Chemical Crystallography

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Lecture – 48
Identification from Intensity Statistics the presence of 2 fold axis in Lattice

Welcome back to the course of Chemical Crystallography. In the previous lecture we have discussed about how, one can identify the correct crystal system by studying the I hkl statistics intensity of every reflection and to correlate different reflections falling in different lave groups. And to identify the corresponding correct crystal system, whether it is monoclinic or orthorhombic, when there is a confusion that the beta is very close to 90 degree or orthonombic and tetragonal where, a and b values are very close, one has to look at the corresponding intensity statistics and confirm the correct crystal system.

Then we discussed about the presence of inversion center in lattice, in the crystal structure using the intensity statistics. In that we discussed the z test for determination of center of inversion. So, in this lecture we will discuss about how one can go about to identify the presence of 2 fold and mirror symmetry in a lattice. As you know the systematic absence conditions are result of different symmetry elements, which result in a translation other than a lattice translation.

So, if you have a centering that is, lattice centering c centered, f centered, or a body centered lattice or if, you have to 1 screw 3 1 screw 4 1 screw or any other glide planes, which involve half translation. Those different symmetry elements would result into systematic absences. And then, when we look at those system absence conditions, look for the systematic absence conditions in the h k l file after data reduction, one can identify the correct space group from systematic absences.

But mind you the symmetry elements like 2 fold and mirror plane do not cause any systematic absence conditions. So, as a result the appearance of 2 fold and mirror does not come from direct observation of any systematic absence. For these two symmetry elements one has to look at the h k l data statistics in a more careful manner as, I am going to discuss now.

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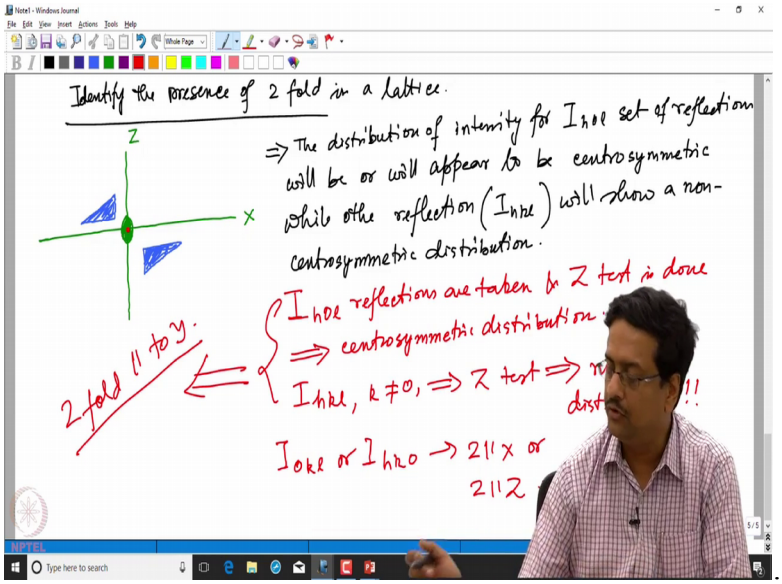

We would like to first identify the presence of 2 fold in a lattice. So, suppose if I have 1 object, suppose if I have 1 object like this, and I then apply a 2 fold symmetry here, it rotates like that. And then if I am trying to project this object on this particular plane, the plane which is perpendicular to the 2 fold then the district then the projection look centrosymmetric. For example, if I have a 2 fold like this and I am rotating this object from here like this, so it is a 2 fold rotation and then, I am projecting it on a plane perpendicular to this 2 fold from top.

So, what if it would look like is that, this object is rotated here and projected. So, how would it look like, I am trying to draw in this 2 dimensional projection. Suppose my 2 fold is parallel to Y, so I am present projecting it in the X Z plane. So, this 2 fold which is along Y is marked here. So, this is my object which I am now rotating about this axis a 2 fold rotation on this would take it here. So, this projection seems to be centrosymmetric about the center there.

So, this appearance of a pseudo center of inversion, results into a certain results into a certain symmetry among a set of reflections. So, this apparent symmetry the apparent center of inversion on X Z plane would imply that, the distribution of intensity for all I h 0 l set of reflections will be or will appear to be centrosymmetric, while other reflections that is the general I hkl will show a non centrosymmetric distribution. So, what do we mean? We mean that if the test for centrosymmetry is done with the reflections which has

Miller indices like I h 0 l, so all h 0 l reflections are taken and the Z test is done like the previous class we did a Z test is done.

This would indicate a centro symmetric distribution, but if, we take general hkl set of reflections where k is not equal to 0 and do the same Z test, we would see that it indicates a non centric distribution. And hence, one can conclude the presence of 2 fold parallel to y. In the same manner one can look at I 0 k l or I h k 0 set of reflections to find out in the presence of 2 fold parallel to X or 2 fold parallel to Z. So, by looking at this distribution of intensities about different set of hol or 0 hl or hk 0 set of reflections, one can identify the presence of 2 fold in a lattice.

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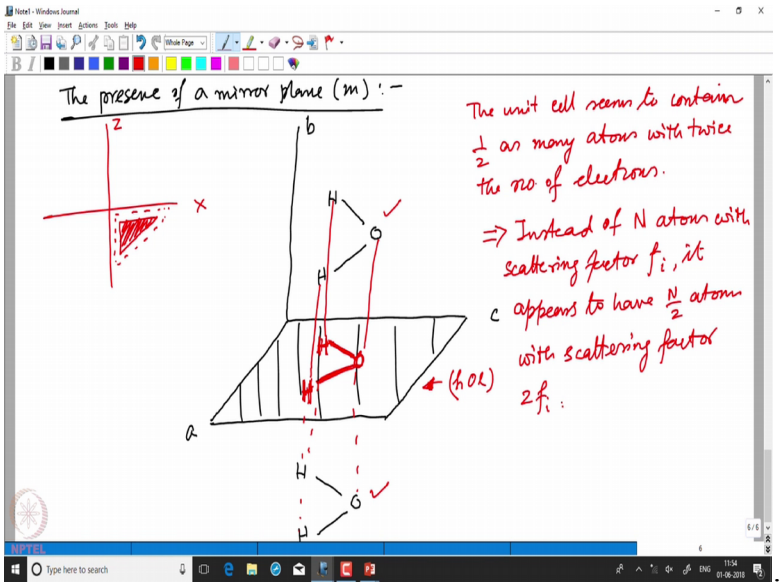

Now, let us see how one can find out the presence of a mirror that is m. A simple mirror without any translational component associated with it. So, in case of a mirror if, this X Z plane is a mirror plane, any object which is above the plane of this mirror gets reflected and goes back in the lower part of the lattice just like, one object having position here and then you have a mirror plane in between, so the object gets reflected like this. So, this object and its reflection are in this orientation and the corresponding projection of both this object and the mirror image on this mirror plane gives an impression of double atom located at same place.

So, what does it mean, it means that if I draw it in 3D if I have suppose, my molecule is a water molecule, the corresponding mirror plane is here; this a c is my mirror plane, the

reflection of that water molecule should come below this mirror plane as, I am drawing here. And the actual projection of this water molecule on this plane from the upper side falls at these 3 places and from the lower side also falls at the same places.

So, what it indicates that, the electron density associated with this particular plane which is, the plane where it is the h 0 l set of planes, it has a projection of one molecule from top and one molecule from bottom, indicating that the unit cell seems to contain half as many atoms with twice the number of electrons. So, this indicates that instead of N atoms with scattering factor, f i it appears to have N by 2 atoms with scattering factor twice of f i.

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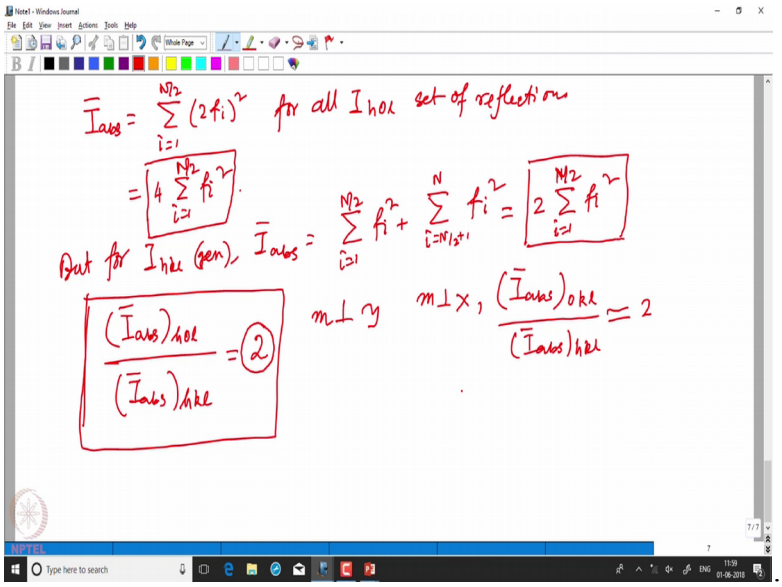

So, in this situation, we can calculate the average I abs as sum over i equal to 1 to N by 2 into twice f i square for all I h o l set of reflections which means, it is equal to 4 sum over i equal to 1 to N by 2 f i square. But for general h k l reflections, one should calculate I abs as sum over i equal to 1 to N by 2 f i square plus sum over i equal to N by 2 plus 1 to N f i square because, in those cases these two sets of atoms are considered to be at different locations and they are different. So, this would indicate that the sum is nothing, but 2 into i equal to 1 to N by 2 f i square. So, now, if I take a ratio of I hol average, I will be done in another 10 minutes.

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So, if I take now the average of I abs for the set of reflections within this as h 0 l to the I abs for the set of general reflections hkl, what we get is nothing, but this quantity divided by the quantity here. So, the number comes out to be just 2. So, if we carefully look at these I abs values for sets of reflections hol and hkl in the reduced data set then, what we get is a number 2 a fraction factor 2 which, then indicates the presence of a mirror plane perpendicular to y.

So, for a mirror perpendicular to X, one should find out the value for I abs for 0 kl set of reflections divided by I abs for hkl and see whether, it is giving you the value 2 that will indicate the presence of mirror perpendicular to x. And similarly, mirror perpendicular to Z also can be found out using this method. So, in these two statistical analysis of your observed data, one can identify the presence of a mirror or a 2 fold axis which otherwise cannot be found using any systematic absence conditions.

So, in today's this part of lecture we have learnt about how to identify the 2 fold symmetry, how to identify the mirror symmetry in the lattice. So, these all are important aspects to find out the correct space group at the end of this data reduction process. As I have already indicated we cannot determine this space group correctly, then the structure solution will not give you correct structure and we will be struggling to get the correct structure without a correct space group.

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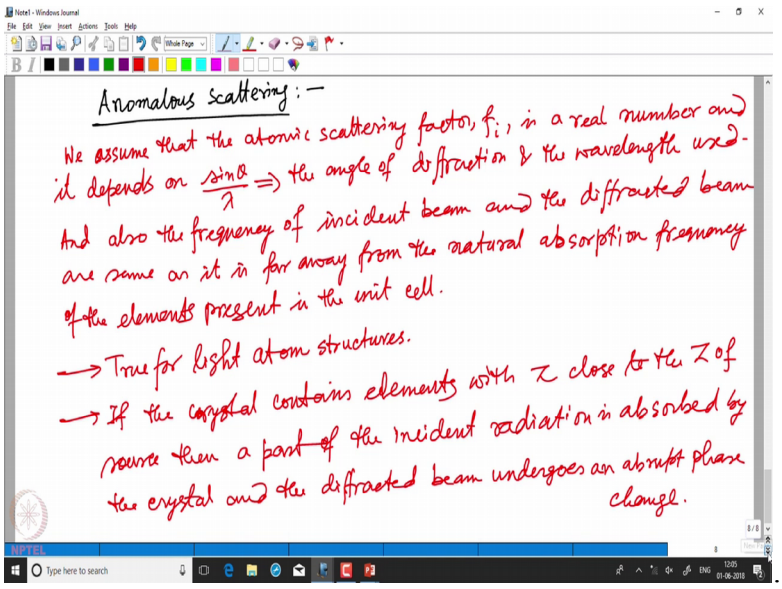

So, now I would like to discuss another different aspect of a crystal data, which we generally encounter with crystals which are containing heavier elements, and specially the elements which contain which are very close to the source element; that means, if I am using copper radiation the metal ions which are close to copper like iron, cobalt, nickel or in case of molybdenum, if we are using tungsten or something like that, these elements give rise to a new phenomena called the anomalous scattering.

So, what we do is we assume that, the atomic scattering factor that is f i is real number and it depends on sin theta by lambda. That is, it depends on the angle of diffraction and the wavelength used. And also the frequency of incident beam and the diffracted beam are same as it is far away from the natural absorption frequency of the elements present in the unit cell.

This is true for light atom structures, but if the crystal contains elements with Z close to the Z of source then, the incident or rather then a part of the incident radiation is absorbed by the crystal and the diffracted beam undergoes an abrupt phase change. So, this effect is called the anomalous scattering of X-rays from a crystal which contains heavier elements.

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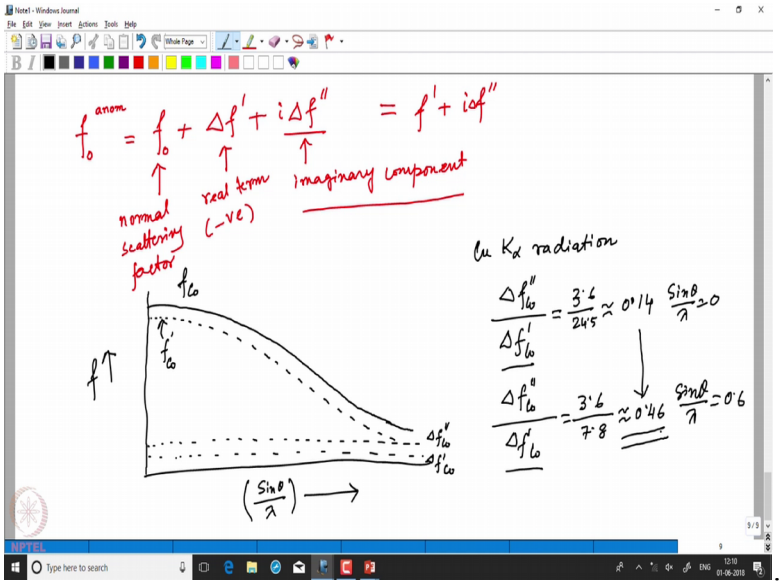

So, then in that case, the scattering factor for an atom with anomalous scattering into taken into account is written as f 0 plus delta f prime plus i delta f double prime where, this f 0 is the normal scattering factor, this delta f prime is the real term and in general it

is negative and this is the imaginary component of this anomalous scattering. So, one can write this as f prime plus i f i delta f double prime.

So, what happens when we try to plot, the scattering factor with sin theta by lambda. This plot may look like this for f cobalt using copper k alpha radiation and the scattering factor of cobalt varies like this if, you consider the corresponding anomalous scattering of radiation. And what we can see that, the values for delta f double prime for cobalt and delta f prime for cobalt are sort of constant over the entire range of sin theta by lambda.

So, what happens is that, when we try to calculate the values for delta f double prime cobalt by delta f, double prime for delta f single prime for cobalt at sin theta by lambda 0, the values are like this 3.6 by 24.5 which is equal to 0.14. But the same this ratio of delta f double prime of cobalt by delta f prime of cobalt at sin theta by lambda equal to 0.6 is 3.6 by 7.8 which is nearly equal to 0.46 indicating that there is a nearly 3 fold increase in this ratio.

So, the anomalous scattering is more significant for high angle reflections compared to the low angle reflection because, at high angle the actual scattering factor of cobalt has fallen so much that, the influence of the second time is taking over and we see a more anomalous scattering at higher angle. So, one has to do a correction for such anomalous scattering during the data reduction as well and then, use the data for further processing.

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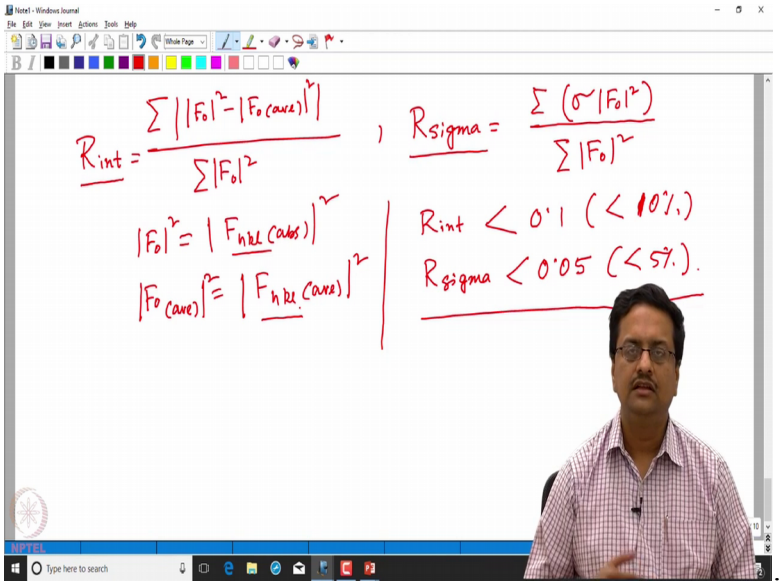

So, once we have done a data reduction, we have taken care of all the problems, we have taken care of absorption, we have discussed about the symmetry determination, we have discussed about the identification of 2 fold and mirror symmetry and so on. So, once all the corrections are applied we have also identified what source it was and what kind of exposure time was given. So, all the relative intensities are now in the absolute scale.

And then, we need to see a few terms to identify how good or how bad the data is. So, to do that we can calculate these two quantities one is R int, which is nothing, but a ratio of these 2 quantities, where we write F o square is actually the F h k l in absolute scale the square of this amplitude and F o average square is nothing but F h k l average square that is the mod of structure factor square that is the intensity. And we also calculate another quantity called R sigma, which also is related to this observed structure factor amplitude square; that means, the intensity.

So, we do the sum of all the standard deviations on the intensity that is F o square and do a sum of all those standard deviations of individual measurements and then the sum of F o square that is the intensity. So, we then worry about these two quantities R int and R sigma at the end of this data reduction process. The acceptable values are R int should be less than 0.1; that means should be less than 10 percent and R sigma should be even less than 0.05, which is very less than 5 percent. These two indicators are very important one has to look at these two indicators at the end of data reduction to identify the quality of the data.

If we see that the R int is very high, that may be 20 percent or 18 percent or 25 percent which indicates that, there must be something wrong; either we have not determined the unit cell correctly or we may not have given a correct scaling or there must be something else which is wrong, which may be even movement of the crystal during data collection, which may be the i's formation during data collection, because i's gives you different kinds of diffraction peaks which can then merge with your crystal data your own intensities. And then, which will actually result in to a wrong measurement of every intensity that you are using in this calculation. So, all these can lead to a very large R R int and this large R int may cause problems during the structure solution as well.

So, today in this lecture we have now learnt about how to identify the 2 fold symmetry and the mirror symmetry. And then we have discussed about the anomalous scattering

and also we talked about the two major important indicators of quality of data that is R int and R sigma. So, in the next class we will start to understand how to do a structure solution using different methods.