Electronic Properties of the Materials: Computational Approach
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Module No # 06
Lecture No # 28
Fermi Surface: Part 3

Hello friends we are going to continue our discussion on the Fermi surface. We already have drawn the Fermi surface for free electrons for a 2 dimensional square lattice. In this lecture, I am going to show how to draw a Fermi surface when we have a periodic potential. We are going to deal with weak periodic potential such that the electrons in a periodic potential, can be treated as nearly 3 electrons.

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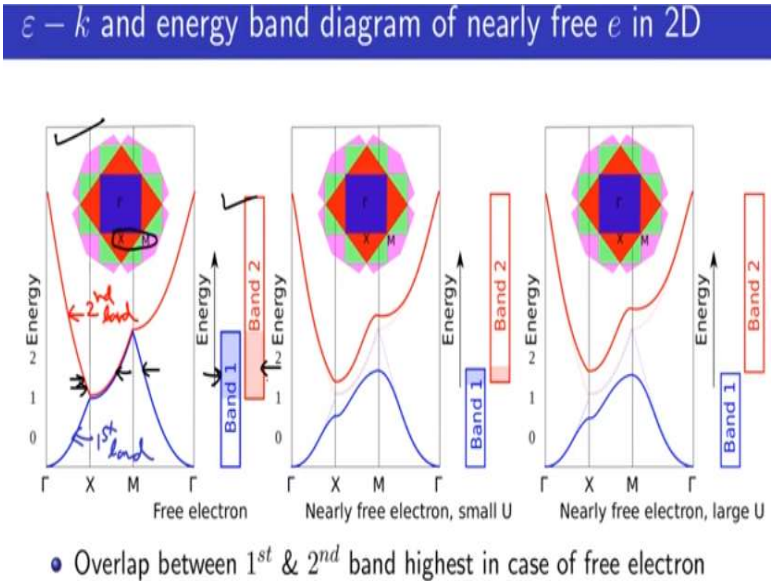

Let us start with the energy dispersion of nearly free electrons in a 2D square lattice. To get the energy dispersion of nearly free electrons we start with the energy dispersion of free electrons in a square lattice, using the empty lattice model. Note that, the X M direction is lying in the boundary of the first Brillouin zone. That is why I have drawn 2 overlapping lines in the e k diagram, along the XM Direction one red and one blue.

The first band is shown in blue and the second band is shown in red. Note that, the second band originally belongs to the second Brillouin Zone and has been brought to the first Brillouin zone according to the reduced zone scheme. Clearly, energy of the first band along the X M line is

higher than energy of some portion of the second band along gamma X. For example, energy of the first band in this region is higher than the energy of the second band in this region.

Same is true for a certain portion of the first band along M gamma, which is higher in energy than some portion of the second band along gamma X. For example, energy of the first band in this region is higher than the energy of the second band in this region. This is known as band overlap. Bend overlap can also be seen in the corresponding energy band diagrams. Blue shaded region of the first band and red shaded region of the second band overlaps in a certain energy window.

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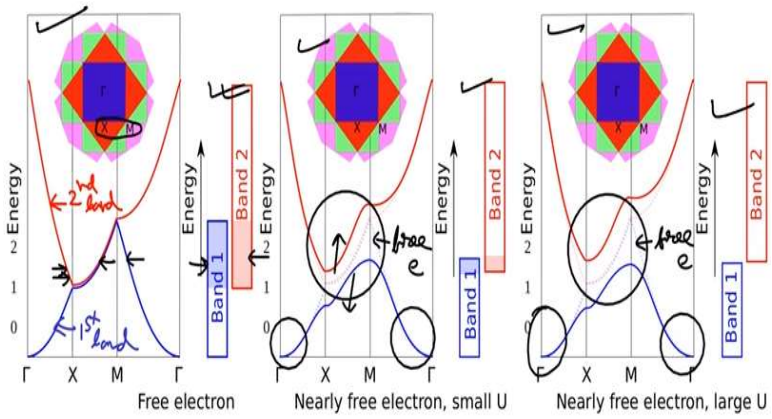

- Overlap between 1^{st} & 2^{nd} band highest in case of free electron
- Overlap between 1^{st} & 2^{nd} band decreases in weak periodic potential
- For sufficiently large U, 1^{st} & 2^{nd} band no longer overlap

So far, we are just following empty lattice approximation for free electrons now, let us consider some weak periodic potential. How can we approximately get the nearly free electron band structure starting from the completely free electron band structure? As we did for 1D we deformed the free electron e k curves only near the backplanes or Brillouin zone boundaries. In these diagrams, free electron e k curves are shown by dotted lines.

So, these are the free electron e k curves and these are the free electron e k curves. Nearly free electron e k curves are shown by the solid lines. Note that, close to the gamma point free and nearly free electron e k curves are identical and coincide with each other, as shown here. Since X M Direction lies on a black plane nearly free electron e k curves do not coincide with the free electron e k curves at all along the X M Direction.

Interestingly, due to weak periodic potential overlap between the first and second band decreases. Because the first band moves downward and the second band moves upwards, compared to the free electron e k curves. Bend overlap is maximum in the case of free electrons, but it decreases with the increasing strength of the periodic potential. If the periodic potential is strong enough, the first and second bands may not overlap at all as shown in the third diagram.

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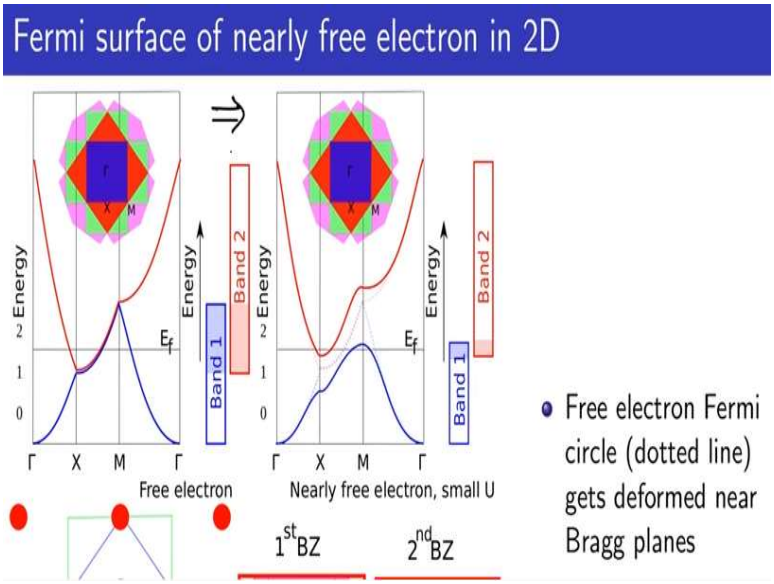

So, starting from the free electron band structure in an empty lattice we have approximately plotted the nearly free electron band structure. We took the EK carbs for free electrons and modified them only near the Bragg planes or Brillouin Zone boundaries to get the e k curves for nearly free electrons.

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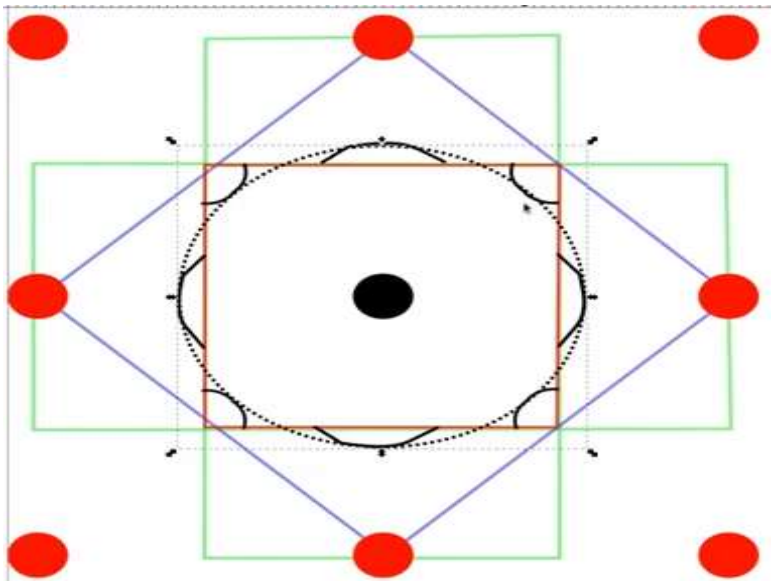

Let us see, how can we draw the Fermi surface of nearly free electrons. Again, we have to start with the free electron for the surface. If the free electron Fermi surface is not crossing any black plane, we have nothing to do. Let us consider a case where the free electron Fermi surface shown by the dotted line crosses the black plains. The free electron Fermi circle gets distorted when it crosses a black plane.

Let us consider this portion of the free electron Fermi Circle. This is crossing the first Brillouin zone boundary at 2 different places. As a result, the Fermi circle gets distorted in this manner. The actual Fermi surface is shown by the solid lines. Let us complete this for the entire Fermi Circle. So this region it will get distorted in this manner and this region will get distorted in this manner and finally, this region will get distorted in this manner..

Thus, whenever the free electron fermi circle is crossing the Bragg planes, we have to start in this manner. Note that the Fermi surface is continuous in the case of free electrons as shown by the dotted line due to the periodic potential Fermi surface gets fragmented.

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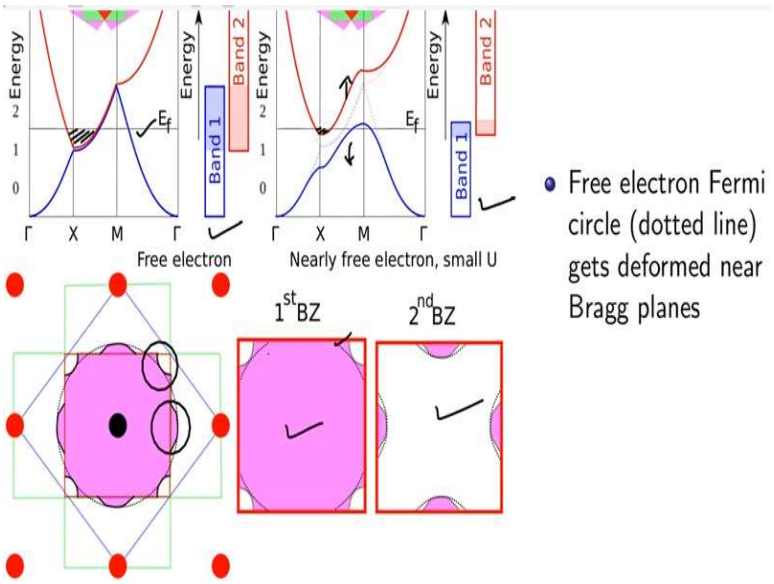

Now, let me give you some justification to support my claim that the free electron fermi circle should get distorted in this manner, due to the periodic potential. As shown in the band diagram band overlap is; maximum in the case of free electrons. When we have some periodic potential band overlap decreases. Because the first band is moving downwards and the second band is moving upwards compared to the free electron bands.

As a result, the number of states occupied in the second band decreases when we have a non-zero cube. For example, if we consider in the case of free electrons then these many states in the second band are occupied where the horizontal line denotes the Fermi energy. On the other hand, less number of states is occupied in the second band, when we have non-zero U. As a result when we draw the Fermi surface area occupied in the second Brillouin zone shrinks.

Whereas, the area occupied in the first Brillouin zone increases the area inside the first Brillouin zone increases because the first bank now has more electrons than compared to the case of the 3 electrons. As we did for the free electrons, we can map the regions in the second Brillouin Zone back to the first Brillouin zone. In that case, this is how the Fermi surface looks in the second Brillouin zone and this is how it looks in the first Brillouin zone. The dotted lines are showing the shape of the Fermi surface in the case of free electrons.

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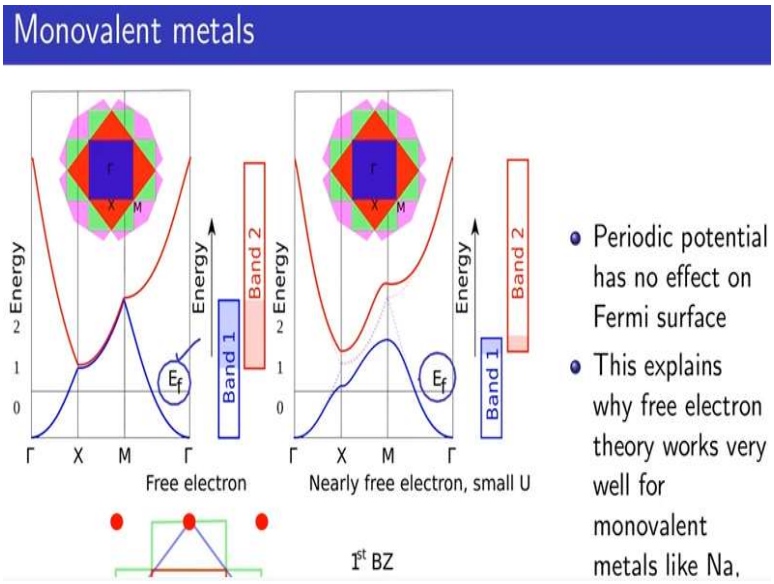

Let us first consider a monovalent metal. The Fermi energy lies within the first band and it does not cross the second band anywhere, both for free electrons as well as electrons in a periodic potential.

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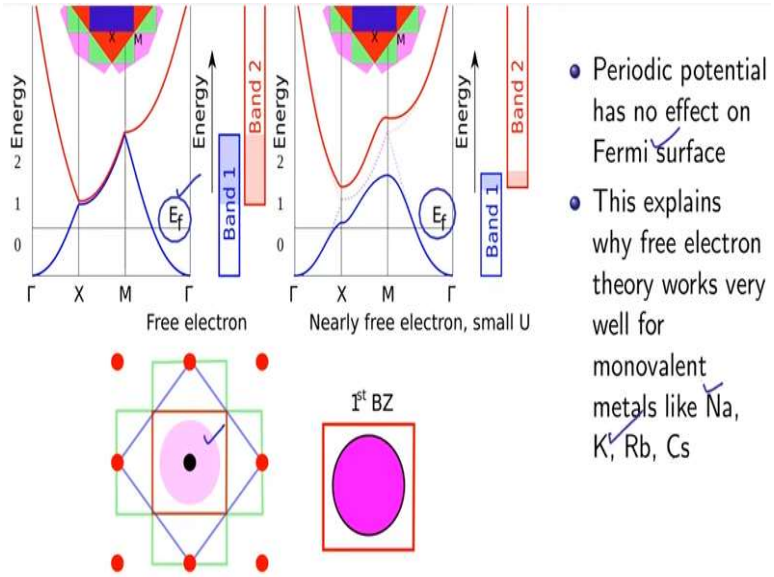

Similarly, the Fermi surface is lying well within the first Brillouin zone. Since the Fermi surface does not cross any black plane. It is very similar to the free electron formic surface. The periodic potential has no effect on the Fermi surface of monovalent metals. This explains why free electron theory works very well for monovalent metals like sodium potassium Etc.

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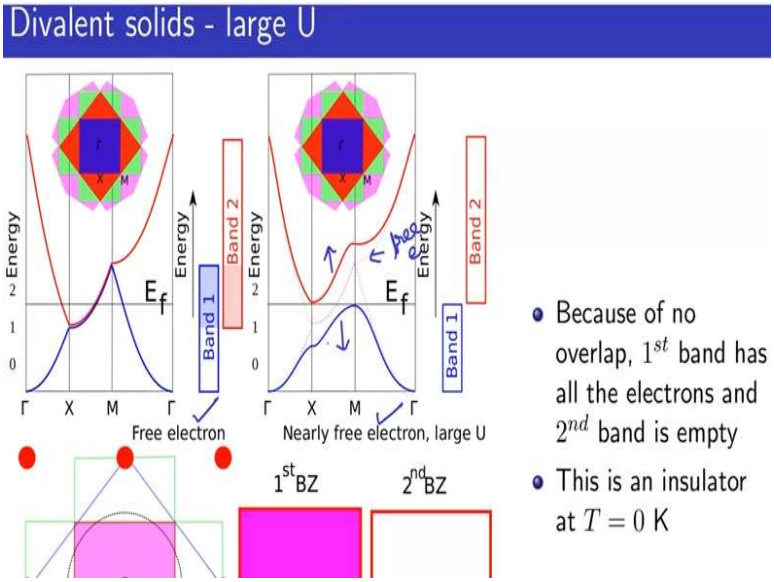

Now, let us consider the case of divalent solids starting with the free electron band structure in an empty lattice. We deform the free electron e k lines, near the black planes to get the nearly free electron then structure. The dotted lines in this diagram show the free electron e k curves. The first band moves downward at the second band moves upward compared to the free electron e k curves.

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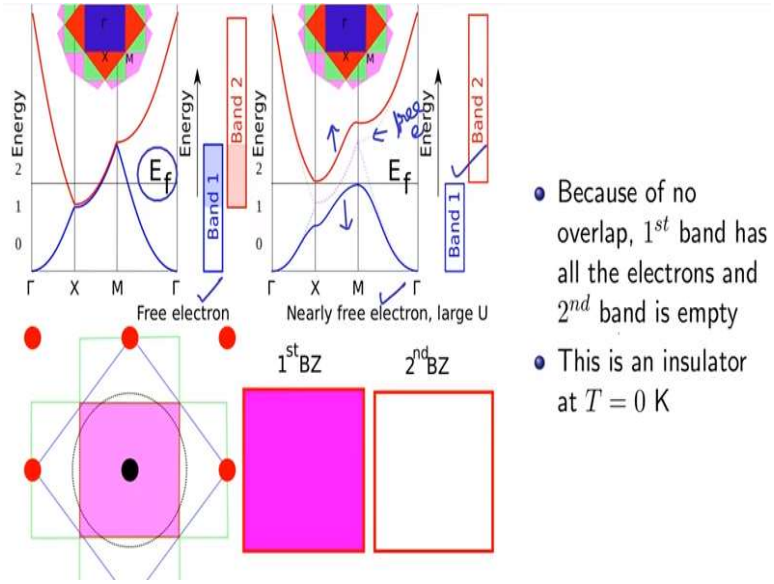

In the case of divalent solid form energy line processes both the first and second band in the case of the free electron band structure. We know that for sufficiently large U, the first and second bands will no longer overlap. Because of no value, the first band has both electrons and the second band is completely empty thus, for sufficiently large U divalent atoms for an insulating solid.

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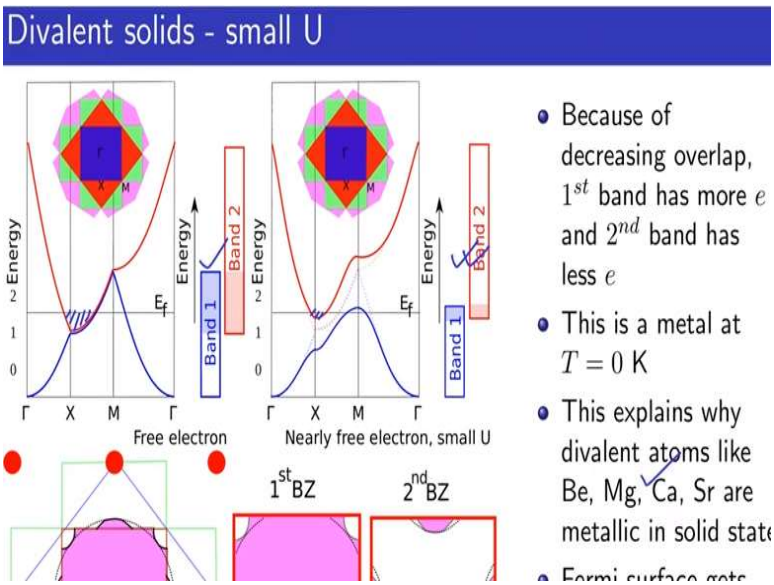

On the other hand, for u, the first and second Band still overlaps as shown in the figure for free electrons the overlap is maximum for u the overlap decreases but, still there is some overlap. Because of decreasing overlap, the first band has more electrons and the second band has fewer electrons when compared to the free electrons. For example, in the case of free electrons, these many states are occupied in the second band.

However, a list number of states are occupied in the second band when there is some periodic potential. As a result of band overlap, we have metal this explains the existence of divalent metals like beryllium, calcium, magnesium, etc.

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In this case, the free electron for the surface shown by the dotted line crosses the bread plains. As a result, the Fermi surface gets fragmented and there is a significant deviation from the free electron Fermi surface. Thus, free electron theory may not work for divalent metals. We can further generalize and say that free electron theory is expected to work only in the case of monovalent metals.

Because the Fermi surface is very similar to the free electron Fermi surface free electron theory is not expected to work for higher valency like divalent, trivalent, or ultraviolet matter because of the shape of the Fermi surface.

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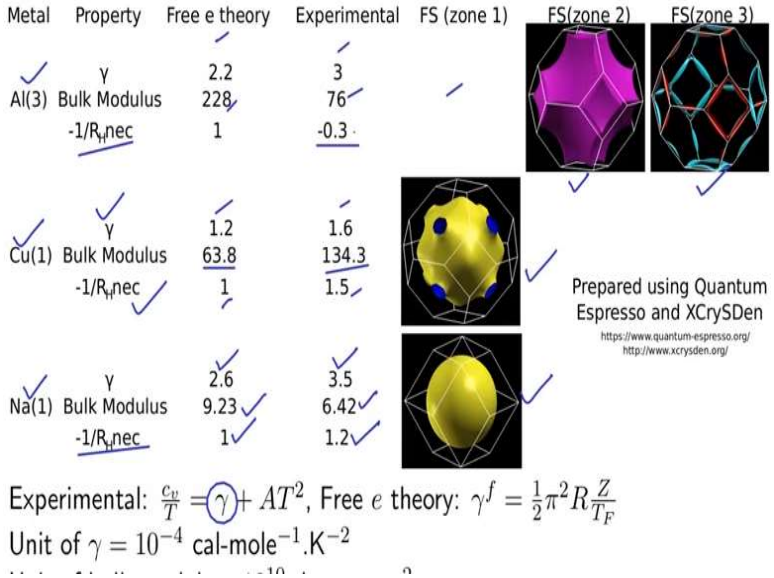

Let us quickly look at some actual 3D metals and their Fermi surfaces. Sodium is a monovalent metal it has a perfect free electron-like spherical formula surface. Now, let us compare the values predicted by free electron theory and actual experimental values. Gamma is the coefficient of the linear temperature-dependent term of heat capacity which can be measured experimentally by plotting heat capacity as a function of temperature.

This is the value of gamma predicted by free electron theory and this is the value of gamma measured experimentally. Experimental and free electron values are not too far from each other. Similarly, bulk modulus can be experimentally measured and estimated from free electron theory values are in good agreement. This is related to the hall experiment. R H is the whole coefficient N is the carrier density, E is the charge of the electron and C is the speed of light.

This number -1 by R H and E C should be equal to 1 and the experimentally measured value is 1.2, which is very close. Thus, experimental values are in good agreement with free electron predictions in the case of sodium because the Fermi surface is very similar to the free electron-forming surface. Next, we look at copper bulk modulus predicted by free electron Theory and measured experimentally differ to some extent.

However, gamma and this value predicted from free electron theory and measured experimentally are in good agreement with each other. This is not surprising as copper is also a monovalent metal although the Fermi surface is not a perfect sphere. It has approximately her spherical shape. Next, consider the case of aluminum, which is a trivalent metal. The first Brillouin zone is completely full.

This is how the Fermi surface looks in the second reloading zone and this is how it looks in the third reloading zone. Clearly, the Fermi surface is nowhere close to the spherical free electron-like fermi surface now let us look at some properties. Experimental and predicted gamma value match well. Experimental and free electron bulk modulus has a large difference and we have a serious problem with the whole coefficient as this quantity is -0.3.

If we measure experimentally, not only the magnitude deviates from one the sign is also negative. In conclusion, if we have free electrons like a spherical Fermi surface then free electron theory works very well otherwise, free electron theory may not work.

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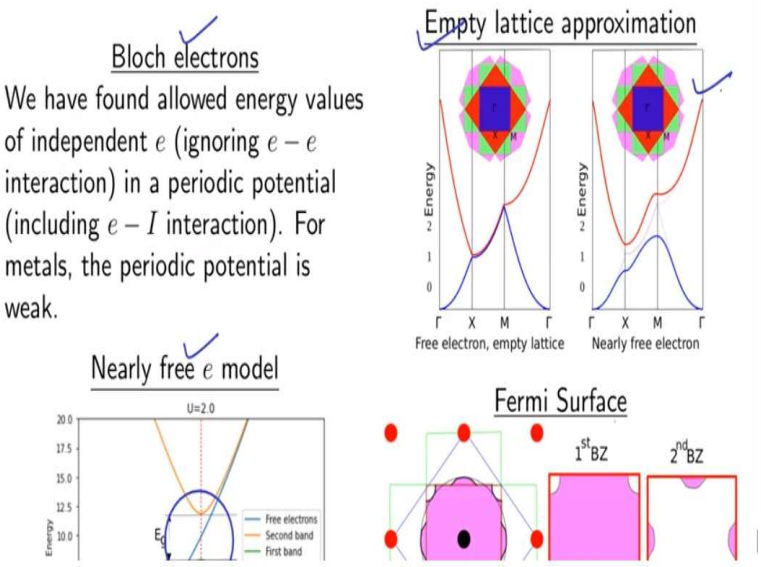

Let me summarize the main Concepts that helped us to understand the metals. First, we have to accept the presence of periodic potential in a solid and we have to solve the allowed energy values of an electron in a periodic potential. These electrons are known as block electrons. For Metals, the periodic potential has to be weak. In presence of weak potential free electron results change to nearly free electron results.

The energy values of p and nearly free electrons are identical away from the Brillouin Zone boundary. Thus, we can start with a free electron Parabola and deform it near the Brillouin engine boundary appropriately to get the allowed energy values of an electron in a periodic potential. This is the basis of empty lattice approximation where we plot the free electron energy along High symmetry directions in the first Brillouin zone of our reciprocal lattice.

Then we define the free electron e k curves appropriately to get the actual band structure. We have seen that it works very well for metals like aluminum.

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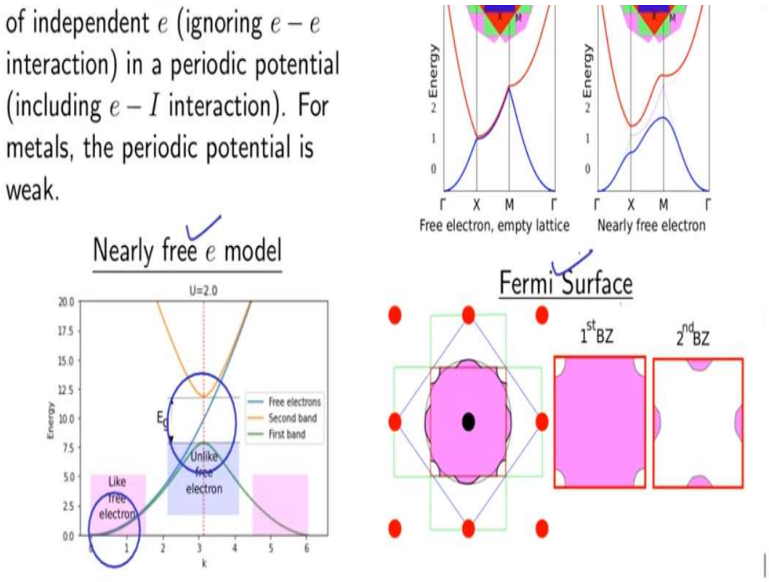

Finally, we learned how to draw the Fermi surface of free electrons and how to deform free electron Fermi surface to get the actual forming surface of a metal having a weak periodic potential. We have found that if the Fermi surface of a metal is free electron like the metal can be described using free electron theory. This happens in the case of mono-direct alkyl metals like sodium, and potassium etc and monovalent noble metals like copper, silver, and gold.

However, for divalent and trivalent metals free electron theory may not work. For example, we get anomalous all coefficient complications arise because of the shape of the Fermi surface.

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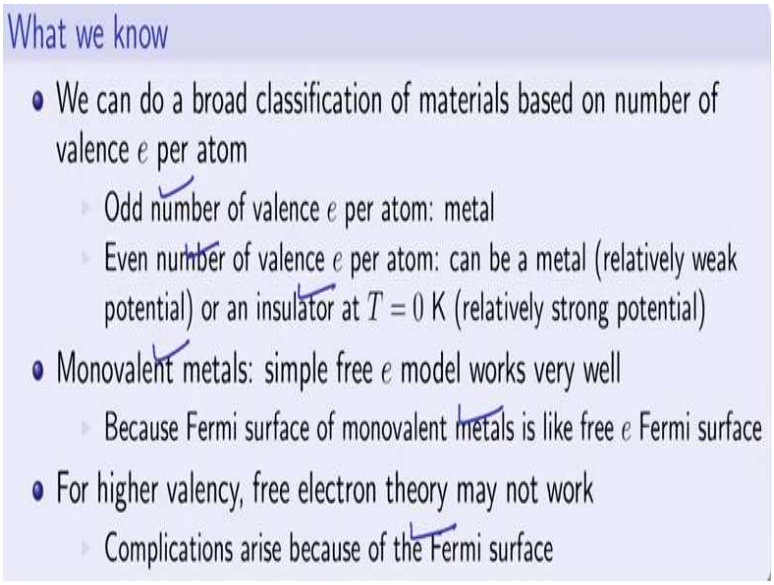

We have come to the end of our discussion, related to electrons in a periodic potential. Let us take a stop at our progress so far. In the first lecture, I showed a schematic diagram of transistor components which can be classified into three broad classes of materials, metals, semiconductors, and insulators. We wanted to know, what determines whether a material will be a metal or an insulator, or a semiconductor.

Based on what we have learned so far, we can do a broad classification based on the number of valence electrons per atom. In the case of the odd number of valence electrons per atom we definitely have a metal. In the case of an even number of valence electrons per atom, we may have a metal if the periodic potential due to the underlying lattice is weak. The metallic nature is due to the band overlap. On the other hand, if the periodic potential is relatively strong we get an insulator.

In addition to the broad classification, we also know that in the case of monovalent metals, free electron theory works very well. Because the Fermi surface of monovalent metals is like a free electron for the surface. For higher valence free electron theory may not work for example, in the case of the Hall coefficient complications arise because of the Fermi surface.

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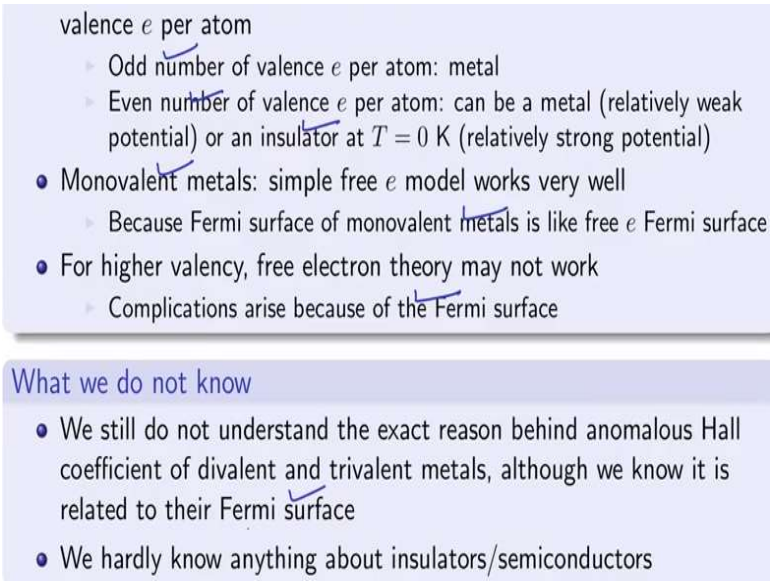

Let us also look at what we do not know so far. We still do not understand the exact reason behind the anomalous all coefficients of divalent and trivalent metals, although we know it is related to the Fermi surface. We would like to pinpoint the reason we hardly know anything about insulators

or semiconductors other than the fact that the constituent atoms have an even number of valence electrons. We would like to know about them in detail.