Solar Photovoltaics :
Fundamental Technology and Applications
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Lecture - 06
Band Theory in Semiconductor Physics

Welcome everyone. You remember in the last class we have started discussing about some preliminary concept of quantum mechanics. So what we have learned that the particle in an infinite square well or particle in a box problem, how to solve the energy eigenfunction and how to get the wave function for that particular case. Very often that is mentioned as quantum free electron theory.

In today's lecture we will learn about how this concept can lead to the formation of band gap or how there are three different kind of solids namely semiconductor, metal and insulator exist.

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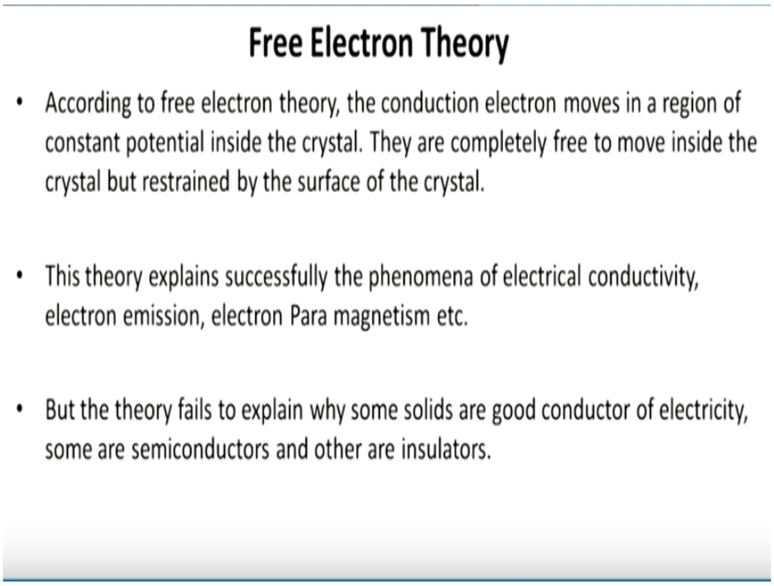

Free Electron Theory

- According to free electron theory, the conduction electron moves in a region of constant potential inside the crystal. They are completely free to move inside the crystal but restrained by the surface of the crystal.
- This theory explains successfully the phenomena of electrical conductivity, electron emission, electron Para magnetism etc.
- But the theory fails to explain why some solids are good conductor of electricity, some are semiconductors and other are insulators.

In free electrons theory, according to the free electron theory, the conduction electron moves in a region of constant potential inside the crystal. They are completely free to move inside the crystal, but restrained by the surface of the crystal. So what is the difference between classical free electron theory and quantum free electron theory? In classical free electron theory we also consider that electron are free to move around inside the crystal, but electron gains energy when we hit them.

But the classical free electron theory was not successful to explain many of the phenomena in solid just like electrical conductivity, thermal conductivity etc. But in quantum free electron theory, we consider again the particle in a box but here particle is free or moving in a constant potential inside the box. Only constraint on the particle is that it is confined in the boundary with boundary has an infinite potential or where the wave function does not exist.

So this problem actually explains pretty well many of the phenomena of the metal like electrical conductivity, thermal conductivity and then electrical paramagnetism etc. So this theory explains successfully the phenomena of electrical conductivity, electron emission, electron paramagnetism etc. But this theory fails to explain why some of the conductors, some of the solids are good conductor of electricity and some of them are bad conductor of electricity.

That means why some of the solids are conductor, some of them are insulator or why some of them are even semiconductor. So that means, the physical properties of the semiconductor cannot be explained by this theory. Secondly, the positive value of the whole coefficient also cannot be explained by the free electron theory. So where is the problem coming from? In the free electron theory, it is an ideal approximation.

We consider that electron moves in a constant or almost free potential inside the solid. But in the practical, in the real life the situation is not like that. The electron moves in a potential which has a periodic form. So in a real crystal solid, we need to modify this problem keeping in mind that the electron not moves in a constant potential, but it moves in a periodic potential. That we will discuss in this class.

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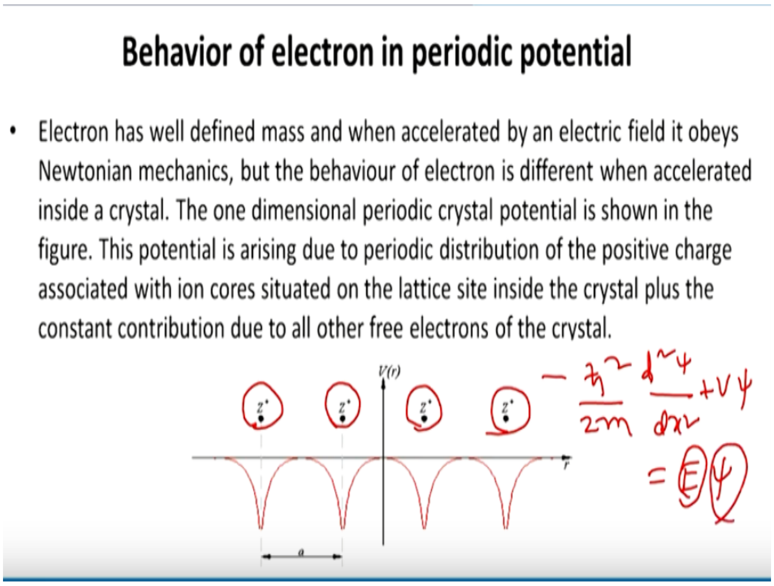

Behavior of electron in periodic potential

- Electron has well defined mass and when accelerated by an electric field it obeys Newtonian mechanics, but the behaviour of electron is different when accelerated inside a crystal. The one dimensional periodic crystal potential is shown in the figure. This potential is arising due to periodic distribution of the positive charge associated with ion cores situated on the lattice site inside the crystal plus the constant contribution due to all other free electrons of the crystal.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V\psi = E\psi$$

The behavior of electron in a periodic potential. Electron has well defined mass and when accelerated by electric field, it obeys Newtonian mechanics. But the behavior of electron is differently when accelerated in a crystal, why? Because in a one dimensional periodic crystal, there is a periodicity in the potential. And because of that the electron interacts with the lattice site and that modulates the energy eigenfunction as well as the wave function.

The one dimensional periodic crystal potential is shown in the following figure. As you can see this is a very ideal potential where the z plus this is showing the positive ion cores. And the distance a is the lattice spacing. That is the distance between two successive lattice sites. This potential is arising due to the periodic distribution of the positive charge associated with the ion cores situated on the lattice sites inside the crystal plus the constant distribution due to all other free electrons of the crystal.

This is very complicated case. So for this particular kind of potential if I need to solve the Schrodinger equation if we remember like the one dimension Schrodinger equation if I write down once again here so this will be like this. So here V is my constant potential in the case of an infinite square well potential. But in this particular case, V has this particular complex geometry.

So it is very difficult to incorporate this exact nature of the V and solve the Schrodinger equation to get my E and psi. To get rid of this problem Bloch came across with a solution. What he said that in this kind of periodic lattice, the wave function is also modulated by the periodicity of the crystal lattice. In order to find out the motion of the electron in a crystalline solid Bloch has solved the Schrodinger equation for periodic boundary condition.

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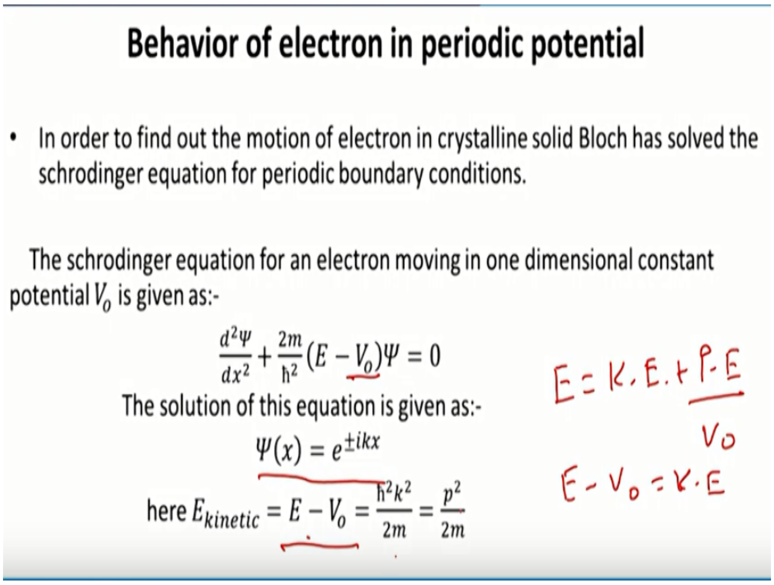

Behavior of electron in periodic potential

- In order to find out the motion of electron in crystalline solid Bloch has solved the schrodinger equation for periodic boundary conditions.

The schrodinger equation for an electron moving in one dimensional constant potential V_0 is given as:-

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}(E - \underline{V_0})\Psi = 0$$

The solution of this equation is given as:-

$$\Psi(x) = e^{\pm ikx}$$

here $E_{kinetic} = \underline{E - V_0} = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$

$E = K.E + \underline{P.E}$

V_0

$E - V_0 = K.E$

So you remember in the case of particle in a box problem or in free electron theory, we have the potential is in finite at the two boundary. That means wave function does not exist at the two boundary. But here we have periodic boundary condition. This kind of model is also called nearly free electron theory. The Schrodinger equation for an electron moving in a one dimensional constant potential V 0 is given by d 2 psi d x 2 plus 2m by h bar square E minus V naught psi is equal 0.

Here your V naught is either zero or constant potential and we all know what is the solution of this equation. The solution of this equation is psi x is e to the power plus minus ikx. So this is basically nothing but a traveling wave which has equal probability to move in the forward direction or backward direction. Remember, in quantum mechanics we consider the electron as a wave.

So associated with every electron there is a electron wave and now this electron wave is interfering with the crystal lattice site. So here the kinetic energy E is E minus V naught, right? Because E is equal to total energy that is kinetic energy plus potential energy. E is your kinetic energy plus potential energy. Here potential energy is V naught.

So if I subtract E minus V naught I will get the kinetic energy of the electron. So E kinetic energy is E minus V naught and that we know is h bar square k square by 2m or is equal to p square by 2m. That was the case of a free electron theory. But in a periodic crystal lattice the potential is also periodic.

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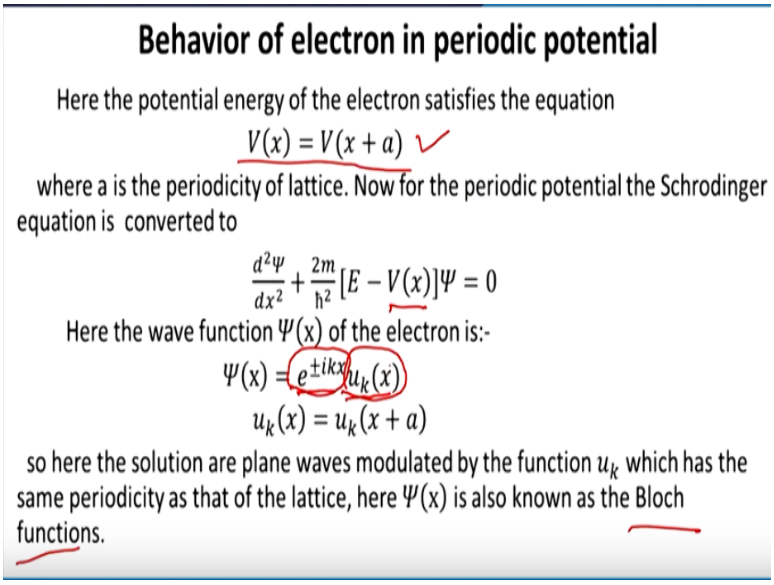

Behavior of electron in periodic potential

Here the potential energy of the electron satisfies the equation

$$\underline{V(x) = V(x+a)} \checkmark$$

where a is the periodicity of lattice. Now for the periodic potential the Schrodinger equation is converted to

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}[E - \underline{V(x)}]\Psi = 0$$

Here the wave function $\Psi(x)$ of the electron is:-

$$\Psi(x) = \boxed{e^{\pm ikx}}\boxed{u_k(x)}$$

$$u_k(x) = u_k(x+a)$$

so here the solution are plane waves modulated by the function u_k which has the same periodicity as that of the lattice, here $\Psi(x)$ is also known as the Bloch functions.

So what we have to do, we have to introduce the periodicity in the potential and that we have done here. The potential of energy of the electron in a crystal lattice satisfies the following equation V x = V(x + a) where a is the periodicity of the lattice. Now for the periodic potential, the Schrodinger equation is converted to d 2 psi d x 2 plus 2m by h bar square E minus V x psi is equal to zero.

Remember, here this V x has this form. Here the wave function psi x of the electron is psi x is e to the power plus minus ikx times u k x where u k x has the periodicity of the crystal lattice, u k (x) = u k (x + a). So if you look at this solution very closely, so, you see this has a traveling part e to the power plus minus ikx modulated by a periodic function u k x.

So here the solutions are plane waves modulated by the function u k which has the same periodicity as that of the lattice. Hence psi x is known as the Bloch wave function. So here in the periodic crystal lattice, the solution of the Schrodinger equation psi x we call it as a Bloch function or Bloch wave function. And what is a Bloch wave function? This is e to the power plus minus ikx into u k x where u k x has the periodicity of the crystal lattice. So Bloch gave this theory to solve the one dimensional crystal lattice problem.

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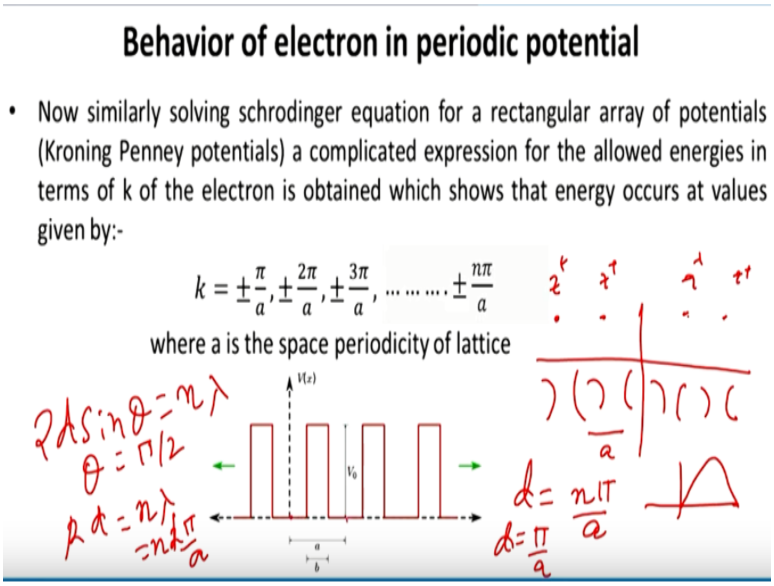

Behavior of electron in periodic potential

- Now similarly solving schrodinger equation for a rectangular array of potentials (Kroning Penney potentials) a complicated expression for the allowed energies in terms of k of the electron is obtained which shows that energy occurs at values given by:-

$$k = \pm\frac{\pi}{a}, \pm\frac{2\pi}{a}, \pm\frac{3\pi}{a}, \dots\dots\dots \pm\frac{n\pi}{a}$$

where a is the space periodicity of lattice

But if you look our original potential, which was like this with a positive ion core right with a positive ion core in between and there is a periodicity of a. That was the real potential in a crystal looks like and considering that Bloch has given an empirical condition and how Bloch came across with the solution? By considering the translational symmetry.

Later on, we can see that this Bloch wave function is also an eigenfunction of the translational operator. Translational operator plays a vital role in solid state physics. We can show that translational operators and the Hamiltonians that is the total energy they commute. From that we can come across with the solution of the Bloch wave function. But still we have complexity in our solutions.

So this particular case where the potential looks like this is very complex although not completely impossible to solve. To get rid of this Kronig and Penney the two scientists they came across with a simplified model for solving the electron in an one dimensional periodic crystal lattice where they consider the potential well as a rectangular well or a square like this and this is called Kronig-Penney model.

So Kronig-Penney model consider here the electron in an one dimensional periodic crystal lattice. So instead of a gradually changing potential in a real crystal case, here the potential is changing like a step function. This kind of problem is solvable mathematically more easily than the real life problem. And we can show later on that this problem pretty much explains most of the phenomena of the solid and many of the three dimensional phenomena can also be explained using this model.

So similarly solve Schrodinger equation for a rectangular array of potential which is a Kronig-Penney potential, a complicated expression for the allowed energies in terms of k of the electron is obtained which shows that energy occurs at the value where k is equal plus minus pi by a, plus minus 2 pi by a, plus minus 3 pi by a. That means plus minus n pi by a where n is the integer.

So what does it physically mean? Let us go back to our original Bragg reflection. In the crystal lattice electron undergoes Bragg reflections. So from our undergraduate science, we have learnt about how the Bragg equation looks like. In a crystal the Bragg equation looks like 2d sin theta is equal to n lambda where n is the order of reflection. Now in a one dimensional lattice theta is equal to pi by 2.

So sin pi by 2 is 1. So this equations gives you 2d is equal to n lambda, right? Now lambda the wavelength associated with an electron can also be written in terms of the lattice vector. The real lattice in many times we convert it to a reciprocal lattice by doing some mathematical transformation and this kind of transformations helps us to calculate different parameters of the lattice very easily.

So instead of lambda we can also write this as n 2 pi over a where this 2 pi over a we have written in a reciprocal lattice space. This 2 and 2 cancels out giving you d is equal to n pi over a, right? Now n is an integer and it gives you the order of reflection. If you put n is equal to 1 the first order reflection so your d is equal to pi by a. Now these values of pi by a, since the crystal has a translational symmetry so plus pi by a and minus pi by a electron wave can move in both directions.

So at these sites plus minus pi by a electron wave undergoes Bragg reflections. Whenever it undergoes Bragg reflections they form a stationary wave. And in the next case, when it comes at the value of the wave vector plus minus 2 pi by a again it undergoes Bragg reflections. So then again it forms a stationary wave. So at this place plus pi by a and plus 2 pi by a crystal is forming standing waves.

We can show that at the position of pi by a, plus 2 pi by a or plus 3 pi by a we can form standing waves. Since there are waves there are energy associated with the waves and in the between place where there is no wave or where we cannot solve the Schrodinger equation that give rise to the energy band gap. So this figure shows a Kronig-Penney potential, a simplified potential in one dimensional crystal lattice.

You see that this is the V naught the height of the potential barrier. From this point to this point we defined a and the width of the potential barrier is considered as b, okay.

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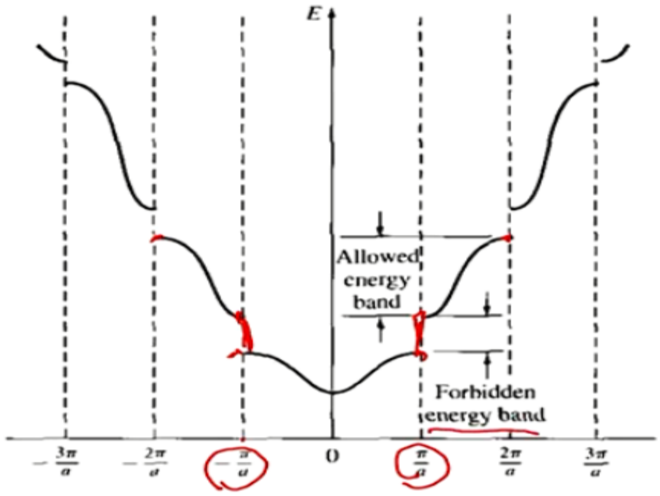

Fig:- Allowed and forbidden bands in E-k diagram for an electron

If we draw now the energy versus k diagram in the Kronig-Penney model so what we can show that at the values of pi by a and minus pi by a the way function is discontinuous that means at this point there are stationary waves formed. The next stationary wave formed at here. We have the allowed energy solutions between minus a to plus pi by a.

We have again the allowed energy values of Schrodinger equation from 2 pi by a pi by a to 21 pi by a and on the left hand side minus pi by a to minus 2 pi by a. But in the between region here, Schrodinger equation does not have any solution. That give rise to the forbidden energy band or band gap. This is the energy versus momentum diagram okay for an electron in a Kronig-Penney potential.

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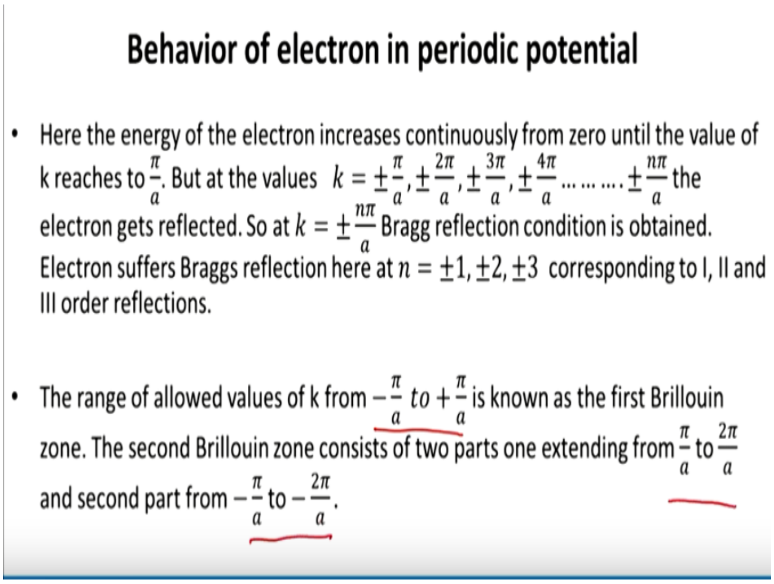

Behavior of electron in periodic potential

- Here the energy of the electron increases continuously from zero until the value of k reaches to $\frac{\pi}{a}$. But at the values $k = \pm\frac{\pi}{a}, \pm\frac{2\pi}{a}, \pm\frac{3\pi}{a}, \pm\frac{4\pi}{a} \ldots\ldots\ldots \pm\frac{n\pi}{a}$ the electron gets reflected. So at $k = \pm\frac{n\pi}{a}$ Bragg reflection condition is obtained. Electron suffers Braggs reflection here at $n = \pm1, \pm2, \pm3$ corresponding to I, II and III order reflections.
- The range of allowed values of k from $-\frac{\pi}{a}$ to $+\frac{\pi}{a}$ is known as the first Brillouin zone. The second Brillouin zone consists of two parts one extending from $\frac{\pi}{a}$ to $\frac{2\pi}{a}$ and second part from $-\frac{\pi}{a}$ to $-\frac{2\pi}{a}$.

Here the energy of the electron increase continuously from 0 until the value of k reaches to pi by a. But at the values of k plus minus pi by a, plus minus 2 pi by a or plus minus 3 pi by a, the electron gets reflected. So at k is equal to plus minus n pi by a Bragg reflection condition is satisfied. An electron suffers Bragg reflection at n is equal to plus minus 1, plus minus 2, plus minus 3.

And they correspond to first order, second order and third order reflection. The range of allowed values of k from minus a to plus a known as the first Brillouin zone.

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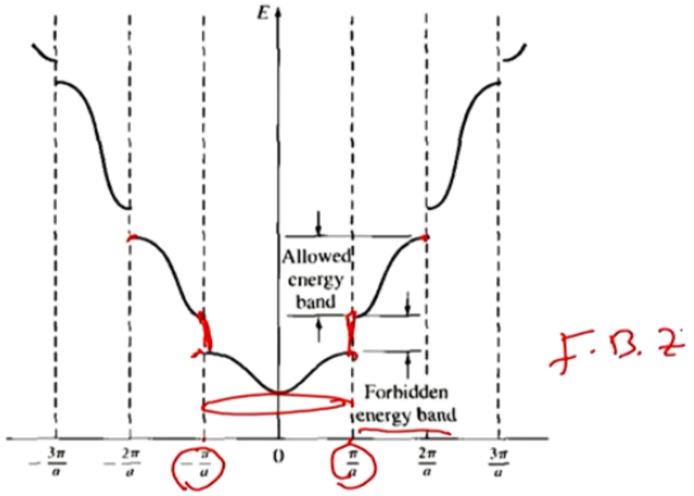

Fig:- Allowed and forbidden bands in E-k diagram for an electron

So if we go back to our earlier site so the region between minus pi by a to plus pi by a this region is called the first Brillouin zone or FBZ. So the region k values from minus pi by a to plus pi by a is known as the first Brillouin zone. The second Brillouin zone is consist of two parts extending from pi by a to 2 pi by a and the second part is on the negative side minus pi by a to minus 2 pi by a, okay. So origin of energy gap.

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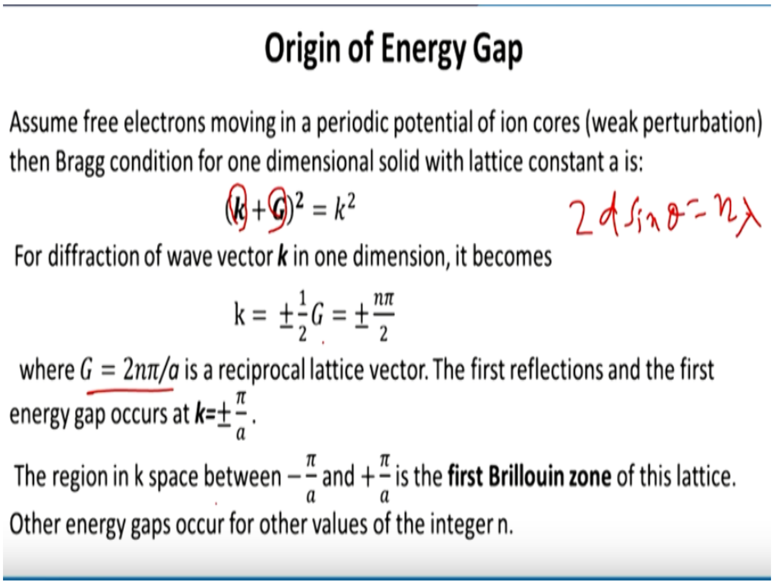

Origin of Energy Gap

Assume free electrons moving in a periodic potential of ion cores (weak perturbation) then Bragg condition for one dimensional solid with lattice constant a is:

$$(k+G)^2 = k^2$$

$2d\sin\theta = n\lambda$

For diffraction of wave vector ***k*** in one dimension, it becomes

$$k = \pm\frac{1}{2}G = \pm\frac{n\pi}{2}$$

where $\underline{G = 2n\pi/a}$ is a reciprocal lattice vector. The first reflections and the first energy gap occurs at ***k***=$\pm\frac{\pi}{a}$.

The region in k space between $-\frac{\pi}{a}$ and $+\frac{\pi}{a}$ is the **first Brillouin zone** of this lattice.

Other energy gaps occur for other values of the integer n.

Assume free electrons moving in a periodic potential of iron cores. Now we consider now this iron cores provide a fairly weak perturbation. So this is a almost nearly free electron theory. Now for the Bragg condition in an one dimensional solid we know in direct space it is 2D sin theta is equal to n lambda. But also we can write down the Bragg reflection condition in reciprocal lattice space.

In reciprocal lattice space Bragg condition is that k plus G whole square is equal to k square. You look that k is the wave vector. For diffraction of the wave vector k in one dimension it becomes k is equal to plus minus half G is equal to plus minus n pi by 2 where G is equal to 2 pi n by a and this is called reciprocal lattice vector. So k is your wave vector and G is your reciprocal lattice vector where G is equal to 2n pi by a.

You can starting from the Bragg equation in direct lattice space that is 2 d sin theta is equal to n lambda. If you convert this equation in a reciprocal lattice space one can also write down that the Bragg condition like that k plus G whole square is equal to k square. The first reflection and the first energy gap occurs here at k is equal to plus minus a, pi by a.

The region in k-space between minus pi by a and pi by a is called the first Brillouin zone of the lattice. Other gaps occurs for the other value of the energy integer n. So if we know plot the how does the energy momentum band looks like for a free electron theory and for a nearly free electron theory. So it is the following.

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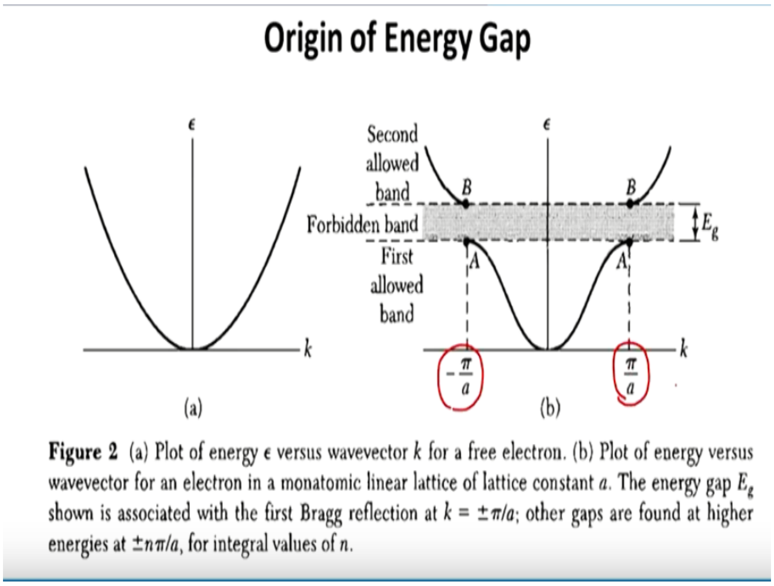

Origin of Energy Gap

Figure 2 (a) Plot of energy ϵ versus wavevector k for a free electron. (b) Plot of energy versus wavevector for an electron in a monatomic linear lattice of lattice constant a. The energy gap E_g shown is associated with the first Bragg reflection at $k = \pm\pi/a$; other gaps are found at higher energies at $\pm n\pi/a$, for integral values of n.

For a free electron theory, energy versus k diagram is almost like a parabola. But in a nearly free electron theory electron does not move in a constant potential but it moves in a periodic potential. So in that case we have learnt right now that electron undergoes Bragg reflection and it undergoes Bragg reflection at the point pi by a and minus pi by a.

So if we draw the energy versus k diagram, so still it is a parabola between minus pi by a and pi by a and the second parabola starts here at the point B. But in the region between a to b there is no solution of the Schrodinger equations.

So the figure number b here plot of energy versus wave vector for an electron in a monoatomic linear lattice of lattice constant a the energy gap E g shown is associated with the first Bragg reflection at k is equal to plus minus a. Other gaps are found at higher energy as plus minus n pi by a for integer values of n.

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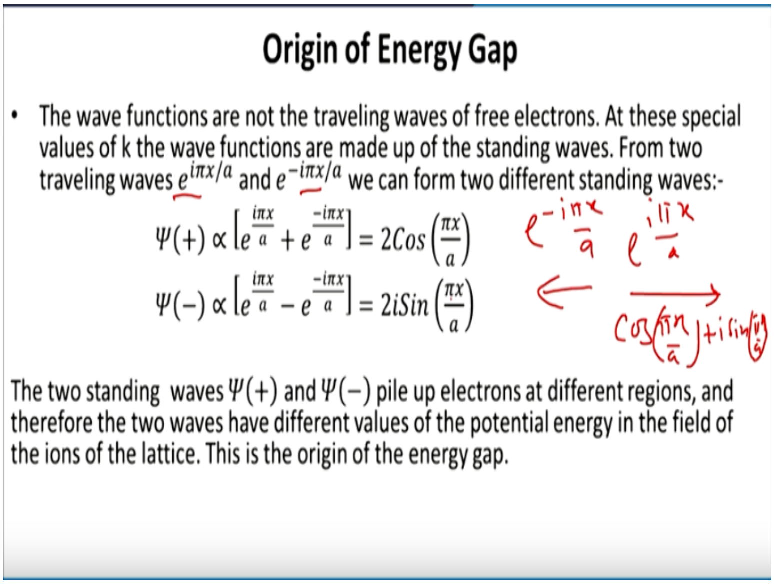

Origin of Energy Gap

- The wave functions are not the traveling waves of free electrons. At these special values of k the wave functions are made up of the standing waves. From two traveling waves $e^{i\pi x/a}$ and $e^{-i\pi x/a}$ we can form two different standing waves:-

$$\Psi(+) \propto \left[e^{\frac{i\pi x}{a}} + e^{\frac{-i\pi x}{a}}\right] = 2Cos\left(\frac{\pi x}{a}\right)$$

$$\Psi(-) \propto \left[e^{\frac{i\pi x}{a}} - e^{\frac{-i\pi x}{a}}\right] = 2iSin\left(\frac{\pi x}{a}\right)$$

$e^{-\frac{i\pi x}{a}}$ $\leftarrow$ $e^{\frac{i\pi x}{a}}$ $\rightarrow$

$\cos\left(\frac{\pi x}{a}\right)+i\sin\left(\frac{\pi x}{a}\right)$

The two standing waves $\Psi(+)$ and $\Psi(-)$ pile up electrons at different regions, and therefore the two waves have different values of the potential energy in the field of the ions of the lattice. This is the origin of the energy gap.

The wave function are not the traveling waves of free electrons in a nearly free electron theory. At this special values of k the wave function are made up of two standing waves. From the traveling waves, e i n pi x by a where n is equal to 1 here. So that is e pi x by a and e minus i pi x by a we can form two different standing waves.

So what we mean here, if we go back to the previous slide, so at this point pi by a and minus pi by a we have two different traveling waves. One is e to the power i pi x by a which is moving in the forward direction and another is e to the power minus i pi x by a moving in the backward directions. So two possibilities can be formed. Either they can summed up or we can differentiate this.

Any linear combinations of the two function according to the quantum mechanics can also be solutions of the function. So there can be two different standing waves here. One let us write down as i plus, which is e to the power i pi x by a plus e to the power minus i pi x by a. And if we expand this e to the power i pi x by a you know that e to the power i pi by x you can write it as cos pi x by a plus i sin pi x by a.

Now similarly you can write down e to the power minus i pi x by a. It will be cosine pi x by a minus i sin pi x by a. Now if I add these two terms, so sin terms cancels out leaving you two cosine pi x by a. Similarly I can form another combinations of these two traveling waves by putting psi as psi minus that is e to the power i pi x by a minus e to the power minus i pi x by a.

In that case instead of plus sign between the two wave function I have to put a minus sign and their cosines will cancel giving you 2i sin pi x by a. So the two standing waves psi plus and psi minus they pile up the electrons at different regions. And therefore, the two waves have different values of the potential energy. Remember, whenever we solved the Schrodinger equation, we solve it for energy eigenvalues and wave function.

Since we have two wave functions here, there will be two values of the energies here in the field of the ion of the lattice. This is the origin of band gap. If we plot these things, this figure will be coming next and that will be more clearer.

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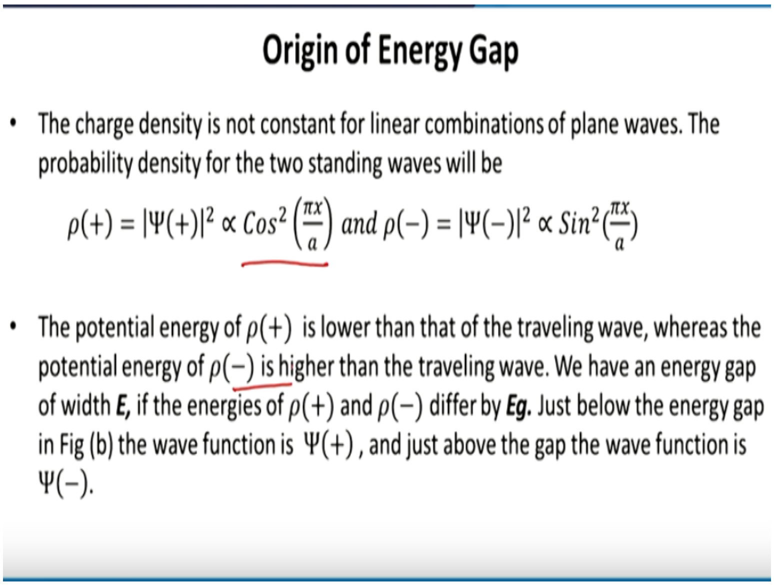

Origin of Energy Gap

- The charge density is not constant for linear combinations of plane waves. The probability density for the two standing waves will be

$$\rho(+) = |\Psi(+)|^2 \propto \underline{Cos^2\left(\frac{\pi x}{a}\right)} \ and \ \rho(-) = |\Psi(-)|^2 \propto Sin^2\left(\frac{\pi x}{a}\right)$$

- The potential energy of $\rho(+)$ is lower than that of the traveling wave, whereas the potential energy of $\rho(-)$ is higher than the traveling wave. We have an energy gap of width ***E***, if the energies of $\rho(+)$ and $\rho(-)$ differ by ***Eg***. Just below the energy gap in Fig (b) the wave function is $\Psi(+)$, and just above the gap the wave function is $\Psi(-)$.

The charge density is not constant for linear combination of the plane waves. The probability density for the two standing waves will be for the case of the positive waves, let us consider is rho plus that is psi plus square is cos square pi x and rho minus this is psi minus square, this will be sin square pi x. The potential energy of rho plus is lower than that of the traveling wave.

The potential energy of the rho plus is lower than that for the traveling wave. Whereas the potential energy of rho minus is higher than that of the traveling wave. So we have an energy band gap of width E if the energies of rho plus and rho minus differ by Eg. Just below the energy gap, the wave function is psi plus and just above the energy gap the wave function is psi minus.

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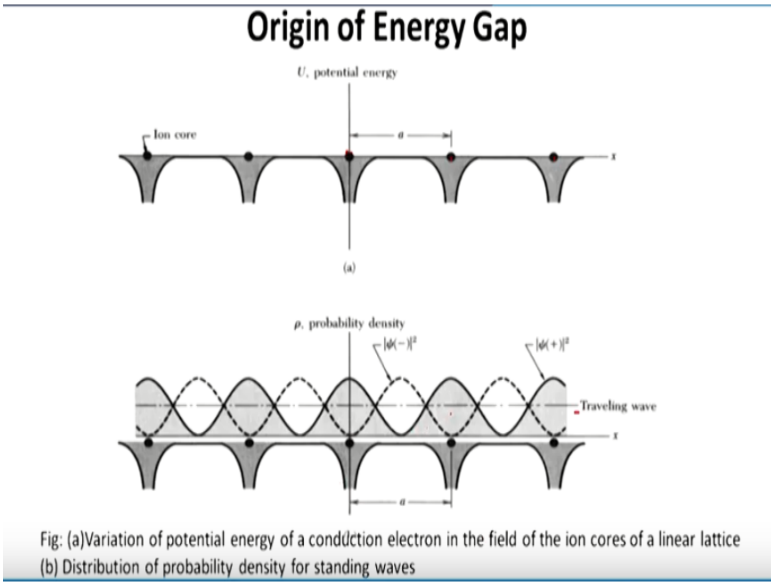

Origin of Energy Gap

Fig: (a)Variation of potential energy of a conduction electron in the field of the ion cores of a linear lattice
(b) Distribution of probability density for standing waves

So here is our potential energy. You look that this is the ion cores. These are the ion cores the black small dots and the distance between these two sites, that is the periodicity, crystal periodicity that is a. Now if we plot the probability density rho which is the square of the wave function psi square and we have plotted that for psi minus square and psi plus square.

So and for a comparison this traveling wave is showing by this straight line. So you see that near that ionic sites psi minus here has a value and which is lower than the traveling value. And at the near the ionic core sites psi plus has a value which is higher than the traveling sites. Just above the energy gap the wave function is psi plus and just above the energy gap the wave function is psi minus.

So that is what we have plotted here. How that standing wave distribute the probability density of the standing wave distributes here.

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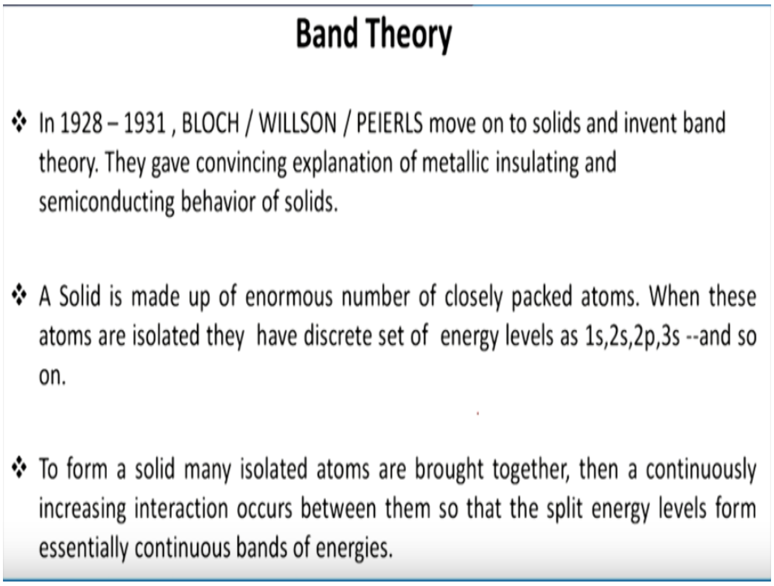

Band Theory

- In 1928 – 1931 , BLOCH / WILLSON / PEIERLS move on to solids and invent band theory. They gave convincing explanation of metallic insulating and semiconducting behavior of solids.
- A Solid is made up of enormous number of closely packed atoms. When these atoms are isolated they have discrete set of energy levels as 1s,2s,2p,3s --and so on.
- To form a solid many isolated atoms are brought together, then a continuously increasing interaction occurs between them so that the split energy levels form essentially continuous bands of energies.

Based on this models or assumptions in between the time period of 1928 and 1931 there are three scientist namely Bloch, Willson, and Peierls extended this concept from the lattice to the whole three dimensional solid and invent the so called band theory. They gave convincing explanations of metallic insulating and semi conducting behavior of solids.

That means the physical origin of the band gap they were able to successfully explain based on their model. A solid is made of enormous number of closely packed atoms. When these atoms are isolated, they have discrete set of energies as 1s, 2s, 3s, 3p and so on. Like you know if you consider silicon, it has 14 electrons and we know we can put these electrons in different atomic levels.

To form a solid many isolated atoms are brought together. Then a continuously increasing interactions occurs between them, so that the split energy levels form essentially continuous band of energy.

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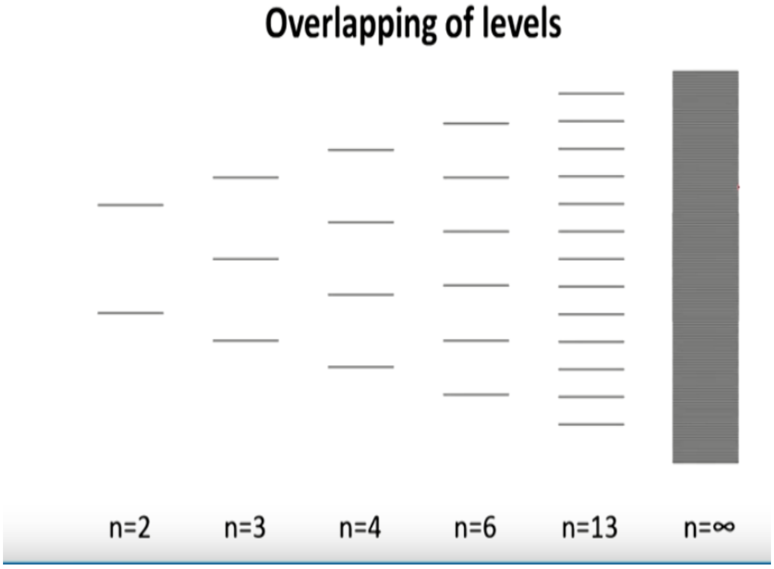

Overlapping of levels

Let us look at it. When n is equal to 2 we have this two energy bands. When n is equal to 3 I have 3. When n is equal to 4, there are 4 energy band; n is equal to 6 there are 6 energy band. If I increase to n is equal to 13 there are 13 energy band. But for an n is equal to infinity so there are all the discrete energy bands but when you look from outside it looks like a continuous energy bands.

This can be an example or analogy can be given to that when we fly in an aeroplane when you are little bit high above we can distinctly see all the different buildings, but when we go high above, then we do not see the different building separately rather we see a stretch of the building. So that is although in the stretch all the different building exist but what it looks like, like a stretch.

Similarly here the energy band gaps looks like a continuous although there are different discrete energy levels lies inside them.

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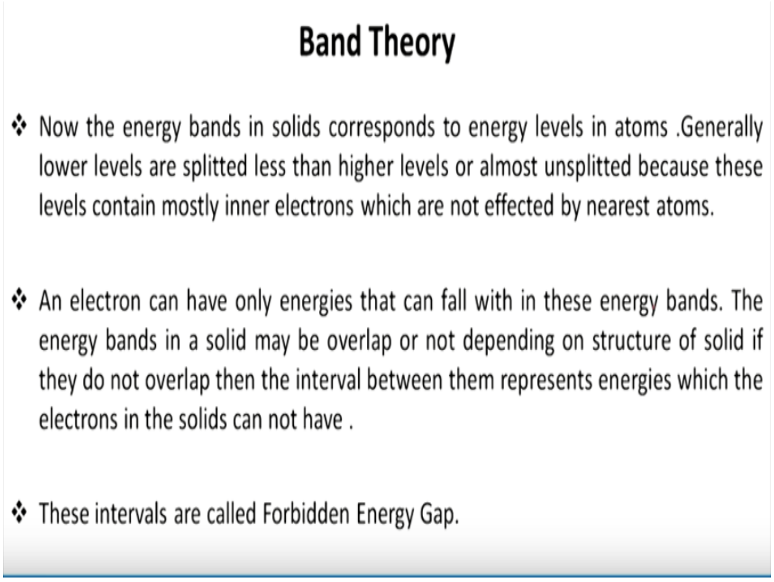

Band Theory

- Now the energy bands in solids corresponds to energy levels in atoms .Generally lower levels are splitted less than higher levels or almost unsplitted because these levels contain mostly inner electrons which are not effected by nearest atoms.
- An electron can have only energies that can fall with in these energy bands. The energy bands in a solid may be overlap or not depending on structure of solid if they do not overlap then the interval between them represents energies which the electrons in the solids can not have .
- These intervals are called Forbidden Energy Gap.

Now the energy bands in solids corresponds to the energy levels in atoms. Corresponding to every energy band, there are the energy levels in the atoms. Generally lower levels are splitted less than the higher level. So almost unsplitted because these levels content mostly inner electrons, which are not affected by the nearest atoms.

So the electrons which are near to the nucleus, they are very tightly bound. So those electrons are not affected by the neighboring atoms. An electron can have only energies that can fall within these energy bands. The energy bands in a solid maybe overlap or do not overlap depending on the structure of solid. If they do not overlap, then the interval between them represents energies, which the electrons in the solid cannot have. These intervals are called forbidden energy gap or the band gap.

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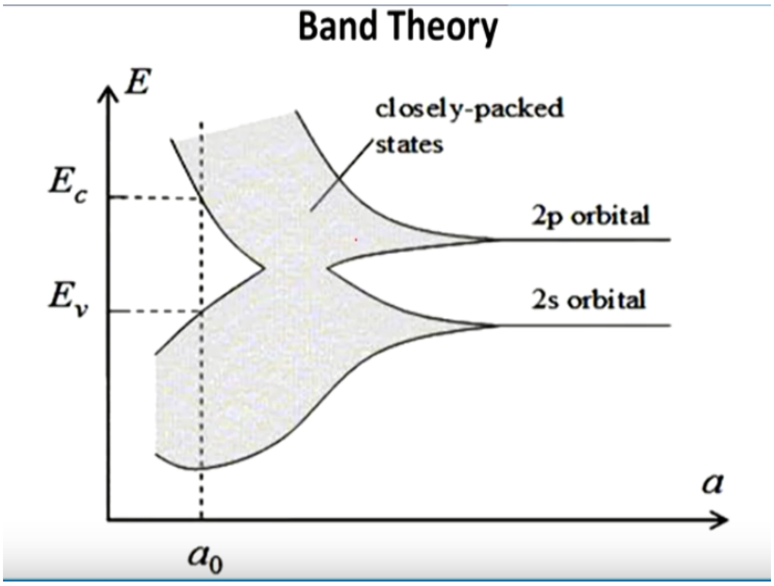

Band Theory

Here we are showing that things. We are considering two closely packed states. We are considering to 2s orbitals and 2p orbitals where these two orbitals has been splitted and you see that in one of them forms an energy band and another of them forms energy band where there is a separation between them two.

Later on we will learn that one of them at T = 0 K is completely filled whereas other of them is completely empty. One of them we will call them as a valence band and other we will call as a conduction band.

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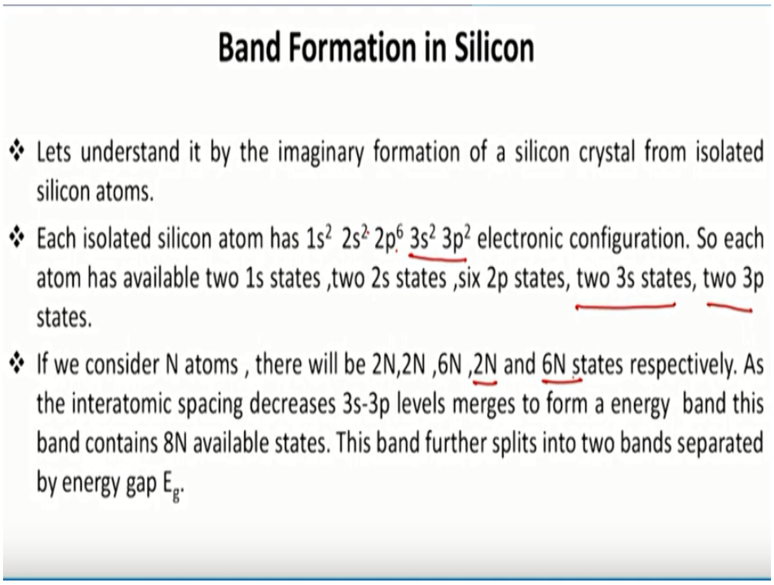

Band Formation in Silicon

- Lets understand it by the imaginary formation of a silicon crystal from isolated silicon atoms.
- Each isolated silicon atom has $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^2$ electronic configuration. So each atom has available two 1s states ,two 2s states ,six 2p states, two 3s states, two 3p states.
- If we consider N atoms , there will be 2N,2N ,6N ,2N and 6N states respectively. As the interatomic spacing decreases 3s-3p levels merges to form a energy band this band contains 8N available states. This band further splits into two bands separated by energy gap E_g.

Let us try to understand this phenomena for a real practical example. Silicon, a semiconductor which is very commonly used to making for making solar cells. Let us understand it by imaginary formation of a silicon crystal from isolated silicon atoms.

So here we are considering a case, you have so many different silicon atoms and you have been given this silicon atoms.

Your job is to put the silicon atoms and make a silicon pistol. How can you do that? Each isolated silicon atoms we know they have 14 electron and where are these 14 electrons stay? They are in different energy orbitals and that we can write as 1s 2, 2s 2, 2p 6, 3s 2, 3p 2. If you add all these electron numbers, 2 + 2 is 4, 6, 10, 12 plus 2 14.

So 14 electrons in one single atoms and they have occupied the different energy level like this. And that is the electronic configuration of a silicon atoms. So in the outermost orbitals, there are 2 + 2 4 electron is there. So each atom has available two 1s states two 2s states, six 2p states, three 2s states and two 3p states. Now if you consider the N atoms, then there will be 2N 1s states, 2N 2s states, 6N 2s states and 6N 3s states respectively.

As the interatomic spacing decrease 3s-3p level merges to form a energy band. This band contains 8N available levels. So again, look at this thing very closely. For one atom in the outer orbitals, I have N is equal to 3. So how many electrons are there, 2+ 2, 4 electrons. How many states is possible. There can be two 3s states and two 3p states, right?

If there are N electrons are there so then there can be responsible, there can be two three states and two TB states right. If there are electrons out there, so then there can 2N and 6N states. 2N state for the s states and 6N states for the p states because p orbital can be sub divided into px, py, pz. So there can be 6N states possible. Now if I have one atom that is the case. If I have N atoms this is the case.

Now if the N is very large, so all the distance between the successive energy level will decrease. So the distance between the 3s-3p level will also decrease and they will march eventually and form an energy band which will ultimately contains 2N + 6N that is the 8N available states. So this band further splits into two bands separated by an energy gap E g.

So when we increase the number of silicon atoms in a crystal let us say 10 to the power 23 silicon atoms in a crystal, so the distance between the successive energy level decrease. Consequently, the distance between 3s and 3p level will also decrease and finally they will merge to form a one energy band gap where everythings have the same energy. You can consider this as a mixture of 8N states where they separate at the same energy. And this band splits into two bands separated by a energy band gap E g.

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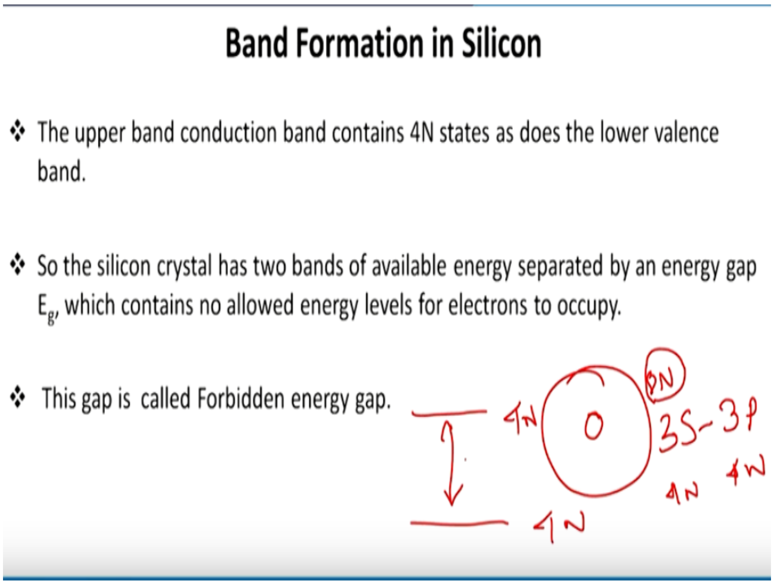

Band Formation in Silicon

- The upper band conduction band contains 4N states as does the lower valence band.
- So the silicon crystal has two bands of available energy separated by an energy gap E_g, which contains no allowed energy levels for electrons to occupy.
- This gap is called Forbidden energy gap.

The upper band conduction band they contain the 4N electrons as does the lower valence band. So there are 8N electrons. So the lower band contains 4N electrons and the upper band contains 4N electrons and they are separated by some energy band gap. So in the silicon crystal, there are two bands of available energy.

They are separated by a distance E g which contains no allowed energy levels for electrons to occupy. So again, if this is the silicon nucleus and this is the outer orbitals, so in outer orbitals now we are considering 8N electrons where there are 3s orbitals and 3p orbitals. Now when n is large in a crystals, so we have learned that the 3s-3p orbital merge and they form 8N electronic states.

Now this 8 electronic states they split into two different states, the lower states contains 4N electrons and the upper states contain 4N electron. So the lower states contains 4N electrons and the upper states contain 4N electrons. In between them, there is a separation and that separation is called forbidden energy gap or energy band gap and we call it as E subscript g that is the expression for the band gap. This gap is called forbidden energy gap.

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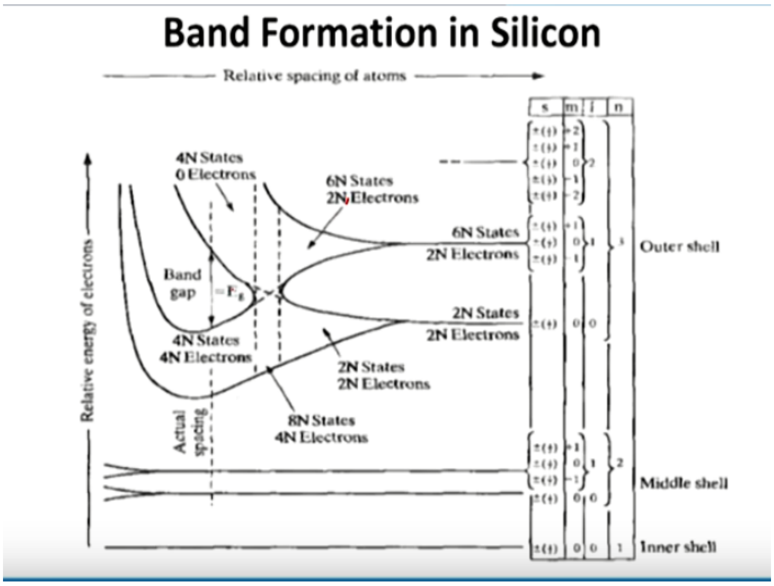

Band Formation in Silicon

We can look this in a in a silicon real silicon crystal and if we plot the relative energy of the electrons along the y axis and along the x axis is here the electronic distance so you can see that how this 6N states and the 4N states has been distributed here. So the 4N states which contains 4N electrons here and 6N states now contains 2N electrons and they are separated by a band gap E g. And along the x axis, we have the relative spacing of the atom.

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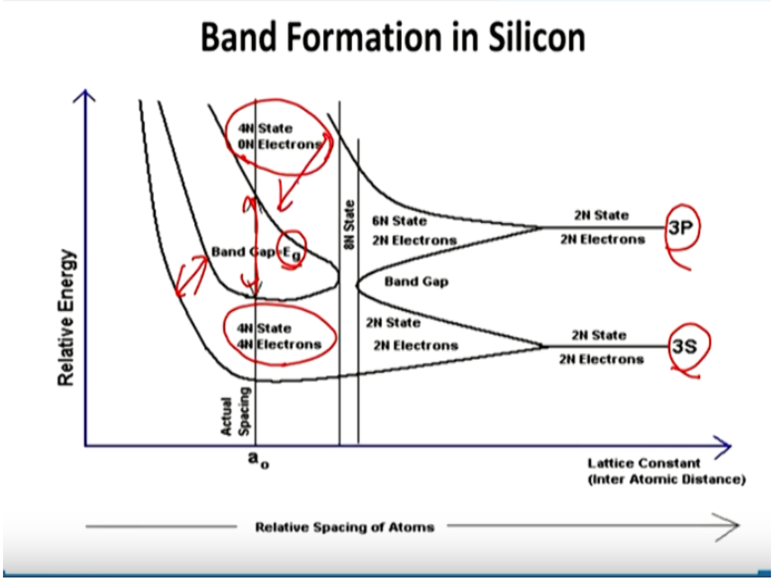

Band Formation in Silicon

So again, y axis is the relative energy, x axis is your relative spacing of the atoms. So you can see that there are two energy states. You have 3s states and 3p states. So 3s states which contains 2N states of 2N electrons; this is 2N state of 2N electrons, right. So this now split into two different states. One is 4N states, which contains 4N electrons and this is also 4N states, but it does not contain any electrons here.

And there is a separation between these two and that separation you call it as a band gap, This energy allowed energy band is called the valence band and this allowed energy band gap is called the conduction band gap.

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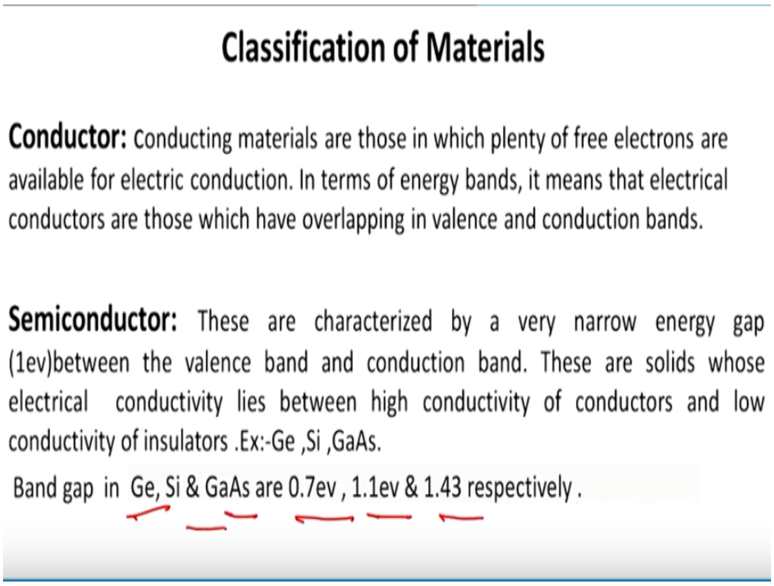

Classification of Materials

Conductor: Conducting materials are those in which plenty of free electrons are available for electric conduction. In terms of energy bands, it means that electrical conductors are those which have overlapping in valence and conduction bands.

Semiconductor: These are characterized by a very narrow energy gap (1ev)between the valence band and conduction band. These are solids whose electrical conductivity lies between high conductivity of conductors and low conductivity of insulators .Ex:-Ge ,Si ,GaAs.

Band gap in Ge, Si & GaAs are 0.7ev , 1.1ev & 1.43 respectively .

Based on this concept, we can classify the solids or materials into three distinct class, conductor, insulator, and in between conductor and insulator semiconductor based on that band gap. So what is a conductor? A conducting materials are those in which plenty of free electrons are available for electronic conduction. In terms of energy bands, it means that the electric conductors are those which have overlapping valence and conduction bands.

So in a conductor or in a metal, valence band and conduction bands overlap each other and Fermi level lies since Fermi level lies in between valence band and conduction band. So in the case of the conductor, Fermi level can lie in between valence band or in conduction band since valence band and conduction band overlaps. So the probability of staying Fermi energy is equal in both of these case.

What is a semiconductor? These are characterized by a very narrow energy gap one electron volt between the valence band and conduction band. These are solids whose electrical conductivity lies between high conductivity of conductors and low conductivity of insulators. For example, silicon germanium, gallium arsenide. So semiconductors are materials whose conductivity is in between conductor and insulator.

So usually the energy band gap is one electron volt to 1.5 electron volt. There are several example of semiconductor and as you have learned that semiconductors are heart of the optoelectronic industry. Band gap in germanium and silicon, gallium arsenide are 0.7 ev, 1.1 ev, and 1.43 ev. So in germanium the band gap is 0.7 ev, in silicon it is 1.1 ev and in gallium arsenide it is 1.43 ev. It is important to remember this number because we will refer to these numbers very often later on.

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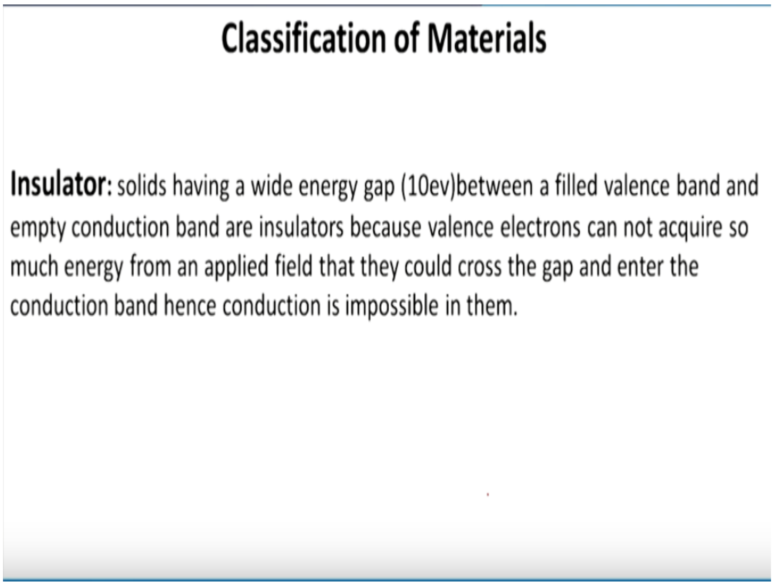

Classification of Materials

Insulator: solids having a wide energy gap (10ev)between a filled valence band and empty conduction band are insulators because valence electrons can not acquire so much energy from an applied field that they could cross the gap and enter the conduction band hence conduction is impossible in them.

And the third part in our classification of materials is the insulator. Insulators are solid having a wide energy gap. Let us say 6 ev or 10 ev between a filled valence band and an empty conduction band and they are insulator because valence band cannot jump or they cannot acquire the required energy from the applied field to move across the band gap and reach to the conduction band for available of the electrons for conductions.

Once the electron jumps from the valence band to conduction bands, so then only electrons will be available for conductions. But in the case of insulator the band gap is such large that this electron cannot jump from the valence band to the conduction band at the room temperature from the applied energy or even if you put some applied energy so that there is almost no electron at the conduction band.

And since the conduction band electron participate in the electricity, so you do not see any electrical conduction in insulator. There are various example of insulator, right? One common example is wood, rock. They are all example of this insulator. So if we draw the energy band diagram for these three different materials, this looks like this.

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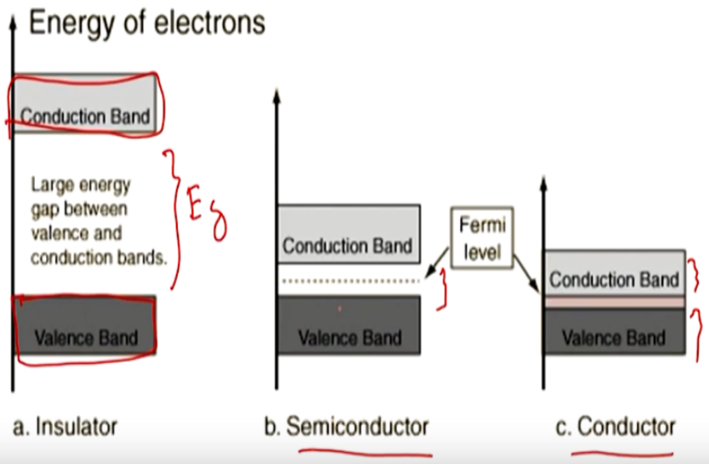
Classification of Materials



Let us say our y axis is the energy of the electron, okay and x axis I am plotting the atomic spacing. So in the case of the insulator, I have this is my valence band and this is my conduction band, right. So the distance between these two that is a band gap E g. So in the case of insulator energy band gap is very large 6 ev or even 10 ev. And the electron has not have sufficient energy to cross this barrier from going from valence band to conduction band.

So that there is no electron available in the conduction band for conduction of the electricity. Now consider the other extreme, that is conductor. Here you see the valence band and the conduction band they almost overlaps with each other. So Fermi levels that can lies in between. So there is almost overlaps between valence band and conduction band.

And at room temperature even there are almost enough amount of electrons which can go to the conduction band and that is why available for conducting the electricity.

That is why metal is a very good conductor of electricity. And in between these two extremes insulator and conductor, we have semiconductor whose conductivity is not as high as conductor but better than insulator. So here there is a finite band gap between the valence band and conduction band, usually from 1 to 1.5 electron volt or in organic semiconductor even it can goes to 2 to 2.5 electron volt.

But if we provide enough amount of energies this electron can cross this band gap and goes from valence band to the conduction band. Once it reaches to the conduction band the electron is available for conduction of the electricity. So that is why the semiconductor materials although in an intrinsic condition, it has a very low conductivity.

When you apply some external bias then it is a very good conductor of electricity. And its conductivity lies between a good conductor and an insulator. Let us compare some of the common properties of a conductor insulator and semiconductor.

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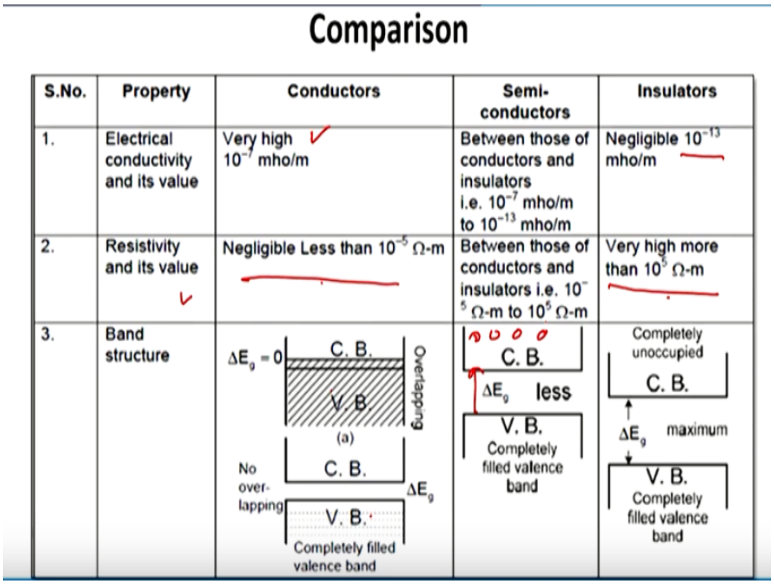

Comparison

S.No.	Property	Conductors	Semi-conductors	Insulators
1.	Electrical conductivity and its value	Very high ✓ 10^{-7} mho/m	Between those of conductors and insulators i.e. 10^{-7} mho/m to 10^{-13} mho/m	Negligible 10^{-13} mho/m
2.	Resistivity and its value ✓	Negligible Less than 10^{-5} Ω-m	Between those of conductors and insulators i.e. 10^{-5} Ω-m to 10^{5} Ω-m	Very high more than 10^{5} Ω-m
3.	Band structure	$\Delta E_g = 0$ C. B. V. B. Overlapping (a) No over-lapping C. B. ΔE_g V. B. Completely filled valence band	C. B. ΔE_g less V. B. Completely filled valence band	Completely unoccupied C. B. ΔE_g maximum V. B. Completely filled valence band

First thing is the electrical conductivity. As I said that for a case of conductor electrical conductivity is very high. But when I say very high, how high it is, it is almost like 10 to the power -7 mho/m. It is the SI unit of conductivity. In case of the insulator the electrical conductivity is negligible, 10 to the power -13 mho/m or in case of semiconductor, this is in between conductor and insulator.

So between those of conductor and insulator and if the value is 10 to the power of -7 mho/m to 10 to the power -13 mho/m. So what will be the resistivity? Since resistivity is reciprocal of conductivity, in the case of conductor, I have a very large value of conductivity. So the resistivity should be very low. So here the resistivity is negligible less than 10 to the power -5 ohm centimeter.

And in the case of insulator the resistivity will be very high because conductivity is low. So it is very high, more than 10 to the power 5 ohm meter. And in the case of semiconductor it is measured between the conductor and insulator. So it is between those of conductors and insulator that is 10 to the power -5 ohm meter to 10 to the power +5 ohm meter.

And there are instruments which can measures this conductivity or resistivity. What about the band structure? In the case of conductor as you have seen that the valence band which is completely filled and conduction band usually which is completely empty. But in the case of conductor valence band and conduction band they overlaps. So their delta E g the band gap is essentially zero and Fermi level overlaps between these two.

In the case of insulator, the band gap is maximum between valence band and conduction band. In the case of semiconductor this is not as large as insulator but not overlapping like as a case of conductor. It has some finite value as I say is 1 electron volt to 2 electron volt depending upon the semiconductor.

And if we provide enough amount of energy electron can cross this level and go from valence band to conduction band and once it reaches to the conduction band these electrons are available for conducting electricity. What about energy band gap? Obviously, as we just mentioned, in the case of conductor it is zero or very small.

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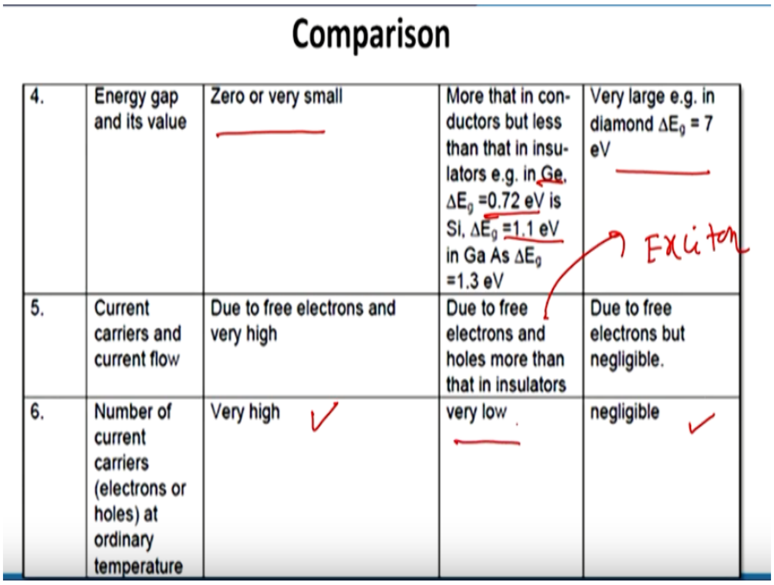

Comparison

4.	Energy gap and its value	Zero or very small	More that in conductors but less than that in insulators e.g. in Ge, ΔE_g =0.72 eV is Si, ΔE_g =1.1 eV in Ga As ΔE_g =1.3 eV	Very large e.g. in diamond ΔE_g = 7 eV
5.	Current carriers and current flow	Due to free electrons and very high	Due to free electrons and holes more than that in insulators	Due to free electrons but negligible.
6.	Number of current carriers (electrons or holes) at ordinary temperature	Very high	very low	negligible

In the case of insulator it will be very large. A common example is diamond whose band gap is 7 electron volt, delta E g is 7 electron volt for the case of diamond which is a very common example of an insulator. In the case of semiconductor we have learned it should be in between conductor and insulator. So more than in conductors but less than insulators. As for example, germanium, the energy band gap is 0.72 eV.

Silicon 1.1 eV right. Gallium arsenide 1.3 eV. Current carriers and current flow that happens in the case of conductor due to the free electrons because electrons are very loosely bound and the conductivity and current flow is very high. In the insulator, the current conduction happens due to the free electrons but there is no available free electrons here. So it is almost negligible.

And in semiconductors, we see the both type of charge carrier, electrons and holes right. We see both types of charge carriers and many often as we will see later on this bound electron and hole pair is called exciton. So this bound electrons and hole pair they are called exciton. So once the electron goes from the valence band to conduction band it leaves a vacancy in the valence band and that vacancy behaves as a positive charge carrier.

And that vacancy is called a hole and electrons and hole together when they are bound by some kind of electromagnetic force, they are called exciton. And this kind of binding energy is called exciton binding energy. Number 6 is number of current carriers electrons or holes at ordinary temperature. At room temperature what is the number of current carriers.

In conductor it is very high. In the case of insulator it is negligible. And in the case of semiconductor at room temperature it is very low. That means for an intrinsic semiconductor if I do not do any external doping, or if I do not provide any external bias, so that the electron cannot cross normally the valence band to the conduction band.

There are very few number of electrons are available in conduction bands for current conductions and that is why the electrical conductivity is not very high, also it is not zero, but has a very low value. So that is all we learn for today's class.

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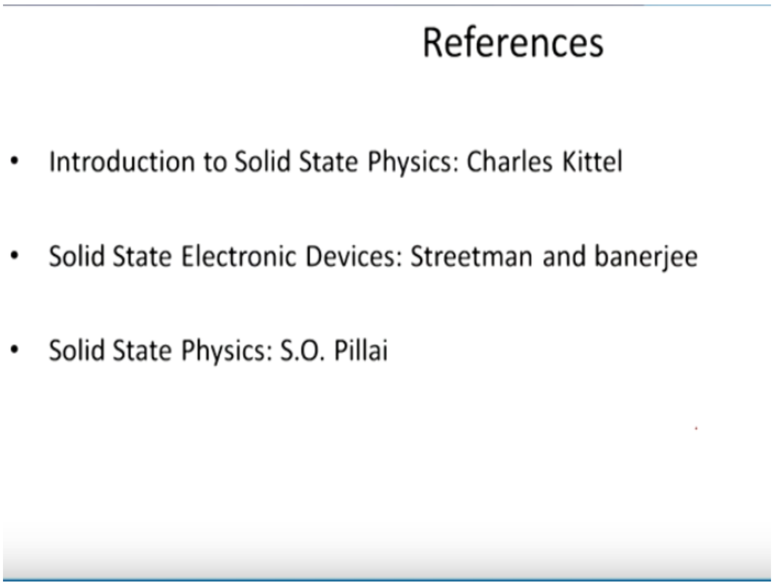

References

- Introduction to Solid State Physics: Charles Kittel
- Solid State Electronic Devices: Streetman and banerjee
- Solid State Physics: S.O. Pillai

And for references, you can look into the Solid State Physics book by Charles Kittel and also by Streetman and in Banerjee’s book and Solid State Physics by S.O. Pillai. And we also have learned that some of the problems which the free electron theory cannot solve, the nearly free electron theory can solve those problems. Like nearly free electron theory can able to explain why some solids are metal, why some solids are conductor and why some of them are semiconductor.

In considering tight binding approximation which is like different from the free electron theory, but gives similar kind of results we can see that in a solid the atomic energy level splits and that gives rise to the energy band gaps. And there are two different types of band gap exist one is called valence band another is called conduction band.

At room temperature usually the valence band is completely filled and conduction band is completely empty and there is a gap between the valence band and conduction band and that gap is called energy band gap. Now depending upon the value of the energy band gap, we classify the materials as conductor, insulator or semiconductor. In the case of conductor, the energy band gap is negligible.

So valence band and conduction band almost overlaps. In the case of insulator the value of the valence band and the conduction band or the energy band gap is very large. So that at room temperature there is almost no electrical conduction. Whereas in the case of semiconductor, the distance or the separation between valence band and conduction band is not overlapping as in the case of metal, but also not very large as in the case of insulator.

But it is in between metal and in between insulator, something like 1 to 2 electron volt. So the electrical conductivity at room temperature is negligible, but if we provide some external perturbation or external energy in terms of doping or electrical current or something, there can be a measurable or some detectable amount of electricity happens in this materials or semiconductors.

And some common example of semiconductors are germanium, silicon, and gallium arsenide. So this theory nearly free electron theory able to explain very easily why some solids are metals, why some solids are insulators or why some solids are semiconductors and in our device physics or in our solar cell photovoltaics devices we will use the semiconductor namely silicon for making our solar cells. Thank you.