Symmetry and Structure in the Solid State
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Lecture – 44
Systematic Absences 1

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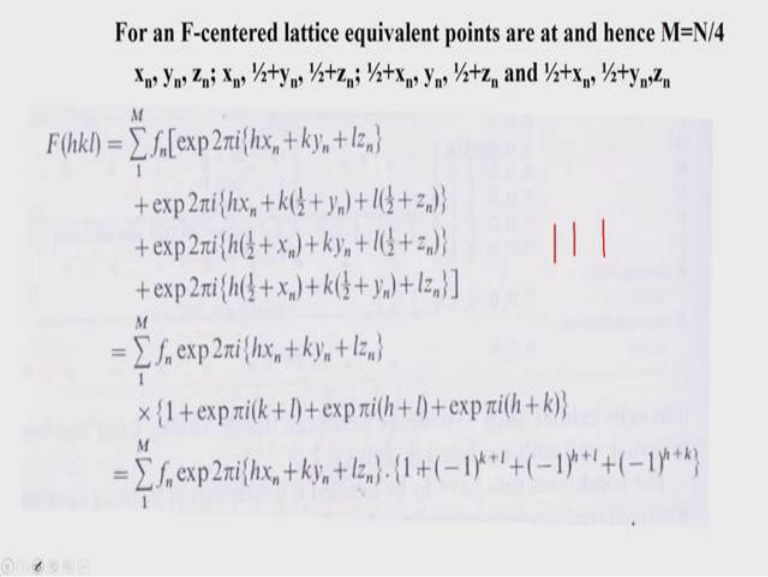

For an F-centered lattice equivalent points are at and hence M=N/4

$x_n, y_n, z_n; x_n, ½+y_n, ½+z_n; ½+x_n, y_n, ½+z_n$ and $½+x_n, ½+y_n, z_n$

$$F(hkl) = \sum_1^M f_n[\exp 2\pi i\{hx_n + ky_n + lz_n\}$$
$$+\exp 2\pi i\{hx_n + k(\tfrac{1}{2}+y_n) + l(\tfrac{1}{2}+z_n)\}$$
$$+\exp 2\pi i\{h(\tfrac{1}{2}+x_n) + ky_n + l(\tfrac{1}{2}+z_n)\}$$
$$+\exp 2\pi i\{h(\tfrac{1}{2}+x_n) + k(\tfrac{1}{2}+y_n) + lz_n\}]$$
$$= \sum_1^M f_n \exp 2\pi i\{hx_n + ky_n + lz_n\}$$
$$\times\{1 + \exp \pi i(k+l) + \exp \pi i(h+l) + \exp \pi i(h+k)\}$$
$$= \sum_1^M f_n \exp 2\pi i\{hx_n + ky_n + lz_n\}.\{1 + (-1)^{k+l} + (-1)^{h+l} + (-1)^{h+k}\}$$

You look the equations the moment, now some people see the equations they get worried here there is nothing to worry about these equations because you are now experts in understanding what we are talking about. *C*- Centered lattice gave you h + k odd absent. So, suppose now you simultaneously see you cannot have *A* center and *B* center and leave it at that because by symmetry *C* center will automatically get centering also done therefore, it become say face centered lattice.

So, either you have *C, A,* or *B* centered lattice which is representing the monoclinic and the orthorhombic systems or you will have a face centered lattice which can come in of course, monoclinic special case *F* can be coming in, but we convert it, which will be probably indicated in some TA class. Then we have the *F*- centered coming in orthorhombic, *F* center will come in cubic as well.

So, depending upon the other symmetry elements, we can decide what crystal system it has to go into and apart from the fact that we have *a b c α β γ* which is also indicators of what crystal system the given the given crystal goes into given system goes into. So, these are the four equivalent points in case of *F*- centered lattice we have x_n y_n z_n this will be equivalent of x_n ½ + y_n ½ + z_n.

This represents the A centered lattice ½ + x_n ½ + z_n y_n this represents the B centered lattice, ½ + x_n ½ + y_n z_n represents the C- centered lattice. So, when all these faces are centered we have a face centered lattice. So, we again do the calculation. So, what we do is again now we divide this into the 4 equivalent points, the number of atoms in the unit cell. So, M now becomes N/4.

So, the summation now is over one-fourth of the total number of atoms in the unit cell. So, the effort becomes lesser when we have a F- centered lattice. So, the F(h k l) is now sum over 1 to M we have the general expression f_n exp $2\pi i$ $(hx_n+ky_n+lz_n)$ and then to this we have to add the centering of each one of them this represents the A centered part this represents the B centered part and this represents the C- centered part.

So, *A* face is centered, *B* face is centered, *C* face is centered and therefore, the expression now becomes sum over 1 to M of x y z associated with x y z that is taken as a common factor from all these four just as we did in the case of the *C*- centered. We have more expressions here and therefore, that becomes 1 + exp (k + l) + exp (h + l) + exp (h + k). So, this expression comes up and this expression now can be substituted with $(-1)^{(k+l)}$ as we calculated in the previous case, exponential with these two integers can be easily evaluated mathematically and the mathematical solution tells us that this can be 1, - 1, - 1, - 1 and therefore, we get this expression for F(h k l).

So, what do you think will happen when we have face centered lattices? Face centered lattices as we see there are four equivalent points which developed because of the face centering. So that means, where the set of atoms we are considering now is reduced to one-fourth. So, these one-fourth atom now will repeat based on the nature of the centering.

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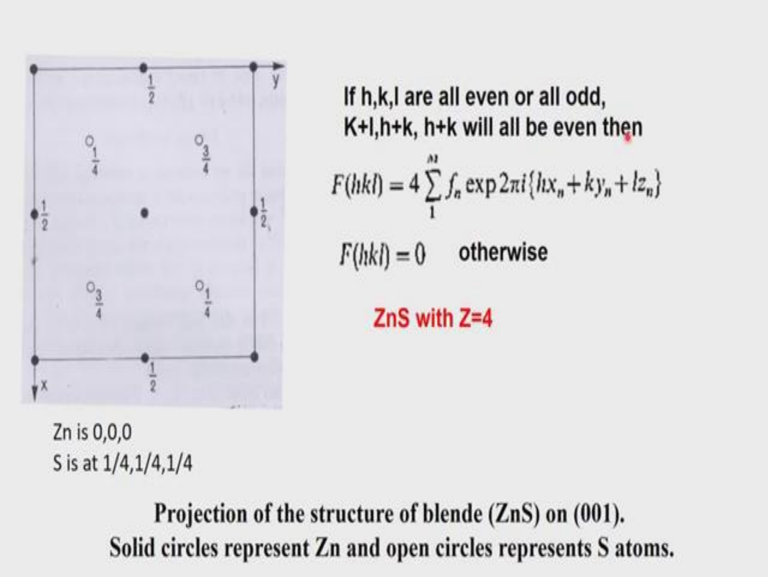

If h,k,l are all even or all odd,
K+l,h+k, h+k will all be even then

$$F(hkl) = 4\sum_{1}^{N} f_n \exp 2\pi i\{hx_n + ky_n + lz_n\}$$

$F(hkl) = 0$ otherwise

ZnS with Z=4

Zn is 0,0,0
S is at 1/4,1/4,1/4

Projection of the structure of blende (ZnS) on (001).
Solid circles represent Zn and open circles represents S atoms.

So, what will happen to this expression what would be the actual F(h k l)? F(h k l) if h k l are all even or all odd then k + l, h + k and l + k will all be even right. So, for example, if you take the value of h k l to be let us take an example, let us take these example of reflection 1 1 1 ok.

So, this tells you h is 1, k is 1, l is 1. So, I take this reflection 1 1 1 now this reflection 1 1 1 has to be fitting into this equation and how it will fits into this equation we will see in a minute. We will go to the next slide and come back again this slide tells me that if F(h k l) are all even or all odd. So, our 1 1 1 is all odd then if you add h + k it is 2. So, k + l will become 2, h + l is also 2, h + k is also 2.

So, they will be all even. So, if it is even let us say if it is 2 2 2, then also these quantities will be even. So, reflections like 1 1 1, 2 2 2 will if h k l are all even or all odd, this value will all be even and then the calculation will be 4 times this quantity. So, the structure factor will have a value whenever this possibility occurs and for all other things for all other things it becomes 0 for all other h k l values it becomes 0.

So, h k l value is like 1 1 1, 2 2 2, 3 3 3 or combinations of other kinds of odd values lets like 3 1 4 cannot be there, 3 1 3 yes, 2 2 6 yes, 2 2 1 no so, such absences therefore, we will develop. So, this is the statement if h k l are all even or all odd, then the value of h + k, k + l and h + k will all be even then you get this systematic absences.

So, this is correct this is the way you have to look at it. So, if h k l are all odd or all even, the summation of each one of the two components will become even and therefore, this exists this expression exists. That means, this systematic absence now will be enormous and the many of them will be absent in this *F*- centered lattice. In fact, this is something which is given later to you in powder diffraction as a what should we call a thumb rule; the thumb rule is that if you have a crystal system which is a simple primitive lattice or if you have a system which is centered like may be face centered the other one is body centered.

Suppose there is 3 polymorphs this is with respect to the pharma people as well as materials people. If it is 3 different polymorphs one crystallizing in primitive cell another crystallizing in face centered cell the third crystallizing in a body centered its quite possible. If such a thing happens then if you take a powder diffractogram of this material you have the same material if you take the powdered diffractogram of the same material you will see more reflections from the primitive and less reflections for the body centered and further less reflections for the face centered.

So, that is how if you record the pattern of sodium chloride you will get only 5 peaks in the powder diffraction pattern. So, the more simplified the powder diffraction pattern is, it represents the symmetry that can be associated with the centering of the lattice. Centering of the lattice is the one which will now reduce the number of possible reflections and therefore, the number of possible observations you can have.

So, more the symmetric the more the symmetric the space group is, the less is the number of observations you will have. And this is an issue which we may have to tackle when we are dealing with diffraction both in single crystal as well as in powder and we will discuss that when we actually do the experimental analysis of these, particularly in powder diffraction this will be very crucial right.

So, now we will take a realistic example. So, you can also say the English language is rather difficult that is why there is always a problem in getting this statement correctly. So, if h k l are all or neither all even nor all odd. So, we can use that phrase as well. So, what happens? If h k l are neither all even nor all odd, then it will be the systematic absence. So, the systematic absences therefore, will now if you add neither or nor here instead of all and or then you get to the definition of the systematic absences.

So, what you should remember here is that in a face centered lattice you add the two indices add h and k, add k and l and also add h and l. When you do that, they should be always even whatever be the value of h k and l individual values; when you add 2 values it should always be even and when those values are even you will get a reflection, you will get the measurement of F(h k l).

So; that means, you will get an intensity I(h k l) all other intensities are 0. So, by just looking at the diffraction pattern now and looking at after indexing, you just easily it is so, easily now to find out the centering of the lattice. We will take an example to illustrate this systematic absences by taking the structure of Zinc Sulphide. In fact, it is the mineral Zinc blende; Zinc Sulphide exists in various forms. So, we will take the Zinc blende, the mineral Zinc blende it has been found by crystallography, that there are 4 Zinc Sulphide units in the unit cell.

So, compound Zn S occurs four times inside the unit cell and that is the information we have from determining the density of the crystal, then we determine the volume of the unit cell by determining a b c α β γ. So, we do the powder diffraction experiment or single crystal experiment, look at the x axis of the powder diffraction and find out the 2θ values and from 2θ values you calculate the d values and from there calculate a b c.

So, the value of a b c will tell us now that the Zinc Sulphide system is going into the crystal system, where there are 4 molecules in the unit cell so; that means, 4 Zinc and 4 Sulphur. So, when one solves the structure we will take the solved structure so, that we can illustrate the occurrence of the systematic absences very clearly. So, when we solve the structure and we show the projection of the Zinc blende. So, Zinc is at 0 0 0, Sulphur is located at ¼ ¼ ¼. So, Zinc is at this position.

So, this Zinc appears at the end of the a axis as well as end of b axis and then it also appears at the ½ the distances along the axis and then the Sulphur because it we are already checking out that Zinc Sulphide is face centered ok. Now let us see what happens to the systematic absences. So, what happens to the reflections which comes from Zinc Sulphide? Zinc Sulphide is Zinc blende is a face centered cubic lattice ok. So, we have Zinc at 0 0 0 Sulphur at ¼ ¼ ¼. So, if we look at the projection diagram down 0 0 1. So, this is very clear now this is distribution of atoms. So, we will see what happens to the structure factors or in fact, the intensities and therefore, the structure factors.

See what is very important now is that we are directly getting the expression for the structure factor, which now can be undergoing a Fourier transform to give the electron density, what we are not worried about at this moment still which we should worry about is how to determine the face. We have the value of f_n, we have the value of h k and l we do not have x_n y_n and z_n in this example we are taking we have x_n y_n z_n. So, we can get the expression for F(h k l), because we can get the expression for I(h k l) and from that we can get the expression for F(h k l).

So, remember that part because what we are now trying to discuss is given the structure of Zinc Sulphide which Zinc is sitting at 0 0 0 Sulphur is at ¼ ¼ ¼ how do we get the systematic absences satisfying the *F*- centered lattice that is all we are now examining and that we can see from this set of equations.

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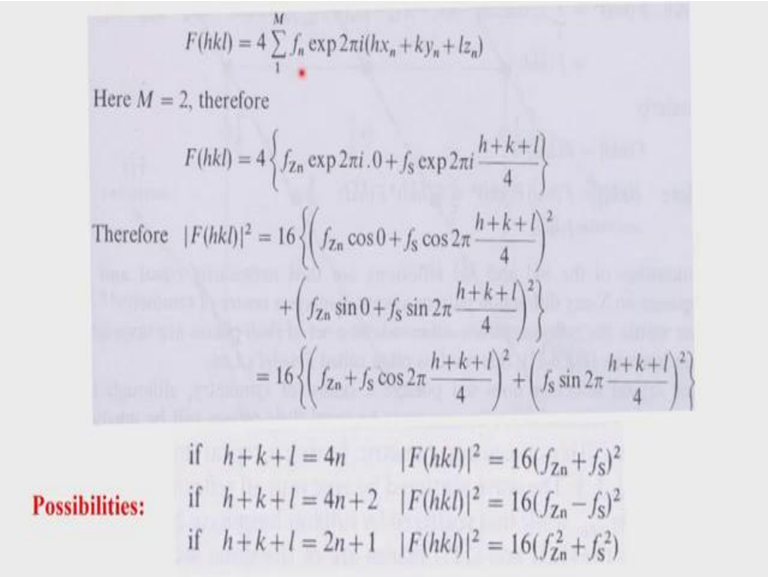

$$F(hkl) = 4\sum_{1}^{M} f_n \exp 2\pi i(hx_n + ky_n + lz_n)$$

Here $M = 2$, therefore

$$F(hkl) = 4\left\{f_{Zn} \exp 2\pi i.0 + f_S \exp 2\pi i \frac{h+k+l}{4}\right\}$$

Therefore $$|F(hkl)|^2 = 16\left\{\left(f_{Zn}\cos 0 + f_S \cos 2\pi \frac{h+k+l}{4}\right)^2 + \left(f_{Zn}\sin 0 + f_S \sin 2\pi \frac{h+k+l}{4}\right)^2\right\}$$

$$= 16\left\{\left(f_{Zn} + f_S \cos 2\pi \frac{h+k+l}{4}\right)^2 + \left(f_S \sin 2\pi \frac{h+k+l}{4}\right)^2\right\}$$

Possibilities:

if $h+k+l = 4n$ $|F(hkl)|^2 = 16(f_{Zn} + f_S)^2$

if $h+k+l = 4n+2$ $|F(hkl)|^2 = 16(f_{Zn} - f_S)^2$

if $h+k+l = 2n+1$ $|F(hkl)|^2 = 16(f_{Zn}^2 + f_S^2)$

You see F(h k l) is = to 4 times f_n exp 2πi $(hx_n+ky_n+lz_n)$ that we know now because from the previous slides here F(h k l) is that expression.

So, we take this expression and we have written it down here; now how many atoms are there in the unit cell that is the summation 1 to M total number of atoms is 1 to M. Now the number of atoms here are only 2, there are 2 atoms they associated with the structure mark my words the unit cell has Z = 4. So, there are 4 Zinc atoms and 4 Sulphur atoms associated with the unit cell, but with the structure there is 1 Zinc and 1 Sulphur. So, the summation has to be done over two of them 1 for Zinc and 1 for Sulphur.

So, here M is 2 therefore, F(h k l) is 4 times $f_{Zn,}$ Zn is at 0 0 0. So, just like our caesium chloride example the phase associated with it is 0. Now f_S is sitting at the position ¼ ¼ ¼ and you know how to do this calculation now it will come at (h + k + l)/4. So, this is now the expression for Zinc Sulphide the structure factor expression for Zinc Sulphide.

So, there are 4 such Zinc Sulphide units. So, it is 4 times f Zn and so, on there is a little error in the textbook here I have taken it from the textbook, M is actually 4 and when once we write 4 here it is then M = 2 is correct that is not an error M = 2, f_{Zn} and f_S is the scattering factor associated with Sulphur.

So, there are 2 atoms with Zinc Sulphide Zinc and Sulphur and the summation is done over those 2 atoms. But 4 times because we have now or going to distribute this into four equal parts; one coming from x y z another coming from the ½ + x ½ + y another one coming from ½ + y ½ + z and the last one coming from ½ + x ½ + z. So, therefore, we get into four such values and then we calculate the intensity. See eventually what we see in the diffraction pattern is the intensity or for that matter the powder pattern will give us, the intensity I versus 2θ . So, we have to calculate the intensity.

So, when we calculate the intensity, it is $F(h\ k\ l)^2$. So, 4 becomes 16, now square of that $\{f_{Zn} \cos 0 + f_S \cos 2\pi(h + k + l)/4\}^2$. So, this now this adds up in case of each one of these. So, f of whole square + $\{f_{Zn} \sin 0 + f_S \sin 2\pi(h + k + l)/4\}^2$. So, what we have done here is to express it as a cosine + sine function you remember we are looking at the intensity. So, there is no imaginary component that gets associated with it.

So, this gives us the solution to the problem, we get the intensity value as 16, $\{f_{Zn} + f_S \cos 2\pi(h + k + l)/4\}^2$ + this. So, this quantity therefore, is something which we will have to now see what are the possible reflections that come? Now why I am showing this, I am showing this because Zinc and Sulphur even though they are *F*- centered lattice alright because of the fact that there are only 4 units of Zinc and 4 units of Sulphur they are sitting in special positions.

Because they sit in special positions effectively you will see more systematic absences the major systematic absences are coming from the *F*- centered lattice, but the fact that Zinc and Sulphur are sitting in special positions, they will also add to the possibility of systematic absences.

So, remember we have been discussing systematic absences in terms of lattice centering so, far. We will also discuss the systematic absences which will come because of translations associated with the 2_1 screw axis or any screw axes and glide planes. This is with respect to the symmetry elements, but when once we have this symmetry elements identified in the space group, we already know that there are some what we call as special positions. So, these special positions therefore, will have additional systematic absences.

So, if atoms have to be confined to special positions then the structure will show over and above the systematic absence required for the symmetry, it will also show systematic absences because the atoms are sitting in special positions. This is something we will write down now as the value. So, it is either $16 (f_{Zn} + f_s)^2$ whenever h + k + l is 4n and if (h + k + l) is 4n + 2 then you will have this value and (h + k + l) is 2n + 1 you will have this value.

So, these now are very special to Zinc and Sulphur, the general systematic absences come from this expression. So, one can calculate this expression and we know that h + k, k + l, l + h should be all even then only we will get these reflections coming up. Among these reflections because Zinc is at 0 and Sulphur at ¼ ¼ ¼ that happens to be special positions in that space group, you will get additional absences. And they look as though they are systematic, but they are systematic only with respect to the atom positions. They are systematic of course, therefore, to the special positions in the unit cell.

So, let us go back to the discussions on the special positions for a few minutes. Because I think we discussed it sometime ago and probably you would have you know over the days you would have forgotten. So, the special position when we discuss this special position issue, we found that the number of equivalent points suppose $P\ 2_1/c$ we take, 4 equivalent points are there.

Now, if the special position is there in the system which is there, it is let us say sitting on the mirror symmetry, then the number of equivalent points will get reduce to 2 so; that means, what was 4 before has now reduced to 2. So, the atoms are now restricted by the symmetry again and that symmetry restriction is coming due to the presence of the 2_1 screw and the *c* glide.

So, whenever we have again translational symmetry associated with the space groups will get special positions. We do not get special positions for example, in case of *P* 1, but we get special positions in $P\ \bar{1}$, because x y z and now can give rise to several centers of symmetry positions which are independent of each other. And therefore, if the atoms sit there they are very special, in other words they give Z = 1 rather than Z = 2 and that gets reflected in terms of the systematic absences we see.

So, these are not now to be called systematic absences; what we should call systematic absences are with respect to the crystal system. So, if it is a *F*- centered lattice whatever are the systematic absences associated with *F* centered absence has to be checked. But then if we find additional systematic absences like what we see here the special conditions there are three possibilities in which the reflections can occur, and those three are indicated here. Only those reflections will come because Zinc and Sulphur are sitting in special positions in the *F* lattice.

So, lattice anyway exists and over and above you will have additional as though they are absences, but they are not really absences they are additional conditions over and above the conditions that are present in the *F* lattice. So, when we reexamine the international table entry, we will see what is the effect of special positions and how additional symmetry elements develop because of that effect.

So, this is something which we have to keep in mind and then we will come back and re visit it, when we reexamine the international tables. So, what we have done so far is therefore, to take the face centered lattice find out how the systematic absences come up. And then we took the example of Zinc Sulphide which is very special, because Zinc and Sulphur are sitting in special positions and we worked out the possible systematic absences as a consequence in the *F*- centered lattice.

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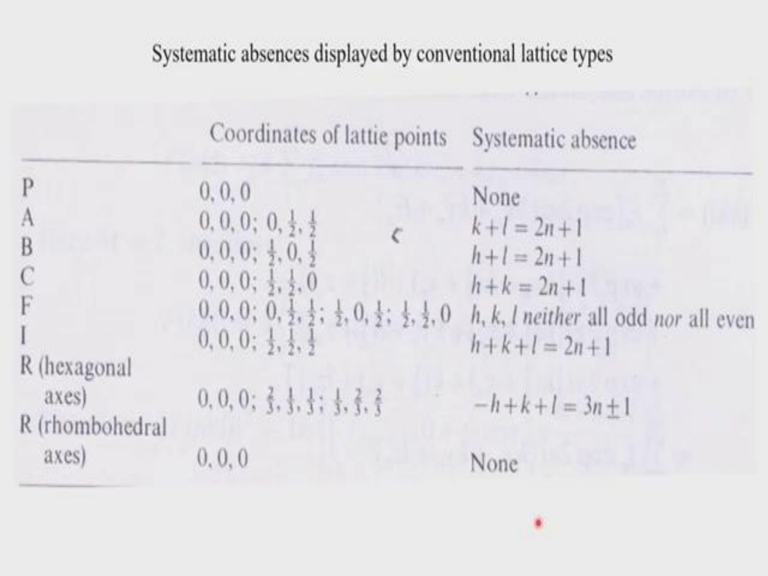

Systematic absences displayed by conventional lattice types

	Coordinates of lattie points	Systematic absence
P	0, 0, 0	None
A	$0, 0, 0;\ 0, \frac{1}{2}, \frac{1}{2}$	$k + l = 2n + 1$
B	$0, 0, 0;\ \frac{1}{2}, 0, \frac{1}{2}$	$h + l = 2n + 1$
C	$0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0$	$h + k = 2n + 1$
F	$0, 0, 0;\ 0, \frac{1}{2}, \frac{1}{2};\ \frac{1}{2}, 0, \frac{1}{2};\ \frac{1}{2}, \frac{1}{2}, 0$	*h*, *k*, *l* *neither* all odd *nor* all even
I	$0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$h + k + l = 2n + 1$
R (hexagonal axes)	$0, 0, 0;\ \frac{2}{3}, \frac{1}{3}, \frac{1}{3};\ \frac{1}{3}, \frac{2}{3}, \frac{2}{3}$	$-h + k + l = 3n \pm 1$
R (rhombohedral axes)	0, 0, 0	None

So, now we will have to see how to evaluate these or observe these systematic absences. So, let us now generalize it, when once we generalize it we see that the systematic absences can be put in this form of a table. So, whenever we have a primitive lattice we have no systematic absences. Primitive lattice can exist in all 7 crystal systems. So, in all the seven crystal systems we go ahead and collect the data, we look at all the h k l reflections try to align them with respect to h even, h odd, k even and so on. And when such an arrangement is done we find that there are no systematic absences in those reflections then we say it is a primitive lattice.

So, the primitive lattice therefore, will have no systematic absences. So, space groups like *P* 1, *P* $\bar{1}$, *P* 2, *P m*, *P* $2_1/c$ will have systematic absences not because of the centering, but it will have systematic absences due to the 2_1 and *c* which we will examine later. At this moment whenever there is a primitive lattice, systematic absences will not occur in general reflections by general reflections I mean h k and l all having values no projection reflections and no axial reflections are considered in this evaluation.

Special the projection reflections and also the axial reflections come may come as a consequence of centering and that was indicated to you when we discussed the *C*-centered lattice. I told you that there is a suppose there is a *h k l* which is 1 4 and 0. So, that is actually a projection reflection, but what is important is to consider the addition of

1 and 4 and I said 1 4 0 is absent. So, that 0 there is actually a referring to a projection reflection 1 4 0, but now we are considering the systematic absences in the overall h k l.

So, we call these as general planes. So, under the general planes we also have the projection reflections as well as the axial reflections. So, when you have a centering of the lattice you will have both of these coming up and that you must remember. And that is something which we have to evaluate. So, when we analyze the data the way in which we analyze the data is we put the crystal, X ray X rays come through do the scattering I will keep on repeating this whenever required. So, we get the scattering and when the scattering occurs we get the reciprocal lattice points, we index the reciprocal lattice points we measure the intensities of the reciprocal lattice points.

Then we organize the intensities in a certain order, let us say even reflections, odd reflections and so on. Then if there is a systematic absence coming in the general h k l reflections, then we will be able to identify the presence of centering. It could be one of the faces centered or all faces centered it could be body centered and so on. So, whenever such a thing happens we should have systematic absences.

So, this particular table which I have given here tells you what are the types of systematic absences that occur when this coordinates where there is a mistake in the textbook it should be lattice points, e is not there its c, lattice and there should be any after that. So, c is missing here. So, its I have copied it from the textbook.

So, many almost all the equations I have copied in the textbook because I thought that if I write the equations you know my handwriting and that will be terrible. And if I prepare the equations that will be an enormous effort for me number 1 and number 2, it may not be it may be more error prone when we prepare it ourselves. So, best is to take the make sure that there are no other serious errors in the text book and take it from there. And so, this has been taken from the textbook of Mackie and Mackie and in fact, most of the equations which we have shown before are also coming from the textbook of Mackie and Mackie.

So, let us now examine this table once more so, that we have now a complete hold on systematic absences coming due to centering. And I think that will take us to one particular stage where we can now diversify and see how this structure factor behavior comes. And then take up the systematic absences which come due to the axial systematic absences the 2_1 screw as well as the glide planes.

So, let us see how this appears. So, the primitive lattice no systematic absence you are very clear about it. So, if it is *A* centered lattice we will have coordinates of lattice point 0 0 0 and 0 ½ ½. So, since the ½ is associated with the k and l direction we will have k + l odd reflections absent. So, those only those values for k and l we will have the when it is even we will have the reflection coming otherwise it would be absent.

I do not think I need to take an example to illustrate it, you can take some h k l examples to find out how this systematic absences coming. *B* centered lattice likewise and *C*-centered lattice likewise and *F* we have learnt just here I have written the English explanation h k l neither all odd nor all even; that means, they have to be either all odd or all even to get the systematic presence.

So, they will be present only this systematic absence. So, we can say neither all odd nor even. So, the I centered is fairly straight forward ($h + k + l = 2n + 1$). Now these systematic absences occur in all general reflections be it projection be it axial it will occur in all h k l reflections. So, we have to consider all the h k l reflections in this particular case.

I have given here 2 additional entries we have not discussed that all in detail the rhombohedral and hexagonal systems, because I just thought that this is slightly away from the plan of this course. However, we should remember that those symmetry also occurs and in fact, there are many materials which go with a rhombohedral symmetry. But there many systems which go into hexagonal symmetry; particularly when we when people are talking nowadays about organic ferroelectrics and so, on there is a large number of compounds which go with hexagonal axis, rhombohedral cell, but hexagonal axis.

So, the hexagonal systems therefore, will have the coordinates of the lattice points are 0 0 0, 2/3 1/3 1/3, 1/3 2/3 2/3 in the case we have a rhombohedral setting of a hexagonal lattice. What I mean by that is that we have a rhombohedral system where a = b = c, $\alpha = \beta = \gamma \neq 90^0$. So, effectively it is a distorted or pushed around cube it is not a distorted cube, its a turned around cube about a given axis.

So, we will have therefore, three values coming up for equivalent points of the coordinates and therefore, we have 3 lattice points and therefore, the systematic absence will come up as $- h + k + l = 3 n \pm 1$. So, this is a very special case we are not going to discuss it in detail here, but you should know that systematic absences can occur in a rhombohedral system not in a hexagonal system.

And particularly when the rhombohedral axis are referred to straight away if we describe the system in rhombohedral axis, then there is no. But if we describe the rhombohedral axis in a hexagonal system; that means, we have a rhombohedral system, but we say $a = b \neq c$, $\alpha = \beta = 90^0$ γ at 120^0 that is the unit cell we fix.

That means we now have actually a rhombohedral cell, but we have fixed it in a hexagonal lattice. If we have a rhombohedral cell and fix it in a hexagonal lattice then we have this problem and this problem is because the rhombohedral axes now will show coordinates of these three positions and that is the property of the rhombohedral cell. It is a special case of the hexagonal lattice all hexagonal lattices will not show. So, in principle we if we have a hexagonal system which is indexed as a hexagonal system you have $a = b \neq c$, $\alpha = \beta = 90^0$ γ at 120^0 and then it shows rhombohedral symmetry, then you will have the systematic absences.

So, this is very interesting suppose you want to find out the crystal system whether it is hexagonal or rhombohedral, you use this test. So, you use this test if you see these systematic absences it is rhombohedral axes, then you go down and set it to rhombohedral axes then you have no systematic absences any more. So, this is a way in which you can actual distinguish the rhombohedral axes with respect to a hexagonal system. So, this in a nut shell is what we see a for systematic absences which are displayed by conventional lattice types.

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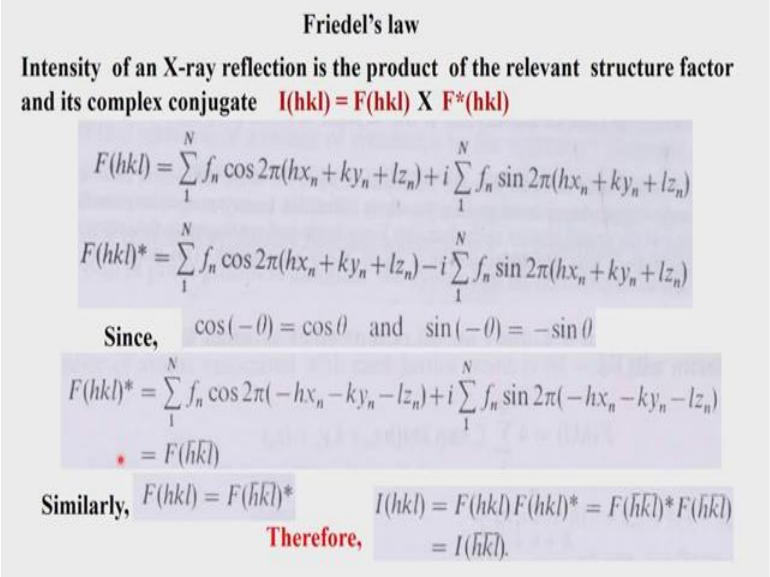

Friedel's law

Intensity of an X-ray reflection is the product of the relevant structure factor and its complex conjugate I(hkl) = F(hkl) X F*(hkl)

$$F(hkl) = \sum_{1}^{N} f_n \cos 2\pi(hx_n + ky_n + lz_n) + i \sum_{1}^{N} f_n \sin 2\pi(hx_n + ky_n + lz_n)$$

$$F(hkl)^* = \sum_{1}^{N} f_n \cos 2\pi(hx_n + ky_n + lz_n) - i \sum_{1}^{N} f_n \sin 2\pi(hx_n + ky_n + lz_n)$$

Since, $\cos(-\theta) = \cos\theta$ and $\sin(-\theta) = -\sin\theta$

$$F(hkl)^* = \sum_{1}^{N} f_n \cos 2\pi(-hx_n - ky_n - lz_n) + i \sum_{1}^{N} f_n \sin 2\pi(-hx_n - ky_n - lz_n)$$

$$= F(\bar{h}\bar{k}\bar{l})$$

Similarly, $F(hkl) = F(\bar{h}\bar{k}\bar{l})^*$

Therefore,

$$I(hkl) = F(hkl)F(hkl)^* = F(\bar{h}\bar{k}\bar{l})^* F(\bar{h}\bar{k}\bar{l})$$

$$= I(\bar{h}\bar{k}\bar{l}).$$

Now, let us go further and see what we have further to offer from X ray diffraction. You see we are talking about structure factors the systematic absences in structure factors and so on. So, what we now do is to see what is the way in which structure factors behave; you see we have seen the intensities how they behave.

In other words we have seen that when you do an X ray diffraction experiment I have already mentioned several times that the I(h k l) will be equal to I(-h -k -l) and that we call as the Friedel's law; that means, that we have the 2 systems where we can now take the h k l reflections we have observed, it could be centered or face centered or body centered those systematic absences will be there. But for any h k l measurement if you also measure -h -k -l these 2 will always be equal for as intensities are concerned and that is the Friedel's law.

Of course Friedel's law can also be violated and if this equation is not satisfied in a certain circumstance. We now invoke a situation where the electrons are now inside the crystal systems are now very close to the incoming radiation frequency the incoming radiation has a frequency, we are ignoring the frequency change because we assume only coherent scattering, but what happens is if the frequency is very close to this the atom now absorbs the X rays.

Because its it does not know the difference you know its there is a frequency coming, that frequency matches the frequency associated with the atom vibration or atom the K shell of the atom and the and the nucleus transition.

So, if both are same the waves cancel each other out and therefore, you will not get any diffraction you get severe absorption at that situation what happens is the electrons do not know what to do. So, the K shell electrons you see we the characteristic X rays we get for copper which we discuss as 1.5418 Å or Molybdenum 0.7107 Å they come due to the fact that we say it is K_α radiation; that means, the K shell electrons are the ones which get knocked out by the incoming X ray this is known as Moseley's law I do not think we will have time enough to do it in detail.

So, I will measure it now in the next few minutes I will do the orally I will explain how the Moseley's laws comes, but I think it is something which is very fundamental and which can be very easily understood.

So, let us say we have an atom inside the crystal and the copper radiation is sent inside the crystal, I will make it as simple as possible copper radiation is sent inside the crystal and then there is a nickel atom which is the next fellow in the periodic table. By the way you must all remember and appreciate that this year is the year of international tables. So, United Nations have decided to call this year as the year of international tables.

So, this is a real recognition for the work done by Mendeleev and the periodic table. Now the fact that we have scattering factors, structure factors intensities are all due to the fact that we have electrons we have nuclei, we have different kinds of elements and therefore, our scattering depends upon the different kinds of elements and the amount of electron density that is associated with them. All these are present in the periodic table. So, periodic table is in fact, the fundamental requirement for any of these courses which we discuss this way.

So, its so, happens that this year is the international year for periodic table. So, lots and lots of international levels activities will be organized may be in the next present part of the presentation may be I will show you a picture of Mendeleev with his periodic table, just to remember that it is the year of periodic table just at the passing. It is not relevant to our course, but why obviously, it is relevant to our course because we are dealing with atoms and the electron density associated with atoms. So, I thought just as a memory I will show it.

So, we will see now what happens to the structure factors. Intensities we know become equal. So, if you have a reflection plane which is 1 1 1 and a reflection plane which is -1 -1 -1, the intensity from this will be equal. I was talking about the violation of this intensity the violation of the intensity comes because the absorption edge associated with an atom inside the crystal is very close to the incoming radiation.

Then happens is that the K shell electron should get knocked out from the incoming radiation and then there should be a transition from the K shell from the L shell to the K shell and that transition gives raise to the characteristic radiation which is 1.5418 Å which we use.

There are 2 electrons in the K shell and therefore, we have effectively 2 radiations that should come one for the one electron the other for the other electron, but the 1 and the 2 electrons are not distinguishable and therefore, when we get this diffraction coming out we will get the α_1 and α_2 which are very closely spaced. So, for all practical purposes we decide to use them as an average α.

So, when this is happening and if it is close to the absorption edge, the 2 electrons which are now getting knocked out they do not know what to do whether they should stay with the incoming radiation and get out or they should go now and generate the characteristic radiation. So, the consequence is these electrons now reach relativistic speed if there is relativistic speed they do not know how to go about and this whole scattering now becomes anomalous and this process this methodology is called anomalous dispersion. And when anomalous dispersion occurs it will occur in any crystal.

It will occur to a very small extent so, we can ignore it, but if we do very accurate measurements of I(h k l) and I(-h -k -l) every atom is associated with an anomalous component and these anomalous component can also be with respect to the Argand diagram. So, we can have both real and imaginary components associated with this anomalous scattering, and anomalous scattering is very useful to determine the absolute configuration of a crystal.

So, we will discuss it when we come towards the end of the course, I do not know whether we will have time enough to discuss such details, but essentially we will mention how to determine the absolute configuration for sure. And when we do that we will bring in and invoke this variation or in other words the violation of the so, called Friedel’s law. So, we will stop here.