

MME 467: Ceramics for Advanced Applications

Lecture 23

Superconductivity

Ref: Richerson, Dekker, 2nd Ed., 1992, pp.239–248.

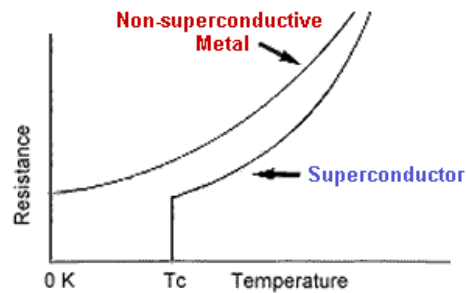
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Topics to discuss

- Discovery and development
- Properties and theory
- Applications

What is a Superconductor ?

- ❑ Superconductivity is the ability of certain materials to conduct electrical current with no resistance.
- ❑ Thus, superconductors can carry large amounts of current with little or no loss of energy.
- ❑ Most materials will only superconduct, at very low temperatures, near absolute zero.
- ❑ Above a certain **critical temperature, T_c** , the material may have conventional metallic conductivity or may even be an insulator.
- ❑ As the temperature drops below the critical point, resistivity rapidly drops to zero and current can flow freely without any resistance.



Linear reduction in resistivity as temperature is decreased:

$$\rho = \rho_0 [1 + \alpha(T - T_0)]$$

ρ = resistivity

α = the linear temperature coefficient of resistivity.

Resistivity: $\rho_s \sim 4 \times 10^{-23} \Omega \text{ cm}$ for superconductor.

Resistivity: $\rho_m \sim 1 \times 10^{-13} \Omega \text{ cm}$ for non-superconductor metal.

Superconductors have two outstanding features:

[1] Zero electrical resistivity

- ❑ This means that an electrical current in a superconducting ring continues indefinitely until a force is applied to oppose the current.

[2] The magnetic field inside a bulk sample is zero (the Meissner effect)

- ❑ When a magnetic field is applied, current flows in the outer skin of the material leading to an induced magnetic field that exactly opposes the applied field.
- ❑ The material becomes strongly **diamagnetic** as a result.
- ❑ In **the Meissner effect** experiment, a magnet floats above the surface of the superconductor.

Discovery & Development



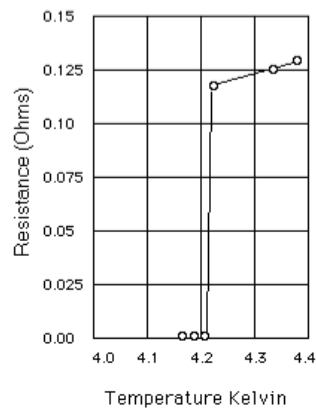
Heike Kamerlingh Onnes
(1853 – 1926)

1908: Liquid He with a boiling temperature of 4.2 K

1911: Mercury with liquid He cooling
→ No resistance measured ($<10^{-27} \Omega \cdot m$)

“When the temperature cooled to ~4.2 K, mercury has passed to a new state, may be called the superconductive state”

Noble Prize on low temperature physics in 1913



The Kamerlingh Onnes resistance measurement of mercury.

At 4.15K, the resistance suddenly dropped to zero.

- ❑ Sn: ~3.8 K; Pb: ~6 K
- ❑ Current was running after one year in a loop of Pb wire cooled in liquid He.
- ❑ V & Nb were also found to be superconducting with low superconducting temperatures and current densities. Once a current exceeds the critical current density, or if there is a magnetic field which exceeds the critical field, the material becomes non-superconducting.

Alloys and metallic compounds (from 1950)

- ◆ V₃Si : 17 K (1952)
- ◆ Nb₃Sn : 18 K
- ◆ Nb₃Ge : 23 K (1973)
- ❑ Have much higher critical temperature (T_c), current density (J_c) and critical magnetic field (H_c)
 - ➔ **Essential for providing high magnetic fields.**
- ❑ Nb₃Ti & Nb₃Sn : $J_c = \sim 10^6 \text{ A/cm}^2$
 - ➔ **Superconducting magnets** for magnetic resonance imager (MRI) & scientific research.

Other chemical compounds:

- ◆ NbN : 17.3 K
- ◆ PbMo₆S₇ : 15.2 K
- ◆ MoC : 14.3 K

High temperature superconductors

La-Ba-Cu-O system:

- ❑ Bednorz and Müller in IBM Zurich in January 1986; $T_c \sim 30$ K
- ❑ Further confirmed by the researchers from Tokyo University on the Fall Meeting of Materials Research Society (MRS) in Boston.



K. A. Müller

J. G. Bednorz

The discovery of superconductivity in ceramic materials

The Nobel Prize in Physics in 1987

Y-Ba-Cu-O system (YBCO)

$\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ Y123 $T_c = \sim 92$ K

Has two crystal structures:

- $d < 0.5$, orthorhombic; $a = 3.827$, $b = 3.882$, and $c = 11.682$ Å; this phase is superconductive;
- $d > 0.5$, tetragonal; $a = b = 3.9018$, and $c = 11.9403$ Å; this phase is non-superconductive

T_c is a function of oxygen contents, an oxygen annealing is needed to ensure high oxygen contents in order to achieve the highest possible T_c ;

The lower critical field H_{c1} is low, but H_{c2} is high, ~ 200 - 300 Tesla at 0 K;

Single crystal : $J_c = 1.5 \times 10^6$ A/cm² at 4 K, 1×10^4 A/cm² at 77 K

Polycrystalline : 100-1000 A/cm² at 77 K

Film : 5×10^7 A/cm² at 4 K at 0-1 T field, 5×10^6 A/cm² at 77 K

$\text{YBa}_2\text{Cu}_4\text{O}_8$ Y124 $T_c = \sim 85$ K

$\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{14}$ Y247 $T_c = \sim 92$ K

Bi-Sr-Ca-Cu-O system: 1988 by H. Meada (Japan)

$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	Bi2201	$T_c < 30 \text{ K}$
$\text{Bi}_2\text{Sr}_2\text{CaCuO}_7$	Bi2212	$T_c = \sim 85 \text{ K}$
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	Bi2223	$T_c = 110 \text{ K}$

- Bi2212 & Bi2223 have perovskite structure with tetragonal unit cells; Bi2212 has 2 layers of Cu-O and Bi2223 has 3 layers of Cu-O
- Comparison between YBCO and BSCCO:
 - i) Bi2223 has a higher T_c than YBCO;
 - ii) BSCCO crystals cleave easily along (001) planes, making it easy to be textured with mechanical deformation;
 - iii) No “oxygenation” process is needed because the oxygen content in BSCCO is relatively stable
 - iv) BSCCO compounds have better stabilities in water containing environments

Tl-Ba-Ca-Cu-O system

By Shen & Hermann with $T_c = \sim 125 \text{ K}$;

- Have a higher T_c than YBCO and BSCCO superconductors;
- Their crystal structures are similar with tetragonal unit cells;
- J_c and H_c are also high
- Highly poisonous

Hg-Ba-Cu-O system

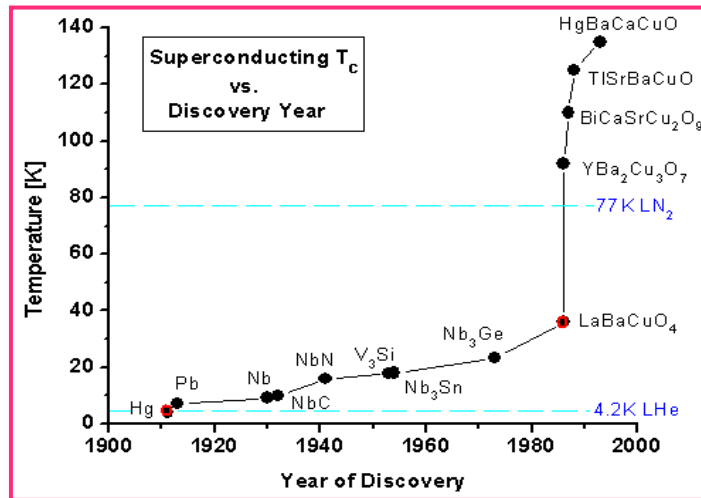
Hg-Ba-Ca-Cu-O system

By Houston University with $T_c = \sim 130\text{-}160 \text{ K}$

- Superconductors with T_c around 200 K, 250 K, and even 0°C were reported but were too difficult to reproduce.

HTSC thin films:

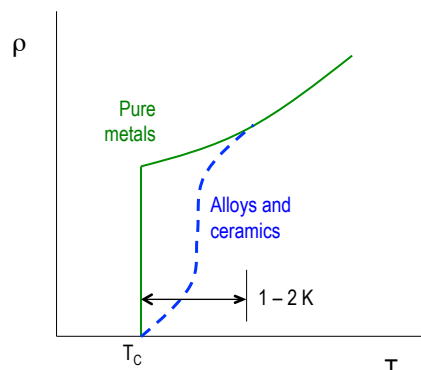
YBCO thin films by sputtering, laser deposition, molecular beam epitaxy, and metal-organic chemical vapour deposition



Properties & Theory

1. Critical temperature (T_c)

- ❑ The critical transition temperature below which a normal conducting material loses its resistivity and begins to be superconductive.
- ❑ T_c is definite for a material.
- ❑ The superconducting transition is reversible !!
- ❑ The transition temperature often varies with the atomic mass, m_a , according to



$$(m_a)^\alpha T_c = \text{Constant} \quad \alpha = \text{material constant (isotope effect)}$$

As an example, T_c for mercury varies from 4.185 K to 4.146 K when m_a changes from 199.5 to 203.4 atomic units.

Critical Temperatures of Some Superconducting Materials

Materials	T _C (K)	Materials	T _C (K)
<i>Elements</i>		<i>Compounds</i>	
Tungsten	0.01	PbTl ₂	3.8
Titanium	0.53	V ₃ Si	17.1
Zirconium	0.70	Nb ₃ Sn	18.3
Zinc	0.79	Nb ₃ Ge	23.0
Uranium	0.80	<i>Ceramic compounds</i>	
Aluminium	1.14	La ₂ Ba ₂ CuO ₄	40.0
Tellurium	2.38	YBa ₂ Cu ₃ O ₇	92.0
Mercury	4.15	Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₁₀	110.0
Lead	7.26	Tl ₂ Ba ₂ Ca ₂ Cu ₃ O ₁₀	125.0
Niobium	9.22	HgBa ₂ Ca ₂ Cu ₂ O ₈	133.0

- Depending on T_C, two types of superconductor:
 - [1] Low T_C superconductors
 - [2] High T_C superconductors

Effect of Variables on T_C

Effect of Pressure

Pressure ↑, T_C ↑

High T_C superconductors – High pressure

Thermal Properties

Entropy & Specific heat ↓ at T_C

Disappearance of thermo electric effect at T_C

Thermal conductivity ↓ at T_C – **Type I superconductors**

Stress

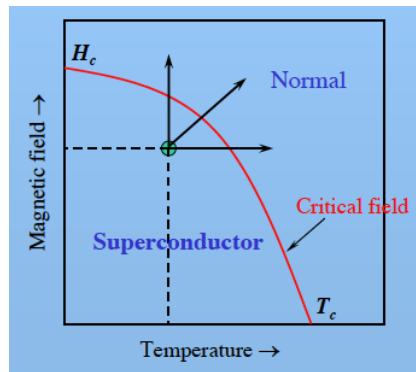
Stress ↑, dimension ↑, T_C ↑, H_C affected

Frequency

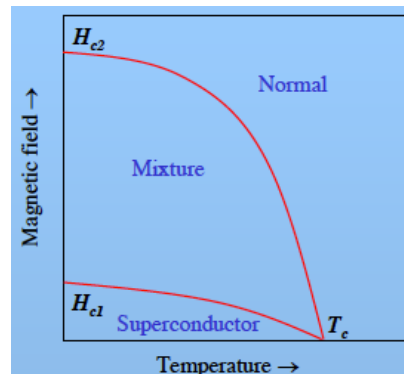
Frequency ↑, Zero resistance – modified, T_C not affected

2. Critical magnetic field

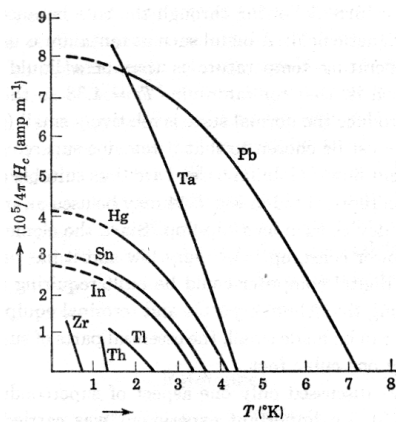
- ❑ The “critical field” or maximum magnetic field that a superconductor can endure before it is “quenched” and returns to a non-superconducting state.
- ❑ Usually a higher T_c also brings a higher H_c .



Type-I superconductor: metals (exclusive V & Nb)



Type-II superconductor: V, Nb, alloys, compounds and HT SC



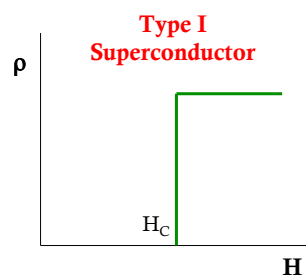
$$\left. \begin{array}{l} T = 0 \text{ K} \quad \frac{dH_c}{dT} = 0 \\ T = T_c \quad H_c = 0 \\ 0 < T < T_c \quad \frac{dH_c}{dT} < 0 \end{array} \right\} \longrightarrow H_c(T) = \frac{H_c(0)}{1 - \left(\frac{T}{T_c}\right)^2}$$

↓
 Critical field at $T = 0 \text{ K}$

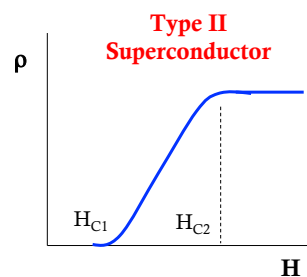
The critical magnetic flux density (B_C) and magnetic field at 0 K (H_0) of a number of superconducting materials

Materials	B_C (telsa)	H_0 (A/m)	Materials	B_C (telsa)
Tungsten	0.0001	91.5	Nb-Ti alloy	12
Titanium	0.0056	4450-7960	Nb-Zr alloy	11
Aluminium	0.0105	8360	$Pb_8Mo_6S_8$	45
Tin	0.0305	24300	V_3Ga	22
Mercury	0.0411	32700	Nb_3Sn	22
Lead	0.0803	63900	Nb_3Al	32
Niobium		156800	Nb_3Ge	30

- On the basis of magnetic response, superconducting materials may be divided into two classifications designated as type I and type II.



- ❖ Sudden loss of magnetisation
- ❖ Exhibit Meissner Effect
- ❖ No mixed state
- ❖ $H_c \sim 1$ tesla
- ❖ Soft superconductor
- ❖ Eg. – Al, Pb, Sn, Hg



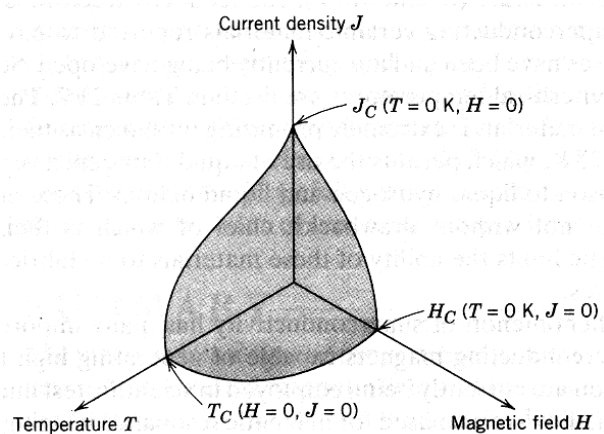
- ❖ Gradual loss of magnetisation
- ❖ Does not exhibit complete Meissner Effect
- ❖ Two H_C s – H_{C1} & H_{C2} (≈ 30 tesla)
- ❖ Mixed state present
- ❖ Hard superconductor
- ❖ Eg. – Nb-Sn, Nb-Ti, ceramic SCs

3. Critical current

- ❑ The magnetic field that causes a superconductor to become normal is not necessarily an external applied field; it may also arise as a result of electric current flow in the conductor.
- ❑ superconductivity in a long circular wire of radius r may be destroyed when the current I exceeds the value I_c , which at the surface of the wire produce the critical magnetic field H_c .

Hence, the critical current

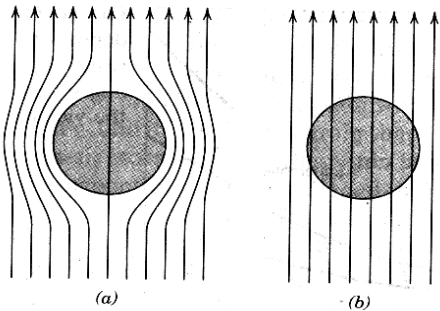
$$I_c = 2\pi r H_c \quad \text{Silsbee's rule}$$



The superconducting envelope, showing the combined effects of temperature, magnetic field, and current density. Conditions within the envelope produce superconductivity.

4. Meissner effect

Diamagnetism tied to zero electrical resistance (i.e., $\rho = 0$ and $B = 0$) in a superconducting material results in special behaviour referred to as the *Meissner effect*.



Representation of the Meissner effect. (a) While in superconducting state, a body of material (circle) excludes a magnetic field (arrow) from its interior. (b) The magnetic field penetrates the same body once it becomes normally conductive.

- When a magnetic field is applied to a conducting material, the changing flux creates an electric field that sets up eddy current, which opposes the applied magnetic field.
- Because of the resistivity of material, eddy current decays, and the lines of magnetic force penetrate the material as if it were not there.
- In case of superconductor, because of the absence of resistivity, eddy currents do not decay. They produce a mirror image magnetic field that completely cancels the applied magnetic field.

Thus, a semiconductor may be regarded as a perfect **diamagnet**, where the magnetic field does not penetrate, but is repelled.

Magnetic Levitation

- Magnetic fields are actively excluded from superconductors (Meissner effect).
 - If a small magnet is brought near a superconductor, it will be repelled because the induced supercurrents will produce mirror images of each pole.
 - If a small permanent magnet is placed above a superconductor, it can be levitated by this repulsive force
-
- The Meissner effect is limited by the strength of the flux.
 - Strong fields will destroy superconductivity and the Meissner effect will disappear.

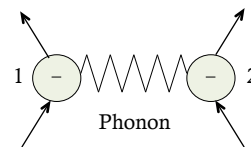


BCS Theory of Superconductivity



Bardeen, Cooper & Schrieffer - BCS theory, 1957
Received the Nobel Prize for Physics in 1972

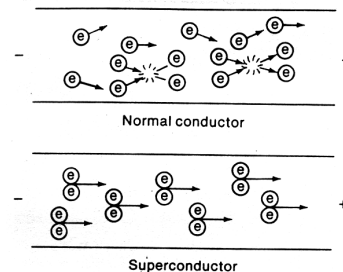
- ❑ A pair of electrons close to the Fermi level will couple into a **Cooper pair** through interaction with the crystal lattice.
- ❑ This pairing results from a slight attraction between the electrons related to lattice vibrations.



Schematic of a Cooper pair

- ❑ The motions of all of the Cooper pairs within a single superconductor are correlated; they constitute a system that functions as a single entity.
- ❑ Application of an electrical voltage to the superconductor causes all Cooper pairs to move, constituting a current.

- ❑ When the voltage is removed, current continues to flow indefinitely because the pairs encounter no opposition.
- ❑ For the current to stop, all of the Cooper pairs would have to be halted at the same time, a very unlikely occurrence.



Schematic illustration of the BCS theory illustrating the difference between normal conduction and zero-resistance superconduction

- ❑ A finite amount of energy is needed to break Cooper pair apart into two independent electrons. This means there is an “energy gap” for “single-particle excitation”.
- ❑ As temperature increases, more electron pairs will be broken up, and the attractive force in the unbroken pairs will be decreased.
- ❑ At a critical temperature, all the electron pairs will be broken, the energy gap vanishes and superconductivity ceases to exist. This temperature is the **critical transition temperature** of superconductivity.

Applications

1) Superconductor magnets:

- ❑ A small magnet can provide a huge magnetic field; the energy loss is minimum
- ❑ Current & potential industrial applications: Magnetic resonance imaging system (MRI) for medical diagnostics and research; Ore refining/separation; Radio-frequency devices for navigation; Magnetic shielding

2) Electric power utilities:

- ❑ Power transmission; Superconducting generators & motors; Superconducting magnetic energy storage (SMES); Transportation tools; Josephson effect; Superconducting quantum interface devices (SQUID)

Trade off between:

Cost Saving

and

Cost Increase

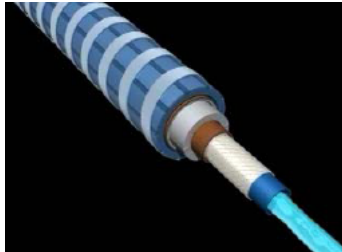


*Zero resistance,
no energy lost,
novel uses...*

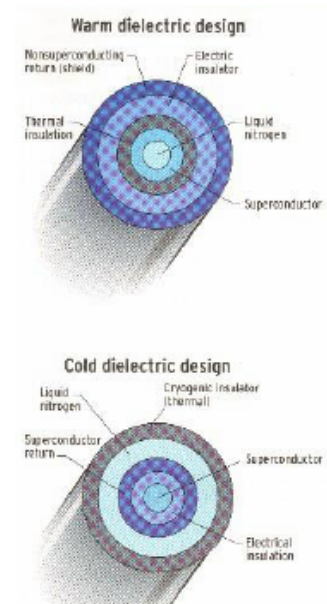


*Need refrigeration,
fabrication costs....*

Superconducting Cable



- ❑ The cable configuration features a conductor made from HTS wires wound around a flexible hollow core.
- ❑ Liquid nitrogen flows through the core, cooling the HTS wire to the zero resistance state.
- ❑ The conductor is surrounded by conventional dielectric insulation. The efficiency of this design reduces losses



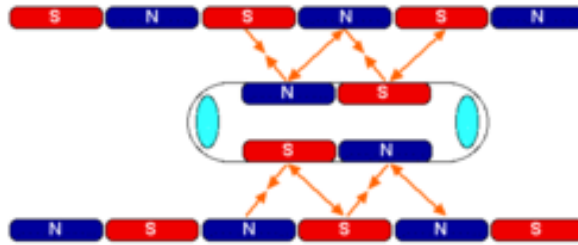
Magnetic Levitated Train

- ❑ 1960s, Dr. H. Kolmat MIT suggested that a train would fly along a frictionless track supported by a powerful magnetic field
 - ➔ magnetically levitated train
- ❑ 1987, the Japanese demonstrated a prototype maglev train, MLU-002, travelled 520km/hour and flew ~10 cm above the track

Principle: Electro-magnetic induction

Magnetic levitation transport, or **maglev**, is a form of transportation that suspends, guides and propels vehicles via electromagnetic force. This method can be faster than wheeled mass transit systems, potentially reaching velocities comparable to turboprop and jet aircraft (500 to 580 km/h).





- ❖ The track are walls with a continuous series of vertical coils of wire mounted inside. The wire in these coils is not a superconductor.
- ❖ As the train passes each coil, the motion of the superconducting magnet on the train induces a current in these coils, making them electromagnets.
- ❖ The electromagnets on the train and outside produce forces that levitate the train and keep it centered above the track. In addition, a wave of electric current sweeps down these outside coils and propels the train forward

Advantages

- No need of initial energy in case of magnets for low speeds
- One litre of liquid nitrogen costs less than one litre of mineral water
- Onboard magnets and large margin between rail and train enable highest recorded train speeds (581 km/h) and heavy load capacity. Successful operations using high temperature superconductors in its onboard magnets, cooled with inexpensive liquid nitrogen
- Magnetic fields inside and outside the vehicle are insignificant; proven, commercially available technology that can attain very high speeds (500 km/h); no wheels or secondary propulsion system needed
- Free of friction as it is “Levitating”

Medical Applications



- ❑ MRI (Magnetic Resonance Imaging) scans produce detailed images of soft tissues.
- ❑ The superconducting magnet coils produce a large and uniform magnetic field inside the patient's body.

Next Class

Lecture 27
Magnetic Properties