Experimental Physics - III
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Lecture – 60
X – Ray Diffraction and Crystal Structure (Contd.)

In earlier class, I have discussed about the X ray production and its properties, and then I have discussed the diffraction of light and Diffraction of X Rays. Now we have seen that from diffraction of X ray, so there nature are grating we use the crystal; crystal of some materials.

The diffraction is that to the synthetical to lambda that is the Bragg condition for getting the inference maxima that we tell the Bragg peaks, so henceforth I will call it Bragg peaks. from X ray diffraction we get Bragg peaks at different angle theta, that we tell Bragg angle and that each Bragg peak, since we are considering only first order n equal to 1.

each Bragg peak corresponds to the to a particular set of parallel planes which is having a particular d. different Bragg peaks we will get, so the different Bragg peaks are from different set of parallel planes ok, so they have different d. analysing, so from X ray diffraction we measure d; we measure d. Experimentally we measure d not d, experimentally we measure Bragg angle theta; Bragg angle theta. Theta for different Bragg peaks, if you know theta for different Bragg peaks, then since lambda is known to you.

2 d sin theta equal to lambda; lambda is known, theta we are measuring from the experiment, then we can calculate d. d is the planar separation. there are few Bragg peaks in one experiment, so we will get different d, d value; different d value Now, d is the planar spacing, so d is related with the lattice parameter say a b c and their angles, alpha, beta gamma

In addition, from that relation from, so solving you see solving these 2-3 equations, which will come from for 2-3 Bragg peaks; 2-3 Bragg peaks will get d 1, d 2, d 3. Now, d 1 is related with the Miller indices and the lattice parameter

If you solve them then you will get; you will get these lattices, we can find out the lattice parameters. What is the a value, what is the b value, what is the c value, what is their angle? That means, if you know them then you can tell what is the structure of the crystal.

That is what I want to discuss now. One should know one should have clear idea about the crystal structure, then only you will be able to analyse the X ray diffraction data and extract the information. All materials in universe in the universe whatever the materials you see, so they are in different form page of form

You can see this gaseous form, liquid form, solid form, plasma form And some other forms are there, but in nature generally these 4 forms we see other forms in laboratory one can generate now this let us concentrate in the solid-state part; solid state form. solid state materials, so all materials are made up atoms.

Generally made of 92 types of atoms. Now, later on there are more atoms are discovered in the laboratory. For the time being let us just consider these 92 types of atoms ok all materials they are made from these 92 types of atoms

Now, this question is, so atoms this material is made of atoms this how these atoms are arranged in the material. whether they are arranged in regular way or throughout the material they are ordered in ordered in throughout the material or they are ordered in just region wise or they are randomly oriented there is no ordered. That way we classify the material this amorphous, single crystalline, and poly crystalline

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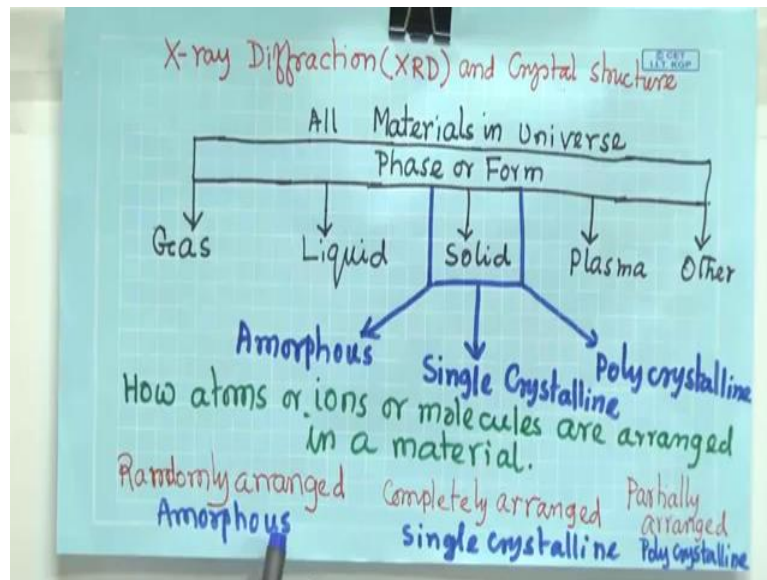
Amorphous however these atoms are randomly oriented in the material, so then we tell this the amorphous, that poly single crystalline, if May it at atoms are completely arranged in the material throughout the material this arrangement are perfect, then we tell single crystalline. Now, in between these two, then there is a partially arranged then we tell is the poly crystalline, so region wise is in some region. I have a picture; I have a picture to tell it.

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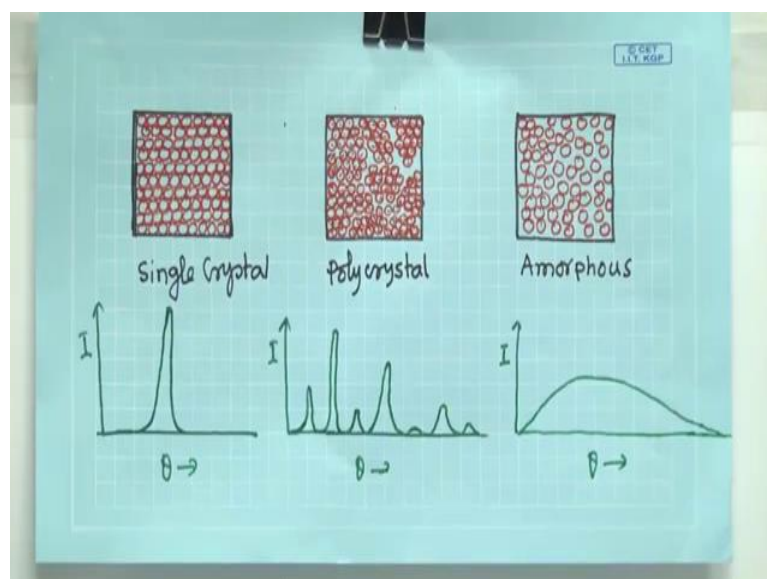
Here you can see the atomic arrangement. See if atoms are perfectly arranged like this; perfectly arranged like this. Then we tell you see clearly you can see they are arranged their ordered ok, so it is a single crystalline. If region wise in this region this is ordered, in this region this is ordered; so this will tell the grain.

this grain are ordered, but there is a difference in direction of this ordering direction from this region to this other region, so this we tell these there the this is another grain. then itself is these atoms in these grains are ordered, but grain to grain there is a boundary because this boundary comes because of their different slightly different orientation

This type of material is called its not throughout the material, it is not following a same ordering. region wise there they are ordered and as if they are randomly oriented these gains are randomly oriented in the material, so then we tell the poly crystalline And if it is randomly disordered you cannot find any ordering of this atoms in this material, then we tell amorphous.

Now in case of extra diffraction; diffraction already I mention that this there are planes; there are planes where the electron density of maximum ok, means the atoms are arranged on this plane. Now, then the same arrangement is found in another plane, it is parallel to it, same arrangement same intensity

Now, electron density variation is there in between this as if this electron density is very low and these are electron density are. High electron density then low electron density, then high, low, high, low, so set of parallel planes. this is only possible if atoms or ordered in the material. Otherwise, this type of distribution of the electron density will not find out and you will not expect; you will not expect the diffraction, you will not expect the diffraction

X ray diffraction if you; if you get like this very sharp peak; very sharp peak ok for a one peak, if you get one peak. For a particular orientation, one peck if you get an this is a very sharp peak, then it can tell this is the single crystalline if we if you get this multi peaks we get multi peaks from this sample, then we tell this is the poly crystalline and if we get this broad peak; broad peaks, then we tell this is the amorphous material.

Seeing the pattern of the diffraction; seeing the diffraction pattern from the materials, so one can tell whether the material is single crystalline or poly crystalline or amorphous

that means, this using X ray diffraction we can identify material, what is the crystal structure of the material. If it is amorphous, there is no question of crystal structure, because there is no order of atoms in the material

Now this crystal this X ray diffraction only it can study the crystalline material. that is why I wrote X ray diffraction and crystal It is not to study amorphous material, so crystal structure crystal. Now crystal structure as I told these two materials have 2 types of structures; one is single crystalline structure, another is poly crystalline structure

Seeing the diffraction pattern one can immediately tell whether it is single, crystalline material or it is poly crystalline material.

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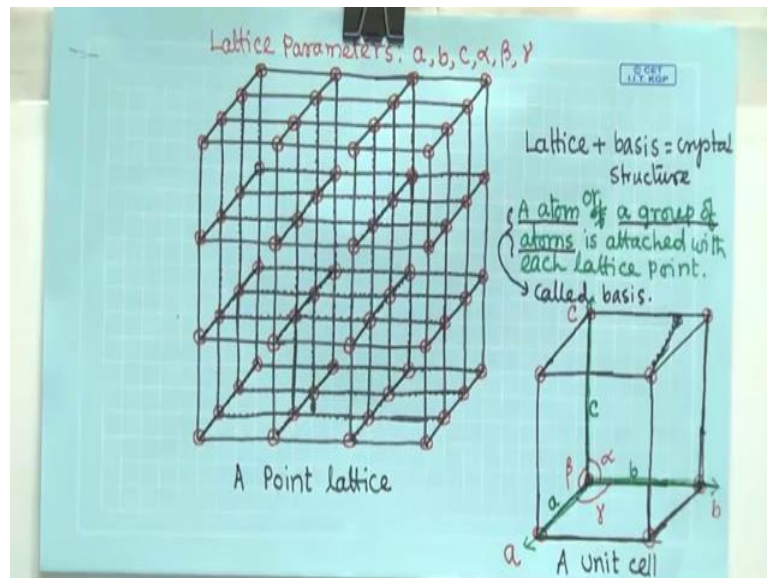
Hopefully you know but still again, I am revising, I am telling in my own way just keeping m to correlate with the X ray diffraction. Here I have drawn a lattice this is called a point lattice, it is the point lattice, you see in space in space I arrange atoms; I arrange the atoms. In addition, this from that arrangement you can see there are it has a one can divide these whole materials, into some units you know; into some units.

Now, one can tell that it's a this lattice, one can; one can get repeating this unit; repeating this unit in space one unit I have taken from here and drawn here you know, so this is called unit cell, so this is nothing but the repetition of this unit cells in all three directions

it will give the lattice. if you know, if you know about the, about the one-unit cell that means, you will know about the whole crystal; whole that crystal material

When we tell that, we want to know about the crystal's crystal structure that means we want to know the unit cell of a crystal. In unit cell, how we define unit cell? We define you see it is a 3 axis; a axis, b axis, c axis and angle between them is alpha, beta, gamma. You see alpha, beta just a opposite of that a this angle is alpha, opposite to b angle is beta, opposite to c angle is gamma.

the these are called the lattice parameter; these are called the lattice parameters and this lattice parameters is a, b, c alpha, beta and gamma if I know this lattice parameters and this lattice parameters are related with the d, d equal to so there is a relation for different structures. if you know d you can find out this lattice parameters, if you know lattice parameter you can find out d. Now, in between you need another things, so lattice parameter and d ok, this in that relation there is another parameters, we need that is called Miller indices.

What is Miller indices? hkl that also I will tell you. Now, one important things I am talking about the lattice and lattice point, lattice is made up lattice points and this lattice points are orderly place in a space now, what is crystal structure? Lattice is not the crystal; the real crystal is lattice plus basis. Lattice the structure is the mathematical concept ok, if I tell you the a, b, c value and alpha, beta, gamma value just you can produce lattice points in space.

Now, real crystal is this one atom or a group of atoms; a group of atoms attached to each lattice point that is total this lattice and basis together is called the crystal structure, so this is very important. as if this lattice points are reference points and we have to put real atom one atom or the group of atoms to the each; to the each lattice point in same way we have to attach ok, then well get the real structure of crystal. That is why I have written lattice plus basis equal to crystal structure.

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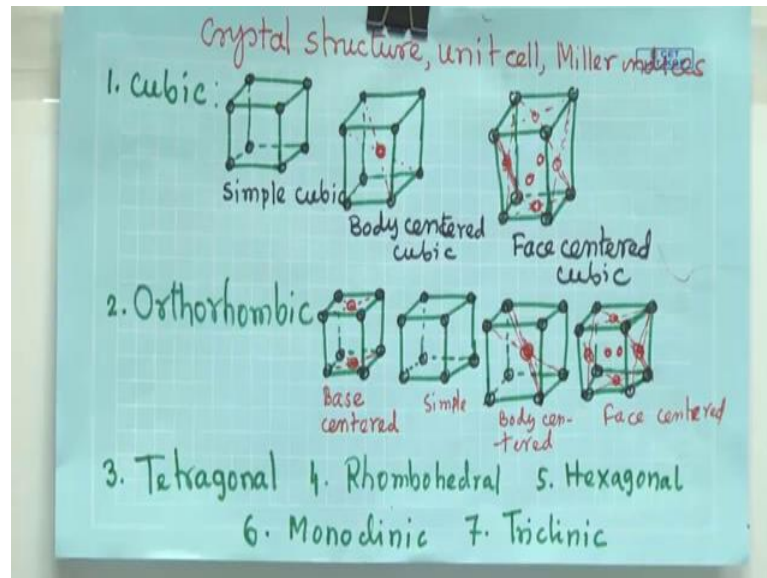
now this crystal structure this fortunately this thousands and thousands materials and they have different types of separate separation, different type of structure ok, but fortunately these all structure, it can be. all materials whatever the structures are there it's a similar to these whatever the material, but they are made of 1 or 2 or 3 or some n number of atoms ok, but that atoms is from this 92

Similarly, this all materials whatever the structure is there, so that structure in terms of unit cell. Only 14 types of unit cells are from symmetry, only 14 types of unit cell exist now can you imagine these 14; 14 lattices are there is called Bravais lattice.

real crystal of a material, so if structure it unit cell or its lattice it will be one of this 14 these 14 Bravais lattice is they have different, they have 14 they have different type of lattice parameters that is why here this cubic, orthorhombic, tetragonal, rhombohedral, hexagonal monoclinic, triclinic. these are the; these are the system these are the system. And in those system this how this lattice parameters are different? How the lattice parameters are different?

| System	Lattice Parameters and relation	Bravais lattice	Lattice symbol
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	Simple, Body centered, Face centered	P, I, F
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	Simple, Body centered	P, I
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	Simple, Body centered, Base centered, Face centered	P, I, C, F
Rhombohedral (also called Trigonal)	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	Simple	P
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90°, \gamma = 120°$	Simple	P
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$	Simple, Base centered	P, C
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	Simple	P

here this we tell cubic this cubic system when a, b, c are equal and they are angles alpha, beta, gamma 90 degree It has 3 types, 3 types Bravais lattice. So it is a simple, body centered, face centered, and just symbol you say you use P, I, F similarly tetragonal a equal to b is not equal to c, so this way you know but still I am I have mentioned here.

When you are studying your crystal your sample what is the structure of this sample? From X ray diffraction I can get I can get different Bragg peak, means I can get different d value. Now, the d value is equal to some relation of this a, b, c this angle and the and the hkl Miller indices

let me just tell about the Miller indices you know but still let me tell you what is the Miller indices, Miller indices is how we have defined Miller indices
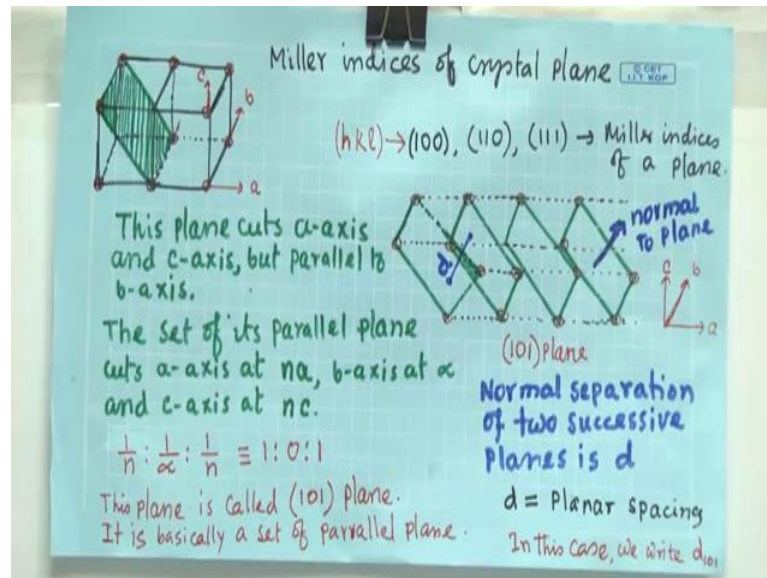
This is the now in crystal; in crystal this lattice points are arranged lattice points are arranged. Now, there you can you can choose a plane and now how we give name of this planes, so you see that planes or all other planes parallel to these. Where they have kept; where they have kept this a axis, b axis, and c axis?

Here I have shown one plane here if it is a axis, it is b axis, it is c axis. Here you can see this plane it cuts; it cuts; it cuts you see c axis, its cuts c axis and it cuts a axis, it cuts a axis and it is parallel to the b; it is parallel to the b. while it will cut? It will cut at infinity unit here one unit of, so you can you can tell that this it cut at this lattice constant along this a axis, this is it is a unit length is a.

It may cut n a, so at a or 2 a or 3 a or a n a Then it can cut b at infinity and c at n c n is either 1, 2, 3 like this ok, but in units of c what is the a distance? a distance is you see this distance between these two; between these two lattice points along on this a axis what is the distance between 2 lattice points. A minimum distance 2 lattice point on the a axis, so that is the a similarly b and c and their angle of course it is there.

we take whatever the factor whatever the factor with a, b, c we take inverse of those factors if it is n. 1 by n ratio 1 by infinity ratio 1 by n in this case both cases is a same, so that is why I have taken n otherwise one has to take different value. if you take from there, so here you can simplify and you can get 1 is to 0 is to 1; 1 ratio 0 ratio 1 this

plane then we tell this 1 0 1 plane, 1 0 1 plane, 1 0 1 plane means it is not 1 plane it is a set of parallel planes; it is a set of parallel planes like this

Similarly you have 1 0 0 plane, you have 1 1 0 plane, you have 1 1 1. Many planes are possible and one can find out from a you know a, b, c value, so what is the planar distance what is the normal distance between these two planes? That is the planar distance d and these d have relation with a, b, c alpha, beta, gamma.

For different structure for cubic, for tetragonal, for orthorhombic. different structure relations are one has to it is given in book you have to find out, you have to just read it or one can one has to derive. I have not shown here this is the standard things how planar spacing d is rated with the lattice parameters a, b, c alpha, beta, gamma. that is there.

When X ray is diffracted from a crystal grating, from a crystal plane. These shifts are parallel planes you see X ray if it falls like this, so it will see; it will see this is the space between these two planes is it's the like a slit width ok, it's like a slit width. it's the but this width is, it is edge is 2, 3, 4 maximum 5 angstrom which is comparable to X ray wave length, so that is why this is the very god gift natural grating for X ray you know.

And it's a so tremendous powerful technique fraction each and every one who do research they use this X ray diffraction and to know their structure of the sample, not only structure of the sample some other important information also one can find out this is the Miller indices hkl ok, so planar spacing we write d h k l; so d h k l. d h k l why we write? Because in one crystal there are many numbers many numbers of plane planes.

In addition, we get different Bragg peaks and we measure the angle of the Bragg peak and we calculate d and d is related with h k l a, b, c alpha, beta, gamma. If 7 unknown is there, so you need at least 7 Bragg peak to set 7 equation. you can solve it then you can know all parameters

Depending on that number of in cubic case, it is a simple only one parameter a equal to b equal to c. only a you have to know and hkl of course. fortunately this there is a data; there is a data X ray diffraction data for all sorts of structure that is called g c I think some internationally acceptable some database are there.

They are for all sorts of data these Bragg diffraction patterns are given their intensity their Bragg angle position, Bragg peak position all are given for all sorts of structure. generally what we do? We just do the experiment get all diffraction pattern from our from our sample. And that diffraction pattern we compare with the database comparing with the database directly, that the database itself will tell us what is the; what is the crystal structure of the sample

However, the database is that is a it is made from that calculation the things the things I told you. it is that just to save time we use that database and get the information if I have the experimental XRD pattern of my sample, comparing with the database I will be able to find out the crystal structure. However, there are some other things, which you cannot find out from the database.

Is it just application of this X ray diffraction this is only for determining these lattice parameters or something else? there is something else what else you can find out from the X ray diffraction experiment.

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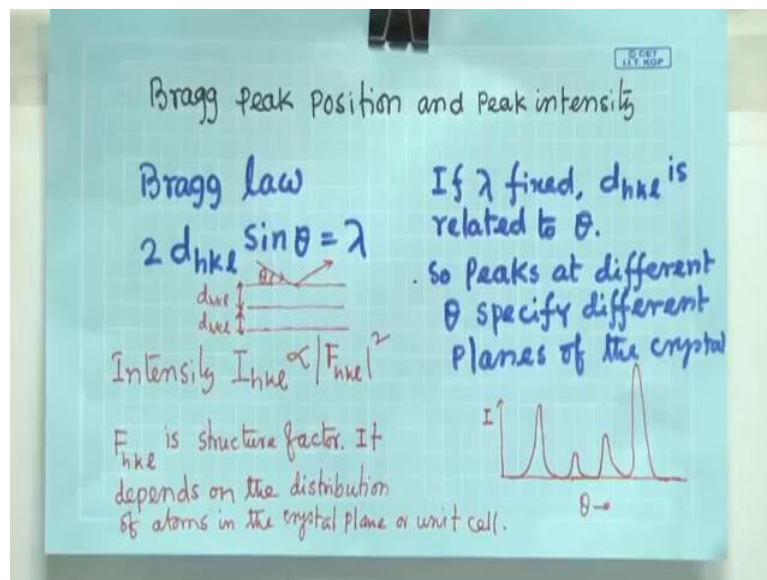
Here so Bragg so from so we have to, so here I have shown the typical XRD patterns form a sample; from a sample. these either from single crystalline sample you can get also this kind of pattern, in that case you have to vary the angle of the sample with respect to the X ray direction And then you are varying and satisfying the Bragg condition for different planes.

That time I told this for poly crystalline and this for so this looks like poly crystalline, but it may not be. Without varying the angle; without varying the angle of the sample with respect to the X ray if we keep this sample fixed, X ray also fixed. Then just the detector if we move if we move at different angles and if you find different Bragg peaks, like this then it is poly crystalline; then it is poly crystalline.

In addition, if it is single crystalline then what will happen. If it is, single crystalline, then if you just rotate this one; if you rotate this one this your detector. Then you may or you may not find the; you may or you may not find any peaks Because this all planes are fixed with respect to the surface of the sample, so here to study the single crystalline we need option to vary the angle.

If you just vary angle, so then you will get one peak. If you vary, more than only you will get another peak if you just vary at fixed at a one phase and if you are moving this your detector. you will see only one peak, then it is single crystalline. In addition, without varying the sample or just you are vary it and fixed it, now you are rotating your detector with all sorts of angle. Then if you see the many peaks at different angles of the detector, so then it is the poly crystalline anyway.

Here the peak here this we tell this Bragg peak, now this Bragg peak for a particular sample these peaks have come different planes. However, their intensity are different you know; their intensity are different. These intensities of Bragg peak carries the information. not only; not only the angle of the Bragg peak carries the information intensity of the Bragg peak also carries the information.

Bragg law as I told 2 d hkl now I have written d hkl, so this hkl plane. hkl it can be 1 0 0 or 1 1 0 or whatever. sin theta equal to lambda as I told we would take only first order. what is theta and what is d hkl that I have shown here. Now, you have done experiment following this geometry and you got this kind of XRD patterns

If lambda is fixed k alpha d hkl is related to theta at different theta you will get different Bragg peak, which specify the specify different planes of the crystals as I discussed. Now, intensity of this Bragg peak, so for different planes is the different. Intensity will depend on hkl, so it is proportional to the F hkl square what is F hkl. This is the structure factor, its called structure factor; F hkl is the structure factor, it depends the structure factor depends on the distribution of atoms in the crystal plane or unit cell

This the atoms how atoms are arranged on the plane? depending on that that is the it will depend on the position of the atoms in on a plane positional information; positional information is we get from these we express in terms of F hkl these this is called structure factor, it's a it will tell about the structure of this of the structure of distribution on the atoms on a particular set of planes for that is why for different sets of planes there their distribution of atoms are different, so that is why the intensity will be different.

From intensity one can actually find out the distribution of atoms on the planes means of distribution the atoms in the. If any displacement crystal may not be, perfect if any distortion of the crystal means ah the arrangement of the distribution of atoms the way we expect for a particular structure it may not be slightly changes. that change will come in the intensity; will come in the intensity.

In case of single crystalline crystal were it is the very where it is very it is a nicely ordered. as I mentioned that this peak become very sharp this intensity here intensity say it's a it become very sharp and in case of if it is order are not perfectly arranged, so these peaks become broad this peak become broad some disorder is there.

these are the, so there are this Bragg, this angle of the Bragg peak, intensity of the Bragg peak, broadening of the Bragg peak, all these are important to study the crystal structure

I think yes, one more things I can tell you that from what are the things we want to get. I kept somewhere let me see this application. Applying the crystal applying the X ray diffraction I have a one slide here I got it. This now at least we know what is the X ray diffraction, what is the crystal structure

Application said there will people used for different many to study the samples for different ah structural aspect, so but main aspect we study using the X ray diffraction.
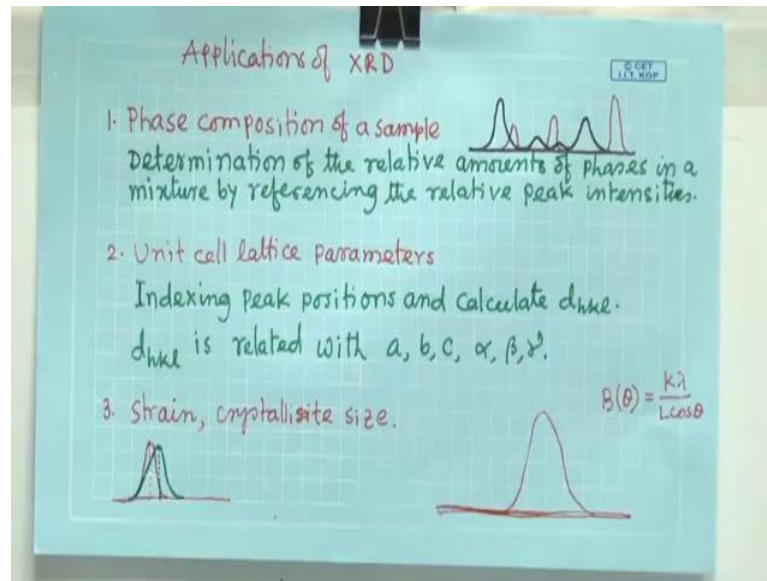
That is that phase composition of a sample this is the very simple. If we you have taken a mixture of two materials say aluminium and copper dust of copper and dust of aluminium and then mixed it.

Now, if I mixed it and give you that what is the ratio of these two ratio? What are the elements are there; what are the; what are the materials are there in this mixture you have to tell. In addition, what is the ratio of these 2 or 3 phases, 3 phase; 3 phase in this in this mixture?

These are called is the phase composition of a sample. Determination of the relative amounts of phases in a mixture by the referencing the relative peak intensity first if you take this XRD pattern, so this kind of pattern one I have shown the red and another black. say one for say aluminium and another set of Bragg peaks red one and black one. This one is for copper and another is for aluminium

Now, you just raise these two peaks Two peaks you have to consider one peak from this from black one and another peak from the red one you choose the same plane this which plan are common in these two, say 2 2 0 or whatever the plane. for a particular plane for a particular hkl since they are d are depends, so they will come at different angle Bragg angle.

One as to identify this using the database one has to identify that this Bragg peaks for which structure. Then you can know this structure of the material and then structure of that metal you can identify the material also it is an aluminium and it is the copper. Now, the intense relative intensity of these two peaks ok, you can find out the amount of the material because the amount of material is higher.

Scattering of X ray or diffraction diffractive rays from that material will be higher the diffracted rays from these from the materials, which amount, is higher. the intensity of refractive rays will be higher. Bragg peaks whatever you will get, so that intensity will be higher compared to the for same kind of plane of the other one

from the ratio relative ratio of this intensity of the peaks of the peaks referencing the here that is why have written, referencing the relative peak intensity we can find out that phase composition of a sample And of course, these the unit cell lattice parameters as I told only on this I told that indexing the peak; indexing the peak, means 1 1 0 peak, 0 0 3 peak etcetera.

Indexing peak positions and from there theta you will get and calculate d hkl; d hkl is related with this one can find out the lattice parameter. Also one can study the strain in the sample, one can study of the in poly crystalline sample, what is the strain size of the sample one can find out

This is one formula I have shown here this is the B as a function of theta is a broadening it is a broadening of the peak. if peaks are broadening, so that means, higher the broadening this crystals strain size will be lower. Order region will be smaller ok, so that is why in case of single crystal as I told peak will be very sharp because this crystal size is order that region is very large.

L that is the order this length of the crystallite crystalline length L, L in single case this L is very large. it's it the broadening is inversely proportional to the size of the crystallite say L, see in case of single crystal it is L is very large. broadening will be very small, so that is why in case of single crystal get very sharp peak, and if it is polycrystalline gain size will be smaller that else will becomes smaller this broadening will be higher.

That is why for polycrystalline sample ok; for polycrystalline sample this crystallite size are limited. that is why this peak will be get peak broadening measuring the peak

broadening one can estimate the crystallite size from this formula And a strain ac strain, strain means the in our sample you are perfectly order 5 ok, it has a particular lattice constant.

Now, if some by some reason whatever the reason, so if metal is strained If it is strained them it is a dimension is different than a normal dimension normal. Lattice parameter will be slightly different from the normal one. That is what we tell this system is under strain that means, when system is under strain, and then its lattice parameter is slightly change. is d is affected, so if d is affected 2 d sin theta equal to lambda. For the same lambda and d is slightly different, so theta will be slightly different.

For unstrained sample unstrained material, whatever the Bragg peak position of the Bragg peak Bragg angle if it is strained. This Bragg position Bragg angle it will be slightly position will be change that is why here I have shown that red peak and this green peak if red one is for unstrained one, so the strained one will be this green one from the shifting of the peak one can study the strain of the system

I told because these are very important these experimental tools to study the structure of the material lot of things I told and unfortunately, I will not be able to show the data or just because this I will show the machine our XRD machine and how we do the experiment. But only data I will I will not take from the system because the system is slightly down now for in next class I will just demonstrate the experiment mainly I will show the system.

Thank you.