Chemical Crystallography
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Lecture – 36
Single Crystal X-Ray Diffractometer

Welcome back to the course of Chemical Crystallography. Today in this class today we are here in the Single Crystal X-Ray Diffractometer room. This is a Bruker kappa apex two diffractometer, which is a four circle diffractometer. So, let me start by explaining different parts to you.

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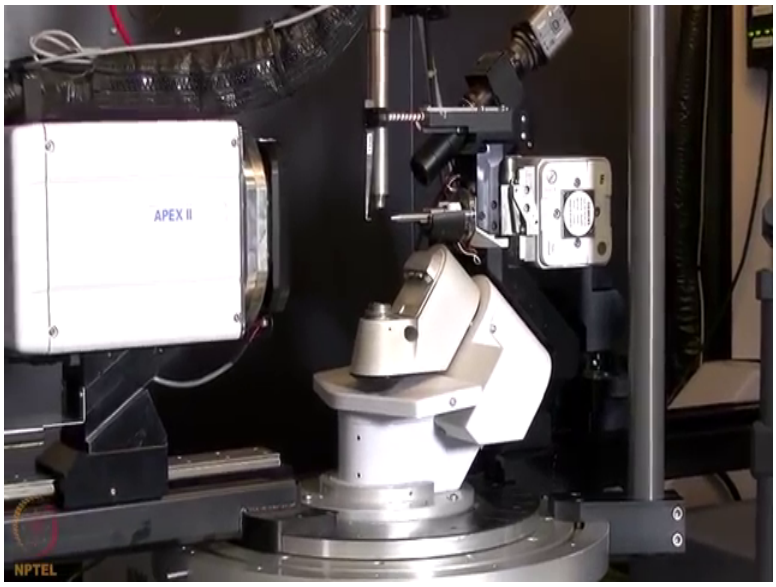

Is it too much on me you are not seeing me right now. So, this is the single crystal x ray diffractometer, it is equipped with a molybdenum steel tube x ray source, which is mounted here in the horizontal direction unlike the powdered x ray tube which was mounted vertical. This horizontally mounted tube is connected at the backside with the chiller, so that the chiller water comes and pulls this anode and goes back warmed up.

The same principle works here as well. In front of the x ray tube we have the optics which then does a fine focusing of this x ray beam. So, it makes it a circular beam and we have a monochromator installed inside this optics region which then monochromatices the beam. And is collimated through this collimator and it is made to fall on the crystal mounted on this base.

This base is the base for the mounting crystal where it can be rotated which I will show when I start operating this instrument. Here what happens is that, the base which is here it can rotate. So, that is my omega circle, when the crystal is mounted here the crystal can be rotated about it is vertical axis that is the phi axis and what we have here is this one, which can rotate left and right that is the kappa axis.

So, there are three axis on this goniometer, which we can see and then the source with this then the detector which is here can be rotated in the positive and negative direction. So, that is my fourth axis of rotation. So, this is a four circle diffractometer. Now, you can see here, the beam stop is mounted directly on this holder and this beam stop is now exactly in front of the direct beam. So, that the direct high intense beam is blocked by that particular piece of metal which is then not allowing the x ray beam to go and fall on that detector.

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Now, I am going to mount the cryst; now, I am going to mount the crystal which we want mounted in the lab under microscope on the diffractometer. So, this is the goniometer head on which we mounted the loop and this loop is a magnetic based loop. So, it can be fitted here by magnetic force. So, this goniometer head has to go and sit on the goniometer.

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You can see here at the bottom, there is a notch here and on that goniometer base there is a notch which go should go and sit along with this gap here. So, that is the locking mechanism which holds the goniometer head on the diffractometer constant then we turn the screw and just hand tighten it. And then you can see the crystal is mounted here, it is in front of the beam and then there is a beam stock.

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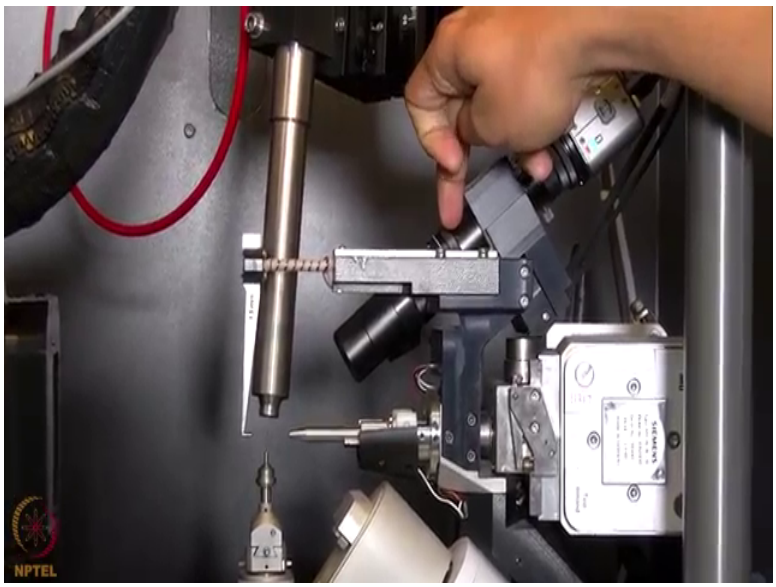

Of course, we need to do a physical alignment of the crystal in front of the beam by rotating some screws which we will show when we start operating the diffractometer.

This is the video camera which is focused on the crystal to view the crystal on the computer. So, using this video camera we can do the alignment of the crystal in front of the beam.

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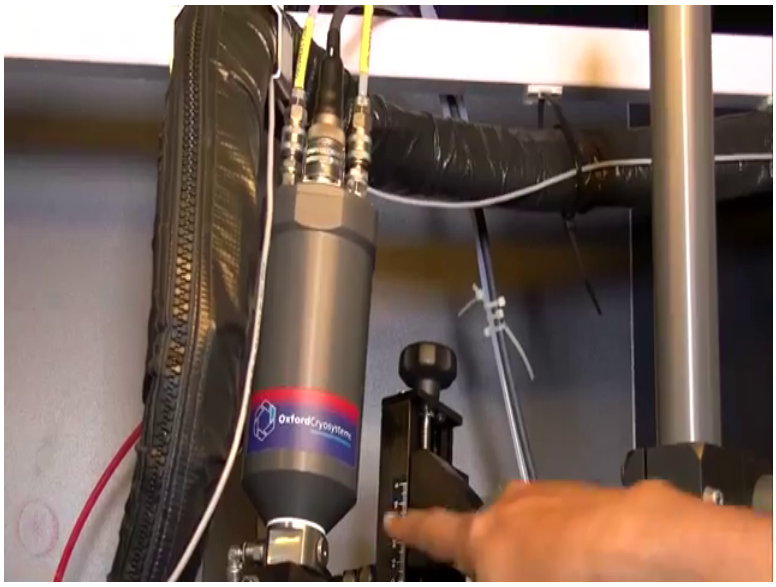

Here, we have the cryo head of oxford cryosystem that you can see; this oxford cryosystem helps us to cool the crystal to a very low temperature. We can go as low as 100 Kelvin using liquid nitrogen as coolant and collect data at 100 Kelvin temperature.

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This is the cryo controller for the cryo system, that can be operated either using these knobs or using a software, so, that we can reduce the temperature in a desired rate. So, we can cool the crystal as fast as 360 Kelvin per hour to 1 degree centigrade per minute or even 30 degree centigrade per hour kind of cooling rate can be used for sensitive samples.

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This is the indicator showing that the shutter is closed. So, the green lights are on, when the orange lights are on, it says x ray on; that means, the tube is on, it is generating x ray and it is keep kept at the lowest voltage and current the standby condition. And when the shutter is open, this red light will be glowing, which indicates that the x ray is inside the chamber so, we should not open the door. Just like powder x ray diffractometer, we would not be able to open the shutter until and unless we close the door in front of the diffractometer.

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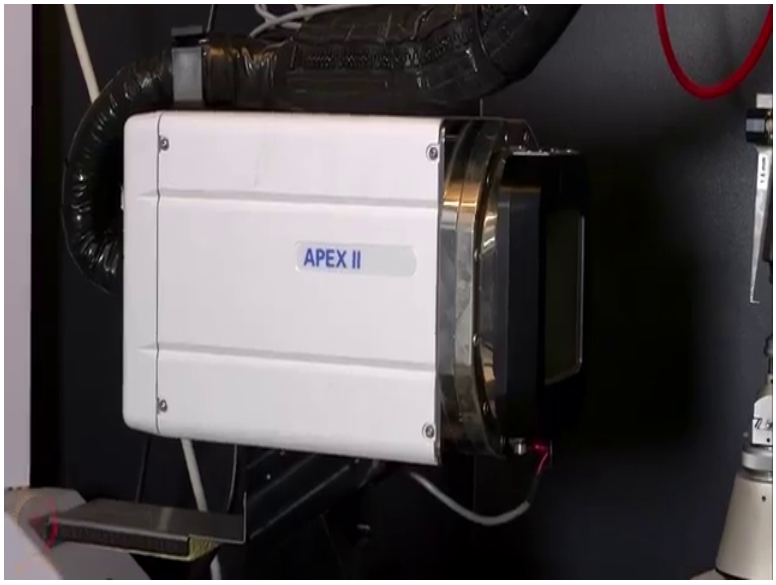

So, this is the apex two CCD detector which is connected with this instrument this detector can be moved back and forth from about 34 millimeter to 180 millimeter to the farthest end. And when the detector moves this side is 2 theta positive and if it moves to the other side it is 2 theta negative.

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So, it makes it possible for us to record data with all four possible orientations of the three possible orientations of the crystal and detector is moved at very high angle. So,

using this there detector one can record charge density quality data with high angle position of the detector like about 90 degree or 100 position of the detector.

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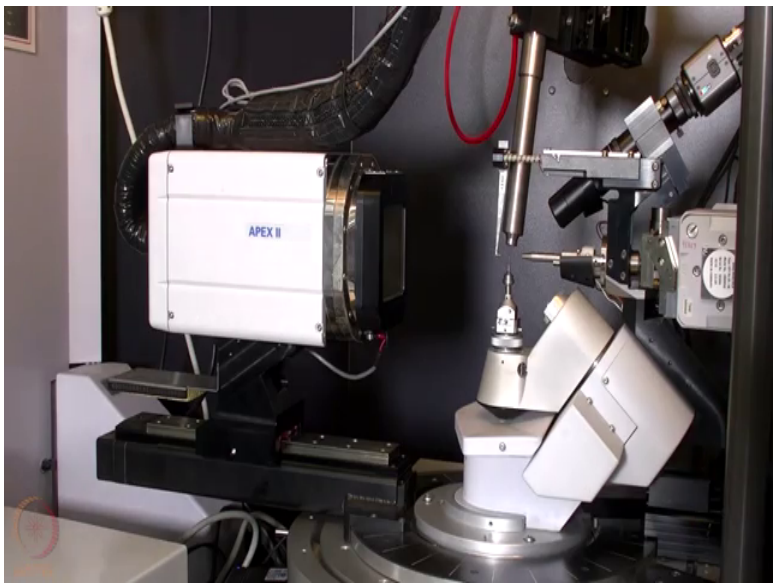

At the moment the goniometer is at 0, so, that omega is 0, kappa is 0, phi is 0 and 2 theta is 0. So, this is the 0 point for all the circles on the diffractometer.

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So, this is the setup of optical heating and crystallization device where we have one CO 2 laser placed in front of the diffractometer here.

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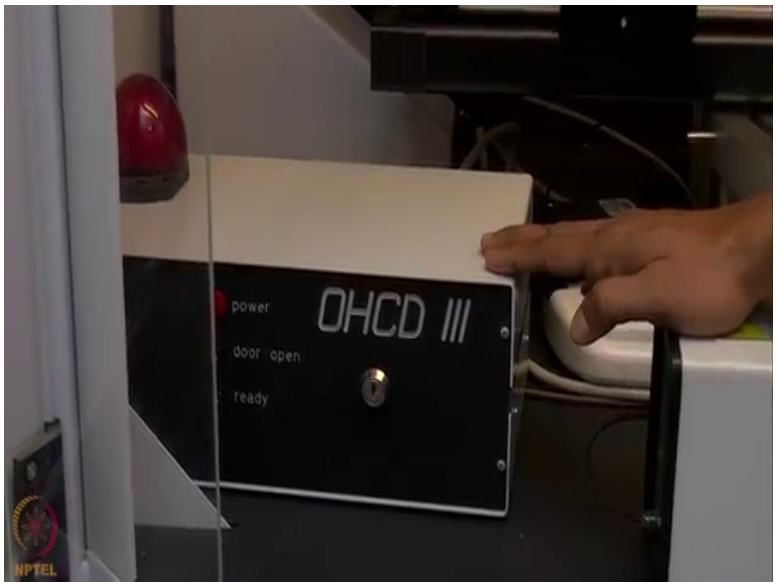

This is the controller of the OHCD which is then connected to the computer. So, that the voltage power supply to the laser is controlled and then this laser is placed inside this cabinet CO2 laser comes in this direction, gets reflected from here there is a mirror and that reflected beam comes up and again here it is convolved.

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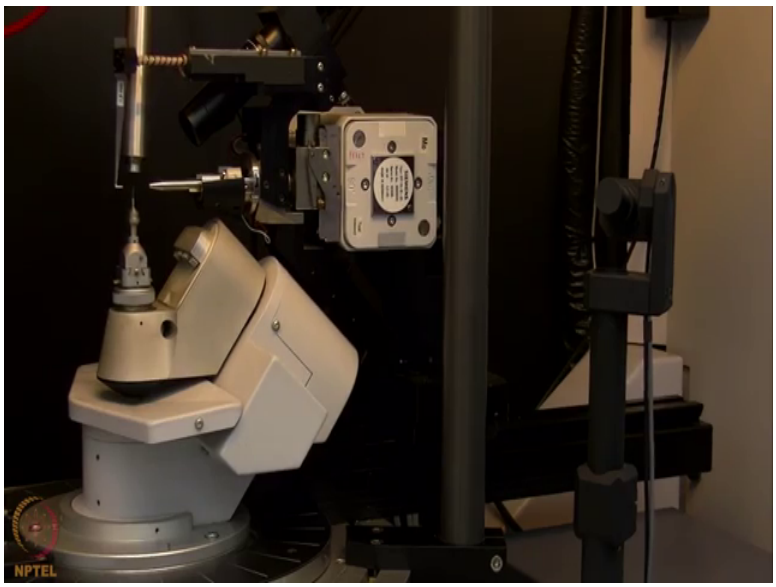

And then, there is another mirror here which then reflects the CO2 laser towards the capillary of in situ crystallization experiment. So, what we do is? We try to align this beam that is CO2 laser from here by rotating this mirror carefully using hand and

tightening and or loosening the screws. And then align it on the beam align it on the capillary and then slowly increase the laser power to such a value that it can melt the material inside and then we can do in situ crystallization using the laser.

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So, what can then do we done is that this particular mirror which is located here is connected to a motor behind. So, with that motor, the mirror can be rotated very slowly in this direction. So, in the mirror rotates like this, the beam travels like that. So, in the beam travels from down to up of the capillary the molten zone moves from bottom to top and the lower zone again crystallizes and forms a single crystal. This process we have discussed in the class and here you can see this is how it is done.

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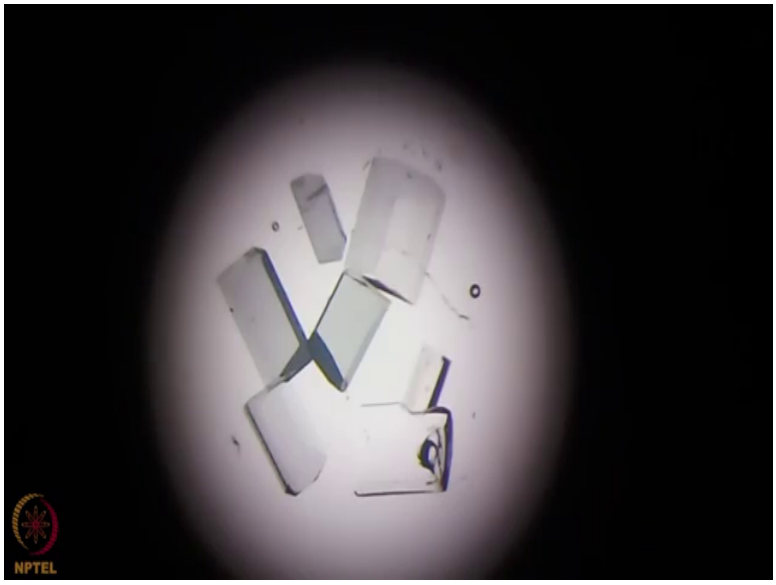

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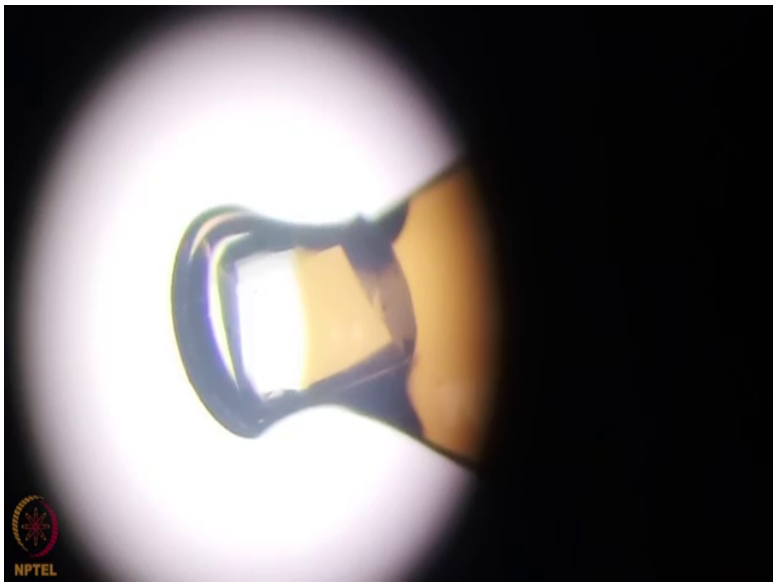

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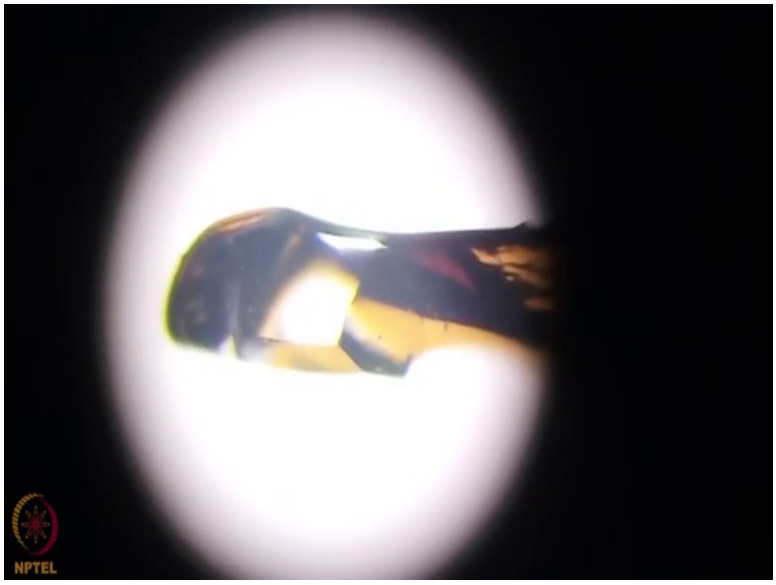

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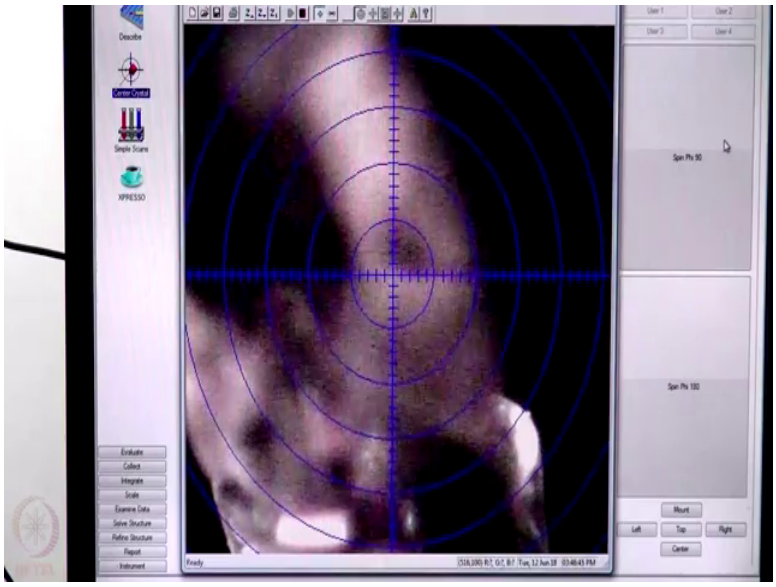

So, on the screen what we can see is the defocused crystal which means that the crystal is not centered. So, we need to center the beam in front center the crystal in front of the x ray beam. So, from the current position I would take this crystal to a different orientation which is called the center orientation.

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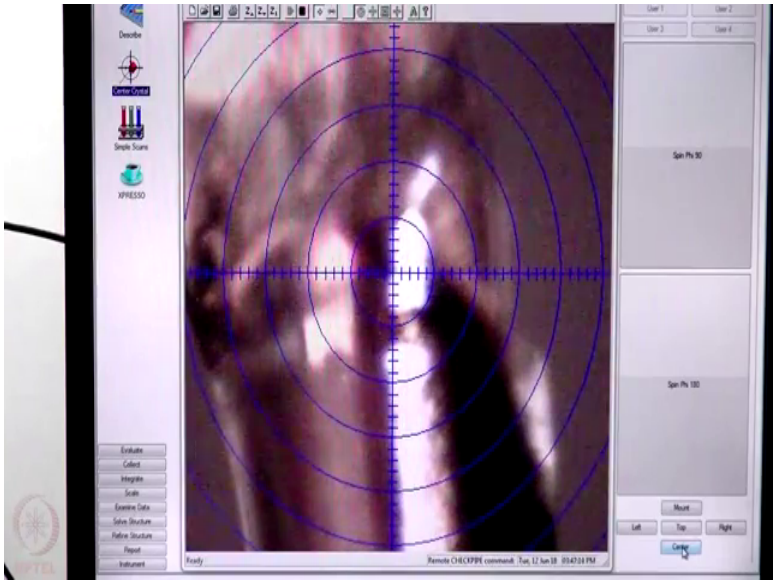

So, what we can now see is the crystal is still defocused. What we need is now to align the crystal on the beam.

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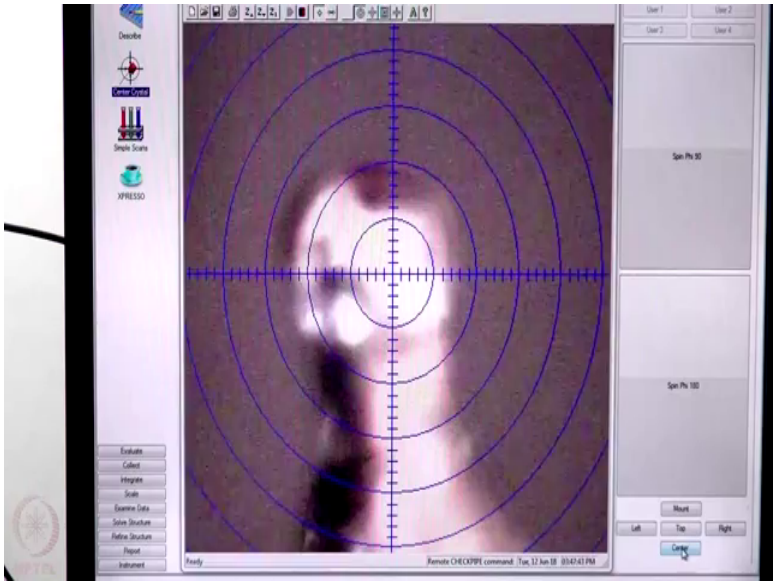

So, we can lower the height, bring it to the center, but still it is defocused which means that in one direction it is far away from the center location. So, now, I will rotate the crystal by 90 degree about the 5.

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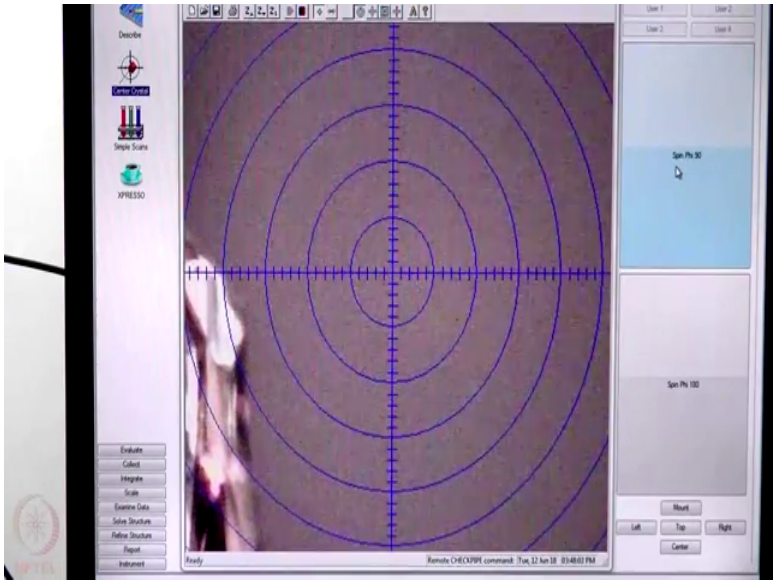

So, now it has gone out of the view, so, what we need is to bring that crystal in the view.

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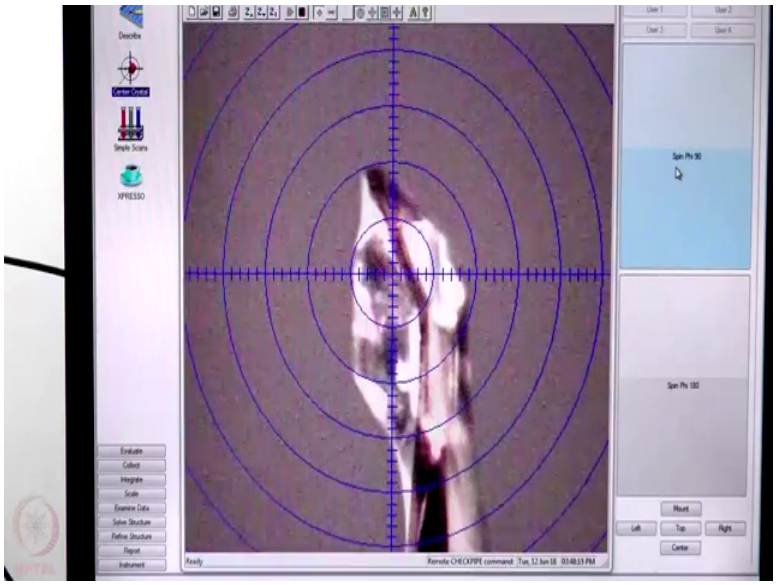

So, now it is sort of focused and we can see that the crystal is somewhere here to there which means the crystal is not at the center it is at a much lower position. So, this means we need to increase the height of the crystal further.

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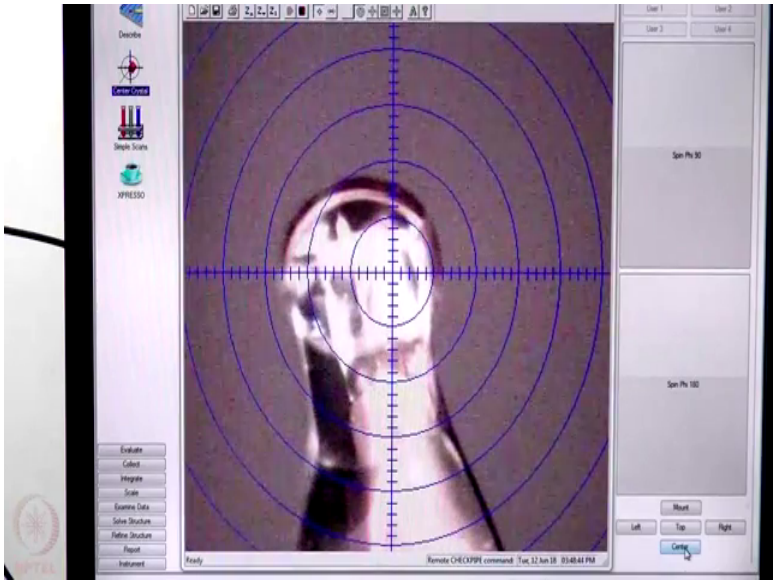

So, now again we come back to the old position, increase the height of the crystal little bit and then fix it here for the time being.

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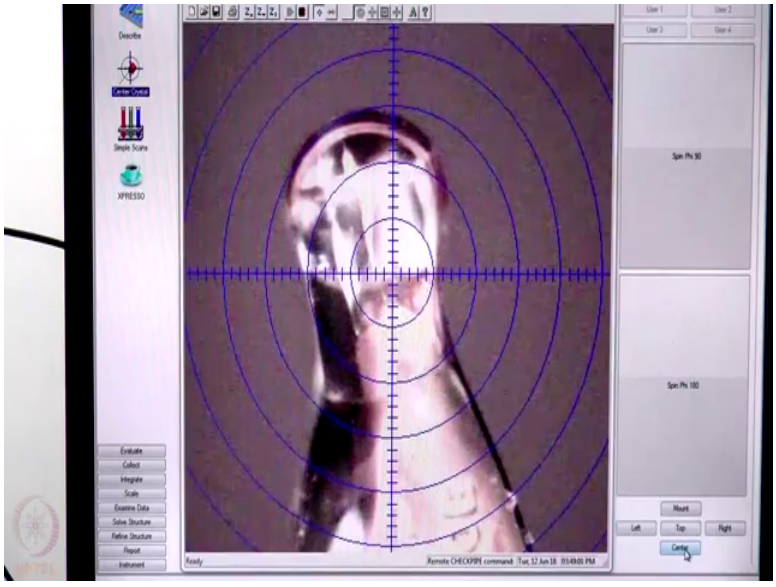

And then it is not at the center so, we further bring it to the center. Then we need to see what has happened to the 90 degree with respect to this.

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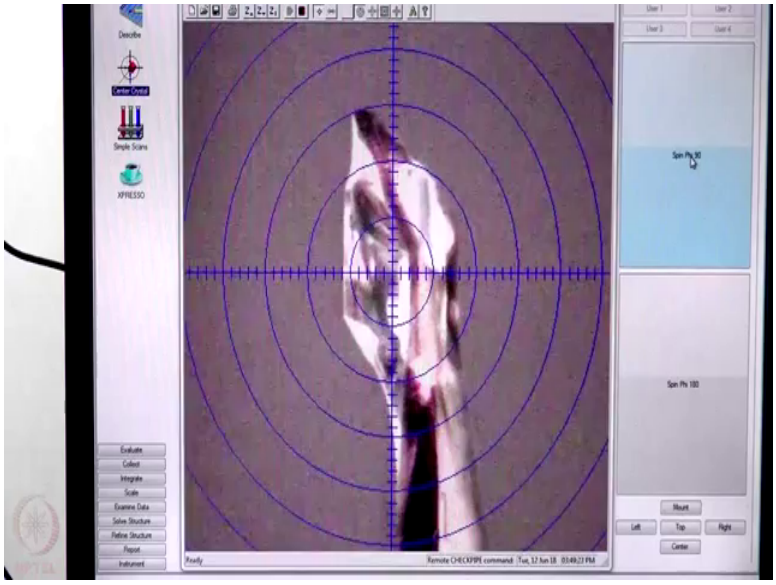

Now, we can see that the crystal is in between to reasonably centered locations and from the top and bottom. So, the crystal is here and between these two points at this 90 degree location so, I rotate the crystal by another 90 degree.

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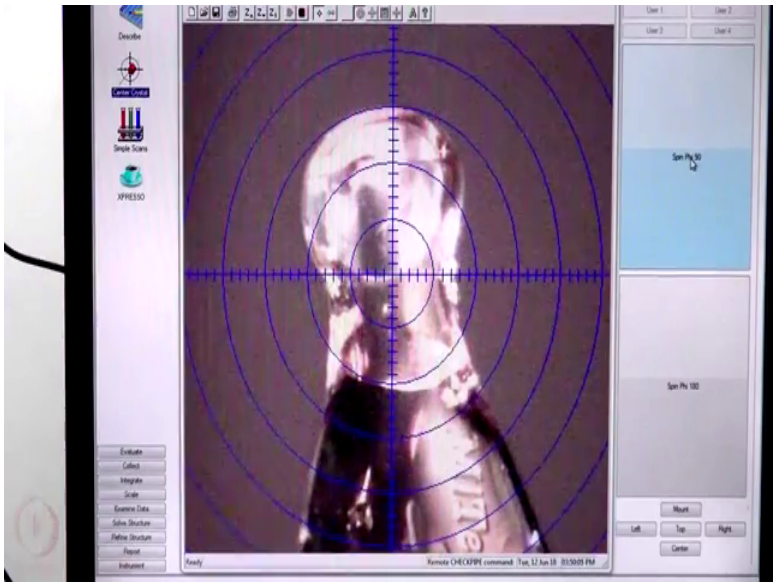

So, here you can see that the crystal is from here to there. So, this is the reasonably big crystal to get an idea, this particular ring is about 400 micron so, crystal is about 450 micron in length and it is about 350 micron in width.

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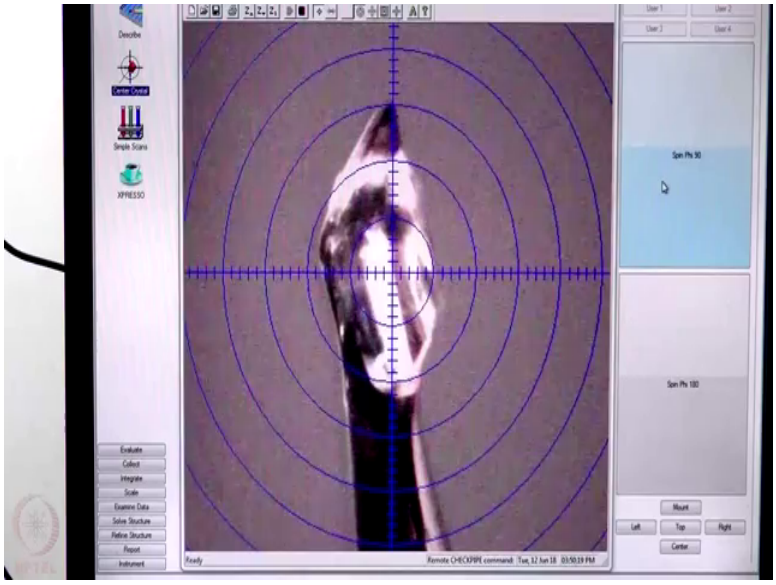

We need to check all the 90 degree rotation positions for centering the crystal. Here what we see is it is slightly more towards the left compared to the right. So, we slightly move it to the right and rotate it by 180 degree to confirm fine it is also and then we change it to 180 degree it goes there. Now I want to see the crystal in a left position so, if I click left the goniometer will readjust its position it will change the orientation of the crystal and bring it to a new position.

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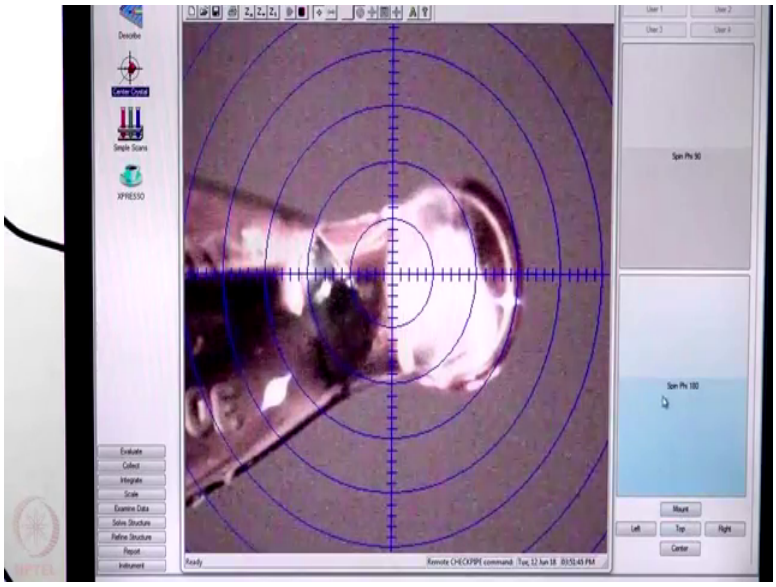

So, here also we can see, whether the crystal is aligned or not by rotating it about phi, because you remember when you doing this data collection, we will be collecting the data with all possible values of phi and all possible values of omega and kappa.

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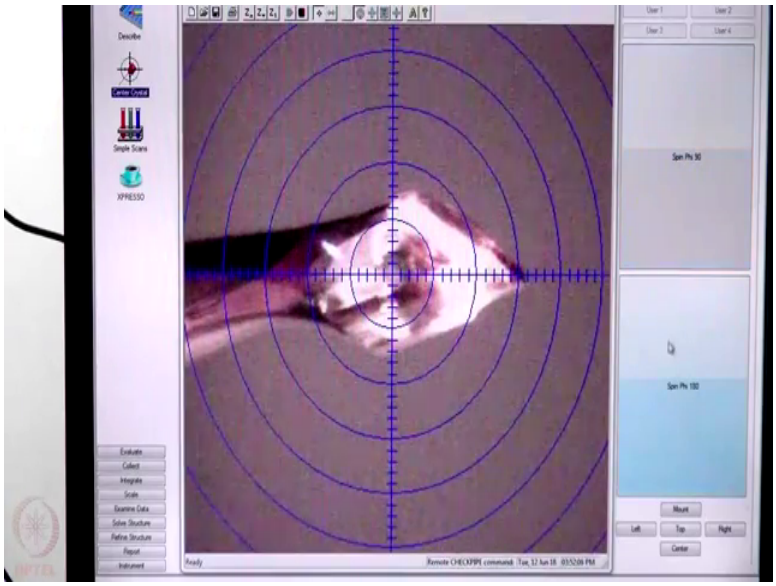

So, at any point of time this crystal should not be out of the beam during the data collection.

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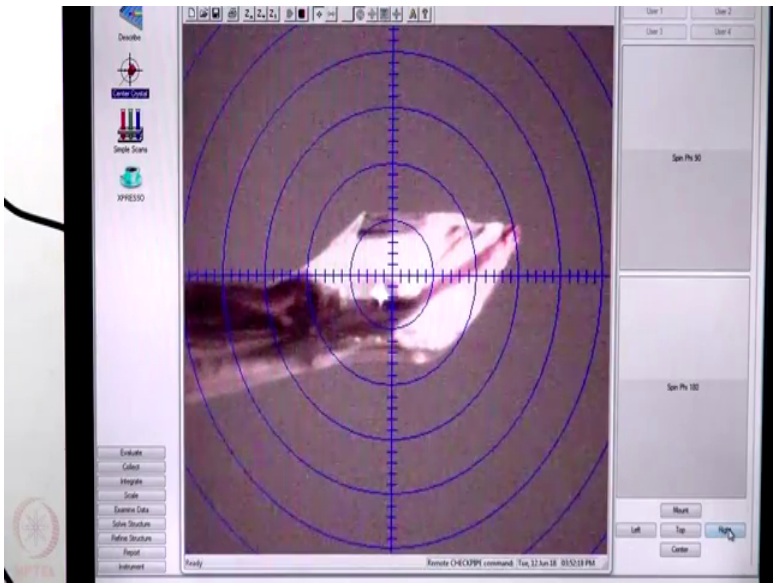

So, now we will check the right position with respect to the screen and here although we should check the rotation about phi and make sure that the crystal is not out of the beam. So, once it is done we can see the crystal in another orientation which is the top orientation, which means the crystal, will now be directly facing the video camera which is now used to collect to which is used to align the beam.

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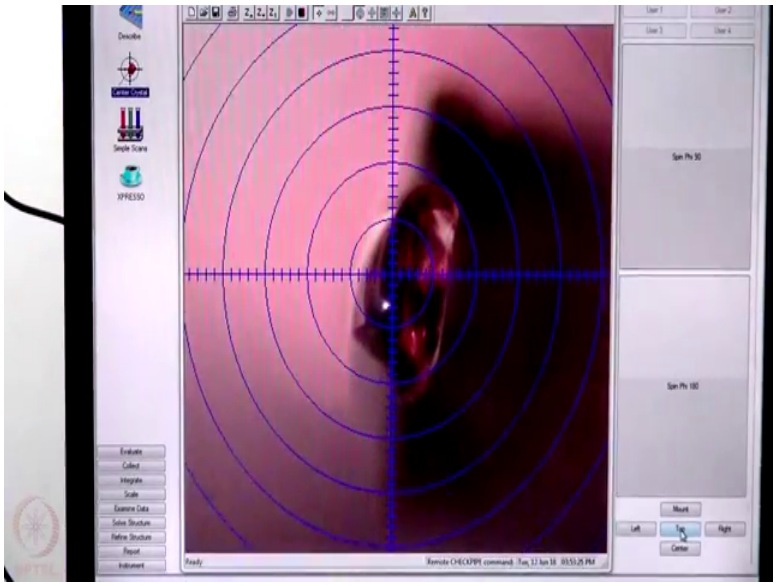

So, this shows that the crystal is not exactly on the line, but it is slightly shifted to one side, which probably can be corrected here fine.

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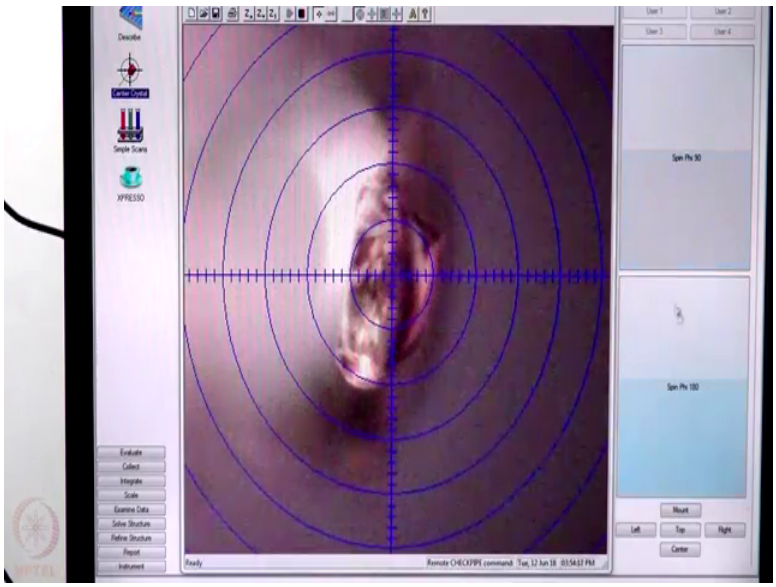

So, from here we again go back to our original mount position, first we go to the center position.

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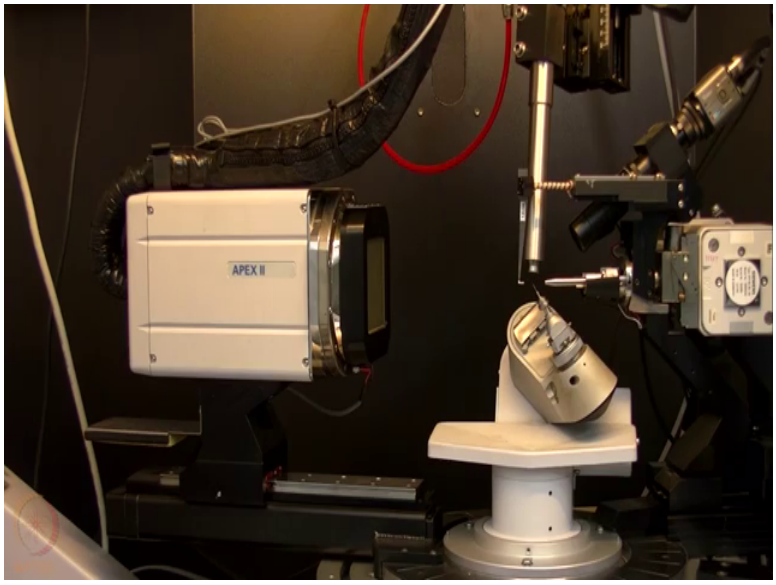

So, this is now at phi equal to 0, we rotated by 90 degree. So, here if we rotate from this point it is then changing the direction along x, if I rotate the screw here it changes the crystal along x, I came back to 0, if I rotate from here it changes the orientation along y and then if I move from this top point, top screw then it goes up and down so, it is the z direction.

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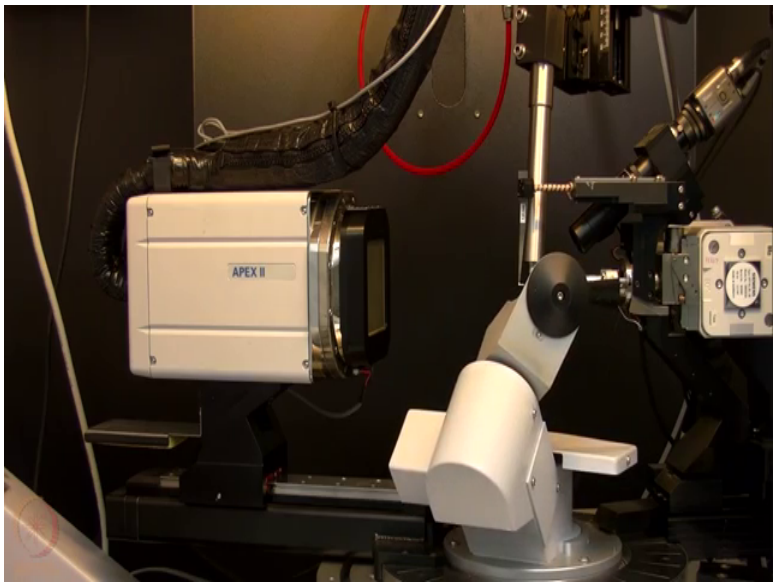

So, in this way one can align the crystal, after aligning one should see the left orientation see here the kappa is changing and coming to a plus 90 orientation. This is the plus 90 degree orientation of kappa axis which is now horizontal like that. If I go back to right

orientation, then again the goniometer readjusts and go goes back the other side with a kappa of minus 90.

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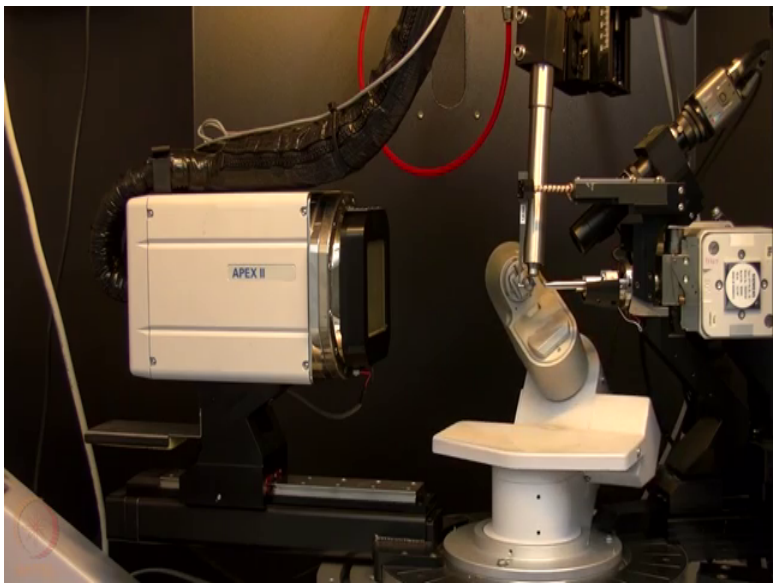

So, now the crystal is pointing towards hours and kappa is at 90 degree with horizontal axis. The base which is rotating here is the omega base and now if we go back go to the top orientation.

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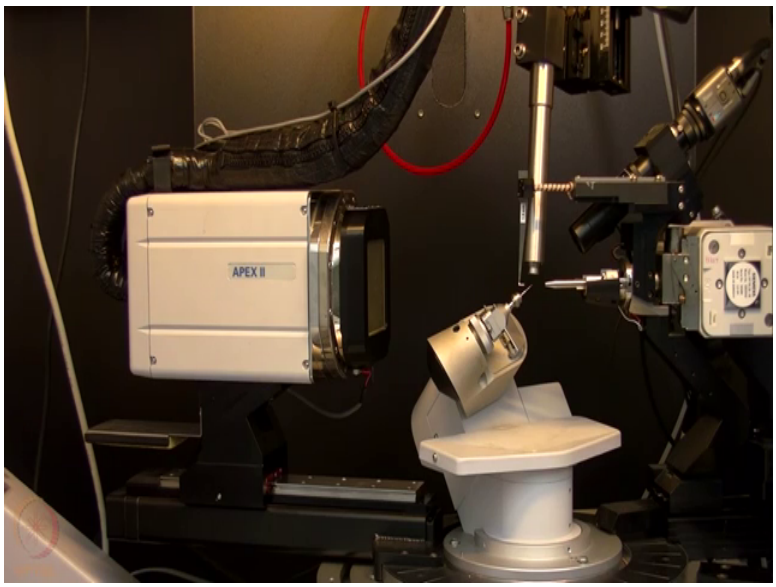

So, this is the top position of the crystal then we again go back to the centered position. So, once we have completed the centering of the crystal, we should close the door and

then start recording the initial frames to get the unit cell and indexed. So, this door need to be closed from both sides we bring it then the middle and then lock it like this so, now, it is locked.

So, now, one can switch on the x ray inside the chamber, you can turn on you open the shutter and let the x ray beam come and we could get diffractions from the crystal that we have mounted. So, now we are going to start the recording of initial three frames, when our aim is to collect about 20 frames in one orientation and then three different orientation. So, 3 into 20 total 60 frames will be recorded with and width of 0.3 degree and expose of time that we will be used is 10 seconds and the detector will be kept at 60 millimeter that is 6 centimeter.

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So, now I am going to start collect, you will see on the screen that how the axis moves? You can see that two theta has come to an angle about 30 degree and omega has gone to about 30 degree kappa is in an new position. And now the detector is moving closer and it is coming to a distance of 6 centimeter. So, now, the sample to detector distance is 6 centimeter.

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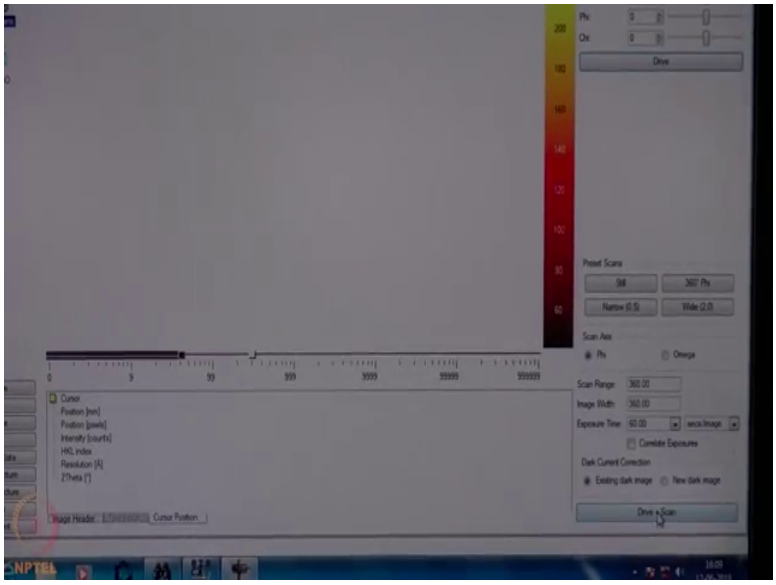

So, before going to collect few frames for the indexing one can do a rotation photograph. So, for that we use at a 0 position and then we record a 360 degree rotation for about 1 minute and then we determine whether the crystal is a good single crystal for data collection or not. So, why it does that, it will show you that the goniometer will move define about it is axis for 60 seconds and the 360 degree rotation mode.

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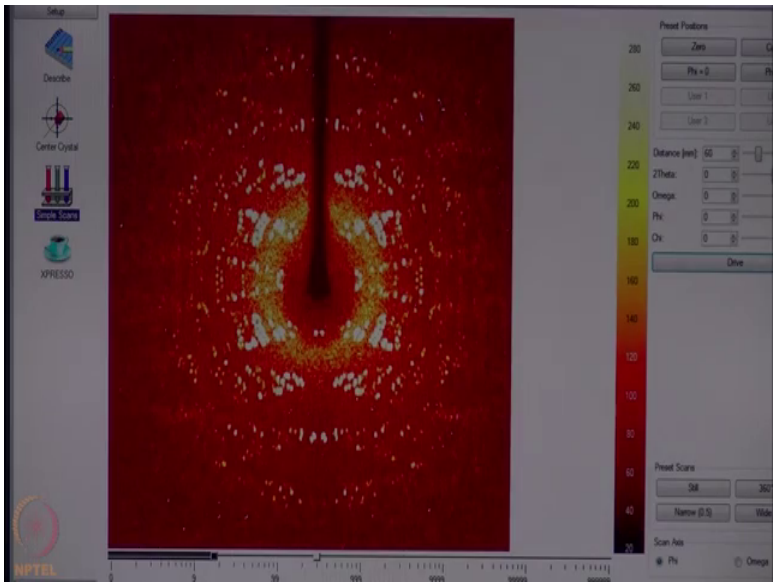

So, this is the rotation photograph which we have recorded by rotating the crystal about phi by 360 degree in about 1 minute.

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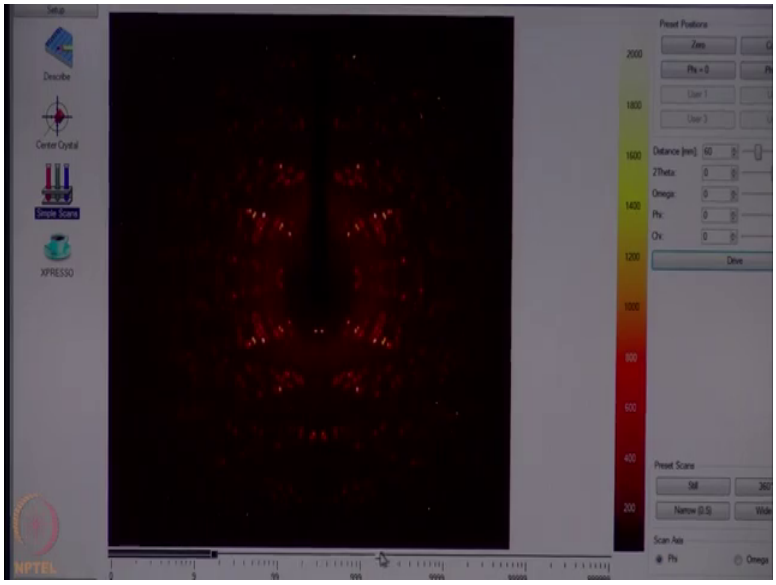

So, what you can see are the diffraction spots and those are centrosymmetric in nature, if you remember the class we are have shown you a rotation photograph of course, that rotation photograph was on a crystal of sodium chloride, which has a very high symmetry. And that is why the spots were highly symmetric and distinct here it may be a monoclinic or triclinic lattice, which has a very low symmetry and large number of spots and many spots are getting merged in this window.

So, to decide on the exposure time, we should take a steel photograph with say about 10 second exposure time and see how the crystal is defect. If it gives reasonable spots with 10 second exposure, we will collect the initial frames with 10 second exposure.

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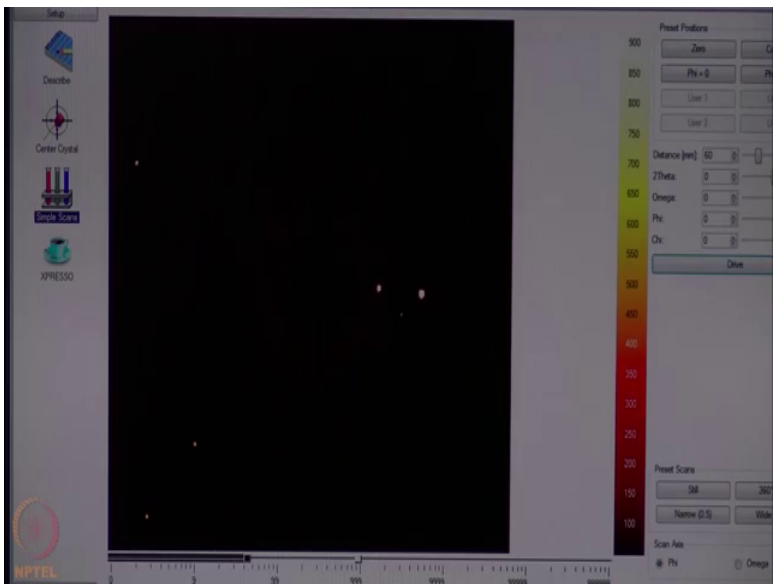

If it does not give good diffraction with 10 second we may have to increase it or we if it is twos intense then we have to decrease it. So, if here what we can see is that the crystal is deflecting reasonably well with this 10 second exposure and the spots are nice and circular.

So, we will use this ten second as a standard for getting the unit cell measured. So, we should go to evaluate determine the unit cell and then click on collect data and then record these images. So, there will be three sets of 20 frames recorded with 10 second exposure each which would take about 12 to 13 minutes to record.

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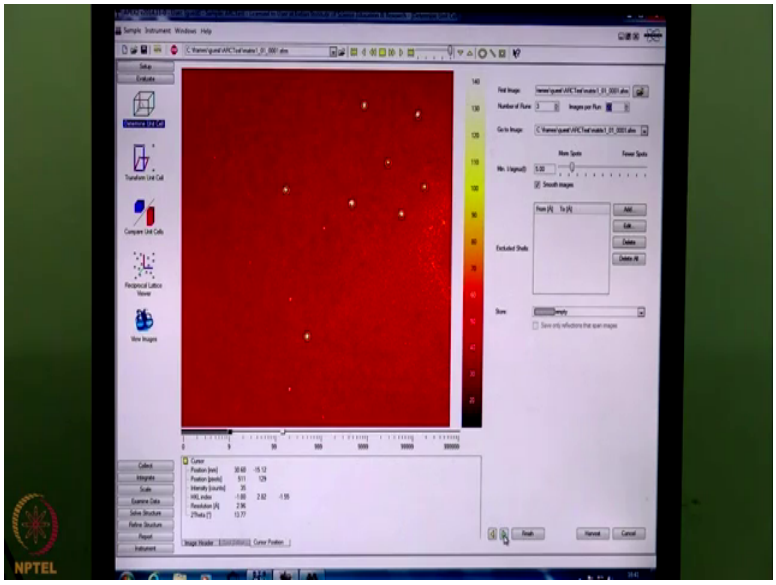

So, now the initial frame recording is over and it has brought to this window. So, what we can see here some spots are started with a green one and some spots are not. This is because, the mean i by sigma that is set here is set to 20, which means only the very strong reflections are selected. So, if we make it to 10 and presenter then it selects some of the weaker reflections also, if we make it 5, it will furthers it will go down further and select some other weaker reflections as well.

So, now, it has recorded three sets 20 times each so, total 60 frames. So, now, we would like to process these 60 frames to get the indexing of this particular crystal. So, out from those 60 frames it has got 269 reflections for indexing, we choose all the three different methods for indexing and see whether the same unit cell is thrown by all the three different methods.

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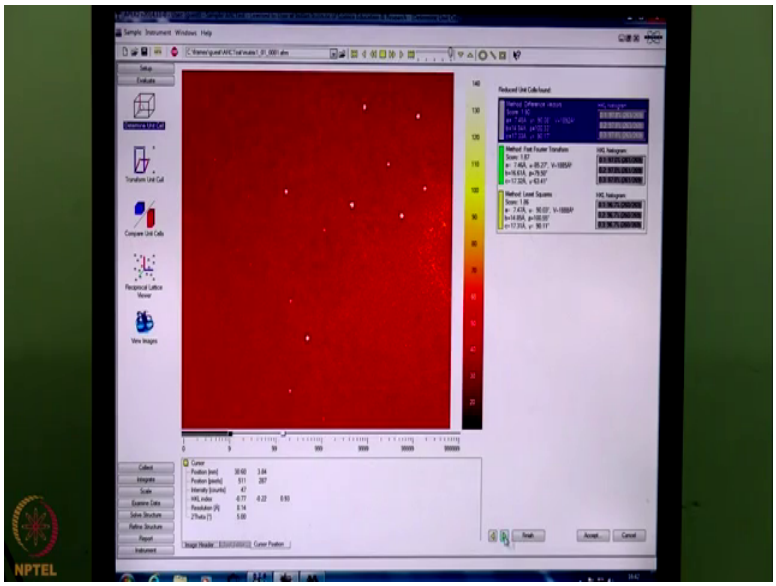

So, initially, it gives a monoclinic unit cell with 90.08 90.17 and 100 beta, this is a try climbing unit cell; this is again a monoclinic unit cell. You will see that these three yarn of sort of same volume 1888 1885 1892 so, one should take the higher symmetry cell which is a monoclinic cell probably it is blue one. And the other one which is here is a score of 1.86; here the score is 1.90 which indicates it is slightly better than that. So, we take that unit cell proceed further make the tolerance to one to include more number of reflections, look at the histogram of all the spots and refine.

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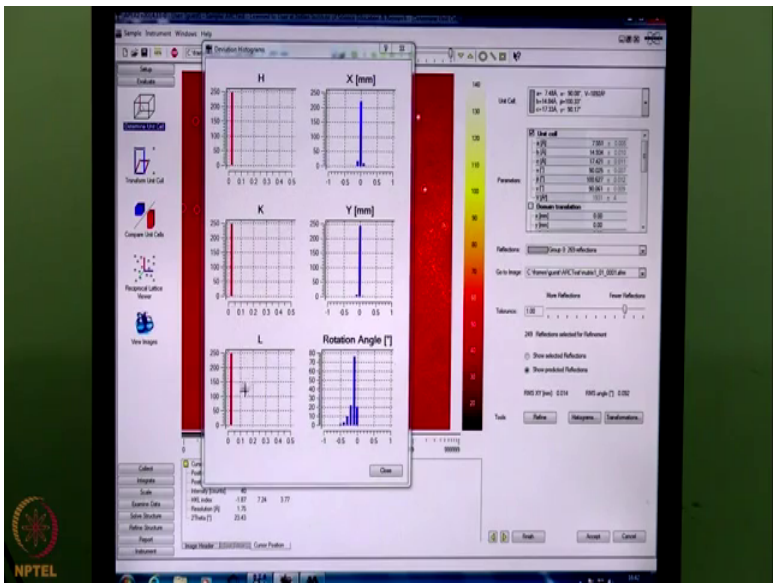

This indicates that the crystal is not fully centered, it is bit off centered and that is why this Gaussian distribution of rotation angle with respect to the centering is slightly towards the left. But the indexing HK and L are single towered; that means the crystal is a very good quality single crystal.

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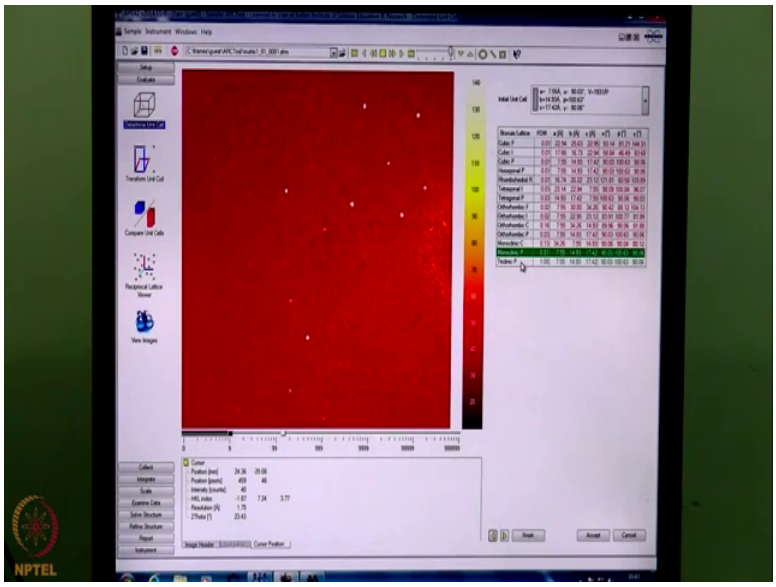

So, now when we try to determine the Bravia lattice, it finds that it is a monoclinic lattice with 90.03 and 90.06 as alpha and gamma with a high figure of merit of 0.81. So, we choose that monoclinic lattice and go forward and do the refinement once again with tolerance 1 and refine still we see that this rotation angle is slightly on the left which indicates that the crystal is not properly centered.

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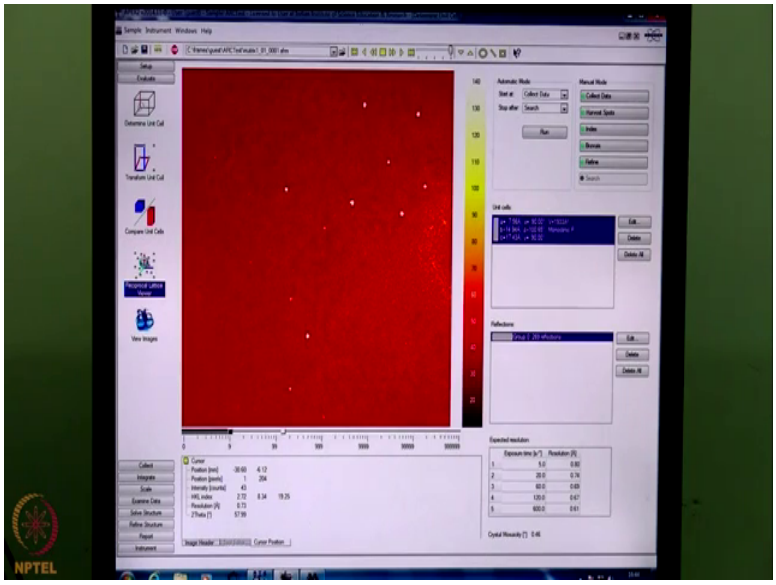

So, now, what we have got is a monoclinic lattice volume of 1933 cubic angstrom, we would like to see these spots in the reciprocal lattice viewer. So, it will show all the spots in reciprocal lattice and we will be able to see a lattice formation by all these spots that are harvested here.

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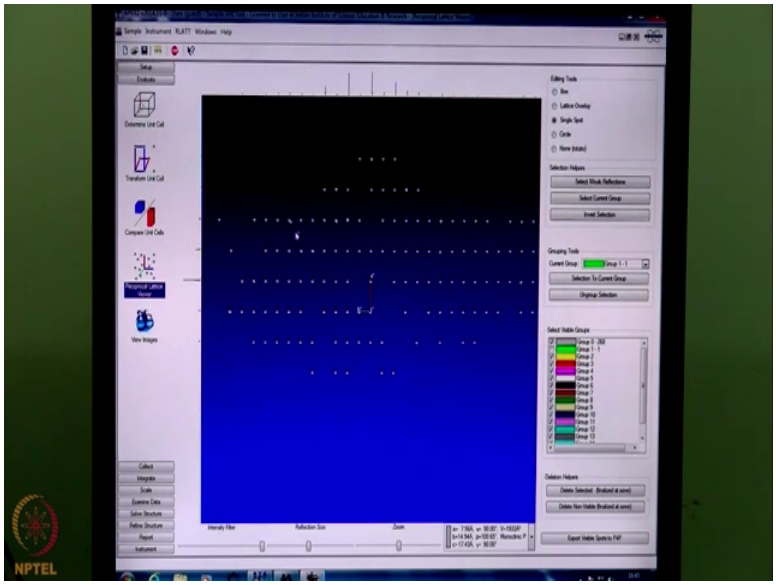

So, these are the spots in the reciprocal space and here you have the information about the unit cell. So, this can be arranged are oriented along the a star axis, if you can zoom it is the a star axis here, this is along b star and this is along the c star axis. If we zoom out and carefully look at the reciprocal sphere in a star b star and c star directions what we

see? That all the spots are falling in an array and there is no spot which is falling outside the array.

What I can see with my experienced eye that this particular spot is falling outside the array. So, I can select that spot and eliminate it from this set and make it invisible. And there is one more spot which is here that can also be removed and then you see all these spots in f 1 f 2 and f 3 orient f 1 orientation, they are all falling in one line.

This indicates that this is a very good single crystal, see what has happened is this data that was collected using three different orientations of the crystal it has scanned the three different regions of the reciprocal sphere. These spots which are here represent one part of the reciprocal sphere, these spots which are here represent the second part and the spots which are here represent a third part of the reciprocal sphere.

So, this is how this defractometer geometry is pre aligned and pre adjusted that the data collection strategy for unit cell determination scans at least three different regions of the reciprocal lattice and gives us very accurate unit cell dimension information. So, with this information; if we want to collect data we need to determine the strategy. So, for that we go to collect and go to data collection strategy module.

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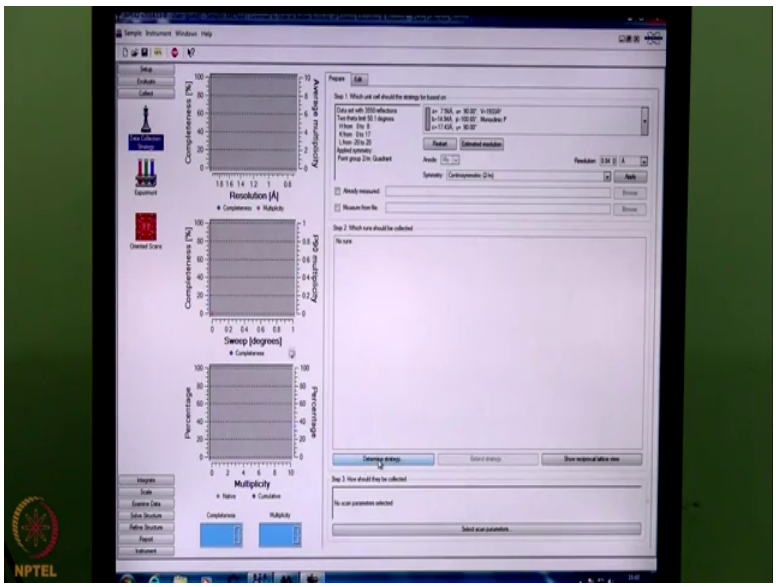

In the strategy module, it is asking whether we should look for a chirals compound or we are looking for a and achiral compound, of course, from the chemical knowledge I know it is not a chiral compound.

So, I am assuming it to be centrosymmetric, I want to collect data up to a resolution of 0.84 that is the requirement for a for IUCR quality data for IUCR valid data. So, with this restriction and that particular unit cell and the corresponding orientation of the lattice it is predicting that the data set will have for 56 39 reflections with h ranging from 0 to 10 k ranging from 0 to 20 and l ranging from minus 24 to plus 23.

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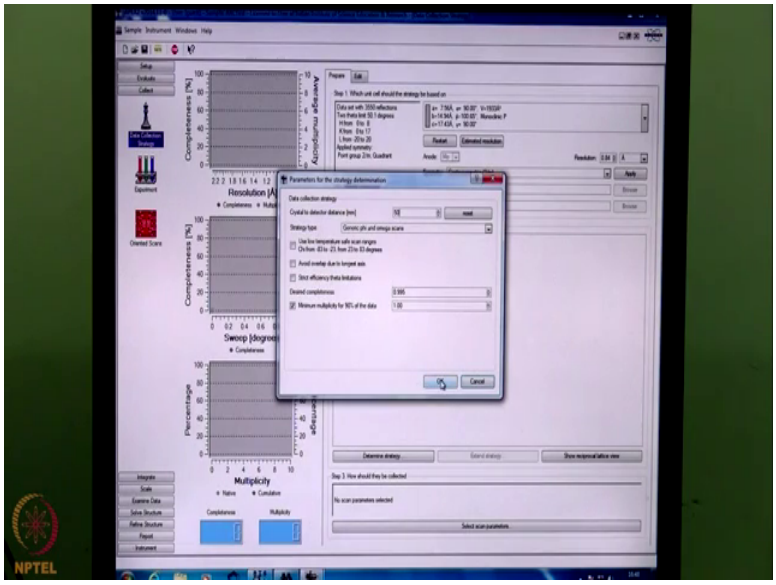

So, we click on determine strategy, it then asks us what is the detector distance at which we are going to collect the data? We can collect the data with 50 millimeter distance, we will use a generic phi and omega scan. And if we want to collect a room temperature data then we do not need to do any requirement adjustments here. And we just say ok, it will then try to find out the best possible data collection strategy based on the orientation of the crystal and the unit cell that have been determined.

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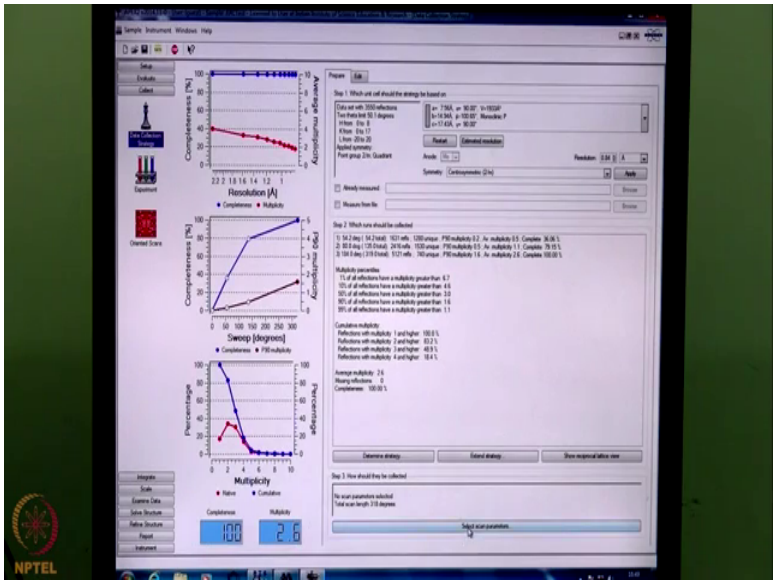

So, now it shows that here we have three sets of runs, in the first set it will give us a completeness of 36 percent, second set we will give us a completeness of 80 percent and third set we will give us and 100 percent completeness.

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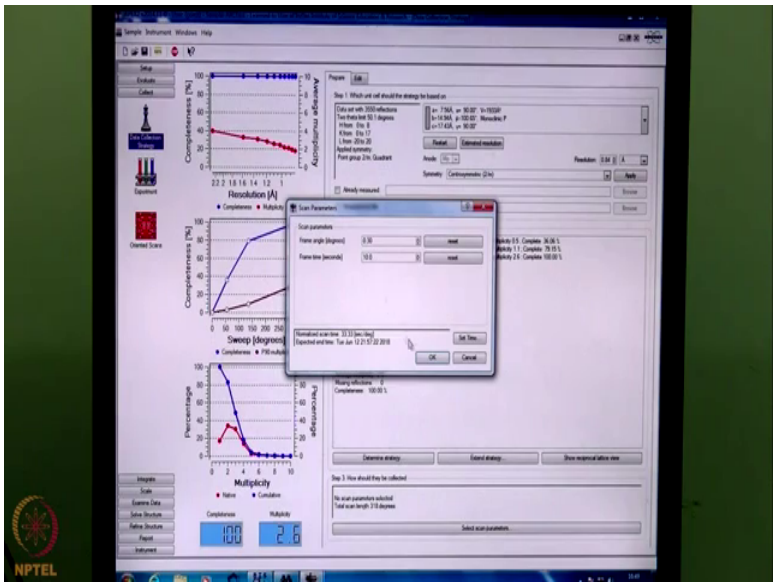

So, now we need to decide on the time that is the exposure time for data collection. And the frame width normally we collect a data with frame width of 0.3 degree and a 10 second expose data; that means, every frame will be measured for 10 seconds. So, if we put those two information, then, what it gives is the total amount of time that is going to be needed for this particular data collection. So, overall data collection time is 52

seconds for 52 minutes for the first run 78 minutes for the second run and 3 hours for the third run. So, altogether the data collection will take about 5 hours.

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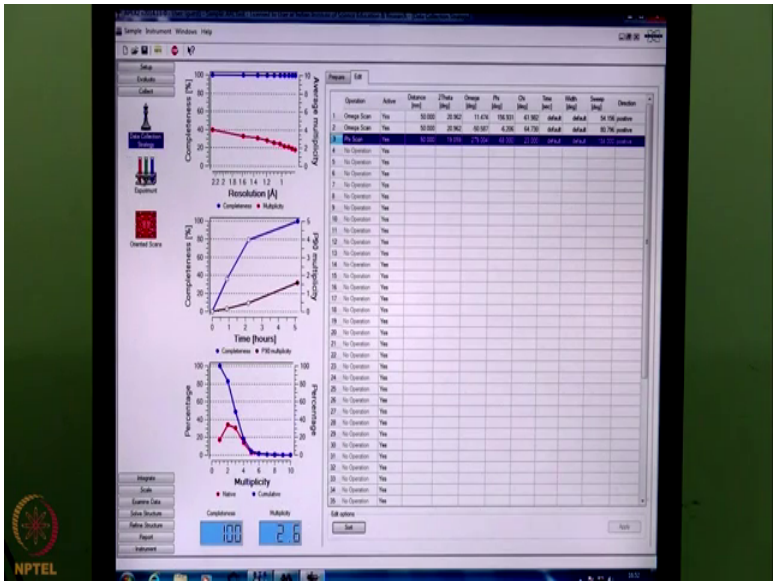

So, if we now try to see the runs, what we can see here is the first run is omega scan at a distance of 50 centimeter, 50 millimeter with a two theta of 20.9 omega starting at 11.747 phi and chi are two different values and it will sweep for 54.156 degree with a scan width of 0.3 degree.

Then it will move to a different position of omega this second run, will have 50 millimeter distance 2.962 that is the detector position remains the same. The omega value changes to minus 50 phi changes chi slightly changes and it records about 80.79 degree in omega. And a third run that it has determined is going to be a phi scan which means the crystal will be rotated about it is own axis that is the phi axis. And the position of omega will be 19.85 sorry two theta will be 19.85 omega will be 179 and phi will start at minus 68 degree with a fixed value of chi at 23 and it will have 184 degree sweep with 0.3 degree width.

So, that means, the phi scan will take the maximum amount of time, the plots here on the left hand side indicate that the completeness percentage completeness is shown in blue is 100 percent with respect to completeness with respect to resolution. So, the completeness is going to be 100 percent for all the resolutions that we want, the average multiplicity for high resolution is going below.

But it is very high at low angle. Similarly, the completeness versus time is plotted here and also the percentage versus multiplicity is plotted here. So, we can click on sort and it sorts these set of runs and then, if we go to the experiment on the left hand side column.

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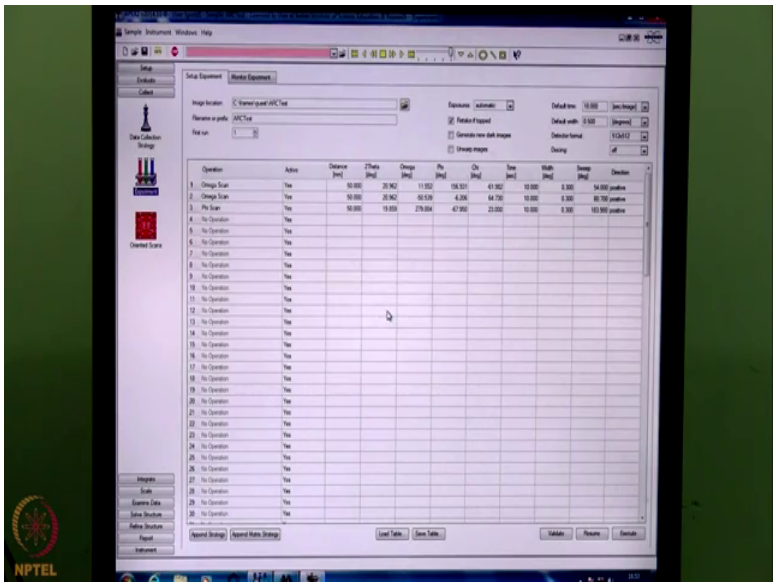

And then happened the strategy that it has been that it has found say it brings this strategy to this window. So, at this point we must validate all these runs because, it should all be valid it should not lead to any collision between the different axis on the diffractometer.

So, to do that when you click validate, the diffractometer collision limits are checked with this data collection strategy and when sure that during this data collection none of those collision limits will be crossed. At this window, we do not change anything manually because these are fixed by the data collection strategy module.

And if we change anything manually it may so, happen that the manually entered number can cross the collision limit and hence a collision may occur. So, we must always avoid a collision on the diffractometer of this kind where all the four circles are movable. So, on clicking that validation it says all operations are valid which means that the data collection strategy is acceptable.

So, we can start a data. So, when I click execute, it starts to execute the operation that is it will move the diffractometer angles to the desired settings. And move the detector to

the desired distance that is 5 centimeter and then it starts to record the data. And you focus on this part only so, that I can show the beam stop.

So, here you can see that the data is getting recorded we have started a data collection. So, at these point on the detector surface you can see a black shadow, this black shadow indicates that the beam stop is in place and the load hydrate beam is falling on the detector. So, this is how we have we can start a data on a single crystal x ray diffractometer, we have a different video where we will discuss how this recorded data is processed and structure is solved.