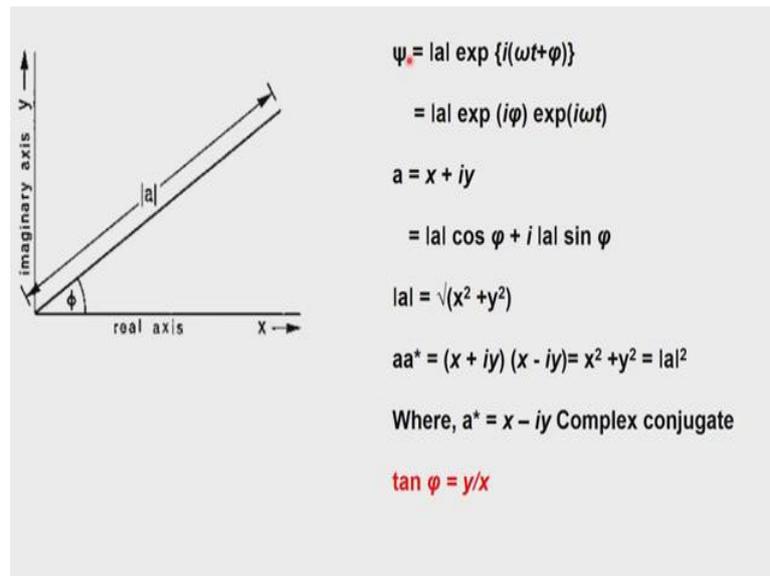


Symmetry and Structure in the Solid State
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Lecture – 43
Concept of Structure Factors

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The fact that the magnitude of the amplitude is given by the expression, which is equal to square root of $x^2 + y^2$ and the intensity therefore, can be expressed as a multiplication of the real and the complex conjugate parts of a ; $a \cdot a^*$ giving us this modulus of a^2 . With a defined as $x + iy$ and a^* defined as $x - iy$, this is now telling us that we can get to the intensities from any scattering. So, this is representing one single wave, but we can have multiple waves. The phase that is associated with its $\tan \phi = y/x$.

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$$\begin{aligned} a_R &= \sum_1^N a_n \\ &= \sum_1^N |a_n| \exp(i\phi_n) \\ &= \sum_1^N |a_n| \cos\phi_n + i \sum_1^N |a_n| \sin\phi_n \end{aligned}$$

For an atom at x, y, z the amplitude is f and the phase change is $2\pi (hx+ky+lz)$

$$\begin{aligned} F(hkl) &= \sum_1^N f_n \exp 2\pi i(hx_n + ky_n + lz_n) && \text{Structure factor} \\ &= \sum_1^N f_n \cos 2\pi(hx_n + ky_n + lz_n) + i \sum_1^N f_n \sin 2\pi(hx_n + ky_n + lz_n) \end{aligned}$$

Now, if there are large number of such amplitudes. So, because that is what happens in a crystal than the overall amplitude which comes out the so, called resultant amplitude is sum over individual amplitudes. So, the resultant amplitude is sum over individual amplitudes and that is given over sum over 1 to N of modulus of $|a_n| \exp(i \phi_n)$.

So, you see that this resultant is the representation of $F(hkl)$. So, therefore, you see that it is sum over 1 to N we can write it as a real part + 'i' times the imaginary part which is associated with 'i'. So, the real part and the imaginary part together will define our resultant 'a'. So, now, you can imagine a situation or you can create a situation where you write here the overall structure factor F and then this will be $F(hkl)$ individual $h k l$ going from 1 to N the total number of reflections, this also could be an individual $h k l$ value $F(hkl)$; $F(hkl)$ this is (Refer Time: 02:24) $F(r)$, F of overall resultant, capital F .

So, for an atom at $x y z$ the amplitude is f and the phase changes 2π which we have calculated in the previous classes to be $2\pi (hx+ky+lz)$. This we worked out with the fact that it can be done for any plane $h k l$ and any position of the atom $x_n y_n z_n$. So, if there is an atom at $x y z$, the amplitude of course, is always f depending upon the content of the electron density at that position vector $x y z$. So, if there is a carbon atom there will be 6 electrons in nitrogen atoms have 7 and so on.

So, we can therefore, write the expression for the structure factor. Remember until now we were discussing the intensities because that is what we measured and now we are

writing the expression for the structure factor. So, the structure factor is 1 to N, $f_n \exp 2\pi (hx+ky+lz)$. So, what you therefore, see is that how the phase factor can also include the imaginary component.

In the case of a centrosymmetric structure this imaginary component will not be there it will become a cosine function only, but in case of the general crystal structures where we have non centrosymmetric materials also this will be expression. So, this is another key expression for our calculations in the future.

So, this is the expression for the structure factor you see that there is no modulus written here. So, it is actual structure factor modulus and the phase together, and this is the expression we need to dump it into the Fourier transform expression of $\rho(r)$ so, that we can get to the $\rho(r)$. So, this is the value which we need to compute electron density.

So, this structure factor therefore, can be also written conveniently in this form $\cos + i \sin$ for the centrosymmetric system as I mentioned again and again only this term will be there. And this term now will be 2 times that because this will vanish and this will be now there 2 times over N by 2, but it is equal to 1 to N, $f_n \cos 2\pi (hx+ky+lz)$ how does that came about we will see as we go along.

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For a centrosymmetric structure, atoms at x_n, y_n, z_n has $\bar{x}_n, \bar{y}_n, \bar{z}_n$

$$F(hkl) = \sum_1^N f_n \{ \exp 2\pi i(hx_n + ky_n + lz_n) + \exp 2\pi i(-hx_n - ky_n - lz_n) \}$$

$$= 2 \sum_1^N f_n \cos 2\pi(hx_n + ky_n + lz_n)$$

$$F(hkl) = \sum_1^N f_n \cos 2\pi(hx_n + ky_n + lz_n)$$

We will see this right away. So, for the centrosymmetric structure atoms are at $x_n y_n z_n$ and the $-x_n -y_n -z_n$ so, that is the definition; that means, we are taking the origin as 0 0 0

as coincident with the inversion center for the any crystal structure which is centrosymmetric. So, there are so, many centrosymmetric space group as we have already learnt and all these space groups will have this property of having $x_n y_n z_n$, $-x_n y_n -z_n$. Apart from other equivalent positions which will come due to the operation of symmetry elements.

So, if it is $P \bar{1}$ these are the only 2 positions, but if we go to higher systems like $P 2_1/c$ and so, on you will get other equivalent positions. But the common factor is that we have the $x_n y_n z_n$, $-x_n y_n -z_n$ which therefore, defines our center of symmetry to be at the origin. If the center of symmetry is at the origin then $F(hkl)$ is sum over 1 to $N/2$ because now we do not have to consider $x y z$ separately and, separately and if we do separate them than its summation is over only the half the number.

Because for every $x y z$ there is a $-x -y -z$ present in the crystal lattice or in the unit cell. And therefore, this summation is over the unit cell and this now you see is $N/2 f_n \{ \exp 2\pi i (hx_n+ky_n+lz_n) + \exp 2\pi i (-hx_n-ky_n-lz_n) \}$.

So, if one evaluates this the sine terms vanish as we showed just a few in the previous discussion and therefore, you see that this is equal to 2 times sum over 1 to $N/2 f_n \cos 2\pi (hx_n+ky_n+lz_n)$. So, what you do is you consider half the number of atoms somethem over 2 times and get the cosine function or the most easy way to program it in (Refer Time: 06:37) of programming is $F(hkl)$ is equal to summation 1 to $N f_n \cos 2\pi (hx_n+ky_n+lz_n)$.

So, the complete disappearance of the dependence on the imaginary axis is gone. So, this is no complex quantity that is associated with the with the centrosymmetric structures. So, this value of $F(hkl)$ can be plugged in to our Fourier transform equation and we can get the electron density distribution. So, that is where we have arrived. So, we have arrived at a very fairly after safer position now, we do an experiment we do an X ray experiment calculate the intensities and having measured rather measure the intensities having measured the intensities calculate modulus of $F(hkl)$.

So, what is left out is to find out the value of $\cos 2\pi (hx_n+ky_n+lz_n)$ in case of centrosymmetric systems and the exponential value corresponding exponential value in the case of non centric systems. We also know how to calculate this $\cos 2\pi (hx_n+ky_n+lz_n)$ with the example we took for caesium chloride. So, it is a fairly straight forward one if

you have only 2 atoms, in the unit cell and that is the centrosymmetric unit cell it was a very easy calculation. But you can imagine that if there are 100s of atoms the calculations will be a little more tedious, its not going to be a fairly straight forward.

The second issue is the unknowns here are x_n , y_n and z_n what you have in this information is the information about the modulus of $F(hkl)$, but as long as we do not know x_n y_n z_n we cannot get the phase and therefore, we have only the magnitude of the scattering that is coming up and that is why we say it is the structure amplitude. So, the magnitude of $F(hkl)$ is called structure amplitude. So, the structure factor is the one which includes the amplitude as well as the phase. So, the amplitude as well as the phase included will be the structure factor right.

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Systematic absences

**For a C-centered lattice, N atoms fall into two equivalent groups,
Each with $M=1/2 N$**

$$\begin{aligned}
 F(hkl) &= \sum_1^N f_n \exp 2\pi i(hx_n + ky_n + lz_n) \\
 &= \sum_1^M f_n [\exp 2\pi i\{hx_n + ky_n + lz_n\} \\
 &\quad + \exp 2\pi i\{h(x_n + \frac{1}{2}) + k(y_n + \frac{1}{2}) + lz_n\}] \\
 &= \sum_1^M f_n \exp 2\pi i\{hx_n + ky_n + lz_n\} \cdot \left\{ 1 + \exp 2\pi i \frac{h+k}{2} \right\}
 \end{aligned}$$

Now, $\exp 2\pi i \frac{h+k}{2} = \cos \pi(h+k) + i \sin \pi(h+k)$

$$= (-1)^{h+k}$$

We go further now the there are lots of equations which will come, but I will go very slowly systematically of course, hopefully so, that we will follow each other. See again we come back to the symmetry that is why you know we entitle this structure as in the in course as structure and symmetry in the solid state or symmetry and structure in the solid state in that order. Because symmetry governs the structure and structure governs the symmetry and then both of them now coexist and handshake in the case of a solid state and that is why we have given the title other than saying crystal structure determination or chemical crystallography or whatever even though the last part of the course we will cover mostly chemical crystallography.

So, systematic absences is something which we will now introduce. Its a very nice statement systematic absences something which is absent systematically. Well I have an example in my group there is one person who is systematically absent in all these talks there others are attending this talks, but there is one fellow who is systemically absence. In fact, using him I can determine the symmetry in the group and that as a joke I am telling you this, but essentially systematic absences help in determining the space group of a given crystal system.

So, we need to study it in more detail. See one of the things I will make a statement now it is like making a statement and giving a proof like in mathematics you know we give the proof and say QED (Quod Erat Demonstrandum) right. And similar thing we will do here the statement that I am going to make is that if in your crystal system, the space group involves translation components watch my words; if in your crystal system the space group involves translational components whether it is a centering associated with one direction or Face centering or Body centered.

So, in other words the translation is associated with a lattice or whether it involves the translational symmetries in the presence of screw axis and or glide planes and if all these operates simultaneously in the space group generating over space group like for example, if you take $P 2_1/c$ in $P 2_1/c$ we have the presence of a primitive lattice. So, there is no translational component associated with the primitive lattice; that means, primitive lattices will have all the reflections with respect to $h k l$.

So, there are no systematic absences that will come. So, the fact that there are systematic absences coming is a consequence of the presence of translational components in the space group. So, it is not obviously, there in the point group, so, it is in the space groups. Luckily for us crystallization ensures that we have three dimensional periodicity. So, the presence of periodicity, the presence of lattice centering will ensure that will have systematic absence. So, using X ray diffraction and finding out how the $h k l$ values is appear, it is possible to see the translational component associated with a lattice.

So, it could be a C - centered lattice, it could be an F centered lattice, it could be an I lattice we will see how it develops. The other aspect is of course, the presence of 2_1 screw axis as well as the glide planes. So, let us now take the structure factor expression

which we have and see how the structure factor expression reorganizes itself when we have a centering. So, we will start from a *C*-centered lattice.

So, in the case of a *C*-centered lattice what are the extra components you will get for every $x y z$ you will get a $\frac{1}{2} + x \frac{1}{2} + y z$. So, if there are 8 equivalent points, you will get 8 other equivalent points associated with the addition of $\frac{1}{2} + x \frac{1}{2} + y$ no addition along the z axis. So, this is the concept of *C*-centering in the lattice. We will take the international tables later on probably later on during the coming classes it probably will not happen now, but in the coming classes.

So, that we now understand the underlying mathematics behind this and the underlying principle behind it and then we will not have to worry about it when ones we have this understanding then we will go and examine the international tables for a crystallography, which we have already seen with respect to equivalent point diagrams and the symmetry diagrams.

We have seen the diagram associated where we see only the symmetry that is associated with the space group on the left hand side and the appearance of the equivalent points on the right and we are now reasonable experts to go one from one to the other given the crystal system point groups symmetry and so on. So, here what we will do is we will get the expertise on understanding how this systematic absence appear. In fact, what international table gives is not the systematic absences, but it gives you the what we could call as systematic presences.

So, whatever is present is indicated in the international table please remember that. Do not look at the international table and look for systematic absences because what is given in the international table are the systematic presences. So, you have to look for once which are not going to follow what is given in the international table before we go to that.

So, let us not hurry up and see and go to the international tables right now what we will see is what happens to the structure factor when there is a *C*-centered lattice that is offering itself in the crystal system. We sent an X ray beam we got the diffraction pattern the diffraction pattern gave us the reciprocal lattice positions as well as the intensities. I measured the intensities, I also got a list of all the $h k l$ values I have.

Now, I am going to examine that list of hkl values what is important for us to remember is that if there is a C -centered lattice, the n atoms just like we discuss the case of centrosymmetry just now. The atoms there are $x_n y_n z_n$, for every $x_n y_n z_n$ there is a corresponding $-x_n -y_n -z_n$. There are no translation components with that and therefore, the presence of the centrosymmetry or otherwise is not going to be indicated by the so-called systematic absences. We will notice that when we look at the international tables and see what are written, what are what is all written in that systematic absence column.

So, if similarly here the n atoms are divided into 2 parts; there is one part which is associated with $x y z$ and the other part which is associated with $\frac{1}{2} + x \frac{1}{2} + y z$ representing the C centering in the lattice. So, what is the effect of that on the structure factor? One is of course, each of them has half of N . So, if N is the total number of equivalent points M is half of N .

So, I hope this equations are fairly clearly seen in the projection, you see it alright ok. So, $F(hkl)$ therefore, can be written as sum over 1 to N this is our general expression which we just now derived f_n exponential $2\pi i$ for any crystal system. Be it centrosymmetric or non centrosymmetric for any crystal system sum over 1 to N is f_n exponential $2\pi (hx_n+ky_n+lz_n)$ we now know this is the factor which is the phase factor and this is the corresponding amplitude coming due to f_n and we know also that f_n falls with $\sin \theta/\lambda$.

So, it depends upon the scattering angle θ as θ increases the value of f_n keeps on decreasing, we know that and we have understand it thoroughly. So, now, what we will do is, because of the fact that there is C centering we factorize this into 2 components. So, we have sum over one to M the first part corresponds to $x_n y_n z_n$. So, this is exponential $2\pi i (hx_n+ky_n+lz_n)$, the second part corresponds to $\frac{1}{2} + x_n \frac{1}{2} + y_n z_n$.

So, we separate these two. So, this is sum over M now, but there are 2 components one corresponding to half of N the other corresponding to the other half of N . So, we have therefore, this expression exponential $2\pi i \{h(\frac{1}{2} + x_n) + k(\frac{1}{2} + y_n) + lz_n\}$. I hope the speed with which I am going is ok. So, you are all with me. So, this is important particularly when you are looking at the video and trying to get the hang of it if I hope I am trying to adjust to the speed, with which we one can interact because in a class room you can sit in front of me and I can see your heads nodding, but when a in a case where you are

observing it on a video, I do not know whether your head is nodding or whether you are sleeping right.

So, I will go adjust the speed in such a way I hope that you will be with me all the time and please follow this indicator which is a nicely red in color. So, I will be following that with the equations. So, let me repeat this part to keep your concentration intact. So, when we go to the general expression of $F(hkl)$ this is the general expression for $h k l$. So, it is 1 to N ; N is the total number of atoms in the unit cell.

Now, this N is becoming $N/2$ in a C -centered lattice and therefore, I have now the summation over 1 to M , M is equal to $N/2$. And then I write the expression which is associated with $x_n y_n z_n$ and this is the expression which is associated with $\frac{1}{2} + x_n \frac{1}{2} + y_n z_n$. So, there are n atoms associated with the entire system half of it with respect to this and half with respect to that and that defines a C -centered lattice.

See this is the advantage of symmetry, this is the advantage of crystallization in a C -centered lattice. Effectively what it means is that if once you have this 1 to M measured; that means, the number of atoms which you are looking for is now halved because we have to determine only the M positions because the other half is generated by this that is advantage number 1. The advantage number 2 is something will happen to these $F(hkl)$, what will happen to these $F(hkl)$ is what we see in the next part.

What will happen is I can write rewrite this the expression as 1 to M , $f_n \exp 2\pi i (hx_n + ky_n + lz_n)$ So, what I do is I take the common factor out of this. So, once I have this common expression $f_n \exp 2\pi i (hx_n + ky_n + lz_n)$, then this will be multiplied by this now becomes value equals 1 . So, because we have this taken out, so, it is $1 + \exp 2\pi i$.

Now, what is left in this expression is $(h+k)/2$. So, this is the additional half values associated with h and k . So, this is $\exp 2\pi i (h+k)/2$. Notice that h and k are integers and therefore, this is a mathematical quantity which can be evaluated the $\exp 2\pi i (h+k)/2$ we can evaluate mathematically. And that is given here we can expand this as $\cos \pi(h+k) + i \sin \pi(h+k)$.

So, this exponential factor with the integers can be calculated straight away and it so, happens that this has a value $(-1)^{h+k}$. So, if you evaluate this expression mathematically we get this as $(-1)^{h+k}$. So, this $(-1)^{h+k}$ can replace now this quantity. So, we will have this

as $1 + (-1)^{h+k}$. So, the value of h and k therefore, will get restricted by this condition, how they get restricted by this condition is shown here.

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Since, h and k are integers,

$$F(hkl) = \sum_1^M f_n \exp 2\pi i \{hx_n + ky_n + lz_n\} \cdot \{1 + (-1)^{h+k}\}$$

Therefore for $h+k=2n$,

$$F(hkl) = 2 \sum_1^M f_n \exp 2\pi i \{hx_n + ky_n + lz_n\}$$

And for $h+k=2n+1$,

$$F(hkl) = 0$$

130 131
140
250

$F(hkl)$ is systematically absent for reflections with values of $h+k$ odd

Since h and k are integers, $F(hkl)$ is equal to this is clear $F(hkl)$ is equal to 1 to M , $f_n \exp 2\pi i (hx_n + ky_n + lz_n)$ times $1 + (-1)^{h+k}$. So, now, the value that comes up for a $h k l$ reflection depends upon whether this value $(-1)^{h+k}$ is evaluated the way it is has to be.

So, we substitute different values of h and k . So, if $h + k$ this quantity $h + k$ is even; that means, if suppose you have a reflection like in the let us take an example, suppose there we have a reflection in the diffraction experiment which is $1 1 0$. So, it is $h = 1, k = 1$. So, $h + k$ is what $h + k$ is 2; that means, it is even 2 times n , n is equal to 1 here. So, $h + k$ is 2.

So, when it is that value then this $(-1)^{h+k}$ will just give an additional 1 to this quantity and therefore, you will have $F(hkl)$ as equal to 2 times, 2 times this value that will be $1+1$. So, it will be 2 times sum over 1 to M , $f_n \exp 2\pi i (hx_n + ky_n + lz_n)$. So, you notice that this is now 2 times and we are summing it over only the half the number of total number of atoms in the unit cell.

So, the effort is reduced to 50 percent and only for the even values of $h k l$; 1 is immaterial in this calculation because its a C - centered lattice. So, in the C - centered lattice therefore, we have $h + k$ is equal to $2 n$ and whenever it is odd let us say we take a

reflection $1\ 2\ 0$ in case of a reflection $1\ 2\ 0$, $1 + 2$ is odd. So, the value of $F(hkl)$ is 0; that means, there is no structure factor value; that means, there is no intensity. So, that is why we call this as systematic absence.

So, all those reflections in among the $h\ k\ l$ all the general reflections we call them as general reflections, $h\ k\ l$ reflections which are measured in the entire experiment if you measure them, you will see that all those values for which $h + k$ is odd will not be there. So, if you just now display your reciprocal lattice in such a way, in which you look at the way in which the reflections appear all the $h + k$ odd values will not be there at all; that means, you do not see any reflection that is coming out from the experiment.

So, experiment generally now dominates of half the set of reflections and they come twice 2 times sum over 1 to M , f_n exponential will allow us to calculate the $F(hkl)$ values. So, what is very interesting here? What is very interesting here is the fact that if we have the C - centered lattice, the presence of the C - centered lattice will give us what we call as systematic absences and those systematic absences occur when $h + k$ is equal to $2n + 1$.

So, let us take a few examples and see how this happens. So, suppose I am now trying to measure in a C - centered lattice, I let us say I want to get a value of $F(hkl)$; that means, I measure the intensity of $h\ k\ l$ what I measure are the intensities of $h\ k\ l$. So, I measure have the diffraction experiment done some spot appeared. So, I indexed the spot, so, indexing again is a very crucial factor.

So, I indexed the spot and when once I indexed the spot, I will identify the $h\ k\ l$ values. If I know already that C centering is present or if I do not know anything about the presence of this let us look at it that way. I have a data and this particular data tells me that suppose I look at this reflection statement which you have made here, $F(hkl)$ is systematically absent for reflections with values of $h + k$ odd by taking some examples. Suppose I give you $1\ 4\ 0$. So, this $1\ 4\ 0$ will be $h + k$ is 5 so; that means, it belongs to this category.

So, whatever be the structure which crystalizes in a C - centered lattice please note the words, whatever be the system which crystalizes in a C - centered lattice whether it is monoclinic, orthorhombic and what other is possible in a C - centered lattice monoclinic, orthorhombic, tetragonal does not have a C - centered lattice. So, also hexagonal and

cubic; cubic can have a C - centered lattice, but then it becomes a F centered lattice by symmetry.

So, it is only in a case of monoclinic and orthorhombic systems, we can have this kind of systems. So, you see that you can cross check the $a b c \alpha \beta \gamma$ which you have got in some sense, so, $1 4 0$ will be absent ok. Now if we look at the reflection like $2 5 0$ that will also be absent. So, if you look at something like $2 4 0$ it will be present.

Now, reflection like $1 3 0$ will also be present. Now why I am taking 0 's not necessary to take 0 . So, I can take for example, $1 3 1$ what will happen to this reflection $1 3 1$? That $1 3 1$ will have to worry only about $h + k$ even. So, therefore, for all $h k l$ values whether it is 1 can have any value including 0 , these $h + k$ odd will be absent and that therefore, characterizes a C - centered lattice.

So, now you see the importance of how diffraction can be used to identify the symmetry that is associated with the diffracting crystal. So, the system into which the diffracting material goes in to. Now clearly says that this has to belong to a C - centered lattice and depending upon the other the distances and angles it could be either monoclinic or orthorhombic. Of course, the other symmetry elements which come are not associated with the centering, they are associated with the a and b and c directions depending upon the nomenclatures we have for different crystal systems.

So, that part we will discuss later. What happens with respect to those three components which describe only the symmetry associated with directions. Those 3 or sometimes 2 sometimes 3 sometimes the same thing repeating 3 times those symmetry elements if they also have translational component those symmetry elements will also show systematic absences.

But please note that those systematic absences will not affect all of $h k l$, it will effect only either projection reflections or axial reflections. This is the statement I am making do not worry too much about it we will discuss it in full detail as we go along. So, right now what we have discussed is a C - centered lattice.