Lecture - 12

Cuprate Superconductors, electron vs hole doped Superconductors

We have looked at the conventional superconductivity in some details, where these superconductors are very adequately described by the BCS theory, and we have looked at the phenomenon of pairing, how the, the Cooper pairs are formed, which is which a mediated via by the phonon, the phonon mediated super conductivity so far, and we have also looked at the Meissner effect, then the quantization of flux, then various other things associated with the super conducting experiments, the experiments that determine the superconducting gap, and then the ultrasonic attenuation, the IR absorption spectrum, and the Andreev reflection in a junction made of normal insulating and a superconductor or a normal superconductor Junction, and now this time for us to review some of the unconventional superconductivity, that people have observed and they have formed a very important part of this study of superconductivity, and so far unfortunately a large amount of data are still unresolved that is people haven't been able to make sense of a number of things at, I mean, mostly related to the normal state of these unconventional superconductors, and mostly we will review the what are called as the high-temperature superconductors, by high temperature we of course mean temperatures which are of the order of liquid nitrogen temperature, which are 77Kelvin and above or around that temperature, in fact reasonably large T_c or the superconducting transition temperature has been achieved using these Cuprate superconductors or high T_c superconductors we are going to look at. So, the title for this discussion is unconventional superconductivity. So, just once more reviewing,

Refer Slide Time: (02:50)

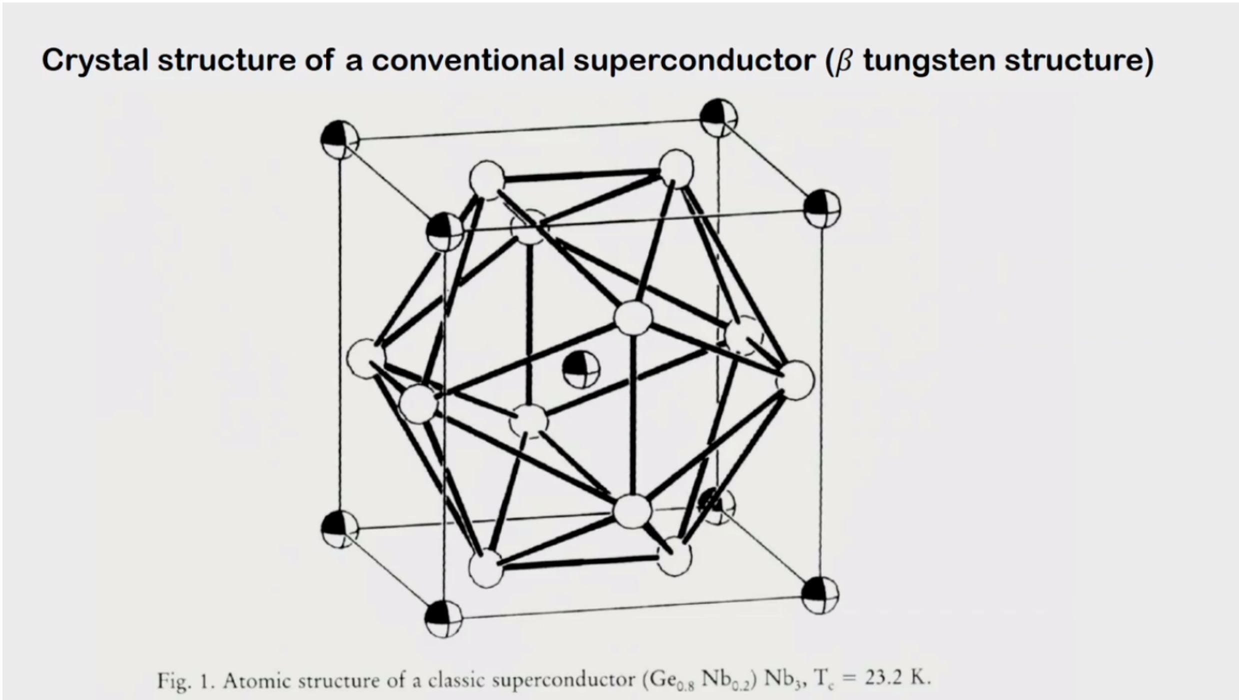
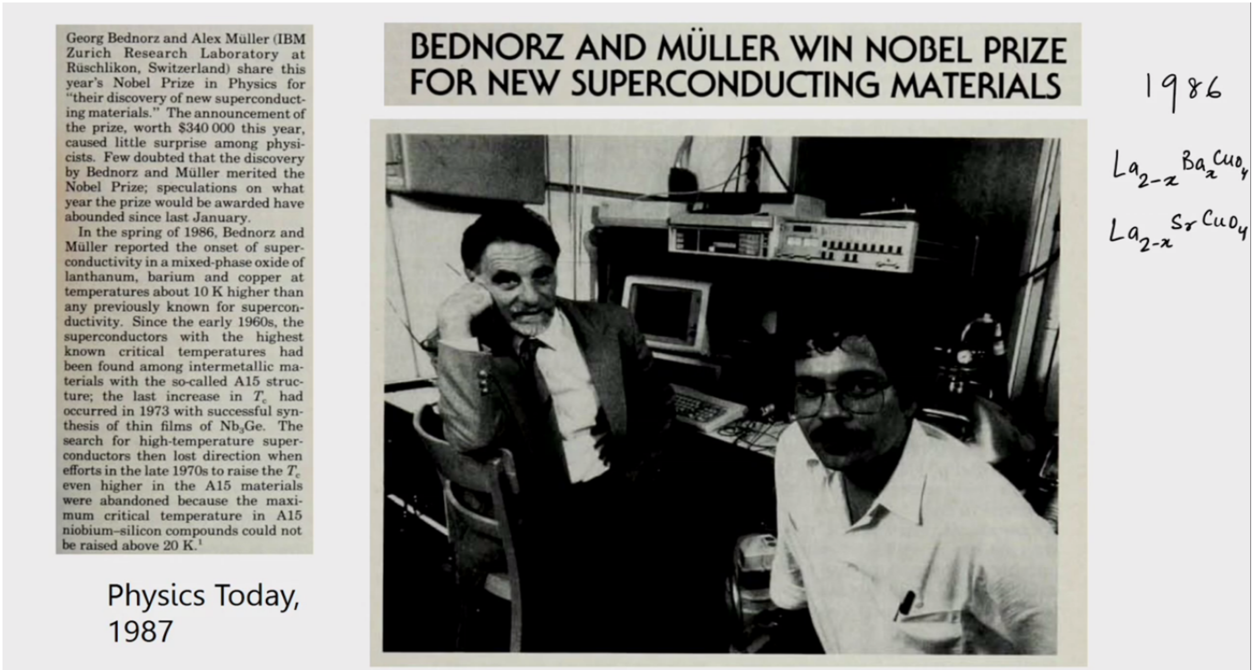


Fig. 1. Atomic structure of a classic superconductor $(Ge_{0.8}\,Nb_{0.2})\,Nb_3$, T_c = 23.2 K.

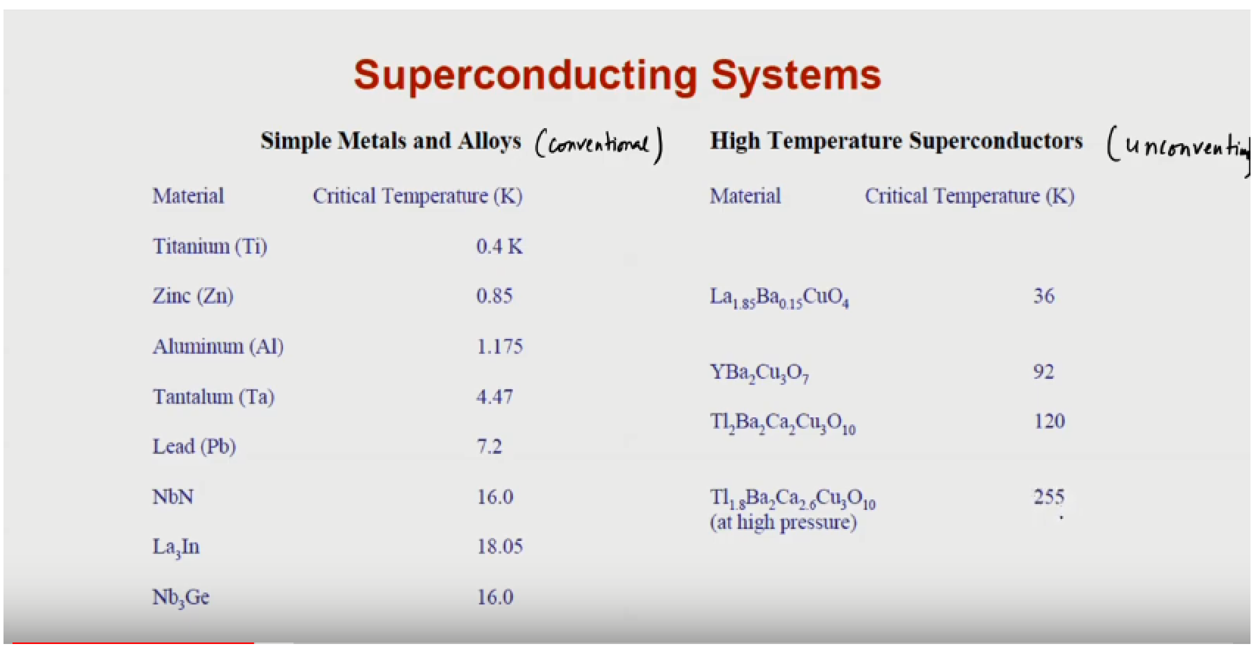
the conventional superconductors, we have shown that there is a significant amount of structural emphasis is there in the conventional superconductors, and this beta tungsten structure or what is called as A15structure, which looks like this gives T_c, which is high as, high as 23.2 Kelvin. So, this is the classic superconductor it's called the germanium niobium Nb_3. So, it's 0.8 germanium and niobium is 0.2. So, that's a ger, that's a superconductor and the T_c is recorded to be the highest among this or one of the highest among these conventional superconductors which is 23.2 Kelvin, and this has an A15 or a beta tungsten structure, this is what we have seen.

Refer Slide Time: (3:46)



So, these all these superconductors were discovered all the way between 1908, when it the superconductivity was first seen in ultra-clean mercury by Dutch scientist, which we have told and then on the discovery of many superconductors which fall into this conventional superconductivity, and in the year of 1986, these two gentlemen called Bednorz and Muller, they got super conductivity which is in the lanthanum barium copper oxide and lanthanum strontium copper oxide. So, we'll just write these, these are lanthanum barium copper oxide and lanthanum strontium copper oxide, and they obtain transition temperatures, which is for the barium doped compound it's 36 Kelvin, and for the strontium doped compound, it came out to be out 40 Kelvin maybe 39 Kelvin, and they were awarded Nobel Prize in 87. So, this is that physics today article which says that Gorge Bednorz and Alex Bullard from the IBM Zurich Research Laboratory in Switzerland, they share this year's Nobel Prize for the discovery of superconducting materials, then it's really the amount of the, the money that they get for these discovery or for this Nobel Prize and few doubted, that the discovery by Bednorz and Muller merited Nobel Prize speculations on, what year the prize would have been, would be awarded have abounded since last January, and the spring of 1986, Bednorz and Muller reported the onset of superconductivity in a mixed phase of oxide of lanthanum, barium and copper at temperatures about 10 Kelvin higher than the previously known temperature for the Supercon for superconductivity, as I said that in this compound it was 36 Kelvin, it was 36 Kelvin and it was 39 Kelvin for this. So, this is about, typically about 10 to 12 degree more the transition temperature. So, that's why it says that so it's about 10 Kelvin more or higher than the previously known superconductivity. Since, the early 1960s the superconductors with the highest known critical temperature, had been found among the inter metallic materials this so called A15 structure, this is what I showed you in the last slide, the last increase in T_c has occurred in 1973, with successful synthesis of thin films of Nb_3Ge, which is what I told, the search for the high temperature superconductors then lost direction, when efforts in the late 1970s to raise the T_c even higher in the A15 materials were abundant, because the maximum critical temperature in A15 niobium-silicon compound could not be raised beyond 20 Kelvin. So, this was a big jump going from 20 or 23 Kelvin to about fa, say about 40 Kelvin and this jump had been recorded by them, and it was reproducible, the data were represents reproducible, and then they got a lot of exciting phenomena associated with the super conductivity, and that formed the basic theme for our discussion for at least for a day or two, All Right! So, just to have an idea of this critical temperature in simple metals and alloys,

Refer Slide Time: (07:57)



Superconducting Systems

Simple Metals and Alloys (conventional)

Material	Critical Temperature (K)
Titanium (Ti)	0.4 K
Zinc (Zn)	0.85
Aluminum (Al)	1.175
Tantalum (Ta)	4.47
Lead (Pb)	7.2
NbN	16.0
La_3In	18.05
Nb_3Ge	16.0

High Temperature Superconductors (unconventio

Material	Critical Temperature (K)
$La_{1.85}Ba_{0.15}CuO_4$	36
$YBa_2Cu_3O_7$	92
$Tl_2Ba_2Ca_2Cu_3O_{10}$	120
$Tl_{1.8}Ba_2Ca_{2.6}Cu_3O_{10}$ (at high pressure)	255

and these are still, as I said that these are conventional, like titanium give a 0.4 Kelvin, it's less than a Kelvin, zinc is about 0.85 Kelvin, look all these things are very difficult to see it, because the liquid helium which is an expensive thing, this liquid helium temperature is 4 Kelvin. So, all these things are very difficult to see even something which is like 7.2 Kelvin, one has to use the liquid helium, then it's zinc 0.85, Aluminum it's 1.1, Tantalum it's 4.47, Lead it's 7.2, Niobium nitride it's 16, Lanthanum indium is 18, and then Nb_3Ge is 16, and then of course they have doped it, and they have increased the germanium concentration, and this has gone up to 23 Kelvin as we saw, whereas the high temperature superconductors, which we are going to study and they are called as the unconventional ones, and these are 36 for the barium doped compound, and then there are $YBa_2Cu_3O_7$, I gave a 92 Kelvin temperature but there is a 7 minus X. So, basically it's an oxygen deficient compound which recorded the maximum T_c for X equal to about 0.15, which is what will see them, then there Thallium barium calcium copper oxide which $Tl_2Ba_2Ca_2Cu_3O_{10}$, which recorded a pretty high transition temperature which is 120 Kelvin, and then of course the same compound with a different stoichiometry and at high pressure, it had builted a really large T_c, which is nearly minus 20 Kelvin, minus 20 degree centigrade. So, it's minus 255 Kelvin which is minus 20 degree centigrade. So, more complete list is that

Refer Slide Time: (10:13)

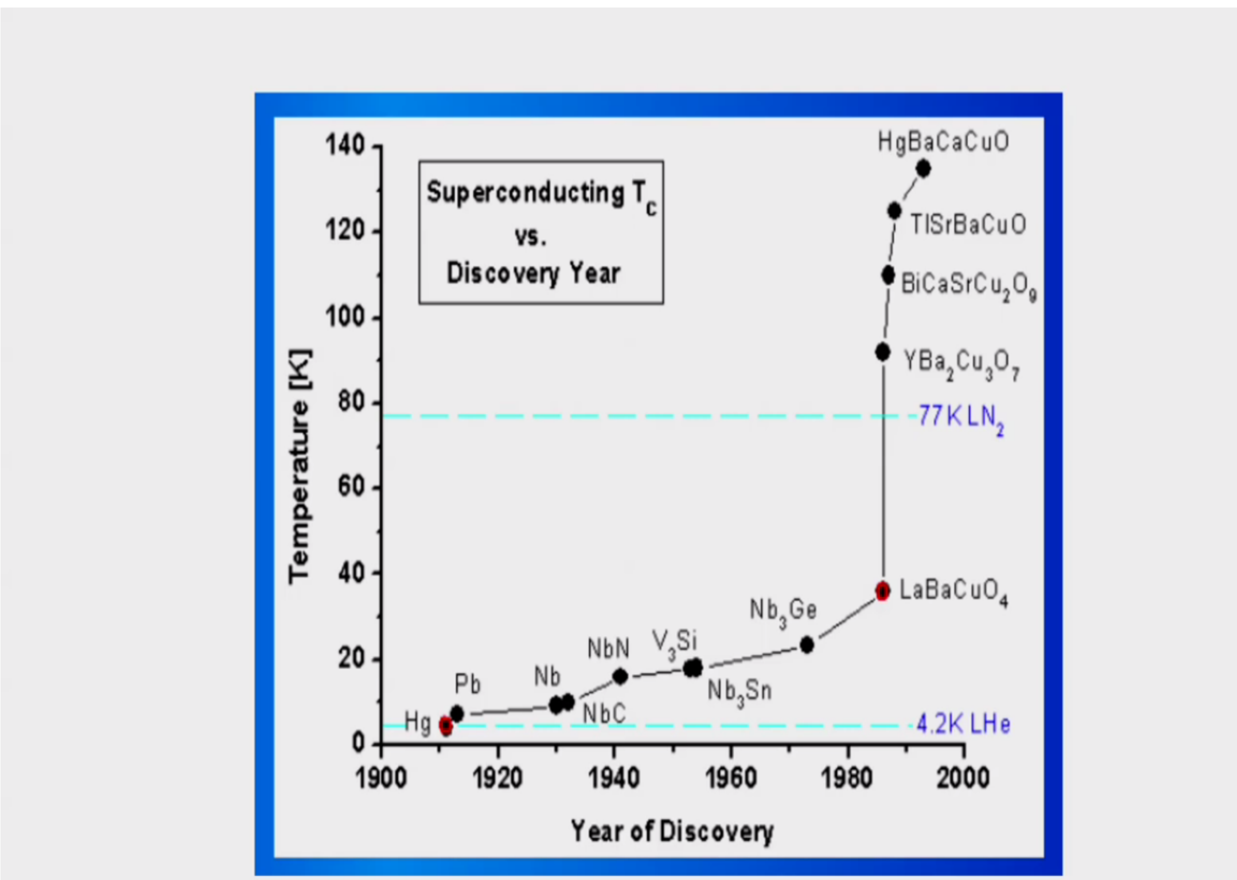
A more complete list

Table 1. High-temperature superconductors, differing in their crystal structure and their maximum superconducting transition temperature.

Chemical formula	Symmetry	a, A	b, A	c, A	Tc, K
$(La, Ba)_2CuO_4$	I4/mmm	3.782	–	13.249	36
$(Nd, Ce)_2CuO_4$	I4/mmm	3.948	–	12.088	24
$(Nd, Ce)(Nd, Sr)CuO_4$	P4/mmm	3.856	–	12.490	20
$IBa_2Cu_3O_7$	Pmmm	3.820	3.886	11.688	94
$IBa_2Cu_4O_8$	Ammm	3.842	3.871	27.240	80
$Y_2Ba_4Cu_7O_{15}$	Pmmm	3.842	3.881	50.500	40
$(Ba, Nd)_2(Nd, Ce)_2Cu_3O_8$	I4/mmm	3.875	–	28.600	40
$Bi_2(Sr, Ca)_2CuO_6$	A2/a	5.362	5.362	24.300	40
$Bi_2(Sr, Ca)_3Cu_2O_8$	Amaa	5.408	5.413	30.871	80
$Bi_2(Sr, Ca)_4Cu_3O_{10}$	I4/mmm	3.811	–	37.080	100
$TlBa_2CuO_5$	P4/mmm	3.847	–	9.600	17
$TlBa_2CaCu_2O_7$	P4/mmm	3.847	–	12.730	91
$TlBa_2Ca_2Cu_3O_9$	P4/mmm	3.853	–	15.913	116
$TlBa_2Ca_3Cu_4O_{11}$	P4/mmm	3.847	–	18.730	122
$Tl_2Ba_2CuO_6$	I4/mmm	3.866	–	23.225	85
$Tl_2Ba_2CaCu_2O_8$	I4/mmm	3.856	–	29.186	110
$Tl_2Ba_2Ca_2Cu_3O_{10}$	I4/mmm	3.850	–	35.638	125
$Tl_2Ba_2Ca_3Cu_4O_{12}$	I4/mmm	3.850	–	41.940	108
$Pb_2Sr_2YCu_3O_8$	Cmmm	5.394	5.430	15.731	70

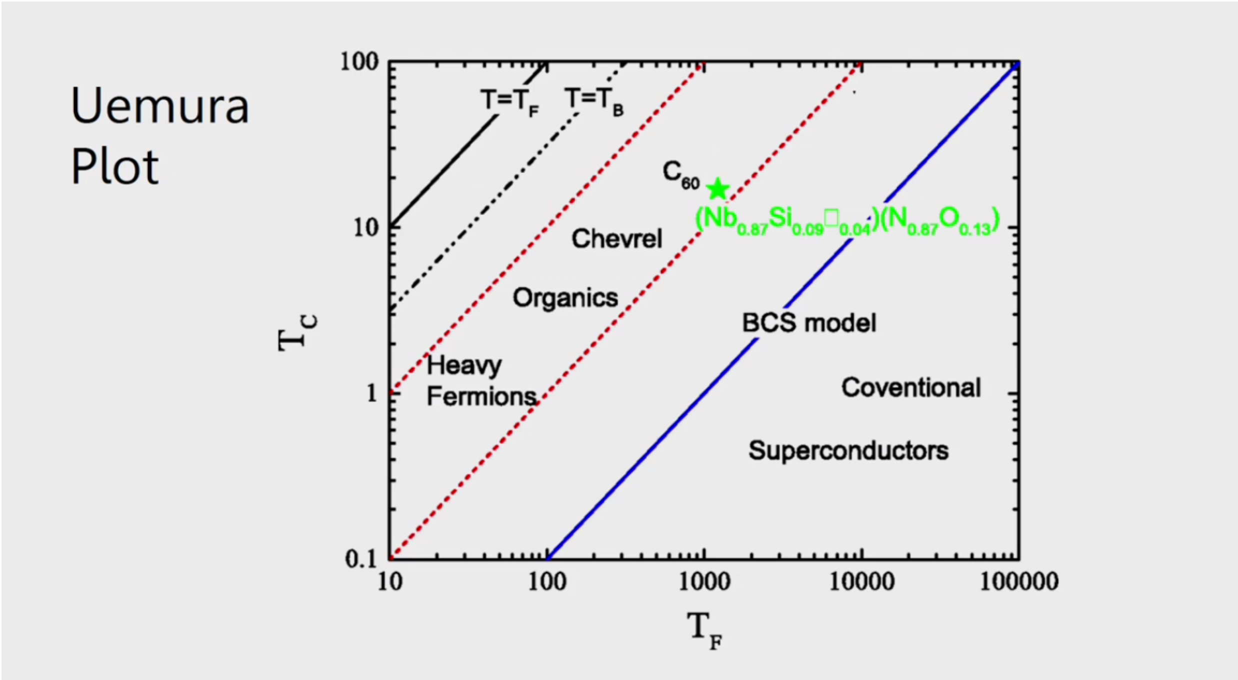
there are in addition to the transition temperatures, here there the symmetry of these crystal structure is recorded here, and these ABC's which are called as the lattice constant, in various directions are also noted here, what is important for us is that if you look at the left most column and the rightmost column, the where the right most column records of course the T_c, one can see that the maximum T_c here is about on 125 Kelvin, there are some numbers which are pretty close by like 122 Kelvin, 116 Kelvin, 110 Kelvin, 108 Kelvin, 100 Kelvin and so on, and then there are other things which are even close to 100, like 80 Kelvin and things like that. So, these are the transition temperatures that have been recorded for these compounds which are on the extreme left. It's important to note that all these compounds, which are recorded in the left panel or the left column, are they have one thing in common, there is a copper oxide plane, there are a number of copper oxide planes, which has rendered a T_c, which is high. So, what is common in all of these things are these copper oxide planes, and these copper oxide planes, hence were thought to give rise to a number of important concepts or other directions in the study or in the discovery of high temperature superconductivity. So, they must be playing an important role, is what people have realized. So, this is nice a

Refer Slide Time: (11:57)



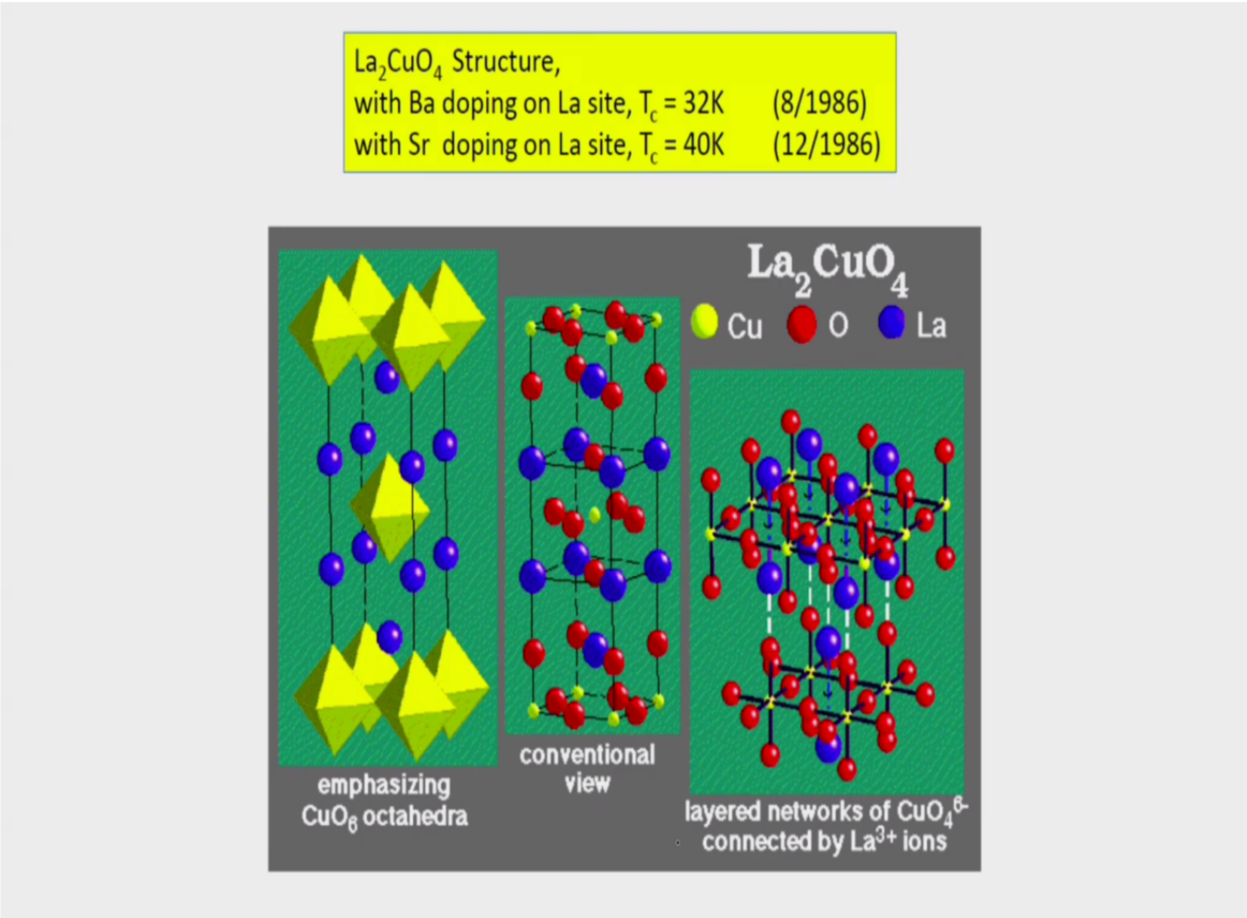
Diagram, showing that the T_c increased, as the years have passed by, because of the discoveries that have occur, occurred in this from all the way from1908, till about 2000, and beyond 2000 and so on. I have not recorded data beyond that wat, what is important is that. So, it started with these, red dot is the liquid helium temperature or rather this these blue line dashed lines, is the liquid helium temperature, which is 4.2 Kelvin, and there's a liquid nitrogen temperature, which occurs at 77 Kelvin. Now, you see that these, all these conventional superconductors excluding this Lanthanum Barium Copper Oxide, they are in the vicinity of this liquid helium temperature, and it's harder to perform the experiments and become expensive, whereas more abundantly available quantities are these, these liquid nitrogen, and you see the, the Yttrium Barium Copper Oxide, or the these are called the YBCO, and these are called the, 'Bisco', and so on, and these are thallium based compound, and these are mercury based compounds, they show T_c of 100 and close 140 degree or even higher than that and there's a jump that had occurred, I mean we are taking this as a discovery. So, there's a there's a sharp jump in the, so let us show this here. So, there is a jump that has occurred here, and all the way up to 140 and 150 Kelvin, in this mercury based, thallium based, bismuth based and the yttrium-based compounds. So, this all these up till all the way up till this Nb_3Ge, it was around 1900 and 70's, maybe 73, 74 and then 86 onwards, there is this discovery that had taken place, as we have said that this discovery took place in 8, 1986 and the Nobel Prize was awarded in 1987.

Refer Slide Time: (14:14)



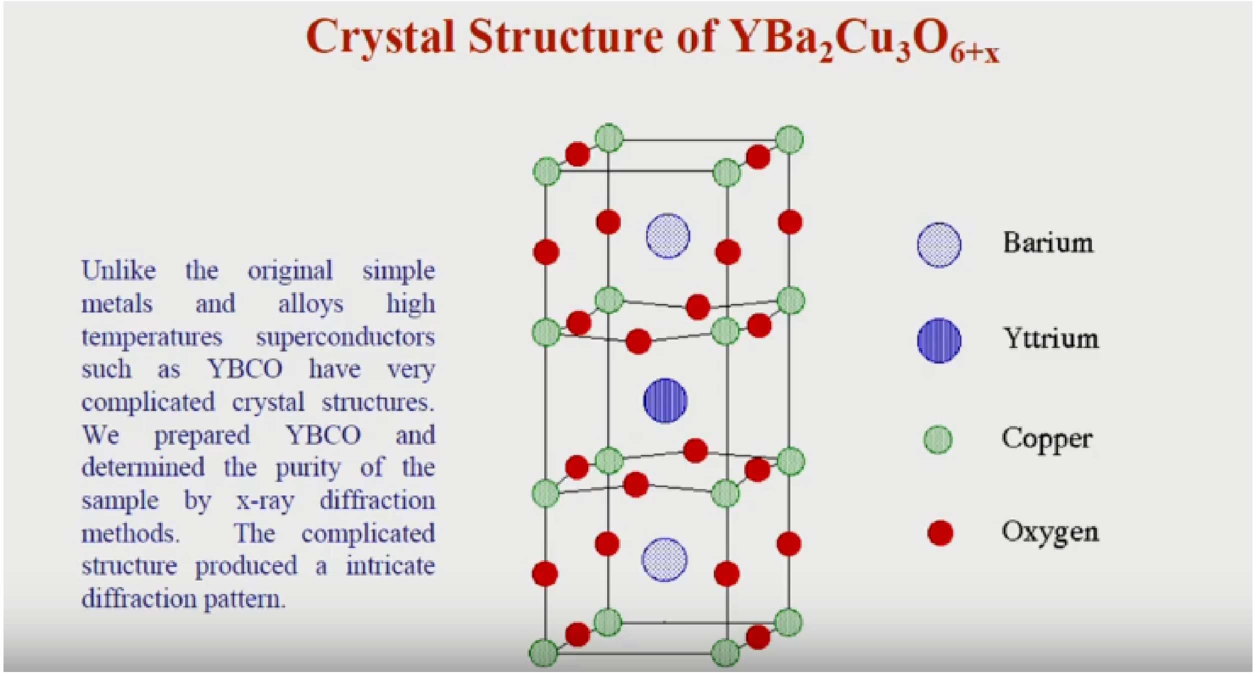
This is a plot which is known as the Uemura plot, it plots what are called as the T_c versus T_F, it's an empirical plot, which had taken into account a large number of superconductors and so on, and one can actually see that so it's a T_c versus T_F in a log-log scale. So, both are in logscale and it shows that this red dotted line, is along the unconventional superconductors and also the the BCS superconductor, the high T_c superconductors also lie in this vicinity of this, Okay? And these are organics, these are heavy fermion, these are called fullerenes or fullerides and so on, and then of course the conventional superconductors are here, which means that the T_c is rather it's much smaller than a T_F, it's of the order of 10 to the power minus 4, whereas this falls along the line, that T_c versus T_F in the log scale falls along a straight line. So, this is a way to distinguish between the conventional and unconventional superconductors. So, in this plot the conventional superconductors are in this, you know occupying there's this region of the space, and the unconventional superconductors are lying between the these dotted lines, and most of these unconventional superconductors lie int his dotted line, and this blue line is pretty much what is called as a BCS model or rather the BCS theory of superconductivity, it agrees well with this line, for the T_c versus T_F. T_F, I remind you is a Fermi temperature. So, if you have a distribution function which is like this, so this is your occupancy, and this is your E. So, this has a discontinuity at, so these are T equal to zero, these are the discontinuity at epsilon equal to epsilon F, which is the Fermi energy, and if you equate the Fermi energy to the Fermi temperature, then itis related by this, and so this T_F, is what is recorded here.

Refer Slide Time: (16:41)



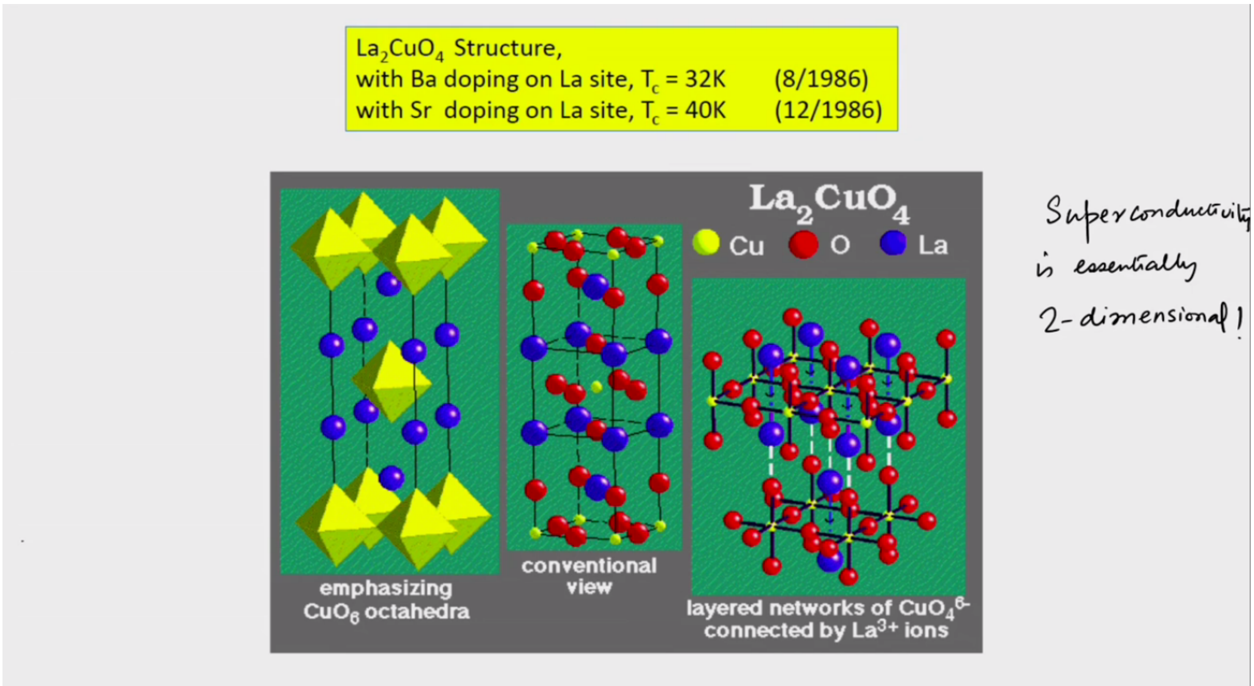
So, let's have a look at some of the known structures, which are discovered, these are the Lanthanum Copper Oxide, this is the simplest of the Copper Oxide Superconductors, and look at it carefully, there is a Copper Oxygen 6, octahedra that are present, and so these are the more conventional view is actually shown here, where these yellow dots that you see, so there is a copper oxide layer on the top, and there is a. Let me use a laser. So, this is a, this is a copper oxide layer, the yellow dots are or the yellow balls are the copper, and there is a, oxygen which are given in the, in the bond positions which are given by this red slightly bigger ones, and this is similar thing there. So, there are two copper oxide layers and besides there are lanthanum, not only sitting in the chains between the copper oxide layers, but also in this position, that is between two such layers there is a copper oxide, and there are, also oxygen here. So, these are the conventional, this is the easiest one to follow, the conventional structure of a lanthanum copper oxide material is shown. Now, it becomes, this is not a superconductor, this is an antiferromagnet, it's an antiferromagnetic insulator, when one dopes this lanthanum or replaces this lanthanum atom by strontium or barium which are rich with holes, then superconductivity is induced in this in these planes, copper oxide planes. So, these are the structures of these lanthanum copper oxide, and

Refer Slide Time: (18:41)



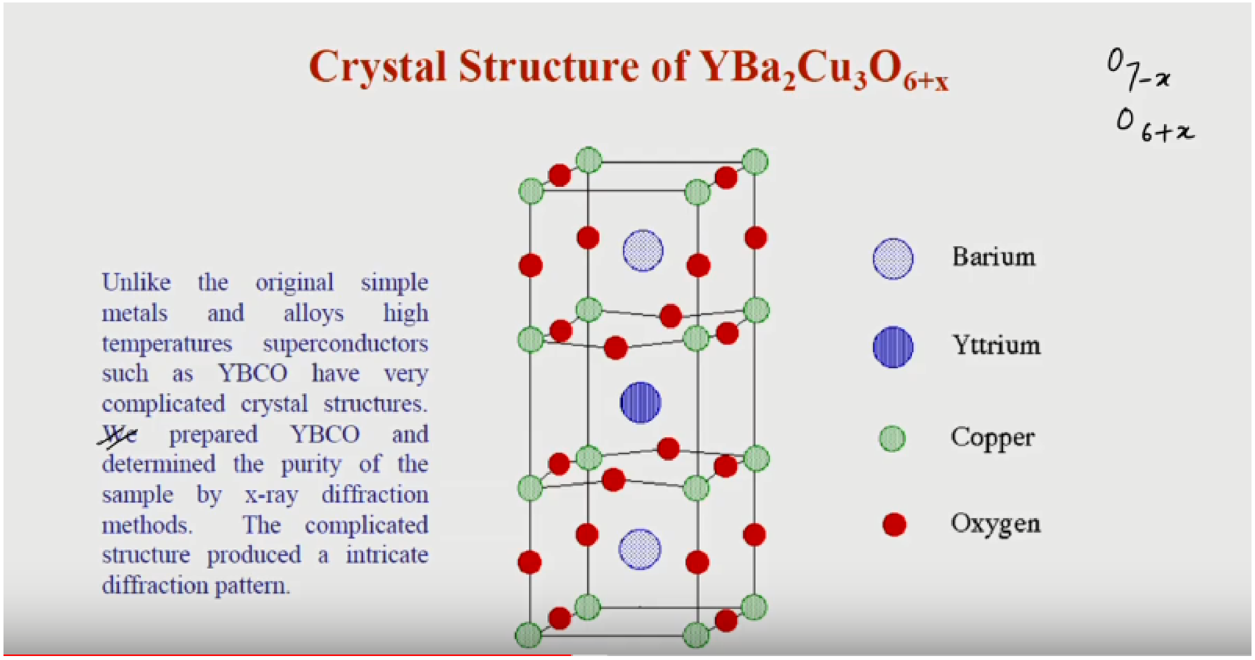
let us look at the crystal structure of YBa_2, before that

Refer Slide Time: (18:48)



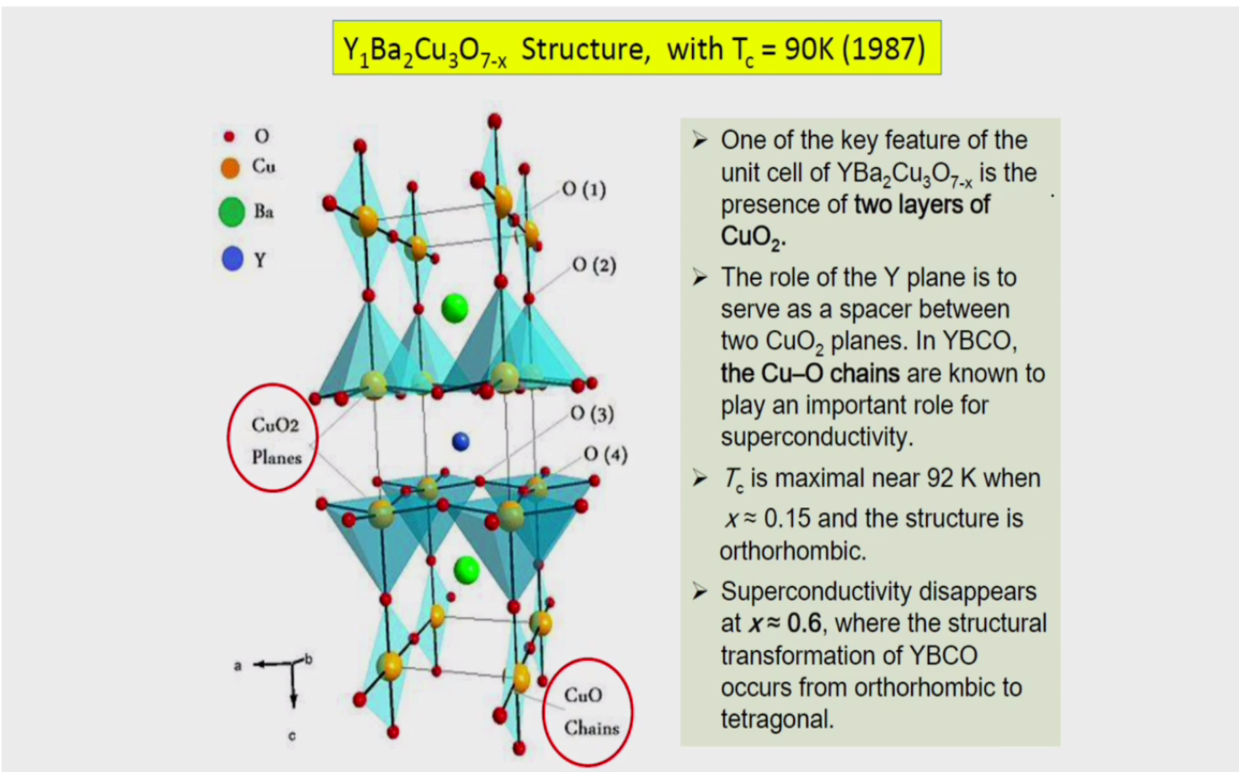
let us look at this thing once more. So, basically this lanthanum they impart, so lanthanum, are actually replaced by the strontium. So, the strontium sit, does not sit in the copper oxide layer, strontium or barium is rich with holes. So, they while being replaced by the lanthanum sites, they impart holes to the copper oxide planes, and hence these super conductivity is actually considered as two dimensional, and why this is more interesting is that there is a theorem which is called as a, Mermin-Wagner theorem, which says that it, it is hard to form order, a long range order in two dimension, or rather it excludes the possibility of having a long range order in two dimension, unless with a with a sort of microscopic order parameter, but there could be other orders, which could give rise to long range order in two dimensions, which are even proposed as some kind of a vortex antivortex pair, some kind of topological order which could give long range order in two dimensions. In any case, the here the super conductivity, which is of course a long-range correlation between the, the pairs, the Cooper pairs, that is happening in two-dimension.

Refer Slide Time: (20:35)



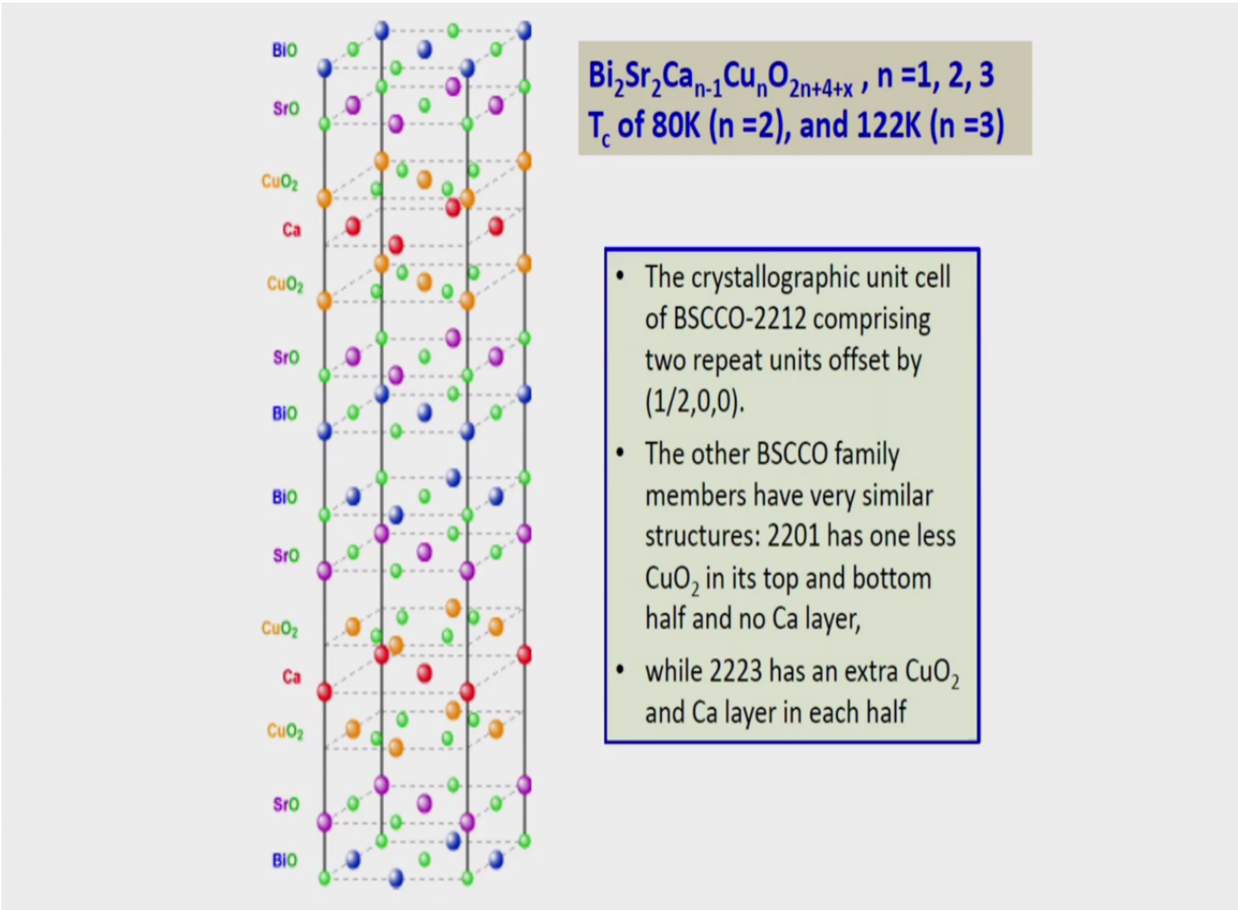
This is the crystal structure of $YBa_2Cu_3O_6$, $O_{6\ \text{plus}\ X}$, it can be could be written as $O_{7\ \text{minus}\ X}$ or $O_{6\ \text{plus}\ X}$, they pretty much mean the same thing, it's one is called as oxygen deficient, the other is called as oxygen rich, if you write it it's written as oxygen rich compound with X to be varying from zero to one, and so it basically it shows superconductivity for X equal to about point maximum T_c, is about X equal to 0.15, and for X equal to what point six or something around that value superconductivity completely disappears, in any case let us look at the structure, and it says that unlike the original simple metals and alloys, high-temperature superconductors such as YBCO is called Epco or YBCO, you have very complicated crystal structures, and there are groups that are prepared YBCO and determine the purity of the sample by x-ray diffraction methods, and so basically this means that we haven't done it, it's only that there are groups that have done it, the complicated structure used as an intricate diffraction pattern, how is this structure determine? This determined by the x-ray diffraction, and sometimes by the neutron diffraction. So, what does x-ray diffraction do? X-ray diffraction in a crystal gives rise to Peaks, as a function of that scatter, the intensity as a function of two theta, which is the scattered angle and then this Peaks are assigned some Miller indices and these Miller indices are the features of where the atoms or the ions are present, and it's pretty accurate in determining the crystal structures and in case of some magnetic elements, one can also use the the neutron diffraction, this is which is of course more expensive and more sophisticated tool to determine structures, but they are used as well. So, let us look at now of course there are color combinations have changed, the oxygens are still in red, but the copper are not in yellow, but they are in a light green, and in the hatched box, and then one has these are the positions of these copper and the oxygen, and then there is a barium that sits here. So, this barium Ba_2 sits here, there's an Yttrium, which sits in the, so there are four such copper oxide layers, these two are middle layers and then there are two barium, which are at the top and at the bottom, and there's an Yttrium at the center. So, this contains, at least this cell that we have drawn contains four copper oxide layers, and that's why it's called as more complicated, we have already told that the lanthanum copper oxide is the most simple of these copper oxide

Refer Slide Time: (23:57)



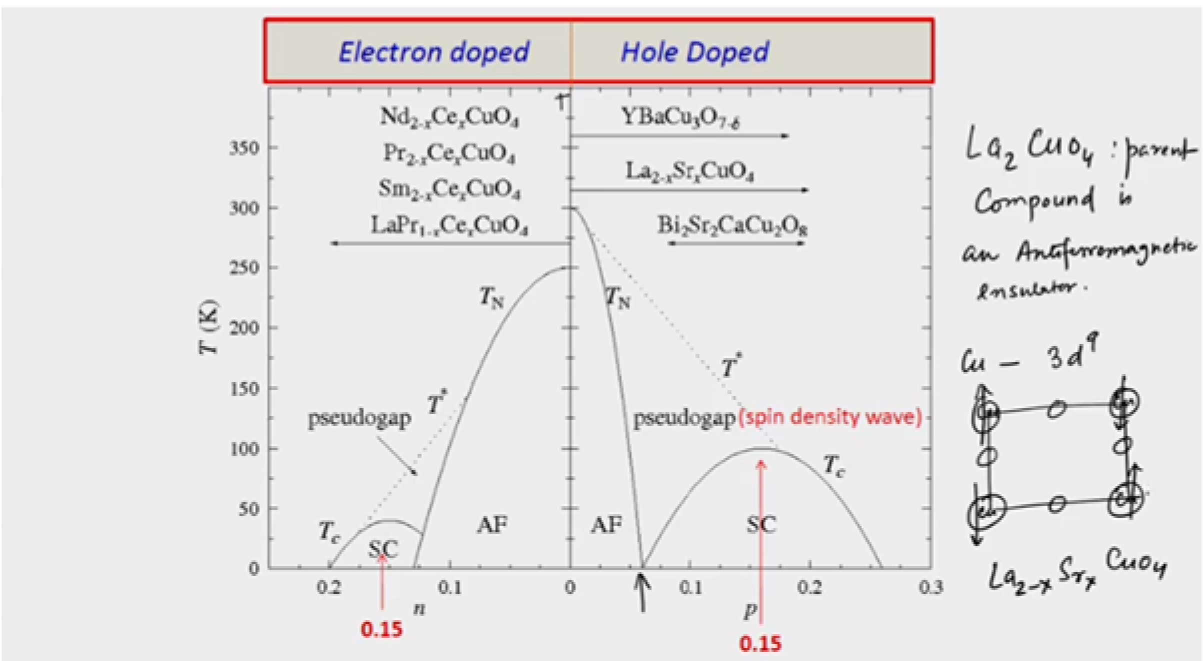
Superconductor in terms of the crystal structure. So, let us look at the, there's another as the nomenclature changes, it's called $YBa_2Cu_3O_{7\ \text{minus}\ X}$, and this was discovered with the T_c of 90 Kelvin in 1987 just one a year after the discovery of these the lanthanum barium and the lanthanum strontium copper oxide, one of the key features of the unit cell of $YBa_2Cu_3O_{7\ \text{minus}\ X}$ this called as an oxygen deficient compound, is a presence of two layers of copper oxide. So, these two layers of copper oxide are written. So, these are the copper oxide planes, which are shown here, so these are the copper oxide planes, oxygen is still in red, copper is now in orange, and this barium is here and so on, and this, this is just a more colorful view of what we have shown you earlier, the role of the Y plane that is containing the Yttrium atoms, is to serve as a spacer between the two copper oxide planes. So, its serves as a spacer which means that there's a barrier which between the two copper oxide planes, in YBCO, the copper oxygen chains are known to play an important role in super conductivity. So, there are copper and oxygen chains as well, T_c is maximal near 92 Kelvin or 92, 92 Kelvin something like that, when X is equal to 0.16 or 15. So, X is equal to 0.15 it's 92 Kelvin and the structure is orthorhombic, in fact this is an important thing, that there is also a structural phase transition along with the disappearance of superconductivity, it disappears at X equal to 0.6, when the structural transformation of YBCO occurs from an orthorhombic to at a trigonal form. So, this is one of the small, yet important difference with the conventional superconductors mostly we have seen that in undergoing a superconducting transition from a superconductor to metal, there is no structural phase transition that is involved,

Refer Slide Time: (26:26)



however, there is a structural phase transition here, more complicated structure is a $Bi_2Sr_2Ca_{n\ minus\ 1}Cu_n$ and oxygen 2 n plus 4 plus X, of course X is the doping, X is the variable that is changed in experiments, n equal to 2, and n equal to 3, yield n here. So, this is equal to Ca_1 or Ca_2, along with oxygen 4 or oxygen 6, 6 plus 4 is 10, 10 plus X or it is equal to, if it's equal to 8 plus X, if n equal to 2 is 8 plus X, and so on. So, n could be 1, 2 and 3, and there's a reasonably large T_c, that is obtained at least for n equal to 3, which is 122 Kelvin, and T_c is equal to n, n equal to 2, for n equal to 2, T_c is 80 Kelvin. So, you see the, the bismuth are given by the green ones, then there's strontium, there is a copper oxide plane, then there's a calcium, then there's another copper oxide plane, then there's a strontium, bismuth, bismuth, strontium, copper oxide plane, calcium, copper oxide plane, strontium, bismuth. So, there's a very large unit cell, so the crystallographic unit cell of it's called Bisco or BSCCO-2212 compounds, this is 22 and n equal to 2, it's equal to 1, and so 221, and then there is a 2 there. So, this is called as a 2212 compound, it comprises of 2 repeat units offset by (1/2, 0, 0). So, there are the, the two units are repeated, but there is an offset of by this distance is there, which is half in the X direction, and nothing and I mean, only in the X direction, there is a, there is a shift in the half of the lattice spacing, the other Bisco family members have very similar features 2201, has one less copper oxide in the top and bottom, and, and bottom half no calcium layer, the calcium that you can you saw here, that is not there in the 2201. So, 2201 means, n equal to 1, layer where the 2223 layer which means that n equal to 3, has an extra copper oxide and a calcium layer in each half. So, this is that the, the differences in the crystal structure, for n equal to 1, n equal to 2 and n equal to 3, these are of course more complicated structures.

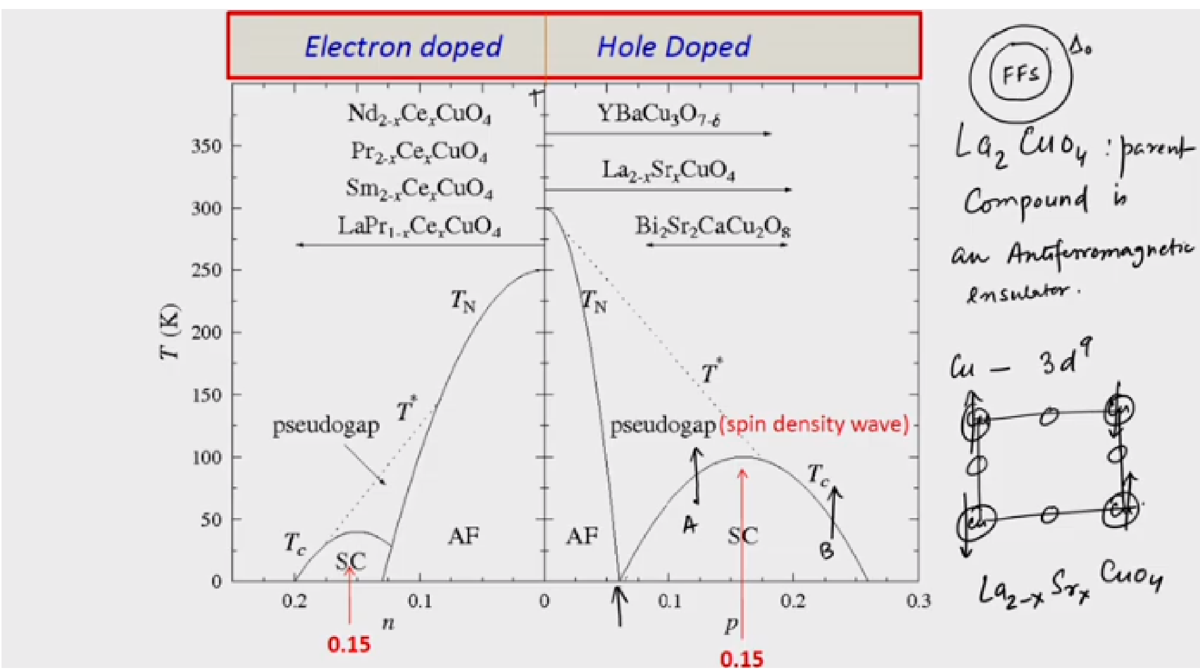
Refer Slide Time: (29:04)



So, let us look at a very important thing, which has caused a lot of discomfort and in understanding of the physics of this super conductivity, or the physics of this high temperature superconductors, and these are called as a phase diagram. So, what is the phase diagram consisting of? Phase diagram is consisting of temperature in this axis, and the doping which of course often we record it as P or we can also call it as X, the X that we have seen in the earlier slides, and this is the, the most important feature of the high T_c superconductors, which have really made people wonder that what the normal state consists of, at least in the under dope transition. So, the left panel consists of electron doped superconductors, which are $NdCe_x$. So, Ce is full of electrons, so they give electrons as charge carriers to the copper oxide planes or there's a praseodymium, and again Ce_x samarium, Ce_x and lanthanum proceed, praseodymium C_x, and all that, we are mostly concerned with the hole doped super conductivity, which we have told that these are the the strontium holes or the, which gives rise to this super conductivity in the copper oxide planes. So, let us look at that see the important thing is that that at if the if, we have X equal to 0, then we have the parent compound which is La_2CuO_4, is a parent compound, undoped and this parent compound is an anti-ferromagnetic insulator, in fact, this is one of the most important differences between the high T_c and the conventional superconductors, that the undoped is not a metal rather it's an insulator, and with anti-ferromagnetic ordering. So, who gives this anti-ferromagnetic ordering? The copper, if you look at it, the copper has it's in a $3d^9$ configuration, it has 29 electrons. So, it's a $3d^9$ configuration, so it has one electron less, which says that it has like one hole more, and this hole has got magnetic moments which alternate, so if we draw the copper oxide plane as this. So, these are the copper which we have shown by various colors in various slides. But they of course meet this mean the same thing. So, there is an up there. There is a down there. There is an up there. There is a down there and this is called as an anti-ferromagnetic ordering. So, the undoped compound has this structure of width of course the oxygen in the P orbital, which are occupying the bonds. So, as you dope with say strontium. So, if you replace this sum of these lanthanum by strontium and keep doing, that in a controlled manner. Then, thus this anti ferromagnetism is destroyed at this temperature. Okay? At this temperature the anti-ferromagnetism completely vanishes. So, all these up down orders ,that we have talked about for the copper moments spin magnetic moments they are and they no longer exist and so the there is a lot of fluctuation in the order parameter or rather in the spin magnetic moment, which kills the anti-ferromagnetic ordering. Immediately after, that maybe there is a small gap which not has not been you know exemplified here, which is called as a spin glass. But we'll forget, that for the moment. The superconductivity starts. So, an insulating behavior ends, an antiferromagnetic insulator behavior ends here. And superconductivity starts. This is something, that's very, very strange. Because, superconductivity is known to be the property of the metals, which below certain temperature they would form or you know, as a function of doping they would form a reasonable the conducting or rather it's a superconducting behavior would set in whereas, this is just followed by or rather the superconductivity is preceded by the anti-ferromagnetic insulating. Now, the, the super conductivity is also somewhat strange, it has a dome structure which means, this dome let me show you this dome structure means, that there is a non-monotonicity about this point. So, here the super conductivity is maximum, or rather it records the maximum T_C here whatever, that TC's for a given compound. So, that is the T_C, that we often say. So, it's actually the T_C max and if you are here. Then, of course there's a T_C which is here. But we don't report, that one reports the T_C, that is corresponding to the the top of the dome. Now, after that, so it reaches a maximum as a function of doping and then, you still continue to be to increase the doping. Then, super conductivity goes down or the TC goes down and finally the T_C vanishes, and it is going to be a metal that is what the understanding is. Now, the important point is, that that this thing happens around 0.1516 depending on material. But it's an around point two in most of the materials, that this maximum T_C happens and Then, it of course disappears also about 0.3 and so on.

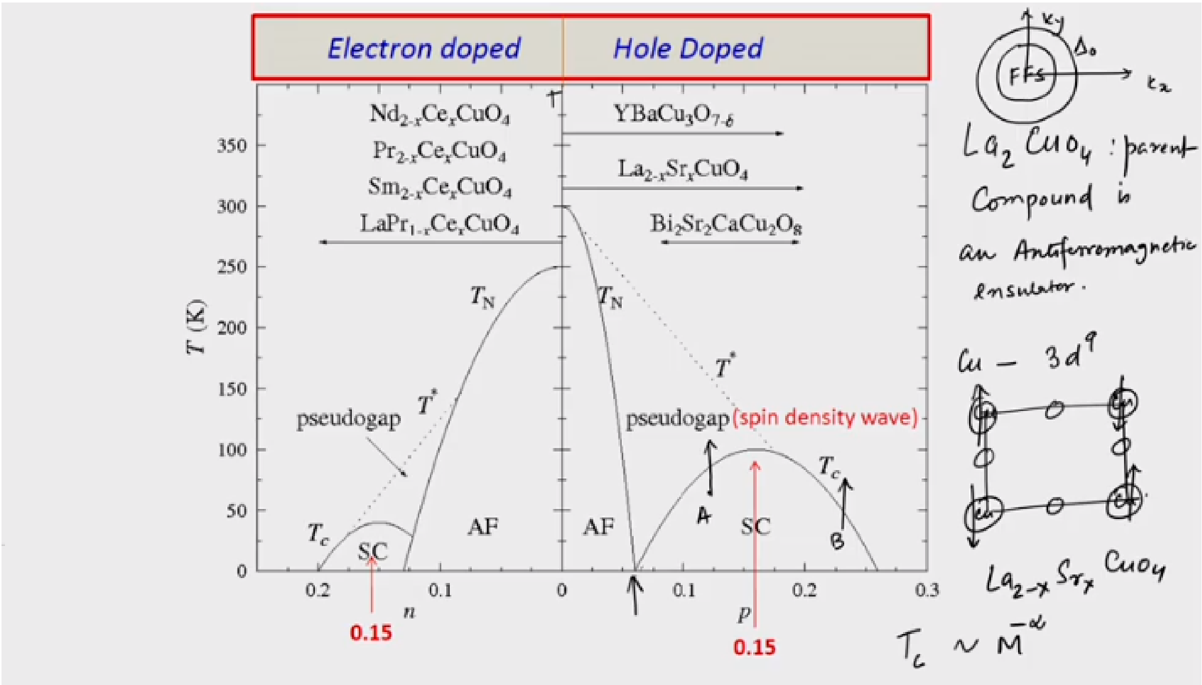
So, this is a feature of this compound or rather this all these generic unconventional high T_C super conductors. This is a feature. Now, you see there is a dotted line, that has been drawn and it says the shades a scale which is given by T star. it's hard to understand what is this Okay? the reason ,that this is drawn is the following ,that ideally when you are when you are here say, that means you are in the superconducting regime for this compound, whichever compound you are talking about may be talking about y busy or you're talking about the lanthanum strontium copper oxide or the bismuth compound.

Refer Slide Time (36:08)



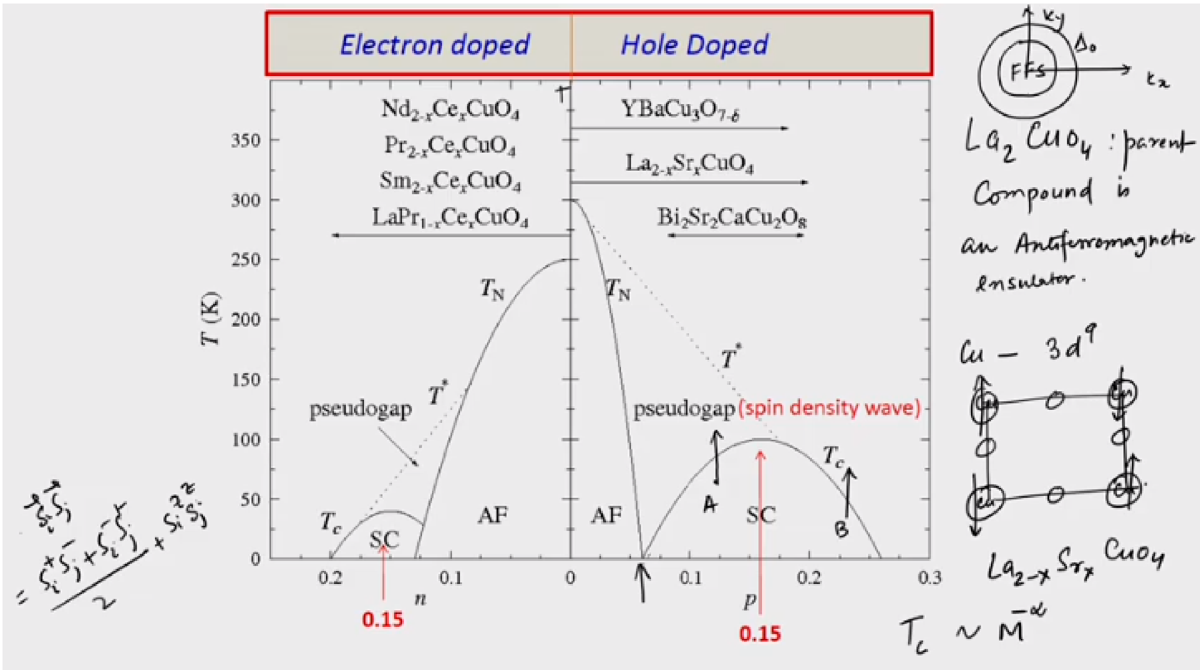
If you heat up the substance you should go to a normal state. So, will happen if you heat the substance. Which means, that if you increase the temperature at this point let's call this point as A and let's call this point as B. one should actually equivalently go to a normal phase. But it does not happen. It does not happen, that one goes to a normal phase from being heated up from this point A goes out of the superconducting dome, and this is a very different phase, which we are going to be talking about in the later lecture, and this is not a metal in the conventional sense or what we know as the metal not from the the free electron theory. But from the landau forma liquid theory. So, we'll give a small recap of Landau's form a liquid theory and we'll show ,that such these region of the space ,that violates all the properties of these a land of Fermi liquid theory and it's a very strange metal whereas if you are in the over doped regime. So, so about this point 1 5 below this is called under doped and above this is called over doped. in the over doped regime, if you heat up the substance, that is if you take it out of the super conducting dome you actually meet a normal state and the normal state is pretty normal or it's very close to what is followed by or what is prescribed by the form a liquid theory Okay? In addition to, that there are notions of preformed pairs here. So, there are a formation of pairs which could have happened here and there are experiments which saw this indication of these pairing happening there. So, if so, this remained as the problem, that one actually gets a state which is not a Fermi liquid. So, you don't know, the what the metallic state is. So, you don't know what the starting point is? if you don't know what the starting point is understanding the material including superconductivity is going to be very difficult one should at least have a good idea of what the normal state is, and the normal state would hence, would give rise to superconductivity. So, if the normal state is not well understood, then the superconductivity becomes even more difficult. There's another thing, that is so it's called as a, 'Pseudo Gap', there and there is another thing, that is important in this context is, that the symmetry of the order parameter is not found to be of the s wave form or an isotropic form. So, the we know in conventional superconductor we have discussed this also the fill Fermi surface looks like this, and the gap function looks like this. So, this is the FFS and this is the Delta zero which is same at all parts of the case space if we really talk about this as a kx and ky. However, this shows a D wave symmetry, and, that's why it's this super conductivity is not taught to be arising out of phonon mediated coupling. But it's more like spin fluctuation mediate coupling and the reason, that the phonon mediated coupling is negated or not believed is, that the isotope effect is extremely small in these superconductors.

Refer Slide Time (39:50)



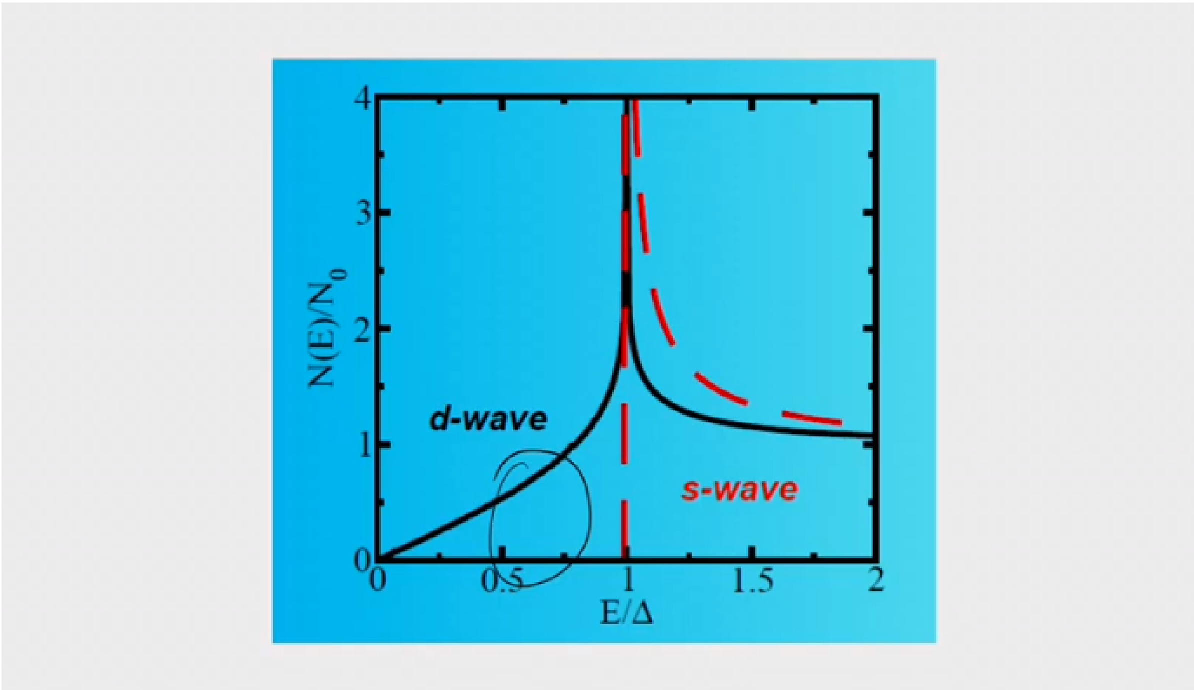
So, just to remind you ,that the isotope effect says ,that the T_C is proportional to M to the power minus alpha where m is the ionic mass and the involvement of the ionic mass in the expression for T_C where alpha is some constant alpha is typically of the as a value which is half and T_C involving the ionic mass is a hallmark feature of the isotope effect and the reason is, that the phonons the frequencies of the phonons ,that involves M as well and So, there's a phonon mediated superconductivity and it's also said, that the phonon mediated super conductivity does not take you beyond Something like 25 Kelvin to 30 Kelvin. So, if we are getting90 Kelvin and 120 Kelvin and 140 Kelvin and so on. So, these cannot be mediated by spin the the phonons rather they are mediated by spin fluctuations.

Refer Slide Time (41:03)



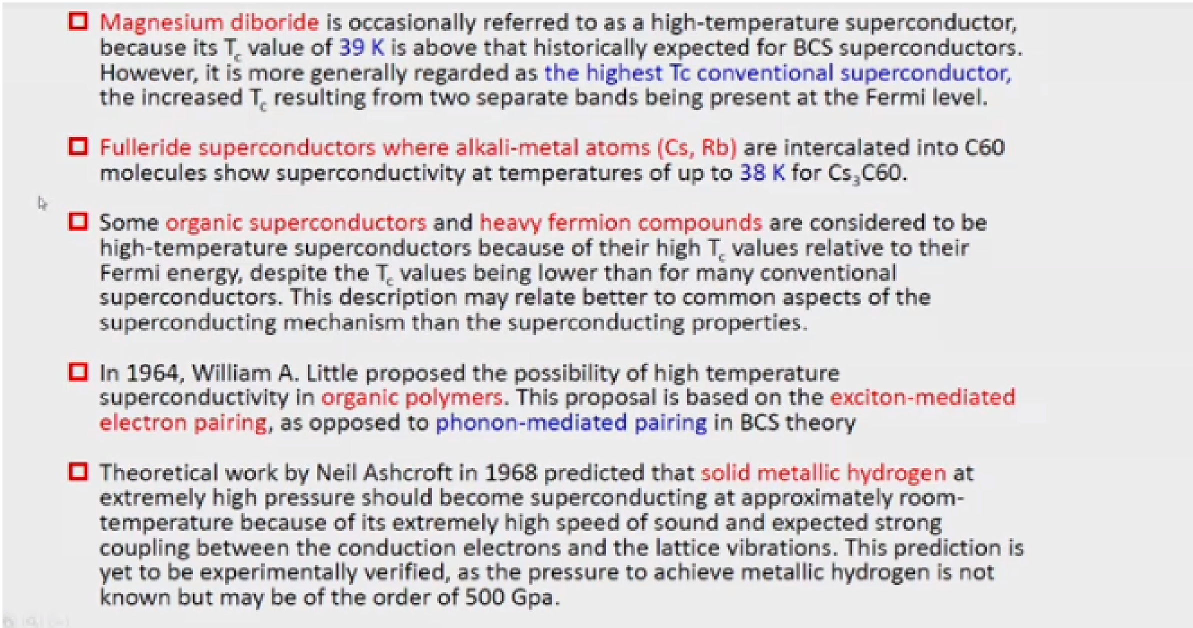
That is the proposal and in a simple model in the TJ model ,that we have discovered or rather discussed in this last class which showed, that there is a term which is like si dot sj which can be written as si plus sj minus plus si minus sj plus with a factor of half and there is a si^z sj^z what one should keep in mind , that hat these are like the spin fluctuation operators, or spin wave operators, which raises or lowers a spin at a given site or a site I or a J. So, these are and from this model we have gotten a d-wave super conductivity. So, a D wave super conductivity unknown normal state pairs being formed in the normal state and then, this dome-shaped super conductivity, d-wave features, undoped tape state being the anti-ferromagnetic insulator. All these things put together made this study of these convention unconventional superconductivity extremely interesting.

Refer Slide Time (42:14)



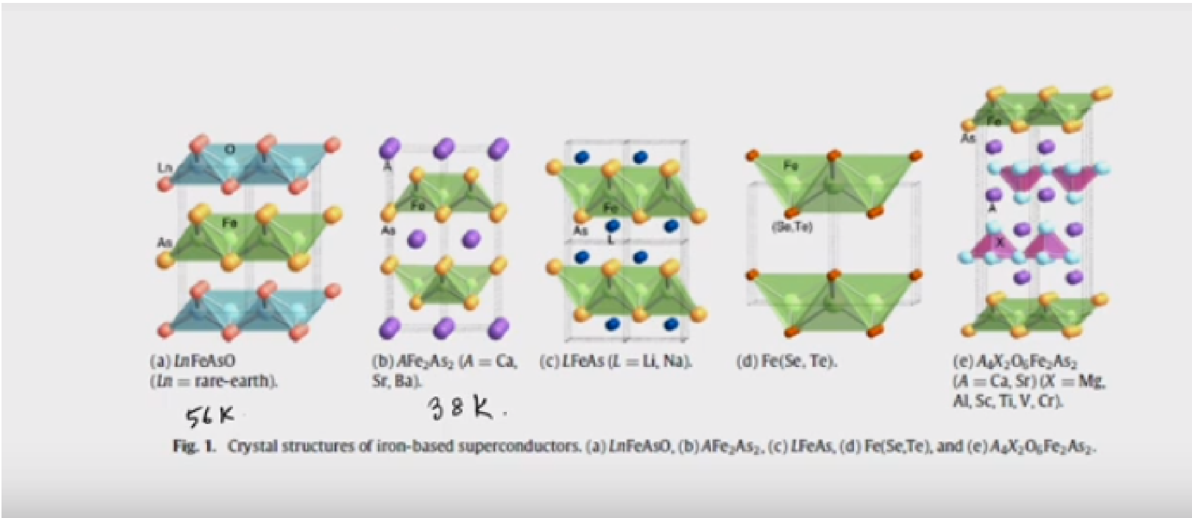
the d-wave has gotten a boost by calculating the density of states. We have seen this the density of states for S wave superconductor is as in the red curve. So, it rises at E by Delta or E equal to Delta and then, it falls off as you go beyond, that whereas for the d-wave it's gently decays to zero. So, even there is a significant density of states for E less than Delta. So, this is the density of states and this density of states can be obtained experimentally. So, this are the features or rather the proof, that the superconductivity is indeed unconventional.

Refer Slide Time (42:58)



Then, there are other materials Sometimes they are referred to as the high-temperature superconductors and, and the magnesium diboride is occasionally referred to as the high-temperature superconductors the T_C value is about 39 Kelvin and is above, that it's historically expected for BCS a superconductor. However, it's more generally regarded as the highest conventional T_C superconductor. So, it's not really an unconventional. But it's a high T_C superconductor. The fulleride of the fuller ends which are intercalated with alkali atoms. So, these are C60 big molecules which show superconductivity up to 30 Kelvin. Then, there are organic superconductors heavy fermion superconductors which are also high T_C superconductors because of the high T_C values and relative to the Fermi energy. Despite, the T_C values being lower than for many conventional superconductors. Now, they are unconventional. But the $T_{C's}$ are not very high. However, the normal state is still unknown. Then, there are inorganic polymers high T_C superconductivity is discovered and this proposal is based on the exit unmediated electron pairing, and this So, as opposed to a phonon mediated pairing as we have been telling time and again for the BCS theory. Then, there are very interesting aspects long back nearly fifty years back, by Ashcroft the same Ashcroft whose proof you read for saw the solid-state physics. Ashcroft thermoman and he proposed in 1968, that solid metallic hydrogen at extremely large pressure could become superconducting at approximately room temperature because of its extremely high sound and expected strong coupling between the conduction electrons and the lattice vibrations. So, this would still be phonon mediated and it would give rise to nearly two hundred fifty plus Kelvin temperature. But pressure, that is needed is extremely high, and one cannot think of, that metallic hydrogen is can be actually subjected to this kind of pressure of five hundred Giga Pascal.

Refer Slide Time (45:21)



So, very quickly we will go through this crystal structure of the iron-based superconductors. So, these are LnFeAsO and so on and these are the, the Nictogens and the, the Chalcogens the Nictogens are your As and so on. So, you're as or the phosphorous or the Nictogens. So, in this, so, these in these iron-based superconductors where ln is a rare earth and so on. So, these are some of the structures, that we have and for this super conductivity. So, these are these rare earth ln the rare earth elements and Then, there's FeAsO and Then, there are these Fe_2As_2 and so on, and so, these are some of the iron-based superconductors which were discovered in early 2000. The $T_{C's}$ around fifty Kelvin. But so, when la is replaced by La replaces Ln the T_C is about 56 Kelvin for this. Then, it's BA or a CA when they are replacing this. Then, the T_C is about 38 Kelvin and so on, and then, there are Chalcogens, which are called as the, the Se, Te. They are called Chalcogens and the Chalcogens also give T_C which are which are around fifty Kelvin Okay?

Refer Slide Time (47:06)

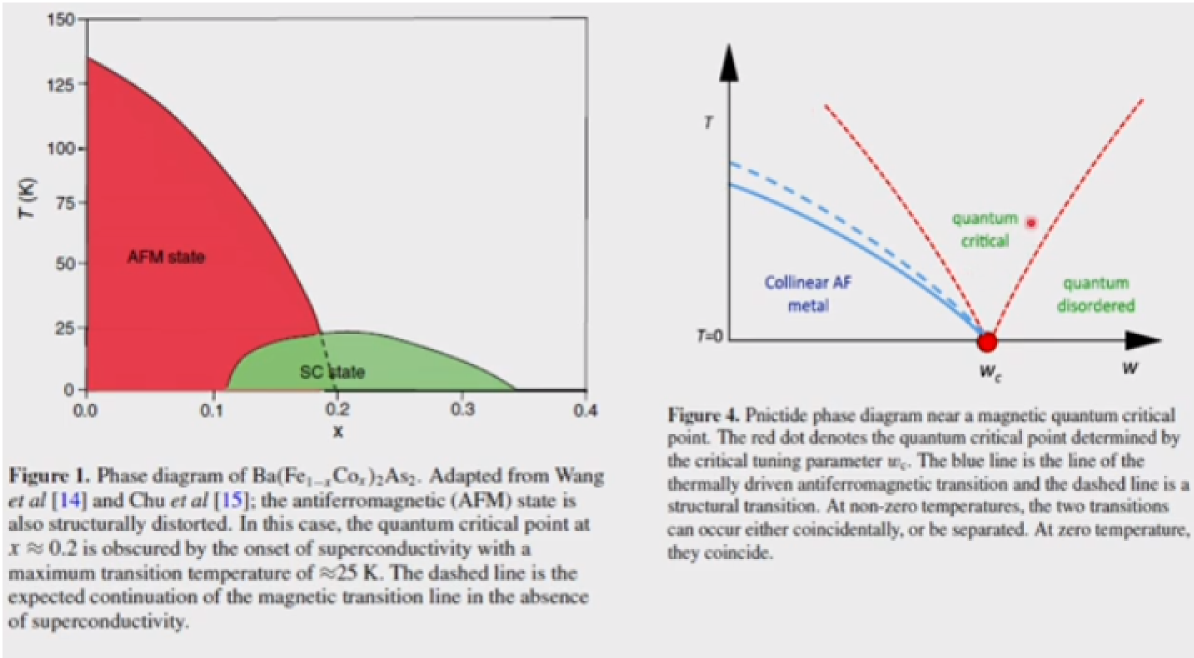


Figure 1. Phase diagram of $Ba(Fe_{1-x}Co_x)_2As_2$. Adapted from Wang *et al* [14] and Chu *et al* [15]; the antiferromagnetic (AFM) state is also structurally distorted. In this case, the quantum critical point at $x \approx 0.2$ is obscured by the onset of superconductivity with a maximum transition temperature of ≈25 K. The dashed line is the expected continuation of the magnetic transition line in the absence of superconductivity.

Figure 4. Pnictide phase diagram near a magnetic quantum critical point. The red dot denotes the quantum critical point determined by the critical tuning parameter w_c. The blue line is the line of the thermally driven antiferromagnetic transition and the dashed line is a structural transition. At non-zero temperatures, the two transitions can occur either coincidentally, or be separated. At zero temperature, they coincide.

So, these are in a nut shell about the iron-based superconductors, something interesting about the phase diagram as well. So, there is an anti-ferromagnetic state, that is seen at zero doping or zero substitution and Then, before the anti-ferromagnetic state and the superconductivity starts and it again shows a dome and not only, that there are Some presence of quantum critical points which were of both experimental and theoretical interests the NIC sites which are by the As and the P this iron based superconductors are replaced by As and p. So, NIC tied phase diagram near a magnetic quantum critical point the red dot denotes the quantum critical point determined by the critical tuning temperature WC is the temperature is a parameter tuning parameter not temperature this tuning parameter the blue line is the line of the thermally driven anti ferromagnetic transition. So, this is, that antiferromagnetic transition here and the dashed line is the structural transition. So, there is also a structural transition. So, along almost along the antiferromagnetic line, which is here almost along this line there is also a structural transition and these two in fact they actually coincide at T equal to zero. But they may be slightly different at T not equal to zero and then, they finally go and come to a quantum critical point and where this is a disordered quantum disordered regime, and this between there red lines there is a quantum critical regime, that one has noted.

Refer Slide Time (48:44)

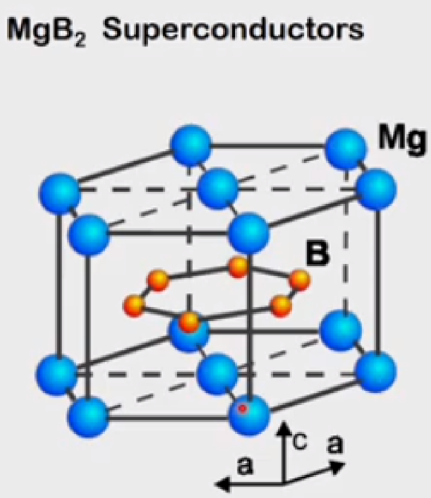


Figure 1. The structure of MgB_2 containing graphite-type B layers separated by hexagonal close-packed layers of Mg.

So, the last thing for us to discuss is this magnesium boride superconductors and we will not say anything simply show you the structure this is honeycomb structure. So, there are boron or the magnesium atoms which are at the honey comb position and also at the middle. And so, is, is it for like a hexagonal cylinder. So, it is on the top and the bottom of the hexagonal cylinder whereas there is a boron honeycomb ring which lies in the middle and so, this is the, the a B c or rather the a a and c are shown there, a and a are same. Because, it's a honeycomb structure and it's, so, basically it is has a similar structure as graphene or graphite. Now, I mean graphene is of course a two-dimensional structure graphite this is more relevant to graphite and this also shows super conductivity. So, we will try to understand, that what gives rise to this rather un explainable sort of features of the normal state of these unconventional, that is the high-temperature superconductors. We mostly talk about the copper oxide superconductors and as I said, that the physics is not the same for all classes of superconductors. But it is good enough for us to understand at least one class and see, that where the Fermi liquid theory fails and why it fails.