Symmetry and Structure in the Solid State
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Lecture – 39
Calculation Intensities 2

So, what we have been looking at is to see, what is the contribution of the intensity, what is the contribution towards the intensity, when ones atoms are found in some positions. For example in the case of a caesium chloride, we discussed the issue that caesium is at 0 0 0, chlorine is at ½ ½ ½ and then we calculated the intensities associated with various reflections like I (1 0 0), I(2 0 0) and so on.

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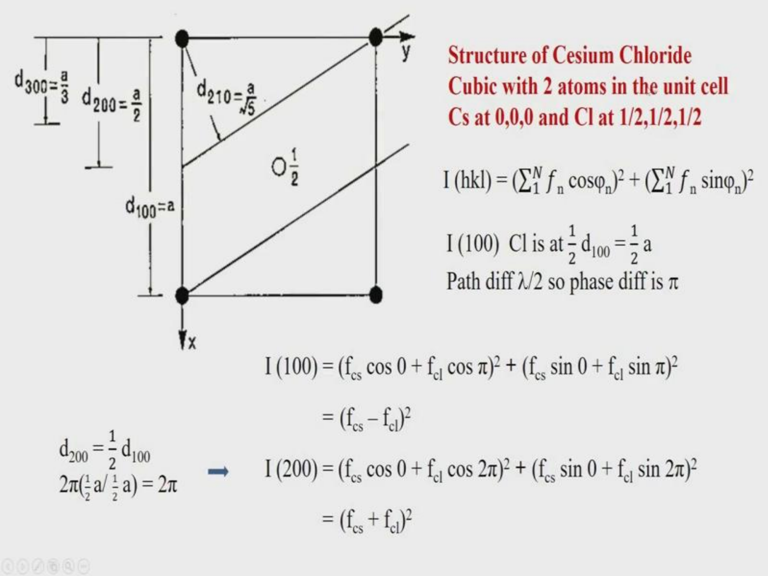

Structure of Cesium Chloride
Cubic with 2 atoms in the unit cell
Cs at 0,0,0 and Cl at 1/2,1/2,1/2

$$I(hkl) = (\textstyle\sum_1^N f_n \cos\varphi_n)^2 + (\sum_1^N f_n \sin\varphi_n)^2$$

I (100) Cl is at $\frac{1}{2} d_{100} = \frac{1}{2} a$
Path diff $\lambda/2$ so phase diff is π

$$I(100) = (f_{cs} \cos 0 + f_{cl} \cos \pi)^2 + (f_{cs} \sin 0 + f_{cl} \sin \pi)^2$$
$$= (f_{cs} - f_{cl})^2$$

$d_{200} = \frac{1}{2} d_{100}$
$2\pi(\frac{1}{2}a/\frac{1}{2}a) = 2\pi$ ➡

$$I(200) = (f_{cs} \cos 0 + f_{cl} \cos 2\pi)^2 + (f_{cs} \sin 0 + f_{cl} \sin 2\pi)^2$$
$$= (f_{cs} + f_{cl})^2$$

We found that in all these expressions, the intensity gets simplified mainly, because of the fact that the caesium is sitting at the origin, which makes caesium to be at 0 0 0 and chlorine is sitting at ½ ½ ½. So, it makes it contribute to various planes depending on it's location.

So, remember we have to use the expression D $_{hkl}$/d $_{hkl}$ that is the one which gives us the ratio of how the position of the atom is with respect to the given plane. For example, if you take 2 1 0 here, the chlorine atom is positioned exactly midway between the parallel planes, which pass through this point, defining 2 1 0 and this is again 2 1 0, so, these are parallel planes. So, this was a methodology with, which we developed that the intensities can be calculated and if we indeed calculated several intensities.

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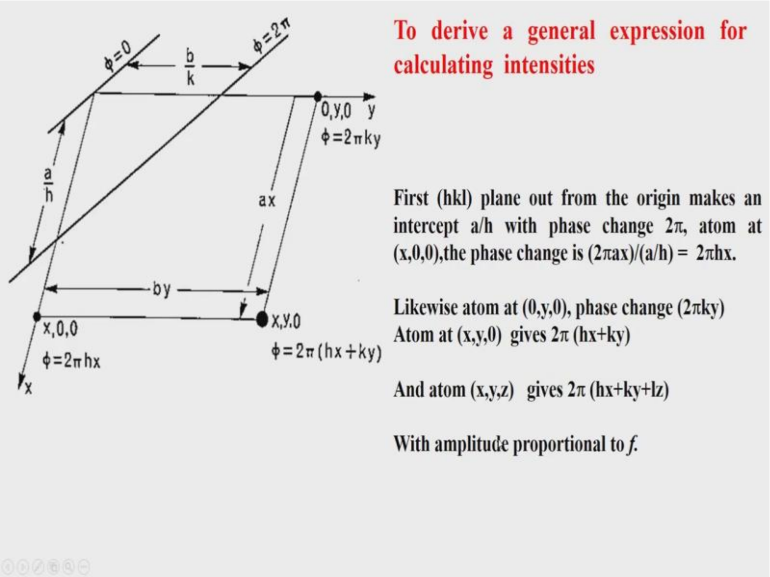

To derive a general expression for calculating intensities

First (hkl) plane out from the origin makes an intercept a/h with phase change 2π, atom at (x,0,0),the phase change is $(2\pi ax)/(a/h) = 2\pi hx$.

Likewise atom at (0,y,0), phase change ($2\pi ky$)
Atom at (x,y,0) gives 2π (hx+ky)

And atom (x,y,z) gives 2π (hx+ky+lz)

With amplitude proportional to *f*.

But in a general case, it is not always caesium chloride we are worried about. We are worried about hundreds of atoms and these hundreds of atoms by symmetry or generating. Let us say more than 4 or 5 molecules in the unit cell. So, it is a very large assembly of atoms and each and every atom now, from our discussion contributes to a given plane. The interference issues with waves coming out of these atomic positions, because it is the electrons which scatter X rays.

So, depending on the electron density, we get contribution into various planes and these are now constructively or destructively interfering and therefore, the intensity associated with a plane gets calculated. The issue is now, how can we get a general expression, because we cannot just every time go and find out where the atoms are sitting and then calculate instead there should be a very general expression depending upon wherever the atom is sitting in the unit cell.

We should be able to calculate the contribution to the plane and that is the idea with which we will now, develop a general expression as I have written here; a general expression for the calculation of intensities. This will be applicable to all three dimensions and therefore, it is in a unit cell depending upon where the positioning of the plane is, we should be able to calculate the contribution to that plane from all the atoms that are present in the unit cell.

So, this is therefore, a very important calculation, which will sort of generalize, how we approach the various issues of how to calculate the intensity. So, what we will do is, we will first derive the general expression and then incorporate the general expression for finding the contribution to various planes the intensity contribution from the presence of 100's of atoms or 1000's of atoms or whatever it is. So, this in principle is easily programmable, so, we can develop packages with which we can calculate intensities.

Whenever I am saying calculating intensities, it means that we already know the positions of the atoms. So, it is only after the structure is determined we can calculate intensities that we must remember. So that means, we should know the positions of the atoms if before we calculate intensity, but the general expression for calculating intensity will always be automatically coming and that is obtained by this obtained by this diagram in which I show, a two dimensional projection, x along this direction and y along this direction, this is the angle between x and y and of course, z is coming in the direction away from the plane of the projection.

So, if you consider a plane passing through the origin as we have always discussed, this particular plane will have a phase difference of 0, because there is no path difference at 0 0 0. We also have shown that all atoms lying on this plane will scatter in the same phase. So, the phase is 0 associated with atoms lying in that plane. What then we will do is to take by definition of the Braggs law. We take the first plane, which comes out of this particular 0 0 0 position and let us take a general position, where we will have the first position coming, which is shown here. This is the first plane out of it; that means, the phase change will be 2π.

So, whenever the phase change is 2π, we have the λ as the path difference and therefore, we satisfy the condition $2\ d_{hkl} \sin\theta$ equals λ. So, we satisfy that expression, which is the Braggs expression. So, suppose, we have an atom at x 0 0 along the direction of x. We locate an atom x 0 0 the contribution of this atom to this plane. We know already how to calculate, what we do is we draw a line parallel to this plane passing through the x 0 0 like that and then we calculate the distance of this particular plane from the origin and then we take the a/h of course, a/h b/k and c/l will be the intersections for the first given plane.

So, depending upon what is the value of *h k* and *l* we can define this particular plane. So, the first plane, which obeys the Bragg equation will come at a distance of a/h, where *a* is the unit cell, *h* is the Miller index, *b/k* wherever *k* is the miller index, *b* is the unit cell and of course, in the third direction it will be *c/l*. So, if we now consider this as the *x* 0 0 then what is the phase that is associated with this, because that is what we want to calculate the intensity. So, the first *hkl* plane out from the origin makes an intercept *a/h*, which is what we are shown here with a phase change of 2π.

So, the first phase change is 2π. Atom is at *x* 0 0, so, what would be the D_{hkl}/d_{hkl} the D is 2π*ax*, because that is the distance, which we which up to the *x* 0 0. 2π*ax* divided by *a/h,* which is the value here. So, if we take this 2/*ax* divided by *a/h*, this will give rise to 2π*hx*. So, 2π*hx* is now, the plane, the phase that is associated with this particular atom its contribution to the plane, which is the first plane out of 0 0 0.

So, the contribution to this plane is 2π*hx*, if there is a atom sitting at x 0 0 likewise, if there is an atom sitting at 0 *y* 0. It will become 2π*ky*, because it will be 2π*by* divided by *b/k*. So, that will become therefore, 2π*ky* and similarly, if it is in the l direction, it will become 2π*lz*. So, in the case, where the atom is sitting at *x y* 0. Let us say we have an atom here. So, what we have to do is, to line draw a line parallel to that calculate the D_{hkl} and the small d_{hkl} is already available and therefore, that will be the atom is at *x y* 0.

So, the corresponding phase will be 2π(*hx* + *ky*), *hx* due to this direction, *ky* due to that direction and therefore, we have *x* contribution *y* contribution both taken into account. So, the phase change will be φ equals to 2π(*hx* + *ky*). So, this diagram therefore, is a general picture of any crystal structure, which will have this kind of disposition. We have considered the positions of three different atoms corresponding to their contributions to this particular plane and the phase changes have been calculated. When once we have the phase changes, we can always calculate the intensity that is associated with it, because an atom at in a general position *x y z* will give rise to a phase change of 2π(*hx* + *ky* + *lz*). And of course, the amplitude will be proportional to that of f, which is the atomic scattering factor corresponding to the scattering angle θ about, which the reciprocal lattice vector is located.

So, what is important here is, the location of the reciprocal lattice point. The location of the reciprocal point is this associated with the plane and the amplitude therefore, has to be read proportional to that. So, whatever is the value of f, at that particular corresponding scattering angle, which is corresponding sin θ/λ has to be read out and then we substitute it to calculate the intensity, this is something which we will now consider and see whether we can do this in very simple terms.

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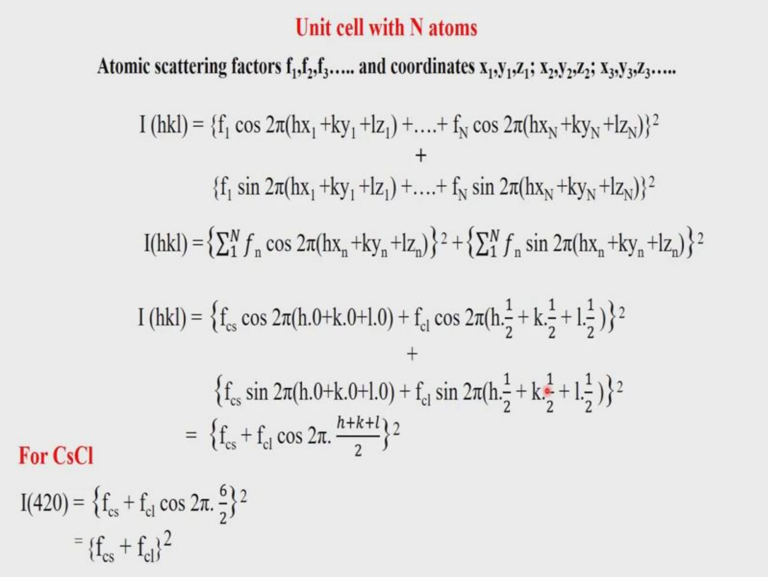

Unit cell with N atoms

Atomic scattering factors f_1, f_2, f_3..... and coordinates x_1, y_1, z_1; x_2, y_2, z_2; x_3, y_3, z_3.....

$$I\,(hkl) = \{f_1 \cos 2\pi(hx_1 + ky_1 + lz_1) + ... + f_N \cos 2\pi(hx_N + ky_N + lz_N)\}^2$$
$$+$$
$$\{f_1 \sin 2\pi(hx_1 + ky_1 + lz_1) + ... + f_N \sin 2\pi(hx_N + ky_N + lz_N)\}^2$$

$$I(hkl) = \left\{\textstyle\sum_1^N f_n \cos 2\pi(hx_n + ky_n + lz_n)\right\}^2 + \left\{\textstyle\sum_1^N f_n \sin 2\pi(hx_n + ky_n + lz_n)\right\}^2$$

$$I\,(hkl) = \left\{f_{cs} \cos 2\pi(h.0 + k.0 + l.0) + f_{cl} \cos 2\pi(h.\tfrac{1}{2} + k.\tfrac{1}{2} + l.\tfrac{1}{2})\right\}^2$$
$$+$$
$$\left\{f_{cs} \sin 2\pi(h.0 + k.0 + l.0) + f_{cl} \sin 2\pi(h.\tfrac{1}{2} + k.\tfrac{1}{2} + l.\tfrac{1}{2})\right\}^2$$
$$= \left\{f_{cs} + f_{cl} \cos 2\pi.\frac{h+k+l}{2}\right\}^2$$

For CsCl

$$I(420) = \left\{f_{cs} + f_{cl} \cos 2\pi.\frac{6}{2}\right\}^2$$
$$= \{f_{cs} + f_{cl}\}^2$$

Let us take a unit cell with N atoms. So, now, we have a unit cell with N atoms, we have various planes passing through this crystal. It is any general crystal. So, the cell dimensions are *a b c α β γ*. So, in such situations what we have is, we have a variety of atoms in our structure. So, let us say we have N type of atoms at N different positions, a very general discussion. So, the atomic scattering factors are f_1 f_2 f_3 so on and the coordinates are x_1 y_1 z_1; x_2 y_2 z_2; x_3 y_3 z_3 and so on. So, if there are N atoms we have therefore, the f_n corresponding to the atomic scattering for nth atom and x_n y_n z_n as the coordinates, then we write the expression for I(*h k l*).

Now, remember the I(*h k l*) expression, we should contain contributions from every one of these items and therefore, we have f_1 cos 2π. Now, this is the phase change, we have already calculated the phase change to be 2π (hx + ky + lz). Now, the atom is at x_1 y_1 z_1. So, we get this first term as $f_1 \cos 2\pi(hx_1 + ky_1 + lz_1)$ + etc.., for second third fourth atom, until the Nth atom, $f_n \cos 2\pi(hx_n + ky_n + lz_n)\}^2$. Notice that it has to be whole square. This is the cosine term, we will also have the sine term, because we know in our wave is a complex number. We will come to the discussion of structure factors in a later time, a few may be in about an hour and hour and half of discussions on this. So, what we therefore, see here is the intensity consists of cosine functions and the corresponding sine functions, cosine function square + sine function square. So, this is the intensity associated with any *h k l*. So, what is the job we have at hand? We have a crystal, we have done the diffraction experiment and we want to now, calculate the contributions of atoms lying at various positions x_1 y_1 z_1 , x_2 y_2 z_2 and so on to the overall intensity that is developing at a given plane *h k l*. So, for any given general plane, it should be possible to calculate the contribution coming from various atoms. So, there are N atoms here, so, all the N atoms are summed up here, in this contribution.

So, this can of course, be written as equal to sum over 1 to N f_n cosine $2\pi(hx_n + k\,y_n + lz_n)^2$ + sum over 1 to N f_n sin of 2π the corresponding sine term square. Let us take the example of our caesium chloride again, to verify whether we are doing it correctly, whether we are doing this calculation or whether this particular expression, which is a general expression for any crystal any crystal with N atoms and it's contribution to any *h k l* plane. So, therefore, I call it as the general expression for calculating the intensities.

So, we take the case of caesium chloride, caesium is at 0 0 0, chlorine is at ½ ½ ½. So, what all we have to do is to substitute the values here. So, f_{cs} the atomic scattering factor of caesium cos 2π (h*0 + k*0 + l*0), because 0 0 0 is the position of x_1 y_1 z_1 then f_{cl} cos 2π $(h*½ + k*½ + l*½)^2$ and of course, the corresponding sine terms. What happens in this situation is that the sine terms will vanish, we will in fact, make a general discussion of why sine terms vanish in situations where which is, which are similar to the structure of caesium chloride. In fact, sine terms generally, vanish in case you have a centrosymmetric crystal.

So, if there is a inversion centre in the crystal and that inversion centre coincides with the origin, then all the centrosymmetric structures therefore, will not have any contribution from the sine terms. On the other hand, the cosine terms does do contribute in the following way for example, the f_{cs} since, it is at 0 0 0, there is no phase change. So, f_{cs} remains as such. So, f_{cl} now gets modified with this change in the phase and the change in the phase happens to be $\{\cos 2\pi\ (h + k + l)/2\}^2$.

So, this is a general expression for deriving the intensity in case of the caesium chloride. So, all possible *h k l* planes, which come out from the caesium chloride diffraction experiments can be calculated and this particular value is now absolute value, because we are reading out the corresponding atomic scattering contributions from individual atoms, chlorine and caesium. So, one ones we take an example here, we want to calculate the intensity of some plane 4 2 0. So, what all you have to do is to substitute that expression in this expression the values.

So, you take the f_{cs} as corresponding to that value in our f versus sin θ/λ picture. So, we cannot take the z value we have to take that value of f_{cs}, which corresponds to the scattering angle. So, if scattering angle is θ, the corresponding sin θ/λ value has to be read for the f_{cs} similarly for f_{cl}. So, one ones we have those values fitted in then the cos value of 2π now, h + k + l here is 6 so, 6 divided by 2. So, 6 divided by 2 happens to be 3 times.

So, it is essentially this. So, happens that it turns out to be a factor of cos of 2π. So, the sign becomes +. So, you will have $(f_{cs+} f_{cl})^2$. So, for any given I(*h k l*) you can calculate again for 1 0 0 or 2 0 0, whatever contributions will come from any general *h k l* plane. So, those *h k l* planes, which will contribute to this will the intensity can all be calculated. So, if we now do an experiment, let us say with caesium chloride either a powder diffraction experiment or a single crystal experiment. Let us take the case of a powder diffraction experiment, then we will get a powder pattern corresponding to caesium chloride and that particular powder pattern will be, we will able to index it in terms of where the *h k l* planes are coming by looking at the *x* axis of the X ray plot. Let me show you that plot.

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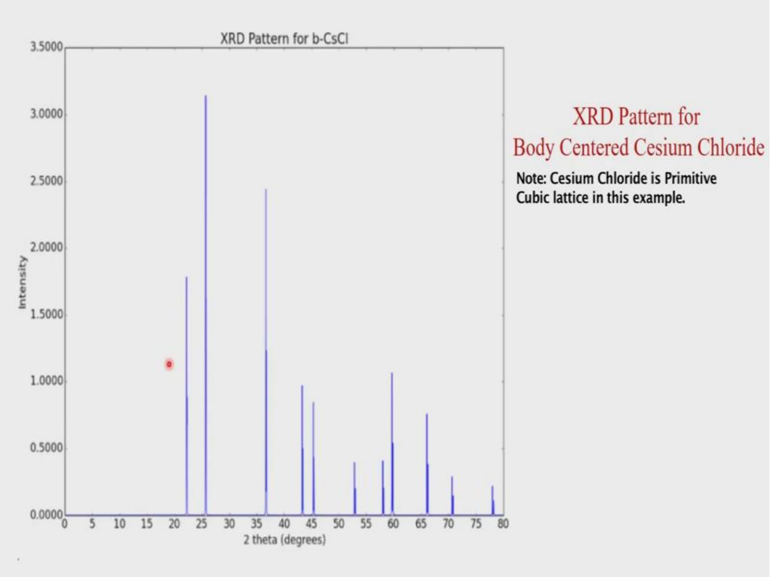

XRD Pattern for
Body Centered Cesium Chloride

Note: Cesium Chloride is Primitive
Cubic lattice in this example.

So, let us say this is the XRD pattern is in fact, the simulated XRD pattern using the coordinates of caesium chloride. We have calculated, what are all the contributions to the to individual reflections. Since, it is a powder pattern you will see the lines. In fact, in a typical recorded powder pattern each line will have a certain width. We will discuss those issues later when we do powder diffraction, but for our discussion now, each of these endpoints will represent our lattice points, if it is a single crystal. So, in principle at various values of these 2θ values you will find the reflections appearing and those appearance of reflections will have this amount of intensity.

So, this is the arbitrary intensity, because this is done on some equipment, whether you do it in, an equipment in Bangalore or some other place or your place, wherever you want to go and do the experiment, the intensities will change depending upon the intensity scale will change depending upon which instrument you are using what are the experimental conditions that are available and so on. So, this is actually a relative intensity and this has to be scaled and brought onto the actual intensity to the absolute intensity, which we get from our calculation, because in the calculation we are using the f_{cs} and f_{cl} as they should be at that scattering angle and therefore, we get the absolute value (Refer Time: 18:30). We will not worry about that aspect.

What we worry about this aspect is the following and what we should know about any powder diffraction, we will when we do it in detail later we will also see that this is that the geometry that is associated with the diffraction, that is the dimensions of caesium chloride, the nature of caesium chloride, the appearance and disappearance of these peaks in case of sodium chloride all that will be indicative in the *x* direction.

So, *x* direction therefore, gives you the geometry of the diffraction, the *x* direction is the place where you can actually see the presence of 2dsin θ = nλ reflections, which are satisfied. So, you do not get continuous pattern here, you get discrete patterns, whenever there is Braggs law obeyed, we will get the diffraction and that diffraction, whether it is constructive or destructive, it is decided by the positions of the atoms with respect to the planes from which we are doing this locating the measurements. So, we therefore, have all the planes which are coming out in the *x* direction. So, the *x* axis represents the geometry of our diffraction condition, the *y* axis represents the intensity that is associated with the diffraction measurement.

So, because of this we see that the associated corresponding intensities will come with respect to the individual calculations, which we did for I(1 0 0) and I(2 0 0) and so on, we calculated those intensities. So, they will come, because of the of fact that caesium is at 0 0 0, chlorine is at ½ ½ ½. So, this discussion therefore, assumes that we know the structure. This discussion also tells us that the way in which the XRD pattern can appear, because the XRD pattern will appear as a relative intensity versus 2θ in all experiments, which you have performed in a normal diffractometer. And therefore, the 2θ degrees, which we plot in the *x* axis, the values associated with *x* axis will therefore, represent various 2θ values.

Now, these 2θ values are the ones, which will tell us what are the d values correspondingly, because we use the formula to 2dsin θ = nλ, where λ is the wavelength we have use so; obviously, this pattern will be different for different wavelengths. Suppose, we use copper radiation, it will have this pattern, if you use molybdenum radiation the pattern will be different, the θ values will come at different positions. So, you should remember that.

But if you plot let us say the relative intensity against the d value, d is already incorporating the corresponding sin θ expression and so on, then the two patterns will be similar and this is something which you must remember. So, when you what is plotted along the *x* axis is important.

But basically what is given in the *x* axis direction, in this plot is the value that is associated with the geometry. So, the geometry of the diffraction condition we can determine; that means, we can determine the unit cell, the dimensions we can determine. Therefore, the crystal system we can determine where the diffraction spots are coming, and therefore, the geometry of the diffraction. So, entire geometry of the diffraction is conserved in along the *a* axis along the *x* axis.

So, that way we know when we do a *xy* plot of this kind that all information on the geometry is here, all information about the structure is along the y direction. Because the intensity is the one, which is the, which is telling us, which item is where and therefore, the electron density distribution is covered along the *y* axis. So, the information that is present along the *y* axis therefore, incidentally tells us about the way in which atoms are distributed inside the unit cell.

So; obviously, the appearance of these relative intensities depend upon the symmetry associated with the material and therefore, when we have found out the space group and in the unit cell dimensions, the number of molecules in the unit cell etc.., which about which we are already reasonable experts. So, this will now tell us how that contributes to the intensity measurements.

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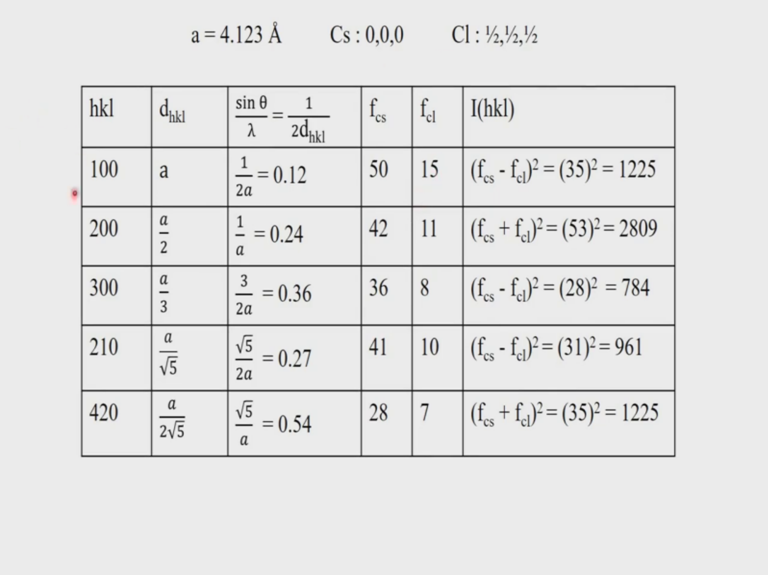

a = 4.123 Å Cs : 0,0,0 Cl : ½,½,½

hkl	d_{hkl}	$\frac{\sin\theta}{\lambda} = \frac{1}{2d_{hkl}}$	f_{cs}	f_{cl}	I(hkl)
100	a	$\frac{1}{2a} = 0.12$	50	15	$(f_{cs} - f_{cl})^2 = (35)^2 = 1225$
200	$\frac{a}{2}$	$\frac{1}{a} = 0.24$	42	11	$(f_{cs} + f_{cl})^2 = (53)^2 = 2809$
300	$\frac{a}{3}$	$\frac{3}{2a} = 0.36$	36	8	$(f_{cs} - f_{cl})^2 = (28)^2 = 784$
210	$\frac{a}{\sqrt{5}}$	$\frac{\sqrt{5}}{2a} = 0.27$	41	10	$(f_{cs} - f_{cl})^2 = (31)^2 = 961$
420	$\frac{a}{2\sqrt{5}}$	$\frac{\sqrt{5}}{a} = 0.54$	28	7	$(f_{cs} + f_{cl})^2 = (35)^2 = 1225$

So, this tells us that these are the possible reflections associated with caesium and chlorine and *a* is equal to 4.123 and this is the calculated values, which we get for sin

θ/λ, based on the presence of where the d values are and therefore, we can calculate based on our general expression which we derived just now. This general expression will tell us how to go about determining the intensities for any given X ray diffraction pattern. So, this is a key equation. Now, if we take the square root of this $I(hkl)$, we will get what is known as the structure factor, it is the modulus of the structure factor.

We will now take up a discussion on the structure factor, but I taught that before we go into the detail of the structure factors associated with any diffraction condition, which essentially is an important factor, because we remember we had 2 expressions, we called them Fourier transforms of each other. We showed that $F(h\ k\ l)$ or F(R) at that time $F(h\ k\ l)$ is related by a Fourier transform to ρ(r) where ρ(r) is the electron density.

And vice versa that is if we from ρ(r) we can get to the F(R). So, those two equations are the major fundamental equations, which we need in order to solve the structure. So, for example, if we know the structure factors, we can determine the structure in principle and if we know the electron density, we can determine the structure factors. So, this Fourier transform equations tell us clearly that when we do a structure determination protocol, the structure determination in order to determine where the electron density is, should have structure factors not the intensities.

So, here what we have done is to shows the general equation by means of which we can calculate the intensities, because that is what we experimentally measure in a diffraction experiment. So, since we have the intensities that is available with us, we can use these intensities and then determine the structure factors. The major problem which comes up, there is the phase problem. We get the magnitude of $F(h\ k\ l)$, we do not get the α associated with $h\ k\ l$.

So, here how did we solve the phase problem in calculating the intensities? We solved the phase problem by looking at the fact that if depending upon where these atoms are the variation is with respect to $2\pi\ (h\,x + k\,y + l\,z)$. So, that gave us the phase issue this is, because we know where $x\ y\ z$ is since, we do not know where $x\ y\ z$ is the modulus value, which we get for structure factor is devoid of phases. No experimental way is available with the way we do the experiment, no experimental approach can be developed to find the phase.

So, therefore, we have to determine the phases or guess the phases that are associated with the structure factors. So, you might ask a question, why not use the intensities and do a Fourier transform. What is what happens if we do the Fourier transform of intensities? If we do the Fourier transform of intensity, we will get what is known as a Patterson function. We will be discussing details of the Patterson function, because that is also an extraordinarily useful function provided, we know certain things about the structure. See the I(h k l) gives rise to the so called Patterson function and that Patterson function is one in, which we get the inter atomic distances as vectors. So, it is a vector map and in that vector map, we get inter atomic distances.

So, in other words what we will get if we do the Patterson of a caesium chloride example we have taken here it is not the positions of the atoms, but the position of the end vectors between caesium and chlorine. We not only get the position of the vector between caesium chlorine, we will also get vectors associated with caesium and caesium itself, chlorine and chlorine itself, chlorine to caesium and then all the other equivalent points, which get generated in this space group and their vectors.

So, if there are N atoms we will get N^2 vectors out of which N will be self vectors. So, the total number of independent vectors will be N^2 - N. It is very easy in case of the caesium chloride to guess what should be the Patterson map, because there are only 2 atoms in the unit cell. On the other hand, if there are 100s of atoms, we will get N^2 - N if 100 atoms are there.

So, we will get N^2 - N peaks and all these peaks will originate from the same origin and therefore, Patterson is also a very useful tool, because we do not have the phase problem there to solve; however, the tool that can be used there is to sort of extract information from the vector map. Since, there is a severe, large number of vectors coming from a single origin, it becomes a severe overlap between vectors and structure solution is not very straightforward, it can be done, but it is not a straightforward methodology. So, the generally recommended methodology is to measure the intensities, identify the magnitude of the structure factors by taking the square root of the intensity and then solve the phase problem to get to the structure.

So, this now is the general methodology that is available for the structure determination. So, what have we done so far? What we have done so far in terms of the structure determines. In fact we did not determine the structure, we assumed the structure of caesium chloride and then did the substitution of various types to get to the intensity calculations. We in fact, got the absolute intensities, because we have used the realistic atoms inside the unit cell. The idea of this particular calculation was to show that, we can get to the intensities given the positions of the atoms. So, even if you have 1000s of positions you can write a computer program, which will use this for general formula for calculating the structure factor, the intensity and it will calculate all possible intensities.

So, there is an advantage since we have fast speed computers and so, one once we know the positions of the atoms we can calculate all possible intensities that come out from the experiment, but that is not our motive. Our motive is to find out the positions of the atoms. So, it is we have now got ourselves into a situation, where if we do not have the positions of the atoms, we cannot get to the intensities. So, that is something which we do not want to face, but we do get the intensities from the experiment.

You see, we have an experiment we performed an experiment we sent a beam of X rays onto the crystal, the crystal did the diffraction. We know the geometry of the diffraction, because it obeys the Braggs conditions, we know where there a particular peak has to come with respect to the 2θ axis of the powder pattern we have a relative intensity measured. So, eventually we should find out a way in which we can put these relative intensities to absolute scale.

All that is possible, but will it lead to the structure determination is a question of is question which is going to be very difficult to answer. Very-very simple structures can be determined, but as we go to higher complexities, if we go to large organic molecules, inorganic coordinate systems (Refer Time: 30:23) MOFs and then eventually to proteins and viruses. It looks an (Refer Time: 30:28) arduous task.

So, the task is cut out here for us to use the intensities and use the information about the geometry which we have derived from the Braggs law conditions and use these two aspects to find out the structure, find out where the atoms are, the challenge lies there. So, the rest of the structure determination protocol which we are going to develop will depend upon, how we develop this whole theoretical approach to find out the positions of the atoms.

What is the plus point? The plus point is that we have done an experiment on with X ray diffraction techniques. So, we have the machine, we generate the X rays, I spent a little time on how we generate the X rays, but maybe we will assume that we have the X rays coming in, because of the number of classes limited in this course. Suppose, something sometime is available with the TAs they may discuss how X rays are generated. So, the X rays will be generated, they will fall onto the crystal, the crystal now diffracts and the intensity are measured the positions of where the peaks come, the points come.

Now, can be can be indexed by in terms of the *h k l* values, because we know the scattering is now giving us the reciprocal lattice. So, we use the *h k l* values using the collection of *h k l* values, we determine the geometry of the diffraction. So, we now know what is the crystal system and what is the various ways in which we can now attempt to determine the space group using the information that is available on the reciprocal lattice. `

So, that will be the next aspect, how are we going to use this information to find? What is the space group that is available for us to handle and then we will know one, once we know the space group you know how many molecules are there in the unit cell, because we eventually have to solve for only 1 molecule the other molecules in the unit cell can be generated by equivalent points, which we know very well.

So, this in a nutshell is what we will have to be doing and therefore, 2 things are important; one is the accuracy that is associated with indexing procedure. So, if you go wrong in that everything will go wrong, that is the first thing that indexing procedure therefore, will tell us where the atom, where the *h k l* planes are coming and in what way those *h k l* planes help us in understanding the geometry of the diffraction.

One once we have that handled, then we can look at the intensities, handle the intensities by taking their square root and going over to the structure factor, the magnitude of the structure factor. Guess the phases and then go and compute the electron density using the Fourier transform expression, that will give us the final structure which we are looking for. So, what then we will do is there is one issue which I always wanted to discuss before we go further and that is something which we have been looking at earlier, in the earlier classes the concept of reciprocal lattice.

Since, we have been now saying that the there are 2 lattices; the direct lattice and the reciprocal lattice we have also formulated the relationship between the direct lattice and the reciprocal lattice, but I think we should have a relook at this reciprocal lattice concept a little more closely.

So, that we now are able to see how diffraction is occurring and how we can get an access to the reciprocal lattice geometry by means of which we can index the pattern and then the distribution of the intensities to individual reflections. Has it got any information, regarding the space group information? Can we derive a space group by looking at the intensities, which have come in our three dimensional reciprocal lattice, because the main direct lattice has this information.

So, can we get that information out of our reciprocal lattice. So, we now go in over to that region. So, before we go over to the region, where we now look at what is the information the reciprocal lattice can give, with respect to the space group determination and in what way we measure the intensities and how we put it put them on the relative scale. All these aspects now are automatically done on diffractometer. I always keep selling that telling all the time that crystallographers are their own enemies that is, because they have made it.

So, very simple now a chemist or any other person who wants to determine a crystal, what all he has to do is put the crystal on the machine and wait for some time and maybe a few hours nowadays, in order to get to the final structure, by just sitting at the keyboard and pressing enter buttons whenever it is asked for. So, effectively the thing is that we do get information regarding the structure.

Without knowing any of the background we have here and that is where the interpretation of the determined structures becomes a challenge to chemists, to physicists to engineers and so on. And that is very important, because one once we have the structure information available, it is always related to the property, the material exhibits.

So, the next step therefore, will be to see, what information we can get from the reciprocal lattice analysis. So, we will go into the details of the reciprocal lattice as we go further.