Physics of Functional Materials and Devices
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Lecture – 31, Week 8
CMR materials

In this lecture 2 of week 8, let us continue our discussion on GMR and CMR materials. In the previous lecture, I gave you the introduction to the phenomena of magnetoresistance. We had talked to you about the GMR materials. Let us move a step forward and in today's lecture, let us talk about the CMR materials, various types of CMR materials and how does the phase diagram of a CMR material impact its magnetoresistive response characteristics. Finally, you will also see in today's lecture, how to synthesize these CMR materials and the synthesis protocols are quite simple. So, you can make them in the lab quite easily.

What did we see in the previous lecture? We had seen that magnetoresistance is a phenomenon where the application of a DC magnetic field changes the resistance of a material. And the effect was quite evident when the magnetic field strength is strong enough to curve the electron trajectory within the length of its mean free path. And we had talked about the reasons why you have to either go to very low temperatures or very high fields to observe the magnetoresistive behavior. But there are materials which show significant modulation in their resistance value even at room temperature and at reasonably low fields.

These kinds of materials are classified under GMR that is Giant Magnetoresistive Materials or CMR materials that is Colossal Magnetoresistive Materials. The term colossal is used because the change in the magnetoresistance, the change in the magnetoresistance value is much larger than the one observed in the giant magnetoresistive materials and therefore, the term colossal is used. So, let us see today, what are these CMR materials. These are the materials which were discovered and they have much larger magnetoresistive effects than those observed in layered materials and therefore, they were called as Colossal Magnetoresistive Materials. They are finding applications in large areas, areas where even GMR materials are used, but CMR have larger change in the resistance because of the applied field and hence they are more liked for such applications such as magnetic recording heads or even as sensing elements in magnetometers.

One of the most common examples are the perovskite like material that is lanthanum manganese oxide. As I said, one of the most common materials which is used is the perovskite like lanthanum manganese oxide. What are perovskite materials? We have seen

this earlier also, but let me very quickly repeat it. So, these are materials which are ABO_3 type structures. What is it? You have an arrangement in a way where the A atoms occupy the cube edges.

The B atom occupies the body center position whereas, the oxygen atom occupies the face center positions. So, this is oxygen, this is the B atom and these are the A atoms. So, these are the typical perovskite type structures. Now, if you have a material that is lanthanum manganese oxide, what would be the valency state? Please remember to have a charge neutral condition, you will have the valancy state of manganese as 3 plus, oxygen 2 minus and lanthanum as 3 plus. So, if you see manganese 3 plus, lanthanum 3 plus, oxygen 3 into 2 minus, minus 6, plus 6, they cancel each other and you ensure the condition of charge neutrality.

So, you have a charge neutral material. Now, I ask you and give you a very simple task that make a material where you replace certain fraction of lanthanum 3 plus by not trivalent, but divalent ions such as calcium or barium or strontium or lead or cadmium. What will happen? You will immediately say this is not possible. Why? Because then you are moving away from the condition of charge neutrality and the material will become unstable, but these strategies are quite routinely used to obtain new materials. Why? Because if you have transition elements such as manganese in your system, then they can have very interesting changes in their valance states.

So, manganese can go from 3 plus to 4 plus. So, what has happened? You replace certain fraction of lanthanum by let us say calcium. So, the effective charge which was expected to come from the lanthanum positions has reduced because certain of lanthanum has been taken out and calcium has been made to sit on those Wyckoff positions. To compensate this loss, what will happen? Certain fraction of manganese will then transform from 3 plus to 4 plus So, as to compensate the loss in the positive charge and this would result in appearance of many mobile charge carriers. And this mixed valance systems have been shown to exhibit very large magneto resistive effects.

So, as I said this is a typical structure of lanthanum manganese oxide, the green circles represent lanthanum, the red circle is representing manganese and the blue circles are representing the oxygen atoms. This is a typical unit cell of a LMO molecular formula. We had talked about calcium replacing certain fraction of lanthanum. So, let us take an example of $La_{0.67}Ca_{0.33}MnO_x$. Now, why do we write x and not 3 in here? It should have been O_3 because when you are inducing loss of charge neutrality condition, there is an additional factor which can appear in this kind of systems, where the loss in positive charge can also be compensated by the appearance of oxygen vacancies and so, you can move away from the condition of O 3 to a condition of O_3-delta, where delta is actually the fraction of oxygen which have been taken out. So, you get a condition where your material is oxygen deficient and that is why you tend to write X also, X can be 3 or it can be less than 3 and then it

could become 3 minus delta. So, if you make this composition, here if you see nearly 1000-fold change in resistance was observed by the application of 6 Tesla DC magnetic field. So, if you see the resistivity curve as a function of magnetic field, huge change in the value has been observed and this is a typical curve of dependence of resistivity which is normalized in LCMO structure, but at 250 degree K.

So, huge change in the value. The temperature dependence of the resistivity also displays another unusual behavior that is near the Curie point, Curie point where these perovskite-based unit cells or structures are undergoing a phase transition or transformation. So, near the phase transition temperature, the resistivity also displayed an unusual behavior. If you are saying that the transition temperature is around 250 K, then you can clearly see that around the phase transition temperature, there was significant modulation in the response characteristic of this LCMO material when the parameter which was being measured was resistivity. Ideally, you would have seen that either resistivity is increasing or if you are cooling, it is decreasing.

One of the things should have happened, but now you are seeing a lambda type of transition. Why is this happening? This is one thing which was observed and why this was happening? It took some more studies to come to the answer why this was happening. This we will discuss in a minute, but let me first just quickly tell you how these materials are fabricated. We have seen the fabrication protocols. Why I am teaching about synthesis before explaining the observation that was seen in LCMO? Because that is the way we have proceeded in our course.

We have talked about materials, we have talked about the phenomena which should change in these materials So, that they become a functional material and you saw that we spent significant amount of time on the synthesis protocols of these materials. So, we must move in the same order So, that we understand that everything which is being talked about till now is also true for such GMR and CMR materials. These LCMO materials are routinely made using a sol-gel synthesis protocol, where you can use metal nitrates, a few like citric acid and ethylene glycol as a binding agent. Mix these three in certain ratio. In typical case it is 1 is to 2 is to 4.

Now you have these things mixed using deionized water and then you adjust the pH to 2. Now you stir this salt which is formed at 80 degrees in a water bath to obtain a homogeneous gel. So, salt now transforms to a gel. Use this gel and heat it to 300 degrees before sintering the material at 700 degrees for 4 hours to obtain the desired product. So, this is what you can easily perform and, in the lab, and you will get a high performing LCMO particle.

You have the X-ray diffraction data shown by the black curve and the red line is the fitted curves obtained curves obtained after Rietveld refinement. Although this is beyond the

scope of this course let me very quickly tell you what is Rietveld refinement. So, if you get an X-ray diffraction pattern and you do not know what is the crystal structure it is stabilizing in, you must simulate a structure and then you have a simulated curve related to that unit cell. For example, if you say it is rhombohedral cell R3C, then for a given ABC that is for lattice parameters ABC and alpha beta gamma you know where the atoms LC or M or O would occupy in a rhombohedral cell. Then you simulate the expected diffraction pattern.

Now you take the diffraction pattern which is simulated not the observed, the simulated data and superimpose it over the observed data. If both of them actually merge or you see a difference profile which are shown by the blue solid line here that means they are superimposing on each other, then the structure which you are seeing from a material has the same unit cell as that you have simulated. But if there is clear mismatch then you need to propose another unit cell, simulate a data and then superimpose over the observed data. And you need to do this exercise till you get the matching which minimizes the R fitting parameters. So, you then do the statistical chi-square test and when for typical values for chi-square for Rietveld refinement curves done using X-ray diffraction data are in the range of 2 or less and if you use neutron diffraction data or high-resolution synchrotron data then it is less than 1.

Then once you have chi-square values which are quite low then the fitting is considered to be of good quality and then you can say that the structure of the material which is forming is the same to that what I have proposed. This is a typical way of doing a refinement. So, you can see that for x equals to 0 and 0.1 you have rhombohedral R3c structure which stabilizes, but if you go to X 0.2 to 0.3 you will find that the structure transforms to an orthorhombic Pnma structure. You can clearly see that you have the change in the nature of the peaks and this is directly related to the unit cell and hence you can find out that the structure is changing. Structure changing I repeated three or four times in last one minute. Why? This is an indication that there is a phase transformation taking place and if there is a phase transformation taking place does it have an impact on the magnetoresistive behavior of the material. This is what we will answer in few minutes.

Now as you make different types of material you can clearly see that the particles can have the same shape and size or they can also change in shape and size. Ideally, when you are comparing these materials, you would like to have materials with similar shapes So, that you do not have to take into consideration various other confinement effects which comes in as you go from one shape to the other and if you go from bulk to nano materials. And now you will see this is a phase diagram for LCMO. What is the thing which is being done? You are plotting various structures and the physical response which are associated with those structures as a function of changing calcium. So, you have this is basically x in $La_{1-x}Ca_xMnO_3$ or Mn_γ.

So, x is what is the composition or concentration of calcium. You can clearly see that as you go beyond 160 degrees and you are at 10 percent concentration what are you seeing? You transform from ferromagnetic insulating behavior of LMO to paramagnetic insulating behavior of LCMO. But if you take a composition let's say around 23 percent to 40 percent in this region and you are in the range of temperatures let's, say around 180 degrees in this range. What is the nature of the material which you are seeing? You are going to see a ferromagnetic metallic behavior of these materials. It is only beyond 250 degrees that you start seeing the paramagnetic insulating behavior in these systems.

If you go beyond 50 percent of calcium in lanthanum manganese oxide matrix you transform to anti ferromagnetic insulating behavior. And, you therefore see that the nature of the material changes as you change the concentration of calcium in the lanthanum manganese oxide matrix. And if you want now to have a material which is showing a ferromagnetic type behavior at room temperature what is the typical composition you would like to take? You would like to take let's say LCMO where calcium is around 30 percent and you can clearly see at room temperature or so, you will get materials which have the ferromagnetic metal type behavior. So, you can tune the temperature range in which you want certain characteristic behavior in LCMO. Similarly, you can talk about the behavior in another divalent ion-toped LMO and that is lanthanum strontium manganese oxide.

Similar it has a similar perovskite type structure and you have the unit cells which are shown in these two curves. Similar perovskite structure. You can use a similar Sol-gel synthesis protocol to obtain the LSMO material. Again, you are using nitrates, citric acid and ethylene glycol as the precursor, the gelating agent and the binding agents. The ratios are also similar 1 is to 2 is to 4.

But instead of calcium nitrates what have been taken? We have taken the strontium nitrate as the precursor. Now you stir at a temperature of 80 degrees using a water bath to obtain a gel. Then you heat it at 300 degrees and then sinter again at 700 degrees for 4 hours to obtain the required material. You will have an extra diffraction pattern and you will see that you can obtain the pure single-phase material of LSMO up to higher concentrations of strontium doping. And along with that you will find that there is some modification in the size of the particles as a function of strontium doping, but the shape remains the same.

That is all. This is what you will see. Now you would have expected that if everything is remaining the same the phase diagram should also look exactly the same as that of LCMO, but no that is where the change is significant. You will find that the nature of phase diagram for LSMO is very different from that of LCMO. You can clearly see that if now I want to have a system which is showing around 300 degrees of ferromagnetic behavior, then I will be in a range of let's say x 0.20 to x around 0.48 or so. So, this would become the range. If now you want to have a system which is showing a paramagnetic insulator behavior, then

which composition will you use and in which temperature range you can find out by the phase diagram. So, you have the temperature versus composition curve and you can clearly find out the Curie temperatures as well as mean temperatures in from this curve and you can find out what is the composition which you would like to make if you want to see the magnetoresistive behavior which is very large. What are we calling this kind of behavior that is colossal magnetoresistive materials then for this composition you will be able to determine the corresponding application. I hope now you clearly understand the phenomena of magnetoresistance.

How we move from GMR to CMR materials? We have discussed two very common CMR materials. You have seen that they are easy to fabricate. Again, I will ask you a question. How can you make new CMR materials? You can clearly make new CMR materials by changing the divalent ion. Along with that you can also go a step forward and you can start modulating the manganese ion concentration and playing with the doping of manganese ion itself and if you do that if you are able to get solid solutions then you would be making a phase diagram.

From there you will be measuring the magnetic phase diagram. You can do the neutron diffraction and then you can make the magnetic phase diagram that is temperature versus x curve and you will know what is the magnetic behavior of a given material and that will give you an indication how to choose a CMR material that has very large change in the response characteristics as a function of applied field. I will give you a task. Please find out what is the nature of change in the delta R by R value as a function of applied field in LCMO and LSMO materials. You will find that the change is something of this curve.

We will talk about this curve more in detail during the live sessions, but this is the exact curve which is obtained and this curve is such that the change in the magnitude is as high as six orders and the change in $\frac{\Delta R}{R}$ values as a function of applied field is directly linked to the change in the phase of the LCMO or LSMO unit cell. So, as you move from one unit cell to the other you see significant change in the response and why that is happening because as you move let us say from rhombohedral to orthorhombic cell, the nature in which the manganese ion is aligning and distributed in the unit cell changes and the alignment of these magnetically responsive elements to an applied field then changes and therefore you have the change in the behavior of these materials because for example if you have a double unit cell in Pnma type structures then you have the tilted structures where the magnetic fields can get cancelled. So, you have canted structures, but when you apply these fields to such canted structures then the spin structure aligns and that leads to significant change in the flow of the charge carriers through these materials. So, you can see large change in the magnetic behavior along with that you can see large change in the resistance value as you change from one structure to the other structure of these materials.

These are the references which you can refer to for developing more understanding and I thank you once again for attending the second lecture of week 8. Thank you very much.