Solid State Chemistry
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Lecture - 53
Band Theory of Solids

Now, I will start the third lecture of week 11. In the last lecture, we learnt about Bloch's theorem and how Bloch's theorem can be used to describe electrons in a typical solid and we qualitatively saw how bands, how we can roughly understand what bands are. So, in today's lecture, I will be talking about the Band Theory of Solids and we will go into slightly more details and we will try to do it a little bit more formally ok. We still will not be able to do it in a you know very accurately, because the problem is not solvable exactly, but we will be able to see how bands appear ok. So, today's lecture will be on band theory of solids.

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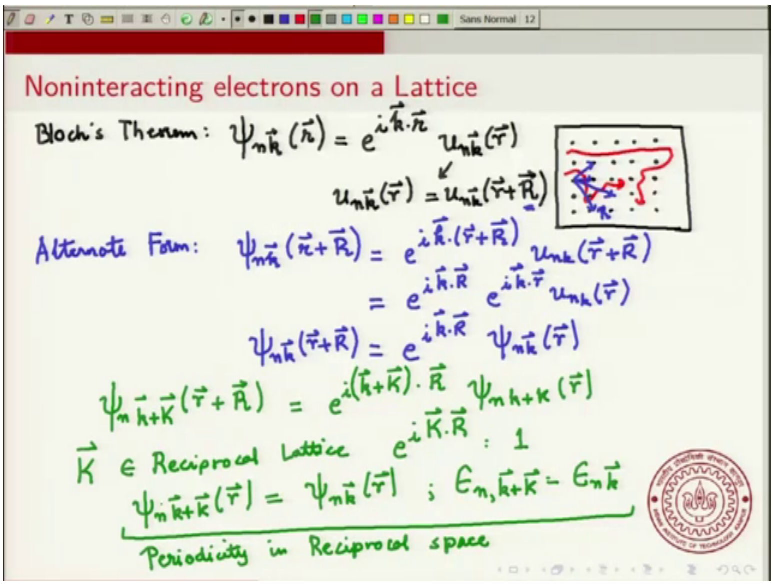

So, let us, we will talk about the system of a non interacting electrons in a lattice. So, what I mean is that, you have a solid and you have all these ions ok. I am just showing them as black dots here and you have a lattice of ions and in this lattice you have electrons which are essentially, except for the lattice they are just moving freely and we want to think about how, what this will look like ok. We want to think about what this will look like and what we said is that according to Bloch's theorem, the presence of a lattice, the presence of a lattice implies that these electrons can be described individually by a wave function ok that has the following form. So, psi n k of r, this is equal to e to the i k dot r times u nk of r.

So, this is Bloch's theorem and I am not going to prove this ok, you can look up standard reference, standard texts for the proof, but that is not important, what Bloch's theorem also says is that you can write the wave function of these electrons moving in a lattice by this ok, where u nk of r is equal to u nk of R plus some vector belonging to the Bravais lattice ok. R is some vector belonging to the Bravais lattice. So, this is a lattice translation vector ok. So, R could be any of these vectors.

So, you could have R like this, like this any of these could be R ok, you could have R is one of the lattice translation vectors and what Bloch's theorem says that you can take any lattice translation vector and add it and since and this u nk, which appears in the solution of the wave function is a periodic function. So, you have a periodic function multiplied by e to the i k dot r ok. Now, let us ask, we are going to write this in an alternate form. So, alternate form of Bloch's equation, which is actually very useful and very incisive ok. Now, let us ask a question what is psi nk of r plus R. So, suppose I ask what is this, ok?

So, now if I do the same on the right hand side of the wave function ok, then you will get e to the i k dot r plus R times unk of r plus R ok. Now, we know that u n k of r plus R is just unk of r and I will write this in the following way. I will write it as e to the i k dot R multiplied by what I will have is e to the i k dot small r and since unk of r plus R is same as unk of r, I will just write this as unk of r ok. So, this is written as e to the i k dot r times psi n k of r.

So, this is what we had here was just psi n k of r. So, we have this alternate form of Bloch's wave function, alternate form of Bloch's theorem is that your wave function can be written in this form ok. So, whether you write it in whether you write Bloch's theorem in this form or this form, it is actually the same. Now, there is something that something nice that happens, when you write it in this form ok. That is the following. Suppose, you ask the question, what is psi n k plus capital K of r?

So, let me ask the question, what is psi nk plus capital K of r plus R,? So, now, from this form of Bloch's theorem, this can be written as e to the i k plus capital K dot R times psi n k plus capital K of r ok. Now, we have a very nice theorem that states that e to the i capital K.

So, capital K now, what I mean by capital K is that capital K is a it belongs to the reciprocal lattice. So, the reciprocal lattice that we talked about earlier. So, K is a vector of the reciprocal lattice and now, what this says is that is since it is a vector of the reciprocal lattice, you have e to the i a vector of the reciprocal lattice dot R into vector of the normal lattice should be equal to 1.

And so, if you expand this and you take it to the next step, you will see that this has an implication that psi n k plus capital K of r is equal to psi n k of r ok. I am not showing the intermediate steps, but you can use this and you can manipulate this to show this final result and the other relation that we get is that e the energy of the Bloch electron epsilon n k plus capital K is equal to epsilon n k.

So, these two equations here, they describe the periodicity in reciprocal space and this is a consequence of Bloch's theorem ok, that your wave functions are periodic not only in real space, but they are also periodic in reciprocal space ok. And again let me emphasize that I have not shown all the steps going from here to here, but you can work it out ok. Now, what else do we want to say so now, let us use this, these ideas in looking at electrons on a one dimensional lattice ok.

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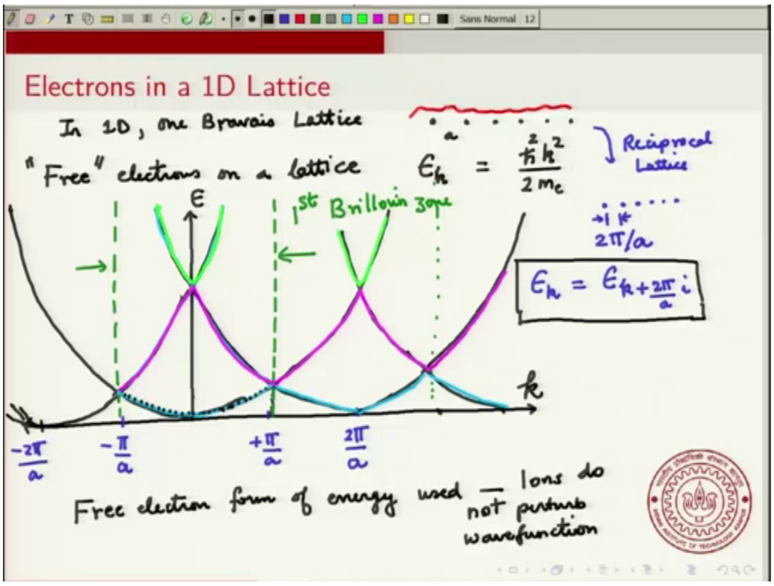

Now, if you have only one dimension ok. So, in one dimensions there is only one Bravais lattice only one Bravais lattice and this lattice is you can think of it as just we can we can take atoms on a line equally separated by distance a ok. So, they are equally spaced by distance a and if you have all these ions and now, you have this electrons that are going in this ok. So, this will be a very nice illustration we will see how bands naturally appear ok.

Now, so, these electrons ok, they are like so except for the ions the electrons are just moving freely. So, there are ions ok, which impose a periodicity. So, let us look at free ok and I am putting free in quotes, because these are free electrons on a lattice ok and in what sense do we mean that they are free; that means, in between that there is no interaction potential ok. They do not feel any forces in between, but there is a periodicity up that is imposed on the wave function ok.

So, what we have is that your we have epsilon k. So, for a given wave vector k the free particle solution say that this is h cross square k square, in this case this is k is just a scalar h cross square k square by 2 m e the mass of the electron ok. Now, so on this lattice these electrons are not really free, there are some periodic, there are some there is a periodicity of the lattice, but now let us just look at this. Let us look at this relation.

So, I will put epsilon as a function of k and let me do this in the following way. I will, choose ok, now, notice that in the reciprocal lattice ok. So, that looks like it is equally spaced points in k space ok. So, this is in, k space in wave vector space, but the spacing between the points is actually 2 pi by a ok. Now, in other words, the, what we are going to say is that this energy of k is equal to energy of k plus 2 pi by a and basically, it is 2 pi by a times any integer times any integer ok.

So, it can be plus 2 pi by a, it can be minus 2 pi by a, plus 2 into 2 pi by a, minus 2 into 2 pi by a and so on ok. So, what we are saying let me extend this graph a little bit on this side ok, just to illustrate the illustrate the point that if you look at this energy versus wave vector ok, you will get some relation that looks like so, it looks like this ok. So, this is the this is just it is a parabolic function E ks h h cross square k square by 2 m e. So, it is just a parabolic function and it will look like this ok. Now, since, you have this Bloch condition ok, what you will get is you will get another parabola in energy.

So, this is 2 pi by a and here, I have a another parabola that looks exactly like this. So, since the wave function here, should look exactly like since this wave function should look exactly the same at 2 pi by a ok. So, at 2 pi by a just due to periodicity, I will have exactly the same form of the wave and it will go out ok and they will cross each other exactly at pi by a. So, I have to draw this properly, we will cross each other exactly at pi by a ok.

So, now, we will have a similarly, we will have something coming from the other side that will also look like this ok. That is coming from the left from minus 2 pi by a, this is minus 2 pi by a ok and so and so, you have this form of the wave function. Now, since the energy is a periodic function ok, you only need to describe the energy in this interval ok and notice we have just used a free particle form of the energy. So, this energy form that we have used is a it is actually corresponds to the free particle. Now, if you just look in this region ok, then you see what the energy looks like ok, I will let me show it in a different colour.

So, it looks like this ok and then there is another band that looks like this and a third band that looks like this ok. So, you can let me show the bands in different colours again just to; so, you can see that just due to periodicity, you see you see this kind of bands forming ok. So, again let me emphasize that we have used free electron form of energy.

So, free electron form of energy used ok and the other point I want to emphasize is that, though we show these k as a continuous variable, it is actually discrete variables ok. This is due to the bond one, carbon boundary condition. So, actually there are only discrete values of k ok, but they are very very closely space. So, it looks like a continuous set of values of k ok. So, again just using the free electron picture ok and we are just so, the role of the lattice is just to bring this periodicity ok. And we see that if you look in this region and then we see the we see a band like picture appearing. Now, incidentally this region from here to here, this region ok, this region of k from minus pi by a to plus pi by a is called the first Brillouin zone ok. This is in 1 D the first Brillouin zone just looks like a region in k minus pi by a 2 plus pi by a.

So, if you know the energy in the first Brillouin zone, you can actually show the you can actually calculate the energy everywhere else ok, just by imposing the periodicity of this first Brillouin zone ok. And I should also emphasize again that there will be more I mean

I have shown only some of the periodic some of the parabolas, but there will be also be more parabolas ok and that will they there will be for example, there will be another parabola that passes through this, that starts at 4 pi by a and it goes like this ok. And so, essentially, what I want to say is that, this whole thing will just keep repeating.

So, you will see that again, again you will have exactly the same kind of behaviour in each of the zones, each of the Brillouin zone ok. So, even in this zone, it will be exactly the same ok. Now, with this basic framework ok, we can go to the so, here we the free electron form of the energy is used ok and so, the lattice actually causes a very little, the ions do not perturb the electronic wave function ok.

So, in this form, in this description the ions do not, it is as though the ions are not perturbing the wave function, but now, we can take this and we can add the idea of perturbation ok. And so, if we think that the ions that are there, they will actually add a weak perturbation ok, then what you can say is the following so, what you can say is that this weak perturbation will actually affect, will actually change the band structure right where these lines cross each other ok.

So, like this region, this region etcetera there will be some perturbation ok. We will see that, in a few minutes ok.

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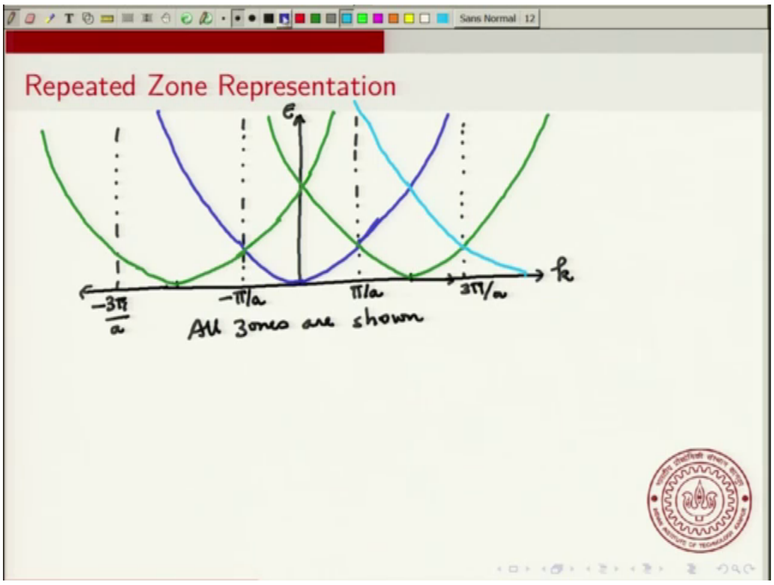

Now, let me so based on this depiction of bands ok, you can, there are a few different ways to represent bands ok. Now, one is called a repeated zone representation, where you show all the zones ok, where all the zones are shown so, for example, if you have the first Brillouin zone, the second Brillouin zone and so on.

Now, then what the idea is that, you show all the zones, you do not only show in the first zone ok. So, you are in the first zone, if you have something like this and a similar thing and this again I am considering the free particle form of the functions. Now, in the second zone, you will have a similar thing ok, you will have something like this. Similarly, in this zone also you will have something like this ok, this is called a repeated zone representation, where you show all the zones ok. So, all zones are shown ok.

So, this is called a repeated zone representation of the bands and again let me emphasize that here I have considered non interacting or a free electrons ok, but you can do this for arbitrary bands ok. So, for arbitrary bands and arbitrary dimensions, you can do this ok, pi by a minus pi by a minus 3 pi by a. The alternative to this repeated zone representation is the reduced zone representation, where you essentially focus on one zone and you show the band in that zone and we already saw what this look like ok. I will just show this again.

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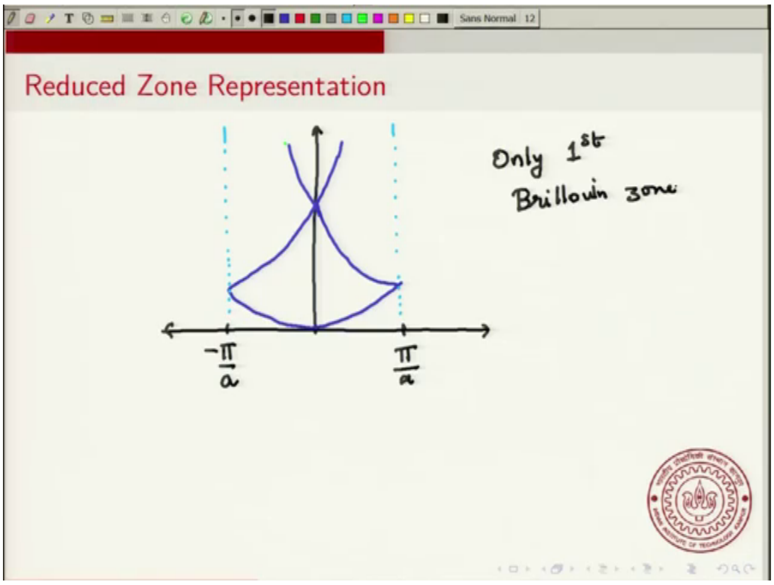

So, you just show the first Brillouin zone, which is minus pi by a to pi by a and if you look at the bands ok, they will go like this and then they will go like this and so on and you will have more bands ok. You will also have bands due to things that are even further away. So, we will see you will have things like this well ok.

So, I am showing here, here I just showed the first two bands and or the first two just due to this blue curve and this green curve ok, but you could have more band structure ok, due to another band that is centered here ok and it will again go and eventually it will come into the first Brillouin zone ok. So, you will also have more bands ok.

And so, in general the in the repeated zone, you will have several bands ok. And this so, this repeated zones representation is also often used to describe bands ok. So, you can either or the reduced zone where reduced zone means only first Brillouin zone ok. Now, let us ask the question what happens if there is a small interaction, if there is a weak interaction in this band structure ok.

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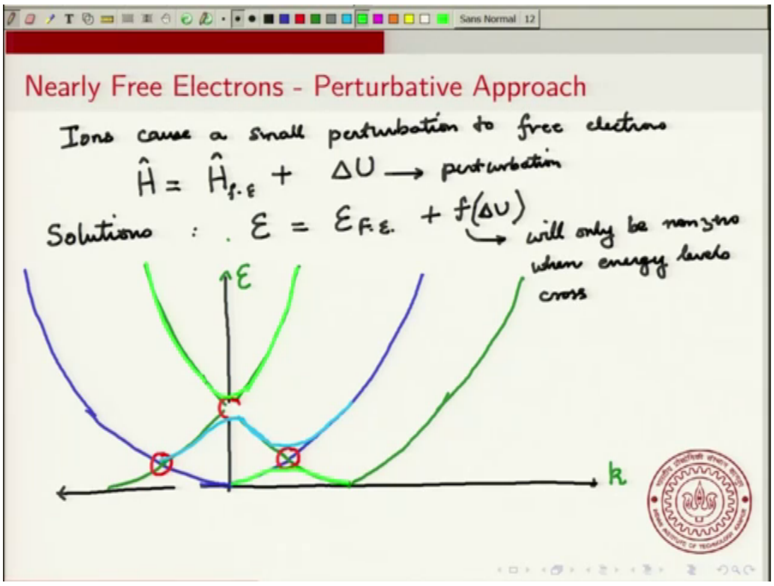

So, what happens in to the band structure, if there is a weak interaction and formally this is done using nearly free electrons, it is a perturbative approach ok.

So, the ions cause a small perturbation to free electrons ok. So, the Hamiltonian is the Hamiltonian of the free electrons plus some small perturbation I will just write delta U, this is a perturbation ok and without going into too many details ok, you can understand this in a very similar way to how you understand, how you understand orbital theory, molecular orbital theory ok. The basic idea is that if this perturbation is very small ok, it will only affect. So, the solutions ok, will look like a the energy is equal to energy of free electron ok, plus something that is related to delta u times I will just well, I will just write some function of delta u ok. Now, so what is important in this perturbative approach is that this function ok, will only be non zero, when energy levels cross and I again I will just show this qualitatively ok.

So if you go back to, if you go back, let us look in the repeated zones representation. So, we had a wave function, that look like this ok and you had you had a second wave function that is let us say starting here, that looks just like this, but shifted by 2 pi by a. This is k energy ok and you have a similar one, on this side also ok. So now, what I want to say is the following that right at these points, where the energy levels cross ok. This is where, this is where the perturbation will be active ok and what the perturbation we will do ok, we will do something with that is very that should be very familiar to you ok. you might have seen this in energy levels of molecules ok.

So, what it will do is that, it will the perturbed energy and let me show this, let me show this in light green ok. So, it will look very much like the free electron ok except close to here, it will move away ok. So, in some sense these two energy levels will repel each other and one will be pushed down the other, which I will show in a different colour ok will be pushed up ok. The same thing is going to happen here to; same thing is going to happen here ok.

So, this energy level will be pushed down here and it will become like this ok and whereas, the this energy level will not be perturbed far away from the, intersection point, but right near the intersection point, it will be pushed like this ok. So, our final energy, our final band structure, we will now, look like this.

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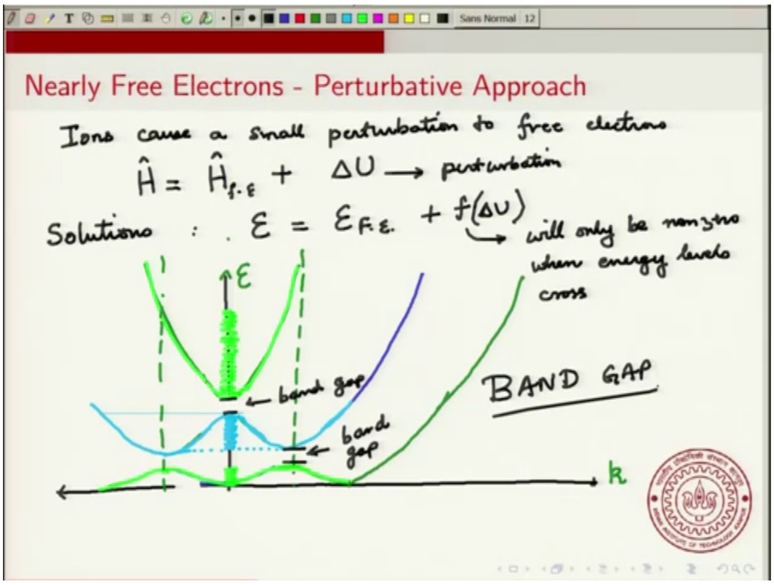

So, let me erase this, it will look, we will erase this to look like this ok. So, that is what the band structure will look like and if you look in the, reduced zsone, if you just look within one, within the first Brillouin zone ok, then what you see is you see a band ok, you let us go to the lowest band.

So, you see a band of energy. So, this is a band of energies from here to here ok and then you see something here, which is caused due to the perturbation that is a. This is called a band gap ok and what has happened is that, because these, because of this perturbation and then you have another band of energies from here to here ok and again, you have a band gap again you have a band gap here and then you have another band of energies here ok. These are continuous ok and the point is that this explains the origin of band gap ok.

So, this nearly free electrons a perturbative approach explains origin of band gap, how band gap appears ok and notice, that we have just used a free electron one dimensional free electron picture ok and just putting this perturbation and I have not done the mathematics of the perturbation, but I have just qualitatively told you that this perturbation leads to a band gap.

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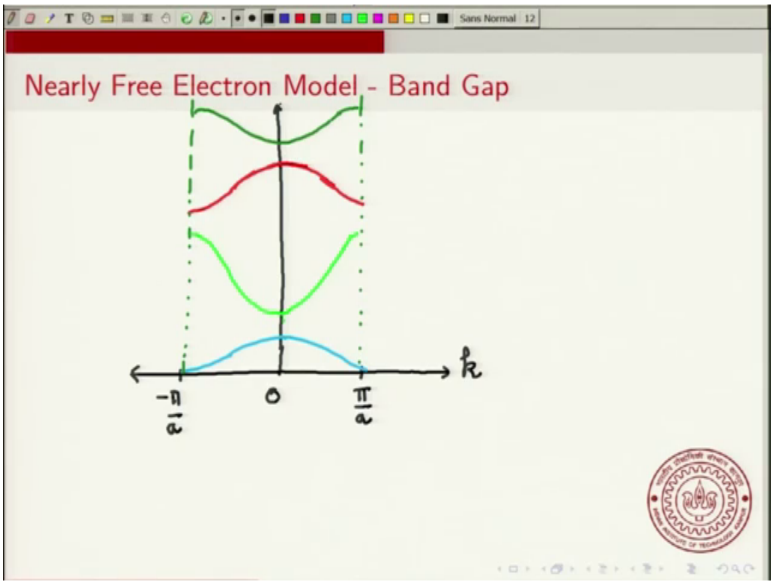

And so now, if you look at the, if you look at just in the first Brillouin zone ok, then you will have and what we had was something like this and then something like this and again you will get something like this ok, if you extend the bands you will keep getting things like this. You will keep getting this alternation of bands that are either going, either like this blue, which going from going from 0 to pi by a, it goes down or it goes up ok and you will see this band gap in the several places ok.

So, we see that this nearly free electron model ok, which is a basically, a free electron with this small perturbation ok, that gives a nice band structure in 1 D ok. So, we have both the origin of bands and the origin of the band gap seen in this ok. So, with this I will conclude this lecture in and so and so, in this lecture, we have seen, how you can understand the origin of bands and band gap in one dimensions ok.

Now, in two dimensions things become a little more complicated in two and three dimensions ok, but so, in the next lecture, I will just briefly show you what happens in two and three dimensions and we will come to the concept of a path in reciprocal space.

Thank you.