Solid State Chemistry
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Lecture – 41
XRD – Analysis of Pattern

Now, I will start the 9th week of this course. In this week I will continue the discussion on x-ray diffraction that we started in the last week and we will complete the discussion with on x-ray diffraction, x-ray crystallography and electron microscopy. So, I will first I will continue where we left off with x-ray diffraction and we will see how to analyze the diffraction patterns. So, in this first lecture of week 9 we are going to do analysis of XRD patterns.

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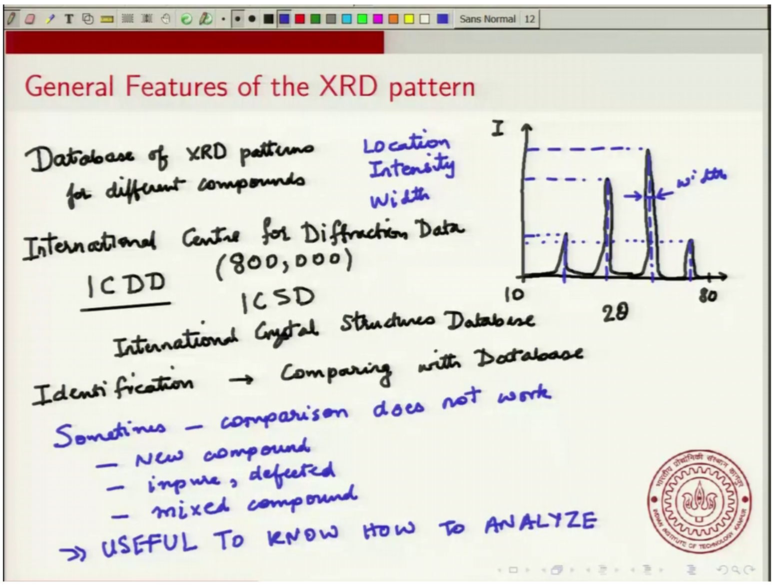

General Features of the XRD pattern

Database of XRD patterns for different compounds

Location
Intensity
Width

International Centre for Diffraction Data
(800,000)
ICDD

ICSD
International Crystal Structures Database

Identification → Comparing with Database

Sometimes – comparison does not work
- New compound
- impure, defected
- mixed compound

⇒ USEFUL TO KNOW HOW TO ANALYZE

So, what are the general features of an XRD pattern? So, suppose you look at a typical XRD pattern ok, then it looks something like this. So, there is an intensity on 1 axis and there is 2 theta which is the angle on the other axis, and typically this looks like there are lot of peaks in this intensity and so on ok. Typically the range of any powder xr, x ray diffraction pattern is from 10 to 80 the theta scale is linear ok. And the range of theta is about is typically from 10 to 10 to 80 ok. And the intensity shows up as such peaks ok.

So, what is important about these peaks? So, what is important is what is the location of this peak? So, what is the 2 theta value at which this peak is located ok. That is one important important property of this peak ok. In fact, that is the main that is the most important property is where the peak is located. Where the maximum that is a peak is located the other properties relate to the intensity of the peak ok. So, what is the intensity of the peak? Ok. What are the relative intensities of the different peaks? Ok. So, that is the other property of interest. And finally, the other the third property is actually related to the width of the peaks. So, you have the, location intensity and width of the peaks ok. Now we will be talking we will be analyzing a lot about the location of the peaks ok.

The very fact that it is a peak means that the intensity is high, but then there are also the relative intensities of the different peaks and these are generally slightly harder to analyze, but we will analyze that also, and the width we will not be talking much about ok. So, what the general way to do is that there is a huge database of XRD patterns, for different compounds ok. This is called the, this is called the International Center for Diffraction Data this is ICDD ok.

So, this and then now there is also the International Crystal Structures Database ICSD ok. This is the international crystal structures database. So, why I am mentioning these 2 databases is that is that, the every every compound that has been crystallized ok will not powder diffraction data is available on this international centre for diffraction data. So, if you want to identify your compound ok. So, if you want to identify. So, so if you want to identify your compound you can compare with this database. Identification can be obtained by comparing with database ok. So, this can be done ok.

Now in fact, the number of number of databases number of compounds right now is greater than 800,000 compounds. 800,000 compounds whose powder diffraction data is available ok. And you can compare with them and you can identify your compound, but sometimes this does not work ok. Sometimes comparison does not work ok.

And what would be the cases? So, one case would be that you have a new compound which is not in the database ok, or your compound might be impure, defected so, the diffraction data is actually not exactly the same as the as the pure compound or it might be a mixed compound ok. It might be a mixture of 2 compounds ok. So, essentially we need a way to what this means is that, it is useful to useful to know how to analyze ok. So, that is what we meant what we are saying is that yes, yes you can directly compare with the database, but still it is useful to know how to analyze ok. And this is knowledge can also help you help you verify that the analysis that is obtained by comparison is actually correct.

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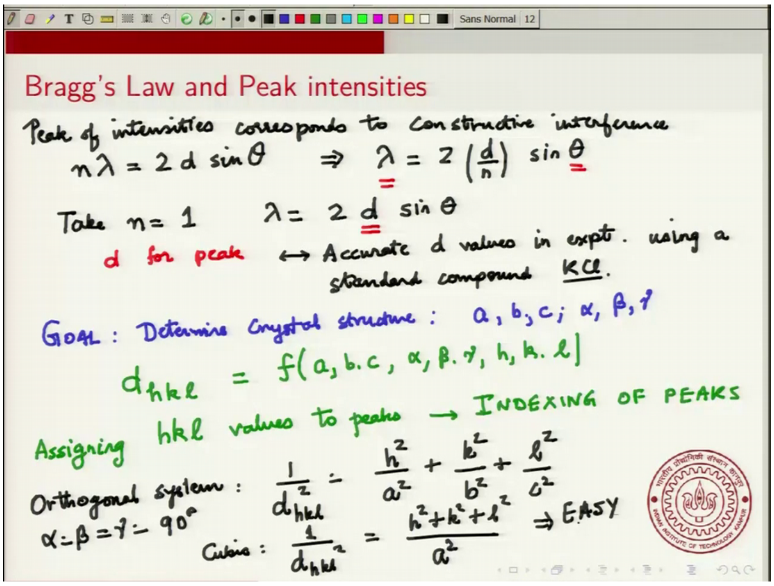

Bragg's Law and Peak intensities

Peak of intensities corresponds to constructive interference

$$n\lambda = 2d\sin\theta \Rightarrow \underline{\underline{\lambda}} = 2\left(\frac{d}{n}\right)\sin\underline{\underline{\theta}}$$

Take $n = 1$ $\quad \lambda = 2\,\underline{\underline{d}}\,\sin\theta$

d for peak $\leftrightarrow$ Accurate d values in expt. using a standard compound $\underline{KCl}$.

GOAL : Determine Crystal structure : $a, b, c; \alpha, \beta, \gamma$

$$d_{hkl} = f(a, b. c, \alpha, \beta. \gamma, h, k. l]$$

Assigning hkl values to peaks $\rightarrow$ INDEXING OF PEAKS

Orthogonal system : $\alpha = \beta = \gamma = 90^\circ$

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Cubic : $\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2} \Rightarrow$ EASY

Now, one of the ways to analyze is I mean the whole analysis is based on Bragg's law and so so Bragg's law and peak intensity. So, so what the basic idea is that, the peak intensities, peak of intensities corresponds to constructive interference. And so, we have n lambda equal to 2 d sin theta ok. This gives this gives you I can rewrite this as lambda equal to 2 and d by n sin theta ok.

So, now, what you have at the peaks you know the wavelength of light used. You know the wavelength of light used and you know the theta ok. So, so you can you can determine the distance between planes up to this n factor. Now what is done is usually we take n equal to 1 ok, and this does not change anything, I mean if you can take if you can think n equal to 2 will just mean a d spacing of half of the of n equal to 1.

So, so we can just take n equal to 1 and that will give you the relation lambda equal to 2 d sin theta ok. So, so we can use this to analyze the patterns ok. So, what we will get is, we will get we will obtain. So, we know lambda and we measure theta the theta where the intensity is maximum and from that you will get values of d ok. So we obtain d for peak ok and now what next? So, now the d spacings ok.

If you these this ds. In fact, one way to get accurate ds, an experimental way to get accurate d, d values in experiment ok. So, these are obtained using a using standard compound. So, KCl is used ok. So, for example, KCl ok. So, KCl can be used. So, what is done is that you take you take potassium chloride whose ds, d values are very accurately known and you mix it with this compound ok. So, that you can actually check that the d values of KCl are accurately reproduced in your in your XRD pattern ok, and if there are any shifts in the d values, then you accordingly you have to shift the d values for your compound ok.

So, let us let us say that we have all these d values, let us say that we have all these d values accurately then what can you do? So, the point is we would like to determine. So, goal is to determine crystal structure and for a start we will determine a, b, c and alpha beta gamma ok. But what is the problem? The problem is that your d d of h k l ok. This is a function of it is a function of a, b, c, alpha, beta, gamma, h, k, l. So, this distance between lattice planes that we that we get ok.

Now this depends not only on a, b, c, alpha, beta, gamma, but it also depends on hkl ok. And so, and so, we have to determine all these quantities ok. All these quantities have to be determined from. So, if you do not know what hkl it corresponds to or what or what a, b, c alpha, beta, gamma are correspond to, then how can you actually get any of these? How can how can you get all these values? Ok. So, clearly that this becomes very complicated. So, this process of this process of assigning hkl values to peaks is called indexing. Indexing of peaks, so that means, you are assigning miller indexed to the peaks.

So, so I mean if once you know once you know a, b, c alpha, beta, gamma ok. Then you can easily you can easily assign this hkl values to the peaks ok. But if you do not know a, b, c alpha, beta, gamma then, it is general in general it is very difficult now and we will see we will see some simple cases where this can be done.

So, obviously, the simple case of let us say if you have a cubic order or let us say you have an orthogonal system. And that means, alpha equal to beta equal to gamma equal to 90 degrees ok. Then you have one over d hkl square is equal to h square over a square plus k square over b square plus l square over c square, and now and now you have to determine a, b and c and by looking at all the peaks ok. You can imagine that you could be able to do this ok.

In the simplest case for the cubic case it is really simple for cubic ok. You just have the relation that one over d hk l square is equal to h square plus k square plus l square divided by a square and you can easily just by trial, but just by trying different values of hkl you can determine the lattice parameter a ok.

And what you have to do is, you have to take each of the peaks and for each of the peaks you try different values of hkl ok, and you try and and using that you can you can identify both the type of crystal and the lattice parameter ok. So, this is easy to do, and this I would expect you to be able to do ok. We will do some exercises on this. So, we will get some practice ok.

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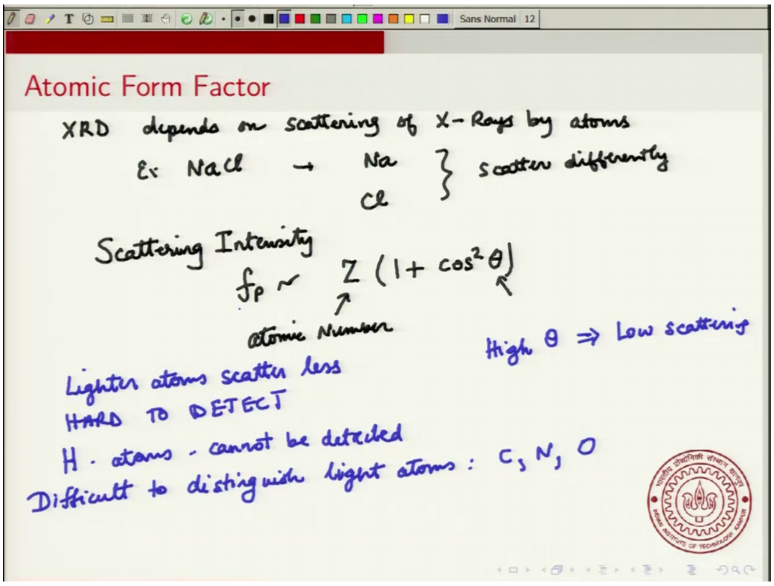

Atomic Form Factor

XRD depends on scattering of X-Rays by atoms

Ex NaCl → Na, Cl } scatter differently

Scattering Intensity

$f_p \sim Z(1+\cos^2\theta)$

atomic Number

High θ ⇒ Low scattering

Lighter atoms scatter less

HARD TO DETECT

H. atoms - cannot be detected

Difficult to distinguish light atoms : C, N, O

Now, there are a few more things that affect the x ray diffraction pattern ok. And I will just mention these here the first is something called an atomic form factor. So, basically your x ray, XRD depends on scattering of x rays by atoms of x rays by atoms, and different atoms scatter differently. So, different atoms scatter differently. So, for example, if you have NaCl then, then Na and Cl atoms they scatter differently. That means, the intensity of scattering ok, the scattering intensity of Na and the scattering intensity of Cl will be different ok. In general, the scattering intensity f p is proportional to Z times 1 plus cos square theta ok. So, there is a factor of z which is the atomic number ok.

So, and then there is also a factor of theta and this is I should say it is approximately proportional to ok. So, it is approximately proportional to ok. So, what that means? What that means is that since it is approximately linearly proportional to Z what you can say is that lighter atoms, scatter less And hence they are hard to detect. In fact, for this reason you may have heard that hydrogen atoms are very hard to detect, almost impossible to detect ok. So, hydrogen atoms cannot be detected the other point is that high angles high theta implies low scattering ok.

So, if theta is large then the scattering is very low because theta is close to 90 degrees then the scattering intensity will be very low. So, usually we stick we do not go to very high theta values. So, the other point is that it is difficult to distinguish light atoms. Light atoms such as carbon, nitrogen, oxygen which have very similar which have very similar atomic masses ok. They are light atoms it is very similar atomic masses and they are hard to distinguish. So, if you have an organic compound that has carbon nitrogen and oxygen it is usually quite hard to determine the structure. So, the atomic form factor will also affect the scattering intensity which will also affect the intensity of the XRD peaks ok.

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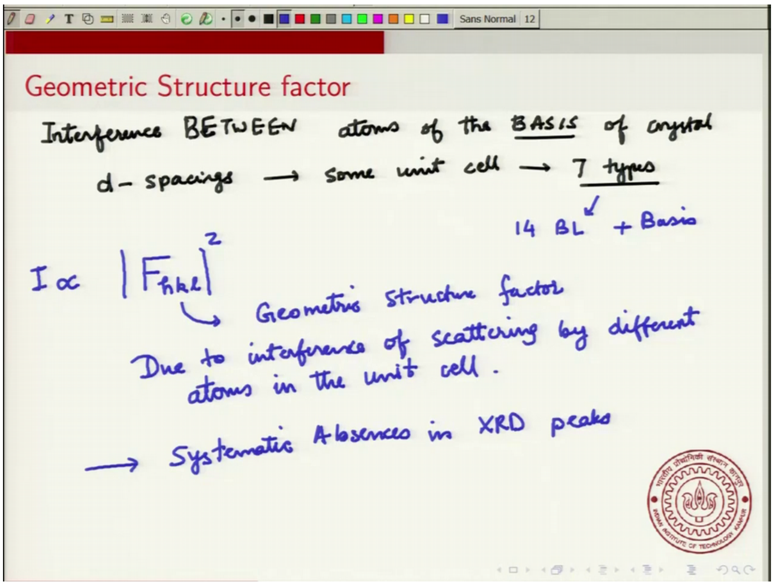

Geometric Structure factor

Interference BETWEEN atoms of the BASIS of crystal

d-spacings → Some unit cell → 7 types

14 BL + Basis

$I \propto |F_{hkl}|^2$

→ Geometric structure factor

Due to interference of scattering by different atoms in the unit cell.

→ Systematic Absences in XRD peaks

There are additional factors that affect the intensity of XRD. So, one is called the geometric structure factor ok, and this refers to this refers to the phenomena of interference between atoms of the basis of crystal ok. And here what I mean is that, you we have a unit cell, you have this unit cell and so, these spacings are with spacings are with respect to some unit cell ok. And so, the unit cells basically there are only 7 types. 7 types corresponding to seven crystal systems and so, now, now within these seven types there are 14 bravais lattices ok. So, there are 14 bravais lattices and then and then you have all the space groups and so on ok. Now you can also have plus you can have a basis ok.

So, this geometric structure factor is a factor ok, so this is a factor it is denoted by capital F of hkl ok. So, this is a factor that. So, so we say intensity is proportional to capital F, F of hkl square ok. This is called the geometric structure factor ok. This arises because of because of because the intensity is due to different atoms within the unit cell ok. So, this is due to interference of scattering by different atoms in the unit cell ok.

So, the different atoms of the same unit cell they each of them scatter the x rays and it is interference due to scattering of these atoms that leads to something called a geometric structure factor. We look at this in more detail, but I will just mention that this leads to something called systematic absences in XRD peaks ok. So, some and and this is a very very crucial factor that is used to identify the compounds or identify the structure. So, in certain structures certain values of hkl that the peaks you would expect a peak, but that would be missing. Because of this geometric structure factor we will see this in more detail in the next lecture ok.

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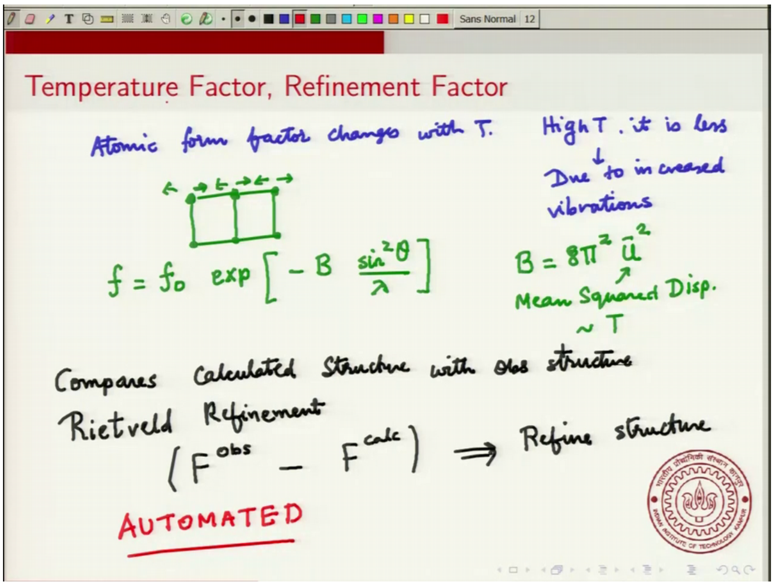

Temperature Factor, Refinement Factor

Atomic form factor changes with T.

High T. it is less
↓
Due to increased vibrations

$$f = f_0 \exp\left[-B\,\frac{\sin^2\theta}{\lambda}\right]$$

$$B = 8\pi^2 \bar{u}^2$$

Mean Squared Disp.
$\sim T$

Compares Calculated Structure with obs structure

Rietveld Refinement

$$\left(F^{obs} - F^{calc}\right) \Rightarrow \text{Refine structure}$$

AUTOMATED

Now, I will just mention two more things two more factors that affect the intensity of XRD patterns. One is called a temperature factor and this tent temperature factor basically says that the atomic scattering factor atomic form factor changes with temperature, changes with temperature in particular at higher temperatures. High T it is less. And the reason for this is that when you increase the temperature ok, then the atoms vibrate more ok. So, due to increased vibration of atoms. So, I mean what we mean is the following that if you have the atoms of a solid ok.

Now these atoms are not actually exactly fixed at their lattice positions here they have some vibrations, they have some vibrations and the amplitude of this vibrations increases with temperature ok. And this leads to a lowering of the structure factor and this is given by this temperature factor and so and so, what is true typically an expression is written that the atomic form factor at a some high temperature is the atomic form factor at 0 temperature multiplied by exponential of minus B sin square theta by lambda ok.

Now this factor of B this factor of B is equal to 8 pi square and u bar square, u bar square is a mean square displacement. So, the mean square displacement of the atom that is how much how much it displaces, what is the typical displacement and this mean square displacement is it is proportional to the temperature ok.

So, the scattering the form factor, atomic form factor decreases with temperature ok. Now in addition to this there is something called a refinement factor which is often used in I mean which is now routinely used in all x ray diffractometers ok. And this is a factor that is used to, that is used to actually has the name suggest it is used to. So, it compares calculated structure with observed structure ok. So, it compares a calculated structure with the observed structure and I will not spend too much time on this, but basically the idea is that there is a very well known procedure called Rietveld refinement. So, Rietveld refinement and this is actually it is an automated program that is there in most of the modern x ray diffractometers this is named after the scientists Hugo Rietveld ok.

So, the idea is that you compare the structure factor that you, that you observe with some model calculated structure factor ok. And this difference is used to is so you try to minimize this difference ok. So, this you difference is used to actually improve the structure. So, if the difference is too large then you sort of modify the structure a bit till this difference is very less ok. So, used to refine the structure now it is actually quite a complicated program and I will not be getting into the details of how this program works ok, but it is good to know that there is such a procedure that that is there in all the x rays ok. So, I will just mention here that it is automated in most instruments in most modern XRDs.

So, we will not discuss about it anymore ok. But it is good to know that these are all these factors are there. So, we saw that you have a temperature factor refinement factor and this is in addition to the atomic form factor and the structure factor and all these factors affect the intensity of the x ray diffraction pattern. So, with this I will conclude this lecture ok. The first lecture of week 9 and in the next lecture we will I will do I will talk in more detail about the geometric structure factor.

Thank you.