

# Superconductive Materials

## Part 2

### Fundamental Properties of Superconductivity



**Leiden, the coldest place on earth (from 1908 to 1923)**

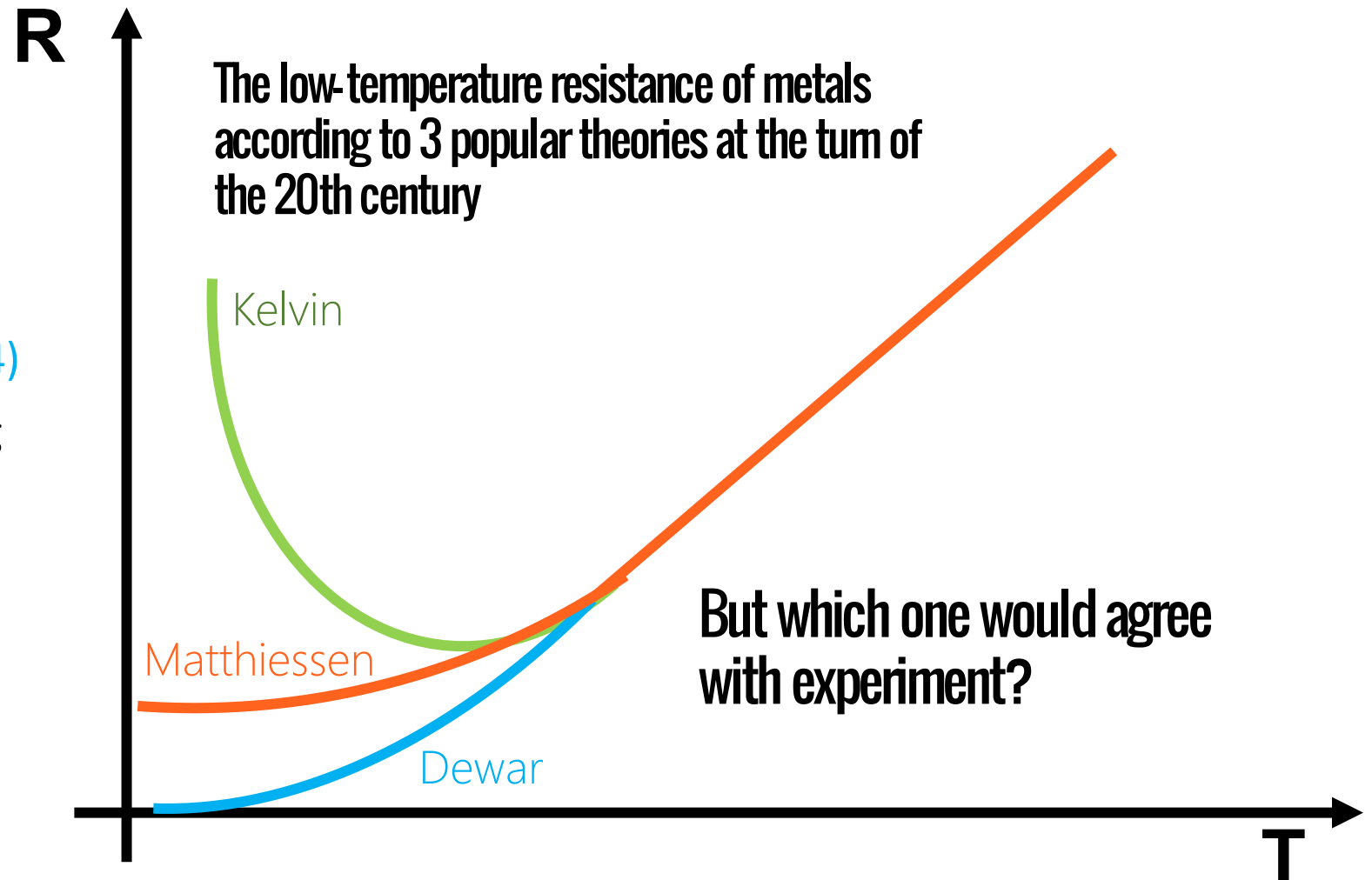


**Leiden, the coldest place on earth (from 1908 to 1923)**

# What would happen to the resistance of a metal as it was cooled to absolute zero?

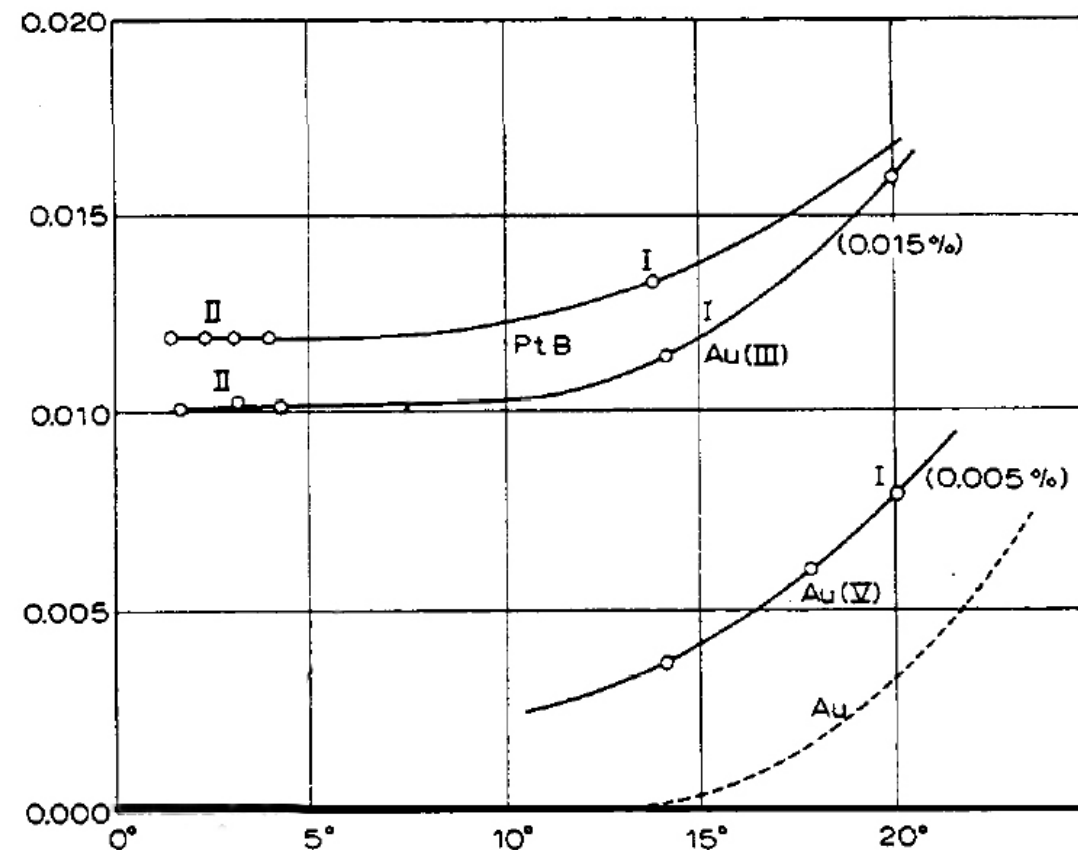
## THREE MAIN THEORIES IN 1908

1. The resistance could approach zero value with decreasing temperature ([James Dewar, 1904](#))
2. It could approach a finite limiting value ([Heinrich Friedrich Ludwig Matthiessen, 1864](#))
3. It could pass through a minimum and approach infinity at very low temperatures ([Lord Kelvin, 1902](#))



# Au and Pt measurements

- Initially, Kamerlingh-Onnes studied Pt and Au samples (easy to purify)
- **Presence of Residual Resistance**
- **Residual Resistance related to sample purity (RRR concept)**
- At the Third International Congress of Refrigeration in Chicago in 1913, he reported on these experiments and arguments. There he said: *“Allowing a correction for the additive resistance I came to the conclusion that probably the resistance of absolutely pure platinum would have vanished at the boiling point of helium.”*



The Kamerlingh Onnes plot from his Nobel lecture showing the low temperature measurements of the resistance in various metals (Au of different purity, Pt and Hg). The dashed curve shows the expectations for the pure gold. The original text describes the axis of the figure in the following way: “The resistance, in fractions of the resistance at zero Centigrade, is shown as the ordinate and the temperature as the abscissa.”

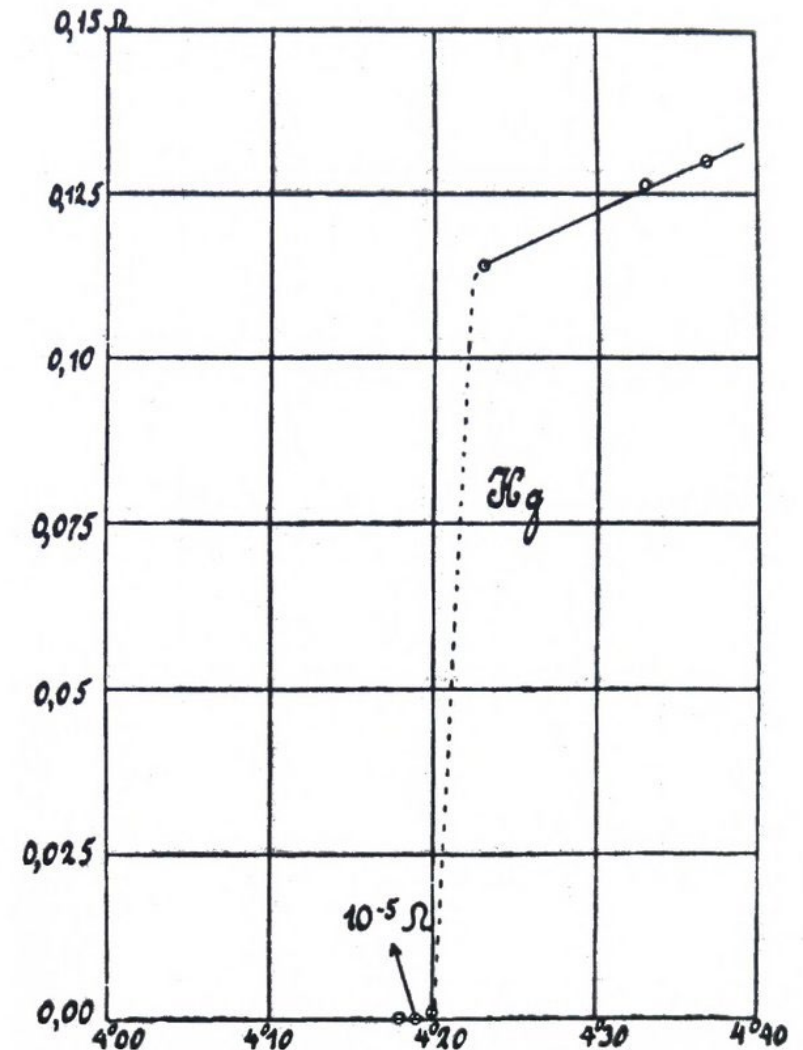
<https://arxiv.org/abs/1111.5318>

# Mercury

- Kamerlingh-Onnes decided to study **mercury**, the only metal at the time that he hoped could be extremely well **purified by means of multiple distillation**
- The initial experiments carried out by Kamerlingh-Onnes, together with his coworkers Gerrit Flim, **Gilles Holst**, and Gerrit Dorsman appeared to confirm the Onnes concepts (Dewar theory)

# Mercury and discovery of Superconductivity (1911)

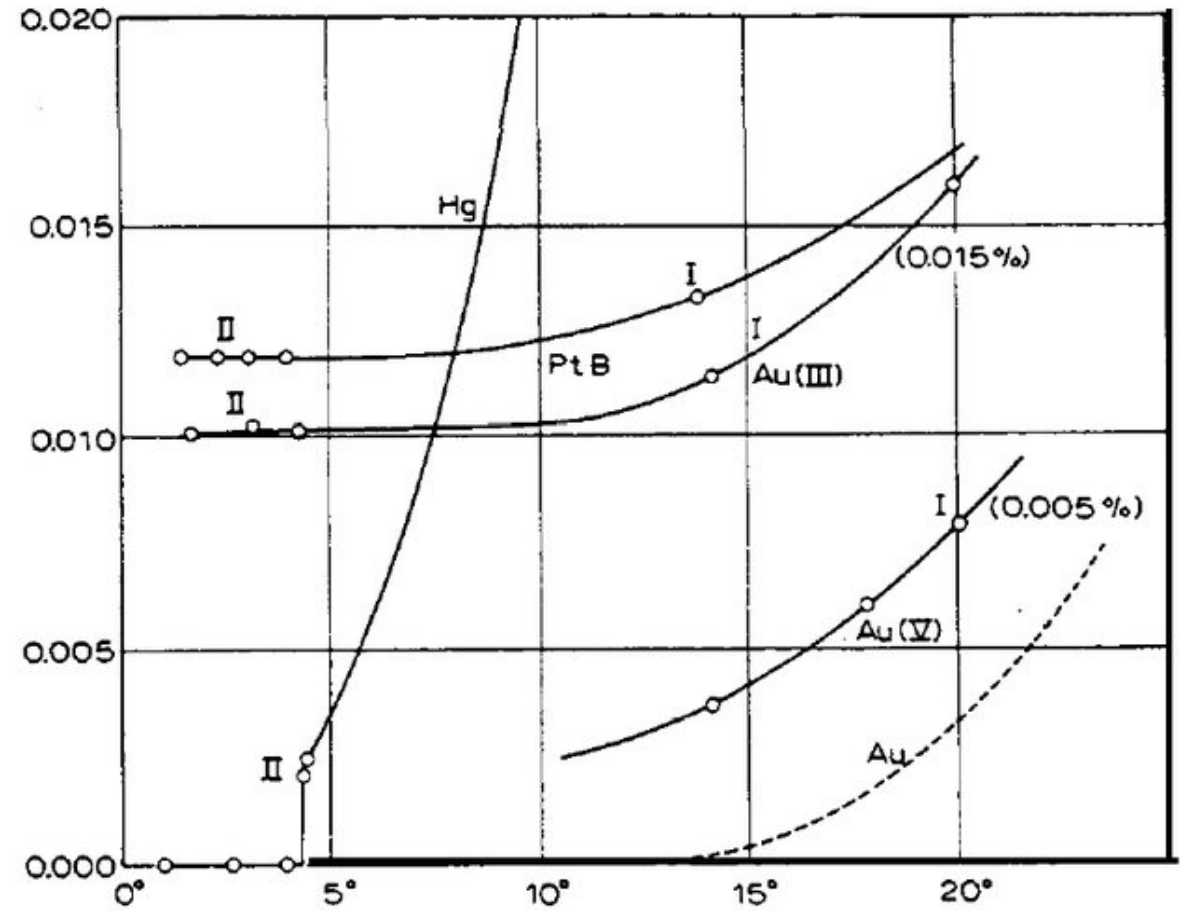
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- Further experiments using improved apparatus shows that the **behavior is completely different compared to Au and Pt**
- **A resistance jump to zero** appears slightly below 4,2 K



# The discovery of Superconductivity (1911)

*“At this point [slightly below 4.2 K] within some hundredths of a degree came a sudden fall not foreseen by the vibrator theory of resistance, that had framed, bringing the resistance at once less than a millionth of its original value at the melting point. . . . Mercury had passed into a new state, which on account of its extraordinary electrical properties may be called the superconductive state.”*

Kamerlingh-Onnes, 1911





# How to measure $R=0$ ?

If  $R=0$    $I$  flows permanently

If not:  $I(t) = I_0 e^{-\frac{R}{L}t}$

$I(t)$  Current at time  $t$

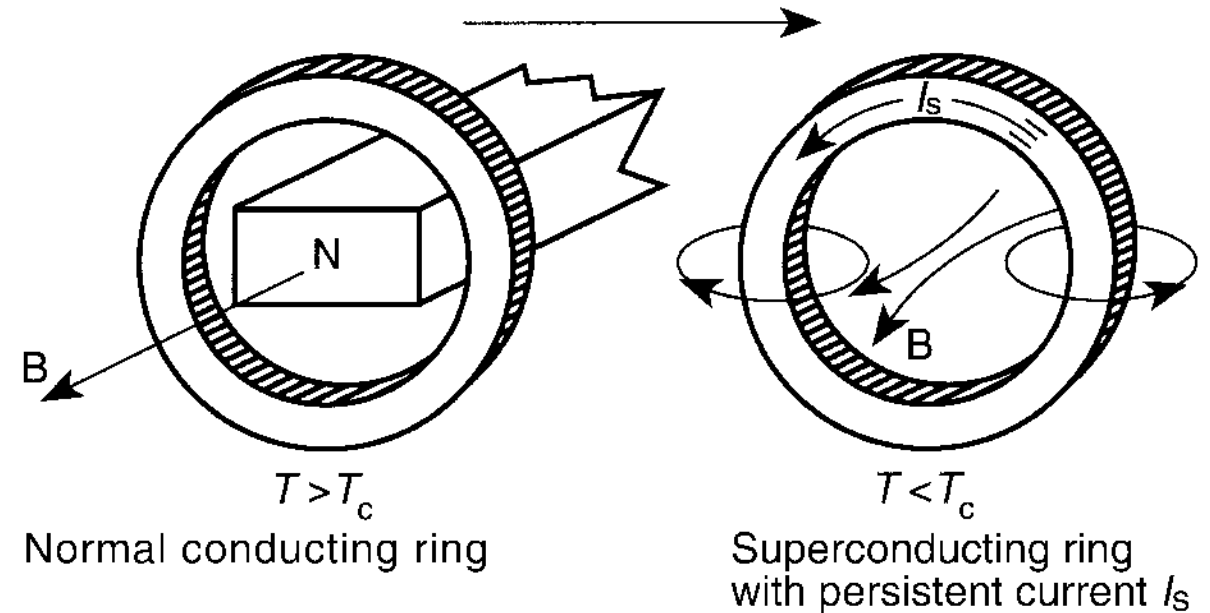
$I(0)$  Current at time zero

$L$  Self-induction coefficient

$R$  Resistance of the ring

## Induced current

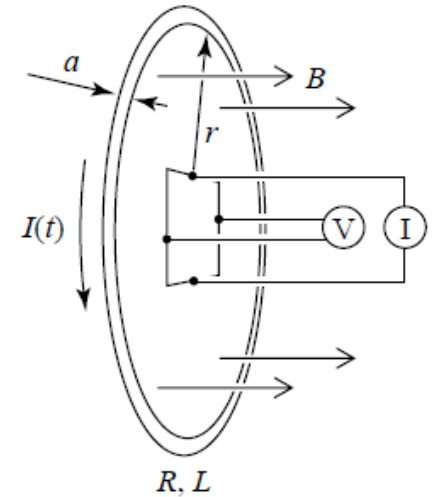
First cool down – than take magnet away



# How to measure R=0? Some numbers

$$I(t) = I_0 e^{-\frac{R}{L}t} \quad \rightarrow \quad \tau = \frac{L}{R}$$

$I(t)$  Current at time  $t$   
 $I(0)$  Current at time zero  
 $L$  Self-induction coefficient  
 $R$  Resistance of the ring



Comes from the conservation of energy:

$$\frac{d}{dt} \left( \frac{1}{2} LI^2 \right) + RI^2 = 0$$

**After  $t_1=1$  year  $\rightarrow I_1=I_0$  Actually we can not say that**

We must to take in account the **measure sensibility**

$$\delta I > I_0 - I_{t1} = I_0(1 - e^{-\frac{R}{L}t1})$$

$$\delta B > B_0 - B_{t1} = B_0(1 - e^{-\frac{R}{L}t1})$$

$$\frac{\delta I}{I_0} = \frac{\delta B}{B_0} > 1 - e^{-\frac{R}{L}t1}$$

Sketch of a simple setup to monitor the possible decay of current  $I(t)$  via its associated magnetic induction  $B(t)$  in a closed loop of inductance  $L$  and resistance  $R$ . The wire has a diameter  $a$  and a loop radius  $r$ . The field  $B$  is normal to the loop area. The magnetic sensor is a Hall probe.

# How to measure $R=0$ ? Some numbers

$$\frac{\delta I}{I_0} = \frac{\delta B}{B_0} > 1 - e^{-\frac{R}{L}t_1}$$

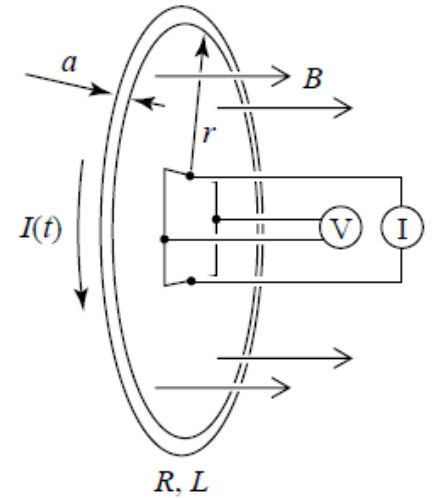
Solving for R

$$R < \frac{L}{t_1} \ln \left( 1 - \frac{\delta B}{B_0} \right) = \frac{L}{t_1} \ln \left( 1 - \frac{\delta I}{I_0} \right)$$

where all quantities on the right can be determined from the experiment

For  $r \gg a$   $\rightarrow$   $L \approx \mu_0 r \ln(r/a)$

$$R < \frac{\mu_0 r \ln(r/a)}{t_1} \ln \left( 1 - \frac{\delta B}{B_0} \right) \rightarrow R < 10^{-19} \Omega$$



$$r = 50 \text{ mm}$$

$$a = 1 \text{ mm}$$

$$t_1 = 1 \text{ year} \sim 3 \times 10^7$$

$$L = 1,3 \times 10^{-7} \text{ H}$$

$$\delta B/B_0 = 10^{-5}$$

# How to measure R=0? Some numbers

$$R < \frac{\mu_0 r \ln(r/a)}{t_1} \ln\left(1 - \frac{\delta B}{B_0}\right) \rightarrow R < 10^{-19} \Omega$$

$$\rho < 10^{-19} \Omega \left(\frac{A}{\ell}\right) \approx 2.5 \times 10^{-25} \Omega m \leftarrow R = \rho \frac{\ell}{A}$$

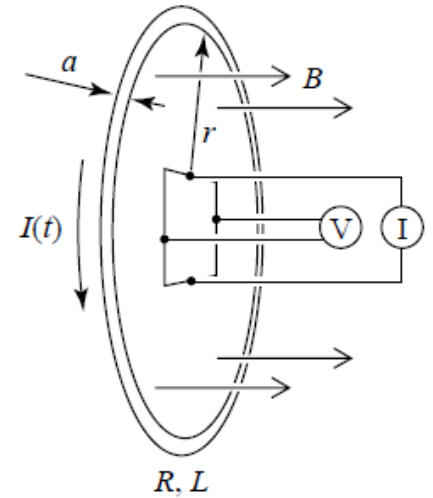
$$\rho_{Al}^{4,2K} = 10^{-12} \Omega m \quad \text{13 order of magnitude less than Aluminum @4.2 K!}$$

$$\rho_{Cu}^{273K} = 10^{-8} \Omega m \quad \text{17 order of magnitude less than Copper @300 K!}$$

$$\tau = \frac{L}{R} > 5.8 \times 10^{13} s \rightarrow \text{More than 2 milion of years!}$$

But remember that the limit is the measure sensibility

With more sensible measure (SQUID),  $\tau$  approach the lifetime of Universe



$$r = 50 \text{ mm}$$

$$a = 1 \text{ mm}$$

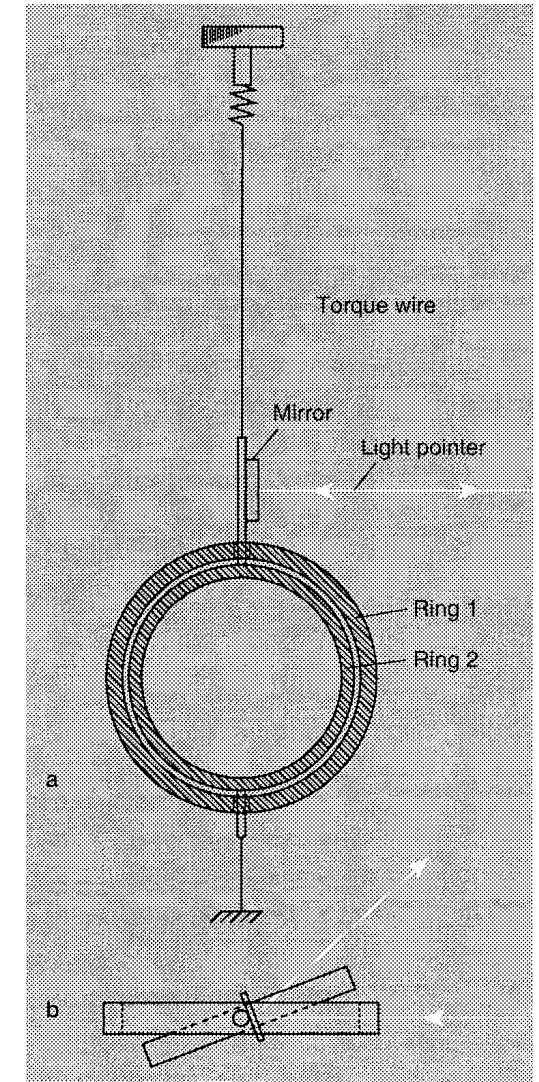
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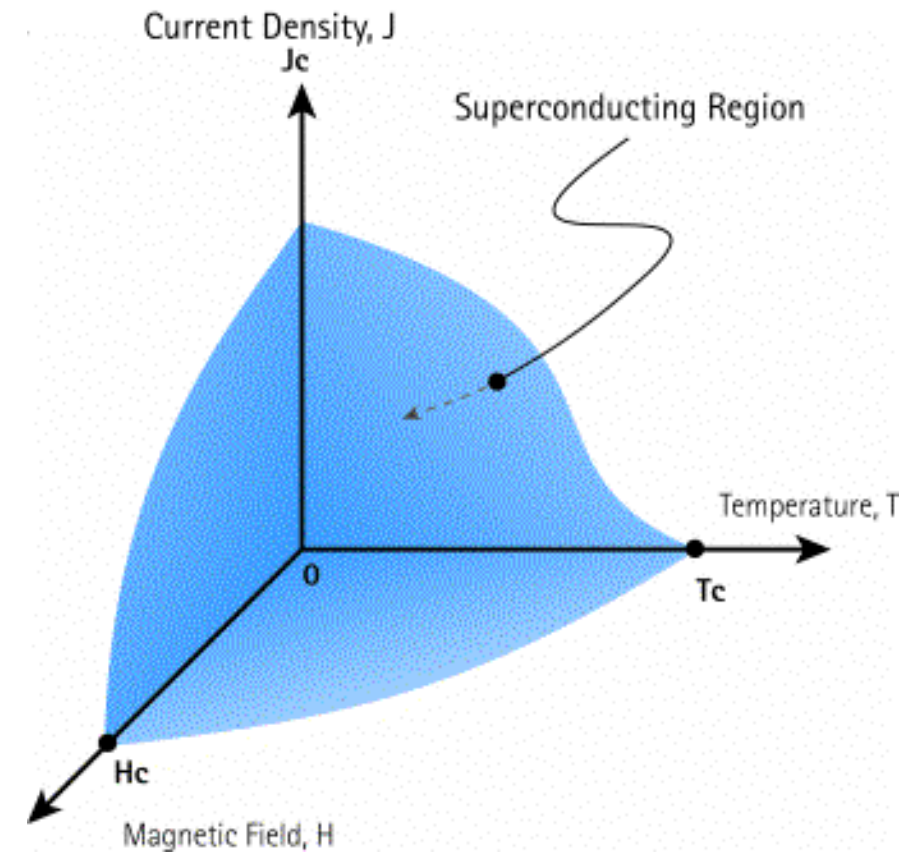
# How to measure $R=0$ ? Further improvements

- Kamerlingh-Onnes enhanced the measure sensibility with a new set-up
- An equilibrium position is established in which the angular moments of the permanent current and of the torsion thread balance each other. This equilibrium position can be observed very sensitively using a light beam.
- During all such experiments, no change of the permanent current has ever been observed
- Today we know that a **SC** has a specific electric **resistance** about **17 orders of magnitude smaller** than the specific resistance of **Cu!!!**
- **The difference in resistance of a metal between the superconducting and normal states is at least as large as that between copper and a standard electrical insulator**



# New superconductors and new critical parameters appears

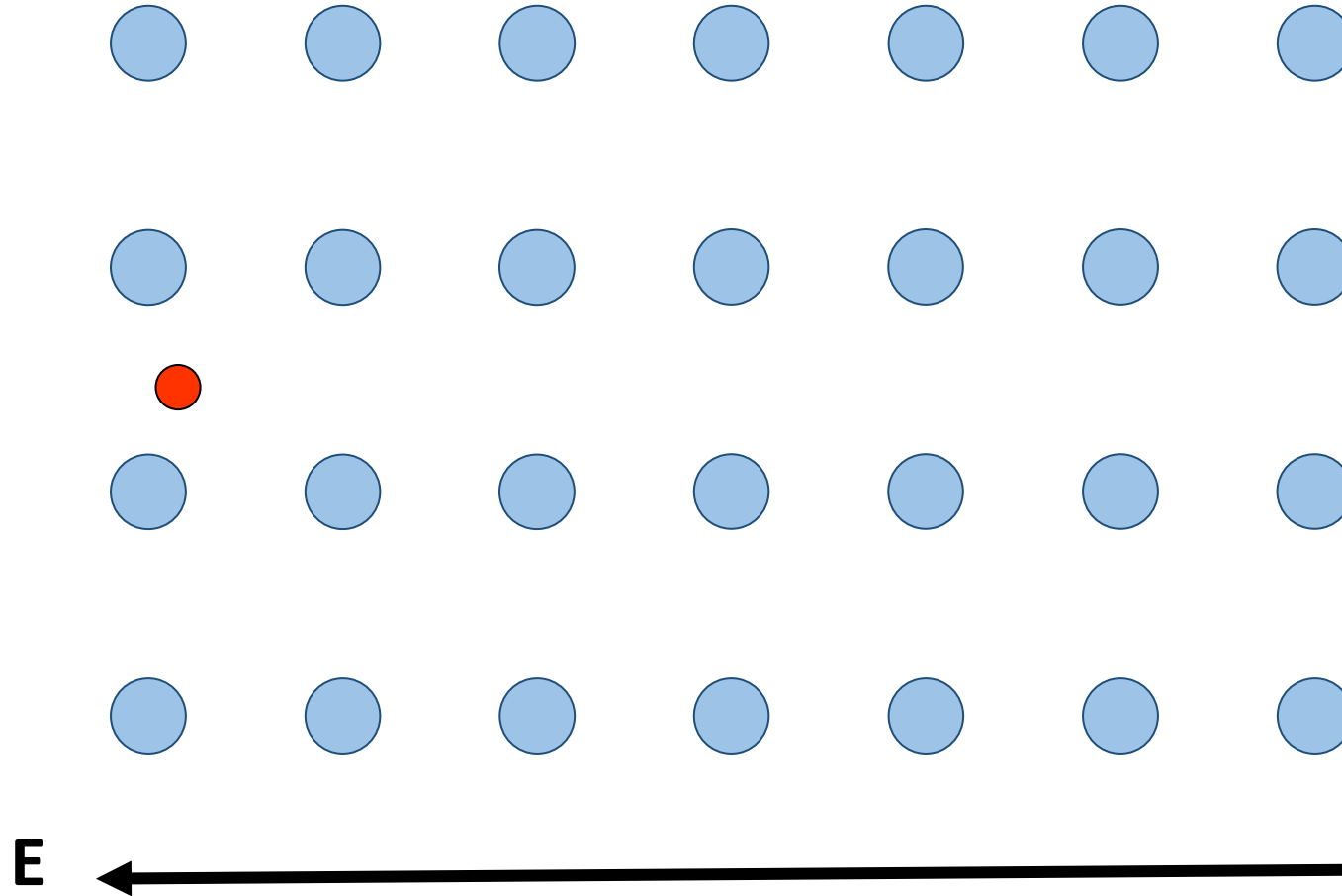
- Onnes' team discovered that **small impurities to mercury had no effect on  $T_c$** . This implied that the effect was intrinsic to mercury.
- In 1912 Kamerlingh Onnes discover **superconductivity in Tin (3.7 K) and Lead (7.2 K)**
- Leiden group works to built high magnetic field superconducting coils (up to 10 T)
- However, experiments showed that **SC could be destroyed** if the material was subjected **to a sufficiently large magnetic field ( $B_c$ )**
- The **critical magnetic field** which would destroy superconductivity (in Sn and Pb) **was rather small**
- Francis Silsbee had showed in 1916 that **the critical current and critical magnetic field were two sides of the same coin**
- None of the discovered SC is a particularly good conductors of electricity (**Au, Ag, Cu are not SC**). This in itself was an important piece of the puzzle, but no-one could understood its significance at the time
- Onnes died in 1926, but work on superconductivity continued at the Leiden laboratory
- In 1931, W. J. de Haas and W. H. Keesom, **discovered SC in an alloy**



A close-up, slightly blurred photograph of a soccer game. In the center, a white soccer ball sits on a green artificial turf field. Several players are visible, some in red jerseys and others in blue. The players are in various dynamic poses, suggesting active play. The background is out of focus, showing more of the field and possibly spectators or stadium lights.

**And what about the Drude Model?**

# Electrons in Electrical Field





# Ohm Law (for metal conductors)

- $V = RI$

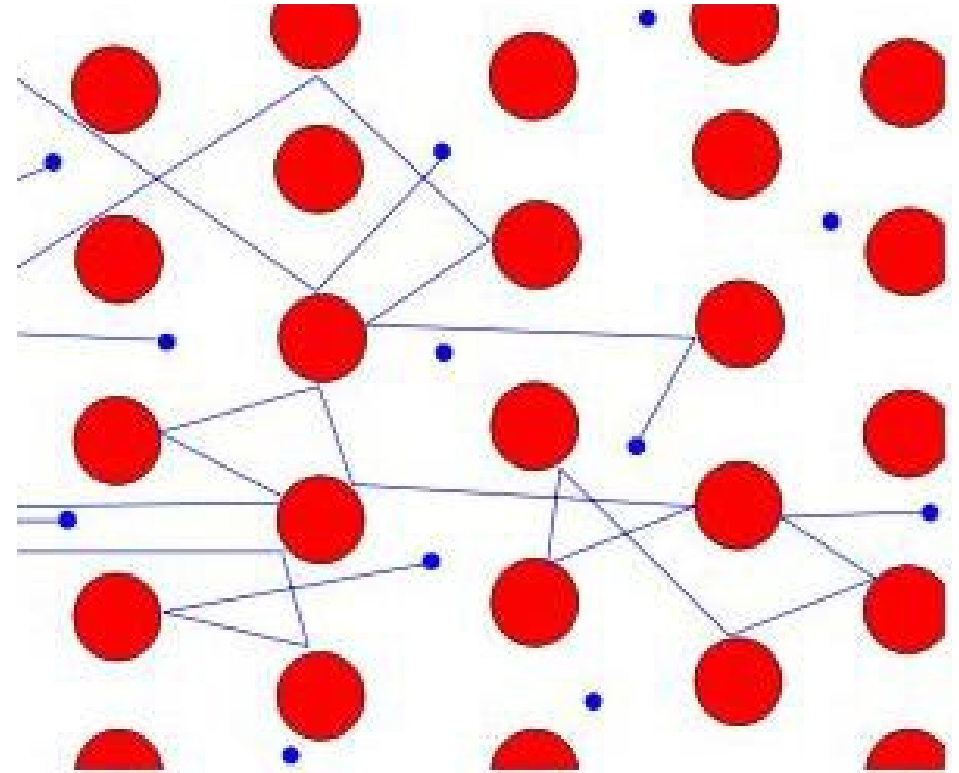
- $R = \frac{\ell}{A} \rho$

- $\rho?$

- $\mathbf{p} = e\mathbf{E}\tau$

- $m\mathbf{v}_d = e\mathbf{E}\tau$

- $\mathbf{j} = -n_e e \mathbf{v}_d = \frac{ne^2\tau}{m} \mathbf{E} \Rightarrow \sigma = \frac{1}{\rho}$



Drude Model

# Electrical Resistance and Resistivity

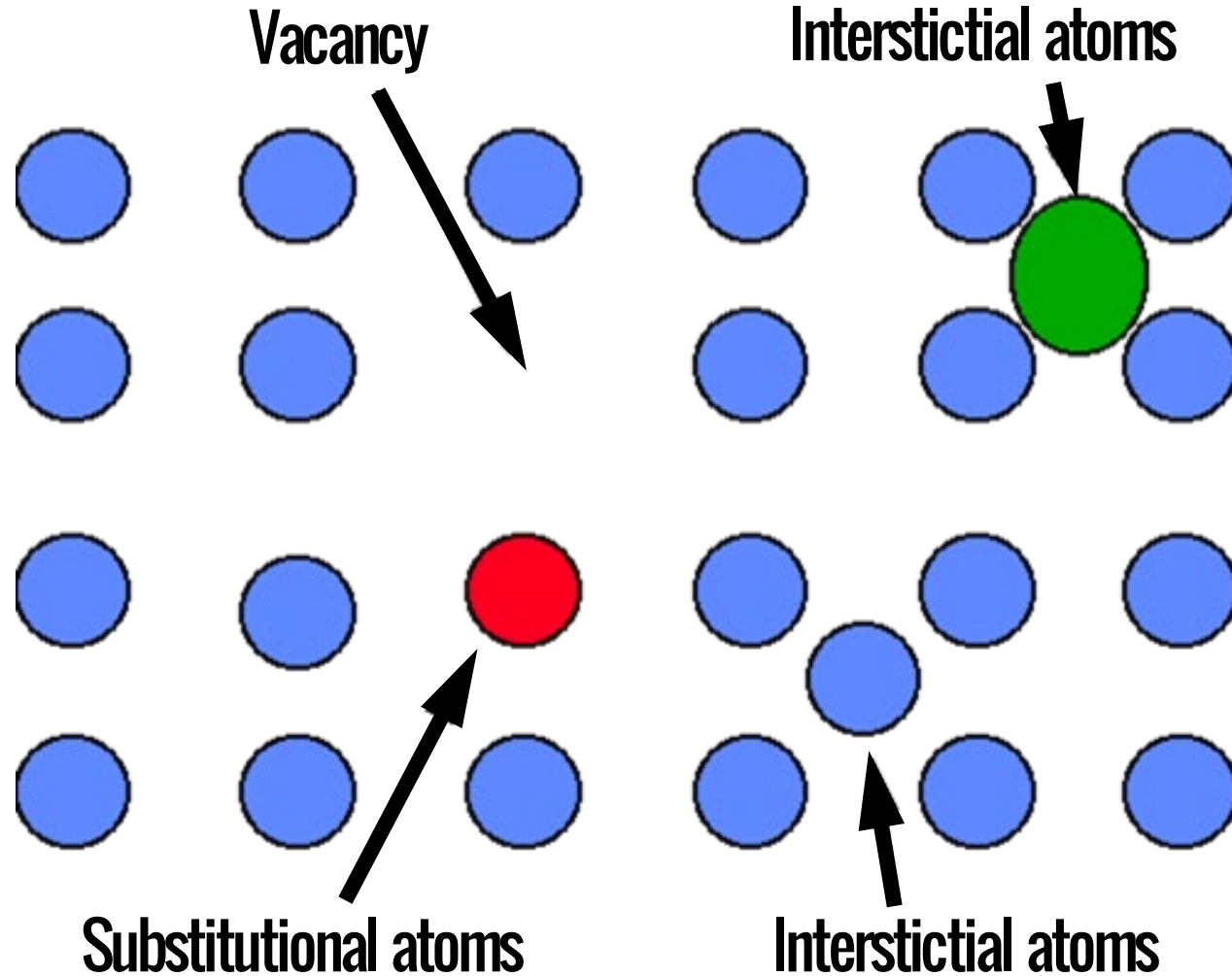
*Electrical Resistance is due to  
hit between electrons and lattice*

**Sum of two contributions:**

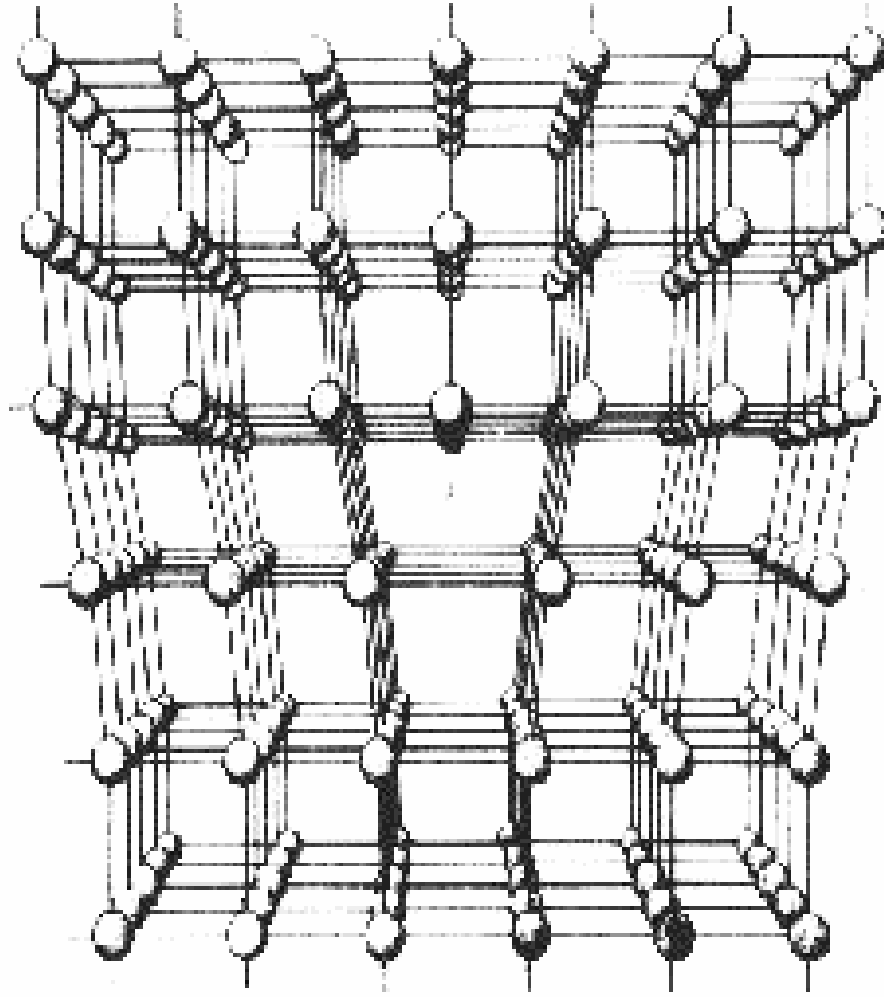
- **Lattice vibration (phonons)**
- **Defects and lattice distortions**



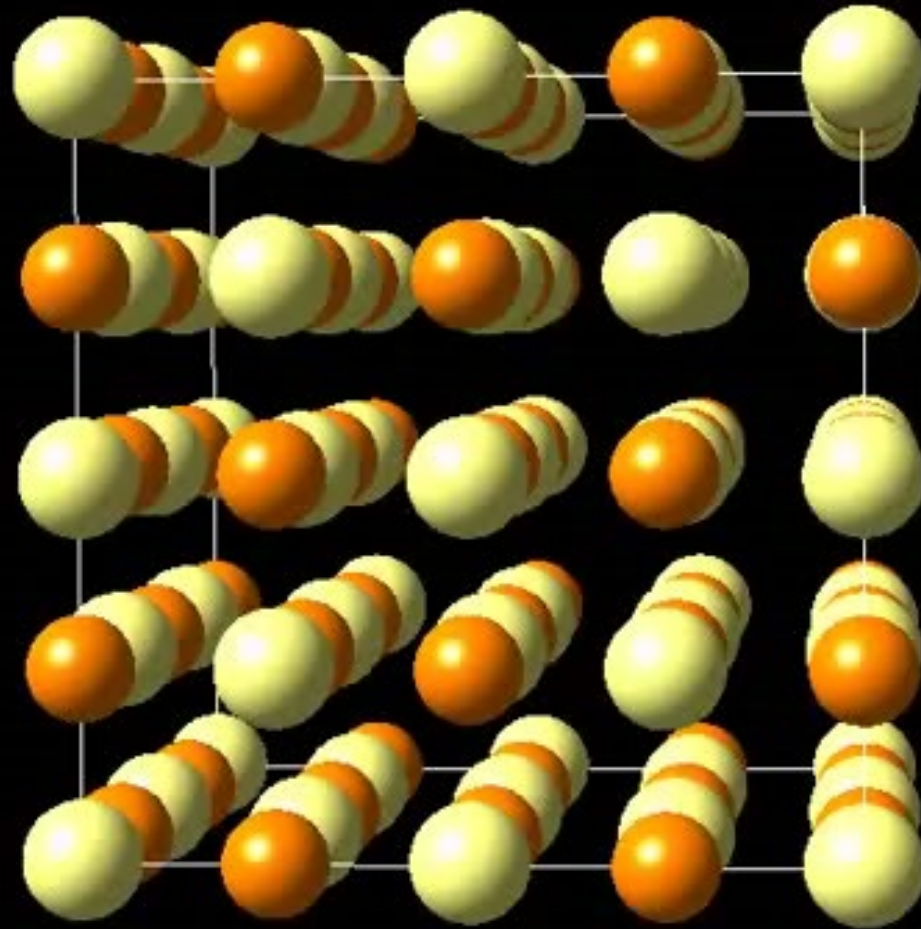
# Punctual defects



# Dislocations

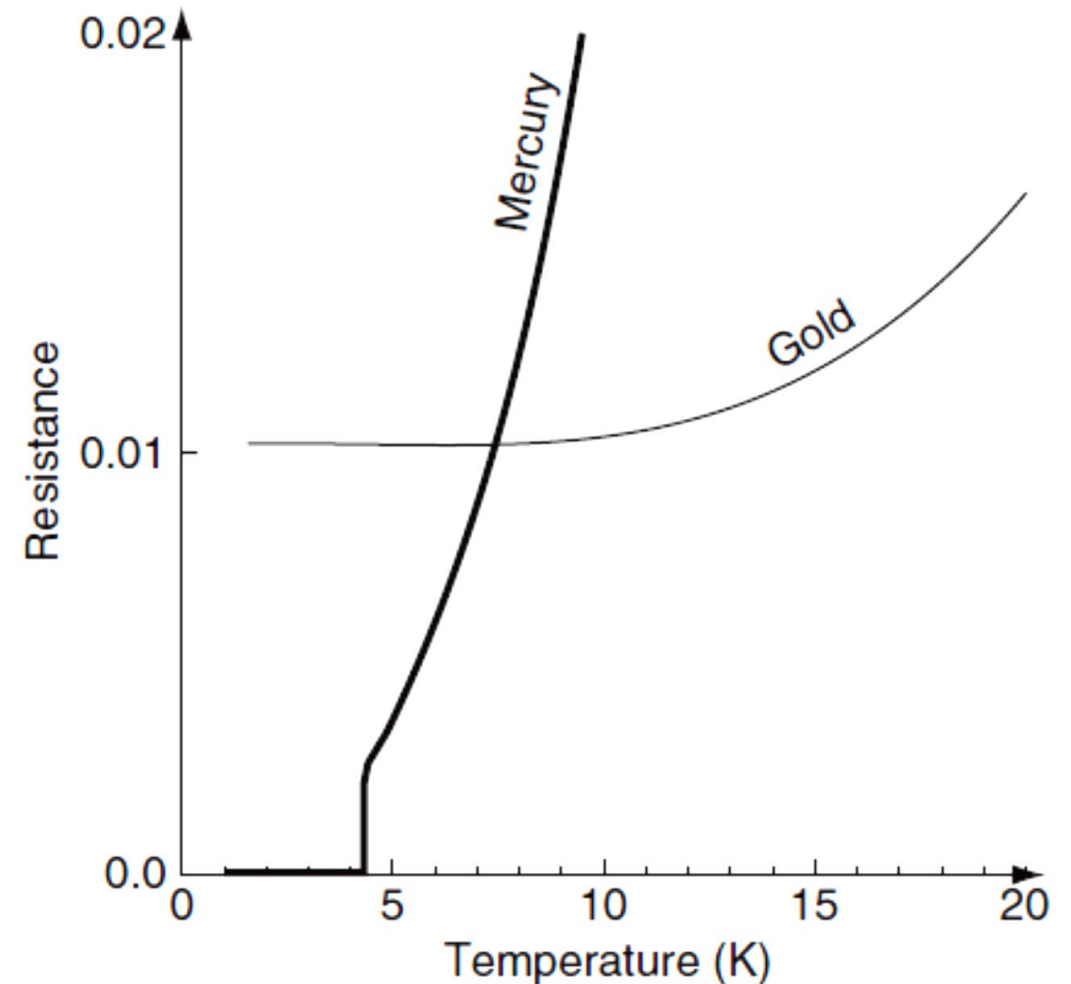


# Lattice vibrations due to Phonons

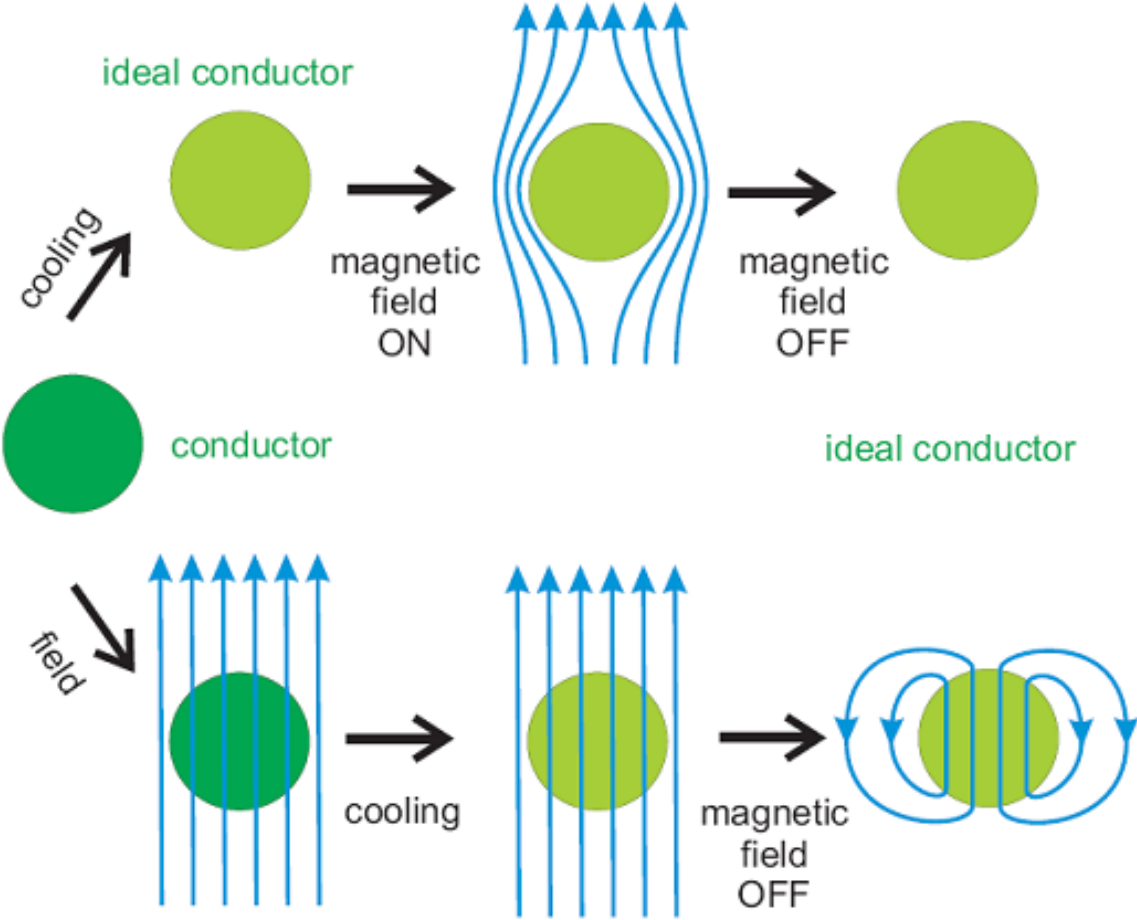


# How to explain superconductivity?

- **Drude model can not explain superconductivity**
- Many scientist tried (without success) to develop a theory to explain superconductivity. Sir J. J. Thomson and Frederick Lindemann are two of those
- Bloch found his attempts to formulate a satisfactory theory of superconductivity were doomed to failure; Bloch concluded that *“the only theorem about superconductivity that can be proved is that any theory of superconductivity is refutable”*. His equally facetious second theorem was: *“Superconductivity is impossible”*
- Albert Einstein, reviewing the situation in 1922, concluded that *“with our wide-ranging ignorance of the quantum mechanics of composite systems, we are far from able to compose a theory out of these vague ideas. We can only rely on experiment.”*
- **We must to wait other experiments and Quantum Mechanics (and a couple of weeks too...)**



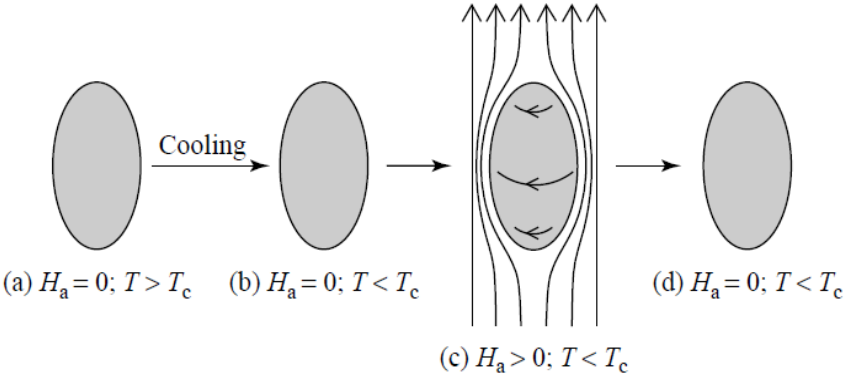
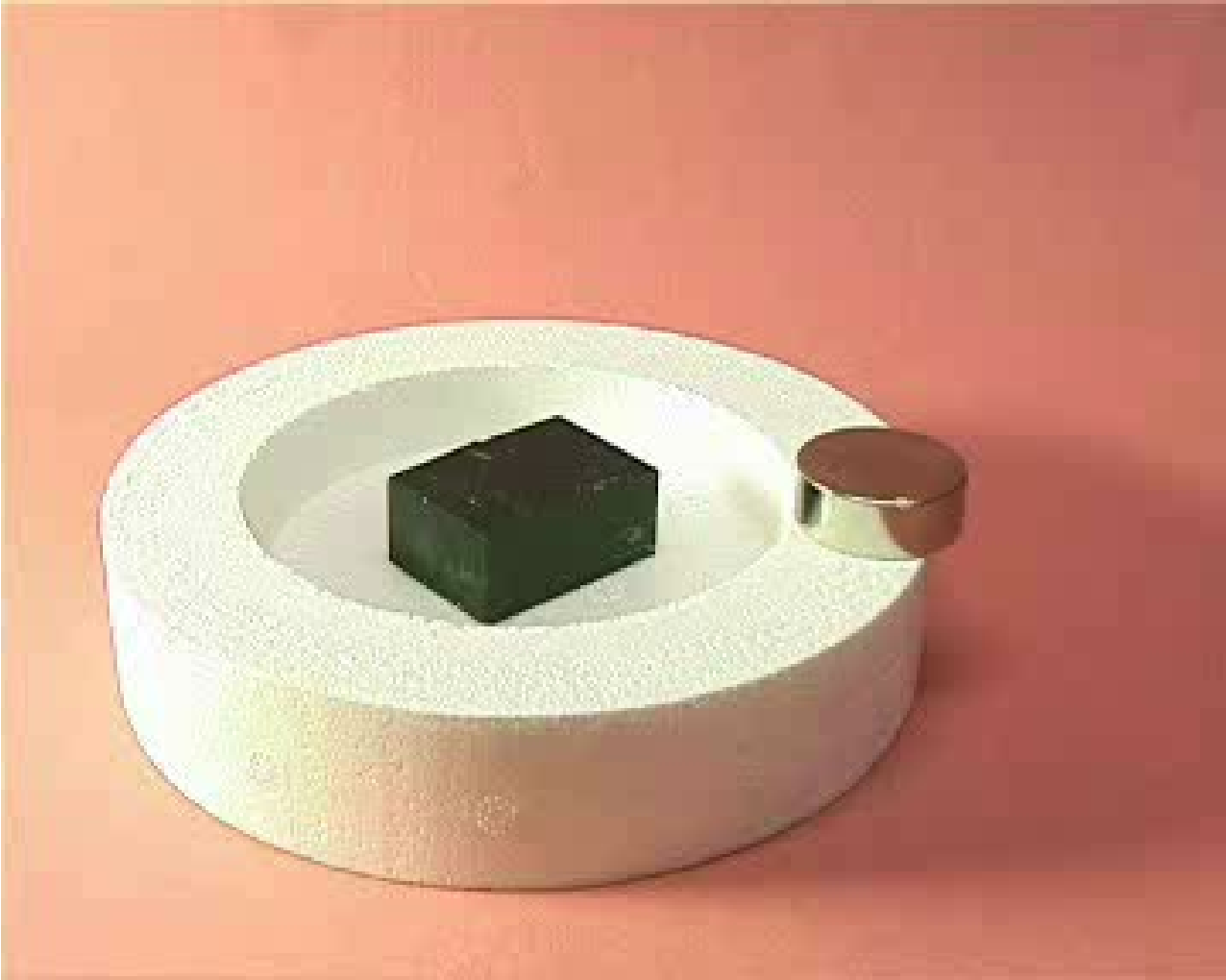
# Superconductors are ideal conductors?



1

2

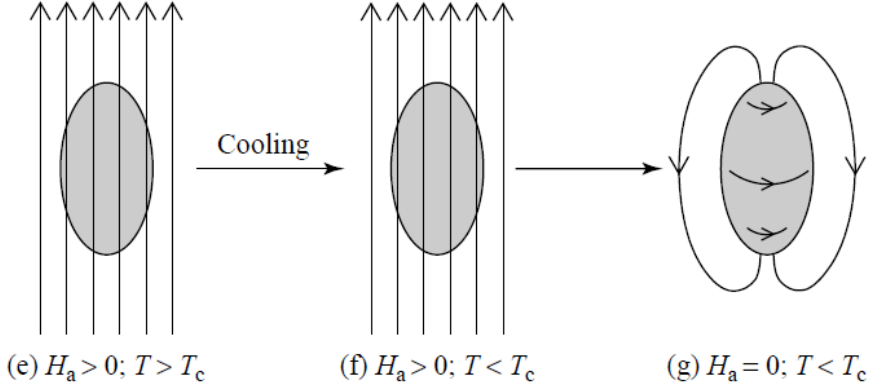
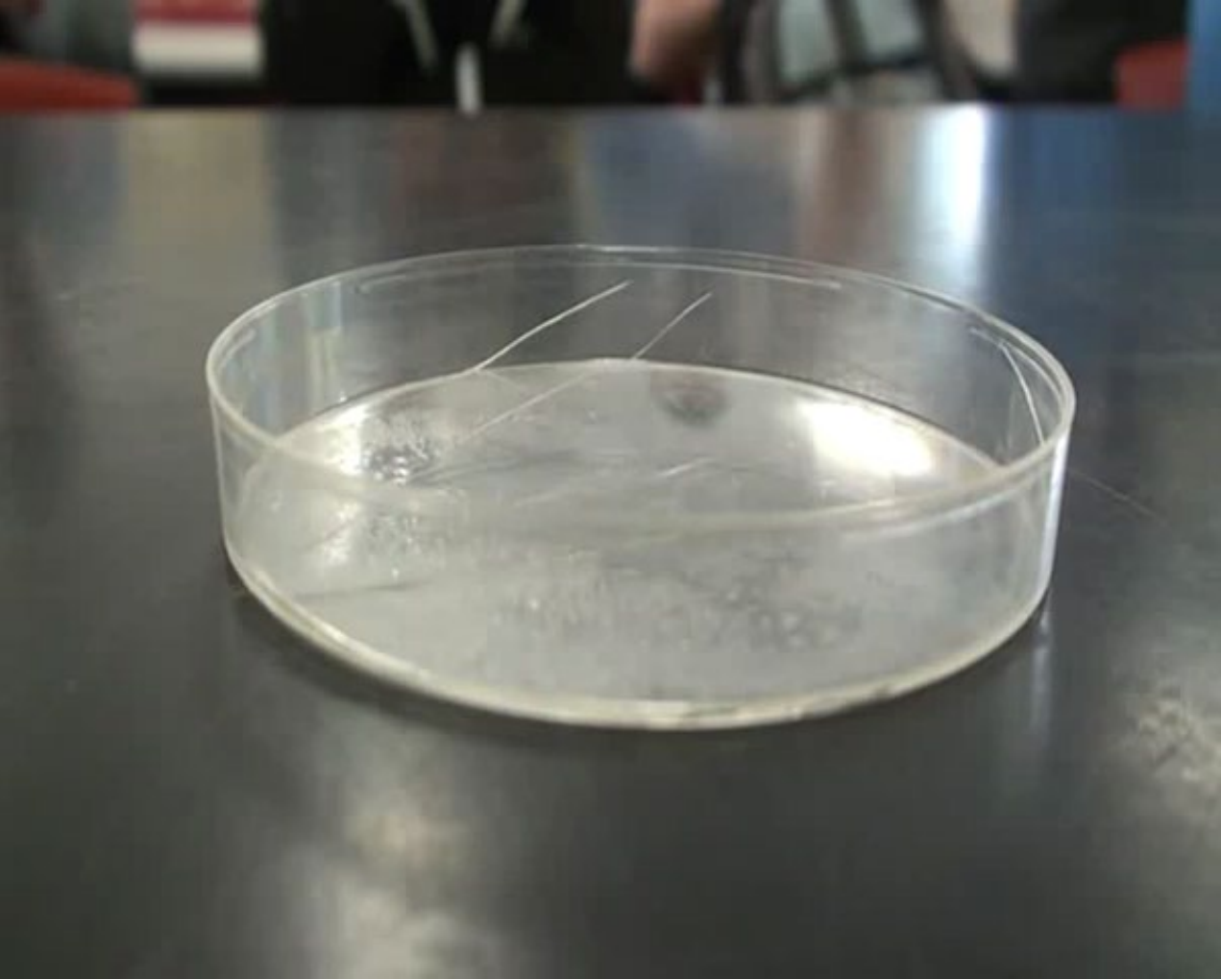
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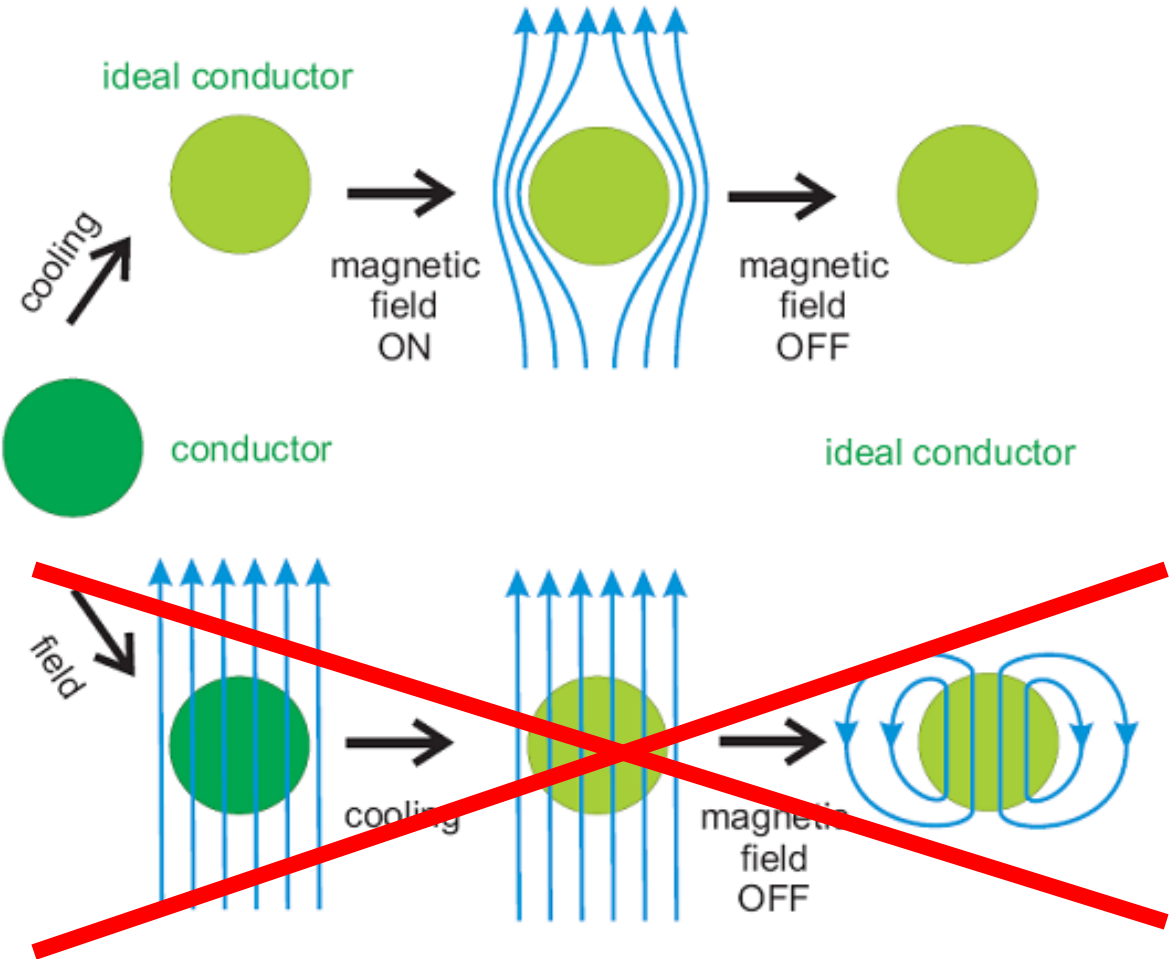


# Superconductors are ideal conductors?



2

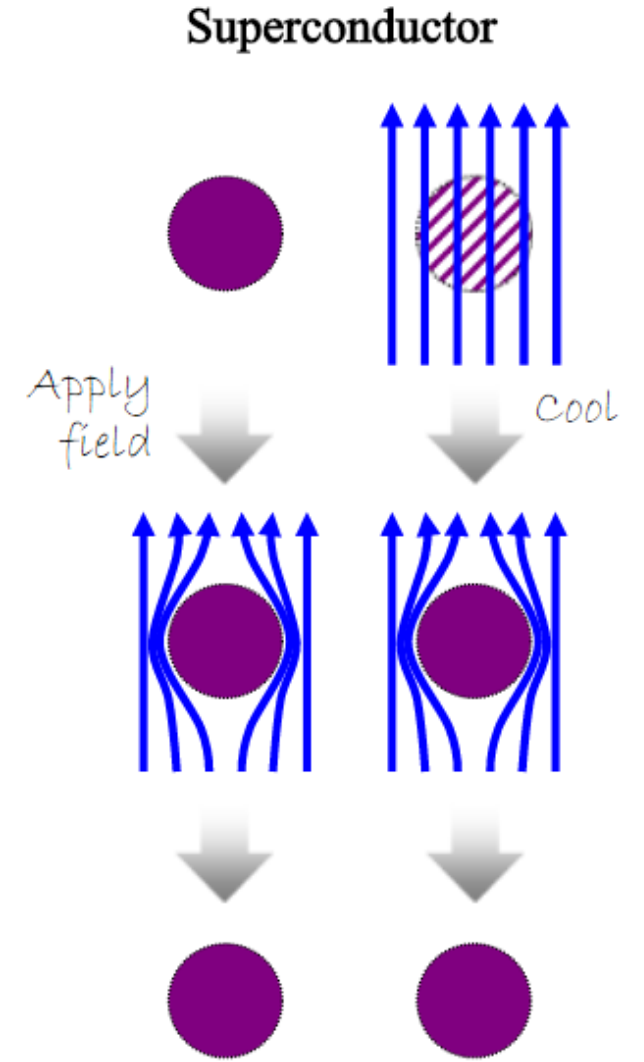
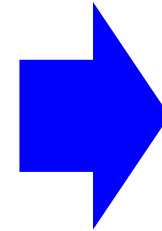
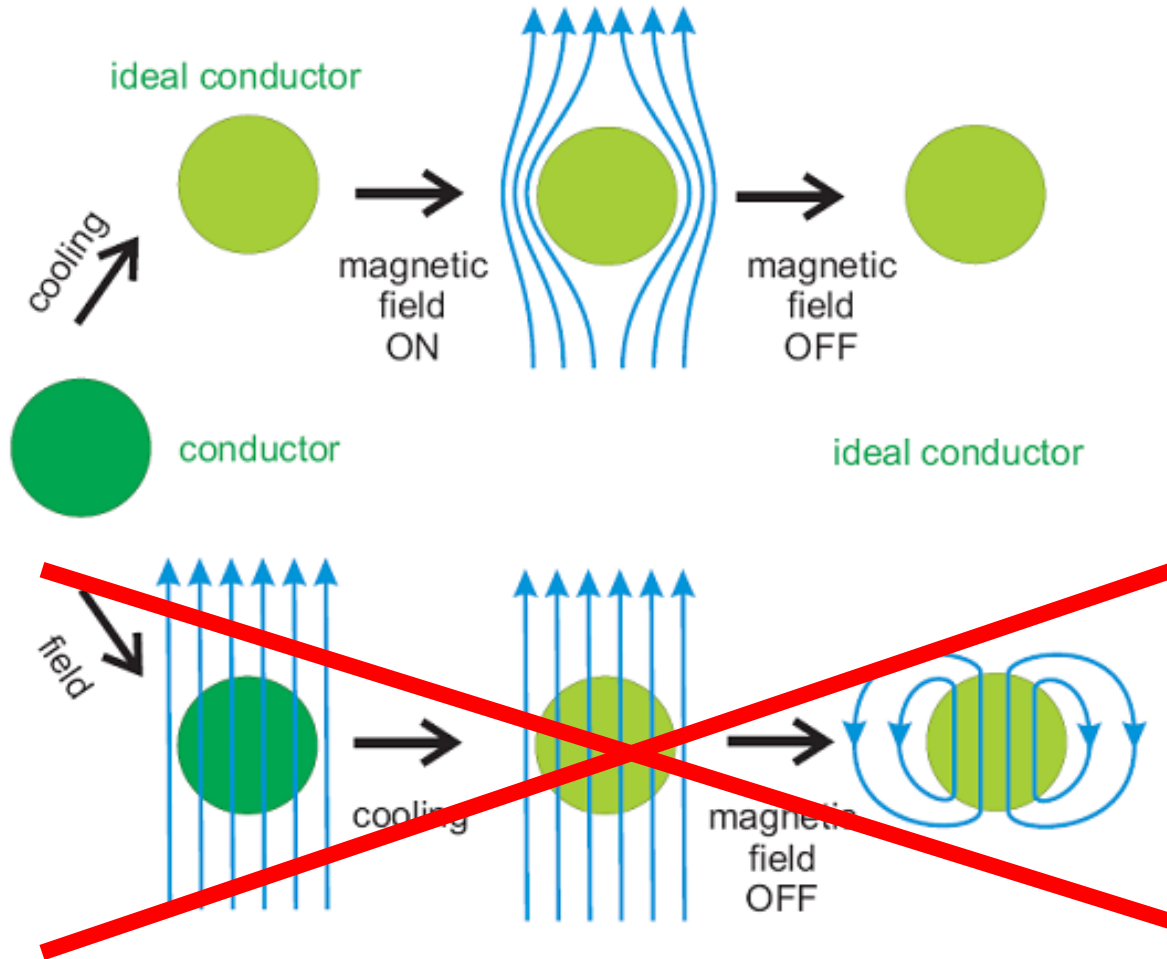
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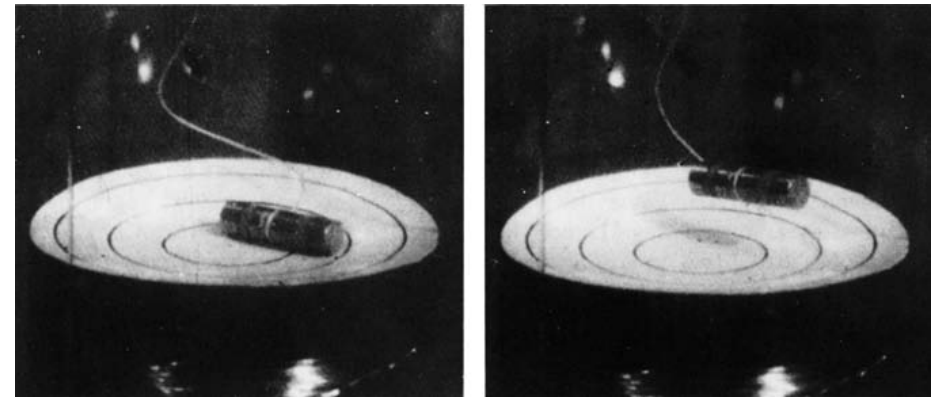
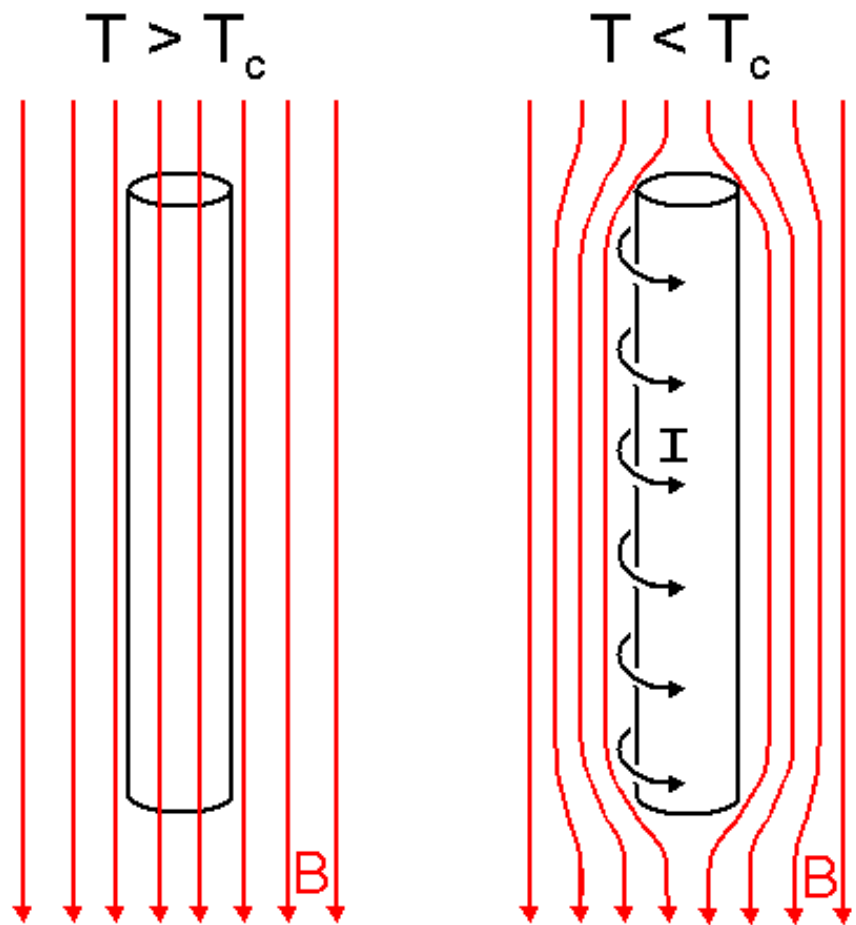
~~2~~

# Perfect diamagnets



# Meissner Effect

- **Ideal diamagnetic state**
- **Independent of the temporal sequence of cooling or magnetic field application**
- This ideal diamagnetism was discovered in 1933 by Meissner and Ochsenfeld for rods made of lead or tin
- Kamerlingh-Onnes in 1924 choosed the wrong shape to test it... a ring



“Levitated magnet” for demonstrating the Meissner-Ochsenfeld effect in the presence of an applied magnetic field.

*Left:* starting position at  $T > T_c$ . *Right:* equilibrium position at  $T < T_c$

# Perfect diamagnetism

Below  $T_c \rightarrow \mathbf{B}=0$  inside the superconductor

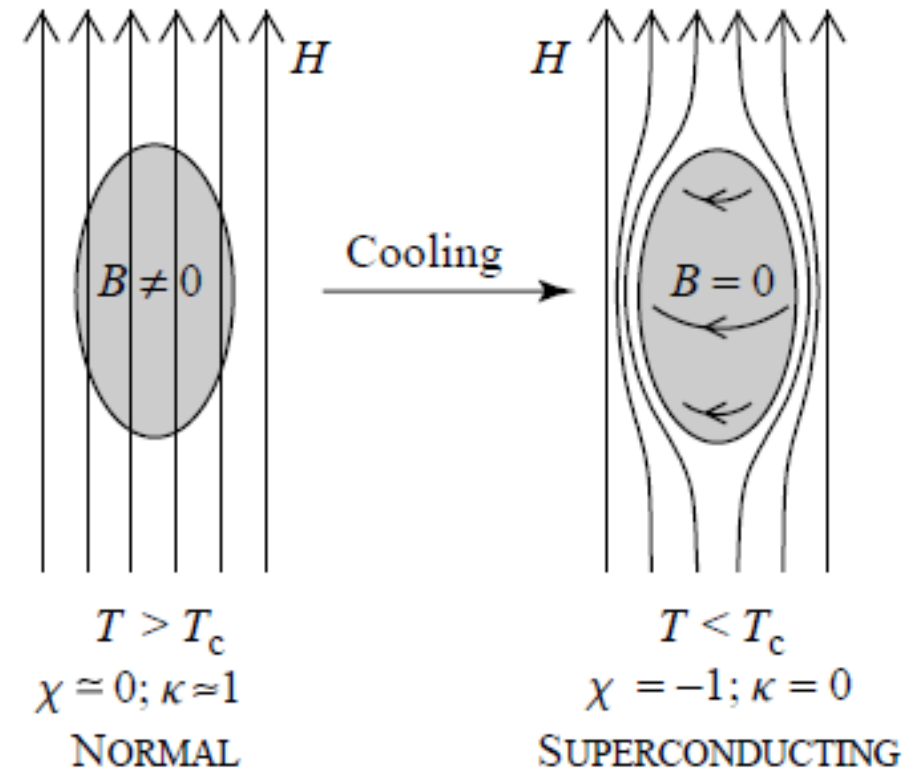
$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) = \mathbf{0}$$

Which implies that in the superconductor

$$\mathbf{M} = -\mathbf{H}$$

And the susceptibility is

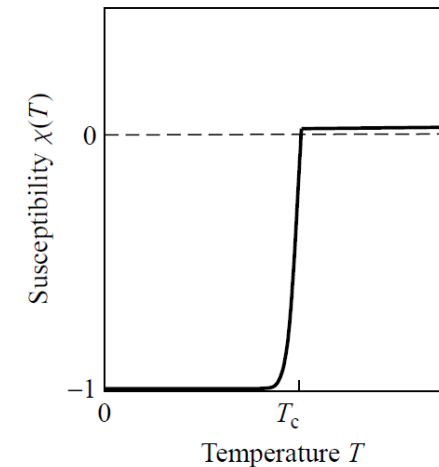
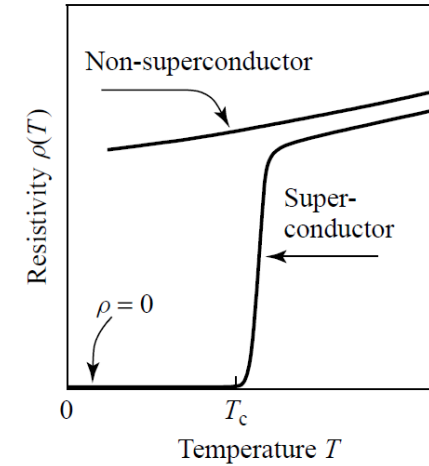
$$\chi = \frac{dM}{dH} = -1$$



# Consequences of Meissner effect

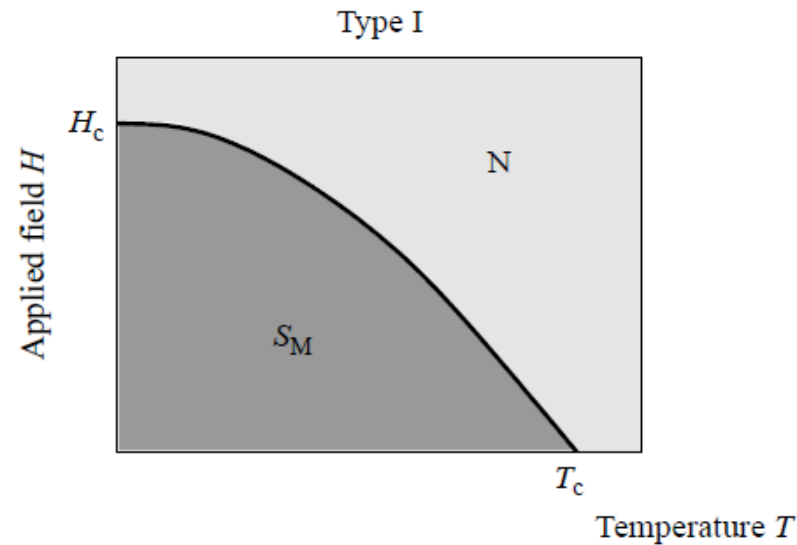
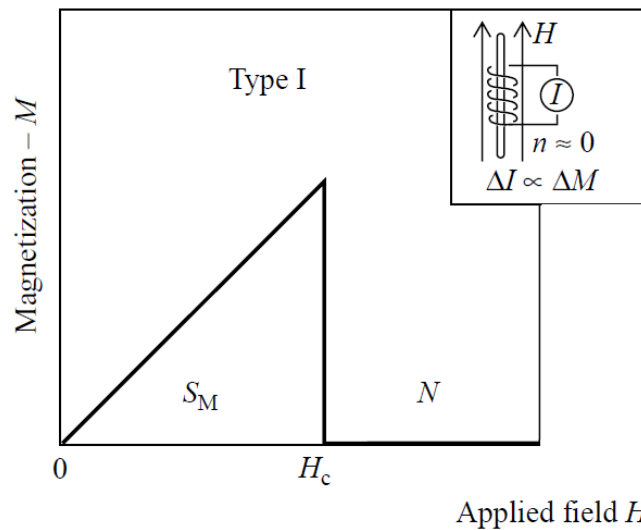
Superconductivity is **more than just  $\rho = 0$**

Superconductivity is a **thermodynamic state**, contrary to a state characterized by just  $\rho = 0$



# 2 types of Superconductors

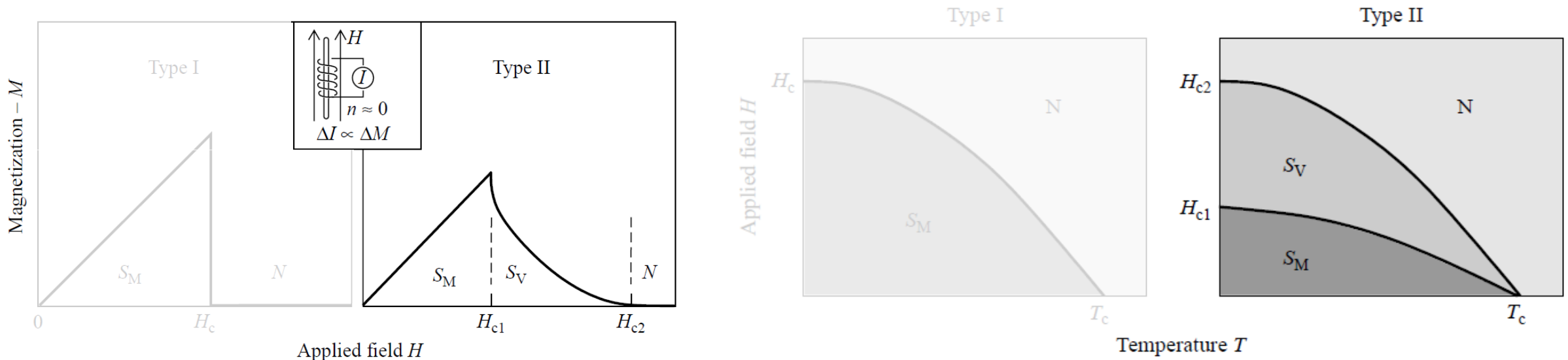
**Type I** The superconductor **switches abruptly** over from the Meissner state to one of **full penetration of magnetic flux**, the normal state, at a well-defined critical field,  $H_c$ .  
Examples of such materials are Hg, Al, Sn, In



# 2 types of Superconductors

**Type I** The superconductor switches abruptly over from the Meissner state to one of *full penetration of magnetic flux*, the normal state, at a well-defined critical field,  $H_c$ . Examples of such materials are Hg, Al, Sn, In

**Type II** The superconductor switches from the Meissner state to a state of *partial penetration of magnetic flux, the mixed state (aka Shubnikov phase)*, at a critical field  $H_{c1}$ . Thereafter it *crosses over continuously to full flux penetration*, the normal state, at an upper field  $H_{c2}$ . Examples: Nb, Nb<sub>3</sub>Sn, NbTi, and all high- $T_c$  cuprates

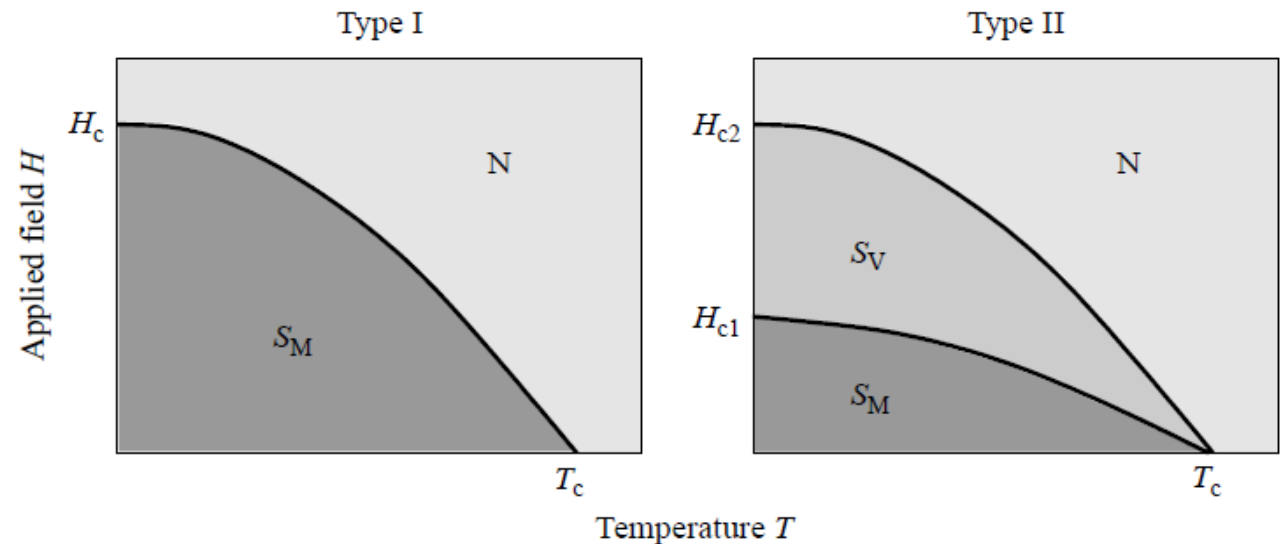
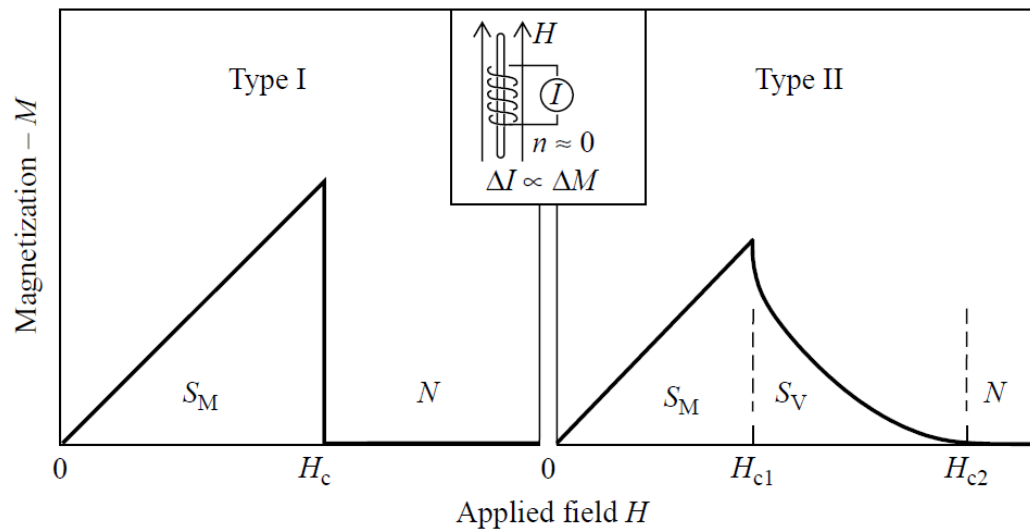




# 2 types of Superconductors

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**Type II** The superconductor switches **from the Meissner state to a state of partial penetration of magnetic flux, the mixed state (aka Shubnikov phase)**, at a critical field  $H_{c1}$ . Thereafter it **crosses over continuously to full flux penetration**, the normal state, at an upper field  $H_{c2}$ . Examples: Nb, Nb<sub>3</sub>Sn, NbTi, and all high- $T_c$  cuprates



# Vortex in Type II Superconductors

*Abrikosov, Nobel Prize in 2003*

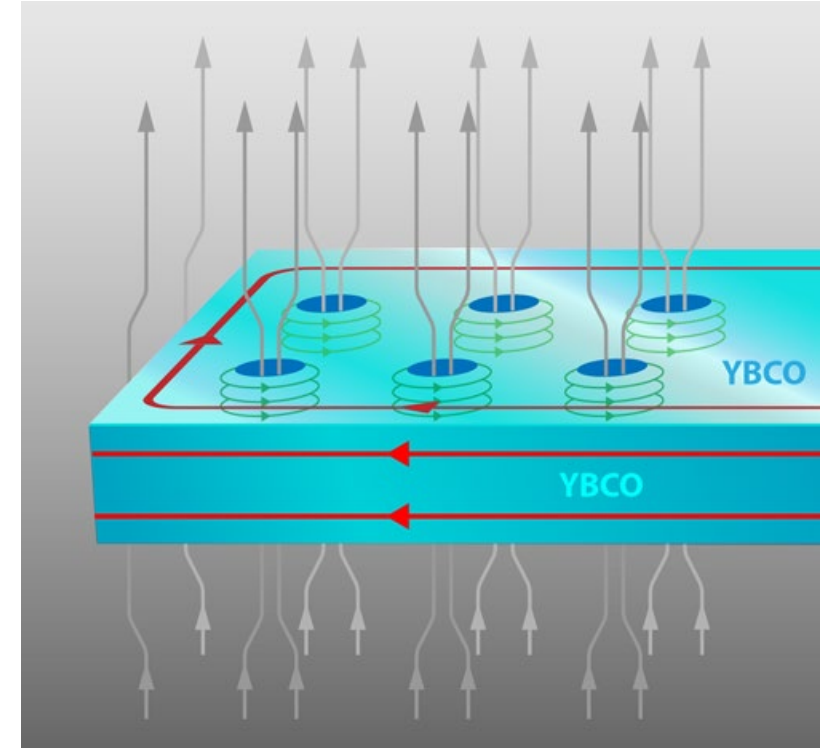
Magnetic field only partly penetrates into the sample

Flux penetrates in tiny, precisely **quantized units of flux**

$$\Phi_0 = \frac{h}{2e}$$

$h$  = Planck's constant

$e$  = magnitude of electronic charge

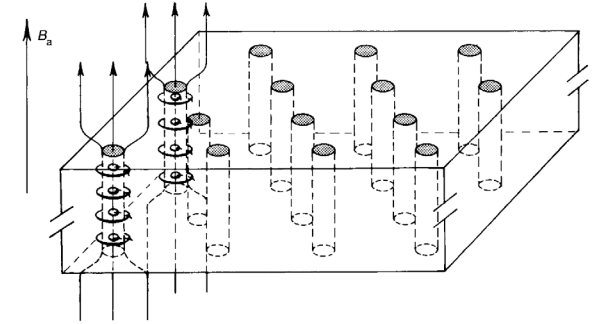


Shielding currents flow within the superconductor and concentrate the magnetic field lines

The density of flux lines increases with increasing applied magnetic field

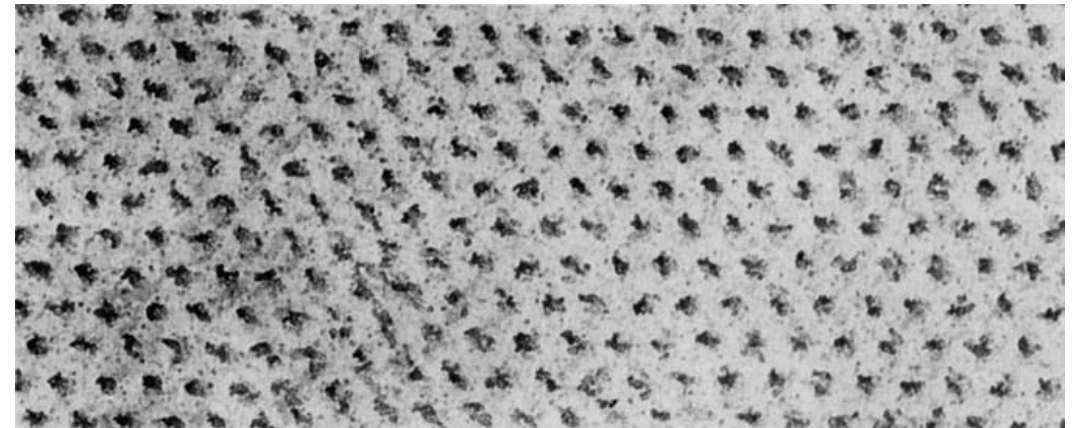
# Vortex in Type II Superconductors (2)

- Abrikosov in 1953 predicted the existence of the so-called mixed phase
- Landau was not convinced (looks like pseudoscience for him)
- Richard Feynman 2 years later explained some properties of superfluid helium using vortices
- This work convinced Landau and Abrikosov's work was published in 1957
- Real images of the Shubnikov phase were generated by Essmann and Träuble using an ingenious decoration technique in 1967



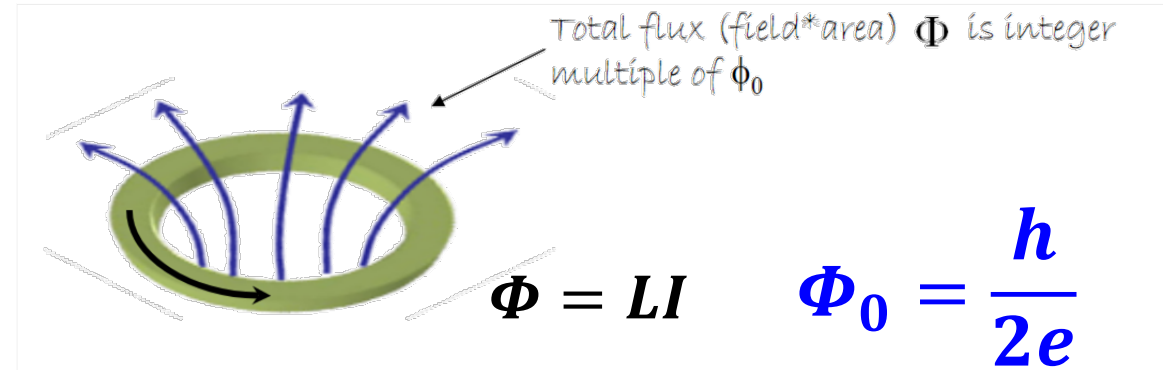
*Magnetic flux structure images were obtained as follows:*

- Above the superconducting sample, iron atoms are evaporated from a hot wire
- During their diffusion through the helium gas in the cryostat, the iron atoms coagulate to form iron colloids
- These colloids have a diameter of less than 50 nm, and they slowly approach the surface of the superconductor
- At this surface the flux lines of the Shubnikov phase exit from the superconductor
- The ferromagnetic iron colloid is collected at the locations where the flux lines exit from the surface, since here they find the largest magnetic field gradients
- In this way the flux lines can be decorated. Subsequently, the structure can be observed in an electron microscope



# Quantization of the flux

Doll and Nabauer / Deaver and Fairbank, 1961



Already expected by Fritz London almost thirty years before

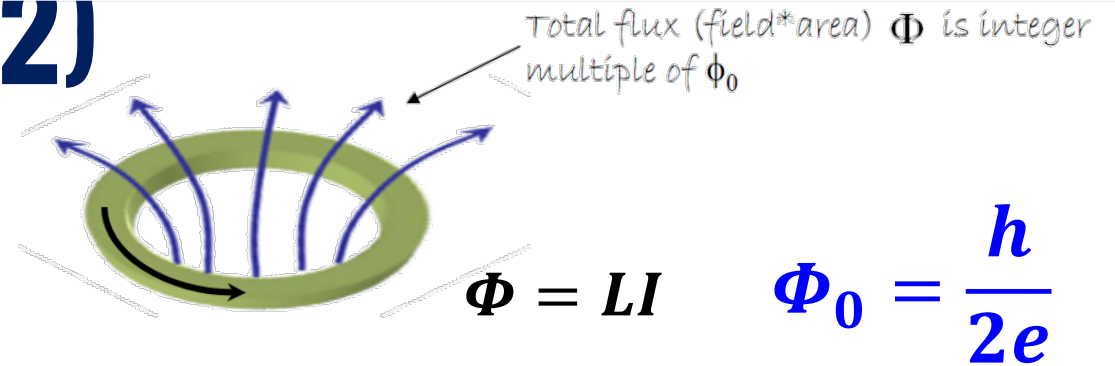
*(We will meet him soon)*

In macroscopic systems magnetic flux through the ring could take any arbitrary value

In **type-II SC** magnetic fields are concentrated in the form of **flux lines**, each of which carries a single flux quantum  $\Phi_0$

# Quantization of the flux (2)

Doll and Nabauer / Deaver and Fairbank, 1961



Extremely difficult to prove due to small **B** necessary

$$\Phi_0 = \frac{h}{2e} = \frac{6.626 \cdot 10^{-34} \text{ J s [C V s]}}{2 \cdot 1.602 \cdot 10^{-19} \text{ C}} = 2.07 \cdot 10^{-15} \text{ V s} = 2.07 \cdot 10^{-15} \text{ T m}^2$$

$$\Phi_B = \vec{B} \cdot \vec{S} \text{ (in the case of omogeneous B field)}$$

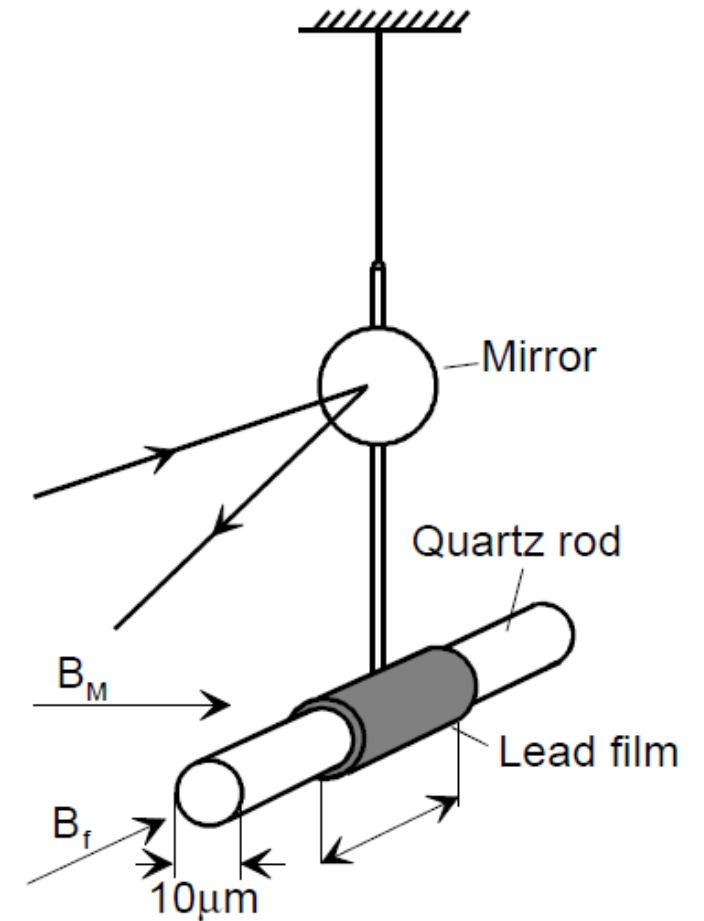
Both groups used thin tubes with  $d \sim 10 \mu\text{m}$

$$B = \frac{\Phi_0}{\pi r^2} = \frac{2.07 \cdot 10^{-15} \text{ T m}^2}{7.85 \cdot 10^{-11} \text{ m}} = 2.6 \cdot 10^{-5} \text{ T} \quad \text{Same order of magnitude of Earth's magnetic field}$$

# Quantization of the flux (3)

## Doll and Nabauer experiment

- Permanent current is generated by cooling in a freezing field  $B_f$
- Torque values were too small to be detected in a static experiment
- They measure the field to excite a torsional oscillation of the system



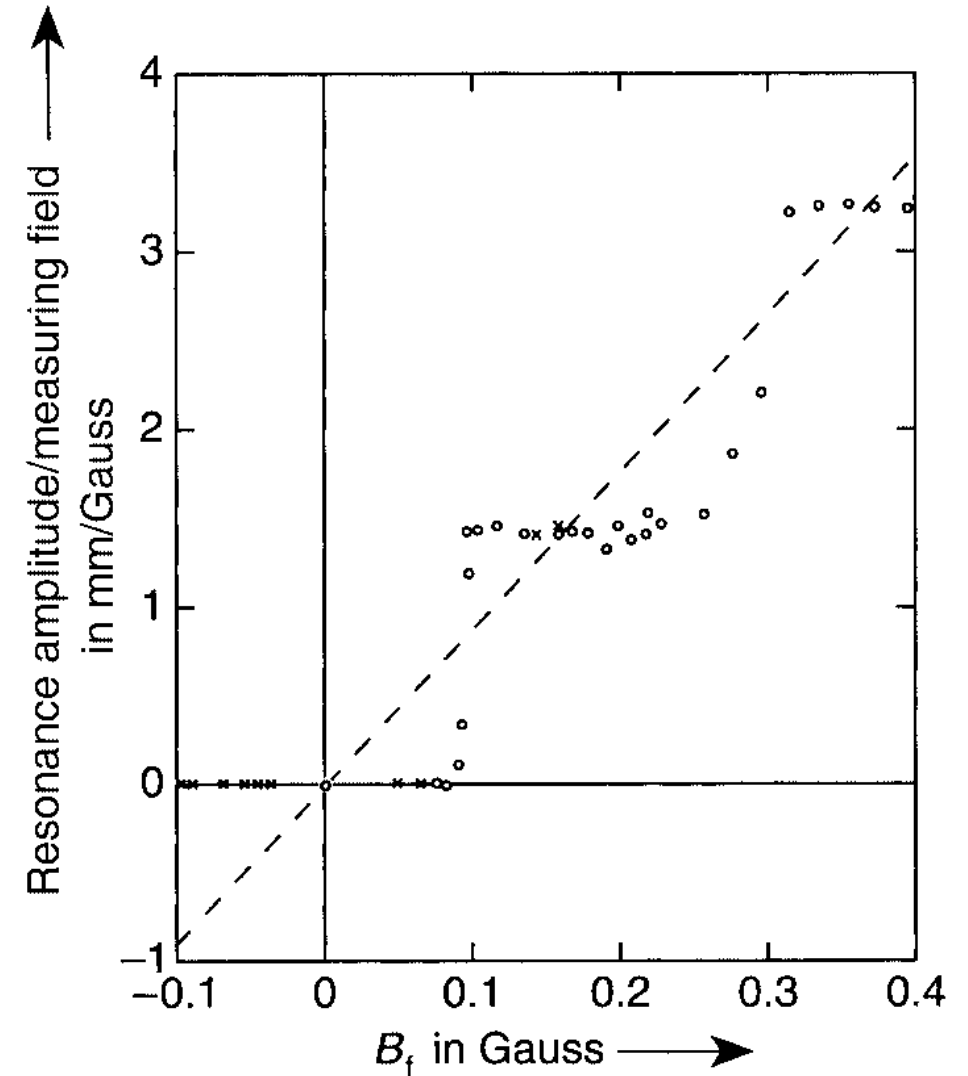
*Schematics of the experimental setup of Doll and Nabauer*

*The quartz rod carries a small lead cylinder formed as a thin layer by evaporation. The rod vibrates in liquid helium*

# Quantization of the flux (4)

## Doll and Nabauer experiment

- Permanent current is generated by cooling in a freezing field  $B_f$
- Torque values were too small to be detected in a static experiment
- They measure the field to excite a torsional oscillation of the system
- The experiment clearly indicates a quantization of the flux in the SC cylinder



# 3 hallmarks of superconductor

1. Zero resistance
2. Complete diamagnetism
3. Flux quantization

But there is something more



# No changes in crystal structure below $T_c$

The X-ray diffraction pattern does not change when crossing the transition temperature showing **no transition in the lattice structure**

**No appreciable change in the reflectivity** of the superconductor can be detected (Although the optical properties of normal metals are strictly connected with resistivity)

**Photoelectric properties remain unchanged too**

**The elastic properties**, the thermal expansion **does not change** with transition and no latent heat or volume change in absence of a magnetic field are observed.

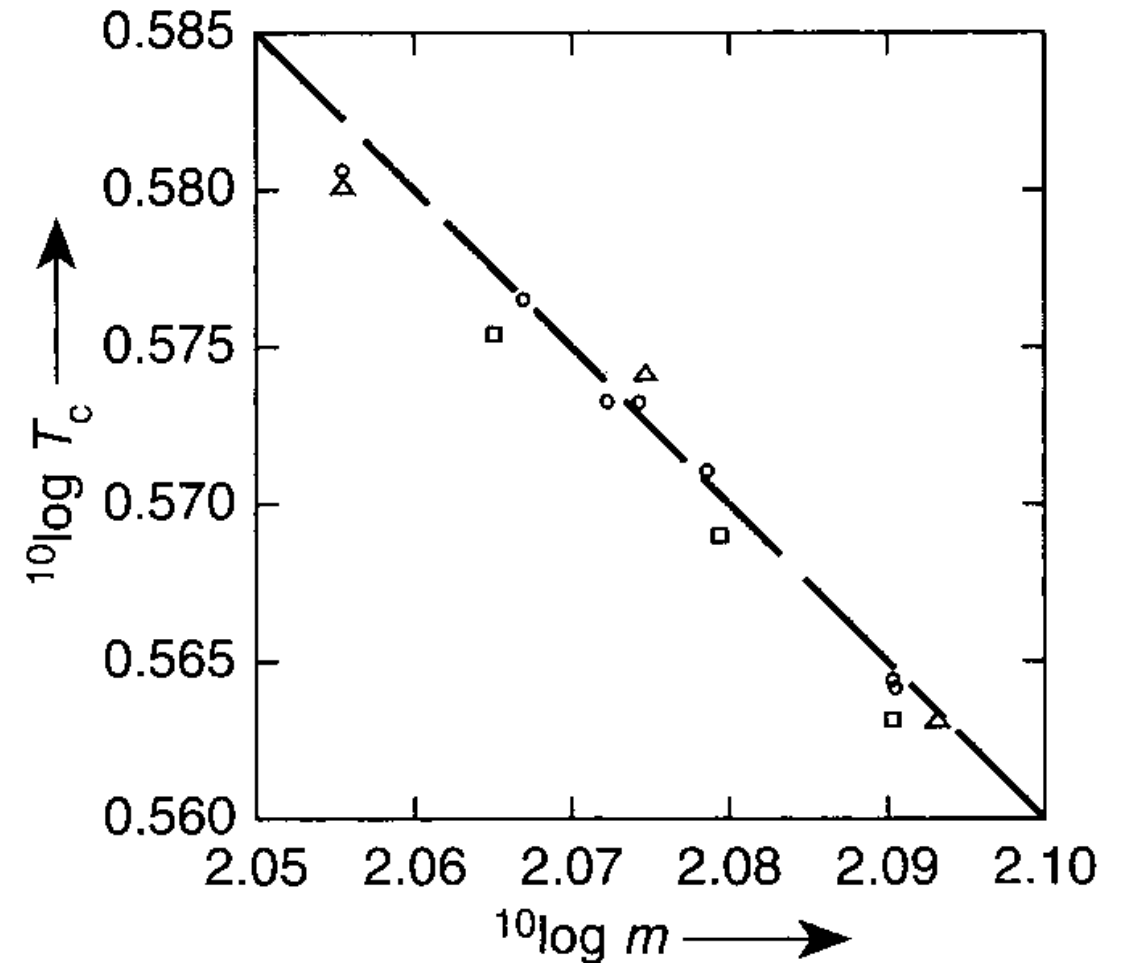
# Isotopic effect, 1950

In 1950 Maxwell as well as Reynolds, Serin, Wright, and Nesbitt almost simultaneously observed in mercury a dependence of the  $T_c$  on nuclear mass

Average atomic mass	199.7	200.7	202.0	203.4
Transition temperature $T_c$ in K	4.161	4.150	4.143	4.126

$$T_c \propto M^{-1/2}$$

*As suggested by Frohlich and Bardeen*



Isotope effect in tin: ○ Maxwell; □ T Lock, Pippard, and Shoenberg; D Serin, △ Reynolds, and Lohman

*E. Maxwell: Phys. Rev. 86, 235 (1952); B. Serin, C. A. Reynolds, C. Lohman: Phys. Rev. 86, 162 (1952); J. M. Lock, A. B. Pippard, D. Shoenberg: Proc. Cambridge Phil. Soc. 47, 811 (1951).*

# Isotopic effect (2)

$$T_c \propto M^{-1/2}$$

In a crystal lattice, the **frequency of vibration** is **inversely proportional** to the **square root of the mass of the atoms (Debye frequency)**

$$\omega_D = \pi \left( \frac{C}{M} \right)^{1/2}$$

The 'isotope effect' was a piece of evidence demonstrating that one should **not ignore the presence of the nuclei that make up most of the mass in atoms**

Whereas the non-transition metals display well the exponent  $\beta = 1/2$ , the transition metals show strong deviations from this value

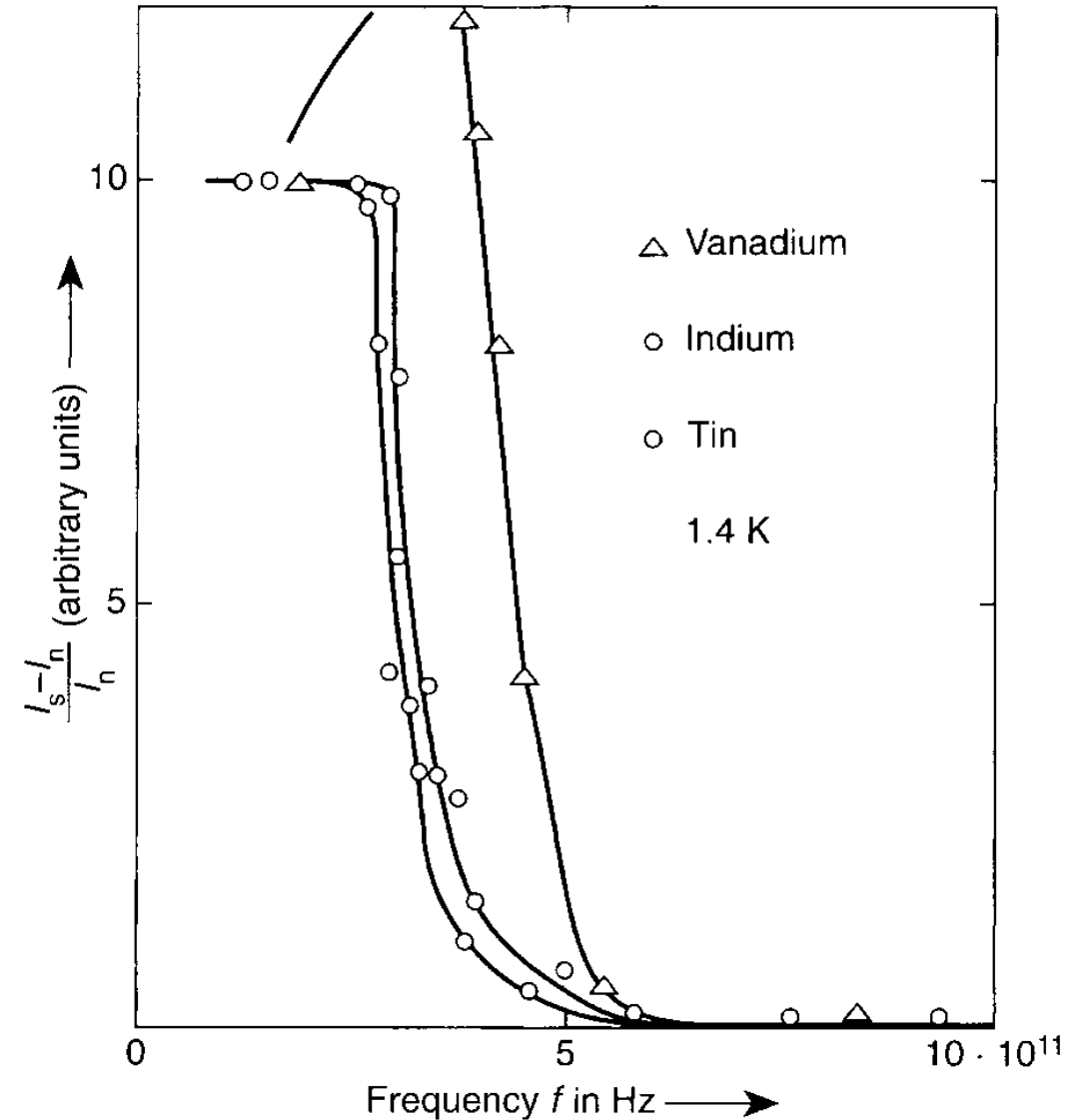
Element	Hg	Sn	Pb	Cd	Tl	Mo	Os	Ru
Isotope exponent $\beta^*$	0.50	0.47	0.48	0.5	0.5	0.33	0.2	0.0

\*) The exponent  $\beta$  is obtained from experiment by fitting to the relation  $T_c \propto M^{-\beta}$ . The values shown are taken from R. D. Parks, "Superconductivity", Marcel Dekker, New York, 1969, p. 126.

# Infrared absorption, 1956

In 1956, Tinckham and Glover demonstrated that **SC absorb IR radiation only above a certain threshold value**

The results of the experiment suggest the presence of an **Energy gap** between the Normal and the Superconducting State

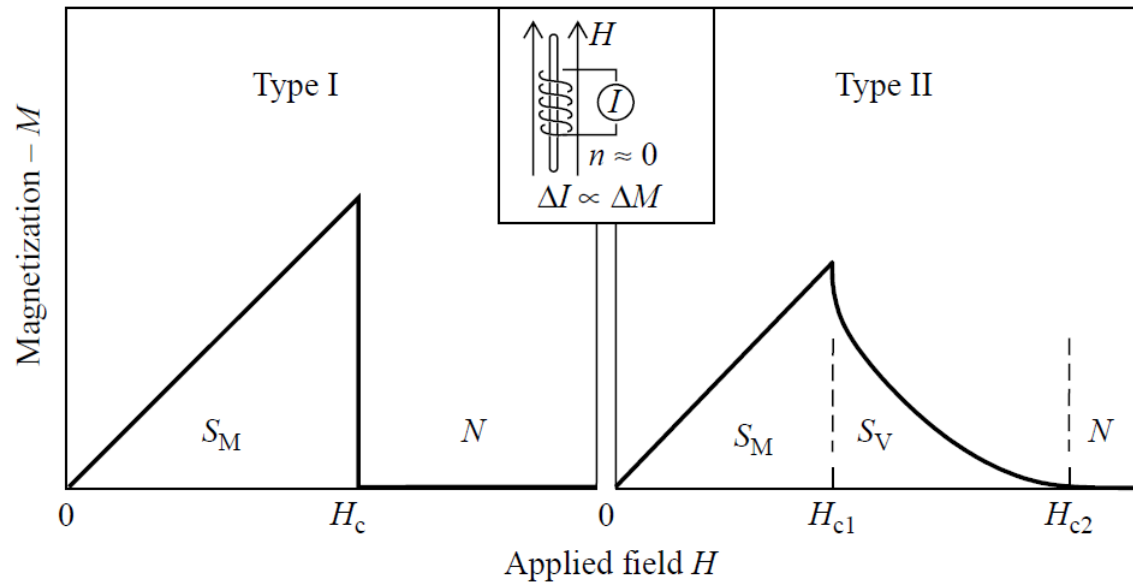


*Infrared transmission of thin superconducting films*

# Thermodynamic of the SC state

SC state appears as a **thermodynamic state** with a **Energy gap** that **separates** it from the NS

Magnetic diagrams can be read as **phase diagrams**



# Thermodynamic of the SC state (2)

In thermodynamics you can derive

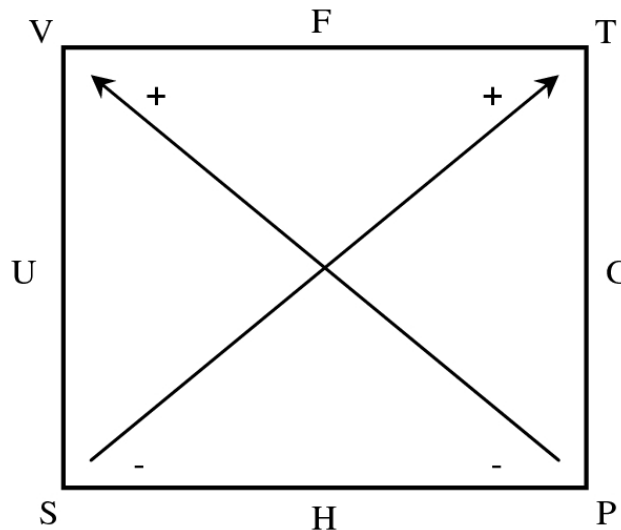
**relationships between measurable quantities by analysis of free energy**

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_S = V$$

$$\left(\frac{\partial G}{\partial T}\right)_P = \left(\frac{\partial F}{\partial T}\right)_V = -S$$

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P = T$$

**Thermodynamics square** is a useful tool to remember the basic relationships



- V** Volume
- F** Helmotz free energy
- T** Absolute Temperature
- G** Gibbs free energy
- P** Pressure
- H** Enthalpy
- S** Entropy
- U** Internal Energy

# Thermodynamic of the SC state (2)

In thermodynamics you can derive

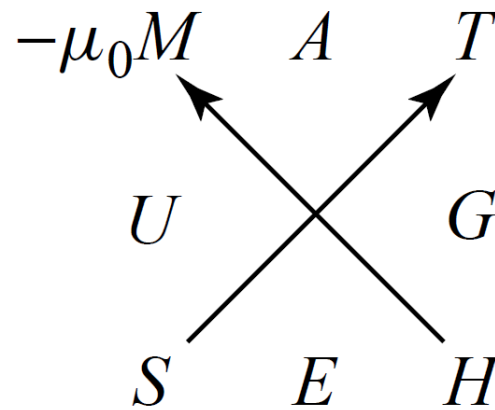
**relationships between measurable quantities by analysis of free energy**

$$\left(\frac{\partial G}{\partial H}\right)_T = -\mu_0 M$$

$$\left(\frac{\partial G}{\partial T}\right)_H = -S$$

$$\left(\frac{\partial U}{\partial S}\right)_M = T$$

**Thermodynamics square** is a useful tool to remember the basic relationships

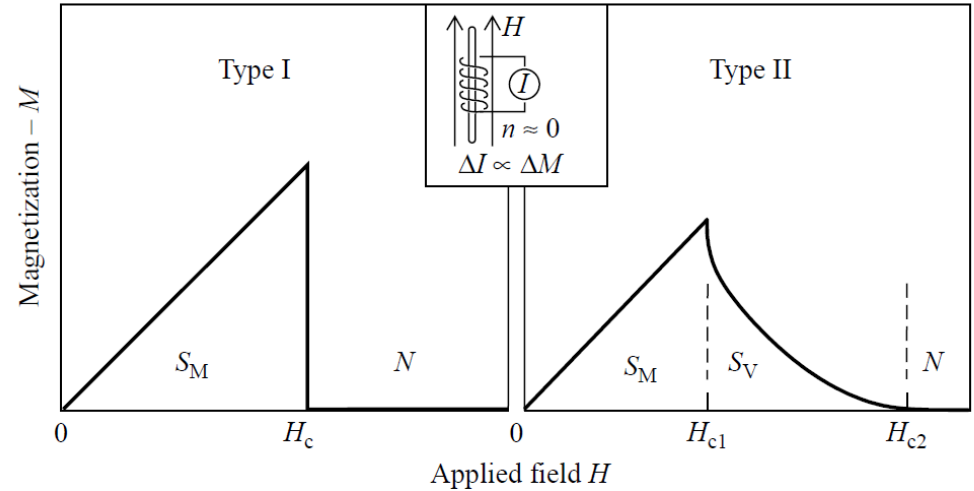


- M** Magnetization
- A** Helmotz free energy
- T** Absolute Temperature
- G** Gibbs free energy
- H** Applied magnetic field
- E** Enthalpy
- S** Entropy
- U** Internal Energy

# Thermodynamic of the SC state (3)

We can obtain the Gibbs' energy  $G$  of the superconducting state starting from the magnetization, consider  $G$  dependent on  $T$  and  $H$

$$\left(\frac{\partial G}{\partial H}\right)_T = -\mu_0 M \quad \rightarrow \quad dG = -\mu_0 M dH$$



The relation is valid both in SC and NC. Integrate from 0 to  $H_c$  at constant  $T$

$$\int_0^{H_c} dG_S = -\mu_0 \int_0^{H_c} M_S(T, H) dH$$

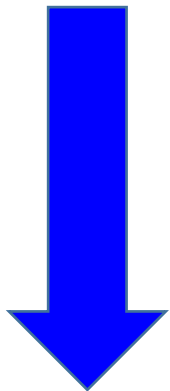


# Thermodynamic of the SC state (4)

$$\int_0^{H_c} dG_S = -\mu_0 \int_0^{H_c} M_S(T, H) dH$$

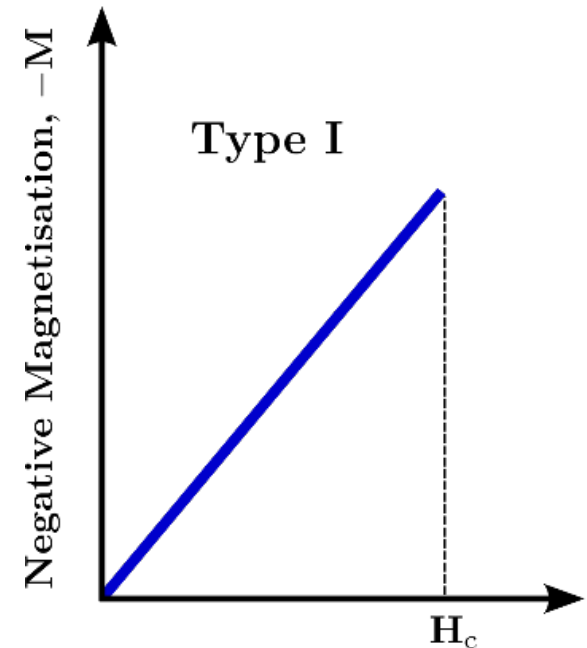
In **type I superconductor**, the Meissner state is characterized by  **$M = -H$**

$$\int_0^{H_c(T)} dG_S = -\mu_0 \int_0^{H_c(T)} (-H) dH$$



$$-\mu_0 \int_0^{H_c(T)} (-H) dH = \frac{\mu_0}{2} H_c^2(T)$$

$$\int_0^{H_c(T)} dG_S = G_S(T, H_c) - G_S(T, 0)$$




# Thermodynamic of the SC state (5)

$$G_S(T, H_C) - G_S(T, 0) = \frac{\mu_0}{2} H_C^2(T)$$

If exist an Energy Gap, we can calculated it from the energy difference between the NS and the SC states

Remember that  $dG_n = -\mu_0 M dH$

For a normal metal  $\chi \ll 1$    $G_n(T, H_C) = G_n(T, 0)$

$$\int_0^{H_c} dG_n = -\mu_0 \int_0^{H_c} M_n dH \quad \text{} \quad \cong 0$$

# Thermodynamic of the SC state (5)

From the fact that the two phases coexist in the intermediate state of type I (with a field  $H_c$  in the normal lamina and zero in the superconducting ones):

$$G_n(T, H_c) = G_s(T, H_c) \quad \text{and} \quad G_n(T, 0) = G_s(T, H_c)$$

Substituting it in  $G_s(T, H_c) - G_s(T, 0) = \frac{\mu_0}{2} H_c^2(T)$

we obtain:  $G_n(T, 0) - G_s(T, 0) = \frac{\mu_0}{2} H_c^2(T)$

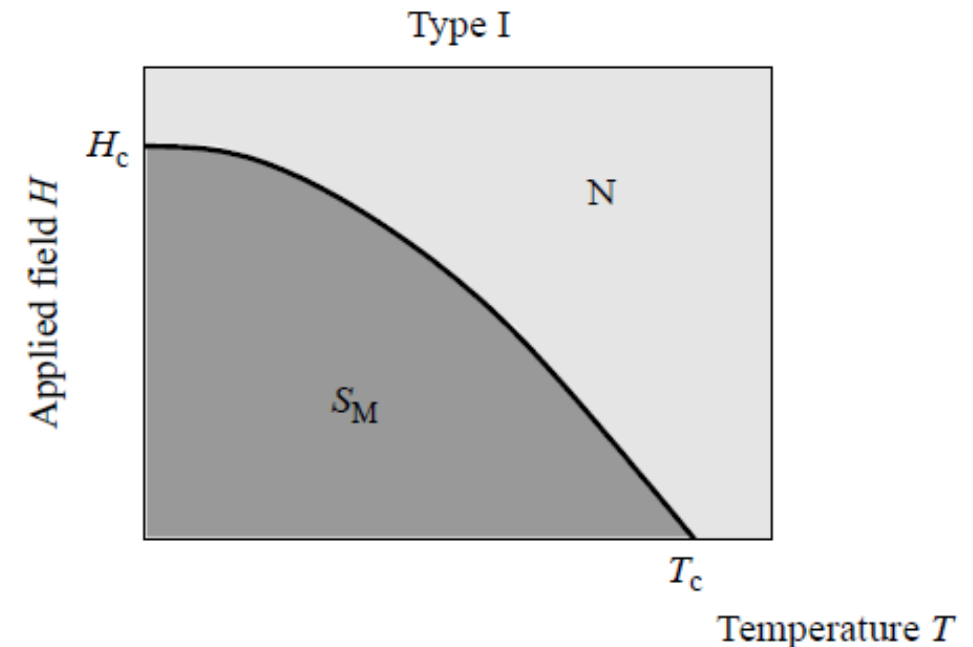
# Thermodynamic of the SC state (6)

$$G_n(T, \mathbf{0}) - G_s(T, \mathbf{0}) = \frac{\mu_0}{2} H_c^2(T)$$

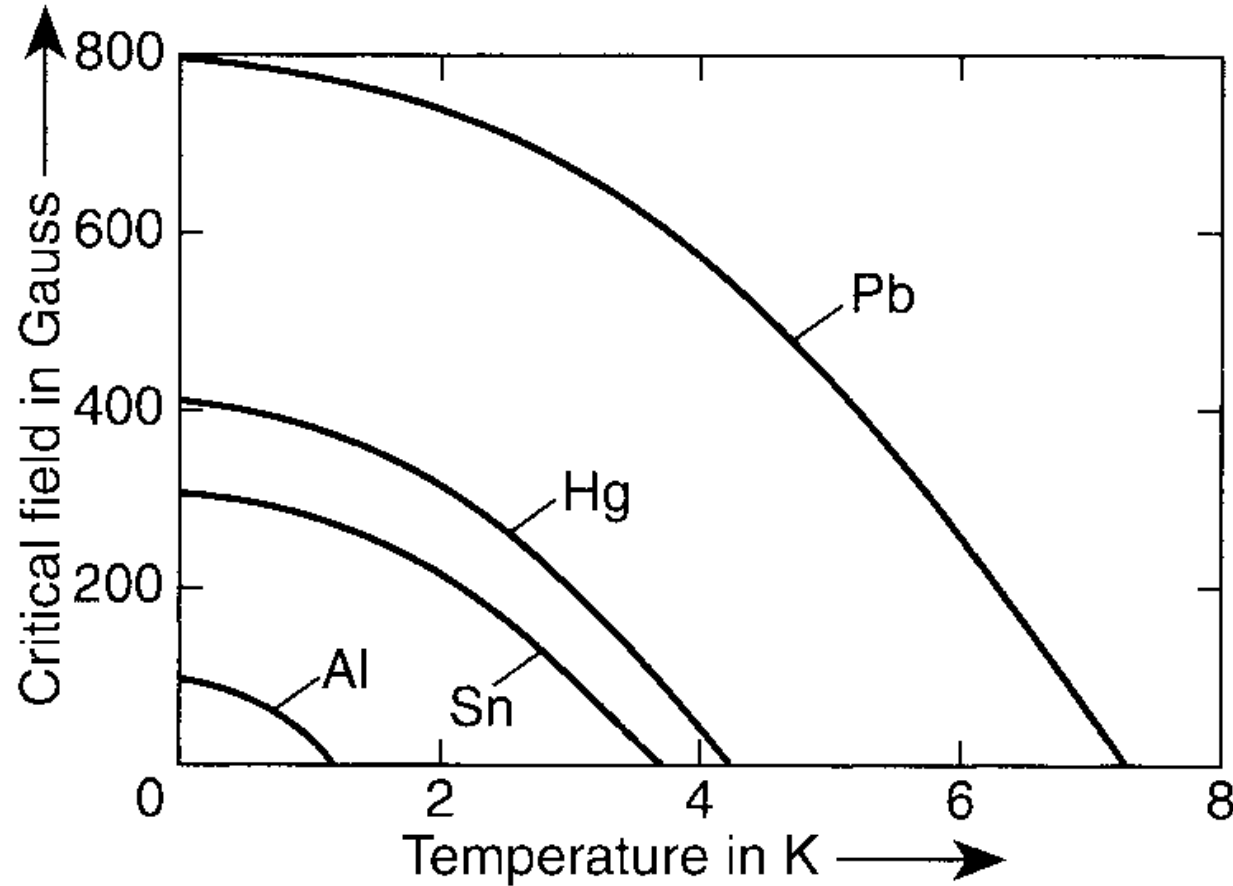
$H_c^2$  is in a deeper sense a measure of the “**condensation energy**” of the Meissner state

$H_c(T)$  from experimental data could be express as:

$$H_c(T) = H_c(0) \left(1 - \frac{T}{T_c}\right)^2$$



# T dependence of $H_c$



$$H_c(T) = H_c(0) \left(1 - \frac{T}{T_c}\right)^2$$

# Thermodynamic of the SC state - Entropy

$$S_s = - \left( \frac{\partial G_s}{\partial T} \right)_H$$

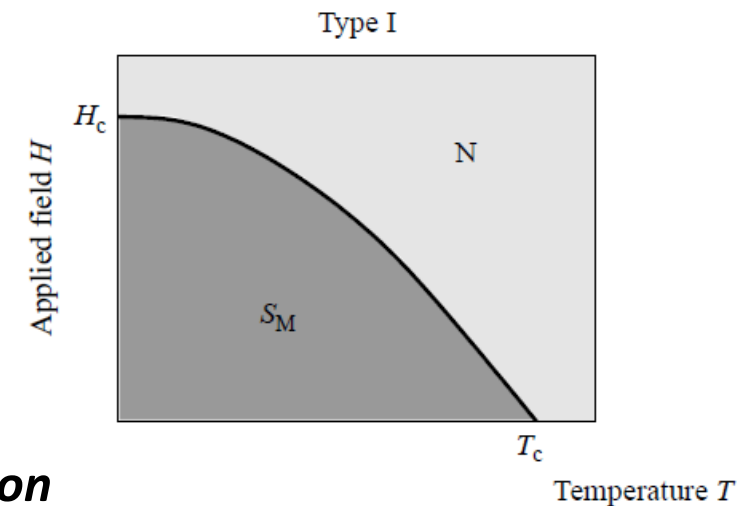
We can now calculate entropy change

from the temperature derivate of:  $G_n(T, 0) - G_s(T, 0) = \frac{\mu_0}{2} H_c^2(T)$

$$S_n(T, 0) - S_s(T, 0) = -\mu_0 H_c(T) \frac{dH_c}{dT}$$

$$-\mu_0 H_c(T) \frac{dH_c}{dT} \geq 0 \quad \longrightarrow \quad S_n(T, 0) - S_s(T, 0) \geq 0$$

At  $T_c$ , where  $H_c = 0 \rightarrow \Delta S = 0 \longrightarrow$  *Second order or continuous transition*



The superconducting state is characterized by **greater order than the normal state**

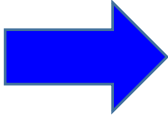
# Thermodynamic of the SC state - Heat Capacity

$$C_H \equiv T \left( \frac{\partial S}{\partial T} \right)_H \quad \text{Remember that} \quad S_s = - \left( \frac{\partial G_s}{\partial T} \right)_H$$

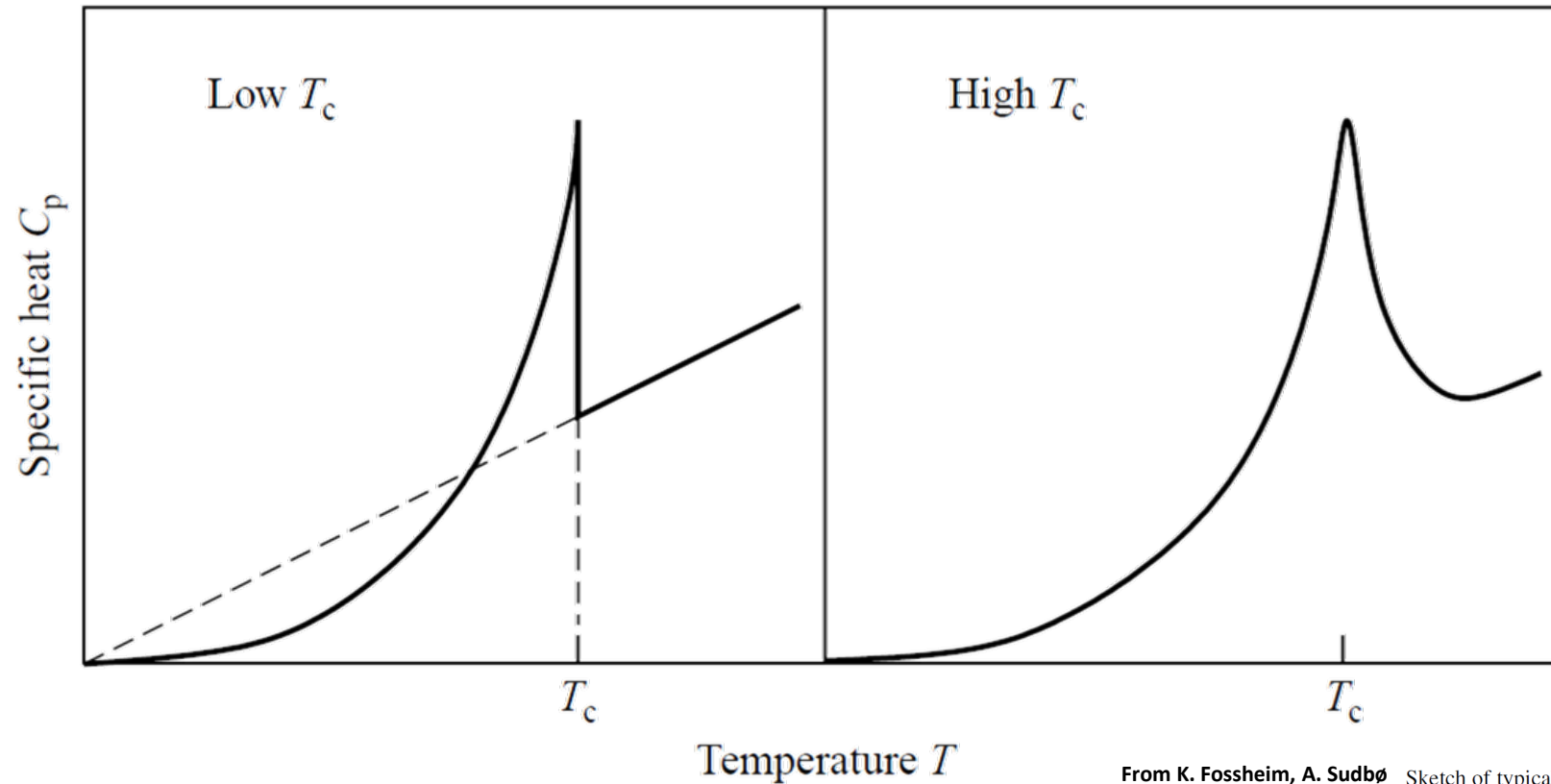
We can calculate HEAT CAPACITY

from the 2<sup>nd</sup> temperature derivate of:  $G_n(T, 0) - G_s(T, 0) = \frac{\mu_0}{2} H_c^2(T)$

$$C_s(T) - C_n(T) = \mu_0 T \left[ \left( \frac{dH_c}{dT} \right)^2 + H_c \frac{d^2 H_c}{dT^2} \right]$$

At  $T_c \rightarrow H_c=0$    $C_s(T) - C_n(T) = \mu_0 T \left( \frac{dH_c}{dT} \right)^2$  **A discontinuity at  $T_c$  is expected**

# Thermodynamic of the SC state - Heat Capacity



From K. Fosheim, A. Sudbø Sketch of typical forms of specific heat curves measured from above the superconducting transition in a mean-field low- $T_c$  metallic superconductor like Al (left), and in a substance with strong superconductivity phase fluctuations like the high- $T_c$  compound YBCO (right).

**Discontinuity at  $T_c$  verified in the experiments**



# Heat capacity

Element	$T_c$ in K	$(C_S - C_N)$ thermal data	$(C_S - C_N)$ magnetic data
		in $10^{-3} \text{ W} \cdot \text{s} / (\text{mol} \cdot \text{K})$	
Sn <sup>a)</sup>	3.72	10.6	10.6
In <sup>a)</sup>	3.40	9.75	9.62
Tl <sup>b)</sup>	2.39	6.2	6.15
Ta <sup>a)</sup>	4.39	41.5	41.6
Pb <sup>b)</sup>	7.2	52.6	41.8

<sup>a)</sup> Mapother, D. E.: IBM Journal 6, 77 (1962).

*From Buckel-Kleiner*

<sup>b)</sup> Shoenberg, D.: »Superconductivity«. Cambridge University Press 1952.

# Bibliography of this part

- W. Buckel, R. Kleiner, "[Superconductivity - Fundamentals and Applications](#)", Wiley  
**Introduction**  
**Chapter 1 - Fundamental Properties of Superconductors**  
**Paragraph 4.6.1 Critical Field and Magnetization of Rod-Shaped Samples**
- K. Fossheim, A. Sudbø, "[Superconductivity - Physics and applications](#)", Wiley  
**I – Basic topics**  
**Chapter 1 - What is superconductivity? A brief overview**