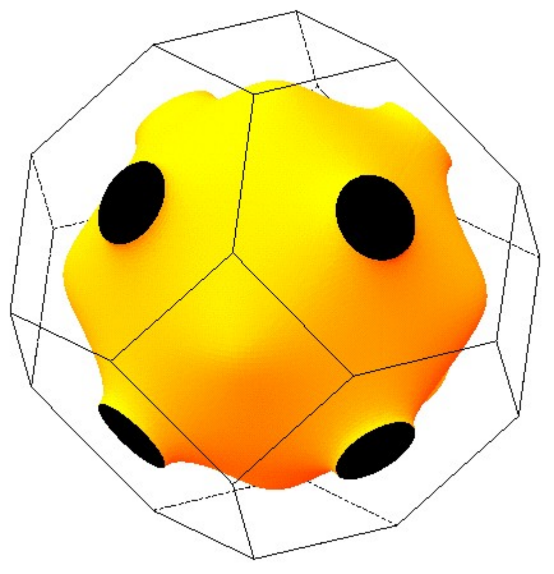
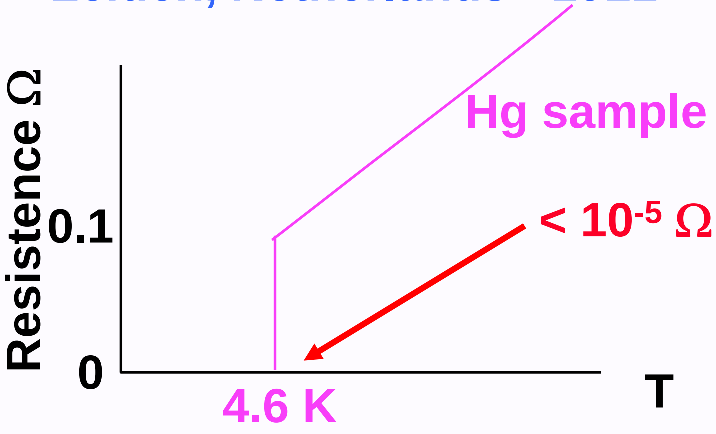
Lecture 22:
Metals (Review and Kittel Ch. 9)
and
Superconductivity I (Kittel Ch. 10)



Leiden, Netherlands - 1911



Outline

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

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

- (Kittel Ch 10)

What is special about electrons?

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

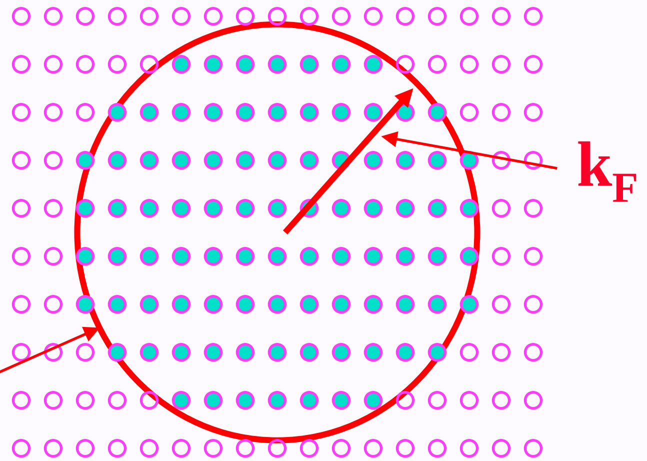
Electron Gas

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

  $N_{elec}/V = (1/3\pi^2)\, k_F^3$

  The Fermi energy is

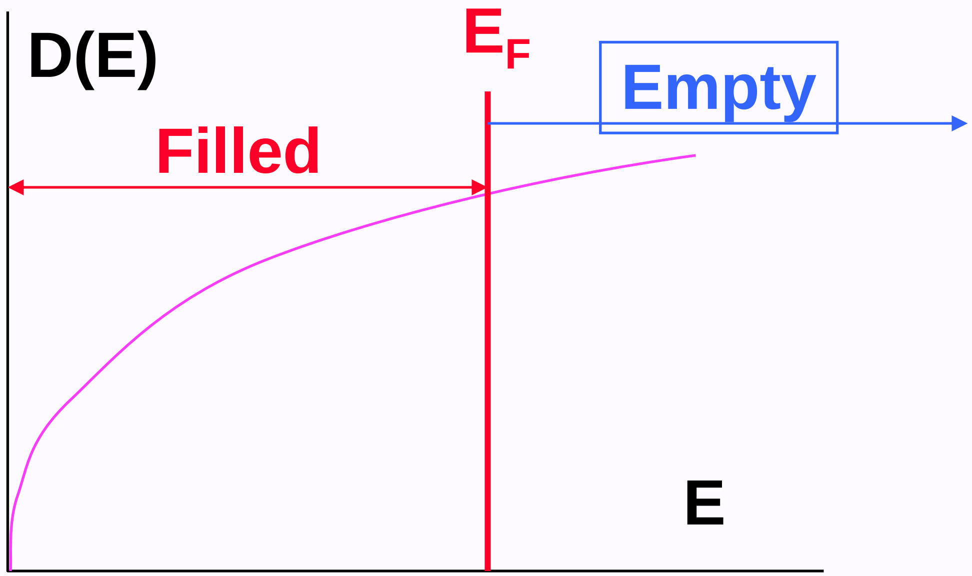
  $E_F = (\hbar^2/2m)\, k_F^2$



Fermi Surface

Recall - Electron Gas
Density of States 3 dimensions

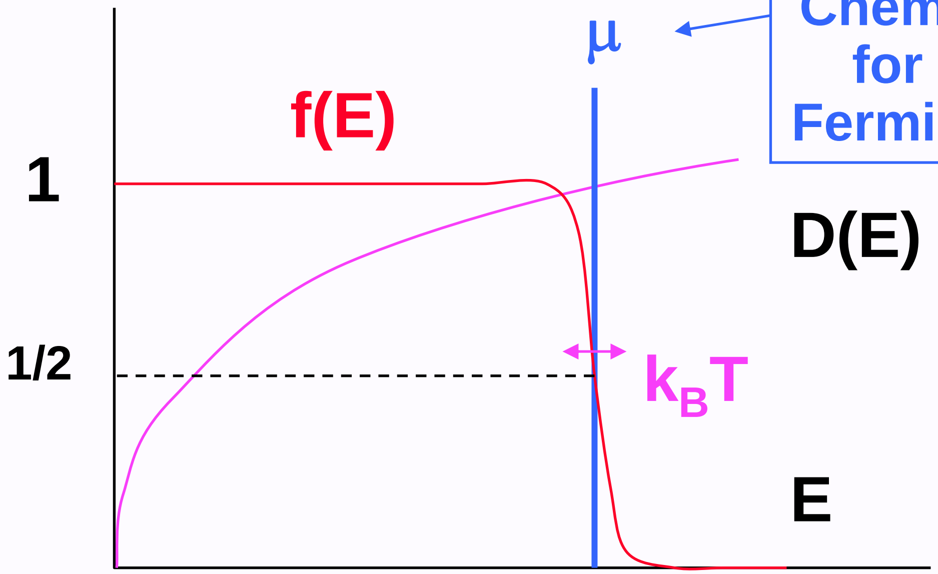
- D(E) = $(1/2\pi^2) E^{1/2} (2m / \hbar^2)^{3/2} \sim E^{1/2}$



Fermi Distribution

- At finite temperature, electrons are not all in the lowest energy states
- Applying the fundamental law of statistics to this case (occcupation of any state and spin only can be 0 or 1) leads to the Fermi Distribution (Kittel appendix)

$$f(E) = 1/[\exp((E-\mu)/k_BT) + 1]$$



Chemical potential for electrons = Fermi energy at T=0

Typical values for electrons

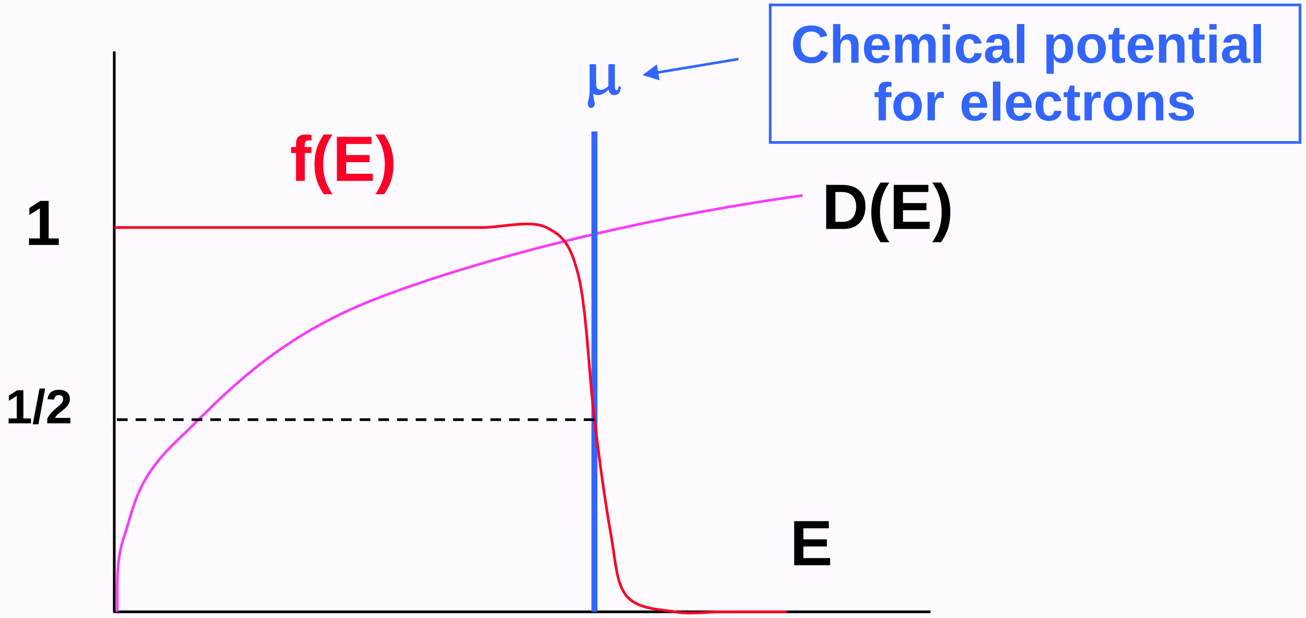
- Here we count only valence electrons (see Kittel table)

Element	N_{elec}/atom	E_F	$T_F = E_F/k_B$
Li	1	4.7 eV	5.5 x10^4 K
Na	1	3.23eV	3.75 x10^4 K
Al	3	11.6 eV	13.5 x10^4 K

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

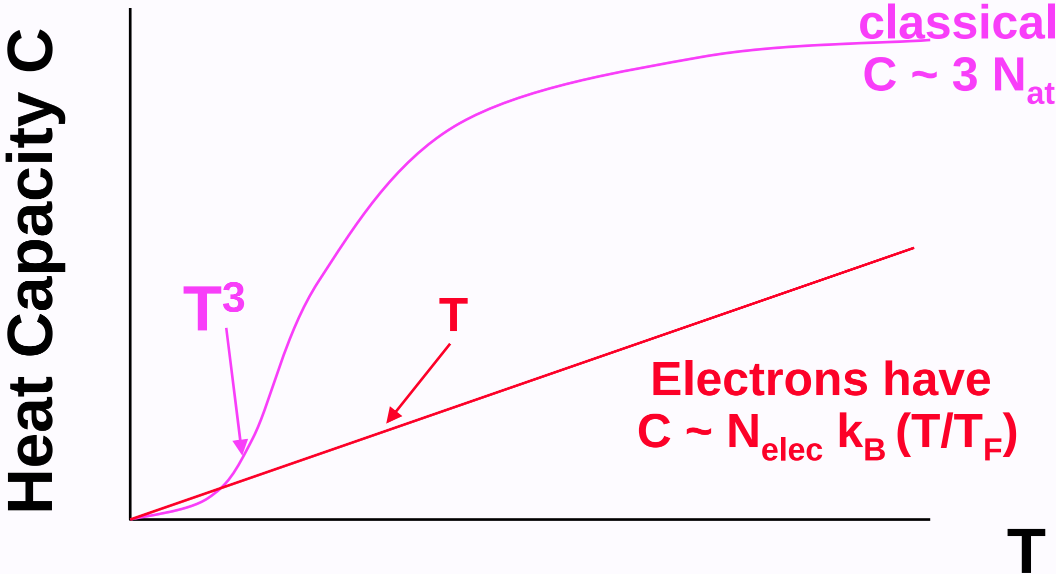
Heat Capacity for Electrons

- Just as for phonons the definition of heat capacity is $C = dU/dT$ where U = total internal energy
- For $T << T_F = E_F / k_B$ it is easy to see that roughly $U \sim U0 + N_{elec} (T/ T_F) k_B T$ so that $C = dU/dT \sim N_{elec} k_B (T/ T_F)$



Heat capacity

- Comparison of electrons in a metal with phonons



Phonons approach classical limit
$C \sim 3\, N_{atom}\, k_B$

Electrons have
$C \sim N_{elec}\, k_B\, (T/T_F)$

Electrons dominate at low T in a metal

Phonons dominate at high T because of reduction factor (T/T_F)

What about a real metal?

- In a crystal the energies are not $E = (h^2/2m) k^2$
- Instead the energy is $E_n(\mathbf{k})$, where **k** is the wavevector in the Brillouin Zone, and n = 1,2,3,… labels the bands
- The energy $E_n(\mathbf{k})$ is different for **k** in different directions
- **The concepts still apply**
  The states are filled for $E_n(\mathbf{k}) < E_{Fermi}$
  The states are empty for $E_n(\mathbf{k}) > E_{Fermi}$
- **This defines the Fermi surface: the surface in k-space where** $E_n(\mathbf{k}) < E_{Fermi}$ **– the boundary between filled and empty states**

The Fermi surface in copper

Cu has the fcc crystal structure

The figure shows the Brillouin Zone and the Fermi Surface

Note that the Fermi surface is nearly spherical!

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

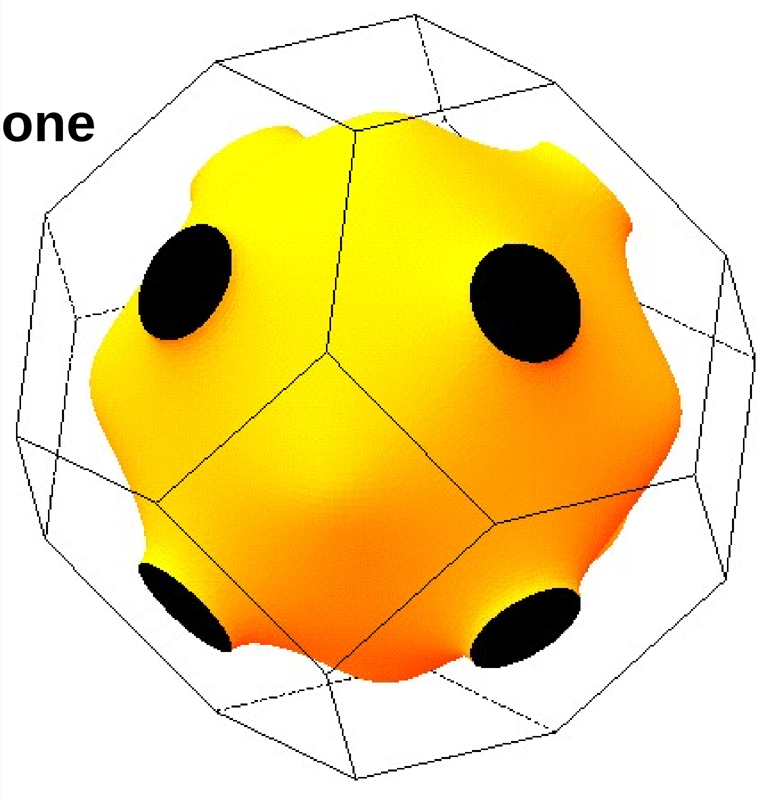


Figure from Nara Women's University
www.phys.nara-wu.ac.jp

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

Heat capacity

- Experimental results for metals

$$C/T = \gamma + A\,T^2 + \ldots.$$

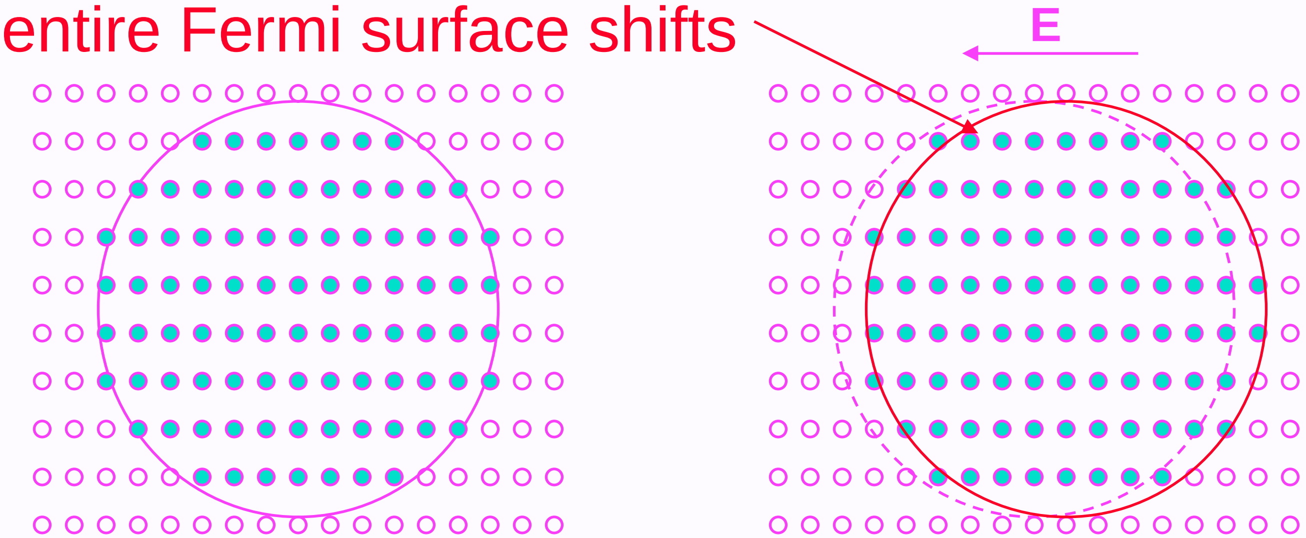
- It is most informative to find the ratio $\gamma / \gamma(\text{free})$ where $\gamma(\text{free}) = (\pi^2/2)\,(N_{elec}/E_F)\,k_B^2$ is the free electron gas result. Equivalently since $E_F \propto 1/m$, we can consider the ratio $\gamma / \gamma(\text{free}) = m(\text{free})/m_{th}^*$, where m_{th}^*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

Metal	$m_{th}^*/ m(\text{free})$
Li	2.18
Na	1.26
K	1.25
Al	1.48
Cu	1.38

- m_{th}^* close to m(free) is the “good”, “simple metals” !

Electrical Conductivity & Ohm’s Law

- Consider electrons in an external field E. They experience a force F = -eE
- Now F = dp/dt = $\hbar$ dk/dt , since p = $\hbar$ k
- Thus in the presence of an electric field all the electrons accelerate and the k points shift, i.e., the entire Fermi surface shifts



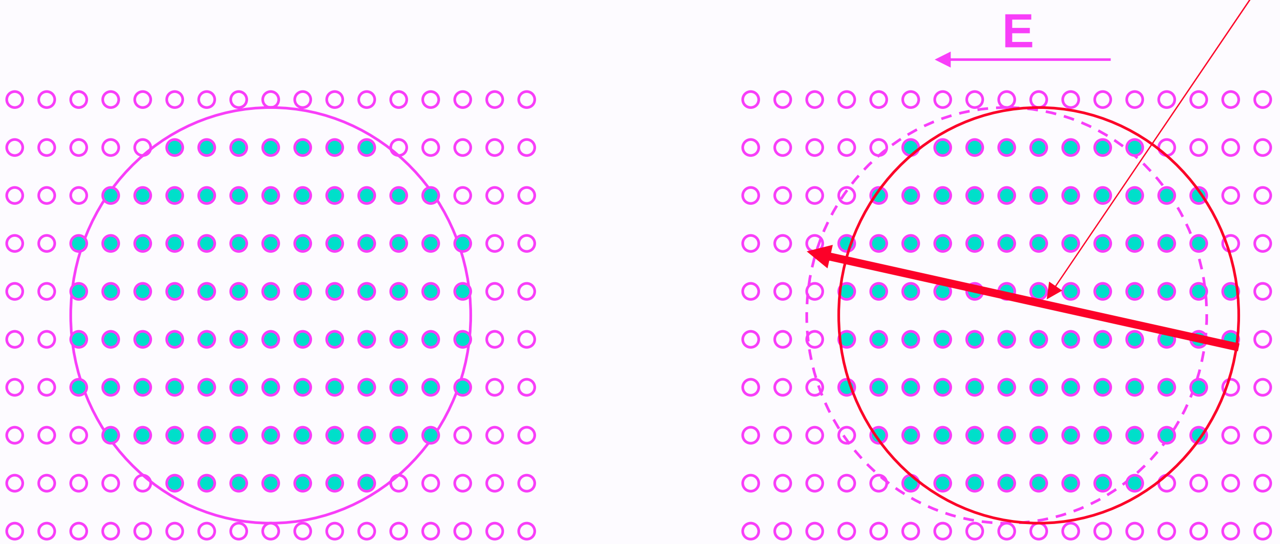
Equilibrium - no field

With applied field

The same ideas apply to real metals with non-spherical Fermi surfaces

Electrical Conductivity & Ohm’s Law

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



Equilibrium - no field

With applied field

Electrical Conductivity and Resistivity

- The conductivity σ is defined by $j = \sigma E$,

  where j = current density
- How to find σ?
- From before $F = dp/dt = m\, dv/dt = \hbar\, dk/dt$
- Equilibrium is established when the rate that k increases due to E equals the rate of decrease due to scattering, then $dk/dt = 0$
- If we define a scattering time τ and scattering rate $1/\tau$

  $$\hbar\,(dk/dt + k/\tau) = F = q E \quad (q = \text{charge})$$
- Now $j = n q v$ (where n = density) so that

  $$j = n q (\hbar k/m) = (n q^2/m)\, \tau E$$

  $$\Rightarrow \boxed{\sigma = (n q^2/m)\, \tau}$$
- Resistance: $\rho = 1/\sigma \propto m/(n q^2 \tau)$

Scattering mechanisms

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

  Proportional to concentration

- Lattice vibrations - atoms out of their ideal places

  Proportional to mean square displacement

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

Electrical Resistivity

- Resistivity ρ is due to scattering: Scattering rate inversely proportional to scattering time τ

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

- Matthiesson's rule - scattering rates add

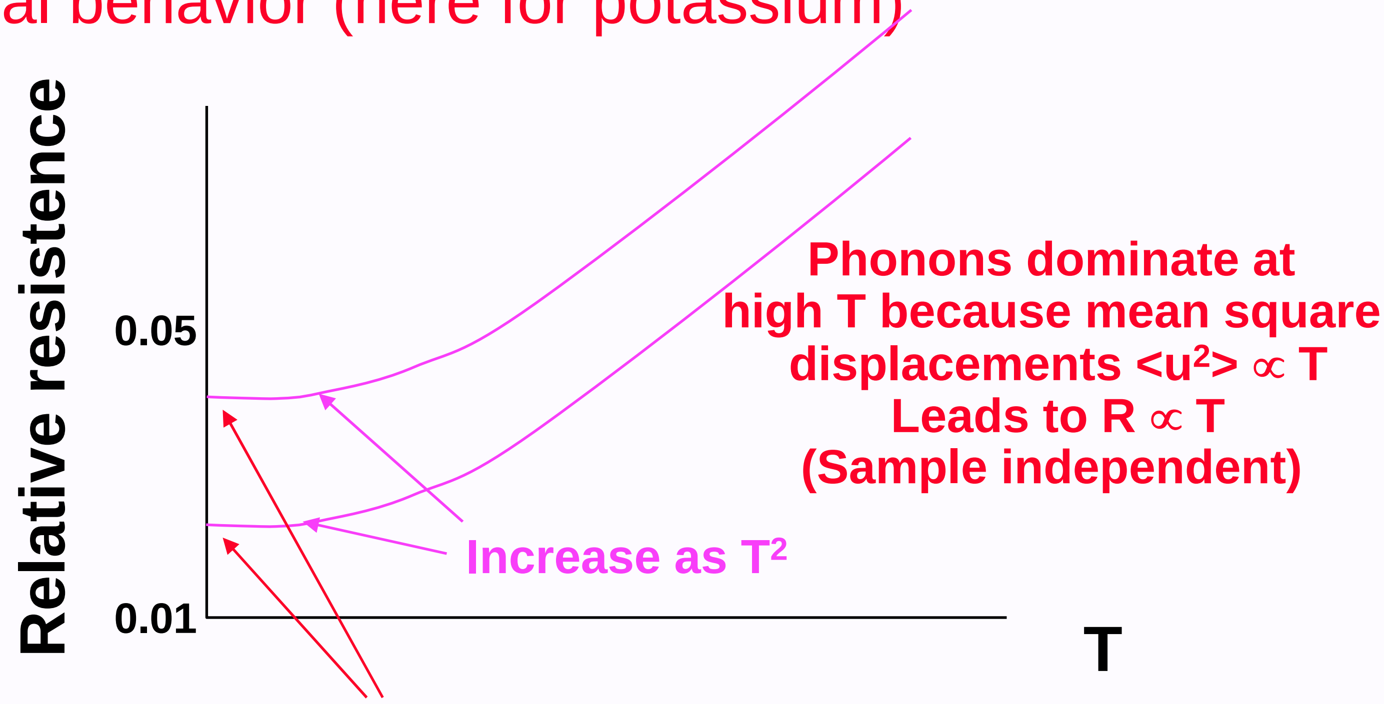
$$\rho = \rho_{\text{vibration}} + \rho_{\text{impurity}} \propto 1/\tau_{\text{vibration}} + 1/\tau_{\text{impurity}}$$

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

Temperature independent
- sample dependent

Electrical Resitivity

- Consider relative resistance R(T)/R(T=300K)
- Typical behavior (here for potassium)



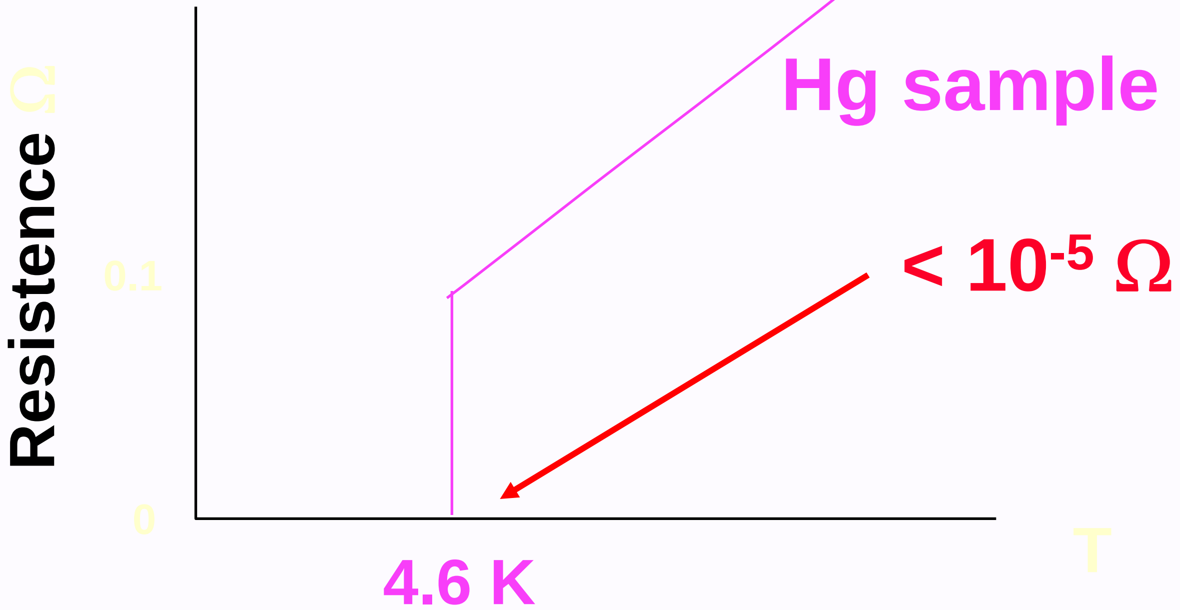
Phonons dominate at high T because mean square displacements $\langle u^2 \rangle \propto T$
Leads to $R \propto T$
(Sample independent)

Increase as T^2

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

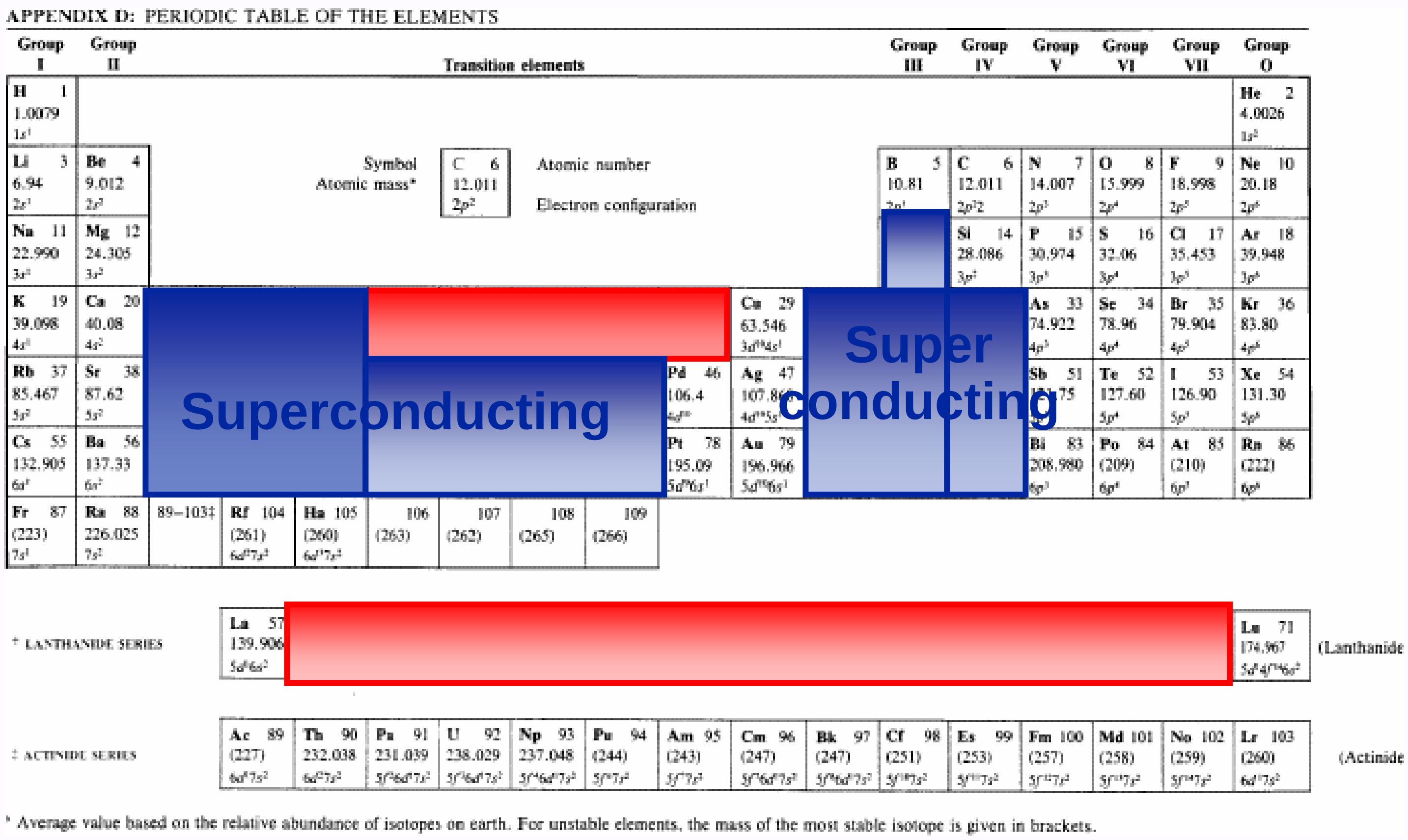
1911

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



Superconducting elements

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



APPENDIX D: PERIODIC TABLE OF THE ELEMENTS

Symbol / Atomic mass* — C 6 / 12.011 / $2p^2$ — Atomic number / Electron configuration

Group I	Group II	Transition elements										Group III	Group IV	Group V	Group VI	Group VII	Group 0
H 1 1.0079 $1s^1$																	He 2 4.0026 $1s^2$
Li 3 6.94 $2s^1$	Be 4 9.012 $2s^2$											B 5 10.81 $2p^1$	C 6 12.011 $2p^2$	N 7 14.007 $2p^3$	O 8 15.999 $2p^4$	F 9 18.998 $2p^5$	Ne 10 20.18 $2p^6$
Na 11 22.990 $3s^1$	Mg 12 24.305 $3s^2$												Si 14 28.086 $3p^2$	P 15 30.974 $3p^3$	S 16 32.06 $3p^4$	Cl 17 35.453 $3p^5$	Ar 18 39.948 $3p^6$
K 19 39.098 $4s^1$	Ca 20 40.08 $4s^2$									Cu 29 63.546 $3d^{10}4s^1$				As 33 74.922 $4p^3$	Se 34 78.96 $4p^4$	Br 35 79.904 $4p^5$	Kr 36 83.80 $4p^6$
Rb 37 85.467 $5s^1$	Sr 38 87.62 $5s^2$								Pd 46 106.4 $4d^{10}$	Ag 47 107.86 $4d^{10}5s^1$				Sb 51 121.75	Te 52 127.60 $5p^4$	I 53 126.90 $5p^5$	Xe 54 131.30 $5p^6$
Cs 55 132.905 $6s^1$	Ba 56 137.33 $6s^2$								Pt 78 195.09 $5d^96s^1$	Au 79 196.966 $5d^{10}6s^1$				Bi 83 208.980 $6p^3$	Po 84 (209) $6p^4$	At 85 (210) $6p^5$	Rn 86 (222) $6p^6$
Fr 87 (223) $7s^1$	Ra 88 226.025 $7s^2$	89–103‡	Rf 104 (261) $6d^27s^2$	Ha 105 (260) $6d^37s^2$	106 (263)	107 (262)	108 (265)	109 (266)									

† LANTHANIDE SERIES	La 57 139.906 $5d^16s^2$														Lu 71 174.967 $5d^14f^{14}6s^2$	(Lanthanide
‡ ACTINIDE SERIES	Ac 89 (227) $6d^17s^2$	Th 90 232.038 $6d^27s^2$	Pa 91 231.039 $5f^26d^17s^2$	U 92 238.029 $5f^36d^17s^2$	Np 93 237.048 $5f^46d^17s^2$	Pu 94 (244) $5f^67s^2$	Am 95 (243) $5f^77s^2$	Cm 96 (247) $5f^76d^17s^2$	Bk 97 (247) $5f^86d^17s^2$	Cf 98 (251) $5f^{10}7s^2$	Es 99 (253) $5f^{11}7s^2$	Fm 100 (257) $5f^{12}7s^2$	Md 101 (258) $5f^{13}7s^2$	No 102 (259) $5f^{14}7s^2$	Lr 103 (260) $6d^17s^2$	(Actinide

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

Superconducting transition

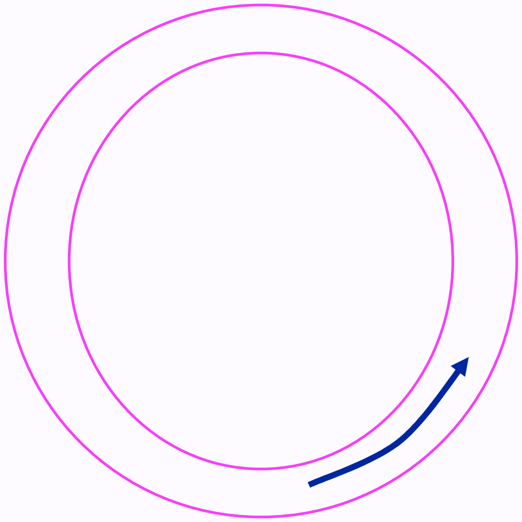
- **Transition is VERY narrow - $\Delta T < 10^{-4}$ K**
- **Reversible (unlike magnet)**
- **Transition Temperatures T_c**
- Al 1.2 K Hg 4.6 K Pb 7.2 K

Au < 0.001 K - not found to be superconducting!

Na_3C_{60}	40 K	(1990)
$YBa_2Cu_3O_7$	93 K	(1987)
Record today	140 K	

Is Resistance Really ZERO??

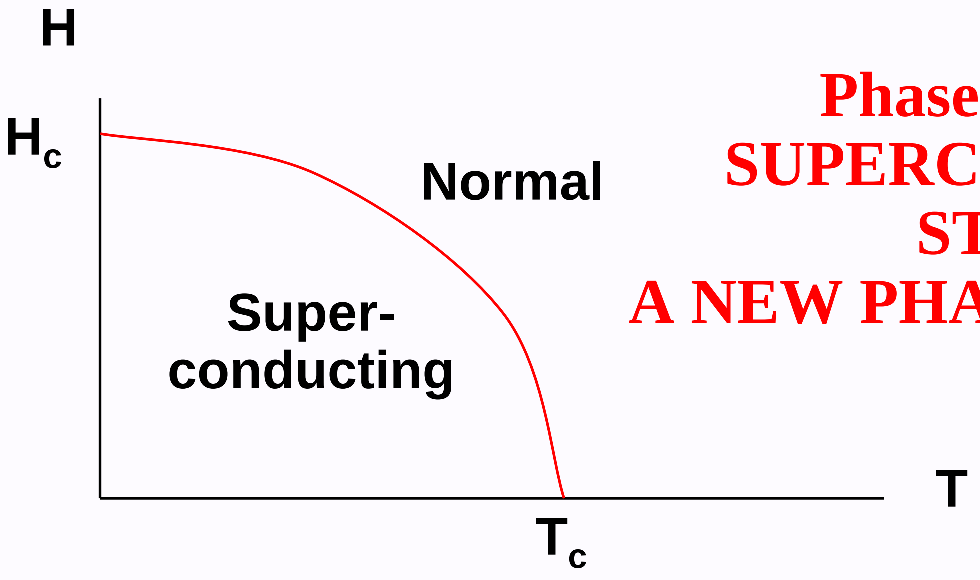
- Currents have been flowing in rings in laboratories with no detectable loss for > 50 years !
- Theory says the current can continue for T > age of universe



Effect of a Magnetic Field

- Magnetic fields tend to destroy superconductivity

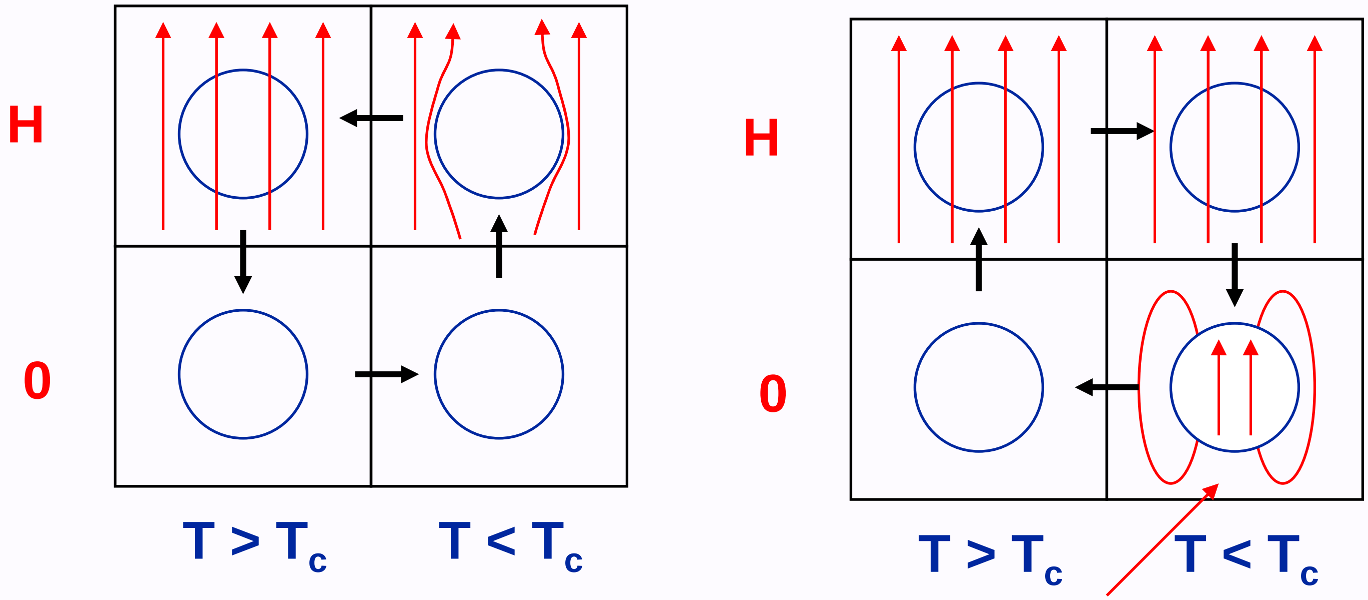
Note: H = external applied field
B = internal field
$B = H + \mu_0 M$
M = Magnetization



Phase Transition
SUPERCONDUCTING STATE IS
A NEW PHASE OF MATTER

Not just a perfect conductor!

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



Zero Field Cooled

Field Cooled

H

0

H

0

$T > T_c$ **$T < T_c$**

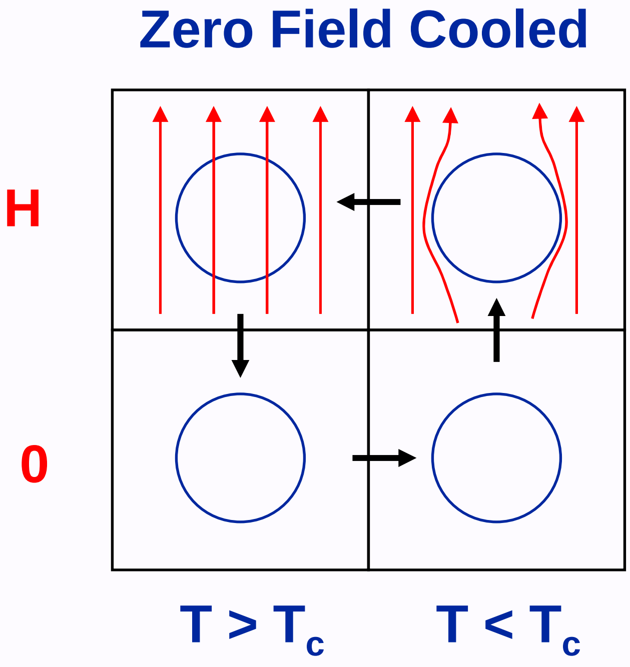
$T > T_c$ **$T < T_c$**

Trapped Field

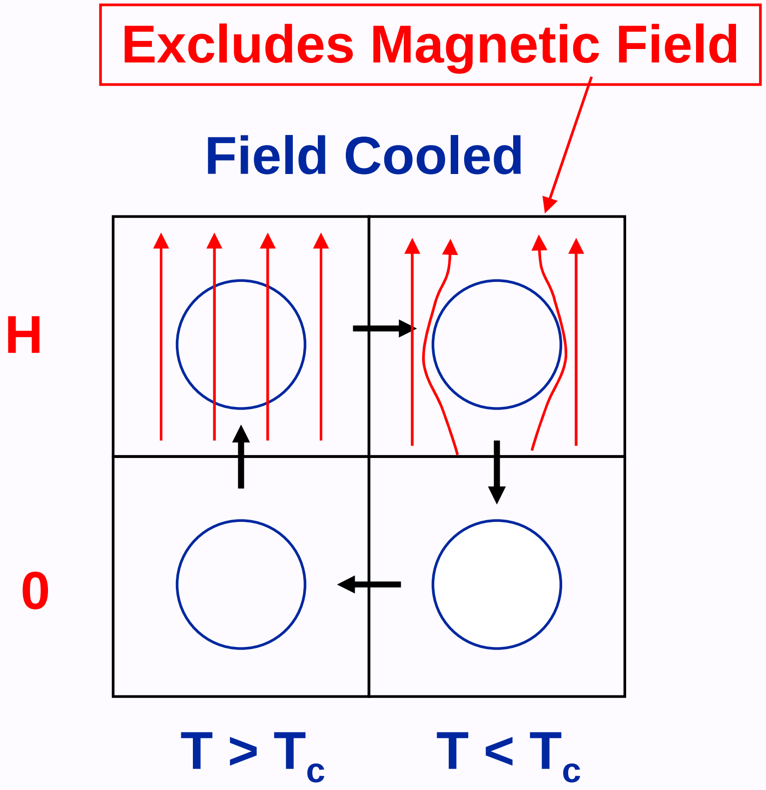
A superconductor is different!

Meisner Effect (1934)

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



Zero Field Cooled



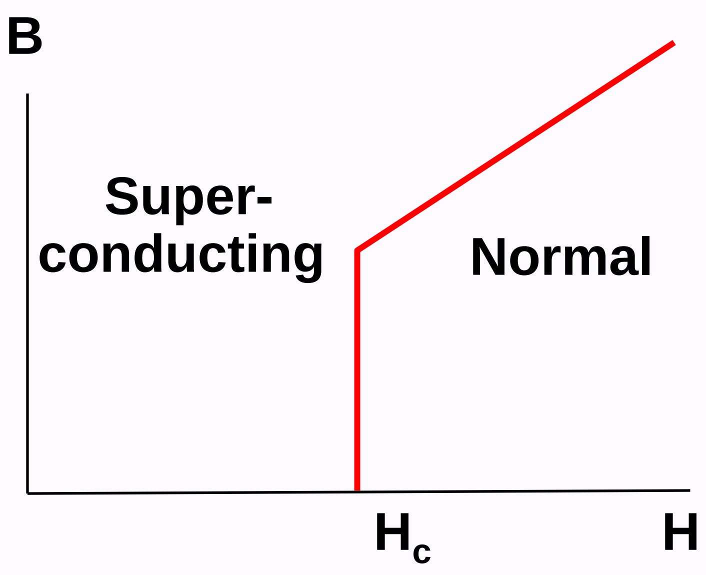
Excludes Magnetic Field

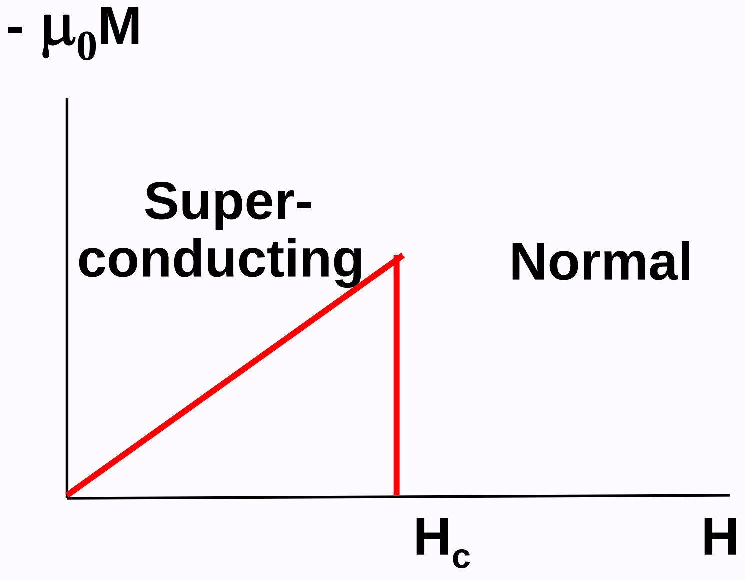
Field Cooled

The superconductor can exclude a magnetic field up to a “critical field” H_c

Meisner Effect

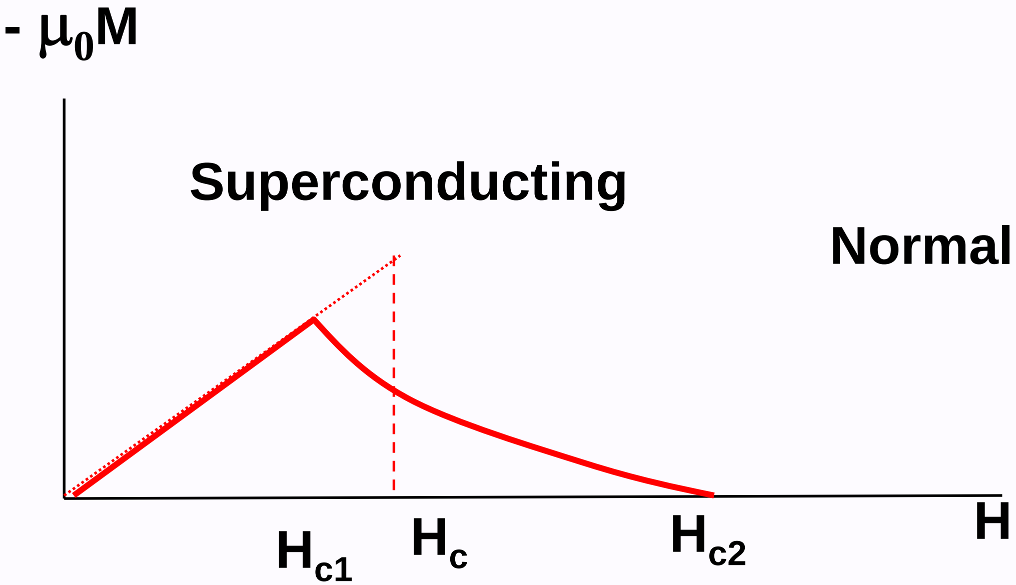
- Magnetic field B is excluded for fields less than a "critical field" H_c where H is the external applied field
- The total internal field is B = H + μ_0M
- For "type I" superconductors B=0 for T < T_c
- **Perfect Diamagnetism !**





Type I vs Type II

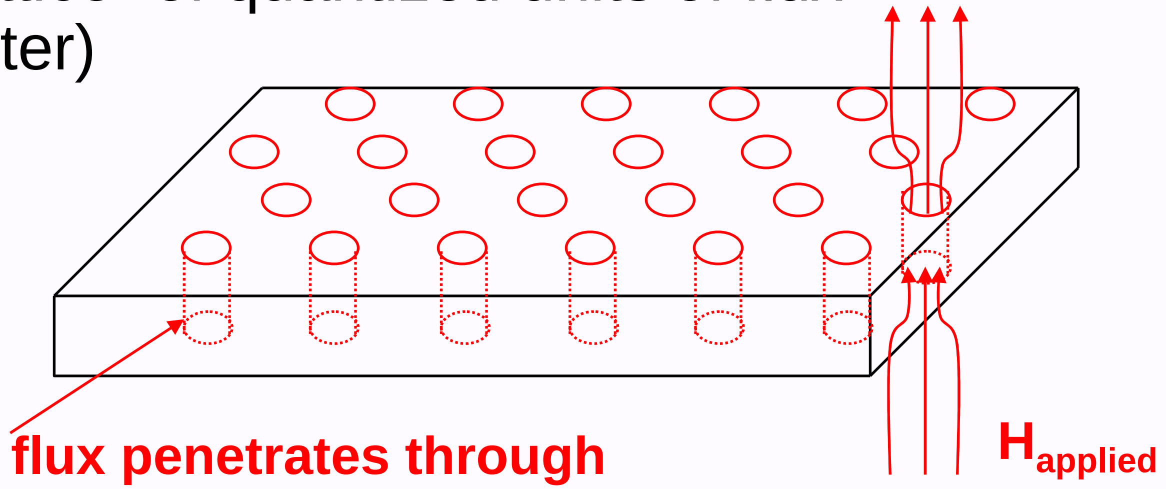
- Magnetic field B is excluded only up to a critical field H_{c1}
- For type II superconductors, at higher fields there is penetration of the field coexisting with superconductivity up to H = H_{c2}



Type II

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

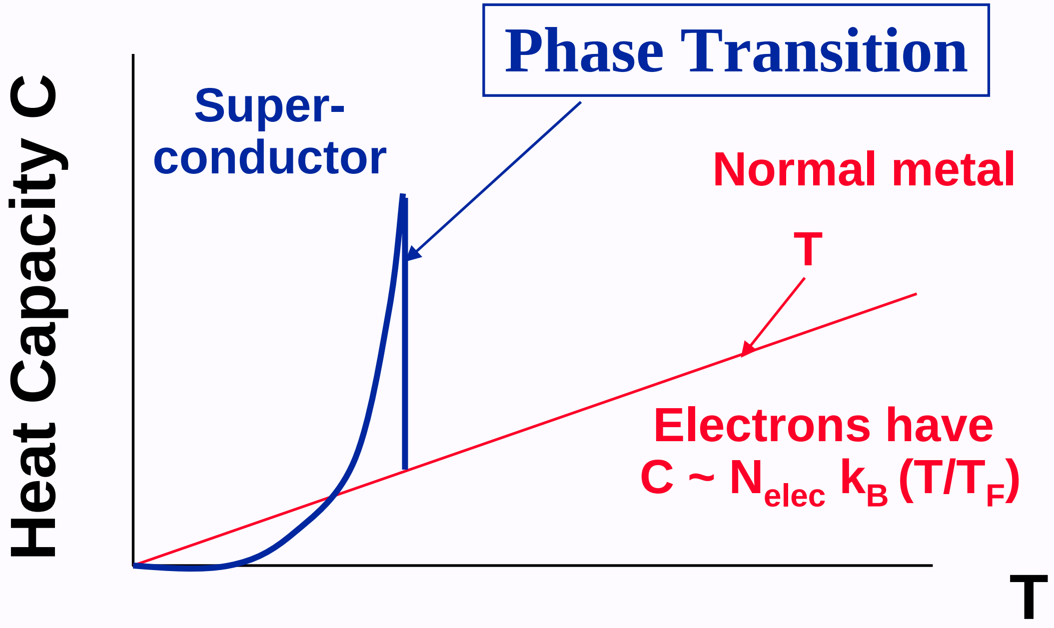
- "Flux Lattice" of quantized units of flux (more later)



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

Heat capacity (Specific Heat)

- Comparison of electrons in a superconductor and a normal metal



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

Isotope Effect (1950)

- For materials made from the same elements - but **different isotopes** - **T_c changes !**
- Experiment - $T_c \sim 1/ M^{1/2}$
- **MUST be connected to MOTION of the nuclei**

Summary

- Normal metal - Recall properties

  No special magnetic properties for non-magnetic metals, $\mu \approx 1$, $B \approx H$

  Resistance vs T

  Heat capacity vs T

- Superconductivity - Experimental Facts

  ZERO resistance at nonzero temperature

  NEW PHASE OF MATTER Meisner Effect (expulsion of magnetic fields) - shows a superconductor is not just a perfect conductor

  Heat Capacity - shows there is a phase transition - below T_c a gap, like an insulator!

  Isotope effect - something to do with MOTION of nuclei

Next time

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

- (Kittel parts of Ch 10)