Chemical Crystallograhpy
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Lecture – 29
Diffractometers and Detectors

Welcome back to this course of Crystallography. In the previous lecture I was discussing about the data collection strategies for different types of diffractometers with 2 circle, 3 circle, and 4 circle diffractometer. So, in this context, I would like to continue discussing the data collection methodology is along with the basic aspects of a diffractometer.

See when we are using X-rays and we are trying to collect data using X-rays in a diffractometer on a crystal, we need to be very much careful about the methodology we need to be very much careful about the instrumental setup and we should know; what are different parts of that instrument. An X-ray diffractometer consists of one X-ray generator which is then connected to the X-ray tube.

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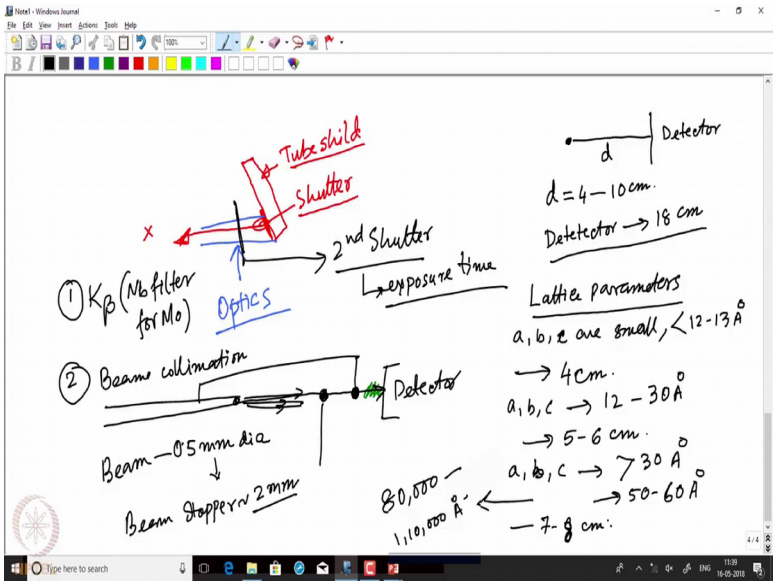

Which is suppose placed on a horizontal axis like this and the beam comes out in this direction.

So, when the X-rays are generated the X-ray beam directly comes out of the source and when we are trying to align or mount the crystal, we do not want this beam to be inside

the diffractometer chamber. So, to stop that what we have is a shutter mounted on the tube shield which is here mounted on the 2 shield to block the X-ray beam inside the tube only. So, this is one main shutter that one operates during a data collection the main shutter opens and it allows the X-ray to come in outside the tube. And then in the beam part here we have a set of optics. What does this optics do?

This optics has a number of jobs to do. The first thing is to eliminate the corresponding k beta radiation and that is done by putting a filter of niobium in case of molybdenum, niobium filter for molybdenum source. And then number 2 is to collimate the beam. So, beam collimation is done beam collimation is done in this optics region. And the beam is made to come out of the collimator as a set of parallel rays. Remember, this beam that is coming out the collimator and directly falling on the crystal is of very high intensity.

So, the beam that comes out from the collimator is capable of penetrating through the crystal and go straight and hit the detector, if kept in the beam path. This direct beam is a very very high intensity we have discussed about the intensities in the previous lecture probably in the first week. And we know that this intensity can be very very high if we have a rotating anode source. So, this intensity can damage the detector. So, to stop that direct beam which is passing through the crystal one has to place a beam stop. So, what it does is it stops the direct beam from falling to the detector and this beam does not reach the detector at all. The beam is blocked by this beam stop

So, the size of the beam stop is very important if the beam is of 0.5 mm diameter then the beam stop or other beam stopper should have a diameter of about 2 millimeter.

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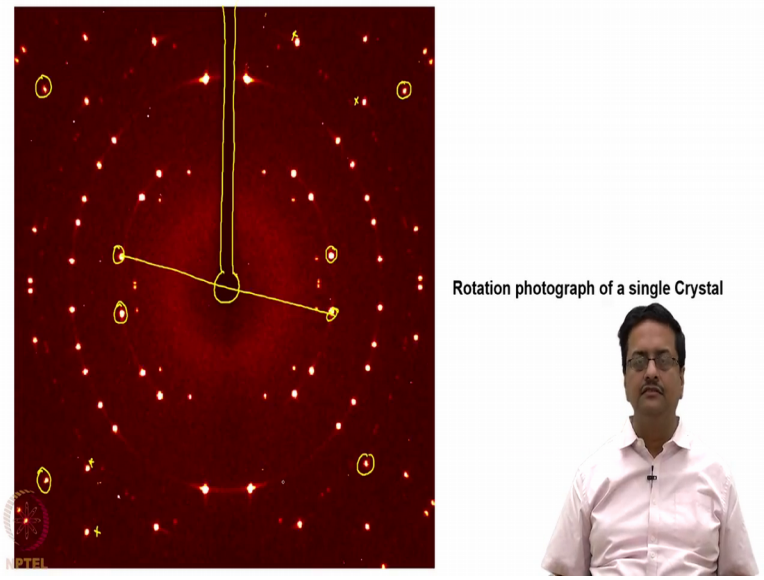

So, if you remember the figure we displayed here we have shown that there is a shadow region. There is a shadow region present in this nice rotational photograph of a single crystal. The shadow region represents the shadow of the beam stop which is coming which is actually mounted on the collimator and coming like that and stopping the direct beam from going through the beam stop.

Now, there is another shattered placed inside this optics, which controls the exposure time. The second shutter on the optics the second shutter on the optics controls the exposure time. So, during one particular run of data as we have seen in the previous day previous class that, we are saying that the exposure time is about 10 seconds.

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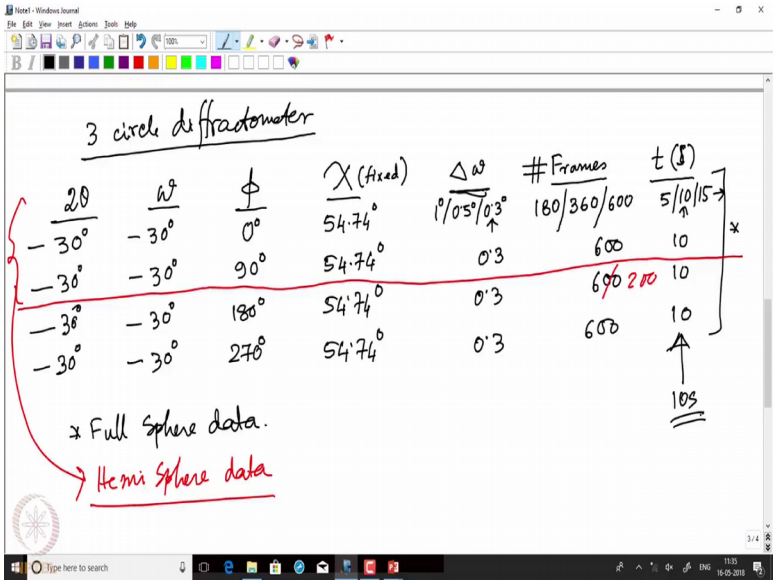

So, this particular shutter remains open for 10 seconds closes and opens again.

So, this regulates the exposure time on this particular experiment. The next important aspect is the sample 2 detector distance, if we have a crystal located at this point, the distance at which the detector is kept is called this sample to detector distance small d. This distance for any routine data collection can be between 4 to 10 centimeter. And the detector can move maximum up to 18 centimeter for various purposes. How do we decide what should be my detector distance? The detector distance is determined based on the lattice parameters. If the lattice parameters are small that is abc are small maybe less than 12 to 13 angstrom all of them; that means, the unit cell is very small.

So, in that case a smaller detector distance is suitable. Because what happens when we increase the (Refer Time: 08:58) to detector distance the intensity of the diffracted beam which is traveling after diffraction through air drastically reduces it is intensity with distance. So, the intensity falls off with 1 by r to the power 6 rule following. So, with larger and larger distance the intensity should fall so; that means, to get higher diffracted intensity one has to use larger exposure time.

So, there is no point in doing it at a higher distance for small molecules. Rather it is better we do it at a smaller distance, but depending on the size of the unit cell one can determine the size. If abc are in the range from 12 to 30 angstrom, the most suitable distance can be 5 5 to 6 centimeter, but then if they same value for a b c is greater than

30 angstrom maybe even up to 50 to 60 angstrom, which means we are actually talking about a very, very large unit cell having volume 80 thousand to one lakh 10 thousand cubic angstrom volume.

In that case, the detector distance must be increase to about 7 to 8 centimeter to achieve a good resolution on the spots that are coming out of this. Because, when you have large spacing between the diffraction in crystallographic planes different hkls 1 by ds are very small. And 1 by ds for too large distant planes are extremely close.

So, to resolve between the 2 planes with 2 different 1 by dhkls one has to go to a larger distance.

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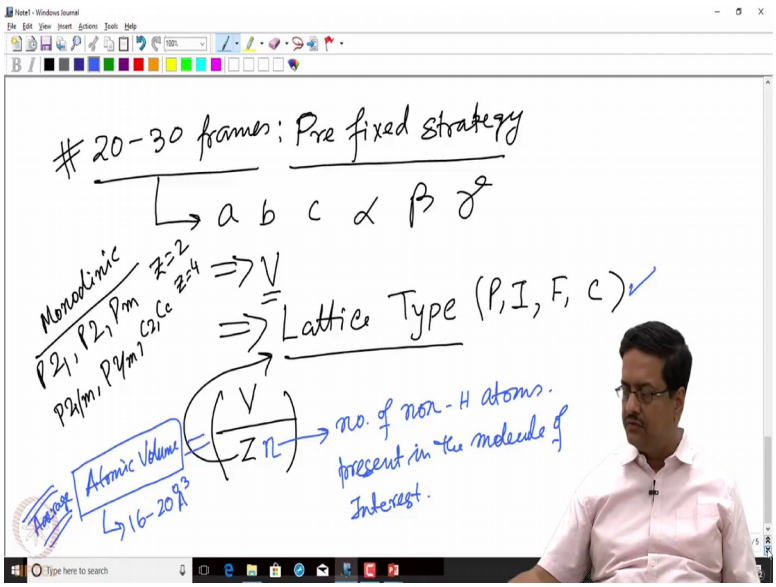

So, depending on the unit cell parameters one has to choose the detector distance. Now let us go see what is required before we collected data. When we have mounted a crystal and we want to know the unit cell parameters, there are different diffractometers following different strategies. In some cases, the diffractometer has a default process of recording a set of starting reflections starting frames.

So, in some cases it simply records about 20 to 30 frames with prefixed strategy. In most of the cases that strategy cannot be edited. And in some cases you can extend the strategy. So, with this pre fixed strategy what it gives a tentative values of abc, alpha, beta, gamma and from that one can calculate the volume. And in this process it also

indicates the lattice type. That means whether it is a primitive lattice or a body centered lattice or a face centered lattice or a c centered lattice in case of monoclinic system you can have c centered lattice as well.

So, based on this information a crystallographer like us would now try to find out whether the molecule that we have can be fitted in the given volume with particular lattice type. So, what we then do is, we take the volume of the unit cell divide it by the value z corresponding to that particular lattice type. And we consider possible space groups because in case of monoclinic suppose, if it is p 2 1; p 2 pm etcetera these z value is 2, but if it is p 2 1 by m p 2 by m c 2 cc z equal to 4.

So, depending on what kind of lattice is possible and what kind of lattice is coming we divide it by z. So, the volume being divided by z, it means it gives you the volume of the asymmetric unit that is the smallest unit. That is required to represent the lattice and that asymmetric unit must contain my total number of atoms. So now, if in a molecule you have a certain number of atoms containing nitrogen hydrogen carbon oxygen etcetera. We exclude the hydrogens and we calculate the number of non-hydrogen atoms has small n which is the number of non hydrogen atoms present in the molecule of interest and we calculate this number.

So, the volume of the unit cell is divided by z. That means, it is the volume of the asymmetric unit which contains my molecule. And then we are dividing that volume of the asymmetric unit probably the molecular volume divided by number of non-hydrogen atoms. So, this number results into the atomic volume. This atomic volume should range between 16 to 20 cubic angstrom. This is the average atomic volume I would say. So, this average atomic volume should range between 16 to 20 cubic angstrom if the desired molecule has crystallized in this particular lattice which we have determined from first few sets of reflections or first few sets of measurements. If the number does not match, then one has to think; what is the reason behind it. There may be some solvents present in the asymmetric unit.

So, depending on what solvent was used how many number of atoms non hydrogen atoms could be present in the solvent and how many such solvents may be present one can redo this calculation and check whether with the corrected calculation whether that number is matching. If this number is not matching, then one has to change the crystal

and then redo this measurement of initial few reflections. Once one has recorded these initial reflections and then recorded then is convinced with the identity of the crystal one goes for data collection as we have discussed in the previous slide.

So now, when we try to collect the data, historically there were lots of different methods of data collection.

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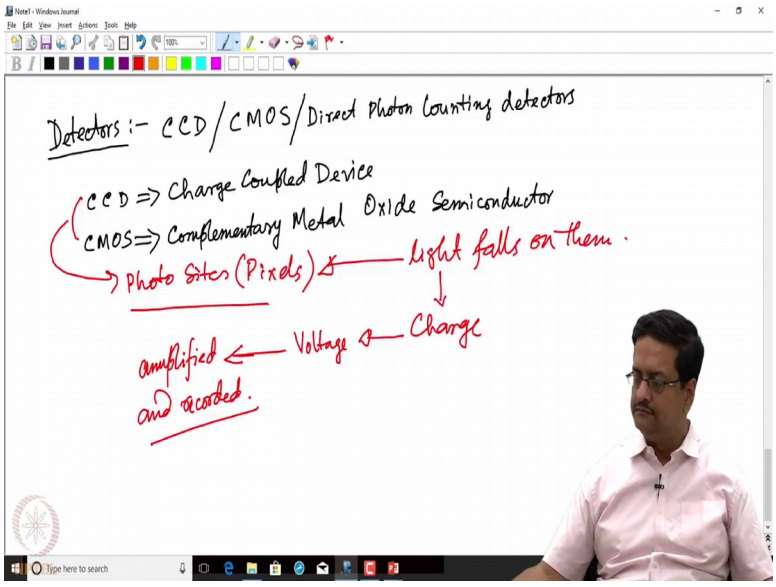

Initially all these X-ray diffraction data used to be collected using a photographic film. If you remember I have shown one of the photographic film data of this powder diffraction data which shows a concentric set of rings, but on today's date in modern times we record these data sets using various area detectors and those area detectors are also of different types.

. So, let us discuss about the recent detectors. So, in X-ray diffractometers we can use detectors like CCDs which are called charge coupled device or CMOS which is the complementary metal organic semiconductor set of detectors. And there are other detectors which are direct photon counting detectors. So, if we use a CCD which is charge coupled device or CMOS as a detector; which is complimentary sorry metal oxide semiconductor detectors, both these detectors are essentially photo sites and they have pixels. What both the detectors do is that when light falls on them they convert this light into charge? And then the charge is then converted to voltage. And then this voltage is

amplified and recorded. So, this general method is used in both CCD and CMOS type of detectors.

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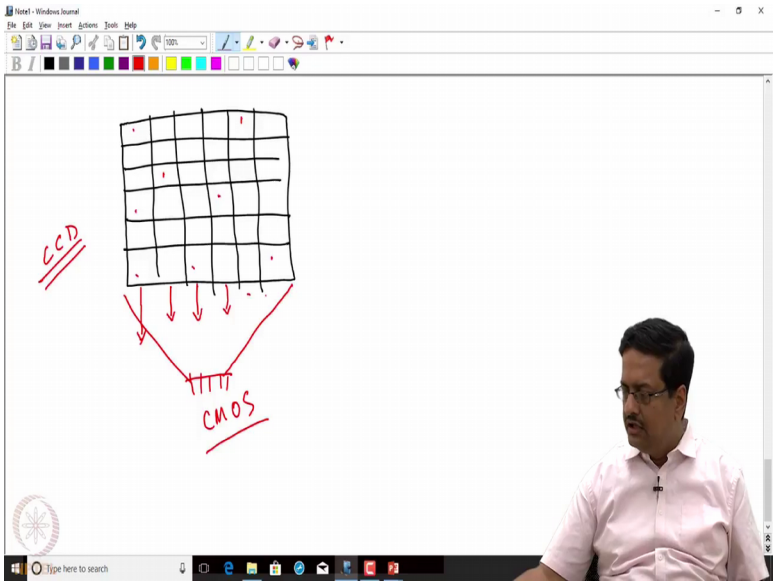

So now let us understand a little bit of underlying principle between these 2 different detectors and why one prefers CMOS against a CCD detector. As I indicated that both the detectors suppose it is square detector like this, has lots of photo sites which we call as pixels. And all these pixels are responsive to X-ray radiation. These are responsive to light and in this case these are responsive to X-ray radiation and wherever the diffracted beam falls suppose somewhere there here there here and so on a particular information is immediately recorded that is the intensity of that diffracted beam which is actually the number of photons that is falling on these surface.

So now once this these photons have impinged on that, immediately the CCD starts to process and because of these impinging photons a certain amount of charge is associated with those points with those diffracted beam positions. And the charge is then transferred. In case of CCD what happens is the readout happens column wise. So, once all the pixels all the photo sites have been read in one column then the second column is read then the third column is read 4th column is read and so on.

So, this process takes a certain amount of time; that means, reading out the data from each and every pixel for a CCD takes a longer time because the readout happens column wise and not simultaneously. In case of the CMOS detector a similar thing happens X-

rays fall on the detector, but then each one of those photo sites are simultaneously working as the converters. So, these sensing sites the pixels convert the charge to the voltage immediately. And then that voltage is transmitted simultaneously to the amplifier. So, in case of CMOS the entire readout is done simultaneous. And as a result the readout is much faster and hence one prefers a CMOS detector over a CCD detector on today's date.

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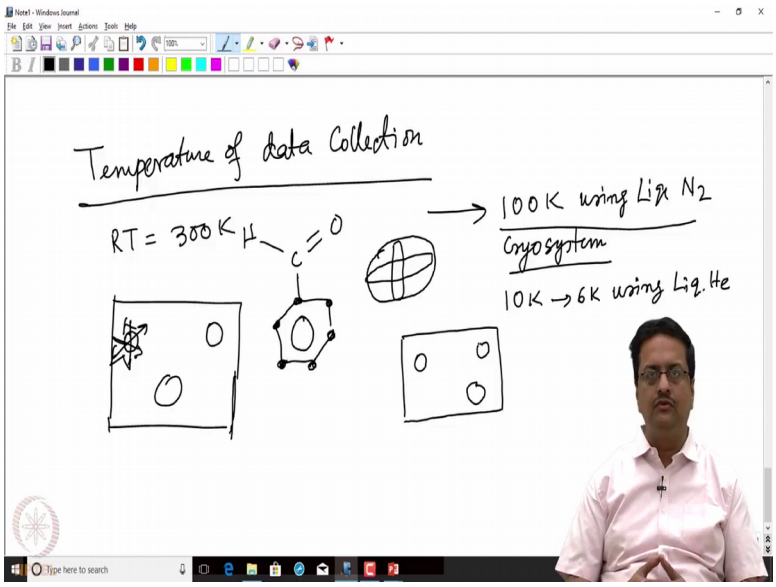

The next point that one needs to understand in case of single crystal X-ray data collection is the temperature of data collection.

A crystal kept at room temperature has the atoms or ions or molecules at room temperature which is about 300 Kelvin. At this particular temperature all the atoms ions or molecule has some significant thermal vibration. So, as a result if we consider one particular plane which suppose contains some atoms at various positions, at room temperature these atoms will vibrate about it is own axis in all the 3 directions; so because of that thermal vibration along x along y along z.

The electron density associated with each one of those atom is largely diffused in that particular plane. And when the electron density is largely diffused the diffraction from that plane is weak, because the X-ray diffraction happens from the interaction of X-rays with electrons. And if the electron density, because of atomic vibration because of thermal vibration of the atoms is diffused over a range of x y and z about that plane the

overall planar density is depleted and the intensity of X-ray diffraction from that plane at room temperature is diffused. And what we end up getting is if we try to determine the structure at room temperature suppose we have determined the structure of benzoic acid what we may see is that the carbon atom located at 6 positions of the aromatic ring and the carbon located as carboxylic acid group.

Those carbons will have a large thermal ellipsoid structure, and it looks like a big rugby ball or a extended sphere. So, this happens because of the thermal motion of each and every atom present in a molecule. So, that is why one tries to collect data at much lower temperature. Ideally one should collect the data at 100 K using liquid nitrogen triode system to reduce the thermal vibration and, but for very high quality very high accurate charge density measurements, one can go even down to 10 Kelvin or lower down to 6 kelvin using liquid helium as a source of cooling.

So, what happens at much lower temperatures maybe 50 degree to 100 degree or maybe 170 degree lower than room temperature this thermal vibration is reduced as a result the atoms corresponding to one particular plane has more spherical nature. And the electrons are confined more close to the nuclei. Because the nucleus is not vibrating so much the electron density is confined in 1 plane.

As a result, the diffraction quality that is the intensity of diffract beam increases. So, for any crystal if you reduce the temperature to 100 K it must improve the quality of diffraction from this crystal. Another point that might happen is that on decreasing the in temperature of a data collection that is the decreasing the temperature of a crystal you are reducing the volume of the lattice. And once you reduce the volume of the lattice the number of reflection changes.

So, temperature has an important role to play in each data. The bond lengths and bond angles have also influenced from this temperature. So, the bond lengths and bond angles determined from a data collected at 100 Kelvin is much more reliable than a data collected at room temperature. That is why we tend to collect data at much lower temperature.

So today we have learnt about data collection strategies. We have learnt little bit about the detectors. I would request all of you to go through other YouTube videos which are available online to know more details about the CCDs and CMOS and other types of

detectors. Because those are beyond the scope of this course the technical details of those detectors. And in the next lectures we will start once again the theory of X-ray diffraction, we will see how these X-ray diffraction data can be handled how the Braggs Law and structure factor scattering factors can be brought into, in solving these crystal data.

So, we will learn how to first understand these diffraction data in terms of scattering powers of different atoms and from there we will proceed further.