PHYS3080 – Part II
Semiconductors 5/Superconductors 1

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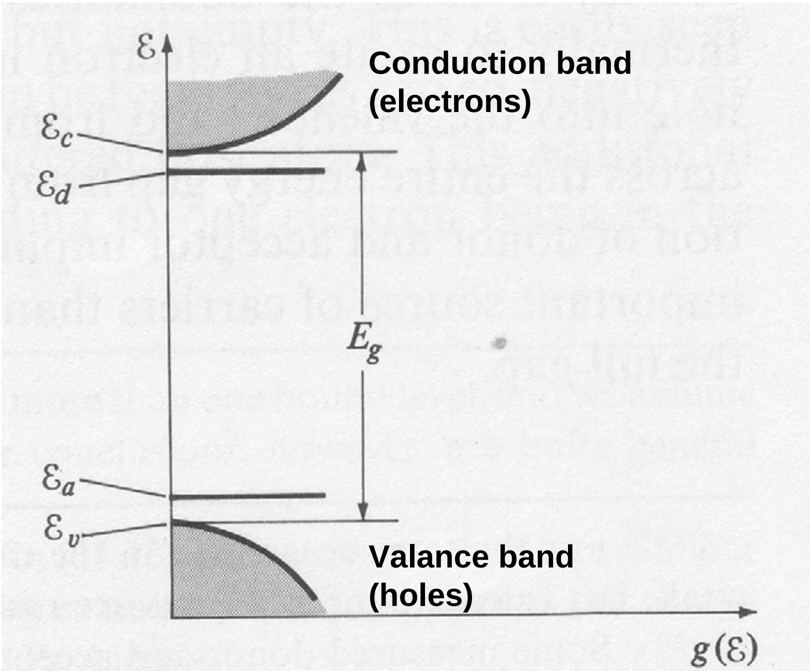
Thermal excitation of carriers



Calculation of number of charge carriers at any temperature T, makes use of this diagram

Notation

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

Some textbooks refer to this term as the chemical potential, μ, while others refer to it as E_f or ε_f.

Either is fine but note that in statistical mechanics Fermi level ε_f describes μ specifically at T=0.

Carrier concentration of electrons

We apply Fermi-Dirac statistics to the appropriate set of 1 electron levels
Certain relations hold regardless of impurity and we start with those

Impurity levels produce new bands below/above the conduction band/valance bands, but conduction is entirely from e^- in conduction band and h^+ in the valance band so regardless of impurities, total number of carriers (electrons in this example) are

Impurities effect n, only through μ used in f(E)

$$n(T) = \int_{E_c}^{\infty} f(E)g(E)dE$$

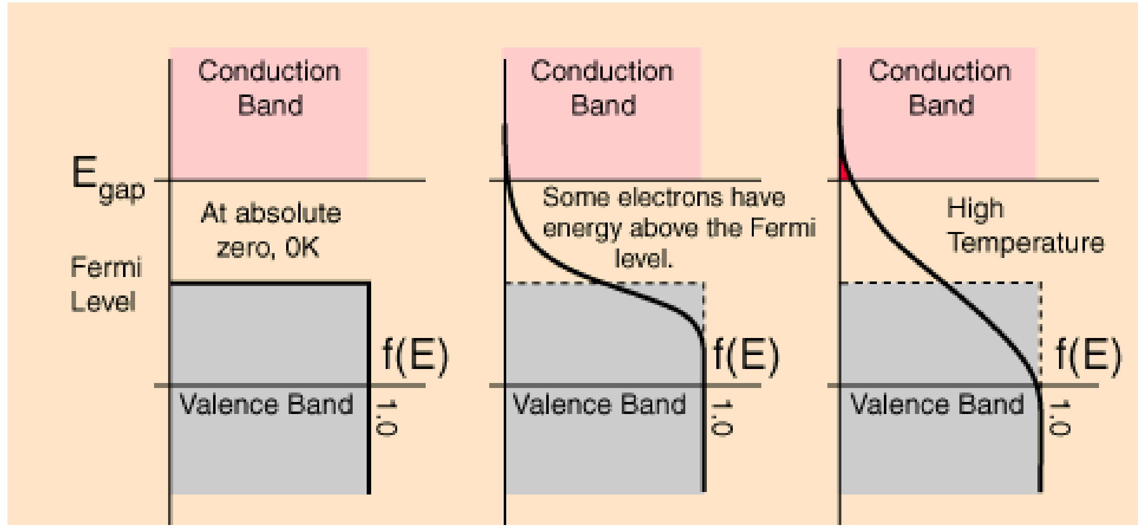
Probability of occupation of electron states at temperature T (the Fermi function)

Density of electron states in the *conduction* band

Fermi distribution

$$n = \int_{E_c}^{\infty} \boxed{f(E)}\, g(E)\, dE$$

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

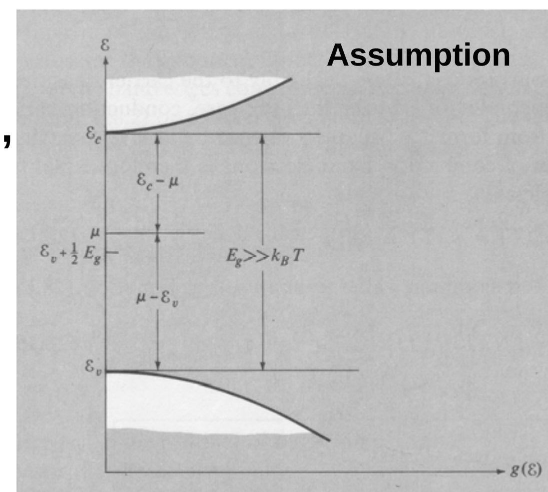


Fermi distribution f(E) is the probability of occupation of a state of energy E at a given temperature T. The chemical potential, μ, adjusts to give the correct number of particles.

At room temperature, $E_g \gg K_B T$
So f(E)~1 in valance band and is very small in conduction band, so we assume that μ is far from E_c (cf $k_B T$) and thus make the following approximation for f(E);

For an electron in the conduction band, $E - \mu \gg k_B T$

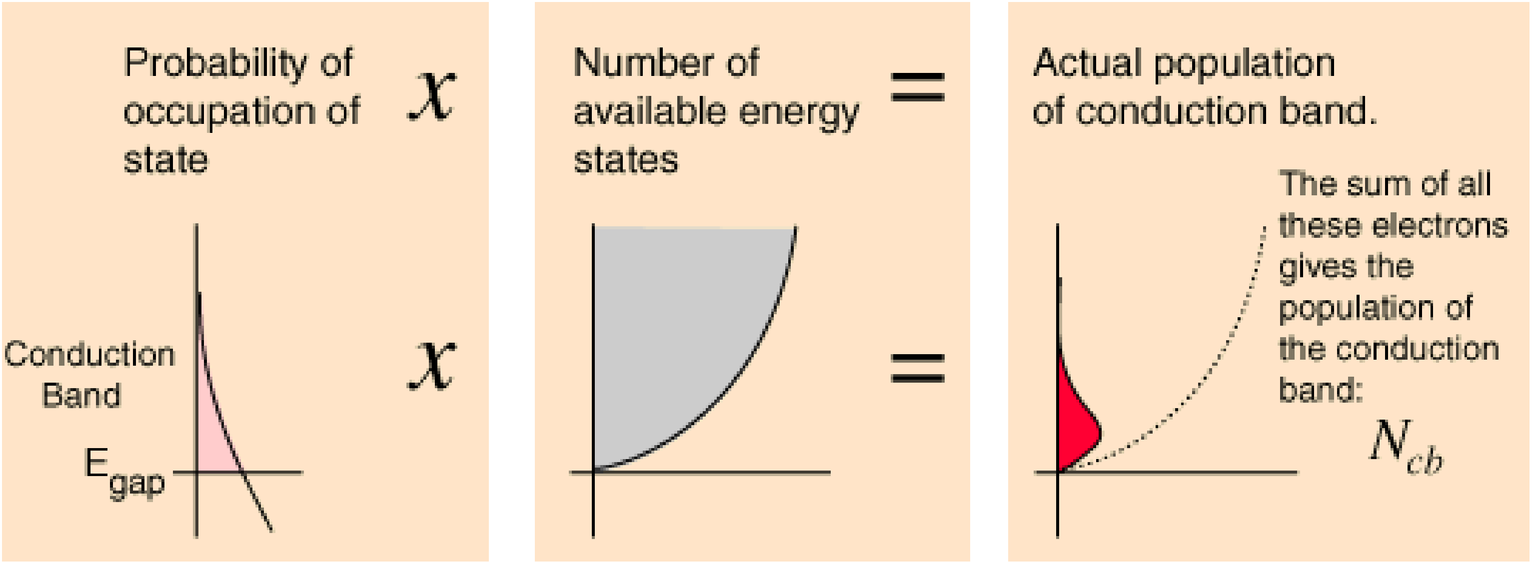
So $e^{(E-\mu)/k_B T} \gg 1$ and $\boxed{f(E) \approx e^{(\mu - E)/k_B T}}$



Carrier concentration of electrons

$$n = \int_{E_c}^{\infty} f(E)g(E)dE \approx \int_{E_c}^{\infty} e^{(\mu - E)/k_B T} \, (2m_e)^{3/2}(E - E_C)^{1/2} dE$$

$$\boxed{n = N_C e^{(\mu - E_C)/k_B T},} \text{ where } N_C = 2\left(\frac{2\pi m_e k_B T}{h^2}\right)^{3/2}$$



N_C is the effective number of levels per unit volume in the conduction band if we assume they are all concentrated at the bottom of the band, $E=E_c$

Carrier concentration of holes

The probability that a state in the valance band is occupied by a hole is 1-f(E), which can be written

$$1-f(E)=1-\frac{1}{e^{(E-\mu)/k_BT}+1}=\frac{e^{(E-\mu)/k_BT}}{e^{(E-\mu)/k_BT}+1}=\frac{1}{e^{(\mu-E)/k_BT}+1}$$

For μ-E >> k_BT, the above equation can be approximated, in a similar manner to the electron case, as $1-f(E)\approx e^{(E-\mu)/k_BT}$

So, the number of holes in the valance band is

$$p=\int_{-\infty}^{E_V}[1-f(E)]g(E)dE \ = \int_{-\infty}^{E_V} (2m_h)^{3/2}(E_V-E)^{1/2}e^{(E_V-\mu)/k_BT}dE$$

$$\boxed{p=N_V e^{-(\mu-E_V)/k_BT},} \quad \text{where } N_V=2\left(\frac{2\pi m_h k_BT}{h^2}\right)^{3/2}$$

N_v is the effective number of levels per unit volume in the valance band if we assume they are all concentrated at the bottom of the band, E=E_v

Law of Mass Action

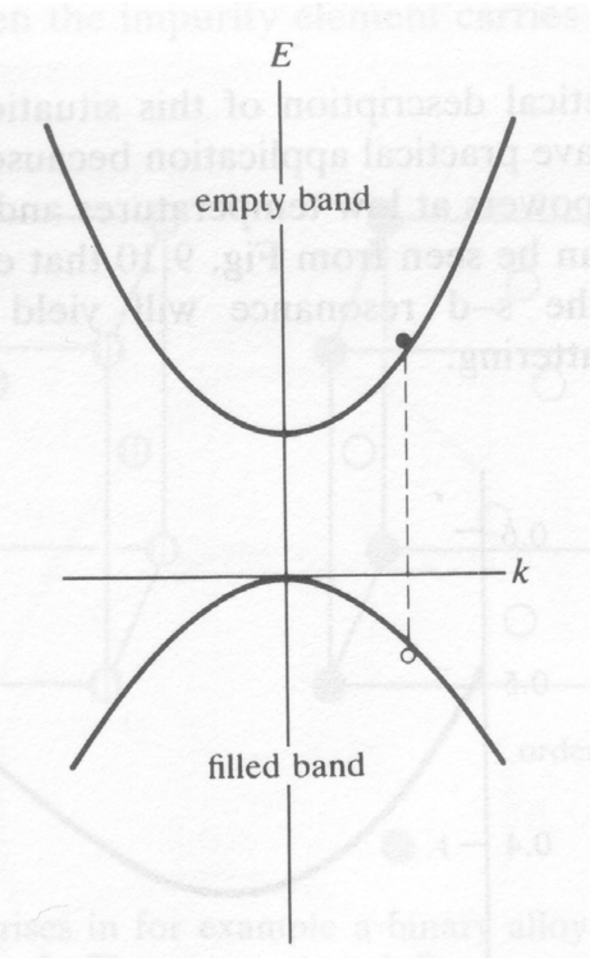
We still need to know μ, to infer n(T) or p(T) but the μ dependence disappears if we multiply the two densities together

$$np = N_C e^{(\mu - E_C)/k_B T} N_V e^{-(\mu - E_V)/k_B T}$$

$$= N_C N_V e^{-(E_C - E_V)/k_B T} = N_C N_V e^{-E_g/k_B T}$$

- So if you know one carrier density you know the other
- What this says is that at any fixed temperature there is a equilibrium between the number of carriers thermally generated and number lost due to electron-hole recombination (called annihilation)
- Note that *np is independent of μ, and so independent of impurity concentration*. The if more electrons are added via additional dopants, the number of holes will be reduced via annihilation, keeping np constant

Intrinsic behaviour



$$np = N_C N_V e^{-E_g/k_B T} = n_i^{\,2}$$

where n_i is the electron concentration for an *intrinsic* semiconductor

so $n_i = p_i =$ $\sqrt{N_C N_V e^{-E_g/k_B T}} = \sqrt{N_C N_V}\, e^{-E_g/2k_B T}$

We can now establish the validity of our initial $E_c - \mu \gg k_B T$ assumption by determining the intrinsic chemical potential μ_i

Chemical potential of an intrinsic semiconductor

We have already determined that,

$$n = N_C e^{(\mu - E_C)/k_B T}$$ **and** $$p = N_V e^{-(\mu - E_V)/k_B T}$$ **and since $n_i = p_i$**

$$N_C e^{(\mu_i - E_C)/k_B T} = N_V e^{-(\mu_i - E_V)/k_B T} \Rightarrow \frac{N_V}{N_C} = e^{(2\mu_i - E_g)/k_B T}$$

thus we re-arrange to give the chemical potential,

$$\mu_i = \frac{1}{2}E_g + \frac{1}{2}k_B T \ln(N_V / N_C)$$

since $N_V = 2\left(\frac{2\pi m_h k_B T}{h^2}\right)^{3/2}$, $N_C = 2\left(\frac{2\pi m_e k_B T}{h^2}\right)^{3/2}$

gives $\mu_i = \frac{1}{2}E_g + \frac{3}{4}k_B T \ln(m_h / m_e) \longrightarrow$

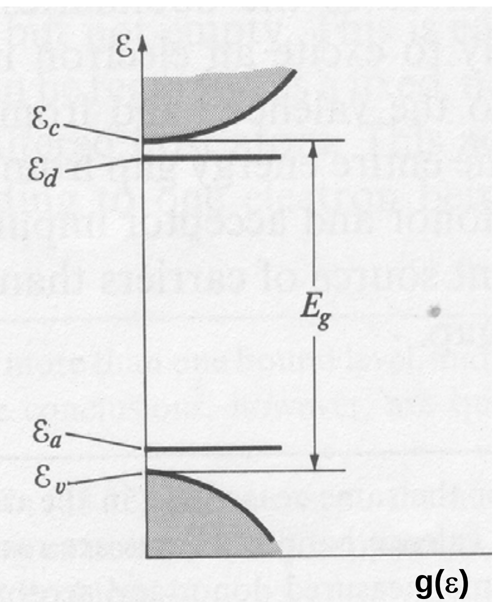
so, as $T \to 0$ $\boxed{\mu_i \to \frac{1}{2}E_g}$

Since $\ln(m_h / m_e)$ is of order 1, μ_i will not stray further than $k_B T$ from the centre of the bandgap, therefore our initial assumption that $E_c - \mu >> k_B T$ is valid for intrinsic semiconductors (bandgaps typically 0.5-1 eV)

Extrinsic semiconductor

For extrinsic semiconductors the value of $\mu(T)$ is different from $1/2E_g$ and we go about determining it by considering the charge neutrality of the semiconductor

Charge neutrality $\rightarrow$ $n + N_A^- = p + N_D^+$



$$N_D^{\ +} = N_D\underbrace{[1 - f(E_C - E_D)]}_{\text{Probability that state at } E_C\text{-}E_D \text{ is unoccupied by an electron}} = N_D \frac{1}{e^{(\mu-(E_C-E_D)/k_BT}+1}$$

Total number of donors

$$N_A^{\ -} = N_A \underbrace{f(E_A - E_V)}_{\text{Probability that state at } E_A\text{-}E_V \text{ is occupied by an electron}} = N_A \frac{1}{e^{((E_A-E_v)-\mu)/k_BT}+1}$$

Total number of accepters

$$n = N_C e^{(\mu-E_C)/k_BT} \qquad p = N_V e^{-(\mu-E_V)/k_BT}$$

Solving these equations to get $\mu(T)$ is complicated so we just consider specific cases

Chemical potential of an extrinsic semiconductor

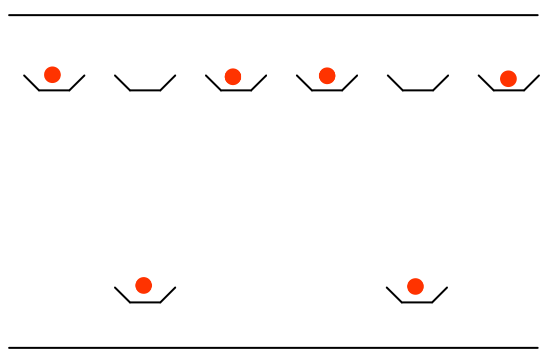
If both types of carrier are present, e.g. $N_D > N_A$, at $T=0$

Conduction band empty →

N_D - N_A unionised → **← $\mu = E_C - E_D$**

Acceptor band full →

Valance band full →



At low T, μ is relatively unchanged and putting $\mu = E_C - E_D$ in our equation for n, gives

$$n = N_C e^{(\mu - E_C)/k_B T} \approx N_C e^{((E_C - E_D) - E_C)/k_B T} \approx N_C e^{-E_D/k_B T}$$

Comparing with n_i the intrinsic electron concentration $n_i = \sqrt{N_C N_V} e^{-E_g/2k_B T}$

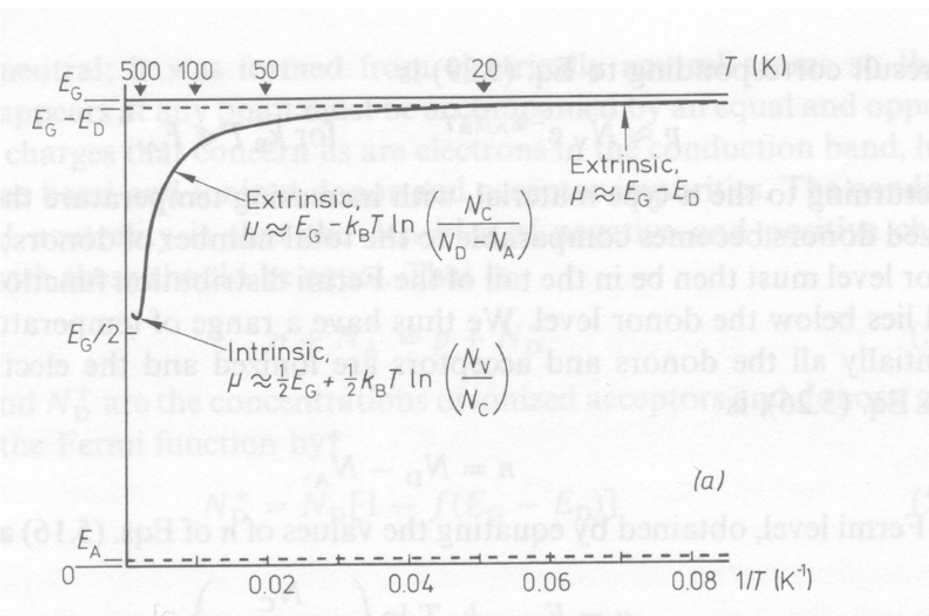
E_D << E_g so the extrinsic electron concentration is much greater than the intrinsic one. From the law of mass action $p_{extrinsic}$ must be << n_i so electrons are the *majority carrier* and the material is *n-type*

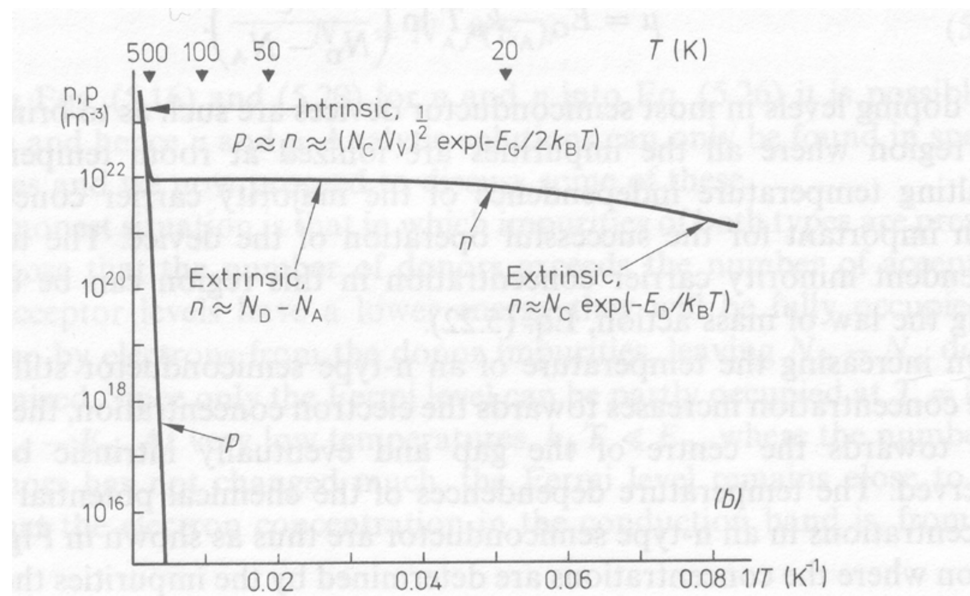
Chemical potential of an extrinsic semiconductor

Raising the temperature , i.e. T>0, results in all the donors being ionised

n = N_D - N_A so, using $n = N_C e^{(\mu - E_C)/k_B T} = N_D - N_A$

$$\Rightarrow \mu = E_g - k_B T \ln\left(\frac{N_C}{N_D - N_A}\right)$$





μ as a function of 1/T

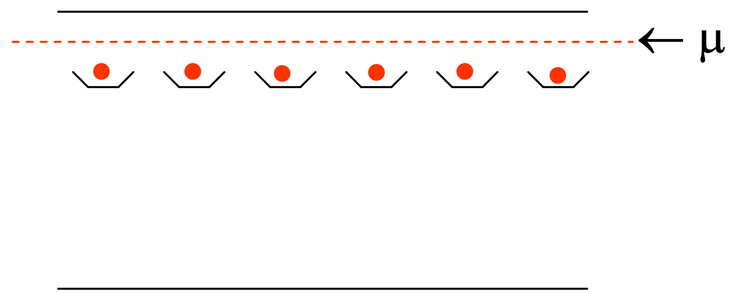
n as a function of 1/T

If only one type of impurity is present

e.g. electrons, at T=0 and very low T

Conduction band empty →

Donor level full →



Valance band full →

This is similar to the intrinsic case with the donor level taking the place of the valance band

$$N_D^{\ +} = N_D[1 - f(E_C - E_D)]$$

$$1 - f(E_C - E_D) = 1 - \frac{1}{e^{((E_C - E_D) - \mu)/k_B T} + 1} = \frac{e^{((E_C - E_D) - \mu)/k_B T}}{e^{((E_C - E_D) - \mu)/k_B T} + 1} = \frac{1}{e^{(\mu - (E_C - E_D))/k_B T} + 1}$$

assuming $(E_C - E_D) - \mu >> k_B T \quad \Rightarrow N_D^{\ +} \approx N_D e^{((E_C - E_D) - \mu)/k_B T}$

Since there are no holes, electrical neutrality requires $n = N_D^+$ so using

$n = N_C e^{(\mu - E_C)/k_B T}$ **gives** $n = (N_C N_D)^{1/2} e^{-E_D/2k_B T}$

Different from both carriers case by factor of 2

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Superconductors 1

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Superconductivity lectures: overview

Our previous descriptions of metals and semiconductors have assumed the 'independent electron approximation' i.e. we have ignored electron-electron interactions. A spectacular failure of the independent electron approximation occurs when trying to explain the low temperature properties of *superconductors.*

Most striking features of superconductors are

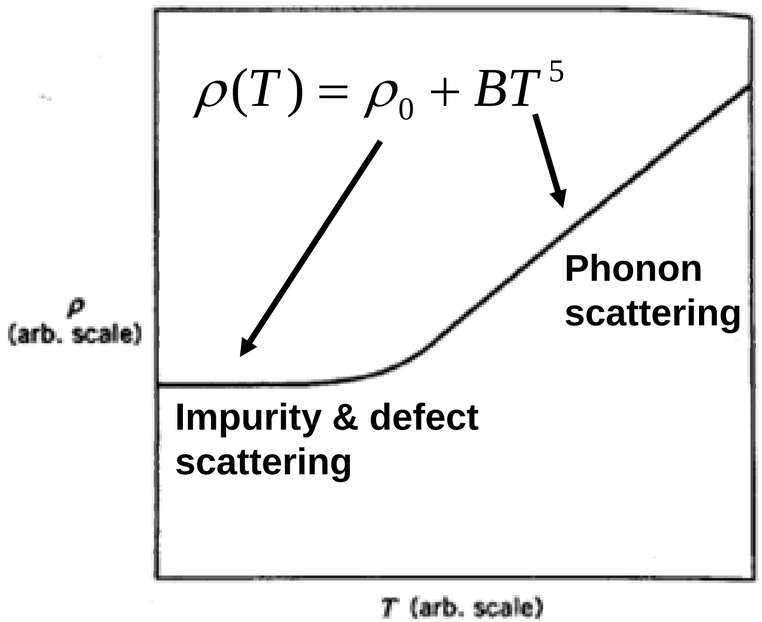
- A superconductor can behave as if it has no DC resistance. Currents can be established which, in the absence of a driving field, do not decay. Record is 2½ years!
- A superconductor can behave as a perfect diamagnet. In an applied magnetic field a superconductor carries electrical surface currents. These currents give rise to an additional magnetic field which precisely cancels the applied magnetic field within the magnet.
- A superconductor usually behaves as if there were a gap in energy of width 2Δ centred about the Fermi energy. So electron can only be extracted from a superconductor if E_F-E exceeds Δ.

Theory of superconductivity: hard! Superconductivity is explained by the BCS model which is based on the idea that electrons are bound in pairs, by lattice vibrations. We will explore these ideas qualitatively later.

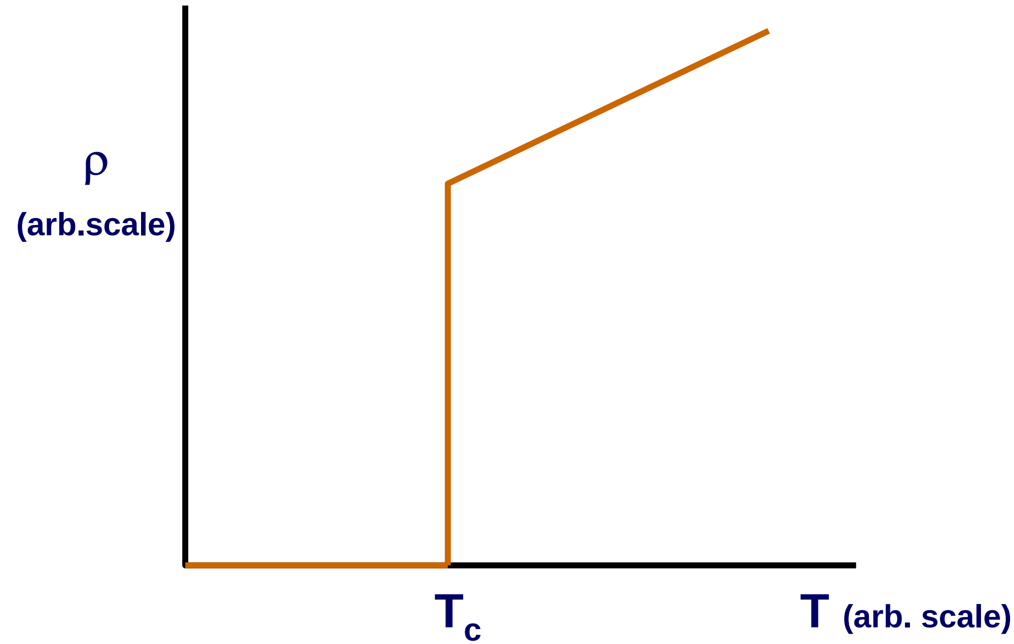
First we look at the experimentally determined properties of superconductors.

Discovery of superconductivity

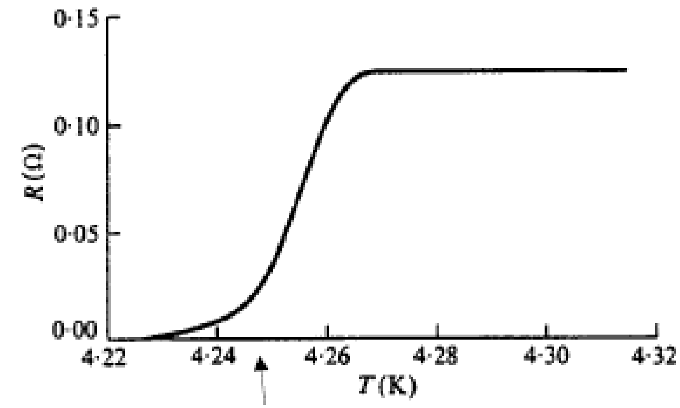
Electrical resistivity of a typical metal



Electrical resistivity of a superconductor

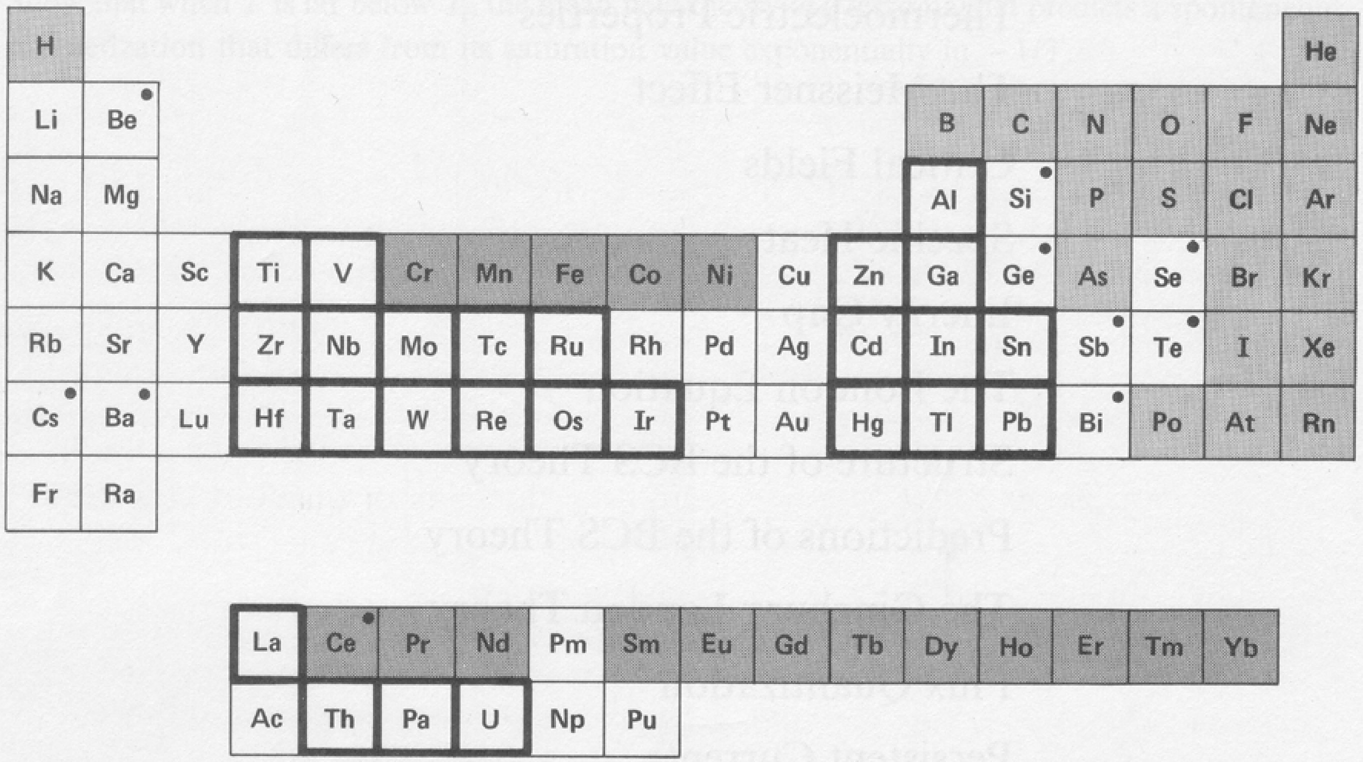


- **Discovered in 1911 by H Kamerlingh-Onnes, 3 years after his 1st liquefaction of helium**
- **First measured in mercury.**
- **Very sharp transition at 4.2 K**
- **Not related to high purity**



Which elements are superconductors?

SUPERCONDUCTING ELEMENTS[a]



[a]Elements that are superconducting only under special conditions are indicated separately. Note the incompatibility of superconducting and magnetic order. After G. Gladstone, et al. Parks *op. cit*, note 6.

Legend:

Al — Superconducting

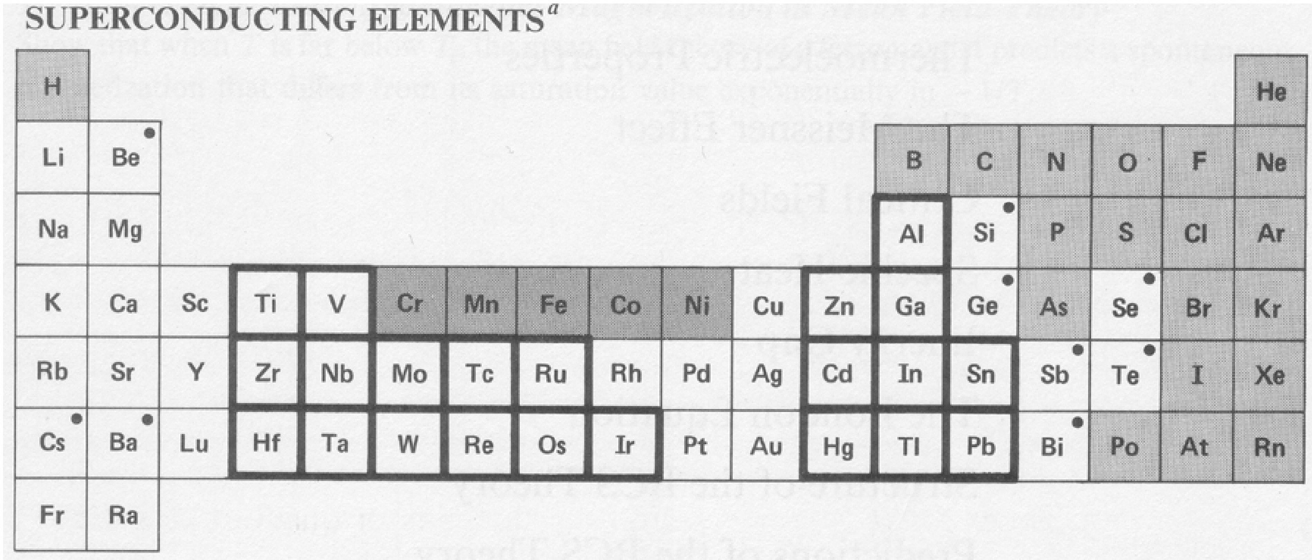
Si — Superconducting under high pressure or in thin films

Li — Metallic but not yet found to be superconducting

B — Nonmetallic elements

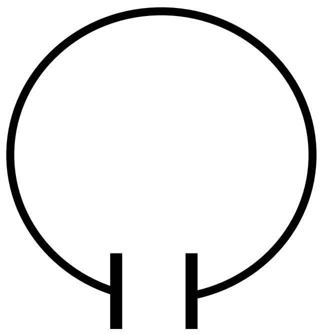
Fe — Elements with magnetic order

Which elements are superconductors?



- **More than 20 metallic elements are superconductors**
- **Cu, Au, Ag, Na, K and magnetically ordered metals (Fe, Ni, Co) *are not* superconductors**
- **Certain *semiconductors* are superconducting at high pressures or as thin films**
- **Highest T_c of an element is 9.3 K for Nb**
- **There are thousands of alloys and compounds that exhibit superconductivity**
- **The highest T_c superconductors tend to be poor conductors in the normal state**
- **Record T_c is currently ~ 125 K**

Persistent current of a superconductor



Most sensitive method of measuring a small resistance;

$\rightarrow$ Look for the decay of current around a closed superconducting loop

R = Resistance of the loop
L = Self-inductance

Current should decay with time constant τ = L/R

No decay observed!

$$V = -L\frac{dI}{dt} = IR \qquad \frac{d}{dt}\log I = -\frac{R}{L} \qquad \boxed{I(t) = I_0 e^{\frac{-R}{L}t}}$$

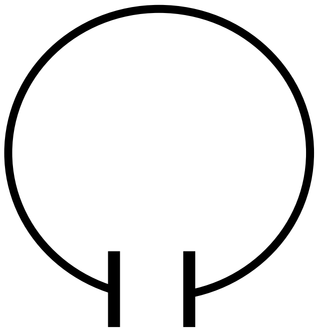
This gives an upper value on the value of R

Resistivity $\rho < 10^{-26}$ Ω-cm for a superconductor

Compare with $\rho < 10^{-8}$ Ω-cm for Cu

18 orders of magnitude difference!

Limitations of persistent current flow



Persistent currents will flow in a superconductor unless;

1) A sufficiently large magnetic field is applied

2) The current exceeds a certain critical current, I_c, (the Silsbee effect)

The size of I_c, depends on the nature and geometry of specimen but can be as large as 100 amp for a 1-mm wire

3) An AC electric field above a certain frequency is applied

The transition from dissipationless to normal response occurs at $\omega \sim \Delta/\hbar$ where Δ is the energy gap

Thermoelectric properties of superconductors

Superconductors are poor thermal conductors

Figure 34.2
The thermal conductivity of lead. Below T_c the lower curve gives the thermal conductivity in the superconducting state, and the upper curve, in the normal state. The normal sample is produced below T_c by application of a magnetic field, which is assumed otherwise to have no appreciable affect on the thermal conductivity. (Reproduced by permission of the National Research Council of Canada from J. H. P. Watson and G. M. Graham, *Can. J. Phys.* **41**, 1738 (1963).)