

Physics of Functional Materials and Devices
Prof. Amresh Chandra
Department of Physics
Indian Institute of Technology Kharagpur

Lecture – 14, Week 4
Theory of Solids

Welcome to the first lecture of week 4. We have seen till now as to how you can synthesize various types of solid materials. And why you need to have different types of materials and what are the ranges of applications for these materials. We have seen that contrary to the belief, you do not always get ideal materials and you will have some defects in those materials. We have also talked to you about the various types of defects and imperfections which are seen mostly in crystalline solids. Let us now move towards the next topic of this course where we will start understanding the classifications of solids and what are the models which actually define these classifications.

For example, we will start with the Drude Lawrence classical theory, then we will move to Sommerfeld's quantum theory and then we will explain to you what is the concept of free electron gas and the free electron gas model. We have seen till now that a solid is a matter which has fixed shape, mass and volume. And if you change temperature, then you will see that the materials will expand or contract depending upon the nature of expansion coefficient, but the overall changes would be smaller than the size of the material. Similarly, we can have another way of classifying the materials.

This can be on the nature of band occupation. Based on the nature of band occupations by electrons, the solid materials can be either metal, semiconductor or insulators. In the first case that is metals, you will find that you have a condition where the valence band and the conduction band are overlapping. Whereas, in the other two cases that is semiconductors and insulators, depending upon the formative gap which is known as energy band gap, you have the classification under semiconductor or under insulator. For example, if the band gap that is the gap between the valence band and the conduction band is more than 3 eV, then you classify these materials as insulators.

If you have materials which have band gap in the range of 0.1 to 3 eV, then you call them as semiconductors. This value has been written just to show you why certain materials which have a band gap of the range of 1.5 eV have become quite important in recent times and this will become clear to you as we go on talking about the applications of functional materials. But to be precise or use the definitions which are mostly used in books, semiconductors have a band gap ranging from 0, 1 to 3 eV. So, this value, the choice of this value will become clear to you bit later. Schematically, you can understand the same concept if you have metals, you have the conduction band and the valence band which are

overlapping. So, you have an overlapping region. If you have insulators, then the band gap is much larger than the band gap of the semiconductor.

So, again what is the value in semiconductor? It is 0.1 to 3 eV whereas in insulators you are talking about more than 3 electron volt eV s. As you know, how do we broadly classify metals? Metals will have certain well-defined properties which are common to all or nearly all metals that is high electrical and thermal conductivity. In addition to them being malleable, they can be ductile and they also show high reflectivity of light. The theory of metals was actually postulated by Drude in 1900 and this theory is called as the free electron gas model.

Let us now understand the free electron gas model and then we will extend this theory to understand the concepts of band gap, the origin of band gap and then we will proceed to the topic of nearly free electron gas models or nearly free electron model and its importance. Whenever you have a theory, how do you proceed? You proceed by defining certain postulates which are associated with that theory. These postulates are the basic ideas which the theory is built upon. Similarly, for the free electron gas model, Drude also had certain basic postulates. What were those? The first said that a metal basically consists of a positive ion core with valence electrons moving freely amongst these cores.

So, positive cores and electrons moving amongst these cores. The electrons are bound to move within the metal. They just cannot leave the metal. Free electron does not mean that if the metal is a metal, then the free electron does not mean that these electrons which are coming on a surface are just leaving out of these surfaces on their own. Therefore, the electrons are bound to move within the metal due to the electrostatic attractions between the positive ion cores and the electrons.

So, there is an electrostatic interaction which is preventing the exit of the electron from the metal surface. The potential field of these ion cores which is responsible for such an attraction is assumed to be constrained throughout the metal. So, you believe that the potential field as you move from one point to the other remains same, which is not always the case if you have two different types of elements coming together and forming a metallic alloy or you have a different sized elements coming together to form an alloy. But for simplicity, we believe that the potential field of these ion cores were same. The mutual repulsions amongst the electrons is neglected.

So, same charges repel, but for the simplicity in the free electron gas model, we believed that the mutual repulsions among these similarly charged electrons were negligible. The behavior of the free electron inside these metals is considered similar to that of atoms or molecules in a perfect gas. So, this was a very important assumption and because of this, you call these models as free electron gas model and you had this condition of electrons moving freely inside the metals just like atoms or molecules move in a perfect gas, you

called it a free electron gas. This was discussed, but if you compare the ordinary gas, then obviously there are certain clear distinctions between the ordinary gas and free electron gas. What are these differences? The basic differences between the ordinary gas and the free electron gas is the following.

The free electron gas is negatively charged, whereas the molecules of an ordinary gas are mostly neutral. So, you have electrons moving freely. What is the charge of electron? It is a negatively charged entity. Hence, see you will get a case where the free electron gas would be negatively charged. What is the second? The concentration of electrons in this electron gas is quite large compared to the concentration of molecules in an ordinary gas.

That was critical to understand. Why? Because around the positive core, you have the electrons and this is forming the electron cloud and there are large number of electrons and then as you move from one atom to the other to the other, then you have large number of electrons. That is why the concentration of the electrons is much higher than the molecules in the ordinary gas. Hence, you come to certain important points which must be understood about these free electron gases. The valence electrons are responsible for the conduction of electricity through metals and hence they are called as conduction electrons.

Since the conduction electrons move in a uniform electrostatic field of iron cores, their potential energy remains constant and is normally taken as zero ignoring the existence of the iron core. As the movement of the electron is restricted within the crystal only, you cannot have electrons going outside and coming back. So, what is the condition? This means the potential energy of a stationary electron inside a metal in comparison to the identical electron which is just outside, would it be higher or lower? Obviously, if the movement is restricted within the crystal, the potential energy of a stationary electron would be less than the potential energy of an identical electron just outside it. The energy difference V_0 serves as a potential barrier and stops the inner electrons from leaving the surface of a metal. So, there is a inbuilt potential energy barrier which is preventing the electrons to leave the surface.

Thus, the movement of the free electron in metal is similar to the movement of free electron gas inside a potential energy box. What do I mean by this? This is a very simple concept and you can understand that as we move along. In 1909, Lorenz postulated that the electrons constituting the electron gas obey the Maxwell Boltzmann statistics. And the Drude-Lorenz theory of electron gas is called as the classical theory because of this reason. This model is able to explain certain phenomena in metals which are commonly observed.

For example, the electrical conductivity, the thermal conductivity, the thermionic emissions, the thermoelectric effect, the galvanomagnetic effects. But it could not explain certain observations. For example, temperature dependent resistivity changes, heat capacities and paramagnetic susceptibility. These are common observations associated

with certain metals of different types. Now, if you are unable to explain observations which are routinely seen by experimentalists, then obviously there are certain limitations to a given theory.

To overcome the limitations of the free electron gas model, Sommerfeld's quantum theory was adopted. And what was done in that? There was a slight modification. The modification was that Sommerfeld treated the quantum mechanical problem which is associated in the particle in a box using the Fermi-Dirac statistics. So you have a free particle. If you have the potential in the y direction and the dimension of the box in the x direction, so starting from 0 to the value l that is the dimension of a one dimensional potential, you have this particle which will remain within this box.

So this was the concept which was utilized. So you have a particle in a box problem which you all have studied probably in the first year of your physics course, the BSc or BS or BTech first year course. How do you define particle in a box? You have potential $V(x)$. If you have the condition x is less than or equal to 0 or x is more than or equal to l, then at the boundaries, that means at the boundaries you see V_0 and within the box you have potential which is 0 and particle will remain inside this box and is able to freely move. The potential in a box problem is solved using what? It is solved using the Schrodinger equation.

So you write the conventional Schrodinger equation for particle in a box problem. The general solution of this Schrodinger equation is $\psi(x) = a \sin(kx) + b \cos(kx)$. By solving this equation, what will you get? You will get the values of a and b and then you have the variation of the wave function and you will know what is the probability of finding a particle at different points within the box. You should remember that there are two boundary conditions which are there. The wave function at 0 or l that is at the boundaries is vanishing.

Why? Because the probability of finding the particle beyond the box or before the box is 0. It is only within the box. The solution of this equation gives me what? If I take the condition that is within the box, you have the wave function varying as $\sin \frac{n\pi x}{l}$. If you use these equations, then you will find that the energies which you will get associated with the quantum state $E(n) = \frac{h^2}{2ml^2} \cdot n^2 \pi^2$. So the bound electron can only have discrete energy values corresponding to what? n is equal to 1, 2, 3 or so on so forth and that is why discreteness in the energy levels appear.

The lowest energy of the particle is obtained as what? As $\frac{h^2}{8ml^2}$. The spacing between the two consecutive levels would be what? Would be basically $(2n + 1) E_1$. Now if you move further and plot these wave functions, then you can clearly see for different quantum numbers you have discrete energy levels and corresponding to each quantum number you

have a wave function that is telling you about the probability of finding the particle within the box. Now electrons, can they be put in one level, all the electrons? No. We know from Pauli's exclusion principle that that is not possible.

Hence more than one orbital may have the same energy but you will have the condition that electrons of different spins would be placed in those numbers. So orbitals having the same energy actually tells you the degeneracy of the system. The topmost field energy level at 0 k is known as the Fermi level and the energy corresponding to this level is called the Fermi energy and hence the Fermi energy is given as $\frac{\hbar^2 k^2}{2m} \cdot (\pi n_f / 2l)^2$. where n_f represents the principal quantum number of the Fermi level. Now according to the Fermi Dirac statistics, one energy state can be occupied by maximum of two electrons. Spin up spin down, you can differentiate the two electrons and hence according to Fermi Dirac statistics one energy level can be occupied by a maximum of two electrons.

Hence the total number of a commutated electrons up to the Fermi level would be what? Would be equal to $2n_f$. Hence what would be the corresponding Fermi energy? This would become $\frac{\hbar^2 k^2}{2m} \cdot (\pi n_f / 2l)^2$. What do you see? Thus the Fermi energy depends on the length of the box and the number of electrons in the box. For example, if we accommodate 5×10^{12} electrons in 1 centimeter length of line, the Fermi energy of the topmost electron would be 3.7×10^{12} eV that is equal to 2.4 eV. Therefore, if you have a large particle of any system, let us say system which has a crystal unit as ABO_3 . You can make a nano size particles with this. The boundary of this particle is defined by l . The boundary of the smaller particle is supposed defined as l' , small l' . What would be the energy levels? You will find that in the first case it will vary proportional to what?

l square l by l square and in the second case it will vary l by l .

So, you have the reason why when you go from the large size particles to smaller size particles, the energies change quite dramatically and you need to move from the classical theory to quantum mechanical theory because the concept of discreteness comes into picture and that is where the origin of nanotechnology lies. Similar concepts can be extended to three dimensions and in that case you will have variations in x direction, the y direction and the z direction and you will get the corresponding energy E_k in the case as $\frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$ where k_x , k_y and k_z take the form as $\frac{\pi n_x}{l}$ or $\frac{\pi n_y}{l}$ or $\frac{\pi n_z}{l}$ respectively. Several combinations can yield the same value of energy. So, you can have different values of k_x , k_y , k_z and you can get the same result. Each of the combinations of quantum numbers is called as a quantum state and the several states which we were talking about if they have the same energy then they are called as degenerate states.

So, you can have various combinations of k_x , k_y and k_z but end up getting the same E_k value that means you have a degeneracy in the energy levels. The applications of the free electron gas model using the Pauli's exclusion principle. So, what are the available quantum numbers? You have k_x , k_y and k_z and you have the spin. So, you take the spin up or spin down. So, each level can accommodate two electrons with a set of k_x , k_y and k_z and plus minus half.

So, each energy level is doubly degenerate. For total n non-interacting electrons at 0 K it would need how many energy levels? It would therefore require n by 2 energy levels to fill up because each level can take two electrons. Unlike the classical theory what did the Sommerfeld theory do? It does not allow condensation of all electrons into the 0 energy level even at 0 K. It does not allow the condensation of electrons and the electrons are distributed amongst the discrete energy levels having energies ranging from 0 to E_f that is the Fermi energy at 0 K. That was the modification. Using this model you can then go on and you can find out the density of states that means you can then calculate the number of electronic states or orbitals per unit energy and then you can calculate a lot of things.

For example, let us take the example of an electron in k space. Linear momentum is $\hbar \nabla$. Now $\nabla \varphi$ would be equal to what? It would be minus $-i \nabla \varphi(r)$.

That is equal to what? $\hbar k \varphi(r)$. From eigenvalue the particle velocity in orbital k is given by $\frac{\hbar k}{m}$. Let us take the electrons in the ground state and you have n free electrons. The occupied orbitals of a system fill a radius k_f . So, you have the electrons filling around the ion core which is positively charged and this sphere which is formed has a radius of k_f in the k space. What would be the corresponding Fermi energy? At the surface of the sphere this would be $\frac{\hbar^2 k_f^2}{2m}$.

What are the allowed wave vectors? That is k_x , k_y and k_z . They would occupy a volume element which would be equal to $\frac{2\pi}{l^3}$ of the k space. So, the total number of orbitals in the Fermi sphere of volume $\frac{4\pi k_f^3}{3}$ that is the volume of the sphere $\frac{4\pi k_f^3}{3}$. What is the volume of the sphere? $\frac{4\pi r^3}{3}$ that is where this calculation is coming from because you have the k_f being taken as the radius of the sphere. So, this would be equal to $2 \cdot \left(\frac{4\pi k_f^3}{3}\right) / \left(\frac{2\pi}{l^3}\right)$ that would be equal to $\frac{V}{3\pi^2 k_f^2} = n$. So, this is what the number would be. From these equations what would you get? You will get the values of the Fermi energy and the number of electrons. How do you define density of states? It is the density of states is defined as the number of available electronic states or orbitals per unit energy range at energy E . Hence, you have dN/dE or $dN/d\epsilon$ in this case. So, if you differentiate what will you get? You will get $dN/d\epsilon$ is equal to $\frac{3}{2n\epsilon}$.

This is what you obtain. So, what have you seen? You have seen that there is a difference between the conventional gas and free electron gas. There are models which are used to explain the observations. You started with Drude's model which was taking the Maxwell Boltzmann distribution, but was unable to explain certain features observed in the metals and then you moved on to Sommerfeld theory which used the Fermi Dirac statistics and a quantum mechanical formulation and you were able to explain many observations. You have also understood the requirement for Sommerfeld quantum theory and then how it leads to a condition from where you can calculate the number of available orbitals and from there you can go on to find out the density of states. These are the references which were used for today's lecture and in the next lecture we will extend this concept further and we will start talking about of nearly free electron model and why it is useful. Thank you very much.