Materials Chemistry
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Module - 5
Lecture - 2
Spintronic Materials I Colossal Magnetoresistive Oxides

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Electronic and magnetic properties of Rare earth Manganites: for Spintronic materials

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We are now into module 5, and I would like to give some topical studies on the properties of solids, especially with respect to conductivity and magnetism. One of the oxides that we have seen in the earlier module is the perovskite oxides and among perovskites there are class of compounds; those which are super conducting, those which are showing interesting magnetic and electrical properties.

And today, I will give a case study on rare earth manganites, which is a very popular perovskite type of compound, and what is interesting is a combination of both electric and magnetic property coupled together, this makes it a very special series of compounds for spintronic applications. So, today we will be actually dealing with manganites, and see what is important in this manganites, and how this can functionally become useful for applications.

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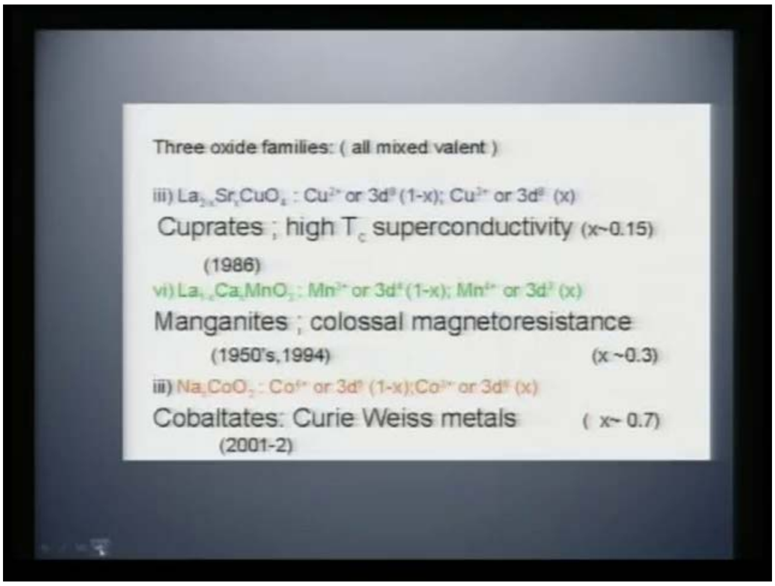

Three oxide families: (all mixed valent)

iii) $La_{2-x}Sr_xCuO_4$: Cu^{2+} or $3d^9$ (1-x); Cu^{2+} or $3d^8$ (x)

Cuprates ; high T_c superconductivity (x~0.15)

(1986)

vi) $La_{1-x}Ca_xMnO_3$: Mn^{3+} or $3d^4$ (1-x); Mn^{4+} or $3d^3$ (x)

Manganites ; colossal magnetoresistance

(1950's,1994) (x ~0.3)

iii) Na_xCoO_2 : Co^{4+} or $3d^5$ (1-x);Co^{3+} or $3d^6$ (x)

Cobaltates: Curie Weiss metals (x~ 0.7)

(2001-2)

And before, I take you through there are three class of compounds, which are useful as far as conductivity is concerned, electrically they are more conducting, as a result they stand out among the class of oxides, and notably lanthanum strontium cuprate. And afterwards, high temperature cuprates like yttrium barium copper, and mercury based super conductors have taken the limelight, where phenomenal change in resistance leading to super conductivity is noted, and this was seen in 1986.

And the other group of compound which is of interest for today’s class is the manganites, which was reported as early as 1950’s by Jonker, who has done a phenomenal amount of pioneering studies in this manganites, and who first noticed that manganites which are insulators can also transform into a metal and a ferromagnet.

So, what is the property that is of importance for us in the present scenario, since 1994 many groups of researchers including us have reported a colossal change in magnetoresistance and which means there is a huge change in resistance on applying magnetic field. So, this will be the topic of our study today and another class of compounds, which was inferred in 2001, 2002 is cobaltates which shows curie weiss metals.

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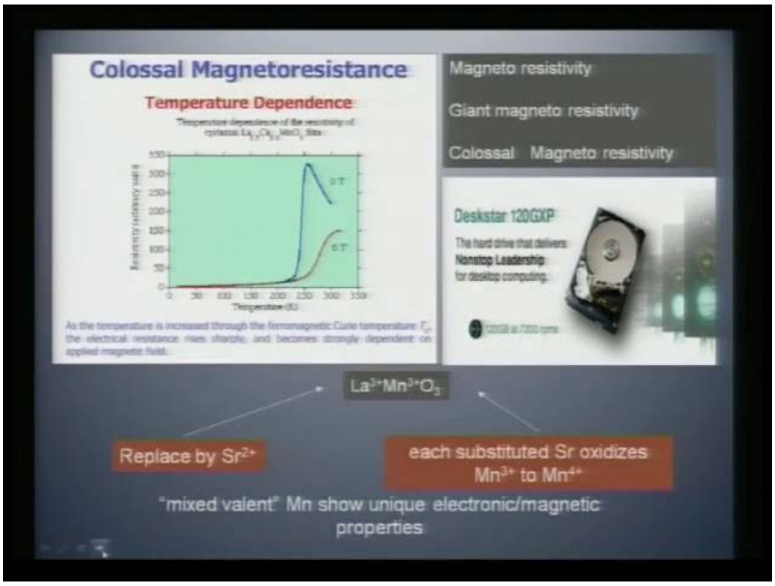

Colossal Magnetoresistance

Temperature Dependence

As the temperature is increased through the ferromagnetic Curie temperature T_C, the electrical resistance rises sharply, and becomes strongly dependent on applied magnetic field.

Magneto resistivity

Giant magneto resistivity

Colossal Magneto resistivity

$La^{3+}Mn^{3+}O_3$

Replace by Sr^{2+}

each substituted Sr oxidizes Mn^{3+} to Mn^{4+}

"mixed valent" Mn show unique electronic/magnetic properties

So, what is this colossal magnetoresistance, this is a cartoon that clearly tells us that there is change in the resistance or change in resistivity, when you apply magnetic field or when you have a absence of field at the 0 tesla, that is absence of magnetic field. This is the insulator to metal transition that you see here, but once you apply a very high field of the order of 6 tesla, you see that the transition shifts to the right side to higher temperature.

And also the resistivity falls down by orders, and this is the term which is used for colossal magnetoresistance meaning, there is a huge loss in resistance when you apply a magnetic field which has never been observed or reported in any oxides thus far. So, as the temperature is increased through the ferromagnetic curie temperature, the electrical resistance rises sharply and becomes strongly dependent on the applied magnetic field.

Now, this is coined in different ways it is called magnetoresistivity or it can be called as giant magnetoresistivity, because of the huge loss in resistance or it can be called as colossal magnetoresistivity. It is popularly known as CMR manganites or CMR oxides mainly, because this term is actually used for another class of compounds which are called metallic multilayers.

So, this GMR term is actually attributed to metallic multilayers, the CMR is generally referred to manganites, so what really brings about such a colossal change in the resistance, it is the substitution of divalent alkaline earth metals in the lanthanum site, which is La 3 plus Mn 3 plus O 3. If you substitute strontium in the La 3 plus site then you can see for charged neutrality part of Mn 3 goes to Mn 4 plus as a result, you have mixed valency which brings about this unique colossal magnetoresistance, so mixed valent manganese shows unique electronic magnetic properties, which we will be seeing from now on.

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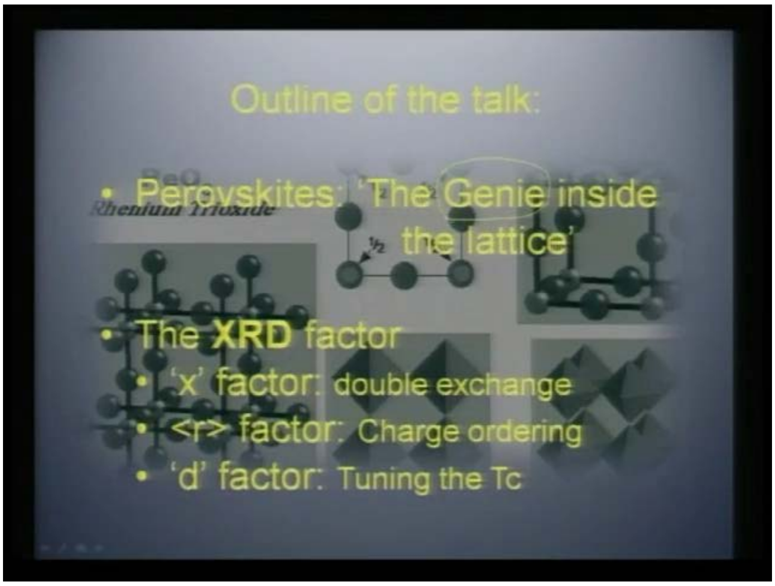

Outline of the talk:

- Perovskites: 'The Genie inside the lattice'
- The **XRD** factor
  - 'x' factor: double exchange
  - <r> factor: Charge ordering
  - 'd' factor: Tuning the Tc

As, a outline of this talk I want to call this perovskite manganite to have a genie inside the lattice, because something very, very unusual of this lattice is simple lattice unit cell, but just by mere substation a big genie comes out of this lattice. So, I call this as the genie inside the lattice, because there are several things that one can learn, one can infer and also one can use this judiciously to extend it for practical applications.

The three factors that really control this unit cell or this manganites, I have identified as the x factor because its easy for us to remember x factor, which really brings about a magnetic interaction called double exchange interaction. And there is a r factor which brings about charge ordering or a electronic traffic jam of the itinerant electrons, which suddenly converts a metal into a insulator and the d factor which we call it has dimensionally, which will be helpful for us to tune the curie temperature. So, there are three factors as we are conversant with the x ray diffraction, I just coin this as x r d factor just to make sure that we remember it, so three factors are there which governs this genie inside this lattice, which we call it is x r and d factor.

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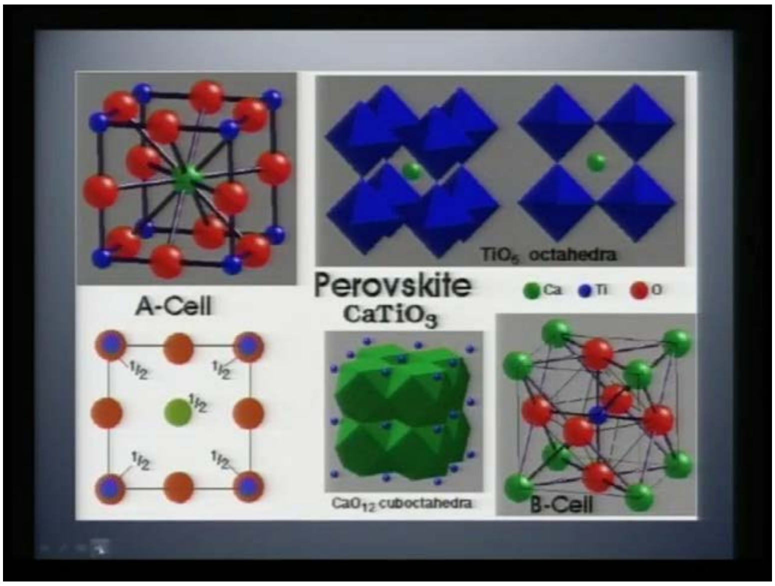

Now, as I told you in the earlier classes we have seen the structure of this perovskites, the basic structure that we will be time and again looking at is this Mn O 6 octahedra and this is your rare earth that is sitting in the middle, and this is made of a edge corner shed polyhedra of Mn O 6 octahedra, so this is the unit cell and in this you would see a phenomenal change in the properties.

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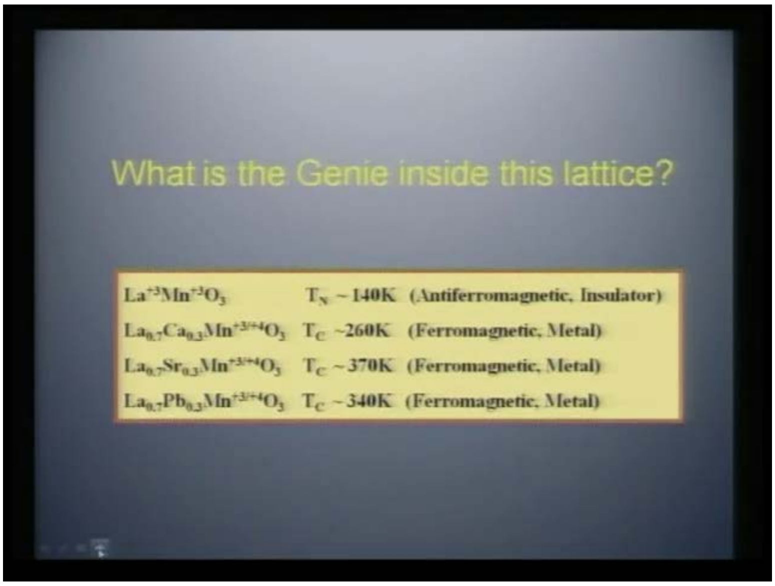

What is the Genie inside this lattice?

$La^{+3}Mn^{+3}O_3$	$T_N \sim 140K$	(Antiferromagnetic, Insulator)
$La_{0.7}Ca_{0.3}Mn^{+3/+4}O_3$	$T_C \sim 260K$	(Ferromagnetic, Metal)
$La_{0.7}Sr_{0.3}Mn^{+3/+4}O_3$	$T_C \sim 370K$	(Ferromagnetic, Metal)
$La_{0.7}Pb_{0.3}Mn^{+3/+4}O_3$	$T_C \sim 340K$	(Ferromagnetic, Metal)

So, what is the genie inside this lattice let us ask this question again, La Mn O 3 is there which has La in 3 plus Mn in 3 plus and this is known to show antiferromagnetic ordering, in other words they show a neel temperature at 140 Kelvin. And at antiferromagnetic transition, it is also a insulator from then on, so if you cool this compound you will see this compound showing a insulating property, but what happens then on is interesting.

If you suppose vary the a site by substituting either with calcium or if you substitute with strontium or with the lead, you will see phenomenally something happens to the magnetism, and to the conductivity of the solid. What happens from a antiferromagnetic state, it goes to a ferromagnetic state, and from a insulator it goes to a metal. So, two things happen when you try to substitute at the lanthanum site, one is it brings about a magnetic transition, and then it brings about a electronic conducting transition.

Now, this T N now becomes T C, because it is ferromagnetically ordered as you may see here I am not changing the La composition or the Mn I am only changing the alkaline earth, but you could see as a function of the ionic size of in the a site you can see the curie temperature is increasing. Therefore this is merely a chemical pressure effect that transcends in this lattice and therefore, you can play around with n number of substitution, to realize a choice ferromagnetic metal which will give you a transition that you decide.

For example, if you are looking for applying this in practical purpose, then one would resort to using this compounds for practical application, which is usable at room temperature. In such a case one would resort to compounds like strontium doped or lead doped manganites, so that you can play around with the curie temperature which is close to room temperature. So, it gives a range of properties, which are fundamentally and from application point of view it is very important.

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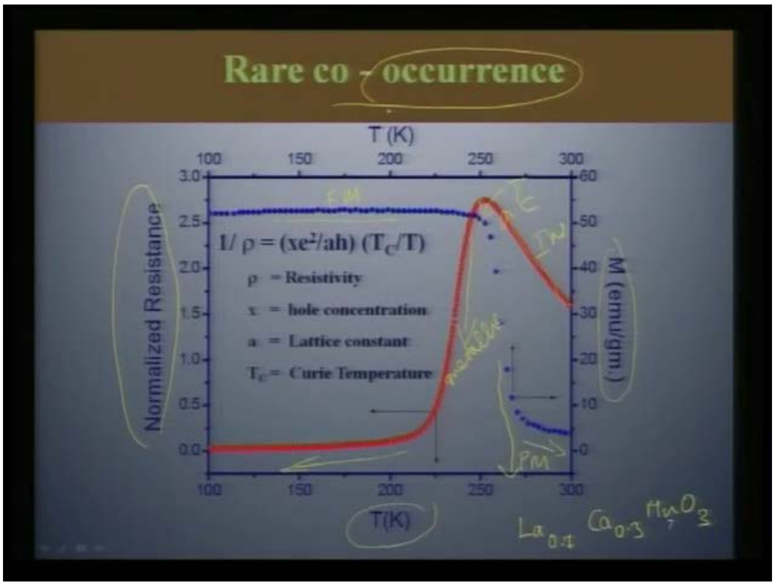

Rare co - occurrence

$1/\rho = (xe^2/ah)\,(T_C/T)$

ρ = Resistivity

x = hole concentration

a = Lattice constant

T_C = Curie Temperature

We look into the next slide and see what is this trench co-occurrence that happens which distinguishes this manganites this is a plot of normalize resistance versus temperature, and also I am plotting on the other y axis magnetization versus temperature. Now, let us take this magnetization which is temperature, which is given in this blue curve as you decrease the temperature from 300 to lower temperature.

You can see a transition where magnetization switches from a very low value to a sudden increase, and then on it shows a practically no change or temperature independent ferromagnetism. So, this change is called ferromagnetic to paramagnetic transition, this is your paramagnetic state this is your ferromagnetic state, and this is the transition which you call as curie temperature.

So, curie temperature is precisely somewhere around 260 or so and this is for a compound, such as La 0.7 Ca 0.3 Mn O 3, which shows a curie temperature at 260 to 270 Kelvin, but what is interesting is if you see the normalize resistance, as a function of temperature. You would see that there is a insulating phase and then at this particular temperature where it matches with T C, the resistivity curve changes its direction and becomes more metallic and it is metallic down to low temperatures.

So, from a insulating state it goes to a metallic state, at the same temperature where a ferromagnetic to paramagnetic transition occurs, so two things happened which I call it as co-occurrence. Two things occur at the same time the ferromagnetic transition and the metal to insulator transition, that makes this group of manganites very special.

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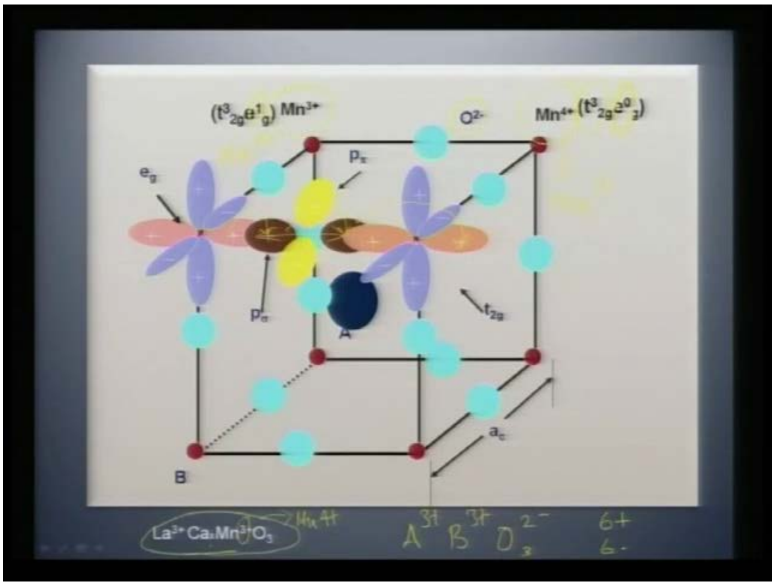

Now, this we can understand from this cartoon where I have tried to mention what exactly happens for this co-occurrence to effect, now if you substitute calcium here as I told you Mn 3 plus part of it has to go to Mn 4 plus, because it has to preserve the charge neutrality in this compound. Because, charged neutrality comes when a is 3 plus B is 3 plus and oxygen is 2 minus, so essentially you have 6 plus and 6 minus making this lattice electrically neutral.

So, when you have calcium doped here part of the manganese 3 plus is actually promoted to manganese 4 plus, now in that case you have the e g orbital of 3 plus which has a odd electron e g 1, and you have a Mn 4 plus core which has a m t e g orbital. Now, when that happens there is a tendency for this e g to go to e g 0 vacant orbital via this oxygen 1 p orbital, so the exchange has to happen from here to here, and here to here and this has to happen here to here.

In such a situation what is required of the symmetry is that this odd electron e g electron has to have a same spin as that of the spins of t to g electron, because this t to g 3 electrons are more localized, and with respect to this electrons this e g electron has to get ferromagnetically coupled. So, this happens when this electron gets promoted to the m t e g orbital of Mn core, then another thing happens this Mn 3 becomes Mn sorry Mn 4 plus becomes Mn 3, and this Mn 3 now becomes Mn 4 plus.

As, a result now a back exchange can happen where the e g 1 here, can go to e g 0 there therefore, a itinerancy is initiated, in other words the electron becomes itinerant, so you would see the transfer is happening back and forth which we call it as double exchange.

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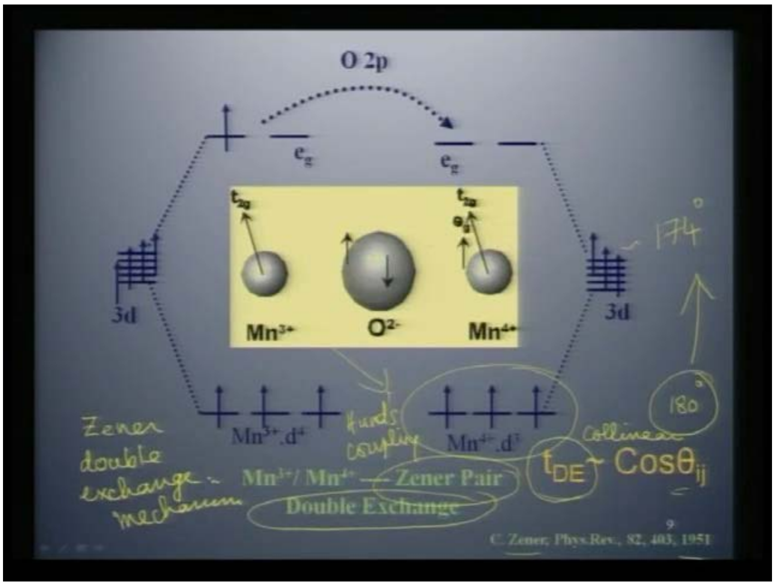

C. Zener, Phys.Rev., 82, 403, 1951

In the next slide we can see this more clearly this is the cartoon, which tells how this exchange happens and as you noticed, this up spin e g electron has to be ferromagnetically coupled to the 3 t to g electrons of the Mn 4 plus core. And this is done by strong Hund's coupling we call it, Hund's coupling and because of this Hund's coupling you have a ferromagnetic exchange that is initiated, and this was actually proposed by Zener, who said that for the transfer integral to happen it depends on cos theta i j between these 2 core spins.

So, if these spins are going to be at 180 degree, then there is a collinear ferromagnetism that can be effected, it is called collinear ferromagnetism, when this angle theta i j is equal to 180 degree. When, it deviates from 180 degree lower than 144 degrees, you will see that this exchange is no more happening, the maximum that this exchange can happen is somewhere around approximately 174, beyond that you will get the spins locked up and there would not be any transfer happening between these 2 core spins.

Therefore, this is very important the transfer of this double exchange integral transfer integral has to be comparable, such a way that you are cos theta i j facilitates such a interaction. And that is crucial for this double exchange to happen and this was proposed by Zener as early as 1951 and therefore, this is popularly called as Zener double exchange mechanism.

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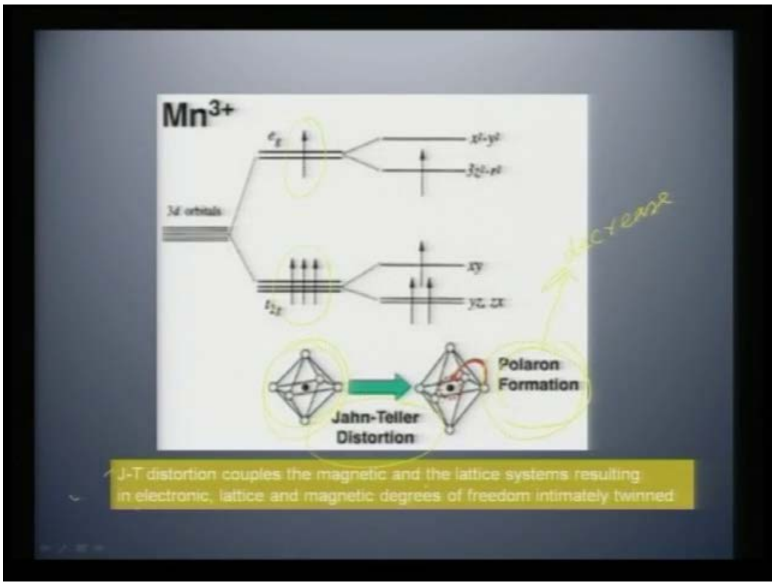

J-T distortion couples the magnetic and the lattice systems resulting in electronic, lattice and magnetic degrees of freedom intimately twinned

Now, we will see that this is not the only condition that governs the metal to insulator transition, and this is not the only thing that is responsible for the paramagnetic to ferromagnetic transition. But, there is another cooperative effect, which is acting in this manganites, which is crucial for this ferromagnetism and for the magnetic property to coexists, one thing that is popularly inferred is the Jahn-Teller distortion. As, we know that is Mn 3 plus has degenerate 3 d orbitals which in the crystal field is split into t to g 3 and e g 1.

And in such a case you actually have a cubic Mn O 6 octahedra which is undistorted, but what happens when this electron is now transferred to another Mn 4 plus site, now there is a distortion happening between the e g orbitals. In other words the e g orbital is spit into further into 3 z square minus r square, and s square minus y square and as a result there is a lowering of symmetry happening during the hopping.

So, this octahedra further gets distorted when such a hopping take place, in such a situation what happens the electron which is conducting which is responsible for conduction is now dragged by this lattice distortion and results in a polaronic formation polaron formation. And because of this polaron which is much bigger in size, the it travels slowly and as a result the metal slowly becomes a insulator.

So, if you want to freeze this polaron what you can do, apply a magnetic field and on application of magnetic field, there is more and more of ferromagnetic ordering initiated, as a result the polaron formation will decrease. When polaron formation decreases, then again the insulating condition fades out and then the system becomes more and more metallic, so the double exchange or the CMR property in this oxide can be explained by 2 ways.

One is by say by understanding with respect to Zener double exchange mechanism, and then you can also understand it based on Jahn-Teller distortion, both are operating in this small unit cell. And therefore, we can sort of some up to say that the Jahn-Teller distortion couples the magnetic and the lattice systems resulting in electronic lattice and magnetic degrees of freedom intimately twined therefore, this cooperative issues present in the unit cell of manganites makes this a more interesting system to study.

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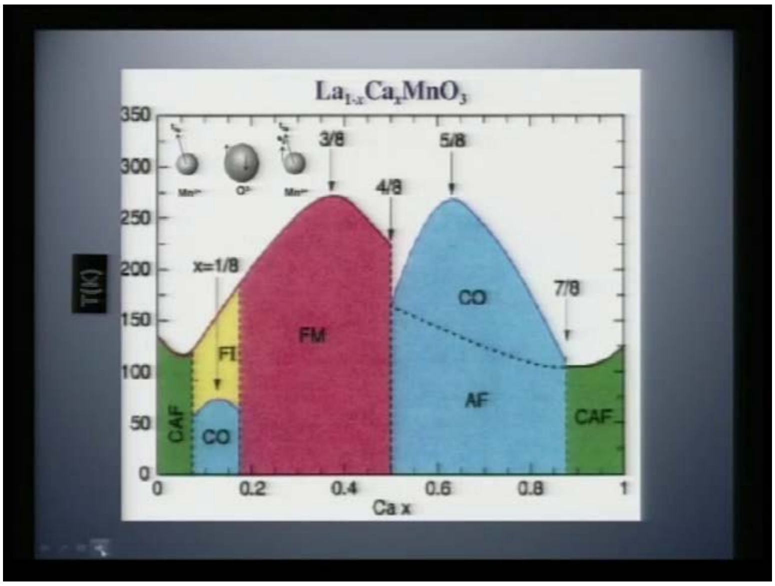

So, what in essence happens here is a situation, where if I start doping calcium in lanthanum calcium manganite series, you would see as you increase the calcium content across the cartoon here, you would see there is a change in the magnetic and electrical resistivity phenomenally. When you substitute for up to 10 percent you see there is a change from a canted antiferromagnetic state, to a ferromagnetic insulator state, it is ferromagnetic, but not necessarily it is metallic.

And there is some amount of charge ordered state that is there, which I will explain later, and once you go further doping with calcium from a ferromagnetic state it goes to a ferromagnetic metallic state. And this is the regime of in interest for us because this is the place, where lot of application can be harvested. This can be used for variety of applications, because this is the state at which there is huge loss in resistance, and as you would see in this regime for a nominal composition of 0.33 calcium the ferromagnetic transition becomes maximum.

And after that its start fading down, but then it is also effected by another big domain, which is either charge ordered or which is antiferromagnetically order. So, the system does not necessarily remain in metallic state for a long time, there is a critical composition which falls incidentally at 0.5 beyond 0.5 still there is some amount of magnetic exchange, but it is all taken in a reverse direction. In other words the it from a ferromagnetic it becomes a antiferromagnetic state, and it also shows unusual charge ordered manganite state, so in a simple system if you keep changing calcium, you come across a variety of magnetic and electrical transition.

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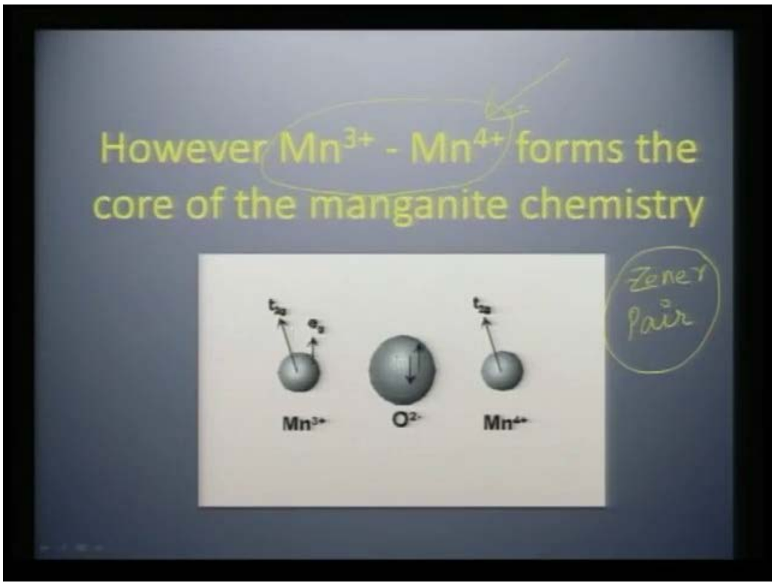

However Mn^{3+} - Mn^{4+} forms the core of the manganite chemistry

Zener Pair

Now, to sum up what is crucial for this manganites, how can I tailor this manganites or what really happens in this manganites I would like to sum up to say, that despite all the fundamental changes that happens during substitution, what is important are the core of the manganite chemistry is this Mn 3 Mn 4 plus pair, which is called Zener pair.

Now, the Zener pair if it is disturbed then the magnetic and conductivity immediately changes, so that is very important. So, what we are going to see in the next few slides we are going to sort of disturb this Mn 3 Mn 4 plus ratio, such a way we will either lose the magnetic property or lose the metallic property, and try to see how we restore it back.

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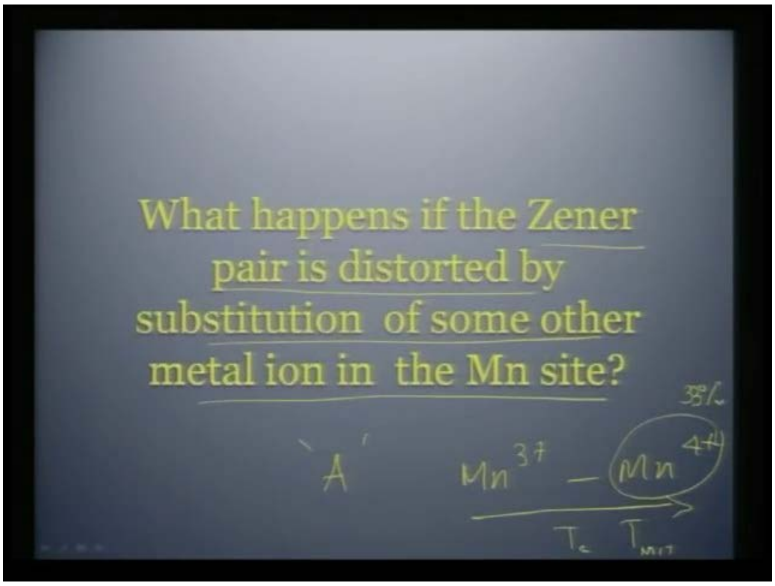

What happens if the Zener pair is distorted by substitution of some other metal ion in the Mn site?

So, this is what I am going to sum it up in the next few slides, what happens if the Zener pair is distorted by substitution of some other metal ions in the manganese site, as I told you if you substitute in a site that is lanthanum site, then Mn 3 plus goes to Mn 4 plus which is advantageous for us. And therefore, you see a ferromagnetic ordering and a metal insulated ordering which is increasing, as you generate more and more of Mn 4 plus up to a critical concentration of say 33 percent of manganese 4 plus. Beyond, 33 percent of manganese 4 plus, you do not see any net change or a spectacular change, in other words sometimes it becomes detrimental, so this is the optimum at which you can get a maximum T C and maximum metal to insulator transition.

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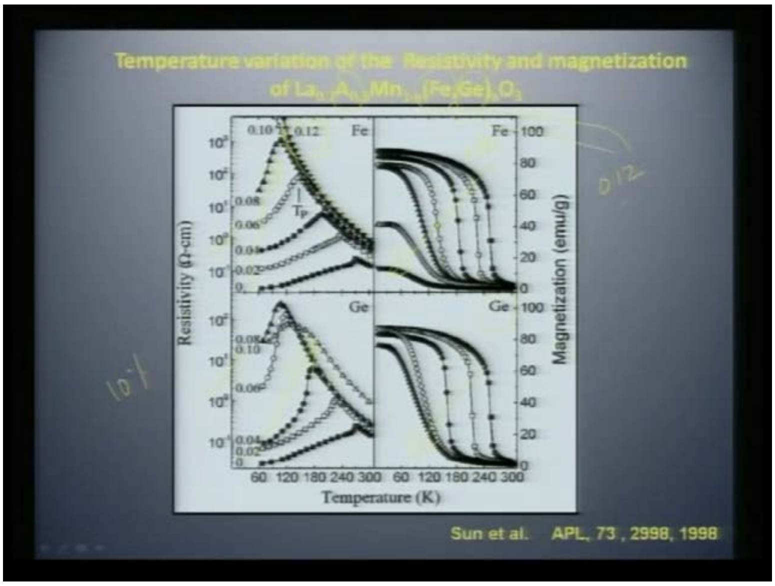

Temperature variation of the Resistivity and magnetization of $La_{0.7}A_{0.3}Mn_{1-x}(Fe,Ge)_xO_3$

Sun et al. APL, 73 , 2998, 1998

In the next slide I will show you suppose I substitute iron or germanium in manganese site, where I am going to keep this A value constant, A is constant therefore, the changes anything that happens will be as a result of iron or germanium. What happens here these are the two magnetization versus temperature plot, these two cartoons are to show they are the resistivity change as a function of temperature. As, we see here when you dope iron starting from the parent compound, you can clearly see that the T C decreases as a function of iron and what is the concentration up to the 0.12, iron 0.12.

Which, means just for 12 percent of iron substituted in manganese you almost kill the ferromagnetic ordering, practically it goes very weakly ferromagnetic. And the same situation is there when you look at the resistivity versus temperature function, as you increase the iron concentration to 12 percent it completely transforms into a insulator.

Same situation for germanium, as you substitute you see the T C decreasing and as you substitute for germanium you see the resistance going almost to a insulating stage, so even in this case you can see that it happens at ten percent of germanium. So, you have either 12 percent of iron or ten percent of germanium totally killing the ferromagnetism and the metal insulated transition.

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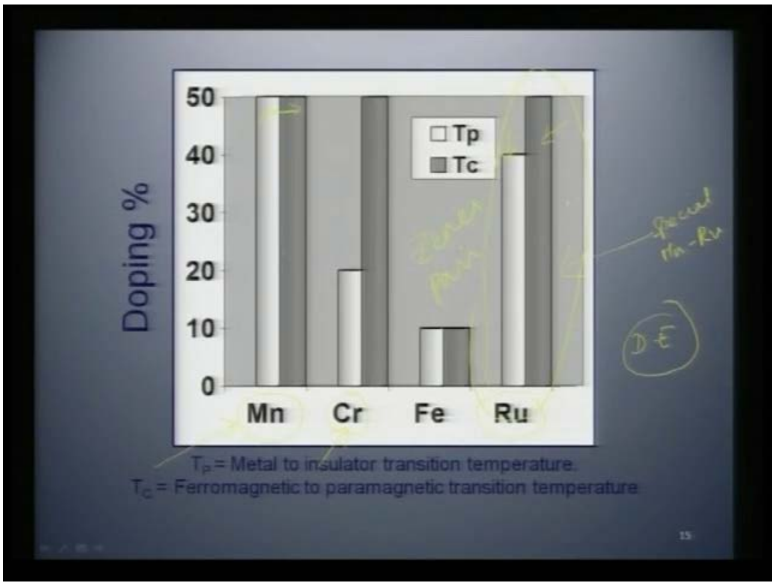

T_P = Metal to insulator transition temperature.
T_C = Ferromagnetic to paramagnetic transition temperature

In the next graph, I will show you for other transition metals, suppose it is only manganese, then manganese 3 plus manganese 4 plus concentration is like this and therefore you can see a double exchange mechanism very strong in manganese. But, if you are going to substitute chromium in the site of manganese, you can see that the metal insulator transition is happening up to 20 percent, although ferromagnetic transition is still there up to 50 percent.

This is a very strange thing that you can see ferromagnetism equally strong up to 50 percent of chromium, where as for the metal insulator transition it deviates, but the real signature for a double exchange mediated ferromagnetism is that, both the T C and T P or the metal insulated transition has to coexist like this. Both has to be like this if it is truly mediated by a double exchange model, but this is not happening in chromium, and if you see iron as I showed you in the previous slide both are killed at around 12 percent.

Another, interesting substitution comes from ruthenium, if you substitute for ruthenium metal insulated transition is taken up to 40 percent, and you also see a strong ferromagnetism up to 50 percent of ruthenium. Therefore, something very interestingly happens in the case of ruthenium substitution, but by and large when you try to disturb the Zener pair, then the metal insulator transition is decoupled from the ferromagnetic to paramagnetic transition that is T C.

So, I am going to show you some examples of ruthenium substituted ones to understand, what all chemistry that we can understand from these manganites, if you substitute ruthenium. And in the end I will also try to make some conclusions what is so special about ruthenium and manganese, especially in manganites, I am taking this case of ruthenium, because we can understand many more things about this genie in the manganite lattice, and also we bring special correlations between two dissimilar metals.

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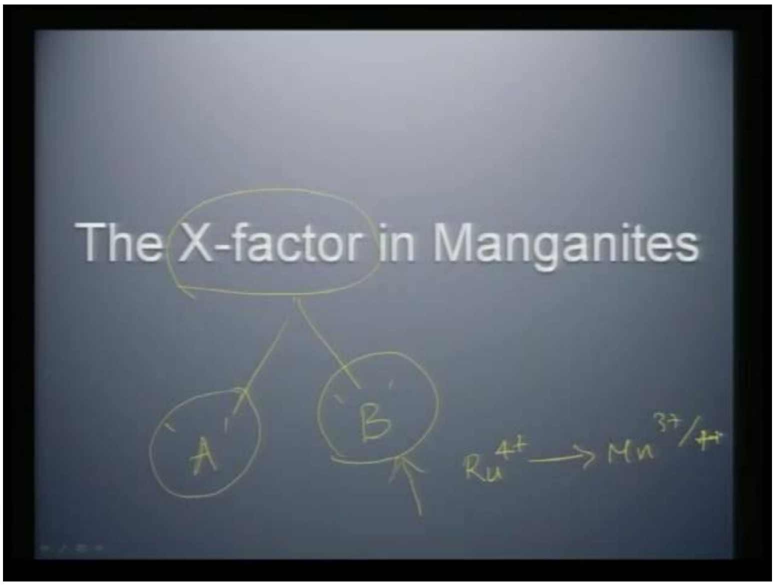

The X-factor in Manganites

Now, the first point that I want to cover is the x factor in manganites, very easy to register because x is something that you would like to always mention. So, x factor in manganites this has both to do with a site cation, you can substitute 1 minus x or B side cation, you can substitute 1 minus x, I have shown you lot of examples of A side substitution. So, I will be by enlarge, I will be focusing on b side substitution, mainly substituting ruthenium 4 plus in the manganese site, in the manganese Mn 3 plus Mn 4 plus site. So, what would happen if you substitute in equal proportions, I take a case study of strontium ruthenate and strontium manganite, because this is more of a reverse doping effect.

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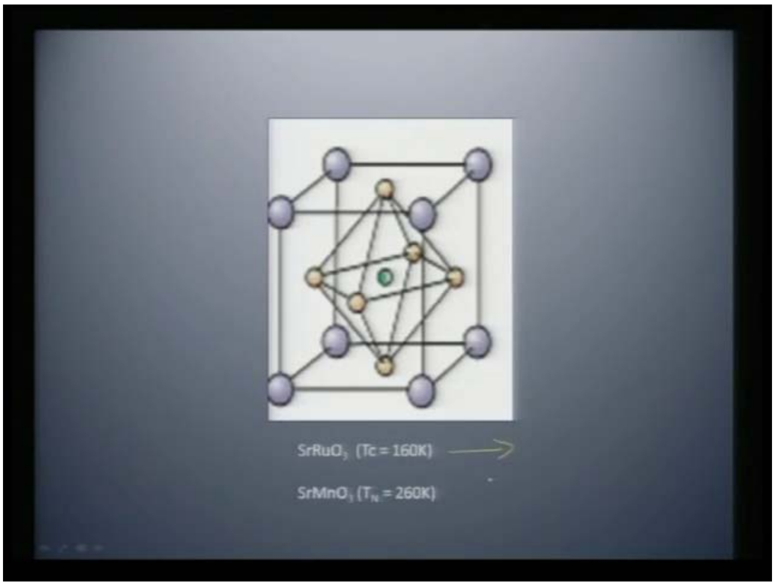

$SrRuO_3$ ($T_c = 160K$) →

$SrMnO_3$ ($T_N = 260K$)

This is a ferromagnetic metal, which is known and one of the very popular ferromagnetic metal known in the ruthenate series or among ruthenium oxides, and on the contrary if you take Sr Mn O 3 it does not show ferromagnetic metallic state it rather shows a ferromagnetic antiferromagnetic insulator state. Now, I am going to substitute manganites in this ruthenate, ruthenium here is already in 4 plus, now I am going to put manganese here.

I can do the other way also take Sr Mn O 3, and I can start putting ruthenium 4 plus here both are possible, but I am going to start with the ferromagnetic metal to see how long I can sustain ferromagnetism, and how long I can maintain this metallicity. So, that is another way of seeing what happens to the Zener pairs, and when the Zener pair becomes operative.

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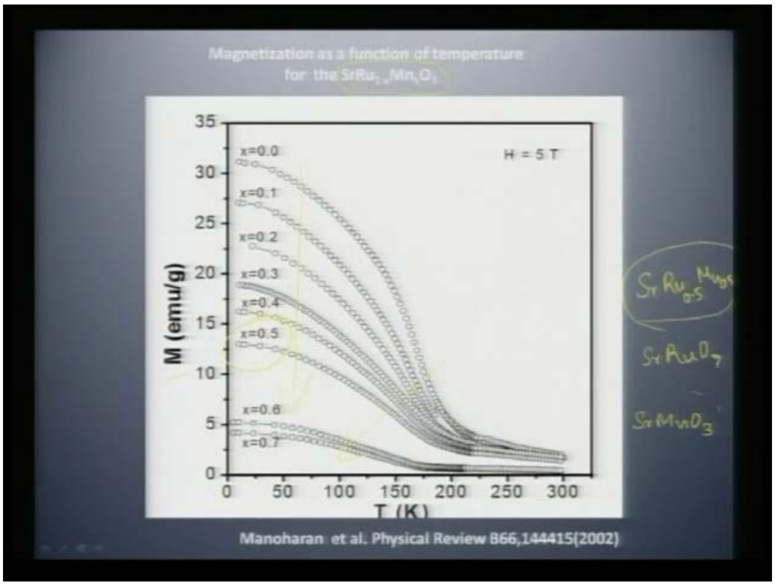

Magnetization as a function of temperature for the $SrRu_{1-x}Mn_xO_3$

Manoharan et al. Physical Review B66,144415(2002)

So, this is a magnetization versus temperature curve for Sr Ru Mn O 3, where we systematically keep substituting manganese down the series, and if you plot magnetization versus temperature. You can see there is a strong ferromagnetic loop that is coming, which is characteristics of this ruthenates and as a function of this manganese substitution the ferromagnetium keeps going down, nevertheless even at 70 percent of manganese, you still see a very strong or a clear ferromagnetic exchange happening.

So, why it has to happen because the n member that is Sr Mn O 3 is a antiferromagnetic insulator, but something special should be happening as you substitute. For example, let us take the case of x is equal to 0.5, in a Sr Ru 0.5 Mn 0.5 you will see that both are in equal proportion in other words for every ruthenium you see a alternate ion should be a manganese ion.

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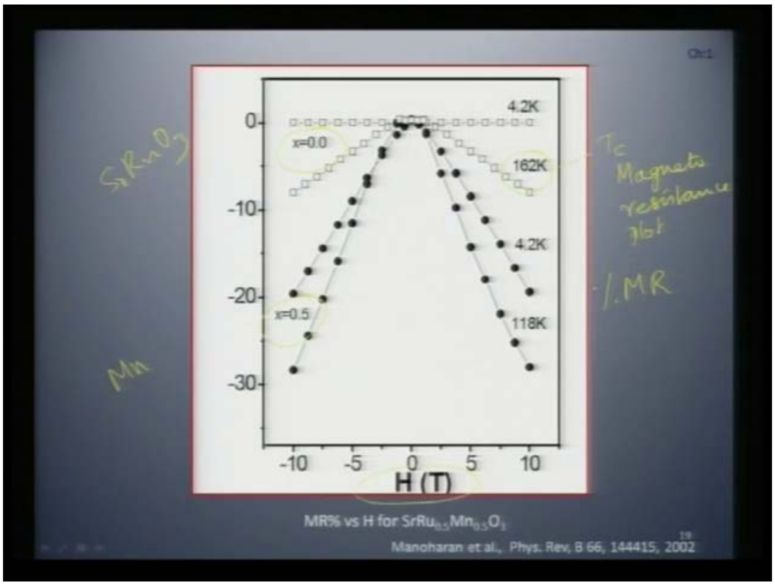

MR% vs H for $SrRu_{0.5}Mn_{0.5}O_3$

Manoharan et al., Phys. Rev. B 66, 144415, 2002

So, in that case you we can see what is really happening compared to Sr Ru O 3, the best way to understand that is do the magnetoresistance curve, this is the magnetoresistance plot, as a function of magnetic field. So, when you swipe the magnetic field in both directions you will see a enormous loss in the resistance, but what is surprising here is if you take the x is equal to 0, that is Sr Ru O 3 case where there is no manganese.

You can see that the M R ratio, percentage M R ratio at the curie temperature T C is only upto 10 percent approximately and at 4.2 k, it is still lower whereas, in the case of Sr 0.5 Mn 0.5 O 3. You see there is a almost three times the magnetoresistance compared to the parent compound, so there should be something unusual happening, when you substitute manganese in the place of ruthenium compared to the parent oxide strontium ruthenate.

That we will see what exactly happens, and let me take you through another example also and show you suppose, if I substitute ruthenium in manganese site then keeping lead concentration constant. As, a function of ruthenium concentration you still see a very strong ferromagnetic loop, in other words even upto 40 percent I am seeing almost for every ruthenium, there is a nearest neighbor manganese in such a unit cell you would see a strong ferromagnetic transition happening.

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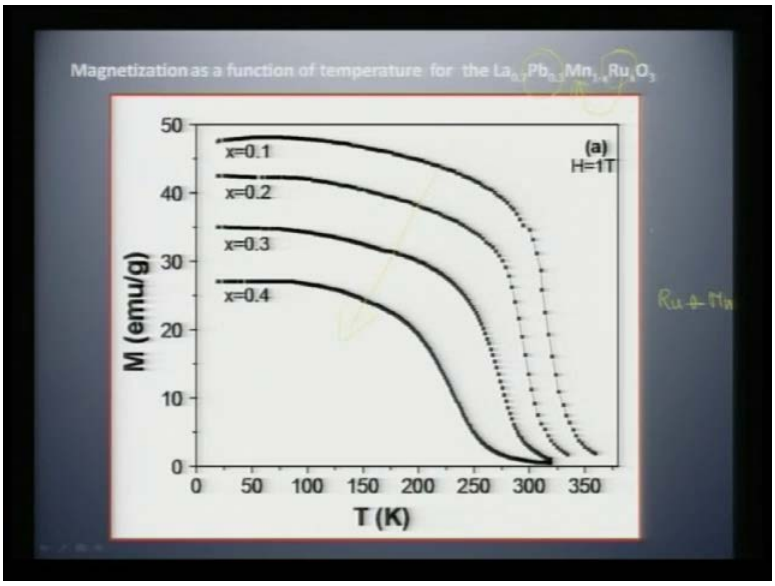

Magnetization as a function of temperature for the $La_{0.7}Pb_{0.3}Mn_{1-x}Ru_xO_3$

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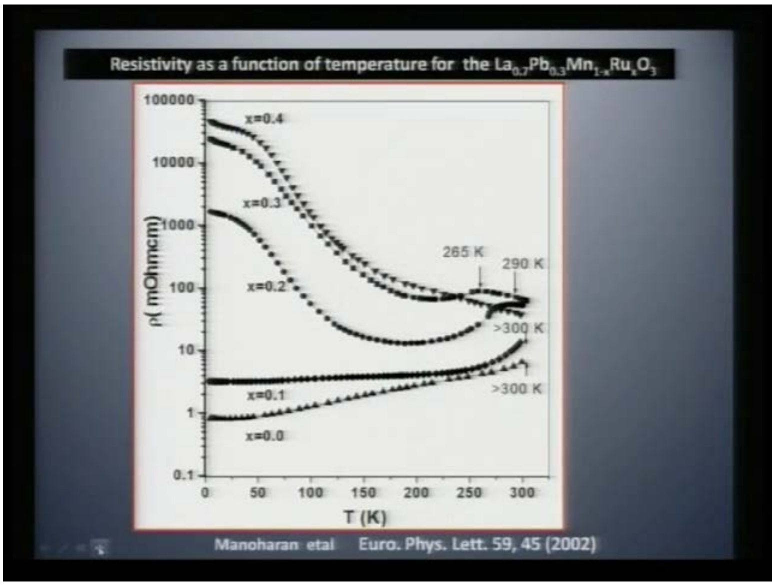

Resistivity as a function of temperature for the $La_{0.7}Pb_{0.3}Mn_{1-x}Ru_xO_3$

Manoharan etal Euro. Phys. Lett. 59, 45 (2002)

So, what is that, which makes it important, this is also pronounced in the resistivity as a function of temperature plot, where you can see the parent compound is showing a clear metallic transition, whereas, 10 percent, 20 percent, 30 percent, and 40 percent of ruthenium, still shows a clear metal insulated transition corresponding to the magnetic transition, which we saw in this case.

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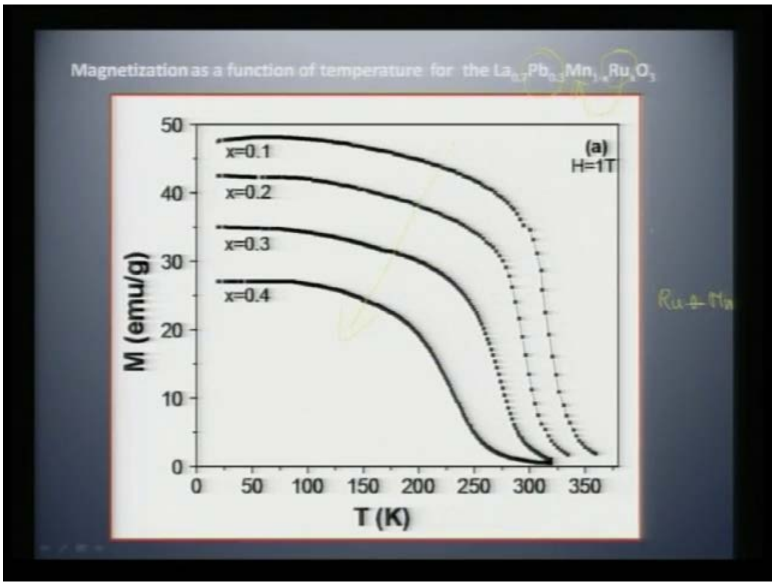

Magnetization as a function of temperature for the $La_{0.7}Pb_{0.3}Mn_{1-x}Ru_xO_3$

So, if you take these metal ferromagnetic transitions, and if you compare, in the next curve with the resistivity plot you still see a clear correlation happening, so something is very unusual of that. We can also try to verify that by keeping ruthenium 0.2 constant in all these cases, and we can try to vary the lead concentration 0.2, in this case 0.3, in this case 0.4, you can clearly see there is a change in the metal insulated transition, but nevertheless they are still ferromagnetic and they are showing a metal insulated transition. And if you also look at the fall of resistance, say for 0.2 and 0.3, there is a huge fall in the resistance for both this compositions.

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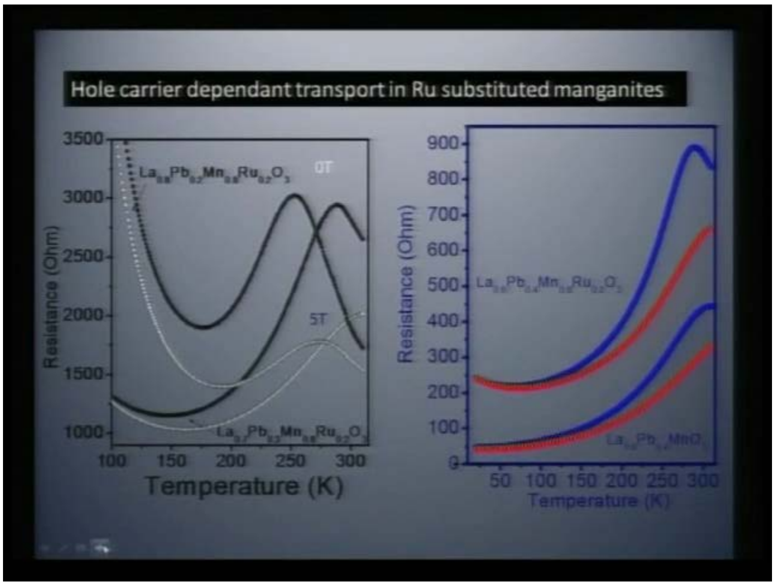

Hole carrier dependant transport in Ru substituted manganites

So, what is happening is there is unusual correlation that is happening between manganese and ruthenium, which we should take note and we can try to see what exactly is responsible. So, we need to make some correlation now to see why such a spectacular systematic change is happening, whenever ruthenium is substituted specially when we try to alter the Mn three Mn 4 plus concentration.

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The R-factor in Manganites

In the next slide, I will take you through the other factor called R factor in manganites, so far we have seen the X factor, where either you substitute in the A site, which improves the ferromagnetic transition or in the B site, which tries to destroy the ferromagnetic alignment.

So, in case of R factor we will try to see what is the influence, R factor is nothing but the average size of a site cation, that is what I call it as R factor, suppose I take calcium or I take strontium or I take barium in the place of lanthanum. Then the average size of this or this or this will keep changing, because you are going from a smaller cation to a bigger cation, as I change this what will happened to the ferromagnetism and metal insulated transition.

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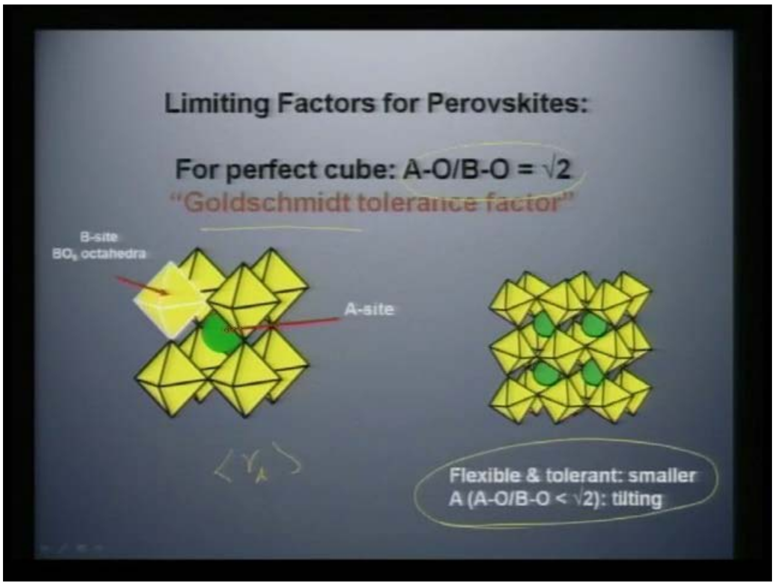
Limiting Factors for Perovskites:

For perfect cube: A-O/B-O = √2

“Goldschmidt tolerance factor”

Flexible & tolerant: smaller A (A-O/B-O < √2): tilting

As, you know in the previous slides in the other modules, I have discussed with you about the perovskite structure and what is important for the perovskite structure is the tolerance factor, which was proposed by Goldschmidt. And this tolerance factor is very critical and if you have the optimum average r A size then you would get a perfect octahedra this is a cubic unit perovskite cell, but once you swap substituting bigger ions in lanthanum site or smaller ions, they can get distorted and therefore, there is a critical tolerance limit to which we are bound.

And that is actually mentioned by this tolerance factor, which has to be not less than 0.89 and it should not be more than 1.02, in that case anyway beyond this extremes this perfect Mn O 6 octahedra gets distorted and this is what we have seen in the earlier stage.

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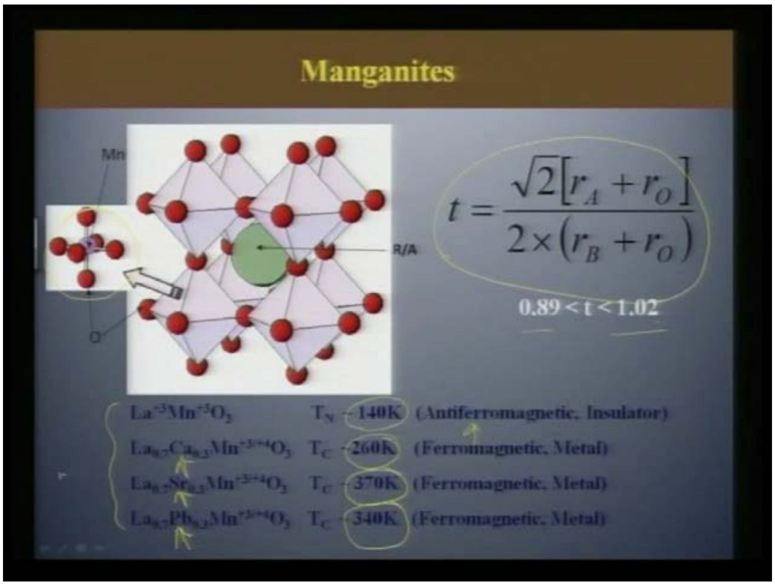

Manganites

$$t = \frac{\sqrt{2}\left[r_A + r_O\right]}{2\times\left(r_B + r_O\right)}$$

$0.89 < t < 1.02$

$La^{+3}Mn^{+3}O_3$ T_N ~ 140K (Antiferromagnetic, Insulator)

$La_{0.7}Ca_{0.3}Mn^{+3/+4}O_3$ T_C ~ 260K (Ferromagnetic, Metal)

$La_{0.7}Sr_{0.3}Mn^{+3/+4}O_3$ T_C ~ 370K (Ferromagnetic, Metal)

$La_{0.7}Pb_{0.3}Mn^{+3/+4}O_3$ T_C ~ 340K (Ferromagnetic, Metal)

So, whenever we are increasing the size average size there is a positive influence where a ferromagnetic T C is increased from antiferromagnetic state, and if you go further than this ferromagnetic state again transforms back to antiferromagnetic state. Therefore, this average a site value is critical which we will see in the next few slides.

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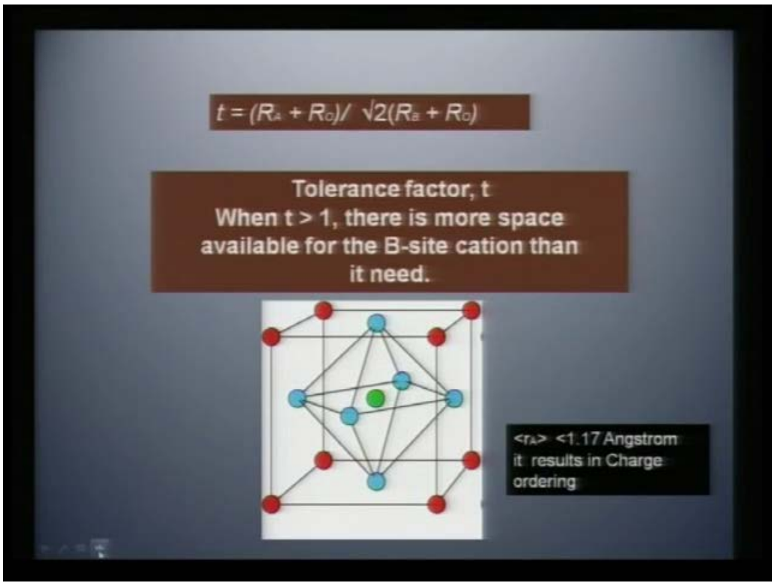

$t = (R_A + R_O)/ \sqrt{2}(R_B + R_O)$

Tolerance factor, t
When t > 1, there is more space available for the B-site cation than it need.

$\langle r_A \rangle$ <1.17 Angstrom
it results in Charge ordering

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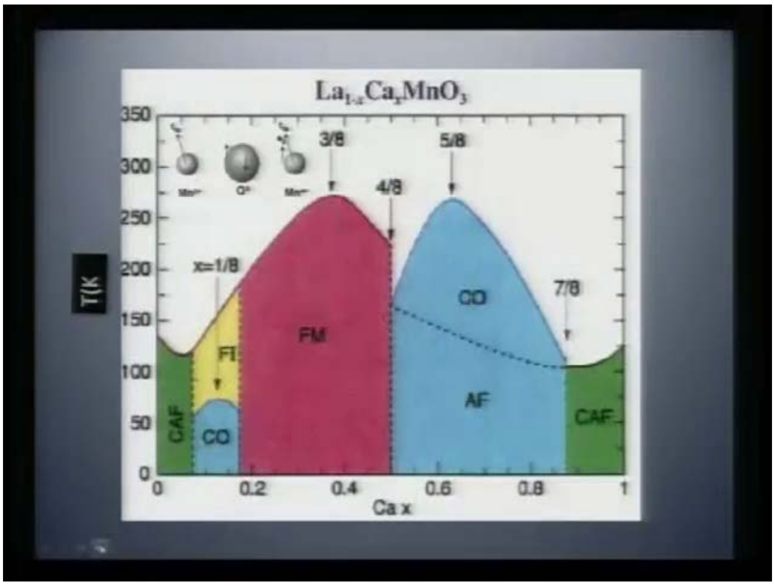

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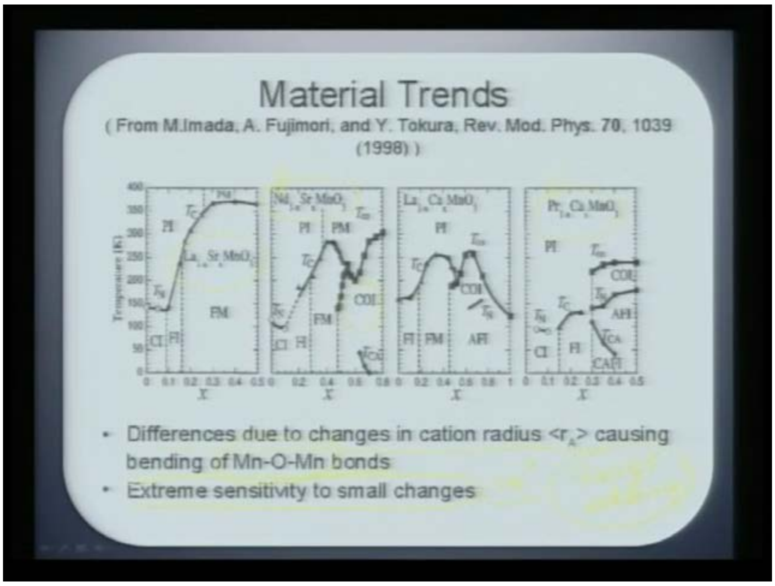
Material Trends

(From M.Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998))

- Differences due to changes in cation radius $<r_A>$ causing bending of Mn-O-Mn bonds
- Extreme sensitivity to small changes

So what is the average r a site, that is needed the critical one is 1.17 angstrom, if it is less than 1.17 angstrom then the compound immediately becomes a paramagnetic insulator. ...which we have already seen in this phase diagram earlier. And this is also seen in other stoichiometries or other compositions, La Sr Mn O 3, you can see upto 0.5, you can have T C and then it slowly transforms to charged out of the state. Neodymium strontium manganite here, I am changing the lanthanum by neodymium again, you would see after a ferromagnetic state around 0.5 you see a charge ordered insulating phase coming.

Similarly, the case for praseodymium it is more complex than other series, because praseodymium itself has a variable valance, as a result the M I T N ferromagnetic transition gets distorted. So, differences due to changes in cationic radii r A this brings about a charge ordering, because there is bending of Mn O Mn bonds, so when Mn O Mn bonds are distorted or it deviates from 174 degrees as I told you earlier.

Then you would actually go into a charge ordered state, which means there is a competing interaction between the itinerant electrons, which causes a double exchange mediated ferromagnetism. And a super exchange competing magnetic ordering, which will actually bring about a charge ordered state, the super exchange mediated ordering leads necessary to a antiferromagnetic state. The double exchange mediated ordering leads to ferromagnetic state, and because you are distorting this Mn O Mn bond you are actually going into a situation, where it is charge ordered. In other words, there is a sudden twist in the Mn 3 plus and Mn 4 plus orbitals and they become orthogonal, as a result there is no collinear magnetism, and there is no exchange a transport of electrons as a result the system suddenly transforms to a insulating stage.

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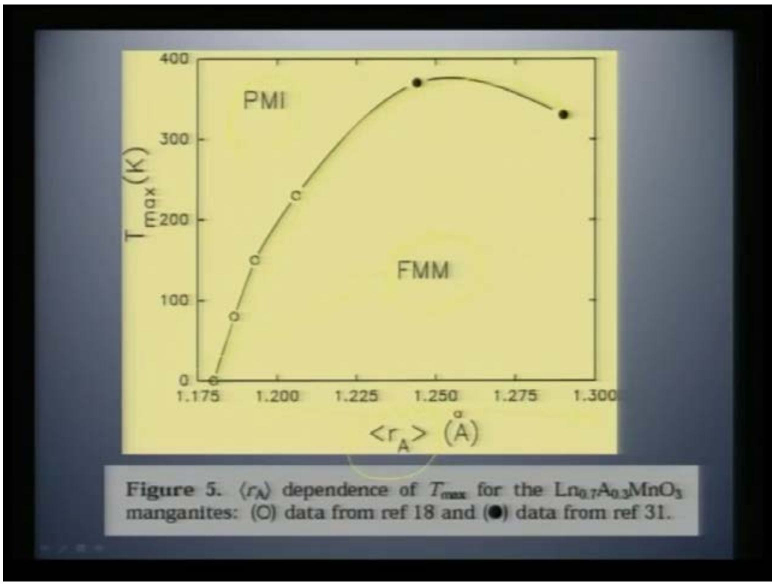

Figure 5. $\langle r_A \rangle$ dependence of T_{max} for the $Ln_{0.7}A_{0.3}MnO_3$ manganites: (○) data from ref 18 and (●) data from ref 31.

So, it is a extremely sensitive composition to small changes, which brings about such a drastic change, now this is another figure that I have taken from paper of Ravo from France, this is appeared in chemistry of materials volume 10. And this curve also shows a plot of T C that is curie temperature as a function of r A, because if you keep on varying the r A value from 1.17. As, you know here, it is gone into a paramagnetic insulating stage whereas, if you start increasing this way then you again transform to a ferromagnetic metallic stage. So, from a paramagnetic metal to a ferromagnetic metal, the critical tie line seems to be something like this, where you have a critical boundary, which separates both this behaviors, so average r A is very important.

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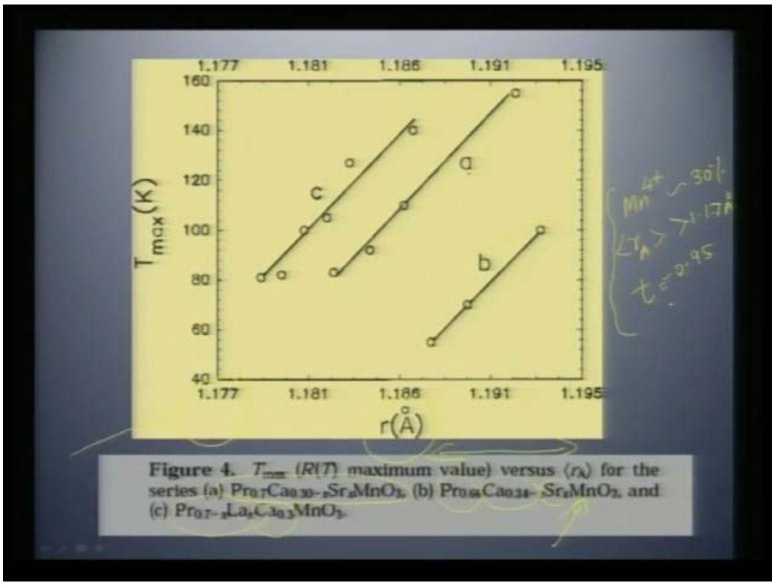

Figure 4. T_{max} ($R(T)$ maximum value) versus $\langle r_A \rangle$ for the series (a) $Pr_{0.7}Ca_{0.30-x}Sr_xMnO_3$, (b) $Pr_{0.66}Ca_{0.34-x}Sr_xMnO_3$, and (c) $Pr_{0.7-x}La_xCa_{0.3}MnO_3$.

We can also make a function of T C as a function of r A, where you can actually try to chose different sort of compounds praseodymium 0.7, calcium 0.30, lanthanum you can substitute little bit for praseodymium and you can keep the calcium constant. Then you can vary sorry praseodymium kept constant, you can vary calcium for strontium, you can see a variety of trend that is available.

For example, take the case of C, where a bigger ion is brought in which has 3 plus immediately you see the transition is increasing on the higher side. Where, as if you take B which is the lowest because you are bringing in more and more of a divalent iron, you are seeing the average a size although here, but it is essentially decreasing the curie temperature.

So, it is not just necessary that you play around in this domain, where the values are low because you are essentially trying to disturb the Mn 3 plus Mn 4 plus ratio there. So, what is, so critical here in this R factor is that magic value of 1.17, so it is possible when you are trying to make new compositions always to have two things in mind. One is you should always have Mn 4 plus ratio which should be approximately 30 percent, and you should have here average a s s value, which should be always above 1.17 angstrom.

So, this you do not even need to do the experiment, you can actually calculate if you know the ionic size and ionic and the valency of your substituting metal, you can principally calculate this. And also the tolerance factor you can calculate, which should be approximately 0.95 or so to keep up with the perovskite phase, so this is more like a mantra, more like a thumb rule for manganites that you need to comply with all three to look for a ferromagnetic metal.

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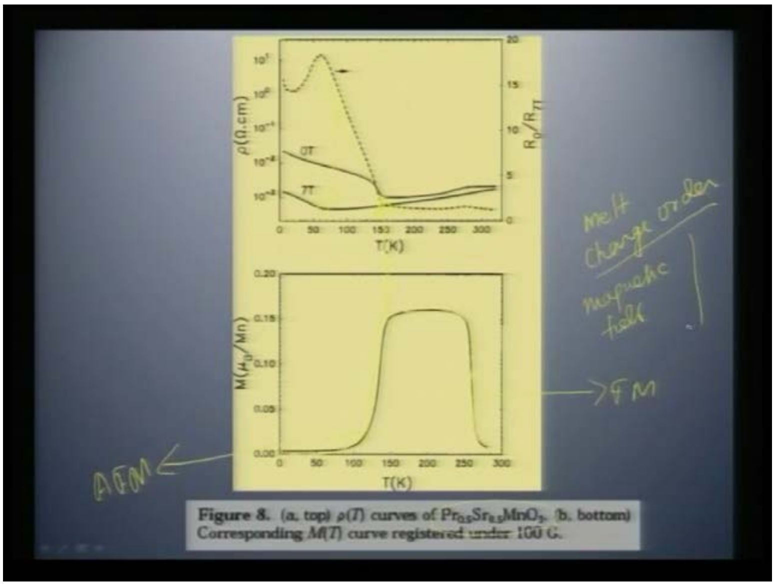

Figure 8. (a, top) $\rho(T)$ curves of $Pr_{0.5}Sr_{0.5}MnO_3$. (b, bottom) Corresponding $M(T)$ curve registered under 100 G.

This is another very interesting case, where you see praseodymium is in a charge ordered state, because you have substituted upto 0.5 therefore, this is a charge ordered situation, where this is your ferromagnetic transition, and this is your antiferromagnetic transitions. So, from a paramagnetic it goes to a ferromagnetic transition and then it comes to a antiferromagnetic transition, this is clearly seen because if you do the resistivity versus temperature plot upto this place it is more or less a weakly metallic state, and then immediately it goes to a insulating state.

At the neel temperature there is also a insulating phase now what can we do about it, if you try to apply magnetic field you can see immediately you can meltdown this insulating phase to a metallic phase. If you are going to apply 7 tesla a very high magnetic field in other words, you can melt the charge ordering mainly using magnetic field.

There are other reports, where you can melt this charge ordering by applying very high pressure, it is called pressure effect, but from chemistry point of view this pressure effect can be brought in simply by altering the cubic lattice, in other words the pressure can be exerted within the unit cell by substituting a smaller or a bigger ion, which we can see.

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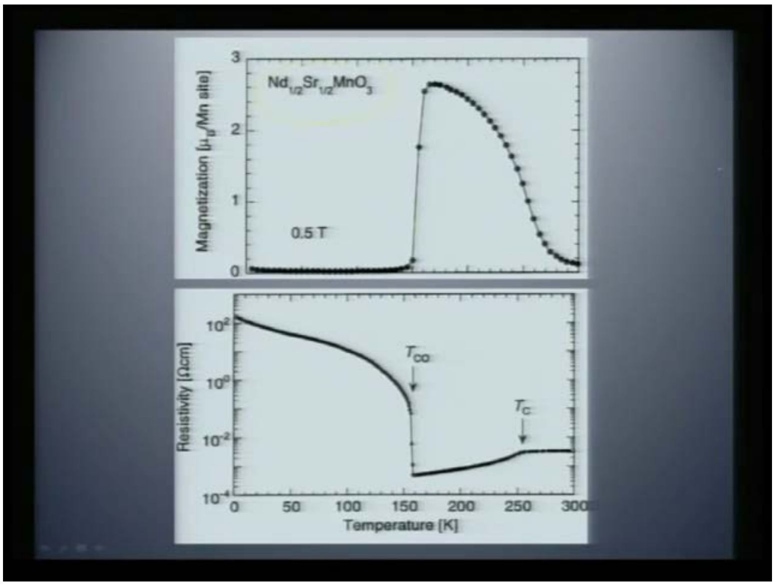

So, this is another compound neodymium strontium manganite, which is a very popular example for a charge order manganite, where it goes from a ferromagnetic state suddenly falls down. And same is true for the resistivity temperature plot exactly at the neel temperature you also see the charge ordered state that is coming which makes it.

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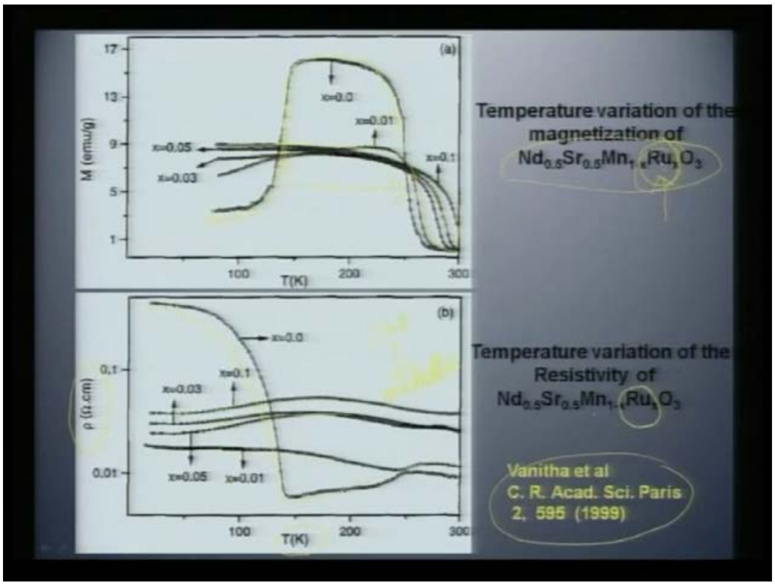

Temperature variation of the magnetization of $Nd_{0.5}Sr_{0.5}Mn_{1-x}Ru_xO_3$

Temperature variation of the Resistivity of $Nd_{0.5}Sr_{0.5}Mn_{1-x}Ru_xO_3$

Vanitha et al
C. R. Acad. Sci. Paris
2, 595 (1999)

But the classic example comes from professor Rao’s group in 1999, they did this work, where they have taken the neodymium strontium manganese, and they have substituted for little amount of ruthenium. What is the amount of ruthenium that is added it is 1 percent, 3 percent, 5 percent and they have gone upto 10 percent, what is interesting here is the moment you start putting just 1 percent of ruthenium, in this charge ordered manganite.

Immediately, this charge ordering is removed and the system becomes a ferromagnetic metal, and as you substitute more and more of ruthenium the system is becoming more ferromagnetic and therefore, from a charge ordered or a antiferromagnetic state, you can make it a ferromagnet by simply substituting with ruthenium. Same is true when you look at the resistivity versus temperature plot, where you can clearly see that from a charge ordered situation, where it is a insulating you can melt this by substituting with ruthenium. So, from a insulating phase you can go to a metallic phase by substituting for ruthenium in the place of manganese or you can drive the antiferromagnet to a ferromagnet by ruthenium substitution.

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The D-factor in Manganites

Dimensionality

Why this happens, we will look at it shortly from now, but before that let me touch on the other aspect that is dimensionality which I call it as d factor in manganites.

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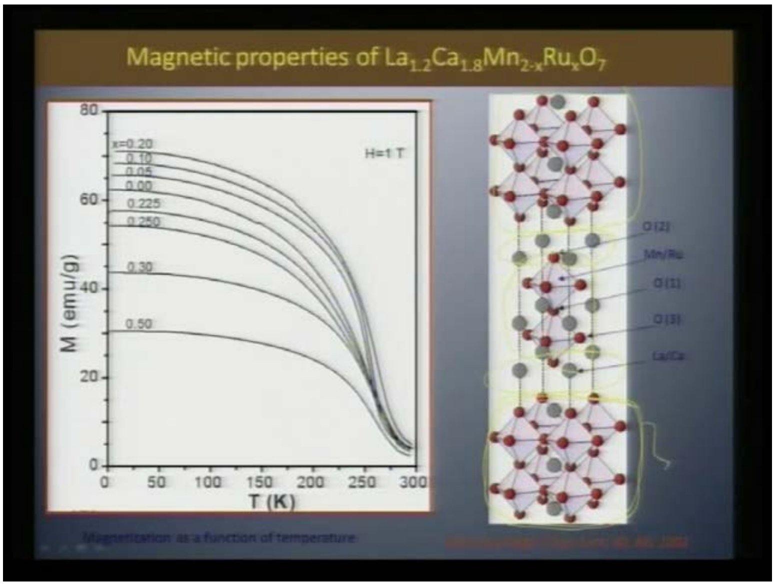

Magnetic properties of $La_{1.2}Ca_{1.8}Mn_{2-x}Ru_xO_7$

Magnetization as a function of temperature

Take the example of a layered perovskite, this is a two dimensional ferro manganite where the Mn O 6 octahedra is here, there is another Mn O 6octahedra here in a polyhedral fashion, you also have a Mn O 6 octahedra here, but it is separated by lanthanum ions.

So, the ferromagnetism present in this polyhedra's is confined only in two dimension and it is not coupled in the three dimension, because it is separated by the lanthanum oxides. In such case you would see for a parent compound the ferromagnetic transition is somewhere here whereas, if you start substituting ruthenium here in manganese site you would see that there is a increase in the ferromagnetic transition up to 20 percent and then the ferromagnetic transition drops down.

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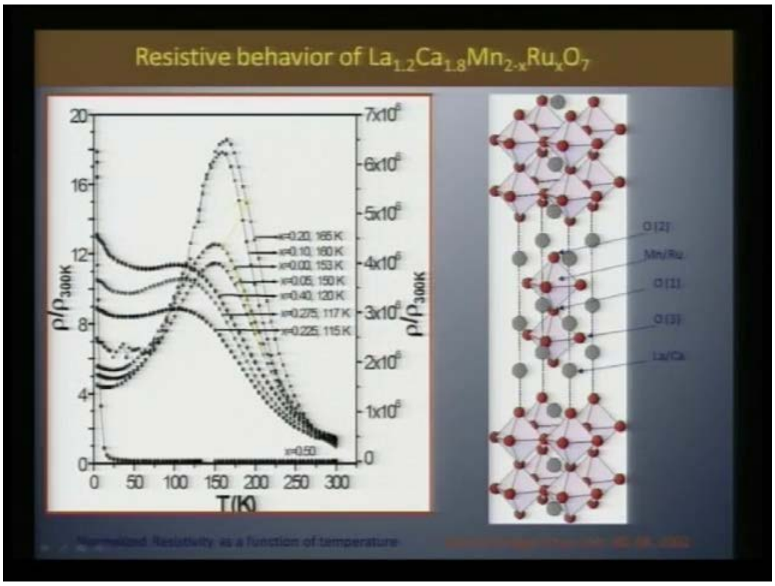

Resistive behavior of $La_{1.2}Ca_{1.8}Mn_{2-x}Ru_xO_7$

Normalized Resistivity as a function of temperature

Now, if you look at the metal to insulator transition, that is again interesting you would see this as the metal insulated transition for your parent compound whereas, if you substitute for ruthenium the metal insulated transition shifts to the right side for when you have calcium. And it is much more interesting, if you are going to substitute ruthenium keeping strontium instead of calcium, you would see the ferromagnetic transition is now on the increase from 110 to nearly 170 Kelvin increase of about 60 Kelvin, you can bring about if you substitute ruthenium for with the bigger size cation.

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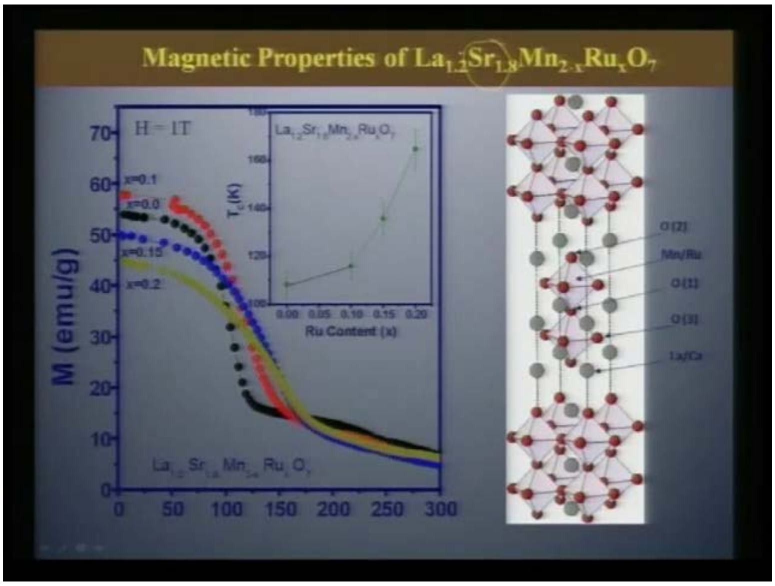

Magnetic Properties of $La_{1.2}Sr_{1.8}Mn_{2-x}Ru_xO_7$

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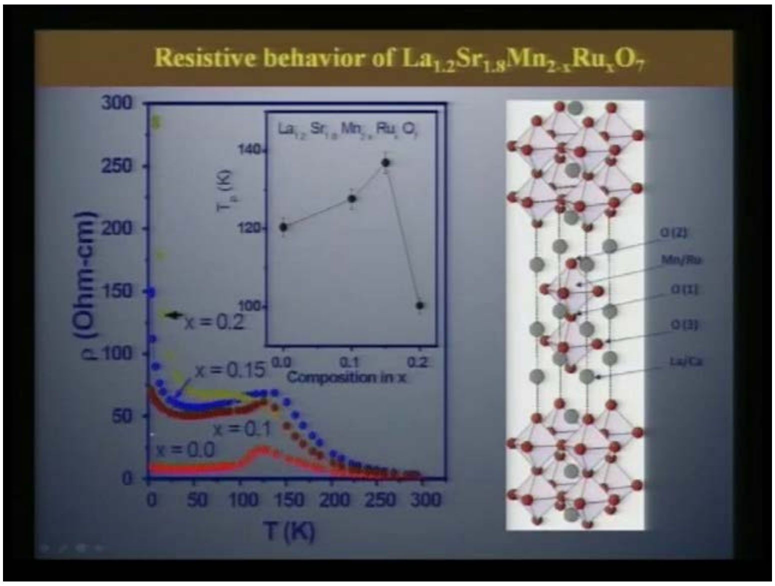

Resistive behavior of $La_{1.2}Sr_{1.8}Mn_{2-x}Ru_xO_7$

The same is true in the metal insulated transition, where you see a clear increase in your metal insulated transition going hand in hand with your magnetic ordering, so what really happens in this case why ruthenium has to increase the ferromagnetic transition.

As, I told you manganese 3 plus manganese 4 plus is very intricate, when you substitute it should actually kill ferromagnetism and metallicity, where as in this case it is actually on the reverse gear it is increasing the metal insulated transition, and it is increasing the ferromagnetic transition. Therefore, there should be something unusually happening with ruthenium and specially in this layered perovskite and that is what we will see in the next few slides.

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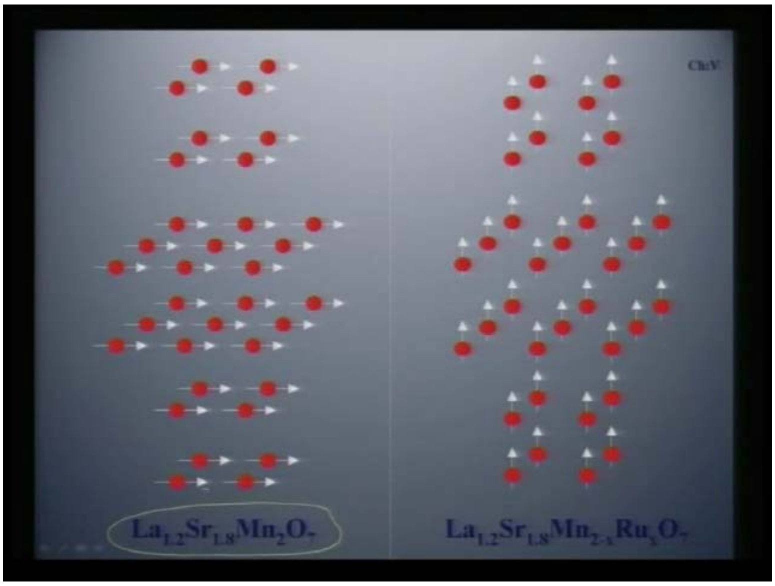

You can see here the spin orientation of the manganese coarse spins are actually confined in the a b plane whereas, when you substitute ruthenium from the neutron diffraction studies, it says it clearly tells us that this there is a rotation of the spins along the c direction it is no more confined in the a b plane, it is now coupled in the c axis.

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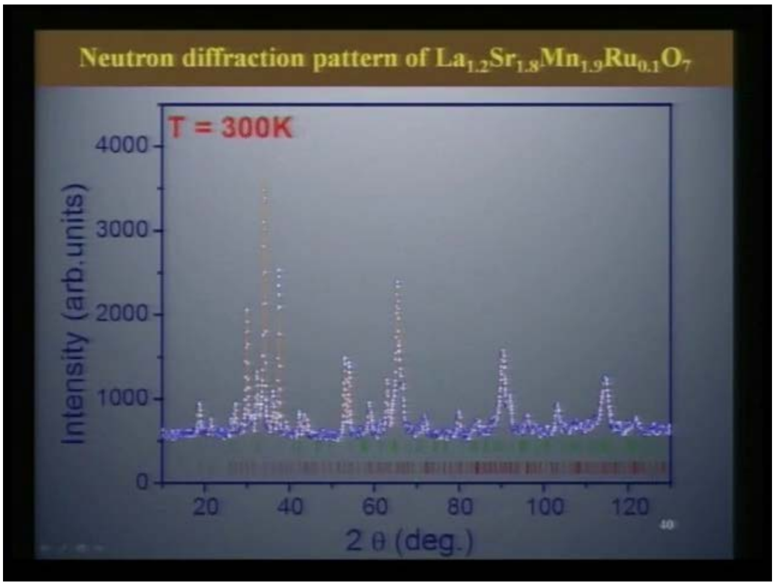

Neutron diffraction pattern of La$_{1.2}$Sr$_{1.8}$Mn$_{1.9}$Ru$_{0.1}$O$_7$

Now, when it is coupled in the c axis this can promote or enhance your ferromagnetic ordering and your metal insulated transition it is not a guess, we can see that from the neutron diffraction case this is the neutron diffraction profile at 300 k. But, let me take you to the low temperature neutron diffraction profile, where you clearly see that in the case of the substituted compound this 0 0 4 neutron reflection or magnetic reflection is absent whereas, this 1 1 0 is actually increasing.

What is true about that 0 0 4 is absent, which is actually representing the a b plane orientation spins aligned in a b plane will have a characteristic 0 0 4 reflection therefore, if it is turning more magnetic in the layered perovskite this intensity should keep increasing. On the other hand what happens in ruthenium is this is nearly absent, and you have this 1 1 0 which is present which means there is a interaction along the c axis nevertheless we confirm this spin state.

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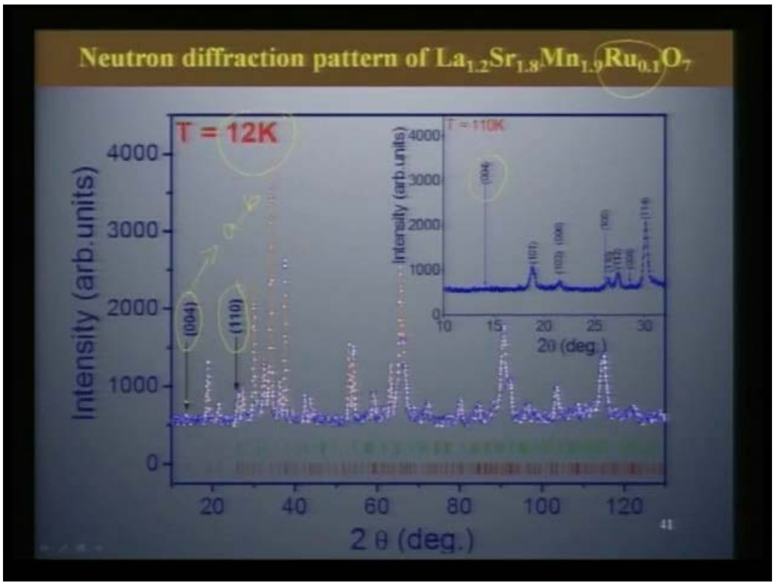

Neutron diffraction pattern of $La_{1.2}Sr_{1.8}Mn_{1.9}Ru_{0.1}O_7$

So, in when you substitute for ruthenium in the manganite site you are actually rotating the spins ferromagnetic alignment along the c axis, as a result you are enhancing the properties.

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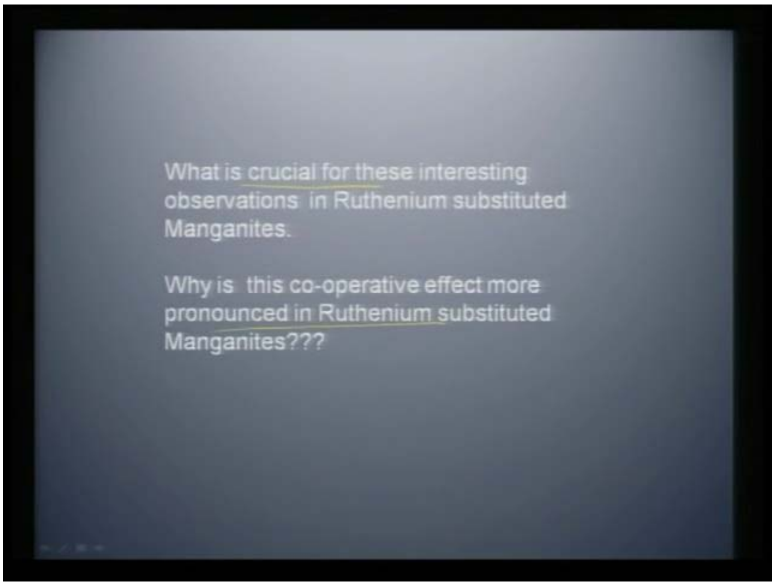

What is crucial for these interesting observations in Ruthenium substituted Manganites.

Why is this co-operative effect more pronounced in Ruthenium substituted Manganites???

So, what is crucial for these interesting observations in ruthenium substituted manganites, the next question we can ask why is this co operative effect more pronounced in ruthenium substituted manganites, these two questions we will try to understand from the spectra.

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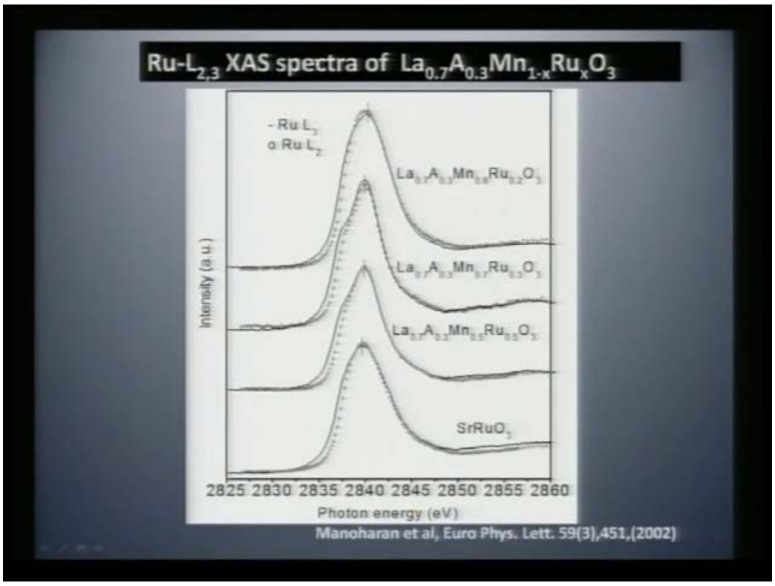

Ru-$L_{2,3}$ XAS spectra of $La_{0.7}A_{0.3}Mn_{1-x}Ru_xO_3$

Manoharan et al, Euro Phys. Lett. 59(3),451,(2002)

This is a XAS spectra of ruthenium L 2 3 h, which actually shows there is a systematic change in the ruthenium image, when compared to your Sr Ru O 3, because Sr Ru O 3 actually is supposed to be 4 plus, whereas in this case you would see the peak maximize shifting to the right side.

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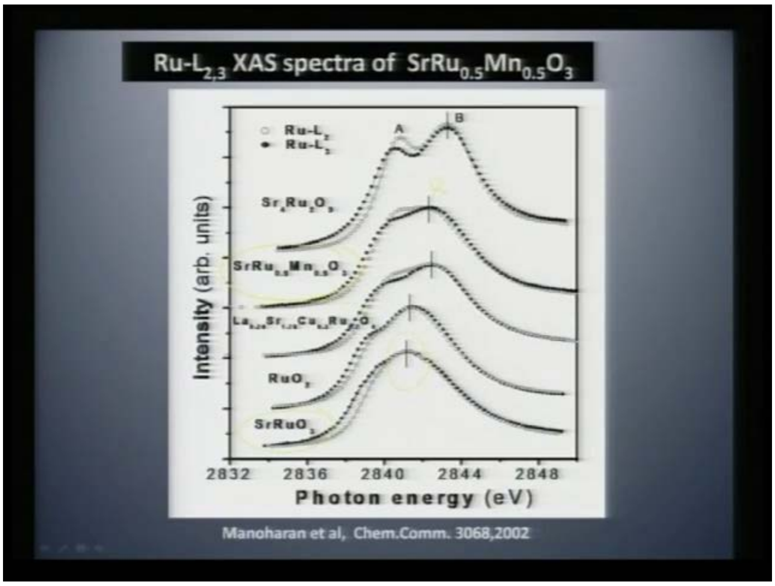

Ru-$L_{2,3}$ XAS spectra of $SrRu_{0.5}Mn_{0.5}O_3$

Manoharan et al, Chem.Comm. 3068,2002

Another example, this makes it more apparent this is Sr Ru O 3 which is a standard which shows your Ru L 2 3 h here, and in this case you have where we have substituted for Sr Ru O 3 it is lying between 4 plus and 5 plus state therefore, your ruthenium is in 5 plus 4.5 state, it is neither 4 nor 5.

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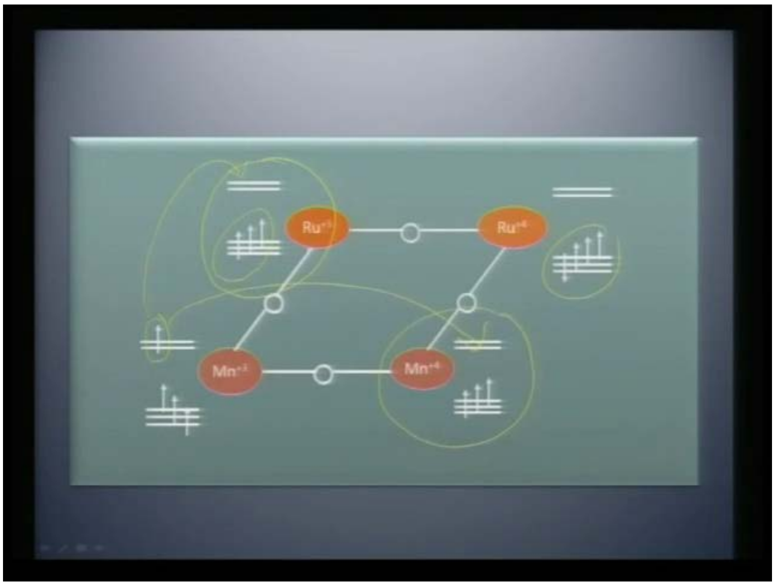

So, we can sort of sum up with a new double exchange model, where we say that Mn 3 plus e g electron now has both ruthenium 4 plus and ruthenium 5 plus, and as a result this e g electron, either can go here or this e g electron can go to this empty orbital. Therefore, you have a two double exchange pathway, where you can drive this compound metallic and ferromagnetic, because you are providing a similar state. In other words this Mn 4 plus is isoelectronic and having iso orbitals like ruthenium, which makes this a more important compound to study.

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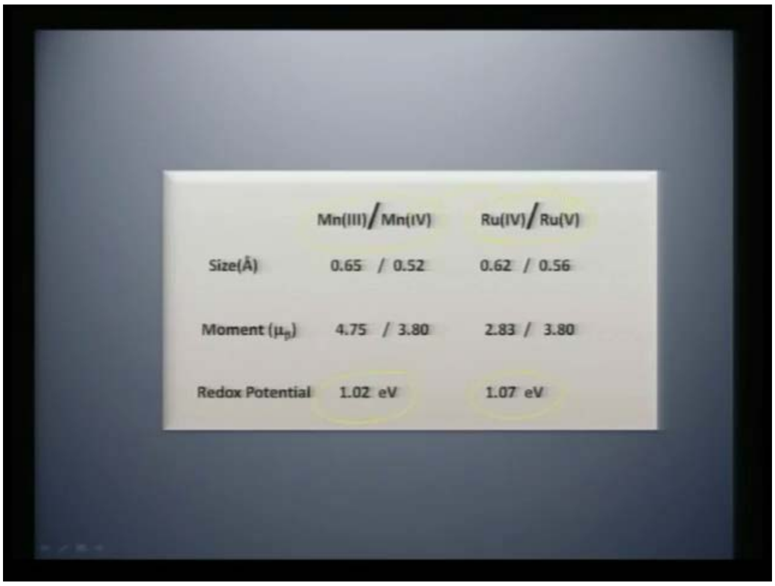

	Mn(III)/Mn(IV)	Ru(IV)/Ru(V)
Size(Å)	0.65 / 0.52	0.62 / 0.56
Moment (μ_B)	4.75 / 3.80	2.83 / 3.80
Redox Potential	1.02 eV	1.07 eV

Not only that ruthenium 4 plus and 5 plus is comparable to that of Mn 3 plus 4 plus, as a result you will have a redox mechanism that is happening, so whenever you substitute ruthenium 4 plus into this Mn 3 Mn 4 plus pair you will see part of your ruthenium 4 is promoted to ruthenium 5, as a result you are clearly providing a two exchange pathway in this manganites.

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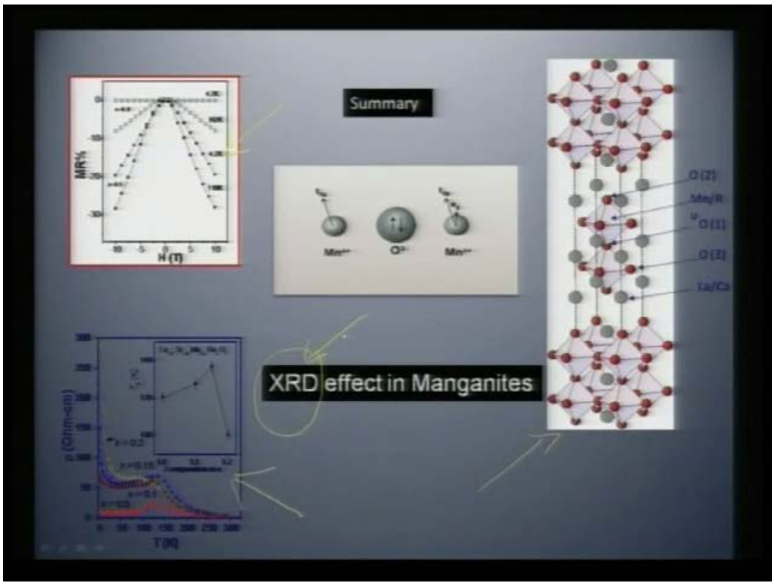

Summary

XRD effect in Manganites

So, to conclude let me put it that we have seen XRD effect in this manganites, which I call it as the genie in this manganites, and we have taken example to see how this manganites 3 plus 4 plus core, when it is disturbed. It can still bring about a very rich chemistry specially with substituting ruthenium, and we have seen how the dimensionality works especially when you substitute with ruthenium, where you twist the spins along the c axis. So, in essence manganites are a very interesting set of compounds that provides you rich chemistry and physics, and there are lot more examples that we can study along the XRD effect in manganites with this I conclude this talk we will look at the other aspects later.