Physics of Functional Materials and Devices

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Lecture – 09, Week 2
Crystal structure - I

Welcome to the final lecture of week 2. Till now this week we have learned various fabrication methods or synthesis protocols by which we can obtain materials. Once we have materials then we can move to the next step and understand their properties. Following that we can then envisage the application of those materials. But once the material has formed you have got something formed it can be in the shape of a powder or any other structure you must understand what is the nature in which the atoms are first arranged. Then only you will have different types of materials.

I have made a sentence that will become clear to you in this lecture. It seems to be complicated, but it is very simple and it is essential to understand the concepts such as lattice, bases, and unit cells which are associated with the materials. Once you have materials we have seen in the first week that you can have two types of materials either crystalline or non-crystalline. If you obtain crystalline materials, then they show certain well-defined symmetry operations.

What are symmetry operations? Also, we will introduce to you in today's class. And based on symmetry operations you can then have various types of structures which can be classified under seven crystal systems in a 3D lattice. Each point in a unit cell can be defined using Miller indices. Why do we require them and what are those? How we calculate them will also be discussed in today's lecture. So, you start with the atom.

This is what we have seen in the synthesis protocols you start with atoms and then you want to have a material out of it. So, you will have atoms. Now, suppose what you do you have a fabrication route by which you are arranging the atoms in one line, in one line only. What will you get? You will get a 1D lattice. A lattice is what is a collection of atoms which have well-defined rotational and translational symmetry.

So, you have this lattice. So, it is a well-defined arrangement of atoms that defines a lattice. Now, you want to make a slightly more complicated structure and in that structure, you do not arrange atoms only in one dimension, not only in one dimension, but you also arrange the atoms in the second dimension. Let us say in the x direction as well as in y direction. So, what will you get? You will get a plane-like arrangement and therefore, you will get what? You will get a 2D lattice periodic arrangement of atoms in two dimensions and the distance between the two atoms may be defined as a in one direction, and it can be defined as b in the other direction if they are not a cubic lattice and you have a slightly different arrangement of atoms in the two directions.

Now, what is the logical step forward? I not only arrange in 1D and 2D, but I also arrange in the third direction. So, what do I get? I have atoms arranged in this direction, this direction as well as in the third direction. So, if you arrange the atoms over each other, then what will you get? You will get a 3D lattice. So, you have a 3-dimensional lattice. If you have a small number of atoms arranged, you will get a small crystal, and if you have a very large number of atoms arranged you get a very large size crystal.

So, that is what it is, but you can clearly see you have arrangements in all three directions and the lattice is such that you will have rotational and translational symmetry in this lattice. So, if I choose any point, then if I perform a rotation or if I have a certain translational along the direction in which the translational symmetry is defined, I will reach the same atom and two atoms of similar species cannot be differentiated and therefore, you can choose origin anywhere. I can choose the origin at this atom, somebody else may go and choose the origin at any other blue atom, does not matter. So, because these atoms of the given species cannot be differentiated, then you can choose the origin at any point this depends on the person who is analyzing this structure and you will still get the same lattice because the translational symmetry and rotational symmetries will hold good. So, if I move forward what are the various kinds of structures which I can get? This is a simple cubic structure.

It is a simple cube-like structure which you will have. So, you can get a simple cubic structure, you will have atoms at the cube corners, and then you can go to body-centered cubic. You have a cube which is formed by this atom and at the center of this body you have one more atom. So, it is called so, you have a cube with a, b, and c, equal to a, but at the center of the body, you have one another atom. So, it is called body-centered cubic.

So, BCC. Then you can have cross section of BCC looking like this because the front face will include these atoms and just behind that you will see the other atom which is of let us say solid in this cube, but it can be blue in the figure shown in the bottom left. And if you repeat this structure you can clearly see it just grows in one dimension and forms the whole crystal. So, this is a unit cell and if you repeat the unit cell one after the other you get the crystal out of the unit cell having a BCC structure. The formation of the whole material and the way electrons or free electrons move in this structure has been successfully explained using free electron model. This model is able to explain electrical conductivity, the thermal conductivity, the thermionic emissions, the thermoelectric effect and Galvomagnetic effects.

We will discuss this model in detail. It is a very important concept which we will discuss in detail in weeks 3 and 4, but the only concept that is required for today's lecture which is being utilized out of this model are that a metal crystal consists of positive metal ions whose valence electrons are free to move between the ions and the crystal is held together by electrostatic forces of attraction between the positively charged ions and negative charged electron gas. So, this concept is being utilized and we will try to understand some more things related to crystals. Now, we started with this example of 1D lattice. You had interatomic distance as a.

So, if you consider an atom, what do you have? You have a nucleus and you have an orbital electron, very simple picture we are considering. Then, if you plot the probability of finding an electron around a nucleus as a function of distance of nucleus, this same information comes out in this nature. So, this is what you have. There is still a vacant space on the left hand side. The figure will just emerge in few minutes.

Let me give you some information before I put that figure. Now, you have atom A, you have two atoms of species A now. They are forming a material. Now, there is if they are forming an a material what is happening? That means, they are coming towards each other. If two things are coming together and towards each other, what do you say? There is an attractive force acting on those species.

So, in this case, two atoms are facing or feeling the consequence of attractive forces. But we know that there is a distance of closest approach beyond which two atoms cannot come nearer to each other. So, two atoms will come nearer to each other, but after a certain distance, you will find that two species of similarly charged nature will repel each other. So, they repel each other. What is this? Initially an attractive force and then a repulsive force.

At which point will they stabilize where the magnitude of these attractive and repulsive forces are such that they are going to get minimized. And this was actually proposed by Lennard and Jones and therefore, it is defined as Lennard Jones potential. So, force there are two types of forces acting attractive forces and repulsive forces. If you plot these curves that is the attractive force and the repulsive force as a function of inter atomic separation. Now, two atoms do not feel this force individually that first they will feel the attractive force, then they will feel the repulsive.

No, they see a convoluted picture and therefore, if you add the contributions of attractive forces and repulsive forces, you get a net curve that is the convoluted curve which gives you the nature in which the force is acting. And that is where they come and stabilize at a distance r_0. So, the force exerted by the atoms or molecules on each other is the derivative is the derivative of the Lennard Jones 6-12 potential. Why it is called 6-12 potential? Because of the exponent which you have. So, you have the Lennard Jones 6-12 potential, the attractive force varies as a function of 6 and the repulsive force varies as a function of 12 and therefore, it is called as 6-12 potential.

And these sigma and epsilon are parameters which correspond to the bond energy and length respectively. So, if two atoms are near to each other there is a bond length. So, and both the atoms feel certain amount of energy. So, depending upon this energy and length you define the term sigma and epsilon respectively. And they are obtained by fitting to the known properties of material.

So, you know what are the properties of the materials and you extract sigma and epsilon from those concepts. Hence, if you look into the plot of potential energy as a function of attraction and repulsive forces you have similar concept, you have repulsive energy and you have attractive energies and the net energy is coming as the curve shown in brown. And this is what you have all read and seen in the book. The potential energy function of a lattice or a material. What is the potential energy function as a function of r? This is what you have seen the potential energy function as a function of r.

So, you have been plotting the potential energy function as a function of r. So, I hope you understand from where this curve comes. This curve is a combination of two contributors one is the repulsive energy term and the other is the attractive energy term. Now, the atoms have arranged themselves. Once they have arranged themselves they can either arrange themselves in crystalline form or non-crystalline form.

And in physics, there is a branch known as condensed matter physics or solid state physics, which particularly deals with crystals and the properties of these crystals as a function of size, as a function of shape, or as a function of electron motion in these solids. So, there is a whole branch of physics that deals with these kinds of materials. Now, we have synthesized the material we know that they can be either crystalline or noncrystalline. What are crystalline solids? They are homogeneous solids in which the constituent particles or atoms or ions or molecules are arranged in a definite repeating pattern. They are arranged in a definite pattern.

So, if you move from one region to the other you will find the same environment. So, it is a definite pattern whereas, in noncrystalline or amorphous solids that does not happen. The atoms molecules or ions are arranged in an order which is called short-range ordering an if you move from one region to the other you will find that the environment within that arrangement may be very different. For example, if I take this structure region and if I take a similar region here you will find that it looks to be very different. So, within this region you can have certain orders you can have small range ordering, but if you talk from one region to the other you will have dissimilarities they are not similar.

But if I look into a crystalline solid then they all look the same. So, as I move through the lattice they are similar. So, they have long-range ordering, and noncrystalline systems have short-range ordering. These kinds of materials include glasses, plastics, gels, polymers and melts, which we will discuss later. As we had seen in the first week single crystal and polycrystalline solids are sub-classification of crystalline solids.

Now, we want to understand mathematically what we understand by the crystal. There are a few terms that were introduced and you must understand them before we start talking about crystals. The basis is an ideal crystal constructed by the infinite repetition of identical groups of atoms. This group is called basis. So, in an ideal crystal if you construct that crystal then there is a small repeating unit that you will repeat continuously and that small unit is called the basis.

And it need not be just one atom, it need not be one atom it can be anything it can be four atoms. But then if you repeat this unit at each lattice point you just go on putting this unit then this group of atoms that are repeating is forming the basis. Lattice the set of mathematical points to which the basis is attached is called the lattice. So, this is a lattice it can be a 2D lattice. If I have a lattice point this basis is attached to a lattice point which means at a lattice point you will end up having maybe five atoms.

This will form one lattice point. It is not necessary that one lattice point has only one atom. You can take this example a simpler example of two atoms of slightly different sizes. And what are we doing? We are repeating this atom at each lattice point. So, what would be the basis? This unit would be the basis which is being placed at each lattice point. So, lattice plus basis gives you the crystal structure.

And if you have a crystalline solid you will find that the lattice of this solid will have identical surroundings which means that the lattice contains a small group of units called the pattern unit which repeats itself by means of translational operation t. So, as you move forward you just go on repeating this unit. What is the consequence? It means as you move along any direction then you will find a similar environment throughout the lattice. So, if you define t as the translational operator then if you have $n_1\vec{a}$, $n_2\vec{b}$ and $n_3\vec{c}$, where n_1, n_2 and n_3 are integers then what do you have? You have the translational operator $\vec{T}$, which will give you that when you move by this distance you will get another lattice point. Hence $\overrightarrow{r'}$ would be $\vec{r}$ plus $\vec{T}$ that is equal to $\vec{r} + n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$.

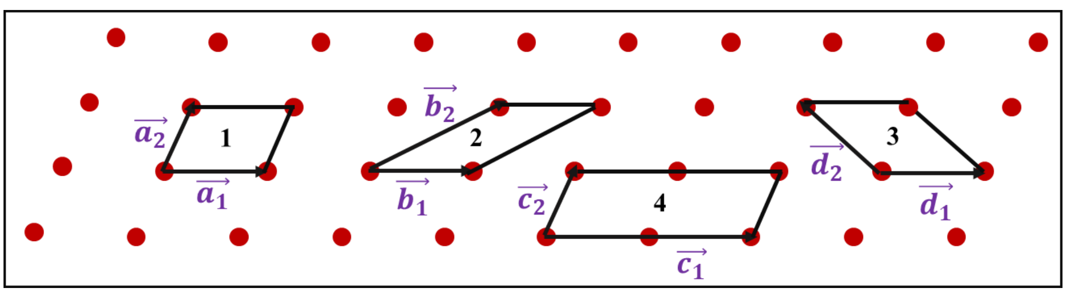
So, from one point to the other if you translate by this value you will get the same point or a similar environment once again. This equation is satisfied for a perfect lattice and $\overrightarrow{r'}$ can be obtained from $\vec{r}$ by the application of operation 1 which is given by equation 1 in this case. In an imperfect lattice, it is impossible to find the sets of $\vec{a}$, $\vec{b}$ and $\vec{c}$ for which the arbitrary choice of n_1, n_2, and n_3 can give $\overrightarrow{r'}$ which is similar to $\vec{r}$. The set of vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$ are called the crystal axis or basis vectors. So, you will find if you have a lattice given by the arrangement of red solid structures then the set of vectors $\overrightarrow{a_1}$, $\overrightarrow{a_2}$ or $\overrightarrow{b_1}$, $\overrightarrow{b_2}$ or $\overrightarrow{d_1}$,

$\overrightarrow{d_2}$ are all sets of primitive vectors, but the set of vectors $\overrightarrow{c_1}$, and $\overrightarrow{c_2}$ are non-primitive translational vectors.

What is it? These values c_1 and c_2 are quite different. The parallelograms marked as 1, 2 and 3, 1, 2 and 3 have the same area and any one of them can be taken as a primitive cell. What does it mean? It has only one atom per unit cell. So, it is a primitive cell and you can calculate the values of r dash and r double dash.

Then comes the concept of unit cell. What is a unit cell? It is the smallest group of atoms that has the overall symmetry of the crystal and from which the entire lattice can be built up by the repetition in three dimension. So, unit cell is the building block of the whole crystal and it is a building block means unit cell has the same symmetry or properties as that of the large crystal. So, this is what it means. It is the unit cell which can be used to create the entire lattice by putting and arranging the unit cells in all the three directions. So, a unit cell will become primitive or non-primitive type unit cell.

A primitive cell is the smallest volume cell. All the lattice points belonging to the primitive cell reside at its corner. The effective number of lattice points in a primitive cell is 1. The effective number of lattice point in a primitive cell is greater than 1. The unit cells marked as p represent primitive unit cells and NP represent the non-primitive cell. You will understand this concept which is given in point number 3.



Representation of primitive and non-primitive translational vector

In detail as we move further. So, any type of crystal structure always satisfies the symmetry operation and what are symmetry operations. We talked about certain concepts when we were introducing lattice and what was that? That the lattice is formed by arranging atoms in a periodic manner or in a given manner such that you have rotational and translational symmetry. So, you have already understood certain things rotational and translational symmetry. The concept of symmetry basically describes the repetition of structural features. What do I mean by that? As I move from one point to any other point in the lattice and if that point has similar environment as the initial point, what is the feature which relates point number A to point number B in the lattice? So, these give you the structural features of a unit cell and crystals therefore, possess symmetry and much of the discipline of crystallography.

You have heard about the subject crystallography. The subject crystallography is concerned with the describing and listing the different types of symmetry which are obtained in various types of materials. So, if you make materials with different types of methods and if they have conditions where atoms arrange in different manner then their symmetries are different that means, the environment in which the atoms are different. And how will they affect the properties? Suppose there are two atoms which are at a given distance shown by my fist. So, there is a distance A, but now I arrange the atoms by which the distance between the two atoms become much larger. Obviously, the bond energy and bond lengths are very different and hence the properties of this material would be different.

Therefore, the symmetry of the crystal also defines the properties of the materials. The crystal symmetry hence can be defined as translational symmetry and point symmetry. This describes the periodic repetition of a structural feature across the length or through an area or volume of the unit cell. So, it is through and through the crystal. It is not only at one point you move from one region to the other the crystal symmetry remains the same if you have a crystalline solid.

And it describes the periodic repetition of a structural feature around a point. These can be reflection, rotation or inversion. So, you can have inversion symmetry about the point. If you have a plane lattice then you will produce these lattices by translation along two vectors.

So, you have a plane lattice. So, if you have a plane how will you produce? You have to move in this direction as well as in this direction and therefore, you will consider two vectors. The constituents it can be atom or an ion or a molecule are repeated with constant distance and angles that produce five unique plane lattice. They are hexagonal, square, rectangular primitive or centered rectangular and oblique. This is a typical square lattice which is of plane lattice type. Then you have a rectangular lattice can you see the difference between the two? Obviously, you can see A and B that is the lattice parameters or the dimensions of square and rectangular are different in x and y directions.

So, you have two types of lattices which are described. Then you can create an oblique lattice, you can have a hexagonal lattice or you can have a centered rectangular lattice. So, you can see that there is a atom in the center of the rectangle. So, it is centered rectangle lattice. Then you have space lattices.

Space lattices are produced by translations along three vectors. In translations around two vectors what were you getting? You were getting a plane like structure sheet like structure. If I also consider the three dimension that is the third dimension c axis what will you get? You will get a three dimensional structure that is what it is. So, here the repeating units are such that they repeat after a constant distance and angles in 3D and because of this you have 14 unique space lattices which are also known as Bravais lattices. So, they are also known as Bravais lattices and they are compatible with 7 symmetry systems and 32 symmetry classes. So, all these lattices which are there in 3D can be classified under 7 crystal systems or symmetry systems.

Let us consider a typical crystal symmetry. Consider the following crystal and then see what happens when we move it from one point to the other following different symmetries. So, let us consider this lattice and we are just marking it at one point as a red dot just to differentiate and explain the feature to you. You rotate this lattice and you will see that after rotation of 360° you came back to the original point you came back to it. So, we see that after the crystal is rotated by 360°, it comes back to its initial position. Now, I do not want to repeat it by 360° I want to repeat it by 90°, but 4 times let us see what happens.

So, we start from condition 1 then we rotate by 90°. So, you rotate around by 90°. So, you have reached this point. So, around an axis you have rotated by 90° then you rotate again by 90° you find that atom has translated to this point. Again you rotate by 90° what do you get? You find that the atom has now come here and finally, if I rotate again by 90° I come back to the original point which is defined.

Hence, we can say that the crystal has 4-fold rotational symmetry. If you rotate the crystal 4 times then you will come back to the original symmetry and then you call it a 4-fold rotational symmetry. This is an example of symmetry operations in a crystal. In general, there are 3 symmetry operations in crystals which we have defined as rotational reflection and inversion. In some cases, you will find that the combination of these 2 also exists. In rotational symmetry, the imaginary axis along which the rotation is performed is an imaginary axis around which the rotation of the crystal is performed is an element of symmetry referred to as a rotation axis.

This rotation symmetry axis which is possible in the crystal is 1, 2, 3, 4, and 6. You see we do not write 5 in there. Why? Because if you have lattice and when I perform the rotational symmetry then by that you should not end up in a condition where you have lattice where the whole space is not being filled and you are leaving voids in the middle. Then it is not a lattice formation and hence you do not have 5, 7, 8, or higher order symmetries because they do not fill the space completely.

But if you look into nature, nature is very different. It actually gives you examples where you see objects with 5, 7, 8, or even higher-order symmetries. So, you can see that there are examples in nature and to replicate these structures is not easy. Hence crystalline structures are routinely synthesized in the lab and the ones we will be discussing in this course will be mostly those that have 1, 2, 3, 4, or 6 rotational symmetries. So, can you understand what is one-fold rotational axis? An object that requires a rotation of a full 360° to restore its original appearance.

So, you will see it will rotate and then you will get it original symmetry. Then two-fold what would it would be? It would be basically that you will have to rotate it twice to come back to its position. So, 360° brings you back to the origin. If you have two-fold then what would be the rotation? It would be rotation by 180°. If you have three-fold rotation, what it would be? An object that repeats itself after a rotation of 120° is said to have a three-fold axis of rotation. So, you will find an atom here rotating at 120° there will be an atom, rotating by 120° there will be an atom and then you rotate by 120° you will again have an atom and the atom is the one which you started from.

So, you will have atoms at 120° after rotation from the original point. Four-fold symmetry you will have atoms after rotation of 90°. So, you will have atoms once you rotate by 90° you will find an atom, rotate this atom by 90° you will find an atom, rotate this atom by 90° you will find an atom, and then rotate again the atom at point D let us say you will come back to the original lattice and a filled square is used to similar symbolize the location of the four-fold rotational axis. Similarly, you can define a three-fold rotation axis, and some other examples which are there which give you examples of atoms are 1, 2, 3, 4, or 6-fold symmetry-based atoms are shown in the curves given below. And the famous painting by Leonardo da Vinci which is of the Vitruvian man can you now understand why this picture is so important and how this tells you about the symmetry operators which are there in materials and you will be amazed to see how this painting actually describes the symmetry operation. Try to find the answer if you cannot we will discuss more about that in the online interaction sessions.

And finally, you have the operation that is called inversion and this is through a point. In this operation, lines are drawn from all points on the object through a point in the center of the object called the symmetry center, and it is symbolized by the letter I. And once you invert that means, you move from your invert about this point you will find the atom once again. So, you will have the atoms once again you can clearly see if you look into these two examples around this point the atoms have inverted and you have the inversion symmetry. In today's lecture, we have talked about the concepts of lattice, bases, and unit cells.

We have also talked about crystals the types of crystals and the symmetries associated with those crystals. Also, what are the various operations that can be performed to get crystalline solids and how does a noncrystalline solid differ from a crystalline solid? We have also given you the basic concepts of Bravais lattices, point groups, and space groups. In the next lecture which we will start in week 3, we will go a step further and try to understand more about the unit cells and types of unit cells that are there. These are the references which you can follow to get more information about the topics that were discussed today and. Thank you very much.