Materials Chemistry
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Module - 5
Lecture - 5
High Tc Superconductors

In the previous lectures, we have looked at materials with different interesting electrical properties.

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And we covered on giant magneto resistance, we covered some issues on colossal magneto resistance which is typical of a perovskite based compound. And we have looked at the possibility of tunnelling magneto resistance in multilayer's, and one of the other lectures we also looked at the possibility of inducing magnetism, and therefore making a semiconductor a magnetic material.

In today's lecture I am going to cover little bit from the materials chemistry point of view on one of the other exciting field, which has brought more focus into fundamental issues on mixed metal oxides, that is the issue of super conductivity, in oxides otherwise not known until 1986. So, this is a discovery which has almost brought a fresh look at all the research, that is going around metal oxide chemistry, and the cartoon that you are seeing in the front screen here is a unmanned maglev train, which is running at the speed of 930 kilometres, which is actually operated using a superconducting coil.

So, the fascination of superconductivity can go to any extent right from basic research to the other issues of materials world, where we can really feel it and experience it. So, in this lecture I am going to tell you more about the chemistry point of view of superconductivity, and what are all the fascinations, that we can look in one single crystal lattice.

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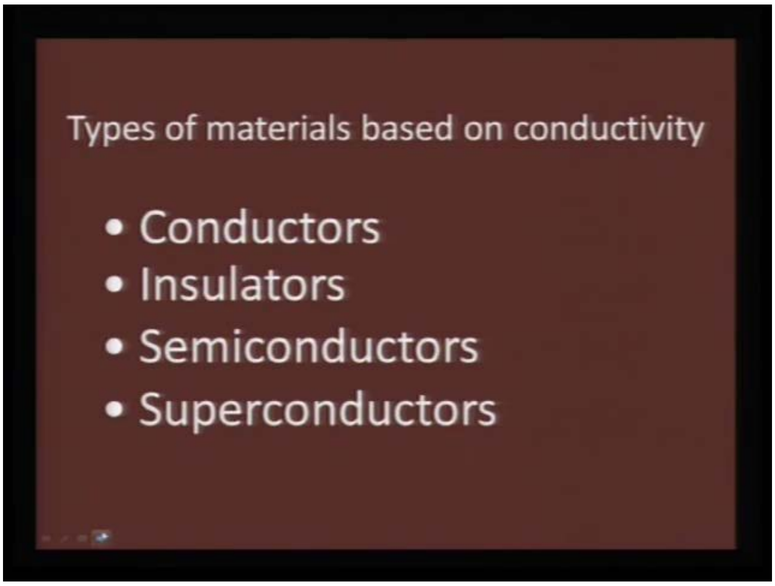

Before I start with issues pertaining to superconductors, just to familiarize our self of the range of materials, that we have starting from simple conductors to insulators to semiconductors. And then we have a special place for superconductors, which usually normally behave as a metal, at a particular point this metal transforms into a superconductor.

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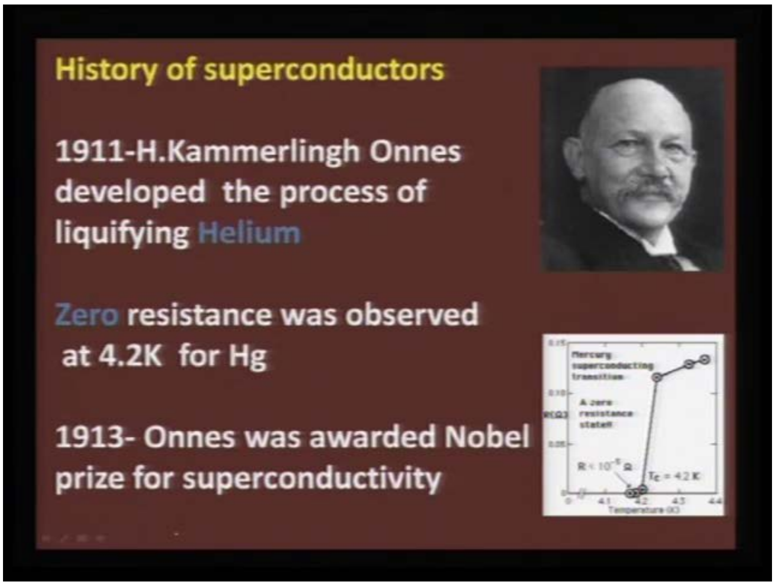

If you look at the history of superconductors, it is almost 100 years since the discovery of super conductor has been made, it was exactly 100 years back in 1911, Kammerlingh onnes developed the process of liquefying helium. And when we liquefied helium he found that mercury was going to a 0 resistivity, in other words it shows 0 resistance at 4.2 K that is the boiling point of liquid helium. Since then this area has picked up and in 1913 onnes was awarded the noble prize for superconductivity.

And this is one of the first results from Kammerlingh onnes where you can see there is a metallic state as you cool the mercury, and at 4.2 K there is a sharp drop in the resistance. And the resistance is of the order of 10 power minus 5 ohms, 0 resistance state it achieves as a result mercury behaves like a superconductor, and as you know mercury is one of the metal which is existing in liquid state. So, there have been lot of studies on other metals.

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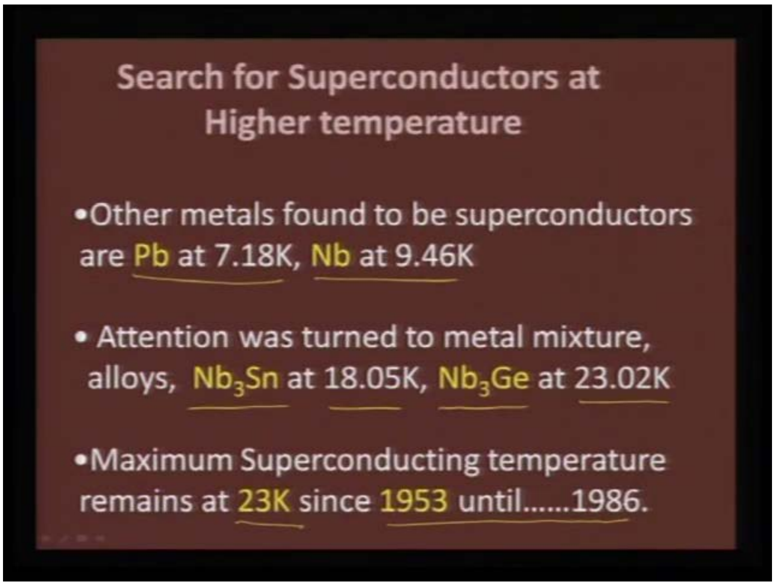

So, the search for superconductors at higher temperature has been the focus since this discovery, and other metals found to be superconductors are lead at 7.1 K niobium at 9.46 K. And then came this a 15 type metals or alloys, this is niobium stannide alloy and then you have niobium germanium, all this shows around 1823 Kelvin, and maximum superconducting temperature that has been achieved up to 1953. Since, the discovery has been only 23 K.

And nevertheless with this finding several useful applications have happened over the years, and these metals are malleable therefore, you can make it into any shape. Therefore, these alloys have been made into some device purposes, and specially in superconducting coils these alloys have been used, and they are applied in even NMR instruments. But, this excitement lasted only until 1986 when there was a paradigm shift, in this work or in this field.

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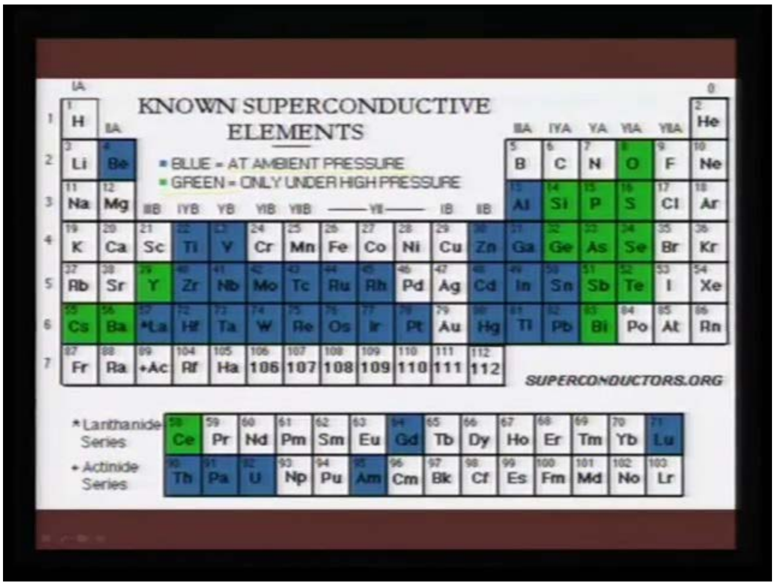

Mainly because of that discovery that struck in 1986 before we look at the major discoveries in this field, I just want to show you that most of the elements in the periodic table do show superconductivity at some temperature. And all the ones which are marked blue here, those are superconducting at ambient temperatures, but if you actually go for non metallic regions specially 4 a, 5 a and 6 a elements they do show superconductivity at high pressure. So, quite a good number of elements do show this strange property.

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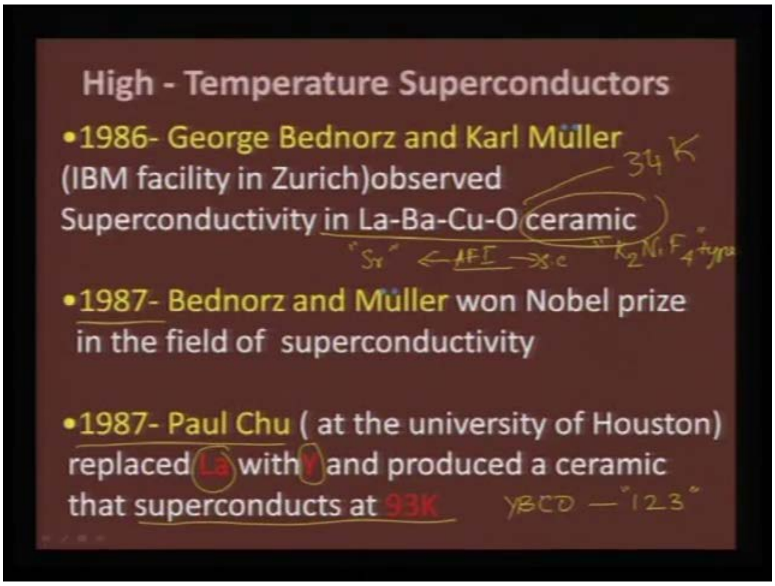

But, what really was the break through is the high temperature superconductors in 1986 George Bednorz and Karl Muller, they are from IBM facility at Zurich. They observed superconductivity in a compound, which is called lanthanum barium cuprate, it is a K 2 N a F 4 type of a compound, the crystal structure resembles that of a K 2 N a 4 type. And this ceramic compound is actually considered to be a anti ferromagnetic insulator.

Because, if you look at the crystal structure the copper oxygen planes, which are inter stacked in this unit cell, they are actually anti ferromagnetic ally aligned and the electrical conductivity actually shows it is a antiferromagnetic insulator. So, you cannot get anything out of this compound, all you can try to do is you can try to increase the whole mobility by substituting with some divalent metal, in the lanthanum site. And as a result you can improve little bit of the conductivity, where you can take it from a insulating state to a semiconducting state this was all known.

So, the breakthrough was when you try to cool the sample at low temperatures, then you see from the metallic state it goes to a superconducting state and in 1981 because of this path breaking discovery Bednorz and Muller won the noble prize in the field of superconductivity. The reason why it was path breaking is, ceramics are not supposed to be showing any metallic property, and it is not just showing metallic nature, but it is also superconducting in nature.

Therefore, a ceramic which is considered to be a rather insulator turning to a superconductor has been the path breaking discovery there. Nevertheless the excitement that generated lead Paul Chu and his co-workers at the university of Houston, to replace some of the lanthanum with yttrium, and then they produced another ceramic that super conducts at 93 Kelvin instead of the one which shows at 34 Kelvin. So, it this was a quantum jump, when this discovery was made.

If we now relate to yttrium barium copper oxide, you would see most of the applications are now based mostly on this compound, which is named as YBCO or YBCO which stands for yttrium barium copper oxide or some people also nickname this as 1, 2, 3 compound. Because, the stoichiometry of yttrium to barium to copper is 1 is to 2 is to 3 therefore, this is popularly referred to as 1, 2, 3 compound or YBCO compound. And many of the practical applications today in this field is based on yttrium barium copper oxide.

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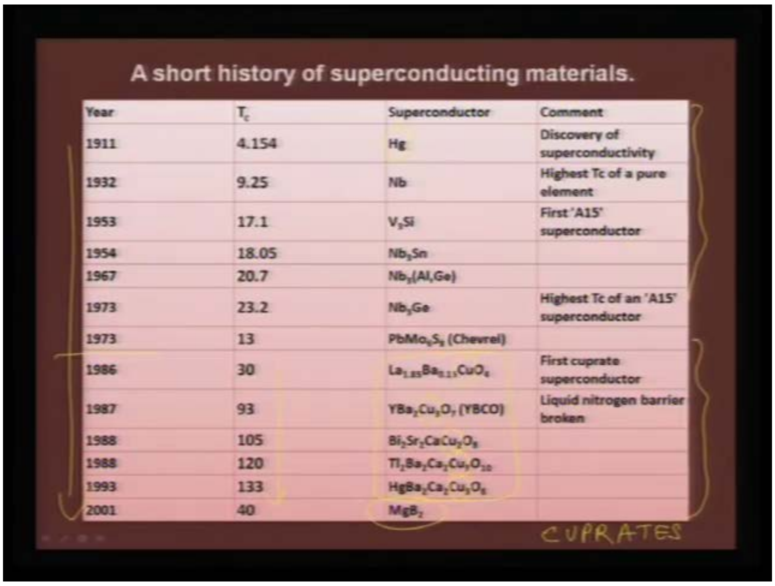

Year	T_c	Superconductor	Comment
1911	4.154	Hg	Discovery of superconductivity
1932	9.25	Nb	Highest Tc of a pure element
1953	17.1	V_3Si	First 'A15' superconductor
1954	18.05	Nb_3Sn	
1967	20.7	$Nb_3(Al,Ge)$	
1973	23.2	Nb_3Ge	Highest Tc of an 'A15' superconductor
1973	13	$PbMo_6S_8$ (Chevrel)	
1986	30	$La_{1.85}Ba_{0.15}CuO_4$	First cuprate superconductor
1987	93	$YBa_2Cu_3O_7$ (YBCO)	Liquid nitrogen barrier broken
1988	105	$Bi_2Sr_2CaCu_2O_8$	
1988	120	$Tl_2Ba_2Ca_2Cu_3O_{10}$	
1993	133	$HgBa_2Ca_2Cu_3O_8$	
2001	40	MgB_2	

Now, if you look at this short history of superconducting materials you would see from finding the superconductivity in mercury way back in 1911, as you scan through there is a shift in focus after 1973. Since then it has always been mostly on the oxide chemistry whereas, in the previous years decades you see it is mostly on several phases or inter metallic compounds. So, there is a paradigm shift after 1986 where you start looking at the oxide chemistry in greater detail.

And as you would see here, in most of the compounds that are listed we have transcended from 30 Kelvin all the way up to 133 Kelvin. So, the quest is to go as close to the room temperature, so that the implications of superconductivity can be realized in energy sector and in many other electronic environments. If you look at the type of oxides that you we have listed here, what you would clearly see is that these are all mainly based on copper.

So, these are popularly known as cuprates, because the basic structure revolves around the copper oxygen planes or sheets. So, mainly this is copper chemistry where this bivalent and trivalent a side cations are providing the required chemistry of the lattice structure, for this strange phenomena to occur. So, by and large if you look at the oxide chemistry it is only cuprates, and there has been no other report on a non oxide, non copper oxide lattice or compound, which is showing high T c.

And lastly in 2001, the part decade we had another strange discovery of magnesium bromide, which shows superconductivity at 34 Kelvin that again is a serendipity we will come to this issue later.

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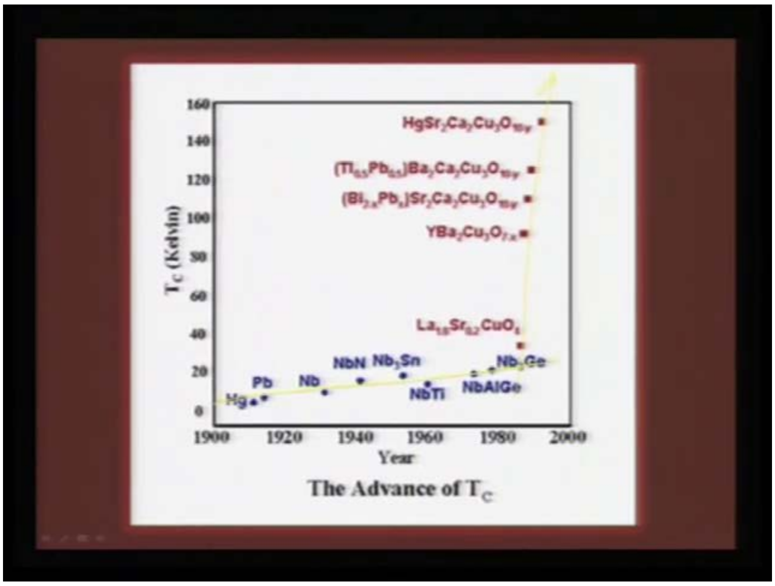

If you try to mark from the previous table a plot of years versus T c in Kelvin, you would see that there are two plateaus, one with all the metals a marginal increase has been aimed at. And then from 86 onwards you see a phenomenal jump in the T c, so there are two plateaus for this range of a compounds, one is to do with the metallic's and then you see a skyrocketing influence of this cuprates in increasing the high T c.

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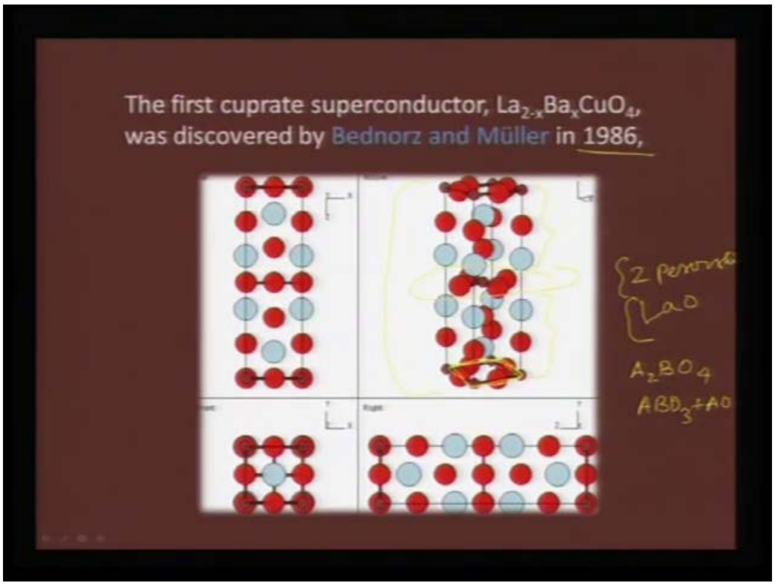

So, the first cuprate superconductor L a 2 minus x B a x C u O 4 was discovered by Bednorz and Muller in 1986, and if you view the crystal lattice in different perception this is what you would see. And as you see here, this is a nothing but a perovskite two perovskite layers are sandwiching a L a O layer. So, you have a two perovskite layers and in between these two perovskite unit cells, you have a lanthanum oxide sheet, which is separating and that's what's you would see here. Roughly this is one perovskite and this is one perovskite, and the intermediate layer is here lanthanum oxide.

So, that's exactly what would bring in the layered nature, so A 2 B O 4 is nothing but A B O 3 repeat with a interlayer A O. So, this forms you k A 2 O N A 4 structure, and as you would see here this is one unit cell, and in this unit cell you have copper in the a b basal plane, and its not along the c axis and this is the a b plane interaction which makes this a superconducting compound.

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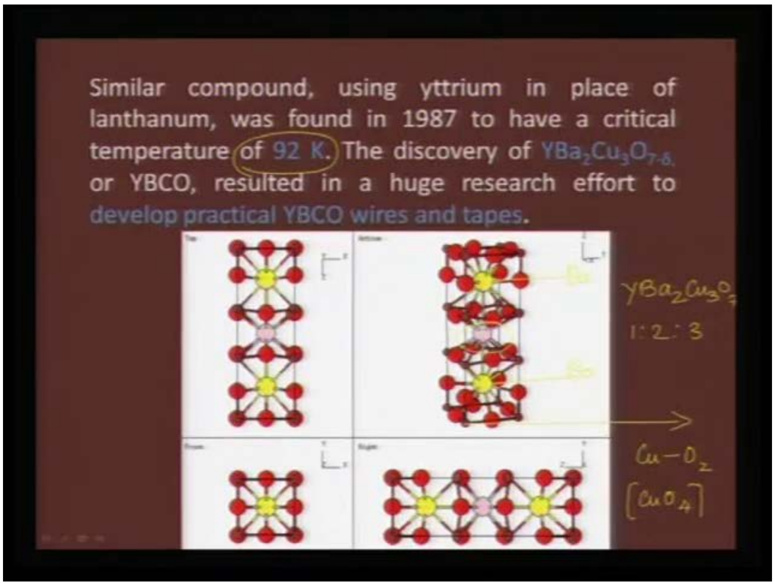

Similarly, yttrium barium copper oxide which actually shows the superconductivity at 92 Kelvin, this also has a very unique perovskite lattice and in this lattice you can see, yttrium barium copper in 1 is to 3 is to 2 is to 3 proportion. So, it is that's why it is called 1, 2, 3 compound, you can see here these two are the barium and in between you have the yttrium, and copper oxygen planes are in the terminal edges.

So, basically this unit is actually based on C u O or C u O 2 planes or C u O 4 pyramidal units this C u O 4 units is what brings about this sort of a crystal structure, with inter planes coming from yttrium oxide and barium oxide. So, this is another projection of the yttrium barium copper, we will look into the chemistry because what is fascinating from the materials chemistry point of view, is the constituents in this lattice. And how when we vary the this crystal structure, how the property can be adversely affected.

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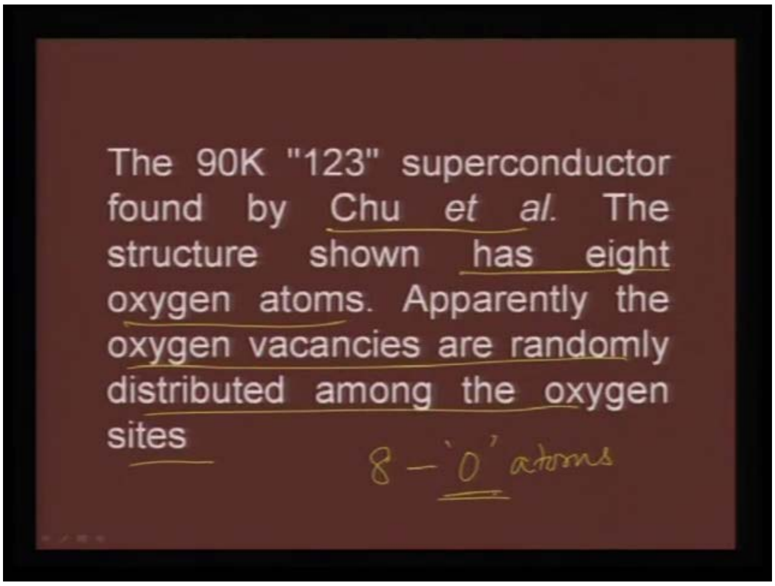

The 90 K 1, 2, 3 super conductor actually was found by chu et al, if you calculate the number of oxygen in this lattice, you would see that apparently the oxygen vacancies are randomly distributed among the oxygen size. And this unit cell actually has 8 oxygen atoms,, and this 8 oxygen atoms their random occupancy and how they can be taken out of the lattice, put inside the lattice will determine whether this particular compound will be superconducting or not.

In the next few slides I will show you, when we discuss about the chemistry of it how vulnerable this oxygen atoms could be. And if your not very careful in maintain this oxygen’s in the preferred lattice sites, you will end up with a insulating compound which is not going to even be metallic. So, that is the chemistry which is rich in this lattice cell.

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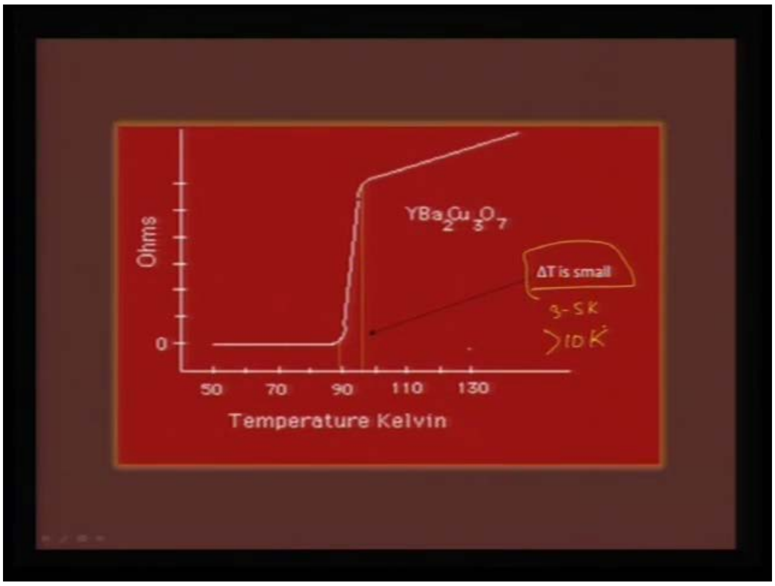

And then we will look at it, typically this 1, 2, 3 compound shows a very excellent transition and the onset is somewhere around 93, and it goes to a 0 absolute 0 state as close as 90. And if look at the delta T it is very, very small and this transition shows that the whole sample is superconducting, and it is not a biphasic compound it is a monophasic compound. As a result the delta is very, very narrow of the order of just 3 to 5 Kelvin. And smaller the delta T then you can be sure that your whole compound, the bulk is actually superconducting, you would also find out that if there is a biphasic compound or some impurities are there delta T can be more than 10 K, which clearly indicates that there is a insulating phase that is present in the compound.

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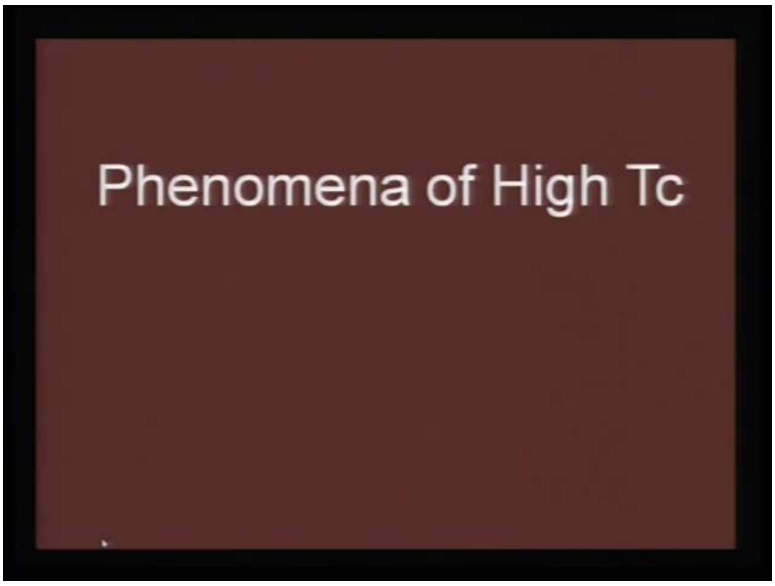

So, what is the phenomena of high T c? And what do we learn from here?

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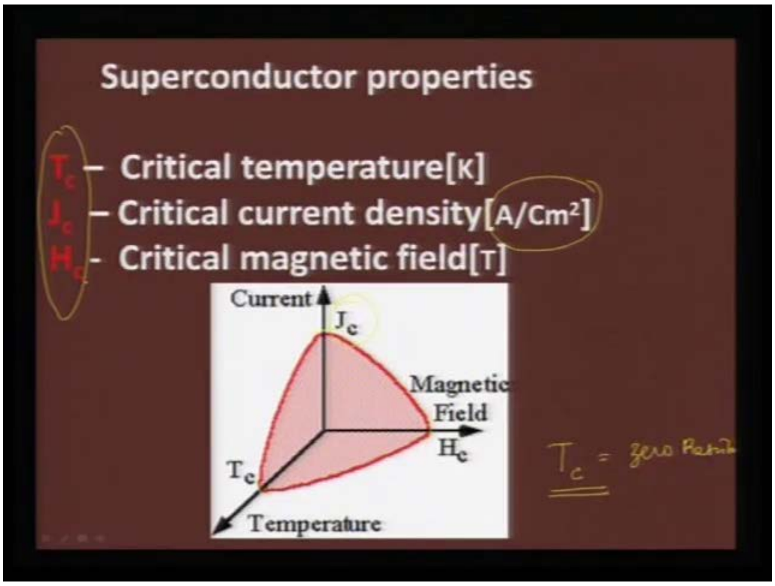

When we think of superconducting properties, there are three parameters that we need to familiarise our self, and these three are critical to decide whether this can actually be transformed or used into used in the applications. And whether they can really contribute to making devices, so when we think about this three parameters, all three are critical therefore, it is called critical temperature, critical current density and critical magnetic field.

Critical temperature T c is this is not curie temperature this is critical temperature, meaning the temperature at which the substance goes to 0 resistance. So, it has to show 0 resistance therefore, that is what we call it as T c and in such a state what is the critical current density, in other words how much of the current that this material can hold it can hold without a loss. So, that measure that can also be measured using physical experiments, so critical current density is one way to map whether your materials can be used for application or not.

And then critical magnetic field is another issue, where the material can sustain only a particular amount of magnetic field, beyond which the flux density of the applied field can go into the compound, in other words it will remove that diamagnetic state. So, when the compound can ripple that particular amount of field that is called as critical magnetic field and that is the strength of you superconductor the diamagnetic state. So, all this three has to be measured, so when we think about superconducting oxide we need to have this three issues in picture.

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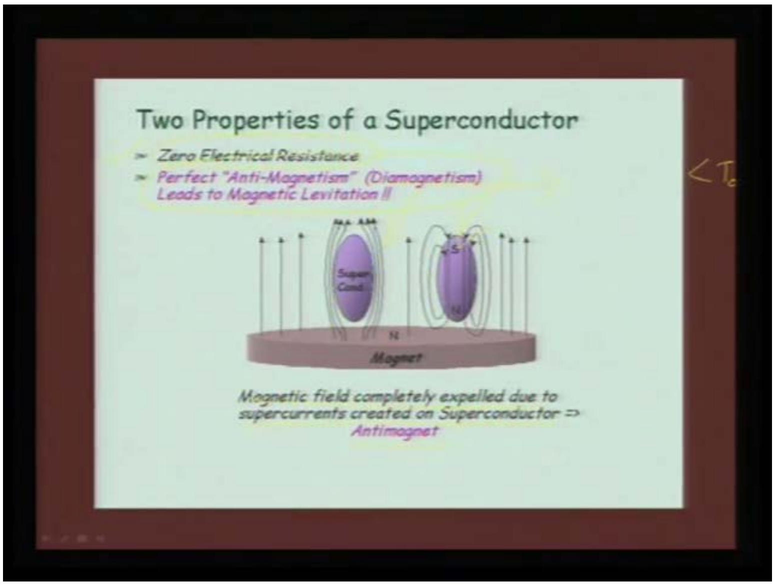

Now, when I talk about this critical field then the first thing that comes to our mind is the property that governs this superconductor, one is the most important property is the 0 electrical resistance. And the next one is the anti state, anti magnetism is nothing but a diamagnetic state, in other words the material may not be diamagnetic at room temperature. But, when you cooling there is something happening with the lattice which makes this material a diamagnetic material, as a result it will expel the magnetic field.

And when it is in a diamagnetic situation that is below the critical T c point that is below T c, it is in a perfect diamagnetic state and in that state one of the manifestation is the magnetic levitation. So, as you would see here, this is a superconductor, superconductor actually when it kept inside when it kept in a field it will ripple. So, the flux will not permeate through the sample and this is the diamagnetic situation.

But, over the critical field then the flux can actually go into the superconducting material, and this is not the high T c phase. So, in at high T c you would see this expulsion of the flux density, so magnetic field completely expels due to super currents created on the super conductor, and this is termed as a antimagnetic state.

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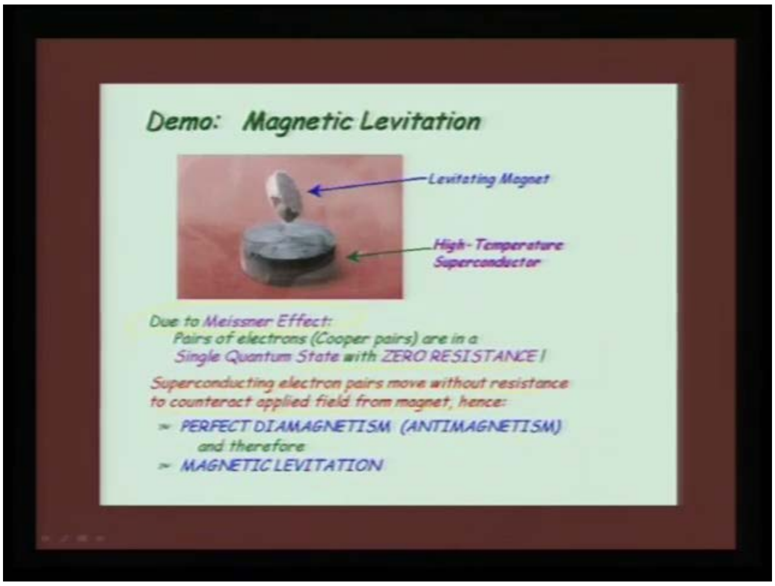

So, if the sample is in a levitated situation or in a diamagnetic situation one of the most important manifestation is it can actually lift up a magnet. So, in this cartoon you would see this, and in the next cartoon a animation is there where you will understand this. So, if there is a magnetic levitation, then it is actually due to meissner effect where the pairs of electrons are in single quantum state with 0 resistance. As a result since they are paired up they attain a diamagnetic situation, which will actually ripple the magnetic field.

So, superconducting electron pairs move without resistance to counteract the applied field from magnet, hence we get this perfect diamagnetism and as a result it manifest with the magnetic levitation. In fact, this magnetic levitation is the true response of a superconductor, of any superconductor therefore, the magnetic levitation is one of a very fundamental application that we can derive from a any super conducting material. In the next cartoons I will show you a demo of how this superconductor works, and how this issue of magnetic levitation can be extended to practical application, and after than we can look at the chemistry of this oxides.

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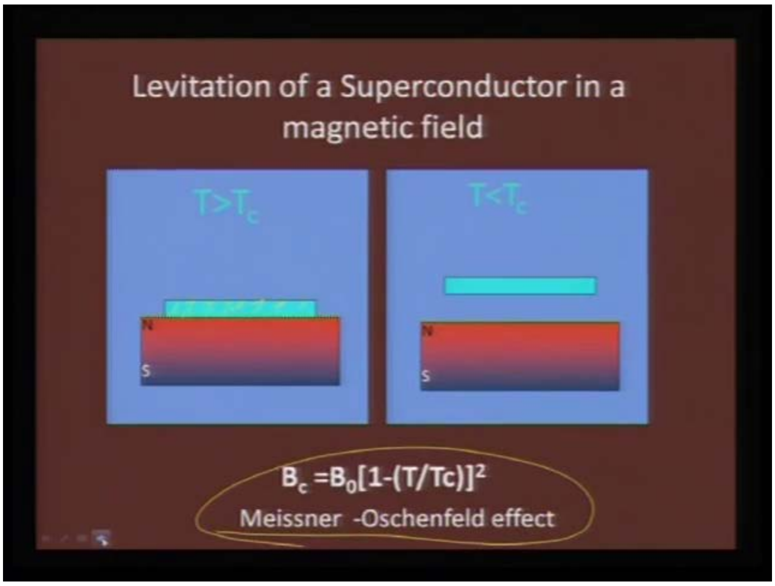

So, levitation of a superconductor in a magnetic field, if you place a superconducting compound on a bar magnet, you would see nothing happens when temperature is above T c. But, when temperature is below T c this material is actually lifted up and it can float, and this is called the Meissner Oschenfeld effect, which is popularly known as magnetic levitation.

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You would see in this cartoon a demonstration of how magnet can float on a superconducting object, as you see here this is this is your magnet and this is the superconducting compound, which is a black block. And now, in the cartoon you would see nitrogen, liquid nitrogen will be poured into this block, so you can see this magnet is now actually placed on the superconductor. And nothing happens a magnet a the there is no repelling response there.

Now, we can pour some liquid nitrogen on this block and cool that black block, which is nothing but your superconductor. So, now, the material is going to liquid nitrogen state, and now if you place that magnet you can see the magnet is actually floating, and you can also see the magnet is rotating. So, there is a field that is expelling the magnet and when the material is actually in a superconducting state.

Now, if we can take the block out then the material will again come back towards room temperature, and in that state you would see than the material does not behave like a superconductor. You can see here the force that is applied on the magnet, but still magnet is being rippled by the superconductor, so the currents inside the super conductor is very strong to through away this magnetic force. Now, you can see even you can lift it in such a situation, and suppose you keep it out say the liquid nitrogen, you can see this black block is now getting back to room temperature.

And as it crosses the critical temperature then the magnet comes and falls back. This is the Meissner effect that you can see, and critical issues there is that the whole phase the bulk of this material has to be superconducting in order to eject or ripple the magnet. You would see same manifestation in a form of a train.

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Where you can realize a floating train using the same issue of superconductor, and here you can see a small engine sort of a stuff is made, and the belt is actually made of a magnet. So, you can see that this engine is actually now floating on the magnet, and now we can freeze this superconducting material, and you can put it on the magnet pathway then you can see that it is actually hanging on the track. So, if you place this superconductor on the track and if you give a small momentum, you would see this high T c superconductor is actually going around the track.

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You can see here that this single pellet of 1, 2, 3 compound is actually going and the moment it loses it is critical temperature it falls down on the track.

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Now, you can do the same thing put the black material a engine sort of a module, and we can see how this can rotate friction less, and still it is bound by the influence of the magnetic field. And this is the way the magnetic levitation works and this is a prototype of engine, which can be operated and this is the module that has been used by this group, which is meant to accelerate, the propulsion actually comes from a device which is hanging there. So, when the floatation occurs depending on the propulsion it can go faster or lower and that is shown here.

Now, you can again put some superconducting material inside the engine, and we can try to bring it to critical current and based on the propulsion that you use we can now maximize the acceleration and it can go in any speed. And you can try to de-accelerate and bring it again to a controlled speed, so both are possible and this is the phenomena of levitation that is useful to apply a in many of the applications.

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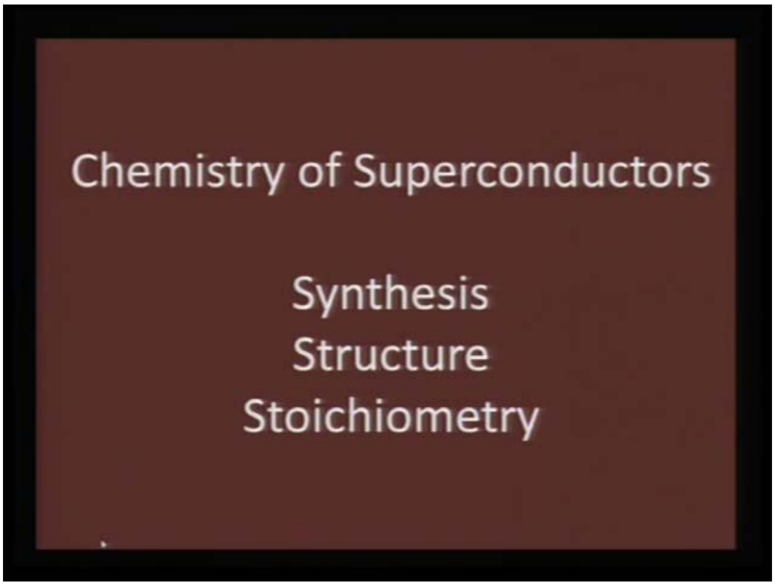

Now, let us go more into the structural aspects and find out what is the essence of the superconductivity? And what is really controlling this phenomena in oxide materials. As you know, yttrium barium copper oxide is not a simple oxide, it is a complex oxide therefore, making this material itself is a herculean task, although no any undergraduate labs can even perform this experiment.

In the initial days it was very difficult to understand the chemistry of this because even if you miss out little bit on the synthetic part, you might end up with a non-superconducting phase, which will be a green compound. So, synthesis is important and then once you have a feel on synthesis you can try to play around with this structure, and also on the stochiometry. So, I will tell you how everything progressed over the years.

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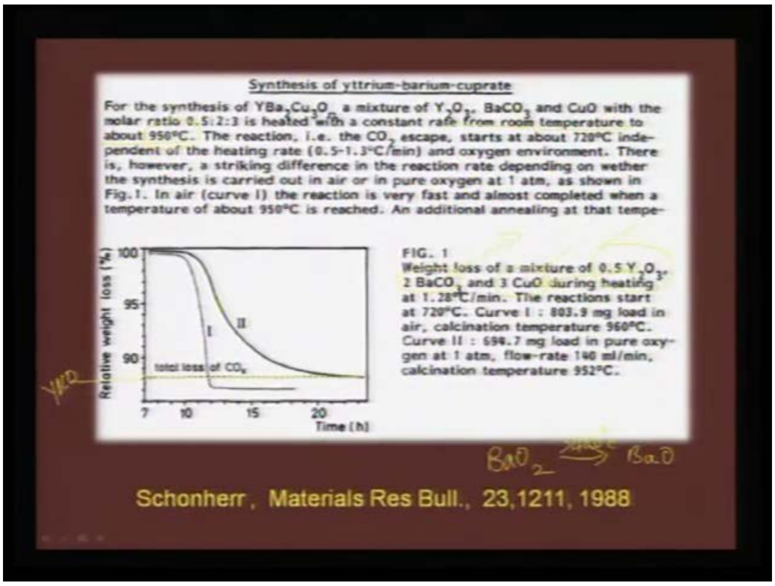

This is a cartoon, where you can find out how critical making this material is, and as you would see here this is a thermo gravimetry just gives you an idea, how the solid state reaction happens. You take 0.5 moles of yttrium oxide, and 2 moles of barium carbonate and 3 moles of copper oxide, and this has to be ground intimately for many hours. And then once this is intimately mixed then you can heat this material, and the material has to be heated, from room temperature up to 950 degree C.

And during this time, you would see carbon dioxide going out of barium carbonate, other than that all the other mixtures are oxides. So, once the carbon dioxide escapes than you would see, there is a weight loss of say around 13 percent and then the final compound is actually formed here. The final compound actually corresponds to YABCO, but problem here is if barium oxide is also stable, then it is easy to take all the component oxides into picture, and make the phase much more easier.

But, barium oxide is very reactive therefore, always it ends up with barium carbonate and barium carbonate undergoes decomposition only above 800 degree C. Therefore the reaction between yttrium, copper and barium has to happen only above 800 and the nominal temperature is achieved at 950 degree C. Problem is when the mixture is being heated there are chances that some intermediate compounds can form between, reactive yttria and copper oxide, and when that happens then the stochiometry suffers.

So, this is the problem with such a superconductor, so many chemical routes wet chemical routes have been brought, where barium carbonate can be avoided and reactive barium oxide can be used. One of the convenient way that this has been achieved is take barium peroxide, and barium peroxide above 400 degree C releases reactive barium oxide. As a result then above any temperature above 400, you will have a very reactive mixture of yttrium oxide, barium oxide and copper oxide. Therefore, the single phase compound can be made with ease. So, there are lot of intricate issues that are involved in synthesis I will not run through every detail, but then show you how to make such a single phase compound from solid state method.

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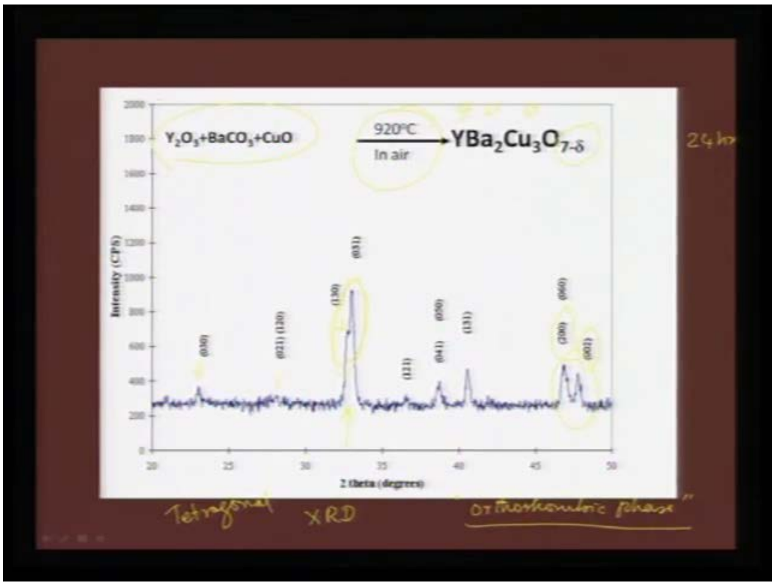

Once you take yttrium barium copper oxide, and then you heat it at 920 degrees in air for say 24 hours, the first pattern that you would see from the XRD powder XRD pattern, is a peak resembling something like this. This is corresponding to 0, 3, 0 and you would see a small reflection here, and then the major peak that comes here will be around 32 degrees, which corresponds to 1, 3 , 0 and 0, 3, 1.

As you would see here, this major peak actually has a splitting and this splitting actually corresponds to, so if you see a splitting the main peak then; that means, a this is orthorhombic phase. And that orthorhombic phase is actually a superconducting phase, but what you would notice here is that it should be O 7 according to this formula. Because, yttrium is 3 plus, barium is 4 plus and copper is in 6 plus because of 3 cooper.

So, 6 plus 4, 13 you as actually get 6.5 as the stochiometry compound, but you would see the range is anywhere between 6.5 to 7, and that is what makes this particular compound very interesting. Because, you have labile oxygen's which can be incorporated or removed, which controls the superconducting state therefore, this becomes a rich chemistry to achieve a fully oxygenated compound, good enough to give a clear T c at 90 Kelvin.

One of the other signatures that you should follow, when we look at orthorhombic phase is this splitting, and the splitting comes somewhere comes somewhere around 46 degree which is indexed to both 2, 0, 0 or 0, 0, 2. If this peak is a single peak, then it resembles it is a tetragonal phase and in that case even this major peak will not have this splitting. So, if there is no splitting then it is a tetragonal phase, and if there is splitting it is a orthorhombic phase. So, you can easily map whether you are working at a critical oxygen containing compound, if it is not the orthorhombic compound you can be sure that it is not going to be superconducting. So, you can have fine tuning done just by looking at the x ray mapping.

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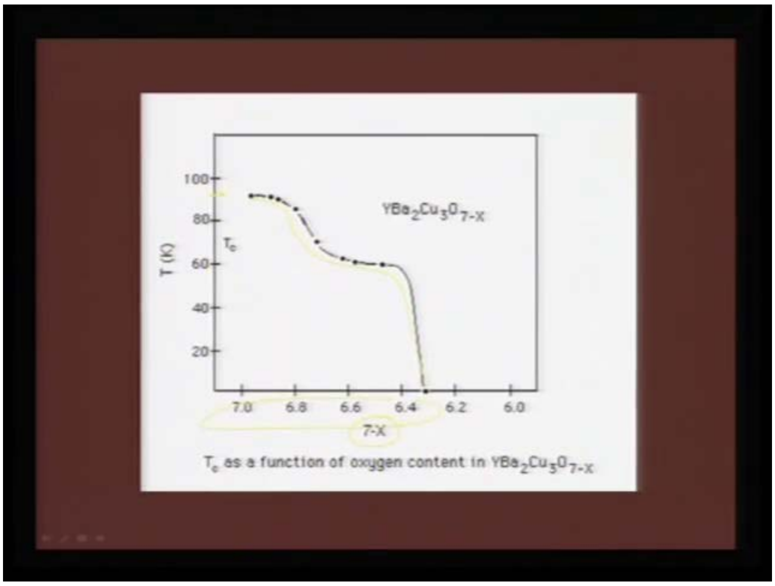

As you would see here, this 7 minus x or 7 minus delta is very critical because as you vary from 7 down to 6.5 according to the stochiometry, you can also see the T c drops to a non-superconducting state. When it is a superconductor you can clearly get a 90 Kelvin

T c, and that is nearly as oxygenated compound. So, where does this oxygen go that we can see from the crystal lattice if you take a closer look at it.

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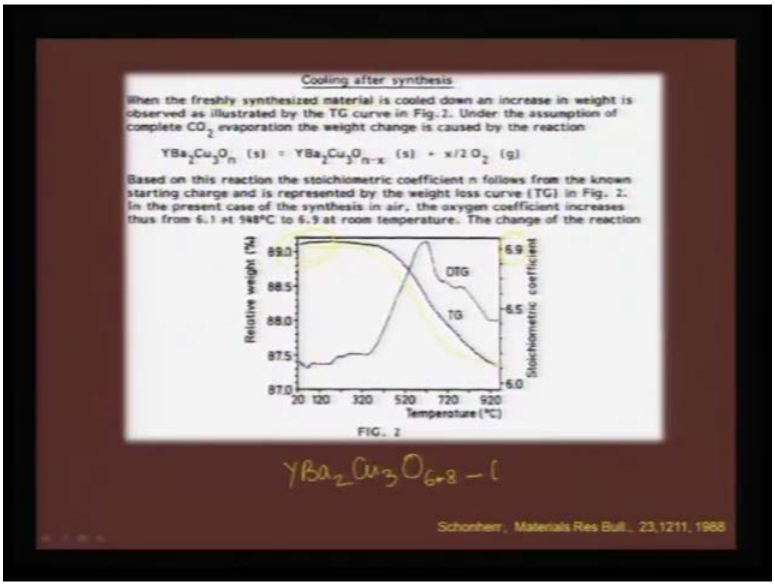

Now, one more thing we need to understand if you do a TG and DTG, you would find out that it loses oxygen, when you heat up to 920 degree. And therefore, freshly synthesized sample at 920, when it is actually cooled down at room temperature it will actually be a fully non stochiometric compound, with oxygen value ranging from 6.8 to 6.9. So, 6.9 Y B a 2 C u 3 O 6.8 to 6.9 is very critical for the superconducting phase to occur.

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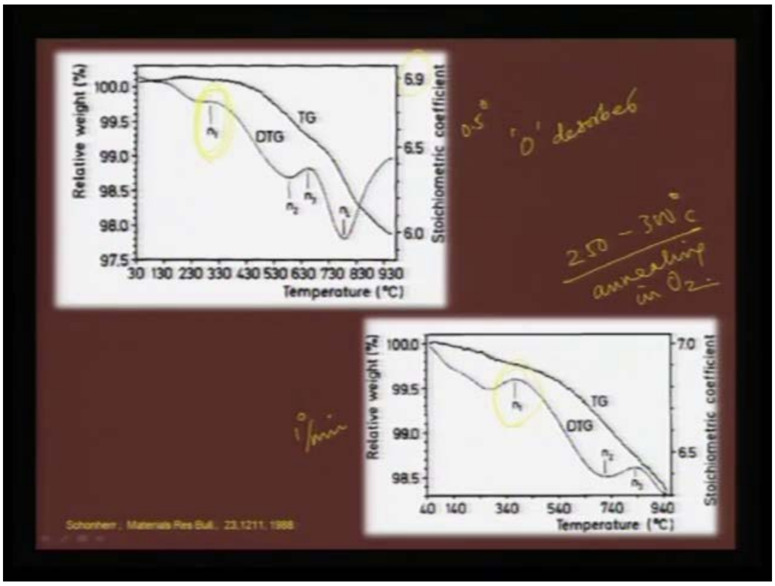

You would also see, if you do the same TG at 0.5 degree per minute and at 1 degree per minute, there are many useful inflection that are coming. If you look at the derivative TG graph at n 1 there is a peak, at n 2 there is a peak, n 3 there is a peak and n 4, so there are four different temperature zones at which oxygen is getting desorbed. So, we need to be very cautious about this desorption that is occurring, we cannot control this 730 degree C because it is at high temperature.

Therefore, it is important if we need to achieve this 6.9, we need to be very careful to anneal this compound at 230 because that is where the oxygen exchange is happening. So, any sample which is prepared before we measure the superconductivity you need to make sure that there is a post annealing that is done, at around 300 degree C for a long time. So, that enough oxygen's are getting incorporated into the lattice, and that is what we see if you do it at a faster rate, probably you do not see the n 1, n 2, but there are only three zones, but nevertheless n 1 is still there. Therefore, this range say from 250 to 300 degree C the annealing has to be done in oxygen, annealing in oxygen has to be done. So, that you get a fully oxygenated sample to achieve 6.9 stochiometry.

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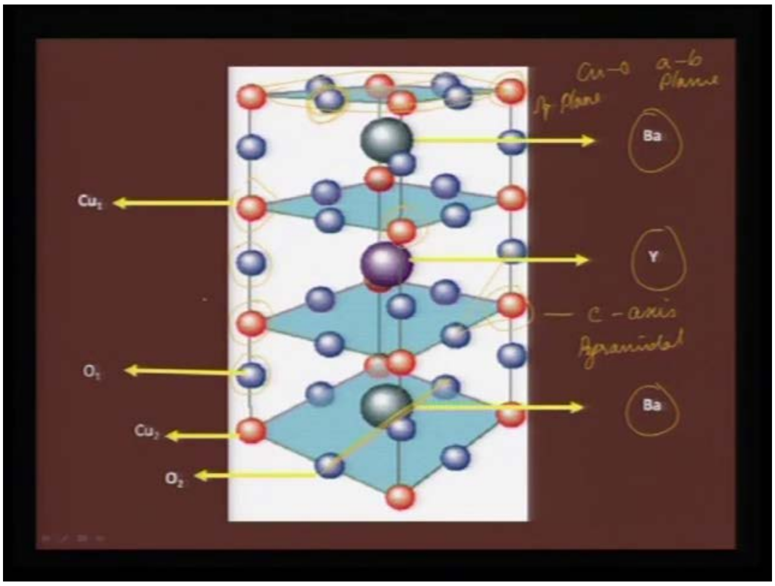

So, the issue of a oxygen content actually brings us back into focus what sort of a unit cell that we have. And if we take a close look at it, we see that the barium ions are placed here and the yttrium ions is actually separating these two perovskite units cell, and then you would see copper in this n chain, and also copper along the c axis. So, this is a copper oxygen unit, in the a, b plane and we also have copper oxygen unit in the c axis.

So, the coordination of this copper oxygen unit actually is different, in this case this is of a square planar nature, and this is pyramidal because it is actually getting linked with the apical oxygen. So, two types of coordination's are there apart from that we would also try to take a close look at the oxygen occupancy, you would see here this is mainly based on the copper oxygen sheets that are prevailing in the a, b plane.

And there are also oxygen's along the c axis, and the number of oxygen's that were getting desorbs, as we saw in the earlier slide denotes oxygen can actually be lost here, oxygen can be lost between these two sites, oxygen can be lost her also. So, there are different places oxygen's can be labile. But, as you saw with each temperature region one particular type of oxygen is actually going, now we will see more closely which of this oxygen's are labile and how they control the superconductivity.

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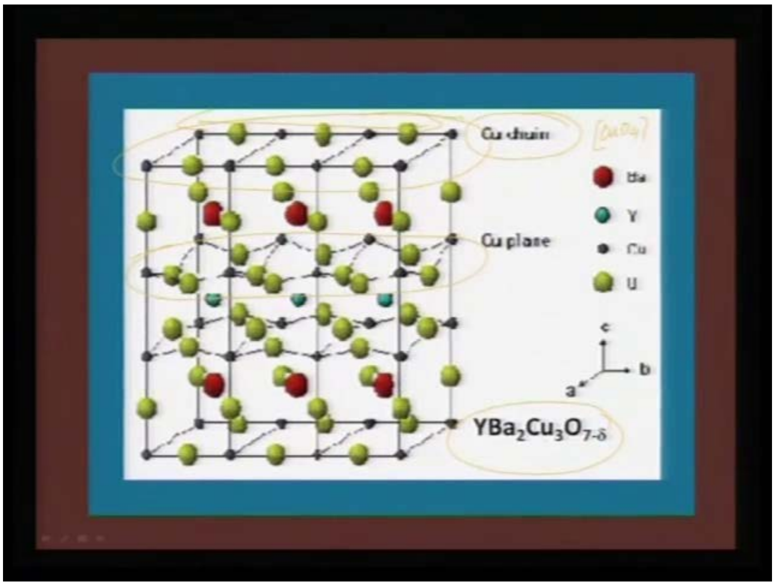

And therefore, if this is one particular unit cell with full composition of yttrium barium copper oxide, and in this you can easily observe that this is the copper oxygen chains that are there. These are the copper oxygen chains, and these are the copper oxygen planes and their coordination is actually different here, but what you would see that the high T c is actually controlled by the copper oxygen chains, which are a C O 4 type of units which are placed here.

This copper oxygen chains are critical to the high T c, and no matter what happens in the copper oxygen plane it does not seem to adversely affect the high T c. So, the core of the superconductivity is the issue of controlling the oxygen stochiometry in the copper oxygen chains because this is your a, b plane.

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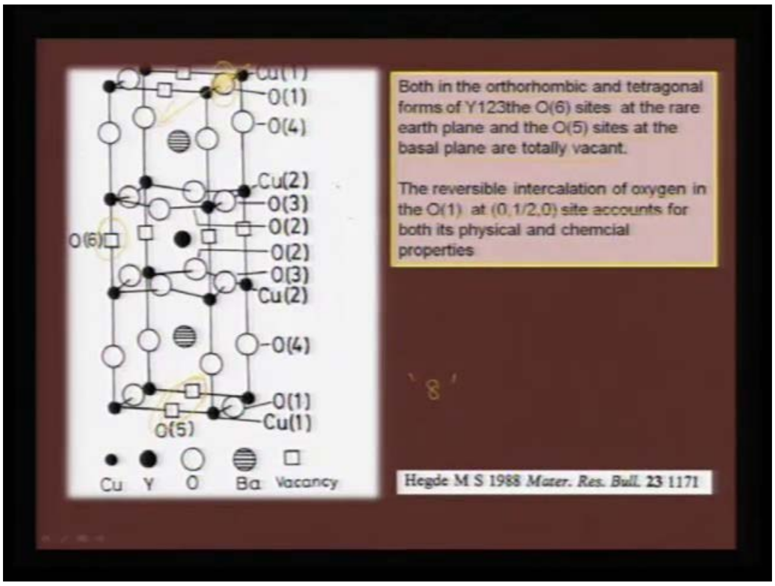

This is a nice view graph which will tell us, where does the oxygen deplete in the first place, both in the orthorhombic and tetragonal forms of the y 1, 2, 3. The O 6 sites as you would see, O 6 sites at the rarerth plan and the oxygen five sites at the basal plane are totally vacant. So, that’s why it is denoted with the square here the squares indicate that these are places where oxygen’s are missing, and that is why you get a total number of 8 oxygen atoms because there are enough vacant sites.

And in this vacancy the places where oxygen can be easily put, and easily taken is this O 5 vacancy, the reversible intercalation of oxygen in O 1 that is here, and at O 5 actually amounts for the physical and chemical properties of this yttrium barium copper oxide. And this can be studied, using temperature program desorption, you can clearly find out that it is possible for us to incorporate oxygen in this region. The moment oxygen is taken out of O 1 which is your copper oxygen chain immediately the T c is lost.

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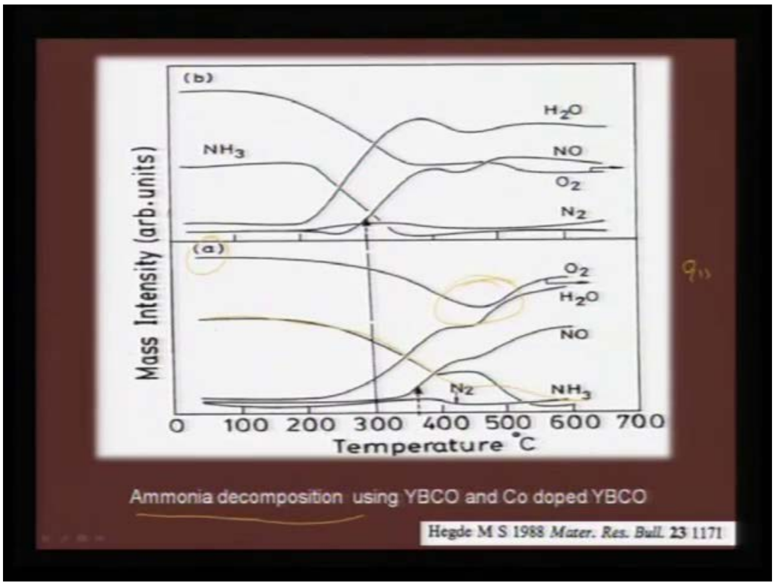

This is another cartoon which tells us, how critical the oxygen stochiometry is and if your using, ammonia as a test gas for ammonia decomposition using yttrium barium copper, you would find out from this plot a which is for YBCO compound. And this is for the cobalt doped YBCO compound, the oxygen depletion is somewhere around 400 to 500 degree C. And this particular oxygen is actually coming out of the woven site which we saw in the previous cartoon, and the more the lattice oxygen is actually taken the more the faster is the conversion of ammonia to nitrogen and to N O and other related oxides. So, the place where oxygen is actually missing comes from the copper oxygen chains.

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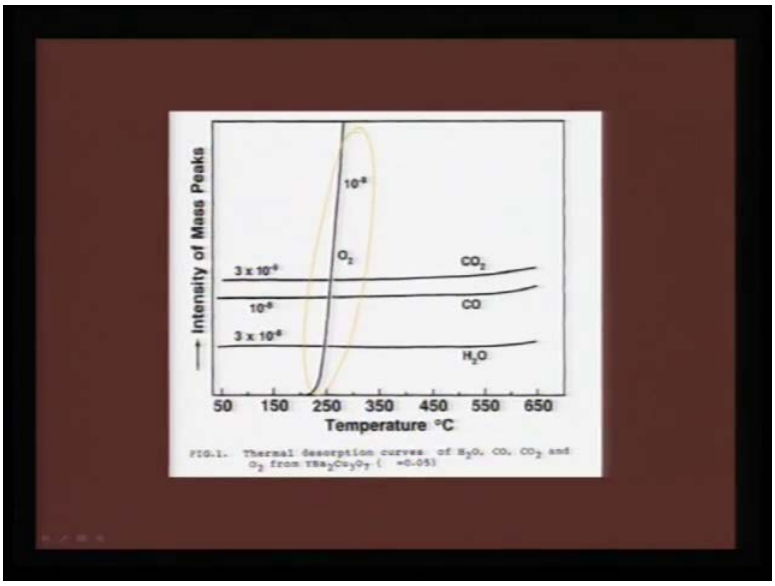

And you can also find out the relative proportion of carbon monoxide or carbon dioxide that is coming out, there is a very steep increase in oxygen coming out of the yttrium barium copper oxide, somewhere around 250 degree C.

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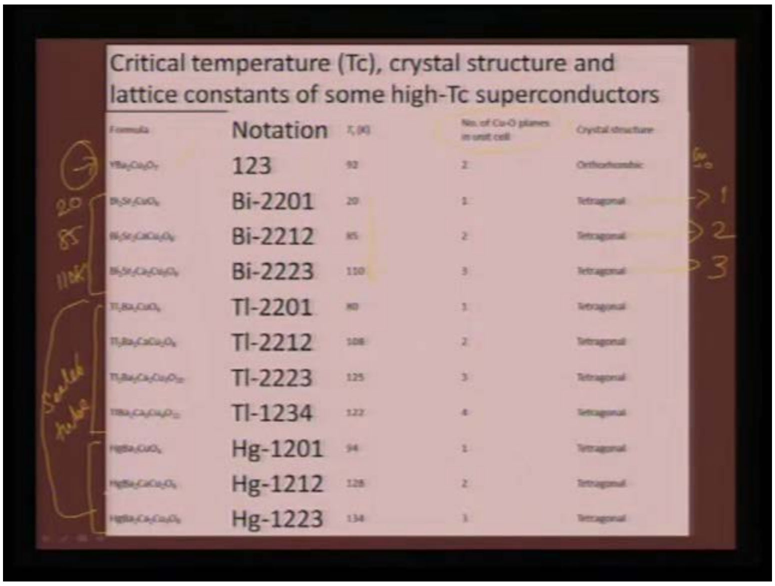

Now, having said that we can actually map some general behaviour in all the high T c superconductors that are reported. For example, you take the 1, 2, 3 compound Y B a 2 C a 3 O 7, and from there you can see there are three other compounds which are mentioned, those are bismuth related compounds, but they are nevertheless cooperates.

And bismuth related compounds, actually shows a increase in T c and if you compare the T c with the number of copper oxygen planes in the unit cell, you would find out that with increase in the copper oxygen planes from 1 to 2 to 3, the T c is actually increasing from 22 85 to 110. So, this is a very clear proof that copper oxygen planes are very critical for the superconductivity, so copper oxygen planes are very critical for superconductivity. So, when you try to make a material if you can make a repeat of this copper oxygen planes, then there is a possibility for us to increase the T c.

But, it has also been found out that the number of copper oxygen planes which can be incorporated into the stacked perovskite layer, that T c actually seems to saturate beyond three. So, there is a limiting situation for such stackings because it is possible to decorate such perovskite interlayer's with the copper oxygen sheets or planes, using some physical vapour deposition, but it has been found that the T c does not seem to increase more than three copper oxygen planes.

Another group of compound that has really attracted interest is thallium based cooperates, and mercury based cuperates as you can see, the maximum has been achieved for mercury based, cuperates which shows T c at 134 K. Main problem with bismuth thallium and mercury is that they really evaporate therefore, you can end up with the non stochiometric or non-chemically homogeneous compound.

So, most of the reactions that are done here is actually achieved in sealed tube conditions, and that imposes a problem of making this in bulk and that's why yttrium barium copper is still preferred for practical application because you do not have stringent requirements, in terms of synthesizing this you can just do it in open air. And you can make it in kilogram quantities or gram quantities which is not a problem therefore, although these superconductors do hold a potential because of their high T c, but because of the processing limitations the applications are very few.

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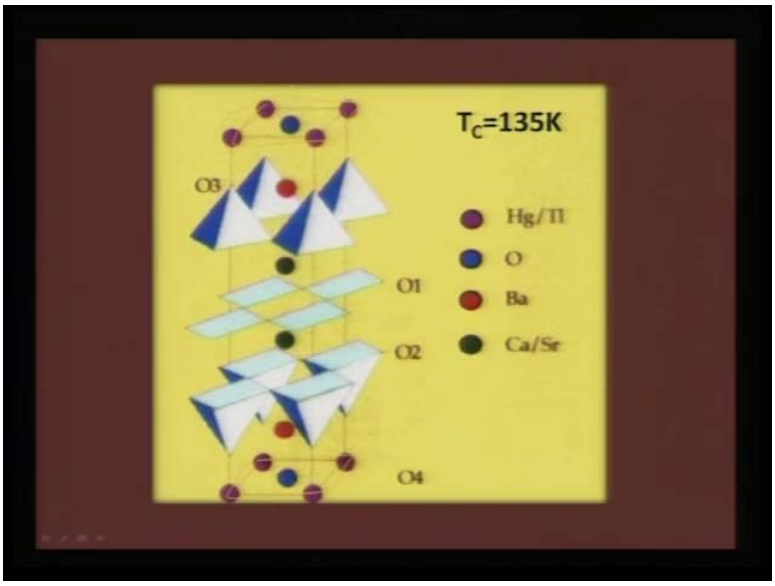

And this is typically the unit cell of your mercury based mercury or thallium based superconductors, you can see here again the copper oxygen planes which actually control the superconductivity. And in between if you can actually incorporate a copper oxygen plane, then the T c actually can be modified.

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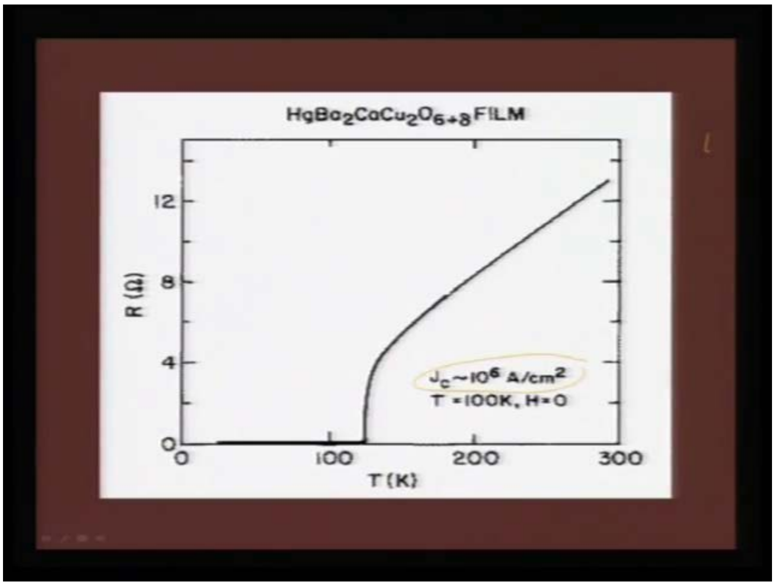

And the typically for a mercury based superconductor the T c can be seen here, and they have very high critical current density of 10 power 6 ampere per centimetre square and the T c is somewhere around 130 Kelvin.

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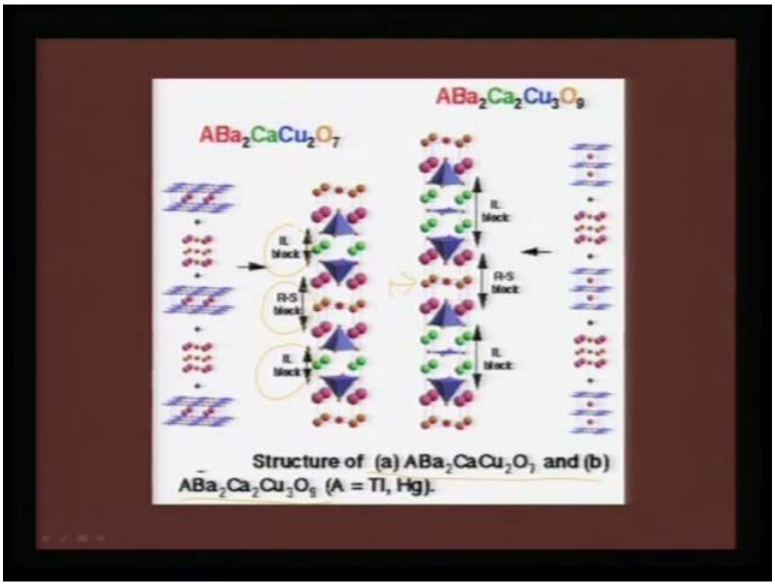

As I told you these are perovskite blocks which can be modified, so if you can this is a illuminate block and the rock salt block, illuminate block. So, it is very easy for us to incorporate copper oxygen sheets in between to increase the superconductivity and therefore, many compositions have been reported for thallium and bismuth based compounds.

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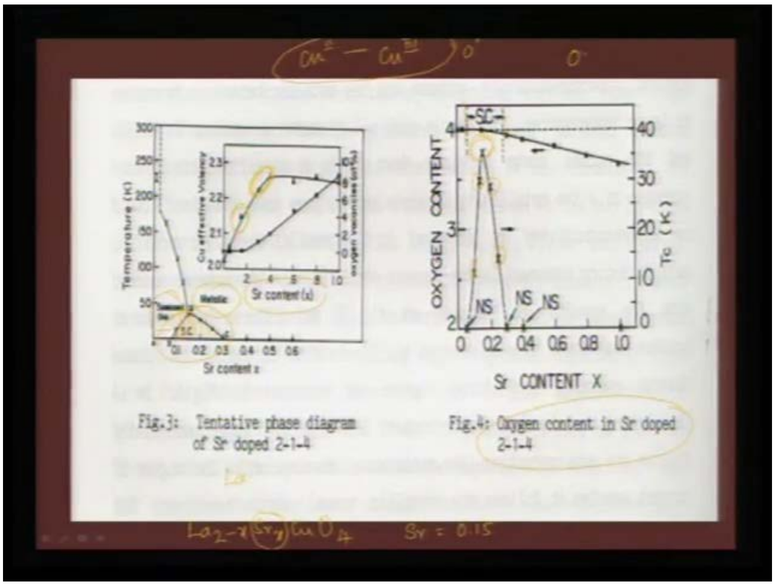

Coming to the phase diagram, then we can understand how critical the doping concentration is as I told you, lanthanum I will write it here, lanthanum two minus x S r x C O 4, actually has the critical concentration of strontium. So, if you actually make a substitution of strontium in the lanthanum site, then you can look at the T c maxima and you would find out, the T c is maximum only for a critical composition of say 1.5. Beyond that, if we keep doping then the superconductivity actually takes them, so this is the region, where you can aim at strontium doping.

So, strontium with 0.15 x is the compound which will actually give you maximum superconductivity, beyond which you would see it is in a metallic range, if it is below 0.15 then it is in a semiconducting like state. So, this is critical for us to understand what is the compositional limit because in strontium content if you increase, you can see that it is fully oxygenated. And therefore, the oxygen vacancies are at it is maximum somewhere around this region.

And this is critical for high T c and you would also find out somewhere around this the nominal composition of your copper valency or copper valence state is somewhere around 2.1 or 2.2, which means copper is actually having both copper 2 and some amount is partially substituted with copper 3 plus, and that is coming because of oxygen deficiency to bring about the right neutrality, charged neutrality some of the copper gets oxidized to copper 3 plus.

And this is again another plot, which tells about the oxygen content in strontium doped L a 2 C o 4, and you can see very well here that this is the superconducting region where the oxygen content is very close to 4. And the T c at is at it is maxima, if you actually bring down either way then the T c falls rapidly and it goes into a non superconducting state. So, the incorporation of oxygen in all this cuperates is very critical and that governs also partially the oxidation state of copper 2, copper 3 which is actually a affecting the copper in the copper oxygen chain, which is in the a b plane.

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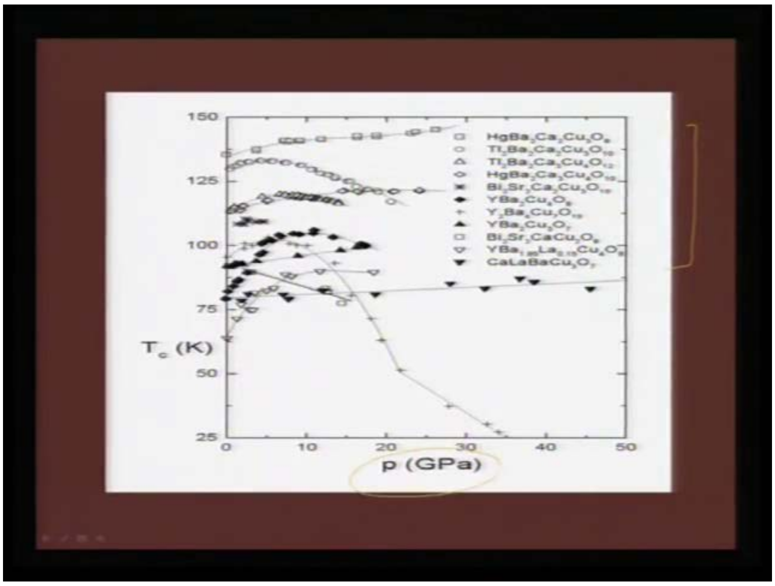

And here again the we see a several other ways that we can enhance the T c for all this compounds that we see here, yttrium barium copper or bismuth based or mercury based or thallium based. We can actually try to maximize on the T c by applying pressure, this is not various chemical pressure effect, this is a physical pressure effect by which we can enhance the T c.

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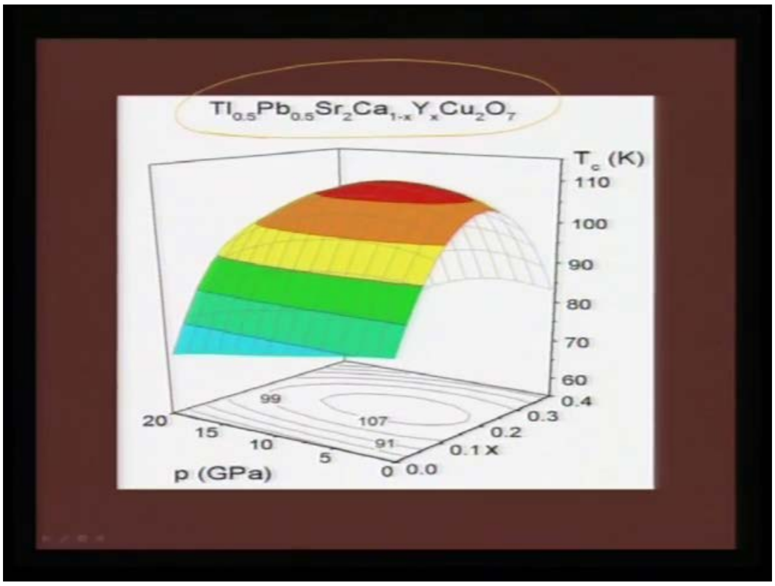

And here, thallium based compound is same here and this is a three dimensional plot of T c versus composition of yttrium versus pressure. You can see only at critical compositions you can get a maximum T c.

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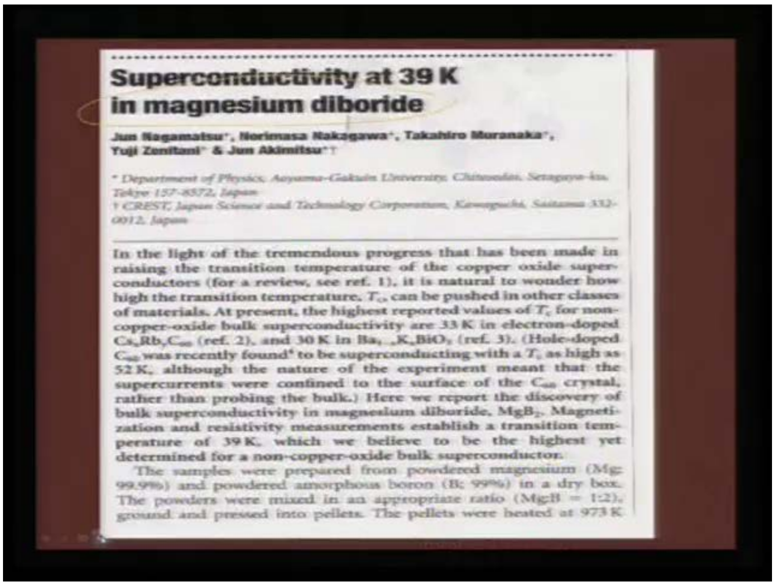

Superconductivity at 39 K in magnesium diboride

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In the light of the tremendous progress that has been made in raising the transition temperature of the copper oxide superconductors (for a review, see ref. 1), it is natural to wonder how high the transition temperature, T_c, can be pushed in other classes of materials. At present, the highest reported values of T_c for non-copper-oxide bulk superconductivity are 33 K in electron-doped $Cs_xRb_yC_{60}$ (ref. 2), and 30 K in $Ba_{1-x}K_xBiO_3$ (ref. 3). (Hole-doped C_{60} was recently found[4] to be superconducting with a T_c as high as 52 K, although the nature of the experiment meant that the supercurrents were confined to the surface of the C_{60} crystal, rather than probing the bulk.) Here we report the discovery of bulk superconductivity in magnesium diboride, MgB_2. Magnetization and resistivity measurements establish a transition temperature of 39 K, which we believe to be the highest yet determined for a non-copper-oxide bulk superconductor.

The samples were prepared from powdered magnesium (Mg: 99.9%) and powdered amorphous boron (B; 99%) in a dry box. The powders were mixed in an appropriate ratio (Mg:B = 1:2), ground and pressed into pellets. The pellets were heated at 973 K

Lastly I just would like to bring to your focus that this is one the recent discovery although it is 10 years old, but this is again a serendipity where magnesium dibromide has been found to show superconductivity, at nearly 40 K. And this is a black compound incidentally the group which was working in Japan, they did not have the proper starting material to synthesis one of the superconducting compound. When they found, magnesium diboride in the shelf and they just took that and studied they found that this diboride also shows a superconductivity. Therefore, the game has always been a serendipity as far as this superconductivity is concerned.

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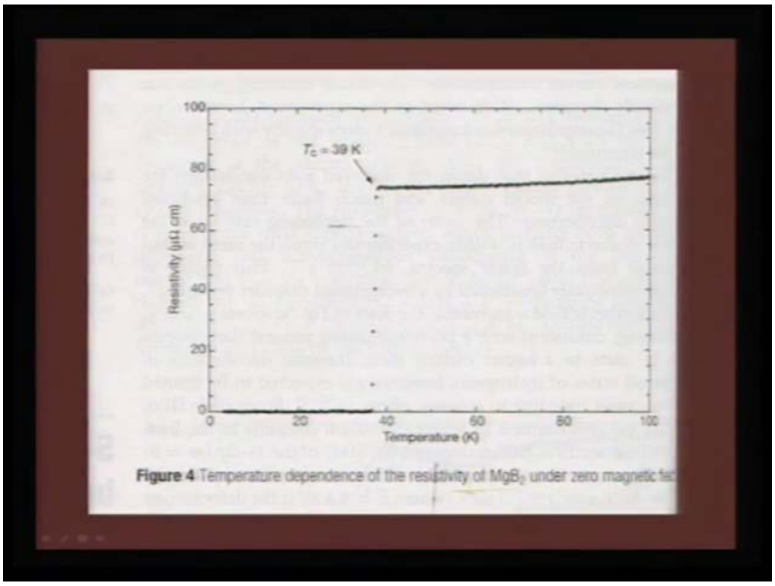

And this is the T c curve which clearly shows a 40 K super conductor for magnesium boride.

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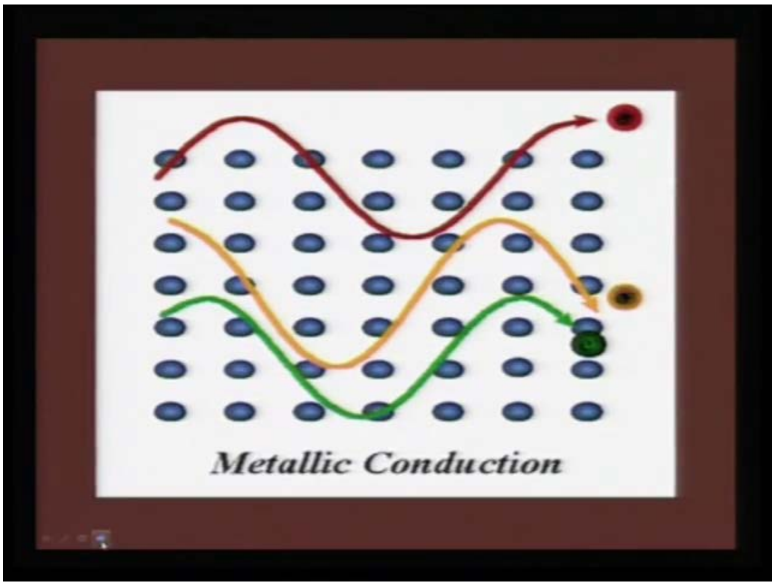

And mechanism it is based on metallic conduction, you would see electrons are going through the lattice with minimum scattering.

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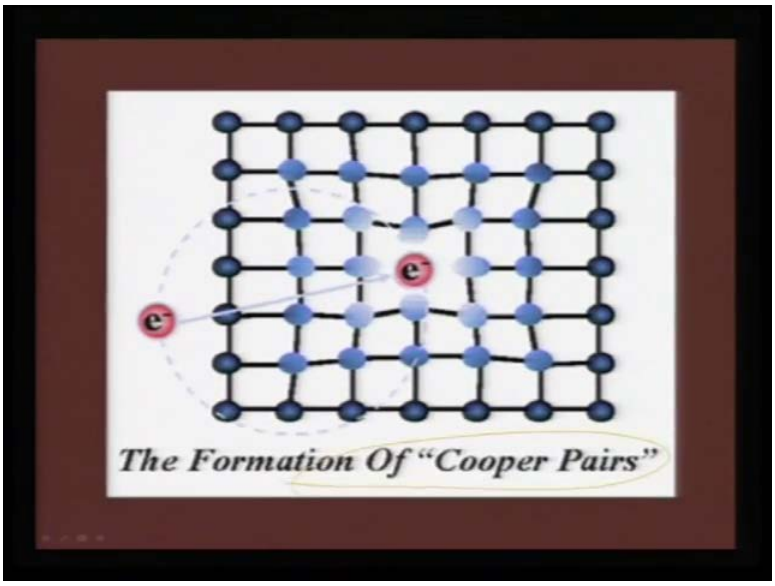

But, what really governs the superconductivity is the formation of cooper pairs, and this cooper pairs really govern the issue of superconductivity.

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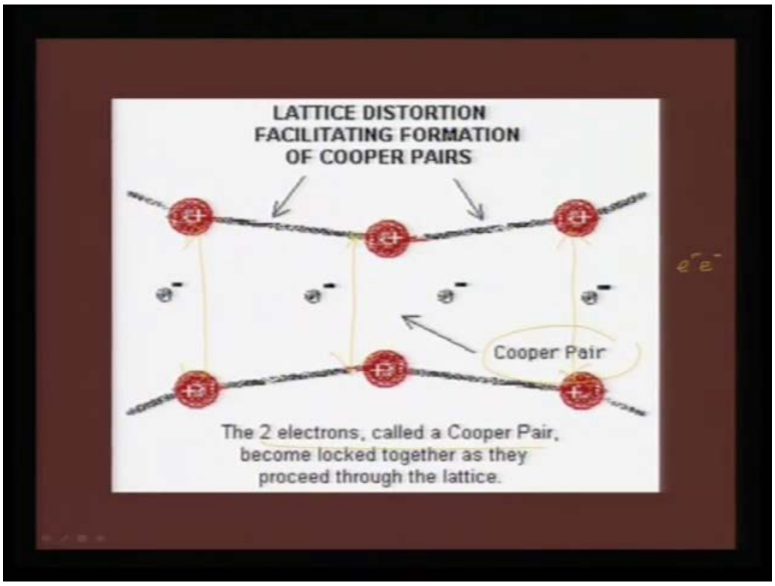

And how does this copper pair formation occurs, cooper pair is nothing but two electrons going hand in hand they are running through the channels, and they induce a super current. And this formation of copper pair is actually facilitated by the lattice contraction here, these are your atoms and when there is a distortion in the lattice. Then a cooper pair is actually formed the two electrons called the cooper pair belong becomes locked together as they proceed through the lattice which gives us strong super current.

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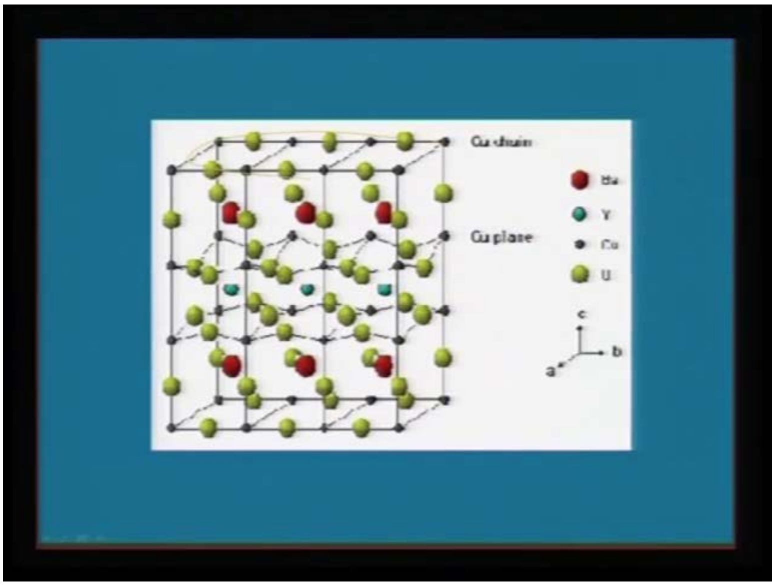

And this is actually confined in the copper oxygen chain which is the cause.

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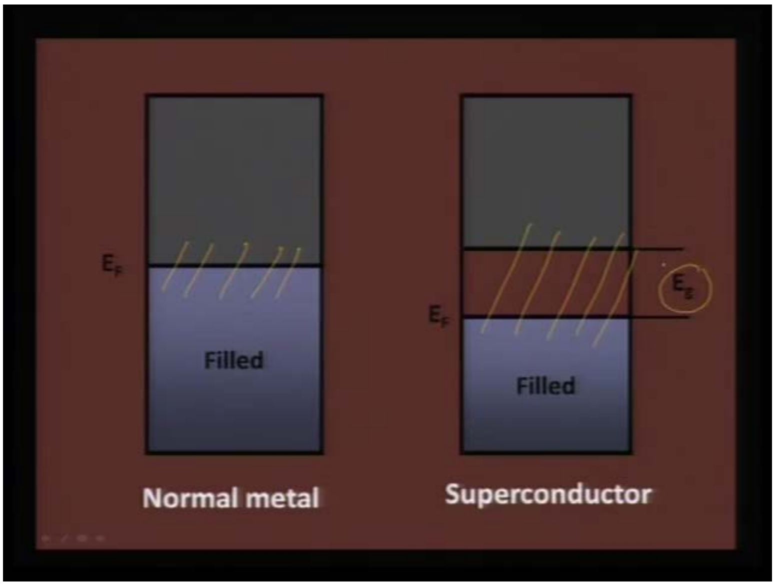

And one way to identify how this differs from a normal metal is there is no band gap in this case whereas, in the superconducting case because a cooper pair has to form there is a opening of band gap which is called E g.

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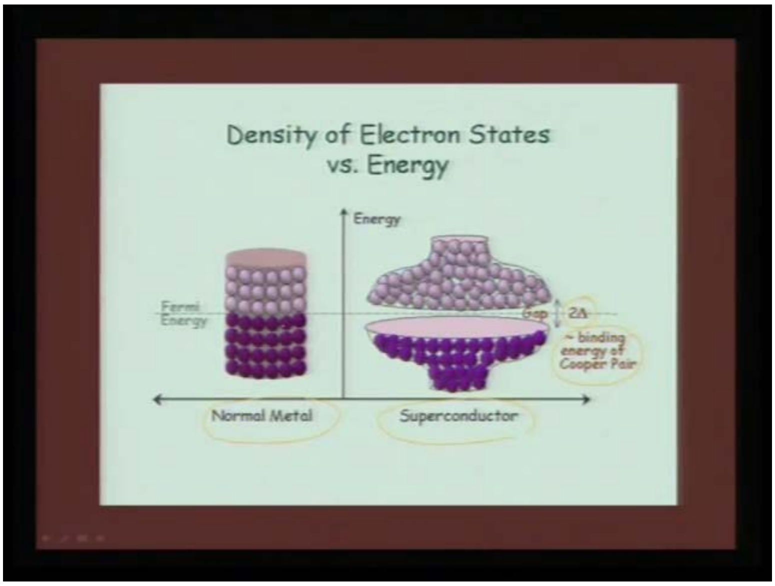

And that is once it is taken care then you can get the super conducting states. So, compared to a normal metal how do we identify a superconductor because this amount of 2 delta is actually a narrow band gap opening, which is the binding energy of the cooper pair. Once one this is formed then the binding energy of the cooper pair will sustain the super current. So, the opening of band gap between the valance and conduction band compared to a normal metal is the in essence the mechanism for superconductor.

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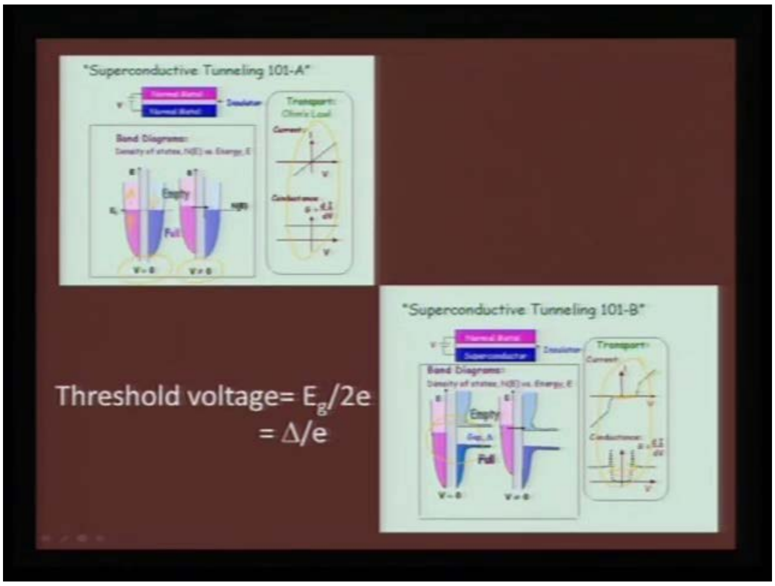

And as you would see here, the spin up and spin down bands are given here spin up spin down bands, and in a normal metal both at v is equal to 0 and v is when potential is supplied. You would see there is a very small variation between the majority and minority spins whereas, in a superconducting state you would see that this is varying. The spin up and the spin down band they open up a band gap, and that will actually give you band gap of this order, which will be the binding energy for the cooper pairs. So, in a typical situation you I V curve for a metal will look like this whereas, for a superconductor you would see a opening up of a band gap that would determine whether this cooper pair can be formed.

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Applications of superconductor I will just finish with few mention.

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One of the important application is in the field of medical imaging, this is a MRI scan where a superconductor is actually used for MRI’s. And not only that superconductor can be made as a real, this is a tape they call it in this rolling assisted texture tapes, you will see the superconductor can be coated. And therefore, we can try to render this superconductor not just as a bulk material, but also in tape form.

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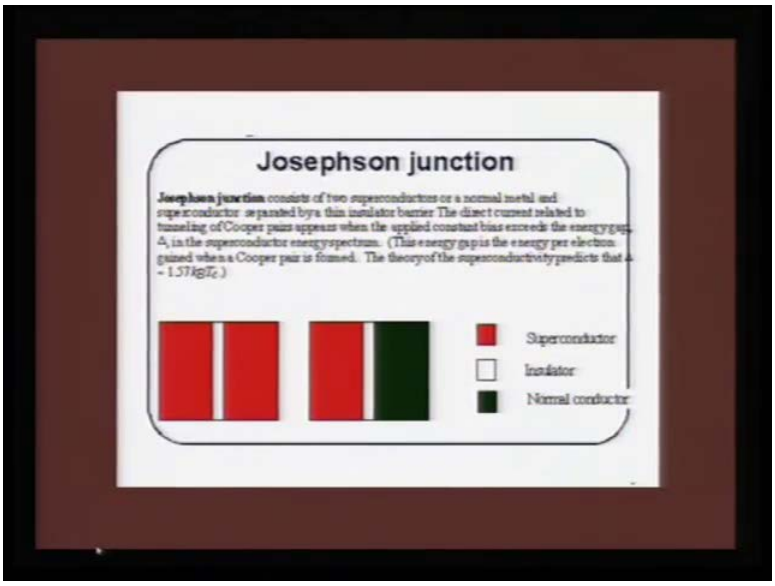

And it is also used in Josephson junction.

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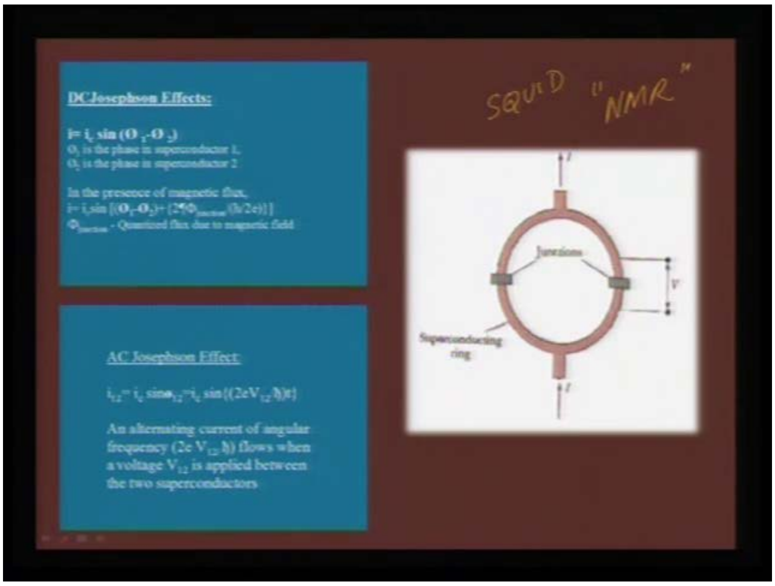

And that's where the principle of NMR application is used, where squid is actually this is nothing but superconducting quantum interferon device which is actually used for measuring very small changes in the magnetic filed in local environment. Therefore, this is actually used in NMR.

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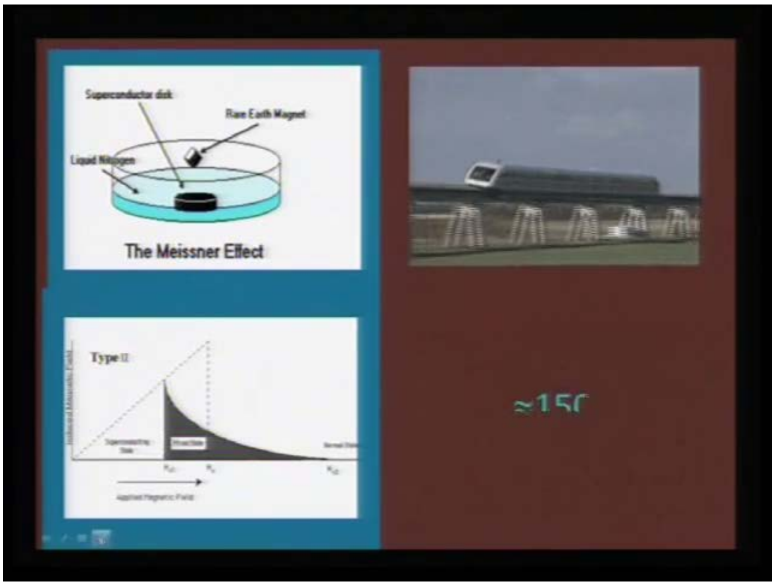

And lastly as I told you - the floating train. The trains run without wheels and this is already experimented between two states in USA and this is a unmanned train, which travels at the rate of 930 kilometres per hour, where Meissner effect or the magnetic levitation is actually used to demonstrate this effect.