Nanomaterials and their Properties

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Lecture - 26
Optical Properties of Nanomaterials (I)

So, welcome to lecture number 26. Students and you know; so we have been discussing about the Properties of Nanomaterials for the last ten lectures. And so, couple of more will be going on for the properties of nanomaterials. As I have been interacting with you during online sessions, I found that some of these topics are not easy for you to understand; because you may not have read or probably have been exposed to these topics.

I would like to tell you one thing very clearly, nanomaterials is indeed the subject of multidisciplinary nature; that means it encompasses fields of physics, chemistry, engineering, biology. So, therefore, it is not possible for you to understand everything when you study this subject at the first time; but you must make an effort to learn as much as possible, that is will be my you know suggestion to you for this.

Today we are going to discuss about mostly about that the optical properties of material.

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In the last lecture, we completed our discussion on the Magnetic Properties of Materials. We shall start a new topic on Optical Properties of Nanomaterials.

Recap:

Effect if size on coercivity and Remanance

Superparamagnetism vs Superferromagnetism

And on the last lecture, we completed our discussions on the magnetic properties of materials. And we shall start a new topic on optical properties of nanomaterials. Before that, we need to have some recap, you know what we did? We just talked about the effect of size on the two important properties that is coercivity and remanance.

And then we also deliberated on superparamagnetism as well as super-ferromagnetism, how the size can make an strong effect on the evolution of these new properties. Super word means high or extra right; the superparamagnetism means very extreme level of paramagnetism or superferromagnetism means extreme level of ferromagnetism.

Please do collect your questions and keep it for the interaction sessions; in fact, I must tell you, I am not satisfied with the interaction sessions, I expect you to ask me more questions, so that we can discuss and learn more on these subjects. Well, you know magnetic materials divided into diamagnetic, paramagnetic, Ferro or ferrimagnetic based on the magnetic moments, ok.

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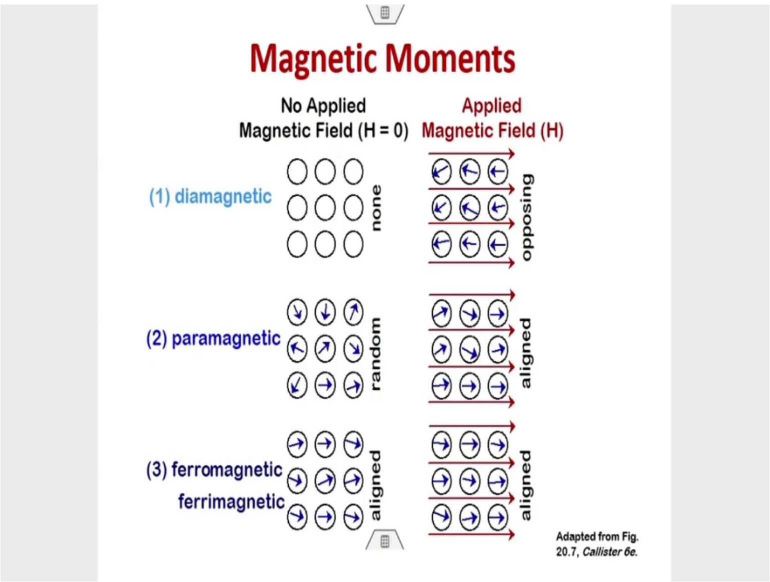

Magnetic Moments

Adapted from Fig. 20.7, *Callister 6e.*

So, when you apply magnetic field vis a vis when you do not apply magnetic field; in diamagnetic materials, effect is not at all significant. Zero magnetic field, there will be no effect; when you apply magnetic field, the diamagnetic materials normally oppose the magnetic field. That is why we call this materials, we do not discuss much of these materials, that is what something you should remember that.

But that is not the only issue about super the paramagnetism, diamagnetism; there you know all the metal in the world show some kind of a diamagnetic behaviour, because of the spin, electron spin around the nucleus. Now, second class of material is paramagnetism, the paramagnetic. In absence of magnetic field, they show random spin alignments; but when you apply magnetic field, there is some kind of alignment happens, but alignment is weak. So, therefore, magnetic moments are very weak.

So, normally they are not useful, the useful magnetic materials are ferro or ferromagnetic; in case of both, these materials the spins aligned for both zero and nonzero magnetic field. And for the nonzero magnetic field, spins can be aligned in a particular directions very nicely; this can lead to very high magnetic moments and these are used.

Difference between ferro and ferri in terms of strength of these you know up and down spins of these materials that we have discussed already.

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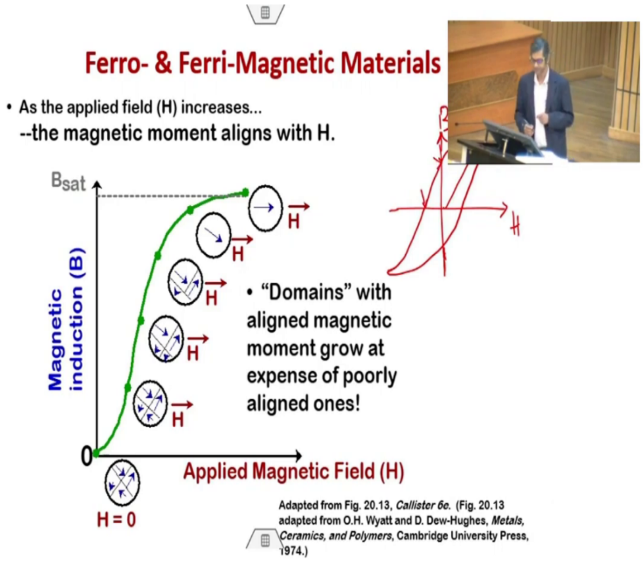

Ferro- & Ferri-Magnetic Materials

- As the applied field (H) increases...
  --the magnetic moment aligns with H.

Adapted from Fig. 20.13, *Callister 6e.* (Fig. 20.13 adapted from O.H. Wyatt and D. Dew-Hughes, *Metals, Ceramics, and Polymers*, Cambridge University Press, 1974.)

So, by the way for the ferromagnetic materials, if you apply field; the magnetic induction happens and the magnetic interaction follows a certain specific trend. So, basically this has happened because of the alignment of the domains or the spins in a part in a along the applied field directions. And the domain with aligned magnetic fields moment, magnetic moment grow at expense of poorly aligned ones.

So, that is why initially it rises and then it reaches the saturation when the all the magnetic moments aligned to the direction of the applied field and this is very common. And this leads to what is known as the B-H loop, we popularly call; this is H and you fill this induction.

So, you see this is what is shown here and then it goes back like this ok and it comes back like that. So, that is the magnetic loop; depending on the size of this loop, we can actually have soft or hard magnetic material. Soft magnetic materials will have very thin loop with a small value of coercivity ok; this is what is known as the coercivity and this is what is known as the remanence magnetic field right; that we know.

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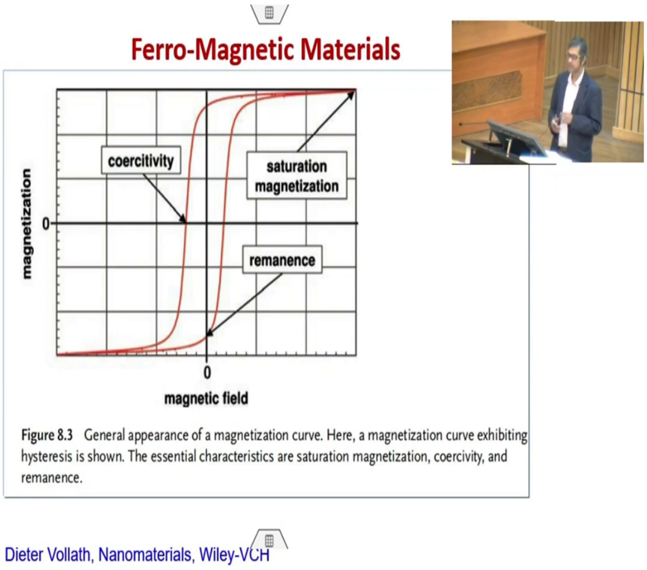

Ferro-Magnetic Materials

Figure 8.3 General appearance of a magnetization curve. Here, a magnetization curve exhibiting hysteresis is shown. The essential characteristics are saturation magnetization, coercivity, and remanence.

Dieter Vollath, Nanomaterials, Wiley-VCH

So, this is all the important things, saturation reaches once you value apply certain field; then you have a coercivity, coercivity is the negative field required to demagnetize the material, remanence is when the field is 0, some amount of magnetic moments remained that is what is (Refer Time: 06:04). This is general appearance of magnetization curve, magnetization curve exhibiting hysteresis loop shown there and the important parameters already I have told about it, ok.

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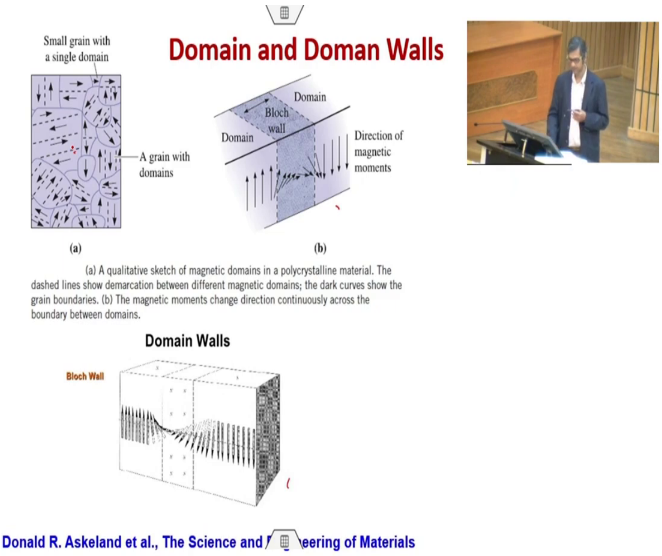

Domain and Doman Walls

(a) A qualitative sketch of magnetic domains in a polycrystalline material. The dashed lines show demarcation between different magnetic domains; the dark curves show the grain boundaries. (b) The magnetic moments change direction continuously across the boundary between domains.

Domain Walls

Donald R. Askeland et al., The Science and eering of Materials

So, now why does it happen? As we discuss this is because of the domain alignments to the field. And you know domains cannot be very large then it is energetically very expensive. So, there will be there will be domain of walls. So, what is known as a Bloch walls. And in Bloch walls actually demarcate the spin reversal ok, a spin change; as you can see here in this case also in this case also.

So, in a multi grain materials or a poly grain materials, you can have spins aligned in different way in one grain itself; like you could see here if the grain size is pretty big. And that means, what in the grain you can have several domains presence and each domain correspond to certain domain wall and they differentiate by domain wall. So, therefore, there is a energy associated with it and that is something which is very important.

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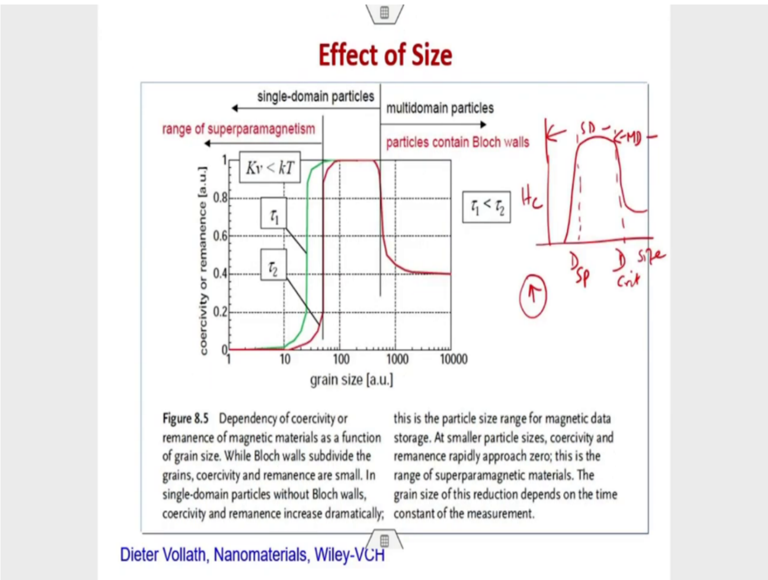

Effect of Size

Figure 8.5 Dependency of coercivity or remanence of magnetic materials as a function of grain size. While Bloch walls subdivide the grains, coercivity and remanence are small. In single-domain particles without Bloch walls, coercivity and remanence increase dramatically; this is the particle size range for magnetic data storage. At smaller particle sizes, coercivity and remanence rapidly approach zero; this is the range of superparamagnetic materials. The grain size of this reduction depends on the time constant of the measurement.

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So, that means when you apply, when you talk about effect of size what actually happens; big size there is no effect ok, there is only both coercivity and the remanence, there is no effect. But as the size, because they are very big particles and they have large number of domains present in each of these grains.

So, therefore, the both the coercivity, remanence does not change much with the grain size; but there is as you know range below which both of them should stop. Why? That is because then your particle size become very small and each of these single particles will become a single domain particle right; that is what it is, the single domain particle happens.

And then the there is no domain of wall exists between the in the particle; because these are all single size is so small that, the one domain is one particle. So, because of that, remanence and the coercivity increases very rapidly and reaches a very high value, correct. But as you reach a smaller size than that, the thermal effect comes into picture, ok.

So, remember this alignment of the spin is basically treated by the magneto crystalline anisotropy right; that is nothing but equal to K×v, v is the volume, K is the magneto crystalline anisotropy parameter. But at the same time, we have a thermal effect coming into picture; because of temperature, the thermal randomness try to play a role and this can make the spins misaligned ok or spins to be randomly aligned, it can randomize the spins basically the effect of temperature is.

And this can lead to reduction of the alignment of the spins in a direction of the field and that can lead to reduced reduction of the as the coercivity remanence drastically. In fact, it can reach zero value also below a certain size little size. So, that is what is very important and that is what is we have been talking about it, you know a lot and you must remember that this size thing is very critical here; I am plotting it again here, this is what is suppose the coercivity and this is a size, ok.

So, as you see here what will happen is like this; you have a no change, then drastic rise and then there is a decrease automatically. So, that means, there is a two domains or critical size; one is called D critical, below which the single particles becomes single spin particle ok and there is a size, below which superparamagnetism happens, that is what. So, these are the multi-domain particle and these are the single domain particle, ok.

So, this single domain particles once they align, spins align in a particular directions; thermal effects can make them misaligned and this can lead to reduction of the coercivity at remanence.

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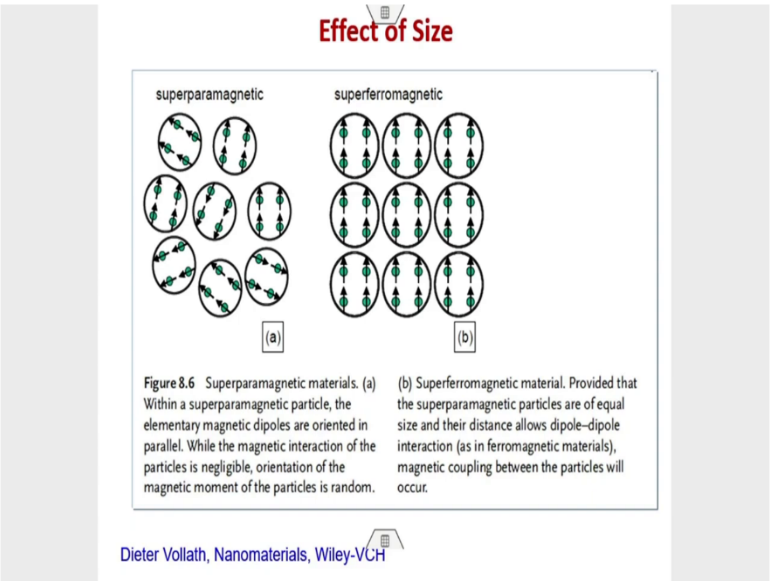

Effect of Size

Figure 8.6 Superparamagnetic materials. (a) Within a superparamagnetic particle, the elementary magnetic dipoles are oriented in parallel. While the magnetic interaction of the particles is negligible, orientation of the magnetic moment of the particles is random. (b) Superferromagnetic material. Provided that the superparamagnetic particles are of equal size and their distance allows dipole–dipole interaction (as in ferromagnetic materials), magnetic coupling between the particles will occur.

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This is what is shown here; in a superparamagnetic material you can see, the spins are you know in each particle aligned differently and therefore, they do not add up to the magnetic moments, ok. Within a superparamagnetic particle, the elements of magnetic dipoles are oriented parallel; but while magnetic interaction of the particle negligible, orientation magnetic moments of the particles are random. And this randomness leads to substance reduction of the coercivity.

On the other hand you can have superferromagnetic material, which can also possible in this domain ok, in this domain here ok, in this domain. So, there the superparamagnetic materials particles are equal size and their distance allow them dipole interaction.

That means, each of these dipoles can interact with each other and make them align in one directions without any randomness. And this can lead to huge increase of remanence of the coercivity; that has been observed and superferromagnetism also has been observed. Well, that is about the recap of magnetic materials. Now, we go into ok, ok by the way, yes.

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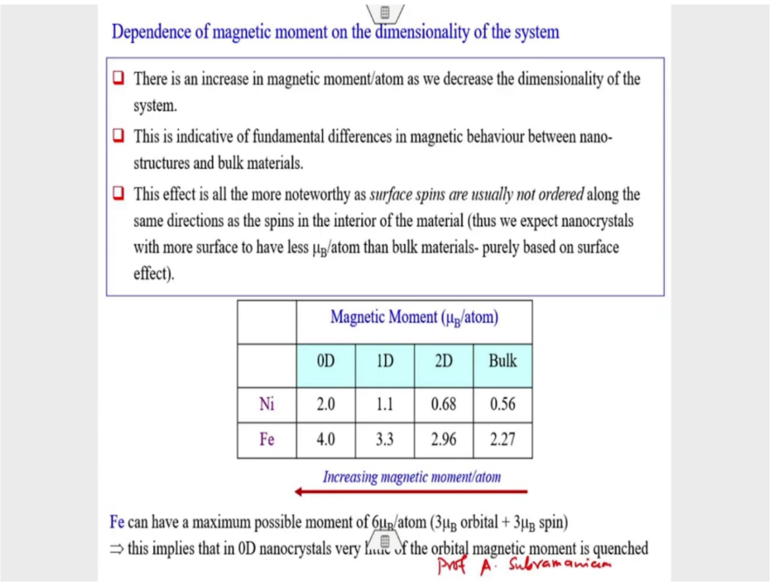

Dependence of magnetic moment on the dimensionality of the system

- ❑ There is an increase in magnetic moment/atom as we decrease the dimensionality of the system.
- ❑ This is indicative of fundamental differences in magnetic behaviour between nano-structures and bulk materials.
- ❑ This effect is all the more noteworthy as *surface spins are usually not ordered* along the same directions as the spins in the interior of the material (thus we expect nanocrystals with more surface to have less μ_B/atom than bulk materials- purely based on surface effect).

	Magnetic Moment (μ_B/atom)			
	0D	1D	2D	Bulk
Ni	2.0	1.1	0.68	0.56
Fe	4.0	3.3	2.96	2.27

Increasing magnetic moment/atom

Fe can have a maximum possible moment of $6\mu_B$/atom ($3\mu_B$ orbital + $3\mu_B$ spin)

⇒ this implies that in 0D nanocrystals very little of the orbital magnetic moment is quenched

Prof A. Subramaniam

Let me give you some example also, because this is something, which is very important. These slides are taken from Professor Anand Subramaniam of our department; he has put his on his website, ok. A you see here for nickel iron, when you have a size 0 D, 1 D and 2 D and bulk; you can see from bulk to 0 D magnetic moment is increasing very very significantly, this is given as Bohr magneton per atom, iron is effect is even more substantial, ok.

So, if you can have a maximum possible moment of 6 Bohr magneton per atom, 3 orbital and 3 spin; by the means what, the 0 material is very I, basically it gives you the limit orbital magnetic moment, ok. So, that means what? Effect is very significant for this you know type of materials which are predominantly ferromagnetic.

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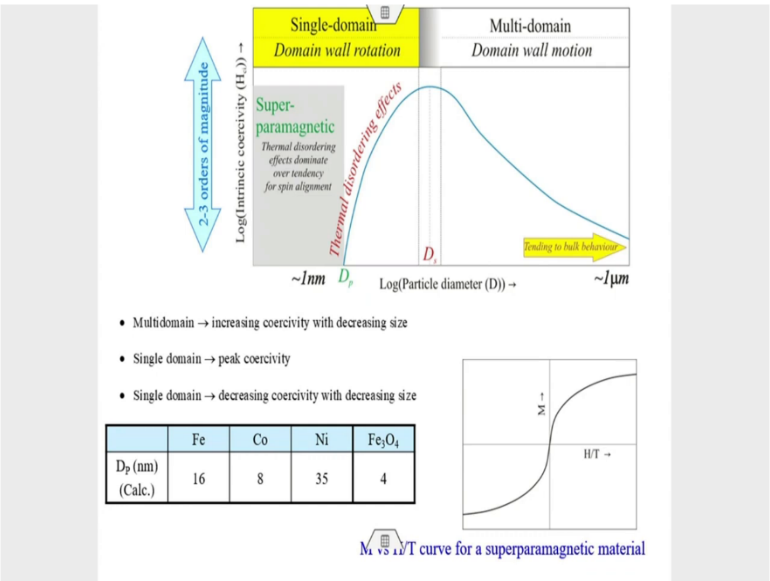

- Multidomain → increasing coercivity with decreasing size
- Single domain → peak coercivity
- Single domain → decreasing coercivity with decreasing size

	Fe	Co	Ni	Fe_3O_4
D_P (nm) (Calc.)	16	8	35	4

M vs H/T curve for a superparamagnetic material

Well, this is again shown in a very nicely manner, ok. You can see the bulk behaviour, then it is increases; super ferromagnetism behaviour comes in picture, then the thermal disorder takes in over and then what is happens, the coercivity goes to zero.

So, these D p is correspond to superparamagnetism and D s is called the single domain particle that is lead to superferromagnetism basically. And for the superparamagnetic material you have a B-H loop like this; because there is no remanence or there is no coercivity. So, therefore, there is no possibility of any B-H loop in these cases.

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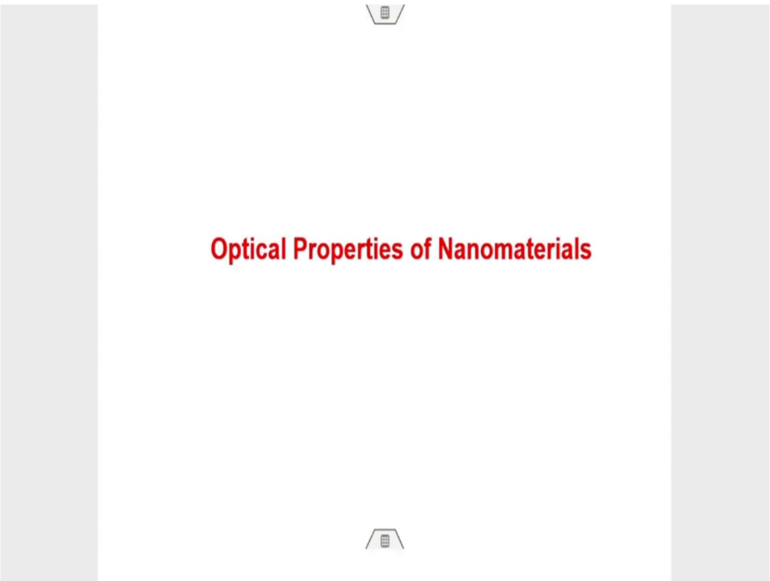

Optical Properties of Nanomaterials

Well, that is about the magnetic materials, we have spent about 12 to 15 minutes on that, let us talk about a optical properties. Let me first tell you how I am going to discuss about this at this particular topic or particular aspects. First I am talking about some aspect of general, some aspect of optical properties of materials; then I will look into the size effect ok, because I understand some of you may not have exposed to optical properties extensively.

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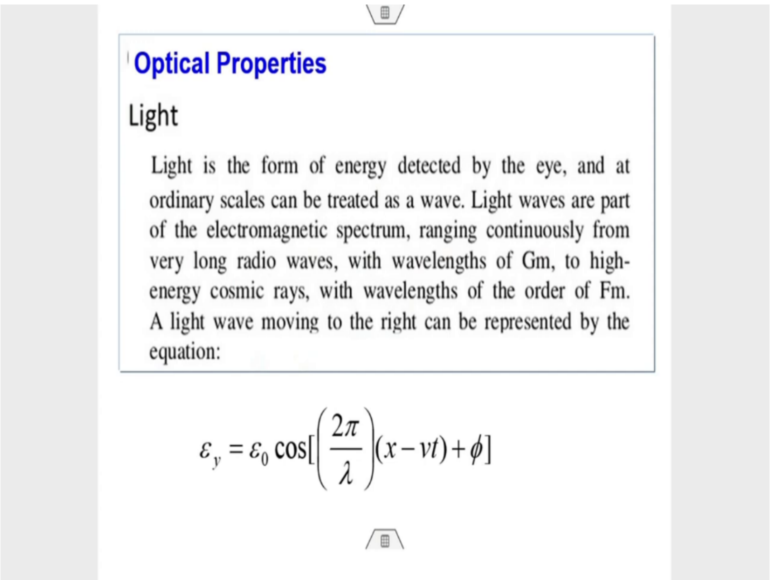

Optical Properties

Light

Light is the form of energy detected by the eye, and at ordinary scales can be treated as a wave. Light waves are part of the electromagnetic spectrum, ranging continuously from very long radio waves, with wavelengths of Gm, to high-energy cosmic rays, with wavelengths of the order of Fm. A light wave moving to the right can be represented by the equation:

$$\varepsilon_y = \varepsilon_0 \cos[\left(\frac{2\pi}{\lambda}\right)(x - vt) + \phi]$$

Well, you know optical properties are something to do with light. Light is what? Light is a form of energy detected by an eye by the eye, and at ordinary scales can be treated as a wave basically. It is just nothing but a wave we know; light waves are basically part of electromagnetic spectrum, which we will see soon.

And you know then it has many, basically it is can be described using an equation like this; $\varepsilon_y=\varepsilon_0 \mathrm{Cos}[(\frac{2\pi}{\lambda})(x\text{-}vt)+\phi]$

So, that is what is the light can be described as a wave formalism, but light also is can be considered to be a particle issue as you know; in quantum mechanics light is considered as a particle and so therefore, but in this case of optical properties mostly it is considered to be a wave.

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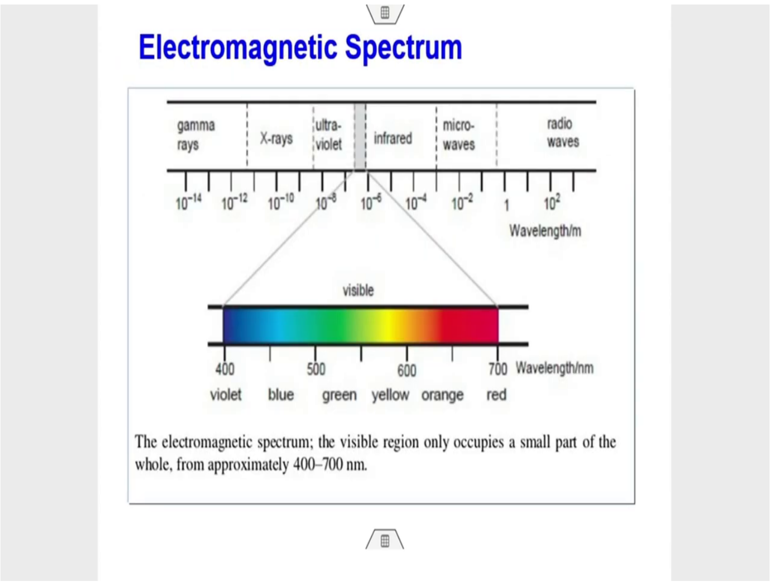

Electromagnetic Spectrum

The electromagnetic spectrum; the visible region only occupies a small part of the whole, from approximately 400–700 nm.

What is the electromagnetic spectrum by the way? It starts from radio waves to gamma rays; radio waves can be very big like meters, even it can reach actually 1 to 100 meters and then you can have microwaves, which is in the range of centimetres. If infrared which is in the mid which is say micrometre to centimetre millimetres and then you have ultraviolet X-rays and gamma rays.

But in between this infrared and ultraviolet we have light waves, ok. The wavelength varies from 700 to 400 nanometres; 700 correspond to red, which is the highest wavelength possible and 400 corresponded to basically violet. So, electromagnetic spectrum has these small range.

So, one is that we can we have visible lights or lights can be, the colours can be seen by our naked eyes. Well, then, but in a nutshell it can also include when you are talking about optical properties of nano materials can also include ultraviolet also. But it will not include X-rays, infrared, microwaves, gamma rays ok, when we are discussing about optical properties of nanomaterials. Please keep in mind those aspects.

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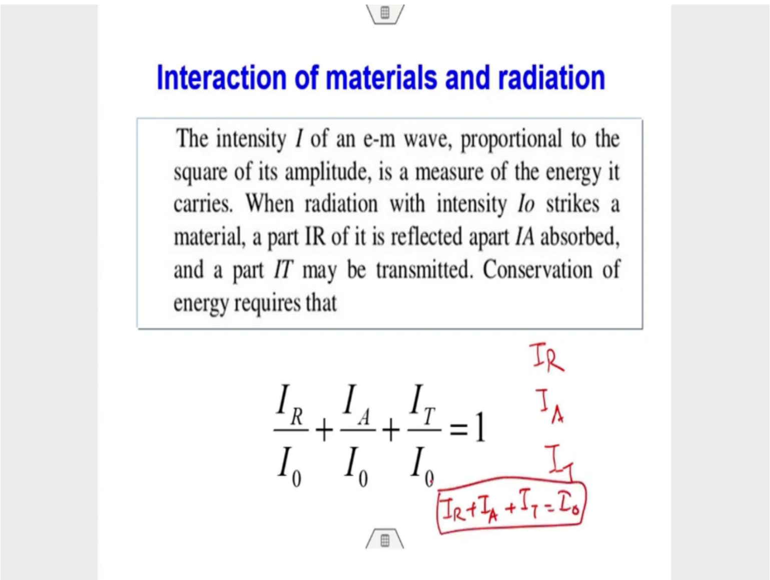

Interaction of materials and radiation

The intensity *I* of an e-m wave, proportional to the square of its amplitude, is a measure of the energy it carries. When radiation with intensity *Io* strikes a material, a part IR of it is reflected apart *IA* absorbed, and a part *IT* may be transmitted. Conservation of energy requires that

$$\frac{I_R}{I_0}+\frac{I_A}{I_0}+\frac{I_T}{I_0}=1$$

I_R

I_A

I_T

$\boxed{I_R+I_A+I_T=I_0}$

Well, you know how does the material and the radiation interact. You know when any electromagnetic wave falls on somebody or some material with the intensity I and its intensity depends on the amplitude square of you know wave, wave has a amplitude, an amplitude square is what is gives you the intensity and you know. So, therefore, the intensity tells you the measure of energy the wave carries.

So, when the radiation is intensity I_0 strikes a material, a part of radiation basically reflected part is absorbed and part is transmitted. So, these things means I_R is basically corresponded to reflection, I_A is absorbed and I_T is transmitted this is what happens.

So, $\frac{I_R}{I_0}+\frac{I_A}{I_0}+\frac{I_T}{I_0}=1$; that means what, whatever the total radiation falling on any substance or any material it is going to be either absorbed, reflected or transmitted. But these three added intensities will be equal to intensity corresponding to incident beam ok; that is very clear ok, that is something must happen, otherwise energy will not be conserved.

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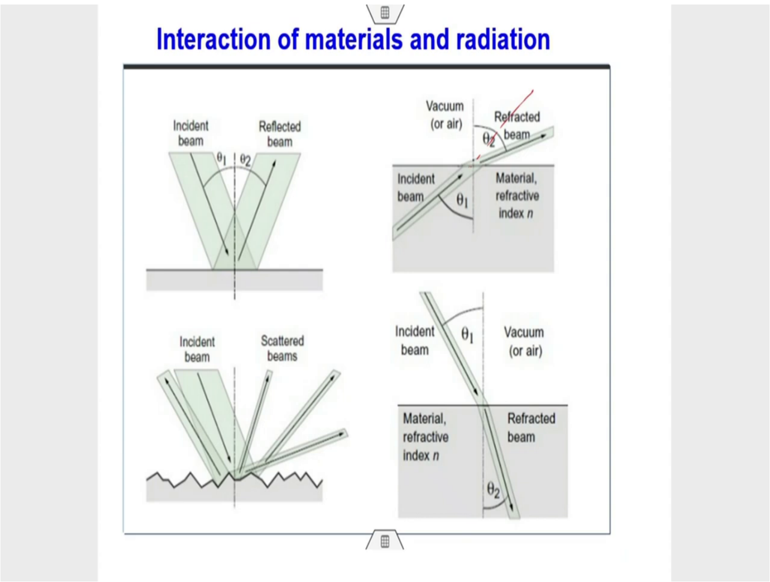

Interaction of materials and radiation

So, how it interacts? If it reflects you know light falls at an reflect at an angle and then reflects with the same angle. If it is refract, light falls on this interface then it is the direction of changes ok, you can change that, ok right. It can also have both reflection and refractions and on a basically rough surface reflection will happen in different angles, ok. So, therefore, depending on whatever things happening, it can be described in this form and in this way how the interaction happens.

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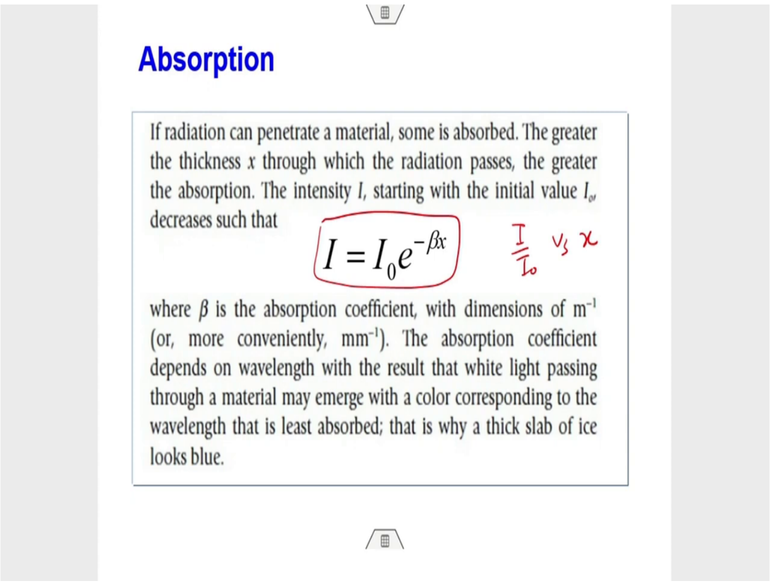

Absorption

If radiation can penetrate a material, some is absorbed. The greater the thickness *x* through which the radiation passes, the greater the absorption. The intensity *I*, starting with the initial value I_o, decreases such that

$$\boxed{I = I_0 e^{-\beta x}} \quad \frac{I}{I_0} \text{ vs } x$$

where β is the absorption coefficient, with dimensions of m^{-1} (or, more conveniently, mm^{-1}). The absorption coefficient depends on wavelength with the result that white light passing through a material may emerge with a color corresponding to the wavelength that is least absorbed; that is why a thick slab of ice looks blue.

So, then next important thing is that the absorption, that is about reflections and they are refractions. Radiation can penetrate any material; if it is can be penetrated, then only it can be absorbed, right. So, greater the thickness through which the radiation is passes through greater is the absorption.

This is something also very interesting; the larger is the thickness through which the a light is passing through, more will be absorption. So, therefore, intensity of light which is starting with initial value I_0 can decrease basically by this equation $I=I_{0e}{}^{-\beta x}$; this is very-very standard equations which has been followed in optics for long time.

And here beta is nothing but the absorption coefficient. So, that means a basically if I plot I/I_0 versus x, this will be exponential curve with negative sign; because β is the absorption coefficient is a value positive value. The absorption coefficient depends on basically wavelength of the light passing through the material with the colour corresponding to wavelength.

That is least absorbed, that is why thick slops slabs of ice looks blue ok; thicker the slabs, it absorbs more, therefore it absorbs more means you have blue of light will be coming out of it, ok. So, that is something which is very common. So, you understand that, this is the absorption equation which is normally used in most of the kind of experiments.

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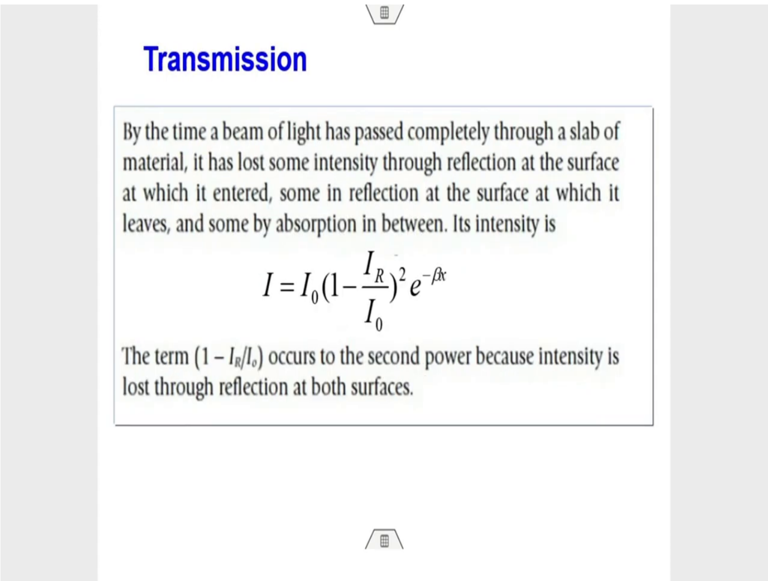

Transmission

By the time a beam of light has passed completely through a slab of material, it has lost some intensity through reflection at the surface at which it entered, some in reflection at the surface at which it leaves, and some by absorption in between. Its intensity is

$$I = I_0(1-\frac{I_R}{I_0})^2 e^{-\beta x}$$

The term $(1 - I_R/I_0)$ occurs to the second power because intensity is lost through reflection at both surfaces.

So, what about transmissions? Ok. So, we have discussed about reflections, we have discussed about absorption, we have discussing about now transmission. By the time a beam of light has passed completely through a slab of material, it must have lost some intensity because of reflections, the surface which is entered and also because of absorption in between.

So, it intensity will be obviously, like this ok; you can clearly see, this equations comes, I= $I_0(1-\frac{I_R}{I_0})^2 e^{-\beta x}$ ok, the second part, because intensity loss to reflections by the both surfaces ok, that is why. So, that is why it has to be multiplied twice, that is what a square come, ok. I_R is cosmic reflections and I_0 exponential beta is basically absorptions ok, you understand that, right.

So, this is very simple equation, but normally you have not seen it; that is something which you should remember it and I have explained also why this square comes into picture.

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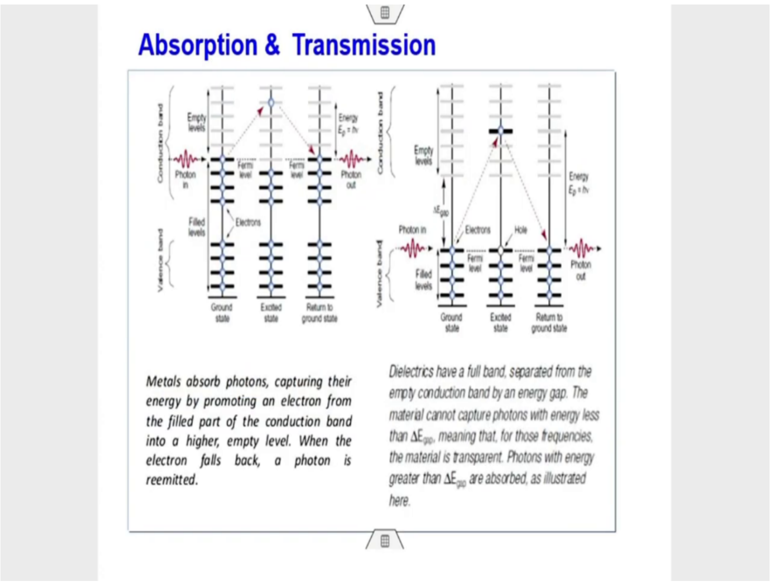

Absorption & Transmission

Metals absorb photons, capturing their energy by promoting an electron from the filled part of the conduction band into a higher, empty level. When the electron falls back, a photon is reemitted.

Dielectrics have a full band, separated from the empty conduction band by an energy gap. The material cannot capture photons with energy less than ΔE_{gap}, meaning that, for those frequencies, the material is transparent. Photons with energy greater than ΔE_{gap} are absorbed, as illustrated here.

So, now, let us talk about this absorption and transmission effect in a material. What happens in a material? Metals normally absorbs photons, because metals have lot of free electrons; these electrons are not localized and they are not bound to a particular atom.

So, they are like a free electron gas. So, the metals can absorb easily photons, capturing the energy by promoting the electrons from a filled part of the conduction band with a higher, empty level, that is what happen. If it photon, this electron will absorb this photon and go to the higher part of the conduction band, ok.

And when the electron then falls back, a photon is reemitted, that is what you see here correct; that is what the interaction happens when it is absorbs and it is re-emits, ok. And emission energy will be same as like the decrease of the energy, because of the this jump from the higher to the lower.

Now, dielectrics ok like basically insulators, they have full band; that means they are their valence band is full, conduction band is empty right, that is what happens. So, what happens when you put when you basically shine them with a light, so there what will happen? Material cannot capture any photon, ok.

So, therefore, it cannot capture photons with energy less than delta gap ok; the gap whatever is the between the valence and the conduction band, it cannot absorb. So, meaning that for those frequencies material is transparent, ok. If you up, if you are shining the lights with frequency corresponding to energies less than E gap; then it will not absorb, it will allow it to transmit through. But it is better; because why to absorb the energy, which are not going to be useful, right.

So, that means the material will be transparent to those frequencies; but photons with energy greater than delta E gap will be absorbed and then it can the electron will go to higher energy level in the conduction band. And once the electron jumps back with valence band, energy is released; this is something which is very frequently absorbed in materials.

So, you can see that optical properties of bulk materials can be explained very easily using these band theories of electrons, the conduction and the valence bands.

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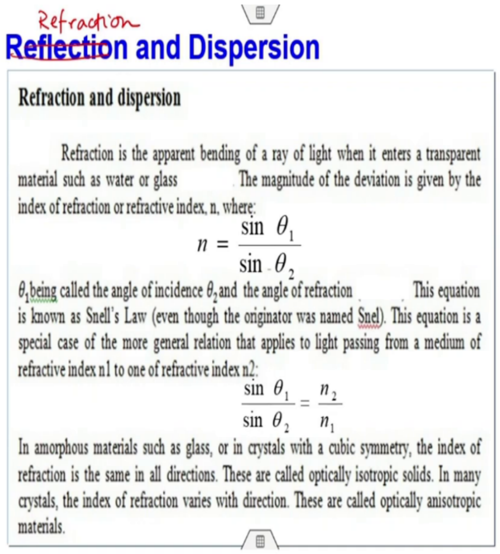

Refraction

~~Reflection~~ and Dispersion

Refraction and dispersion

Refraction is the apparent bending of a ray of light when it enters a transparent material such as water or glass The magnitude of the deviation is given by the index of refraction or refractive index, n, where:

$$n = \frac{\sin\theta_1}{\sin\theta_2}$$

θ_1 being called the angle of incidence θ_2 and the angle of refraction This equation is known as Snell's Law (even though the originator was named Snel). This equation is a special case of the more general relation that applies to light passing from a medium of refractive index n1 to one of refractive index n2:

$$\frac{\sin\theta_1}{\sin\theta_2} = \frac{n_2}{n_1}$$

In amorphous materials such as glass, or in crystals with a cubic symmetry, the index of refraction is the same in all directions. These are called optically isotropic solids. In many crystals, the index of refraction varies with direction. These are called optically anisotropic materials.

Well whatever reflections and dispersions; reflection also important, reflection refraction not reflection, refraction I am sorry, this is wrong. This should be refraction; refraction is apparent binding of ray of light when it enters a transparent medium, such as a water or glass, ok.

The magnitude deviation is obviously given by the refractive index and that is nothing but $n_1 = \sin\theta_1/\sin\theta_2$.

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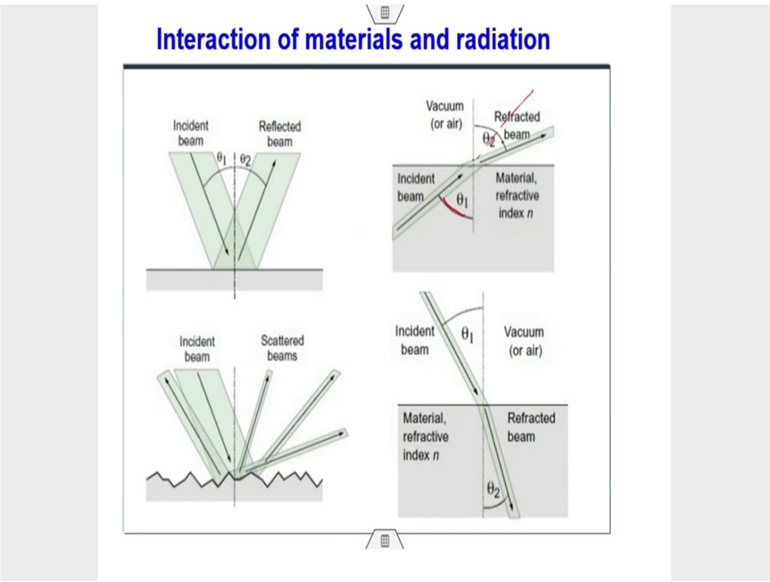

Interaction of materials and radiation

You could have seen this picture ok; this is sin theta 1 and sin theta 2 ok, that is this what it tells you about it. The equation is known as the Snell's law, all of you have studied in class two physics or maybe in class tenth standard; this equation is a special case of general relations that applies to light passing through the medium or refractive index n_1 to n_2, that is nothing but $\sin\theta_1/\sin\theta_2 = n_2/n_1$.

In amorphous material such as a glass or a crystal with a cubic symmetry, index of refraction is same in all directions; there is no difference of refractive index because of crystallographic directions. They are called optically isotropic solids, but some other crystal basically, this is not show. So, they are called optically anisotropic materials.

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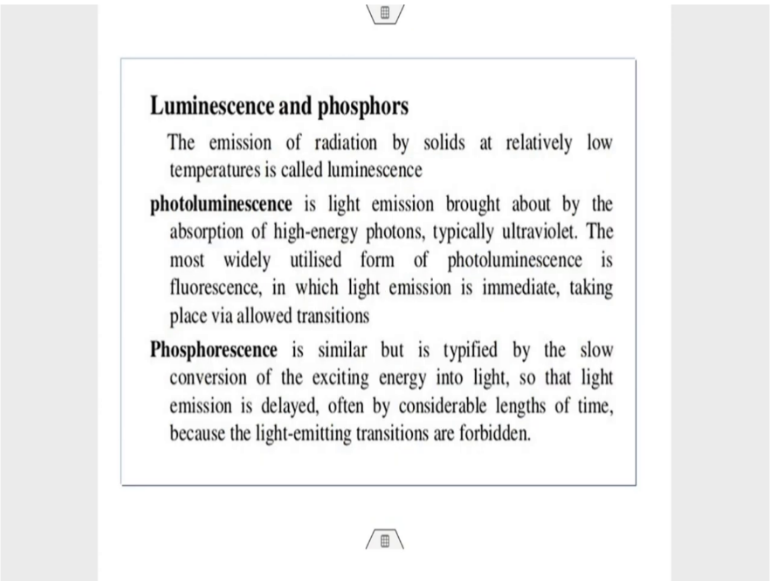

Luminescence and phosphors

The emission of radiation by solids at relatively low temperatures is called luminescence

photoluminescence is light emission brought about by the absorption of high-energy photons, typically ultraviolet. The most widely utilised form of photoluminescence is fluorescence, in which light emission is immediate, taking place via allowed transitions

Phosphorescence is similar but is typified by the slow conversion of the exciting energy into light, so that light emission is delayed, often by considerable lengths of time, because the light-emitting transitions are forbidden.

So, that is about the refraction and dispersions. Now, you also have luminescence and phosphorescence; emissions of radiation by solid at relatively low temperature is called luminescence. Photoluminescence is what? The light emission brought about by absorption of high energy photons, typically ultraviolet rays. The most widely utilized form of photoluminescence is fluorescence, in which light emission is immediate and taking via allowed transitions.

Phosphorescence is what? This is similar to this photoluminescence, but is typified by the slow conversion of the excitation energy into light. In this photoluminescence it is immediate ok; this it is not be slow, it will be very immediate, but in case of phosphorescence it is slow.

Like those of you have seen the you know any microscope, scanning electron microscopes or maybe trans electron microscope; electron falls on a white screen and then you see their pictures, this is nothing but the phosphorescence. You have a phosphorous screen with you with which the electron interacts and then it gives you light.

So, the light its emission is delayed here in case of phosphorescence and that is basically because of the light emitting transitions some are formatting. Some are allowed, some are not forbidden and that is makes the deliver photoluminescence, is empty number of light emission modes available, so that is why it is immediate, ok.

These are the three things two things you must remember ok, they are not same; some of you always will tell photoluminescence and phosphorescence are same, these are not basically same well.

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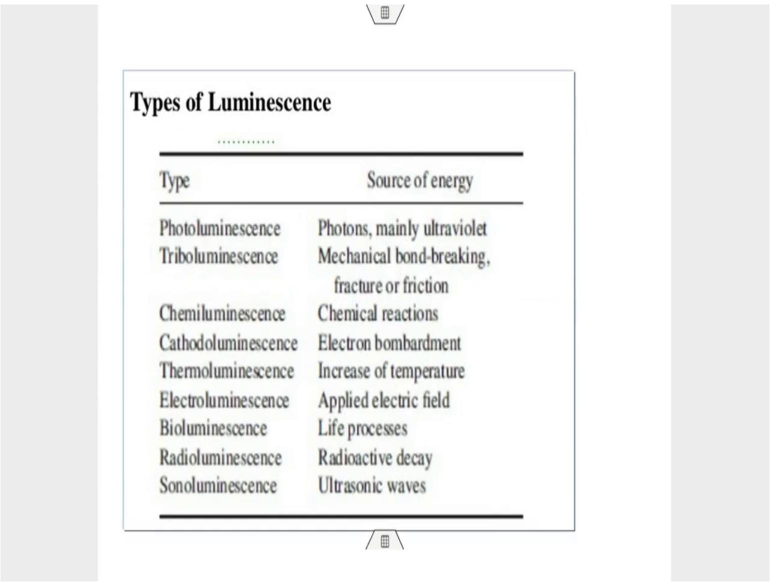

Types of Luminescence

....

Type	Source of energy
Photoluminescence	Photons, mainly ultraviolet
Triboluminescence	Mechanical bond-breaking, fracture or friction
Chemiluminescence	Chemical reactions
Cathodoluminescence	Electron bombardment
Thermoluminescence	Increase of temperature
Electroluminescence	Applied electric field
Bioluminescence	Life processes
Radioluminescence	Radioactive decay
Sonoluminescence	Ultrasonic waves

There are different types of luminescence; photo luminescence, tribo luminescence, chemiluminescence, cathodoluminescence, sonoluminescence depends on the source of energy. So, you have radioactive sources the decay is the main thing it is called radioluminescence; if it is applied electric field is called electroluminescence, all kinds of luminescence are possible depending on the energies, ok.

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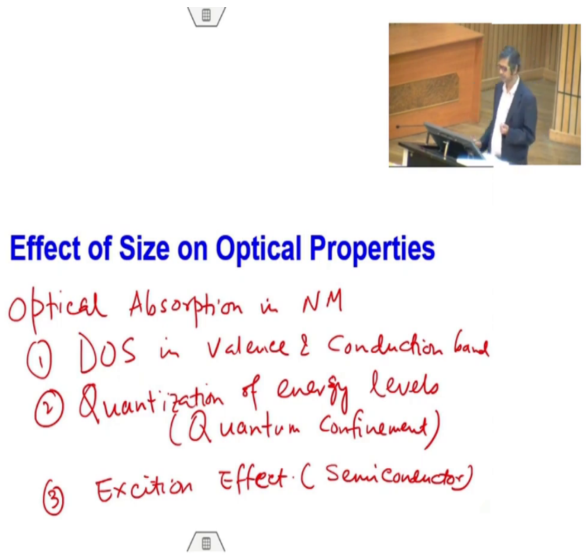

Effect of Size on Optical Properties

Optical Absorption in NM

① DOS in Valence & Conduction band

② Quantization of energy levels
(Quantum Confinement)

③ Excition Effect (Semiconductor)

So, that is something which gives you some amount of introduction to the subject. Now, optical properties of material, size effects. Well, by the way optimum size effect comes into pictures in three ways ok for the nanomaterials. What are the these things? There are three things happens in nanomaterials and basically optical absorption are always associated with three important aspects.

Optical absorption in nanomaterial let me write it in NM, it depends on three factors, ok. First, one is, first one is the density of states in valence and conduction band; we already have discussed that, density of states or DOS in valence and conduction band, right.

Second one is what? Second one is basically what is known as a quantization of energy levels or quantization, sorry quantization of energy levels right; in a nutshell this tells you the quantum confinements, energy levels or I write down quantum confinement, right. And third aspect is what? Third aspect is a new thing; it is exciton effect, which is new which I have not discussed so far and this is mostly happens in case of semiconductor.

So, dos you know that density of states in valence and conduction band bands, that is what dictates the electronic transitions and electronic transitions are basically responsible for optical spectrum, optical absorption, ok. And the nanomaterials you can have quantum confinement effects; because of the size or because of the dimension of the nanomaterials, that has a strong role to play and third thing is exciton.

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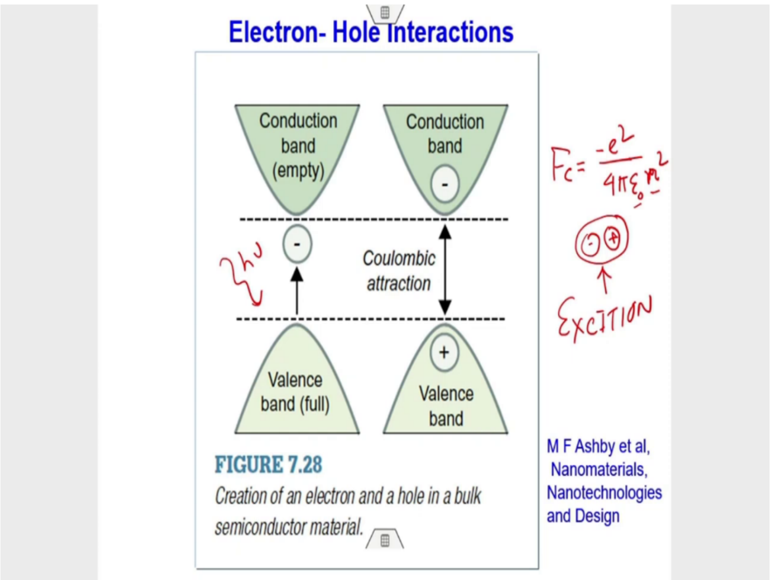

Electron- Hole Interactions

FIGURE 7.28

Creation of an electron and a hole in a bulk semiconductor material.

$F_c = \frac{-e^2}{4\pi\varepsilon_0 r^2}$

EXCITION

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So, first let us talk about what is exciton, ok. What is it? You know let us talk about a semiconductor with a certain band gap; that is it is easy to understand because of semiconductor that is what I am taking the example, otherwise I could have taken the examples of insulator, ok.

So, as we know, semiconductor has a band gap and this is gone given shown here this band gap, right. So, therefore, if I have incident photon energy, which is higher than the band gap what will happen; electron will be excited from the valence band and then it can jump into the conduction band, which is mostly empty in case of semiconductors ok at room temperature or low temperature, they are the empty mostly.

So, photon energy is higher than this band gap; electron and the valence band absorb the photon energy and then excited to the conduction band, correct. So, and under these conditions, photon is absorbed very easily correct, with a while a hole is left in the valence band. Once the electron leaves the valence band, if it leaves a hole gap. So, if inversely an electron in the conduction bands returns; suppose electron in the conduction band returns to the valence band, what will happen? Ok.

So, it will recombine the hole the which is present there and then photon is released with the energy equal to the same as the band gap of the semiconductor. So, these two things can happen easily; the moment you have a photon energy, which is more than the band gap.

So, photon energy can excite the electrons and valence band and then it can go to the conduction band, ok. So, one is goes to a conduction band, leaves behind a hole in the valence band, right. Similarly, the electron in the conduction band can jump back to the valence band, recombining the hole, leaving away the photon energy; this is very standard thing can happen in a bulk material like a semiconductor, am I clear.

Now, question is, how about low temperature what has been observed for the bulk summary on semiconductors; you know it shows often this optical absorption, just now we discussed absorption of these optical you know photon at a just below the band gap.

It you do not need to excite these electrons in the valence band by energy or the photon higher than or equal to the band gap. It can actually get excited even very lower than or very close to the energy band gap, just below actually, just below the band gap energy.

So, this something which is against the intuition, just now I told you; why does it happen? Well, this process is basically leads to a new concept; that is why it happens. What this process? So, it is a formation of an electron and a hole bound to each other ok, am I clear. This process basically because it is happening at energy level lower than the below the just below the band gap; this can lead to formation of a species, which combines electron and the hole.

And this bounding state of electron on hole is known as a exciton ok, this is what is known as a exciton, ok. So, you understand that. So, that means electron and hole can bound each other; they do not you know recombine and produce a photon energy, they just bound each other and remain there.

As per the many particle, exciton has mobility; obviously it can even this whole thing can move as a recombined, as a as a combined thing, not a recombined thing combined thing. And binding between this electron hole is because of the electrostatic things; electric charge between the electron and the negative charge and the whole positive charge.

So, therefore, the you know coulombic energy is nothing but $F_e = \frac{-e^2}{4\pi r^2 \epsilon_0}$, right. So, here e is electronic charge, epsilon naught is basically dielectric constant for the free space and r is the separation distance between the electron hole.

So, it basically tells you an electron and a hole can remain together without recombining and that is what is known as a exciton. The reason they remain together is because there is a bonding, electrostatic bonding between them; positive charge of the hole and negative charge of the electrons, they can basically attract each other and then they can have a coulombic interactions, ok.

The electrostatic interaction basically this electrostatic interaction between the holes and the electron can reduce the energy required for the excitation formation, ok. And that is what causes the this effect that, even if you have a photon energy, photon energy, which is below the band gap energy; still this you know phenomenon can happen, electron can move into the conduction band ok, electron get excited, ok.

So, that is what can happen; electron can get excited, even if you put an energy which is less than the band gap energy of the material. So, that is what it is. And so, therefore, the electrostatic interaction will reduce the energy required for the excitation formation with respect to the unbound electrons and the whole energy bringing the electron energy level, energy level closer to the conduction band, ok. What is that, ok?

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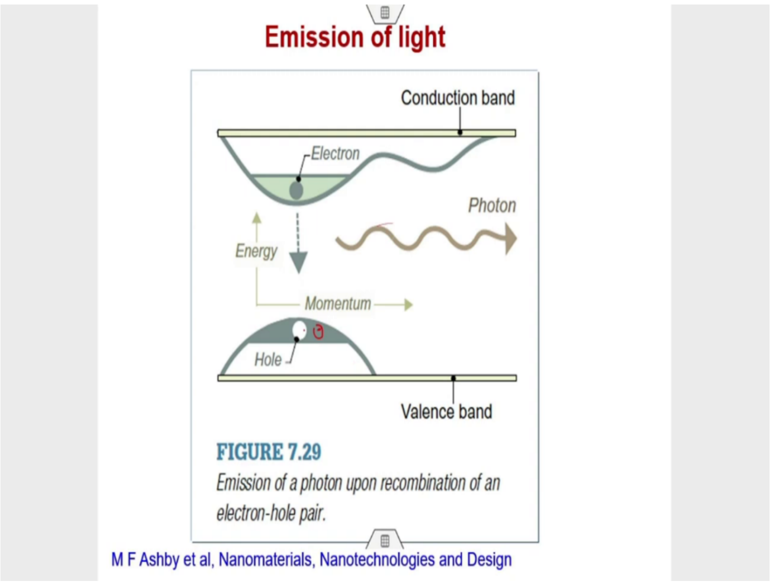

Emission of light

FIGURE 7.29
Emission of a photon upon recombination of an electron-hole pair.

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Well, this is something which I need to show you. So, therefore, you know electron once it jumps here, it can recombine and gives a photon that is what we said. But electrons may not jump here, it can remain here ok; do not recombine and create a electron hole pair, that is what is known as a basically.

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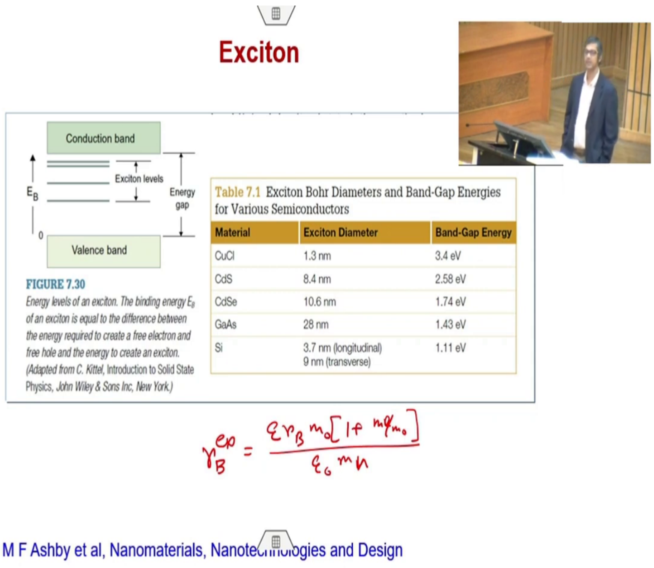

Exciton

FIGURE 7.30
Energy levels of an exciton. The binding energy E_B of an exciton is equal to the difference between the energy required to create a free electron and free hole and the energy to create an exciton. (Adapted from C. Kittel, Introduction to Solid State Physics, John Wiley & Sons Inc, New York.)

Table 7.1 Exciton Bohr Diameters and Band-Gap Energies for Various Semiconductors

Material	Exciton Diameter	Band-Gap Energy
CuCl	1.3 nm	3.4 eV
CdS	8.4 nm	2.58 eV
CdSe	10.6 nm	1.74 eV
GaAs	28 nm	1.43 eV
Si	3.7 nm (longitudinal) 9 nm (transverse)	1.11 eV

$$r_B^{ex} = \frac{\varepsilon r_B m_0[1+m_e/m_0]}{\varepsilon_0 m_h}$$

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Now, just now what I have said, because of this electrostatic interaction between the hole and the electron; what can happen? This can lead to reduction of energy required for the excitation formation with respect to the unbound electrons or the whole energy that is the band gap energy basically.

So, bringing the energy level closer to the conduction bands, ok. This these energy levels will be, electron hole energy levels will be closer to the conduction band; because you know, because it has already attractive force, so this can lead to reduction of the energy levels or the band gap energy.

And so, that means what; the energy band for this excitation will be closer to conduction band, it is same thing like if you have a impurity in the silicon. The moment you add a impurity energy band, sorry the energy levels of the impurity can go closer to the conduction band and that can lead to easy transfer of the electrons from the to the conduction band right, that is normally observed in case of this.

But nonetheless as a result, the basically Bohr radius increases ok; you know the Bohr radius basically. So, Bohr radius increases and the new Bohr radius is normally Bohr radius is given by this excitation Bohr radius epsilon r_Bm0 1 plus m v by m naught; you know these are v means electrostatic and epsilon sorry epsilon naught, epsilon naught m v, right.

So, u is the u is the dielectric constant, epsilon naught is the basically dielectric constant of this free space; r B is the Bohr radius here of the absorption of the excitation, in the absence of excitations, this r B, ok. And m g is the mass of electron, m is the effective mass of electron and m h oh sorry this is m h, this is m h m b, m h, oh this is m m 0 is the mass of the free electron. m e, this is m e; m e is the effective mass of the electron and m h is the mass of the hole, that is what it is.

$$r_B^{exp} = \frac{\epsilon r_B m_0 (1 + \frac{m}{m_0})}{m_h \epsilon_0}$$

So, this equation little bit complex, but this is the modified Bohr radius. And as you can see here, this table for the different material like copper chloride, cadmium sulphide, cadmium selenide, gallium austenite, even silicon also; the excitation radius are in nanoscale, right.

So, therefore, for a nanomaterial, excitation radius may be confined; because the dimensional nanoscale, for nanomaterial this radius can be confined also. The interaction between the hole and electron can be modified. This is something which is very very new to you right, you may not have heard about such kind of concepts; but is nicely given in chapter 7 of Ashby's book, you can read it up and understand, ok.

So, in general, so this is what is called excitation, exciton and this can affect it the optical property is very significant, right. So, like let us talk about these aspects in next 10 minutes or so in detailed manner, correct. So, as we have discussed, the three effects three things which can affect the optical properties of nanomaterial; first is the dos, density of states in the valence and the conduction bands ok, and second is these quantum confinements of the electronic level, energy levels because of nano structuring.

Third is this exciton. And exciton actually basically has a diameter basically is nano scale or dimensional like 1.3 to about 20 nanometres. Therefore, therefore, these can actually lead to part; this can also be confined, just as electrons can get confined, electron ionic states. The excitation exciton energy states also get confined depending on the nano material and the dimension, ok.

So, how does it can be observed in the real scale? Ok so, you know as the nano material changes from three dimensional to zero dimensional; quantum confinement is very severe, you all of us seen that ok in our last discussions on even on magnetic properties or electrical properties or even thermal properties, these effect we have already seen it, right.

So, therefore, the as the dimension decreases from 3-D to 2-D to 1-D to 0-D; this quantum confinement become very severe and it can lead to various density of states become quantized and the band gap of the material can sit upward ok, it has been seen.

So, as a result you can have blue shifts ok, in the absorption spectrum as the size of the material decreases and rate shifts when the size of material increases. This is what has been observed also and this is understandable; because as the you know then the energy bands are getting quantized, the band gap will be increasing; it will go to higher up upper side as the band gap increases you have a blue shift ok and as the band gap decreases, because of size increase red shift happens.

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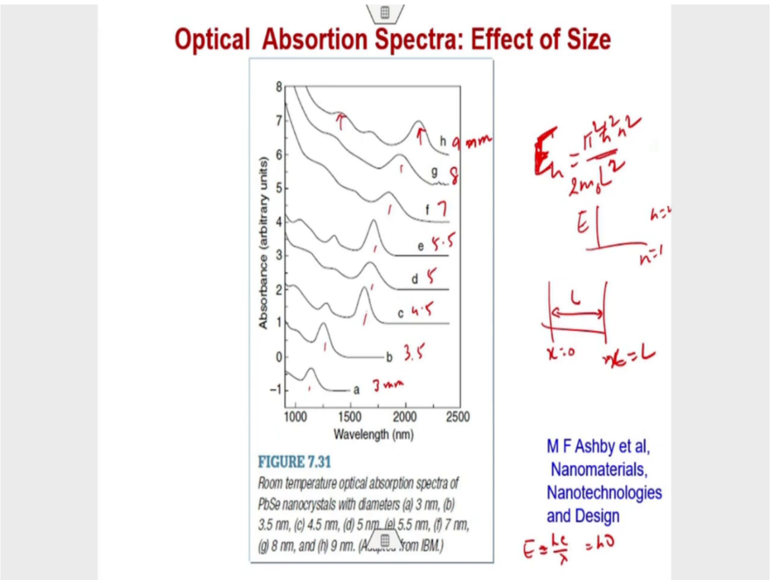

Optical Absorption Spectra: Effect of Size

FIGURE 7.31
Room temperature optical absorption spectra of PbSe nanocrystals with diameters (a) 3 nm, (b) 3.5 nm, (c) 4.5 nm, (d) 5 nm, (e) 5.5 nm, (f) 7 nm, (g) 8 nm, and (h) 9 nm. (Adapted from IBM.)

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$E = \frac{hc}{\lambda} = h\nu$

So, effect is more visible in the this picture, which is shown here. You see this is nothing but a room temperature optical absorption spectra of lead selenide tunnel crystal. So, different diameters starting from 3 nanometres here, a corresponding to 3 nanometre ok and the h corresponding to 9 nanometre. So, b is again 3.5, this is 4.5, this is 5, this is 5.5, 7 very very close placed size in this of lead selenide crystals, ok.

So, what do you observe here? As you see here the visible this basically shows the highest absorption region ok shortest wavelength shortest wavelength correspond to is thousand. So, therefore, this is the highest absorption regions, ok. And look at this band what is happening, it is slowly shifting to the a lower size.

Even at lower size you cannot see even this band at all, this band has moved below 100 nanometres wavelength or so, that is something, which is always. So, that is what is called blue shift correct as the size decreases these absorption edge, corresponding to the absorption highest energy, absorption region is shifting to the blue region; that is shifting to the lower wavelength regions ok.

You remember the optical spectrum red to blue right red 700 blue is 400. So, blue is lower size that is what is called is the blue shifting, ok. So, these kind of absorption edges is shifting towards the lower aeroplanes that is what is called blue shifting, am I clear as the particle size decreases. And this is the understandable; why? Because of the, because of the quantum confinement of the electrons; as the size decreases, electrons are getting more and more confined.

So, electrons cannot take up the energy levels, which are allowed at higher values than a lower value at 9 nanometres the confinement is much less severe than at 3 nanometres or 2 nanometres right, that is we know because as the size decreases confinement become very serious.

Because you're the it is basically nothing but related to the in the potential well this is the x =0, x=L, right. So, this is the length right, you know the energy $E_n = \frac{\pi^2 \hbar^2 n^2}{2m_0 L^2}$ right, that is what you see.

So, this as you decrease the L, the energy E energy E ok is more severely confined right; this is the factor of L right as you can see here; only depends on n, but the confinement, basically as you plot E versus n; if you plot that ok n is equal to 1 n equal to 2 n equal to 3, the nature of the energy curve will depends on also L, right.

So, that is what I am telling. As the size decreases, this effect will be more significant in the field than for this absorption edge. Finally, for the higher absorption peaks like this one ok; this is the higher absorption peaks here, higher absorption peaks are associated with the formation of exciton ok, this is something which is to understand.

This is low absorption peaks can be easily understand understood using this density of states and the quantization of the energy levels, because of the size effect. But higher absorption peaks cannot be explained by that; it is can only explained by the exciton and which can shift to lower wavelengths.

As you can see here it is shifting from 2000 to about one close to 1200 nanometre ok; that is what is this absorption band is shifting ok, this peak is slowly shifting you can clearly see that ok, this peak is slowly shifting that side. So, this shift is and can be understood using the excitation exciton ok; just now I discuss what is the exciton, it is basically combinations of electron holes together and they are bound together because of the electrostatic energy between themselves, which is nothing but a coulombic force.

Now question is this, the how are how this effect is observed? Well, that is why I need to discuss this; we always consider two designs, one is called you know strong confinement design, other is called weak confinement designs. So, weak confinement and strong confinement are determined basically degree of coupling between the hole and the electron how they are strongly bonded.

That depends on the distance obviously r square, depends on the you know media what is that called you have seen probably no, that, depends on this distance r square and depends on this epsilon 0. E is obviously constant, it does not change for the you know electron and hole.

So, anyway, so that means the strong and the weak confinement will depends on how they are strongly they are bonded with each other. Well, let us now discuss each of these cases and then we can wind up this lecture, correct.

So, weak; so, therefore, in case of weak confinement, a dimension of nano materials are greater than the excitation exciton radius, ok. They will be at least greater than a factor at 1 or 2 ok, at least double or triple. So, exciton radius is 1.3 to about 5 or 6 nanometres. So, the particle size should be double of that, at least 12 or maybe or maybe it will can be a 3, 4. If it is 1.5, it should be 3 and if it is a 6, it will be 12 nanometres, ok.

So, if it is so, then this can happen. Under these conditions coulombic interaction between the electron and the hole leads to increase of the excitation energy, binding energy, ok. And obviously, this causes a shift to the exciton exciton peaks the toward the blue ok; because electron hole are binding very strongly at that energy, which is the binding energy between the electron hole can shift the energy level to the higher sides and that can lead to blue shift, ok.

Higher energy means lower wavelengths ok, you know that; this energy is nothing but E is nothing but what? h c/λ right, that is nothing but h nu. Thus, the higher energy means well lower wavelengths, ok. The band it goes to higher energy levels compared to the valence band.

So, therefore, the blue shifts happens am I clear and the this is what we see here. But on the other hand higher degree of confinements is observes in case of. So, the, but these confinements will be very easily filled in case of nano films or nano wires than the nano particles correct.

But on the other hand, if the dimension of nano particles are bigger than, sorry smaller than the excitation radius; then this whole thing you know will be not correlated properly, that means the excitation will not exist at all, that is what is called the strong correlation or strong confinement effects.

So, weak confinement effects is more widely seen, weakly they are confined to each other; but when the size is smaller than the exciton radius, this effect will not be Seen. So, that means you know this absorption spectra is very important tool to investigate the optical behaviour of the nanoparticles, ok.

So, with this I stop here and then we will come back with some more on the optical absorption spectra in the next lecture. So, that you will understand, but before I wind up this lecture; I would like to say these are the things which are really new to you have never probably come across such a kind of concepts.

But fact is that, these are used in your research area. So, it is better you learn these aspects. And at least try to understand how and how they can form, how we can explain them and what is the effect of size on these properties.

Thank you.