Historical Development of Superconductivity: Conventional, High Temperature Superconductor and its Various Applications

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Abstract: A brief historical development to phenomenon of superconductivity. Main discovery and Nobel prize winner with their contribution in this field is also discussed. main feature of superconductivity like as transition temperature for different material, Meissner effect, Isotope effect, type I and type II superconductor, penetration depth, coherence length, London equations, energy gap, entropy, flux quantization etc is briefly discussed. This review research paper take a very simple approach to explain the various properties of conventional superconductor and high temperature superconductor and its various application in many field. Recent development with proper sequencing in the phenomenon of superconductivity is also elaborated here.

Keywords: Superconductivity, high temperature superconductor, SQUID etc

Introduction: Kamerlingh Onnes in 1911 discovered the superconductivity in mercury at extreme low temperature 4.2K. In this phenomenon resistance of the substance drops to zero and substance also shows the diamagnetic behavior .temperature below which a substance shows superconducting behavior is known as transition temperature. Generally superconducting behavior is shown by the substance at extremely low temperature and high pressure. Superconductivity is found in many metallic elements of the periodic system and also found in mix alloys, intermediate compounds and semiconductors. Mixed compound like as Nb_3Sn, Nb_3Ge and Nb_3Al shows the phenomenon of superconductivity at temperature 18K, 32.2K and 17.5K respectively. Cesium become a superconductor at temperature Tc = 1.5K at a pressure of 110Kbar. Generally materials having high normal resistivity exhibit superconductivity and $n\rho > 10^6$ is a best criteria for existence of superconductivity where n= no. of valence electron per cubic centimeter and ρ is the resistivity at 20℃. When the critical current $I_c(t)$ passing through the superconductor then again it like a normal conductor. Amorphous thin film of Be, Bi and Fe show superconductivity and at very high pressure, amorphous thin film of Be,,Bi and Fe shows superconductivity. Good conductor like as Ag, Au, Cu do not show superconductivity even at very low temperature. Ferromagnetic and antiferromagnetic material are not superconductor at all.

Historical Development of Superconductivity: In table 1.1 we have discussed year wise development in the field of superconductivity and it also contain name of scientist and their contribution. In table 1.2 we have discussed year wise Nobel prize winner in the field of superconductivity and their contribution.

Table 1.1: Important events in the field of superconductivity

Year	Scientist	Contribution
1911	H.Kamerlingh Onnes	Discovery of superconductivity
1933	Walter Meissner and Robert Ochsenfeld	Magnetic flux expelled from superconductor below transition temperature
1935	London Brothers	London equations, Penetration depth and existence of energy gap
1944	Gorter- Casmir	Superconductor as a mixture of superconducting and normal electrons
1950	Vitaly Ginzburg and Lev Landau	All the electron pairs condensed into a macroscopic quantum states
1952	Frohlich	Electron could attract each other due to distortion of the lattice
1955	Bardeen, Cooper and Schrieffer	Explanation of superconductivity
1960	Giaever	Measuring the energy gap
1962	Brain Josephson	Josephson effect
1975	Sleight, Gilson and Bierstadt	Superconductivity at 13 K in mixed compound of Ba, Pb, Bi and oxygen
1980	Juri Matisoo	Josephson computer
1986	Binning and Rohrer	Scanning tunneling microscope
1987	George Bednorz	Superconductivity in perovskite crystals
1988	Robert Cava and Bertram Batlogy	Superconductivity around 30K in mixed compound of Ba, K, Bi and O

Table 1.2: Nobel Laureates in Superconductivity

Year	Scientists	Contributions
1913	H.Kamerlingh Onnes	Discovery of superconductivity
1962	Lev Landau	Theories for condensed matter specially helium
1972	Bardeen, Cooper and Schrieffer	BCS Theory of Superconductivity
1973	Leo Esaki and Ivar Giaever	Tunneling phenomenon in superconductivity
1978	P.L Kapitsa	Discovery of superfluidity in helium
1987	J.Georg Bednorz and K.A.Muller	Discovery of superconductivity in ceramic materials
1996	David Lee, Douglas.Osheroff and R.C.Richardson	Discovery of superfluidity in He-3
2003	Alexei Abrikosov, V.L Ginsburg, A.J Leggett	Contribution to theory of superconductor and superfluids

Main features of Superconductivity:

1. Generally superconductivity is shown by those substances which have number of valence electron between 2 and 8.
2. A sufficient strong magnetic field will destroy superconductivity and critical magnetic field B_c depends upon the temperature T.

$$B_c(T) = B_{c0}\left[1 - \left(\frac{T}{T_c}\right)^2\right]$$

3. Isotope Effect: according to this effect critical temperature T_c depends upon the mass of atom constituting the crystal lattice by the expression
$M^{\alpha}T_c$ =constant

Table 1.3:Isotope effect in Superconductors

Substance	α
Zn	0.45±0.05
Cd	0.32±0.07
Sn	0.47±0.02
Hg	0.50±0.03
Pb	0.49±0.02
Tl	0.61±0.10
Ru	0.00±0.05
Os	0.15±0.05
Mo	0.33
Nb_3Sn	0.08±0.02
Mo_3Ir	0.33±0.03
Zr	0.00±0.05

Ref. J.W. Garland Jr Physical Review Letters 11,114(1963) revised by Dr. V.Compton

4. **London Equations:** Superconductivity is a purely macroscopic phenomenon and according to this theory total number of electrons per unit volume is equal to sum of normal electrons and super electrons.
n = n_s+n_n where n_n = number of normal electrons per unit volume n_s = number of super electrons per unit volume
from the Newton's equation of motion $m\dot{v_s} = eE$

$$J_s = en_s v_s \text{ and } \frac{dJ_s}{dt} = en_s\left[\frac{dv_s}{dt}\right]$$

$$\dot{J_s} = n_s e\dot{v_s} = \frac{n_s e^2 E}{m}$$

This is known to be first London equation and according to this expression steady current exist in a superconductor even in the absence of electric field.

According to second London equation we have $\nabla^2 B = \frac{\mu_0 n_s e^2}{m} B$ or $\nabla^2 B = \frac{1}{\lambda_L^2} B$

Where $\lambda_L = \left(\frac{m}{\mu_0 n_s e^2}\right)^{\frac{1}{2}}$ is known to be London penetration depth and solution of above equation

is $B_z(x) = B_z(0)\exp\left[\frac{-x}{\lambda_L}\right]$

This expression shows that flux density or magnetic field decreases exponentially inside the superconductor falling to i/e th of its initial value at a distance equal to London penetration depth. however magnetic field inside the bulk of the superconductor is totally absent.

5. Type I and Type II Superconductor: a good type I Superconductor excludes a magnetic field until Superconductivity is destroy suddenly, and then the magnetic field penetrates completely. A good

type II Superconductor excludes the field completely upto a field up to a field H_{c1} and above this field substance remain Superconducting at a very high field H_{c2}, the magnetic flux penetrates completely and superconductivity is completely destroyed. In type I Superconductor coherence length is longer than penetration depth and most of the pure metal falls into this category. In type II Superconductor coherence length is smaller than penetration depth and most of the alloying elements and mixed compounds falls into this category. In type I superconductor surface energy is always positive and in type II superconductor surface energy becomes negative as magnetic field is increased.

Table 1.4: Properties of some selected superconducting elements

Element	T_c	Type
Be	0.03K	I
Ir	0.11K	I
Cd	0.52K	I
Zn	0.9K	I
Mo	0.92K	I
Ga	1.09K	I
Al	1.19K	I
Sn	3K	I
In	3.40	I
Hg	4.12K	I
Pb	7.175K	I
Nb	9.2K	I
Osmium	.70K	II
Zirconium	0.80K	II
Thorium	1.40K	II
Rhenium	1.70K	II
Thallium	2.40K	II
Tantalum	4.50k	II
Niobium	9.30K	II
Nb-44%Ti	10.5K	II
Nb-25%Zr	10.8K	II
NbN	16K	II
V_3Ga	16.5K	II
V_3Si	17K	II
Nb_3Al	18K	II
Nb_3Sn	18.5K	II
Nb_3Ge	23.2K	II

6. According to BCS theory of superconductivity the cooper pair do not have spin half and so pairs do not follow Pauli exclusion principle rather than such pairs behaved as bosons and they remains in stable collective state and thermal energy is sufficient to destroy this collective state of cooper pairs. The electron –lattice-electron interactions leads to an energy gap and this is responsible for critical field, the thermal properties
   and most of the electromagnetic properties. Basically penetration depth and coherence length emerges as natural consequences of BCS theory.
7. In superconductor, the field states are occupied by cooper pairs and empty band having energy gap E_g is occupied by broken cooper pairs. The band gap or energy gap E_g measures the binding energy of cooper pairs and it can be denoted in terms of critical temperature T_c

$E_g = 3.53\ kT_c$. Cooper pairs have the identical wave functions, the electron system is denoted by macroscopic wavefunction Ψ with which many wave functions of the Cooper pairs overlap and can be denoted as $\Psi = |\Psi_0| \exp i\phi$ where ϕ is the phase between cooper pairs and $|\Psi_0|^2$ is the density of cooper pairs.

8. Entropy is the measurement of the disorder of the system. Since superconducting state is more ordered than the normal state hence entropy is lesser in superconducting state in comparison of normal state.
9. **Josephson Effect:** it is found in two forms DC Josephson effect and AC Josephson effect.
   DC Josephson effect: a Dc current flows across the junction in the absence of any magnetic field or electric field.

AC Josephson effect: when two sheets of superconductor are in close contact through a very thin insulating layer. For example- Nb-NbO-Nb, the due to tunnelling of cooper pair current $i = i_o \sin\theta$ passes through the Josephson junction even without no voltage. Where θ is the phase difference between the wavefunctions of the cooper pair on either side of the junction. Here io is the maximum junction current depends on the thickness of insulating layers and it has the order of microampere to milliampere.

When a voltage V is applied then phase difference θ increase with time around the Josephson junction and then we have frequency $f = \frac{d\theta}{dt} = \frac{2eV}{h}$ since current I change according to sign rule with time t. this is said to be AC Josephson effect. Josephson shared the 1975 nobel prize of physics for this work.

10. **Organic Superconductor:** Jeroem et al in1980 discovered the first organic Superconductor with Tc approximately 1K and around 1990 an organic Superconductor with Tc of 12K was reported. Now a days we are using two known class of organic
    Superconductor
    a) $(TMTSF)_2X$ where TMTSF = tetra methyl tetra selena full Valene, X= PF_6, NbF_6
    b) $(BEDT\text{-}TTF)_2X$ where BEDT-TTF means bis, ethylene dithio tetra thia full Valene and X is a mano valent anion.
11. Heavy Fermion Superconductor: Steglich et al in 1979 reported superconductivity in $CeCu_2Si$ at 0.5K, UBe_{13} at 0.85K and UPt_3 at 0.5K. In these type of Superconductor electronic heat capacity decreases exponentially with temperature.
12. In the mid 80's, copper oxide mix together with the elements lanthanum and barium reported the superconductivity even at temperature greater than 30K, when scientist used strontium instead of barium then superconductivity was shown by temperature greater than 30K. Yttrium-barium-copper-oxide became the first material which shows superconductivity at temperature 92K. now for cooling liquid nitrogen can be used instead of helium and this nitrogen gas is easily available and cheap too.

Table 1.5: Superconducting Materials

Materials	T_c	Pair Symmetry	Crystal Structure
LaH_{10}	260K	s	Under Pressure
H_3S	203K	s	Under Pressure
$HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$	135K	d	Perovskite
$Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$	125K	d	Perovskite
$YBa_2Cu_3O_{6+x}$	90K	d	Perovskite
$NdFeAsO_{1-y}$	54K	ZrCuSiAs type	ZrCuSiAs type
MgB_2	39K	s	Hexagonal
$La_{2-x}Sr_xCuO_4$	36K	d	Perovskite
$Ba_{1-x}K_xBiO_3$	30K	s	Perovskite
$LaO_{1-x}F_xFeAs$	26K	s	ZrCuSiAs type
$CeRu_2$	6.2K	s	Lavis Cubic
$Na_xCoO_2\text{-}YH_2O$	5K	p	Triangular Lattice

13. In 2018 compound involving lanthanum and hydrogen at very high pressure shows the Superconductivity greater than 250K and this was the highest crack temperature in the field of Superconductivity.
14. Recently in October 2020 Rocherster University Ranga Dias et al reports Superconductivity in mixed hydrogen sulphide-hydrogen in methane under extreme high pressure and team observed that photoochemically transformed carbonaceous sulphur hydride system showing the Superconductivity upto the temperature of 288K first time.
15. Critical temperature of the superconductor depends upon debye temperature Θ_D, density of electrons on the fermi surface $N(\varepsilon_F)$ and interaction between electrons V.

    Mathematically we have $T_C = 1.13\theta_D \exp\left[\frac{-1}{N(\varepsilon_F)V}\right]$
16. The first C_{60} superconductor discovered was $K_3\,C_{60}$ with a critical temperature of 18K however $Cs_3\,C_{60}$ have the critical temperature of the order of 38K. experimentally it has been found that when lattice constant increases then critical temperature tends to rise because lattice spacing extension leads to narrow band width and so it resulting in the increase of $N(\varepsilon_F)$.
17. The distance ξ_0 by which the electron moves to form the cooper pair is known to be BCS coherence length. It is given by the expression $\xi_0 = tv_f$ where t is the scale of time to forms cooper pairs and v_f is the fermi velocity. Coherence length is of the order of micrometer to nanometer depending upon fermi velocity.
18. Superconducting state can be described by the magnetic field. Consider a straight wire in which current I is flowing then magnetic field B created by it $B = \frac{\mu_0 I}{2\pi r}$

    At the surface of wire r = R , $B = B_c$ and $I = I_c$ then $I_c = \left(\frac{2\pi R B_c}{\mu_0}\right)$
19. Penetration depth does not have a fixed value rather than it depends upon the temperature T and can be described as $\lambda(T) = \lambda(0)\left(1 - \frac{T^4}{T_C^4}\right)^{-1/2}$

At low temperature it is nearly independent upon the temperature however it increase rapidly and tends to infinite when temperature approach to transition temperature.

20. The thermal conductivity of superconductor under goes a continuous change between the normal and superconducting state and its value is found to be lower in the superconducting state because electronic contribution drops, the superconducting electrons could not play any role in heat transfer.
21. The specific heat in superconducting state can be denoted as $C_{el}(T) = Aexp\left(\frac{-\Delta}{k_B T}\right)$

    this exponential form tell us the existence of finite gap. The specific heat of the material shows in abrupt change at $T = T_c$ and it has a large value below the critical temperature.
22. Consider a superconductor of area A that carries a current I then the amount of magnetic flux B.A passes through the ring. According to Faraday law of induction changing flux will responsible for change the current in the ring so as to oppose the change in flux. Since the ring has no resistance due to superconductivity so change in flux will be perfectly canceled and flux φ is permanently trapped in the ring and this flux is quantized because the phase of wave function of the cooper pairs in the ring must be continuous around the ring.

    Mathematically we have $\varphi = n\left(\frac{h}{2e}\right) = n\phi_0$

$$\phi_0 = \frac{h}{2e}$$

23. Josephson junction are used in making sensitive magnetometers called SQUIDS (superconducting quantum interference devices). Magnetic field change as small as 10^{-21} tesla can be detected by SQUIDS. This device is highly useful for detection of heart and brain disease.
24. Quantized magnetic flux can penetrate the inside of the material beyond the critical magnetic field H_{c1}, on the other hand, if the magnetic field reaches the upper critical field H_{c2} the superconductivity disappears. The region between H_{c1} and H_{c2} is known as the mixed state, in this region superconducting state coexist inside the material.
25. The history of high temperature superconductivity starts in 1986 with discovery of superconductors in Ba-La-Cu-O system by Bednorz and Muller in 1986 and they were awarded Nobel prize for the same.
26. Superconducting magnets are used in MRI and most particles accelerators are cooled with liquid helium but helium is a very rare and expensive substance.

Chronological Development in the field of superconductivity: In table 1.6 different mixed compounds with their transition temperature is discussed and in this table we have discussed name of discoverer and year of discovery. In table 1.7 different mixed compounds with their transition temperature is discussed. In table 1.8 different mixed compounds with their transition temperature with period is discussed.

Table 1.6: Discovery of Mixed Compounds

Material	Highest T_c	Year of discovery	Discovered by
$Ba(Pb,Bi)O_3$	13K	1975	-
$(La,Ba)_2CuO_4$	35K	1986	J.G Bednorz & K.A Muller
$Yba_2Cu_3O_7$	90K	1987	M.K Wu & C.W Chu
Bi-Sr-Cu-O	22K	1987	Micheal et al
Bi-Sr-Ca-Cu-O	100K	1987	Maeda and Tarascan
Tb-Ba-Ca-Cu-O	122K	1988	Sheng & Hermann
Hg-Ba-Ca-Cu-O	130K	1992	Putilin & A. Schililing
$L_{2-x}Ce_xCuO_{4+y}$ Lx= Pr,Nd etc	25K	1989	Tokura, Takagi & Uchida

Table 1.7: High Temperature Superconducting Mixed Compounds

Mixed Compound	Transition Temperature
$BaPb_{0.73}Bi_{0.27}O_3$	13K
$Nb_3Al_{0.75}Ge_{0.25}$	20.7K
$Ba_{1-x}K_xO_{3-y}$	29.8K
LaBaCuO	90K
$Y_1Ba_2Cu_3O_7$	92K
$(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$	105K
BiSrCaCuO	110K
TlBaCaCuO	125K
$Hg_1Ba_2Ca_2Cu_3O_y$	135K
Transformed Carbonaceous Sulfur Hydride	287K(Recently discovered)

Table 1.8: High Temperature Superconductor

Period	Substance	Critical temperature Range
1910-20	Hg and Pb	4-6 K
1937-38	Nb	9.50K
1940-80	NbN, Nb_3Sn,V_3Si	10-20K
1980-90	BkBo	32K
2000-05	MgB_2	41K
2005-10	SrFFeAs	53K
2010-15	FeSe	100K
2015-20	Carbonaceous Sulphure Hydride System	288K

Recent Development in field of Superconductivity: Cava et al in 2000 reports that copper oxide superconductors are the most important high temperature superconductors and they have wide practical applications in various fields. Schilling and Cantoni discovered the superconductivity in the Hg-Ba-Cu-O system at T_c =153 K. Manfred Sigrist in 1988 reports time reversible symmetry breaking states in various type of high temperature superconductor. Bellcore in 1987 observed the superconductivity in the mixed compound YBa2Cu3O7-δ around the temperature 90K and Japnese Scientist observed the superconductivity in BiSr-Ca-Cu-O compound with a temperature around 120K A.M Hermann and Z.Z.Sheng at the University of Arkansas observed the superconductivity in a compound Tl-Ba-Ca-Cu-O with an onset temperature near 140K in the resistivity transition and at temperature 118 K in the diamagnetic transition. Japnese Researchers team in the leadership of H.Maeda announce the superconductivity in Bi-Sr-Ca-Cu-O compound with an onset at 120K in the resistance transition and at 110K in the transition towards perfect diamagnetism.

Application of Conventional and High Temperature Superconductors

1. Magnetic Resonance Imaging: this is a medical imaging technique that provide a 2D picture of tumors, fractures and other abnormalities in different part of the body. In Magnetic resonance imaging method we needed a magnetic field in appropriate amount for recording images. Therefore superconducting magnet which have no power requirement due to zero resistance phenomenon- once electric current flow in the superconducting wire the power supply may be switched off because current can persist now upto infinite time till then temperature is kept below the transition temperature of the superconductor.
2. Diagnosis using SQUID: SQUID is highly sensitive to small magnetic fields and it can be able to detect the magnetic field from the heart which is of the order of 10^{-10} Tesla and even in the brain which is of the order of 10^{-13} Tesla so it can detect the heart and brain disease at initial stage.
3. Magnetic Levitation: high temperature superconductor behaves as a diamagnetic substance therefore when any magnetic field comes in contact with HTSC then they repelled and this phenomenon could be used in creating vehicles that moves using the principle of Levitation, on this principle peoples have developed Maglev trains. These trains have a very high efficiency because train never touch the track and therefore fraction losses are negligible. Now a days China and Japan are leading in the field of Magnetic Levitation, trains supremacy is found in Asian countries. James Powell and Gordon Danby of Brookheaven received the first patent for a magnetically levitated train design in late 1960 and China was the first country which create the magnetic levitation system.
4. Superconducting Transmission System: Below critical temperature , HTSC shows zero resistance , therefore transmission Superconducting wire can reduced the ohmic losses and so efficiency could be increased.

5. Magnetic Accelerators: Particle accelerators are needed to accelerate small particle to high speed for physics research experiment specially in nuclear physics then scientist can study their collision and corresponding phenomenon. Large Hadron Collider is an example of such experiments.
6. HTSC Motors: These type of motors are highly useful because such motors have more power efficiency, lower noise, lesser weight and lesser size too.
7. Bearing and Flywheel Energy storage: Various type of HTSC material are used for this purpose and this mechanism are highly useful in various mechanism.
8. Electronic and small Devices: Superconducting materials can be used for making Josephson devices like as square law detector, parametric amplifier, mixer. Superconducting materials also can be used as electromagnetic shielding and they can also be used as a bolometer.
9. Computer and Information Processing: Superconducting materials can be used as a semiconductor, Superconductor hybrids and active Superconducting elements like FET. They also can be used for voltage standard in optoelectronics and can act as a Malched filters.
10. Energy related mechanism: Superconducting materials can be used for production of energy by magnetic fusion and magnetohydrodynamics. They also can be used for magnetic energy storage and electric power transmission.
11. Transformation: Superconducting materials can be used in high speed trains and ship drive systems.

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