Chemical Crystallography
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Lecture – 27
Single Crystal X-Ray Diffraction Data Collection

Welcome back to this course of Chemical Crystallography. In last about 4 weeks we have learned some basic aspects of X-ray diffraction, we have discussed about crystallographic symmetry. We have talked about point groups, space groups. We learnt about how to draw those point groups and space groups in a 2 dimensional projection we called it as stereographic projections. And I have given you a set of homeworks which I think you must have tried.

In the previous lecture we were talking about the crystallization methods, different ways one can crystallize different types of materials. In that, we discussed about the crystal growth from a pure solvent, crystal growth from a mixture of solvents, vapor diffusion method, then we talked about crystallization of inorganic materials. And then we discussed about the in situ crystallization using optical heating and crystallization device.

So, while discussing about crystallization processes we also talked about how one should identify and choose a crystal for a diffraction experiment. One should look at the crystal under optical polarizing microscope, use the analyzer efficiently to identify the crystals which are showing extinction as is seen in the case.

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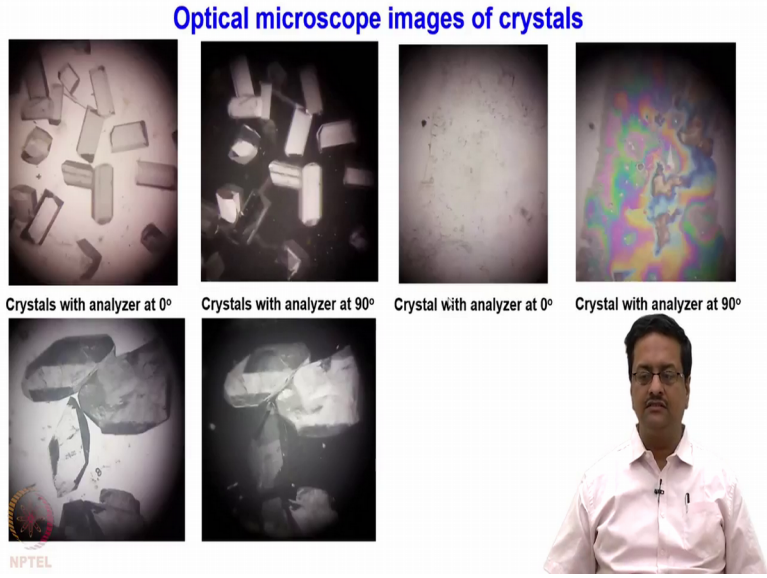

There, it is seen in the case of this crystal which shows extinction, when the analyzer is rotated by 90 degree. In the same way another crystal which is of irregular shape, also shows extinction when the analyzer is rotated by 90 degree.

Here in the case of right hand side crystal as we have seen, the analyzer when it is at 0 degree, it shows that the crystal is transparent. But, when we rotated the analyzer by 90 degrees shows multiple colors, indicating that there are different domains on in which the crystal unit cells are oriented.

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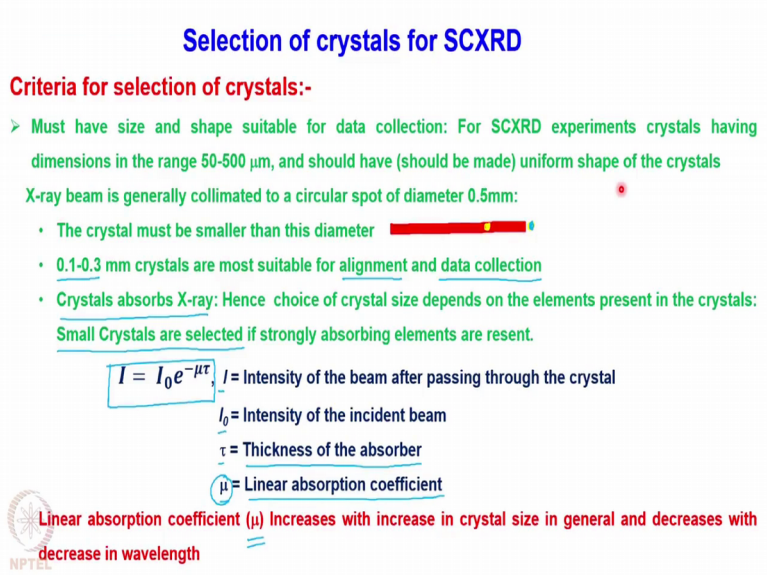

Then we learnt about selecting a crystal.

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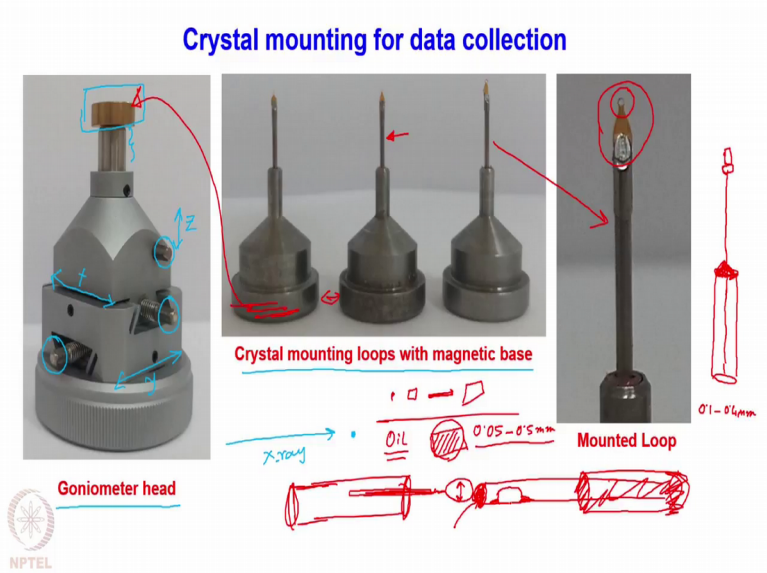

And, we learnt about how to mount a crystal. In this part of the lecture I think I did not mention another way of mounting which we used to use at some point of time. But even now one can use it for data collection, in case you do not have access to these loops. What one does in that case is, you take a thin glass fiber, mount it on a brush pin; which is available with every diffractometer facility and then glue it at the bottom so that the glass fiber does not move.

Mind you this, the diameter of that fiber will be from about 0.1 to 0.4 millimeter. So, this is a very thin glass fiber. And one can use some glue which hardens very quickly something like epoxy or the glue available from different suppliers with that glue we take little bit of glue at the tip of this glass fiber, and then stick the crystal on top of it as vertical as possible. And then we mount this brass pin with the crystal on that diffractometer and try to collect data.

The other option is that if you have a sensitive crystal which is maybe moisture sensitive or air sensitive, then one can use the Lindeman glass capillaries which we used in case of liquid samples. So, what we can do is, we can take a piece of a Lindeman glass capillary of a desired diameter, and then insert this capillary in the same brush pin a cylinder like this, and close it with glue the bottom is also closed with glue, and then we insert the crystal from top.

We choose the loop such that the crystal of fits inside the loop, and we put this crystal along with a bit of oil which holds the crystal on the wallbecause of surface tension. And then, we can close the top of this capillary with glue so that the crystal can be isolated from the external atmosphere and we do not have any contact of the crystal with the air or moisture which is there outside.

So, by doing these different types of mounting one can then do the data collection on any diffractometer.

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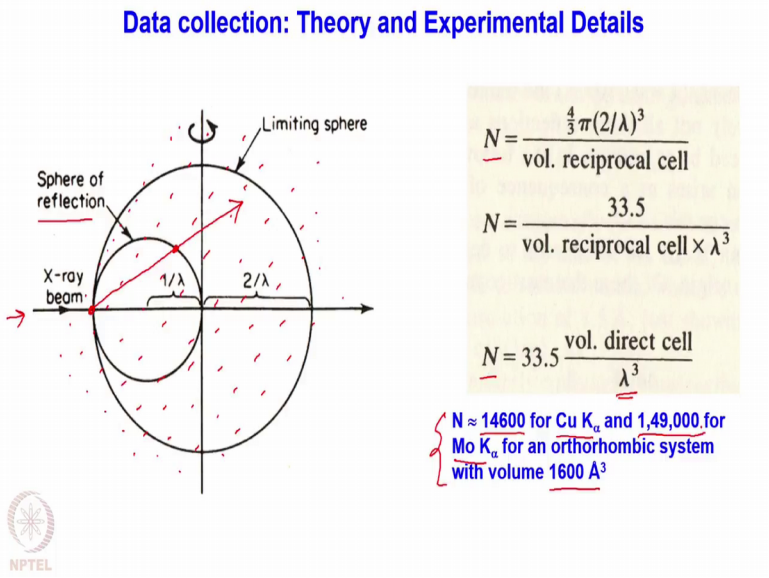

So now, let us try to understand the theory and experimental details behind this data collection methodology. When we are saying that we would like to collect a crystal data; that means, we are trying to collect the diffracted intensity out of all the reciprocal lattice points which are falling within the, which are falling within this limiting sphere as we have learnt in the previous lecture. This limiting sphere contains reciprocal lattice points at a given distance. And those lattice points represent direct planes in the real crystal, and when these reciprocal lattice points coincide with the sphere of reflection or the Ewald sphere which is here diffraction occurs.

Hope you remember that we have shown one animation where it was shown that, if we shine X-rays from one side. And the crystal is kept here as soon as one of the points meet the circumference of this Ewald sphere a reflection is generated. This is the X-ray diffraction X-ray diffracted beam that is then recorded using a detector. We have also to

discussed that the total number of reflections that one can have from a given crystal is limited. And that limitation comes from the volume of the direct cell and the wavelength that is used.

So, for crystals with larger unit cell dimensions; that means, having a very large volume, will have large number of reflections compared to the crystals having a very small unit cell. Once again if we change the wavelength from molybdenum to copper or copper to molybdenum there is a drastic change in the number of reflections, as we discussed in one of the previous lectures using copper k alpha radiation for an orthorhombic system if we can get 1600 reflections. Sorry, if we take one orthorhombic system with 1600 cubic angstrom volume and use copper k alpha radiation. We may get about 14,600 reflections, whereas if we use molybdenum k alpha radiation it increases by about 10 times.

So, what constitutes the unique data? These total number of reflections that one can achieve is called the overall data, but then all these h, k, l values that are being measured are not independent of each other.

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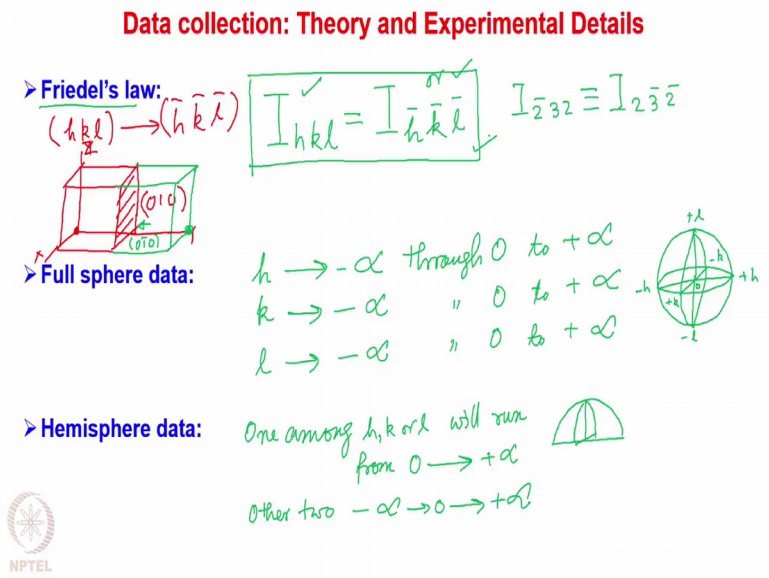

As we know the plane if we represent a plane h, k, l and another plane h bar, k bar, l bar, what are they? These 2 planes are one and the same, but the miller indices was generated using a different set of origin. Just to make you understand, suppose I am talking about the 1 0 0 or maybe we talked about let us let us draw it as this. And this particular plane is 0 1 0 with respect to the origin here.

But the same plane if we are considering from the other side. So, with that origin we are talking writing this as 0 1 0, but then if we; and then with respect to the new origin located at this point the same plane looked from the right hand side would have miller indices 0 1 bar 0. What does it imply? It implies that a plane h, k, l and it is all negative indices like h bar, k bar, l bar represent the same plane. And once these 2 are same plane the planar density of h, k, l is same as planar density of h bar, k bar, l bar; that means, the diffraction from the plane h, k, l is going to be same as from the h bar, k bar, l bar.

So, the deflected intensity that is I h, k, l that is the intensity of the diffracted beam from that particular planet with indices h, k, l is going to be same as the intensity of diffraction from h bar, k bar, l bar, which means, in case of a data in case of a particular crystal where we have a reciprocal lattice, it forms a sphere and that sphere has a large number of reflections. But half of them represent the other half, because every h, k, l has it is equivalent reflection h bar, k bar, l bar.

So, any reflection suppose I 2 bar 3 2 is same as I 2 3 bar 2 bar. And it is true for all values of h, k and l; which means when we collect a full sphere of data which means collecting all the possible values of h, k and l ranging from minus infinity to plus infinity through 0 corresponds the full sphere data. And which is already an excess amount of data because the Friedel's Law which we have indicated here which is mathematically written as that I h k l equal to I h bar, k bar, l bar is valid for all the crystals no matter whether it is centro symmetric or non-centro symmetric.

So, when we say that we are collecting a full sphere data; it means that we have h ranging from minus infinity through 0 to plus infinity; K ranging from minus infinity through 0 to plus infinity and l also ranging from minus infinity through 0 to plus infinity. This means if we consider the reciprocal lattice as a sphere like this, with h, k and l running from origin to either side. So, if this is the origin if we say that this is plus h 2 minus h plus k 2 minus k plus l 2 minus l this corresponds the full sphere of data.

So now if we try to collect only the one part of Friedel's Law; that means, if we either want to collect this or that we only need to collect half of this entire sphere. So, that means, one among these h, k and l we can start from 0 and collect up to infinity. So, one among h 1 among h, k or l will run from 0 to plus infinity. And other 2 will run from

minus infinity through 0 to plus infinity which would mean that we are actually collecting the data one of the 2 parts of a sphere.

So, what we understand from here is that the distribution of intensity among the sphere that is the reciprocal lattice sphere is centro symmetric in nature, the distribution of intensity being centro symmetric; following Friedel's law we only need to collect the hemisphere of data.

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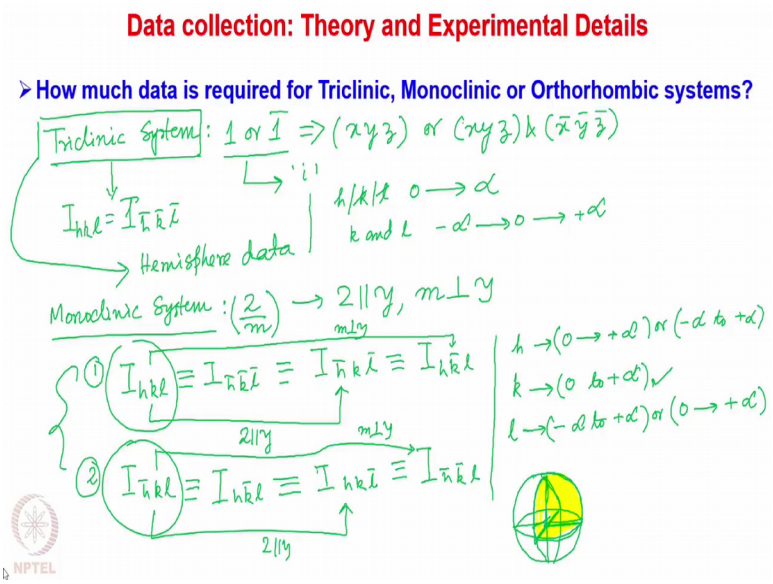

So now, when we have a triclinic system, what symmetry do we have? We can have one or maximum 1 bar which means we can only have x, y, z or x, y, z and x bar, y bar, z bar as equivalent points.

So, these means we have only to a maximum of inversion symmetry. So, in case of triclinic the only symmetry that the intensities can have is the Friedle's law. And no other symmetry is present in case of triclinic lattice. So, that means, for a triclinic system we should only collect the hemisphere data. And that will constitute the maxima, the full amount of data that was needed for a triclinic system.

So, in case of triclinic either h, k or l should run from 0 to infinity. Suppose, if h is running from 0 to infinity then k, and l will run from minus infinity through 0 to plus infinity. For monoclinic systems what do we have? For monoclinic system the symmetry is 2 by m. The maximum symmetry is Laue symmetry is 2 by m. So, this 2 by m

indicates that we have a 2-fold axis parallel to y, and we have a mirror plane perpendicular to y.

These 2 symmetry conditions give rise to 2 sets of reflections. One set corresponds to I h, k, l equal to I h bar, k bar, l bar which is nothing but Friedel's law; is equal to I h bar k l bar which is a 2-fold operation from the first point parallel to y. And the corresponding Friedel made of this reflection which is h, k bar l which actually is a mirror operation perpendicular to y.

So, these 4 reflections have the same intensity, and they fall in one particular group. And the second set of reflections will have having indices like this. H bar k l the corresponding Friedel's equivalent or Friedel's opposites h, k bar l and then again we apply 2 fold on this first h, k, l. So, we get h, k, l bar and the corresponding Friedel opposite of this is h bar k bar l.

So, that means, this is a 2 parallel to y and this is a mirror perpendicular to y. So now, we have 2 such sets of reflections which are equivalent. So, this means that we only need to record one among all this and one among all that. And as a result, the amount of data that is needed to collect the total number of reflections which is minimum required for monoclinic is reduced to one-fourth.

So, in this case the values for h, k and l that are required to be recorded is like this. Since, y is the unique axis we should collect k from 0 to plus infinity. And one of those to either h or l from 0 to plus infinity, and the other one from minus infinity to plus infinity, either this, r minus infinity to plus infinity for h, this remains the same this again changes from 0 to plus infinity which means we are only trying to collect the one-fourth of the sphere which I am going to mark now. This is a full sphere, one-fourth would mean that one of these indices is running from minus to plus. This index is running from 0 to plus, and this index is running from 0 to plus.

So, the region covered in this part is the one-fourth of data, let us try to highlight these region with yellow. So, this small region is the one-fourth of this sphere. This can be understood if you consider an orange. And that orange if it is cut from the middle is half of the sphere, which is only the upper half, and that upper half if it is chopped vertical, then what segment we get is one-fourth of the sphere and we are talking about that one-fourth portion in this particular case.

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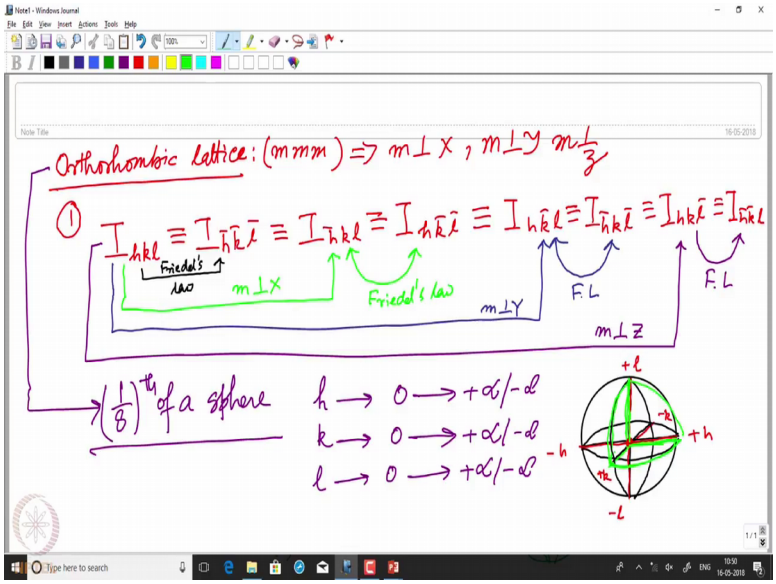

For orthorhombic system what we have? In case of orthorhombic lattice, the symmetry that we have is m m m that is the miller that is the Laue symmetry of orthorhombic system. What does it mean? It means a mirror perpendicular to x, a mirror perpendicular to y and the mirror perpendicular to z.

So, when we have such orthorhombic system, we have the condition satisfying these 3 symmetries resulting into the intensities of different sets of h, k, l reflections to be equivalent. So, i h, k, l is equivalent to I h bar, k bar, l bar which is Friedle's law, then it is equivalent to a mirror perpendicular to x indicating h bar k l is also same as h, k, l; the corresponding Friedle's opposite is h, k bar l bar, is again equivalent to I h, k bar l which is mirror perpendicular to y and the corresponding Friedel opposite is I h bar k l bar; is once again equivalent to i h, k, l bar.

That is mirror perpendicular to z and the corresponding Friedel opposite h bar k bar l. So, let us write down the relationships between these points once again. This is Friedel's law, this I h, k, l being equivalent to this I h bar k bar is because it has a mirror perpendicular to x. Then this h bar, k bar, l bar equivalent to this indicating mirror perpendicular to y, and this indicates mirror perpendicular to z. And the corresponding pairs here are related by Friedel's. What does it mean? There are 8 different sets of h, k, l's which are equivalent.

So, if you collect any one of these 8, it is going to represent all those 8 reflections in the reciprocal sphere. So, all these 8 reflections need not be collected, but one can only collect one of those 8, which indicates for orthorhombic system we only need one-eighth of a sphere. This one-eighth of a sphere means, we only need h ranging from 0 to plus infinity, k ranging from 0 to plus infinity, and l also ranging from 0 to plus infinity. Or minus infinity does not matter. Because the reflections that you generate that you get in the upper octant is same as the lower octant and so on.

So, what are we trying to mean here? We mean that if this is a sphere, and then we have divided into 8 parts. So, starting from the origin which is here, one can have plus h and minus h plus k minus k plus l 2 minus l. So now, if we just want one-eighth of this particular sphere, we are only trying to record a data falling in this small segment marked in green. See here, in all the cases it is running from 0 to plus h 0 to plus k and 0 to plus l.

So, only one-eighth of the data is recorded for orthorhombic system. As a matter of fact, the number of unique reflections that are needed to be recorded further decreases when you have higher and higher symmetry. And you need lesser and lesser amount of data to represent the actual required data for any crystal structure determination. So, in today's lecture we have learnt about the crystal mounting. Then we talked about the number of reflections that one can achieve using the Ewald sphere and limiting sphere concept, and then we try to understand; what are the unique data that is required for low symmetry cases which are most common in crystallography. Triclinic monoclinic an orthorhombic these 3 different things need only a very limited data.

Why do we need to know this? The reason that we need to know this is that if we are trying to collect a data, we should determine a strategy for data collection. And in that strategy for data collection we should give appropriate input based on the initial information about the unit cell parameters to the diffractometer and then only we should be able to collect the required amount of data. Otherwise the data that we collect will be incomplete.

So, in the following class we will discuss about the actual experimental way of collection of single crystal data, what are the parameters involved in that, what kind of detectors we have etcetera.