potassium)

- Phonons dominate at high $T$ because mean square displacements $<u^2> \propto T$
  Leads to $R \propto T$
  (Sample independent)

- Increase as $T^2$

- Inpurity scattering dominates at low $T$ in a metal
  (Sample dependent)
1911

- Laboratory of Kamerling Onnes in Leiden
  Why there?
  Why then?
- Helium had just been liquified in Onnes’ lab, making possible experiments at temperatures around 4.2K and below

\[
\text{Resistance } \Omega < 10^{-5} \Omega
\]

Hg sample

4.6 K
Superconducting elements

• **NOT** the magnetic 3d transition and 4f rare earth elements - **NOT** the “best” metals - like Cu, Ag, Na

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**APPENDIX D: PERIODIC TABLE OF THE ELEMENTS**

<table>
<thead>
<tr>
<th>Group I</th>
<th>Group II</th>
<th>Group III</th>
<th>Group IV</th>
<th>Group V</th>
<th>Group VI</th>
<th>Group VII</th>
<th>Group O</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1 1.0079</td>
<td>Li 3 6.94</td>
<td>Be 4 9.012</td>
<td>B 10.81</td>
<td>C 12.011</td>
<td>N 14.007</td>
<td>O 15.999</td>
</tr>
<tr>
<td></td>
<td>1s1</td>
<td>2s1</td>
<td>2p1</td>
<td>2s2</td>
<td>2p2</td>
<td>2p6</td>
<td>2p6</td>
</tr>
<tr>
<td>Na 11</td>
<td>22.990</td>
<td>Mg 12 24.305</td>
<td>3s2</td>
<td>Si 28.086</td>
<td>P 30.974</td>
<td>S 32.06</td>
<td>Cl 35.453</td>
</tr>
<tr>
<td>K 19</td>
<td>39.106</td>
<td>Ca 20 40.08</td>
<td>4s2</td>
<td>K 39.106</td>
<td>4s2</td>
<td>4p5</td>
<td>4p6</td>
</tr>
<tr>
<td>Rb 37</td>
<td>85.467</td>
<td>Sr 38 87.62</td>
<td>5s2</td>
<td>Ca 40.08</td>
<td>5s2</td>
<td>5p5</td>
<td>5p6</td>
</tr>
<tr>
<td>Cs 55</td>
<td>132.906</td>
<td>Ba 56 137.33</td>
<td>6s2</td>
<td>Sr 87.62</td>
<td>6s2</td>
<td>6p5</td>
<td>6p6</td>
</tr>
<tr>
<td>Fr 87</td>
<td>226.025</td>
<td>Ra 88</td>
<td>7s2</td>
<td>Ba 137.33</td>
<td>7s2</td>
<td>7p5</td>
<td>7p6</td>
</tr>
</tbody>
</table>

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• **LANTHANIDE SERIES**
  - La 139.906
  - Ce 140.908
  - Pr 140.908
  - Nd 144.242
  - Eu 151.966
  - Lu 174.967

• **ACTINIDE SERIES**
  - Ac 227
  - Th 232.038
  - Pa 231.035
  - U 238.029
  - Np 237.048
  - Pu 244
  - Am 243
  - Cm 247
  - Bk 247
  - Cf 251
  - Es 253
  - Fm 257
  - Md 259
  - No 259
  - Lr 260

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* Average value based on the relative abundance of isotopes on earth. For unstable elements, the mass of the most stable isotope is given in brackets.

Physics 460 F 2006 Lect 22
Superconducting transition

- Transition is VERY narrow - $\Delta T < 10^{-4}$ K
- Reversible (unlike magnet)
- Transition Temperatures $T_c$
  - Al  1.2 K  Hg  4.6 K  Pb  7.2 K
  - Au  $< 0.001$ K - not found to be superconducting!
  - Na$_3$C$_{60}$  40 K  (1990)
  - YBa$_2$Cu$_3$O$_7$  93 K  (1987)
  - Record today  140 K
Is Resistance Really ZERO??

- Currents have been flowing in rings in laboratories with no detectable loss for > 50 years!

- Theory says the current can continue for $T >$ age of universe
Effect of a Magnetic Field

- Magnetic fields tend to **destroy** superconductivity

Note: $H = \text{external applied field}$
- $B = \text{internal field}$
- $B = H + \mu_0 M$
- $M = \text{Magnetization}$

Phase Transition
SUPERCONDUCTING
STATE IS
A NEW PHASE OF MATTER
Not just a perfect conductor!

- A superconductor is NOT just a perfect conductor
- A perfect conductor would do the following:

**Zero Field Cooled**

- $T > T_c$
- $T < T_c$

**Field Cooled**

- $T > T_c$
- $T < T_c$

Trapped Field

A superconductor is different!
Meisner Effect (1934)

- A superconductor can actively push out a magnetic field - the Meisner effect

The superconductor can exclude a magnetic field up to a "critical field" $H_c$
Meisner Effect

- Magnetic field $B$ is excluded for fields less than a “critical field” $H_c$ where $H$ is the external applied field.
- The total internal field is $B = H + \mu_0 M$.
- For “type I” superconductors $B=0$ for $T < T_c$.
- **Perfect Diamagnetism**!
Type I vs Type II

• Magnetic field $B$ is excluded only up to a critical field $H_{c1}$

• For type II superconductors, at higher fields there is penetration of the field coexisting with superconductivity up to $H = H_{c2}$

\[ -\mu_0 M \]

![Graph showing Type I vs Type II superconductors](image)
Type II

• For type II superconductors, at higher fields there is penetration of the field in lines of normal material coexisting with superconductivity in surrounding material up for $H_{c1} < H < H_{c2}$

• “Flux Lattice” of quantized units of flux (more later)

Magnetic flux penetrates through the superconductor by creating small regions normal metal

$H_{\text{applied}}$
Heat capacity (Specific Heat)

- Comparison of electrons in a superconductor and a normal metal

\[ C \sim N_{\text{elec}} k_B \left( \frac{T}{T_F} \right) \]

Phase Transition

- Shows there is an energy gap in the superconductor! (Specific heat is like an insulator!)
Isotope Effect (1950)

• For materials made from the same elements - but different isotopes - $T_c$ changes!

• Experiment - $T_c \sim 1/ M^{1/2}$

• MUST be connected to MOTION of the nuclei
Summary

• Normal metal - Recall properties
  No special magnetic properties for non-magnetic metals, $\mu \approx 1$, $B \approx H$
  Resistance vs $T$
  Heat capacity vs $T$

• Superconductivity - Experimental Facts
  ZERO resistance at nonzero temperature
  NEW PHASE OF MATTER  Meisner Effect (expulsion of magnetic fields) - shows a superconductor is not just a perfect conductor
  Heat Capacity - shows there is a phase transition - below $T_c$ a gap, like an insulator!
  Isotope effect - something to do with MOTION of nuclei
Next time

- Superconductivity - theory
  Basic ideas and phenomena
  Bardeen- Cooper-Schrieffer Theory - 1957
  (Nobel Prize for work done in UIUC Physics)

- (Kittel parts of Ch 10)