Materials Chemistry
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Module - 5
Lecture - 4
Spintronic Materials IV Dilute Magnetic Semiconductors

In the last 3 lectures, we have been looking at the issue of Spintronic Materials and what makes inorganic solids more attractive, mainly because in the presence and absence of magnetic field, you see large changes in the resistance. And to give a classic example we have discussed about manganite chemistry and how in a simple lattice, you have ferromagnetic structures, which can be fine tuned to alter the electronics properties.

In other words we see a large change in the resistance, in the by the influence of magnetic field, which brings about a huge drop in resistance, which we call it as colossal magnetoresistance. Also in metallic samples we have discussed, how the interfaces can help in ordering ferromagnetic compounds, in both ferromagnetic way and in antiferromagnetic way and thereby affecting the electronic properties. Another group of compounds have attracted interest and this is also under the broader area of spin electronics, spintronics and this is called as dilute magnetic semiconductors.

We all know that semiconductor industry is mainly governed by silicon technology and there are lot of additions to silicon technology, which has come up in the last 2, 3 decades. Therefore, in semiconductor industry can there be anything new that can come out, other than the existing silicon based technology.

The most prominently used material other than silicon is gallium arsenide, but it is a very expensive technology, because you cannot accommodate any amount of oxygen as a impurity, therefore this technology is a very, very touchy or very sensitive technology. So, mostly the semiconductor technology involves high vacuum and in conditions, which is normally not exercised for other compounds, that are used in functional applications. So, if we can bring about a magnetic signature in a typical semiconductor, will that affect the semiconductor technology is the question.

Today I am going to take you through some course of slides where, I am going to show you specific examples where, compounds, which were originally thought to be

semiconducting, if it is transformed to a magnetic semiconductor or if we can induce semiconducting property. What are the implications and how we can understand that and also I will give some examples of slightly higher band gap materials, other than the typical semiconductors and show how magnetic properties can be governed and studied in those.

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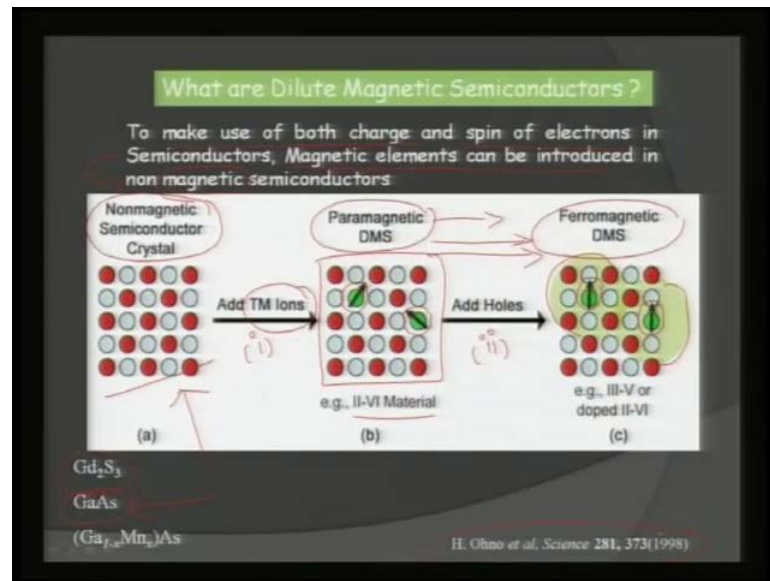
Now, to quickly take you through some of the basic definitions and then some examples, which will form the case for today's lecture, let me ask this question what are these dilute magnetic semiconductors. These semiconductors, they make use of both charge and spin of electrons and there by magnetic elements can be introduced to bring about a situation where a semiconductor, which is nonmagnetic can become magnetic semiconductor.

So, precisely this cartoon will tell us, what such a situation is this is a typical nonmagnetic semiconductor where, the semiconductor material is arranged in a periodic lattice. And suppose, I am going to add some transition metal ions into this semiconductor, then one can see that, these sort of magnetic impurities can be accommodated in the crystal lattice and they are in fact ordered. And in such situation you end up with paramagnetic dilute magnetic semiconductors, because these ions are magnetic, but they are oriented in different fashion.

Now, what is important is the crystal lattice still remains the same, we are not disturbing the lattice and classic example is that of a 2 6 semiconductor. Some of the known ones

are gallium arsenide and this is a typical magnetic semiconductor, which is a gadolinium sulfide, but the most prevalent one is gallium arsenide. Now, if the same paramagnetic D M S compound, we can try to induce some holes and if we can induce some holes here, in this structure.

Those holes will actually turn these paramagnetic signatures to a concerted ferromagnetic signal, thereby we translate a paramagnetic dilute magnetic semiconductor to a ferromagnetic dilute magnetic semiconductor. So, 2 issues are there take a semiconductor and transition metal ions and if you can engineer some holes, if you can add some holes and these holes will stabilize the paramagnetic stuff to a ferromagnetic stuff. So, in essence you will see a concerted magnetic movement or a total magnetic moment, which is prevalent even at room temperature. So, this is a example of a dilute magnetic semiconductor, it was reported by ohno and coworkers in science magazine in 1998.

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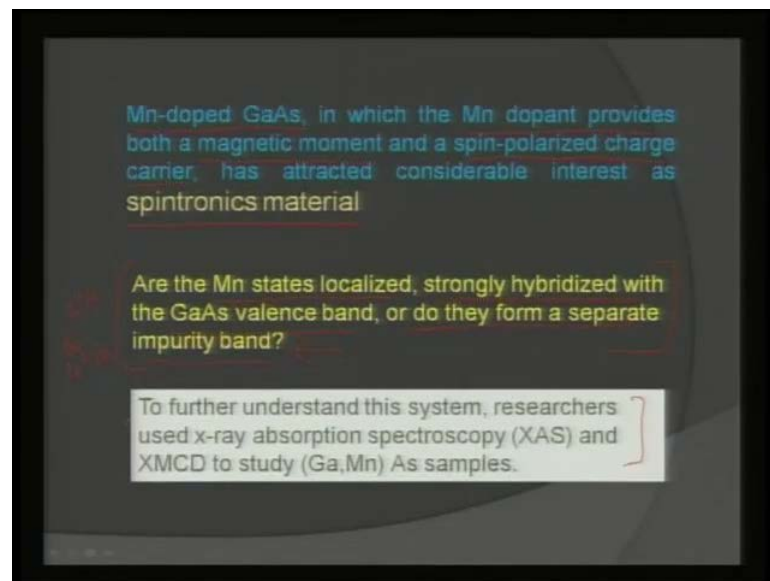
Now questions, that remain to be answered here is if manganese is doped in gallium arsenide, in which the magnetic domain dopant provides a magnetic moment, then a spin polarized charge also comes into picture, because the carrier is now having a spin memory and this can actually bring about a new phase of spintronic materials.

So, transition metal ion doped in a semiconductor matrix, will induce a magnetic moment and there by provide a spin polarized charge carrier, which brings about a spin a spintronic material.

But, there are some primary questions, that we need to address, what is this question, what are the states of manganese, what is the oxidation state, are the manganese states localized or they are strongly hybridized with the gallium arsenide valence band. It can stand a aloof or it can actually, hybridize with the gallium arsenide valence band and otherwise, they can form a separate impurity band.

If they form a separate impurity band, then you cannot call this as a dilute magnetic semiconductor, it has to mingle itself with the valence band of the host material therefore, it is very important to understand where this, manganese is going. Because, you are trying to dope to the tune of 2 percent to 4 percent not more than that, because it has to be dilute.

Now, in such concentration, where is your manganese and what is the nature of this manganese is the question, now to understand this sophisticated techniques, such as x-ray absorption spectroscopy and X M C D, that is x-ray magnetic circular dichroism. These are some of the refined techniques, that are used, to see whether it is truly a magnetic signal or not or whether it is coming from a impurity induced magnetic signature. So, these 2 are synchrotron based analysis, which can give you precise idea about, what is the nature of the interactions in this compound.

This cartoon will tell us, what exactly the signature of manganese doped gallium arsenide is, in the top figure, we see the manganese L 2 3 edge of the absorption spectra, this is from the x-ray absorption spectra. Now, you can actually make this compound, which is manganese doped gallium arsenide and you can look at the manganese L 2 3 H and you can do that in 2 ways, one is magnetization. In the you can actually try to probe this in 2 different directions, one is parallel and antiparallel alignment of polarization and when the magnetization is aligned in 0 0 1, that is this curve and the magnetization, when it is aligned in 1 1 1 direction, that is in this curve green curve.
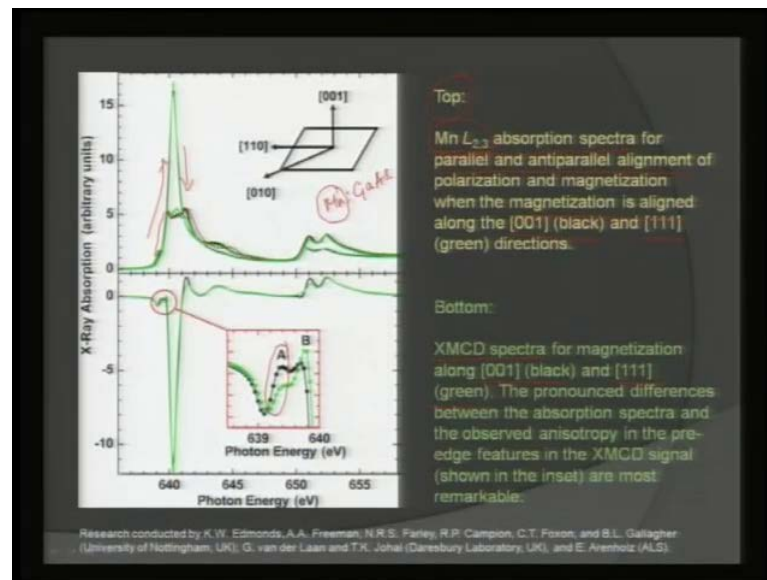
So, if you clearly see that, in 2 directions, 0 0 1 and in 1 1 1 direction, you see that there is a huge drop in the intensity, in other words, they features x-ray absorption features are radically different, when you try to take the X M C D sorry, x-ray absorption spectra of the manganese feature. And in the plane of magnetization, out of plane of magnetization as a result, what happens you can clearly see, that it is magnetized the lattice is magnetic as a result, there is change in the x-ray absorption structural feature.

So, this is one signature, that can tell us that it is truly magnetic, suppose manganese is not doped, then you would see both the intensities in 0 0 1 and 1 1 0, they will be actually the same. So, this is one signature, in the other one you can see X M C D x-ray magnetic circular dichroism, for magnetization along 0 0 1, that is black here and the one in green is in the 1 1 1 plane.

The pronounced differences between the absorption spectra and the observed anisotropy in the features in the X M C D are most remarkable, you can clearly see in this region, that the intensity of the features, in both 0 0 1 and 1 1 1 plane, clearly shows that, there is a remarkable change in the X C M D.
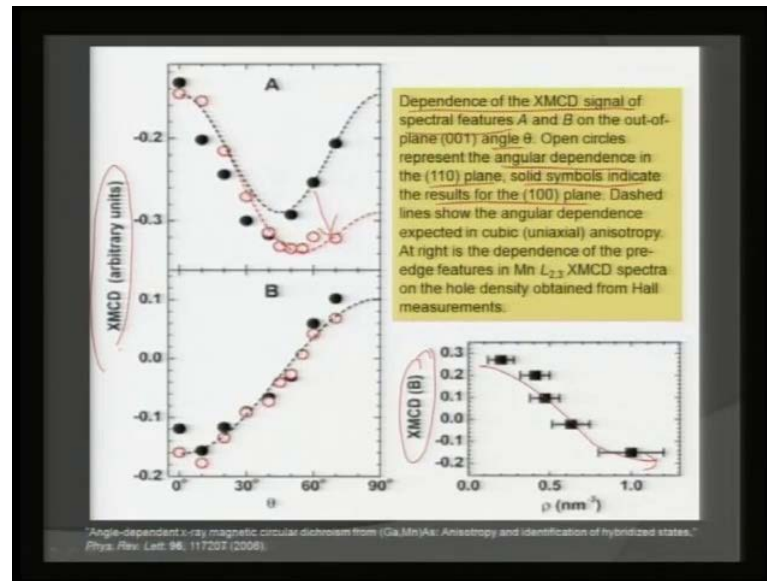
And this work was actually reported by edmonds and coworkers, which is also published in P R L in the year 2006. Now, if you make the X M C D, if you take the X M C D and try to make a plot, against the angle of rotation, then you can see the dependence of X M C D signal, for the out of plane and in plane as a function of angle theta. And you can clearly see that, the open circles, which represents the angular dependence in 1 1 0 plane and the solid symbols indicates, the results in 1 0 0 plane.

So, in the 1 0 0 plane, you do not, you see between here and here, there is a angel of rotation, which means there is a magnetic signature, which is intrinsic of the manganese doped gallium arsenide. And the same is true, if you look at look at the X M C D features here, the hall measurements clearly show that, there is a change in the hall mobility or the hole density, as we take the signature from the X M C D results.

What does this mean, there is a angle dependent x-ray magnetic circular dichroism, which clearly shows that when manganese is doped in gallium arsenide, there is a definite magnetic signature coming. Now, so what do we understand about, this dilute magnetic semiconductors.

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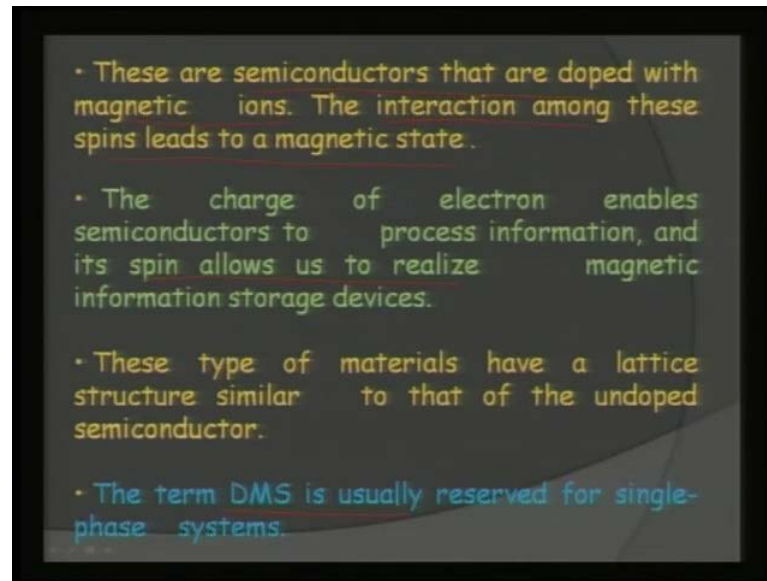
These are semiconductors that are doped with magnetic ions, the interaction among these spins lead to a magnetic state, the charge of the electron enables semiconductors to processes information. And the spin allows to realize magnetic information for storage devices, these type of materials have a lattice structure similar to that of undoped semiconductor.

So, one of the main thing, that one would required or one would look for is the single phase, x-ray single phase, that has to be present not only x-ray single phase, the it should be also magnetically a single phase material. Because, you are dealing with the very small doping and in such situations, you may not be able to trace the impurity ion, in from the x-ray, because it is very, very low. Therefore you need to know whether, it is magnetically a single phase and structurally a single phase.

There are several examples, that can suggest how tricky this situation can become, but before that what one slide I would like to show, what is the implication of this dilute magnetic semiconductor. The possible application is it would create a revolutionary, new class of electronic based on the spin degree of the freedom of the electron in addition to the charge.

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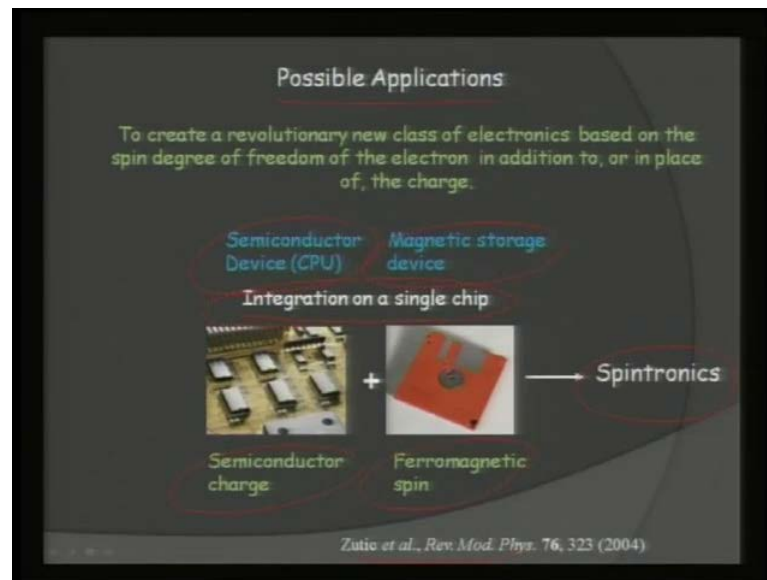
So, far the semiconductor devices, they are more concerned with the charge of the electron, now if you bring about a spin, ferromagnetic spin into this, then you can actually translate, this into a single integration on a single chip, which will comprise of both the semiconducting property and the magnetic property. And therefore, you can bring about a new possibilities in spintronics, this was reported by zutic in review of modern physics in 2004, for a better understanding on all the possible applications of this.

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Now, another question that, we can ask about the usefulness of this, spin and charge in dilute magnetic semiconductors, when will this finally, be as easy as switching on the light, is it a near possibility or a distant reality that one can hope for, many people keep asking this question and whether this can be ably applied to our computer technology in these days. And specially because this can affect the random access memory, this has a direct implication the answer that we can saym as of now based on the results, that we have that using this spin and charge, in semiconductor industry is not too far.

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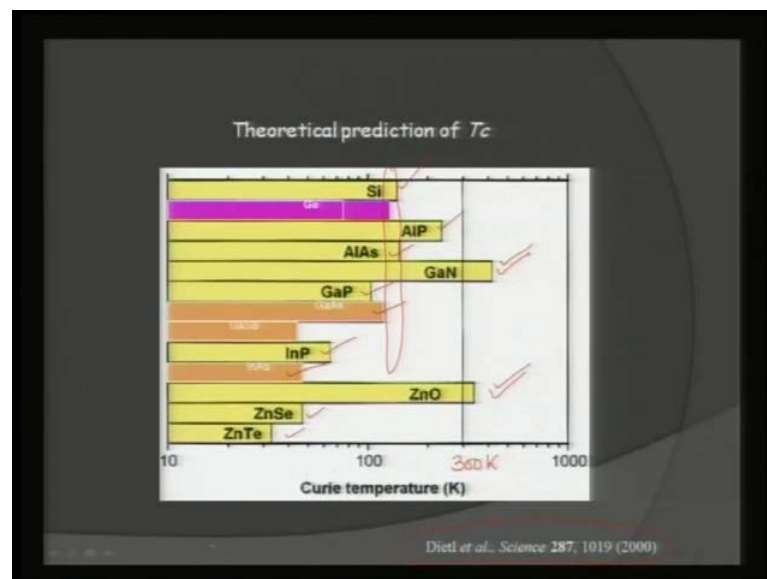
So, why there is such a great interest in these materials, because in year 2000 dietail and coworkers, they reported using theoretical predictions, they run through several of the semiconducting materials and they try to predict if there is a possibility of looking for new materials. In such case you start first with silicon, which is our reference point compare to silicon, you have 2 4 semiconductors or 2 3 5 semiconductors or 2 6 semiconductors.

You can see aluminum phosphide, aluminum arsenide, gallium phosphide, gallium arsenide, indium phosphide, indium arsenide all these combinations are somewhere close to silicon. These are the theoretical predictions indicating that, they can turn ferromagnetic. Now notably, if you see we are somewhere around this region of room temperature, if we have to realize a room temperature ferromagnetic situation, then 2 compounds really cross this line and those are gallium nitride and another one is

astonishingly zinc oxide, both these compounds are known to be ferromagnetic or it is calculated to show, that they possess a definite magnetic moment, beyond room temperature. So, therefore, the target molecules or the target compounds, which have been studied in the recent past or the substituted gallium nitride materials and also zinc oxide. There are other ones based on zinc compounds, which are the zinc chalcogenides namely telluride and selenide, they also show magnetic property.

But, never the less the once, which are around the room temperature carries our attention therefore, I will try to show in the next few slides the some of the research, that has gone into several of these oxides or non oxide base compounds. And we will try to understand, how we can clearly escape from the situation where, we realize a impurity induced ferromagnetic compound. And we will also try to see, what are all the characterization facilities, that are available for us to go into microscopic details to find out, whether they are truly, magnetic signatures are they are impurity induced ones.

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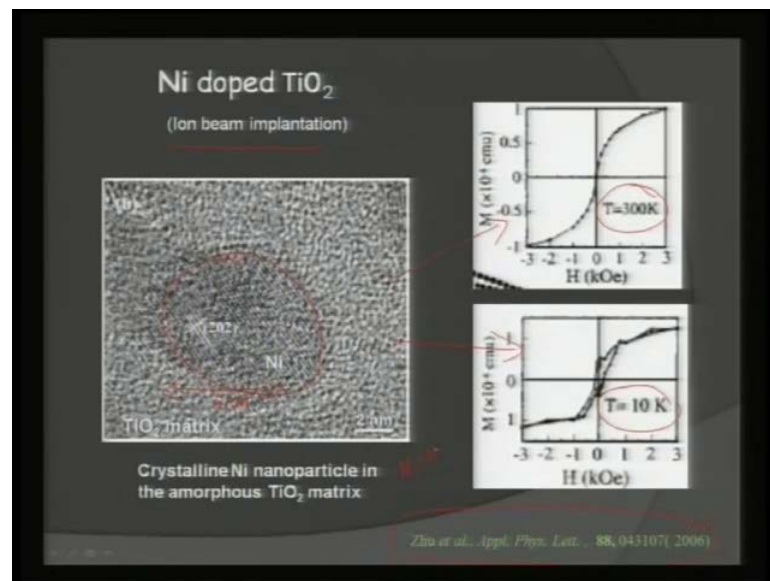
To start with let me show an example of zhu and coworkers, who reported this compound nickel doped titania and this was reported in A P l in 2006, you can see here, they have formed using ion beam implantation technique. They have tried to dope nickel in titanium matrix and this is the T E M picture, which clearly shows that, this is a amorphous titania matrix, because you can see, there is no order, there and in this there are submerged nickel clusters or nickel particles.

And these are of the order of say 6 nanometer or so roughly, they are of 6 nanometer nickel particles, which are actually embedded in titanium matrix, in such case, what will happen, you will see the magnetic signature very clearly, you see a signature at 300 K. And this should have actually blown up, but what you see here even at a 10 K, you do not see a very clear change in the hysteresis, but a very feeble hysteresis is developing at low temperature. This was the first report on nickel doped T i O 2 and in this case you see, that nickel seems, to be in the nickel 0 state as a nickel metallic cluster, it is not a nickel substituted in T i O 2.

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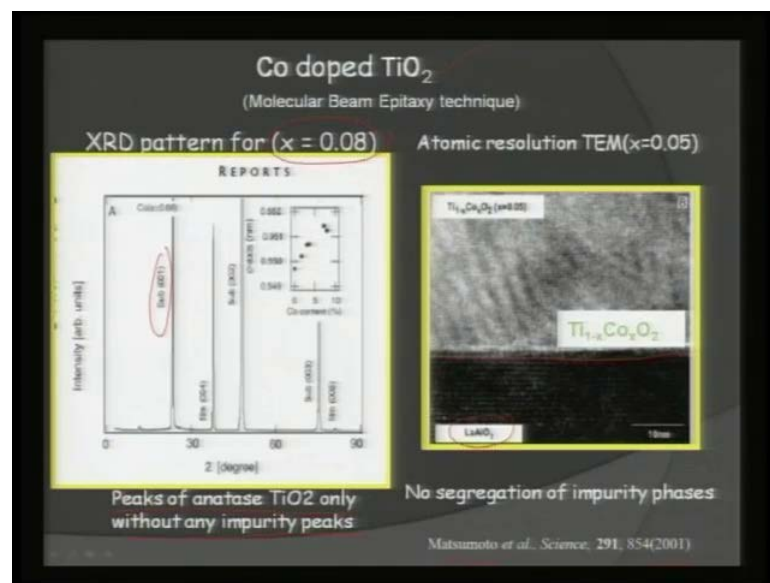
Otherwise another example, that was reported by matsumoto in 2001 and what did they do, they have doped cobalt in T i O 2, because T i O 2 is also a band gap material, wide band gap material. And if you clearly look at the X R D pattern of, 8 percent cobalt doped in T i O 2, you can clearly see the peaks of anatase T i O 2 only, with no impurity peaks. So, if you look at the cobalt signature, you would see that, it is epitaxially growing and there is no signature of cobalt crystallizing out, in any other form. So, in that case, you can look at the high resolution T M also, we do not seemingly see any sort of change in the interface, it is nicely growing on L a A l O 3 substrate, but never the less, we do not have any clear idea where, this magnetic signal is coming from.
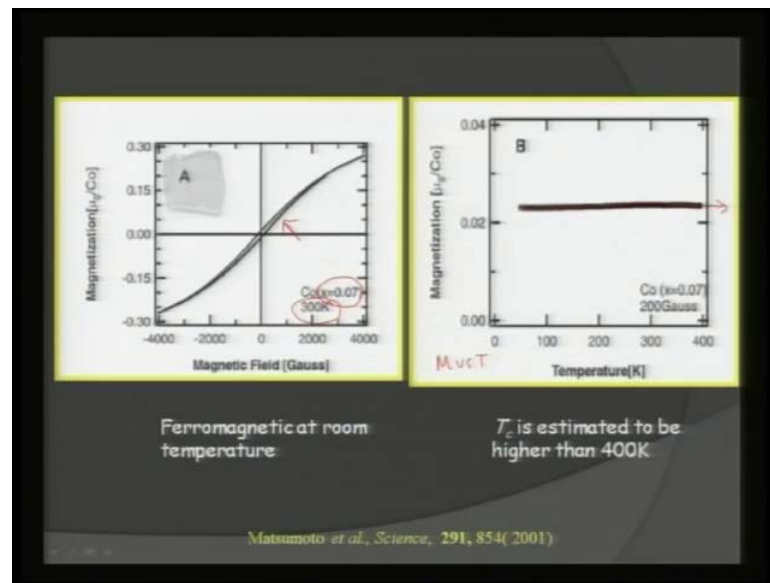
If you look at the magnetic signature M versus H plot, clearly shows at room temperature for a 7 percent cobalt doped one, you clearly see this hysteresis loop coming and if you are going to sweep, the M versus T plot, for the same 7 percent cobalt doped T i O 2, you can clearly see that, there is the ferromagnetic transition is beyond a room temperature. So, just for 7 percent cobalt doped in T i O 2, you see the T c is above room temperature and there is no signal of any cobalt crystallizing out.
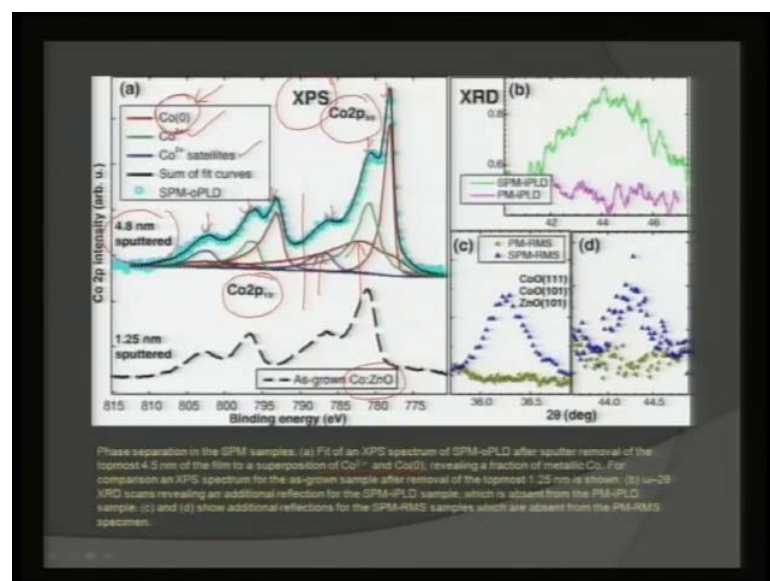
If you look at this cobalt doped zinc oxide, for a change, you would see the X P S, that is x-ray photoelectron spectroscopy results, which was reported in a series of sample, if you look at the cobalt 2 P 3 by 2 and cobalt 2 P half, you see a X P S feature, which is with very fine features. You would be tempted to say is that cobalt is nicely doped, in zinc oxide, but if you carefully, look at the signature, you would find for a 4.8 nanometer sputtered film.

If you deconvolute these features and if you deconvolute these features, you would find that cobalt 2 plus is definitely there, which means it is clearly substituted in Z N O, this is zinc oxide. And you would also see the cobalt 2 plus satellite features here, these are the satellite features, now along with that, you also see a clear feature coming, for C o, which is metallic. In other words, you have apart from cobalt getting doped in the Z N O, you also have a proportion of cobalt, which is staying as a metallic cluster.

So, in this case what you would clearly understand is the magnetic signature, although it can come from substituted cobalt, which can be doped in the valence band region, of your zinc oxide lattice. There is a clear possibility of metallic cobalt contributing to the magnetic property. So, this is very important and we need to be extremely careful, that the magnetic signatures what we observe is actually coming from, the doped situation and not from the metallic clusters.

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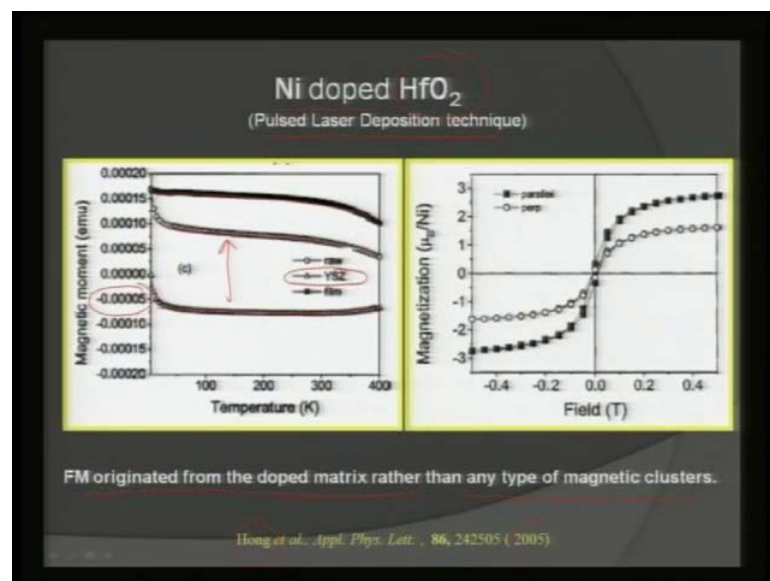
If you take for example, another high band gap material like H f O 2, which is doped with nickel and this can be achieved by pulsed laser deposition technique, you would see that the magnetic moment, for the Y S Z, that is the substrate, substrate is almost showing a very, very weak magnetic moment of the order of 10 power minus 5 e m u. And if you dope, if you take the raw data of the nickel doped one you see, there is a remarkable jump in the feature and if you try to subtract the background, then you can see the film is actually contributing something like this.

Now, between the substrate and the nickel doped sample, the difference is only in this value, never the less, it is a very small feature and therefore, you need to look at the M versus H feature, you can see that in the parallel and perpendicular geometry, there is a change. If in parallel and perpendicular, there is a change, then we can say that nickel is doped inside H f O 2 therefore, you can say that the ferromagnetism is originating from the doped matrix, rather than from any type of clusters, this was reported by hong coworkers in 2005 In A P l.

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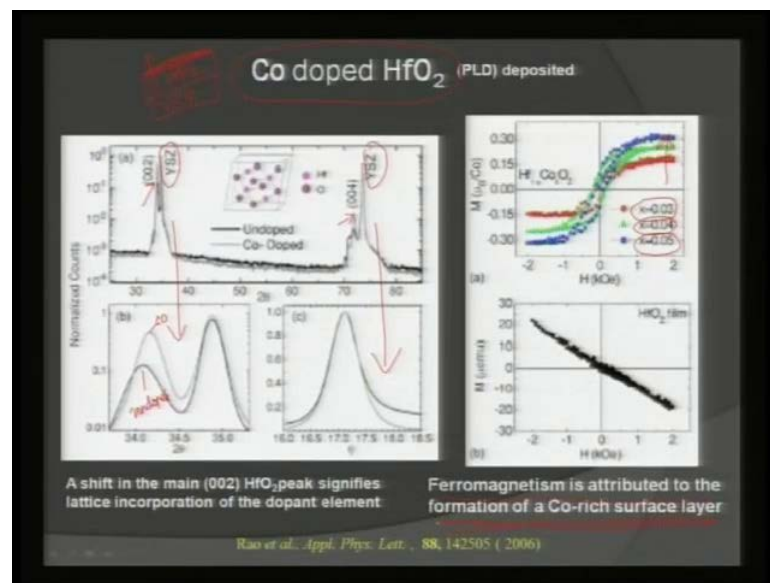
Cobalt doped H f O 2, this also can be prepared from pulsed laser deposition, you can clearly see that, this is clearly a doped situation, because if you look at the x-ray of the thin film, which is deposited in Y S Z. These are the Y S Z x-ray features and along with that comes the reflection for H f O 2, this peak is for H f O 2 and this peak is also for H f O 2, which is 0 0 2 and 0 0 4 features, they nicely grow on Y S Z film.

Now, if you look carefully at this deviation, if you look carefully at this peak, now you would find out that between the doped and the undoped, this is the cobalt doped and this is the undoped. There is a clear deviation in the x-ray pattern showing that, when you doped cobalt then there is a shift which means, cobalt is substituted in H f O 2 matrix, as a result whatever magnetic feature, that is coming, whether it is 3 percent or 4 percent or 5 percent, you see a systematic increase in the moment of this cobalt doped H f O 2 compound.

So, one can say that, there is a possibility of doping this material in H f O 2, but we need to also understand, where this magnetic signatures are coming, it is proved that the ferromagnetism is attributed to formation of a cobalt rich surface layer, because if you do the eels as a function of the thickness of your H f O 2. So, you have your Y S Z here, Y S Z substrate and if you have your H f O 2, thin film and if you keep on doing the eels study across this thickness, as you go towards the surface of this layer, as you go to this surface.

You see the cobalt magnitude or the amount of cobalt is actually increasing the intensity of the cobalt peak is increasing, as you go towards the surface of the H f O 2 peak. Therefore it was a concluded, that it is not purely a dilute magnetic semiconductor, rather it is coming from a rich cobalt surface layer, which is contributing towards the magnetic property.

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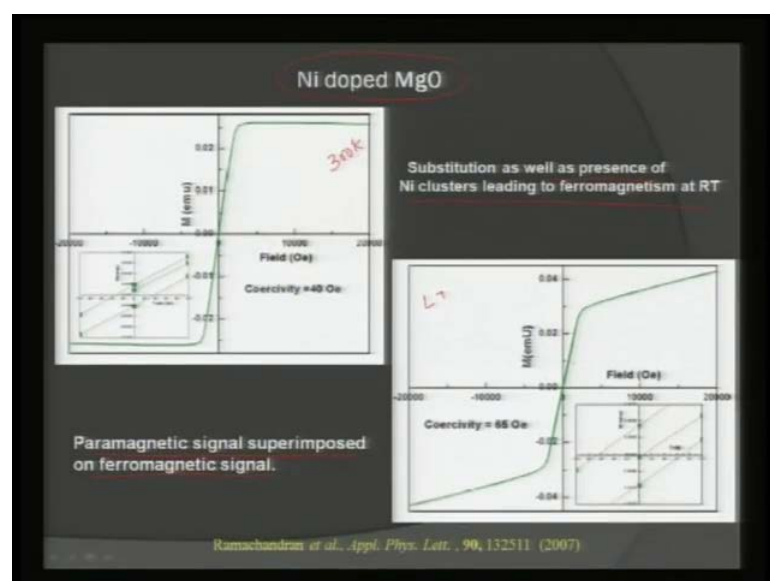
If you take another example, this is a another classic example of a wide band gap material M g o, which is having a band gap above 4 electron volt. And in this case, if you are going to dope nickel, then you can see, that there is a paramagnetic signal, which is superimposed on the ferromagnetic signal. Mainly because this is seen at 300 K and this is seen at a low temperature, substitution as well as presence of nickel clusters lead to ferromagnetism at room temperature.

So, the at the microscopic level, if you look at the magnetic feature, it looks as though you have a very strong ferromagnetic signature. But, if you clearly probe, it these are specially at low temperatures, you could see that there is a paramagnetic signature, which is coupled with a ferromagnetic signature and this was reported by Ramachandran in 2007.
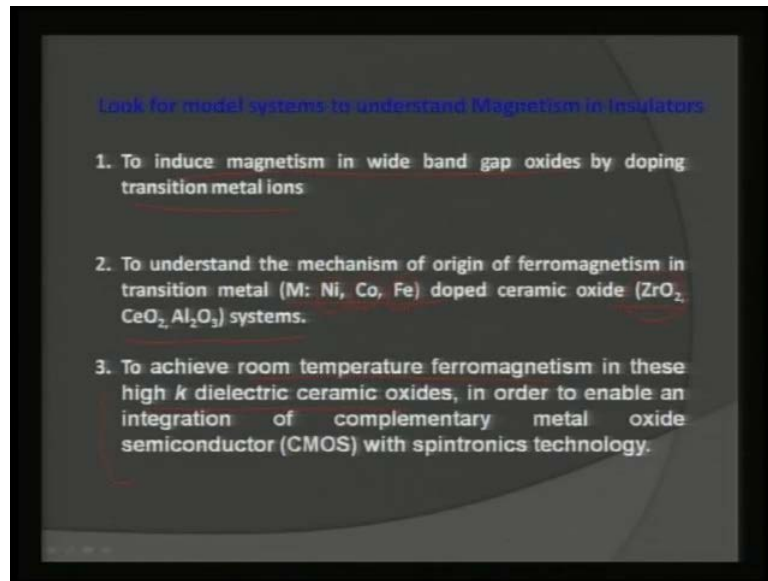
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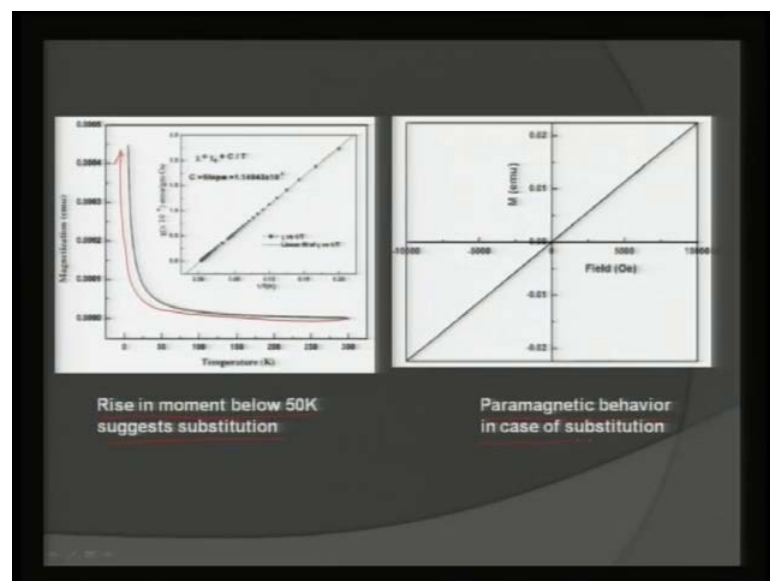
And if that is a case then if you make a plot of magnetization versus temperature, you would see, if there is a sudden upsurge in the magnetic moment at low temperatures, then the indication is, this is due to substitution. And the paramagnetic behavior in the case of substitution comes, at low temperature.

So, with all these confusions around, we do not know whether, the magnetic signature in this sort of wide range of semiconductors, that I have been studied, whether the magnetic information, that we are getting is truly coming from a doped semiconductor or it is coming from a impurity induced magnetic property. If it is induced then it is of no use for the spintronic property therefore, we need to be extra careful to know whether, the magnetic information is a true phenomena or it is a impurity induced phenomena, because in the past, it has been observed, when you are doing magnetic study.

Even, if you are going to pickup these materials with a nickels spatula or a iron spatula or iron forceps, even though small impurities can induce quite a lot of signature. Specially, because the sort of magnetic signal, that you are seeing in a thin film situation is of the order of 10 power minus 5 e m u, you have to be very, very careful where these signatures are coming from.

So, to elucidate this, it is possible for us to study a different sort of compounds, to say what could happen, if there, if it is a transition metal cluster induced ferromagnetism and what would be the signature, if it is truly a ferromagnetic situation. So, for this reason, we can actually try to induce magnetism in wide band gap oxides by doping transition metals, we can try to do that by doping nickel, cobalt, iron in ceramic oxides like zirconia, ceria and alumina, I may not be able to run through all these examples.

But, I will certainly try in the next few slides, to show you, what will happen if you have nickel, cobalt and iron doped in zirconia and try to understand, what is the magnetic signature that we can look for, if you try to dope it in a wide band gap material. In fact, zirconia is not just a semiconductor, we can classify this even as a insulator, because the band gap is more than 5 e v. And we can try to see, if we can achieve room temperature ferromagnetism in this high K dielectric ceramic oxides and we can see whether, this can be used for potential applications in spintronic technology.

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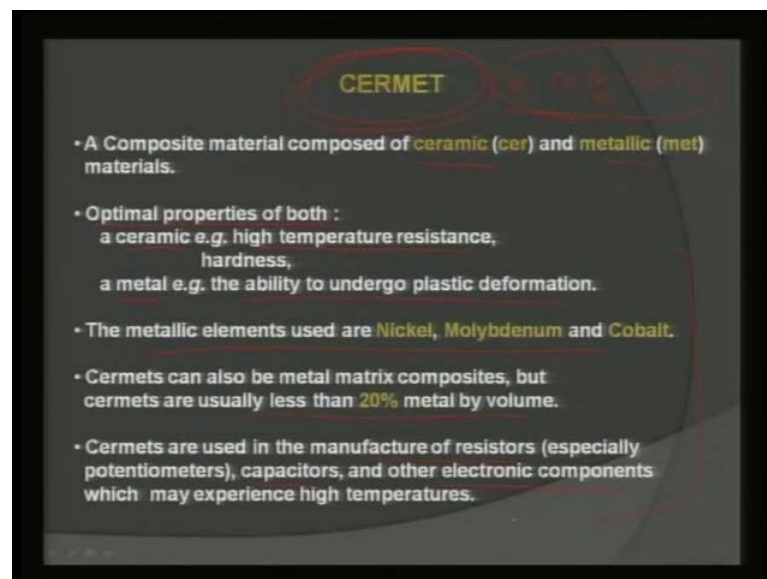
Now, why we are choosing nickel cobalt and iron based Z r O 2, because they form a very important class of compounds called cermets, cermets is nothing but a ceramic and a metal composite, ceramic metal composite, which is known for more than 3 decades, now. And these are used for mechanical applications, because zirconia when it is doped with any transition metal it improves the mechanical strength by orders. Therefore, intentionally people dope, this transition metals including molybdenum, people have used it and this comes under special category called cermets.

So, cermets are nothing but ceramic metal composites and the optimal properties, that you can achieve is one is it is a ceramic. So, you have a high temperature resistance and one is you have a metal, you have the ability to go through plastic deformation. So, plugged in, you have 2 in 1 where a metal is actually interspersed in a ceramic metal, which will add strength to the to the material, but we are going to use such a ceramet

composition to study the magnetic information, in these oxides.

The metallic elements used as I told you are nickel molybdenum and cobalt, cermets can also be made, with a with a concentration of 20 percent metal by volume and cermets are used in the manufacture of resistors, capacitors and other electronic components, which may experience high temperature. So, these are the fundamental use of the cermets, but what we are going to do is use this cermet compounds to see, whether we can understand little bit on the magnetic signature.

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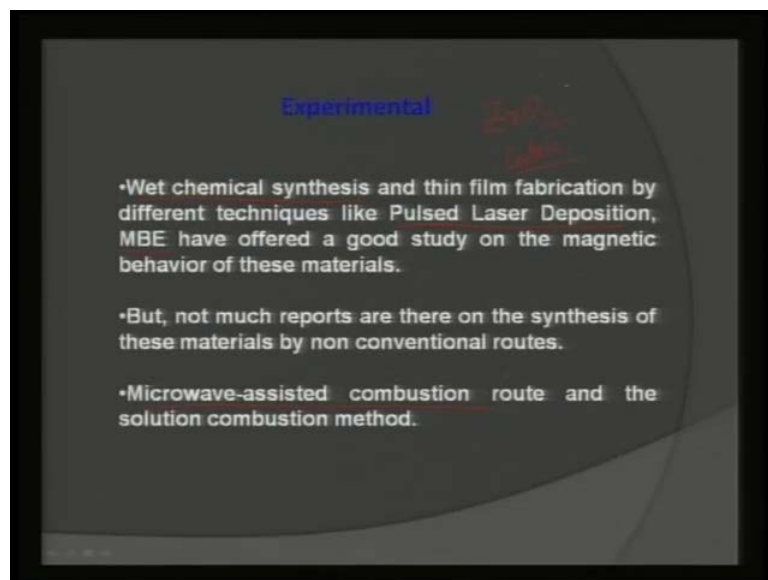
So, how do we do this, because zirconia is a material, which is a high temperature material therefore, you need very high temperatures to prepare these compounds. We are going to show how using wet chemical routes, one can prepare these oxides and there is no need even to make thin films using costly methods like, P L D or M B E. And these materials can be prepared at a very faster rate and we can achieve, even high temperature phases by nonconventional routes.

I will show 1 or 2 examples of how using microwave combustion route, we can prepare these compounds, microwave assisted combustion route, can form a very useful route to prepare this sort of high temperature oxides.

And in the module one in on wet chemical routes, I have already discussed with you the use of microwave combustion, the main advantage of microwave combustion is, you try to generate high temperatures from within the sample, instead of supplying heat to the sample. So, this is the conventional electro heating method where as, this is the microwave heating method.
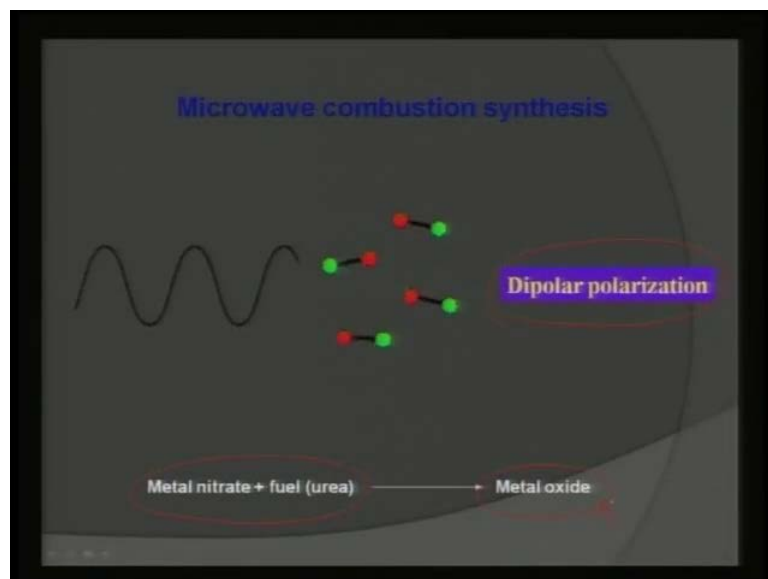
And the reason, why we can use microwave is, you are actually starting with some material, which is made of nitrate and fuel, which is urea and these are materials, which have very high dielectric constant therefore, they absorb the microwave much more easily, due to a mechanism called dipolar polarization. As a result, you can initiate combustion reactions within the sample, which can easily lead to a one step decomposition straight to metal oxide.

So, therefore, if you have to prepare zirconia at even 1200 degree C, you can achieve that in a using a just a microwave, in other words a furnaceless technique can be used to initiate high temperature reactions where, you can make metal oxide. So, let us say that metal oxides are made out of this reaction, then we need to look at the purity and then we need to look at the magnetic signature, that we are going to see in this compound.

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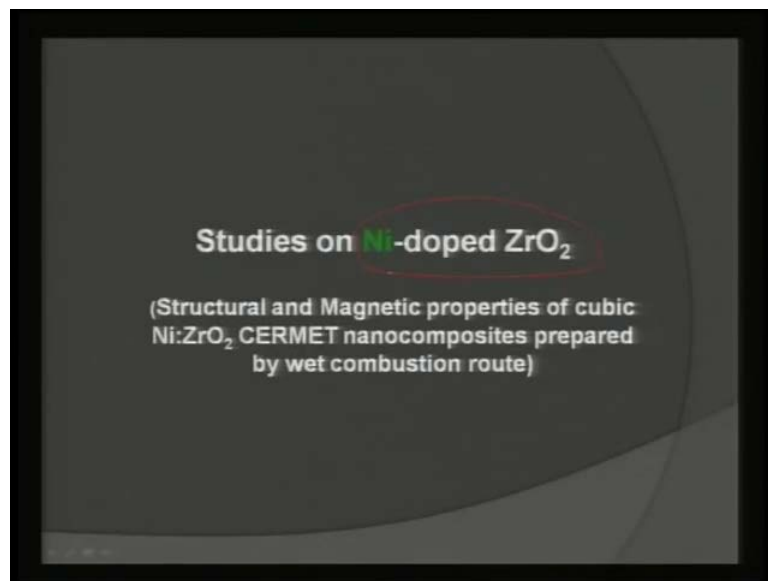
So, we will first start with nickel doped zirconia powders and try to see, if we use combustion synthesis to prepare.
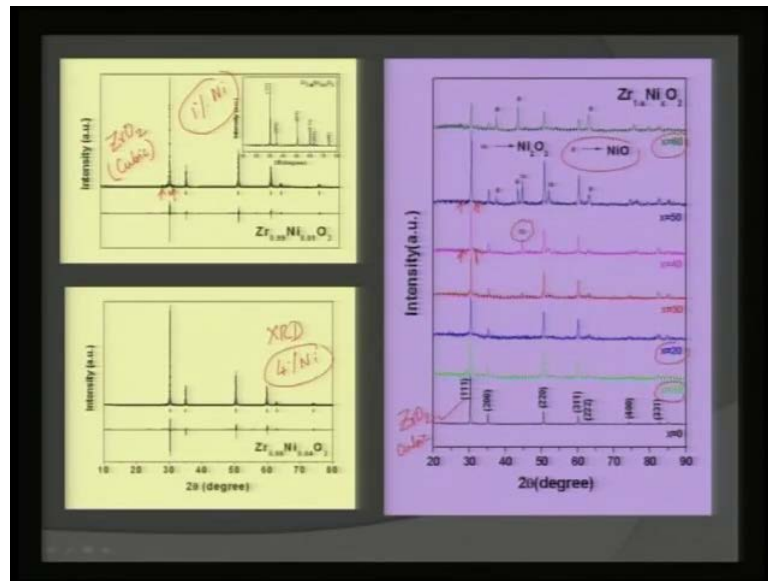
What are the magnetic signatures in this and this is just the residual analysis for 1 percent and 4 percent doped compounds. You can see clearly that the x-ray pattern, X R D pattern that, we see for 4 percent nickel doped and 1 percent nickel doped samples. Clearly show that the x-ray pattern resembles, that of cubic zirconia, if it is going to be monoclinic, which is another phase, which is reported to be stable at room temperature, then you would see signature of the monoclinic phases coming somewhere here.

But, one would clearly see that, there are no features of monoclinic picks present in the samples clearly showing, that just using a simple technique one can prepare cubic zirconia. Now, we do not have to just limit with 1 percent and 4 percent, which is of interest for our D M S study, one can even go to 10 percent or 20 and we can go even up to 60 percent. And try to see in the cermet compositions where, exactly nickel oxide impurity peak is coming, as you see here, 10 percent peak, we do not we still see zirconia in cubic phase.

And if you go to 20 percent, 30 40, you do not see any trace of monoclinic phase coming here, so this is still in cubic, but what you would, you see here above 40 percent, small peaks are coming, these are the nickel oxides peaks. So, these nickel oxides peaks have started coming beyond 40 percent therefore, if we need to look at the magnetic phases one can say that, safely up to 30 40 percent, we can keep looking at these magnetic signatures carefully and try to understand whether they are impurity induced or they are

coming from substituted ferromagnetism.

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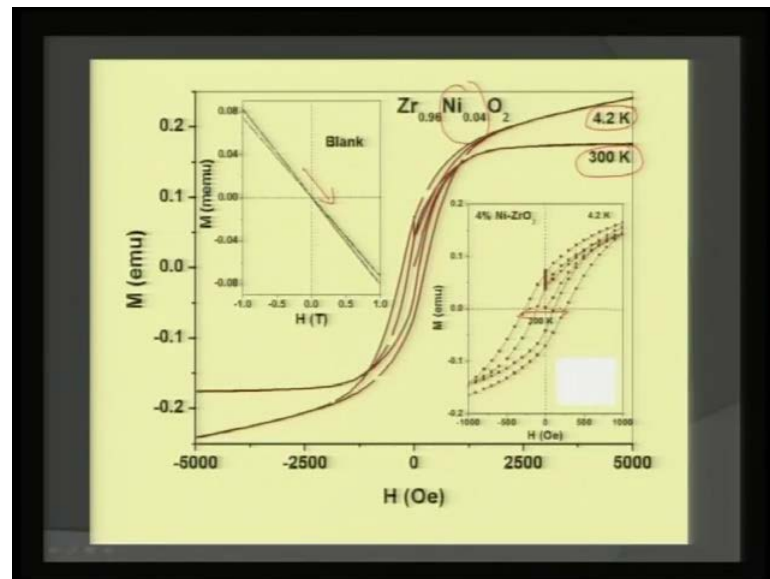
You can see in the first view graph of this magnetic signature, for a 1 percent nickel doped zirconia very clearly, there is a hysteresis loop emerging at 300K and at 4.2 K. Now, to make sure that this is not coming from zirconia itself, because zirconia is actually a oxygen scavenger, in other words, it can easily form Z r 2 minus delta or plus delta, because zirconia takes carries a electron and it can give electron and as a result it is also known as fast ion conductor. But, what is important here is any amount of excess oxygen is present, it can easily go into the Z r o 2 lattice.

So, if we should make sure that, the magnetic signature is not exactly coming from oxygen stoichiometry. So, if you look at the parent compound, parent compound clearly shows a negative trend in the M versus H curve, showing that it is nonmagnetic, so any signature that is coming, is actually coming from nickel doping only. So, for one percent nickel doping, you can clearly see it is showing a room temperature ferromagnetism and if it is room temperature ferromagnetic system, then one would typically see, that the coercivity value is increasing and the moment is increasing, if we measure it at 4.2 K.

But, what we see here is more of a paramagnetic signature, which is coming like this, for 4.2 K indicating, there is a paramagnetic component associated with the ferromagnetic impurity at 1 percent nickel doping. And you can see this is clearly blown, to show how the coercivity is varying with the temperature. So, definitely there is some possibility of

inducing ferromagnetism at this stage.

Now, if you go to 4.4 percent nickel doping, you can see that, it is not showing any more of the paramagnetic signature at 4.2 K and there is a definite change in the hysteresis and hysteresis loop clearly shows that, there is a strong ferromagnetism, that is induced into this zirconia matrix. And just to make sure that we are still playing in the safe domain, you see that the Z r O 2, which is undoped is showing, a negative magnetization slope therefore, whatever is seen here is actually coming from nickel doping.

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Ni conc. (x)	M_s (emu/g)	μ_B/ f.u.	μ_B/ Ni atom	Magnetic particle size (d) in 'nm'	Crystallite size in 'nm' (XRD)
0.01	0.07	0.0015	0.1502	0.95	0.79
0.04	0.34	0.0074	0.1852	0.94	0.75
0.1	0.38	0.0082	0.0817	0.94	0.55
0.2	0.75	0.0158	0.0787	0.93	0.60
0.3	3.14	0.0637	0.2124	0.92	0.51
0.4	6.34	0.1252	0.3128	0.91	0.53
0.5	8.08	0.155	0.3096	0.90	0.53
0.6	0.87	0.016	0.0269	0.89	0.50

So, you can actually run through, from 1 percent, you can go up to 60 percent of nickel and try to see, what is happening, you can see that, the M s value is actually increasing up to 50 percent and beyond 50 percent suddenly, you see the magnetization is decreasing. Why it is happening, I have already shown that beyond 40 percent nickel oxide starts precipitating out and we can try, we can based on the magnetic signature, then you can try to look at the boar magneton.

In terms of formula unit, in terms of nickel atom, you can see, that there is a progressive increase, in this case and then it falls back and then again, it increases therefore, there are some safe domains where we can, look for magnetism, that is truly coming from nickel doping. And there are some domains, where it is coming from the segregated phases.
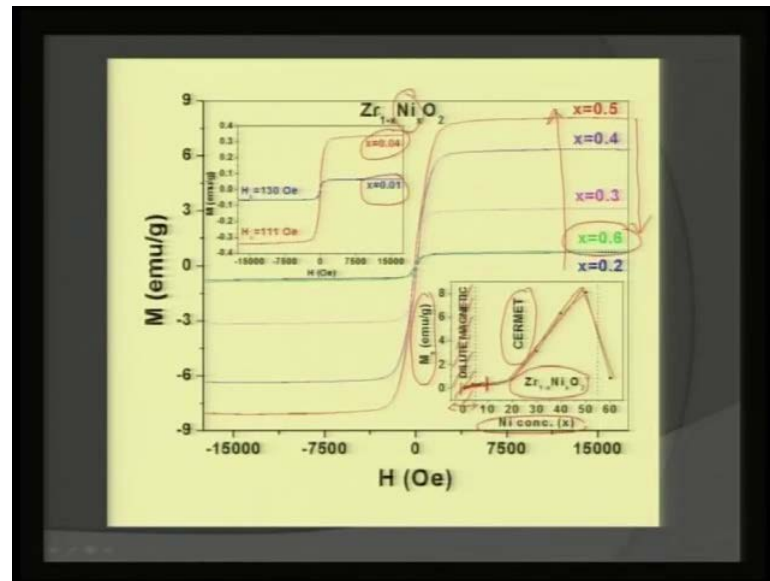
We can see that from this sum up of results, 1 in 4 percent clearly shows a ferromagnetic loop at a room temperature, this we have seen. And if you increase the nickel concentration, you can clearly see that, the magnetization is systematically increasing, but for 60 percent suddenly it is dropping down. So, that means, nickel keeps on going, but if you make a plot of magnetization as a function of nickel concentration, you would see, that there is a region where, the slope is only marginal or we can say it is linear here may be even up to this place.

And then suddenly the linearity goes this way and then it drops down, so we can actually say that, there are 3 regions in nickel doping as a function of magnetization, a region from says 0 to may be 10 percent is 1 region and beyond 10 percent, you see a increase in the magnetization and then it again falls down. So, we can sort of propose a tentative magnetic phase diagram, saying that, if at all we are looking for a dilute magnetic semiconductor, then this is the region, which we can look for, where it is safely nickel, which is clearly substituted into the ZrO_2 matrix.

And beyond, that in this is a cermets region where, nickel is actually precipitating out as nickel clusters and those clusters are embedded in ZrO_2 matrix, as a result, you clearly see with more and more of nickel, nickel coming out as nickel metallic nickel, there is a increase in the magnetization. So, if you look at this magnetic phase diagram, we can clearly say that, if we are talking anywhere about a possibility of a dilute magnetic

semiconductor situation, then we should only be talking about 0 to less than 10 percent phase where, you can clearly substitute nickel in Z r O 2 matrix.

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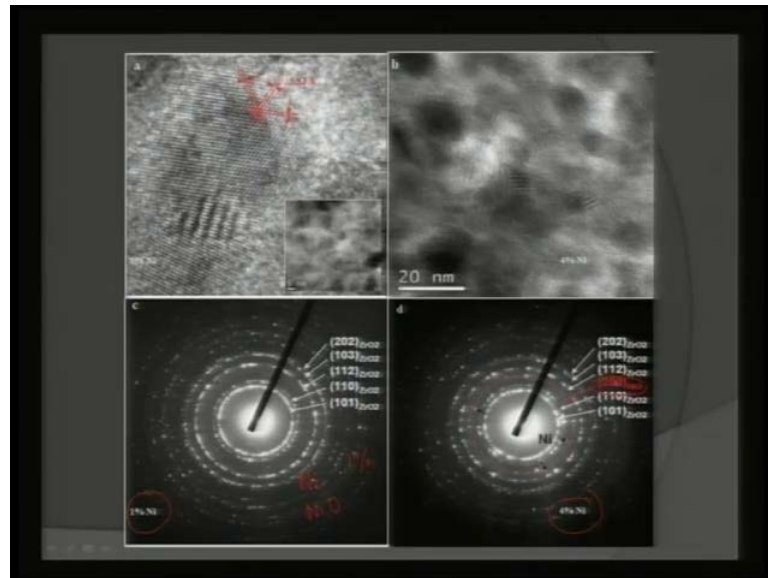
We can clearly see that, from the T E M pictures also, this is for 1 percent nickel, what you would see here is a polycrystalline feature, but you do not see any sort of nickel or nickel oxide phase coming in one percent. But, in 4 percent nickel, you see a small feature of nickel oxide, which is precipitating out, this is clearly evident from the T E M results. So, we can say that even between 1 to 4 percent.

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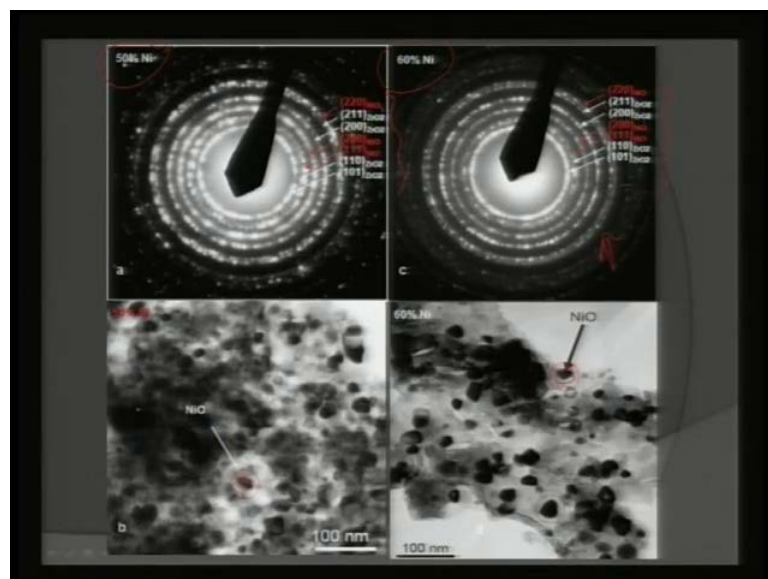
There is a safe compositional limit where, we have to restrict for a dilute magnetic semiconductor and if you go further your T E M clearly shows that, for 50 and 60 percent, there is a clear signature of nickel oxide, that is coming out. And these particles for example, if you map, it these are suppose to be nickel oxide, which is actually showing the sort of nickel oxide features, in the electron diffraction pattern. So, you have a increase in the magnetic moment, but the magnetic moment is essentially coming from nickel metal, rather than nickel substitution.

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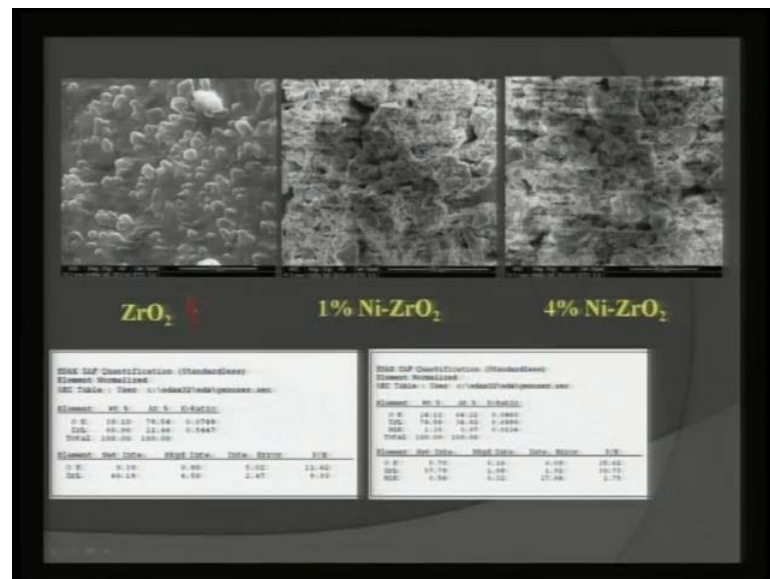
And this we can see from the ferromagnetic resonance as well, you can clearly see for 1 and 4 percent, there is a systematic change in the magnetic resonance therefore, there is a clear possibility of a D M S, that is in picture. And how do we know in a macroscopic way, we can even look at the powders, the morphology of the powders, the moment you doped nickel, you can see zirconia particles, totally the morphology transforms in a very different way when, you dope even 1 or 4 percent of nickel.

And then these are the X P S studies for 1 percent nickel, clearly shows there is no satellite feature, which means there is only 1 oxygen species there. Suppose, there is Z r O 2 and then nickel oxide, then both will actually show 2 different oxygen peaks, so we can clearly say that, there is one only phase and therefore, there is no asymmetry in the oxygen one is oxygen peak. And here again, if you see the nickel 2 P 3 by 2 and nickel 2 P 3 by 2 peaks, for 1 and 4 percent of nickel, there is no satellite features, in the nickel 2
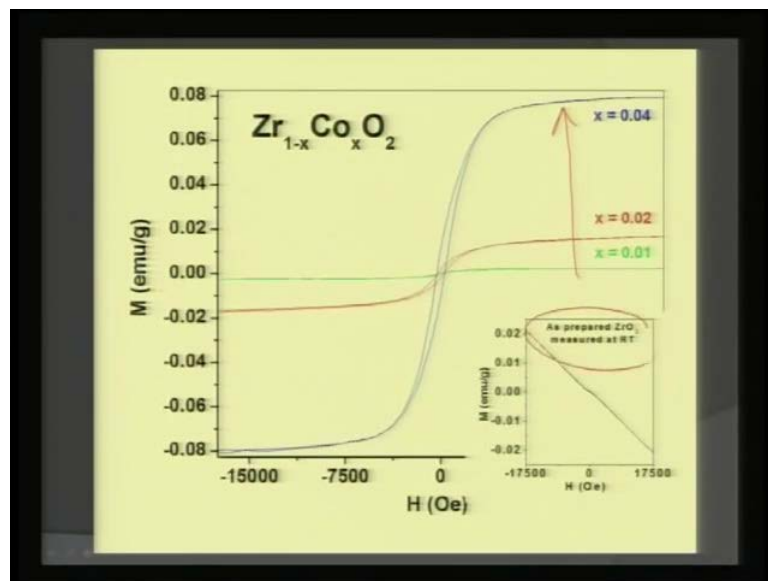
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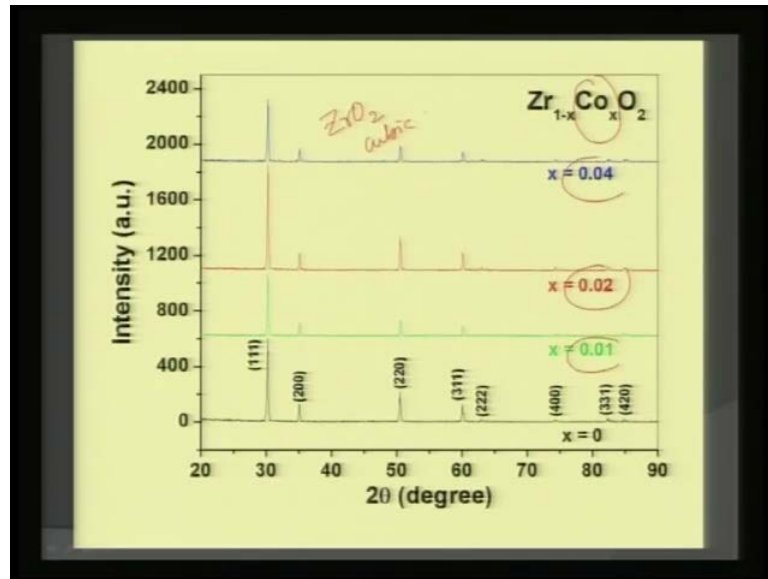
Therefore, we can clearly say that nickel is there only in one oxidation state, which means nickel is in nickel 2 plus only. Same is true, if we take cobalt case, cobalt is another ferromagnetic ion, which can be doped as you can clearly see, whether it is 1 percent 2 percent or 4 percent, it is absolutely a clean Z r O 2 cubic phase.
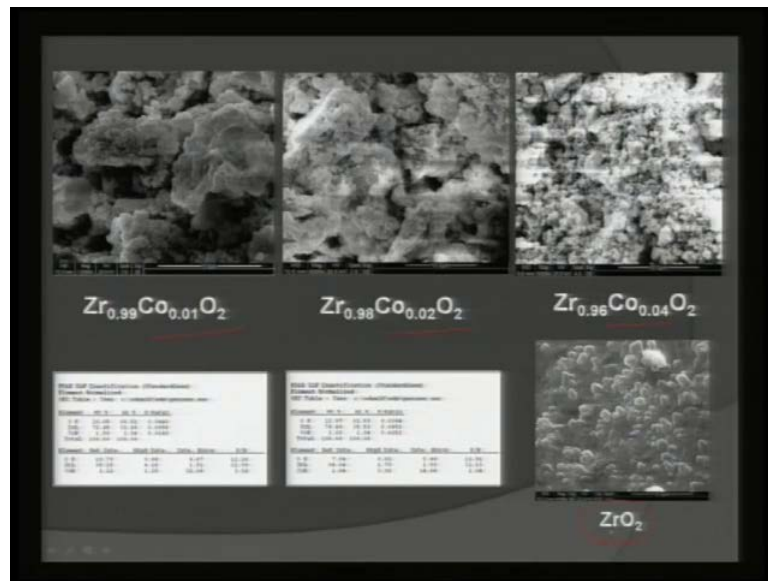
And you do not see any sort of impurity, that is induced here and you can also see the magnetic moment is increasing as a function of cobalt therefore, there is a clear

possibility of a D M S phase, that is emerging out, against a undoped situation.

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Therefore, even cobalt seems to through, a possibility for a clear dilute magnetic semiconductor situation and as I told you earlier, the cobalt substitution can be pronounced in the morphology compared to Z r O 2.
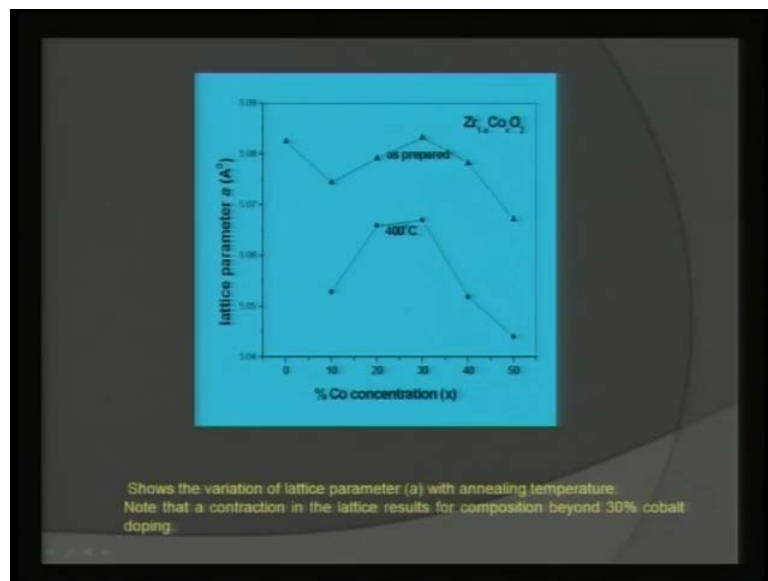
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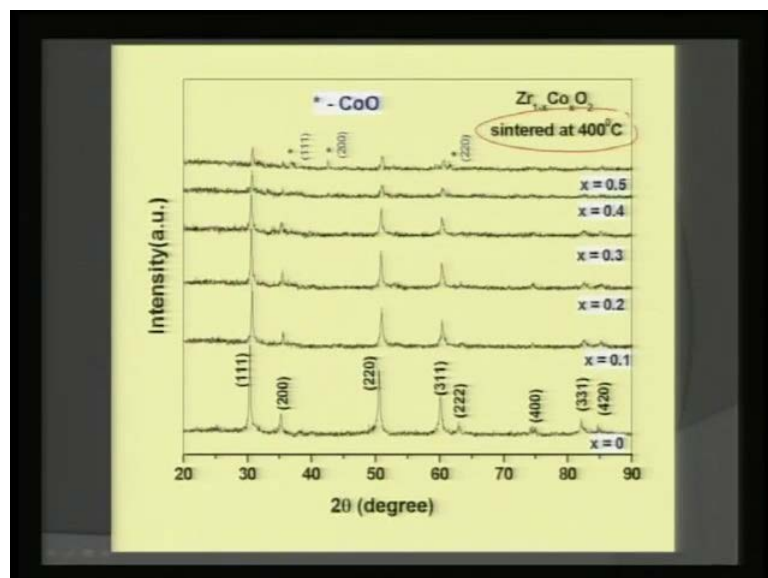
You can see that, cobalt is literally changing the morphology and if you keep substituting cobalt to higher percentage, even up to 60 percent, unlike the nickel case, you can see here, that you have a clean zirconia phase, that is coming, but beyond 40 percent, you

can see that cobalt oxide phase, that is C o O is coming. And it is becoming more prominent and when you substitute for 60 percent, the system instead of increasing in crystallinity, you can see as you would keep doping cobalt, the crystallinity dampens and then you almost get a amorphous phase.

So, cobalt seems to be getting substituted in the zirconia lattice and there is no signature of C o 3 4, which is a magnetic phase, which is present anywhere in the x-ray therefore, we can say that the magnetic signature, if at all anything is there, it is not coming from any of the oxide impurity of cobalt, it is actually coming from a doped situation. And this is the similar thing, you know you can also try to sinter the same powders at a higher temperature, to see whether x-ray is altering, you do not see systematically any change with the sintering conditions.

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Shows the variation of lattice parameter (a) with annealing temperature. Note that a contraction in the lattice results for composition beyond 30% cobalt doping.

And you can also see that, the lattice parameters by and large remains the same, whether it is a as prepared sample or sintered sample saying that, the oxidation state of cobalt does not seem to vary with annealing. In other words, it says that cobalt is not just embedded in the matrix, but it is actually substituted.
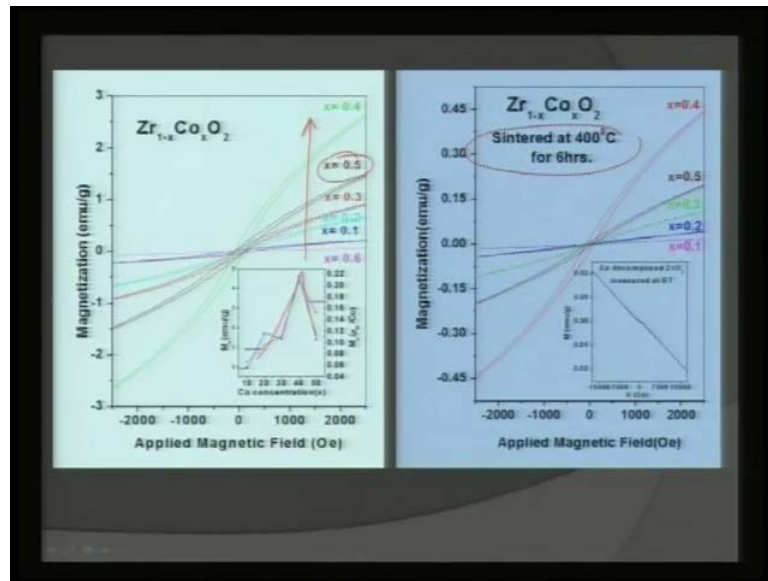
And you can also see from these 2 cartoons, whether it is as prepared samples or whether it is sintered at 400 degree C, you can see the clear trend in the magnetic property. Initially, it is low and then it picks up just like the way, we saw in nickel, there is a increase up to 40 50 percent, and then there is a drop, drop is actually coming from, this drop in moment is coming from impurities of cobalt oxide.
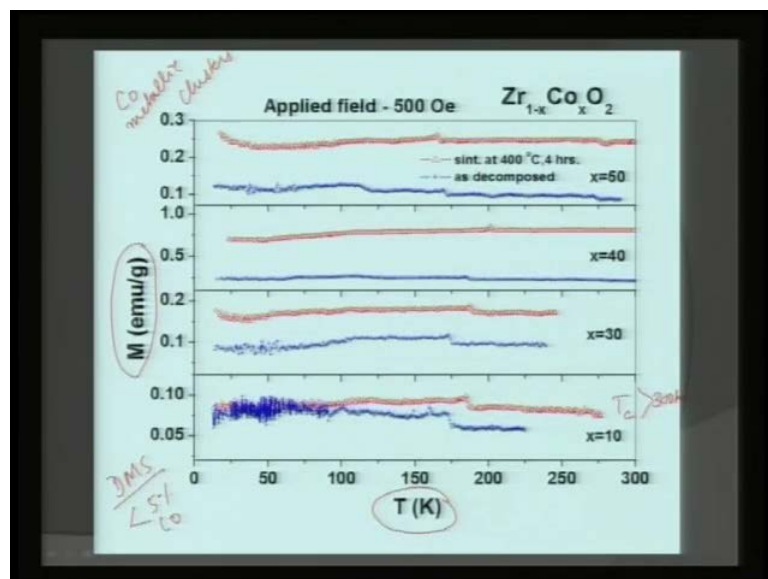
So, what we can see from this cobalt substituted compounds, beyond 10 percent, you can see that the ferromagnetic signature shows that, if you sweep magnetization as a function
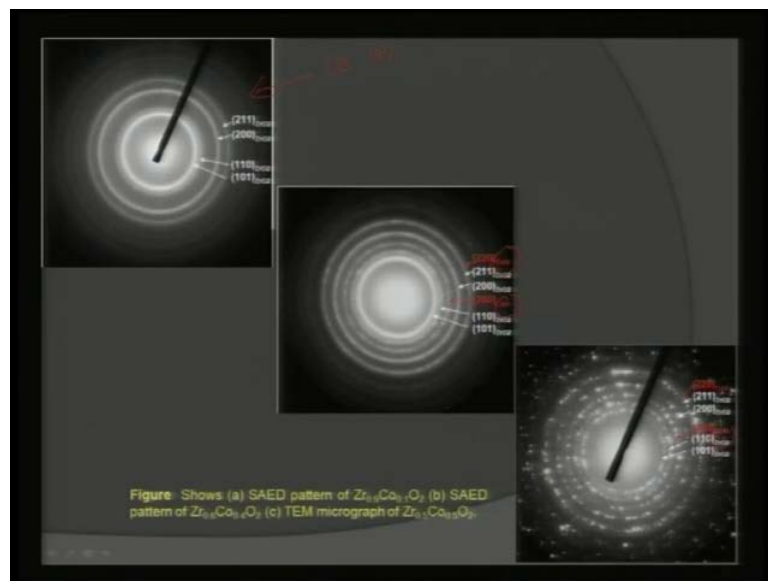
of temperature, they all show a study temperature independent variation, showing that, the T C is above 300 K, in all these compositions. So, these signatures may come from cobalt metallic clusters, whereas D M S phase is possible less in less than 5 percent cobalt doping.

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Co conc. (x)	Mr (emu/g)	μB / Co	μB / Co atom	Magnetic particle size (d) in 'nm'	Crystallite size in 'nm' (XRD)
0.01	0.0022	0.00005	0.0048	1.023	0.51
0.02	0.015	0.00033	0.016	1.019	0.41
0.04	0.0664	0.00145	0.035	1.016	0.56
0.1	0.2478	0.0053	0.0534	0.936	0.57
0.2	1.114	0.0233	0.1165	0.928	0.47
0.3	1.568	0.0319	0.1062	0.928	0.52
0.4	4.393	0.0868	0.2169	0.913	0.63
0.5	2.754	0.0528	0.1056	0.901	0.55

So, we can see this trend, even as we sweep through this.

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Figure: Shows (a) SAED pattern of $Zr_{0.9}Co_{0.1}O_2$ (b) SAED pattern of $Zr_{0.6}Co_{0.4}O_2$ (c) TEM micrograph of $Zr_{0.9}Co_{0.1}O_2$.
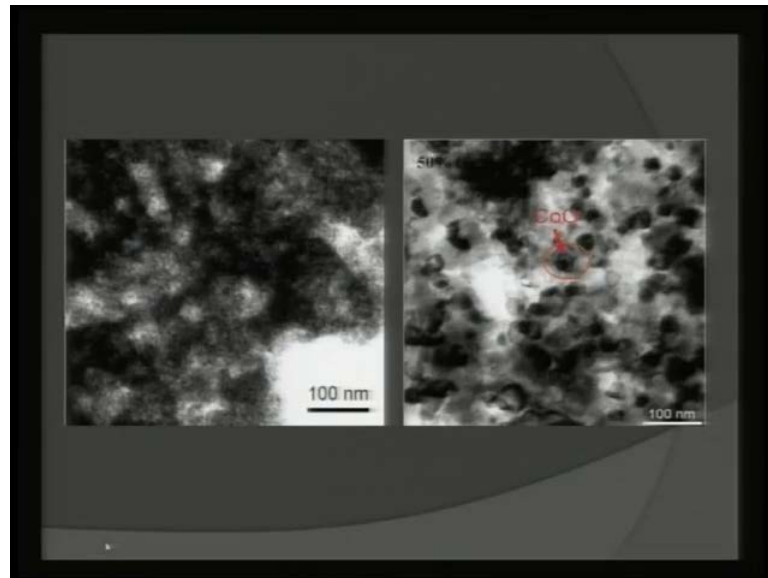
I have already shown you the phase diagram and if you can see the T E M features, even up to 1 10 percent sorry, even up to 10 percent of cobalt doping. You would see there is

no signature of cobalt oxide coming, it is a clean Z r O 2 phase, which means cobalt is substituted and once you go beyond that, you can see the cobalt phase is coming ok.
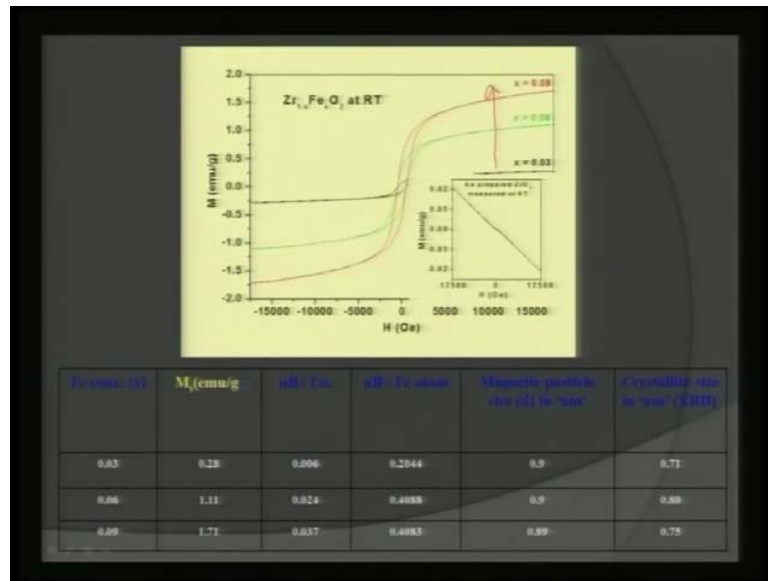
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So, I will quickly go through the last example to show, what exactly we can conclude out of doping magnetic property, in this Z r O 2 matrix, let us take the a example of iron.

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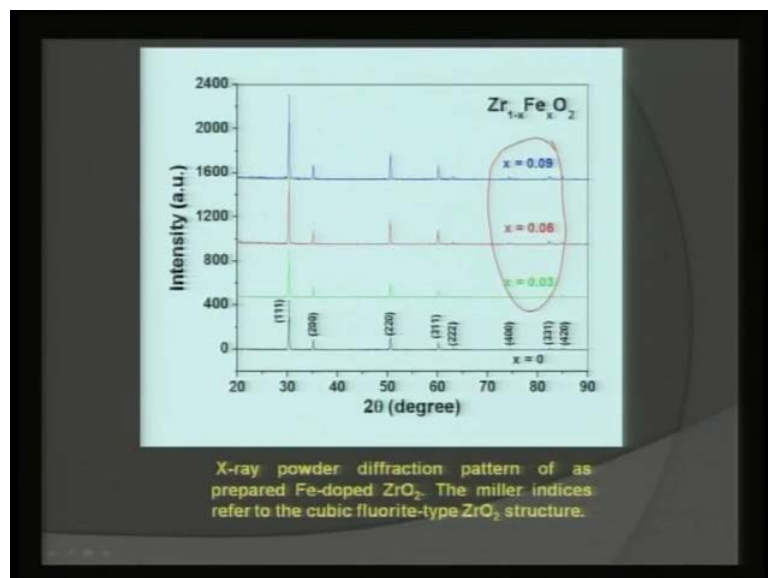
Now, if you dope iron carefully only in low concentration limits say up to 9 percent 3 6 and 9 percent, you can clearly see, it is again showing clean say Z r O 2 cubic phase.

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Now, once you look at the magnetic property, you see that the magnetization steadily increasing, but the clue, whether it is really coming from doped situation or from any other impurity comes from mossbauer.
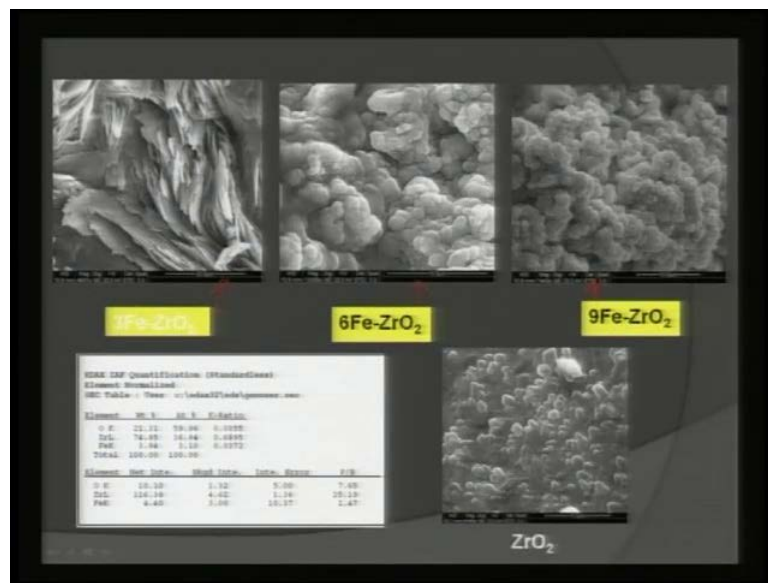
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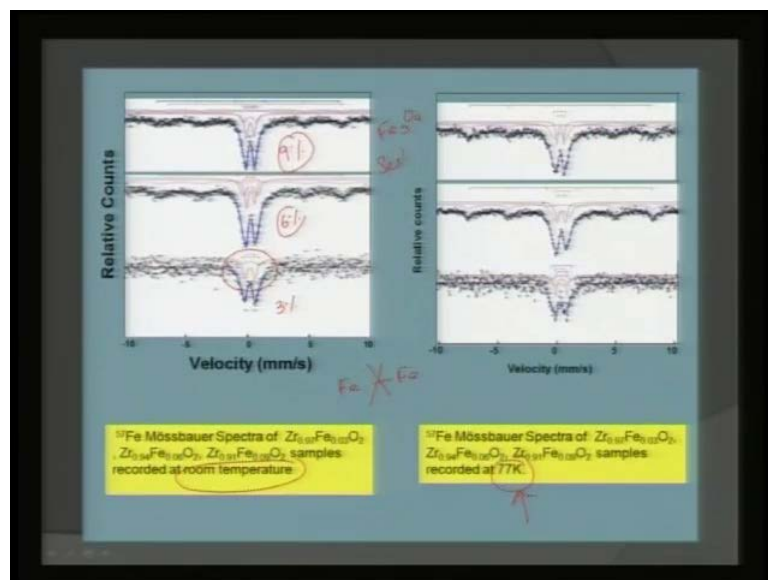
You can see for example, here in this case it is actually, 3 percent, this is 6 percent and this is 9 percent, this is at 77 Kelvin and this is at room temperature. One would clearly see that, for 3 percent, you only see the doublet here, you only see the doublet in this case where as you go to 6 percent, you can see that this doublet is getting split into a 60

and more so in 9 percent.

And similar feature is seen even in the 77 Kelvin recorded mass per peak, what we can say is if, there is a doublet then iron is actually isolated. There is no iron iron interaction in this case whereas, in the case of 6 and 9 percent, we seemingly find F e 3 O 4 impurities, which are creeping up, that is why for 6 and 9 percent, you can see a sextet feature is coming for the iron.

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So, safely we can say, what is the compositional limit, that we can look for, again you see

for 3 percent or 6 percent and 9 percent. The radically the morphology is changing, so what do we can see, for nickel cobalt and iron, we can say that, less than 3 percent of this transition metals doped in zirconia, there is a clear possibility of a dilute magnetic signature, that is coming. Beyond that even though, there is a steady or there is a schematic trend, present in the magnetic behavior, one has to be careful, that this is not actually the true signature, that comes from a dilute magnetic phase, rather it comes from, a impurity induced phase.

So, we can sort of say from this study, that there is a possibility for a dilute magnetic semiconductor, not only in Z n O type of compounds, even in high band gap materials, but we need to be very cautious about finding, what is the limiting concentration, at which this magnetic phase can be found out. So, with this I conclude and we can look into this aspect later, so make some quick analysis.

The analysis of magnetization data suggest that, iron induces room temperature ferromagnetism high temperature phase mossbauer study of 3 percent shows doublet and the corresponding 6 and 9 percent show, superimposed sextet and doublets. The isomer shift and quadrupole moment indicate, iron to be in the 3 oxidation state to occupy different octahedral sites, associated with some amount of disorder. So, in cases where we do not have a clue, here is one classical example that we can use mossbauer study to elucidate, what is a limiting compensation, at which we can realize dilute magnetic phase, I stop here and we will continue in the next lecture.