

Electroceramics
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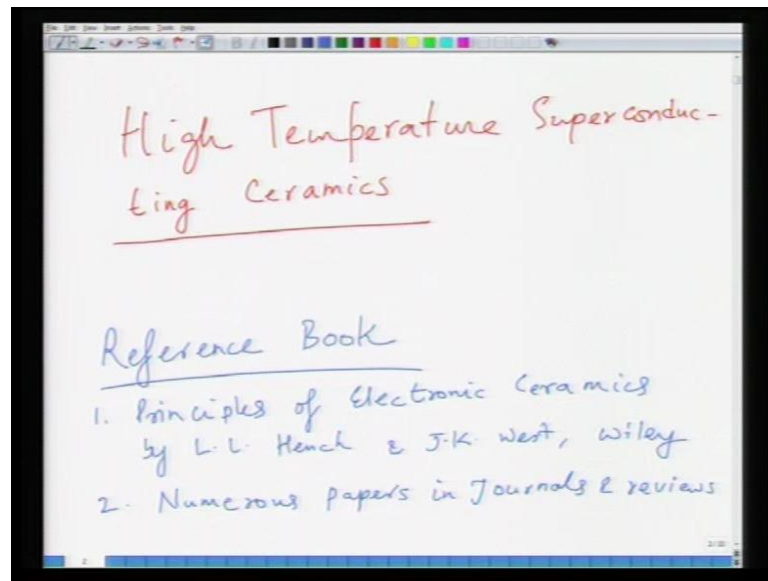
Lecture - 39

So, this is again a start of a new lecture, and in this lecture we start a completely different topic now. So, the past module I think about five lectures or so, we concentrated five to six lectures; we concentrated on magnetic ceramics. So, in that module, we basically discussed the fundamentals of magnetism, what is the origin of magnetic moment? What are the different kinds of magnetism? How do you differentiate between them and what is the origin for those magnetic mechanisms?

And then based on that we moved on to magnetic ceramics, which are essentially ferrites - cubic ferrites, hexagonal ferrites and garnets, and then we looked at some properties with reference to the applications. So, in this module now, we will focus on some of the exotic or a special kind of electro ceramics which are not dealt in any kind of detail in most of the text book except a few and at under graduate level or senior under graduate level or early graduate level there are virtually very few books which mention.

So, in this module we will dedicate about a lecture each to these materials. So, that I introduce you to them and give you some references which you can go and read later on. So, this is module number seven which is based on special or exotic electro ceramics. Now, the first category of materials that we will talk about in this module is essentially high temperature, super conducting ceramics.

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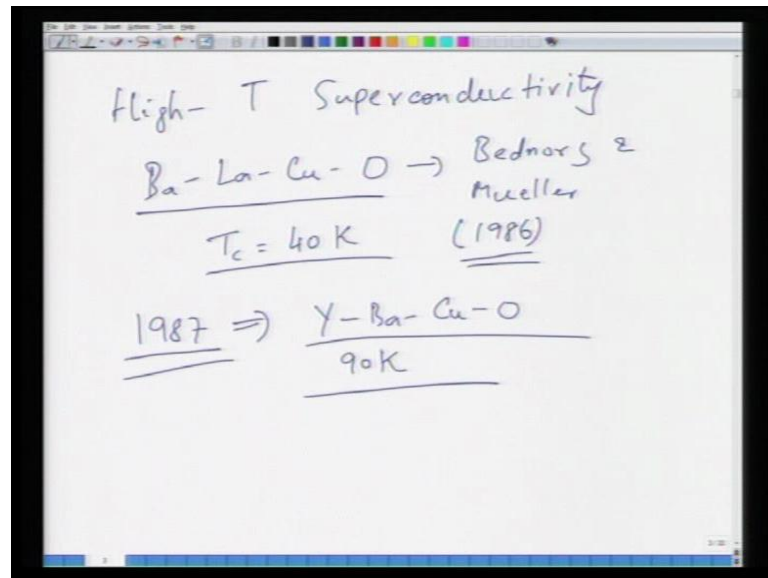
Now, an introduction to high temperature super conducting ceramics does not happen without an introduction to the super conductivity itself. So, what we will do is that we will initially introduce super conductivity talk about low temperature super conductors a bit; some of the fundamental principles behind super conductivity and then we will move on into high temperature super conductivity a bit, and then we will look at some of the application which are useful. Now, the reference book which I would recommend you to read is principles of electronic ceramics by L L Hench and J K west; and this is a Wiley publication.

So, you can read about super conductors in this book and there are numerous papers in journals, and reviews which can help you understand this principle little bit more; and again there are several books other books which can take you through this journey to super conductivity.

Now, super conductivity as a name itself suggests, it is like super conducting materials which are highly conducting and what this essentially means is that these materials have zero resistance in the super conducting state. Now, the super conductivity is essentially has remained very hot topic for more than 50 years or so and this is essentially because this ability to have zero resistance is something which is unique, and this can allow us to develop variety of applications without losing any power, because of the resistance of the material. So, this is something which is essentially a very nice scientific philosophy, but

it is very hard; it is not easy; materials, which exhibit super conductivity are also very rare; every material on the earth exhibits super conductivity.

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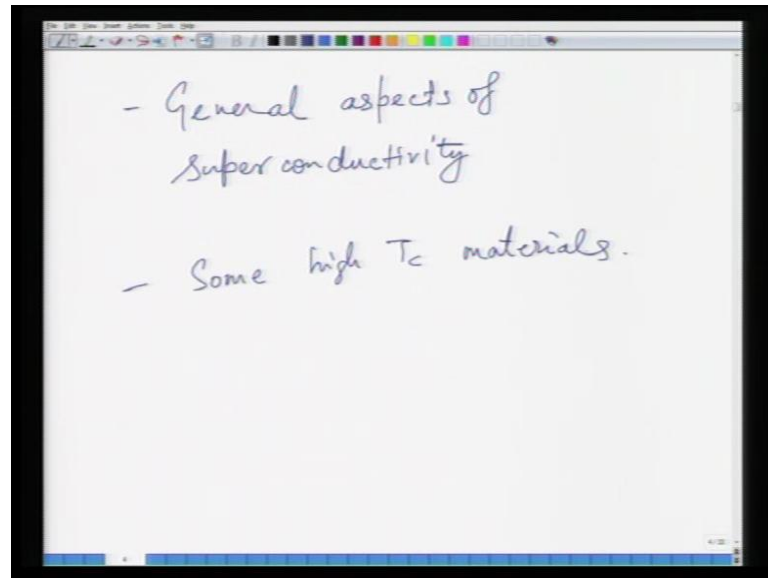


Now, as far as high temperature of super conductivity is concerned this became an intense topic of research after the discovery of super conductivity in materials like high temperature super conductivity; it was discovered in an oxide of barium, lanthanum copper, oxygen by Bednorz and Muller; and this fuelled in 1986 basically not to old phenomena, and this discovery which happened to show a transition temperature of 40 Kelvin which meant that below 40 Kelvin; these materials were super conducting that is they had zero electrical resistance was a major boost to finding super conductivity in oxides.

And followed by this in 1987, super conductivity has discovered an another oxide which is yttrium, barium, copper, oxide and this showed a T_c of about 90 k, and this was a major boost to super conducting research, because this temperature is very high; this temperature is higher than liquid nitrogen temperature and that allows you to operate your devices at liquid nitrogen temperature which is a lot cheaper than liquid helium if you had a T_c below 77 Kelvin.

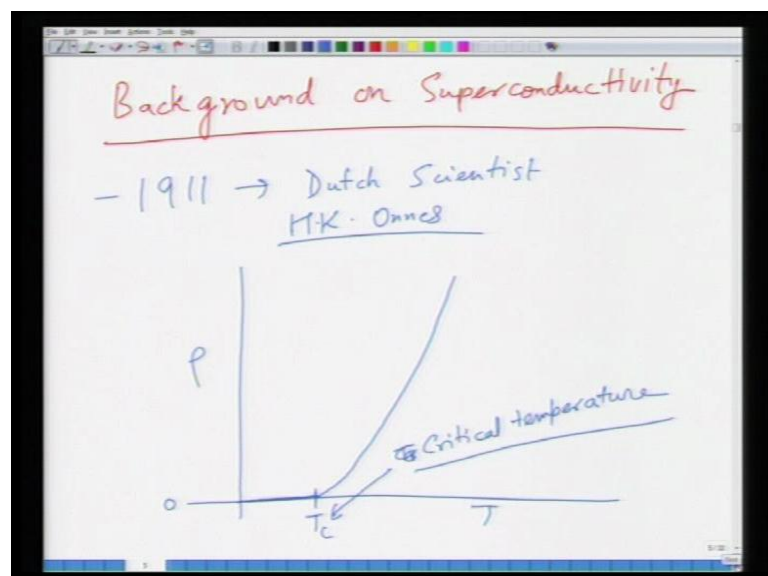
So, commercially this made lot of sense to have this kind of material which have high T_c . So, this sought of set the tone for high temperature super conducting ceramics research as well as development of applications.

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Now, what we will do is that we will first discuss the general aspects of super conductivity which will include a first generation super conductor followed by some of the basic principle such as Meissen effect etcetera and then we will look at some of the high T_c materials.

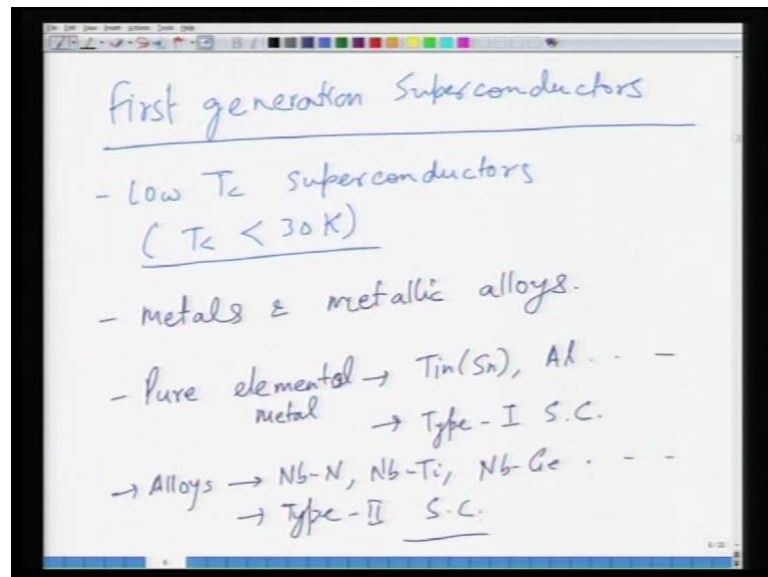
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So, we will start with discussion on low temperature of super conductivity and this low temperature super conductivity discussion, we will essentially give you background information. Now, super conductivity was discovered in 1911 by Dutch scientist H K Onnes, who was basically studying the properties of liquid mercury at liquid helium temperatures and then he suddenly discovered that you know below liquid helium temperatures or around helium temperatures this mercury was super conducting, and that was something which was a surprise to him; and what essentially it meant was that the resistance as a function of temperature suddenly drop to 0 at a particular temperature, and this was called as T_c , a transition temperature or critical temperature in the lingo of super conductivity. So, this is critical temperature. So, beyond this temperature essentially the material remains super conducting and essentially the behaviour is it is not like this, but rather if you take it above T_c it is sort of like this, and then of course, it follows some sort of power law when you reach normal temperatures.

So, essentially what it means is that there is a drop of temperature, below there is a drop of electrical resistance of the material to 0 ohms below a particular temperature which is called as T_c or a critical temperature.

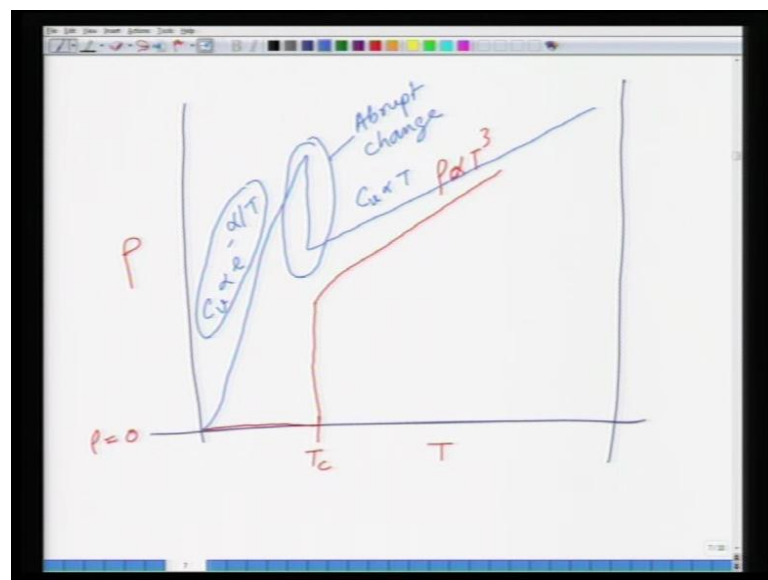
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And these first generation super conductors were essentially metals or metallic alloys and they are typically called as essentially low temperature or low T_c super conductors; and what do you mean by low T_c super conductors is essentially the T_c is lower than 30

Kelvin; that was the definition of these low T_c super conductors and the materials which follow this were you know metals and metallic alloys, and even in this there was a distinction pure elements such as you know tin or aluminium etcetera or mercury. These all pure elemental metals, these were called as type one super conductors and while the alloys such as you know niobium nitride alloy, niobium titanium alloys, niobium germanium alloys and variety of further alloys they were called as type two super conductors. And what is type one and type two that will be clear to you in a while, but this was the definition of low temperature super conductivity in metallic systems before the advent of a high temperature super conductivity.

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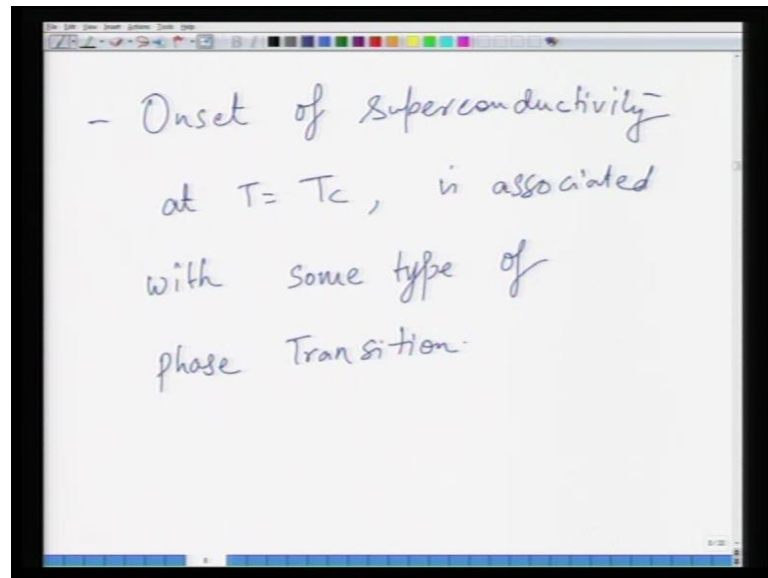
Now, essentially this onset of super conductivity when the super conductivity takes place you of course, have a change in resistance. So, if you plot resistance versus temperature then of course, you reach 0 resistance. So, this is ρ is equal to 0 followed by you know some sort of power law; and this power law could be anything depending upon the material or system typically it goes as ρ is proportional to T to the power 3 or something like that.

So, this temperature would be called as T_c and this line would be actually more like a straight line. So, let me just draw it correctly. So, this line would be more like a straight line before following some sort of power law and this is your temperature dependence of resistance, but this is also accompanied by change in the physical properties; for

example, one of these is super specific heat. So, now, I plot a specific heat, this specific heat now scales an arbitrary.

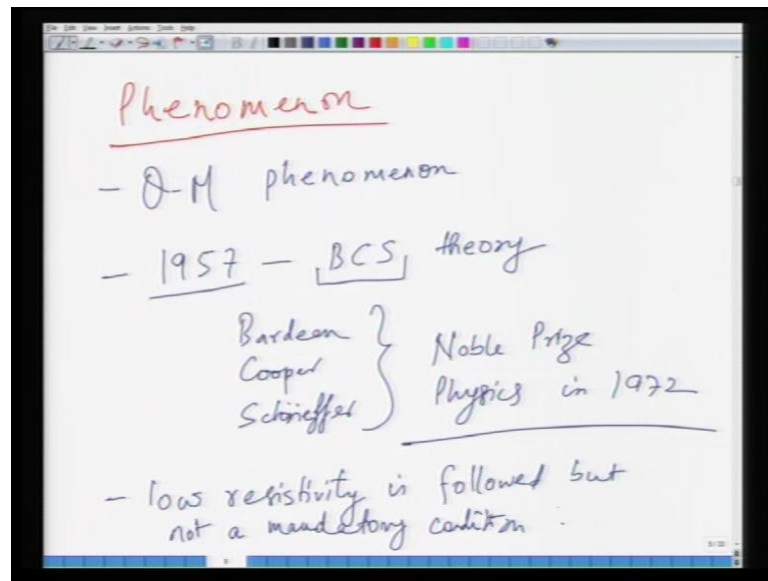
So, except that resistance is 0 below T_c , the specific heat follows a linear relation C_v is proportional to T at temperatures above T_c , but below temperature T_c it follows some sort of behaviour which is exponential of minus alpha by T . So, this alpha is some sort of a constant which depends upon material and this abrupt change in the specific heat; and this abrupt change in the specific heat if you aware of discussion that we carried out during discussion on phase transition inferro electrics such abrupt changes in physical properties like specific heat are signature of some type of phase transition.

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So, essentially what you can say is that onset of super conductivity at T is equal to T_c which is the critical temperature is associated with some type of phase transition. So, this is essentially physically what happens in super conductivity.

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Now, super conductivity as a phenomena it is a purely quantum mechanical phenomena and just like magnetism, and in your modern, and many other modern topics in physics; this is purely a quantum mechanical phenomena it cannot be explain by classical mechanics.

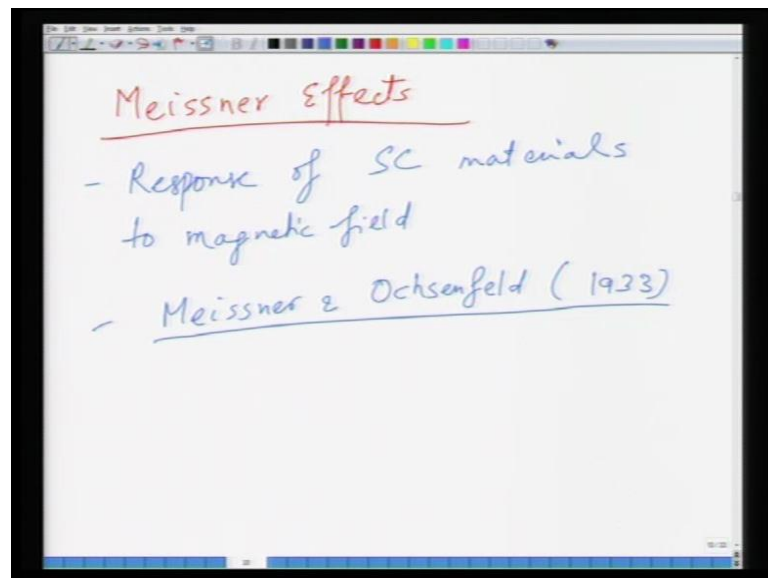
And for some time there was no theory to explain super conductivity; there were few trial attempts made you know just by talking of you know some sort of super fluid or some sort of cooperative movement of electrons or etcetera, but all this attempts which were made to explain super conductivity they went in vain because they could not explain it very well.

So, what happened was in 1957 B C S theory which was coined after Bardeen, cooper and Schrieffer, three scientists; Bardeen was john Bardeen and cooper was Leon cooper, and Robert Schrieffer, these three scientist together they discovered this theory in 1957 based on what is called as a formation of cooper pairs in the super conducting materials which gives rise to this kind of super conducting behaviour; and for which these Bardeen, cooper and Schrieffer all three got noble prize of physics in 1972. So, this was a major discovery in explaining the theory of super conductivity and this was essentially based on flow of some sort of super fluid or you can say the current which flows in the super conducting state is nothing, but due to flow of a super fluid consisting of what is

called as cooper pairs or pair of electrons which essentially interact through the wire lattice interaction; and this was something which was very important to understand.

And another thing which is noticed for many super conductors is that many super conductors have low resistivity; all though it is a condition which is followed in many cases; it is not a necessary condition. So, you can say low resistivity is followed, but not a mandatory condition. So, it is not a constraint as such just like in Ferro electricity you have constraint like you know it has to be non-centro symmetric, it is not a constraint for a superconducting state. Now, we look at the formation of cooper pairs in a while; how the B C S theory came into picture.

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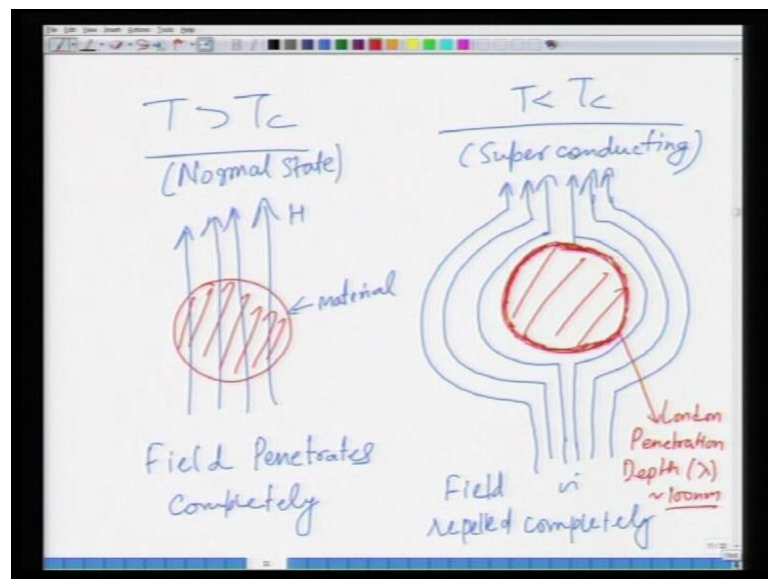


But some other features of super conducting materials is they follow what is called as Meissner effect and this Meissner effect is essentially an effect which distinguishes super conducting materials from the diamagnetic materials. Many times people confuse between these two effects, but they are not similar; they are very different. Meissner effect is essentially describes the response of super conducting material to magnetic field in the super conducting and non super conducting states; or basically in the super conducting states. And this goes after two German scientist Meissner and Ochsenfeld, who discovered this in 1933 and what they discovered was that when a super conductor is placed in a magnetic field beyond a certain field which is called as a critical field H_c super conductivity does not exist, it vanishes. So, even if you are below T_c material

when it is in super conducting state, it does not remain super conducting if you keep on applying the magnetic fields beyond a certain extent.

Now, when the field is below T_c then field does not penetrate the material, it penetrates only partially on the surface of the material; otherwise, it is completely repelled. And this depth of penetration is very small, it is about few 100 nanometre or may be smaller than that and it is called as London penetration depth.

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So, what essentially it is? So, when you have T greater than T_c if you take a super conducting piece of material, it is a normal metal. So, a normal metal when you apply field to it. So, this is normal. So, normal metal means field penetrates completely. So, we can write this is normal state and this is your material, and this is your field H . Now, when T is less than T_c which means you are in super conducting state then when you have this material and when you apply field this field is like this, it bends around the sample like this. So, you have massive flux lines on the surface, but nothing penetrating inside.

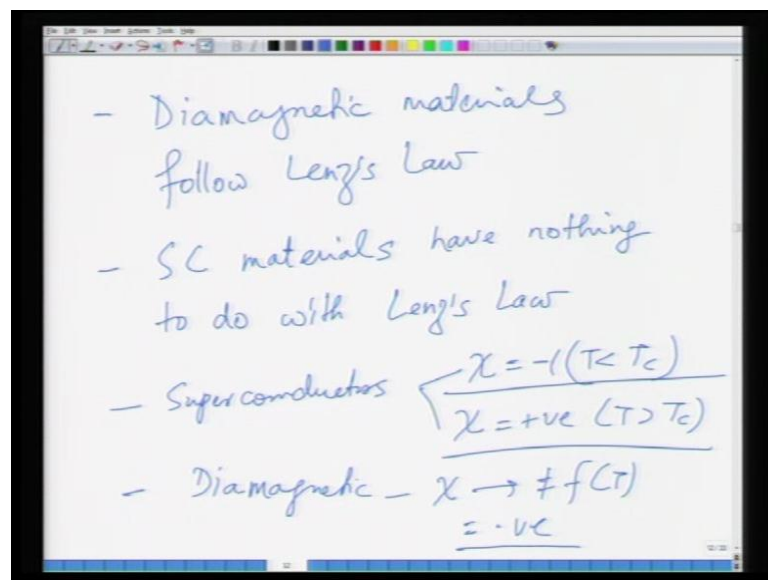
So, the whole of the field that you apply gets repelled and this repulsion give is essentially explained in terms of what is called as an opposite magnetization. So, which means material is doing something which is repelling the whole field; this is like conceptually similar to diamagnetism, but it is not diamagnetism because this is a

dependent; this is a function of temperature. So, when you are below T_c , it is completely repelled; when you are above T_c , it is completely penetrated. So, it is not diamagnetic effect; on the other hand diamagnetic effect essentially based on Lenz's law. When you apply field you essentially create a current which gives rise to a magnetization which is opposing the applied field and this is not which is happening here. So, it is not a diamagnetic effect rather it is called as Meissner effect; the outcome is sort of similar, because you get a magnetization opposing the applied field, but the causes are different.

So, this is your field is repelled completely and this thick skin around the material in which the penetration takes place little bit thin layer. So, there is some interaction which is taking place on the outer surface, this is called as your London penetration depth λ and this is of the order of hundred nanometre or may be smaller.

So, it is only up to this depth, this effect is importance. So, that is why this kind of effect is very important in thin films, because when the dimensions of thin films are very small they are less than hundred nanometre; then there are some strange things which may happen there; so where as in bulk material it is a fairly straight forward thing.

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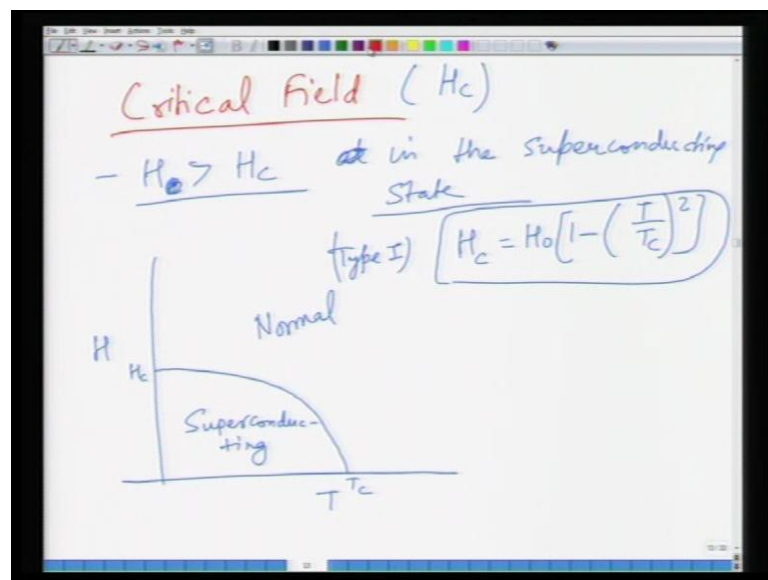
So, essentially the difference with diamagnetic material is diamagnetic materials follow Lenz's law which means they have a current which give rise to magnetization which opposes H ; whereas, super conducting materials have nothing to do with.

So, essentially the effects are similar, but causes are different; both have negative susceptibility. So, superconductors you can say have χ is equal to minus one below T_c , but it is positive when T is greater than T_c . So, this is the essential difference; whereas for diamagnets this χ is not a function of temperature and it is always negative, and also there is a dependence on Lenz's law for a diamagnetic material. So, this is a major difference between these two.

So, essentially, but what you can see that since in the superconducting state when you apply a magnetic field it completely repels a magnetic field which means you can give rise to essentially very large surface magnetization which is opposing the magnetic field and this can be used for lot of good applications which we will see later; and this is a very useful for variety of applications.

So, essentially diamagnetic effect is because of just to summarise; diamagnetic effect is because of orbiting electrons which gives rise to current which in turn gives rise to magnetization opposing the magnetic field in superconducting state, it is not true; it is something else.

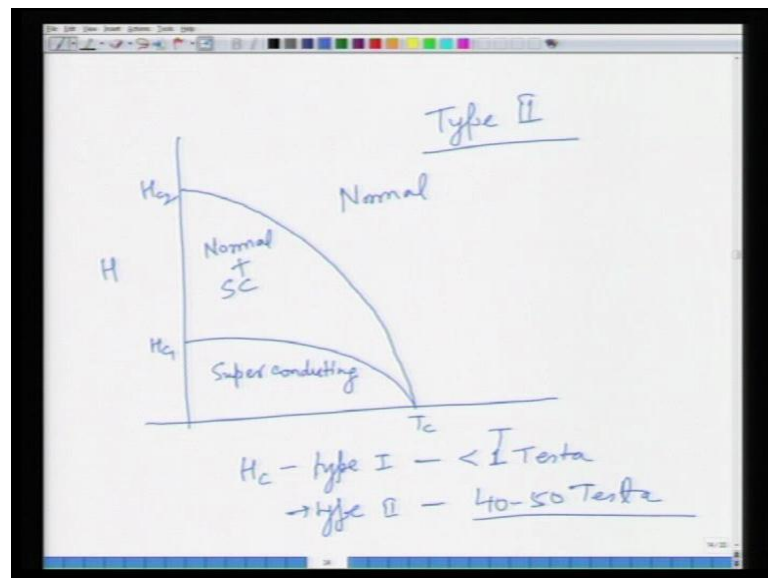
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So, another concept which comes in the wake of this Meissner effect is called as critical field and this critical field is essentially H_c . So, when H is greater than H_c then you can say in the superconducting state the material does not remain superconducting.

So, how essentially you see it as when you apply let us say this is magnetic field; this is temperature. So, there is a correlation here. So, this is H_c and this is T_c . So, of course, at 0 field below T_c the material becomes super conducting. So, this region is super conducting regime; anything above it becomes a normal. So, what you see is that the T_c of a material decreases as you increase the magnetic field. So, this is the correlation of T_c and H_c , and this H_c is given as $H_c = H_0 (1 - T/T_c)^2$. So, this is a relation which relates H_c and T_c in the parabolic form. So, this is true for what we called as type one super conductor this kind of behaviour. In case of type two super conductor there is a slight difference. Now, what essentially it is? In case of type two, I will use different colours or I will use different plot let us say.

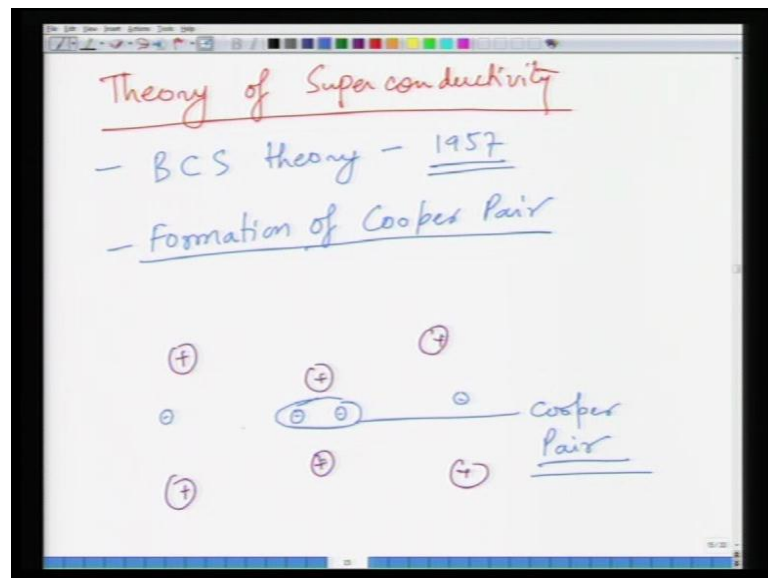
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Now, in case of type two you have similar effect here in the lower field side. So, you have T_c and then H_c , but what you have here is H_{c1} ; and below H_{c1} you have super conducting state, but beyond H_{c1} the region is essentially normal state and beyond these two you have normal plus super conducting. So, essentially this boundary between H_{c1} and H_{c2} below T_c is a region where normal and super conducting states coexist and this is what is found in type two super conductors, and this is where the difference type one and type two came; type one was mostly elemental metals and type two were mostly alloys.

So, basically what this critical field and Meissner effect do is that they essentially define a boundary between when you draw a plot of magnetic field and temperature they define a boundary between the normal and super conducting state, and determine the field above which the material does not remain super conducting. So, this is a very important concept again and the critical fields for instance for type one super conductor; so, H_c for type one could be of the order of less than a Tesla and for type two it could be since they have this region where normal and super conducting phases can exist; the fields can be as high as 40 to 50 Tesla. So, this is the advantage with type two super conductors that you can hold the super conductivity at least some super conductivity upto very high fields; and this is very important from the application point of view.

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Now, we come to what is called as theory of super conductivity. Now, theory of super conductivity as we said was proposed by B C S, Bardeen, Cooper and Schrieffer and this was essentially put forward in 1957 at university of Illinois when these guys were working to explain the reasons, and this was essentially based on the formation what is called as Cooper pair; and this concept of Cooper pair was floated by Leon Cooper who is one of the scientists who put forward this theory.

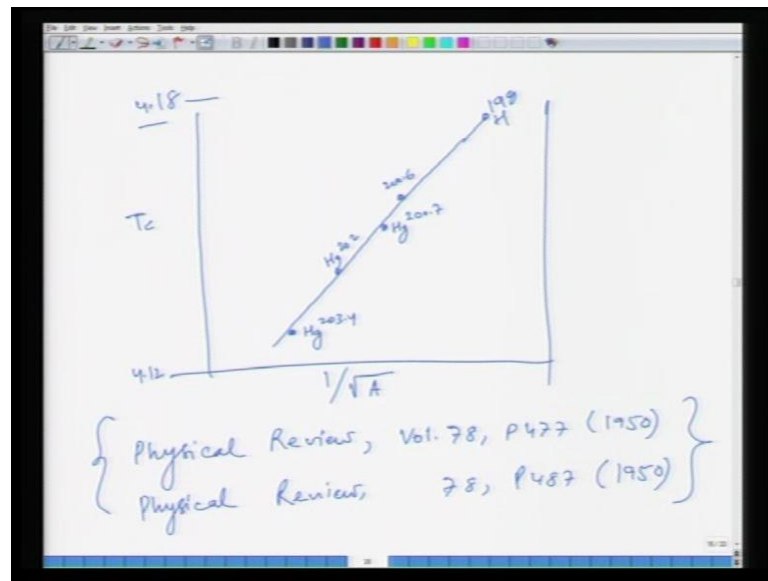
So, this Cooper pair is nothing, but a pair of electrons which moves together in the lattice and this happens by interaction with the lattice. So, how you have here is you have these lattice ions and what you have here is you have this pair of electrons. So, you have this

pair of electrons which interacts with the lattice leads to some distortion in the lattice you can see that these two ions are closer to each other. So, essentially there is an interaction of electrons and lattice which gives rise to formation of this pair of electrons. So, this is your Cooper pair and this Cooper pair is supposed to be formed, because of Coulombic attraction between electrons you might wonder what this Coulombic attraction between electrons is?

So, what essentially it is? Since you have negative charge on the lattice on the electron essentially, this negative charge on the electron in the lattice leads to build up of positive charges around it and which in turn attracts another electron, and this sort of leads to formation of what is called as a Cooper pair, it is a very simplistic explanation that I am giving to you, but this is what it is in summary. And this Cooper pair is essentially stable only when the binding energy of this Cooper pairs smaller than the thermal energy and this is why this super conductivity is a low temperature phenomena.

So, since the binding energies are very small, as a result it does not it is not seen at high temperatures. So, essentially this Cooper pair moves through the lattice by distorting the lattice and this sort of demonstration of electron lattice interaction which was also verified experimentally where experiments were performed by taking different atomic masses, and T_c was noted down, and what the idea was if I change the atomic mass then if there is a lattice interaction the T_c would change, and this is what was observed. So, essentially the beauty of this whole phenomena is you know the coupling of this electrical phenomena with respect to mechanical process such as distortion of the lattice.

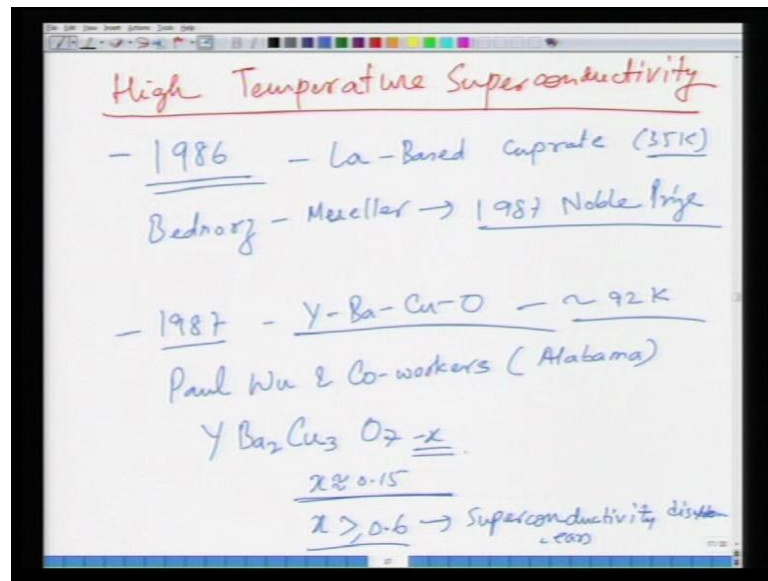
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So, this is what is essentially the theory of super conductivity and the experimental validation which was done was essentially you have a temperature versus T_c versus $1/\sqrt{A}$, and this was done for mercury for instance, and mercury followed a sort of straight line. So, this is for instance somewhere here you have mercury 203.4; here you have mercury Hg 202 and here you have Hg 200.7, and then 200.6 and so on and so fourth until you go to very high like Hg 198; and the transition temperature varies from your 4.12 Kelvin and this goes to right up to like 4.18 Kelvin.

So, the transition temperature was varying when you change the atomic mass of mercury; if you want to know about this you can go to this reference in physical review, volume 78, page 477, 1950 and then another one physical review again, and then volume 78, page 487, and again in 1950. So, you can look at these two papers for experimental validation of the transition temperature in experimental validation of essentially interaction between the electrons and the lattice supporting the idea of formation of cooper pair through the lattice distortion. So, now, what we will do is that we have discussed this theory of super conductivity with the focus on fundamental principles like Meissner effect and critical field. What we will do now is we will look at the high temperature super conductivity.

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And high temperature superconductivity as I said in the beginning of the lecture, it was discovered in 1986 by Georg Bednorz and Karl Muller at I B M Zurich in nineteen eighty six when they discovered the super conductivity in this perovskite oxide which was essentially lanthanum based it was a cuprate layered oxide. So, essentially lanthanum based cuprate and they discovered this as around 35 Kelvin or 40 Kelvin 35 40 Kelvin, and for which Bednorz and Muller they won Nobel prize for physics in 1987 in physics. So, this was just after a year of their discovery one of the quickest Nobel prize ever given.

And this sort of created a lot of vibrations a lot of flurry of research activities in super conductivities especially high temperature super conductivity, because so far before this the super conductivity was limited to elemental metals and alloys. This was the first time when the super conductivity was observed in something not metallic; something which was oxide and previously oxides were studied as a dielectric as a ferroelectrics etcetera, and structures were fairly well studied, but this was the first time when something different was seen, and that to starting with the high temperature like 35 Kelvin it was much higher as compared at that time low temperature super conductivity.

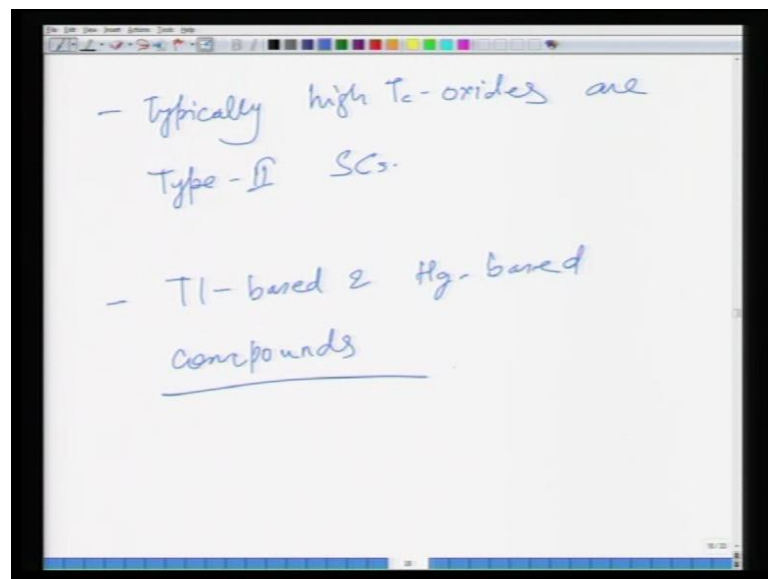
Now, this was followed by discovery of another compound in 1987 which was yttrium, barium, copper, oxide and this was found in university of Alabama where I think Paul Wu and his researchers they made this discovery, and this has a T c of 92 Kelvin; and

this was a landmark discovery, because this gave rise to a hope that you know much more higher temperature transition temperature.

So, materials can be discovered simply, because this 92 Kelvin as I said previously is higher than liquid nitrogen temperature and that makes operation of super conductors much easier, and much less troublesome. And Paul Wu and his co-worker also found that this super conductivity in yttrium, barium, copper, oxide is highly sensitive to the composition. So, what they found was this is essentially the formula is $\text{Y Ba}_2 \text{Cu}_3 \text{O}_{7-x}$ and this x was say very important, and what they found was the super conducting state occurs when x is about 0.15; and this is what shows the highest T_c .

However, when you make x greater than or equal to 0.6 super conductivity disappears. So, this is sort of composition beyond which super conductivity does not remain. Now, followed by these discoveries flurry of activities that took place on understanding the physics of these materials; how the super conductivity takes place etcetera? There have been many attempts which have been made to understand the physics of these materials; however, unfortunately there is no consensus on the physics of operation of these materials. How the super conductivity occurs in these materials? There are typically type two super conductors, but the physics of these materials is not known.

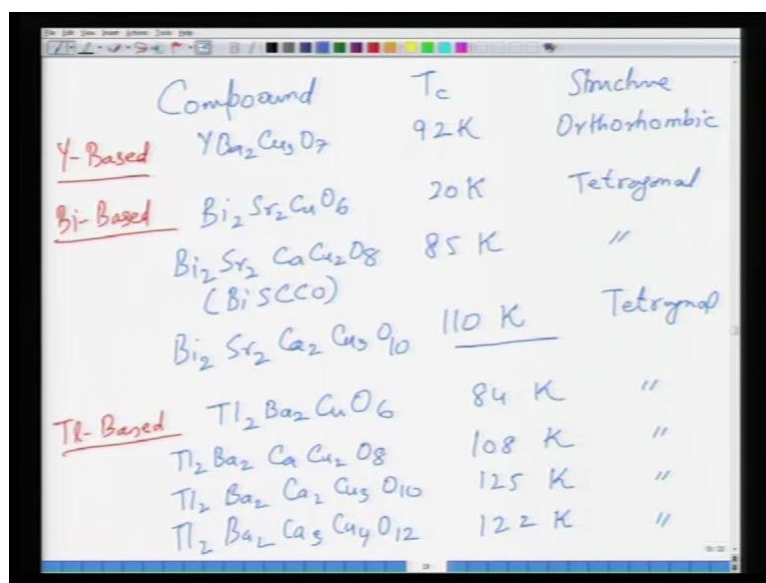
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So, you can say that typically high T_c oxides essentially most of these are oxides are type two super conductors, but the theory of the physics of operation or just like you have a BCS theory put forward to explain low temperature super conductivity. The super conductivity in these materials is not very well understood; there have been some theories which have been proposed; essentially again quantum mechanical theories, but they have not been successful in explaining it completely.

So, I will leave that out at the moment, but following this discovery of lanthanum based cuprate material and then yttrium barium copper oxide; variety of other materials were studied. So, for instance essentially the major focus was on thallium based and mercury based compounds which showed much higher T_c 's. So, I will show you some of the structures.

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	Compound	T_c	Structure
<u>Y-Based</u>	$YBa_2Cu_3O_7$	92 K	Orthorhombic
<u>Bi-Based</u>	$Bi_2Sr_2CuO_6$	20 K	Tetragonal
	$Bi_2Sr_2CaCu_2O_8$ (BiSCCO)	85 K	"
	$Bi_2Sr_2Ca_2Cu_3O_{10}$	110 K	Tetragonal
<u>Tl-Based</u>	$Tl_2Ba_2CuO_6$	84 K	"
	$Tl_2Ba_2CaCu_2O_8$	108 K	"
	$Tl_2Ba_2Ca_2Cu_3O_{10}$	125 K	"
	$Tl_2Ba_2Ca_3Cu_4O_{12}$	122 K	"

So, compound it is T_c and structure; and what you will see is that most of these oxides which were discovered they had this very simple perovskite based layered structure. So, that made life of crystallographers much more easier to understand them. So, the first thing you can have is yttrium based was of course, $YBa_2Cu_3O_7$. Now, I am not giving that non-stoichiometry here. So, most of these oxides show super conductivity in some sort of non-stoichiometry and this T_c highest achieved was 92 Kelvin, and this has a orthorhombic structure; and then you have another category of bismuth based

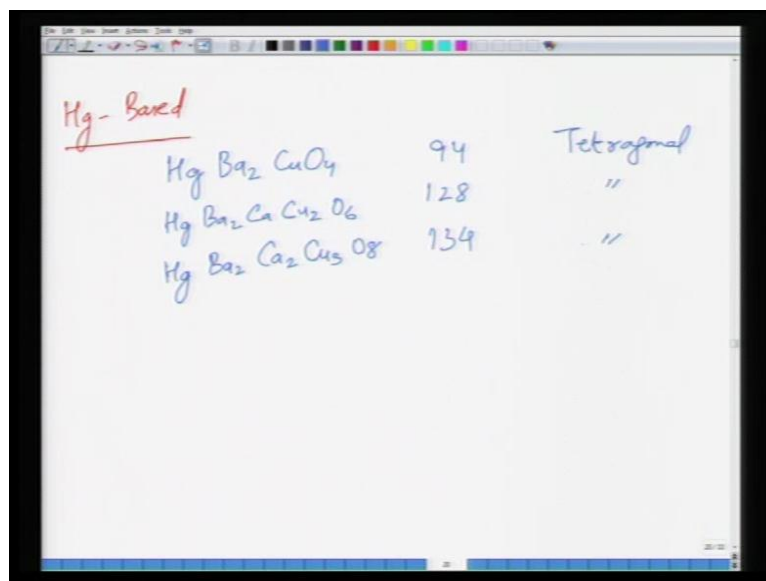
materials, and these bismuth based materials variety of materials $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ which had a T_c of 20 Kelvin, and this was tetragonal in nature.

Now, you can build upon this. Now, this is $\text{Bi}_2\text{Sr}_2\text{CuO}_6$, if you tune the composition little bit then it gets much more bigger unit cell or at the same time the T_c increases. So, for instance if you make $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, you can see that you have increased a layer of calcium oxide and when you put calcium oxide in the unit cell, and increase the number of copper atoms as well then the T_c becomes 85 Kelvin, and this is called as BISCCO; and this again has a tetragonal structure much more bigger unit cell.

Another one you can make some more alterations $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$. So, you can say that you have increased Cu O and Ca O 2. So, you have increased another oxygen and another copper O 10 and this gives rise to 110 Kelvin, and this is again tetragonal. So, if you change the BISCCO composition, you can have the T_c as high as 110 Kelvin. So, this is you know very nice discovery, the problem that these materials is that they are not easy to fabricate and that is why BCO remained still a very popular compound.

And another category is thallium based compounds and in thallium based you start with $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ the parent compound, and this parent compound shows a T_c of 84 Kelvin, and this is again tetragonal structured. You can add some more atoms to it again; you do the same thing that you did in BISCCO. So, this becomes $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ and this has a T_c of 108 Kelvin; and then you have $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ and this increases the T_c further 225 Kelvin; again with the tetragonal structure and finally, when you make $\text{Tl}_2\text{Ba}_2\text{CuCa}_3\text{Cu}_4\text{O}_{12}$ then this decreases the T_c now, any further addition does not increase the T_c and this remains as 122 Kelvin.

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A handwritten table on a whiteboard. The title 'Hg-Based' is written in red and underlined. The table lists three chemical formulas, their corresponding Tc values in Kelvin, and their crystal structure. The first row is HgBa₂CuO₄ with Tc = 94 K and a tetragonal structure. The second row is HgBa₂CaCu₂O₆ with Tc = 128 K and a tetragonal structure. The third row is HgBa₂Ca₂Cu₃O₈ with Tc = 134 K and a tetragonal structure.

Hg-Based	T _c	Structure
HgBa ₂ CuO ₄	94	Tetragonal
HgBa ₂ CaCu ₂ O ₆	128	"
HgBa ₂ Ca ₂ Cu ₃ O ₈	134	"

So, roughly similar another category that you have is of mercury based again there you have Hg Ba₂ Cu O₄; again you can see that all of these are cuprates, they have copper layers in between. So, there is something to do with copper layers which is important barium oxide, copper oxide layers which make them super conducting. So, there is something do with that which has to be understood Ba₂ Ca Cu₂ O₆ and then you have Hg Ba₂ Ca₂ Cu₃ O₈, and these have T_c's of 94, 128 and 134 Kelvin; again all with tetragonal structure.

So, you can see that these cuprates which have layers of copper oxides if you tune the composition by putting in variety of atoms in the structure you can change the T_c quite well. The problem with mercury and thallium based is that mercury and thallium are difficult to handle; they are poisonous and they are not something, and many countries have banned their use or restricted the use. So, as a result they did not pick up too much, but still huge research was done on yttrium based cuprate oxides. I will show you the structure of yttrium based cuprate oxide which we went through in module one just to recap what is the structure like?

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Yttrium Barium Copper Oxide or YBCO

- Parent compound : $\text{Y}_3\text{Cu}^{3+}_3\text{O}_9$
 - Contains perovskite units.
- Doping of Y by Ba
 - Structure modification
 - Reduction of Cu^{3+} to Cu^{2+} state which results in reduction in the number of required oxygen ions and hence creates oxygen vacancies in the structure.
 - This gives a transition temperature of ~ 92 K below which the compound has zero electrical resistance *i.e.* is a superconductor.

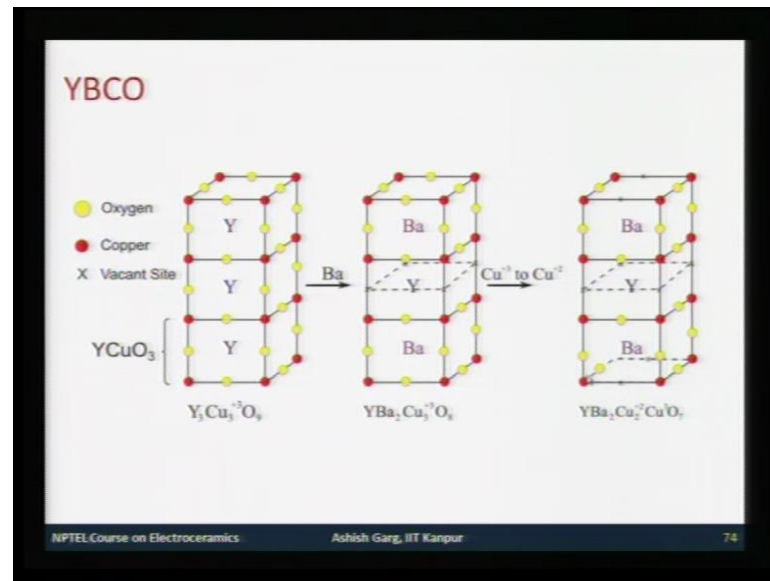
$$\text{Y}_3\text{Cu}_3^{3+}\text{O}_9 \xrightarrow{\text{Ba}} \text{YBa}_2\text{Cu}_3^{3+}\text{O}_8 \xrightarrow{\text{Cu}^{3+} \rightarrow \text{Cu}^{2+}} \text{YBa}_2\text{Cu}_2^{2+}\text{Cu}^{3+}\text{O}_{7-x}$$

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So, if you go through this now, yttrium barium copper oxide, essentially the parent compound is $\text{Y Cu}_3 \text{O}_9$ and here copper is in plus 3 state, and this contains perovskite units where the perovskite units would be some BO_6 or BO_3 kind of units; and these BO_3 kinds of units are sandwiched in the layered form. Now, what you do in this material is you dope this material by replacing yttrium with barium. So, this yttrium is replaced by barium. So, this modifies the structure. So, essentially what you have is as a result now, the difference here is yttrium is plus 3 barium is plus 2 and this leads to reduction in order to maintain the stoichiometry; this leads to reduction of Cu plus 3 to plus 2 and which results in the reduction in the number of required oxygen atoms, and hence what it does is it creates a vacancies of oxygen in the structure.

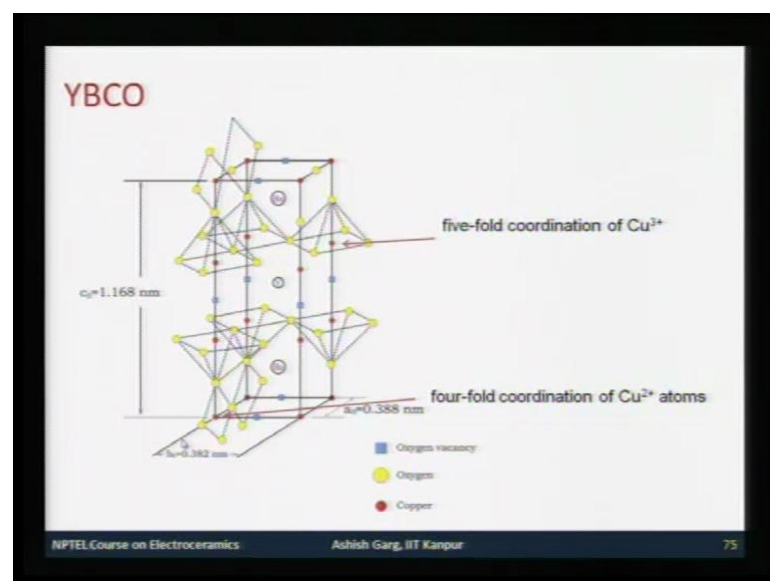
So, you understand that you bring in one barium you of course, reduce the requirement of oxygen. Now, in order to compensate completely copper also reduces itself as a result, because you have one charge deficiency here and another charge deficiency is caused by this reduction $\text{Cu}_2^{3+} \text{Cu}^{2+}$ plus to remove one oxygen. So, the moment you do that $\text{Y}_3 \text{Cu}_3 \text{O}_9$, it becomes $\text{YBa}_2 \text{Cu}_3 \text{O}_8$ and what you have here is followed by $\text{YBa}_2 \text{Cu}_2^{2+} \text{Cu}^{3+} \text{O}_{7-x}$.

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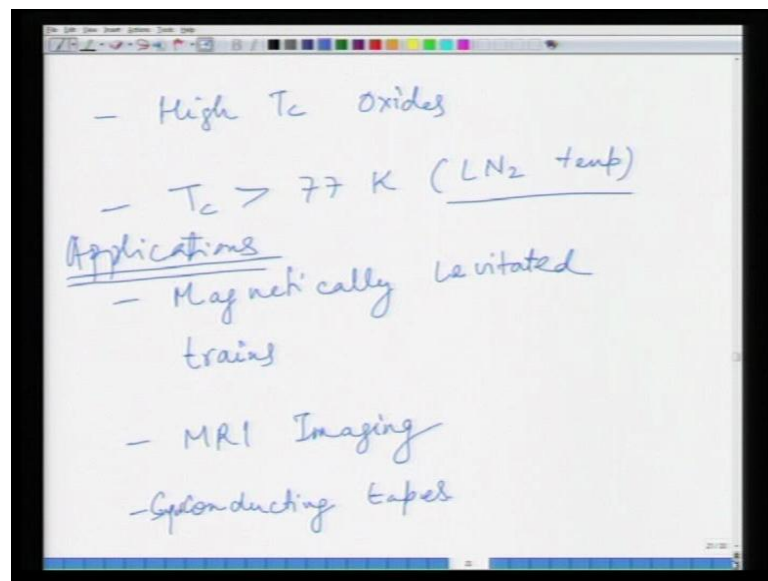
So, the structure changes like this. So, you have this $\text{Y}_3\text{Cu}_3\text{O}_9$ followed by $\text{YBa}_2\text{Cu}_3\text{O}_8$ and then Cu^{3+} plus to Cu^{2+} plus formation of $\text{YBa}_2\text{Cu}_2\text{O}_7$. So, structure remains similar orthorhombic structure, but what you have here is as a result of these substitutions and reduction in the oxidation state. What you have here is vacancies of oxygen and these crosses are nothing, but vacancies of oxygen, and this also leads to change in the coordination of copper atoms.

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So, what you have here is essentially five-fold coordination of copper three plus atoms along these rows and within the plane you have this four-fold coordination of copper two plus atoms. So, this gives rise to an isotropic behaviour in terms of conductivity of these materials. So, this is this is one primer on the structure of these materials. Similar structure or similar kind of tuning can be done in other super conducting oxides to give rise to variety of structures that we have seen. So, essentially just like you have formed $\text{YBa}_2\text{Cu}_3\text{O}_7$, you can start from $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ and then you can keep on building using these copper oxide layers by putting in calcium increasing the number of copper change the T_c , and this can happen when bismuth thallium and mercury based all these three types of compounds. So, this sort of gives you a sort of understanding of what happens in these super conductor oxides.

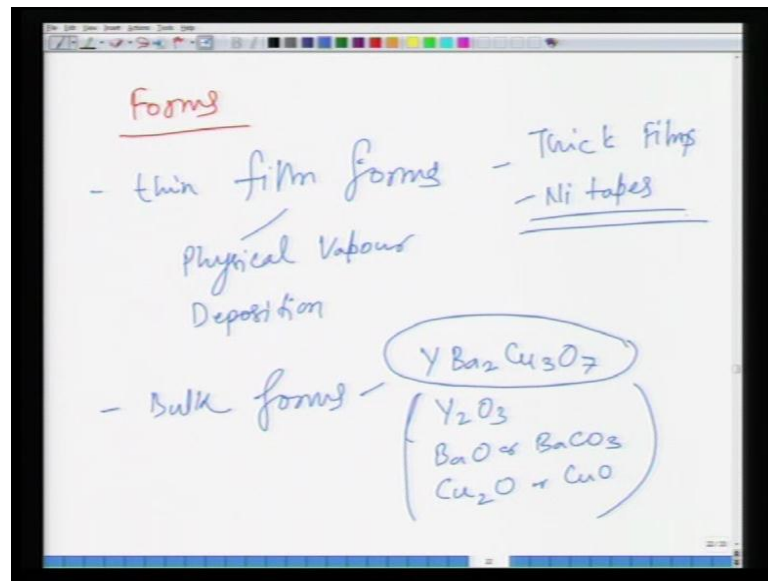
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Now, these super conducting oxides since the T_c 's are typically higher than 77 Kelvin which is liquid nitrogen temperature they have been thought of their used in variety of applications; and these applications could be you know like magnetically levitated trains; you can have MRI imaging; you can have super conducting tapes.

So, variety of applications had been proposed and some of them are already under use. And this is essentially because of this fantastic nature of this material that it has a T_c below which it offers 0 resistance and also below T_c , it offers complete repulsion of magnetic field as long as the magnetic field is below H_c .

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So, this is what is very good quality of this thing. Material can be used in variety of forms, it has been studied in thin film form; thin film forms can be made by variety of techniques, you can use physical vapour deposition methods. So, essentially what you do here is you take a oxide target which you either a sputter or laser ablate on the substrates which are lying under and as a result you can make thin films of YBCO for thin film applications. So, if you want to make YBCO, $YBa_2Cu_3O_7$ for this you take yttrium oxide, barium oxide or barium carbonate and then copper oxide Cu_2O or CuO , mix them together in stoichiometric quantities, and when you mix them together they react with each other at high temperatures to form the desired phase under controlled atmosphere and temperature.

So, under control conditions you do that. Similarly, thin film form made by physical vapour deposition process you can make thick films as well and these thick films are used in super conducting tapes. So, for instance one of the uses of these YBCO is conducting tapes and these conducting tapes of course, you cannot make a tape of standalone ceramic, because ceramic is brittle in nature.

So, as result you have to put it on a substrates and this substrate has to be ductile. So, that it can sustain the weight and it can keep the ceramic crack free, and these thick films are typically deposited on nickel tapes; and these nickel tapes they have some addition layers in between, and the thick films are formed by processes such as liquid phase epitaxy. So,

essentially you melt the YBCO material and you draw the tape through the through the melt, YBCO deposits on the nickel tape and it solidifies, and forms a thick coating on the top of nickel tape. So, this is another form in which YBCO can be used. I will show you couple of pictures of applications of these materials.

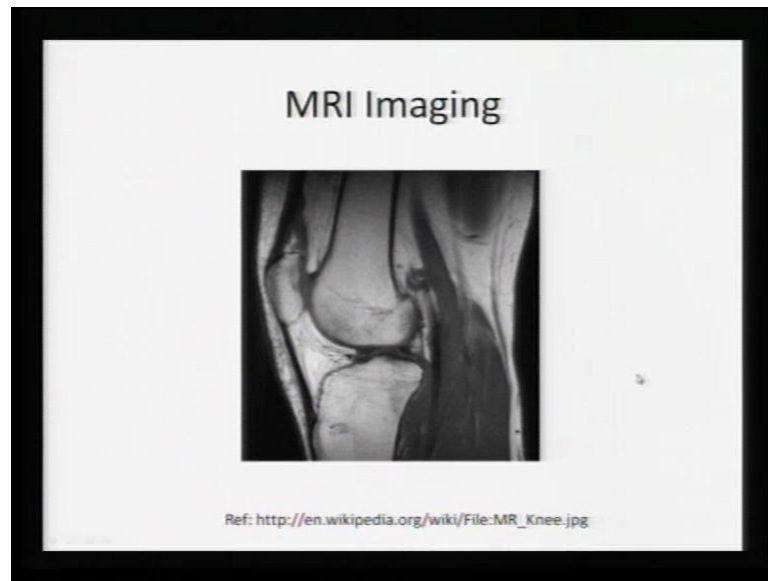
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So, for instance one of the applications of super conducting ceramics is this magnetically levitated trains; as they are called as Maglev's. So, you have this train which is running on the race track. Now, this race track of course, has essentially there is no friction, because of this repulsion. So, you have these race track which can have super conducting material and this of course, has to operate at low temperature, and you can have this train which can have magnets at its bottom, and you know that since the field is repulsed by a super conductor.

So, you can have either of these two things; either the track can be magnetic or the train can be super conducting. But whatever it is because you have repulsion of magnetic field these trains float in this magnetic field without any friction and they can run at very high speeds of 300 to 400 kilo meters per hour easily. And they have been trials which have been done in countries like Japan, and they have been they are running in china and Germany as well. It is not a very common phenomena; it is not a very common mode of operation or travel, but it is something which is been used in some countries and they are trials which are being made in some other countries as well.

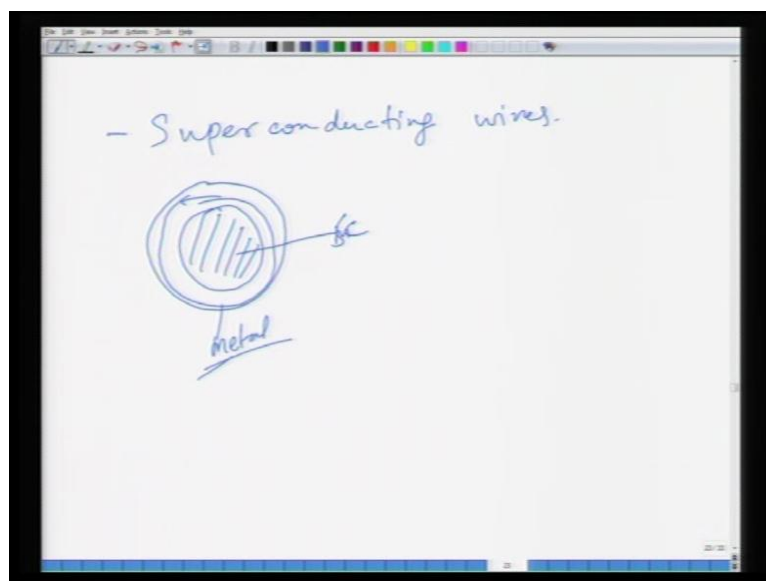
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Another useful application is your MRI imaging and you must be more familiar. MRI is essentially magnetic resonance imaging and this is again essentially if you look at this image, what you can see is various body parts and tissues etcetera, and here you can find out the damage which is been done in the body through this imaging. So, what you have here is essentially when you cool a super conductor below T_c , it repulses this magnetic fields. So, this magnetic field which is repulsed is applied to the body and this essentially what happens is then the fat molecules and the hydrogen atoms which are in the water born things in the body; they are forced to pick up the energy from the from the magnetic field. And these species they release their energy at a certain frequency which can be detected and displayed in the form of a image by a computer. So, what you see here is you can see variety of ligaments and bones etcetera.

So, any kind of damage that happen in any tissues and bones in the body can be very precisely imaged in this technique; this is very essential technique for these health applications. So, essentially you have these two applications which are of course, in use. Super conducting tapes are coming in picture; there are some laboratories in America which are trying to commercialize these some companies as well. So, you can have thick tapes and another application is essentially is super conducting wires.

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And these are essentially composites; what you have is a metal sheet in which you flow a super conducting wires. So, you have metal super conductor; you have a metal and between them of course, you have liquid nitrogen flowing, and this can give rise to composite wire; you have to put a metal, because super conductor is an oxide and brittle material. So, as a result it cannot sustain its weight when you have long cables in the carrying the electricity. But what this will do is that this will minimize the electrical losses and make the electricity transmission much more efficient, and save money in terms of power consumption. So, this is what is basically a primer on super conducting materials with which some emphasis on super conducting ceramics.

I have given you the references, you can go through these books and journals, and reviews. If you are interested you can go and read them. Plenty of literature is available on super conducting materials. So, I think you should not have any problem in getting more up to date knowledge in this area. In the next module, what we will do is that we will take up another exotic class of materials which is multiferroic and magneto electric materials which are again being researched in recent years, because of their some fantastic properties, and that we will take up in next module.

So, just to summarize what we learnt in this module? We learnt in this module, we started with low temperature super conductivity which are nothing, but essentially metals and metallic alloys; type one and type two super conductors. And then we followed with

the effect Meissner effect which essentially tells you about the dependence of magnetic field and critical temperature; and what it tells you is that below T_c when you apply magnetic field above a certain level then the super conductivity ceases to exist. And the theory of super conductivity which is by Bardeen cooper and Schrieffer which is based on the principle of formation of cooper pair through the interaction with the lattice.

And then we looked at high temperature super conductors essentially oxides which were discovered in 1986 not too long ago, but there are some promising compounds like yttrium, barium, copper, oxide. The fantastic features of these materials is that they are a layered materials; so you can keep building layers and layers by chemically modifying them and change the T_c which has been observed in variety of materials.

And however, despite all the advances yttrium, barium, copper, oxide still remains a favourite choice simply, because it can be made easily and it does not contain any toxic elements which otherwise are present in other materials, and it has a T_c which is higher than liquid nitrogen temperature. So, we will stop here and then in the next module we will look at multiferroic and magnetic materials.

Thank you.