Advanced Materials and Processes
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Lecture – 56
Advanced Functional Alloys

Welcome to NPTEL, myself Doctor Jayanta Das from Department of Metallurgical and Materials Engineering, IIT Kharagpur. I will be teaching you Advanced Materials and Processes. Today, we will start a new topic on advanced functional alloys in this particular topic, we are going to discuss the newly developed alloys or compound that exhibit multifunctional properties. Let us say, as an example we have already discussed about shape memory effect, which one can achieve in nickel titanium, shape memory alloys.

However there the interplay between structural phase transition means from austenite to martensite is linked with temperature and stress, but how it will be if we gets, very similar behavior means shape memory effect in a material due to the application of a magnetic field. So, now we are thinking about materials that should be utilized a without application of much stress and temperature interplay by some third parameter or maybe we can think about that entropy change, we have learned quite a long time, ago when we discussed about order of phase transformation or temperature induced phase transformation in metals and alloys.

However we can apply a magnetic field and the phase transition can occur and that may involve a large entropy change ok. So, this could be a, very interesting phenomena in materials or compounds or specifically on a metallurgical aspect, when we think about developing such alloys that exhibit such functional behavior. So, let us start today's discussion on advanced functional alloys.

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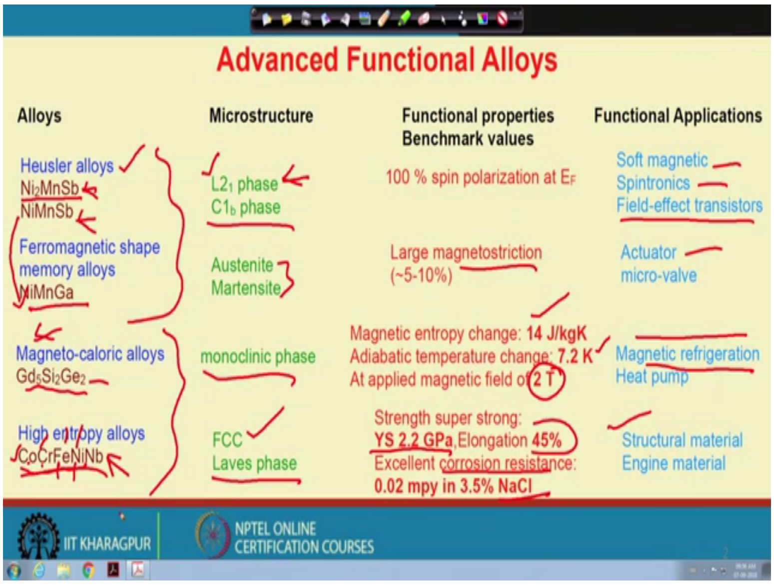

Here, I show you some of the typical alloys like Heusler alloys these Heusler alloys or compounds has a very typical composition like x to y with some half metal like antimony.

Usually this compound exhibit FCC structure here, these are some complex FCC structure ordered structure L 2 1 structure. We will discuss in detail, what is this L 2 1 structure. In this particular case of such Heusler alloys, one can achieve near 100 percent spin polarization at the fermi level. Now what are the application or what are the functional behavior? Because of that we can apply these Heusler alloys for these are soft magnetic materials, we can use them for spintronics also we can use them as a transistor like field effect transistors, where we can apply some external field magnetic field and the properties may change.

Now, very similar type of compounds these are called as half Heusler nickel manganese antimony, which also has a FCC base structure are also called as Heusler alloy. Now very similar alloys here, this is also a half Heusler; however, in these particular case, we can get a shape memory behavior, they have one hand ferromagnetic properties as well as by application of the magnetic field only ferromagnetic materials can heavily interact with the magnetic field yes. So, that is why they are ferromagnetic and there will be a phase transition between austenite to martensite or vice versa and we can get very large shape change or dimensional change or length change the property is called as a magneto restriction.

So, very high means greater than 5 to 10 percent and we can get actually or use this material, which are already being used as a actuator micro valve and so on. Now the third type of material, these are also magnetic material; however, in those magnetic materials or alloys, let us say as an example, we may have some monoclinic type of structures, this is a gadolinium compound, gadolinium silicon germanium, the interesting phenomena here by application of a magnetic field. Let us say, a value of something in the range of 2 Tesla, we can achieve a large magnetic entropy change in the order of 10 14 joule per kg Kelvin.

And that simply changes a adiabatic temperature of the material in the order of 7.2 Kelvin, this is a very a fascinating class of material actually and the benefit is simply enormous because, we can develop a Carnot cycle, where in one side we will generate a hot side other side, it is a cold side. So, we can extract that heat or we can cool a material because of that, we use this material for magnetic refrigeration or in the heat pump. So both way, the Carnot cycle can be used and the major benefit of such material. We will discuss later on.

Now other class of materials like, high entropy alloys here these are, the multi principle element like cobalt, chromium, iron, nickel ok. So, 25 percent, 25 atomic percent cobalt, 25 atomic percent chromium, 25 atomic percent of iron, 25 atomic percent of nickel, can be can be mixed in a liquid state and we can produce an alloy out of these 4 major elements and we will get a single FCC phase and that may have some strength level of 800 or below 1000, which can be further processed to make very nano crystalline size microstructure or may be by adding some niobium into these alloy with these 4 principal element, we can incorporate some laves phase or laves phase may form due to the addition of niobium.

And the yield strength can reach up to 2.2 giga Pascal. So, this strength level is almost reaching to the close of a theoretical strength like metallic glasses and we can also achieve very high elongation, very high corrosion resistance in a aqueous medium. Let us say, 3.5 percent of sodium chloride and these are typical alloys, where due to the presence of various equi atomic a various allowing element, the entropy means we are talking about configurational entropy s is equal to k lnw.

So, there we can achieve a very high entropy values and the material could be multifunctional. So, in those cases the material can be used as a structural material or may be due to different heat conductivity, we can also use for engine material block and so on. The first these 2 different types of magnetic materials, they already find commercial application; however, the magneto caloric alloys for refrigeration purpose and a high entropy alloys are still yet to be developed and there are many different consideration theoretical understanding that is being developed day by day.

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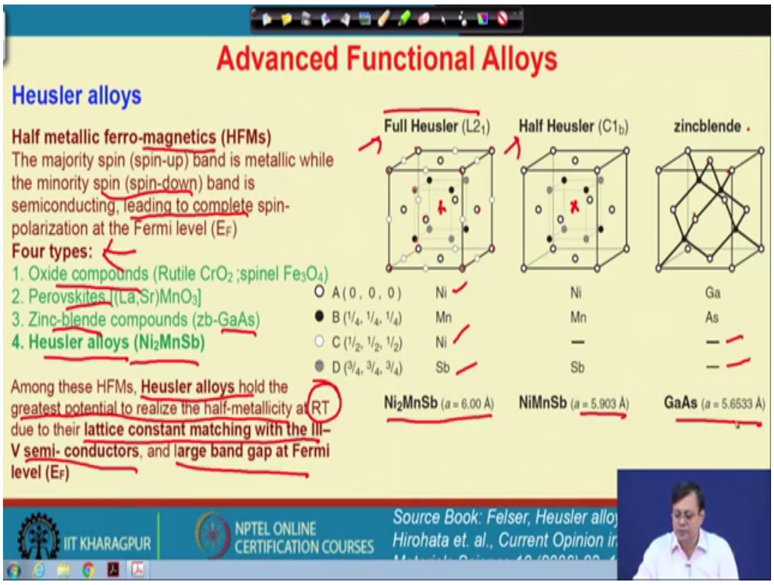

Now, the before going to these Heusler alloys, Heusler compounds we first need to a discuss a bit about the half metallic ferro magnetics here, I specifically used these terminology magnetic, in it include different oxide compounds perovskites structure zinc blende structure like gallium arsenide or alloys. So, in this half metallic ferro magnetic, here the majority of the spin like spin up band is metallic, while the minority of the spin that is spin down, the band is semi conducting in nature ok, what is really the spin up and spin down like metal or semiconducting? We will come in a minute we will discuss.

Ah this basically leads to a complete spin polarization effect at the fermi level there are 4 types of a different ferro magnetics or half metallic ferro magnetics has been observed like oxide compound, rutile, spinel structures, perovskites, zinc blende like gallium arsenide and Heusler compounds. So, among all these half metallic ferro magnetic, heusler alloys hold the greatest potential to realize the half metallicity at room temperature due to their lattice constant matching with the group 3 to group 5 semiconductors and large band gap at the fermi level.

Now, these Heusler compounds has a structure, that is the FCC base structure and let us first try to look at how these structures looks like? So, nickel 2 manganese antimony this is called as a full Heusler, the full Heusler structure is a FCC base structure, you can see these are the A position, the lattice A position and the center of the face centering that contain nickel ok, now the B the sub lattices here, that is located at one fourth, one-fourth; one-fourth whereas, C is located at the center ok.

So here again, nickel is occupying the position that is located at half, half, half and D which is located at three fourth, three fourth and three fourth. So here, is the antimony is occupying the place, now the difference between full Heusler and half Heusler is that the C sub lattice is vacant. So here, C is the, at the center that is vacant where nickel supposed to be there and therefore, there is the presence of nickel manganese and antimony. So, in case of full Heusler, it is 6 angstrom lattice parameter in case of half Heusler, it is 5.9 and in case of zinc blende structure, this is also FCC base structure; however, both the C and D sub lattice are missing ok.

So, zinc blende structure is very famous for this gallium arsenide structure and it has a it has a lattice parameter or lattice constant as 5.65 angstrom and these 3 different compounds or these half metallic ferromagnetic, shows very interesting properties.

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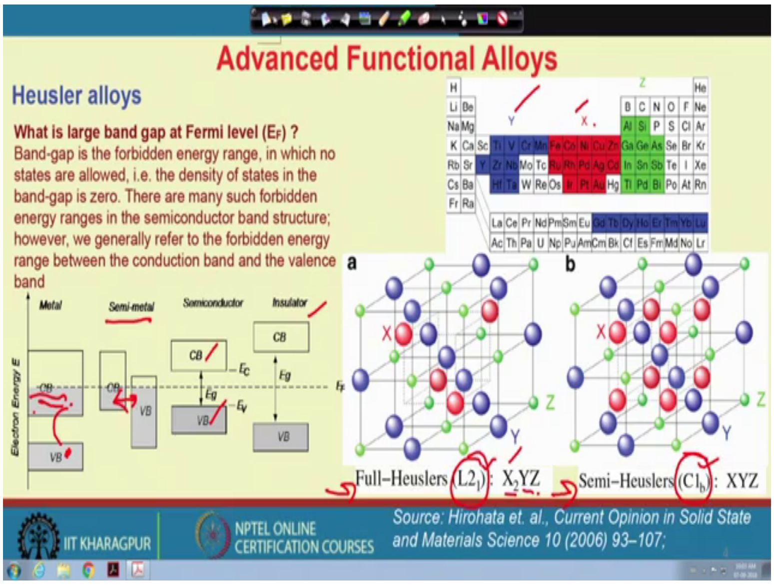

Now, if we think about, what do we mean by this fermi level? Actually the fermilevel means, there is a band gap is the forbidden energy, band gap you know that exists between the conduction and the valence band.

So, in case of a metal there is a very less energy gap. So almost no gap so, all the electron can flow from the valence to conduction and there is enough electrons are present in the conduction band. So, we get a good conductivity electrical conductivity as well as thermal conductivity um, on the other hand if we think about a semi metal, the semi metal here both the conduction band and valence band, they are overlapping with each other. So, electron can easily go from any of the bands, in case of semiconductor there is a large energy gap also which is in the, which is between the conduction band and valence band whereas in case of insulator it is much higher greater than 4 Ev ok.

So, the gap is much higher. So, so almost no electron can jump into the conduction band normally and the energy required is very high. So, this is the difference between the metal, semi metal and semiconductor and insulator. Now the density of the states in a in a band gap, that is 0 like in case of a metal and so; however, we generally refer to this forbidden energy range between a conduction band and the valence band.

So, in case of full Heusler and the and the and the half Heusler or semi Heusler, the structure is different because even though both are FCC base structure, but in one case it is L 2 1 structure and here the centering the C 1 B structure the centering atoms are missing actually. And so, in both these cases the presence of these X 2 Y Z type of element X and Y are taken from the periodic table, which are the transition metals like here Y is titanium, vanadium chromium, manganese, zirconium, niobium, hafnium, tantalum so on.

Whereas the X here is represented by iron, cobalt, nickel and so on. So, we can take nickel or iron, there are many iron base components are also being developed um, now these are the P type of elements like aluminium, silicon and a gallium germanium and arsenic antimony tin and indium. So, these are the P type P type P type metal from taken from the from the from the periodic table.

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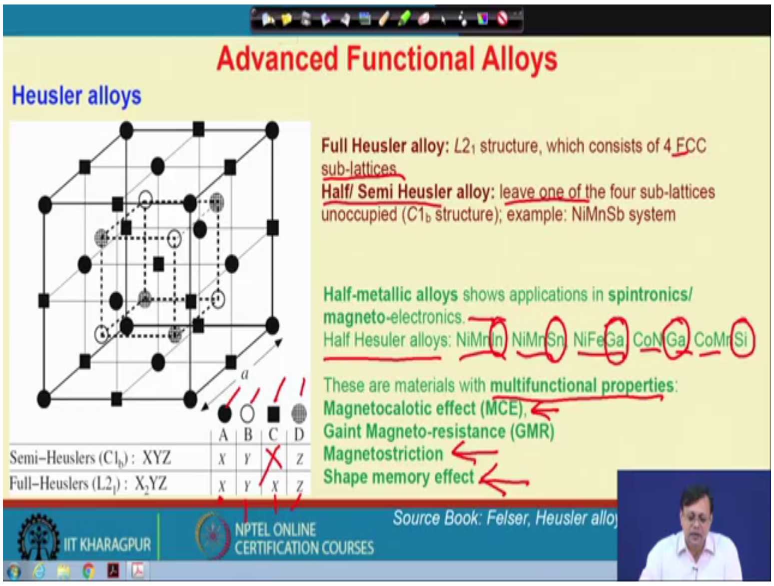

So, that is basically represented by the Z and we can clearly see that difference between these 2 structures and try to look at the other a differences in these full Heusler type of alloy and half or semi Heusler type of compound.

So, in case of full Heusler, we have basically 4 FCC sub lattice ok. So, like A, B and C and D position, which all are occupied by the full Heusler as I said and in case of semi Heusler compound, where we leave 1 of the 4 sub lattice and that is basically the C and here there is absence of a nickel or any of these or iron and so on. So, half metallic alloys shows a large potential for spintronics and magneto electronics and these half Heusler alloys, the typical example like nickel, manganese, indium or nickel, manganese, steel or nickel, iron, gallium, cobalt, nickel, gallium or cobalt, manganese, silicon.

So, you can easily see how these, semi metal or P type of element has been chosen from the periodic table, actually and they also such a behavior and these Heusler compounds are multifunctional compounds or alloys that exhibit magneto caloric effect, which I have explained you a minute earlier, now giant magneto resistance means, we can apply magnetic field and the resistivity will change, a magneto restriction property means length changes as well as by application of magnetic field, we can achieve shape memory effect.

So, these are very interesting properties or multifunctional properties that one can achieve.

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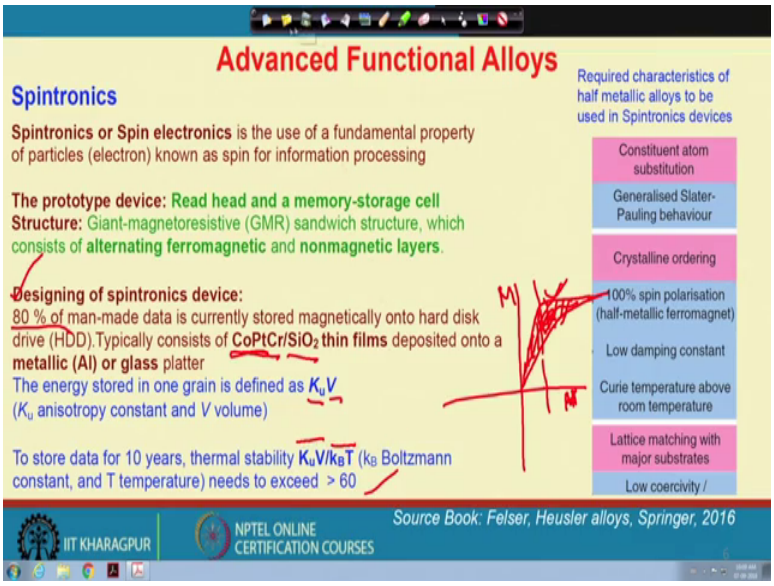

Now, in case of spintronics, the spin electronics is also a fundamental property of the elementally particle. So, elementary particle means basically the electron which are known as spin for information processing. Now the prototype devices for those kind of spintronics application are the memory storage ok, memory storage cells or let us say, the red head and the structure is a giant magneto resistive sandwich structure, which consists of alternating layer of ferromagnetic material as well as non magnetic material.

So as an example, I can tell you we discussed about cobalt platinum for magnetic storage, you may recall here this is a cobalt, platinum, chromium alloy and a silicon dioxide thin film, which are sandwich type of structures that are made for devising those spintronics application. So, far for such a design 80 percent of the manmade data in on today are made out of those magnetically or into the hard disk or a hard disk drive we call and typically they are all consist of this cobalt, platinum, chromium and silicon dioxide thin film, that are usually deposited on a on a metallic aluminium or glass platter.

The important information here that we must keep it in mind that the energy stored in one of the grain is defined by Ku into V, V is here the volume and Ku is the anisotropic constant. So, the magnetic anisotropy generated due to the crystallographic direction, you may recall we have shown you the hysteresis. So, let us say for a particular hkl direction here and this is another direction. So, this is the applied magnetic field and let us say, this is H and here we have V or M magnetization.

So, for this particular direction hkl, we can we can magnetize the material at a much lower field whereas, this particular hkl, we cannot or we need much higher applied magnetic field to magnetize a magnetic material ok. So, this basically generates a anisotropy in the in the material ok. So, this is a area that is somehow linked with the anisotropy and we call it as a Ku. So, Ku is the anisotropy constant and to store a data for let us say something like 10 years thermal stability is very much important and it should need to exceed like 60, which become from the ratio of KuV divided by KB, is the Boltzmann constant at a given temperature.

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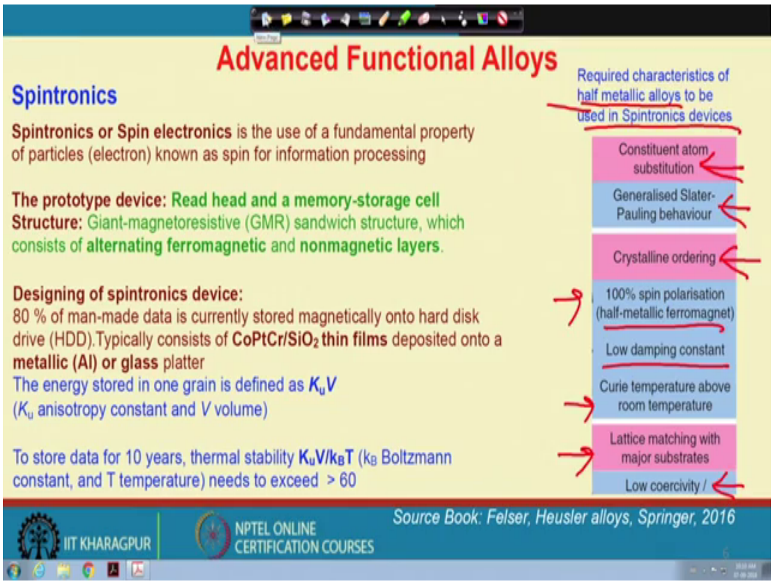

So, that is why one need to consider all these aspect for spintronics application. So, there are some basic requirement for these spintronics like a half metallic alloys to be used for spintronics devices, where we need some constituent atoms substitution, we which we are calling as a half metallic elements and so on and we need a generalized swatter fouling behavior, which we have already discussed during a magnetic material discussion, we also need some crystalline ordering. So, far L 2 1 structures and so on, we have discussed we also need a 100 percent spin polarization, that is a typical feature of let us say, Heusler type of compound or half metallic ferromagnetic materials.

Also we need a very low damping constant; we need a curie temperature above room temperature, because if we have to store the magnetic data and if Curie temperature is very near room temperature, then all hard disk drive will fail right. So, we need a very high curie temperature and to store a room temperature data of that and the lattice matching with the substrate is also important because, we have to grow those films on the top of a aluminum or some glass plate.

So, substrate is also important as well as the low coercivity means, it should be soft magnetic in nature.

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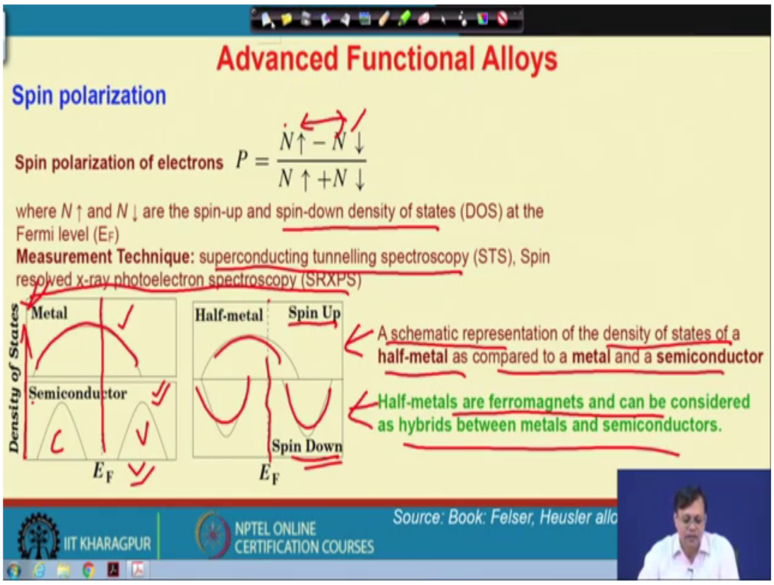

So, so these are the very important aspect of material or half metallic material to be used for spintronics application, now regarding spin polarization the spin polarization are measured with a parameter called P and this P is equals to the difference between the spin up and spin down. This is let us say, spin up and this is spin down and divided by the addition of these 2 different spins, main spin up and spin down.

So, if we need let us say 80 percent spin up spin down then, I basically need 90 10, 90 percent of the spin should be up 10 percent and down. So, let us say, 80 will be the difference divided by a 100. So, the calculation goes in that way. So, where spin up and spin down are represented by the density of the states at the fermi level and measurement technique, what we imply like a superconducting tunneling spectroscopy or spin resolve x ray photoelectron spectroscopy technique like the density of states. If we need to understand in case of a metal, we know that near the fermi level, we have a valence band and conduction band present and electron can easily flow.

And in case of a half metal in case of a half metal actually um. So, they are partly has this metallic type of nature and why we call it as a half metal? You will understand because in case of a semiconductor we have these, conduction band and the valence band ok. So, there is a large energy gap between these 2. So, now these feature of a metal and the feature of a semiconductor both are present in a half metal because, when we have this spin up it is metallic, where there is a spin down, it is basically like a semiconductor like this case actually ok.

So, this is the fermi level. So, both the feature of spin up and spin down here, half of the property is like metal and half of the properties are when it is spin down, it is like semiconductor. So, this is the basic origin of spin polarization effect in a in a half metallic metal or P type of metals. So, P type of elements. So, the schematic representation of the density of the states of a half metal and compared with a metal and semiconductor so, half metals of ferromagnets can be considered as a hybrid between the metal and semiconductor.

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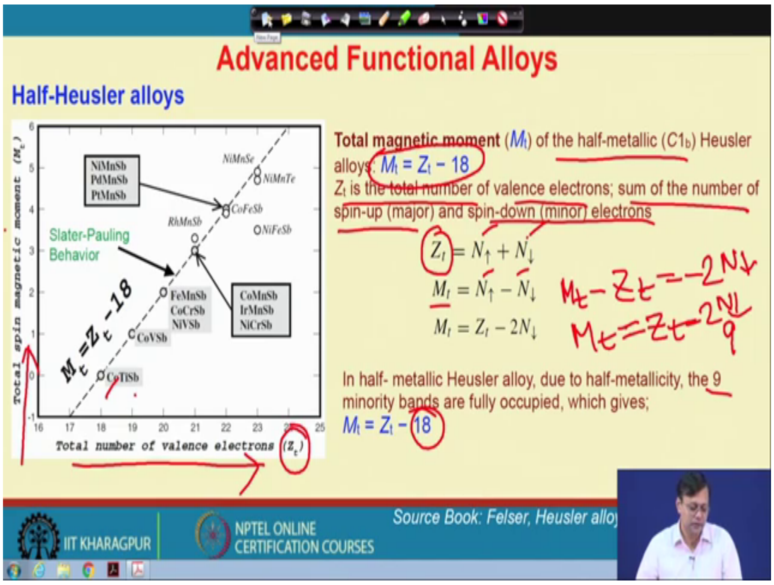

Ah now um if we look at all these a half Heusler alloys and. So, full heusler alloys have a have a 2 X 2 Y and Z type of composition in case of these half Heusler alloys, you see there is this is XYZ type of compound like cobalt titanium and antimony and so on. So, if we simply plot between the valence electron that is Zt and the spin magnetic moment ok. So, there is a correlation between these 2.

So, if the valence electron increases the spin magnetic moment is also increases linearly almost and they basically have a exhibit such a correlation between Mt is equal to Mt is the spin magnetic moment, that is equal to Zt minus 18 and how does this come? Actually you can see this like, let us say we have taken a half metallic Heusler alloy and

Zt is the total number of the valence electron and some of the spin up and spin down minor electron ok.

So, this is actually Zt, which is the summation of both and Mt is the is the difference between the 2 different spin, one is spin up and spin down, now if I subtract that Mt that minus Zt, you can easily see that it will be basically minus 2 N right 2 N. So now, Mt is equal to is equal to Z t minus 2 N. So, this N is basically, the spin down one ok. So, for a for a half metallic alloy due to the half metallicity. Let us say 9 minority bands are occupied and if I put here 9, then it will be basically the total is the 18.

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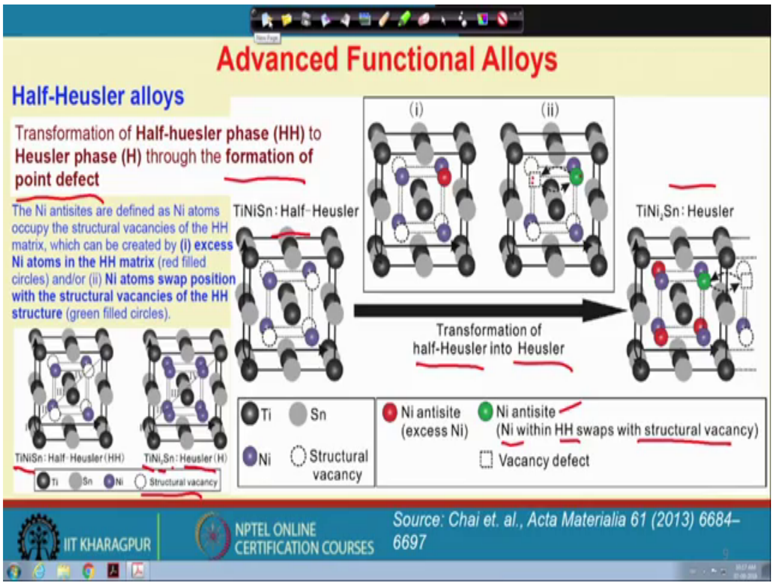

So these are the basic origin of all these different compounds, which are the half Heusler alloys and how these spin magnetic moments, are achieved due to the half metallicity in a compound. However these switching between the half Heusler phase to a Heusler phase, we can we can identify by considering some formation of some point defect. So, this is quite simple because, I have shown you that the C sub lattice, which is missing in a in a half Heusler phase and here there is a need of a structural vacancy. So, titanium, nickel, tin which is a half Heusler compound and titanium, nickel, 2 tin which is a Heusler type of compound.

So in this particular case, you can see that there are some structural vacancy present and for a 2 switch from a half Heusler to a Heusler actually. So, we need to switch between this nickel antisite, nickel with some HH swap that with the structural vacancy that that basically causes the nickel antisite, where we have some excess nickel and so on. So, transformation from a half Heusler to Heusler is also possible.

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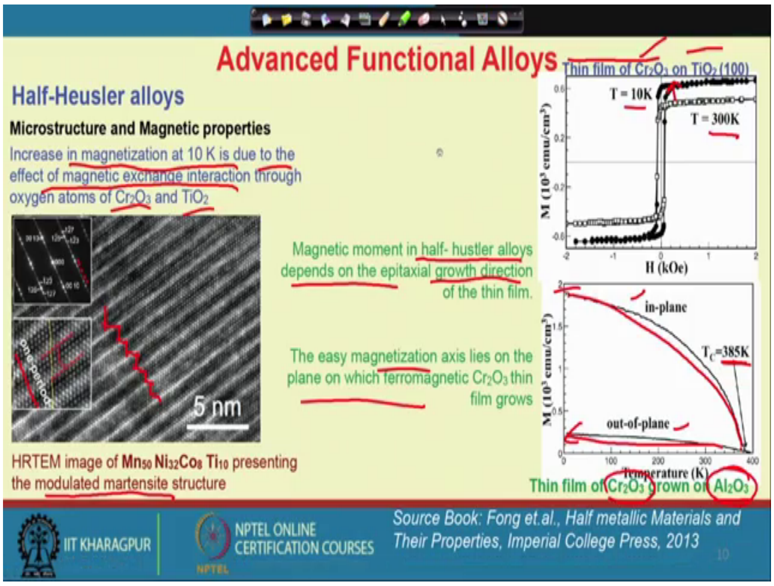

So, they basically changes their positions and we by a vacancy defect from a half Heusler HH to a Heusler phases. Now when we talk about these half Heusler alloys, there are some structural features. So, usually these increase microstructure content mostly, let us say the martensitic structures and these martensitic structures are highly twinned and I show you one of the example of such structure, where we get some modulated martensitic structure it basically, means that there are layer of different martensite, they coexist together and these are the typical twin in a martensite, you can see here one of the such a periodicity is shown and these are the diffraction pattern.

And from here also we can measure, how many number of these weak spots are present? Until the short spot so, let us say this is like a 5 n modulated microstructure. So, increase in the magnetization around 10 K due to the effect of magnetic exchange interaction through oxygen atom like chromium and titania is a is shown here. So, this is a thin film that is grown on a titania 1 0 0 direction and the film is made of chromia. So, from 300 K to 10 K, you can see there is a increase of the magnetic exchange introduction and magnetization.

So, magnetic moment in a half hustler alloy that depends on the epitaxial growth direction of the thin film, very similar behavior people have, observed when they have grown these chromia on a alumina substrate. So, let us say here, it is around 385 K, where out of plane and in plane of the alumina means, whether we are measuring these axis in plane of alumina or out of the plane. So, the difference goes higher ok. So, the magnetic moment in plane is much higher than, the outer plane actually and these are a very typical feature of such kind of a half Heusler alloys in terms of magnetic properties. So, with this we we stop today's discussion on these a half Heusler type of compound, we will continue this discussion in the next class with more detail in terms of very interesting feature of other functional properties of including some of the magnetic properties.

Thank you very much.