Physics of Functional Materials and Devices

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Lecture – 10, Week 3
Crystal structure - II

Welcome to lecture 1 of week 3. In the previous week, we had given you the introduction to crystal structure and why crystal structure is very important to understand the properties of functional materials. In today's lecture, you will see some more details about the crystal structure. We will talk to you about types of lattices, crystal structures and various types of crystal structures and then we will introduce a concept which is called Miller indices and also give you the importance of this concept. In the previous week, we had talked to you about the following concepts. We had introduced the concept of 1D lattice that means, you have arrangement of atoms in one dimension.

Then we had talked to you about two dimensional lattices where you had arrangement in two directions, be it be x y, y z or the combination of any of these. And finally, we had given you the introduction to the real structures or real lattices which you see that is the three dimensional lattices and then we had told what are the differences between small crystals and larger size crystals. It is basically the arrangement of the number of atoms which will decide whether you have smaller size crystals or the bigger size crystals. If you have more number of atoms, obviously, you will get a bigger size crystals.

Following that you had seen that these arrangements of atoms in a solid material can be of two types, mostly a crystalline type or a non-crystalline type. Crystalline means you have periodic arrangements in the directions you are talking about. So, if you have 2D structures, you have periodic arrangements in two dimensions. If you are talking about 3D crystals, you have crystalline materials which are 3D will have periodic arrangements in all the three directions. Non-crystalline materials as you can see from the picture, they have short range ordering and you do not have periodic arrangement of atoms.

Crystalline materials can be of two types, single crystals and polycrystalline type. The concept of these two were also introduced in the previous lecture. Following that you may have understood what is a crystal structure or what is a crystal, how is it built. It is basically a combination of lattice plus basis. So, a basis is an ideal crystal constructed by the infinite repetition of identical group of atoms.

It need not be one atom only. You can have a combination of 3 or 4 or 2 n number of atoms, make it a particular repeating unit and then you can repeat at different points, you will have the crystal and these points where you are going to put these groups of atoms is the lattice points. So, you have a crystal structure which is a combination of lattice plus basis. A crystal structure is talked in a way when you start talking about terms like it has identical surroundings. What does it mean? That means if you go and perform any translational operation or rotational operation about various points in a lattice, you will see the same environment around a given atom.

So, it is not that the origin is fixed. The origin in a lattice can be chosen at different points, but the environment in the lattice will remain the same and this was also discussed in the previous lecture. Once you have the lattice, the concept of unit cell was introduced. What is the unit cell? Unit cell is the smallest group of atoms that has the overall symmetry of a crystal and which becomes the building block of the crystal. That means you will go on repeating the unit cell, then you will get the whole crystal.

That is what a unit cell is defined as. Unit cells can be of two types primitive and non-primitive. We discussed these concepts in the previous lecture and based on these concepts, we had discussed about the effective number of lattice points in a primitive cell or we had discussed about the unit cells which have more than one effective points per unit cell. So, those concepts were also discussed in the previous lecture. Once you have a crystal, it is not necessary that you will only see a translational symmetry, a rotational symmetry.

There are various types of symmetry operations which can be seen in a crystal and different types of symmetry operations were also discussed in the previous class. We had discussed about mirror symmetry, we had discussed about two fold symmetry, three fold symmetry, four fold symmetry and six fold symmetry. We had discussed about the f symmetry, the i and also the inversion symmetries. This is what was covered till the previous lecture of the previous week. Let us move forward and try to understand the crystal structure more in detail and why are we spending so much of time to understand crystal structure and how these will affect the properties of functional materials.

If you see a crystal that means arrangement of atoms, then there can be various types of arrangements and if there are various types of arrangements, then you can see the properties would be very different. For example, wherever you are sitting and hearing this lecture, you are in a room, you can imagine what am I talking about. Suppose you are sitting in a room and you have the corners in this room. Can you see those corners? Now put one ball at each corners of this room. Next you have a ball which is at hanging at the center of the room.

So, right at the center of the room, you imagine there is a ball hanging. Now compare the first example with the second example. First was where the balls were only at the edges of the room. So how many balls you had? You had eight balls at the edges of the room. Now you have another ball hanging at the center of the room that becomes there is one more

ball.
Are the two situations same? No, they are not. They are clearly different and hence the properties of these two conditions or unit cells or crystal would be different because there is an additional atom coming into picture. That is why we have to understand the importance of arrangements of atoms and how do we arrange these atoms so that we get crystalline materials. And is it so that you can have n number of arrangements? This you will see today that it is not true for two dimensional structures or three dimensional structures. If you are talking about crystal structures, there are a set number of arrangements which are possible and this number is not infinite.

There is a fixed number associated with this value and this is what we are going to now understand. So, a crystal lattice can be mapped into itself by a lattice translation T. So, you have a crystal lattice you translate it by T, you will find that similar structure or the same arrangement is obtained. And it can also be generated that means the lattice can also be generated by various other symmetry operations. So, there are other symmetry operations which can also lead to the same lattice.

If you have 2D structures, so 2D structures or 3D structures this is what we are talking about. So, 2D structures or 3D structures. If you consider 2D lattices, then you will find that you can classify 2D structures, crystalline structures into 4 crystal systems. And if you consider 3D lattices, if you consider 3D lattices you can classify them into 7 crystal systems. There are 14 Bravais lattices in 3 dimensional grouped in 7 crystal systems and 5 Bravais lattices in 2D grouped in 4 crystal systems.

I have just introduced a term Bravais lattices. Immediately you will ask what is a Bravais lattice? A Bravais lattice is a lattice in which the atom or all the atoms at a lattice point. So, at a lattice point we have seen previously you can have one atom or a group of atoms. So, a Bravais lattice is the lattice in which atom or all the atoms at a lattice point or at lattice points are identical or if the surroundings of each lattice points are the same. So, you will have that around each lattice point the surroundings would be same.

So, Bravais in 1948 actually showed that there are 14 lattices which are sufficient to describe all crystals in 3D. And hence these 14 lattices were called as Bravais lattices. So now, if I ask you the question is it that you have infinite ways of arranging atoms in a crystalline material in 3D? No, there are 14 lattices which will be sufficient to describe any type of 3D crystalline material which you are going to have. So, if you see the crystal systems and Bravais lattices in two dimensions there are four crystal systems. They are oblique, rectangular, square or hexagonal.

The associated Bravais lattices are you can have an oblique Bravais lattice, you can have a rectangular primitive or rectangular centered Bravais lattice which is going to be clubbed under the crystal system that is rectangular. If you have a square Bravais lattice it is corresponding to a square crystal system in 2D and hexagonal Bravais lattice is corresponding to the hexagonal crystal system in 2D. What is the corresponding conventional unit cell? If you have an oblique crystal system you have a parallelogram type unit cell. If you have a rectangular crystal system you have a rectangular unit cell. If you have a square crystal system you have a square unit cell and if you have a hexagonal crystal structure you have a 60 degree rhombus type unit cell.

And the corresponding lattice parameters A and B. So, you have two dimensions. So, A and B. So, two dimension. And what is the angle between the two lattice directions? Let us see what I mean by this.

So, if you see an oblique type lattice what is the corresponding unit cell? What did we say? We said a parallelogram. So, you have a parallelogram. You have A and B defining the lattice parameters where A and B are not equal and gamma is not equal to 90°. Similarly, if I move to rectangular you have A and B not equal, but gamma equal to 90° If you have rectangular centered you have A not equal to B, gamma equal to 90°, but you will have an additional point in the center.

You have rectangular centered. Then you move to square. What do you have? You have A equal to B and gamma equal to 90°. And similarly you can define hexagonal. What is this unit cell actually representing? For example, if you have a square lattice this means you could choose any point as origin. Let us choose this point as origin then there is an atom here.

If you translate by A you will have another atom. If you then translate by B you have another atom. And if you move back by the vector A, but in the opposite direction you have the fourth atom. So, this is what the arrangement of lattice is. If I now add this which type of lattice have I obtained? Is it rectangular? Is it square? Is it hexagonal? Or is it oblique? So, you will see if you just take that this line had to be straight then you will see that this is more like a rectangular lattice because the vector B and A are not equal.

And hence you have a rectangular type lattice. Similarly, you have crystal systems in three dimensions. And you will find that all the lattices which you see in 3D can be classified in one of these types of crystal systems or associated Bravais lattices. What are these seven crystal systems in 3D? You have cubic, tetragonal, orthorhombic, rhombohedral or trigonal, hexagonal, monoclinic and triclinic.

This you should remember. So, there are seven types of crystal systems in three dimensions. If I have a cubic lattice that means the atoms are arranged in a cube. What is the only meaning you have in a cubic lattice? What do I mean? That means the atoms would be at the cube edges. This is what we are meaning by cubic type crystal system. Then if it is a cubic type arrangement, what would be the lattice parameters? We know in a cube A is equal to B is equal to C.

So, if this is A, this is B and this is C, then A is equal to B is equal to C, the magnitude of the three unit dimensions. So, you have A equal to B is equal to C and corresponding angles alpha, beta or gamma are all equal and that is equal to 90 degrees. There are various types of Bravais lattices which a cubic unit cell can have. It can be a simple cubic, it can be a body centered cubic. A body centered cubic means what? This consider this unit cell as a body.

Then if I am saying that there is a body centered means at the center of this body there is one more atom. So, there is at the center of the unit cell there is one more atom. Remember the first example I was talking to you just to imagine there is one more ball hanging at the center of the room in which you are sitting in addition to the balls at the edges of the room. So, one was simple cubic, the other was the example of body centered cubic.

Third could be you can have face centered. So, you can have face centered cubic that means, you will have atoms at the center of the faces. So, you can have center of the faces. This is what you have. Tetragonal what do you do in tetragonal? A is equal to B that means, the dimension if you see the floor they have both the same values, but the height is different. So, you have displaced and made the height larger than the plane on which the third plane is being constructed that becomes tetragonal.

You have simple tetragonal or body centered tetragonal. Similarly, if you pull a simple cubic along one of its face diagonal. So, one of the face diagonals you pull it then you get a orthorhombic cell and if you do that you have a equal to b equal to c which was the case in cubic that condition is lost and you get a condition because you have pulled the cell along the face diagonal you can get what a not equal to b not equal to c, but alpha beta and gamma are equal to 90°. And you have various types of orthorhombic cells and the symbols which are associated by the face centered, end centered, body centered or simple orthorhombic are P, I, C or F respectively. You can have different types of materials which are showing these kind of arrangements.

Similarly, you can have rhombohedral, hexagonal, monoclinic or triclinic and you have different types of materials. Let me show you schematically what do we mean. So, this is simple cubic then you add one more atom in the middle you will have what is this if I do not give you an example can you tell me what this example is. If I say that it is face centered cubic am I correct or am I wrong? I am incorrect in this because there are no atoms at the faces of the cube then it is in the body centered. So, what type of cell it becomes? It becomes body centered cubic.

So, it becomes body centered cubic. Now if I have face centered cubic what would happen? You will have atoms at the center of the faces. Simple orthorhombic then what is the next example which we will take? This is what? This is the end centered. So, you have the two end sides on which you are putting atoms and therefore, they are called as end centered orthorhombic and you are putting in the height direction. So, you call it a C type end centered orthorhombic. You can have different types of crystal systems as we discussed what are those.

So, if you want to clearly imagine then you can see you have simple tetragonal you have orthorhombic you have simple orthorhombic, monoclinic, triclinic or hexagonal cells. If you look into these unit cells, these unit cells are what? These are representing the arrangement of atoms in a lattice which is then growing to give you the crystal which you will then use for various applications. And just by looking at these unit cells, do you think that the property of a tetragonal type arrangement would be same as the hexagonal type cell? If I apply stress, let us say I apply a stress in the x direction in a on a tetragonal unit cell and I apply stress on a hexagonal cell will they be same? No, they would be different because the forces which are acting in the three directions on a given atom would be different in these two cells and hence their properties would be different. I hope now you understand why the properties of materials would be different if you have different crystal structures. And how are you going to get different crystal structures? Can you answer this question? We get crystals by various synthesis routes.

If I change the synthesis route, I get different types of atomic arrangements. If not arrangements that means, I may get same tetragonal cell, but I may end up getting different values of a and c in a tetragonal cell, b is equal to a. So, therefore, I am only mentioning a and c, b is equal to a in a tetragonal cell. For example, if a is equal to 5 Å in a given case and then somebody synthesizes the same material. For example, lead titanate, a well-known ferroelectric material.

You synthesize lead titanate with lattice parameter a equal to 4 angstrom and c equal to 10 Å. I synthesize the material and I get lattice parameter a equal to 3.5 Å and c equal to 3.7 Å. Will the properties be same? No, you can clearly see that I am moving towards cubic cell.

The difference between a and c are very different in my example, but in your case the c is double the value of a and hence the behavior of the two materials having the same chemical formula would be different because the lattice parameters are very different and hence as you tune the synthesis protocols, you get different materials and hence their physical or chemical properties are different. I hope now you clearly understand why it is important to understand these synthesis protocols and then only move forward. There is one concept which one should understand very clearly. When we were talking about primitive unit cells, there was a term which came as effective number of lattice points in a cell. What is effective number of lattice points? So, if you look into the unit cell which we have constructed, very simple unit cell.

How many atoms do you see? I see 1, 2, 3, 4, 5, 6, 7, 8. There are 8 atoms which are leading to the unit cell. That we are considering. What is this effective number of lattice points? But if you look into a lattice next to this unit cell, there is another cell in this direction, there is a cell in this direction, there is a cell in this direction, there is a cell in the fourth direction as well as fifth and sixth directions. Why? Because lattice means that each atom will have the same environment no matter if I translate from one point to the other. So, if you consider this atom, this atom is actually contributing to how many unit cells? It is contributing to this, then to the next, one on the top, one on the right of it and two more on this directions.

So, the contribution effective contribution of this atom to a given unit cell which we are considering is just one earth. So, this is one eighth because this atom is being shared by another 7 unit cells. So, effective contribution of a atom to a given unit cell in this case becomes one eighth. So, if I now move one step forward, I add more number of atoms, but only at the face centers. If I have a face center, then there is a unit cell here and there is a unit cell on top of it.

You do not see a unit cell on this side, you do not see a unit cell, but on the top. So, this atom which is at the phase center is being shared by how many unit cells? Two unit cells. So, the effective contribution of the face centered atom would be half and the one which is at the body centered which is in the body centered position, it is not being shared by any other unit cell, it is not contributing to a unit cell above it or at the sides of it. It is enclosed within a given unit cell. So, what is the contribution of this body centered atom? It becomes full, it becomes one.

And hence, you will find that the effective number of lattice points n in any unit cell is given by N_i plus N_f by 2 plus N_c by 8. What would be N_i? The number of lattice points which are completely inside the cell. What would be f? These would be the face centered points. And what would be c? That is Nc would be the corner positions of the cell. And therefore, the effective number of lattice points is equal to N_i plus N_f by 2 plus N_c by 8.

Now, you have crystal structure. You can move in x direction, you can move in y direction, you can move in the z direction. And you will find that the arrangements of atoms could be slightly different. Why? Because you may have a condition which is tetragonal, which means a equal to b not equal to c and c is much larger than a or b. Then you may have atoms which are slightly farther away from each other if you move in the c direction.

This was discussed and explained by the concept of Miller indices. The orientation of the planes in a lattice, so you can have a plane. So, you can have in the x direction, the y direction or the z direction. You have the planes. This is simple to imagine, but you can also have a plane starting from the zero point and going along in the direction of the body diagram that also forms a plane. So, what is the way you will describe these planes? This was basically described by Miller indices which specifies the location, the directions and the planes in a crystal.

How do you explain or calculate the Miller indices? First, find the intercepts of the plane on a crystallographic axis. So, if you have let us say h k l as one of the Miller planes, then what is the corresponding intercepts at x, y or z axis. Take the reciprocal of these intercepts, but we do not generally write in fractions. So, simplify and remove fractions if any and enclose the numbers which you obtain into parentheses.

The corresponding notation is for the Miller indices for a given plane. Let us see what we mean. For example, let us take this example. If you have the condition where in the a direction, the lattice parameter is 4 angstrom. In the b direction, you have lattice parameter as a angstrom and in the c direction, you have the lattice parameter as 3 angstrom. You want to construct a cut away which is representing the Miller plane shown by the dashed triangle.

What are we going to do? We see what is the corresponding intercept in the x, y or z direction or a, b or c direction. You see in a direction, the intercept is at 2. So, you have 2 corresponding to b it is at 6 Å and for c it is at the edge. So, it is 3 Å.

What are we supposed to do? Take a reciprocal, the inverse. what are we doing? You have 1 by 2, 3 by 4 and 1. This is what you have. How do you get 1? You get 1 by 3 by 3. You have 3 by 3 is equal to 1. Now, what is the corresponding Miller indices? You will get the values here, you have to remove the fractions.

So, if you remove the fractions, take the LCM, remove the fractions, what are the corresponding values you will get? You will get 6, 4 and 3. This is what the whole calculation is for a Miller indices. So, if I go back, now you understand the steps. You first take the intercepts, then the reciprocal and then you remove the fractions. So, we took the intercepts, then we finally remove the fractions from the fractional intercepts and reciprocal of that we had to remove the fractions.

I hope you can calculate the Miller indices of any given plane in a crystal structure now. If you have planes, the distance between the two planes are called as interplanar distance. This is the concept which you should remember and if you have understood the previous calculation which we discussed, you should be able to clearly discuss and understand the way you calculate the interplanar spacing. Let me give you that answer. So, if I have to calculate the interplanar spacing, how are we going to do that? Simple, let us calculate OA, OB and OC that is 1 by h, 1 by k and 1 by l and multiply by lattice constants A, B and C.

If you are talking about cubic cell, we will multiply it by A. You have the corresponding values as A by h, A by k and A by l. From the figure, you can clearly see what is the value of cos alpha dash that is O n by OA. That is equal to what? d h by A. Similarly, you can write cos beta dash and cos gamma dash.

You have d into k by A and d into l by A for cos gamma dash. You know cos alpha dash square plus cos beta dash square plus cos gamma dash square is equal to 1. And hence, if you use the corresponding values which you obtain, you will get d square is equal to A square divided by h square plus k square plus l square. And what is the value of d? The interplanar spacing becomes d is equal to A by under root h square plus k square plus l square, where h k l is the value of the Miller indices. In Miller indices, please remember the brackets and commas matter a lot. If you have h comma k comma l in parentheses, then it represents a point, it is not representing a plane.

If you have square brackets, then it represents a direction. If you have in brackets h k l, then it is family of directions. If you have under parentheses, but no commas between h k l, then it represents a plane. And if you have curly brackets and no commas between h k l, then it represents a family of planes. Now suppose, if you want to represent the negative, that means if you are writing that you have to take direction opposite to the earlier case.

For example, 1 and minus 1. How do you represent in Miller indices? That you represent by writing 1 bar. So, you put a bar if you want to have negative weight associated with the given indices in the Miller representation. So, in today's lecture, I hope we have discussed about the basis and lattices which lead to crystal structures and the corresponding unit cells. We also revised about the crystal symmetries and then we moved on towards the introduction to Bravais lattices, the point groups and space groups.

And you have seen what are the 7 crystal structures or systems in 3D lattices. I have also briefly introduced the concepts of Miller indices and lattice planes in this lecture. And as we go along, more discussions will follow on these topics as we require them at different points. These are the references which were followed to prepare today's lecture and I thank you for attending the first lecture of week 3.