Nanostructures and Nanomaterials: Characterization and Properties

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Lecture - 24

Electrical, Magnetic and Optical Properties of Nanomaterials (C4)

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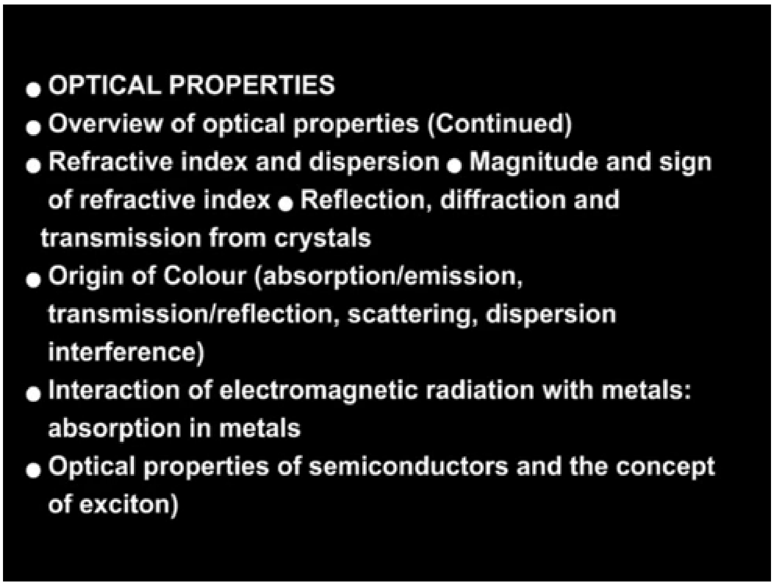

- OPTICAL PROPERTIES
- Overview of optical properties (Continued)
- Refractive index and dispersion ● Magnitude and sign of refractive index ● Reflection, diffraction and transmission from crystals
- Origin of Colour (absorption/emission, transmission/reflection, scattering, dispersion interference)
- Interaction of electromagnetic radiation with metals: absorption in metals
- Optical properties of semiconductors and the concept of exciton)

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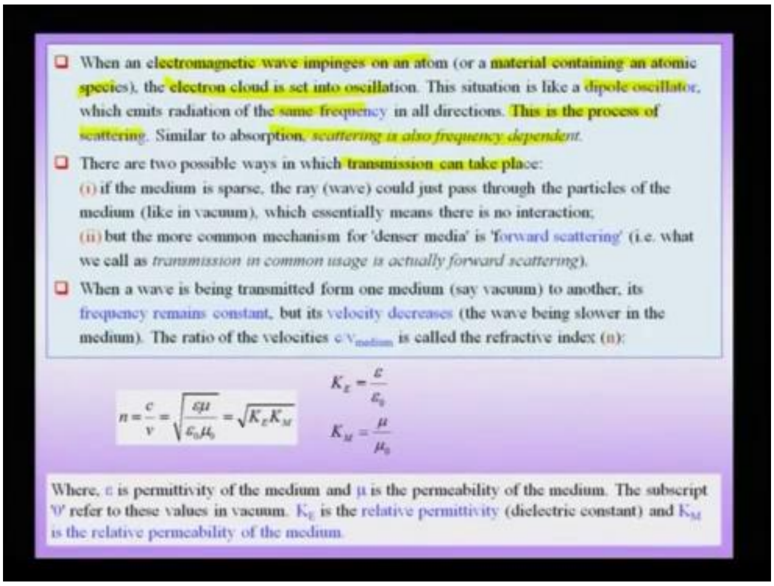

- ☐ When an electromagnetic wave impinges on an atom (or a material containing an atomic species), the electron cloud is set into oscillation. This situation is like a dipole oscillator, which emits radiation of the same frequency in all directions. This is the process of scattering. Similar to absorption, *scattering is also frequency dependent.*
- ☐ There are two possible ways in which transmission can take place:
  (i) if the medium is sparse, the ray (wave) could just pass through the particles of the medium (like in vacuum), which essentially means there is no interaction;
  (ii) but the more common mechanism for 'denser media' is 'forward scattering' (i.e. what we call as *transmission in common usage is actually forward scattering*).
- ☐ When a wave is being transmitted form one medium (say vacuum) to another, its frequency remains constant, but its velocity decreases (the wave being slower in the medium). The ratio of the velocities c/v_{medium} is called the refractive index (n):

$$n = \frac{c}{v} = \sqrt{\frac{\varepsilon\mu}{\varepsilon_0\mu_0}} = \sqrt{K_E K_M}$$

$$K_E = \frac{\varepsilon}{\varepsilon_0}$$

$$K_M = \frac{\mu}{\mu_0}$$

Where, ε is permittivity of the medium and μ is the permeability of the medium. The subscript '0' refer to these values in vacuum. K_E is the relative permittivity (dielectric constant) and K_M is the relative permeability of the medium.

When an electromagnetic wave impinges of an atom or a material containing atomic species that implies that it could be an ion or metallically bonded material the electron cloud is into set into oscillation this situation is like a dipole oscillator. Therefore, this dipole oscillator radiates emission all around it in this having the same frequency and this we can for a first approximant assume is not direction dependent. This process of scattering is basically the process, which we call scattering, in other words it is the electron cloud or an atom which is responsible in combinations ion cores. If I consider initially, the ion core is fixed and the electrons are on which are oscillating and this type of oscillator sense out radiation in all direction.

This is the process of scattering in other words scattering is not merely some kind of reflection it is actually a dipole oscillator at work and similar to absorption scattering is also frequency dependent. In other words, the strength of scattering depends on the frequency, now there are two possible ways in which transmission can take place we had earlier pointed out there are three possibilities. When light falls on a medium or light passes a ray passes through a medium one is reflection other is refraction and third is absorption.

When you are talking about refraction, we are essentially assuming that the ray is going into the second medium which we otherwise we call transmission, of course if we shall see soon if the refractive index is close to 1. In that case, the refraction angle being is the deviation angle is very small the two possibilities are for transmission number one. If the medium is extremely sparse like you are talking about interest hailer space, wherein the atomic density or the matter density is extremely small, then the wave actually pass between the particles so schematically I can draw it like this.

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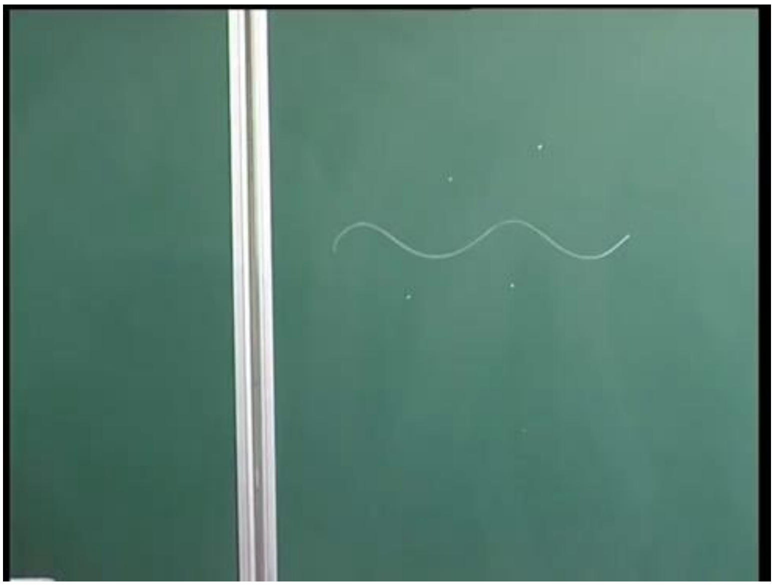

So, I have my medium which is extremely sparse and my wave is actually passing between the particles, so essentially is no interaction and this is what you might call the trivial case of transmission.

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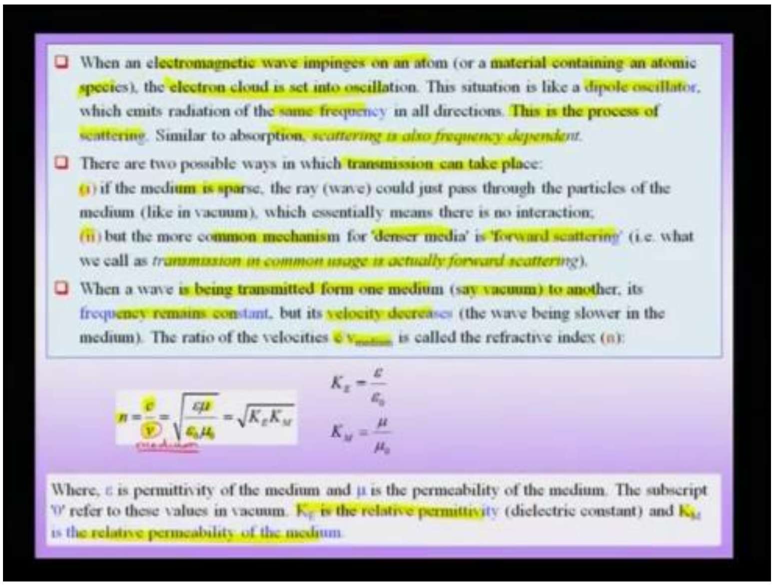

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The more common mechanism of transmission and this is we are talking through a denser medium is the phenomena of forward scattering. In other words, what we normally call transmission like suppose light is coming from the left of this room and going to is the right of this room, we call a transmission. It looks to us as if it is just motion of light through the medium without any interaction at all, but in reality it is dominated by forward scattering. When I am talking about molecules in the atmosphere for instance, the blue colour is coming because of the frequency dependence of scattering.

In other words, this frequency goes as omega power four and the that means that the higher the frequency more will be the scattering and that is why the blue light is scattered. Therefore, we see our sky as blue and this phenomena is known as Roley's scattering the unscattered light which is the longer wavelength red radiation which goes through straight is what is responsible for the reddishness of the sky in the evening. In the evening, what happens is scattered light is lost the unimpaired or the unscattered light the forward scattered light which goes through is the one you which meets our eye. Therefore, red evening sky looks red while the day time sky actually looks blue, so this is the phenomena of Roley scattering.

Therefore, we have to know that what we call transmission in common usage may turn out to be what you might call forward scattering, so this has to be remembered. That means the forward wave is reinforced and if there is no lateral scattering at all that means all the other waves are destructively interfering. Therefore, we essentially have a wave transmission in the forward direction, but as we saw in the case of the scattering through the atmosphere often there is lateral scattering. Though the amount may be small, but this is what is responsible for the colour of the sky when a wave is been transmitted from one medium to another say vacuum to glass.

For instance, to take an example the frequency remains constant, so what is constant when a wave actually propagates from a rarer medium to a denser medium. For instance we take the example of vacuum to glass, it is a frequency which remains constant, but the velocity of the wave is altered. In fact, the velocity of the wave is decreased and the ratio of the velocity is of the wave in vacuum which is a fundamental constant c divided by the velocity in the medium. So, the denominator is the velocity in the medium, this velocity is what we call in common language the refractive index, therefore when the wave enters the medium its velocity decreases.

This ratio we call the refractive index though we will not be talking too much about refractive index per say of nanostructures material, then suppose I take a glass sphere and keep on reducing its size to the nanoscale, what happens to its refractive index? So, I will mention it in the passing that often as we note here that the refractive index is a function of the can be written in terms of permittivity and permeability of the medium with respect to the permittivity and permeability of free space. In other words, they depend on what you may call the relative permittivity and the relative permeability of the medium and because these constants are these characteristics of the medium the permeability and permittivity are not sensitive functions of the size.

Therefore, often you will find that the even when you approach the nano scale, the refractive index is not changed much, but however there is expected to be some change. So, we have this concept called a refractive index which is basically the ratio of the velocity of light in vacuum is a v the velocity in a given medium.

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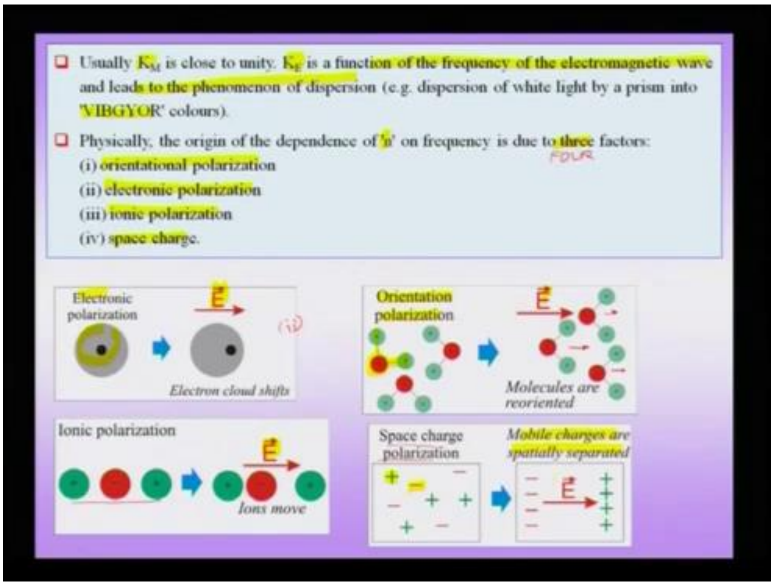

- ☐ Usually K_M is close to unity. K_E is a function of the frequency of the electromagnetic wave and leads to the phenomenon of dispersion (e.g. dispersion of white light by a prism into 'VIBGYOR' colours).
- ☐ Physically, the origin of the dependence of 'n' on frequency is due to three factors:
  FOUR
  (i) orientational polarization
  (ii) electronic polarization
  (iii) ionic polarization
  (iv) space charge.

Now, it in the previous relation the K M the relative permeability or the relative magnetic permeability is actually close to unity. Therefore, K E is what is going to determine the refractive index essentially and this K E is the function of the frequency of the electromagnetic wave. This is what is responsible for the phenomena of dispersion dispersion, essentially implies we are referring to some kind of Newton's experiment wherein we send in white light into a prism. We see that it actually spreads into what you might call the Vibgyor colours and this is coming from dispersion phenomena of dispersion.

This essentially tells you that now my refractive index in is a function of the frequency of the material or frequency of the electromagnetic wave and this dependence of n is coming from K E because K M is essentially close to unity. Therefore, because K E depends on the frequency we see that the refractive index of a material actually depends on the frequency. Physically, if you look where is this dependence of n coming from physically you would note that the dependence of frequency dependence of n is coming from actually four factors if we include three of them are the main factors usually sighted.

There are four factors here, so let me write down this is four totally and these four factors are what you might call orientation polarization, electronic polarization, ionic polarization and phase charge polarization. From these terms, it is obvious that I am referring to for instance like a dielectric medium, wherein polarization is possible and therefore, I am talking about the propagation of an electromagnetic wave like light. Let me for now assume that light is passing through some medium like quads or some other crystalline medium. All these polarizations are responsible for what you might call the frequency dependence of n that means that these polarizations are activated at selective frequency regime.

Therefore, in other words these are not active at all frequency regimes and therefore there is a dependence of n on the frequency of the electromagnetic wave in electronic polarization. Essentially, you see that because the presence of an electric field of course n the case of a wave this electric field and the magnetic field are oscillating quantities. You know that an electromagnetic wave is nothing but a coupled electric and magnetic oscillations, it propagating through space. For now, we will assume example showing it as if is a fixed deal, but we have to remember that is actually we are talking about time dependent e and correspondingly a time dependent h.

Due to this electric field, what happens is that the centre of mass of the electron cloud is shifted with respect to the centre of mass of the nucleus. Essentially it is electron cloud which shifts and this implies that there is a net dipole created in the material. So, this dipole which is instantaneously created at the atomic level is what is responsible for this what you might call electronic polarization. So, this is actually point number two which is electronic polarization the other possibility is what you might call ionic polarization in a. This can obviously can happen only in a dielectric medium having ions, in that case what happens is centre of mass of the negative charges shifts with respect to the centre of mass of the positive charges.

This means again a dipole is created and of course this dipole will oscillate if the electric field d oscillate. Therefore, again there is a dipole being created at the atomic level and this dipole is responsible for the for the frequency dependence where ever. It is clear that suppose I am trying to shift the electron cloud the electron cloud is much less massive compared to an ion.

That means that the electron core shifting is going to take can be operative at higher frequencies as compared to the ionic polarization which may be active at lower frequencies. Third examples is of course the third point is orientation polarization and we have already talked about this orientation polarization when we talked about the case of microwave heating of water when you put that. We now for schematically show the water molecule for instance by this wherein essentially the oxygen molecule is slightly negative. The hydrogens are slightly positive and you have these molecules oriented randomly in a medium like water.

Now, what happens is that when you apply an electric field there is a tendency for the dipoles to align themselves such that of course the positively charged. Therefore, the dipole alignment along this direction all the individual atomic dipoles are molecular dipoles align themselves. This is responsible for what you might call orientation polarization here, obviously when you are talking about entire molecules have to rotate. This implies that this is going to kick in at even lower frequencies as compared to a phenomena like electronic polarization or ionic polarization and this we have also pointed out while heating of water at that when the electric field is actually oscillating.

That implies that these molecules are constantly trying to rotate and align themselves parallel to the field and this when deceptively operates you can see that actually is to heating of water in your microwave oven. The fourth of these is the space charge polarization, wherein at the any positive kelvin temperature, you may have actually dissociation of the positive and negative charges in a medium. This could typically occur at the interface for instance and when you apply an electric field these mobile charges are spatially separated. Of course, this may not be a mobile to a long distance may be the short distance mobile and therefore again you get an net dipole movement in a material and this dipole moment.

For instance, as I pointed out could be localized to an interface, in other words there are underlying atomic mechanisms which are responsible for this frequency dependence of an, and this are the four. We have just now sighted now a few more words about the refractive index, usually the refractive index is greater than 1.

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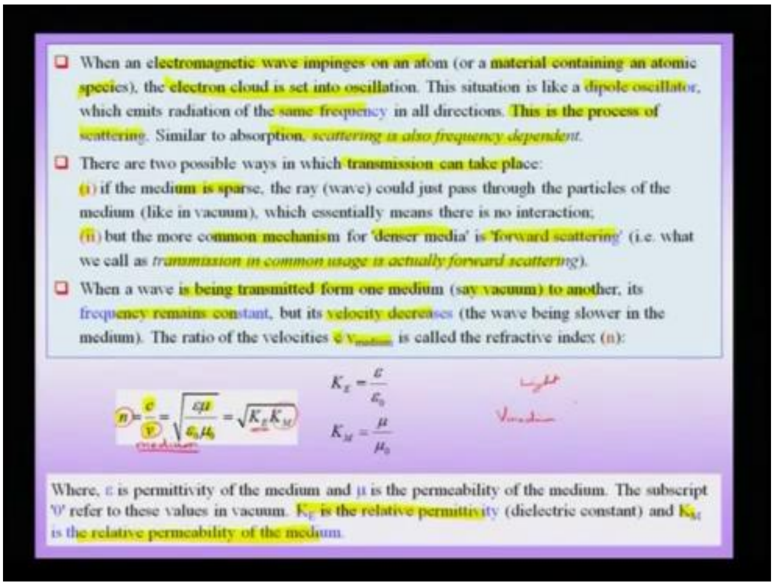

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light

V_{medium}

Where, ε is permittivity of the medium and μ is the permeability of the medium. The subscript '0' refer to these values in vacuum. K_E is the relative permittivity (dielectric constant) and K_M is the relative permeability of the medium.

That means that velocity of light in a medium is going to be greater than is going to be smaller than and this is velocity of light of course, this is true for any electromagnetic radiation, but I am just writing this for light is going to be less than c.

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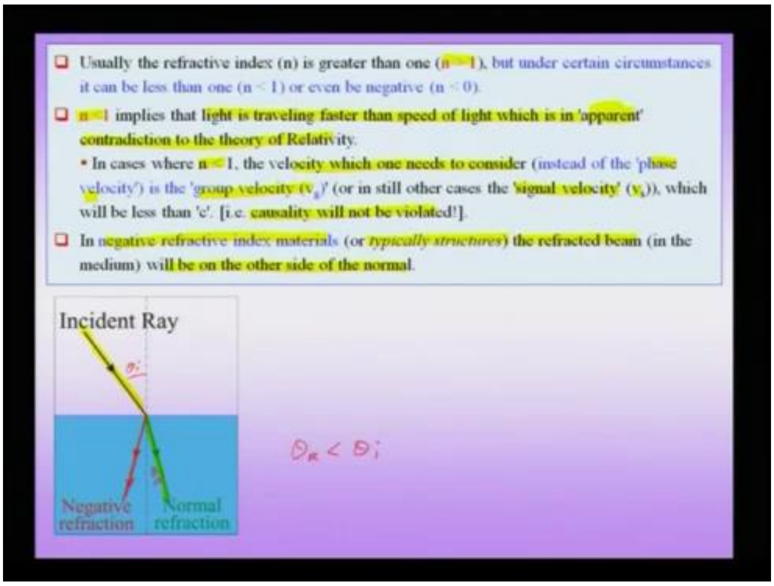

- Usually the refractive index (n) is greater than one ($n > 1$), but under certain circumstances it can be less than one ($n < 1$) or even be negative ($n < 0$).
- $n < 1$ implies that light is traveling faster than speed of light which is in 'apparent' contradiction to the theory of Relativity.
    - In cases where $n < 1$, the velocity which one needs to consider (instead of the 'phase velocity') is the 'group velocity (v_g)' (or in still other cases the 'signal velocity' (v_s)), which will be less than 'c'. [i.e. causality will not be violated!].
- In negative refractive index materials (or *typically structures*) the refracted beam (in the medium) will be on the other side of the normal.

$\theta_R < \theta_i$

It is what we expect because we know c is the upper limit for velocities in nature, now there are materials in which n is less than 1 and still we are talking about a positive kind of an n and this is very surprising because if n is less than 1. It implies that light is travelling faster than the speed of light, which is an apparent contradiction to the theory of relativity and the word apparent is used because in reality it is not in contradiction of the theory of relativity. Wherever the n is less than 1, the velocity one needs to consider in this context is not the phase velocity, but the group velocity and of course in still as still as certain other cases where group velocity even cannot resolve the case.

You actually consider something known as signal velocity and whatever is you either consider the group velocity or the signal velocity you will notice that the signal itself is not propagating faster in the speed of light. In other words, causality is not been violated which is implies that the Einstein’s postulate is correct that c is the fundamental constant of nature beyond which or equal to which we cannot send any signal. So, even though we may have a refractive index less than 1, which implies the velocity of speed greater than or the speed of electromagnetic wave in a medium greater than that of a speed of a light. This does not violate in any sense in principle of causality which implies that the signal or the information cannot be transmitted faster than the speed of light.

So, this is important to keep in mind, but we will briefly consider in these set of lectures not n is less than one materials, but materials wherein and n is less than 1, materials have been found for instance in both say Einstein condensates. I mean there are special materials which have been created where light is been slow down or light has been speeded up, but we will not talk about those materials, but we will briefly take up what is known as negative refractive index material. In reality, these are not really materials and you should note that they are actually typically structures of course we know the difference between materials and structures.

When we refer to the word material, we imply that there is no geometry there is no other parameter, it is kind of an infinite term and no point in the material is different from any other point in the material. Of course, the properties may be direction dependent, but the points in the material themselves are all identical in a structure, there is some geometry. Suppose, I talk a material like copper I assume that it is a big block of copper wherein two points are identical, but suppose I am talking about a copper plate, then there is a geometry involved in it because there is a length there is a plate, there is an thickness to this plate.

Therefore, such a thing would also have a characteristic of a structure, now in this negative refractive index material the refracted beam will be on the other side of the normal. So, this a very strange kind of phenomena wherein and these kind of materials some times are called meta materials in which the incident ray comes normally like this and the normal refracted beam is like this. If you are talking about an optical denser medium, this blue material, then you would notice that if this is the theta incident and this is my theta refracted then theta refracted would be less than theta incident, we know this. In the case of negative refraction, actually the refracted beam lies on the other side of the normal.

So, this is very special kind of refraction, which is known as negative refraction this was theoretically postulate quite some time back, but then it is physically realized especially for radio waves. Other kind of electromagnetic radiation in quite recent times a last couple of decades and it is actually a region area of very active interest because people are talking about making cloaking devices based on negative refractive index materials.

Now, we take about of talk about of few more other aspects wherein we are talking about interaction of electromagnetic waves with what you might call matter and for now we will restrict ourselves to what you might call crystalline form of matter.

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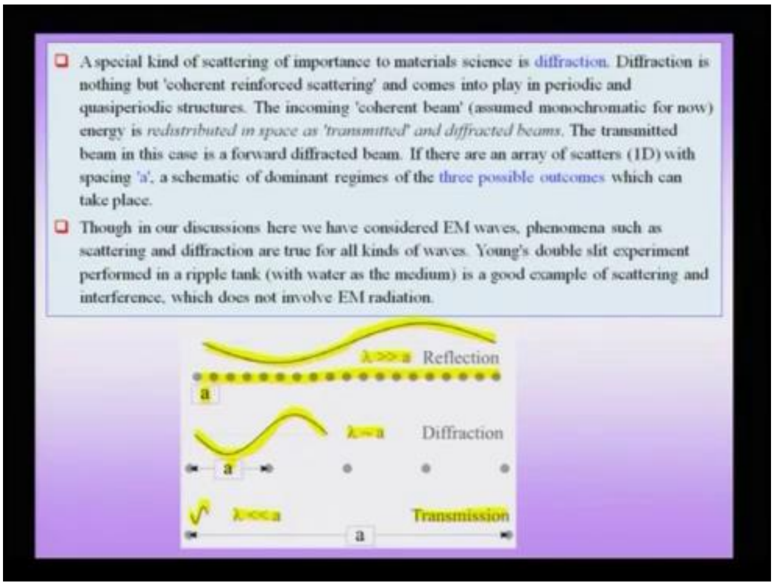

- A special kind of scattering of importance to materials science is diffraction. Diffraction is nothing but 'coherent reinforced scattering' and comes into play in periodic and quasiperiodic structures. The incoming 'coherent beam' (assumed monochromatic for now) energy is *redistributed in space as 'transmitted' and diffracted beams*. The transmitted beam in this case is a forward diffracted beam. If there are an array of scatters (1D) with spacing 'a', a schematic of dominant regimes of the three possible outcomes which can take place.
- Though in our discussions here we have considered EM waves, phenomena such as scattering and diffraction are true for all kinds of waves. Young's double slit experiment performed in a ripple tank (with water as the medium) is a good example of scattering and interference, which does not involve EM radiation.

In other words, there is an periodic array of atoms in material and of course I have just shown one row of atoms and this could be actually a series of rows like in a three dimensional crystal. I assume now for this spacing between the atoms is which is now this inter atomic spacing or the lattice parameter and I have three positions three situations shown here. Case one that the wavelength of the radiation lambda is much larger than inter atomic spacing. The second position is that the wavelength of the incoming radiation is of the order of inter atomic spacing and the third case is when the wavelength is much smaller than inter atomic space.

The easiest of these three to visualize is the fact that the when wavelength is very small, then essentially transmission dominates which is very easy to see like it is a case like we drew here. When you have these points scatters very far apart, then their radiation essentially can go unimpeded through space.

The remaining two are the most interesting case while one example like to say it of transmission for instance suppose I am sending light through a material, then the wavelength is for instance I take copper and send light. Then, you would think that the wavelength of light is much larger than the atomic space, but suppose I send, what you might call an electron beam, which is what you do in a transmission electron microscope. Then, the wavelength of that electromagnetic what you may call the electrons which is basically because they Debroy relationship. We have a wave particle duality and this implies that the wavelength of that electron beam is actually much smaller.

It is of the order of picometers and this depend on of course on the voltage of the accelerating voltage, but this picometer sized or the wavelength radiation can actually pass through matter as if there existed in it. So, there was it, this could be a situation very close to transmission when the lattice parameter say of copper is of the order of the Armstrong. Now, the other two situations the case of the scatter spacing being of the order of the wavelength here or much smaller than the wavelength are of interest to us in other the wavelength is much larger that the scattering spacing are of interest to us. The first case leads to essentially what you might call the reflection, so most of the wave when the lambda is much larger than a is actually reflected.

Of course, a little bit of the radiation will still leak through and this will be a small amount and this amount which leaks through is given is frequency dependent obviously are the wavelength dependent and is given by the bather’s relationship. Now, the important a nice example of this would be again we go back to our microwave oven when you look at the microwave oven, you would notice that in front of the microwave oven, actually you have a mesh a wire mesh.

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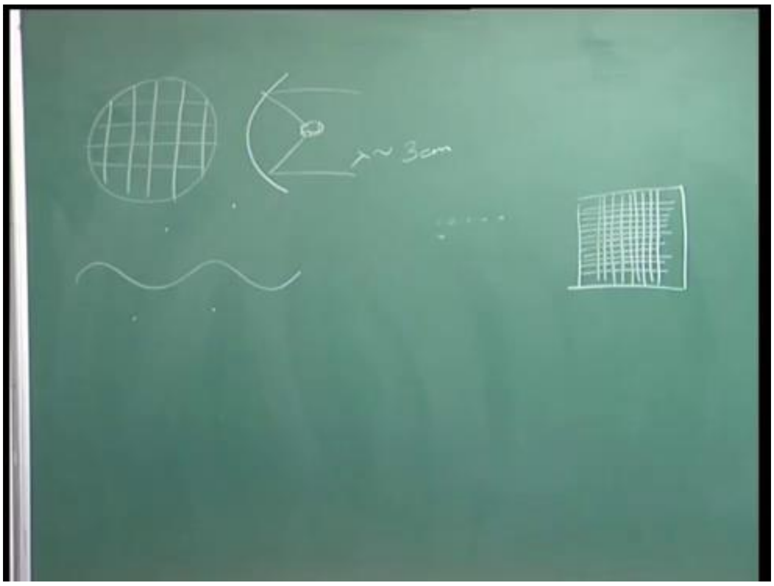

So, it is typically a small there are lot of small holes in the mesh, in other words I schematically draw this wire mesh like this. So, this is my front window we just assume it schematically to be my front window and there are these small holes in the front window. So, you might assume that the electromagnetic radiation in the case microwave is and this microwaves have a wavelength of the order of about lambda of the order of about 3 centimetres would actually come through these holes come out through these holes. Actually, I mean can affect in other words can beat you up or can cause damage to your tissue, but this does not happen because this is the case we are now considering in which case the wavelength is much smaller.

Then, this whole dimensions or in other words the scattering spacing, so because this wavelength is much larger most of the electromagnetic waves actually going to be reflected. In other words, microwave is not much of the microwave is going to be reflected from those measures and nothing is actually going to be or very little is going to be actually transmitted through that kind of a hole kind of a structure in a microwave oven. Another example could be for instance when you are using radio waves to collect, you typically have a radio wave antenna like this and you might have noticed that many of this radio wave antennas actually have a parabolic or a kind of a shape.

They have these what you may call rod like structure or they may even have a meshed like structure and if you look from the side you'll notice that this dish has a collector here in other words electromagnetic waves are reflected. There is a detector here a transponder or transducer which converts this energy into electrical signals, now the question which may be asked is that again if this such a holy structure is most of it is actually a rods or wires here. Then, only electromagnetic waves go through it and very little will be reflected here, again the answer lies because this scattering spacing of the holes are actually much smaller.

Then, the wavelength of the radio waves which implies that you are actually even though it looks like a structure which has practically holes in it. You would actually see that most of it is reflection dominant in other words this can now act like almost like a mirror. We use in a normal telescope the mirror reflecting telescope has this kind of large mirrors and these large mirrors actually reflect, so for what is for light those mirrors is for radio waves these kind of dish antennas.

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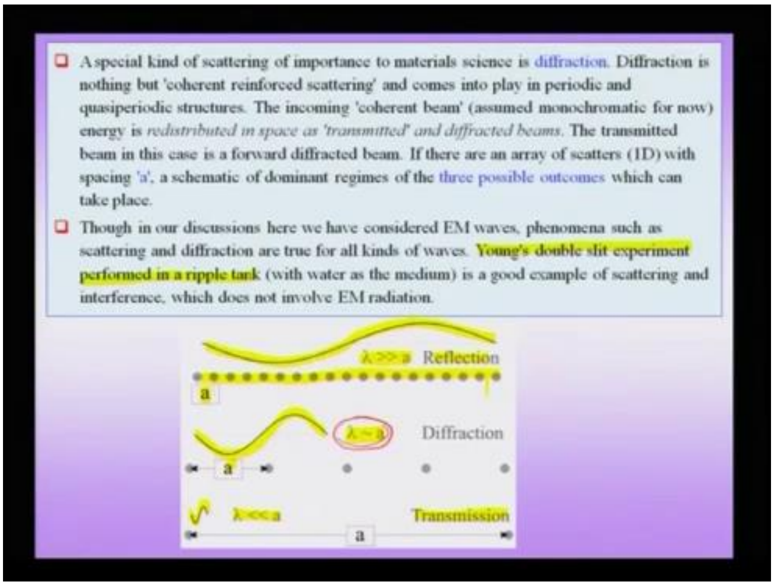

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Now, equally interesting to this case is the case where in the wavelength of the lambda is of the same order of inter atomic spacing and we had we said that we are going to consider actually point scatter as we will have to for.

Now, assume this is slightly different from these cases because here we have finite thickness scatters, but for now for simplicity we will assume that there are point scatters. So, when the lambda is much of the order of a then we note that actually that you have a phenomena on a diffraction in diffraction what happens is that not only you have a transmitted beam, but the energy is redistributed in between a transmitted beam. Many of the diffracted beams and of course the distribution is not equal most of the energy goes into the transmitted beam very little of it can be found actually in the diffracted beams. If it is a crystalline material, then the diffracted beams given by Brag's equation would occur very specific angles and of course we can conduct a diffraction experiment.

Using light in photonic crystals we can conduct, in another words we will have to use laser on photonic crystals to get a diffraction or an optical grating as you call it. You will be using an optical grating and laser to get a diffraction pattern you can use x-rays and you can use crystal like copper to get diffraction patterns, you can use microwaves and you can use a crystal made up of ball bearing balls. In other words, I can take large macroscopic crystals in which there are ball bearing balls and I can use microwaves like we just now pointed out like in a microwave oven and I can do a diffraction of experiment.

So, these three possible outcomes have to be kept in our mind and for now we had been talking about electromagnetic waves, but we have to remember diffraction and transmission are more common or more universal than just for electromagnetic waves. We know that for instance an young's double slit experiment can be performed in a ripple tank, in other words you can use water waves and you can use what you may call wooden blocks as scatters to actually get scattering and interference in a water tank. That means we are using mechanical waves transfers waves on the surface of the water and those we will show the phenomena like a diffraction interference etcetera.

So, these are universal phenomena and we have three regimes in which we can talk about before we go to the origin of colours. Let us briefly summarize what we have been talking about so far in optical properties we noted that there are three phenomena which can take place. One is refraction, another is reflection and then third is absorption and we said that this is basically occurring when you have electromagnetic radiation falling on a medium which we assume to be denser than the outer medium in which it is immersed. We said from a fundamental perspective there are only two kinds of phenomena, one is known as scattering and the other is absorption.

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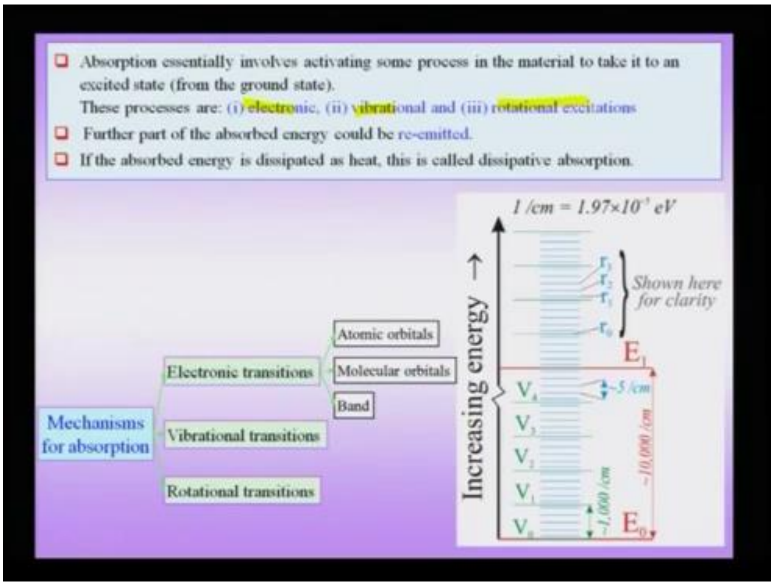

- ❏ Absorption essentially involves activating some process in the material to take it to an excited state (from the ground state).
  These processes are: (i) electronic, (ii) vibrational and (iii) rotational excitations
- ❏ Further part of the absorbed energy could be re-emitted.
- ❏ If the absorbed energy is dissipated as heat, this is called dissipative absorption.

We also said that if the absorption is possible if this external electromagnetic waves sets up some kind of an electronic vibration or rotational resonance within the material. Of course, once the material has been excited using this kind of an external electromagnetic radiation the material may relax back and in the process actually re emit electromagnetic radiation. This re emission of course we noted can take place immediately, which is why it is called scattering basically.

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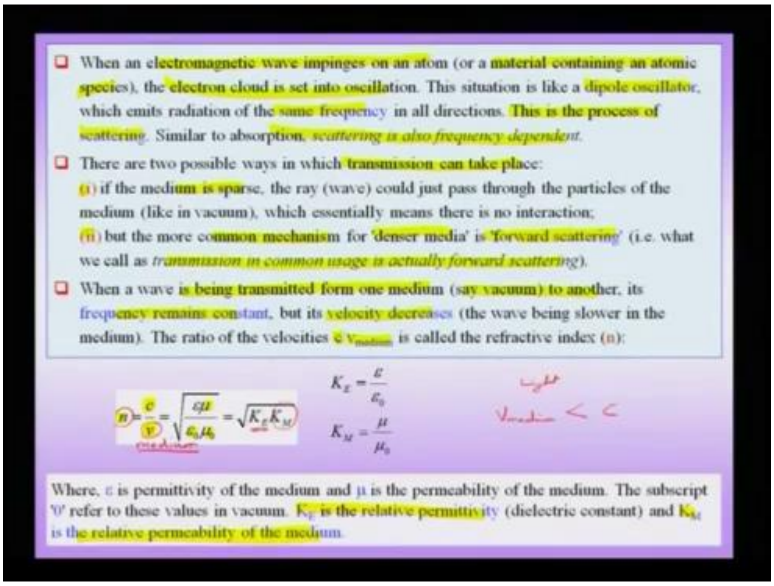

- When an electromagnetic wave impinges on an atom (or a material containing an atomic species), the electron cloud is set into oscillation. This situation is like a dipole oscillator, which emits radiation of the same frequency in all directions. This is the process of scattering. Similar to absorption, *scattering is also frequency dependent.*
- There are two possible ways in which transmission can take place:
  (i) if the medium is sparse, the ray (wave) could just pass through the particles of the medium (like in vacuum), which essentially means there is no interaction;
  (ii) but the more common mechanism for 'denser media' is 'forward scattering' (i.e. what we call as *transmission in common usage is actually forward scattering*).
- When a wave is being transmitted form one medium (say vacuum) to another, its frequency remains constant, but its velocity decreases (the wave being slower in the medium). The ratio of the velocities c/v_{medium} is called the refractive index (n):

$$n = \frac{c}{\underset{medium}{v}} = \sqrt{\frac{\varepsilon\mu}{\varepsilon_0\mu_0}} = \sqrt{K_E K_M}$$

$$K_E = \frac{\varepsilon}{\varepsilon_0}$$

$$K_M = \frac{\mu}{\mu_0}$$

$V_{medium} < c$

Where, ε is permittivity of the medium and μ is the permeability of the medium. The subscript '0' refer to these values in vacuum. K_E is the relative permittivity (dielectric constant) and K_M is the relative permeability of the medium.

In other words, the material behaves like the electron atoms in a material act like a dipole oscillators and it is merely of course with the small time like scattered back in which case you call it an oscillator and this is not called an excitation. We also said that the velocity of light in a denser optically denser medium is smaller than the optical velocity of light in a rarer medium like air or vacuum and which implies that there is a quantity called as refractive index, which is the ratio of the velocities. We also pointed out that this refractive index actually has a frequency dependence which gives rise to a familiar phenomenon known as dispersion. This means that white light is actually spread by a prism into its component colours which is known as the Vibgyor colours.

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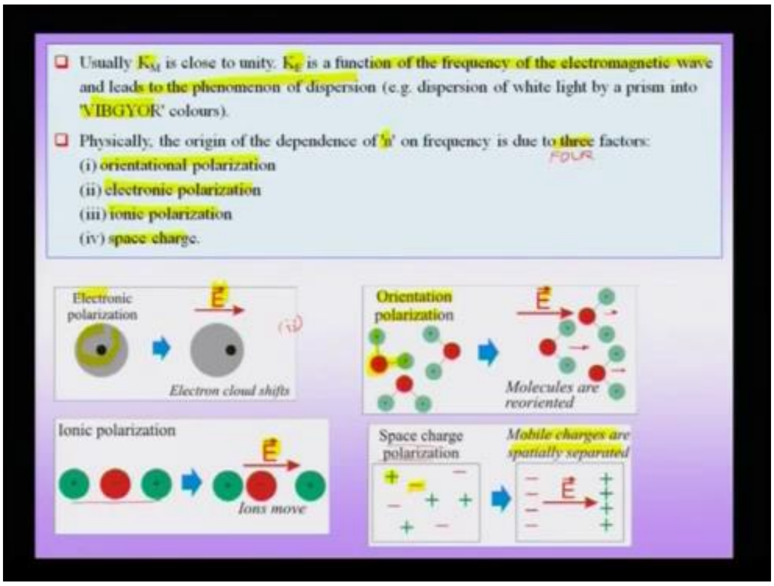

- Usually K_M is close to unity. K_E is a function of the frequency of the electromagnetic wave and leads to the phenomenon of dispersion (e.g. dispersion of white light by a prism into 'VIBGYOR' colours).
- Physically, the origin of the dependence of 'n' on frequency is due to three factors: FOUR
  (i) orientational polarization
  (ii) electronic polarization
  (iii) ionic polarization
  (iv) space charge.

We said that there are mechanisms like orientation electronic ionic and space charge polarization which lies in the heart of this kind of a frequency dependence of an or the refractive index.

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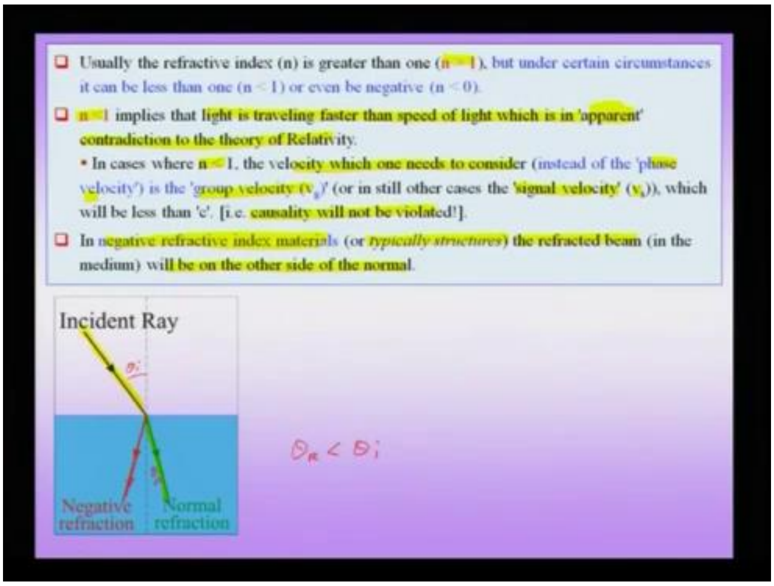

- Usually the refractive index (n) is greater than one ($n > 1$), but under certain circumstances it can be less than one ($n < 1$) or even be negative ($n < 0$).
- $n < 1$ implies that light is traveling faster than speed of light which is in 'apparent' contradiction to the theory of Relativity.
  - In cases where $n < 1$, the velocity which one needs to consider (instead of the 'phase velocity') is the 'group velocity (v_g)' (or in still other cases the 'signal velocity' (v_s)), which will be less than 'c'. [i.e. causality will not be violated!].
- In negative refractive index materials (or *typically structures*) the refracted beam (in the medium) will be on the other side of the normal.

It lies on the same side of the normal as the incoming beam or the incident ray.

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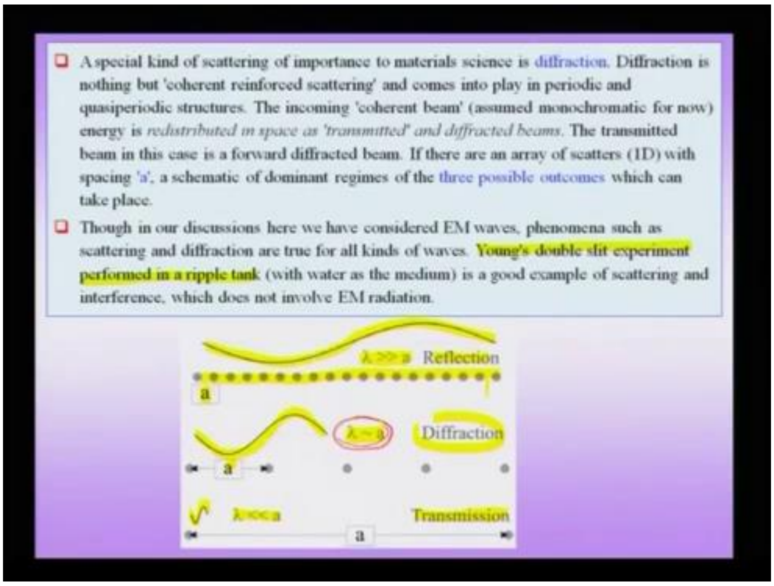

- ❑ A special kind of scattering of importance to materials science is diffraction. Diffraction is nothing but 'coherent reinforced scattering' and comes into play in periodic and quasiperiodic structures. The incoming 'coherent beam' (assumed monochromatic for now) energy is *redistributed in space as 'transmitted' and diffracted beams*. The transmitted beam in this case is a forward diffracted beam. If there are an array of scatters (1D) with spacing 'a', a schematic of dominant regimes of the three possible outcomes which can take place.
- ❑ Though in our discussions here we have considered EM waves, phenomena such as scattering and diffraction are true for all kinds of waves. Young's double slit experiment performed in a ripple tank (with water as the medium) is a good example of scattering and interference, which does not involve EM radiation.

We also said that this when you have an electromagnetic wave interacting with the crystal which is a periodic array of point scatters, then there are three phenomena possible, one is reflection other is the interesting case of diffraction. Finally, transmission also is possible and of course depending on various other parameters all these three might be simultaneously happening. It is not that we are talking about dominant regimes, but is not mean procured that only one will happen even in case where reflection is taking place. There, some amount of matter is actually transmitted and this is has a some kind of a lambda power 4 dependence, so the next topic we take up is the origin of colour.

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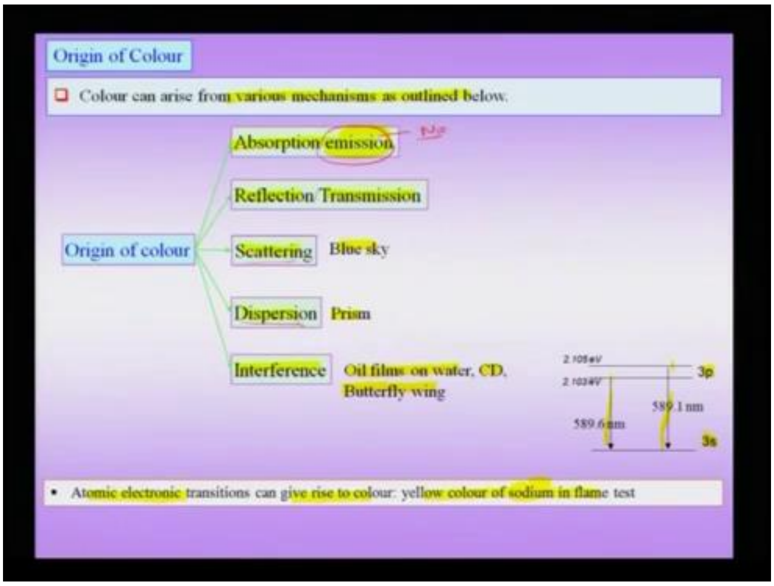

Origin of Colour

- ☐ Colour can arise from various mechanisms as outlined below.

Origin of colour

- Absorption/emission
- Reflection/Transmission
- Scattering — Blue sky
- Dispersion — Prism
- Interference — Oil films on water, CD, Butterfly wing

- Atomic electronic transitions can give rise to colour: yellow colour of sodium in flame test

Colour can arise from various mechanism as outlined below, the most common what we are accustomed to is the absorption or emission colours that means that some part of the electromagnetic spectrum is absorbed remaining is transmitted. Therefore, you see a certain colour or some part of the electromagnetic spectrum is actually absorbed remaining is reflected and you see what is called reflection colours. Of course, these absorption may be followed by emission and these emission can give rise to colours as well and we will take up specially this topic of absorption and emission colours in nanoparticles colour.

Again, if whatever is not absorbed or reflected is transmitted and if some part of the electromagnetic spectrum is actually absorbs some other part is reflected. Then, if you are looking at a transparent material if you are standing on the back side of the transparent material, then what you see is a transmitted colour which could be which is a complementary in some sense. If you are talking about a material which only reflects, absorbs, so if you are one side of the partially absorbing partially transmitting system you will absorb one colour, but the complementary colour would be observed on the other side which is transmitted.

Now, you could also have scattering colours as we pointed out like in this case the blue sky or the red sky in the evening which is basically coming from the scattering phenomena. We will take up one such example of colloidal gold, wherein you see colours because of scattering there would we also know that dispersion itself like in the case of prism can give rise to colours in which case a white light which is being split. Therefore, you have colours also interesting are the cases of interference colours like we know the case of oil films on water they have a certain colour and this colour changes when a viewing angle is changed.

You have colours on a CD, a compact disk you see that on a back side of a compact disk typically you see some kind of iridous and colours which is coming from again from interference the colours of a butterfly wing. For instance many of these monarch butterflies etcetera have a beautiful iridous and colours which is coming from interference. Typically, many of the blues in nature are actually interference colours many of this birds which also have blue colour from this interference colours. We have already noted that if this colours could come from atomic electronic transitions like for instance if you look at the yellow colour of sodium in a flame test, we have for instance a three s state and two closely spaced 3 p state.

When relaxation takes place from these excited states, we have the two famous sodium vapours lying which are the in the yellow division. Therefore, this is coming from emission, so this is a nice example of an emission colour, so this can be a colour for instance the sodium colour sodium in a flame test or a sodium vapour lamp. Now, in other words, there can be multiple origins of colour, it can come from absorption or emission reflection or transmission or a combination of all these factors like absorbs part of a spectrum is absorbs, part of it is reflected, part of it is transmitted.

Therefore, you may have depending on which side of the medium you are you may absorb different kinds of colours. Therefore there could also be scattering colours as we just noted the case of the blue sky or the red sky in the evening. There could be colours because of dispersion and more interestingly there could be iridous and colours be coming because of in the phenomena of interference in other words white light falls on a.

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For instance, on film of oil on top of water for instance we have an oil in a water, so this is my oil on water, and then typically what happens is that some part of the electromagnetic spectrum. This thickness is destructively interfering and some part of the electromagnetic spectrum this delta happens to be integral multiples of lambda. That means that is going to be constructive interference and therefore you will see some colours being removed from the electromagnetic spectrum, while others are enhanced. Therefore, you have colours in this coming rise purely from interference, so we will have a little more talk about this origin of colours in nanomaterials in some of the coming slides.

What happens when an electromagnetic radiation falls on a metal, now this picture we are taking up because we said that when you have a series of scatters and you have an electromagnetic radiations falling on it there are three possible scenarios.

This is assuming that these point scatters are virtually invade point scatters, but then we know that we could actually be talking about these point scatters like ion cores ion cores in a metal residing in an electron gas. That means we are talking about metallic bonding where there are free electrons available in a material.

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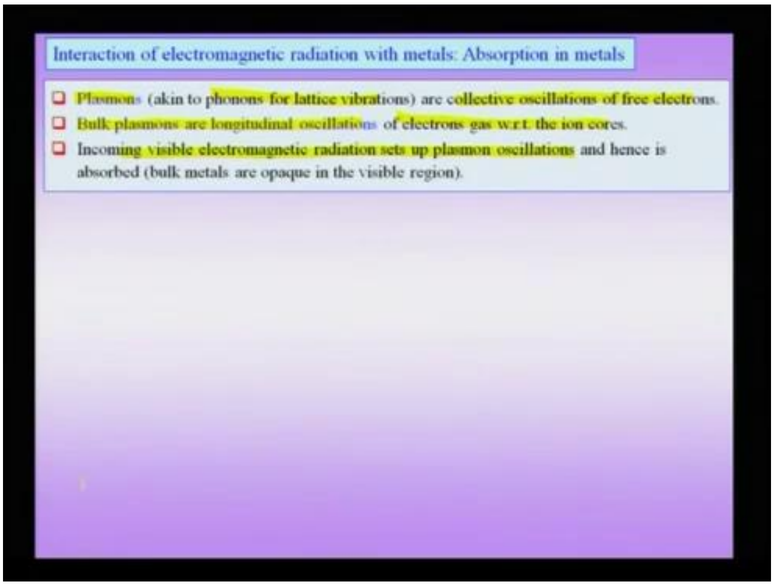

Interaction of electromagnetic radiation with metals: Absorption in metals

- ☐ Plasmons (akin to phonons for lattice vibrations) are collective oscillations of free electrons.
- ☐ Bulk plasmons are longitudinal oscillations of electrons gas w.r.t. the ion cores.
- ☐ Incoming visible electromagnetic radiation sets up plasmon oscillations and hence is absorbed (bulk metals are opaque in the visible region).

In such a behaviour, material obviously the behaviour is more complicated and what really does this electromagnetic wave do to this material is that it actually excites what are known as plasmons like you have phonons for lattice vibrations. Plasmons are collective oscillations of free electrons, so when you have an electromagnetic radiation impinging on a metallic surface it excite Plasmon waves oscillation inside the material. Typically what we call the bulk plasmons are longitudinal oscillations of electrons with respect to the ion cores. So, the a plasmons which is excited in the bulk of the material has a longitudinal character like we have sound waves travelling through a medium like air in this room which are longitudinal oscillations.

On the other hand, suppose I pluck a guitar string we know that is a transverse oscillation now because the incoming electromagnetic wave sets up Plasmon oscillation. This implies that this material there is a resonance happening that means an electron external electromagnetic field a wave is going to be absorbed by the medium.

Now, it is going to set up the electromagnetic or oscillations of the free electrons which we call Plasmon therefore, because of this Plasmon resonance what is happening is that you typically find metals are opaque metals do not transmit light. We will see that this is true for the visible radiation we will have taken the more detail picture that what kind of a wavelength, how it interacts with the metal in the coming slides, but this is true for visible radiation. Typically, we find that metals are opaque to the visible radiation again we will take up one more interesting case later on wherein you make thin films of a metallic material like gold.

So, thin films of metallic material can actually become a transparent and this we when we pointed about what how the properties of nanomaterials come about in those lectures. We talked about a phenomena that when there is insufficient material, then you would have certain effects coming like for instance transmission through gold. This is not really a nano phenomenon, this is not something new physics coming if there is insufficient material.

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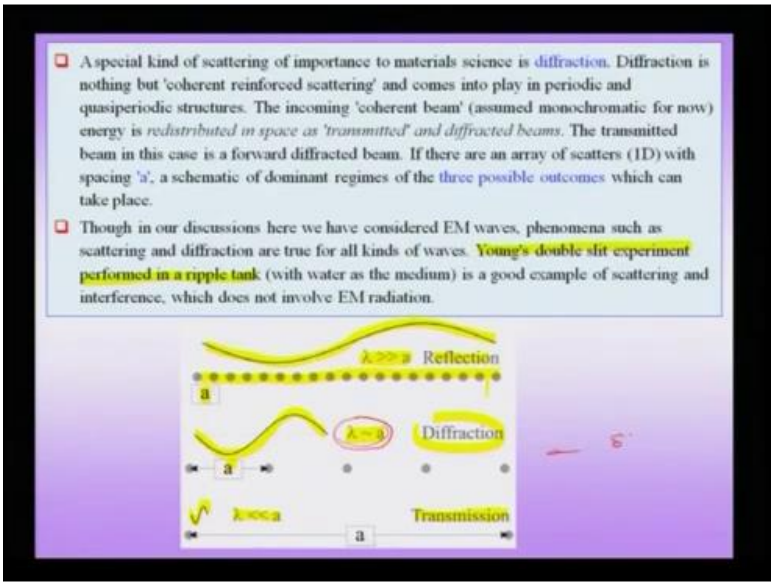

- A special kind of scattering of importance to materials science is diffraction. Diffraction is nothing but 'coherent reinforced scattering' and comes into play in periodic and quasiperiodic structures. The incoming 'coherent beam' (assumed monochromatic for now) energy is *redistributed in space as 'transmitted' and diffracted beams*. The transmitted beam in this case is a forward diffracted beam. If there are an array of scatters (1D) with spacing 'a', a schematic of dominant regimes of the three possible outcomes which can take place.
- Though in our discussions here we have considered EM waves, phenomena such as scattering and diffraction are true for all kinds of waves. Young's double slit experiment performed in a ripple tank (with water as the medium) is a good example of scattering and interference, which does not involve EM radiation.

Suppose, I did a brags equation on a material on a point scatters like this if I had an infinite array a three dimensional crystal and I through electromagnetic radiation then I would obtain sharp delta peaks in reciprocal space. Suppose, now I had a finite crystal there we have peak broadening and this peak broadening is essentially coming from insufficient number of atomic films.

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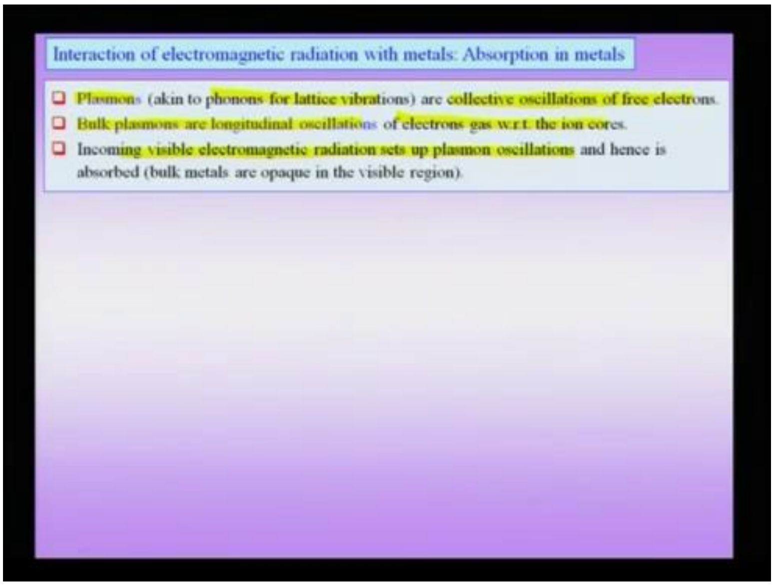

Interaction of electromagnetic radiation with metals: Absorption in metals

- ☐ Plasmons (akin to phonons for lattice vibrations) are collective oscillations of free electrons.
- ☐ Bulk plasmons are longitudinal oscillations of electrons gas w.r.t. the ion cores.
- ☐ Incoming visible electromagnetic radiation sets up plasmon oscillations and hence is absorbed (bulk metals are opaque in the visible region).

There is no new physics out there, similarly you will notice that when you make thin gold foils, they actually can become transparent to some parts of the electromagnetic spectrum, but we will take up the this case in detail very soon. So, we are seeing that when you have an incoming electromagnetic radiation we have to worry about something more than just the presence of the ion cores of the scatters. We have to worry about the free electron cloud surrounding this ion core these free electron clouds are set into collective oscillations and these collective quantise oscillations are called plasmons. These plasmon oscillations or resonance can actually give rise to a absorption and a metal, in other words metals are not transparent as we know.

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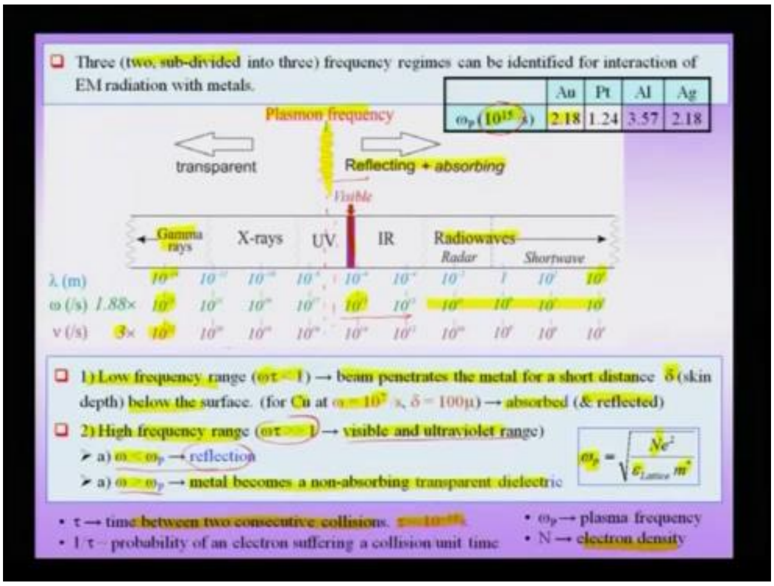

- Three (two, sub-divided into three) frequency regimes can be identified for interaction of EM radiation with metals.

	Au	Pt	Al	Ag
ω_p (10^{15}/s)	2.18	1.24	3.57	2.18

- 1) Low frequency range ($\omega\tau \ll 1$) → beam penetrates the metal for a short distance δ (skin depth) below the surface. (for Cu at $\omega = 10^7$/s, $\delta = 100\mu$) → absorbed (& reflected)
- 2) High frequency range ($\omega\tau \gg 1$ → visible and ultraviolet range)
  - a) $\omega < \omega_p$ → reflection
  - a) $\omega > \omega_p$ → metal becomes a non-absorbing transparent dielectric

$$\omega_p = \sqrt{\frac{Ne^2}{\varepsilon_{Lattice}\, m^*}}$$

- τ → time between two consecutive collisions. [illegible]
- 1/τ – probability of an electron suffering a collision unit time
- ω_p → plasma frequency
- N → electron density

Now, what is the regime of transparency and opaqueness of a metal, so when we talk about visible radiation we have already pointed out what really happens and that is of course for a typical metal like silver. For instance, what is the scenario when you have for instance and the electromagnetic radiation starting from gamma rays with very high frequency of about 10 power 23 in the circular frequency or about 10 power 22, 3 into 10 power 22 in the linear frequency? Then, and on the other hand of the frequency regime you have the radio waves which have very long wavelengths of the order of about 10 power 4 meters.

That means you have wavelengths of the order of kilometres you have this extremely short wavelength 10 power minus 14 meters gamma rays of the spectrum and you have wavelengths for the order of kilometres. Obviously, all these different regions of the electromagnetic spectrum are not going to interact identically with the given metals. So, what are the factors which come into play, so we can actually divide the electromagnetic spectrums into three frequency regimes? In these three frequency regimes two of them come in the range of the high frequency regime and one of them is the low frequency regime, how do I determine my high or low frequency regime?

I multiply my frequency or of course omega being the circular frequency with the mean free collision time which we had encountered before and typically we had noted that the mean free collision time is a collision time between of electrons between. In other words, it accelerates or maintains and maintains increases velocity between two collisions. Then, there are it may and then interact with the phonon or an impurity and gets scattered and the time between the two is called the mean free time more casually or the average collision time. This happens free of the order of about 10 power minus 14 seconds for most metals, so I multiply my circular you can see with my mean free time and note if it is much less than if it is less than 1 or it is much greater than 1.

So, let us take an example for instance of the case of copper and when you are talking about frequency like 10 power 7 Hertz and we see that this electromagnetic radiation is actually absorb and of course,, some of it will be reflected. Now, in making this discussions as I pointed out we have to invoke the concept of Plasmons and Plasmons have a certain characteristic frequency depend on the material. This Plasmon frequency typically lies in the range of about 10 power 15 Hertz, so suppose I am talking about the Plasmon frequency which is given as a function of what you might call the electron density.

They and of course also depend on the free electron mass in the permittivity of the medium this Plasmon frequency lies in the range of about 10 power 15 hertz for gold for instance is 2 power 1, 8 into 10 power 15 hertz. So, what is happening now is that in the low frequency regime the beam penetrates the metal for a short distance, which is called a skin depth and then it is absorbed and some of it is reflected. When I am talking about the low frequency regime, which is a reflecting and absorbing regime I am talking about the regime on the right hand side. So, this my low frequency regime, so here an reflection and absorption is being dominate and what is my switch over dominant or the switch over kind of frequency which you have to monitor.

This is the Plasmon frequency and i noted that this Plasmon frequency is of the order of 10 power 15 Hertz. In other words, in the omega scale it is my 10 power 15 here, so my Plasmon frequencies are approximately in this regime and my visible lies to the right of the Plasmon frequencies. That means that in the visible region metals are reflecting and absorbing they do not transmit any of the radiations.

So, the bulk metals typically we know that we already have this experience that they do not transmit any of the radiation in the high frequency regime wherein the omega tau is greater than 1. We see that this is of course coming in the visible and the ultraviolet region there are two possibilities when omega is less than omega peak. That means this region where the omega is actually less than omega p this region to the right of it the visible and the infrared regime so you have to the right of the Plasmon frequency. You have the visible and the infrared, which is actually the low frequency regime given in the high frequency regime, wherein omega tau is much greater than 1.

In another words, I have the low frequency regime where I know that metals are not going to transmit, then I take up the high frequency regime, but then subdivided into two parts that part where the omega is less than omega plasmon. The case where omega is greater than omega plasmon noting that the omega plasmon is of the order of 10 power 15 Hertz, which lies somewhere in the frequency spectrum here. So, the visible and infrared are actually larger frequencies compared to what you might call the omega Plasmon. So, in this high frequency regime you see that visible an ultraviolet radiation is actually reflected because this regime lies because the plasmon frequency is less than the or greater than the omega of the radiation.

Suppose, you go towards regime where omega is much greater then beam, then the metal becomes the non absorbing transparent dielectric. So, if you are in this regime, wherein the omega is much larger than omega p's, so here somewhere here then you would notice that for radiations like gamma rays and x-rays a metal can actually become transparent. So, you have three kind of interactions possible of radiation with a metal one regime in which is absorbed and reflected. Essentially, other regime wherein the visible and ultraviolet regime where there is reflection. There is another regime wherein you can actually see that the metal actually becomes some kind of a transparent dielectric which happens only in very high frequency regime.

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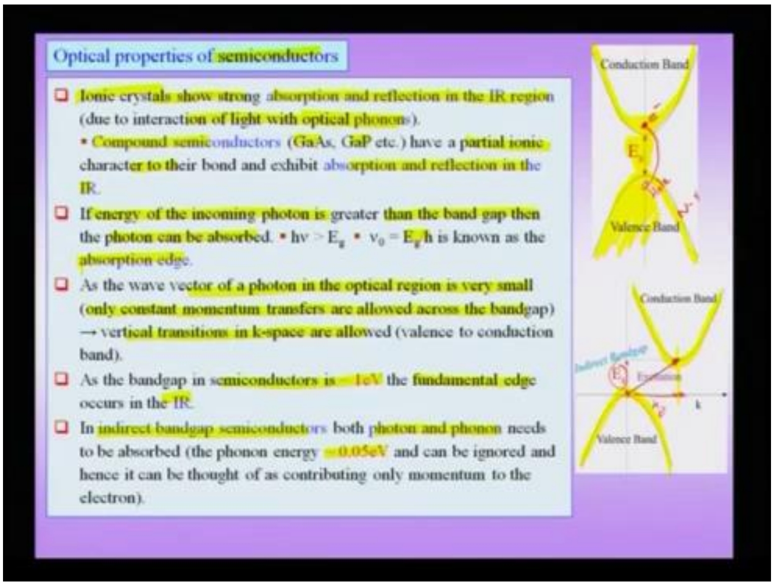

Optical properties of semiconductors

- Ionic crystals show strong absorption and reflection in the IR region (due to interaction of light with optical phonons).
  - Compound semiconductors (GaAs, GaP etc.) have a partial ionic character to their bond and exhibit absorption and reflection in the IR.
- If energy of the incoming photon is greater than the band gap then the photon can be absorbed. • $h\nu > E_g$ • $\nu_0 = E_g/h$ is known as the absorption edge.
- As the wave vector of a photon in the optical region is very small (only constant momentum transfers are allowed across the bandgap) → vertical transitions in k-space are allowed (valence to conduction band).
- As the bandgap in semiconductors is ~ 1eV the fundamental edge occurs in the IR.
- In indirect bandgap semiconductors both photon and phonon needs to be absorbed (the phonon energy ~0.05eV and can be ignored and hence it can be thought of as contributing only momentum to the electron).

Now, having this broad picture we that means metals have to be treated slightly separately from semiconductors and other dielectrics. So, we see when we talk about the dielectric like glass we know or I would to crystal we know that I do not have to worry about Plasmon's at all. That means I can talk about purely in terms of the normal language of a transparent dielectric except close to those resonances wherein the dielectric starts to absorb. We already noted the mechanisms of those resonances, but when you are talking about a metal the predominant behaviour of metal to electromagnetic radiation is coming from free electrons and of course when these free electrons start stop to a response.

In the case when the omega is much greater than omega p, then you would note that actually that the material the metal can also become transmit to an electromagnetic radiation as it may happen to high gamma rays etcetera. The optical properties of a semiconductor as you would expect is going to be very different from that of a metal and this is going to be obviously dominated by the phenomena of the band gap. So, we will take up briefly here what are the issues of the band gap, how is it going to affect my absorption and emission from a semiconductor and we are talking about absorption and emission of electromagnetic waves now.

We will take up in somewhat detail the fact that what happens when I make a semiconductor particle like Cd Se or gallium or Sn It in a very nano form. That means I have particle size of the order of 10 or 20 or 5 nanometres ionic crystals shows strong absorption and reflection and infrared region due to interaction on light with the optical phonons. Now, the absorption is not because of Plasmon because there are no free electrons in this system, this is a semiconductor and this ionic material which is Dielectric tends to absorb in the infrared region.

Now, you are setting up resonances in the optical phonon spectrum compound semiconductors have partial ionic character and also exhibit absorption and reflection in the infrared like in we are talking about compound semiconductor. It can be direct band gaps gallium arsenate or gallium porcine and these have a certain partial ionic character which implies that they also have a partial behaviour which is similar to ionic crystals. Now, if the energy of the incoming photon is greater than the band gap, then the photon is absorbed, so you have the balanced band in the semiconductor which is schematically shown here, you have the conduction band.

The no in semiconductor it is 0 kelvin the valence band is full and the conduction band is empty and if you have, you are at a finite kelvin temperature you know that kelvin temperature. You know that thermal excite excitation of electrons will put some electrons into the conduction band and we know that this fraction is given by the Fermi direct statistics. Now, what is happening is that if I am sending electromagnetic radiation and if the measure of the energy of the electromagnetic radiation is the frequency. If I have the frequency is much smaller than the critical frequency given by Eg by H, then there is no absorption and like that of a metal and because they are always free electrons which can be oscillated.

Now, if you keep on increasing the frequency then the energy in the incoming photon can exceed that of Eg. In other words, an electron can be excited from the valence band into the conduction band and you leave a hole in the valence band a hole is nothing but the fact that there are actually now n minus 1 electrons in the conduction valence band. I can either deal with the motion of these n minus 1 electrons in opposition to the electric field in a direction opposite to an electric field or I can talk about the motion of one hole in the direction of the electric field.

So, this is a convenience I use language of hole is for convenience, so I do not have to deal with n minus 1 electron, but I can just talk about one hole moving in the valence band. Therefore I have would have a strong absorption when my frequency exceeds is critical frequency of the absorption edge and we will therefore, absorb the electromagnetic, the semiconductor will absorb the electromagnetic radiation. Now, as the wave vector of photon in or the optical region is very small and only a constant momentum transfers are allowed across the band gap vertical transition in case space are allowed.

That means that if I have a direct band gap semiconductor I can ignore the wave vector of the photon in coming photon because it is very small and I can only talk about the energy transitions. So, I need to do not worry about what you call the momentum of the photon, but on the other hand suppose I am talking about an indirect band gap semiconductor in which case the conduction band is actually shifted in k space. That means the conduction band minima lies at a certain fixed value of k here compared to the maxima in the valence band in energy. This implies that when I want to excite an electron to the from the valence band to the conduction band, then not only to support, supply the energy Eg.

Additionally, I will have to supply if I will just to add a substitute called a kg kind of a momentum. Now, as I pointed out, the photon itself does not have this momentum, so this would imply that purely by a photonic excite photonic excitation. I cannot excite and electron from the valence band to the conduction band, but luckily a phonon comes to our aid here. That implies that in indirect band gap semiconductors like germanium both of photon and phonon together give rise to the excitation and in this case of the phonon i ignore. It is an actually like for the photon ignored its momentum because it was small for the phonon.

I can effectively ignore its energy because its energy is small and I can think of the phonon only contributing only the momentum to the electron. So, I have now two aspects coming in and I am trying to excite an electron in the indirect band gap semiconductor one is the energy coming from the photon. The other is momentum coming from the phonon and put together they supply the required momentum and the energy to excite electrons from the valence band to the conduction band, typically the band gap of semiconductors of the order of about Ev's a few Ev's.

That implies that the fundamental edge actually is in the infrared and therefore, semiconductors though cannot be used as lenses in the visible region because you know semiconductors are not transparent to the visible region. You can make infrared when you make infrared cameras lenses can be made out of these semiconductors because below the absorption edge they actually would transmit. Therefore, I can make a lens out of a semiconductor, therefore to summarize the optical properties of semiconductor the optical properties of semiconductor are dominated by two factors. One of which is given in this slide other on we will take up in the next slide is the fact of the band gap.

That means any energy or frequency which is lower than the critical energy or the critical frequency is not going to be absorbed. On the other hand, any other in higher energy than the band gap is going to be absorbed by the semiconductor. Later on we will have lot to say about how this band gap actually changes with confinement how do you make it when you make the materials smaller, how the band gap changes. We said that in the context of absorption in semiconductors not only have I have to worry about this band gap energy Eg, I also have to worry about the relative position of the conduction band minima we saw with respect to the absorb valence band maxima.

So, this could be a direct band semiconductor in which the minima lies right above the maxima or it could be indirect band gap semiconductor in which case there is a shift of the minima with respect to the maxima of the valence band. In this case, space in the momentum space which implies that I have to supply the energy coming from a photon ignoring its momentum. The momentum coming from a phonon ignoring its energy and put together the phonon and photon actually give rise to excitation of an electron from the valence band to the conduction band.

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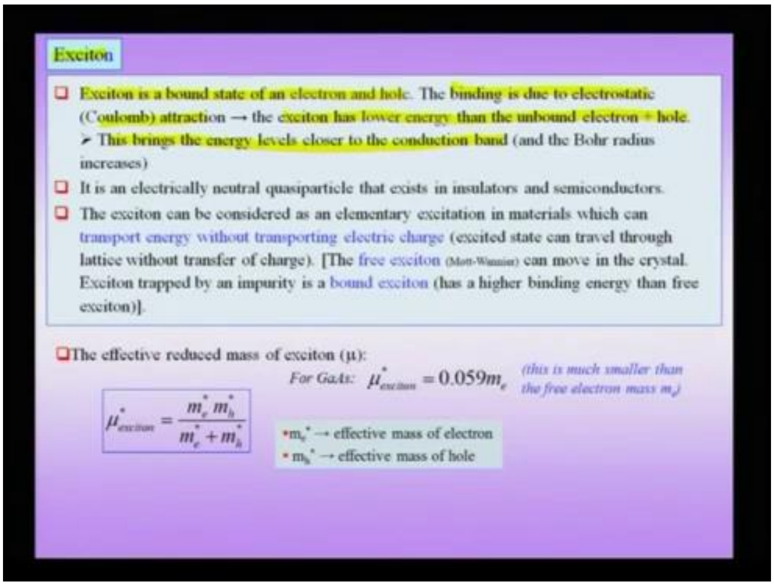

Exciton

- Exciton is a bound state of an electron and hole. The binding is due to electrostatic (Coulomb) attraction → the exciton has lower energy than the unbound electron + hole.
  - This brings the energy levels closer to the conduction band (and the Bohr radius increases)
- It is an electrically neutral quasiparticle that exists in insulators and semiconductors.
- The exciton can be considered as an elementary excitation in materials which can transport energy without transporting electric charge (excited state can travel through lattice without transfer of charge). [The free exciton (Mott-Wannier) can move in the crystal. Exciton trapped by an impurity is a bound exciton (has a higher binding energy than free exciton)].

- The effective reduced mass of exciton (μ):

For GaAs: $\mu^*_{exciton} = 0.059 m_e$ (this is much smaller than the free electron mass m_e)

$$\boxed{\mu^*_{exciton} = \frac{m_e^* m_h^*}{m_e^* + m_h^*}}$$

- m_e^* → effective mass of electron
- m_h^* → effective mass of hole

When I said that two factors come into play when I am talking about absorption in semiconductors the second factor is what is called the exciton. Now, having excited and hole I mean excited electron to the conduction band you are left with an electron in the conduction band and a hole in the valence band. So, you have these two factors you have a hole in the valence band and you have an electron in the conduction band, but in principle. Of course you might assume that this hole would move in its valence band independently in response to an electric field of course dictated by its mobility in the valence band which would be different from the mobility of an electron in the conduction band.

You would assume that this electron would move freely in the conduction band this situation may or may not be. So, in fact there would be an columbic attraction between the electron and a hole and you may form what is called a bound state between the electron and the hole which is called an exciton. So, n exciton is a bound state of an electron in a hole this binding is due to electrostatic or columbic attraction and the exciton has lower energy then the unbound electron plus an hole. So, obviously because there is a lowering of energy that this binding is taking place and this implies a very important things that brings an energy level closer to the conduction band.

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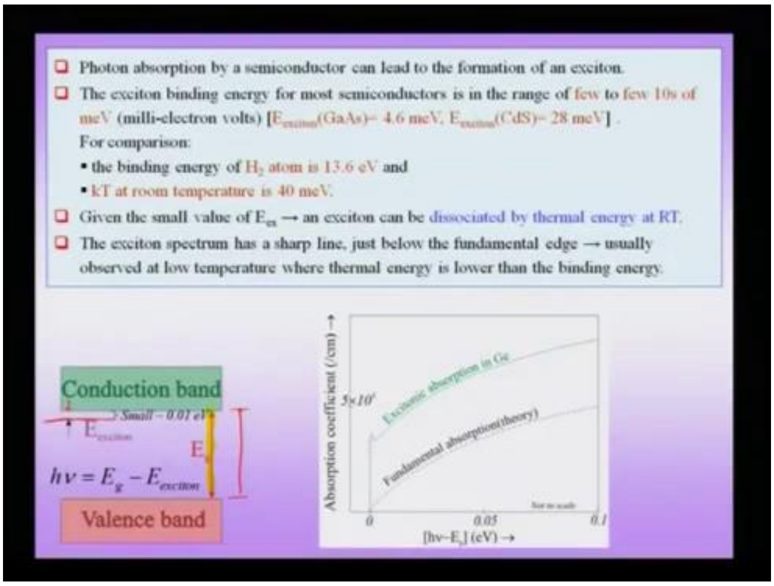

- ☐ Photon absorption by a semiconductor can lead to the formation of an exciton.
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  For comparison:
  - the binding energy of H_2 atom is 13.6 eV and
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- ☐ The exciton spectrum has a sharp line, just below the fundamental edge → usually observed at low temperature where thermal energy is lower than the binding energy.

$$h\nu = E_g - E_{exciton}$$

So, what is exactly happening is that so you have the conduction band edge and you have a certain Eg that means if I do not supply my Eg. Then, I cannot excite an electron from the valence band to the conduction band, but because of the columbic attraction between the hole and the electron. You can have a bound system and this bound system has an lowering of energy with respect to the conduction band and this is now my exciton binding energy. So, this small number here and this exciton binding energy is typically very small it is of the order of 0.01 Ev or about 10 milli electron volts.

This is small binding energy never the less this energy is lower than the conduction band edge energy, this is important consequences to the absorption of semiconductor. We shall see now, but so this exciton forms and we what is this exciton this is a bound state. Typically we will see that this exciton can be thought of an electron and a hole moving around that means a spatially confined and they are moving around each other centre of mass and this can be calculated.

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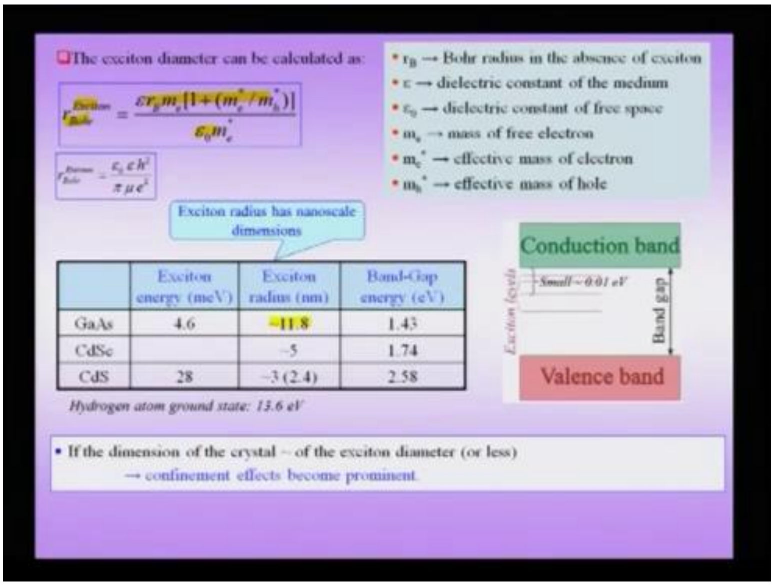

The exciton diameter can be calculated as:

$$r_{Bohr}^{Exciton} = \frac{\varepsilon r_B m_e [1+(m_e^* / m_h^*)]}{\varepsilon_0 m_e^*}$$

$$r_{Bohr}^{Exciton} = \frac{\varepsilon_0 \varepsilon h^2}{\pi \mu e^2}$$

- r_B → Bohr radius in the absence of exciton
- ε → dielectric constant of the medium
- ε_0 → dielectric constant of free space
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Exciton radius has nanoscale dimensions

	Exciton energy (meV)	Exciton radius (nm)	Band-Gap energy (eV)
GaAs	4.6	~11.8	1.43
CdSe		~5	1.74
CdS	28	~3 (2.4)	2.58

Hydrogen atom ground state: 13.6 eV

- If the dimension of the crystal ~ of the exciton diameter (or less)
  → confinement effects become prominent.

This radius around which they move around is can be called as the bore exciton radius which is which is given by some of the fundamental constants of an electron. This Bohr exciton radius is of the order of about eleven point eight nanometres if it is a nanoscale, it is not like the normal Bohr radius of an hydrogen atom it is much smaller as you k, therefore you can have an electron hole in a bound state.

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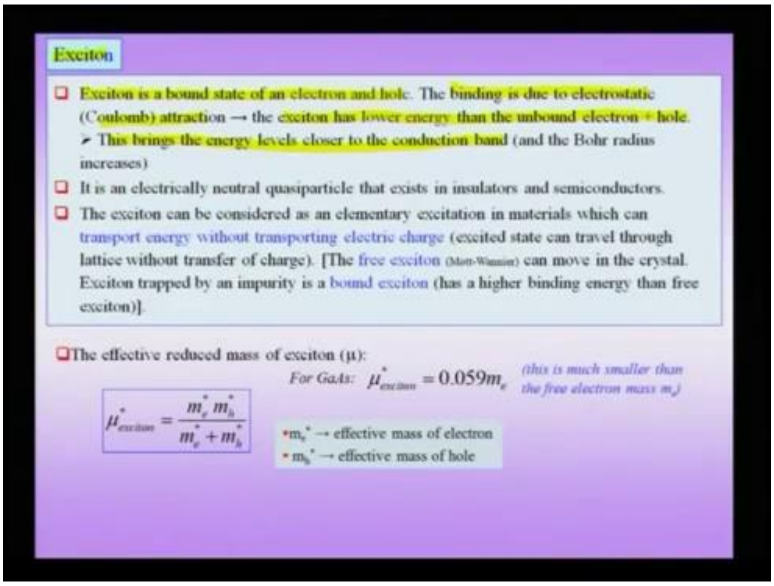

Exciton

- Exciton is a bound state of an electron and hole. The binding is due to electrostatic (Coulomb) attraction → the exciton has lower energy than the unbound electron + hole.
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- It is an electrically neutral quasiparticle that exists in insulators and semiconductors.
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For GaAs: $\mu_{exciton}^* = 0.059 m_e$ *(this is much smaller than the free electron mass m_e)*

$$\mu_{exciton}^* = \frac{m_e^* m_h^*}{m_e^* + m_h^*}$$

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A new concept called the concept of an exciton which is now spatially bound and spatially means that it is spatially bound to a radius of the Bohr radius. We just now pointed out they move around the centre you can think of them as moving around a common centre of mass and this give rise to an energy level the bound level of an exciton in the band gap, so this is very important.

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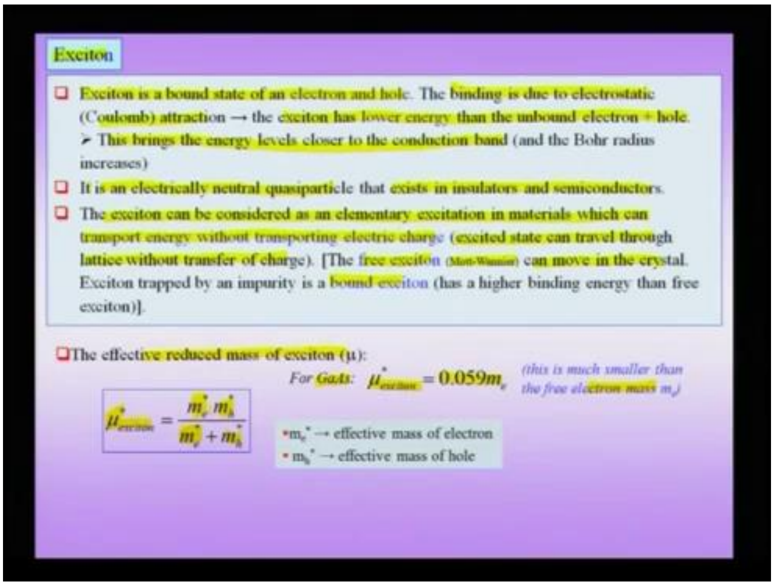

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This exciton in electrically neutral quasiparticle because now there is a hole in an electron together they form a neutral quasiparticle that can exist in insulators and semiconductors. We will talk about the relevance of exciton, so only in semiconductors here the exciton can be thought of as an elementary excitation in materials. This can transport energy without transporting electric charge because this sum total of the electron hole is the neutral particle. When it moves to the crystal as in the bound form this is can be thought of as transporting energy without transporting electric charge this excited state can travel through a lattice without transfer of charge.

So, this is very important and for now we will restrict ourselves to what is known as a free exciton or otherwise given a name as a Mott Wannier exciton which can move through the crystal. There can be other forms of excitons which are known as bound excitons which we will not talk about here the exciton can itself be thought to have as an effective mass. If an effective reduced mass, which depends on the effective mass of the electrons and holes as given in this formula and if you look at the effective mass of an exciton, you can see that and for example, I am taking gallium mass. Here, it is got the mass of about 0,059, in other words it is much smaller than the mass of an electron.

So, exciton can be ascribed an exciton Bohr radius similar to the concept of an Bohr radius in a hydrogen atom an exciton can be given a mass which is the effective mass or mu star of an excitons. This is of course as we just now saw it has a much smaller value than the eletron mass that means a much lighter particle quasi particle as you should be more careful with this terminology because this is a quasi particle as compared to an electron.

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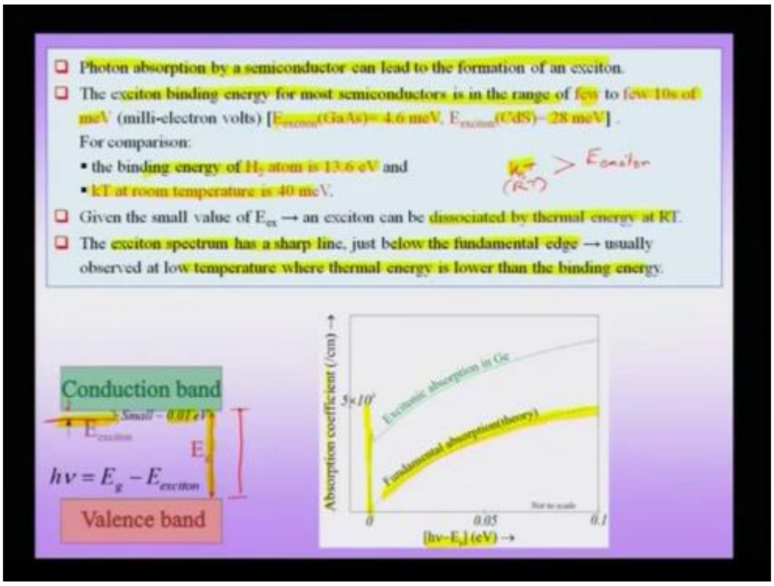

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Cadman sulphide is the order of about 28 milli electron volt, so this is the range of these binding energies of this exciton and if you want for a comparison k t at room temperature is about 49 milli electron volts this tells you directly that since kt at room temperature. I am now talking about kt at room temperature and kb is the Behrman constant is greater than the exciton binding energy. This implies that at room temperature in bulk semiconductors, the exciton will be unbound the thermal energy will overcome the binding energy of the exciton.

This implies that the exciton actually will be dissociated at room temperature, so that we implies we take a room temperature and do the electromagnetic radiation absorption experiment. Then, you would note that there will be no p corresponding to the exciton you and if you want to take a even higher energy scale.

You will note that the binding energy of an hydrogen atom is about 13.6 electron volts much larger than the exciton binding energy. So, we note that we have an important concept like exciton, but it becomes important only at the low temperatures and absorption of semiconductors one of the reasons. We are taking up this discussion excitons in details that often when we read literature regarding nanoparticles semiconductor nanoparticles in there absorption. The word excitonic absorption is used and this sometimes can be misleading because the actual a effect is coming from confinement effect and not from excitonic absorption.

Therefore, we have to be little careful with the terminology and the physics behind it and if you look at semiconductor low temperature then the excitonic absorption spectrum is a sharp line just below the fundamental edge of the semiconductor. This is observed at low temperature where thermal energy is lower than the binding energy, so if I go to low temperature the kt b contribution goes down the exciton binding energy is larger than kt b. This implies that I would absorb observe an excitonic absorption and for now I am just showing one excitonic level a simplified diagram wherein I would have an absorption corresponding to the exciton just below the fundamental edge.

So, I am plotting Hu minus Eg in electron volts as a function of the absorption coefficient and for a normal semiconductor without exciton. You note that the absorption coefficient would go increase like this is theoretical plot, but in the presence of the exciton, you will observe a strong peak here which is now my excitonic peak, which can be observed only at low temperatures. So, because now even though the energy level is only bit slightly below the conduction band edge, but statistically this implies that many more electrons are going to be excited to the exciton level and which gives you a strong absorption, excitonic absorption.

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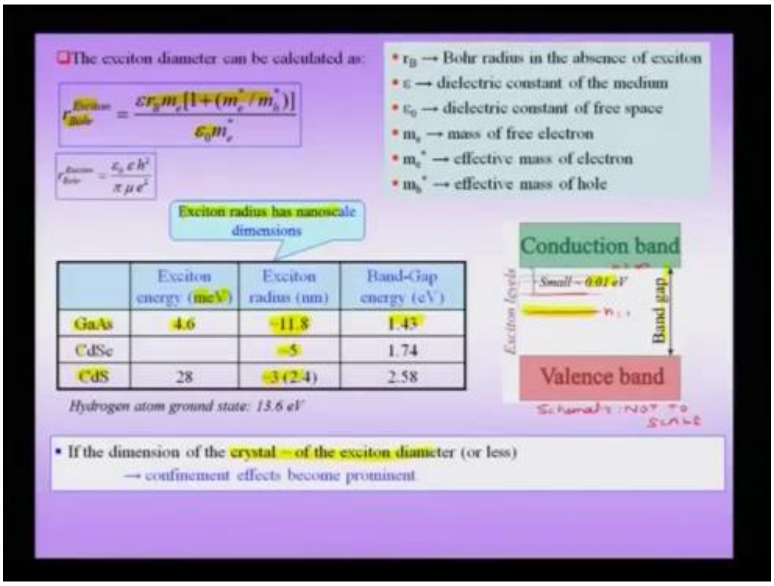

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Now, an important point we already saw in the case of the exciton radius is the fact that the exciton radius itself is a nanoscale sub entity within the semiconductor. So, it is a critical number within a material which the excitons binding radius which is of the order of nanometres for instance for gallium arsenate with an exciton energy of about four 0.6 Ev for a milli electron volts the exciton radius is of the order of 11.8 nanometres. The bulk and band gap is of the one order of 1.43 ev which is much larger than the Ev quantities for Cd Sec. The exciton radius about 5 nanometre for Cd Si T is about of the order of about 3 or 4 nanometres and if you look at a more slightly more detailed picture of the exciton, you can actually see that you can ascribe quantum number to the excitons.

In other words, the lowest and this is of course the exaggerated picture because we know that the exciton energy is very small and we have the compared to the band gap energy this is out of scale diagram. So, we should note that this is like the previous diagram I showed you and you can see that in this you can have multiple quantum numbers. So, this could be the n equal to 1 state and n equal to infinity state is nothing but the conduction band gap edge the conduction edge itself becomes a. Therefore, you can have multiple levels excitonic levels and therefore you can have multiple excitonic absorptions.

They will suppose you look at a spectrum like this the other excitonic absorptions would also show up in such a spectrum and you have to go to low temperature for this. Then, these excitonic levels can also be thought of as quantized levels having quantum numbers of its own.

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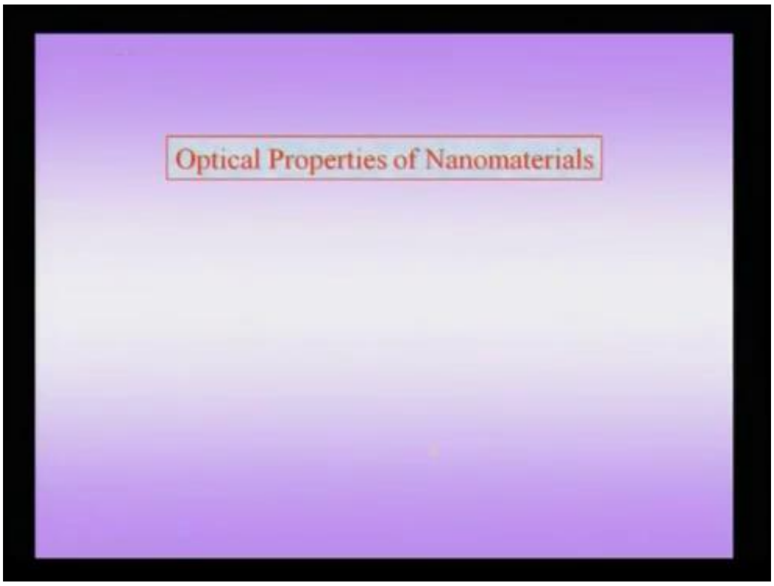

Optical Properties of Nanomaterials

We can note that if the crystal becomes very small of the order of the excitonic radius, then there are important things which we need to consider.