Solid State Chemistry
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Lecture - 56
More about Band Theory, Crystal Momentum

Now, we will start the last week of this course. And in this week, I will talk a little bit more about band theory of solids and we will particularly show how band theory of solids can be use to understand the different kinds of solids ok. In the last week we learnt about the origin of bands, we saw how we can understand why bands arise in a solid and now, we want to actually take that theory and apply it to see the how bands affect the properties of solids ok.

And first, in the first lecture I will make some remarks about band theory of solids ok. This will be sort of summarizing that also making some additional remarks about the band theory of solids. And I will talk about a quantity called crystal momentum and so, this week 12, lecture 1 will be more about Band Theory and Crystal Momentum.

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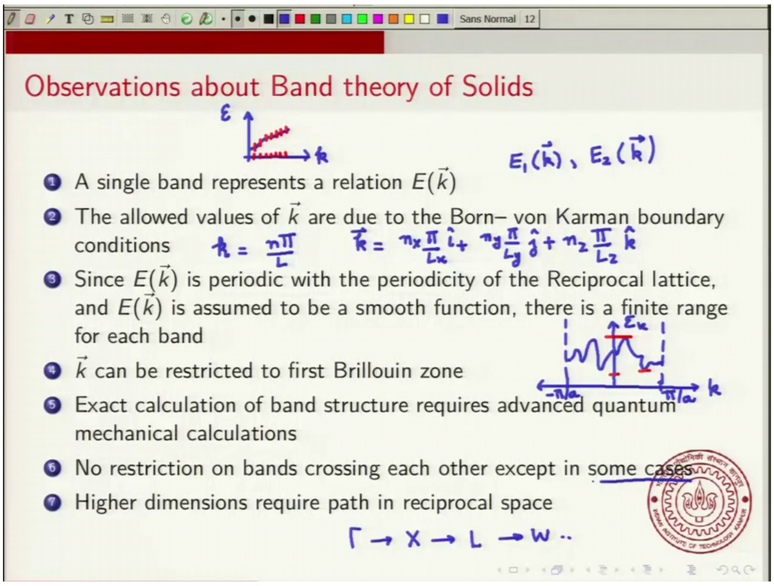

Observations about Band theory of Solids

$E_1(\vec{k})$, $E_2(\vec{k})$

1. A single band represents a relation $E(\vec{k})$
2. The allowed values of $\vec{k}$ are due to the Born– von Karman boundary conditions $k = \frac{n\pi}{L}$ $\vec{k} = n_x \frac{\pi}{L_x} \hat{i} + n_y \frac{\pi}{L_y} \hat{j} + n_z \frac{\pi}{L_z} \hat{k}$
3. Since $E(\vec{k})$ is periodic with the periodicity of the Reciprocal lattice, and $E(\vec{k})$ is assumed to be a smooth function, there is a finite range for each band
4. $\vec{k}$ can be restricted to first Brillouin zone
5. Exact calculation of band structure requires advanced quantum mechanical calculations
6. No restriction on bands crossing each other except in some cases
7. Higher dimensions require path in reciprocal space

$\Gamma \rightarrow X \rightarrow L \rightarrow W ..$

Now, let me make some observations about band theory of solids ok. So, we have already seen how we got bands and what I want to say is that a single band represents a relation E of k ok. And basically, you have different bands, given by E 1 of k, E 2 of k, etcetera. So, each band each particular band will have its relation E of k ok. And now this is a very interesting picture that we have the pictorially what we have is something like this, you have k and you have E, ok and for a band you have some relation between E and k, ok, some relation between E and k that represents the band.

Now, so the allowed vales of k are due to the Born von Karman boundary conditions and so, what we select was that if you are doing an one dimension then k should be n pi by L, should be a multiple of n pi by L. If you are doing an if you are doing an higher dimensions then k should be something like n x pi by Lx plus n x pi by Lx i plus n y pi by Ly j plus n z pi by Lz k ok. This is a Born von Karman boundary condition that says that the Lx, Ly and Lz is the size of the system. And usually Lx, Ly and Lz a very large, so the allowed values of k are very closely spaced ok.

And what you notice is that the allowed values of k are evenly spaced. So, if you look at the allowed values of k, if you look at this energy diagram you have specific values of k, but you have a large number of them. So, we can draw a smooth curve, the which is an approximation, but it is a very good approximation for this band structure ok. So, the allowed values of k are actually very closely spaced and so, that naturally gives us bands, it gives us smooth bands ok. And again, they are closely spaced because Lx, Ly and Lz are very large.

Now, the next point is actually very important it is the fact that E of k is periodic with the periodicity of the reciprocal lattice and we assume E of k to be a smooth function ok. And just these two restrictions, if you have a periodic function that is smooth, ok then basically it implies at there is a finite range for every band. So, you can see this in the following way that if you have this periodic function and let me put this as the period ok. So, if it is starts here then it has to when it comes back to this point it has to come to the same value.

Now, in between you can do anything ok, but what you see since it has to come back to this point and it is smooth function, basically what they say is that there is a finite range of energy. So, you just have a finite range of values ok. So, this is the range of allowed values of this of the energy of this band ok. So, you see that natural consequence of the periodicity is that there is a finite range of energies for each band ok.

The other natural consequence of the periodicity in reciprocal space is that you are k can be restricted to the first Brillouin zone, because this energy as a function of k will be periodic; will be periodic ok. So, it will be the same function over and over again. So, all you need to do is to look at in the first Brillouin zone ok. And in 1 dimensions is first Brillouin zone is minus pi by a to pi by a, in higher dimensions you have to look at the; you have to look at the 3 dimensional object that is a first Brillouin zone. And this is another point I want to make, we do not actually if you want to exactly calculate the band structure, you need to do advanced quantum mechanical calculations.

So, you need to really solve the Schrodinger equation, we actually never solve the Schrodinger equation. We just qualitatively described why band should be there and what their structure is supposed to be. But if you really want to calculated starting from first principles you will have to do a advanced quantum mechanical calculations ok.

The other thing is that there is no restrictions on bands crossing each other exception in some cases ok. In some cases, what I mean by some cases is that when you have bands when you have two wave vectors that are related to each other through the reciprocal lattice, then there is some non crossing conditions, but other than that bands can cross each other.

And the last point is that in higher dimensions you require a path in reciprocal space you cannot just show the band in terms of a simple scalar axis for k for example, you had gamma to X to L to W and so on ok. So, you have some path in k in reciprocal space that is required to depict the band structure ok. So, this is only to depict, only for depiction of the band structure on paper, you require this path in reciprocal space ok.

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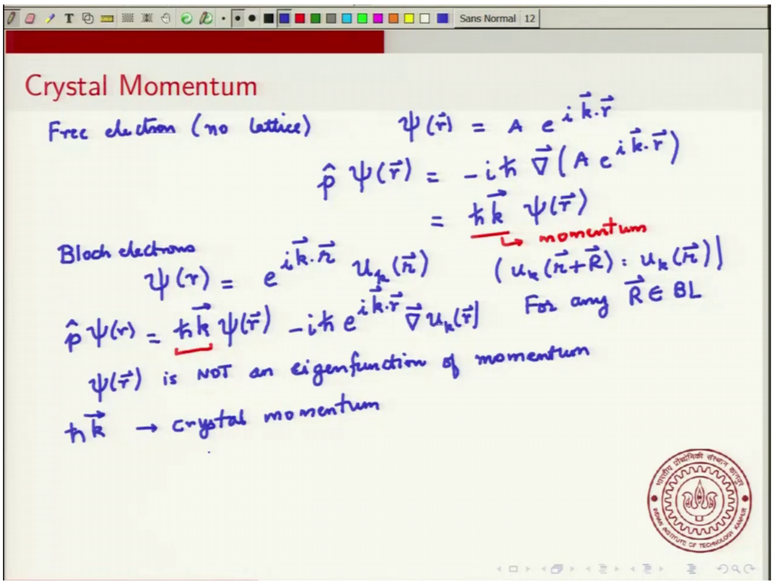

Crystal Momentum

Free electron (no lattice) $\psi(\vec{r}) = A\, e^{i\vec{k}\cdot\vec{r}}$

$$\hat{p}\,\psi(\vec{r}) = -i\hbar\,\vec{\nabla}\left(A\, e^{i\vec{k}\cdot\vec{r}}\right)$$

$$= \underbrace{\hbar\vec{k}}_{\to \text{momentum}}\,\psi(\vec{r})$$

Bloch electrons

$$\psi(r) = e^{i\vec{k}\cdot\vec{r}}\,u_k(\vec{r}) \qquad \left(u_k(\vec{r}+\vec{R}) = u_k(\vec{r})\right)$$

For any $\vec{R} \in BL$

$$\hat{p}\,\psi(r) = \underbrace{\hbar\vec{k}}\,\psi(\vec{r}) - i\hbar\, e^{i\vec{k}\cdot\vec{r}}\,\vec{\nabla} u_k(\vec{r})$$

$\psi(\vec{r})$ is NOT an eigenfunction of momentum

$\hbar\vec{k}$ → crystal momentum

Next, I will come to the concept of crystal momentum ok. Now, if you take a free electron, for a free electron, for a free electron without a lattice, this is no lattice ok. The wave function is given by some constant times e to the i k dot r. And if you calculate the momentum ok, so to calculate the momentum you have operated by the momentum operator and the momentum operator is minus i h cross times gradient ok. Now, gradient of this whole thing, we will just give the same function multiplied by i k ok. So, this will just give you minus i h cross times the gradient of A e to the i k dot r and this gradient is just equal to i k times the same function ok.

So, I can write this as i k into minus i h cross that is just h cross k times psi of r ok. And so, you immediately you identify that this is the momentum ok. So, this is the eigenvalue of the momentum and that is the value of the momentum, in any experiment you will see this value for momentum of free electron ok.

Now for what about Bloch electrons? Now, we have psi of r given by e to the i k dot r multiplied by some periodic function, where u k has the periodicity of the Bravais lattice; u k for any R contended Bravais lattice, any R. So, you can take any lattice translation vector and you will get you will have this relation ok.

So, now if you calculate p operated on psi of r ok, now you will have minus i h cross and you will have the gradient operated on this product of functions and so, you will get 2 terms; one involving the gradient of e to the i k dot r and the other involving the gradient of u k of r. The term involving the gradient of e to the i k of r will simply look like h cross k and you will have psi of r. But you will have another term that looks like this. It looks like minus i h cross e to the i k dot r times the gradient of u k of r ok. The point I am making is that this is not an eigen function of; so, psi of r is not an eigen function of momentum. However, we still see that if you look at this there is at least one term that looks like an eigenvalue expression. So, you still have that looking like an eigenvalue expression, but there is an additional term ok.

So, put a vector here h cross k will be a vector ok. So, you identify h cross k is like a momentum and you call it the crystal momentum ok. And so, it is like this momentum of this electron that is in this whole crystal ok. It is not the true momentum, but it is momentum with the restriction that it takes that it experiences this periodic lattice ok. And there is a connection; there is a connection with the full momentum ok, but we will not talk about it ok.

But this is called the crystal momentum and it is the it is so you can really think of k as in some ways related to the momentum it is not a true momentum, but the term used is crystal momentum ok. In fact, you can do more advanced quantum mechanics to explore the connection between crystal momentum and real momentum, but that will not be covered in this course.

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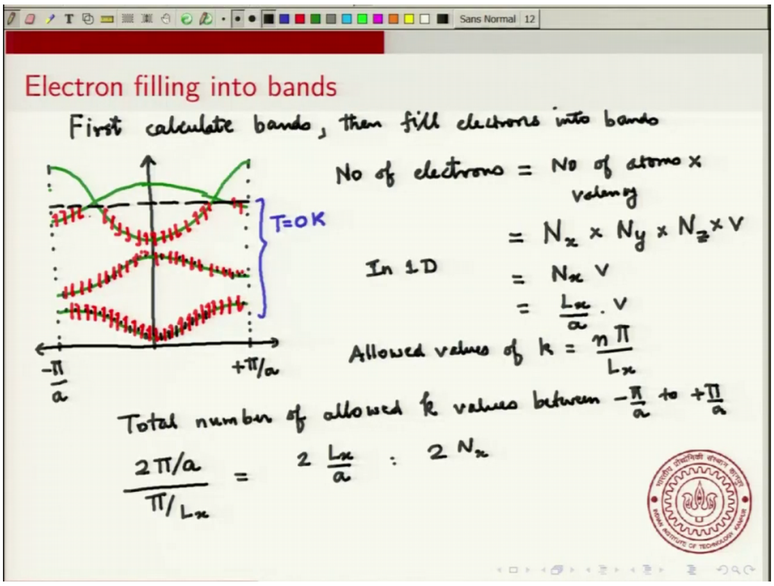

Electron filling into bands

First calculate bands, then fill electrons into bands

No of electrons = No of atoms × valency

$= N_x \times N_y \times N_z \times V$

In 1D $= N_x V$

$= \frac{L_x}{a} . V$

Allowed values of $k = \frac{n\pi}{L_x}$

Total number of allowed k values between $-\frac{\pi}{a}$ to $+\frac{\pi}{a}$

$\frac{2\pi/a}{\pi/L_x} = 2\frac{L_x}{a} : 2N_x$

The next important idea is the following that the way we are; the way we are describing the band theory what we do is you first make the bands then fill electrons and this is the picture that will be using ok. So, for example, if you look at let us look at the 1 dimensional case that is easy if to illustrate ok.

So, what you do first is you calculate the entire band structure and you just need to restrict to the first Brillouin zone because of the periodicity. And now, what you do is you start making the bands and let say I will just give some examples of bands, let say you have something that looks like this. I am just showing of your bands ok.

Now, how do you fill electrons into these bands? Now, so first thing you have to do is to calculate the number of electrons equal to number of atoms times valancy ok. And in the born von Karman boundary condition we wrote the total number of atoms as N x times N y times N z times the valancy and just say V for valancy ok. So, now, you can see in 1D, in 1 dimension this is just the. So, in 1D number of electrons is equal to N x times the valancy and N x is just the length in the x direction divided by a times a valancy ok.

So, now, let us see what does looks like ok. So, basically you have this is a total number of electrons. Now, again we recall the allowed values of k of k is equal to n pi by Lx and so and so, if you go from number of; so, if you ask how many k values are there from minus pi by a to plus pi by a. So, total number of; total number of k values between minus pi by a to plus pi by a ok. So, if you can do this in the following way. So, you see that this spacing this from minus pi by a to plus pi by a you have a range of 2 pi by a ok.

And if you look at this number the allowed values of k is n pi by Lx, so the spacing between k values is pi by Lx. So, if you just divide this by pi by Lx you will get the total number of value allowed values of k and this is equal to twice Lx by a ok. That means, Lx by a, so you take the, so you have this many values. So, this is equal to twice number of Lx number of atoms, Lx by a is nothing but the number of atoms ok.

So, basically in this range from 0 to pi by a you have the number of you have a total of N x states ok, here you have N x states and so on ok. And again for the other you can show this for each other bands there are total of N x states ok. I am just showing some of the states here. Now, if you want to start filling electrons, now, you have to fill N x into V electrons ok. So, what you will do is depending on your value of V you will start filling from the lowest. So, you start filling from here you start filling electrons starting from the lowest state ok.

Then you go to the next state, if you have more states you fill the next one and depending on how many hour you have then you start filling from here. Once you get here then you start filling this also ok. So, you start filling this way and then you keep going on till you exhaust all the electrons ok. This is a very central idea to the band theory of solids that you start filling electrons from the lowest energy and fill them up ok.

Now, this is the band structure this is the electronic configuration at, this gives the electronic configuration at T equal to 0 Kelvin that is at T equal to 0 Kelvin only the lowest energy configuration is allowed. At finite temperatures you have some electrons that might be excited to higher bands ok, so at finite temperature they could be excitations of some of these electrons to higher levels ok. So, in that case the electronic configuration is more complicated.

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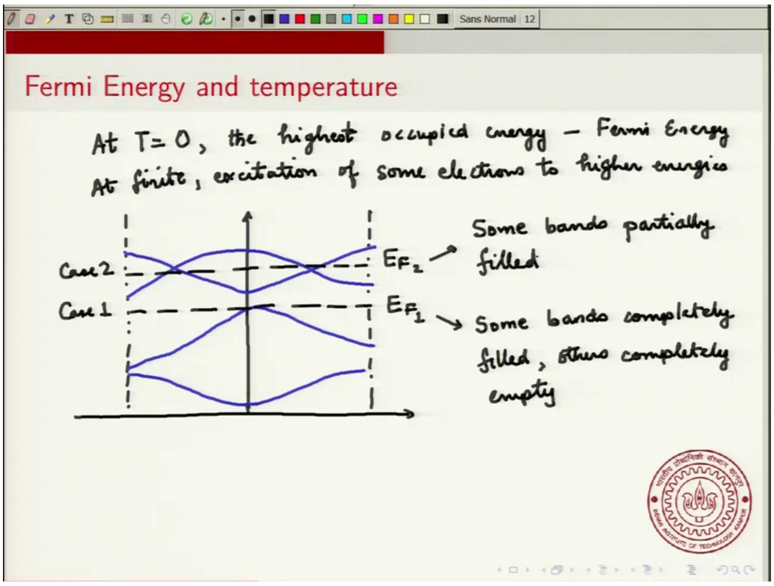

Fermi Energy and temperature

At $T = 0$, the highest occupied energy – Fermi Energy

At finite, excitation of some electrons to higher energies

Some bands partially filled

Some bands completely filled, others completely empty

So, now, you can ask what is a Fermi energy and what is the role of temperature? So, as we saw in the last figure, you can have; you can have these bands and you can have. So, you can say at T equal to 0, the highest occupied energy is called the Fermi energy ok. So, if you go back to what we saw, then this would be the in this case this would be a Fermi energy because I mean we assume that all the when you fill all the electrons you reached up to this level ok.

So, now obviously, if you have; if you have temperature then you knows you have some excitation of electrons and but the easiest way to define the Fermi energy is through T equal to 0 ok. At finite temperature you have excitation of electrons of some electrons to higher energies ok.

So, now, there are various cases that can happen and we will look at this in more detail a little later ok. Now, it could happen that when you fill, I am showing; I am using 1D for illustration, but you can do this for arbitrary dimensions ok. Now, when you take these bands and you start filling them ok, it could happen that your Fermi energy is right here ok, it could happen that your Fermi energy is right here, it could or it could happen that your Fermi energy is here. For this is case 1, case 2; E F in case 2, E F in case 1 ok.

And in the first case you see that you have some bands that are you have in this case you have some bands completely filled others completely empty and in this case you have some bands one or more bands can be partially filled ok. So, you have one or more bands; in this case I showed two bands at a partially filled you could also have a case where only one band is partially filled ok and this information about how the Fermi energy is related to the band structure ok. So, this will turn out to be very crucial in describing the electronic properties of solids ok.

So, with this I will conclude this lecture for today and here in this lecture we sort of summarize some of the points about band theory of solids and we look back and we also looked at how to fill electrons into the bands. In the next lecture I will talk about the concept of density of states.

Thank you.