Chemical Crystallography
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Lecture - 47
Identification from Intensity Statistics
The Correct Crystal System and Presence of Inversion Center

Welcome back to the course of Chemical Crystallography. In the previous lecture we have discussed about the data processing.

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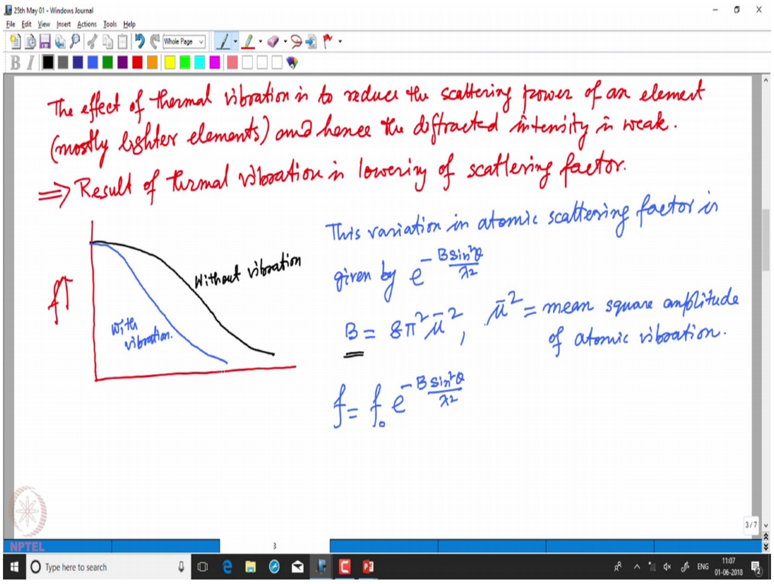

The effect of thermal vibration is to reduce the scattering power of an element (mostly lighter elements) and hence the diffracted intensity is weak.

⇒ Result of thermal vibration is lowering of scattering factor.

This variation in atomic scattering factor is given by $e^{-\frac{B\sin^2\theta}{\lambda^2}}$

$\underline{\underline{B}} = 8\pi^2\bar{u}^2$, $\bar{u}^2$ = mean square amplitude of atomic vibration.

$$f = f_0 e^{-\frac{B\sin^2\theta}{\lambda^2}}$$

And how to derive the expression for the relative intensity from absolute intensities and then in that during this process we were talking about how to understand or how to account for the thermal vibration using the thermal vibration parameter B, B mean square amplitude of atomic vibration. And we have discussed that the atomic scattering factor with vibration falls more rapidly compared to the situation, where there is no vibration all at 0 Kelvin temperature and then depending on various values of B.

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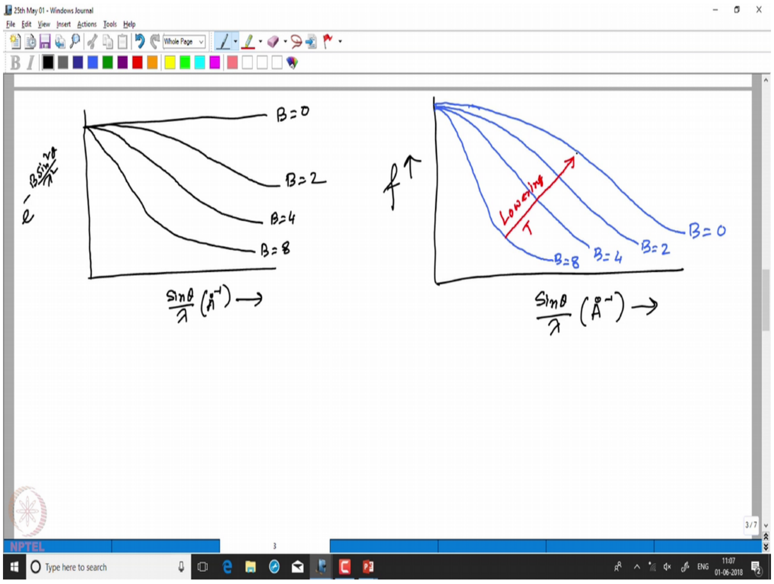

We have discussed how the scattering factor falls with increasing with how is scattering factor falls with increasing temperature and then on lowering the temperature the scattering factor which is the maximum at when B equal to 0.

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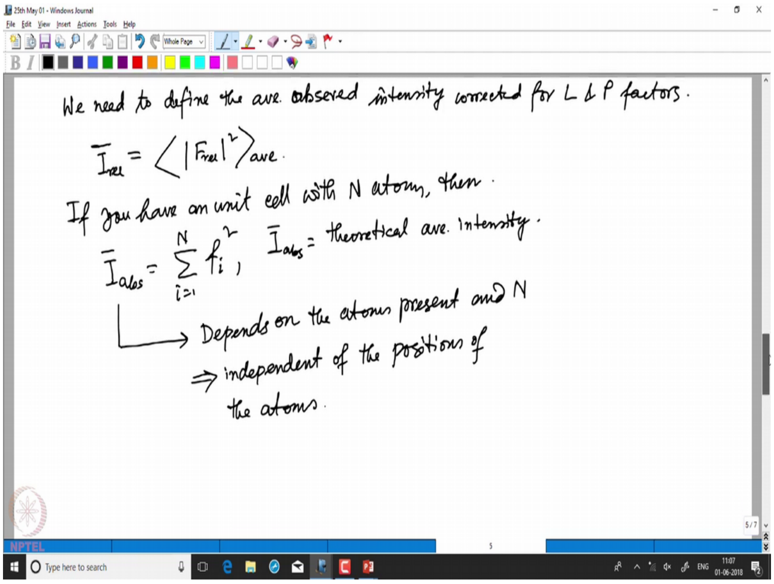

We need to define the ave. observed intensity corrected for L & P factors.

$$\bar{I}_{rel} = \langle |F_{rel}|^2 \rangle_{ave}.$$

If you have an unit cell with N atoms, then.

$$\bar{I}_{abs} = \sum_{i=1}^{N} f_i^2, \quad \bar{I}_{abs} = \text{theoretical ave. intensity.}$$

→ Depends on the atoms present and N

⇒ independent of the positions of the atoms.

So, then we try to understand how one can do the relationship between I relative verses I absolute and in that process we have ended up seeing a plot called Wilson plot which is given here

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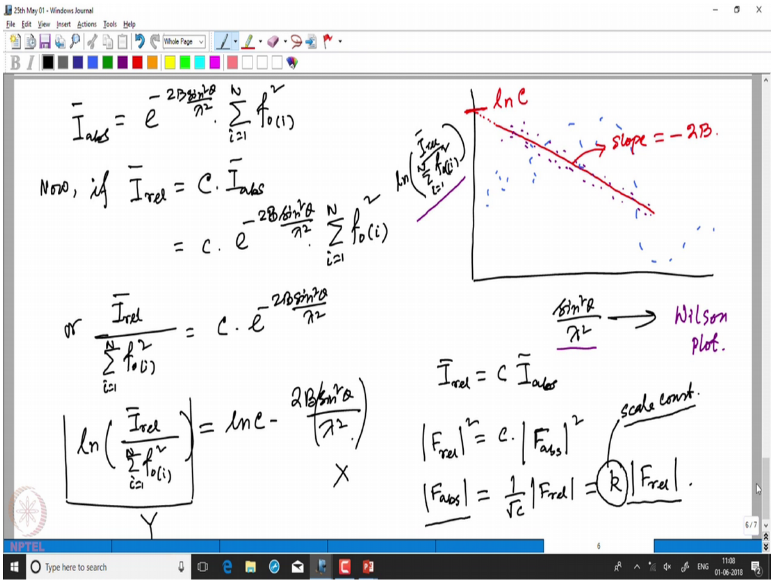

$$\bar{I}_{abs} = e^{-2B\frac{\sin^2\theta}{\lambda^2}} \cdot \sum_{i=1}^{N} f_{0(i)}^2$$

Now, if $\bar{I}_{rel} = C \cdot \bar{I}_{abs}$

$$= C \cdot e^{-2B\frac{\sin^2\theta}{\lambda^2}} \cdot \sum_{i=1}^{N} f_{0(i)}^2$$

$$\text{or } \frac{\bar{I}_{rel}}{\sum_{i=1}^{N} f_{0(i)}^2} = C \cdot e^{-2B\frac{\sin^2\theta}{\lambda^2}}$$

$$\underbrace{\boxed{\ln\left(\frac{\bar{I}_{rel}}{\sum_{i=1}^{N} f_{0(i)}^2}\right)}}_{Y} = \ln C - 2B\underbrace{\left(\frac{\sin^2\theta}{\lambda^2}\right)}_{X}$$

$\frac{\sin^2\theta}{\lambda^2} \longrightarrow$ Wilson plot.

$$\bar{I}_{rel} = C\,\bar{I}_{abs}$$

$$|F_{rel}|^2 = C \cdot |F_{abs}|^2$$

$$\underline{|F_{abs}|} = \frac{1}{\sqrt{C}}|F_{rel}| = \underbrace{\textcircled{k}}_{\text{scale const.}}\underline{|F_{rel}|}.$$

This Wilson plot is generated to identify a good dataset from a bad dataset and also to identify the corresponding constant the scale factor or the scale constant which is related to the C. So, ln C is calculated from the data by extrapolating it to sin theta by lambda square equal to 0 and the slope of the straight line gives you the an estimate of the thermal parameter B.

So, in today's lecture we are going to now discuss about 2 more aspects where we will now try to see how one can identify the correctness of the lattice parameters, whether it is monoclinic orthorhombic or something else. And how then one can identify the symmetry elements like inversion symmetry, 2 fold symmetry and middle symmetry which do not cause any systematic absence. But, it gives you an indication of these symmetry elements present in your lattice through the values of I hkl that we are going to record in case of a crystal data.

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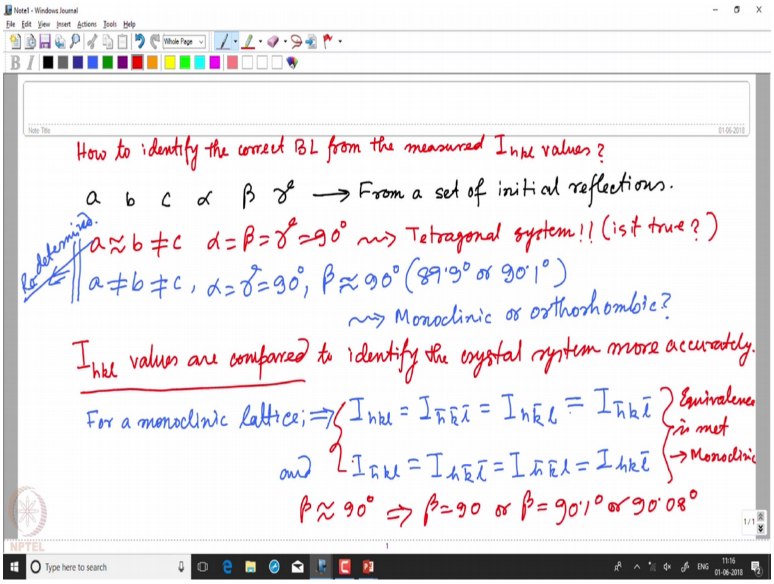

How to identify the correct BL from the measured I_{hkl} values?

$a \quad b \quad c \quad \alpha \quad \beta \quad \gamma \longrightarrow$ From a set of initial reflections.

Redetermined.

$a \approx b \neq c \quad \alpha = \beta = \gamma = 90^\circ \rightsquigarrow$ Tetragonal system!! (is it true?)

$a \neq b \neq c, \ \alpha = \gamma = 90^\circ, \ \beta \approx 90^\circ \ (89.9^\circ \text{ or } 90.1^\circ)$

$\rightsquigarrow$ Monoclinic or orthorhombic?

I_{hkl} values are compared to identify the crystal system more accurately.

For a monoclinic lattice; $\Rightarrow \begin{cases} I_{hkl} = I_{\bar{h}\bar{k}\bar{l}} = I_{h\bar{k}l} = I_{\bar{h}k\bar{l}} \\ \text{and } I_{\bar{h}kl} = I_{h\bar{k}\bar{l}} = I_{\bar{h}\bar{k}l} = I_{hk\bar{l}} \end{cases}$ Equivalence is met $\rightarrow$ Monoclinic

$\beta \approx 90^\circ \Rightarrow \beta = 90$ or $\beta = 90.1^\circ$ or 90.08°

So, today we would like to learn the first point is how to identify the correct Bravio lattice from the measured I hkl values. See there may be situation when we start index apart x ray index some a index diffraction pattern we may get the values of a b c alpha beta and gamma from a set of initial reflections. On physical observation it may turn out that a is very close to b and is not equal to c and alpha equal to beta equal to gamma equal to 90 degree, which may look like it is a tetragonal system is it true; is it true that.

In case of tetragonal system or from the initial measurement it means look like a not equal to b clearly not equal to c very clear, alpha equal to gamma equal to 90 degrees also very clear. But beta is very very close to 90 degree maybe 89.9 degree or 90.1 degree so; the confusion is it monoclinic or orthorhombic. This confusion cannot be solved that the beginning when we are trying to determine the itself because, we do not have enough number of reflections to talk about and we have not reduced the data to get the relative intensities of all I of h of all hkl values that are going to be recorded during the data connection.

So, once the data is collected these parameters are redetermined and what is done is that then we compare various I hkl values to identify the crystal system more accurately. So, at this point after the data reduction is done once again reindexing of the lattice is done, the reindexing of the unit cell is done and then one looks at the statistics of all the hkl and tries to see what kind of information can be found from those reflections.

So for example, in case of a monoclinic lattice for a monoclinic lattice we should have I hkl equal to I h bar k bar l bar which is Friedels law, I hk bar l which is the mirror operation. And the corresponding Friedels law Friedels opposite is I h bar k l bar which is a twofold operation parallel to v and for I h bar k l set of reflections, should have because for the equivalence with I h k bar l bar then you apply the middle symmetry, so it is h bar k bar l equal to I h bar I hkl bar.

So, if we see that in the data that we have recorded this 2 set of equivalence is met then we conclude it as monoclinic. So, this confusion is avoided that whether beta when it is close to 90 degree should we consider it as beta equal to 90 degree or we take it as beta equal to something like 90.1 degree or 90.08 degree which is very very close to 90 degree. So, in case if it is really monoclinic then these 2 conditions will be met, if it is not monoclinic if it is orthorhombic then a different condition will be met and what is that different condition.

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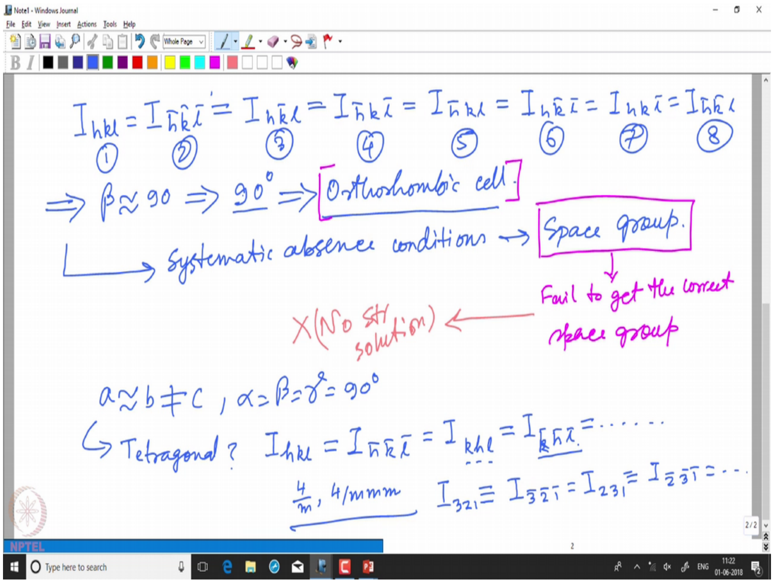

$I_{hkl} = I_{\bar{h}\bar{k}\bar{l}} = I_{h\bar{k}l} = I_{\bar{h}k\bar{l}} = I_{\bar{h}kl} = I_{h\bar{k}\bar{l}} = I_{hk\bar{l}} = I_{\bar{h}\bar{k}l}$

① ② ③ ④ ⑤ ⑥ ⑦ ⑧

$\Rightarrow \beta \approx 90 \Rightarrow \underline{90^\circ} \Rightarrow$ Orthorhombic cell.

→ Systematic absence conditions → Space group.

Fail to get the correct space group

X (No str solution) ←

$a \approx b \neq c \, , \alpha = \beta = \gamma = 90^\circ$

↳ Tetragonal? $I_{hkl} = I_{\bar{h}\bar{k}\bar{l}} = I_{khl} = I_{\bar{k}\bar{h}\bar{l}} = \cdots\cdots$

$\frac{4}{m}$, $4/mmm$ $I_{321} \equiv I_{\bar{3}\bar{2}\bar{1}} = I_{231} \equiv I_{\bar{2}\bar{3}\bar{1}} = \cdots$

In case of orthorhombic what we know is that the reflections which are hkl corresponding Friedel opposite I h bar k bar l bar and orthorhombic has mirror symmetry that is mmm symmetry in the lave group. So, it should have the equivalence as I h bar k l equivalent to it is Friedel opposite I h bar k l bar equal to I h bar k l equal to it is Friedel opposite I hk bar l bar is equal to I hkl bar should be equal to I h bar k bar l. So, all these 8th group of reflections 1 2 3 4 5 6 7 8 all these 8 group of reflections will have the same intensity. And this will then conclude what beta we were seeing very close to 90 degree, I actually 90 degree hence we take it as orthorhombic cell thus this state is very important. If we do not determine the correct crystal system which then would be taken to find out the systematic absence conditions to determine the space group, so if our unit cell that we are determining here is not right we will fail to determine the correct space group.

So, the systematic absence condition will fail to determine the correct space group. What can happen in term because of incorrect space group no structure solution because, our structure solution in general works based on this space group that we have written. Of course, now a day's x t model latest version of Feligs can do structure solution without the correct space group being determined, it determines the structure based on space group p1. Then applies the different systematic conditions observe and then applies a suitable space group and then gives us the solution in appropriate space group.

So, now the other point that we would like to looks highlight here is situation is when a is very close to b and is not equal to c with alpha equal to beta equal to gamma equal to 90 degree, in the same way we need to see whether it is a tetragonal or not. So, for that we should look for reflections which are I hkl should be equal to I h bar k bar l bar should be equal to I khl should be equivalent to I k bar h bar l and the other conditions which comes for the tetragonal symmetry which could be either 4 by m or 4 by mmm.

So, one has to look at those I hkl corresponding to different kind different point groups the different lave groups of fort lave groups of tetragonal system and see those equivalence are met or not using this particular data. If those equivalence are not met strictly then it is orthorhombic, that means the interchange of axis a and b is not allowed if all these conditions are met together then it is tetragonal.

See here what I have written k h l what does it mean, suppose I am talking about a reflection I 3 2 1 should be equivalent to I 3 bar 2 bar 1 bar which is Friedels opposite, then it should be equivalent to I 2 3 1. That means, a and b interchanged and the corresponding Friedel opposite I bar 3 bar 1 and so on.

So, this is what is meant by k h l or k bar h l bar k bar h bar l bar because, the in indices got get changed but the numbers remain the same. So, this way one can actually identify the correct Bravais lattice at the end of data reduction. So, now we would like to see what happens if we have a centre of inversion or if we do not have a centre of inversion.

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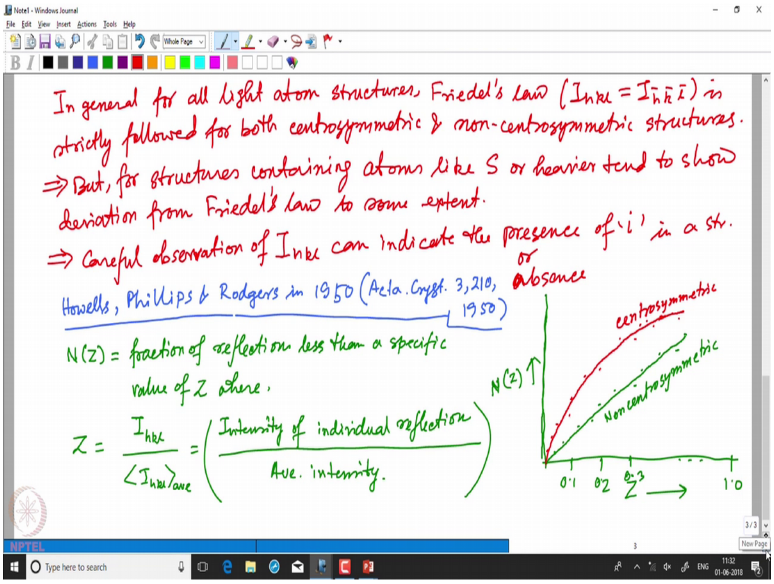

In general for all light atom structures, Friedel's law ($I_{hkl} = I_{\bar{h}\bar{k}\bar{l}}$) is strictly followed for both centrosymmetric & non-centrosymmetric structures.

⇒ But, for structures containing atoms like S or heavier tend to show deviation from Friedel's law to some extent.

⇒ Careful observation of I_{hkl} can indicate the presence or absence of 'i' in a str.

Howells, Phillips & Rodgers in 1950 (Acta. Cryst. 3, 210, 1950)

N(Z) = fraction of reflection less than a specific value of Z where,

$$Z = \frac{I_{hkl}}{\langle I_{hkl} \rangle_{ave}} = \left(\frac{\text{Intensity of individual reflection}}{\text{Ave. intensity.}} \right)$$

So, what we know is that in general for all the light atom structures, Friedels law that is I h k l is equal to I h bar k bar l bar is strictly followed for both centrosymmetric and non centrosymmetric structures. But for structures containing atoms like sulphur or heavier tend to show deviation from Friedels law to some extent. So, then it becomes easier to identify the centric and non centric structures by looking at the I hkl and I h bar k bar l bar. So, what we need is a careful observation of the intensities I hkl can indicate the presence of or rather presence or absence of I in a structure.

To determine the presence of this inversion centre in a structure there are a few different methods that are known in the literature. So, now here I am going to discuss one such method which is called the Z test or N Z test and it was introduced by Howell Howells Phillips and Rodgers in 1950 because it introduced in this.

Act crystallographic Gannel volume 3 page number 2 1 0 year 1950. So, what they proposed is that from the general observation that the intensities for I hkl are more tightly packed for no centrosymmetric structures about the I average. Whereas, the I hkl values are more deviated from the I average value for the centrosymmetric structures.

So, what they try to do is that they calculated the number N Z which is the fraction of reflections less than a specific value of Z, where Z is nothing but the ratio of the corresponding I hkl to the average I hkl. So, first we need to see the value of Z for each and every reflection, it is the ratio of the intensity of individual reflections; intensity of individual reflections by the average intensity.

And then they proposed to plot these 2 quantities against each other, where one plotting Z along x axis and the corresponding N Z along y axis, so then it was shown that for a non centrosymmetric structure the line is more straight compare to the centrosymmetric structure which is bent. So, this observation is made from the data set that was collected and reduced.

And then the corresponding relative I hkl are taken into account the I hkl average is done and you take the ratio of those I hkl with respect to the average. So, we calculate the value of Z and then from there we calculate the fraction of reflections less than a specific value of Z; that means, the specific value of Z can be made to fall within 0.1 0.2 0.3 and so on 1.0.

So, the number of reflections that is N Z is the fraction of reflections having the value less than Z of 0.1 is then plotted and a best fit line is done. So, in case of centrosymmetric structure it may be the case that the points were following like that, so the best fit line represents a straight line. Whereas, for a noncentrosymmetric structure these lines indicate a deviation from a straight line and rather go like curve which is around here. So, the best fit curve that goes is goes higher than the noncentrosymmetric structure and from there one can conclude whether it is centrosymmetric or noncentrosymmetric.

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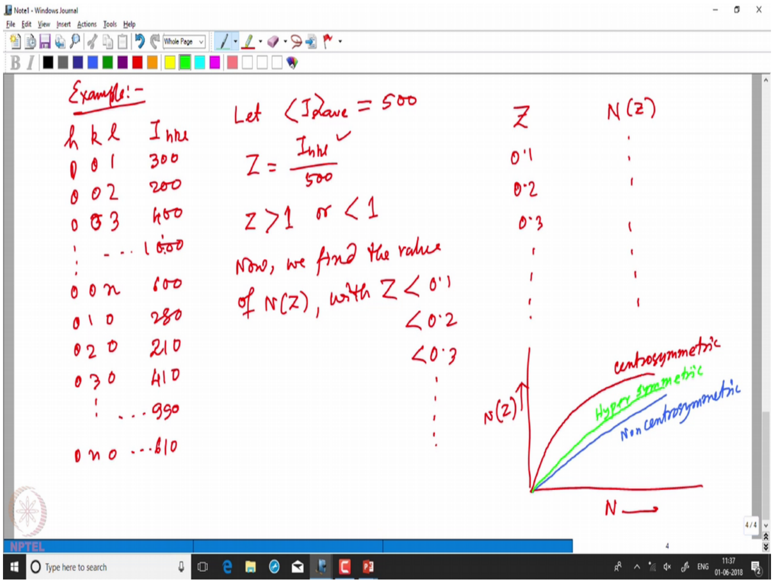

Example:-

h k l	I_{hkl}
0 0 1	300
0 0 2	200
0 0 3	400
⋮	… 1000
0 0 n	600
0 1 0	280
0 2 0	210
0 3 0	410
⋮	… 990
0 n 0	… 610

Let $\langle I \rangle_{ave} = 500$

$$Z = \frac{I_{hkl}}{500} \checkmark$$

$Z > 1$ or < 1

Now, we find the value of $N(Z)$, with $Z < 0{\cdot}1$

$< 0{\cdot}2$

$< 0{\cdot}3$

⋮

Z	N(Z)
0·1	⋮
0·2	⋮
0·3	⋮
⋮	⋮

To understand this let us take one example suppose in case of in this particular example, suppose in one data set we have the corresponding hkl and the I hkl values from the data reduction software. We have numbers for 0 0 1 0 0 2 0 0 3 and so on reflections up to 0 0 n, the values may be something like for example 300 200 400 like that these may be 600 the somewhere in the middle the maximum may be 1000 and so on and then the set of reflections where it is 0 1 0 0 2 0 0 3 0 and so on with 0 n 0.

Also has values very similar like 280 210 410 somewhere in between you have 990 somewhere here you have like 610 and so on. So, then it may we may find that let average that is I average is equal to say 500, so we calculate Z for each and every reflection with I hkl by 500. So, that is my value of Z, so Z can be greater than one or less than one depending on the actual intensity of I h l.

So, now we find the value of N Z, that is the number of reflections that has Z value less than 0.1 less than 0.2 less than 0.3 and so on and make a table. So, what we need what we are is we have Z and N Z say for Z equal to 0.1 0.2 0.3 and so on we have some numbers here and then we plot those 2 quantities against each other and we end up getting a plot like this.

If we get a plot in this manner then we would call it as centrosymmetric, if we get a more or lies a straight line we can call it as we will recognise it as non centrosymmetric. And here at this point I would like to just sensitize you that there may be something which is called hypercentric. The hypercentric structure means that there is no centre of symmetry in the lattice but, there is a centre of inversion in your molecule or in the pair of molecules which are there in the lattice, so you have a pseudo centre of symmetry in your lattice. So, in that case this statistics will show a very minor deviation from noncentrosymmetric plot, but it will not so be as deviated as like centrosymmetric.

So, it will go nearly a straight line but with some curvature in it and it will then you identify it as hyper symmetric structure. So, this happens when either your molecule has a centre of inversion, but that centre of inversion does not need to a centrosymmetric structure or that centre of inversion does not coincide with the centre of inversion of your lattice, in that case you end up getting an high percentage distribution. So, in this lecture we have learnt how to identify from the intensity statistics the correct unit cell parameters, how to identify the correct Bravais lattice that is whether it is rather correct crystal system.

Whether it is monoclinic orthorhombic or tetragonal or anything higher symmetric and then we under we try to understand how one can identify the presence of inversion centre in a crystal. So, in the next lecture we will discuss about the study of this hkl, in I hkl values from which we can then identify the presence of 2 fold and mirror symmetry in crystal structures.