# **PYU44P13 Magnetism and Superconductivity**

J. M. D. Coey

- 1. Introduction
- 2. Magnetic fields and forces
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- 4. Magnetism of atoms
- 5. Magnetism in solids.
- 6. Simple models of metals
- 7. Superconductivity
- 8. Theory
- 9. Tunnelling
- 10. Applications



Comments and corrections please email: jcoey@tcd.ie

# **Magnetism and Superconductivity; Part 2**

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- 6 Simple models of metals
- 7. Superconductivity
- 8. Theory
- 9. Tunnelling
- 10. High T<sub>sc</sub> Applications





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# Superconductivity

This part of the course provides a basic account of the phenomena and theory of superconductivity in metals, and discusses applications such as SQUIDS, levitation and high-temperature superconducting materials. It will be of interest the experimental and theoretical physicists, and to materials scientists. Requirements are elementary electromagnetism, quantum mechanics statistical and solid state physics.

Recommended books; General solid state texts

• J. R. Christman: *Fundamentals of Solid State Physics*, Wiley 1988: Clearly-written and succinct

• C. J. Kittel *Introduction to Solid State Physics*, Wiley 7th edition 1994 The classic text with useful appendices. Units are a confusing mixture of cgs and SI

• N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Holt, Reinhart and Winston 1976: An excellent advanced text. cgs units

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Elementary Texts.

- M. Cyrot and D. Pavuna *Introduction to Superconductivity and High-T<sub>c</sub> Materials*, World Scientific 1992 A modern introduction.
- A. C. Ross Innes and E. H. Rhoderick *Introduction to Superconductivity and High-T<sub>c</sub> Materials*, World Scientific 1992 An excellent introduction to the physics of superconductivity
- J. F. Annett. *Superconductivity, Superfluids and Condensates,* Oxford 2004 Ch 3 6. A more advanced treatment of all the main macroscopic quantum phenomena

Advanced Texts.

- M. Tinkham, *Introduction to Superconductivity*, Dover . 2004.
- P. G. de Gennes, *Superconductivity of Metals and Alloys* Benjanin 1966

- Dirac statistics and the Fermi Surface. Conductivity, mean free path, Ohm's law, Pauli susceptibility Stoner criterion in a metal Electronic specific heat. Temperature-dependence of resistivity of a metal. Matthiesen's rule. Impurity scattering and electron-phonon scattering
- 7 Superconductivity. Transition to zero resistance, critical field and critical current. Meissner effect. Difference between perfect conductors and superconductors. Surface currents and magnetization. Shape effects. Heat capacity and energy gap. High-frequency properties. Isotope effect. Type I and Type II superconductors. Hc1, Hc2 and Hc(0)
- 8 Macroscopic Theory. Thermodynamics and entropy. London postulate. Penetration depth. Ginzberg-Landau theory of the phase transition. Coherence. Energy of the superconductor/ normal interface. The vortex state. Microscopic Theory. Attractive electron-phonon interaction. The Cooper pair. BCS Ground state, Gap at the Fermi surface. The superconducting wave function. Phase. Coherence length. Explanation of persistent currents
- 9 Superconducting Tunneling. Flux quantization, Giaver tunneling, direct measurement of the gap. Josephson tunneling. AC and DC Josephson effects
- 10 Applications. Superconductors: Levitation, SQUIDS, High-Tc materials. Magnets: Electromagnetic drives, Magnetic recording, Spin electronics

# I. Simple Models of Metals (review)

# 1 Introduction

Three quarters of the elements in the periodic table are *metals*. Metals transport electrons freely under the influence of an electric field Normal metals are opaque and highly reflecting at all wavelengths



Most metals enter a ground state at low temperature (  $\leq 1$  K) which is magneticallyordered or superconducting, but *never both*. 18 elements order magnetically, 32 are superconducting (more at high pressure or in thin film form), some are neither (Na, K, Ne, Ar....), *none* are both at once.



## **1.1 Electrons**

The properties of metals reflect the electrostatic, Coulomb interactions among the electrons, and between the electrons and the nuclei. Metal physics is the physics of the Coulomb interactions of the outer electrons, subject to the constraints of quantum mechanics – but there are  $\sim 10^{20}$  atoms per cubic millimeter! As usual in physics we develop simplified models to treat the essential physics, and reproduce the rich variety of physical phenomena.

An electron is a point particle which possesses:

mass  $m = 9.109 \ 10^{-31} \text{ kg}$ charge  $-e = -1.602 \ 10^{-19} \text{ C}$ angular momentum (spin)  $\frac{1}{2}\hbar = 0.527 \ 10^{-34} \text{ J s}$ 

In metals, we are concerned with the outermost, weakly-bound conduction electrons of the atoms which have a binding energy of just about an electron volt.

```
e.g. {}^{29}Cu 1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}3d^{10}4s^{1} Ato

/ Core electrons Conduction electron n

Binding energy ~9 keV Binding energy ~1 eV fce
```

Atomic density  $n = 8 \ 10^{28} \text{ m}^{-3}$   $fcc, a_0 = 0.36 \text{ nm}$ atomic spacing 0.25 nm



Spin

Why is the last electron delocalized.?

 Confining an electron to an atom introduces an uncertainty in its momentum given by the Heisenberg relation

$$\Delta p \Delta x \sim \hbar$$

Take  $\Delta x \sim 0.25 \ 10^{-9} \,\text{m}$ ,  $\hbar = 1.054 \ 10^{-34} \,\text{Js}$  $\Delta p \sim 4.2 \ 10^{-25} \,\text{Jsm}^{-1}$  $(\Delta p)^2/2m \sim 18 \ 10^{-50}/2 \,\text{x} \ 9 \ 10^{-31} \sim 1.0 \ 10^{-19} \,\text{J} \approx 1 \,\text{eV}$  (1 eV = 1.602  $10^{-19} \,\text{J}$ )

#### — but

binding energy of a Bohr atom  $E_b = Z^2 R_0 / n^2$ 

 $R_0$  is the Rydberg constant, 13.6 eV  $Z_{eff} = 1$ n = 4

$$E_b \approx 1 \,\mathrm{eV}$$



# 2 Independent Electron Models

### 2.1 Drude Model (1900)

Drude considered the conduction electrons as a classical gas, which were involved in occasional collisions with the ion cores.

In an electric field, the electrons acquire a drift velocity  $v_d$  in the direction of E.

**j** = - *n* e **v**<sub>d</sub>

(1)

Current density A m<sup>-2</sup>

Conduction electron density

In a typical conductor, 1 A may flow in a  $1 \text{mm}^2$  conductor,  $j = 10^6 \text{ A m}^{-2}$ .  $v_d = j/ne = 10^6/8 \ 10^{28} \text{ x} \ 1.6 \ 10^{-19} \sim 10^{-4} \text{ m s}^{-1}$ .

Note  $v_d \ll \langle v \rangle$ , the mean velocity of the electrons;  $\langle v \rangle \sim 10^5 \text{ m s}^{-1}$  for classical electrons,  $E = (3/2)\text{kT} = \langle \frac{1}{2}\text{m}v^2 \rangle$  $\langle v \rangle \sim 10^6 \text{ m s}^{-1}$  for Fermi-Dirac statistics ( $E_F \sim 10 \text{ eV}$ ) [kT  $\approx 1/40 \text{ eV}$ ]

### 2.1.1 Ohm's law (1827)

Ohm's law is an experimental result for normal metals, originally written as V = IR, here



conductivity  $\Omega^{-1}$  m<sup>-1</sup>

(2)

For copper, a good metal  $\sigma \approx 10^8 \,\Omega^{\text{-1}} \,\mathrm{m}^{\text{-1}}$ 

Resistivity  $\rho$  is defined as  $1/\sigma$ .



For metals, generally 
$$\rho = 10^{-8} - 10^{-6} \Omega$$
 m

Resistance *R* of a bar of length *l* and cross-section *A* is  $R = \rho l/A$  ( $\Omega$ ) Note that  $\rho$  and  $\sigma$  are extensive properties of the metal.

How far ( $\lambda$ ) do the electrons travel between collisions? How long ( $\tau$ ) between collisions? Equating impulse (F $\tau$  = -e $E\tau$ ) to change of momentum (m $v_d$ ), we find  $v_d \approx -eE\tau/m$ ;

Hence from (1) and (2)  $\sigma = ne^2\tau/m$ 

For Cu,  $\tau = [10^8 \text{x}9.1 \ 10^{-31}]/[8 \ 10^{28} \text{x}(1.60 \ 10^{-19})^2] = 10^{-13} \text{ s}$ 

Define the mean free path as  $\lambda = \langle v \rangle \tau$  (Note *not* =  $v_d \tau$ ) For Cu  $\lambda \approx 100$  nm.

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#### 2.1.2 Hall effect

In a magnetic field **B**, there is an off-diagonal term in the resistivity (or conductivity)



For copper,  $R_{\rm H}$  is very small; measurements of  $R_{\rm H}$  give *n* (provided there is only one band)

$$E_y = R_{xz} B_z j_x$$



#### 2.2 Free Electron Model

We must now apply quantum mechanics to the electrons. They have spin  $\frac{1}{2}$ , and thus there are two magnetic states,  $m_s = -\frac{1}{2}$  (spin up  $\uparrow$ ) and  $m_s = +\frac{1}{2}$  (spin down  $\downarrow$ ), for every electron.

Suppose the electrons are confined in a box of volume V, where the potential is constant,  $U_0$ Electrons are represented by a wavefunction  $\psi(\mathbf{r})$  where  $\psi^*(\mathbf{r})\psi(\mathbf{r}) \, dV$  is the probability of finding an electron in a volume dV.



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Free -electron parabola

k

Only certain values of k are allowed. The boundary condition is that L is an integral number of wavelengths.

 $k_i = 0, \pm 2\pi/L, \pm 4\pi/L, \pm 6\pi/L$  .....

The allowed states are represented by points in *k*-space

There is just one state in each volume  $(2\pi/L)^3$  of k-space, And at most two electrons, one spin up  $\uparrow$  and one spin down  $\downarrow$ , can occupy each state. Electrons are fermions.

The energy of an electron in the box is  $E = p^2/2m$ 

$$E_{\rm k} = (\hbar k)^2 / 2m + U_0$$
 (4)



The points in k-space are very closely spaced; There are N  $\sim 10^{22}$  electrons in a macroscopic sample, so k is effectively a continuous variable.

At temperature T = 0, we fill up all the lowest energy states, with two electrons per state, up to the Fermi level. The energy of the last electron is the Fermi energy  $E_{\rm F}$ . The wavelength of the last electron is the Fermi wavelength  $k_{\rm F}$ .

The *N* occupied states are contained within the Fermi surface. In the free-electron model this surface is a sphere.

We calculate  $E_{\rm F}$ .

$$N = (4\pi/3)k_{\rm F}^3 \times 2/(2\pi/L)^3 \to k_{\rm F} = (3\pi^2 N/{\rm V})^{1/3}$$
(5)

$$(E_{\rm F} - U_0) = (\hbar k_{\rm F})^2 / 2m = (\hbar^2 / 2m) (3\pi^2 n)^{2/3}$$
 where  $n = N/V$  (6)

For Cu,  $(E_{\rm F} - U_0) \approx 7 \, {\rm eV}$ .

An equivalent temperature  $T_F$  is defined by  $kT_F = E_F$ . For Cu,  $T_F \approx 80,000$  K (1 eV =11605 K) The Fermi velocity  $v_F = \hbar k_F/m$  For Cu,  $v_F \approx 1.6 \ 10^6 \text{ m s}^{-1}$  (about 10 x the classical value)

D(E)	A useful concept is the density of states, the number of states per unit sample volume, as a function of k or E. From (5) $k = (3\pi^2 n)^{1/3}$				
E	From (6) $E = \hbar^2 k^2 / 2m = \hbar^2 / 2m (3\pi^2 n)^{2/3}$ $n = (1/3\pi^2)(2mE/\hbar^2)^{3/2}$ $\ln n = \ln E + const$ I/n dn = (3/2E) dE The number of electrons (both spins)between <i>E</i> and <i>E</i> + $\delta E$ is $dn/dE = \mathcal{D}(E) = 3n/2E \propto E^{1/2}$				
At the Fermi level * $\mathcal{D}(E_F) = (3/2)$	$n/E_F$ Units of $\mathcal{D}(E_F)$ are states J <sup>-1</sup> m <sup>-3</sup> (or states eV <sup>-1</sup> m <sup>-3</sup> )				
State occupancy when $T > 0$ is given by the Fermi function					
<i>f(E)</i>	$f(E) = 1/[exp(E - \mu)/k_BT + 1]$ (7)				
$\leftrightarrow k_{\rm B}T$	$\downarrow$ $k_{\rm B}T$ The chemical potential $\mu$ is fixed by $\int_0^{\infty} f(E) dE = 1$				
E	Note: $\mu = E_F$ at $T = 0$ ; also $j = (\sigma/e)\nabla \mu^*$				

Table	Propert	ies of the free-el	ectron gas	
Fermi wavevector	k <sub>F</sub>	$(3\pi^2 n)^{1/3}$	$1.2 \times 10^{10}$	$m^{-1}$
Fermi velocity	$v_F$	$\hbar k_F/m_e$	$1.4  imes 10^6$	${\rm m~s^{-1}}$
Fermi energy	$\varepsilon_F$	$(\hbar k_F)^2/2m_e$	$9 \times 10^{-19}$	J
Fermi temperature	$T_F$	$\varepsilon_F/k_B$	$6.5 \times 10^{4}$	Κ
Density of states	$\mathcal{D}_{\uparrow,\downarrow}(\varepsilon_F)$	$3n/4\varepsilon_F$	$5 \times 10^{46}$	$m^{-3} J^{-1}$
Pauli susceptibility	X <sub>P</sub>	$3\mu_0\mu_B^2n/2\varepsilon_F$	$1.1 \times 10^{-5}$	
Hall coefficient	$R_h$	-1/ne	$1.0  imes 10^{-10}$	${ m m^3~C^{-1}}$

Numerical values are for  $n = 6 \times 10^{28} \text{ m}^{-3}$ . Density of states is for one spin.

k<sub>B</sub> = 1.38 10<sup>-23</sup> J K<sup>-1</sup> I eV ≈ II605 K

### 1.3 The Nearly-free Electron Model.

Now we consider the effect of replacing  $U_0$  by a periodic potential U which has the periodicity of the lattice. The electron waves will be diffracted by the lattice.

- Then (3) becomes

ψ<sub>k</sub>(**r**) = (1/V<sup>1/2</sup>) [exp i**k.r**] U<sub>k</sub>(**r**)

(8)

where  $U_k(\mathbf{r})$  has the periodicity of the lattice.

The effect of a translation by any lattice vector  $\mathbf{R}_i$  is to multiply the wave function by a phase factor exp i $\mathbf{k}$ .  $\mathbf{R}_i$  This is Bloch's theorem

Note: The wavevector k is still a good label for the electron states.

The free-electron parabola develops bands
of allowed and forbidden energy for
the electrons. The gaps occur at values
of *k* corresponding to the edges of the
Brillouin zone, where the electrons are Bragg scattered
The Brillouin zone is the Wigner-Seitz cell of
the reciprocal lattice of the crystal.



k

- The density of states develops band gaps and van Hove singularities.
- Each band contains just two electrons, one  $\uparrow$  and one  $\downarrow$ .
- For monovalent metals like Cu, Na .... the first band is just half full. The free electron model is a pretty good approximation. D(F)





Fermi surface of copper; 4s<sup>1</sup>

### 6.4. Density of States Effects

Some physical properties that depend solely on electrons can be completely explained in terms of the total (both spins) density of states at the Fermi level  $\mathcal{D}(E_F)$ 

#### 4.1 Electronic specific heat

Only electrons within ~  $k_B T$  of the Fermi level can be thermally excited at a temperature *T*. The number of these electrons is ~ $\mathcal{D}(E_F) k_B T$ The increase in energy E(T) - E(0) is ~  $\mathcal{D}(E_F) (k_B T)^2$ 



Note that the electronic entropy  $S_{el} = \int_0^T (C_{el}/T) dT' = \gamma T$  [recall  $C = \delta Q / \delta T$ ;  $\delta Q = T \delta S$ ]

According to the third law of thermodynamics,  $S \rightarrow 0$  as  $T \rightarrow 0$ 

#### 4.2 Pauli susceptibility

Only electrons within ~  $\mu_0\mu_BH$  of the Fermi level can be magnetically excited in a field HThe total number of these electrons is  $\mathcal{D}(E_F) \mu_0\mu_BH$ . We now show the  $\uparrow$  and  $\downarrow$  density of states separately, in red and blue They split in a field  $B = \mu_0H$ 



The splitting is really very small, ~  $10^{-5}$  of the bandwidth in a field of 1 T.

 $M = \mu_{\rm B}(n_{\uparrow} - n_{\downarrow})$ 

*Note M* is magnetic moment per unit volume,  $n_{\uparrow}$ ,  $n_{\downarrow}$  are numbers per unit volume At *T* = 0, the change in population in each band is  $\Delta n = \frac{1}{2} \mathcal{D}(E_F) \mu_0 \mu_B H$ 

> $M = 2\mu_{\rm B}\Delta n = \mathcal{D}(E_{\rm F})\mu_{0}\mu_{\rm B}^{2}H \quad \text{The dimensionless susceptibility } \chi = M/H$  $\chi_{\rm Pauli} = \mathcal{D}(E_{\rm F})\mu_{0}\mu_{\rm B}^{2} \quad \text{It is } \sim 10^{-5} \cdot 10^{-6} \text{ and independent of } T$

In the free-electron model,  $\mathcal{D}(E_F) = (3/2)n/E_F$ 

Hence  $\chi_{\text{Pauli}} = \{3n\mu_0\mu_B^2/2E_F\}[1 + cT^2 + ...]$  (Compare Curie law  $n\mu_0\mu_B^2/k_BT$ )

The ratio of electronic specific heat coefficient to Pauli susceptibility in the nearly-free, independent electron approximation should be a constant *R*.

$$R = \pi^2 k_B^2 / 3\mu_0 \mu_B^2$$

Actually, there is also small, diamagnetic contributions to the susceptibility due to the core electrons and the conduction electrons (Landau diamagnetism), arising from Lenz's law. (In Cu, these diamagnetic contributions actually outweigh the Pauli paramagnetism!)

$$\chi_{Landau} = -1/_3 \chi_{Pauli}$$

Some values of  $R_{experiment}/R_{theory}$  Theory is OK for broad *s*-band, but poor for *d*-band metals

Li	2.0	Pd	4
Na	0.9	Ni	3
Rb	1.1		
Cs	0.9		

# 7.5 Resistivity of Metals



A perfect crystal lattice would not scatter electrons at all – electron states are Bloch waves. Very pure metals have  $\rho(\text{RT})/\rho_0 \simeq 10^4$ .

 $\rho = \rho_0 + \rho(T)$ Scattering by impurities or defects
Scattering by lattice vibrations (phonons)
In noncrystalline metals (metallic glasses) the first term is so large that the lattice
vibrations contribute very little. There  $\rho_0 \approx 10^{-6} \Omega$  m.

#### 5.2 Temperature-dependence of resistance



The Fermi surface is *very* slightly displaced by an applied electric field.

The current decreases in the absence of field by relaxation processes that change the electron momentum by  $\sim \hbar k_{\rm F}$ .

The direction of the momentum of the scattered electron changes but its magnitude remains  $\sim \hbar k_F$  for the effective scattering processes

q

 $\Delta \boldsymbol{k}$ 

K

Inelastic scattering process

**q** is the phonon wave vector

Conservation of momentum  $\boldsymbol{k}_2 = \boldsymbol{k}_1 + \boldsymbol{q}$ 

Energy is also conserved, but since  $E_F >> k_B T$ , the scattering is *quasi-elastic*. Note; A phonon of energy  $k_B \Theta_D$  has  $q \sim k_F$ . Here  $\Theta_D$  is the Debye temperature. Consider two limits:

 $\boldsymbol{k}_1$ 

a)  $T >> \Theta_{D}$ 

The electron mean free path  $\lambda$  will be inversely proportional to the number  $n_{\phi}$  of phonons present in the metal,

The internal energy U of a monatomic solid is ~ 3RT. The energy per phonon is ~  $k_B \Theta_D$   $\therefore$   $n_{\phi} \propto T$  Hence  $\lambda \propto 1/n_{\phi} \propto 1/T$   $\lambda = \langle v \rangle \tau$ 

So  $\rho = 1/\sigma = m_e/(ne^2\tau) \propto T$ . ( $\sigma = ne^2\tau/m_e$ ) see p. 10

### b) $T \ll \Theta_{\rm D}$

At low temperatures the specific heat  $C \sim T^3$  in the Debye model, hence  $U \sim T^4$ . The energy per phonon is  $k_B T$  when  $T << \Theta_D$   $\therefore$   $n_{\phi} \propto T^3$  Hence  $I \propto 1/n_{\phi} \propto 1/T^3$ 

But these low-energy phonons do not possess enough momentum to scatter electrons through a large angle on the Fermi surface.

q <<  $k_{\rm F}$ , hence the scattering angle  $\theta$  is small.

 $\Delta k = k_{\rm F}(1 - \cos\theta) \approx k_{\rm F}\theta^2/2 \propto q^2/2$  for small  $\theta$ .  $\therefore$  the number of collisions required to deflect the electron through  $\theta \sim \pi$  varies as  $(\Theta_{\rm D}/T)^2$  [for a phonon  $E \sim q$  near the origin].  $l_{\rm eff} \sim (\Theta_{\rm D}/T)^2 l \sim 1/T^5$  hence  $\rho \propto T^5$ . Note: In transition metals, *umklapp processes* can occur with  $k_1 + q + G = k_2$  where **G** is a lattice vector, then  $\rho \propto T^3$ .

#### 5.3 Electron-phonon scattering.

See Ashcroft and Mermin

Consider the atoms vibrating about their equilibrium positions  $R_i$ .



 $A = \sum_{i} \exp\{i(\mathbf{K}.\mathbf{R}_{i} - \Omega t)\} + (1/2)i\mathbf{K}. \alpha\{\sum_{i} \exp[(\mathbf{K}+\mathbf{q}).\mathbf{R}_{i} - (\Omega+\omega)t])\} + \sum_{i} \exp[(\mathbf{K}-\mathbf{q}).\mathbf{R}_{i} - (\Omega-\omega)t])...$ 

The next term is of order  $\alpha^2$ 

—The first term gives the *Bragg scattering*, which has a maximum at K = G, any reciprocal lattice vector. It is *elastic* scattering at frequency  $\Omega$ .

$$\boldsymbol{k}_1 \rightarrow \boldsymbol{k}_2 \pm \boldsymbol{G}$$

-The second terms correspond to *inelastic* scattering

 $\Omega \rightarrow \Omega \pm \omega$  and  $\mathbf{k}_1 \rightarrow \mathbf{k}_2 \pm \mathbf{G} \pm \mathbf{q}$ 

The electron is scattered from one Bloch state to another, with the absorption/excitation of a phonon of wave vector **q**.

The frequency of the scattered wave is  $\Omega' = \Omega \pm \omega$ Multiplying by  $\hbar$ ;  $\epsilon(\mathbf{k}_1) = \epsilon(\mathbf{k}_2) \pm \hbar\omega(q)$ 

- Higher order terms represent weaker, multiphonon processes

Similar theory applies to other scattering, e.g. neutron scattering in crystals, where the dispersion relation  $\omega(q)$  can be traced out for the phonons. [What does it look like?]

# Metal Physics and Superconductivity PYU44P13

### 6. Normal Metals

- 7. Superconductors
- 8. Theory
- 9. Superconducting Tunelling
- 10. Applications; High-T<sub>c</sub> superconductors





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# 2. Superconductors

# 1 Introduction

Half the metallic elements have a superconducting ground state, and many hundreds of superconducting metals and alloys exist New ones are being discovered every year; e.g. MgB<sub>2</sub>, FeSe, LaH<sub>10</sub> (under high pressure) ....



The phenomenon was discovered in 1911 by Kammerlingh Onnes, who had recently liquified helium for the first time in Leiden in 1908. Motivated by a desire to investigate van der Waals' s theory of the noble gasses, he became interested in the behaviour of metals at low temperature



Einstein Ehrenfest Langevin Onnes Weiss





Ehrenfest, Lorentz, Bohr, Onnes The Great



 Boiling points (K)

 Xe
 161

 Kr
 121

 Ar
 87

 Ne
 27

 H
 20

 He
 4.2

& the Good

There was the question of whether the resistivity of a very pure metal would tend to zero as  $T \rightarrow 0$ . He chose mercury, which could be purified by multiple distillation, to minimize the residual resistivity, caused by impurity scattering.



He found that the resistivity fell abruptly to zero, as far as he could measure, at a critical temperature  $T_{sc} = 4.2$ .

This was the first observation of the superconducting transition. The transition was reversible on heating



*Kwik nagenoeg nul* 8-iv-1911; 16.00



The maximum  $T_{sc}$  advanced slowly but steadily as more and more superconducting alloys and compounds were discovered. Up to 1987, the record of 22.3 K was held by Nb<sub>3</sub>Ge. There had been no advance in  $T_{sc}$  for 15 years, although progress was made in other ways. The discovery of high- $T_{sc}$  oxide superconductors by Bednorz and Müller was a breakthrough



From the beginning, the implications of zero resistance were quickly grasped — superconducting solenoids to generate magnetic fields, superconducting power transmission lines, superconducting motors and generators ....

However, all the early superconductors, pure metals and alloys (known as type I superconductors) had a severe defect — the superconducting state was was easily destroyed by an applied magnetic field, or electric current flowing in the supererconductor.

Type II superconductors, which had a high extrapolated residual resistivity, were discovered later.  $\mu_0 H_c$ 



Note: Stability of the superconducting state increases as T<sub>sc</sub> increases

 $B_{\rm c}(T) = B_{\rm c}(0) \{1 - (T/T_{\rm sc})^2\}$
The critical current is also related to the critical field.

*Silsbee* 's *Rule*: The current cannot exceed that which produces  $H_c$  at the surface of the conductor. (The critical current may be much less).



Consider the dashed path around the circumference of the wire.

 $\oint H dl = i$  —enclosed current

2πaH = i

 $i_c = 2\pi a H_c$  $j_c = 2H_c/a$ 

This suggests that for a large critical current density we should use separated strands of very fine wire. We discuss where the current actually flows in a superconductor in a later section, Ch 3. 2.2

Impurities and inhomogeneity tend to smear out the superconducting transition.



## 7.2 Zero resistance

Is the resistance *really* zero? Or is it just very small? A good test is to set up a supercurrent in a loop (see below) and check if there any change in the magnetic field it produces.

If the resistance of the loop is *R*, and if its inductance is *L* 

iR + Ldi/dt = 0

 $i(t) = i(0) \exp -(R/L)t$ 



From sensitive experiments using nmr probes to measure *H*, over periods of one year, it has been found that  $(L/R) \ge 10^5$  years and  $\rho < 10^{-26} \Omega$  m

Compare with copper,  $\rho\thickapprox 10^{\text{-8}}~\Omega$  m .

The resistance of the superconductor *really is zero*.

An important property of a resistanceless circuit is that the flux threading a resistanceless circuit cannot change



Apply a field  $B_a$  to the ring in its Area A normal state, and then cool the ring below its superconducting transition  $T_{\rm sc}$  in the field. The flux threading the loop is  $\Phi = B_a A$  (units Tm<sup>2</sup> or Weber)

Now try to change the flux in the ring by changing  $B_a$ .

An emf is induced according to Faraday's law.  $\mathcal{E} = -A dB_a/dt$ , and a current *i* is created.

 $-A dB_a/dt = R i + L di/dt \quad but R = 0,$ 

Therefore  $Li + AB_a = \text{constant} = \Phi$ 

The total flux threading the circuit is a constant. It cannot change. The original flux is maintained indefinitely, provided the ring remains resistanceless, and  $i < i_c$ 

Uses: — Magnetic screening

- Superconducting magnets in the persistent mode.



Very good screening of external magnetic fields can be achieved with superconducting shields. But note  $\Phi = 0$  i.e.  $\int_{S} B_{a}S = 0 \implies B = 0$  everywhere inside.

- Superconducting magnets (persistent mode)



The current in the sc solenoid creates a field  $B_0 \approx \mu_0 ni$ . It is built up slowly to the desired level, and the superconducting switch is closed (heating it above  $T_{sc}$  with a little coil opens it).

The power supply can then be removed, and the current flows through the s/c switch, since  $\Phi$  = constant

#### 2.1 Superconductors in parallel paths



What determines the distribution of the current *i* in the two paths ?

 $V_{ab} = L_1 di_1/dt + M di_2/dt = L_2 di_2/dt + M di_1/dt$   $(L_1 - M)di_1/dt = (L_2 - M)di_2/dt$ Integrating  $(L_1 - M)i_1 = (L_2 - M)i_2 + \text{constant}$ If  $i_1 = i_2 = 0$  at t = 0, constant = 0 Furthermore, if L >> M,  $i_1/i_2 = L_2/L_1$ Current splits inversely proportionally to L

#### 2.1 AC currents in superconductors

Power transmission in a superconductor is truly lossless only for DC. There is no electric field, otherwise the current would change. If there is a changing current, as in AC, some electric field must be present. The superconducting electrons possess mass, so they lag behind the exciting field. This inertia corresponds to a small inductance, adding to that due to geometry

The two-fluid model assumes that both normal and superconducting electrons are present below  $T_{sc}$ , with the proportion of the latter falling to zero as  $T \rightarrow T_{sc}$ .



For DC the normal electrons are completely short-circuited. Typically,  $L/R \sim 10^{-12}$  s, so even in the kHz or MHz range, the fraction of the current carried by the normal electrons is small.

However, at frequencies  $\geq 10^{11}$  Hz, the superconducting properties disappear. This is in the far infrared (terahertz range).  $\lambda = c/v = 3$  mm.

In the visible range,  $\lambda$  = 500 nm, a normal metal and a superconductor are indistinguishable. A superconductor *looks* no different in the superconducting state.

We will see that this crossover from superconducting to normal behaviour occurs at frequencies



 $\Delta$  is the superconducting gap [6.6 10<sup>-34</sup> x 10<sup>11</sup> ÷ 1.38 10<sup>-23</sup> ≈ 5 K]

### 7.3 Diamagnetism (Difference between a metal with no resistance and a superconductor)

The magnetic properties of superconductors are as extraordinary, and actually more important and characteristic than the zero resistance.

They show that a superconductor is something *much more* than a perfect conductor. A superconductor is not just a metal with zero resistance.

We saw in § 7.2 that  $\Phi$  = constant for a resistanceless circuit. This is true for *any* such circuit, hence at every point in a superconductor

$$\nabla \cdot \mathbf{B} = 0$$
  

$$\varepsilon_{o} \nabla \cdot \mathbf{E} = \rho$$
  

$$(1/\mu_{o}) \nabla \times \mathbf{B} = \mathbf{j} + \varepsilon_{o} \partial \mathbf{E} / \partial t$$
  

$$\nabla \times \mathbf{E} = -\partial \mathbf{B} / \partial t$$
  

$$dB/dt = 0$$
  

$$\int_{A} \nabla \times \mathbf{E} \, dA = \int \mathbf{E} \cdot d\mathbf{l} = 0$$
  
No emf  $\mathcal{E}$  around a sc circuit  
(There couldn't be; otherwise  $\mathbf{j}$  would increase without limit)

The flux distribution in a perfect conductor would remain fixed, just as it was when the metal first became resistanceless.



A perfect conductor cooled below  $T_{sc}$  with or without an applied field, which is then reduced to zero.

#### Perfect conductor.

Note that the state of the sample depends not just on the thermodynamic variables  $B_0$  and T, but on the history of *how* it was cooled below  $T_{sc}$  (whether or not a field was applied).

The transition for a perfect conductor would be irreversible, and thermodynamics would not apply!

Note: The applied field  $B_a$  is the field (flux density) =  $\mu_0 H_a$  that would be there in the absence of a specimen. The currents flowing in the superconductor modify *B* in its vicinity.



A superconductor cooled below  $T_{sc}$  with or without an applied field, which is then reduced to zero.

#### Superconductor.

The behaviour of a superconductor is different. Meissner and Oschenfeld in 1933 measured the flux distribution outside Sn and Pb specimens and found that on cooling below  $T_{sc}$  the samples become perfectly diamagnetic, expelling the magnetic flux density from their interior, This is the *Meissner effect*.

B = 0 (for a type I s/c)

Note: The transition at  $T_{sc}$  is now reversible. The state of the system is now determined only by the thermodynamic variables *B* and *T*.

#### Superconducting levitation,

A magnet suspended above a superconductor demonstrates *perfect conductivity*.

A magnet which *rises spontaneously* when the superconductor is cooled below  $T_{sc}$  demonstrates flux exclusion, the Meissner effect.

Because of the Meissner effect, the superconductor acts like a magnetic mirror. B = 0 inside

 $\nabla$ **.**B = 0 (Maxwell 1) means  $B_{\perp}$  = 0

is parallel to the surface outside the s/c





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#### Flux exclusion

There are two alternative ways to consider the flux exclusion from a type I superconductor

Screening current diamagnetism.

The superconductor generates a distribution of electric currents which cancel the applied field everywhere in the interior. Consider a rod-shaped specimen:

$$B_a \ j_s \qquad B_a \ j_s \qquad Am^{-1} \text{ is the surface screening current From}$$
  

$$H_a = B_a / \mu_0 = j_s \quad Am^{-1}$$

- Bulk diamagnetism

We can suppose that perfect diamagnetism is a bulk magnetic property of the superconductor.  $M = -j_s \times e_n$  (right hand rule)

but 
$$B = \mu_0(H + M)$$
  
hence  $B = 0 \rightarrow H = -M$  (units Am<sup>-1</sup>)  
relative susceptibility  $\chi = -1$  'perfect diamagnetism'  
two descriptions are formally equivalent; either one will do.

In the screening current picture, the currents flow only on the surface of the superconductor, not in the bulk.

 $\nabla \mathbf{x} \mathbf{B} = \mu_0 \mathbf{j}$  (Maxwell 3)

Since **B** = 0 inside the superconductor,  $\nabla \times B = 0 \rightarrow j = 0$ 

 $B \neq 0$  outside, so the current must flow on the surface.

Note: There is an analogy with the charge distribution on a conductor (E = 0 inside a metal), and the current distribution in a superconductor; equipotentials ~ flux lines.

Consider a hollow conductor; Flux exclusion depends on whether **B**<sub>a</sub> is applied above or below



#### 3.1 *B*, *H* and *M*

In free space, the distinction between **B** and **H** is unimportant, they are simply proportional, related by the constant  $\mu_0$  the permeability of free space  $4\pi \ 10^{-7} \text{ T A}^{-1}\text{m}$ .

$$\boldsymbol{B} = \mu_0 \boldsymbol{H}$$

*B*, the *magnetic flux density* is taken as the fundamental quantity, because there are no magnetic poles in nature, hence  $\nabla . \mathbf{B} = 0$ . The B-field is created by electric currents and may be calculated from the Biot & Savart law:  $\delta \mathbf{B} = -\mu_0 I \mathbf{r} \times \delta \mathbf{l} / 4\pi r^3 \qquad P \otimes \delta \mathbf{B}$ (follows from M3)

In free space, Ampères law follows  $\oint B.dl = \mu_0 l$ , where l is the enclosed current.

enclosed current

but in a magnetic material, both *conduction currents* and *magnetization* currents contribute



If a solenoid contains a bar of magnetic material with magnetization (magnetic moment m<sup>-3</sup>) *M*, the flux density in the bar is the sum of that produced by the solenoid, and that produced by the atomic (or superconducting) currents in the material. When the

bar is magnetized along its length, the contribution of the magnetization to **B** is equivalent to that of a *surface* current density of  $M \text{ Am}^{-1}$ .

 $B = \mu_0 ni + \mu_0 M$  (there are *n* turns m<sup>-1</sup> on the solenoid) due to solenoid due to magnet

Hence, integrating around the dashed loop,  $\int \vec{B} \cdot dl = \mu_0 (I_f + I_M)$   $I_f = ni$ 

Free (conduction) current threading the loop magnetization current threading the loop (Same as  $j_s l$ ) Since we have no means of measuring  $I_M$  directly, we define another field as  $H = B/\mu_0 - M$ H is known as the magnetic field strength.

 $\boldsymbol{B} = \mu_0 \left( \boldsymbol{H} + \boldsymbol{M} \right)$ 

So Ampère's law for **H** involves only the measurable, free conduction currents  $I_{\rm f}$ .

$$\int \mathbf{H} \cdot \mathbf{dl} = \mu_0 l_f$$

\ enclosed free current

This is the usual form of Ampères law, which applies in any medium.

Note: For the long bar, *H* does not depend on the presence of magnetic (or superconducting) material. The screening currents  $I_M$  influence *B*, but not *H* inside the material. Deep inside a type I superconductor, *B* = 0 (Meissner effect) but  $H \neq 0$  in the presence of an applied field.

1. Summary, in point form:  $\nabla \mathbf{x} \mathbf{B} = \mu_0 (j_f + j_M)$  $\nabla \mathbf{x} \mathbf{H} = i \quad \nabla \mathbf{x} \mathbf{M} = i$ 

$$\nabla \mathbf{x} \mathbf{H} = j_f \quad \nabla \mathbf{x} \mathbf{M} = j_M$$

Note: The *B*-field is *solenoidal*, produced by currents only, whereas the *H*-field behaves as is it were produced by a distribution of fictitious magnetic 'poles' on the sample surface.

What if the sample is *not* a thin rod? Consider a sphere:



In the uniform applied field of the solenoid, *M* is still uniform (as it is for any ellipsoid of revolution) but the contribution to *B* is smaller than before.

 $B=\mu_0 ni+(2/3)\mu_0 M$ 

To retain Ampère's law we keep  $H = B/\mu_0 - M$  as the definition of H within the sphere Hence H = ni - (1/3)M  $H_{int} = H_a + H_{demag}$  where  $H_a - ni$ 

The *H*-field is reduced by end effects, the *demagnetizing field*  $H_{demag}$ . The factor 1/3 is the demagnetizing factor for the sphere.



Maxwell's equations in a medium

 $\nabla \cdot \boldsymbol{B} = 0$   $\nabla \cdot \boldsymbol{D} = \rho$   $\nabla \times \boldsymbol{H} = \boldsymbol{j} + \partial \boldsymbol{D} / \partial t$  $\nabla \times \boldsymbol{E} = -\partial \boldsymbol{B} / \partial t$ 

N.B.  $\boldsymbol{M}$  and  $\boldsymbol{P}$  are implicit  $\boldsymbol{B} = \mu_0 (\boldsymbol{H} + \boldsymbol{M})$ 



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Hence  $B_{int} = \mu_0(H_a + (1 - \mathcal{N})M)$ 

Now consider a superconductor. Here  $B_{int} = 0$ , and M is opposite in direction to  $H_a$ 



 $H_{\rm a}$  =  $M(\mathcal{N}$  -1)

 $H_{\rm int}=-M=H_{\rm a}/(1-\mathcal{N})$ 

So the internal *H*-field in a superconductor is actually *greater* than the applied field, whereas in a ferromagnet the internal *H*-field is *reduced* by the demagnetizing field.

The key point is that it is the H-field that actually determines the state of the material.

The critical field is  $H_c$  not  $B_c$ . Moreover, it is the local (internal) value of H that counts.

**Recall:** The boundary conditions for *B* and *H* at an interface

 $B_{\perp}$  is continuous (follows from Gauss's theorem)

 $H_{||}$  is continuous (follows from Ampère's law)

#### 3.2 The intermediate state

When the specimen is not a long thin rod, the internal field  $H_{int} = H_a / (1 - \mathcal{N})$  e.g., for a sphere,  $\mathcal{N} = 1/3$ ;  $H_{int} = (3/2) H_a$  or for a cylinder  $\mathcal{N} = 1/2$ ;  $H_{int} = 2H_a$ 



Outside the sphere the field lines are bunched at 'x' because of flux exclusion from the superconductor. Hence  $H = B/\mu_0 > H_a$ 

At the surface at 'x', the tangential component of H is continuous, so  $H_x = (3/2) H_a$ 

So what happens when  $H_x = H_c$ ?

Caps at x and y (caps) go normal when  $H_a = (2/3)H_{c_1}$  not the whole sphere. Sc shape changes

When  $(2/3)H_c < H_a < H_c$  the sphere breaks up into normal and superconducting domains



The magnetic flux now runs through the normal domains, while remaining excluded from the superconducting domains. These now have a different shape, and a smaller value of  $\mathcal{N}$ .

At the superconductor/normal interfaces, the normal component  $B_{\perp}$  is continuous. Since B = 0 in the superconducting domains, it follows that B and H lie parallel to the interface on the normal side (M = 0) so the interfaces lie *parallel to the applied field*.



# 7.4 Type I and Type II Superconductors

The superconductors we have considered so far exhibit perfect flux exclusion (at least for long rods) below the critical field  $H_c$ . They are usually pure metals, and the values of  $T_{sc}$  and  $H_c$  are low. These are *type I* superconductors.

There is another, more important class which show *two* critical fields  $H_{c1}$  and  $H_{c2}$  These *type II* superconductors tend to be alloys with a high resistivity in the normal state, and a short electron mean-free path. They are also known as *dirty* superconductors. Flux partially penetrates the superconductor between  $H_{c1}$  and  $H_{c2}$ , but this is an intrinsic physical property, which is unrelated to the shape of the specimen (c.f. § 3.2).



*H* The flux begins to penetrate at  $H_{c1}$ , which may be very low, and a mixed, vortex state forms where tubes of flux, each a quantum h/2e  $\approx 2 \ 10^{-15}$ T m<sup>2</sup>, penetrate to thread the s/c matrix. Superconductivity is *H* finally destroyed at  $H_{c2}$  The difference is basically that the normal/superconducting interface has a positive free energy for type I (so the n/sc interface area is minimized) whereas it has a negative free energy for type II (so the n/sc interface area is maximized).

 $H_{\rm c}$  can still be defined for a type II as the thermodynamic critical field  $H_{\rm c} = (H_{\rm c1} H_{\rm c2})^{1/2}$ 

The material retains zero resistance up to  $H_{c2}$ , which may be very large, so they can be used as practical superconducting materials,



# **7.5. Thermal properties** 5.1 Specific heat and entropy

The heat capacity of a superconductor shows a discontinuity at  $T_{sc}$ , but there is no latent heat. It is an excellent example of a second-order transition (like the Curie point of a ferromagnet)

G = U - TS + PV - BM where  $B = \mu_0 H'$  is the externally applied field dG = -SdT + VdP - MdB since dU = dQ - PdV + BdM (1<sup>st</sup> law) and dQ = TdS (2<sup>nd</sup> law)

1<sup>st</sup> order transition  $\rightarrow$  1<sup>st</sup> derivatives of *G* are discontinuous  $M = -(\partial G/\partial B)_{T,P}$   $V = (\partial G/\partial P)_{B,T}$   $S = -(\partial G/\partial T)_{P,B}$ 

2<sup>nd</sup> order transition  $\rightarrow 2^{nd}$  derivatives of *G* are discontinuous  $C_p = (\partial Q/\partial T) = T(\partial S/\partial T)_{P,B} = -T(\partial^2 G/\partial T^2)_{P,B}$ 



Electronic heat capacity is plotted as a function of T (corrected for the  $\beta T^3$  lattice term)

The normal state can be stabilized by applying a small field, so the two curves can be compared for a type I sc

At low temperature,  $C_{els} = a \exp(-\Delta/k_{\rm B}T)$ , which suggests a gap  $\Delta$  in the electronic density of states;  $\Delta \approx 1.5 k_{\rm B}T_{\rm sc}$ 

Experiments on microwave absorption also indicate that there is a gap at  $hv = 3 - 4 k_B T_{sc} = 2\Delta$ . The microwave experiment creates a pair of excited electrons. The thermal experiment measures the energy per statistically-independent electron.



Entropy  $S(T) = \int (C/T) dT$  (=  $\gamma T$  in normal state)

The entropy is lower in the superconducting state; In some sense it is more ordered.

Note: Only electrons within  $k_B T$  of the Fermi energy contribute to  $C_{el}$ , and the ones within  $k_B T_{sc}$  condense into the ordered, superconducting state.  $n_s \rightarrow 0$  as  $T \rightarrow T_{sc}$ 

The transition is second-order provided there is no applied field.

It actually becomes first-order when measured in the presence of an applied field.

#### 5.2 Thermal conductivity

— At low temperature, most of the thermal conductivity  $\kappa$  of a normal metal is due to conduction electrons.

$$\kappa = (\pi^2/3)(k_B/e)^2 T \sigma$$

This is the Wiedemann-Franz law.  $\kappa/\sigma$  varies as *T* in a normal metal. In a superconductor,  $\sigma$  is infinite but the electronic contribution to  $\kappa$  disappears progressively as  $T \rightarrow 0$  (Two current model). The superconductor is a poor thermal conductor; lead is used as a low-temperature thermal switch.  $\kappa_n \approx 100 \kappa_{sc}$  for Pb at 1 K.

#### 5.3 Thermoelectric effect

—Thermoelectric effects are not found in superconductors. Normally, the thermal emf  $\mathcal{E} = S\Delta T$  where S the thermoelectric power.

This is common sense. Imagine a circuit with junctions of dissimilar superconductors. No thermal current accompanies the electric current. Transport of entropy is zero.

#### 5.4 The isotope effect.

It was discovered in the 1950s that different isotopes of the same element show slightly different values of  $T_{sc}$ .

 $T_{\rm sc} \propto M^{-n}$  where  $n \sim \frac{1}{2}$  M is the isotope mass

There is ~ 1% difference in  $T_{sc}$  between <sup>204</sup>Pb and <sup>208</sup>Pb. (Four stable lead isotopes <sup>204</sup>Pb <sup>206</sup>Pb <sup>207</sup>Pb <sup>208</sup>Pb)

	n
Zn	0.45
Cd	0.32
Sn	0.47
Hg	0.50
Pb	0.49

 $n = \frac{1}{2}$  Is not found in every case, but it helped suggest that superconductivity was not a purely electronic effect.

The isotope effect suggested a phonon coupling mechanism, via the electron-phonon mechanism.

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# 8. Macroscopic Theory8.1 Thermodynamics

We saw that, thanks to the Meissner effect, the normal  $\rightarrow$  superconducting transition is *reversible*. Hence we can apply thermodynamics and obtain an expression for the free energy difference between the normal and superconducting states.

The energy density (J m<sup>-3</sup>) associated with a magnetic field in free space, where  $B = \mu_0 H$ , is  $(1/2\mu_0)B^2 = \frac{1}{2}\mu_0 H^2 = \frac{1}{2}BH$ 

Since the field penetrates a type I when  $H = H_c$  the free energy difference per unit volume is  $\frac{1}{2} \mu_0 H_c^2$ .

In a type II superconductor, where the field penetrates above  $H_{c1}$  we retain the idea of a *thermodynamic* critical field such that  $H_{c1} < H_c < H_{c2}$ .  $H_c = (H_{c1}H_{c2})^{1/2}$ 

The free energy of a phase at a given temperature can also be found by integrating the S(T) curve obtained from the specific heat.

$$G(T) = -\int_0^T S(T') \, \mathrm{d}T' \qquad see \text{ p. 58} \quad S = -(\partial G/\partial T)$$

Note *all* thermodynamic potentials are per unit volume.

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More precisely:  $dU = TdS + \mu_0 HdM - PdV$  1st and 2nd law.  $G = U - TS - \mu_0 HM + PV$   $dG = -SdT - \mu_0 MdH + VdP$ At constant temperature,  $G_s(H,T) = G_s(0,T) - \mu_0 \int_0^H MdH'$   $= G_s(0,T) + \mu_0 \int_0^H H' dH'$  since M = -H ( $B_{internal} = 0$ )  $= G_s(0,T) + \frac{1}{2}\mu_0 H^2$ At the critical field,  $G_n = G_s$  (G is the same for two phases in equilibrium, given  $P_iT_iH$ )

 $G_{n}(H_{c}T) = G_{s}(H_{c}T)$ 

But  $G_n$  does not depend significantly on field since  $M \approx 0$  in the normal state;  $G_n(H_cT) = G_n(0,T)$ 



 $G_{\rm n}(T) - G_{\rm s}(T) = \frac{1}{2} \mu_0 H_c^2$  G is Gibbs free energy per m<sup>3</sup> Thermodynamics:  $(dG/dT)_{H} = -S$  S is entropy per m<sup>3</sup> § 5.1 p.58  $\therefore S_n(T) - S_s(T) = -\mu_0 H_c(dH_c/dT)$ Hence the latent heat of the transition,  $L = T\Delta S$ is given by  $L = -T\mu_0H_c(dH_c/dT)$ N.B. L = 0 at  $T_{sc}$  ( $H_c = 0$ )  $H_{c0}$ and at T = 01st order When H = 0 or T = 0, there is no latent heat; There n transition is *second order*. Elsewhere it is *first order*. SC Furthermore C = T dS/dT $\Delta C = C_{\rm n} - C_{\rm s} = T(dS_{\rm n}/dT - dS_{\rm s}/dT)$  $T_{sc}$ 0  $= - \mu_0 T \{ H_c (d^2 H_c / dT^2) + (dH_c / dT)^2 \}$ At  $T = T_{sc}$ ,  $H_c = 0$ 2nd order  $C_{\rm p} - C_{\rm s} = - \{\mu_0 T (dH_0/dT)^2\}_{T = T_{\rm sc}}$ 

This is the discontinuity in the heat capacity at  $T_{sc}$  c.f. p.58



Note that at  $T_{sc}$  the curves meet with the same slope ( $\Delta S$ = 0) [no latent heat at a second order transition]

e.g. for Al; 
$$\mu_0 H_c$$
 at  $T = 0$  is 10.5 mT,  $T_{sc} = 1.1$  K  
 $(G_n - G_s) = \frac{1}{2} (10.5 \ 10^{-3})^2 / (4\pi \ 10^{-7})$ 

= 44 J m<sup>-3</sup>

This is not a large difference.

For Al,  $\rho$  = 2700 kg m<sup>-3</sup>, AW = 27 the energy difference is just 5 10<sup>-9</sup> eV/atom

Recall 1eV = 11605 K;  $T_{sc} = 1.1 \text{ K} \approx 1.2 \text{ 10}^{-4} \text{ eV}$ 

Since the energy difference is <<  $\Delta$  (10<sup>-4</sup> eV), it follows that *only a small fraction of the electrons participate in the superconducting state*. The fraction is of order 10<sup>-4</sup>

The fraction is just the fraction that are close enough to  $E_F$  to participate in the electronic specific heat.

# 8.2. London Theory

The two fundamental properties of Type I superconductors, zero resistance and zero flux density inside the superconductor, were successfully described by the London brothers in the 1930s. They made a postulate to replace Ohm's law:

 $\boldsymbol{j} = \boldsymbol{\sigma} \boldsymbol{E}$ 

Londons' postulate:

$$\boldsymbol{j}$$
 = -(1/ $\mu_0 \lambda^2$ )  $\boldsymbol{A}$ 

(1)

Check the dimensions [A] = Tm;  $\lambda$  is a length

2.1 Vector potential of the magnetic field, **A** 

The *B*-field is related to the vector potential by

#### $\boldsymbol{B} = \nabla \mathbf{x} \, \boldsymbol{A}$

Usually, in this definition there is some freedom in the choice of **A**, since we can add any term of the type  $\nabla \chi$  where  $\chi$  is *any* scalar. It is known as a *gauge transformation*. It leaves **B** unchanged because  $\nabla x \nabla \chi \equiv 0$ .

 $A' = A + \nabla \chi$  (cf adding a constant to the scalar potential  $\phi$ ). However (1) is *not* valid in any gauge. London pointed out that  $\nabla \cdot \mathbf{j} = 0$ . i.e.  $\int_{S} \mathbf{j}_{\perp} dS = 0$ .  $\therefore$  from (1),  $\nabla \cdot \mathbf{A} = 0$ . so the choice of gauge is restricted to those scalar functions that satisfy Laplace's equation  $\nabla \cdot \nabla \chi = \nabla^2 \chi = 0$  Furthermore, at the surface of any conductor,  $j_{\perp} = A_{\perp} = 0$ ; [c.f (1)] Hence  $\nabla \chi$  is a constant, and **A** is uniquely specified by  $\nabla \cdot \mathbf{A} = 0$  plus the boundary conditions, — the London Gauge.

The other motivation for using the vector potential relates to the momentum of an electron (or other charged particle) moving in a magnetic field;

p = mv + qAkinetic momentum field momentum recall, in quantum mechanics  $p = -i\hbar\nabla$ In the absence of any applied field, we expect the ground state to have no net momentum:  $\langle p \rangle = 0 \rightarrow \langle v \rangle = -qA/m$   $j_s = n_s q \langle v \rangle = -n_s q^2 A/m$   $n_s$  is the number of s/c electrons/m<sup>3</sup>

This is just the London postulate, with  $\lambda^2 = m/(\mu_0 n_s q^2)$  [London theory does not let  $n_s$  vary]

#### 2.2 Londons' equations and penetration depth

Assume  $\mathbf{j} = -(1/\mu_0 \lambda^2) \mathbf{A}$  for a *simply-connected* surface. Extra terms may be added for a ring or hollow cylinder  $\nabla \mathbf{x} \, \mathbf{j} = -(1/\mu_0 \lambda^2) \, \mathbf{B}$  London equation Now  $\nabla \mathbf{x} \mathbf{B} = \mu_0 (\mathbf{j} + d\mathbf{D}/dt)$ 

Maxwell's equation (M3)

neglect the displacement current under static conditions

from London equation,  $\nabla \mathbf{x} \nabla \mathbf{x} \mathbf{j} = -(1/\mu_0 \lambda^2) \nabla \mathbf{x} \mathbf{B}$ 

$$[\nabla \mathbf{x} \nabla \mathbf{x} \mathbf{X} = \nabla \nabla \mathbf{X} - \nabla^2 \mathbf{X}]$$

 $\therefore$  since  $\nabla \cdot \mathbf{j} = 0$  and  $\nabla \mathbf{x} \mathbf{B} = \mu_0 \mathbf{j}$ 



B = constant is not a solution unless B = 0In a region where we go from free space where  $B \neq 0$ superconductor where the solution is

 $B(\mathbf{x}) = B(\mathbf{0}) \exp{-(\mathbf{x}/\lambda)}$ 

 $\lambda$  Is the London penetration depth.  $\lambda = (m/\mu_0 n_s q^2)^{1/2}$  If q = e;  $n_s = n$ ;  $\lambda = 10 - 100$  nm The London postulate implies flux exclusion inside the sample and gives the depth within which the field penetrates and the screening currents circulate.



$$d\mathbf{j}/dt = (n_{s}q^{2}/m) \mathbf{E}$$

$$M4 \qquad \nabla \mathbf{x} \mathbf{E} = -d\mathbf{B}/dt$$

$$\rightarrow \qquad d\mathbf{B}/dt = -(m/n_{s}q^{2}) \nabla \mathbf{x} d\mathbf{j}/dt$$

#### 2.3 Thin films



The London electrodynamic equations. *c.f.* London equation on p. 68.

Consider a film of width 2*a*; *B* is applied || to z.

 $d^2B/dx^2 = (1/\lambda^2) B(x)$ 

$$\begin{split} B(\mathbf{x}) &= c\{\exp(\mathbf{x}/\lambda) + \exp(\mathbf{x}/\lambda)\} \text{ if } \mathbf{a} << |\lambda| \\ \text{The constant c is determined by } B(a) &= B(-a) = B_a \\ B(\mathbf{x}) &= B_a \{\cosh(\mathbf{x}/\lambda)/\cosh(a/\lambda)\} \end{split}$$

Note that in the film, expelled flux density <<  $B_a$ hence  $G_s(B_a) - G_s(0) << B_a^2/2\mu_0$ 

It follows that the critical field of the thin film will be *increased* relative to the bulk, by a factor of order  $\lambda/a$ . (The surface has an even-higher critical field  $H_{c3}$ ). c.f.Type II superconductors.



# 8.3. The idea of coherence length $\boldsymbol{\xi}$

Besides the penetration depth, there is a second fundamental length scale that enters the theory of superconductivity — the coherence length  $\xi$  (xi).

It emerges naturally from the Landau theory, and the BCS theory, treated in later sections.

2.1 Here we give some idea of what is involved physically. The London postulate appears to be a *local* equation relating  $A(\mathbf{r})$  to  $\mathbf{j}(\mathbf{r})$ , but this is a simplification. We really need to *average*  $A(\mathbf{r})$  over a volume of order  $\xi$  to get  $\mathbf{j}$ .

Even Ohm's law  $\mathbf{j} = \sigma \mathbf{E}$  should be written as a nonlocal average over the mean free path l $\mathbf{j}(\mathbf{r}) = (3\sigma/4\pi) \int \{\mathbf{R}[\mathbf{R}.\mathbf{E}(\mathbf{r}')] \exp(-R/l)\}/R^4 d\mathbf{r}'$   $\mathbf{R} = \mathbf{r} - \mathbf{r}'$  The nonlocal form of the London postulate:  $\mathbf{j} = -(1/\mu_0 \lambda^2) \mathbf{A}$  where  $\lambda^2 = m/(\mu_0 n_s q^2)$  is

 $\mathbf{j}(\mathbf{r}) = -(n_s q^2/m)(3/4\pi\xi) \int \{\mathbf{R}[\mathbf{R}.\mathbf{A}(\mathbf{r}')] \exp(-\mathbf{R}/\xi)\}/R^4 d\mathbf{r}'$   $\mathbf{R} = \mathbf{r} - \mathbf{r}'$ In the presence of scattering, the coherence length is reduced:



2.2 An uncertainty-principle argument can be used to indicate the magnitude of  $\xi_0$ .

The electrons involved are those within  $k_B T_{sc}$  of  $E_F$ Their uncertainty in momentum is  $\Delta p = 2 k_B T_{sc} / v_F$  Fermi velocity

 $\Delta x \approx \hbar / \Delta p \approx \hbar v_{\rm F} / k_{\rm B} T_{\rm sc}$ 

$$\xi_0 \approx a\hbar v_F/k_B T_{sc}$$
  
constant a = 0.15 for pure metals,  $\xi_0$  is 100 - 1000 nm; In type I superconductors  $\lambda/\xi_0 \approx 0$ .

1
2.3 An alternative argument is based on the idea that we cannot have a completely sharp interface between a superconducting and a normal region without paying a very high price in energy. It always costs energy to modulate the spatial density of superconducting electrons, just as it does to modulate the spatial density of normal electrons, as in the hydrogen atom, for example.

We suppose that the superconducting electrons can be represented by a wave function  $\psi(\mathbf{r})$ 

with the meaning that  $\psi^*(\mathbf{r})\psi(\mathbf{r})d^3r = n_s$  is the probability of finding the superconducting electrons at  $\mathbf{r}$ . This is just the normal definition of a wave function but the assumption of a wavefunction for the superconducting electrons is pregnant with consequences.



The kinetic energy  $p^2/2m$  in quantum mechanics is obtained by evaluating the operator  $(1/2m)(-i\hbar\nabla)^2$ 

For the plane wave,

 $\mathcal{E} = \int \psi^*(x) \left[ (-\hbar^2/2m)(\partial^2/\partial x^2) \right] \psi(x) dx$  $\mathcal{E} = \int \exp -(ikx) \left[ (-\hbar^2/2m)(\partial^2/\partial x^2) \right] \exp (ikx) dx$  $\mathcal{E} = \hbar^2 k^2 / 2m$  the expected result for free electrons For the modulated wave  $\mathcal{E} = \int \phi^*(x) [(-\hbar^2/2m)(\partial^2/\partial x^2)] \phi(x) dx$  $\mathcal{E} = (\hbar^2/4m)[(k+q)^2 + k^2]$  $\mathcal{E} \approx \hbar^2 k^2 / 2m + \hbar^2 kq / 2m$  if  $k \gg q$ 

The extra energy needed to modulate the wave is  $\hbar^2 kq/2m$ . If this exceeds the energy gap, the superconducting state is destroyed. The critical value of q is given by  $\hbar^2 kq_0/2m = E_q$ Here  $k_{\rm F}$  can be used for k since only electrons near the Fermi energy are involved.

Define 
$$\xi_0 = 1/q_0 = \hbar^2 k/2mE_g = \hbar v_F/2E_g$$
, as before.

## 3.1 Interfaces

The nature of the normal/superconductor interface depends on whether  $\xi_0 > \lambda$  or  $\xi_0 < \lambda$ 



Type II;  $\xi_0 < \lambda$ 



Suppose  $H < H_c$  The interface energy is -ve for type II,  $\xi_0 < \lambda$  the interface energy is -ve, and the interfaces form spontaneously.

## 8.4. Ginzberg-Landau Theory

This is the ultimate *phenomenological* theory. It is very useful, and can be applied to many types of phase transition.

- The idea is to write down an expression for the free energy per unit volume, and deduce whatever is needed from it using thermodynamics. The unknown coefficients in the expression are determined by *experiment*.
- I. In the absence of a magnetic field, the free energy of the superconducting state is  $G_s(0)$
- II. All the sc electrons can be described by a wavefunction  $\psi(\mathbf{r})$  so that  $\psi^*(\mathbf{r}) \psi(\mathbf{r}) = |\psi|^2 = n_s$  where  $\psi(\mathbf{r}) = \psi_0 \exp i\theta$ . Here  $n_s$  is the density of sc electrons., which is uniform in zero applied field (**B** or **E**), except near an interface;  $\theta$  is the phase of the macroscopic wavefunction, which can be *measured*.
- III.  $G_{s}(0) = G_{n}(0) + a_{1}|\psi|^{2} + a_{2}|\psi|^{4} + \dots$

Zero field. This is the simplest choice of free energy, which has to be real. The coefficients  $a_1, a_2$ .....are unknown and must be determined by experiment.

IV The energy is raised in an applied magnetic field  $B_a$  by an amount  $(1/2\mu_0)B_a^{2}$ .  $[\frac{1}{2}\mu_0H_a^2]$ If the flux is not entirely excluded, but if locally it is *B*, the increase is  $(1/2\mu_0)(B_a - B)^{2}$ . V Also the electron density may vary with position in an applied field,  $\nabla \psi(\mathbf{r}) \neq \mathbf{0}$ The associated kinetic energy operator is  $(1/2m)(\mathbf{p} - q\mathbf{A})^2$ , so the energy is  $(1/2m)|(-i\hbar \nabla - q\mathbf{A})\psi|^2$ 

Putting everything together:

 $G_{\rm s}(B) = G_{\rm n}(0) + a_1 |\psi|^2 + a_2 |\psi|^4 + \dots (1/2m) |(-i\hbar\nabla - q\mathbf{A})\psi|^2 + (1/2\mu_0)(B_{\rm a} - B)^{2}$ 

<sup>1</sup>in 1959, Gorkov showed that Ginzburg-Landau theory is the limiting form of BCS theory, valid near  $T_{sc}$  and generalized to allow for spatial fluctuations in electron density.

Also  $|\psi| \sim \Delta$ , the superconducting energy gap.

## 4.1 The phase transition (*B* = 0)

The nature of a phase transition depends on the form of the Landau free energy. For the superconducting transition, there is a small, uniform density of superconducting electrons  $|\psi|^2$  near  $T_{sc.}$ 

 $|\psi|$  is the *order parameter* in the theory

c.f. *M* for a ferromagnet

P for a ferroelectric

Ordering is equivalent to symmetry breaking

 $G_{\rm s}(0) = G_{\rm n}(0) + a_1 |\psi|^2 + a_2 |\psi|^4 + \dots$ 



Second order phase transition; To have a nonzero minimum for  $|\psi|^2$ ,  $a_1 < 0$ ,  $a_2 > 0$ To have a zero minimum for  $|\psi|^2$ ,  $a_1 > 0$ ,  $a_2 > 0$ Hence we need to choose  $a_1$  so that it changes sign at  $T : -|\psi|^2 \neq 0$  for T < T

Hence we need to choose  $a_1$  so that it changes sign at  $T_{sc}$ ;  $|\psi|^2 \neq 0$  for  $T < T_{sc}$ 

$$a_1 = c_1(T - T_{sc}); \quad a_2 = c_2$$

Next choose  $|\psi|^2$  to minimize  $G_s = G_n(0) + a_1 |\psi|^2 + a_2 |\psi|^4 + ...$ 

$$\partial G_{\rm s}/\partial |\psi|^2 = 0 \rightarrow a_1 + 2a_2 |\psi|^2 = 0;$$
  
 $|\psi|^2 = -a_1/2a_2$ 

$$G_{s} = G_{n} + a_{1}(-a_{1}/2a_{2}) + a_{2}(a_{1}/2a_{2})^{2} + = G_{n} - a_{1}^{2}/4a_{2}$$

$$But G_{s} - G_{n} = \frac{1}{2}\mu_{0}H_{c}^{2} \qquad \therefore \quad H_{c} = -a_{1}/(2\mu_{0}a_{2})^{1/2}$$

$$hence H_{c} \sim (T_{sc} - T) \text{ in the vicinity of } T_{sc}$$

The theory is only valid near  $T_{sc}$ , where  $|\psi|^2$  is small



4.2 Example of a semi-infinite slab. (see Solymar & Walsh; *Lectures on the Electrical Properties of Materials*)

The ground state of the superconductor is found by minimizing the free energy

 $\int G_{\rm s}[\boldsymbol{A}(\boldsymbol{r}), \boldsymbol{\psi}(\boldsymbol{r})] \mathrm{d}^{3} \mathrm{r}$ 

A problem in variational calculus, to choose A(r) and  $\psi(r)$  to minimize the integral. Consider the one-dimensional problem of a semi-infinite slab.

**A** is parallel to 0y

$$\begin{array}{c} \hline G_{s}(B) = G_{n}(0) + a_{1} |\psi|^{2} + a_{2} |\psi|^{4} + \dots (1/2m) |(-\hbar\nabla - qA)\psi|^{2} + (1/2\mu_{0})(B_{a} - B)^{2} \\ \hline G_{s}(B) = G_{n} + a_{1}\psi^{2} + a_{2}\psi^{4} + \dots (1/2m) [\hbar^{2}(-\partial\psi/\partial x)^{2} + q^{2}A^{2}\psi^{2}] + (1/2\mu_{0})(B_{a} - \partial_{A}/\partial x)^{2} \ (1) \\ \hline \text{For simplicity, } \psi \text{ is supposed to be real;} \\ \hline G_{n} \text{ is independent of } B \\ \hline \text{Euler 's theorem:} \quad \int F[x,y(x), y'(x)] d^{3}r \text{ is minimized when} \quad \partial F/\partial y - (d/dx)(\partial F/\partial y') = 0 \\ \hline \partial G_{g}/\partial \psi - (d/dx)[\partial G_{g}/\partial(\partial A/\partial x)] = 0 \\ \hline \partial G_{g}/\partial A - (d/dx)[\partial G_{g}/\partial(\partial A/\partial x)] = 0 \\ \hline \partial G_{g}/\partial A - (d/dx)[\partial G_{g}/\partial(\partial A/\partial x)] = 0 \\ \hline \partial C_{2}\psi/\partial x^{2} = (m/\hbar^{2}) 2a_{1}(1 + q^{2}A^{2}/2a_{1}m)\psi + 4(m/\hbar^{2})a_{2}\psi^{3} \ (3) \\ \hline \text{From 1 and 2b, } (1/2m)2q^{2}\psi^{2}A - (1/\mu_{0})\partial^{2}A/\partial x^{2} = 0; \quad \partial^{2}A/\partial x^{2} = q^{2}\psi^{2}\mu_{0}A/m \ (4) \\ \hline \text{The solution of (3) is subject to the boundary conditions } \psi = 0, d\psi/dx = 0 \text{ at } x = 0 \text{ since } v_{x} = 0 \text{ at the surface, } i\hbar\partial\psi/\partial x - qA_{x} = 0, \qquad \text{If we ignore the field in the s/c region, taking  $A = 0 \text{ at } x = \infty, \ (3) \text{ becomes } \\ \partial^{2}\psi/\partial x^{2} = (2m/\hbar^{2})(a_{1}\psi + 2a_{2}\psi^{3}) \\ \hline \Psi \\ \hline \text{VU4P13 2023} \end{array}$$$

The solution is  $\psi(x) = (-a_1/2a_2)^{1/2}$  tanh  $(x/\sqrt{2\xi})$  where  $\xi = \hbar/\sqrt{2ma_1}$  the coherence length

Deep in the superconducting region,  $\psi \rightarrow \psi_0$ 

Using the results 
$$\psi_0^2 = -a_1/2a_2$$
 and  $H_c = -a_1/\sqrt{(2\mu_0 a_2)}$  (3) and (4) become  
 $\partial^2 \psi / \partial x^2 = (1/\xi^2) \{ -(1 - A^2/2H_c^2 \lambda^2 \mu_0^2) \psi + (\psi^3/\psi_0^2) \}$  (5)  
 $\partial^2 A / \partial x^2 = (1/\lambda^2) (\psi^2/\psi_0^2) A$  (6)

where  $\lambda^2 = m/(\mu_0 \psi_0^2 q^2)$ , the usual definition of penetration depth.  $\lambda^2 \sim 1/\psi_0^2 \sim -2a_2/a_1$  (p.79) These are the *Ginzburg-Landau equations*.

Define  $\kappa = \lambda/\xi$ , the *Ginzburg Landau parameter*.

Note that  $\kappa$  is independent of temperature, since  $\lambda^2$  and  $\xi^2$  both vary as  $1/a_1$ 

From (6), provided  $\lambda >> \xi$ ,  $\psi = \psi_0$  and  $A = A(0) \exp -(x/\lambda)$ 

but  $B = \partial A / \partial x$  so  $B = (-1/\lambda)B(0) \exp -(x/\lambda)$  hence the penetration of B, as before.

n general,  $\lambda \sim \xi$ , so that  $\psi$  varies with distance, and the decay of *B* is modified.

f the density of s/c electrons is small,  $\psi^3$  can be neglected, and if  $A(x) = B_a x$ , (field penetrates throughout)  $\partial^2 \psi / \partial x^2 = -(\kappa^2 / \lambda^2) \{ (1 - B_a^2 x^2 / 2H_c^2 \lambda^2 \mu_0^2) \psi \text{ has solution } B_a = \mu_0 H_c \kappa \sqrt{2} / (2n+1) \}$ The maximum value of  $B_a$  is  $\mu_0 H_c \kappa \sqrt{2}$ , hence if  $\kappa > 1 / \sqrt{2}$ , the field inside is  $> H_c$ .  $H_{c2} = \kappa \sqrt{2} H_c$ 

When  $\kappa < 1/\sqrt{2}$  we have Type I When  $\kappa > 1/\sqrt{2}$  we have Type II

# 8.5. Flux Quantization

Well inside a superconductor, the wave function  $\psi$  will give a uniform density of superconducting electrons.

 $|\psi|^2 = |\psi_0|^2 = n_s$ 

Hence there is a wavefunction of the form  $\psi = \psi_0 exp \, i\theta$  where  $\theta$  is the phase, a macroscopic variable.

Consider a ring carrying a supercurrent of density **j**.

Since  $\boldsymbol{p} = m\boldsymbol{v} + q\boldsymbol{A}$   $\boldsymbol{v} = (1/m)(\boldsymbol{p} - q\boldsymbol{A}) = (1/m)(-i\hbar\nabla - q\boldsymbol{A})$   $\therefore$  The particle flux is  $\frac{1}{2} \{(\psi^* \boldsymbol{v}\psi) + cc\}$  [number/m<sup>2</sup>/s] Hence the current density is  $(q/2m)\{\psi^*(-i\hbar\nabla - q\boldsymbol{A})\psi + [(-i\hbar\nabla - q\boldsymbol{A})\psi]^*\psi\}$  $\therefore \boldsymbol{j} = (n_s q/m)\{\hbar\nabla\theta - q\boldsymbol{A}\}$  (1)



This resembles the London postulate:  $\mathbf{j} = -(1/\mu_0 \lambda^2) \mathbf{A}$  where  $\lambda^2 = m/\mu_0 n_s q^2$ except for the extra term  $-i\hbar \nabla \theta$ 

Taking the curl of both sides of (1),  $\nabla x \mathbf{j} = -(1/\mu_0 \lambda^2) \mathbf{B}$  – the London Equation.

*Recall*  $\nabla x \nabla \theta = 0$  for any scalar  $\theta$ .

A dramatic consequence of (1) is flux quantization in a superconducting ring



Consider the dashed line buried deep inside the superconductor, where B = j = 0

$$\oint \mathbf{j}.\mathrm{d}\mathbf{I} = (n_s q/\mathrm{m}) \oint \{\hbar \nabla \theta - \mathbf{q}\mathbf{A}\}.\mathrm{d}\mathbf{I} = 0$$

By Stokes's theorem,  $\oint \mathbf{A} \cdot d\mathbf{I} = \int_{S} \nabla \mathbf{x} \cdot \mathbf{A} \cdot d\mathbf{S} = \int_{S} \mathbf{B} \cdot d\mathbf{S} = \Phi$ 

 $\Phi$  is the enclosed flux, which is independent of path, provided we avoid the penetration depth.

Also  $\int \nabla \theta d\mathbf{l} = \Delta \theta$ , the change of phase on going once around the ring.

But  $\psi$  has to be single-valued, hence  $\Delta \theta = 2n\pi$  or  $\hbar \Delta \theta = \hbar 2n\pi$ 

$$\hbar 2n\pi - q\Phi = 0$$

 $\Phi = \hbar 2 n \pi / q = n h / q$  The flux is a multiple of a fundamental quantum h/q

 $\Phi_0$  = 2.07 10<sup>-15</sup> T m<sup>2</sup> the flux quantum or *fluxon* 

### Measurement of the flux quantum:



The fact that the flux quantum is actually observed is good evidence for the description of superconductivity in terms of the complex order parameter  $\psi(\mathbf{r})$ .

Furthermore, the charge q must be 2e, not e, in order to explain the value of  $\Phi_{0.}$ 

This means that the charge carriers are electron pairs.

How long does the flux remain trapped in a superconducting ring?

The probability for escape for a flux quantum is attempt frequency x activation probability The activation probability is  $P = \exp -(\Delta G/k_BT)$ 

d

The activation volume that has to go normal for a fluxon to escape is ~  $d\xi^2$ .

$$\therefore \Delta G = (\mu_0 H_c^2/2) d\xi^2$$

Suppose  $d = 100 \,\mu\text{m}$  (~ thickness of a hair)

 $\xi = 10 \text{ nm}$   $\mu_0 H_c = 100 \text{ mT} \longrightarrow \Delta G \sim 10^{-16} \text{ J}$   $T = 100 \text{ K} \longrightarrow -\Delta G / k_B T = -10^5$ The attempt frequency is of order  $k_B T / \hbar \sim 10^{13}$ 

 $P \sim 10^{13} \exp -10^5 = 10^{13} 10^{-43000}$  This is immense; the age of the universe is only  $10^{18}$  s.

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- 6. Normal Metals
- 7. Superconductors
- 8. Theory (microscopic)
- 9. Superconducting Tunelling
- 10. Applications; High-T<sub>c</sub> superconductors





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# 8.6 Microscopic Theory (Bardeen, Cooper and Schreiffer)

## 4.1. The Cooper pair

The essential element of the BCS theory of superconductivity is that the electrons form *pairs* Consider two electrons, each with  $s = \frac{1}{2}$ , somehow bound together with opposite spin to form an entity with S = 0, known as a *Cooper pair*.

The Cooper pair should behave as a boson, with all the pairs condensing into the same ground state. All of them are then described by the same wave function  $\varphi_p(\mathbf{r})$ .

We need some attractive force between the electrons to provide the coupling, and reduce the energy below that of the normal electron gas.

In the original BCS theory, the attractive force was provided by the electron-phonon interaction, although other possible attractive interactions exist. The strong Coulomb repulsion between electrons in a metal is screened out at large distances.

Normally, when no supercurrent flows, the Cooper pairs have no net momentum.



Cooper pair: 
$$q = 2e$$
  $m = 2m_e$   
 $K = 0$   $S = 0$ 



Attractive electron-electron interaction mediated by the ion cores in a crystal

The Cooper pair is a quasi-bound state. The energy is lowered compared to that of two free electrons.



Unlike a single electron, the total momentum of a pair is unchanged by exchanging a phonon.

The  $\{k, -k\}$  pair is scattered into another Cooper pair state  $\{(k - q), -(k - q)\}$ 

k for the electrons in the Cooper pair is  $\sim k_F$ 

The energy of the *virtual phonon* exchanged is ~  $\hbar \omega_{\rm D}$ 

The spatial extent of the pairing is  $\xi$ , the coherence length!

Virtual phonon exchange

Energy is needed to break up a Cooper pair into two electrons.

These are called *quasi-particle excitations* of the fully-paired bosonic ground state.

The energy required is  $2\Delta$ 

Hence the energy gap  $E_g = 2\Delta$ .

## 4.2 Energy of the Cooper pair.

We now calculate the energy reduction of a pair of electrons due to electron-phonon coupling.

The free electron wave functions are of the form  $\psi = \exp i\mathbf{k} \cdot \mathbf{r}$ ; They have momentum  $\hbar \mathbf{k}$ 

In the absence of any attractive force, the wave function of the pair of electrons is

 $\psi_{p} = \{ \exp i \mathbf{k} \cdot \mathbf{r}_{1} \} \{ \exp i (-\mathbf{k}) \cdot \mathbf{r}_{2} \}$ 

$$\psi_p = \exp i\mathbf{k} \cdot \mathbf{r}_p$$
 where  $\mathbf{r}_p = (\mathbf{r}_1 - \mathbf{r}_2)$ 

*Note:* It looks like a single-electron state, but it actually represents a pair.

If there is a supercurrent, all the electrons have an additional net momentum  $\hbar \,\delta \mathbf{k}$  in the current direction. Hence there is an extra factor exp i $\delta \mathbf{k}$ .( $\mathbf{r}_1 + \mathbf{r}_2$ ) in the pair wavefunction.

We suppose that the individual electrons making up the Cooper pair have  $E \approx E_F$  and  $k \approx k_F$ 

The interaction with the phonons scatter the electrons from one pair state to another, so the appropriate pair wavefunction is a linear combination of the individual  $\psi_p s$ , where  $A_k$  does not depend on  $r_p$ 

$$\varphi_{p}(\boldsymbol{r}_{p}) = \sum_{k} A_{k} \exp i\boldsymbol{k}.\boldsymbol{r}_{p}$$
(1)

Suppose the attractive force is associated with a potential  $U(r_p)$ . We also assume, for simplicity, that the electrons are in states at the Fermi energy. The Schrödinger equation is

$$-(\hbar^{2}/2m)\{\nabla_{1}^{2} + \nabla_{2}^{2}\}\phi_{p} + U(\boldsymbol{r}_{p})\phi_{p} = (2E_{F} + \delta E)\phi_{p}$$
(2)

Schrödinger's equation can now be solved to give the change of energy  $\delta E$  due to the attractive force. Set  $\nabla_1^2 \phi_p = \nabla_2^2 \phi_p = -k^2 \phi_p$  and use (1) and (2)

$$\sum_{k} \{ (\hbar^2 \mathbf{k}^2 / m) - 2E_F - \delta E \} A_k \exp i\mathbf{k} \cdot \mathbf{r}_p = -\sum_{k} U(\mathbf{r}_p) A_k \exp i\mathbf{k} \cdot \mathbf{r}_p$$
  
Set  $\varepsilon_k = (\hbar^2 \mathbf{k}^2 / 2m - E_F)$   
 $\mathbf{r}_p = (\mathbf{r}_1 - \mathbf{r}_2)$ 

$$\sum_{k} (2\varepsilon_{k} - \delta E) A_{k} \exp i\mathbf{k} \cdot \mathbf{r}_{p} = -\sum_{k} U(\mathbf{r}_{p}) A_{k} \exp i\mathbf{k} \cdot \mathbf{r}_{p}$$

Now x by exp-ik '. $r_p$ , integrate over the sample volume and use the identity  $\int \exp i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}$ d<sup>3</sup> $r = \delta_{kk'}$  V The integral = V, sample volume, when  $\mathbf{k} = \mathbf{k}'$ ; when  $\mathbf{k} \neq \mathbf{k}'$  it is 0.

$$\therefore (2\varepsilon_{k'} - \delta E) A_{k'} = -\sum_{k} U_{kk'} A_{k} \text{ (sum over } k \text{)}$$
(3)  
where  $U_{kk'} = (1/V) \int U(r_{p}) \exp i(k - k') \cdot r_{p} d^{3}r_{p}$   
Now the states with  $k' < k_{F}$  are all occupied, hence  $A_{k'} = 0$  for  $k < k_{F}$ .

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Also the electron-phonon interaction cannot scatter electrons in states with  $E > E_F + \hbar \omega_D$  or  $E < E_F$  (A<sub>k</sub>= 0 for  $k < k_F$ ). Therefore the scattering is within a narrow band of k near  $k_F$ 

Take  $U_{kk'}$  = constant = -U if k and k' lie within this narrow shell, zero otherwise

From (3) 
$$A_{k'} = U \sum_{k} A_{k} / (2\varepsilon_{k'} - \delta E)$$
 (*U* is +ve for an attractive force)

To find  $\delta E$ , sum over all states k' within the narrow shell, and divide by  $\Sigma_{k'} = \Sigma_k$ 

 $1 = U \sum_{k'} 1/(2\varepsilon_{k'} - \delta E)$  Now use  $\mathcal{D}(\varepsilon)$  to convert the sum to an integral;

 $1 = U \int_0^{h\omega_D} \{ \mathcal{D}(\varepsilon)/2(2\varepsilon_k - \delta E) \} d\varepsilon$  where  $\mathcal{D}(\varepsilon)$  is the density of states near  $E_F$  (both spins)

Take 
$$\mathcal{D}(\varepsilon_{\rm F}) \approx \text{constant}; \quad 1 = (U\mathcal{D}/4)\ln[(\delta E - 2\hbar\omega_{\rm D}/\delta E]]$$
  
 $\delta E = -2\hbar\omega_{\rm D}/[\exp(4/U\mathcal{D}) - 1]$   
 $\delta E \approx -2\hbar\omega_{\rm D}\exp(-4/U\mathcal{D})$  when  $U\mathcal{D} << 1$  (4) (~ true for all known s/c)  
The change of energy is -ve, so the electrons in a Cooper pair are bound. For

high  $T_{\rm sc}$  the Debye frequency should be high (light elements), and U,  $\mathcal{D}(\varepsilon_{\rm F})$  should be large

#### 4.3 The superconducting ground state

The above treatment is for a single Cooper pair. The treatment of the collective interaction of all the pairs in the superconducting ground state is more complicated. We do not treat it here, but simply state some of the main results.

— The Cooper pair with energy ( $2E_F + \delta E$ ),  $\delta E < 0$  mixes states at  $E_F$  with states above  $E_F$ . This leaves some states at  $E_F$  free, so that electrons below  $E_F$  can also form pairs. If states below  $E_F$  are unoccupied, electrons can scatter into them, and this tends to break up the pair, so the binding energy is lost.

— The range of one-electron states that are partly occupied in the BCS ground state is  $\pm \Delta_0$  around  $E_{\rm F}$ . at T = 0. (smearing looks rather like the Fermi function for nonzero temperature)

$$\Delta_0 = 2\hbar\omega_{\rm D} \exp(-2/U\mathcal{D}(E_{\rm F})) \qquad \text{c.f. Eq (4)}$$

This is the binding energy of a Cooper pair, but it reflects the collective interaction of *all* the electrons.

- It can be shown that  $G_n - G_s = (1/2) \mathcal{D}(E_F) \Delta_0^2$  but  $\mathcal{D}(E_F) = (3/2)n/E_F$  (see slide 15)  $G_n - G_s = (3/4) n \Delta_0 (\Delta_0/E_F)$   $(= (1/2)\mu_0 H_c^2)$ 

This is consistent with the idea that only a small fraction ~  $(\Delta_0/E_F)$  of electrons form a quasibound state near  $E_F$  with a binding energy  $\Delta_0$  But it is nonetheless a *collective* ground state. How much energy is needed to break up the Cooper pair, and create two quasiparticle excitations (electrons) ?



Above the gap the electrons are quasiparticles - unpaired

Below the gap, the electrons are superconducting.



Note that the gap is tied to  $E_{\rm F}$ , not like a semiconductor, where it is fixed to the lattice in reciprocal space.



## Energy-level diagrams



Superconducting ground state

Excited quasiparticles are usually produced two at a time, hence the gap is usually  $2\Delta_{0.}$ 

One electron can be injected from a normal electrode (Andreev reflection)





3

Semiconductor representation. An added electron (at *T* > 0), can go into the nearly-empty upper state or the nearly full lower state (and form a Cooper pair). Both are singleelectron bands

## 4.4 Summary of BCS predictions

- 1)  $k_B T_{sc} = 0.57 \Delta_0 = 1.13 2 \hbar \omega_D \exp(-4/U \mathcal{D}(E_F))$  Note The bigger U, the higher  $T_{sc}$  and the bigger the resistivity in the normal state.
- 2)  $\Delta$  varies with *T* 3) Isotope effect follows since  $\omega_D \propto 1/M^{1/2}$   $T_{sc}$  *T*
- 4) Zero resistance arises because scattering with small loss of energy is impossible because of the gap
- 5) Flux quantization with  $m = 2m_e$ , q = 2e,  $\Phi_0 = h/2e$
- 6)  $T_{sc} \propto \Delta_0 \propto H_c(0)$   $H_c(T) = H_c(0)[1 1.06(T/T_{sc})^2]$  for  $T << T_{sc}$  $H_c(T) = 1.74 H_c(0)[1 - (T/T_{sc})]$  for  $T \approx T_{sc}$
- 7)  $\lambda$  and  $\xi$  emerge from the theory;  $\xi$  is the real-space extent of the Cooper pair
- 8) Nothing sacred about phonon pairing. *Any* mechanism that provides an attractive interaction between electrons might do.
- 9) The macroscopic wavefunction follows from the unique BCS ground state for all electrons





# Metal Physics and Superconductivity PYU44P13

- 6. Normal Metals
- 7. Superconductors
- 8. Theory
- 9. Superconducting Tunelling
- 10. Applications; High-T<sub>c</sub> superconductors





www.tcd.ie/Physics/Magnetism

Comments and corrections please: jcoey@tcd.ie

# **Magnetism and Superconductivity; Part 2b**

J. M. D. Coey

- 6 Simple models of metals
- 7. Superconductivity
- 8. Theory
- 9. Tunnelling
- 10. High T<sub>sc</sub> Applications





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# **5 Superconducting Tunneling**

Tunneling is a familiar phenomenon in quantum mechanics. The wave function of the electrons in a metal does not disappear abruptly at the surface, but it decays exponentially - an evanescent wave. There is a significant probability of detecting an electron up to about a nanometer away from the surface.

Normal tunneling across a vacuum or air gap is the basis of scanning tunneling microscopy (STM) [1986 Nobel Prize for Binnig and Rohrer] 5.1. Two normal metals

Consider a tunnel junction made from two normal metals,  $m_1$ ,  $m_2$ :



# 5.2 A normal metal and a superconductor - Giaver tunneling.



tunnel into the unoccupied quasiparticle states of the superconductor, above

# 5.3. Two superconductors. Josephson tunnelir

(PhD work of Brian Josephson in 1963 — Nobel Prize 19 Consider a tunnel junction made from two superconductors





Cooper pairs may now tunnel across the insulating barrier

Assume  $sc_1$  and  $sc_2$ are made of the same metal

The two superconductors are weakly coupled across the insulating barrier. How does a supercurrent flow?

Suppose the two superconductors are made of the same material, so  $\Delta_0 = \Delta_0'$ . The density of superconducting electrons  $n_s$  is the same in both, so they are described by a wave function with the same amplitude  $\psi_0$ . What may be different is the phase  $\theta$ .

 $\psi = \psi_0 \exp i\theta$ 

If a supercurrent is crossing the junction, in zero applied field  $j = (q/2)\{(\psi^* \mathbf{v} \psi) + cc\}$  (see § 3.5 p.83)

Set q = 2e,  $m = 2m_e$ ,  $p = -i\hbar \nabla$  No magnetic field, A = constant $i = -(iq\hbar/2m)[\psi^*\nabla\psi + \psi(\nabla\psi^*)] = -(e\hbar/m_e)n_s\nabla\theta$ (1) If  $\nabla \theta = 0$ , there is no current, and  $\theta = \text{const.}$  If  $j \neq 0$ ,  $\nabla \theta \neq 0$ When a constant supercurrent flows in the x-direction,  $\theta = a + d$  $\psi = \psi_0 \exp i\theta = \psi_0 [\cos(a + bx) + i \sin(a + bx)]$ bx.  $\psi = \psi_0 \exp i \,\delta \mathbf{k.r}$  (See § 4.2 slide 91)  $\theta = \delta \mathbf{k} \cdot \mathbf{r}$  $\nabla \theta = \delta \mathbf{k}, \quad \mathbf{j} = -(e\hbar/m_{\rm e})n_{\rm s}\,\delta \mathbf{k} \quad \text{from} (1)$ X 106 PYU44P13 2023



The two superconductors are supposed to be identical, but with different phases. The barrier introduces a phase difference  $(\theta_1 -$ 

 $\psi(x) = A \exp \alpha x + B \exp \alpha x$   $\alpha$  depends on barrier height u (Joules);  $\alpha =$ (2mu)<sup>1/2</sup>/ħ

Let  $\theta_1$  and  $\theta_2$  be the phases on either side of the insulating barrier.

Continuity conditions: A exp - $\alpha a$  + B exp  $\alpha a = (n_s)^{1/2} \exp i\theta_1$  on the left side and A exp  $\alpha a$  + B exp  $-\alpha a = (n_s)^{1/2} \exp i\theta_2$  on the right side

Hence  $A = (n_s)^{1/2} \{ \exp i\theta_2 \exp \alpha a - \exp i\theta_1 \exp -\alpha a \} / \{ \exp 2\alpha a - \exp 2\alpha a \} \}$  $B = (n_s)^{1/2} \{ \exp i\theta_1 \exp \alpha a - \exp i\theta_2 \exp -\alpha a \} / \{ \exp 2\alpha a - \exp -2\alpha a \} \}$  Then and current in gap  $j = (ie \hbar \alpha/m) \{AB^* - A^*B\} = (4e \hbar \alpha/m)n_s \sin(\theta_1 - \theta_2)/(exp2\alpha a - \theta_2)$  $exp2\alpha a)$ 107

> where  $i_0 = (42\%\%\%)^{1/2}(\exp 2\alpha a - \exp 2\alpha a)$ (1')  $i = i_0 \sin(\theta_1 - \theta_2)$

A supercurrent flows across the junction when V = 0. It depends on the properties of the insulating barrier, a and  $\alpha$ . (~ $\sqrt{u}$ ) !  $j_0$  is the maximum possible supercurrent density. It is the critical current of the junction. When  $\alpha a << 1$ , exp $2\alpha a = 1 + 2\alpha a + ..., , j_0 = (e\hbar/ma)n_s$ . The magnitude of the supercurrent depends on the phase difference ( $\theta_1 - \theta_2$ ) across the junction.

The junction carries a normal current and a supercurrent, Below  $j_0$  the supercurrent dominates. If the current is increased, when it reaches  $j_0$  the junction switches to the normal state (b c). On decreasing



the device the low to the sected and, then returns to a. The Josephson junction is a fast bistable switch. Only the dc current is plotted in the figure. This is the dc Josephson effect. Capacitance of junction is tiny, so switching is extremely fast. RC ~ ps.

But when a voltage V is applied cross the junction, there is also a rapidlyoscillating ac supercurrent, the ac Josephson effect.
## 5. 3.1 ac Josephson effect.

When a voltage is applied to the junction, electrons may:

i) tunnel as normal individual electrons when V >>  $2\Delta_0$ /e ii) Tunnel as Cooper pairs. When a pair crosses the junction, it must lose its extra energy to attain the condensed state, which it does by emitting a photon

with onoray

$$hv = 2eV$$
(2)

V is typically 1 mV (≈ 10 K) 1 mV → v = 2 x 1.6 10<sup>-19</sup> x 10<sup>-3</sup>/6.6 10<sup>-34</sup> = 484 GHz, hence v is in the high microwave range. The junction emits microwaves when a voltage is applied across it. An ac tunnel current of this frequency also appears across the junction. Since frequency can be measured very accurately, the Josephson junction is used in standards laboratories worldwide to define the volt.

When the energy of the centre of mass of the pair is E, a factor exp -iEt/ $\hbar$ must be included in  $\psi$ .  $\theta = 2eVt/\hbar$ . Time varying current  $\rightarrow \Delta\theta(t)$   $2eV = \hbar d\Delta\theta/dt$ implies a voltage. The Josephson junction equation becomes The supercurrent is now sinusoidal in time with v = 2eV/h,  $\omega = 2eV/h$ 

Finally, if the Josephson junction is irradiated with microwaves of frequency  $\omega'$ and amplitude  $V'_0$   $V' = V'_0 \sin \omega' t$  the equation becomes

$$j = j_0 \sin\{\theta_1 - \theta_2 - 2eVt/\hbar + (2eV'_0/\hbar) \sin \omega't\}$$

Expand using sin (A + B) = sin A cos B + cos A sin Bwhere  $A = \theta_1 - \theta_2 - 2eVt/\hbar$  and  $B = (2eV'_0/\hbar) \sin \omega' t$ Also expand sin  $(2eV'_0/\hbar)$  sin  $\omega't$  and cos  $(2eV'_0/\hbar)$  sin  $\omega't$  as Fourier series.  $\rightarrow j = j_0 \Sigma_0^{\infty} A_n \sin\{\theta_1 - \theta_2 - (2eV/\hbar - n\omega')t\}$ Hence, as V increases, a dc current flows when  $V = n \hbar \omega'/2e$  $J_0$ Shapiro steps occur when V is a multiple of  $\hbar\omega'/2e$ This gives  $\hbar/e$  from  $\bigvee'_{0}(\omega)$  measurements 110 Z///e PYV44P13 2023 5.3.2 Superconducting quantum interference devices (SQUIDS) Now we combine Josephson junctions with the idea of flux quantization in a ring. There must be two junctions in the ring if we are to be able to apply or measure a dc voltage across ita

The junctions may be tunnel junctions, or point contacts (weak links) with a much reduced  $i_c$  (or  $j_c$ ) denoted  $i_{ca}$ 

NB from (1) on 
$$p$$
 83,  $j = (n_s q/m) \{ \hbar \nabla \theta - q \mathbf{A} \}$ 



in sc Suppose the two junctions are identical. The phase jumps across the junctions are  $\Delta \theta_a$  and  $\Delta \theta_b$ . These decide the supercurrent flowing in the ring. The phase change within each superconductor is negligible, since the current is so small. There is a phase difference when a field is applied. It is across the sc, not the Jj, which is very thin.

When the field is first is applied, a supercurrent flows in the ring so as to exclude it. However, if  $i > i_{ca}$  for the weak links, the flux cannot be entirely excluded from the ring. It penetrates, one fluxon at a time, and the direction of the current in the ring changes sign periodically as  $B_0$  is increased, but the flux in the ring is  $\approx$ the applied flux. The weak circulating current introduces  $\Delta \theta$  at the weak PYC44P13 2023 If the weak links were absent, the applied field would cause a supercurrent to flow in the loop in order to exclude the flux. The flux would only penetrate the ring when the critical current density  $j_c$  of the superconductor is reached. ( $j_c \sim 1000$  A/mm<sup>2</sup> in Nb at 4K) c.f p.99

When the weak links are present, the flux penetrates as soon as the critical current density of the junction  $j_{ca}$  is reached. Flux penetrates one fluxon at a time, and the sense of the supercurrent in the ring reverses periodically as B increases. In general L  $i_{ca} << \Phi$ , and in the the device we consider L  $i_{ca} << \Phi_0$  so all flux penetrates the ring.

From § 3.5, we can write the condition for flux quantization around the ring,  $\int \mathbf{J} \cdot d\mathbf{I} = (n_s q/m) \int \{\hbar \nabla \theta - q\mathbf{A}\} \cdot d\mathbf{I} = 0$  (3)

The phase change around the superconducting circuit is  $2n\pi$ .

 $\Delta \theta_{tot} \begin{bmatrix} (\Delta \theta_a - \Delta \theta_b) + 2\pi n ] - q\Phi = 0 & hence \Delta \theta + 2\pi n \operatorname{Since} \Phi / \Phi_{ca} < \langle \Phi \phi_0 = h/q \rangle \\ \text{Two currents can make A a multiple of } 2\pi; & induced circulating \\ phase differences appear across each weak \\ link. & generate one fluxon. \\ The flux in the ring ~ \Phi = B\mathcal{A} & The flux in the ring is <math>2n\pi$  is satisfied because of the phase differences at the weak links.  $\Delta \theta (B) = \int_{0}^{12} \Phi / \Phi$ 



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Pass a sense current I across the SQUID. Half of it passes in each arm. There is a current of I/2 - i in junction a, and a current of I/2 + i in junction b From (3)  $\int {\hbar \nabla \theta - 2e\mathbf{A}} .d\mathbf{I} = 0$ 

If  $\theta_0$  is the phase difference between X and Y associated with I.  $\Delta \theta_{XY} \approx \Delta \theta_a \approx \Delta \theta_b$ 

$$\Delta \theta_a = \theta_0 - \pi \Phi / \Phi_0 \qquad \Delta \theta_b = \theta_0 + \pi \Phi / \Phi_0 \qquad \text{Phase change is the same if} \\ B = 0 \qquad B = 0$$

 $J_{a} = j_{0} \sin (\theta_{0} - \pi \Phi/\Phi_{0}) \qquad J_{b} = j_{0} \sin (\theta_{0} + \pi \Phi/\Phi_{0}) \qquad \text{from the J J Eqn (1')}$   $J = J_{a} + J_{b} = j_{0} [\sin (\theta_{0} - \pi \Phi/\Phi_{0}) + \sin (\theta_{0} + \pi \Phi/\Phi_{0})] \qquad j_{0} \text{ is max } j \text{ in either junction}$ 

$$J = 2 j_0 \sin \theta_0 \cos (\pi \Phi/\Phi_0) \qquad \text{since} \\ \sin(A \pm B) = sAcB \pm cAsB \qquad 114$$

$$J_{c} = 2i_{0} |\cos(\pi \Phi/\Phi_{0})|^{13 2023}$$

SQUIDS are used a very sensitive magnetometers, flux changes of  $\Phi_0/100$  can easily be detected.

Suppose the area of the loop is  $1 \text{ cm}^2$ ,  $10^{-4} \text{ m}$ 

 $\Phi_0 = 2 \ 10^{-15} \ T \ m^2$ 

$$B_{min} = (1/100) \times 2 \ 10^{-15} / 10^{-4} = 2 \ 10^{-13} \ T!$$



Hence we use SQUIDS to detect the very weak fields produced by the biological currents produced in the heart, brain etc.

Geological prospection. SQUIDS are used to map anomalies in the Earth's magnetic field that reflect buried iron ores.

The SQUID is used as a sensitive ammeter to measure very tiny currents via the fields they produce. Small voltages are measured by passing currents through a known resistor.

There are various types of 'weak links', all of them showing a small critical current across the constriction, where magnetic field can penetrate.



Nanoconstriction Point contact Grain bouundary Tunnel junction RSJ

A supercurrent can pass through the weak link, and the phase difference  $\Delta\theta$  increases with current, reaching the critical value when  $\Delta\theta = \pi/2$ . Only for the tunnel junction does the current vary as the sine of  $\Delta\theta$ , but otherwise all the weak links resemble eachother.

A short weak link has  $d < \xi$ . The ideal Josephson effect is seen only in short links

The point contact junctions are most suitable as rf radiation sources and detectors, as the radiation can be easily coupled in and out of them. Rf SQUIDS use a point contact.

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A layer of normal metal can also be used to see  $\frac{PY144P13}{10}$  and the two superconductors.

A single Josephson junction or point contact is sensitive to the magnetic field. There is a dc current which depends on the flux threading it.



— Switching of a Josephson junction can be very fast; We can estimate the switching time from the junction capacitance C, and its critical current  $I_0$  and the switching voltage  $V_{switch} = 2\Delta_0/e$  (§ 5.3)

$$\tau_{switch} \approx R_n C = C V_{switch} / I_0$$

 $C = \varepsilon \varepsilon_0 a/d$  where *a* is the junction area and  $d = 2a \approx 1$  nm;  $R_n \sim 1/a$ 

Hence the switching speed is independent of area. This means that a scalable technology could be built around superconducting electronics. The switching speed depends on the superconducting material, and the barrier thickness d. (which must be as thin as possible)  $I_0 = (2\Delta_0/eR_n)$ . A 100 x 100  $\mu m^2$  junction may have  $R_n \approx$ 

0.1 
$$\Omega$$
 and C  $\approx$  4 10<sup>-10</sup> F ( $\varepsilon_0 = 1/\mu_0 c^2 = 8.85 \ 10^{-12}$ ) For a conventional superconductor  $2\Delta_0/e \approx 1 \ mV$ ,  $I_0 \approx 0.1 \ mA$ ,  $j_0 = 10^6 \ A \ m^{-2}$ 

 $\tau_{\rm switch} \approx 4 \, 10^{-12} \, {\rm s}$ 

rf SQUID

ac

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- Suppress the hysteresis of a Josephson junction by placing a resistive shunt X across the junction (RSJ) R

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dc SQUID dc JE

— Flux transformer. A superconducting circuit. The flux threading the loop cannot change.



The gradiometer has a figure-of-8 pickup coil, which eliminates the effect of any uniform (fluctuating) field  $B_0$  and responds to the local field  $B_0$ . It

measureşy BP13 2023

— Superconducting logic

A and B are control lines which produce a field which is sufficient to switch the nearby junction.



We make the junctions so that any one can carry a supercurrent of i/2, (but not 2i/3)

The structure acts as an AND gate. When A and B are on, then a voltage appears at

If the junctions switch between i/3 and i/2, it acts as an OR gate.

The gate is dissipative, and can be reset with a -ve current pulse.

— Microwave resonant cavities, antennae

# Metal Physics and Superconductivity PYU44P13

- 6. Normal Metals
- 7. Superconductors
- 8. Theory
- 9. Superconducting Tunelling
- **10.** Applications; High-T<sub>c</sub> superconductors





Comments and corrections please: jcoey@tcd.ie

# 6.1 New Superconductors

The record for T<sub>sc</sub> (23.2 K) was held by Nb<sub>3</sub>Ge up to 1 Many attempts were made to find new superconducting materia these included – Organic materials – Heavy fermion metals

Cubic A15 Nb<sub>3</sub>Ge

La 🔵

Cu 🔿

None yielded a higher T<sub>sc</sub> until Müller and Bednorz came up with an oxide material in April 1986 that showed signs superconductivity above 30 K. They were awarded the Nobel Prize the following year! Their material

 $(La_{1-x}Ba_x)_2CuO_4$ 

has the tetragonal  $K_2NiF_4$  structure, with planes of copper and oxygen. The end-member  $La_2CuO_4$  is an antiferromagnetic semiconductor. The formal valences are  $La^{3+}_2Cu^{2+}O^{2-}_4$ .  $Cu^{2+}$  has a  $3d^9$  configuration.

It has a strong preference for square-planár coordination. The composition was  $(La_{1.8}Ba_{0.2})_2CuO_4$  or  $La^{3+}_{1.8}Ba^{2+}_{0.2}Cu^{2+}_{0.8}Cu^{3+}_{0.2}O^{2-}_4$  $Cu^{3+}$  has a 3d<sup>8</sup> configuration. A mixed-valence compound.<sup>22</sup>



Then, in 1988 a new family of superconductors  $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$  was discovered:

n= 1

$$Bi_2Sr_2CuO_{6+\delta}$$
  
 $Bi_2Sr_2CaCu_2O_{8+\delta}$   
 $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ 

These are layer compounds with a structure made up of building blocks of (BiO)<sub>2</sub> double layers and stacks of  $n(CuO_2)$  layers, intercalated by (n-1)Ca atoms.

 $T_{sc}$  is lower in the n = 4 compound.

Related compounds with TI and Hg exhibit  $T_{sc}$  of up to 148 K. c=24.6 A



$Cs_{3}C_{60}$	40 K	(1990)
$MgB_2$	39 K	(2001)
Ba <sub>0.3</sub> K <sub>0.2</sub> FeAs	37 K	(2008)





#### 6.1.1 Bipolaron superconductivity.

The idea of Bednorz and Muller was to develop a new coupling mechanism coupling for a high  $T_{sc}$  superconductor using Jahn-Teller polarons. They tried mixed-valence oxides which exhibit hopping conduction (Their idea turned out to be wrong!).



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#### 6.1.2 Electronic Structure.

The chemical systematics of high- $T_{sc}$  superconductivity establish that it is the CuO<sub>2</sub> layers that are the common feature. There is a strong twodimensional character to all these high- $T_{sc}$  oxides.



If we remove an extra electron from copper to make Cu<sup>3+</sup> '3d<sup>8</sup>' it is an experimental fact that the extra hole is mainly localized on the oxygen. The configuration of 'Cu<sup>3+</sup>' is closer to

 $3d^9\underline{L} - 3d^92p^5$  (<u>L</u> is a ligand hole) than  $3d^8 - 3d^82p^6$ 

The holes formed by adding Ba or Sr to LaCuO<sub>4</sub> have mainly oxygen 2p character.

The nature of the holes was determined by electron photoemission experiments.

# 6.1.3 Ceramics.

The cuprate superconductors are oxide materials. They are black ceramics, usually prepared by solid state reaction of powders of the constituent oxides. They are formed of tiny crystallites sintered together in a brittle porous mass.

The bulk ceramics are formed of superconducting crystallites with grain boundaries between the grains forming a network of weak links.

They cannot be fabricated into wires by normal metallurgical processes. Superconducting tapes are made from composites of the oxide with silver. It is possible to grow single crystals for studies of fundamental physical processes, and thin films can be grown on single-crystal substrates such as  $SrTiO_3$  by pulsed las<sup>2</sup> - 2<sup>-2</sup> - 2<sup>-2</sup> - 2<sup>-2</sup> - 2<sup>-2</sup>

SrTiO<sub>3</sub> has the perovskite structu The lattice parameter is very that oi

The structures of all the high- $T_c$  o. are derived from perovskite.



# 6.1.4 Tunelling

A key question was whether the high-T<sub>sd</sub> materials show the same electron pairing as in normal superconductors.

It was possible to make a Josephson junction from Nb and  $YBa_2Cu_3O_7$ Hence Cooper pairs with S = 0 also exist in the oxide.

However the electrons at the Fermi energy have  $d_{x^2 - y^2}$  character, rather than s character. It is d-wave rather than s-wave superconductivity.







There are four nodes around the gap in the Fermi surface, where the wavefunction changes sign.  $\Delta_k = \Delta \{ cosk_x a - {}^1 e^0 sk_y a \}$ 

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### 1.5 Anisotropy of the physical properties.

### a) Conductivity.

All the discussion in the first five chapters has been in terms of the free-electron model. The metallic character of the high- $T_{sc}$  oxides is clearly very anisotropic or even two-dimensional — two-dimensional in the plane, and tunelling from plane to plane along the tetragonal c-axis.



NB  $\rho_{ab}$  ( $\rho_{\perp}$ ) is or order 3  $\mu\Omega$  m at room temperature  $\rightarrow$  mean free path  $\approx$  lattice spacing. (see Ch1 §2.1.1 p.10)

A bad metal makes a good superconductor.

The conductivity along the c-axis is clearly semiconducting.

c) Critical Fieldth the slope near  $T_{sc}$ , the values of  $H_{c2}$  at T = 0 can be estimated using  $H_{c}(T) = 1.74 H_{c}(0)[1 - T/T_{sc}]$  (§ 4.4 p97)  $H_{ll}$   $H_{c2} = 53 T$   $Slope -4 T/K}H_{c2}^{L} = 211 T$  These are enormous!  $H_{ll}$   $H_{c2} = 1 T$  (Thermodynamic critical field) The corrolary is that the coherence lengths are very small.

Ginzburg Landau theory gives  $H_{c2} = \Phi_0/2\pi\mu_0\xi^2$ . (The maximum possible packing of fluxons in the vortex state determines  $H_{c2}$ )

*Hence*  $\xi^{||} = 1.8 \text{ nm}$   $\xi^{\perp} = 0.5 \text{ nm}$  <sup>132</sup>

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The penetration depth depends on the conduction electron density in the isotropic case  $\lambda^2 = m/(\mu_0 n_s q^2)$ 

$$\lambda_{\parallel} = 210 \ nm$$
$$\lambda_{\perp} = 60 \ nm$$

Hence  $\kappa_{||} = 120$ 

 $\kappa_{\perp} = 120$  It is an extreme type II superconductor. Recall  $\kappa > 1/\sqrt{2}$  is the condition for type II

Now the pinning energy is  $\Delta V \mu_0 H_c^2/2$ 

 $\Delta V = \xi_{\parallel} \xi_{\perp}^{2} \sim 10^{-27} \, m^{3}$ 

Hence the activation energy  $10^{-27} 1^2/1.38 10^{-23} 8\pi 10^{-7} \sim 30 \text{ K}$ 

Flux flow (creep) occurs near  $T_c$ . The flux lattice has to be pinned, by structural defects, in or H



# 6.2. Applications

A major application of low- $T_c$  superconductors is superconducting magnets. 10<sup>6</sup> km of NbTi wire has been used for 20,000 Magnetic Resonance Imagers



<del>5 T split pair</del>

Large hadron collider quadrupole magnetsU44P13 2023

'10<sup>6</sup> km of NbTi wire has been used for 20,000 Magnetic Resonance Imagers'

Q. Estimate the magnetic field B in the bore of an MRI machine, given that the current passing in the NbTi superconducting wire is 100 A. A. The H--field in a long solenoid is H = nl Units are Am<sup>-1</sup>

number of turns/m current in the windings

Hence  $B = \mu_0 n I$ 

Estimate from the photo: Length of coil 1.8 m; Average radius 0.4 m

Length of wire used in one MRI;  $10^{6}/20,000 = 50 \text{ km}$  ! One turn is  $2\pi r = 2.5 \text{ m}$ . No of turns 50,000/2.5 = 20,000n = 20,000/1.8 = 11,111 turns/m. H = nI = 1.1 MA/m $B = \mu_0 H = 4\pi \ 10^{-7} \text{ x} \ 1.1 \ 10^{6}$ 

B = 1.4 T.

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SQUID sensors for magnetometers, nondestructive testing, geophysical prospection... incluing high- $T_{sc}$  SQUIDS and microsquids





High-T<sub>sc</sub> microwave resonant cavities, bolometers ...

Electrical interconnects:



High  $T_{sc}$  leads are often used with low- $T_{sc}$  superconducting coils

#### Electrical transmission lines.







500 MW high  $T_{sc}$  YBCO power transmission lines (up to 800 m long)

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#### An exciting prospect; Compact fusion reactors in 10 years!

<u>https://www.theguardian.com/environment/2018/mar/09/nucl</u> <u>ear-fusion-on-brink-of-being-realised-say-mit-</u> <u>scientists?CMP=share btn link</u>

Current nuclear fusion experimental facilities (JET, ITER) are tokamaks that inertially confine a plasma at enormously high temperature ( $\sim T_{sun}$ ) in a toroidal magnetic field. 3.45 T at JET, 11.8 T at ITER for the toroidal field. Bigger fields will be possible with high-Tc superconductors. Opening the possibility of much smaller  $\sim 1GW$ ) - one in every city.



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#### Another really exciting prospect; Quantum computing with Josephson junction Q-bits

.A JJ behaves as an 'artificial atom' at low temperatures – a simple 2-level system with a ground state  $|0\rangle$  and and an excited state  $|1\rangle$  which can be modelled as if it is was a pseudospin S =  $\frac{1}{2}$ , oriented in a direction  $\theta$ ,  $\phi$  relative to the quantization axis z.

*Tn* general the state if the system is a quantum superposition

 $\Psi = \cos\theta |0\rangle + \exp^{i\phi} \sin\theta |1\rangle$ 

This state, with a long coherence time, is the requirement for a Q-bit

There are many possible realizations of pseudospin  $S = \frac{1}{2}$  systems, but the *Jj* is currently the most promising.