Physics of Functional Materials and Devices

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Lecture – 11, Week 3
Crystal structure - III

Welcome to lecture 2 of week 3. We have seen till now the details of various synthesis protocols which are used to obtain different types of materials. These materials can have crystalline or non-crystalline type character. If you consider crystalline materials, then they can be single crystalline or polycrystalline type. And all the crystalline materials, if they are in three-dimensional type arrangement, then they can be classified under seven crystal systems which show one of the fourteen possible Bravais lattices. Let us continue and now understand what happens and how do you actually determine the way the atoms are arranging in a given manner.

That means if they are arranging in cubic type lattice, that means you have atoms arranging in a way that the unit cell would have the lattice parameter a equal to b equal to c and alpha beta gamma equal to 90 degrees or you can have arrangements where the atoms show a tetragonal type arrangement in a given unit cell. So, in today's lecture, I will start with the discussion on X-ray diffraction. Why this technique is useful for determining the crystal structures? Why do we introduce the concept of reciprocal lattice? From real lattice, we go and introduce the concept of reciprocal lattice. And finally, using the concept of geometrical structure factor, how do you determine the intensities what you see in X-ray diffraction measurements? We have already seen the difference between single crystalline solids, the polycrystalline solids and amorphous solids.

And they are primarily depending upon the growth mechanism and the ordering. So if you have growth only in one of the preferred directions and you have long range ordering, you get single crystal. If you have growth in such a way, you do not have any preferred direction of growth, but you still show long range ordering, then it is polycrystalline. And if you do not have long range ordering, then you see amorphous solids. And you can have various types of crystal structures, which are belonging to different types of crystal systems.

And if you see different types of materials, you will find that the atoms are arranging themselves in different ways in these unit cells and hence the properties of these materials are very different. You can clearly see that iron oxide is arranging very differently to itself if you see manganese oxides or sodium iron phosphates or cobalt oxides or copper 2 oxide or tin oxide. These are just the examples which I have taken because these are the materials which we will be talking about as we move forward in this course. So they do not have a specific reason that only these have to be mentioned. Because these would be useful for us in this course, so I took them as an example, you can take any other material to amplify your understanding.

So how do we actually visualize the arrangement of atoms? This was very nicely done by understanding the concept of X-ray diffraction. What is diffraction? If you see diffraction, diffraction is basically the interference or bending of waves around the corners of an obstacle or through an aperture and the wavelengths have a similar size of or magnitude as that of the aperture. The diffraction patterns are such that you will have a series of bright regions and dark regions and X-ray diffraction was used to understand how the atoms are arranging, but how it was used and why this became such an important technique for all of us. If you look into the arrangement of atoms in a crystal, so what do you have? You have atoms, they are arranged. What type of lattice are we seeing here in this example? This is a typical two dimensional lattice, but now please also imagine that there are atoms arranged in the plane coming out of the screen or inside going inside the screen.

So you have a 3D lattice. You have distance between two atoms that is the atomic spacing, but one layer of atom and then you have another layer of atom. There is a distance between the two. So you have an additional thing. What is that? That is called the interplanar spacing.

Mathematically we had seen in the previous lecture what is the value of d in a cubic type unit cell and you can similarly calculate for other unit cells also just by changing the value of h, k, l and a, b and c. This phenomena of diffraction in crystals was first suggested by a German physicist von Laue in 1912 and Friedrich and Knipping successfully demonstrated the diffraction of x-rays from a single crystal of zinc blend type structure which we studied in the first week and the whole theory was verified experimentally. For diffraction conditions you will see that the wavelength of the incident radiation is similar to the lattice constant or less than that. Now in a crystal what do you have? You have atoms which are arranged. The distance between two atoms are of the order of what? Are they millimeters? No, they are of the order of angstrom.

Angstrom means what? 10 raised to the power of minus 10 meter. So you have atoms separated from each other by values which are of the order of 10 raised to the power of minus 10 meter. Therefore if this condition has to be satisfied then the wavelength range which you should consider to observe diffraction in crystal should have what values in this region? This region means what? Let us say from 0.1 to 10 Å. If you see the spectrum you will find that x-rays have wavelengths in the range of 10^{-10} meters while the visible spectrum gives you the values of wavelength in the range of 10^{-6} meter or so.

So optical wavelength is approximately from 4000 to 7000 Å. In this case what it means that lambda becomes much much greater than d if the d value which we are considering, are in the range of let us say 0.1 to 10 Å. So will you see diffraction in crystals using the visible light? Yes or no? You will not be able to see that. You will mostly see ordinary optical reflection.

Then came the famous work by Bragg which is now known as Bragg's law and that explained the way you will see the diffraction pattern and from there you can go on to calculate the d spacings and if you know the d spacings you can then calculate the atomic arrangements and then from there you can calculate or estimate the crystal system to which that lattice belongs to. Bragg's law tells you that $2dSin\theta = n\lambda$. As $Sin\theta$ is much much less than 1 or equal to 1 at the most lambda is equal to less than or equal to d and this is the condition which was required. Let us see how this was actually calculated mathematically. What is a grating? A grating is a large number of slits arranged in a small area and that leads to high intensity diffraction patterns because you have multiple diffraction beams falling at one point because you have large number of diffraction beams coming in from these apertures they convolute and hence the intensity goes up and that is the diffraction grating experiment which you have been doing in your first year.

Now, if you look into the arrangement of atoms you have these arrangement of atoms. In between these two atoms there is a space. So, what do you actually simulate? You actually simulate the condition of a grating and if this atomic arrangement is simulating the condition of a grating can you have the same behavior and see the diffraction pattern. If you can do that then you can easily determine the conditions of maxima and minima and as you change this value of aperture width the maxima and minima will change their position and you can then go on making various combinations and you will be able to determine the values of d. This was basically done in this mathematical calculation of diffraction conditions.

So, let us consider a collimated beam of monochromatic x-rays of wavelength lambda. If you do not consider monochromatic waves then you may have conditions where diffraction maxima coming in because of the first wavelength is superimposing on the third maxima coming in from any other wavelength if you had an source which was giving you heterogeneous wavelengths. So, you had a series of wavelengths coming in. Then you can never find out the intensity is coming in from which wavelength and then the whole experiment falls apart and therefore, you have to use a monochromatic x-rays. You will see that the most common target which is used is copper and copper has $k_{\alpha 1}$ and $k_{\alpha 2}$ and you need to actually consider the contributions of both $k_{\alpha 1}$ and $k_{\alpha 2}$ while determining the intensity which you see in a diffraction pattern coming in from material if you had the copper as the target from which the wavelength was originating.

Else you have to use filters to eliminate $k_{\alpha 2}$ so that the highly intense $k_{\alpha 1}$ only falls on the sample. So, there are cases where you may see a closely spaced wavelengths which are originating from the target, but then you can use filters to eliminate one of them and you will have only one wavelength that is monochromatic wavelength falling on the sample.

So, you take a collimated beam, parallel beam of monochromatic x-rays and they are made to be incident on the diffraction grating which is formed by the periodic arrangement of atoms. So, this is let us say beam 1 which is p and beam 2 is q. Now, beam 1 which is p gets reflected from the first plane and you have a diffraction beam as r.

The second beam crosses the first plane and is diffracted from the atom in the second plane and the beam which you get is s. But if you calculate the extra path which beam 2 has to traverse, then it turns out to be that this is the extra path which beam 2 has to traverse before it reaches the screen. This path difference is basically what is coming in if you have O and O' as the two points from which the diffractions were taking place for beam 2 and beam 1 respectively, then the path extra path which beam 2 has to traverse is MO' + $O'n$. So, if you take the projection of this wavelength the path by considering d, then that MO' = d$Sin\theta$ and $O'n$ = d$Sin\theta$ what is equal to δ that is 2d$Sin\theta$. Now, for constructive interference of beams we know what that delta should be an integer should be an integer and hence if you have constructive interference 2d$Sin\theta$ should be equal to what λ, 2 λ, 3 λ, 4 λ that is an integer and hence you have the value n mentioned here.

2d$Sin\theta$ is equal to nλ this is the way you have the mathematical explanation of Bragg's law and the integer n is called the number of order of diffraction. So, if you have n equal to 1 this first order n equal to 2 second order n equal to 3 third order and so on so forth. As I mentioned earlier since $Sin\theta$ is less than equal to 1 and λ is also satisfying the condition that it is nearly equal to the d spacing or less than d spacing you have the condition of diffraction taking place. This mathematical formulation was converted into experimental tool and this was used to determine the phase of a crystalline material and in today's world this is one of the most fundamental technique which is used to determine the structure of a crystalline material which is solid. So, what you will have? You will have an X-ray source, you will have a sample and you will have a detector.

Because you have various planes which are forming in a crystal, the diffraction beam will be at different angles. So, you scan and you find the various conditions of maxima and from there you can then calculate the d values because you know the value of the theta, you know the value of lambda and by changing the values of n you will find out what would be the value of d which will satisfy that diffraction patterns. But please note X-ray is an extremely extremely powerful technique. People only use it for phase determination and it is not true. It is extremely powerful and it can be used for various other experiments.

Just to give you an overview of what X-ray diffraction pattern carries. It carries two types of features. It has a background, it has reflections. Do not ignore background. Even the background from an X-ray diffraction experiment has certain information.

It carries information about the sample, which is count and scattering, TDS, the amorphous content, the PDF, the local order disorder. If you look into reflections, it has three points.

It has a position, it has the profile and it has the intensity. If you analyze just the position, you can determine the unit cell parameters, the symmetry associated with the given lattice, the space group which is leading to that particular kind of diffraction pattern and you have the ability to actually analyze the phase if not quantification is possible, but qualitatively you can determine the phase which is resulting in a given diffraction pattern. If you look into the profile, you have the capacity to determine the particle size and which is very important for many features you will see later on.

If you determine the profile shape correctly, then you will be able to find out the strain inside a lattice. It has its own consequences. And finally, by analyzing the intensity of the diffraction profiles, you can find out about crystal structure, atomic positions, the temperature factors, the occupancies and quantify the phase which is leading to a given diffraction patterns. But when people started talking about diffractions, then there were certain difficulties which were being observed. If you take the fifth order of a given plane, then you had to draw that on a piece of paper and that plane was becoming difficult to explain.

So, to imagine the plane and explain to the people who were trying to analyze the diffraction patterns, it was becoming very difficult to explain the different orientations and spacings which are observed in a crystal. And these kind of problems was simplified by evolved by developing a new type of lattice which is known as reciprocal lattice. What happens in reciprocal lattice? Each point in a reciprocal lattice corresponds to a particular set of parallel planes of direct lattice. The distance of a reciprocal lattice point from an arbitrary fixed origin is inversely proportional to the interplanar spacing of the corresponding plane in the direct lattice. And that is why it is called reciprocal.

You are taking the inverse and hence you are talking it as reciprocal lattice. And the volume of the unit cell in a reciprocal lattice is inversely proportional to the volume of the corresponding unit cell of the direct lattice. So, if a and b are the lattice parameters in real lattice, in reciprocal lattice you may represent it as a star and b star. If you talk in unit vectors in real space as $\mathbf{a}_1$**,** $\mathbf{a}_2$ and $\mathbf{a}_3$**,** then the unit vectors in reciprocal lattice would be $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$. And the relationship between the two are that $\mathbf{b}_1$ is equal to $\mathbf{a}_2$ cross $\mathbf{a}_3$ divided by $\mathbf{a}_1.\mathbf{a}_2 \times \mathbf{a}_3$ and similarly you can define $\mathbf{b}_2$ and $\mathbf{b}_3$ vectors.

$\mathbf{a}_1.\mathbf{a}_2 \times \mathbf{a}_3$ is what is basically the volume of the unit cell. And hence what would be the value of $\mathbf{b}_3$? That would be $\mathbf{a}_1 \times n\mathbf{a}_2$ by V, while $\mathbf{b}_3.\mathbf{a}_2$ and $\mathbf{b}_3.\mathbf{a}_1$ will be equal to 0 because $\mathbf{b}_3$ is perpendicular to $\mathbf{a}_1$ and $\mathbf{a}_2$ planes. So, simple vector calculations. As I said the volume is $\mathbf{a}_1.\mathbf{a}_2 \times \mathbf{a}_3.\mathbf{b}_3$ is what? $\mathbf{b}_3$ is for example, if you see a unit cell given on this slide, then $\mathbf{b}_3$ is what? Area OA OACB divided by area of OACB into OD that is equal to 1 by OD that is equal to 1 by d_{001} plane.

Similarly, you can get **b_2** which is 1 by d_{010} plane and **b_1** which is 1 by d_{100} plane. The reciprocal lattice vectors for the plane with Miller indices (h k l) is represented by h capital H of (h k l) is equal to **h b_1** vector, **k b_2** vector and **l b_3** vectors. Please remember there are two fundamental properties. (h k l) vector is perpendicular to the plane of h k l that means, the vector h k l if you take the magnitude of this vector h of h k l that is equal to 1 by d_{hkl}. So, if you want to calculate and see what happens if you let us consider a case of simple cubic lattice where the primitive translational vectors would be **a_1** is equal to a **i**, a_2 is equal to a **j** and a_3 vector is equal to a.**k.**

You have the volume as a cube. Let us see what would be the values of **b_1 b_2** and **b_3** vectors they would simply be 1 by a into unit vector **i** 1 by a into unit vector **j** and 1/a into unit vector k respectively. The reciprocal lattice to simple cubic lattice is also a simple cubic, but what have you seen earlier you had a as the lattice constant here what was happening it was just becoming 1 by a. So, this is what was happening. If you see the reciprocal lattice for a body centered cubic then for a body centered cubic what do you have you have vectors a', $b'$and c'equal to body center. Please remember we are talking about there is a atom at the body center a' is equal to what a by 2 i plus j minus k b dash is equal to minus i plus j plus k and c dash is equal to a by 2 i minus j plus k.

The volume is known is what a dash dot b dash vector cross c dash vector. What do you get you basically get the value as a 3 $a^3/2$. You take the reciprocal now what you will get you have **a***, **b*** and **c***. $\boldsymbol{a}^* = (\boldsymbol{b}' \times \boldsymbol{c}')/$ Volume, $\boldsymbol{b}^* = (\boldsymbol{c}' \times \boldsymbol{a}')/$ Volume and $\boldsymbol{c}^* = (\boldsymbol{a}' \times \boldsymbol{b}')/$ Volume.

So, you have the corresponding values. And if you see into this calculation you will find they represent the condition where there is an atom at as if it is simulating an FCC lattice. And therefore, the reciprocal lattice to a BCC lattice is an FCC lattice. Similarly, you can show that for an FCC lattice if I calculate the vectors and from there I calculate the volume you will find that the reciprocal lattice to a FCC lattice is a BCC lattice. This is very important and you must understand it clearly. Reciprocal lattice of an FCC lattice is a BCC lattice and a reciprocal lattice for a BCC lattice is a FCC lattice.

But the next question which comes is the diffraction observed for all set of planes. Let us find out. Before that let us see why the diffraction is taking place and what is the intensity which is associated. The intensity of a diffraction peak from an HQL plane depends on the geometric structure factor and the intensity is proportional to the square of this structure factor. What is structure factor? This is the amplitude of the wave scattered by all atoms of a unit cell divided by the amplitude of wave scattered by one electron.

So, F_{hkl} is basically equals to summation about j that means all atoms $F_j = e^{2\pi i\,(hu_j + kv_j + lw_j)}$where h, k, l, can take all possible values in a given unit. And this scattering amplitude you will find the structure factor if you have F as F_{hkl} then scattering amplitude is F given as amplitude of wave scattered by an atom divided by the amplitude of wave scattered by one electron. And as I said u_j, v_j and w_j are the fractional position of atoms in a unit cell. So, F_{hkl} in a given unit cell shown in this slide would be what? would be what? You will have all possible values which are given by the arrangement of atoms. So, F_{hkl} is equal to summation of small f_j for different values of j.

So, diffraction will only be observed for all sets of plane which are available in a given unit cell. There is no restriction in h, k, l values to the observed diffraction patterns, but the possible h, k, l values are dependent on the arrangement of atoms and hence they are related to the crystal structure. Mathematically there are no restrictions, but physically the restriction comes from the symmetry, the point group and the space groups which are associated to a given crystal. So, this is what you can then find out for a BCC lattice and you will find that the diffraction will only take place if the summation of h + k+ l is equal to even.

You can find out for an FCC lattice. The diffraction pattern will only occur if you have the case when the sets of plane for which h, k and l is unmixed. So, you will have (1 1 1), (2 0 0), (2 2 0). So, either all are even or all are odd. You cannot have a mixed like (2 1 0).

So, you cannot have odd and even mix. So, for a case on a FCC you will have diffraction where h, k, l is unmixed. It is not a combination of even and odd numbers. Now, if an X-ray falls on a material it can lead to various phenomenas. It can lead to heat, you can have fluorescence, you can have transmissions, you can have scattered X-rays, you can have emissions because high energy beam is coming, hitting the material and you can have electron emissions. If you consider scattered X-rays, then you can have coherent or incoherent type scattering.

If you talk about electron emissions, you can have Compton recoil, you can have photoelectrons or you can have Auger electrons which are coming in. So, there are various features which can be observed in materials by the incident X-rays and various experimental techniques have been developed. So, you can have photoelectron emission spectroscopy, you can have Auger electron spectroscopy, you can have fluorescent X-ray diffraction or scattering effects or you can have Compton scatterings. So, you can have various experimental techniques. If you look into the experimental arrangement in the typical laboratories or the master or research level laboratories, you will find that these experimental techniques have a source, a place where you will have the holder for inserting the sample, you will have a detector which would detect the diffraction patterns and based on these combinations, based on these combinations you have various methods.

So, if you have a diffractometer, what am I talking about? I am talking about a monochromatic source, a powder sample mostly, a detector which can be countered and this will give me a diffraction pattern. Similarly, if you have a variable wavelength, a solid sample and the detector is film type, you have a Laue diffraction method. So, these are the diffraction methods which are there depending upon the combination of source, the sample and the detector which are utilized. So, I hope now you understand what are the various methods.

This is the typical way by which you get an X-ray. So, if you have an high energy electron impinging a target which is an anode, then you have the emission of characteristic radiation along with the continuum. This is for copper K alpha. So, how does a X-ray refractometer looks like? What do you have? You have the stabilizers which will stabilize high voltage and high current. Then you have the high voltage generator, you have the X-ray tube. Once they are giving the X-rays, you have the slits which will allow the wavelength to go through.

Then you have the collimators which will make the beams parallel. These parallel beams will fall on a sample. You will have the diffraction taking place. You can have a monochromator here and from there you have a detector. This detector the signals are quite weak and it goes into amplifier and then to data analysis center and finally, you have the data which is obtained.

This is a typical block diagram of an X-ray diffractometer and this is what a diffractometer looks like. You have the source, the filters, then you have the solar slits, the divergence slits so that the beam actually falls on a larger portion of the sample. Then you have the filters. So, if there are any other diffraction peaks coming in from extra wavelengths other than the wavelength which you wanted to fall on the sample, they are eliminated. Then you have the receiving slits, the secondary solar slits and finally, after they go through the scattering slits, the detector analyzes the sample.

You have to be very careful while you prepare the sample. It is not a trivial exercise and you cannot just ignore that you can put any kind of sample and analyze these to get a useful. Let me show you how to obtain a useful data in X-ray diffraction experiments. So, if you want to have a X-ray diffraction data, you need to first take the sample. Crush it into fine and homogeneous powders.

Otherwise, you will see some artifacts. Why? Because the distance from the source to the sample and to the detector is one thing which is used to calculate the values. Now, if you have sample which is up and down, it is having different sized large size grain which is on the surface. Then what will happen? At certain points the distance from the source to the sample for the wavelength which is travelling will be slightly different and same thing will happen when the wavelength travels from the sample to the detector. And hence the d values which you estimate would be slightly different. So, for a powder diffraction data, you must first have a finely grinded powder and then you take the sample holder.

It can be a glass slide or if you have any other large size material, then you can use a steel sample holder. This is a glass slide on which the sample is being prepared. So, you sprinkle the powder on this and then using the glass slide, you make thin sample on the sample holder. You must rub it not only in one direction, but in all the directions so that you do not induce any preferred growth on the sample surface.

Once you have prepared the slide, then you clean the slide. You should not leave any point or space vacant on the sample otherwise again because some wavelength will then travel up to the distance which is hitting the back of the sample and then the two wavelengths which will interfere would be travelling different path and hence you will get different kind of diffraction patterns. You should make sure that the sample holder is such that it is it has a stable sample because as they move in the diffraction experiment setup that is the refractometer, they should not fall inside the diffractometer. This is a typical tabletop x-ray refractometer.

You have the generator. So, you put the sample in the middle. You have the generator. Then you have the detector on the other side. Once you load the sample, the beam will come hit the sample and then it will go in the direction of the detector and the detector will move in the theta to theta direction and you will be able to get the diffraction data. This is the typical way you perform the diffraction experiments.

So, the handling of reactive samples must be very carefully done. Do not use any material which is going to be reacting to the source. Avoid all possible sources of contamination. Seal the sample with appropriate transparent media if you are finding a condition where the sample is not stable or is not sticking to the sample holder. And after the data collection, you have to then carry out the pattern treatment that means peak search, background corrections, smoothening and $k_{\alpha 2}$ stripping. And then you can go on to obtain the data which can correspond to crystals, amorphous solids or liquids or monoatomic gases.

So, you can have single crystalline, polycrystalline or amorphous type diffraction patterns. So, I hope in today's lecture you have understood the importance of determining the crystal structure, how that will affect the properties of materials, the basic technique of X-ray diffraction which is used to determine the phase and the lattice which is resulting in a crystal system, why you need to understand the concept of reciprocal lattice and what is reciprocal lattice vector and how you have the geometric structure factors of simple cubic, body centered cubic or face centered cubic and how reciprocal of BCC is an FCC lattice and reciprocal of an FCC lattice is a BCC lattice. And what is the importance of calculating the various structure factors. These are the books which were used to prepare today's lecture and you can follow them to develop even more understanding.

If you have any queries, you can write to us or contact me during live sessions. Thank you very much. Thank you.