Module 7: High temperature Superconductors

Introduction

In addition to the dielectric and magnetic ceramic materials we discussed in earlier modules, there are a few more ceramics which are rather different and exhibit unusual characteristics about which we normally do not find any mention in the standard text books. One such category belongs to high temperature superconductors, which became an intense topic of research after the discovery of superconductivity in an oxide of Ba-La-Cu-O at 40 K[1]. This was soon followed by discovery of high temperature superconductivity at 90 K[2] in another oxide, Y-Ba-Cu-O, whose structure was shown in Module 1. In this module, we discuss some fundamental aspects of superconductivity in general followed by a brief discussion on high temperature superconducting materials which are typically oxide ceramics.

The Module contains:

Suggested Reading:

- Principles of Electronic Ceramics, by L. L. Hench and J. K. West, Wiley

[1] Bednorz and K.A. Muller, Z. Phys. B, 64, 189 (1986)

[2] M.K. Wu et al, Physical Review Letters, 58, 908 (1987)

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7.1 Background

Superconductors are materials which, when cooled below room temperature, exhibit a sudden drop of electrical resistance of the material to exactly zero at a temperature called as critical temperature, T_C. The phenomenon was discovered by Heike Kamerlingh Onnes in 1911when he was studying properties of mercury at liquid helium temperatures.

Most first generation superconductors were elemental metals and metallic alloys. While most pure elemental materials like tin, aluminum were called as type-I superconductors, metallic alloys like niobium nitride, niobium-titanium, and niobium-germanium alloys were classified as type-II superconductors. However, most of these are superconducting at temperatures below 30 K.

The onset of superconducting transition is also accompanied by abrupt changes in various physical properties such as heat capacity, which can be associated with a phase transition. For instance as shown in figure 1, while in the non-superconducting (normal) regime, the electronic heat capacity is proportional to the temperature i.e. C_V T, at T_C, it shows an abrupt jump and does not remain linear in the superconducting regime, varying as C_V T^{-aT} where a is a constant. The nature of phase transition depends upon the type of superconductor.

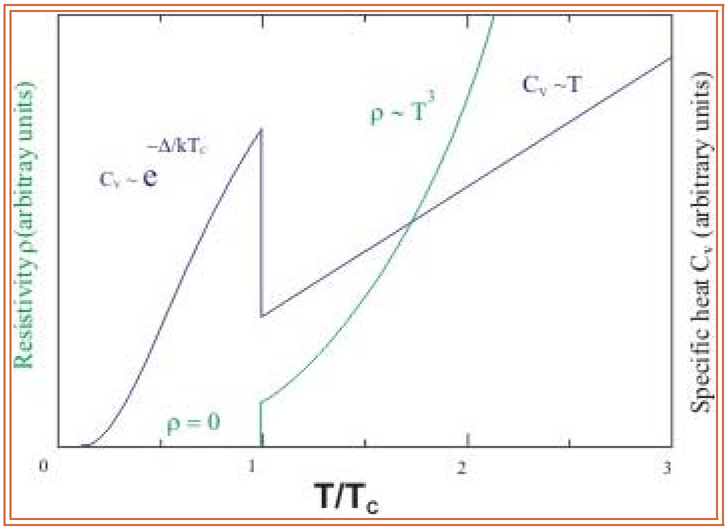

Figure 7.1 Schematic of superconducting transition (green line: resistivity; blue line: specific heat)

Superconductivity is also a quantum mechanical phenomenon like magnetism and a modern well accepted theory was developed by Bardeen-Cooper- Schrieffer[3] in 1957 for which they won Physics Noble prize in 1972. They explained superconducting current as a superfluid of Cooper pairs, pairs of electrons interacting through the exchange of photons.

Another point to note is that while low resistivity is a necessary condition for a material to be a superconductor, it is not sufficient.

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[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175–1204 (1957)

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7.2 Meissner Effect

Meissner effect essentially describes the response of a superconducting material when placed in a magnetic field. It was discovered by W. Meissner and R. Ochsenfeld in Germany in 1933.

When a superconductor is placed in an external magnetic field H ($H < H_c$) and cooled belowT_C, the magnetic field does not penetrate into the material completely. The field penetrates up to a very small depth decaying exponentially and is of the order of 100 nm or so, and is called as London penetration depth, *l*.

The Meissner effect is often confused with the diamagnetism as predicted by Lenz's law which states that application of a changing magnetic field to a conductor induced a magnetic moment which opposes the applied field magnetic field. In a perfect conductor, an arbitrarily large current can be induced, and the resulting magnetization exactly cancels the applied field giving rise to $\chi = -1$.

In contrast, Meissner effect implies spontaneous expulsion of magnetic flux lines which occurs during transition to superconductivity. So when the material is in normal state at $T > T_C$, the flux lines would penetrate but when it reaches superconducting state at $T < T_C$, the magnetic flux lines would be abruptly expelled which is NOT Lenz's law. It is not a diamagnetic effect which, in a normal material, is caused by opposite moment developed due to orbiting electrons.

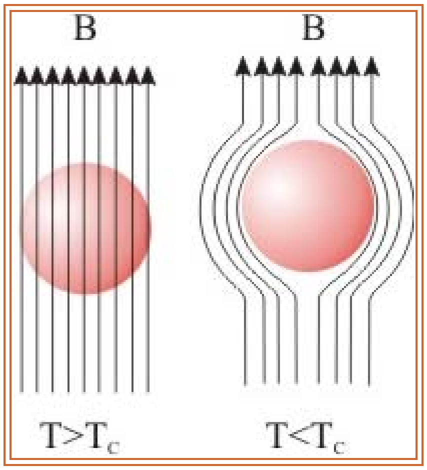

Figure 7.2 Meissner Effect

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7.3 The Critical Field, H_c

Similarly, at a fixed temperature below the critical temperature, superconducting materials cease to remain superconducting when they are placed under an external magnetic field which is greater than a critical magnetic field (H_c). The field follows a parabolic form with temperature T and is given as

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

where H_0 is a constant while T_C is the critical temperature i.e. the onset of the superconductivity. This is shown to be because the Gibbs free energy of the superconducting phase increases quadratically with the magnetic field while the free energy of the normal phase is roughly independent of the magnetic field.

The difference between type-I and type-II superconductors is that while type-I superconductors exhibit a distinct boundary between superconducting and normal state, type-II superconductors show a region of mixed normal and superconducting states. Also Type-II superconductors have much higher critical magnetic fields, as high as 40-50 Tesla than type-I superconductors, typically less than 1 Tesla.

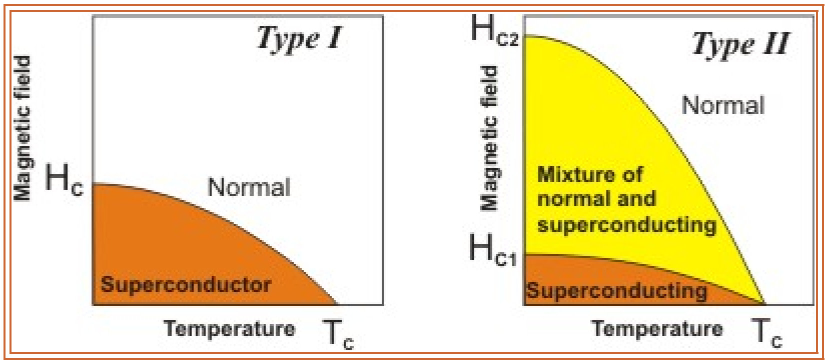

Figure 7.3 Schematic plot of magnetic field vs temperature to differentiate type-I and type-II superconductors

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7.4 Theory of Superconductivity

Originally it was very difficult to explain the origin of superconductivity as then, it was not even possible to explain the zero resistance at 0 K putting the explanation of high temperature zero resistance out of question. Initial theories proposed a qualitative two conduction mechanisms i.e. a normal fluid of electron and another superconducting fluid of electrons. However, the theory did not have any theoretical or analytical basis and was discarded.

An appropriate theory of superconductivity was proposed by J. Bardeen, L.H. Cooper and J.R. Schreiffer in 1957 at University of Illinois (USA) and for which they were awarded the Nobel Prize in Physics in 1972. Following this work, the theory has been called as ***BCS theory***.

BCS theory relies on quantum mechanical calculations which show that in the superconducting state below T_C, there exists an energetically favoured ordered state formed by the electrons and is called as Cooper Pairs. While earlier it was thought that in the superconducting state, the electrons do not interact with the lattice atoms destructively. In the contrast, the BCS Theory supports the interaction of electrons with the atoms but in a constructive manner leading the formation of Cooper Pairs.

The theory makes an important assumption that there exists an attractive force between the electrons in typical type-I superconductors, which is due to Coulombic attraction between the electron and the lattice. It is based on the understanding that due to negative charge an electron in the lattice, there is a build of slight positive charges around it which in turn, attracts another electron and these two electrons are known as a Cooper Pair, as shown schematically in Figure 7.4. The pair is stable only when the binding energy of this pair is energy to keep them together is smaller than that from the thermal vibrations of the lattice which would attempt to break them apart. This is why it is necessary that superconductivity is essentially a low temperature phenomenon.

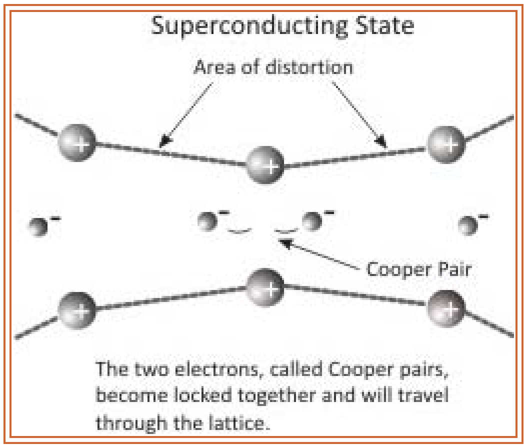

Figure 7.4 Formation of Cooper pair in a superconducting material (Source: Oak Ridge National Laboratory online reports)

7.4.1 Experimental Validation

The experiments were performed on the basis that if electrical conduction in mercury was purely electronic, it should have no dependence on the nuclear masses. The observed dependence of the superconducting critical temperature, T_C, upon the isotopic mass was the first direct evidence for interaction between the electrons and the lattice (see Fgure 7.5). These experiments supported the

BCS theory based on electron-lattice interaction leading to the formation of Cooper pairs. The effect is clearly observed in the case of Type I superconductors while rather weakly in Type II superconductors. At the end, one can observe that it is quite remarkable that an electrical phenomenon such as the transition to zero electrical resistance should be associated with the purely mechanical process of the lattice.

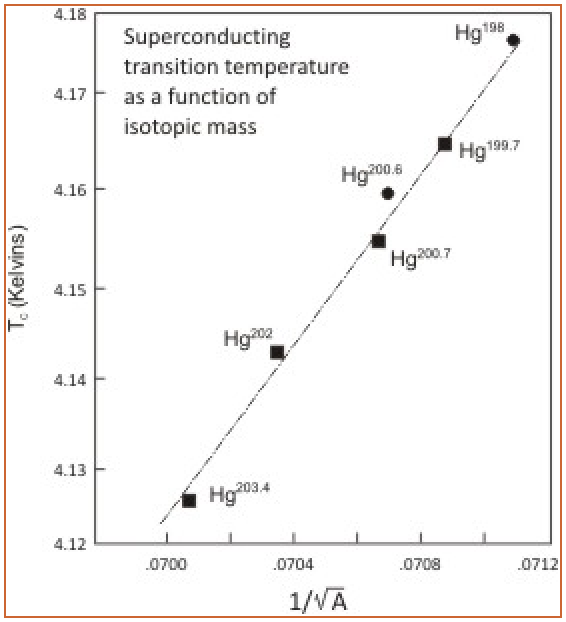

Figure 7.5 Dependence of the critical temperature on the atomic mass A (Reproduced from E. Maxwell, Physical Review, 78, pp 477 (1950); Reynolds et al., Physical Review, 78, pp 487 (1950))

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7.5 Discovery of High Temperature Superconductivity

In 1986, 75 years after the discovery of superconductivity, George Bednorz and Karl Müller at IBM, Zurich demonstrated superconductivity in a perovskite structured lanthanum based cuprate oxide which showed a T_C of 35 K for which the inventors also won Physical Noble prize in 1987. This was a remarkable discovery as it later allowed chemical substitution in perovskite cuprates to push the transition temperatures well beyond the liquid nitrogen temperature (77 K) which is a much cheaper and easily accessible medium as compared to liquid helium.

This was realized by replacement of La by Y to give rise to $YBa_2Cu_3O_{7-x}$(YBCO) which showed aT_C of ~92 K as first shown by Wu and his students at University of Alabama, Huntsville in 1987. The materials show highest T_C when the materials are slightly oxygen deficient *i.e.* when $x = 0.15$. Superconductivity disappears at x ˜ 0.6, when structure of YBCO changes from orthorhombic to tetragonal.

Subsequently many other oxides such as thallium and mercury based oxide compounds showed even higher transition temperatures and these are usually called as type-II superconductors.

A list of important oxide superconductors is shown below with their structures and transition temperatures. If you recall, some of these structures were shown in Module 1. As you can see that critical temperature is dependent very strongly on how the chemical substitutions are made into the parent structure.

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Compound		T_c (K)	Crystal structure
Y-based	$YBa_2Cu_3O_7$	92	Orthorhombic
Bi-based	$Bi_2Sr_2CuO_6$	20	Tetragonal
	$Bi_2Sr_2CaCu_2O_8$	85	Tetragonal
	$Bi_2Sr_2Ca_2Cu_3O_6$	110	Tetragonal
Tl-based	$Tl_2Ba_2CuO_6$	84	Tetragonal
	$Tl_2Ba_2CaCu_2O_8$	108	Tetragonal
	$Tl_2Ba_2Ca_2Cu_3O_{10}$	125	Tetragonal
	$TlBa_2Ca_3Cu_4O_{11}$	122	Tetragonal
Hg-based	$HgBa_2CuO_4$	94	Tetragonal
	$HgBa_2CaCu_2O_6$	128	Tetragonal
	$HgBa_2Ca_2Cu_3O_8$	134	Tetragonal

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7.6 Mechanism of High Temperature Superconductivity

The high temperature superconducting materials are of category of Type–II superconductors and show a gradual change in transition temperature as a function of the magnetic field. There has been intensive research on developing a theory for high temperature superconductivity and consequently a few mechanisms have been proposed, out of whch following two are well accepted.

First mechanism is based on the antiferromagnetic spin fluctuations in a doped system such as cuprates. Spin fluctuation tests yield information on the symmetry of the pairing wave function which, for cuprates, should be of the type $d_{x^2-y^2}$. The second model is the interlayer coupling model which states that superconductivity in a layered structure consisting of BCS-type symmetry *i.e.* *s*-wave symmetry can be enhanced by itself.

However, both of these models do not fully explain the high temperature superconductivity and there is no clear consensus.

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7.7 Applications

Expulsion of magnetic field by superconductors in superconducting state is useful in a variety of applications such as magnetically levitated trains, called as Maglevs (shown below), which are operational in a few countries and can achieve very high speeds because of no friction which is present between normal train's wheels and the tracks. Here, the huge magnetic field that can be sustained by the superconductors is used to levitate and propel the trains.

Figure 7.6 Magnetically levitated train in Japan
(Ref:
http://en.wikipedia.org/wiki/Maglev_%28transport%29)

Another application is magnetic resonance imaging (MRI). In this a strong superconductor-derived magnetic field is applied to the body such that water borne hydrogen atoms and fat molecules in the body are forced to pick the energy from the magnetic field. These species then release this energy at a certain frequency which can be detected and displayed in the form of an image by a computer.

Figure 7.7 MRI image of a human knee
(Ref:
http://en.wikipedia.org/wiki/File:MR_Knee.jpg)

Zero resistance is potentially a fantastic property to have for conductors but since transition temperatures are below RT, the commercial applications are not financially viable. At the same time, wires of only YBCO would be very brittle given that it is a ceramic material. However, a few firms in US are trying to make taped wires where YBCO is grown on top of a nickel tape which provides it the strength without compromising on the T_C and current carrying capacity. However, any commercial products are yet to be witnessed.

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Summary

Superconductors are the materials which show a sudden drop of electrical resistance at a certain temperature when cooled below room temperature. While most superconductors of early generation were low T_C materials, next generation superconductors, layered oxides based on perovskite structure, were called as high T_C as materials showing T_C in the excess of liquid N_2 temperature. These have been successfully fabricated in various forms and examined at various places across the world. While the BCS theory explains the origin the superconductivity in the low T_C superconductors quite well, a well agreed theory for the high T_C ceramic oxides is yet to evolve. These have found applications in magnetically levitated trains and magnetic resonance imaging for medical applications.

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