Optoelectronic Materials and Devices
Prof. Dr. Deepak Gupta
Department of Material Science and Engineering
Indian Institute of Technology, Kanpur

Module - 01
Electronic Structure of Materials
Lecture - 10
Conduction in Relation to Band Diagrams

Welcome to lecture number 10. In the last lecture, I had mentioned that, if time remains, we will cover this conductivity in relation to band structure. So, now, let me try to do it in this lecture and then I will make some comments on conductivity of materials in this lecture. Remember what did we see last time in previous lecture; we defined a quantity called effective mass and we found it to be a strange quantity that, it turned out to be somewhere some places reach going to infinity. Of course, that is one feature; but, more importantly, which I probably did not mentioned in the previous lecture was in the other places, you would have noticed that, effective mass was a negative quantity. This negative quantity is what we will look for and see define what idea… We will try to give the idea of what a hole is.

And, that you have heard of in semiconductors; that you have heard of electrons and you have heard of holes. Remember in metals, we always talk of electrons; whereas, the moment we move on to semiconductors, we start introducing another term called holes. And, commonly, in school, the way it is taught, it is said that, holes are absence of electrons. Fair enough; but, what precisely it means that, I am going now about to explain to you in context of these band diagrams. When we start looking in conductivity in terms of band structure; that comes out naturally. So, what is that I am going to now talk about? Let us look at it again.

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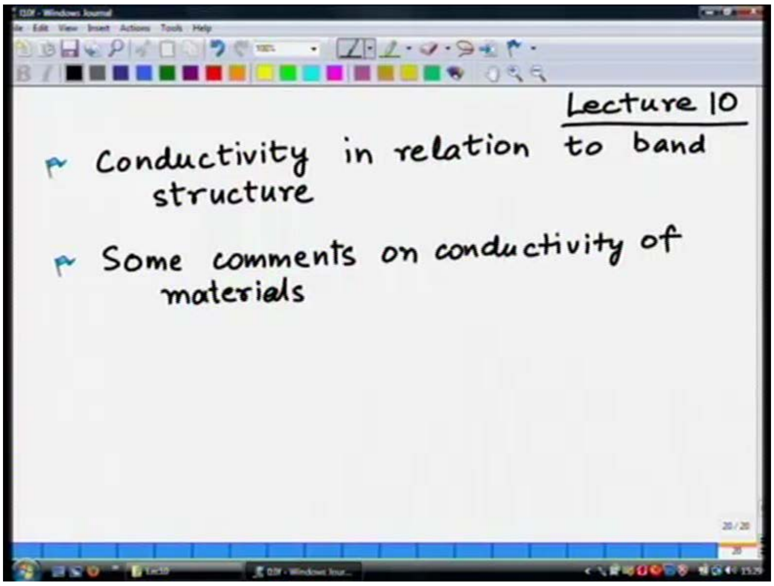

Let us look at the band structure. Let us look at a hypothetical, a schematic of a band structure. We again plot out band structure just like we did for nearly few electrons. So, let us do that and let us look at what happens.

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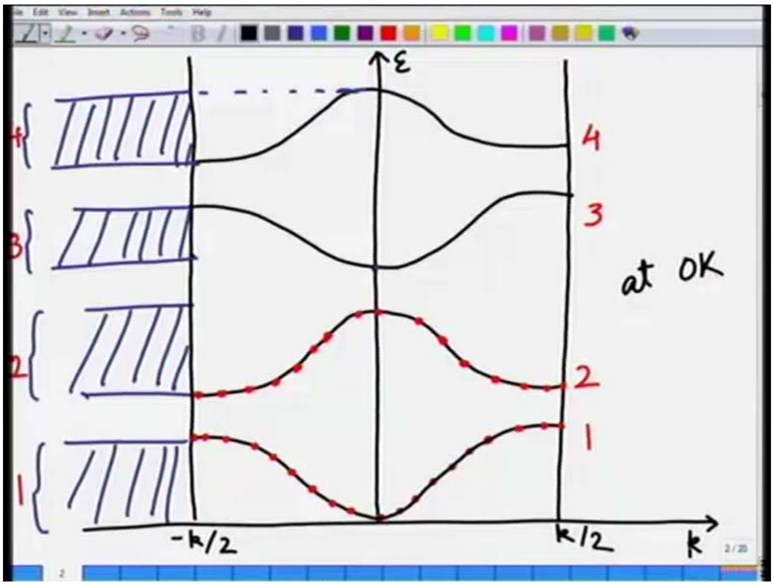

I am going to plot four different bands. So, I am going to take this line E verses k curve. Here is E verses k diagram, which I am plotting. And, in that, I am going to plot out here again up to in the first brillouin zone only. So, I am marking the first brillouin zone. This is k and this is energy; and, here is k by 2 and minus k by 2 showing the brillouin zone;

here is 0. So, that is the brillouin zone. I am now going to draw four different bands. And remember, just like we did it in nearly few electrons, I am going to draw those band right here. It is not important what the precised shape of the band structure is, what exactly the band structure is. But, I am just for schematic, I am going to put down four different bands, whose shape and nature will be exactly like that we did derive in a nearly free electron theory like Kronig-Penney model. So, let me draw that first.

Now, those… Let us draw it like this; second band like this; and then, again somewhere up to here; and then, again somewhere up to somewhere something like this. These are the four bands let us say. What does that mean? That means these are allowed energies; that means up to here to here, these are allowed energies; there is a gap in between. Then, these are allowed energies. There is a gap in between. These are allowed energies right here. These are the allowed energies. And then, there is a gap in between. So, you can keep seeing… You keep seeing gaps in between. And then, that these are the called bands. So, these are the energy bands right here, right here, right here, right here on the allowed energies. This corresponds to this point right here; and, this is of course is right here. So, these are the bands allowed in the values of energies; and, band gap in between; energies which are not allowed for electrons. So, those are the band gaps.

Now, what we are going to do is we are going to start placing electrons on these. So, in order to place electrons, let us choose two different colors. Let us say we choose red color for electrons. So, here is an electron; and, I am going to place electron here; I am going to place electron here; I am going to place electron here; here, here, here; and, let us say here. I have placed all these electrons in here. So, what am I showing? On these bands, there are k's… On these electron bands, on the k-states, in this particular band; let us call it band number 1; let this be called as band number 1. But, let us write it; not roman, but just band number 1. This is band number 2. This is band number 3. This is band number 4. So, 4, 3, 2 and 1. These are the four different bands – energy bands, which we have. What I am showing you is; in energy band 1, different k-states; and, all these k-state electrons are completely filling it; that means band 1 is completely full of electrons, totally filled. Likewise, what I am going to do is I am going to fill up band number 2 also. So, I am going to fill up all the k-states; I am going to fill up these electrons in there as well. Even this band number 2 is completely full. Band number 2 is completely full with electrons; I have put all the electrons in there. What about band number 3 and band number 4?

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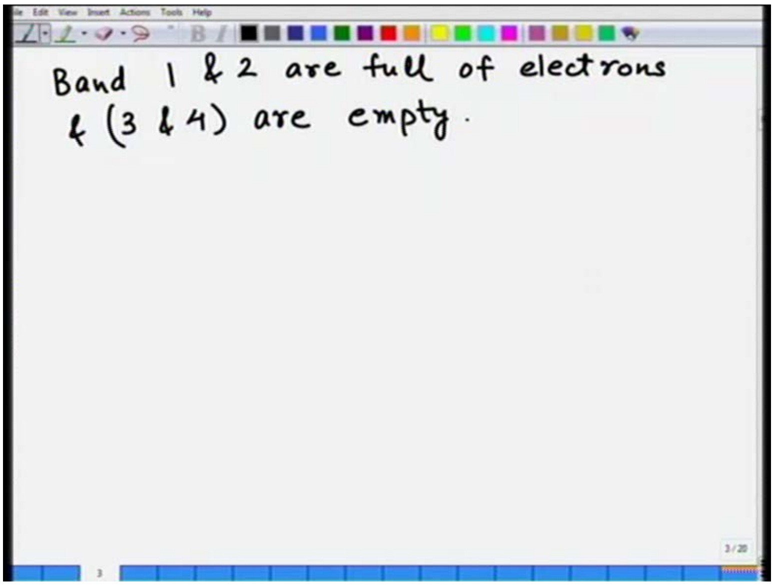

Let us say band number 3 and band number 4 are completely empty; there are no electrons in band number. So, what I am showing you is band 1 and 2 are full of electrons; and, 3 and 4 are empty. So, that is what the picture is. Now, let us say this is picture let us say 0 k at 0 kelvin. That is the temperature. And, bands are completely full. And, that is what the picture is. Now, suppose I go to room temperature; I go to room temperature. And, in this case, what happens; since there is some thermal energy, some electrons, which are sitting right at the top of the band right here' say these electron has the highest energy here; it is sitting at the top of the band. And, these electrons, which are sitting on the top of the band, can now begin to jump. Suppose they begin to jump into the next higher band. So, next higher band they jump. So, let us draw that picture also.

So, if I draw that picture; then, I quickly draw identical picture like this, like this; and, this is the first brillouin zone, which I am drawing right here. So, E verses k diagram; again, k by 2 and minus k by 2 if I draw this minus k by 2; and then, I draw the same bands like this. These are again the four bands, which I have; here four bands, which I have.

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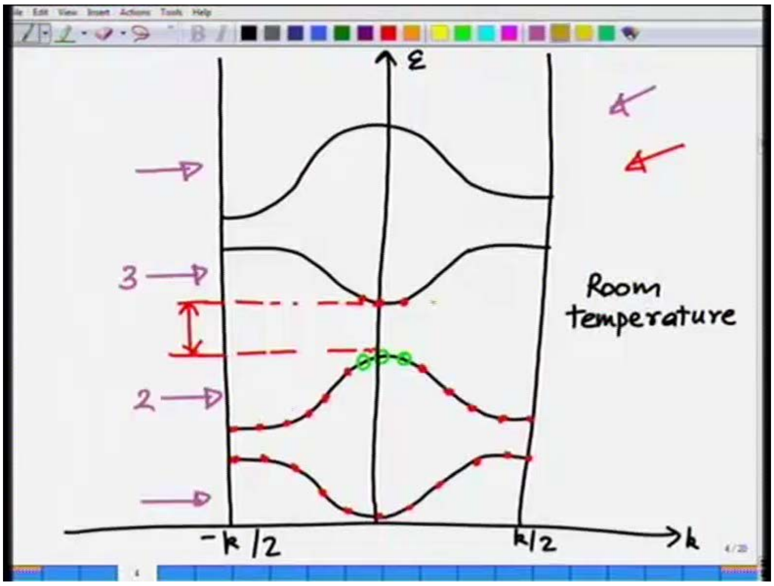

In this case, now, again, what I do; I put all these electrons here. And, what I have done is; what I am going to do is I am going to cause 3 of these electrons to jump up there, because I am at room temperature now. And, what I will do is with the green pen, green dots, I am going to show here 3 states, which will become empty. These electrons have jumped up in the band number 3. And, now, the band number 2 is partially empty. And, this is the picture at room temperature; let us say at room temperature. At room temperature, this has happened; some electrons have jumped up there.

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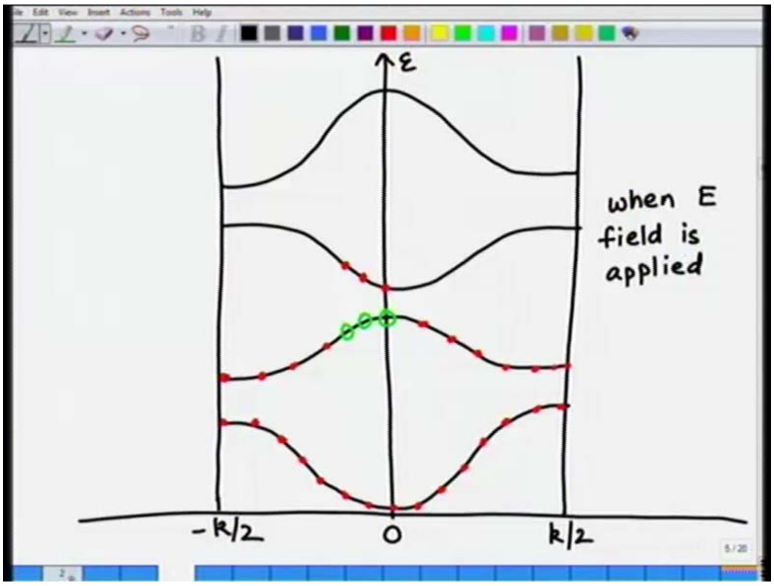

Now, suppose I apply electric field and ask how the conduction will happen. For that, let me draw another third picture also similarly. Exactly similarly, let me draw the third picture. This is k by 2, minus k by 2, 0. And, on top of that, now, I am posing an electric field; I am applying electric field in let us say in k direction. So, if I do that, what will happen? Let us put the electrons again. Now, what I am going to do is; when I apply the electric field, let us say these electrons have drifted on one side. So, I am going to draw this as like this and I am going to plot like this. This is when electric field is applied.

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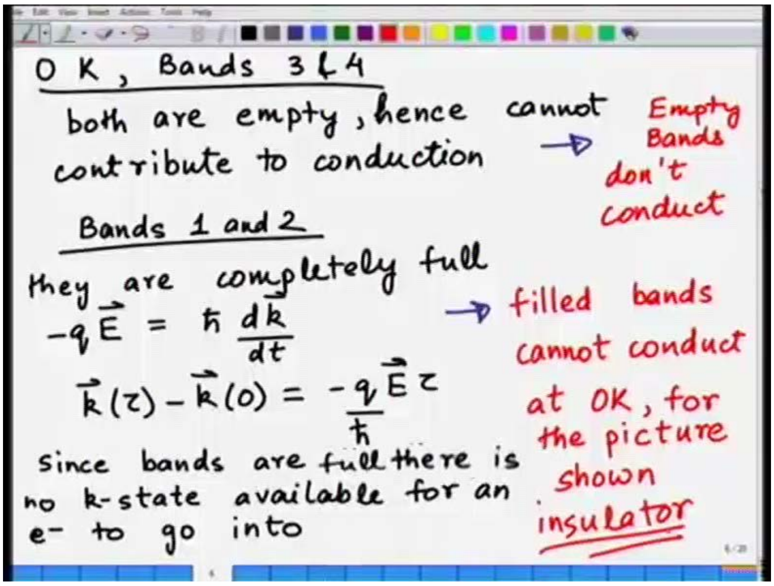

Now, let us look at conductivity. What happens? Let us look at 0 k. So, let us look at this picture right here, which is shown here and let us look at 0 k; what the conductivity will be. Let us look at electrons in each band and see what happens. We will start with band number 4 and band number 3. So, let us look at this 0 k, bands 3 and 4. Both are empty; hence, cannot contribute to conduction. So, they cannot contribute to conduction. What that means is empty bands do not conduct. That is the conclusion. Clearly, if a band does not have electrons, how can it conduct? Those are energy states available. But, if they are not occupied by electrons, electrons are not there; in that case, we cannot have any conduction through those bands. So, band number 3 and 4 in 0k – this picture right here at 0k. Therefore, cannot conduct. In band number 3 right here and 4, cannot conduct.

What about band number 1 and 2? So, let us look at bands 1 and 2 at 0k. Bands 1 and 2 – they are completely full; which means if I apply electric field; which means if I apply a force called – this force on an electron, then that should cause – remember h should be dk by dt – rate of change of momentum. That is what… That means n time the k-state should change; so much so you will recall. Then, k-state at some time tau should be equal to that quantity; should be equal to at 0 time… Whatever the state initially was, if I apply a electric field; in that case, k tau should be equal to k 0 plus some quantity minus q E by h bar into tau. And, remember tau was that time – that average time, which holds the Fermi sphere in place. Because of scattering – different scattering processes, you will recall those we covered in lecture number 3 or 4 something like that. We have written down this equation; that means k-state will change for electron as we apply electric field. However, since bands are full; since bands are completely full; therefore, there is no space for electron to move. Since bands are full, there is no k-state available for an electron to go into or move into. And therefore, this electron cannot move.

An example would be – imagine a class; there are many many chairs; these chairs are like energy states. Now, if all the chairs are occupied by the students; the students come and sit in these chairs and they go completely in there sitting in the chairs. So, these are energy states in which now think of the students as electrons; these students come and occupy the chairs. Therefore, they are completely… The entire classroom is completely filled; that means there is no movement of students possible anymore; they are all… Since all students are alike, we are thinking of electrons as indistinguishable particles. Therefore, even if you interchange two students, which we are assuming to be indistinguishable students; even if you interchange the two of them, the picture remains the same; it does not change. In a sense, nothing has change even if you interchange two students, because they were indistinguishable students. Similarly, electrons are indistinguishable. So, if they are on energy state, even if you interchange them, that does not make a difference; just that they are effectively they have not moved. If their band is completely full of electrons, then it cannot change its k-state. And therefore, you can see that, completely full bands cannot conduct. Filled bands cannot conduct. That is the second conclusion. First conclusion; second conclusion.

What does that mean? At 0k, for the picture shown… What is that? Which picture we are talking about? This picture; the first picture right here at 0 k in which band number 1 and 2 is completely full; and, band number 3 and 4 is completely empty, you cannot have conduction. You cannot have conduction because of that reason; that means that… I have a picture of insulator. I have a picture of insulator, which cannot be conducting at all; except that, now, when we go to room temperature. When we go to room temperature, some electrons…

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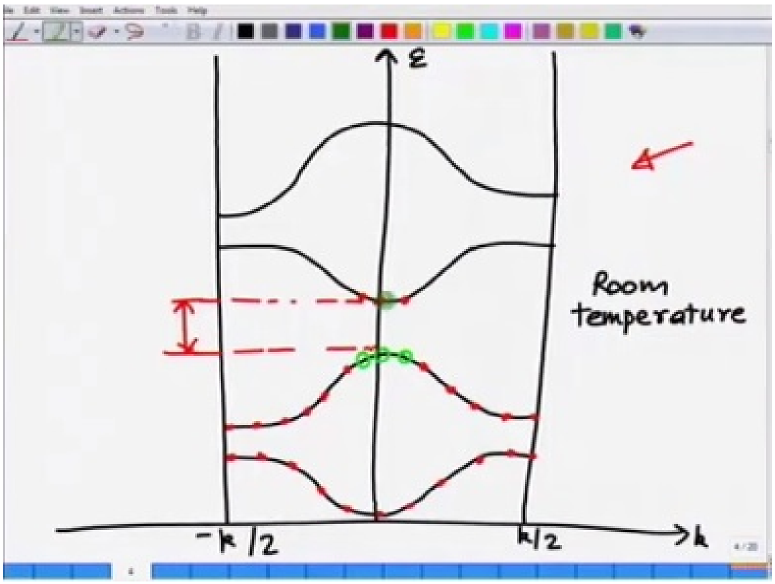

In this case, I am talking about now this picture right here – the second picture in which… Since the gap was not very large… This gap I am talking about; this particular gap was not very large; this point being this point and this point being this point, this gap not being too large. Therefore, in this schematic, 3 electrons could jump to the next energy level. And, notice that, the jump from top of the band below – band number 2 from top of the band into bottom of the third band, which was the lowest energy available. That is the minimum energy jump, which is possible.

And hence, that is where the electrons would like to go. So, since electrons would like to occupy the lowest energy; so, from wherever they jump, the final picture will be like this, because in band 2, all the electrons would have got taken the lowest energy; and, the empty ones would be at empty k-states, would be right at the top. Whereas, in case of band number 3, wherever they jumped, they will roll down to the lowest energy. And hence, those three states I am showing you will be filled. And, if there are 3 electrons jumping, and others will be empty. If that is the case, clearly, in this picture now…

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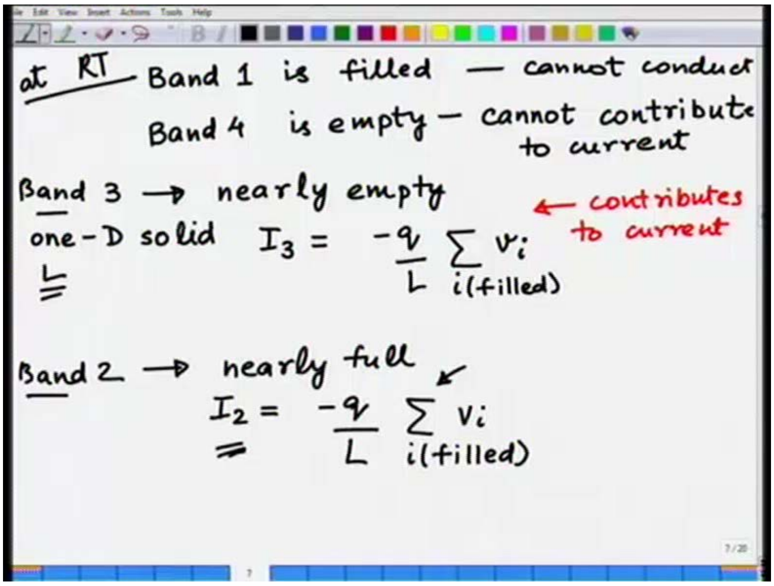

Let us go to this picture at room temperature. At room temperature… So, we talk at room temperature. Now, the picture is band 1 is filled – completely filled, cannot conduct. That is the conclusion we already know. This cannot conduct; and hence, cannot contribute to current. Band number 4 – band number 4 is empty – is completely empty, cannot… You can see that, band number 1 is completely full; band number 4 is completely empty. Therefore, neither of these two bands can contribute to current at all. So, cannot… Instead of saying cannot conduct, I should really say cannot contribute to current; cannot contribute to current.

But, now, see if you look at band number 2 – band number 3 and band number 2 – these band number 3 and band number 2; now, you see they are partially filled. Band number 2 in this schematic has 3 empty states; and, band number 3 has 3 electrons and rest of the states are empty. So, these bands – now, number 2 and 3 could possibly conduct and when I have applied electric field. Therefore, you can see that, k-states begin to change as I have shown you in the third picture. So, what is this current, is essentially that, I want to show you that, how does conduction happened in band number 2 and band number 3. So, that is, let us start looking at it. So, let us say nearly empty band…

Let us look at band number 3. Its characteristic is nearly empty, but not completely empty; band number 3 has some electrons; band number 3 has some electrons right here, right here. In this case or in this case, right here, band number 3 now has some electrons.

It is mostly empty, but it has few electrons. If that is the case, then what happens? In that case, if I write the current in band number 3 and I will call it band number 3; if I think of a one-dimensional example; let us say one-dimensional; one-D – dimensional solid is what we are talking about let us say; whose length is L. L is the length of that solid. In that case, I will write the current through this band, because current contribution from band number 3 as being equal to minus q being the charge… So, q by L is the charge density; and, summation of all the velocities, where i is on the filled states – the states which are filled; the states which are filled if I multiply by the velocity of those electrons. So, there are 3 electrons I have shown. So, this summation over 3 electrons the states on which it is filled. And then, this will give you the current I 3. So, it will start contributing to current. Now, this contributes to current.

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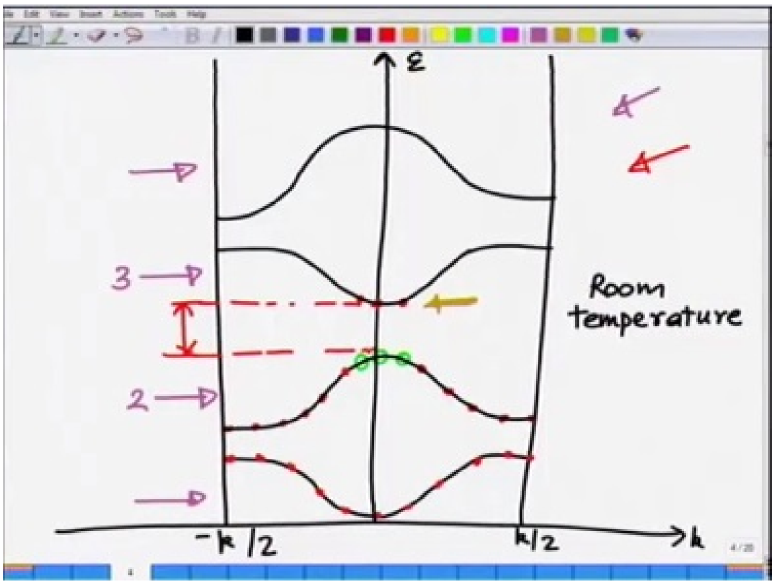

If I now look at band number 2, what is its characteristic? It is nearly full. If you look at this picture, you see green dots, which are green open circles, which are showing you the empty states. But, other than that, it is almost completely full. Therefore, it is a nearly completely full. If I look at this particular band, then what the current will be? Same way I can write this current I 2 to be equal to minus q as the charge divided by L gives me the charge density – linear charge density multiplied by the velocities i, which is filled – overfilled states. Now, I can do a trick; now, I can do a trick.

How many electrons are there? Recall that, whatever is the number of primitive cells in a material, that many k-states are available in the first brillouin zone. That was the consequence of Blaws theorem, which I had taught you; that whatever is the number of primitive cells and if we are talking about only one atom in a primitive cell; if such is the case; in that case, then we will have – whatever is the number of atoms, we will have that many number of k-states in the first brillouin zone. Since number of primitive cells in a material would be on order of Avogadro number, give and take one order of magnitude – 10 to power 23, 10 to power 22; per centimeter cube is the density of atoms. Therefore, we know that, if I take it 1 centimeter cube of material, I will have 10 to power 22 or so primitive cells and that many number of – 10 to power 22 number of filled states. If so, in order to compute this current I 2; since this is nearly full, only few empty states. Therefore, I must carry out this summation over all the filled states – almost Avogadro number of states I must carry out this summation. I can play a trick. Recall that, what is a v i.

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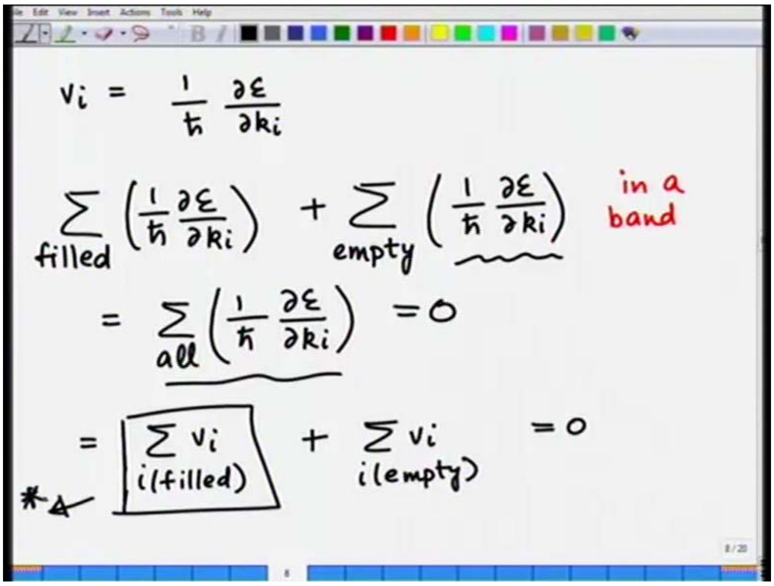

Wherever the electron is v i, we have defined as 1 over h bar del E by del k i. That is what we defined as a velocity of electron if electron is occupying a state called k i. If it is occupying, then that is the velocity. So, now, if I carry out this summation; so, now, if you look at the k-states in a band number 2; if I have band number 2, this is band number… And, if I carry out this del E by del k type of summation on all these k-states whether they are occupied by electron or not occupied by electron; so, then, I am going to write this as del 1 over h bar… So, I am going to write this as 1 over h bar del E by del k i over all summation over all filled states or filled states plus I will do this as summation over 1 over h bar del E by del k i over all the unfilled states or empty states or let me call it empty states. Then, this quantity should be equal to 0; this quantity should be equal to 0, why? Remember, what I am carrying out is essentially this is equal to…

Or, I should write even one more step before I do this. I should write this as over all the k states in a band, this should be equal to 1 over h bar del E by del k i; and, that quantity should be equal to 0. Clearly filled plus empty means all. So, if I look at band number 1, band number 2, then whatever are the… Here are the filled states – the red dots; green open circles are unfilled. And then, again red ones are filled states. And, these are all the states. So, if I do carry out this summation of del E by del k term over all the states; that means I am carrying out a filled state plus unfilled state. But, notice that, for every k state here, whose velocity I always have exactly negative velocity of that on the other side. If you wish, I will show you in this another picture here.

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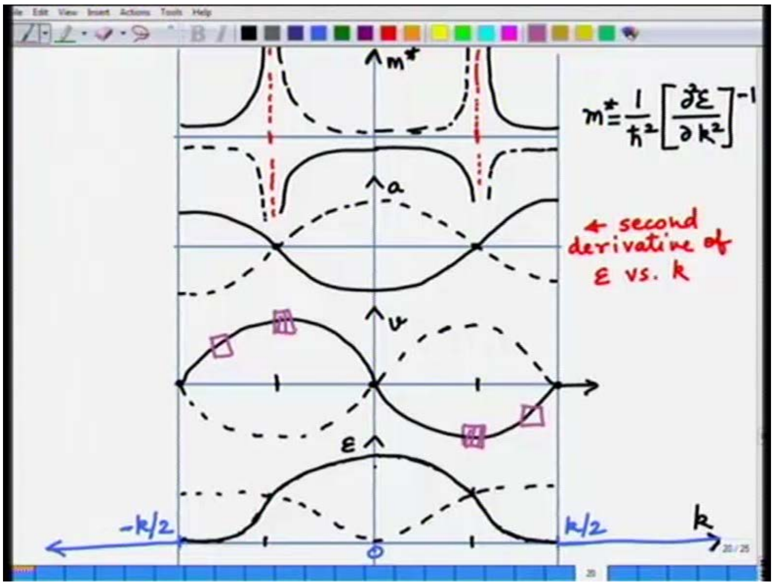

Let us go back to this picture. If you will see that, for every velocity here – I am showing you here this portion here; whatever is the velocity, exactly symmetrical, because about k equal to 0, I will find a point, where there is a negative velocity. If for every positive velocity here like this; I will have a negative velocity E verses k curve – since it is symmetric about k equal to 0, for every quantity del E by del k i on one side; for the negative k i for same value, same negative k value, I will have exactly same magnitude, but a negative sign. And therefore, when I add up over all the states, I should have a picture, where I would have a case, where this over all the state, this whole thing will go to 0. If so, then what I can think of is since…

Remember this filled state is what I recall; I call them as v i. And, I although it is not – the empty states are not filled with electrons; so, I should not talk of electron velocity. But, if I think of this quantity as velocity of some hypothetical particle – those green open circles, which have I shown you; then, I can think of this as empty and I can write v i of those particles, which I define as this basically same in the same way – about this 1 by h del E by del k i. I define then velocity of those hypothetical particles. Then, I will say that, this quantity is equal to 0. If so, I can now substitute this quantity in here; I can substitute in this quantity in here and that I will do in the next page. So, I will write this I 2 current; in which, I will replace this I 2 by this empty sides velocity, negative of that.

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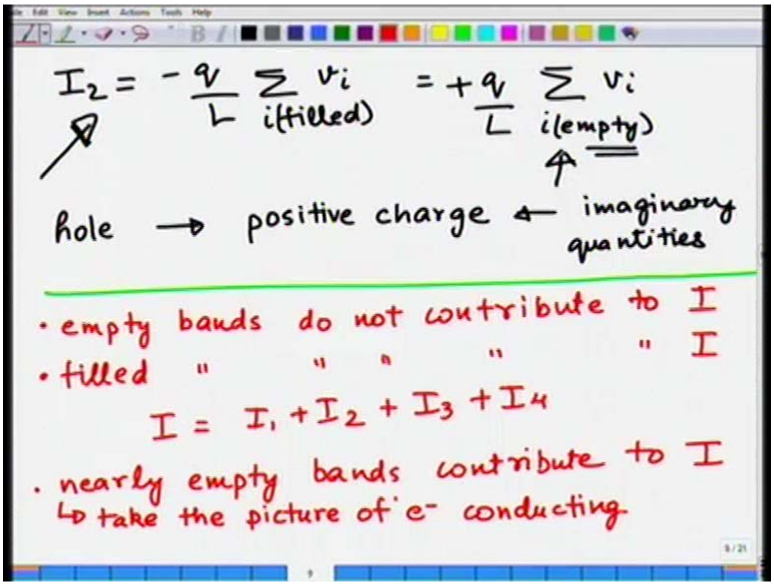

So, I will write I 2 as equal to minus q by L; the way I have written is i filled v i. But, then, I can write this same thing as plus q by L i on empty states v i. Now, notice what have I achieved. What have I achieved is that, instead of having to carry out the summation on Avogadro number of particles in band number 2; in band number 2, instead of carrying out summation over Avogadro number of particles, because it is nearly full. I can get the same value of current by carrying out this summation over not the filled states, but over the empty states. I can carry out the summation over the empty states. Except in that case, I will have to change the sign of the charge. In that case, I will have to change the sign of the charge. And also, I will replace in future, mass also by a positive quantity. In that case, what I define this hypothetical particle. So, if I carry out this summation over empty states; if I think of them to be occupying on a hypothetical particles, which are empty states; in that case, in such cases like band 2, I can define a quantity called holes, which have now positive charge and also mass, which is effective mass, which is inverse, which is positive in this case. Now, this is the part. This is what introduces us to the idea of holes; holes essentially. These are imaginary quantity… Holes are imaginary quantities. These are imaginary quantities, which help us in calculating the currents; which I will like to show you from this plot here.

Recall that; now, notice what happened. If you look at the solid curve; if you look at the solid curve E verses k; remember I was showing you in this case, I was showing you three dots here. Look at the effective mass here. Look at the effective mass of solid. Effective mass here was negative, was a negative quantity. Wherever the slope of the curvature of E verses k curve is concave downwards, which is right here in this case; or, in case of dotted lines, it is right here, right here; or, in case of dotted lines, right here; we find negative masses. In dotted lines right here, we find negative effective mass. This negative effective mass can be treated as a positive quantity; we can convert it into positive and thought of to be occupying, occupied by an imaginary particle, which has a positive charge when it is empty, as empty places. So, remember, if electrons goes away, then electron…

Where will the holes like to live? Empty states would like to live… Because since electron would like to lower its energy, they will roll down to lowest possible energies. So, all the empty states would show up at the top of these bands. So, you can think of that whole energy is lowest at the top of the band. And hence, they will like to reside where the curvatures are concave downwards. In such cases, effective mass of electron is a negative quantity. But, you can think of effective mass of a hole therefore, to be a positive quantity and it carries a charge, which is positive. And, you make the charge to be positive, because, so that you can compute the current by carrying out addition only on the unfilled states rather than on the filled states. So, that is the basic idea of introduction of these holes. So, these holes are basically imaginary quantities, where electrons are not…

And, the advantage you take is that, instead of in band number 2, wherever you have fewer number of empty states; instead of carrying out summation over Avogadro number of filled states, which are right here and here; you could carry out this summation only on the unfilled states and still get the same current I 2. That is what I have proved to you and hence define electrons and in process define the idea of electrons and holes. If that is the case, then let us go back to this picture and see what happens. So, you are free to take a picture. So, now, if I conclude all these together, empty bands do not contribute to total current. Filled bands do not contribute to total current. And, total current of course, in this picture is I 1 plus I 2 plus I 3 plus I 4 because of all four bands. Nearly empty bands contribute to current and what? Take the picture of electrons conducting. Take the picture of electrons conducting, why? Because there are few electrons, nearly empty. There are few electrons; you have to carry out summation over few electrons only.

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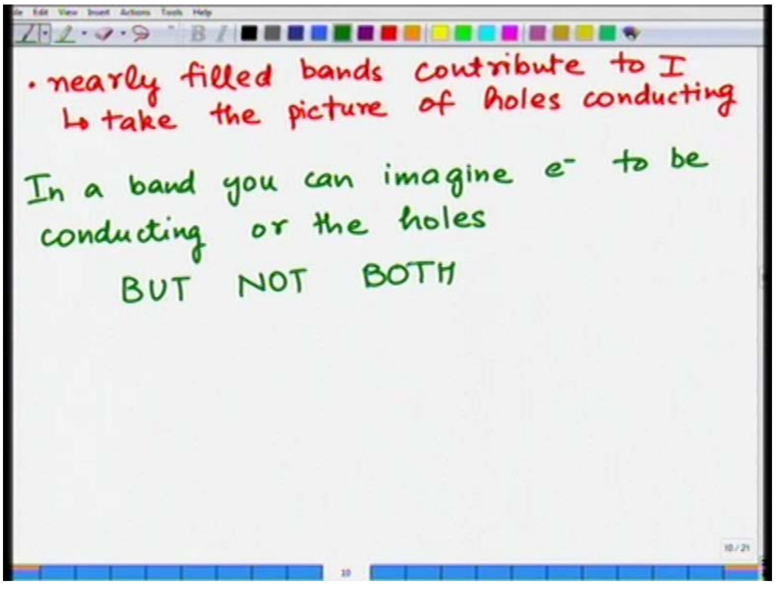

In case of nearly filled bands contribute to current. But, now, you should take the picture of holes conducting. This way you will have to carry out summation over only fewer particles.

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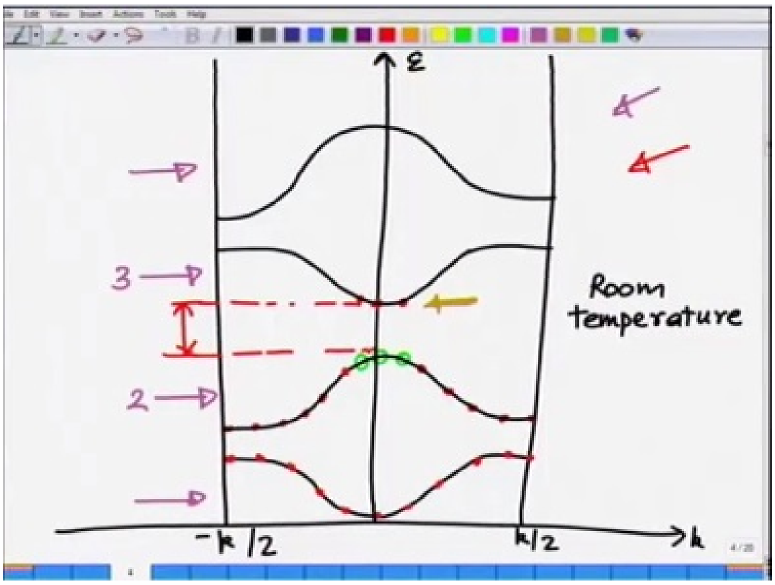

The point being that, whenever you see curvatures of this type – concave downwards, it is worthwhile to think of holes conducting rather than electrons conducting. Wherever the curvatures are concave upwards; in that case, it is worthwhile taking picture of electrons conducting, because electrons will be sitting at the bottom of the band – only few of them at there. And therefore, you can… So, in other words, you can take a picture… So, you can take a picture of… In a band, you can imagine electrons to be conducting or the holes, but not both. For example, in I 2 band, we took a picture of holes; in I 3, for calculation of… In band number 3, for calculation of current I 3, we took picture of electrons. But, you cannot mix them up. Once you said band 3, you would not talk of electrons; then, you have to stick to electrons only. When you want to talk in terms of holes, then you can talk in terms of holes for band 2. So, in a material, for a particular band, you can talk of electrons or holes, but not both in same band. That is basically the conclusion. And that, now, you can see why I semiconductors in valence band – what you call as valence band, you think in terms of holes, because they were very few of them; otherwise, valence band is full of electrons. And hence, you speak in terms of holes.

Whereas, in conduction band, you speak in terms of… In semiconductors, you speak in terms of electrons. And, that is because, there are very few electrons, rest of the states are empty like holes. You could in conduction band, talk of holes, because it is completely empty. But, then you will have to carry out summation over Avogadro number of empty states. Similarly, in valence band, you can speak in terms of in terms of electrons, but then you will have to carry out summation for currents over Avogadro number. And hence, preference is for holes in valence band and electrons in conduction band. Holes you can now imagine, is a mathematical quantity – a derived quantity, absence of electrons, where charged and effective masses are replaced according to the curvature of that particular band. So, that is where what I have introduced. In context of this, now, we will have a brief comment on conductivity of materials. So, now, let us go further. So, I have shown you conductivity in relation to the band structure. So, what I will do is now make few comments on the conductivity of materials.

And now, we will try to complete the full circle from where we started. If you remember, theory, etcetera, etcetera; and, we developed further ideas of conductivity. And now, we are going to talk in terms of band diagrams in context for band structures. So, just brief comments with some comments, I will make briefly in next 5-10 minutes before I end this chapter and move on to the next module, where we will start talking about semiconductors in particular in the carrier densities and optical properties of materials. So, what I am going to do is before that, I will make quick comments.

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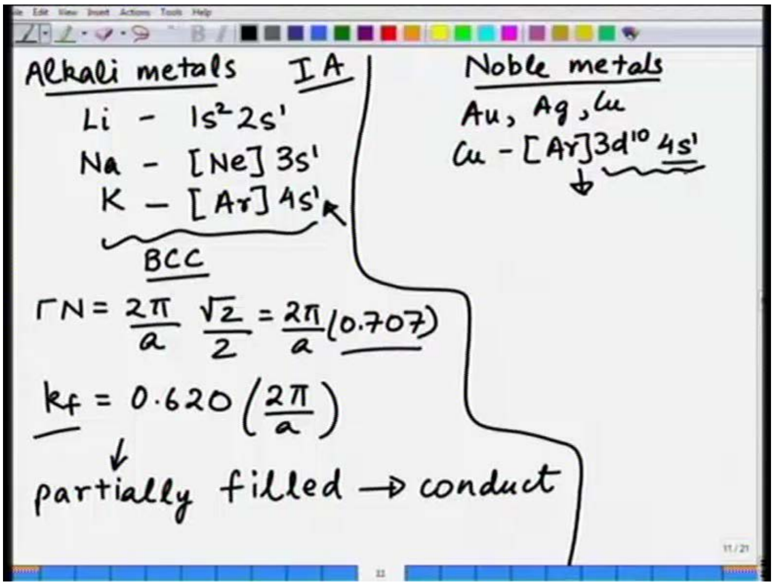

So, let us start with alkali metals. Let us use, let us talk of alkali metals. Remember these are the materials in which theory work fairly well; and, even free electron theory work very well. And, what are these materials? These are lithium; they are lithium, sodium and potassium and so on, many other… So, this is 1 s 2 2 s 1. This is neon configuration and then 3 s 1. And then, this is argon configuration and then 4 s 1 and so on. There are other cesium and other materials also in this. This is group 1 a materials. And then, we also have noble metals such as copper, which have 1 electron in the outer cell like noble metals; you can talk about noble metals also like gold, silver and copper. Also, in this category, copper being of course, equal to… Copper having argon configuration times 3 d 10 and then 4 s 1. So, basically, like potassium, except there are d electrons also involved in it. What happens? This is where roots theory and free electrons theory worked well.

What happened? Why they worked very well? Now, remember this structure of these materials is BCC – BCC series structure. If BCC is the structure, then the reciprocal lattice is like FCC; reciprocal lattice is like FCC. And, how many electrons per atom? There is only 1 outer shell electron, is 1. So, there is 1 electron, which is a conducting electron per atom. It is a BCC. And, if I look at this now, number of k-states that I will have therefore, is equal to essentially number of primitive cell; each primitive cell has 1 lattice point. And, since this is the monovalent, in this particular case, 1 lattice side is occupied by only 1 atom; that means number of atoms is same thing as number of primitive cells. So, whatever is the number of atoms, same is number of k-states. So, if I have n atoms in this, then I have n number of k-states in the first brillouin zone alone; first brillouin zone has n number of k-states. Each k state can take 2 electrons. So, I can have 2n electrons filling the first brillouin zone itself. And, how many electrons do I have? If I have n atoms, each atom gives 1 electron. So, I have n electrons. What is that means? First brillouin zone could have taken 2n electrons. But, I have n electrons; that means first brillouin zone will be only half filled. That is what this means. So, if I look at this… Then, if I look at this…

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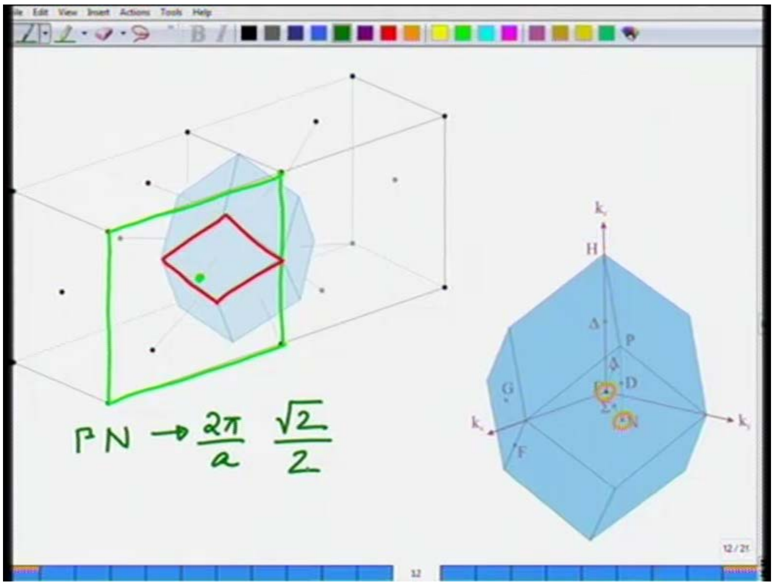

Let me show you. If you look at this; since the structure is BCC; that means… What is that means? That means the reciprocal lattice is like FCC. So, this is the reciprocal lattice for a BCC structure right here. Which is the shortest distance in this? The shortest distance in this is gamma to N; gamma to N is the shortest distance, which is like saying this point from the center point right in the middle. Here is the point, where intersection of this particular plane in… Wherever the line being drawn to this particular lattice point… Just messing up little bit. So, let me draw a little better.

So, if you think of this particular plane for example; and, if you think of this particular as a lattice point here on this particular face; on this face is this… Center point on this face is this point from the center of this zone shown if you draw a line here. This red line is the paint formed by red lines shows you a perpendicular bisector. So, that is what this point N is; that is the point this N is. So, what is the distance gamma to N? This distance of course, is equal to 2 pi by a; 2 pi by a are these distances right here – square root of 2 divided by 2, is the distance gamma to N. So, gamma to N. So, I will write this down here. So, this tau N is a distance, which is to a 2pi by a root 2 by 2, which is equal to about 2 pi by a – in terms of 2 pi by a 0.707.

Now, if I look at the Fermi sphere, then the radius of Fermi sphere – in this case, if I think of Fermi surface to be spherical and I calculate for one… Remember you can now calculate the radius of Fermi sphere; you have all the… We have done all the derivations. If you calculate this part – the radius of the Fermi sphere; then, you will find that, this quantity is 0.620 into 2 pi by a; point being… This is smaller than the shortest distance in the brillouin zone; that means the Fermi sphere will be totally contained in the first brillouin zone. And, since you have only half-filled brillouin zone in shape of Fermi sphere; and, partially filled band therefore. So, you have partially-filled brillouin zone and hence it can conduct. So, this material has a continuous band. First of all, it is a continuous band and it is partially filled. So, then partially filled band will conduct. And, that is why you had this theory working – all these theories – free electron theories, because the surface itself is a sphere since it can be contained fully within the brillouin zone itself. And hence, these alkali metals of group 1a – this theory – roots theory and free electron theory started working well.

Some complications begin to show up when you go to copper. For example, if you go to copper, then instead of thinking of one conducting electron, there are places… And, if you are more interested, you can look at this electronic properties – the reference I have given you electronic properties of materials by R. F. Hummel. So, you can… There is a reference, which has been given to you; you can use this reference. And, there is a band diagram for free electron. There is a band diagram shown for copper; and, you can read there. I will state only in words, because I want to be brief here; you will find that, there are places, where d electrons, d bands start coming very close to the s bands. And hence, they interfere; they also play a part in conduction. So, you might have to think in copper as if there are 11 electrons conducting rather than 1 electron conducting. But, yet there are no band gap in this material; and, these nobel metals also conduct reasonably well.

Now, if we move on to next picture, which is group 2 divalent metals; if we move to divalent metals, example of this will be for example, 2a metals, which are let us say beryllium. Let us take some examples – magnesium, calcium, strontium, etcetera, which is 1s 2 2 s 2; 3 s 2; argon 4 s 2; and, this is 5 s 2; this is the hcp structure – hexagonal close packed structure; this is hexagonal close packed structure; this is fcc; and, this is also fcc structure.

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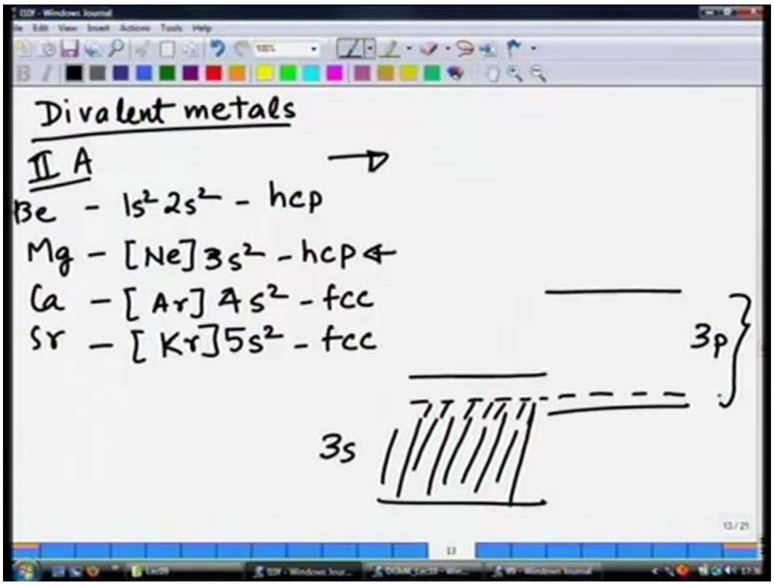

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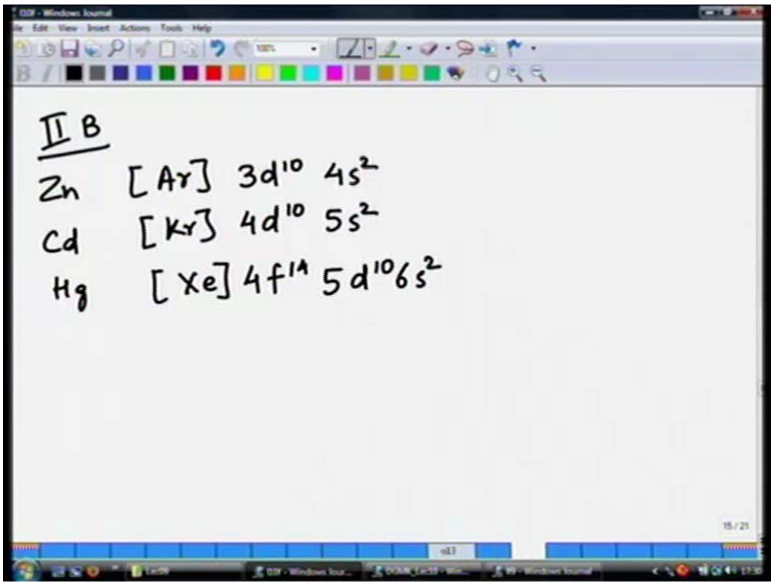

If I take group 2B metals, which have d electrons also in there; so, zinc for example, argon configuration and then 3d 10 and 4s 2 or I take cadmium or mercury, where we talk of xenon here. And, this is 4d 10, 5s 2. This is 4f 14 5d 10 and 6s 2 is this configuration. Let us look at them one by one. Now, what happens here? What happens here? Why do these metals conduct? Notice this; now, we have two electrons. So, if we think of fcc; number of atoms same as primitive cell. If we have 1 atom on each lattice point, then number of primitive cell is same as number of atoms. If that is the case, then first brillouin zone will be able to… If there are n atoms; in that case, I will have n k–

states. Again, I repeat the story. Each k-state can take two electrons: spin up and spin down. Therefore, it can take 2n electrons.

And, how many electrons are there in first brillouin zone? Now, in this case, per atom, there are two electrons, which are going to conduct. So, if there are n atoms, then I will have 2n electrons. So, 2n states in first brillouin zone and 2n electrons in first brillouin zone. What does that mean? The first brillouin zone would be completely full. And hence, we must think of these as insulators. But, your experience tells you that, no, these materials – magnesium, calcium, etcetera, are conductors. So, what is happening? What is happening is this that, since there are continuous band, there are no band gaps. Therefore, take example of… For example, you take example of this magnesium. In this case, what you find is that, you have 2p band; this is 3s band; this is the 3s band, which should have been completely full with 2 electrons. But, there is a partially overlapping next higher band – 3p band, which is next higher band up there; which is now also there. So, there is a 3p band right here in magnesium for example, over lapping. So, what happens is the picture is that, result of this is that, some of these electrons draw a picture little better. Some of these electrons can flow over into this band – also 3p band also. And hence, 3s band is partially empty as is 3p band, which has only few electrons.

Consequence of that says that, this also becomes a partially-filled band; and hence, this can conduct though its conductivity is slightly lower than normal metals we talk about. In group 2B metals, again 4d electrons… This d electrons also playing a part. But, in case of zinc and cadmium, the d electrons are far far below the 4s band if you look at the band diagram 4s of s band. And hence, d electrons do not play too much of a part. Mercury indeed; however, d band are fairly close to the s bands or sometimes they intersect. Therefore, you must think of s and d electrons together in case of mercury. But, the point is that, again in these cases, because there are continuous band, there are no band gap; these materials are still conducting; which bring to me to the point, where you can recall.

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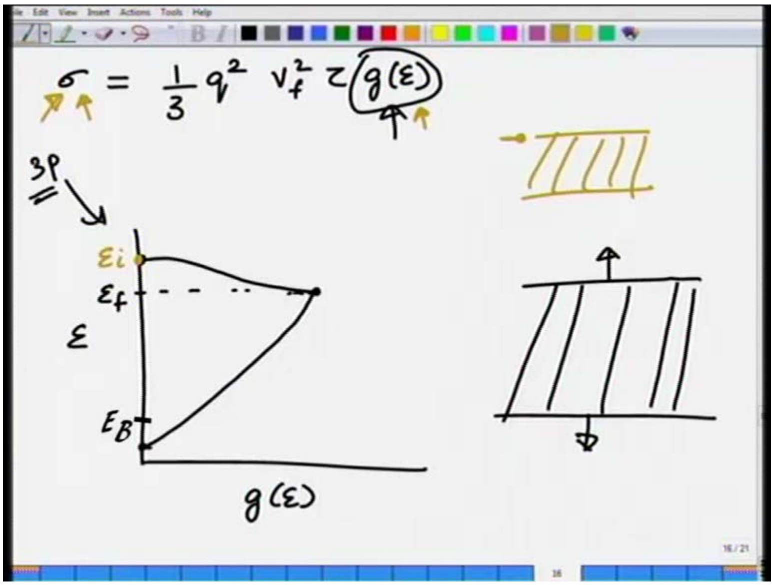

I had written sigma as conductivity as equal to at… After free electron theory, I had derived that, conductivity in context of free electron theory to be approximately 1 over cube q square – charge square times Fermi velocity square times some tau. And, I had written density of states, which are occupied actually. But, nonetheless, density of states also I had included. This is… Notice this density of states. I could think of this. Therefore, something like this; I could think of density of states like this in the energy scale. Remember if I think of a band; if I think of a band; what is that mean? If I think of a band, I mean that, below it there are no energy states; there are energy states not allowed; energy states above it are not allowed; that means those are disallowed energy states; that means density of energy states; there is nearly 0. So, somewhere here is 0. At the top of the band… At the bottom of the band, the energy states are 0. So, if I plot this density of state, it shows a maximum somewhere here; somewhere here in the middle shows the maximum.

And, what happens; in case of monovalent metals, the Fermi energy lies somewhere here – E f for a monovalent; Fermi energy for monovalent metals, because for example, alkali metals of group 1a, where we have only one electron – the half-filled bands. Bands are half-filled. Since they are half filled; so, they are somewhere in the middle, where the density of state is maximum. This g is maximum therefore. And hence, conductivity is very high. In case of bivalent metal, we can think of… If I take a picture of 3 bp band; if I think of this is as 3 bp band; then, I will think of Fermi energy to be somewhere here.

Here is the Fermi energy. So, I will show that Fermi energy somewhere here as energy for a bivalent metal. In that case, I do have some g; I have some g here; some value of density of states. And hence, I have some conductivity, but not as well as good as monovalent metals.

If I think of now bands, which are completely full; if I think of bands, which are completely full; in that case, Fermi energy somewhere in the top. And, I would think of that and for such materials E i to be the Fermi energy, where density of states is nearly 0. And hence, I would think of again conductivity to be very very poor in those materials; let us call them insulators. Therefore, I have written the subscript i for those cases. So, we can take such a picture; show this picture; and, from what we have derived for a free electron theory; from that formula, we can think of conductivity – why there are differences in conductivity in this way.

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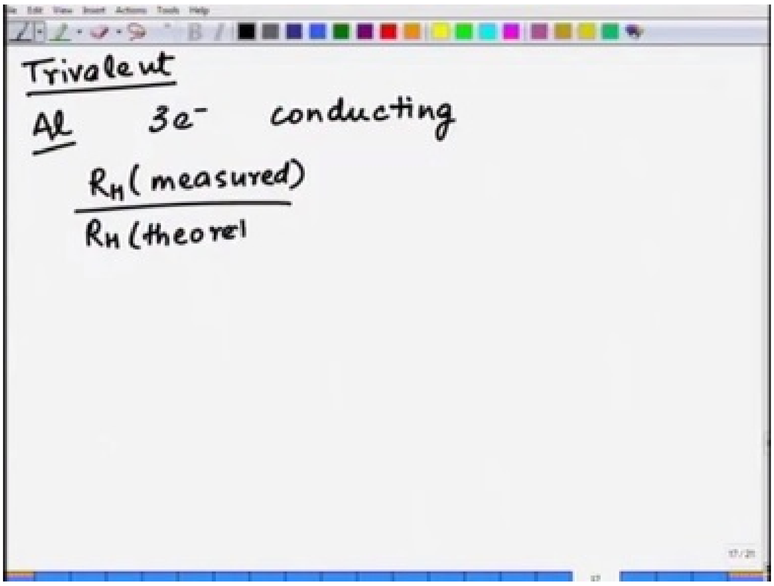

Briefly, I will also mention trivalent metal, because that was a problem, which we never were able to resolve. You will recall in case of aluminum, where we think of three electrons conducting in free electron theory or Drude theory. We found the Hall coefficient to be equal to… Hall coefficient came – multiplied by n times q came out… Or, rather I should write this in different form – R H, which was measured; and R H, which was theoretically predicted…