Nanostructures and Nanomaterials Characterization and Properties
Prof. Anandh Subramaniam
Prof. Kantesh Balani
Department of Material Science and Engineering
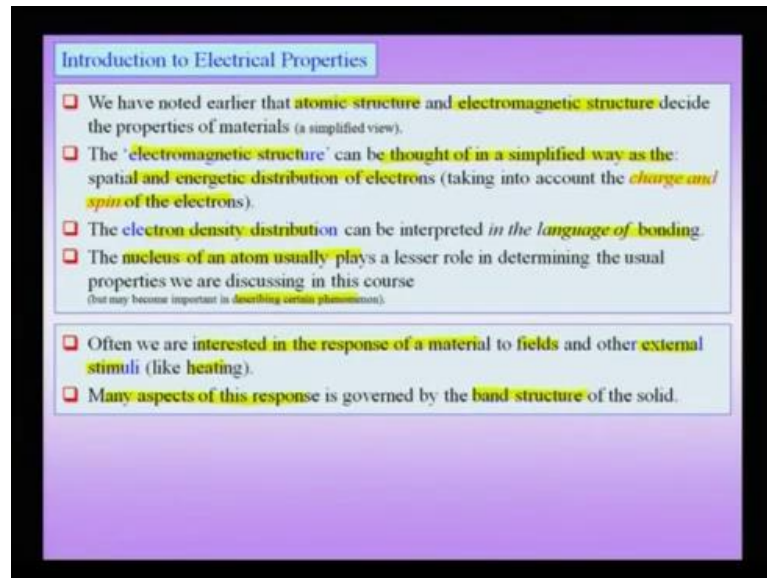**Indian Institute of Technology, Kanpur**

Lecture - 20
Electrical, Magnetic and Optical Properties of Nanomaterials (C4)

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- ELECTRICAL PROPERTIES
- Introduction to Electrical Properties:
- Free electron theory ● Fermi level ● Conduction by free electrons ● Mean free path & average collision time
- Phonon (thermal) and impurity scattering ● Band structure ● Density of states
- Electrical Properties of Nanomaterials
- Conduction in nanoscale materials: quantum confinement effects
- Density of states in 2D, 1D (carbon nanotubes) & 0D nanomaterials
- Electron tunneling & Coulomb blockade

We had discussed in detail about the physical and mechanical properties of not only normal bulk materials, but also of nanostructures and nanomaterials. The next topic we take up is the topic of electrical properties. As before we will first describe some of the basic concepts involved in electrical properties and electronic properties followed by electrical and electronic properties of nano structure materials and nano crystals and other nano entities. Further, we will take up part of this overall gamut of what you might call the electronic structure and electronic properties magnetic properties and also optical properties, that will be in the coming lectures.

Now, if I were to consider electrical properties then before we had already noted the two important factors come into play, when we want to understand the properties of materials. It is of course, at the heart of every all the properties is what we may know as the electromagnetic structure. And crudely we would like to sort of divide this overall electromagnetic structure into what we may call the atomic structure. Where, we will be worried about the atomic entities and their positions. Also, what we may call the electron distribution, which we might call the electromagnetic structure in this specific context.

This electromagnetic structure can be thought of as in a simplified way as the spatial and energetic distribution of electrons, taking into account the charge and the spin of the electrons. In other words when you are talking electromagnetic structure, typically unless we are really interested in very specific properties. Typically, the nucleus of the atom is usually ignored. So, we are worried about the electrons, we are worried about the electron density. We are worried about the spatial and energetic distribution of these electrons. In this process not only the worry about the charge of the electrons in terms of its density, but also we worry about the spin of the electrons.

As we shall see later the spin is the dominant force behind the magnetic properties, which we will take up and usually in the common language. We call the language of bonding this electron density distribution is interpreted as kind of a bonding. In other words if the electron density distribution is high between the two atoms, we call it a

covalent bond. If the electron density distribution shifted towards one atom, we call it a ionic bond. If the electron density distribution is delocalised in other words the electron belongs to the whole solid and not to a particular atom, we call it such a material or such a kind of a bonding as the metallic bonding.

Just to reiterate the nuclear aspects are usually ignored unless of course, we are worried about the certain kind of important phenomena, where in the nucleus may play an important role. In these set of lectures we will not consider that further. Often, when you are talking about electronic properties and electrical properties, we are interested in the response a material to do kind of entities. One is the fields the electromagnetic fields, which is essentially would be, which we would mean we are talking about optical kind of properties and other kind of external stimuli like heating.

So, these two aspects you always keep in mind when you are trying to understand, for instance any kind of properties. Suppose, I am talking electrical conductivity then I will worry how electrons are accelerated, when you apply an electrical field. How this electrical conductivity is actually going to change with temperature, as we shall see soon. Many aspects of this response, that means the response is the material to external stimuli.

These external stimuli could involve fields and heating another kind of stimuli is governed by quantity known as the band structure of the solid. In other words, we have individual atoms, which have discrete energy levels, but when these atoms come together, we have a concept of a band, where in the electrons no longer belong to a single atom, but to belong to a entire solid as a whole. This band structure is going to determine some of the important properties, which include the magnetic, optical and electrical properties of the solid.
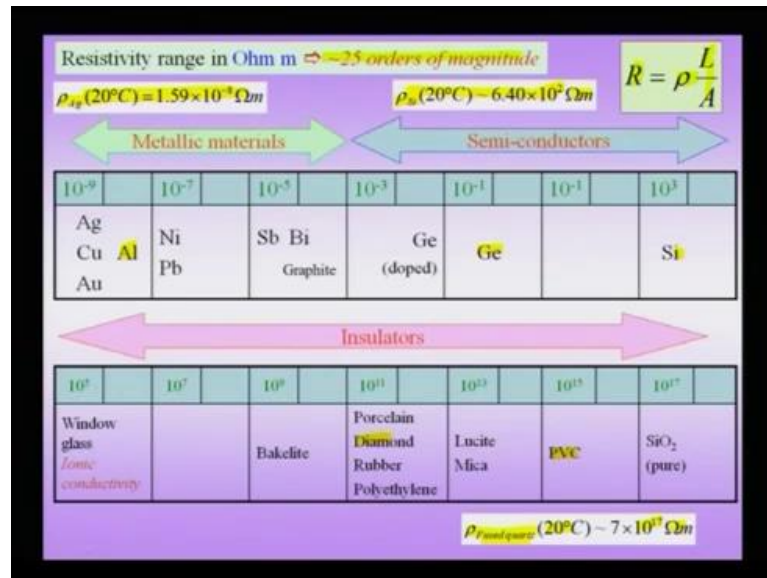
Let us start with understanding what you may call the resistivity and its variation across different kind of elements. You know resistivity is the coefficient when you are talking about the variation of the systems with geometric related terms like the length of the conductor divided by the area of the conductor. Resistivity happens to one of those kinds of one of the rare kind of material properties, which varies to about 25 orders of magnitude. When you go across from one element to the other on one hand, we have extremely good conductors with very low resistivities like silver, which at 20 degree celsius has a resistivity of the order of about 10 power minus 8 ohm meter.

On the other hand we have extremely high insulators like fused quartz at 20 degree celsius as a resistivity of the order of both 10 power 17 ohm meter. So, this is one of those rare quantities, which varies orders of magnitude, which implies. Suppose, I am using aluminium as a conductor. If on the surface of this aluminium conductor you have formed an oxide, which is going to be a 1 2 3. Then you would notice that the resistivity is going to jump by orders of magnitude. This implies that my electrical conduction is going to be very poor just by this mere process of oxidation, at the surface of this aluminium conductor.

There are materials with intermediate conductivity like silicon, which has an conductivity of the order of about 10 power 2 ohm meters. If you look at how this resistivity changes with temperature than the behaviour too here, too is the very different

for instance. If you heat silver than the resistivity would increase on the other hand, when you heat silicon actually the resistivity would drop. In other words, if I do not understand such phenomena, then as we pointed out in previous slide.

We have to look at what is known as the band structure of the solid, which will tell us why such a behaviour of resistivity is formed. When I go from one kind of a material like Silver or Copper or Gold, which is a very good conductor to intermediate conductor. Like Germanium or Silicon to a very poor conductor, like Diamond or P V C or fused quartz as the case may be.

So, even for a simple property like electrical conduction and material property like resistivity I have to look at some of the details of the band structure or the electronic structure of the material. The simplest kind of a theory, which is which been proposed to understand what called a phenomena like conductivity or the variation like conductivity temperature, or the what it might call the origin of resistivity, when you actually apply an electric field is known as the free electron theory.

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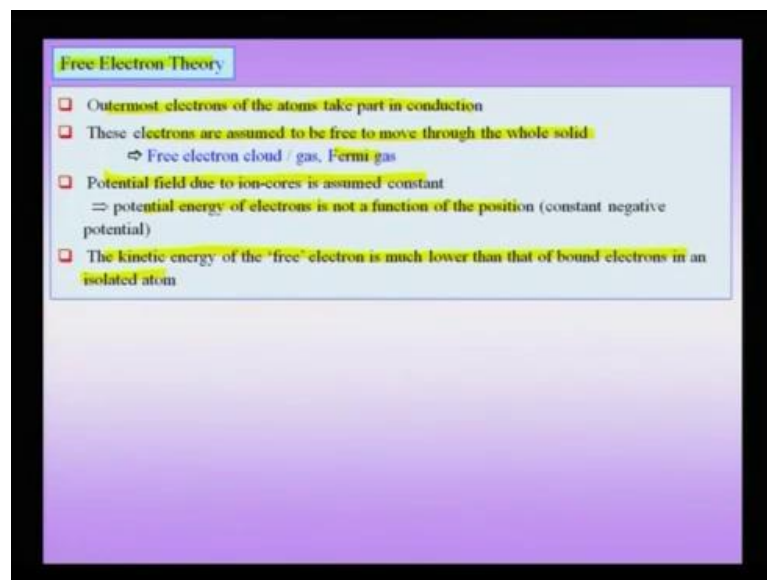
In the free electron theory the outermost electron of the atoms are only considered to be taking part in conduction, or in other words they these electrons belong to the whole solid and not to a particular solids. These electrons are assumed to be free moving through the whole solid. So, they are delocalized they roam belong to the single atom. This electron gas also often called as fermi gas or a free electron cloud and in it is

assumed that the potential field, due to the ion cores is assumed constant. The potential energy of electrons is not a function of the position, though it is moving around enough potential of these ion cores, it is assumed to be constant. That means there is no spatial variation of these what you might call the potential in which these electrons are moving.

It is to be noted that the kinetic energy of the free electron is much lower than the bound electrons in an isolated atom. Now, we have a simplified version of what you might call the real picture, which is called the free electron theory, but interestingly this free electron theory is able to explain many concepts, many simple concepts. We take them one by one. We will slowly build towards what you might call the region, where we need to transcend this free electron theory. Go into a what you might call a band structure, which is will be needed for explaining the conductivity of semiconductors and insulators. The starting point for all this is that we have something known as a wave particle duality of electrons.

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In others words every moving particle has certain wave nature. This wave nature becomes more and more important, when the mass of the particle becomes small, so for a very lightly massed particle like electrons the wave nature becomes extremely important. We will see later on that this wave nature is that the heart of what you might call quantisation of energy levels, where in we were talking about nano crystalline material or a nanostructure, where in we want to understand the conductivity. So, this wavelength

is given by h by m v. Typically, in a free electron theory you would plot what is known as the energy of the various levels. The orbital levels as a function of k, which is the defined as 2 pi by lamda, which is goes as the inverse of the lamda.

So, this wave number or the wave vector is what we plot against energy. In the free electron theory the energy is a function of k square, which are the other constants added on including the mass of the electron. In other words, you have what you might call a continuum of energy levels, which increases parabolically and electrons can occupy these continuum of energy levels. This implies that if suppose an electron sitting at the higher top most energy level. There are energy levels free above that to which it can be excited.

So, they are in proximity to this energy level and if you are looking at an increase in the wave debroi. Debroi wavelength, then you would notice that the k decreases and the energy decreases. So, in this, but of course, if you look little closely you will have to note that these energy levels though have to be from this kind of an equation looks continuous. They are actually slightly discrete, because of the Polly's extrusion principle, which tells that no two electrons can actually have the same set of quantum numbers. Therefore, if you look closely there may be a slope closely spaced electron levels, but nevertheless for now we will assume they are continuous.

Therefore, there is a series of levels, which can be available for the electron to occupy another kind of a diagram, which we will encounter, where in we do not plot energy versus the wave number or wave vector, which is where in we try to notice a different kind plot a different kind of quantity, which is called a density of state, which is also encountered more frequently than the K kind of a diagram. Now, we have to of course, know that when we write down the energy as half m v square. We are ignoring the relativistic corrections. Now, we noted that suppose I fill start filling electrons and I know that there are N number of orbitals, which need to be filled with these electrons. There will be obviously an highest energy level, which is filled.

So, all the electrons in the solid might fill up and still you will only reach a certain energy level, which means all the states below this energy are filled up by electrons. This is the top most energy level, which is filled this top most energy level, which is filled is called the fermi level. Typically, the concept of fermi level is defined as the highest energy level filled, but at 0 Kelvin

Now, if in other words if I look at my energy versus the property of finding an electron. I would note that at 0 Kelvin the curve, which is the green curve is the one, which is valid. In other words upto the highest level of fermi level all the energy levels are filled that means the probability of finding an electron is one, but beyond the fermi level no energy levels are filled at 0 Kelvin, which means the probability of finding an electron, above the fermi level is 0. This is so it is 0 here, now suppose you and this fermi level can be given by a formula like this as E f is h cross by 2 m into k f square where and which is related to n, which is the total number of orbitals, which are available.

In other words in the k k x k y k z space you would notice that the energy of the highest electron, which is a constant energy surface is a sphere. This sphere the electrons lying on that sphere have an energy, which is equal to the E f. Now, if I look at the total number of orbitals with energy below E. Of course, I can replace E by E f at 0 Kelvin is given by the function n, which is v by 3 pi square v is the volume of the specimen. It goes as 2 M e by h cross square and the important thing to note is this exponent 3 by 2.

The importance of this exponent will come, when we do not track actually at the total number of orbitals, but we go to the what I mentioned as the density of states. Now, suppose I heat this specimen above 0 Kelvin, then what will happen progressively with increasing temperature is that more and more electrons will be excited to these higher energy levels.

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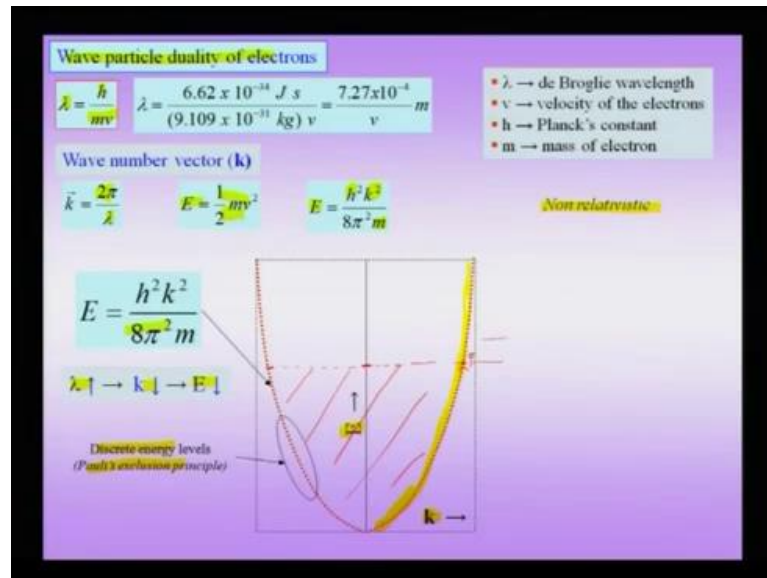
And there is no barrier to this excitation, because these energy levels are closely spaced and are just above the fermi level, which implies that. Now, my probability of finding an electron above E f increases. That means that the probability of finding an electron below the fermi level slightly reduce.

Above the fermi level increases this probability of finding an electron at any finite Kelvin temperature is given by this fermi dirac function. In other words I multiply the probability of finding electron at 0 Kelvin by this fermi dirac function. Therefore, I find the probability of finding an electron at any finite temperature using this fermi dirac function. Therefore, with increase in temperature what happens is that more and more electrons are promoted to higher and higher energy levels, which are now accesible to the system, because the energy are continuous and parabolic.

Therefore, the the tail of the fermi dirac function starts to grow this implies that I can actually increase the energy of the electrons. Of course, at the expenses some of the electrons, which had a lower energy level by merely heating the solid. Now, it can this process be also be done by an alternate method.
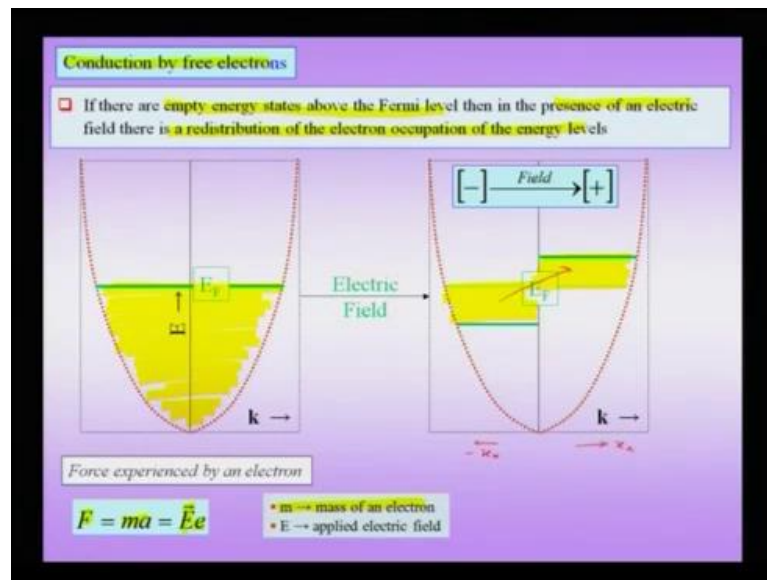
That is by applying an electric field and this application of an electric field with lead to what we know as the conduction of these free electrons. Since, there are empty energy levels above the fermi level, then in the presence of the electric field. There is a redistribution of the electron occupation energy levels in other words in the absence of an electric field. You notice that all the electrons are filled upto the top most level, which is now my fermi level the green line is shown here. All the levels above the fermi level are completely vacant, but what happens when you actually apply an electric field. That there is an asimity between the positive k x direction and the negative k x direction. So, this is my positive k x direction and this is my negative direction. Therefore, more the electron levels are occupied in the positive k x direction.

That means electrons are promoted the electrons, which originally were occupying this level are actually now promoted to this higher energy levels. Since, like before for the thermal excitation there were free energy levels in the what you might call in the E k diagram. Therefore, these electrons, which gain momentum can actually occupy these levels.

Therefore, you will have a electrical conduction and of course, you can write down the force experienced by the electron in the presence of the electric field E as f equal to E into e where e is the electron charge and M is the mass of the electron. If you want to write down the acceleration as M a. So, I have two ways of actually exciting electrons to

higher energy levels. So, point number one of course, is that there are continuous set of energy levels.

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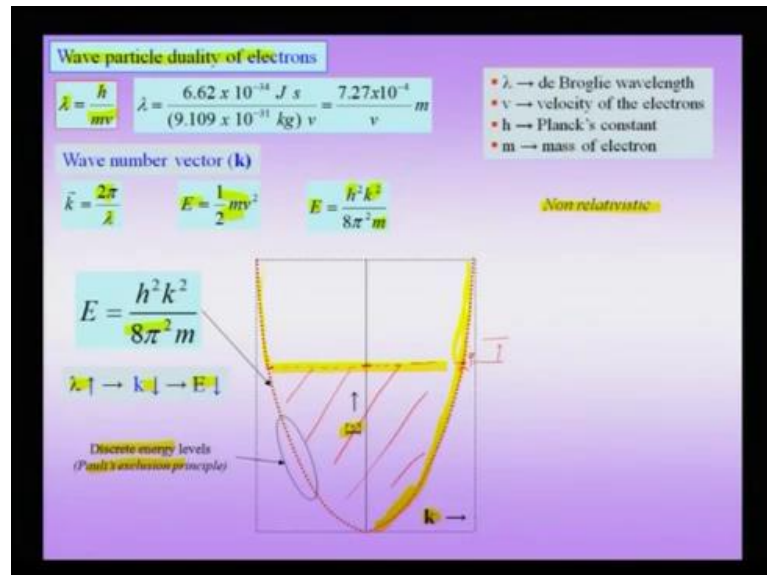
At 0 Kelvin it is filled to a certain energy level known as E f beyond E f. There are no energy levels filled, but there are continuous free energy levels available above the E f also. I can actually excite electrons to these energy levels by either heating the solids or by applying electric field. In the case of heating of the solid there is actually no net flow of electron in any given direction, but when you apply an electric field, electrons tend to flow down the electric field gradient. Therefore, because of the electric field they flow and, because of that you have actually electrical conduction.

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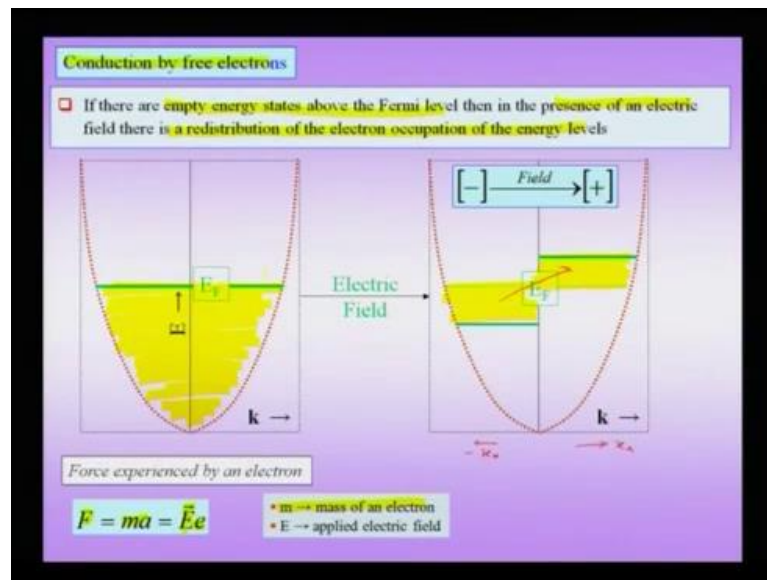
But if you just notice this part that f is equal to M a. That means electrons will be accelerated by the presence of this electric field. What you would expect with time is that the electrons keep on gaining velocity soon they will obtain a very high velocities. Perhaps, they will get to a closed velocity of light, but then that is not what is found this is, because no material is perfect.

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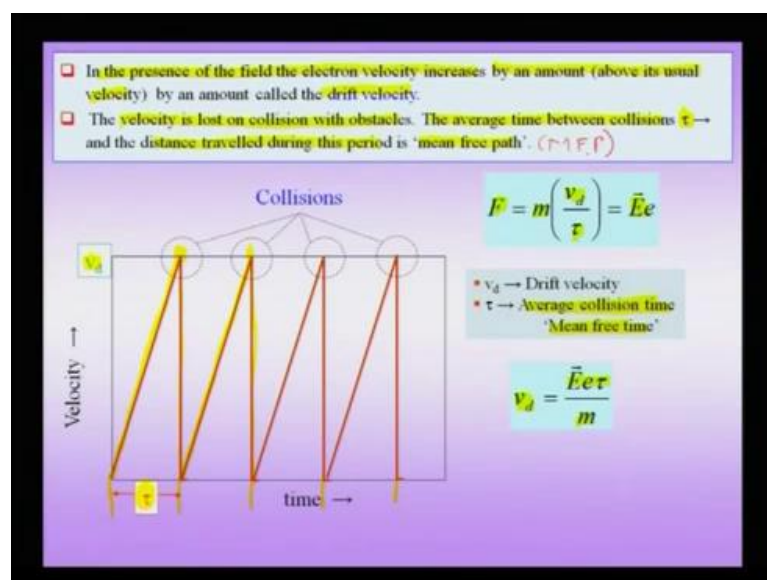
What really happens is that this when the electrons are accelerated at constant acceleration they gain velocity. When they approach a velocity known as the V d they

get scattered they suffer collisions and when a when an electron suffers a collision. It's velocity actually falls down to 0, now, because of the presence of electric field. Again, the electron is accelerated at constant acceleration, we assume it to a velocity V d, but then it again suffers a collision. The velocity comes down to 0 this of course, a idealistic picture in reality.

Of course, you might find that one electron accelerates a little more compacted than other electron before it suffers collision, but what we are talking about is average quantities here. Now, what we are saying is that in the presence of the electric field the electron velocity increases by an amount about its usual velocity, which may get diffusive velocity to an amount called the drift velocity. So, the drift velocity is the velocity acquired in the presence of the electric field.

This velocity is lost on collision with the obstacles we will of course, soon note that what kind of obstacles are these, which are giving rise to these collisions, which is what is leading to what you might call loss in acceleration of the electron. Or in other words this is at the heart of the quantity called resistivity or the origin of resistance, because if there were no collisions then the material will be will be conducting smoothly. What you may have is very good conduction, but, because of these collisions in the Eddy's obstacles. You are actually having the concept of resistivity the average time between collisions, which can be seen as the quantity here between.

So, you have this average time between collisions is given by the quantity tow. The time actually the distance actually travelled during this period is called a mean free path. The word mean is, because as I told you each electron is following a different kind of a time, before it suffers a collision. What is drawn here is for an average kind of a number here. When you statistically average over a large number of electrons. Therefore, we have a mean path, which an electron travels before it gets scattered and the time in which during the period in which it actually experiences an uniform acceleration is given by this tow, which is called the average collision time, or some time you can call it more casually as mean free time.

Now, I can write my F is equal to M a as F is equal to M V d by tow, which we have noted is equivalently written as e e where e is the electric field and not the energy. Therefore, I can write down my V d, which is now my average or the peak velocity

gained as e e tow by M. Now, what is the importance of these two quantities, because there are two important quantities we have introduced in this slide. One is the what you might call the mean free time or the average collision time. Other is what you might call the M f p, which is otherwise known as the mean free path.

So, this slide involves two concepts one concept is a concept of acceleration of electron to a peak velocity V d, which we call the drift velocity. The second important concept is that we can't keep on accelerating electrons, because they suffer collisions, which is the origin of resistance. This time average time over, which the electron is actually accelerated is called the average collision time or the mean free time. The path equivivalent to that is the mean free path.

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Now, I can relate this mean free path to the conductivity as the material by writing noting that the flux of an electron. A flux is nothing but the flux flow of electrons is what do you might call the current density, which is given as J e. The conductivity can be written as flux per unit potential gradient. In other words, J e the flux current density is nothing but conductivity into E the electric field or the potential gradient. This quantity this function is very similar to our Ohm's law. This can actually be verified by using by comparing the dimensional quantities, because on the left hand side you have ampere by meter square, which is now my flux.

On the right hand side I have conductivity, which is one by ohmmeter into volt per meter. On the other hand if I track my V into i r that is vol t per Ohm. On the right hand side is I take the mm Ohm from here to the bottom side. Therefore, the ohm has come here and this is equal to ampere. Therefore, if you compare the two equations you can see that both sides. If you divide by ampere meter square, you can see that volt power of ohm per meter square.

If you take the volt above is similar to this kind of a quantity. In other words, this is some form of Ohm's law, which is very familiar. Now, this current density J can be written as number of electrons into the electronic charge into the drift velocity. Going back to the previous slide we know that b d can be written as e e tau by M. Substituting that I can write it as n e square tau e by M. In other words, I am combining this equation for J with the equation for the flux. I can get the conductivity as n e square tau by m, in other words my conductivity is directly related to my what you may call the average collision time, if I have a longer average collision time.

That means I would have an higher conductivity for the material. If I have a material where, because we will see the origin of all these collisions. Therefore, if the electrons suffers more and more collisions per unit time, that means that such a material is going to be a poor conductor. We should note of course, that we are still talking in the regime of what we might call a free electron kind of a picture. Now, we have a few more things to say about the mean free path, which we had pointed out before.

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The mean free path obviously can be written down as the drift velocity into the average collision time. This is the mean distance travelled by the electron between successive collisions. For an ideal crystal with no imperfections the mean free path we expect at 0 Kelvin to be about infinity. That means in an ideal crystal there are no collisions. The conductivities is infinite.

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Because we know now the mean free path or the average collision time is directly proportional to conductivity.

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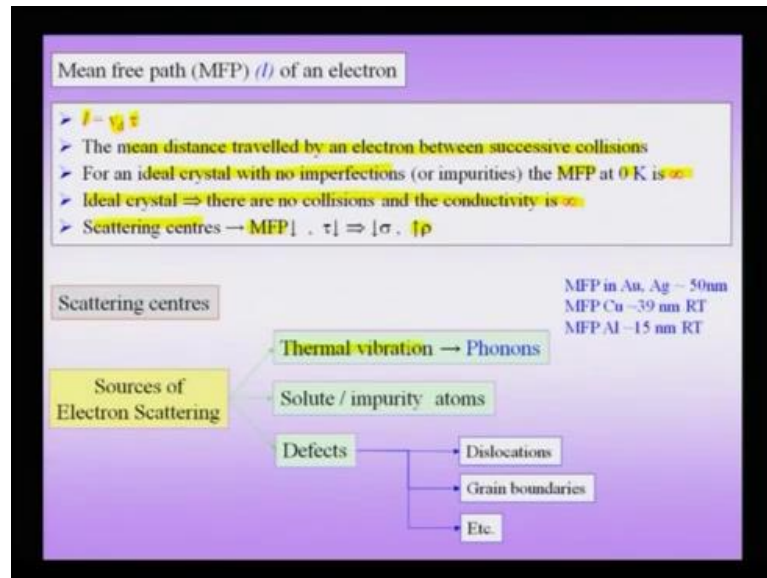
And if the mean free time goes to infinity the conductivity goes to infinity, but as I pointed out there are scattering centres in a material, which reduce my mean free path time is directly proportional to the conductivity. Therefore, increase the resistivity of the material. Now, what are these what is the origin of these kind of a scattering centres? One is obviously thermal vibrations, that means if the there are atomic vibrations and collective quantised modes of these vibrations are called phonons. Therefore, if an electron suffers a collision with the phonon its velocity can be reduced to 0. The second kind of an origin to these kinds of scattering centres is solute or impurity atoms. That means of course, I say impurity or solute I mean it could be a substitutional element intentionally added or it could be an unintentional element present in any material.

This kind of impurity atoms actually distort the lattice. Therefore, cause an imperfection in the lattice and therefore, can act like a scattering centre for these conduction of electrons. Further, we also know that a crystal could have additional kind of defects like dislocations grain boundaries stacking faults. Other kind of defects, which also can act like scattering centers for these electrons. Therefore, instead of the mean free path being infinity the mean free path typically reduces to a very small number.

You would notice that the mean free path typically for a good conductor like gold or silver is about 50 nanometers. On the other hand, even for a slightly less conductorless

conducting material like aluminium. You notice that the mean free path has already reduced to about 15 nanometers.

So, and for mean free path for copper is about 39 nanometers clearly, you see that the mean free path is of the nano scale. So, automatically the question will, which will come to our mind is that. Suppose, I have a nano crystal and if this nanocrystal is of the size of the mean free path, then what happens to its conductivity. So, this is the question, which we will understand try to understand very soon.

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But before that will say a few more things about the quantity, which is the thermal vibration of phononic scattering. Now, at any temperature below above 0 Kelvin the atomic vibration, which leads to the phononic scattering is going to lead to an increase in the resistivity of the material. Now, the mean free path does not have a constant kind of a function. The mean free path is a function of the temperature at which you are making your measurement. It goes as one by t cube approximately at the very low temperatures and at slightly higher temperatures, it goes as 1 by T. The other factor, which we saw was the impurity scattering. We said that the material with an alloying element or with an I am purity is going to have a higher resistivity as compared to completely pure metal. Now, the increase in resistivities approximately proportional to the amount of alloying material added.
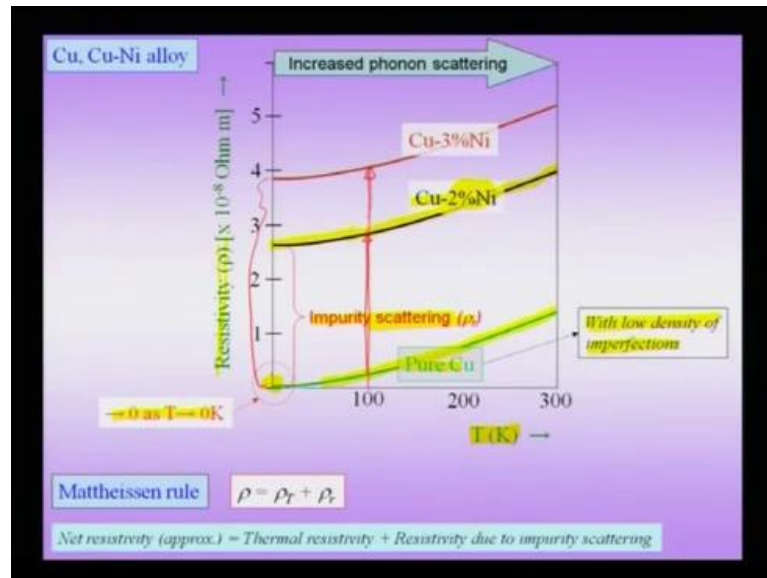
Therefore, if I have a pure material like copper and with a very low defects densities and I plot its resistivity as the function of temperature. Then I would notice suppose I plot the resistivity of pure copper. Now, I am talking about a pure copper with low density of imperfections. That means I am ignoring my stacking faults and dislocations. I track its resistivity as a function of temperature I would note that with decrease in temperature my phononic scattering would reduce and resistivity. Keep on decreasing in other words my conductivity is going to continuously increase. What you would expect at 0 Kelvin or as it tend to 0 Kelvin is that the material will tend to some kind of a superconductor. Because, this is not pure copper and there are no phononic scaterings.

There are no other form of lattice defects, which can gave rise to scatering. Therefore, you expect it to become superconductor, but on the other hand suppose I have a Copper Nickel alloy. This alloy even though the resistivity decreases with temperature, which is what we, because of phononic contribution is going to decrease, but then there is always residual resistivity, even as we tend towards 0 Kelvin. This is coming from the fact that now you have an alloying element like Nickel, which is going to give rise to what you might call the impurity scattering or the alloying element scattering. As you increase the amount of alloying element the resistivities can all.

Suppose, I might have a vertical temperature like about 100 Kelvin you would notice that at this 100 Kelvin. You would notice that my resistivity increases as you add the alloying

element. You add little more of the alloying element resistivity further increases that may increase with more and more alloying element. You going to higher and higher residual resistivity as you tend towards 0 Kelvin. So, we know now that if I want to make a perfect conductor. Then I have to avoid all these scattering entities, which includes presence of solid elements and the presence of defects.

If I reduce my what you may call the phononic scattering contribution by reducing the temperature. Then I would have an increase in conductivity so to reiterate the message of all these slides, so far in the free electron model. There are free energy states available where electrons can be excited. If you apply an electric field then its going to get directed motion of electrons in the presence of what you may call temperature. This is going to be random motion of electrons in the presence of an electric field the electron is accelerated but, suffers collisions, because of which the velocity comes down to 0. This time or the path it travels freely before a collision is suffered is given called a mean free path.

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The mean free path or the equivalent mean free time can actually related to the conductivity.

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That means you increase the mean free path, then the conductivity increases equivalently. Suppose, if I note that the mean free path of most materials good conductors is of the order of about tens of nanometers. If I make a nano material or a nano crystal, which is of vocalised noise with whose size of this order, than I would expect some drastic changes in the properties.

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I had pointed out that the free electron theory cannot explain all kind of concepts. It's a sort of a simplified theory the more or the more rigorous way of understanding the

conduction property is. The overall electronic structure is what is known as the band structure. Now, vocalised noise in a simple physical way of understanding the band structure is to assume, that you have these individual atomic levels.

When the atoms are far apart, so you have an infinite separation here and atomic separation on the x axis. The energy levels on the y axis and when the electrons when the atoms are very far apart here at the infinity. Then these electrons do not talk to each other the electronic energy levels do not talk to each other.

Essentially, you have discrete energy levels, but as the electrons come the atoms comes closer the outer most energy levels start to overlap and given the pauli's exclusion principle. They spread into a band in other words all my 3 D electrons would split into band like this the 4 s electrons would form a band like this. Now, these 3 D and 4 s bands belong to the entire solid and not to the individual atomic levels.

Therefore, there is an equilibrium atomic separation at which you can see that there are energy bands. The 4 s band starts here and ends here and the 3 D band starts here and ends here. There is some more detail about this 3 D four s bands and their overlaps, which does not become obvious, when you look at a diagram like an energy atomic separation diagram. Therefore, we will take up something known as the density of state diagram very soon. So, the message of the slide is that at equilibrium atomic separation the outer electronic energy level give rise to bands, the core levels continue to remain discrete.

That means they have the atomic character still bands may overlap and fill in parallel over a range of energy values as shown in the figure here. That means that once I have when once I am in the energy region between here and here. That implies that I am going to be filling my 3 D and 4 s band parallelly, as a range of energy values are allowed in a band. Of course, we know from Pauli's exclusion principle that they are discrete, but they are closely spaced. Any radiative transition from these outer levels to core level has a broad range of wavelengths.

Now, because if we had if we look at the to mice mission spectra on a absorption spectra that will tend to be very sharp, but suppose you have a radiation radiative transition from these bands. They will have a continuous energy value, because you these band themselves have a continuous range of energy levels. Now, as I pointed that certain

important details are hidden away when you plot a diagram like this, where in you are showing an overlap between the 3 D and 4 s bands.

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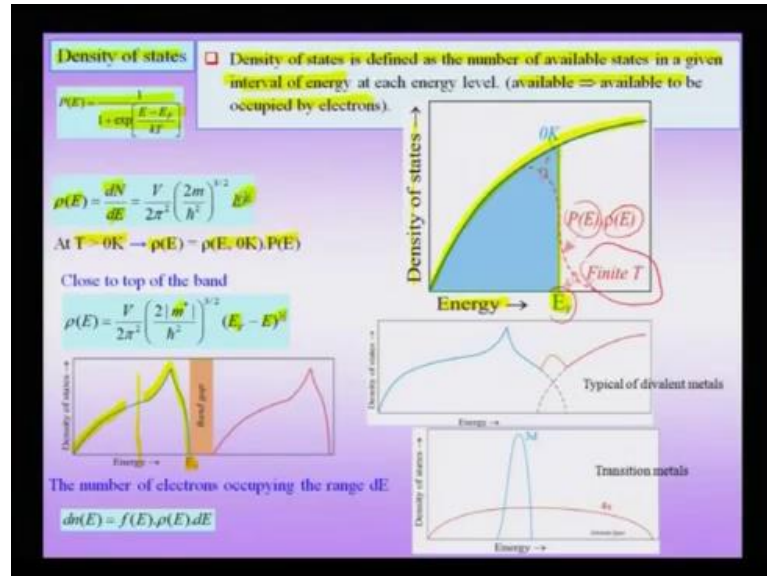
This kind of a diagram would be for a typical transition metal. So, we have to invoke the concept known as the density of states density of states is defined as a number of available states, in a given interval of energy. Previously, we had noted the value N ion the free electron model we noted the N goes as E power 3 by 2, which is scaled by the volume of the material. Now, the density of state is nothing but the number of states available in a given energy interval of energy. This available implies we are talking about available to be filled by electrons. So, I can calculate my density of states as d N by d E. The N formula as I showed you before. And therefore if I do this differentiation I would find that the density of state goes as E power half. In other words, if I plot my density of states with energy in the free electron model.

I would note that the it goes like an e power kind of a relationship and at 0 Kelvin you know that the energy is only upto fermi level are filled, which we pointed out in other words all the level energy levels below the fermi level are occupied, which is given by the blue region in this plot. All the energy levels above the above E f level are all vacant, but we had also pointed out, when I want to track the number of energy levels at any finite Kelvin temperature. Then I need to multiply my function by what is known as the fermi dirac function. I would do the same thing here to find the density of states at any

finite Kelvin temperature. I, that means at t geater than 0 Kelvin to find the density of states.

I will multiply the density of states is 0 Kelvin, which is of course, the region blue shaded region in the curve and multiplied by the P of e which is given by fermi diracfunction. Therefore, this function close to the E f will start to develop this kind of a curved region. Otherwise there will be a small tail now the energy there will be electrons states, which will be vacant go vacant here and there will be electron levels, which will be occupied here at higher energy levels. So, this is at a finite Kelvin temperature in other words I have taken my density of say it is 0 Kelvin and multiplied by the fermi dirac function.

Now, thus kind of a picture is not actually valid, when you are close to the what you might call the bandage. This kind of a picture is only valid when you are in the completely free electron domain. That means the electron is not filling any effect of the potential of the ion course. Once it starts to feel that potential this kind of a function, which is given by E power half has to be modified. The way to do it is by invoking the effective mass of the electron. The new density of state can be plotted instead of E power half then I have the E v minus E power half, where E v is the energy corresponding to the bandage. In other words, close to the what you might call when the fermi surface actually starts to talk to the blown zone.

Then what happen you actually modify the function and the function starts to look something like this. In other words, this is the regime where I can talk about absolutely a free electron. This is a regime where I need to modify this E power half kind of a functionality. Later on when we talk about nanostructure materials we will see how this E power half kind of function is actually modified in the case of a nanostructure material. How we will actually even a very good conductor can actually start to become aninsulator, because of the limitation or quantisation in one or more dimensions. If you look at we had also talked about in the previous slide, that actually bans can fill parallelly that means the 3 D and 4 s bands can fill parallelly.

In that case the density of state function is to be even further modified. It looks a little more complicated as in the case here you can see that, it starts look little more complicated, when more than one band is overlapping. This is typical of divalent metals

and this diagram here corresponds more close you to the transition metals like, Iron in the case of transition metals. You would notice that the foremost band, which is the broad band in the density of states is parallelly filling compared to the. Also, with the 3 D band, which has a high density of states localised to a small region in energy. This has important implications, because now we are not just merely talking about the free electron picture.

We are talking about a picture, where I am taking into account what you might call the density of states. In other words it is the number of states available in a small interval of energy D e. This is going to determine much of my important properties for instance. Now, the fact that this 3 D band is highly localised has a narrow bandwidth tells me that the electrons here the 3 D electrons are not fully. That means they have a partial kind of a localisation character. Later on we will see this plays a very important role in a magnetism of Iron.
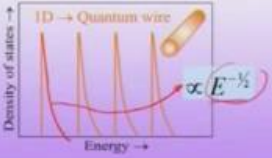
So, to summarize this slide we know that we have normally, what we plot in the case of materials is the what you call the density of states, which is the number of energy levels available in a small interval of energy. This intensity of states function has to be initially of course, looks like a E power half function in the free electron regime, but has to be modified. When I am talking about overlapping of bands and close to a bandage the function becomes little more complicated.

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The density of states function is highly altered with respect to a normal material. So, now what happens in the case of this kind of a wire if I keep on exciting the system. That means that originally in a free electron picture I could keep on exciting the system.

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I would find always energy, there are energy levels to be occupied. That means the material will behave like a conductor, but now you see that upto a certain extent. Of course, I have a density of state, which is now falling with energy not increasing with energy.

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Beyond this kind of a critical energy, there are no density of states available for the electron to be promoted till. Of course, the next quantum level is occupied that implies that this material. Now, starts to behave in some sense like a semi conductor not like it is not like a metallic conductor, which we expect even though we started off with the metal, but we this by reducing dimensions the density of states is been altered. I have developed a band gap in my density of states. We had originally said that this band gap is characteristic of an insulator or a semi conductor. Now, this is a pure metal starting to look like a semi metal or atom. Look like a semiconductor or an insulator purely by the quantum confinement effect, which is coming from fact.

Now, that the density of state functionality has been altered in the case of a what you might call a quantum wire, as you would like it. Now, what happens when I before of course, I take 0 D up nano crystals. It is important to see that there are actual examples of this kind of 1 D nano materials, which are now like for instance my carbon nanotubes.

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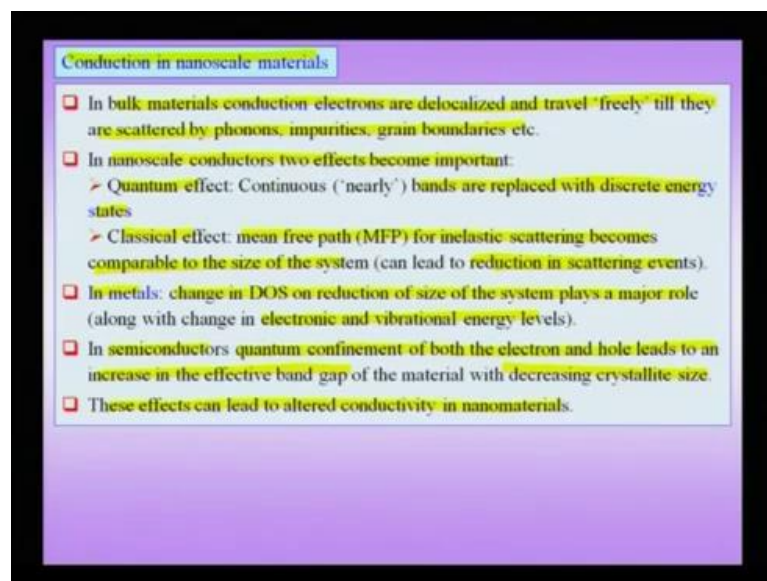
And in this carbon nano tubes you will take up an important phenomena, which is known as the ballistic transport of an electron, which is coming from the second effect, which we talked about here. We had said that there are two effects, which are very, very important in when you are talking about the conduction of electrons or conductivity. one is the quantum confinement of which we have been talking about so far, which determines what you might call the an altered density of states, but additional we also

have this issue, which we talked about the mean free path becoming comparable to the size of the system.

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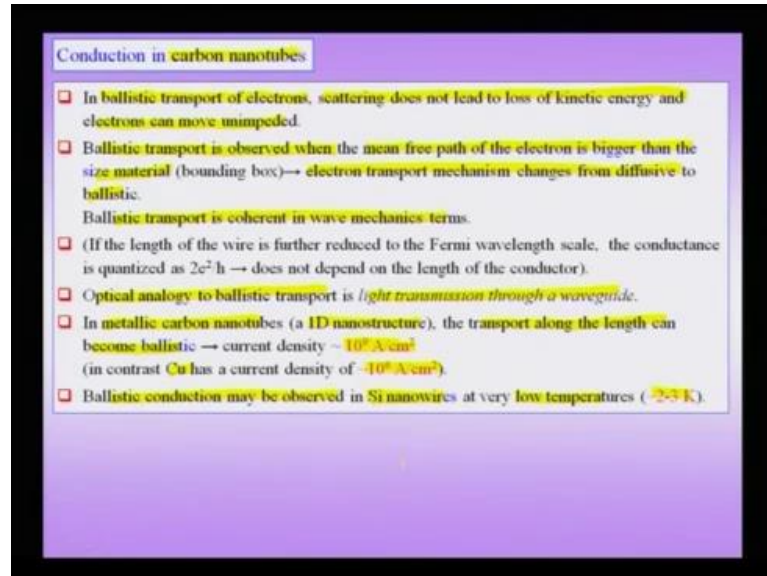
When there are no scattering events within the system, then the electrons can actually just be accelerated or can keep on gaining velocity. That implies that you can have what is known as ballistic transport of electrons scattering, does not lead to a loss of kinetic energy. The electrons can move unimpeded to the system the ballistic transport is observed, when the mean free path of the electron is bigger than the size of the material. In these cases the electron transport mechanism changes from diffusive to ballistic and ballistic transport is coherent in the what you might call, the wave terms of wave mechanics or quantum mechanics terms.

Now, the optical analogy of the ballistic transport is the light transmission through waveguide, where there in there is no loss. In other words, now there is an loss less transmission of in the course will have wave guide, there is loss less transmission of light. In this case there is lossless transmission of electron. There are actual structures, which are metallic carbon nano tubes, which is a 1 D nano structure, where in transport along the length can become ballistic. When this happens you can actually have a current density of the order of about 10 power 9 ampere per meter square. If you compare it with the metal like Copper, which has a current density of 10 power.

You can clearly see that this now this carbon nano tube has become really a very good conductor along the length. We are talking about those kind of where you actually M and N numbers, where in actually have what you call a metallic carbon nano tube. It is alsoseen that ballistic conduction may be observed in silicon nano wires, at very low temperatures like 2 to 3 Kelvin, where phononic scattering becomes small contributor.

So, to summarise this slide we have noted that a system size can become, so small that normal drift transport at diffusive transports, which is to what you may call ballistic transport, where there is no scattering of electron. There are and when this happens you can obtain very high current densities as in the case of metallic carbon nano tubes along the length of the nanotube. This transport this kind of a current density is much higher than, what you typically obtain even in a good conductor like Copper. There are other systems like Silica nano wires too, where in we would expect some kind of a ballistic transport at very low temperatures.

Of course, we had known that this metallic carbon additive has to be defective. Because, all these if there are any defects in the crystal then or a nanotube, that will lead to scattering, which would lead to further, which will not give us this kind of high current density. So, it is indeed surprise that in nano tubes we can get very high conductivities and very high current densities, which is coming from the fact that, now the dense scale of the problem has gone to nano size.

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So, having talked about what you might call bulk materials. Then we have talked about 2 D nanomaterials, then went on to talk about 1 D nanomaterials, wherein we saw that even metallic materials change their behaviour.

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We can now talk about what you might call the 0 D nano materials or quantum dots. Here, all the energy levels are discrete, because now the system is confined in all three dimensions. So, such an system is now a quantum dot and is confined in x y and z all three dimensions. Therefore, this implies that there are no free electrons in the system. There are no free dimensions along, which the electron can freely move about. There is quantisation of confinement in all three directions.

Therefore, now such a system is described by three quantum numbers energy levels n x n y and n z. If you look at the density of states of such a system this becomes, what you might call delta function in the ideal limit. In other words, the density of states for us quantum dot becomes similar to that of an atom and metals start to behave like insulators.

You can see that if I plot my density of states in of course, the ideal situation they start to behave like delta functions. In other words they are discrete and if electrons have promoted, they have to be promoted from one energy level to the other by giving a discrete amount of energy. More realistic of course, if you have the size of the system little larger than you would notice that, there would be a little broadening of the energy

levels. Never the less they remain discrete and such a system you know the electric conductivity would be limited and metals would start to behave like insulators at very, very small length scales.

So, far we have been talking about conduction, which is called the normal conduction, where in you have a free electron or an electron, which is travelling down the potential, but there is another kind of a quantum effect, which is called tunnelling in which case an electron actually has a finite probability of being formed beyond a barrier.

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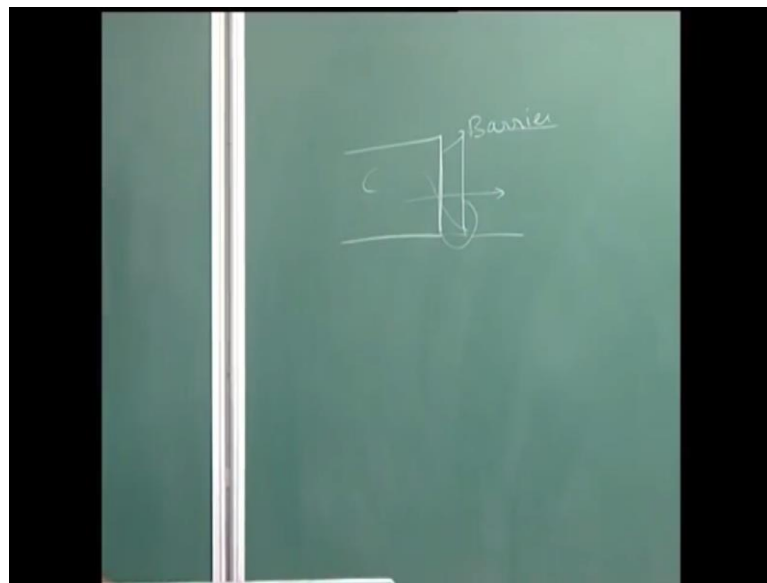
So, suppose if this is my conductor and this is a barrier in classical terms the electron cannot be found this barrier, this potential barrier. So, particularly in quantum mechanics actually there is a finite probability of actually finding this electron outside the barrier. So, this implies that if I have a a small resistor of a thickness smaller than this, what you might call the d k length for this tunnelling than actually, such if this region is conducting. This region is conducting I am actually transport the electrons purely by the tunnelling mechanism. So, this tunnelling has no classic analog, and it is purely a quantum effect.

When you are talking about tunnelling there is a very closely interesting kind of an effect, which is called the coulomb blockade, which is observed. We will take this example, because such an kind of effect can actually put to some kind of a application. There is something called the tunnel junction and this tunnel junction behaves like a resistor.

Now, I can take a metal which is a conductor where in electrons can normally flow and on in between this metal. Another metal I put a insulator and as I just pointed out if this insulator is thin enough. Then actually I can flow tunnelling current from one metal layer to another. If I apply a potential this tunnelling current is obviously going to be smaller. Then the normal current you would observe when you have a flow through the conductor. This resistance in the exponential increases, exponentially with the barrier thickness.

Now, I am talking about barrier thickness, which is very small of the order of nanometer. If this insulating barrier becomes large, then I would find that there is no current, which is transported from this green metallic region, which is shaded green to the next metallic region, which is also shaded green. So, for this kind of a tunnelling current to take place the thickness of this barrier the insulating layer has to be small, but addition to the fact that this layer introduces resistance to this flow of current to this kind of a setup. It

additionally also has capacitance, because this insulator can is also a dielectric. As you know dielectrics can store charges.

Therefore, it can also be behave like a capacitor the important point to note is the current through the junction the tunnel junction passes, as one electron one at a time sometimes. Of course, a co tunnelling can occur, where two electrons can also pass through, but typically it is one electron at a time, which actually tunnels through this tunnel barrier. Now, this implies that the tunnel junction capacitor is charged with one tunneling electron. Once this tunnel barrier has been charged with one tunneling electron.

This implies that if I want to push the second electron into through this system, across its voltage the first electron, which is already built charge, because of the capacitance of the insulating layer work has to be done by the external voltage to push the second electron. That implies for an additional charge cube to be introduced into the conductor work has to be done against the electric field of the pre existing charges residing in the insulating layer. Of course, it should this should be an insulating layer charging an island with capacitor C.

There are island of course, insulating island we are talking about with an electron of requires change E square by 2 C. That implies that if I do not supply this much of energy I cannot push a second electron in an insulating to the insulating layer, which is already been charged with the first electron. That implies if I now plot my voltage current characteristics this becomes very different from the odd, that what we normally observe for normal materials, which is like a normal conductor. We know that V is equal to I R kind of a relationship. That means it goes the current goes linearly with voltage, but you can see that in such a system, where in I have a metal insulator better configuration. You can see that the current voltage characteristics has a starchius kind of a structure.
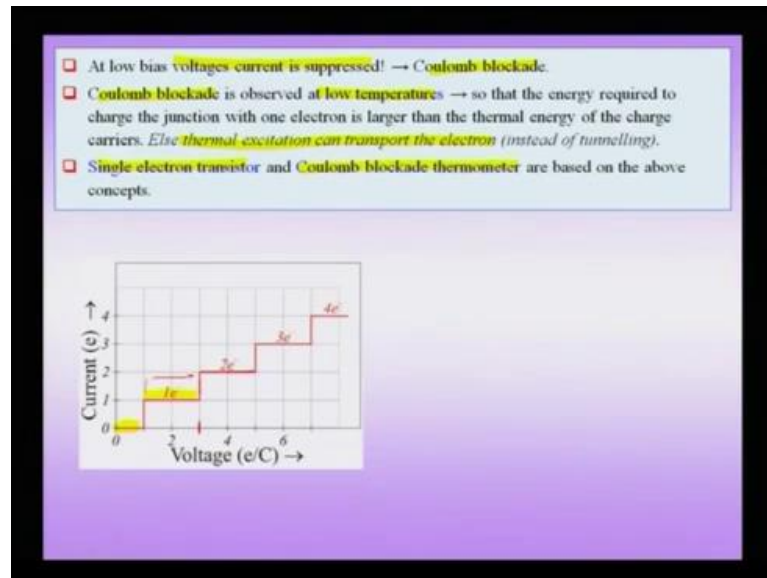
Now, at low voltages; first of all, no there is current itself is suppressed. That means if you have very low voltages, you see that no current passes through the system. This is called the coulomb blockage, that means that I have no current. If I have low voltages in a normal conductor, if you have low voltages you will still have some current. The current value will be small typically for a coulomb blockage to be observed you have to work at low temperatures, because at otherwise at higher temperatures thermal excitation can transport the electrons. Instead of tunnelling that means purely, where thermal excitation this barrier may be broken. Therefore, you will have some conduction thermal excitation. Therefore, you will not you will be not observing the coulomb blockade phenomena.

So, what is essence of this coulomb blockade phenomena, you see that initially. Of course, at low voltages, there is no current at all and when you put sufficient voltage. You can see that the system charges to one electron, but further increase in voltage does not in this regime. We can see that in this regime between from here to here further increase in voltage is not leading in a increase in current, because the pre existing charge in the capacitor is effectively stopping a second electron from entering the capacitive system. That implies that I have to again breakdown this capacitor for which I have to employ our higher voltage.

Once I have charged the system two electrons, again you find that there is a plato in the current voltage characteristics. Therefore, this very interesting system, which has been put to use by in developing devices. Like single electron transistors and coulomb blockade thermometers, but you can clearly see that, there is no classical analog of such a behaviour in the voltage current characteristic phase, which is coming from a thin insulator. The fact that this insulator is now in the nanoscale. It is what you might call you at the heart of this whole process is what you might call tunneling current, which only happens in a nano scale. If I make a thick material then the tunneling current fall down to 0, because the resistance increases exponentially with the barrier thickness.

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Therefore, we can see that there are very, very interesting phenomena, which are very very different from bulk scale materials, which you observe regarding the electrical conductivity in nanoscale materials. Some of this can actually be put to very good use in the form of devices. Various kind of counter connects additionally we have to remember that when you are making a when you are trying to reduce a dimension of a, because when we tried to do a very large scale integration for devices. Trying to reduce the dimensions of various wires and interconnects.

We have to note that some of these quantum effects may come in some of these confinements may come in. Therefore, the materials may start to be have very differently than the bulk. Therefore, newer and newer technologies have to be discovered before the

size can be reduced to very small scale, but addition with those problems, we can see that there are newer possibilities, which are opening up, because of newer phenomena which kick in when you actually go down to the very small scale.