Solid State Chemistry
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Lecture - 57
Density of States

Now, I will go to the second lecture of week 12 of this course. And in this lecture I will introduce the very useful concept called the Density of States. And later on we will see how this density of states can be used along with the band gap information to infer about the electrical and optical properties of the material. So, week 12 lecture 2 will be on Density of States.

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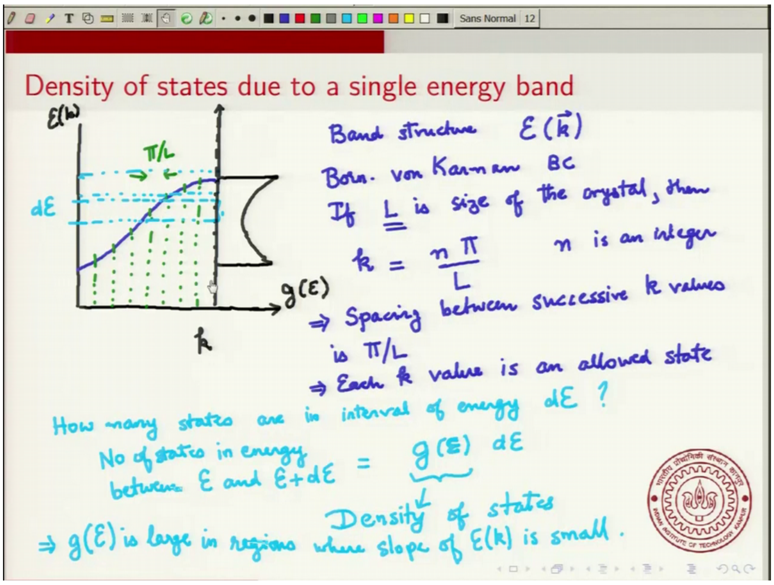

Density of states due to a single energy band

Band structure $\mathcal{E}(\vec{k})$

Born. von Karman BC

If $\underline{\underline{L}}$ is size of the crystal, then

$k = \frac{n\pi}{L}$ n is an integer

⇒ Spacing between successive k values is π/L

⇒ Each k value is an allowed state

How many states are in interval of energy $d\mathcal{E}$?

No of states in energy between $\mathcal{E}$ and $\mathcal{E}+d\mathcal{E}$ = $\underbrace{g(\mathcal{E})}_{\text{Density of states}}\, d\mathcal{E}$

⇒ $g(\mathcal{E})$ is large in regions where slope of $\mathcal{E}(k)$ is small.

So, now let us look at the density of states due to a single energy band first ok, and then we will go to the density of states due to multiple energy bands ok. Now if you have a single energy band then I am just showing schematically relation between the energy and the wave vector ok.

So, imagine I have a k here and let me take do not worry about the origin or origin in this k direction, let us say this is a allowed ranged of allowed values of k. And if you plot this energy as a function of k energy of just 1 band then you will have a graph that looks may be something like this ok.

So, may be you have a graph that looks like this and so this is energy of k is the band structure. So, the band structure is given by the energy as a function of wave vector ok. So, let me just write it down. So, the band structure is given by this relation E of k in general it is k is a vector; in general k is a vector. But just for representation I will show it as those k is a scalar; a k is a scalar. I will just show one dimensional representation, but in principle k is a vector.

So, now, you ask a question, what is a density of states due to what is what do you mean by the density of states ok. Now to do this, we go back to the; we go back to the Born von Karman boundary conditions. What the Born von Karman boundary condition says is that if L is size of the system that is of the crystal, the total size of the crystal is L ok.

So, L is a total size of the crystal then k in one-dimensions should be n pi by L where n is an integer. So, in 1D so this is in 1D, k should be n pi by L; that means, the spacing between successive k values; that means, implies that the spacing between successive k values is pi by L ok. So, pi by L is the spacing between successive k values and the and what you say each k value corresponds to a state. So, each k value this is an important idea each k vale is an allowed state ok.

So, you can have several different k values each of them is an allowed states and according to the Born von Karman boundary the spacing between successive k values is pi by L. So, what this implies, what this implies is that in this band structure, there are various states and I am exaggerating the size such that this spacing between any 2 states is pi by L. So, this is the k axis; so, on the k axis the successive states are separated by this pi by L.

So, you could imagine that there is one allowed value of k here, one allowed value of k in each of these intervals. And since L is very large these intervals are very closely spaced, I am just exaggerating the spacing between the intervals here ok. Now you can ask the question, if you look at some interval of energy ok; so, if you look at some interval of energy let me call this d E, how many case states are there? So, the question is so, how many states are in interval of energy d E? So, if you have d E is the interval of energy and yours how many of states are there in this.

And so; obviously, if d is larger, then the number of states will be more if d is smaller the number of states will be fewer. So, this number of states is represented by; so you can write this as so, the number of states in energy between E and E plus d E ok.

So, this is how you write it. The number of states in energy interval between E and E plus d E is some function g of E times d E; g of E times d E and this function is called the density of states. So, you take the number of states in some interval and you divide by the size of that interval you will get the density of states. So, if I just check d E at that to the denominator here so, I take the total number of states between the energy E and E plus d E and I divide by that interval size I will get the density of states ok.

Now, just by looking at this band structure, you can immediately see that in this region so, if you take this region where the energy is changing very rapidly with k, you have very few states where as if you take the same interval in this region, you have more states. So, if you take if you call if I call this interval d E 1 and I call this other interval d E 2 you can clearly see that the density of states in d E 2 is more, because the band structure is flat. So, you have lot of states in this energy interval ok.

Again you have to imagine that you I mean, I am sure you a only few of these green dotted lines, but actually there are lot more states you have several allowed states in this region whereas, here you have relatively few allowed states, because the slope is high. So, the first thing you realize is that g of E in one-dimensions is large in regions where slope of E of k is small ok. So, this is a very important idea that when the band structure is flat, that is the flat regions are the band will have lot will have a lot higher density of states, than the than the regions where there is a lot of variation ok.

Now, the other point I want to make I am just going to erase this thing here to make this point is that, often in the books and the general articles what is done is the band structure is shown and then side by side right here you show the density of states. Now, the density of states is actually because E is an axis for the density of states. So, the g of E is actually plotted here near is this so, g of E is plotted this way ok. So, basically here you have no states; here you have a very large number of states and then the number of states is very low in this region. So, here you have much smaller states and that is shown this way and again in this region the number of states increases and so, you will get something like this.

So, this is what the density of states looks like ok. So, it is often plotted side by side with the band structure ok. So, again keep in mind high density of states in this graph, high density of states is here because the density of states in this axis. So, large density of states is here, here there is a small density of states again because the slope of the band structure is large and again at this end there is a large density of states.

So, you can at least in this one dimension you have density of states will look like this you can qualitatively argue this just by looking at the slope of the band structure ok. Now they could be more interesting things, they could be multiple bands ok. Now suppose you have band structure that look like this. Again I will just for ease of drawing I will just use one dimensional representation ok. Let me show the E as a function of k here and here I will show g of E ok.

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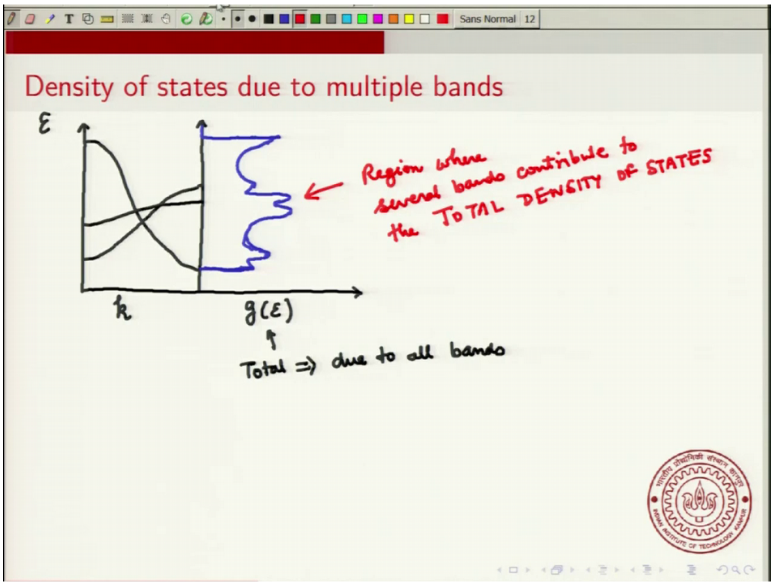
Density of states due to multiple bands

Region where several bands contribute to the TOTAL DENSITY OF STATES

Total ⇒ due to all bands

So, now suppose E as a function of k has something like this suppose you have multiple bands like this ok. So now each of these states will contribute to the density of states. So, the total density of states so, this is the total density of states due to all the bands, because due to all the bands ok. So, this total density of states will look like this so, here it is 0 then it goes high because this is one band which has very small slopes.

So, small slope we said that it means a high density of states and then it goes down then right around this point; around this point so, it goes down and right around this point now you see a second band come. And this band has smaller slope so, it will; so you will see a slight increase in the density of states ok. Then again it will go down and then you will see an increase on the states due to this third band ok. So, you can have something like this due to all these. So, here you have multiple bands contributing so, you have a very large density of states and then it then it will go down. Again here due to the flat region you will see a high density of states and finally, it will go down again it will increase due to this flat region, then due to this flat region it will go like this ok.

So, you can get a much more rich behaviour in the density of states when you have multiple bands ok. So, you can get a much richer behaviour when you have density of when you have multiple bands involve and not just 1 band ok. So, the density of states in this case is due to contribution from each other bands and when all the bands contributes that is where you would expect the highest density of states so, in flat regions and in regions where many bands contribute.

So, let me emphasize that this is region where several brands contribute to the total density of states ok so, this is the picture of the density of states due to multiple bands. Now in three-dimensions you can do the same thing. So, so if can a higher dimensions then you do not have a simple k vector ok. So, the band structure now you can immediately see the advantage of the density of states.

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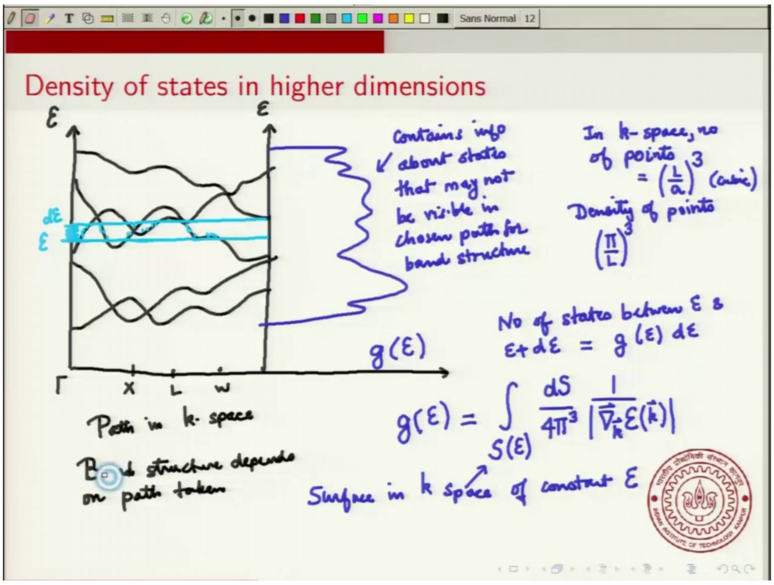

Density of states in higher dimensions

Path in k- space

Band structure depends on path taken

Contains info about states that may not be visible in chosen path for band structure

In k- space, no of points $= \left(\frac{L}{a}\right)^3$ (cubic)

Density of points $\left(\frac{\pi}{L}\right)^3$

No of states between $\mathcal{E}$ & $\mathcal{E}+d\mathcal{E}$ $= g(\mathcal{E})\, d\mathcal{E}$

$$g(\mathcal{E}) = \int_{S(\mathcal{E})} \frac{dS}{4\pi^3} \frac{1}{|\vec{\nabla}_{\vec{k}}\mathcal{E}(\vec{k})|}$$

Surface in k space of constant $\mathcal{E}$

So, in the band structure if you look at the E versus k band structure then you have as we had already seen in higher dimensions you have this whole path from gamma to x, to L, to w, to again to etcetera and you have to some other point. And, so you have a path in k space; so, you have a path in k space ok, but the nice thing about the density of states ok so, the band structure in some sense depends on what path you take. So, this band structure; however, you might get something like this, you might get some complicated behaviour and this band structure really depends on depends on what path that you would take.

So, the band structure depends on path, but the density of states that does not depend on the path taken I mean density of states just counts a total number of states ok. Now what is important here is that you might not see all the bands at any place. So, depending on a path taken you might not see some of the bands ok.

So, the density of states you will have you will get some information that looks and the point I want to make is that they are might be path that are not seen ok. So, this contains information about the states that may not be visible in chosen path for band structure. This is; this really illustrates why the density of states is useful quantity ok. So, the band structure really depends on the path that you choose whereas, the density of states this looks at all possible paths, it just looks at all states ok.

Now, now some of these states might be in along different paths as we at said the path in k space basically sets a certain direction in which you are allowing the wave vector to vary ok, but really if you look at the Brillouin zone, there are lot of wave vectors that that are allowed states which do not fall on the path; which do not fall down on the path in higher dimensions and so, those states will also contribute to the density of states ok.

So, the density of states in some sense it contains a lot more information than the band structure along a chosen path ok. Now, formally how do you understand the density of states ok? So, we said that we need to write the number of states between E and E plus d E as g of E d E ok. So, we had the idea that the number of states between energy E and E plus d E is equal to g of epsilon; g of E d E ok.

Now how do we go about calculating this g of E in the case of higher dimensions ok? Now there is a way to do this by essentially converting this to an integration over volume ok. So, we use the idea that in the in k space, number of points this again comes from the Born von Karman boundary condition and this is equal to L by a cube if you just take for a cubic system, this is for cubic system ok. And what that means, is that the density of points in k space of points; that means, for every as we as we already saw this we saw that every pi by L, pi by L in interval pi by L in 1 d we had 1 k point.

So, in three-dimensions you have pi by L cube you have 1 k point ok. And if you use this information and you convert this to an integral over k and now what you will see is that if you want the density of states, then at any point, then you have to consider one small region around that energy. So, suppose I want the density of states at this energy let us say this is my E, then I basically consider a small shell around this, this is an energy shell this is d of size d E and I count all the states in this region ok. I basically count all the states that are in this region.

And so, I count the states coming from here, from here, from this all the states coming from here, from here and from here ok. So, I count all these states I get the total density of states. So now this can be written as an integral in k space ok integral over the k space ok and using certain mathematical techniques, this can be expressed as an integral over surface of constant energy ok this is a surface in k space of constant energy and what you have is you have d S ok, this is the surface element and divided by 4 pi cube and you have 1 over absolute value of and you have the gradient in of E of k ok.

So, this is the again this derivation is slightly complicated I am not going to do this in detail, but the idea is that you this is the gradient is like d E by d k ok so, this is d k by d E. So, you are writing this in terms of this gradient in k space. So, as we said when the gradient is large that is the slope is very high, then you have very few states ok. So when; so it is inversely; so this exactly the same statement in 1 d where we said that a small slope ok, leads to a large number of points where as a large slope leads to a few number of points, few number of states.

So, the number of states is actually it can be expressed as a surface integral, this is a surface of constant epsilon so, this is actually a surface in k space ok. This is a surface in k space of constant epsilon ok do, constant energy e ok. So, this is a surface in k space of constant energy e and so this g of e is written as an integral, an this integral is over the surface ok so, you basically you look in k space and you look y at a region in k space where the energy is just E ok.

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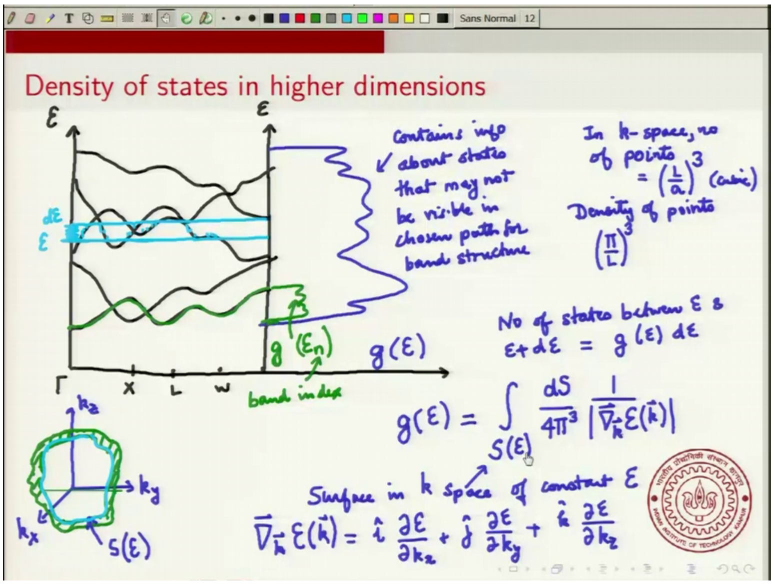

Density of states in higher dimensions

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Density of points $\left(\frac{\pi}{L}\right)^3$

No of states between $\mathcal{E}$ & $\mathcal{E}+d\mathcal{E} = g(\mathcal{E})\,d\mathcal{E}$

$$g(\mathcal{E}) = \int_{S(\mathcal{E})} \frac{dS}{4\pi^3} \frac{1}{|\vec{\nabla}_{\vec{k}}\mathcal{E}(\vec{k})|}$$

Surface in k space of constant $\mathcal{E}$

$$\vec{\nabla}_{\vec{k}}\mathcal{E}(\vec{k}) = \hat{i}\frac{\partial \mathcal{E}}{\partial k_x} + \hat{j}\frac{\partial \mathcal{E}}{\partial k_y} + \hat{k}\frac{\partial \mathcal{E}}{\partial k_z}$$

So, if I show it schematically way; let me just erase some this just to show it schematically ok, I will just erase this region just to show it schematically. So, if you look in k space ok so this is your coordinates of k ok. So, k you can think of this as kx, ky, kz and now if you ask what is the surface of constant energy E ok. So, there will be if you say that energy should be equal to E and you look at that region you will get some surface ok.

And if you ask what is the surface where the energy is E plus d E that will be another surface ok. And basically what you have doing is your you need to calculate the volume of this region; volume of this region again this is in k space. So, you are saying you want to know how many states are there so, that is the number of states can be expressed as the volume of this region times the density of points ok. So, if you multiply the volume by the density, you will get the number of states. And so the idea is that you need the volume of this region in k space and that volume of that region can be written using green serum, this can be converted to an integral over this surface.

So, this is the surface of I will just shade it in a different color this is the surface of constant energy E. So, this integral over this volume can be written as a integral over this surface of constant energy E ok. And the terms and if you work this out, it is not a very difficult exercise, but if you work it out then you can see that what you have is surface integral an integral over this surface.

So, you look at the gradient this a gradient in k space; that means, this gradient in k is expressed as k. So, this is mathematically this is expressed as i times dou e by dou k x plus j times dou E by dou k y plus k times dou E by dou k z ok. So, this is the expression for the gradient and using this expression you can calculate the density of states in higher dimensions ok.

Now I should mention this just for completeness that, I could ask the dens; I could ask for the contribution to the density of states due to the single band. So, if I just look at one band let say I just look at this band and I just look at the density of states only due to this band ok. So, I ignore all the other bands, then the density of states due to this band will look something like this and this is sometimes refer to as g n ok so, this is density of states sorry, g of E n ok. So, the subscript E so, this is the band index ok.

So, this is a density of states due to one; due to just due to this band and what you can see is that if you add up the density of states due to each of the bands, you will get the total density of states. So, the total density of the states is sum of density of states due to each of the bands ok. Again the idea is the same you can use density of states due to one band or you can dues a total density of states it will again it will follow exactly the same procedure. Only if you have just one band here; if you if you just want the density of states due to one band. So, then you will have E n here and you will have an E n here that is the only difference and you will have S of E n.

With this I will conclude this lecture, I hope I have given you an idea of the usefulness of the concept of density of states, I do not again this is very widely used in electrical properties of materials and electrical and even optical properties of materials. We will see a couple of applications but I just wanted you to know that there is a quantity called density of states and what is the physical meaning of that. So, the exact formulas I mean, they obviously depend on the band structure. So, if you want to calculate of density of states, you need the band structure, you need information of how the energy changes with the wave vector.

So, we will just be doing it qualitatively like how we did, we look at the slope of the diagram and then we look at the approximate we just try to qualitatively sketch the density of states. However, we will see in the next class that the information that we get from the band structure and density of states can be use to understand the electrical and optical properties of a material of a solid. So, with this I will conclude this lecture.

Thank you.