Symmetry and Structure in the Solid State
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Lecture – 41
Diffraction and Reciprocal Space (Continued)

So, having seen the relationship between direct space and reciprocal space in several crystal systems, different kinds of crystal systems and the way in which we can derive the values of the reciprocal lattices. We could do a few numerical problems, but then instead of spending more time on numerical problems, because we have to cover the rest of the course content, maybe we could give it as possible exercises during the course evaluation. So, what I will now do is to redo this Bragg's line reciprocal space, we have already done it once.

We have indicated possible occurrences of the Ewald's sphere and the presence of the limiting sphere, and then we showed that so many reflections will come up in a diffraction experiment. Only because of the fact that we just do not keep the crystals steady, but we rotate the crystal. And as the crystal rotates the reciprocal lattice will rotate with it, and then we have this, the limitations coming up due to Bragg's condition.

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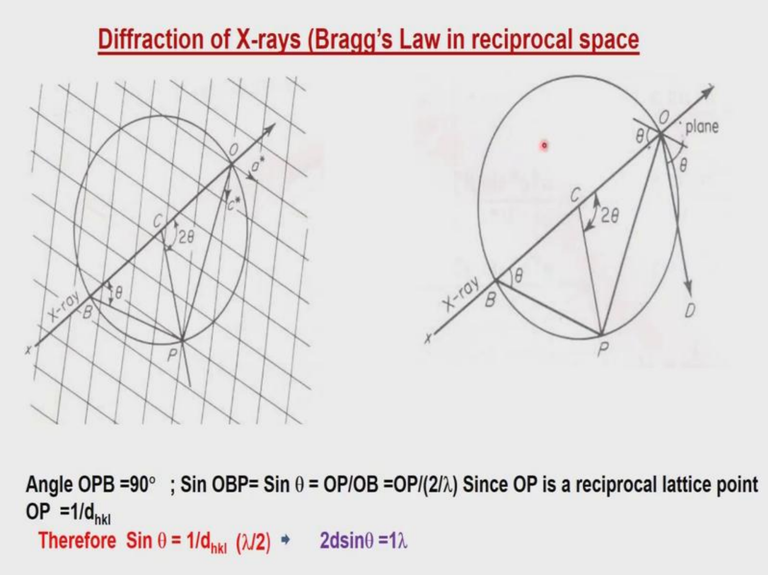

Diffraction of X-rays (Bragg's Law in reciprocal space

Angle OPB =90° ; Sin OBP= Sin θ = OP/OB =OP/(2/λ) Since OP is a reciprocal lattice point OP =1/d_{hkl}

Therefore Sin θ = 1/d_{hkl} (λ/2) ➧ 2dsinθ =1λ

So, this particular slide, we will tell you the entire construction procedure which we do in order to understand the direction and in the reciprocal lattice of the diffracted beam. So, we therefore, consider this as diffraction of X rays. In fact, I should put a, should have put a bracket here Bragg's law in reciprocal space.

Now, as I mentioned again and again that Bragg's law in reciprocal space is more crucial for us, because what we record is I vs 2θ and from 2θ we can get information on the reciprocal lattice and eventually the direct lattice. So, we take now for example, a reciprocal, a direct space lattice, sorry a reciprocal space lattice. Now this reciprocal space lattice is represented by two vectors. This is a 2 dimensional reciprocal lattice. So, b^* is coming towards us in this from the plane. And so in the plane we have drawn the reciprocal lattice. We have drawn the graph of the reciprocal lattice; that means, we have taken O as the origin. And with respect to O as the origin we have two vectors; a^* and c^*, and the angle between a^* and c^* will be γ^*.

So, this is the representation of the reciprocal lattice in the background. So; that means, if you want to find out and index this parts in the a^* c^* plane, how will you do that? We will do it like this, you start from 0. Suppose you go along the a axis in one direction in the positive direction, that particular index will be 1 0 0 in the reciprocal lattice, 2 0 0 in the reciprocal lattice and so on. And in the c^* direction you can have 0 0 1, 0 0 2 and so on.

So, this point therefore will be 1 0 1 right, you got the point. So, this is how we can go and index the various spots. So, they occur in different positions in the background, and now we will see what happens when we send in X ray beam. So, there is an X ray beam which is coming in this direction of XO and XO is go through this direction and I am going to put a crystal at C. Origin I have taken here, but I will discuss that a little later, but at this moment let us say we put a crystal at C.

So, if this is the direction in which the unit vector of the incident beam is coming, this is S_0 and this is the direction at which it goes out, it is S_0 and this is S, this scattering vector the angle between them is 2θ by definition. So, we have given this as 2θ.

So, this is in fact, the CP is the direction of our R vector, the R vector. It is also the direction of the H vector, if it cuts the reciprocal lattice point. So, this is as far as the diagram is concerned. So, we have now CP and there is a reciprocal lattice point cutting this. Apart from that, one more thing is cutting that reciprocal lattice point what is that?

That is the one which is the so called Ewald circle in this particular case, but when we go for 3 dimensions it becomes the Ewald's sphere.

So, we are now discussing this issue again in 2 dimensions, because the reasons which we have been discussing on and off again. So, the 2 dimensional network is shown in the back; that is the reciprocal lattice network. We have the cell dimensions a^* and c^* and the angle γ^* between them, X rays are passing through and there is a crystal kept here so this scattering takes place; otherwise of course, we have the direct beam going through and through. Now we sit at the point C and then take the radius of this circle as $1/\lambda$, where λ is the wavelength which we are using.

Let us say we are using copper k_α radiation, it will be 1.542 Ås or 1.5418 to be exact. So, you take that, the value as 1 divided by that quantity, take that as the radius of this circle and draw this circle. Now this is known as the Ewald circle, this is called Ewald construction and this known as the Ewald circle. So, you see that the origin of the reciprocal lattice point is now taken at on the circumference of the circle at this moment. So, the origin of the reciprocal lattice is taken at the circumference of this circle.

Now, we have said that the crystal is up here and this diffraction direction is that, with respect to that the angle is 2θ. Now what is happening is that if you look at this circle and see where are all the points where the reciprocal lattice is intersecting with the circle. We find at least P is definitely intersecting with the structure, with the circle. So, whenever such intersections takes place by definition, we will have diffraction. So, whenever there is a reciprocal lattice point in this reciprocal mat, which cuts the circumference of the Ewald's sphere which is drawn with a radius of $1/\lambda$, that particular point now will be a point from which diffraction can come out.

That means it will be a point corresponding to the vector H, the H which we have discussed. And therefore, we see that there will be a diffraction in this direction. And since the diffraction is then this direction we have to work out what is the geometry that is associated with this diffraction condition, and that should be the same as Bragg's law, because Bragg's law said what, Bragg's law said that if there is a plane and then incident beam, the direction of the incident radiation characterized by vector S, the scattering vector say characterized by a vector an incident is characterized by S_0 and this scattering by S. We would have had this kind of a discussion, and therefore, it will now give us the diffraction condition satisfied, 2 d sin θ= λ.

So, what we have done now is to go to reciprocal lattice. The once we went to the reciprocal lattice we decided to take 1/λ as our unit and the circle is drawn with a radius 1/λ. Now in this circle there are certain properties, the properties are the following. The angle OPB is an angle in a semi-circle and angle in a semi-circle is always 90° from our school days. So, therefore, OPB is 90°.

Now you see that the sin of OBP, if you consider this as OBP, the sin associated with OBP that is with respect to the angle θ. So, this will be the sin θ. If you consider this triangle the sin θ is equal to, if you consider the triangle OBP. So, we are looking at the triangle OBP; one of the angles is 90° this angle is θ. So, what we are now looking at is the sin of OBP, it will be OP which is this distance from the reciprocal lattice origin, OP divided by the diameter of this Ewald's sphere, Ewald's circle which is equal to 2/λ. So, it will be therefore, OP/OB which is OP/(2/λ).

Now, the thing is OP as by definition is a reciprocal lattice point and that is cutting this Ewald's sphere. So, this OP, the distance from the reciprocal lattice origin to P is $1/d_{hkl}$. Therefore, we can write sin θ which is this as equal to $1/d_{hkl}$ which is OP, and then you see slash 2/λ, it can be written as a multiplication factor λ/2. So, this gives rise to 2 d sin θ = λ. So, you therefore, derive the Bragg's law in reciprocal space in the following way.

I suppose with the explanation given before and the explanation on this diagram it is clear now, how to work out the Bragg's law in reciprocal space. Now there are two issues which we have brought up here; one is we said that we could keep the crystal at the centre then we said the origin is in the on the circumference of the circle and so on, instead of that we can keep one definition.

We can either keep the at this moment with the discussion we have done and with the derivation we have done, we have assumed the origin of the crystal and the origin of the reciprocal lattice to be at O. But we will see this diagram which will tell us how to reorganise the argument with respect to the diffraction from a plane. So, what is happening is now the X rays are coming in and let us say we have a crystal here.

The crystal is consisting of a large number of planes and one of the planes is shown here which satisfies the Bragg condition. So, when once it satisfies the Bragg condition it will generate a H vector in the direction OP. So, we have therefore, a scattering direction OP which is now is the reciprocal lattice vector. So, this is with respect to O as the origin.

So, what will happen now is that since this angle is θ, the other angle is also θ because this inside angle is 2θ. So, we have a plane, it is as though there is a plane and then X rays went in there and a reflected. So, the reflection direction is along the OD. What you see is that OD and CP are parallel to each other, and therefore, this now represents your scattering direction D, OD could be now equivalent of CP.

If you are putting a crystal at C, CP and OD are the directions of scattering and that therefore, is clarifying the fact that it is at an angle of 2θ. So, whether we keep the crystal at O or whether we keep the crystal at C, it does not matter, because what we do is we measure it at very long distances.

We are talking about here the Å inverse lengths in the case of the reciprocal lattice. So, the distance here is in very very small quantities, and what we measure is a diffraction which is coming out from the crystal is at a distance which is far larger than the 1/λ which is involved here, and therefore, whether it comes from this point or that point is immaterial. So, for all the rest of the discussion one this can say that crystal is at the centre of the Ewald’s sphere. So, this is the derivation of the Bragg’s law in reciprocal space

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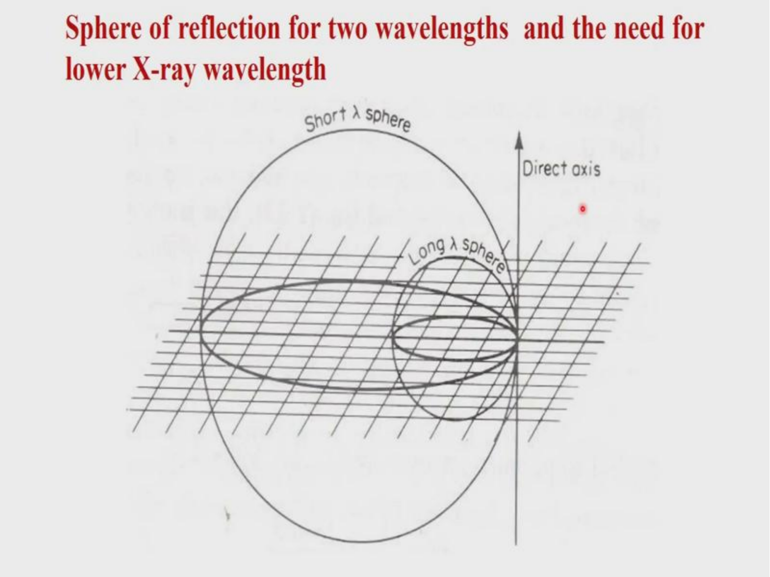

Sphere of reflection for two wavelengths and the need for lower X-ray wavelength

So, having seen this we will go further and see what are the ways in which we can now utilize the fact that these reciprocal lattice points will cut the Ewald’s sphere, and whenever this will happen at the Ewald’s sphere the diffraction condition is satisfied, so we get a reflection. So, now, we have the 1/λ into the picture; that means λ into the picture, the wavelength of light. The wavelength of light we use is anywhere between, let us say 0.4 to 2.5 Ås, they will give similar results. But what is important is, what is the influence of this wavelength on the amount of data which we can get, because we want to get as much data as possible in our diffraction experiment.

So, if we go back to this position, we discuss the issue that this is a stationary a reciprocal lattice, and in the stationary reciprocal lattice we have occasional intersections of the Ewald’s sphere with the reciprocal lattice, and whenever that happens we get scattering. But when we rotate the crystal about the centre of the diffractometer and the crystal rotates, as the crystal rotates the reciprocal lattice also rotates with it.

So, as the reciprocal lattice rotates different points on the reciprocal lattice will have to intersection with the Ewald’s sphere. So, what we have to therefore consider is, those reflections which come in a sphere of radius, double this one. That means those which come in a sphere of radius 2/λ , because the radius of the Ewald’s sphere is 1/λ. So, this will be 2/λ and this 2/λ will be the, what we call? Excuse me.

So, what we were looking at is to see now what is the wavelength which we can use, under what circumstances we can make sure that we get maximum number of measurements, because the whole logic of this X ray structure determination depends upon how many independent reflections you can get in a diffraction experiment. This is the advantage of also the solid state and particularly the crystalline state, because it not only gives the possibilities of diffractions parts, it gives you an option of having a very large number of diffraction spots compared to what is it we have to determine. What I mean to say is, suppose there are 10 atoms in a molecule and this molecule goes into a, let us say a space group $P\ 2_1/c$, Z is equal to 4; that means, we have to determine 40 atoms.

The determination of 40 atoms will mean three coordinates associated with the atom. And since atoms are not rest in a given crystal material, we have to determine their thermal effect parameters also. So, the thermal parameters are not isotropic, because atoms are connected to each other in all three directions, so they will be anisotropic. They are not isotropic they will be anisotropic. And as a consequence there are 6 parameters which come up to describe the atom in the form of an ellipsoid. The uncertainty that is associated with determining the position of an atom therefore, is within that ellipsoid, and that is the one which controls the deviation or the effect of thermal vibrations which are associated with atomic positions.

So, when you say that you have determined a position of an atom at $x\ y\ z$, there is a certain uncertainty that is associated with it, because the atom is not sitting there in the next moment, but your diffraction experiment is a static experiment and therefore, we have to find those error bars. Those error bars are expressed in terms of thermal parameters, so that will be 6 parameters. So, x, y, z plus 6 thermal parameters will be about 9 per atom. So, we have to determine totally there are 40 atoms in the unit cell, but we have to determine 10 position atoms, 10 atoms in the asymmetric unit. So, 10 times 9 will be 90 plus 1 which is now going to put the measurements on an absolute scale, the so called scale factor.

So, totally 91 parameters have to be determined. The way in which we are going to determine and improve the final structure depends on a procedure called the least square refinement. And the requirement of the least squares refinement is that the number of parameters which we have to determine must be very very small compare to the number of measurements we can offer in this experiment. The measurements we can offer in an experiment in a diffraction experiment or the intensities, and the location of them in the reciprocal lattice which is the *h k l.*

So, the number of planes therefore, which we can locate and measure the intensity from should be reasonably large. In fact, the ratio is anticipated to be atleast 10 for a very good structure determination. That means, the number of reflections or number of observations we should have, the number of I(h k l) we should measure which is independent of the diffraction condition that should be at least 10 times more than the number of parameters we have to determine. And this is a logic which therefore, tells us that larger the number of measurements, the better we are. Now here is a situation since our Ewald's sphere is 1/λ, the chance that is given to us to expand the reciprocal lattice is in the times of tuning the λ value.

So, if one as synchrotron radiation we can tune the λ value, but in a typical laboratory experiment we normally have a copper radiation. So, copper radiation will be 1.542 Å sorry 1.5418 Å. So, that will give raise to a reciprocal lattice of a certain volume and dimensions. And the corresponding Ewald's sphere which we construct will be 1/λ, so it will be 1/1.542. Suppose, we now reduce the value of λ, then 1/λ will keep on increasing.

So, the shorter the wavelength, the more reflections in the reciprocal lattice will fall. So, therefore, the more reflections will fall and more reflections will satisfy the Bragg condition. That means, if we use shorter wavelengths, shorter λ we will have a larger sphere of reflection and for the smaller λ or a long λ, longer values of λ we will have smaller sphere of reflection.

So, the larger this sphere of reflections the better it is. So, between copper and molybdenum, molybdenum is preferred radiation for determining the crystal structures in general. Of course, we can use silver radiation which is much more superior. We can also use radiations of different kinds or we can go to synchrotron radiation and tune the wavelength. There are other practical aspects when we do this kind of a thing; that is the design of the instrument itself.

For example, let us say we, because of this logic we go to very very short wavelengths ok, less than 0.2, 0.3, 0.1 and so on. Then the accessibility volume will anyway increase, but our measurement device and the way in which we design the experiment, the diffractometer construction, a mechanical device which is moving the arcs to measure the distances and also the detector capability it limits that value at which we can collect the data. So, normally it is recommended that we use wavelengths of that particular order which will resolve the distance between the two atoms.

So, the most preferred wavelength if you are using the laboratory X ray source is molybdenum. The other issue is of course, the absorption and things like that which we will be discussing in the next few, after probably a few classes, is the fact that we will have absorption, we have in total internal reflection leading to what we call as extinction and such effects. And these effects will also destroy the quality of the intensity we get number 1, and also the quantity of the intensities we can measure.

And therefore, these are all issues which will come up, but in general it is better to use a shorter wavelength to access larger regions of their reciprocal lattice, so that we will get more and more reflections that can be measured within the limits of our Ewald's sphere limitation; that is which will satisfy the Bragg condition. And that is why this construction which we discussed in the previous slide and there the picture which is shown here, is self-clear, is very clear to indicate that the shorter wavelengths are the ones which are preferred.

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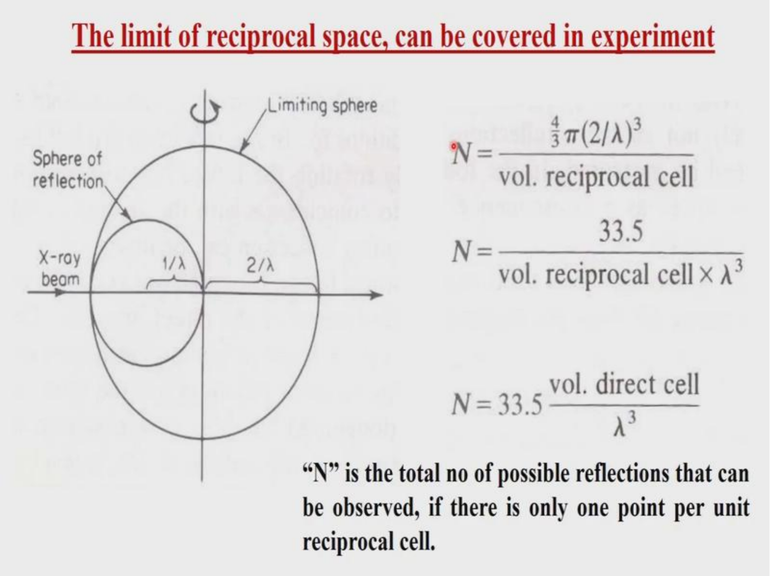

The limit of reciprocal space, can be covered in experiment

$$N = \frac{\frac{4}{3}\pi(2/\lambda)^3}{\text{vol. reciprocal cell}}$$

$$N = \frac{33.5}{\text{vol. reciprocal cell} \times \lambda^3}$$

$$N = 33.5\,\frac{\text{vol. direct cell}}{\lambda^3}$$

"N" is the total no of possible reflections that can be observed, if there is only one point per unit reciprocal cell.

So, the way in which we can express this will be in a slightly different way that will be the way in which we can calculate. In fact, we can calculate how many reflections can come in a given experiment. Suppose we take $1/\lambda$ as the Ewald's sphere and $2/\lambda$ therefore, will be the limiting sphere. All those reciprocal lattice points, so we put, let us say we embed the reciprocal lattice behind this particular sphere or through the particular sphere.

In this example let us say its 2 dimensional, so we put it behind this in the background, that reciprocal lattice will rotate with the as the crystal rotates and different points in the reciprocal lattice. When they intersect with the sphere of reflection we will get the diffraction condition, satisfied and therefore, we will get to the measure of the intensity.

So, what is the number we can access? It is quite interesting to calculate the total number of reflections we can access by this approach. The value of the number of reflections which we can approach depends upon two things; one is of course, the volume of the limiting sphere we have, and the other is the volume of the reciprocal lattice, because volume of the reciprocal lattice is the one which will tell us how many Bragg's spots we have. So, the number of Bragg's spots we have depends upon the volume of the reciprocal lattice; 3 dimensional. And this therefore, is the sphere the limiting sphere now, the volume of the limiting sphere is also a consequence.

So, the volume of the limiting sphere is four-thirds π r cube by definition, any sphere the volume of the sphere is ($4/3\ \pi\ r^3$). In this particular case the value of r is $2/\lambda$, and therefore, ($4/3\ \pi\ r^3$) will be this quantity, so divided by the volume of the reciprocal lattice. The value of ($4/3 * \pi$) and this quantity is fixed ok. So, except that the variability variable here is only λ.

So, we can recast this expression by writing N is equal to 33.5 which is actually calculated as ($4/3 * \pi$) times 2 is 33.5 divided by the volume of the reciprocal lattice times λ^3 , because λ is in the denominator here, it comes down here, so it is multiplied by λ^3.

So, then what we can also rewrite this expression in terms of the direct cell, because we can measure the volume of the direct cell or volume of, it does not really matter, but this is 33.5 *(volume of the direct cell/ λ^3). So, N is the total number of possible reflections that can be observed, if there is only one point per unit cell that is of course, per unit reciprocal cell. So, we can calculate the total number of such reflections that can come.

Now, actually we can do this exercise now. So, if we take for example, the λ value, let us say is 1.542 or 1.5418 Å that of copper. And let us take a unit cell which is 8 * 10 * 20 is orthorhombic let us say. So, $a = 8$, $b = 10$ and $c = 20$. So, what would be the volume? Multiplication of *a b* and *c* if it is an orthorhombic cell; so, 8 times 10 is 80, 80 times 20 is 1600. So, the volume of the unit cell will be 1600 Å^3 .

So, if you now substitute the volume of the unit cell here; 1600 Å^3, this will be therefore, 1600 * 10^{-24} that is the Å^3 in centimetres. And the value of λ is also now expressed in centimetres will be 1.5418 * 10^{-24} in Å ok. So, we can forget the 10^{-24}, so 33.5 volume of the direct cell divided by λ^3 .

So, if we calculate that value of N, N turns out to be from the calculation you will see yourself it is 14,700. So, it means that we can measure 14,700 reflections in principle. If we use the Cu k_α radiation in a unit cell, which is now consisting of 8 * 10 * 20 as the unit cell dimensions; obviously, the unit cell dimensions 8 * 10 * 20 in an orthorhombic system. Let us say we have ¼ all general positions and let us say this space group is $2_12_12_1$. If there are four molecules in the unit cell and the molecule size will be not greater than number of atoms, will be probably around 20 to 25. So, if that is the number of atoms we now know that for 20 atoms in the unit cell in the asymmetric unit; 20 * 9 = 180, plus 1. So, it is 181 parameters to be determined, and we have the in this example the number to be 14,700.

Now, this property that is associated with a unit cell and the property that is associated with the reciprocal lattice, which gives a very large number is referred to as over determination. So, we have to determine 180 plus 1 parameters and we have 14,700 reflections. So, the measurements are over determined and that is in fact, what we require to improve the structure to the accuracies which we eventually report. Mathematically this is a very comfortable situation. The best possible situation would be to now change the wavelength. So, if I change the wavelength of Cu k_α from 1.5418 to 0.7107, let us say its molybdenum radiation. If you calculate the value of N, you will be astounded, because it will now be 1,29,000 possible reflections.

Same crystals, same unit dimensions, but now you see that the number of reflections you get will be an enormous number. Of course, there will always the issue of symmetry and what symmetry can do to these reflections. Not all 14,000 or 1,29,000 reflections are independent of each other. Many of them will be equivalent of each other. So, there will be a reduction of one-fourth or one-eighth of this total value, by the time we actually get to the unique axis, unique number of reflections. We call it the unique number of reflections.

So, by the time we get to the unique number of reflections, it will be reduced by a factor of 4. Even then we have a heavily over determined site and therefore, this methodology of using structure determination to get very accurate positions of atoms, inside the crystal goes up by a very large amount. There is no other method which will give you this kind of an accuracy. You might have seen the results which are published from X ray diffraction studies, where carbon to carbon distance is 1.542 with a standard deviation of ± 0.003 Å. So, the accuracies with which we go, is a real measure of the quality and quantity of data which we have got. So, if we have a good single crystal.

So, the rate limiting step in the entire analysis is the use of a good single crystal. By a good single crystal I do not mean a good looking crystal. A good looking crystal is not sometimes diffracting very well. In fact, a extremely good looking crystal will not diffract at all, because the extremely good looking crystal has many reflecting surfaces. Because it has many reflecting surfaces, there is a good possibility that reflection coming from a plane, maybe again getting reflected within the crystal by another plane. It is oriented in such a way that it will satisfy the Bragg condition again, and so eventually it will be within the crystal and never come out of it.

In fact, there is very clear example of my own personal experience which was the case of the Glucuronic acid. Glucuronic acid I manage to get crystals of very beautiful size and very beautiful shape. Very excited I put it on the diffractometer and waited as usual 45 minutes, 1 hour. Then I lost my patience waited, almost lost my patience, but then I said 2 hours. No diffraction came out, but I was very sure it was looking beautiful. So, I took it to the my polarising microscope, looked under the polarising microscope, there was no extinction visible, because the parallel planes are so well organised that you will not see any extinction of light.

One of the characteristics you should check therefore, when you mount a crystal, is to see the crystal under the microscope. These are practical issues, because many of you are going to determine structures and when you determine the structures you will be using a single crystal. And when you are using a single crystal, first check you have to do is to take the crystal of suitable size, normally the size which is suited for a diffractometer experiment depending on the of course, the contents of your unit cell, assuming it is a let us say a large organic molecule or a small inorganic molecule or whatever and you are using Mo k_{α} radiation.

The size of the crystal should be 0.3 mm^3 in a typical case. It may not be always possible to grow crystals in cubic shape, 0.3 mm^3 would mean it is a cube. It may be a needle, it may be a plate, it may be a flat very flat plate or a thick plate. Depending on that the average overall dimension should come to about 0.3 $Å^3$.

The whole idea is that when you sent in an X ray beam collimated on to the crystal, the crystal should be fully bathed inside the beam, and otherwise you will get other effects. So, the requirement is that the size of the X ray beam which comes in and the size of the crystal should be about the same or slightly smaller than the beam coming, but definitely not too very big. If you have too very big, a crystal that would be severe absorption and in this case of the Glucuronic acid what happened was, that there were several parallel reflections, so everything was internally getting reflected. I then decided let me cool the crystal and when I cooled the crystal I thought that you know the diffraction may be better may be it is large thermal vibration inside the molecule.

Well, it is not the large thermal vibration inside the molecule, but the diffraction itself was now going within the crystal. So, what really happened is when we cooled the crystal, the crystal exploded after the diffraction was done, because the diffraction experiment increase the temperature inside the crystal, because the X rays were going within the crystals so many times that the crystal could not withstand and the crystal exploded on the goniometer.

So, an extremely good crystal is not what we are looking for. We are looking at crystals which have the property of extinction, which have the right kind of dimensions and we take this particular crystal and mount it on the goniometer. First check whether the diffraction conditions are nicely satisfied and we are getting a good quality set of reflections from the reciprocal lattice issue and then continue for the data collection.