4.3 A NOTE ON SUPERCONDUCTIVITY

Metals
• The definitive characteristic of a metal is its ability to conduct electricity that increases as the temperature decreases.
• The temperature dependence of conductivity in a metal is readily explained by the band model of solids.
  - In a partially filled band, there are immediately accessible higher energy states allowing unpaired electrons to move about freely (itinerant electrons) and to be accelerated under the influence of an electric field. (NOTE: the application of an electric field skews the relative energy of the crystal orbitals over the material – electrons flow from higher to lower energy).
  - In a metal, conductivity decreases with increasing temperature because electron scattering caused by interaction with the lattice vibrations (phonons) decreases the “freeness” of the itinerant electrons.
  - Temperature is essentially a measure of the kinetic energy of a medium or sample. Thus, increasing the temperature of a solid increases the kinetic energy of the lattice vibrations.
• Above some critical temperature $T_{IM}$, a metal-to-insulator transition occurs.
Superconductors

- The definitive characteristic of a superconductor is its ability to conduct electricity with an electrical resistivity of zero ($\Omega = 0$).
  - In other words, if you induce a circulating current in a ring made of (an ideal) superconducting material, it will go on indefinitely – no decay!

- As with metallic conductivity, superconductivity is a critical phenomenon. In other words, it occurs below some critical temperature $T_c$. Above this temperature, the material can be a metal, an insulator or a semiconductor.
  
  - NOTE: Many (but not all!) elemental metals become superconductors at low temperatures. (E.g., Hg, Al, Zn, Y, La, Ru, Sn, Pb …)
  
  - NOTE: The ferromagnetic metals, coinage metals and alkali metals do not superconduct at low $T$. (i.e., Fe, Co, Ni, Cu, Ag, Au, Pd, Pt, Li, Na, …)

Source: M&T
EXPLANATION…sort of…**BCS theory** at a glance (Bardeen, Cooper & Schrieffer)

Due to the interactions of the electrons with the vibrations of the atoms in the lattice, there is a small net effective *attraction* between the electrons. The result is that the electrons form together in bound pairs (**Cooper Pairs**)

A single electron is a Fermi particle (spin $\frac{1}{2}$), but a bound pair is a **Bose particle** (spin 0 or 1) and Bose particles are *not subject to the Pauli exclusion principle*!!

Bose particles tend to all adopt *exactly the same quantum state*…the collection of Cooper pairs shows macroscopic occupation of the same quantum state with the *same common momentum*!

When a phonon interacts with a member of the Cooper pair to change its momentum, an equal and opposite change occurs in the other member of the pair with the reemission of a phonon to the lattice…*no net change in momentum (no resistance)!*

The interaction of one electron of a Cooper pair with the lattice vibrations leaves a message for the other electron in the pair and allows interactions over a longer distance (coherence length) and longer time (vibrational relaxation time) than would be possible for free electrons.

So, the two electrons in a pair are *not* held together very closely like a point particle; they are relatively far removed from one another.

A Cooper pair can be considered a wave packet with a diameter corresponding to the coherence length. Overlapping wave packets phase lock the different Cooper pairs. Because of the phase coherence, we may say that the relationship of superconduction to normal conduction is similar to that of a LASER beam to normal light.

The energy of pairing (i.e., net attraction) is very weak. Only a small increase in lattice vibration (i.e., temperature) is enough to throw the electrons apart by thermal agitation and convert them back to “normal” electrons.

- In addition to the vanishing electrical resistance below $T_c$, a number of other phenomena are associated with superconductivity:
  - **Magnetic fields below a critical field strength ($H_c$) are excluded**…
    … they can’t penetrate the superconducting material!! …

**WHY?**

If, as you build up a magnetic field, any of it were to build up inside the material, there would be a rate of change of flux which would produce an electric field, and an electric field would immediately generate a current which, by Lenz’s law, would oppose the flux.
Since all the electrons move together, an infinitesimal electric field will generate enough current to oppose completely any applied magnetic field.

So, if you turn the magnetic field on after you’ve cooled a metal to its superconducting state, the field will be excluded.

- A related phenomenon: for a material that is a metal conductor at high temperature and a superconductor at low temperature, if you establish a magnetic field through it at high temperature and then lower the temperature below $T_c$, the magnetic field is expelled! In other words, it starts up its own current – and in just the right amount to push the field out!

… this is called the Meissner effect: http://www.youtube.com/watch?v=Be3qiux6Dow

- The Meissner effect is often demonstrated by the levitation of a permanent magnet above a piece of superconducting material.

- The permanent magnet is repelled (resulting in levitation) because it induced supercurrents within the superconducting material that exclude that magnetic field brought near it. Effectively, the permanent magnet “sees” a mirror image magnetic field at the superconductor’s surface.

- Because there is zero resistance in the superconductor, the supercurrents can adjust rapidly to maintain levitation of the permanent magnet even if it is in motion.

- At magnetic field strengths above critical $H_{c1}$, magnetic flux will penetrate the bulk of the superconductor and at an upper critical field strength ($H_{c2}$) destroy the superconductivity.

- When $H_{c1} = H_{c2}$, the superconductor is termed type I. Superconducting elements, other than Nb, are type I.

- For type II superconductors ($H_{c2} > H_{c1}$), magnetic flux will penetrate the bulk sample producing a mixed state with magnetic cores arranged in a regular array in the bulk superconductor.

- Also observed: the heat capacity displays a discontinuity at $T_c$.

- Also observed: anomalous effects in the Debye-Waller factor – a measure of the vibrational stiffness – in the vicinity of $T_c$. 
EXAMPLE: YBCO … (pronounced ‘ib-co’)
YBa$_2$Cu$_3$O$_{7-x}$
- so-called ‘123’ superconductor, from proportion of metal atoms
- most well-known HTSC ($T_c = 93$ K)
- structure is like perovskite but with missing O atoms
- the stoichiometric YBa$_2$Cu$_3$O$_7$ unit cell consists of 3 simple perovskite cubes stacked vertically with Y and Ba in the A sites of the original perovskite and Cu atoms in the B sites … but a large number of vacant O sites means that the B sites are not surrounded by an octahedron of O atoms!
- also, the Y and Ba in the A sites have less than 12-coordination

RESULT: some Cu atoms have five O atom neighbors (square pyramidal)
some Cu atoms have only four O atoms (square planar CuO$_4$)
YBa$_2$Cu$_3$O$_7$ readily loses oxygen atoms forming YBa$_2$Cu$_3$O$_{7-x}$ ($0 < x < 1$), but for $x > 0.1$ the $T_c$ drops with increasing $x$.

Source: “Shriver and Atkins”

- We can easily explain the metallic conductivity at RT using band theory.
- We can see a correlation between the YBCO structure and superconductivity:
  - Many HTSC materials have at least part of their structure derived from that of perovskite… i.e., layers of linked CuO$_n$ ($n = 4, 5, 6$) polyhedra