Physics of Functional Materials and Devices

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Lecture – 26, Week 7
Phase and phase transitions

Welcome to the lecture 1 of week 7. In the previous week, I had given detailed description about the thermal properties in solids and how those properties can be tuned and hence you can get different kind of materials and applications. In this week, let us start discussing on a very common topic which we have been studying from our school days that is magnetism. And why this concept, this phenomena which is known for many many centuries is still a very important and widely investigated phenomena and people are trying to fabricate, make new materials so that they can get new and novel magnetic properties which can be then used in new devices or devices as per the requirement of the end user. So in today's lecture, let me quickly revise the basics of magnetism. We will not go in details because that you have studied probably from your school days onwards.

So let us very quickly revise them and then in the next lecture, we will start talking about functional materials which are becoming very important and as we had learned in the first week, what are functional materials? Functional materials are those which have at least one or more than one functionalities. Hence if one of the functionalities is magnetism, if you really want to have a functional material, then you must add another functionality in the same material so that you can call that material a functional material. So in the next lecture, we will see what are the common and most widely investigated functional materials which have magnetism as one of their important properties. But that is for the next lecture.

In today's lecture, let us quickly revise the origin of magnetism, what are the types of magnetism and what are the principles which actually describe the origin of magnetisms. As I said and all of you know, magnetism is a concept which is known for decades and decades and the first point at which magnetism was known to human mankind is probably not known, but it is known that Greeks were probably the first race who documented that and they said that there is a material or a brick or a stone coming from the word lithos stone which can attract certain other kind of materials which are nearby to it. And if you see the documentation, this was probably seen for the first time in lodestone and it could attract the other naturally magnetized pieces of minerals or other materials. And the word magnet comes from the Greek term magnetis lithos. So you have the word magnet coming from there.

In 1600, it was Gilbert who published the first detailed report on the magnet and magnetic bodies and also said that the earth itself is a big magnet. Now before that, people used to believe that it was the pole star Polaris or a large magnetic island on the north pole that attracted the magnetic compass. But Gilbert said no earth has its own magnetic field and then people started giving definitions to what is magnetism and then lot of things were talked about, but initially it is the force of repulsion or attraction between two different substances caused by a motion of charged particles. This was the definition which was accepted in the beginning and then people went on refining this definition. You know magnetic field is the space around a magnet where magnetic effect is felt and it is represented by the magnetic lines of force.

Unlike poles repel and unlike poles attract, this is what we all know. What you know? The lines of force, they emanate from the north pole and then they enter the magnet from the south pole. This is what we had seen and then you had the permanent magnets which were being made or hard magnets and they could attract the magnetic materials or elements or compounds which were near to there. Based on the response characteristics of these magnetic materials, we have three types of magnetic materials. Thiamagnetic, paramagnetic or ferromagnetic.

In ferromagnetic you can have two types, you can have an antiferromagnetic and ferrimagnetic. The value of the magnetic moment of a body is what defined as chi H and is the measure of the strength of the magnetism that is present. If you look into atoms in various transition elements, they have unfilled energy levels where the spins of the electrons are unpaired. This gives rise to the net magnetic moment. The famous example of iron and you will find if you write the electronic configuration, what you get? You get unfilled D levels and that is the origin of magnetic behavior in iron.

Based on the value of chi that is magnetic susceptibility, you can differentiate between diamagnetic and paramagnetic materials. Para magnetic have negative value of chi and paramagnetic have positive value of chi. In ferromagnets or even ferrimagnets and antiferromagnets, in addition to the permanent magnetic moments, there is also a strong interatomic force which acts and that is called as exchange interaction and that leads to the higher order of magnetism in these materials. So if you look into a block diagram or a schematic description of the materials, if you have domains, magnetic domains, then in paramagnetic they are randomly oriented. So if they are randomly oriented means what? Let us say I take one magnetic moment direction, then it is probably getting cancelled by the other magnetic moments which have the magnetic moment in the opposite direction and when they add up, they cancel the magnetic moment.

So the net magnetic moment becomes 0. In ferromagnetic, the domains are aligned in the same direction and therefore they have a net magnetic moment. In ferrimagnetic, although the magnetic moments are oppositely arranged, you will find that the order of these moments of the individual domains are different and hence you have a net magnetic moment in the direction dominated by the larger domain or the domain which has a larger magnetic moment. So ferrimagnetic has magnetic moments which are less than ferromagnet, but they are not having all the domains in the same direction. But then you have anti-ferromagnetic systems which have oppositely aligned magnetic domains and they cancel the magnetic moment of each other and then you have the net magnetic moment going to 0.

Once again what will be diamagnetism? It is basically the materials response to a magnetic field and diamagnetic materials are repelled by magnetic field. Why? Because the applied magnetic field creates an induced magnetic field in these materials which are in the opposite direction and hence causes a repulsive force. Example, water, wood, gold, mercury and many more. In paramagnetic systems you have the objects which are attracted when an external magnetic field is applied. You have unpaired electrons in these materials, but the moment you take magnetic field out then the net magnetism goes to 0.

So they will behave like a magnetic material as long as there is an applied magnetic field. Obviously, greater is the number of unpaired electrons, greater would be the magnetic moment of the substance and greater would be the paramagnetism. You have common elements like aluminum, manganese or solid solutions like copper oxide or you have oxygen which behave like a paramagnetic material. Ferromagnetism, it has long range ordering in which materials strongly attract the magnetic materials which are around them. It is important that these atoms have a permanent magnetic moment.

You have iron, cobalt, nickel and their alloys as the common example and they show a hysteresis loop which is as a function of **M** that is magnetism which is observed as a function of applied field. So, you see saturation, so saturation magnetization, you see remnant magnetization and you have the $\mathbf{H_c}$ value of the hysteresis loop. Please note that this curve is for the first cycle that is when you start from 0, then you go and you reach the saturation magnetization. Then in the reverse direction, you will follow the path given by the curve. But when you reverse the field, you will not go to 0 again and hence you will follow the path now shown in the curve.

So this curve which is in the middle is only observed in the first cycle. This question is many a times asked in your interviews or in many examination. What is the major difference in the hysteresis loop of a magnetic material which is ferromagnetic in the first cycle and the second cycle onward? In the first cycle, you will have a curve like this whereas in the second cycle what onwards, what will be the nature of the curve? You will get something like this. So if you have M-H curve, you will not get the line which is going from 0 to M-S. So remember this very carefully.

Now you must also remember that what is the nature of hysteresis loop in an anti-ferromagnetic material. This is very rarely asked or shown in the books. So a material which is anti-ferromagnetic, so what is happening? You have domains which are oppositely aligned and they have nearly the same magnitude. So initially what will happen when you apply a field, what is happening? These domains which are already in the direction of the applied magnetic field will remain in the same direction, but the domains which are in the opposite direction will be forced to reverse their direction and move in the direction of the applied magnetic field. Above us critical point, you will see that these domains will also reverse and then what would be the condition? You will get the condition that all the domains are now aligned and if all the domains are aligned what type of hysteresis loop will you get? Yes, you will get a ferromagnetic material type loop.

Therefore in anti-ferromagnetic materials you get butterfly type loops which are initially showing paramagnetic character and beyond a critical field then they show a hysteresis loop which is similar to the ferromagnetic material. So these are your anti-ferromagnetic materials. So you can clearly see the difference in the hysteresis loop of these two materials. Now can I ask you a simple question? How will you use an anti-ferromagnetic material in a device? Firstly we have been talking about ferromagnetic. My question is how will you use an AFM material? Very simple.

It can be used as a device to detect magnetic field beyond a critical value. Why? Till suppose you have that device placed in an area where you are sensing the magnetic field. As long as you are getting this linear curve that means you are in the safe region of application for a particular device. But the moment you start seeing the opening of the loop that means you have crossed the critical field and you are entering a region where the material is transforming to a ferromagnetic type. So if you want to have a device which operates up to the region given by the value R of H then you can clearly note that you can have a tracer nearby and as long as you are in this region you will not see a hysteresis loop.

The moment you cross it you have a hysteresis loop and that is instantaneous and you can find out that you have crossed the limit or the safety limit defined for the device. It is only that you have to make a material which has the transition at the point which is defined by your requirement. So the value of H critical is defined by your device and you make a sensing material out of it. In addition to the classification of the materials we know that the magnetic induction B is given by $\mathbf{H+4\pi M}$ that is $\bar{\boldsymbol{\mu}}\mathbf{H}$ where $\bar{\boldsymbol{\mu}}$ is the permeability defined as the ratio of magnetic induction B to the applied field H and the permeability of vacuum of free space is μ_0 that is equal to $\mathbf{4 \times 10^{-7}}$ **Henry per meter**. Then you have relative permeability and that is defined as the ratio between the absolute permeability mu to the permeability of free space that is mu 0 and chi that is defined as the intensity of magnetization that is m to the magnetic field strength H.

So χ is equal to **M/H**. We already know that you have four quantum numbers which were required to define the origin of magnetic field. Those were the principle quantum number n, the azimuthal quantum number l, then you had the magnetic quantum number m_l and then you had the spin quantum number m s and electrons can have plus and minus values of spin that is up spin or down spin and m_s can take values of plus half or minus half. The spin with which electrons are actually represented, the orbital angular momentum and change in the orbital momentum induced by the applied magnetic field leads to the origin of magnetism in the materials. This is what we know. Now if you see the origin of permanent magnet dipoles, according to Ampere the magnetic dipoles have their origin in the flow of electric currents.

A stationary loop current flowing in a plane produces a magnetic field that at a large distance may be described as resulting from a magnetic dipole. That is μ if you write magnetic dipole moment $\boldsymbol{\mu = IA}$, where **I** is $\boldsymbol{-e\omega_0/2\pi}$ where ω_0 is the angular frequency and that will give $\boldsymbol{\mu = \frac{-e}{2m^*} m\omega_0 r^2}$ and $\boldsymbol{\mu = \frac{-e}{2m^*}}$ that is the angular momentum. So the minus sign indicates that the dipole is points in the direction opposite to the direction represented by the vector of angular momentum and this is valid for any electron orbit. So as I said you will have m, l, m_l and m_s the four quantum numbers which will define the nature of magnetization stabilizing in a material. The possible components of the angular momentum along any specified directions are determined by the magnetic quantum number m_l and if you see $\mathbf{m_l}$ can take values from l to -l that is **2l+1**, **l** can take values from 0 to **n** minus 1 where n is the principle quantum number, m s can take values as what plus half or minus half.

So the electron itself has a angular momentum known as its spin and the possible angular momentum component of the spin along an external field directions would be $\hbar/2$ and you have plus minus because they are either plus spin or minus spin. And the angular momentum and the spin add up vectorally to give the total angular momentum J. This is just the representation of what I said. So if you look into the splitting factor which is spectroscopic splitting factor what do you get? You have this splitting factor the gyromagnetic ratio defined as $\boldsymbol{g}$ you will find that the orbital angular momentum and the spin add up vectorally to give the total angular momentum J as we said earlier. Hence what is the consequence? For an electron with a certain l the total angular momentum would become l plus minus half.

In an atom you can have more than one electron. Hence l vector combines to form the resultant orbital angular momentum vector as capital L. This is called the Russell Saunders coupling. Similarly S vector combines to form the resultant spin angular momentum given as capital S vector. And the resultant l and s combine to form the total angular momentum J.

And you have the Landes g factor given as $\mathbf{1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+!)}}$. As we had been saying the whole concept was then easily understood when Pauli's exclusion principle was combining with Hund's rule and you understood that no two electrons in the same state can have the same quantum numbers. Which quantum numbers? n, l, m_l and m_s. So that is what Pauli's exclusion principle actually said. Therefore what happened for if you have this consideration you will find that when you write the electronic configuration for example for chromium which has z equal to 24 you get as the unfilled orbital as $3d^5$.

So this is the electronic configuration of chromium. Now if that is the case if you say chromium 2 plus then you have there is the presence of four unpaired electrons because paired electrons should have meant that they have the opposite spin electron also there. But it is not there so they are not there. So you have four unpaired electrons only in the 3d shell and therefore you have unpaired electrons and that is giving you the value of l and s. Now if you have an atom that is less than half occupied then J is equal to l - s that is equal to 0 you can see from the above equation.

So you can write for all combinations and you will be able to write the values of l and s and from there you can find the possible magnetic behavior of a material. So I hope I have given you the quick revision to the origin of magnetism, how you can make different materials which can be used in different devices and the use of Pauli's exclusion principle and Hund's rule to explain the arrangement of electrons in the orbits around the nucleus. These are the books which you can refer to for further understanding and I thank you for attending this lecture.