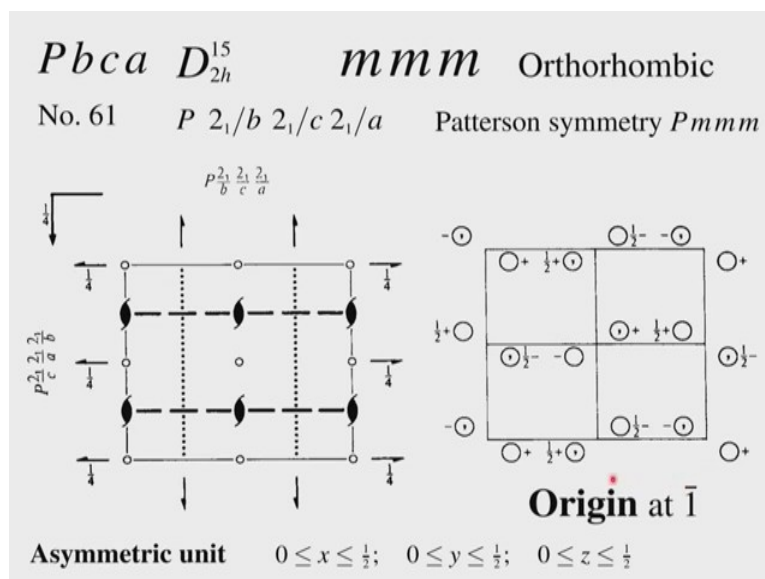


Symmetry and Structure in the Solid State
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Lecture – 47
Friedel's Law and Laue classes

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Let us go to another example which is *Pbca*. This is because this is one of the see I have taken all the common crystal systems, which come across which you come across particularly chemist come across and also in pharma industry. You will come across only lower symmetry systems, because you are dealing mostly with organic compounds. And the pharmaceutical compounds have all these functionalities which make the molecules very flexible. And so the crystals systems into which they go into a lower symmetry space groups and therefore, I have considered the monoclinic triclinic monoclinic and orthorhombic systems.

So, among these systems I have considered only the most commonly occurring systems. So, we discussed $P2_1/c$ as a most commonly occurring center symmetric monoclinic system, the non center symmetric $2_12_12_1$ in the orthorhombic case is very often occurring and *Pbca* is the one which is its counterpart as far as center of symmetry involvement is concerned. So, it is actually $P 2_1/b 2_1/c$ and $2_1/a$; that means, it is a *b* glide perpendicular to the *a* axis, *c* glide perpendicular to the *b* axis, *a* glide perpendicular to the *c* axis.

So, this in this particular system of course, we have studied the way in which the symmetry elements come up, additional symmetry elements show up which are not really indicated here they will also show up. And as a consequence we get eight equivalent points in the unit cell.

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Positions Multiplicity, Wyckoff letter, Site symmetry	Coordinates		Reflection conditions	
8 c 1	(1) x, y, z	(2) $\bar{x} + \frac{1}{2}, \bar{y}, z + \frac{1}{2}$	General: $0kl : k = 2n$ $h0l : l = 2n$ $hk0 : h = 2n$ $h00 : h = 2n$ $0k0 : k = 2n$ $00l : l = 2n$ Special: $hkl : h + k, h + l, k + l = 2n$ $hkl : h + k, h + l, k + l = 2n$	
	(5) $\bar{x}, \bar{y}, \bar{z}$	(6) $x + \frac{1}{2}, y, \bar{z} + \frac{1}{2}$		
	(3) $\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$	(4) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z}$		
	(7) $x, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$	(8) $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, z$		
	4 b $\bar{1}$	$0, 0, \frac{1}{2}$		$\frac{1}{2}, 0, 0$
		$0, \frac{1}{2}, 0$		$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
	4 a $\bar{1}$	$0, 0, 0$		$\frac{1}{2}, 0, \frac{1}{2}$
		$0, \frac{1}{2}, \frac{1}{2}$		$\frac{1}{2}, \frac{1}{2}, 0$

So, those equivalent points are the general points and therefore, there 8 equivalent points, which represents the multiplicity of this site x y z. And then the symmetry associated with the site is 1. This particular space group has two possible special positions. So, again associated with -1, as you see it is a consequence of the value becoming 1/2 or 0, depending upon the generation of the symmetry associated with these 8 equivalent points.

So, what are the conditions? The general conditions are 0 k l: k even, h 0 l: l even and h k 0: h even. So, what does this represent? This represents a, b and c glides. In the association of these three with respect to the a b c makes it *Pbca*, but the systematic absences are with respect to a b and c all three together. Now the special reflections to actual reflections h 0, 0 and 0 k 0, 0, 0, l will also develop because it is the system is $2_1/b$ $2_1/c$ $2_1/a$ the full system. Because, the point group symmetry associated with this unit cell is m m m, $2/m$ $2/m$ $2/m$ and so these are the general systematic absences.

Ones it occupies this special position, the central symmetry in *Pbca* it takes up two possible Wyckoff positions a and b, c be in the general Wyckoff position. And this

Wyckoff position will generate 4 equivalent points $0\ 0\ \frac{1}{2}$. So, you see that the conditions look as though what? It looks as though they are *F* centered lattices you remember the conditions for *F* centered. So, this looks as though they are *F* centered lattices. So, what you have to do is never look at these special absences, look at only the general absences to determine this space group.

So, these are occurring mainly because of the way in which the atoms are positioned inside the lattices. So, suppose you take a *Pbca* lattice and put these equivalent points you will see automatically the generation of the face centered symmetry. Because, you have a $0\ 0\ 0$ you have a $0\ \frac{1}{2}\ \frac{1}{2}$, you have a $\frac{1}{2}\ \frac{1}{2}\ 0$ and you also have a $\frac{1}{2}\ 0\ \frac{1}{2}$. You see here this 4 positions essentially tell you it is a face centered lattice. The way the atoms are located this is what we did in the case of Zinc Sulfide, when we took the example of zinc sulfide in the earlier classes. And, we found that it belongs to *C2/c*, if you want you can go back to that example you will see that the presence of the face centering in *Pbca* comes because the atoms are positioned in such a way they mimic a face centered lattice.

Since, this is now face centered lattice you will get face centered absences in the general reflection and so it is not an *F* centered lattice. It is still a *Pbca* with special position, which is associated with Wyckoff *a* and that is how we have to interpret the symmetry indications shown in the international tables for crystallography. Now you see the importance of analyzing the equivalent points their presences and absences and then identifying the in a space group to the extent possible. So, again and again I have been stressing that if there is an error here you will never get this structure determined. And if the machine also makes the error which is quite possible then also you will never get this structure.

So, this point has to be borne in mind and what you have learnt so far in this particular course is very crucial for this, see once you have this unusual systematic absences coming up, since you have not done the structure you see these are coming up because now you know where the atoms are sitting right in this special position. It does not tell you the structure information you do not have still $x\ y\ z$ that is what you have to determine, but before you even determine the $x\ y\ z$ you know in this particular case the atoms have to sit in special conditions and follow the systematic absence. So, it is an advantage. So, it is the advantage of putting the atom user molecules inside the unit

cell and keep the symmetry information which is very crucial for determining this space group.

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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 $I(hkl) = F(hkl) \times F^*(hkl)$

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

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

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

I think I have stressed enough on this space groups until now and we will wind up the discussion on the space groups at this moment. So, we will now look into the other properties of the structure factors. So, we have actually here when we are discussing the systematic absences we are actually looking at the presence or absence of structure factors right. Because it is F_{hkl} we are looking on to.

So, the F_{hkl} as a special property, that is known as the Friedel's law. So, the Friedel's law is a very special property which makes the diffraction always centro symmetric. So, your crystal system may be non-central symmetric let us say $P2_12_12_1$ is your space group. Then it has to be a non-center symmetric system, but when you do the diffraction and when you do the scattering experiment and get it diffraction done you will get a center of symmetry associated with your hkl distribution; that means, for every F_{hkl} you have a corresponding minus of F_{-h-k-l} . And this is known as the Friedel's law.

The disadvantage with Friedel's law is the fact that you cannot identify the non center symmetric feature, associated with your space group or for that matter the symmetry that is also associated with your crystal system because the data always is centro symmetric. So, when you do the X-ray diffraction experiment your number of point groups will reduce from 32. In fact, it will become only 11 and these 11 are known as the Laue

group. So, diffraction experiment therefore, will not directly give you the 32 point groups.

This is the revelation at this moment, but we will we will have to live with it because X-ray diffraction is centro symmetric, why is it. So, intensity of X-ray diffraction is the product of relevant structure factor and which complex conjugate. Mathematically I_{hkl} is expressed as F_{hkl} times F_{hkl}^* and I have told written down below what is F_{hkl} and what is F_{hkl}^* . So, if you look at F_{hkl} it is sum over 1 to n of the cosine term plus i times sum over 1 to n of the sine term. This is the general expression for the structure factor because now you know we are not expressing in terms of the exponential we are expanding it as cosine theta plus i sine theta.

So, this therefore, is F_{hkl} the corresponding complex conjugate F_{hkl}^* can be written as I equals to 1 to n of the cosine part minus i times the sine part then if you take F_{hkl} and F_{hkl}^* and take their product you will end up with I and therefore, when you take this square root of I_{hkl} what you get is not F_{hkl} directly you get the F_{hkl} modulus. Because, of the fact that there is a face information that is contained in this one we will have only the modulus coming in the phase does not come up when you take this square root of the intensity. And therefore, this expression is can be considered like this since cosine of minus theta is equal to cos theta and sine of minus theta is minus of sine theta, if you substitute you get F_{hkl}^* as equal to sum over 1 to n, $f_n \cos 2\pi (-h x_n - k y_n - l z_n)$.

That means we are taken $-x_n -y_n -z_n$ as the possible coordinates of the atom instead of $x_n y_n z_n$ so; that means, to say we are now considering the centro symmetry equivalent. So, for every x y z there is a -x -y -z in a centro symmetric system. So, here we are bringing that concept into the positioning of the F_{hkl}^* as $f_n \cos 2\pi (-h x_n - k y_n - l z_n)$ plus i times sum over 1 to n of $f_n \sin 2\pi (-h x_n - k y_n - l z_n)$. So, what does this represent this represent F_{-h-k-l} . So, F_{hkl}^* is equal to F_{-h-k-l} and you see that F_{hkl} can be shown equal to F_{-h-k-l}^* . So, the complex conjugates are related to each other by this mathematical fashion.

So, F_{hkl}^* is F_{-h-k-l} and F_{hkl} is F_{-h-k-l}^* . So, we can rewrite this expression for F_{hkl} and then you will see this equivalence coming up therefore, because of this feature of the complex conjugate nature of F_{hkl} you will get I_{hkl} is equal to F_{hkl} times F_{hkl}^* and that is equal to F_{-h-k-l} because F_{hkl} is equal to F_{-h-k-l}^* from this expression and from the other expression you

write F_{-h-k-l} and what does this represent if I_{hkl} is $F_{hkl} F_{hkl}^*$ then F_{-h-k-l}^* times F_{-h-k-l} this should represent I_{-h-k-l} ; that means, I_{hkl} is equal to I_{-h-k-l} .

So, therefore, what we see is that the intensity that you measure is always has a centro symmetric component. So, it is this is where you know we calculated the possible number of reflections by making use of the formula which told us the volume of the limiting sphere and the volume of the reciprocal lattice. And using that we calculated the number of reflections that are possible and that turned out to be for a given wave length λ because it depends on $1/\lambda^3$. And we found out that in case of molybdenum radiation it is 142000 something.

But you see that half of it is redundant because whatever you have measured as I_{hkl} the other half of I_{-h-k-l} is identical. So, actually measured reflection twice and as we will see later the symmetry associated with the system will also make some other equivalence. And because of the fact that there are some other equivalences with high intensities the number of reflections you collect start to reduce. The I_{hkl} equals I_{-h-k-l} is a universal relationship. And it is always valid unless under special circumstances.

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The 11 Laue Classes

System	Laue class	Constituent point groups of the Laue group			
Triclinic	$\bar{1}$	1	$\bar{1}$		
Monoclinic	$2/m$	2	m	$2/m$	
Orthorhombic	mmm	222	$mm2$	mmm	
Trigonal	$\left\{ \begin{array}{l} \bar{3} \\ \bar{3}m \end{array} \right.$	3	$\bar{3}$	$3m$	$\bar{3}m$
Tetragonal	$\left\{ \begin{array}{l} 4/m \\ 4/mmm \end{array} \right.$	4	$\bar{4}$	$4/m$	$4/mmm$
Hexagonal	$\left\{ \begin{array}{l} 6/m \\ 6/mmm \end{array} \right.$	6	$\bar{6}$	$6/m$	$6/mmm$
Cubic	$\left\{ \begin{array}{l} m\bar{3} \\ m\bar{3}m \end{array} \right.$	23	$m\bar{3}$	$\bar{4}3m$	$m\bar{3}m$

Bijvoet
 $f = f_0$
 $+ \Delta f'$
 $+ i\Delta f''$

So, for all practical purposes this is a valid law and therefore, we end up with 11 Laue classes. So, the 11 Laue classes can be followed into the 7 crystal systems and corresponding point groups. So, the triclinic has 1 and -1 the Laue group will have only -1. So, the 2 systems that are associated to point groups will be essentially 1 point group

as far as diffraction is concerned. Similarly in the case of monoclinic system $2/m$ is the only possibility, mmm is the only possibility for orthorhombic and so on. So 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, these are the 11 Laue classes.

So, for a diffraction experiment therefore, there are only eleven point groups symmetry and, so how do we now find out the realistic point groups. The determination of the realistic point groups will come in later, but in the diffraction experiment you will get only the Laue symmetry. Now just in the passing I will also tell you what happens in case the Friedel's law is not valid. Under what circumstances Friedel's law validity goes off.

One of the things which we will notice in a practical experiment is that when we actually measure the intensity of $h\ k\ l$ and measure the intensity of $-\bar{h}\ -\bar{k}\ -\bar{l}$ using a detector the counts which we get on the detector will not be exactly equal. They will be nearly equal if I_{hkl} is very strong, $I_{-\bar{h}-\bar{k}-\bar{l}}$ will also be very strong, but we do not expect the numbers to be; let say 10000 and 10000.

So, there will be a difference between these two, but this difference will be minimal the difference is due to the fact that we have a crystal. So, X-rays are coming from the from here or rarer medium and they are going to the crystal which is a denser medium and then they are scattering. So, even though we treat this as essentially a reflection they are going through a denser to a rarer to a denser to a rarer medium, before they are measured and therefore, there will be differences depending upon where exactly in the crystal $h\ k\ l$ is located and where exactly in the crystal your $-\bar{h}\ -\bar{k}\ -\bar{l}$ is located with respect to the defined origin and therefore, the intensity is will be slightly different from each other, but Friedel's law will still be validated.

So, when you put this data on absolute scale you will see that they are nearly equal, but when you actually do this exercise with a compound where you have a very heavy element. And it is going into a non centro symmetric system. It is possible that the system which now is generated may show I_{hkl} as not equal to $I_{-\bar{h}-\bar{k}-\bar{l}}$. So, what was my example 10000, it may become 4600 there is a huge difference between these two it cannot be mainly due to the absorption or the size of the crystal. It is due to some other affect that some other affect is known as anomalous dispersion and this anomalous dispersion is. In fact, a very useful tool this was discovered by a person called Bijvoet.

So, it goes according to his name let me write it somewhere, very interesting spelling pronounced as by-foot.

So, you can say Bijvoet if you want that is what most of us spell it, but it is pronounced by foot. So, they these gentlemen found out that the difference is due to something very interesting and that is the phenomena of anomalous dispersion. So, what happens in anomalous dispersion, I do not think this is within the purview of our course. So, I will just describe verbally for a couple of minutes what this process is all about. The process is that, when X-rays fall on the given element by the intensity which is falling on the element it is possible that the energy that is associated with the X-rays in coming X-rays is sufficient enough to knock out the k shell electrons.

So, there are 2 electrons in the k shell for any element, so the 2 electrons go away and the immediate action will be that to keep the stability of the atom the immediate action is that there is a transition from the next which is the l shell to the k shell. So, the transition from the l shell to the k shell is accompanied by emission of radiation and that radiation is the so called characteristic radiation which will be a very sharp x radiation which is what we use in our diffraction condition, which is what we use for input for copper radiation or molybdenum radiation and so on, we pick up that characteristic radiation we have discussed this in an earlier class well.

So, what happens therefore, is that this particular wavelength has a certain of course, when we say wavelength it has a frequency associated with it. Now if there is an atom which has a frequency or that difference between the k and l shell is about the same as that of the wavelength which is coming in. Then it does not know whether to stay there or go out because the frequency matches and because the frequency matches these electrons now they do not know what to do they reach relativistic speeds. As a result whatever scatters from the atom becomes anomalous and this anomalous behavior is the one which gets causes the change in the observation of I_{h-k-l} being different from I_{hkl} .

People have estimated the possible effects and we will be discussing it at a later time, if time permits because this is out of the purview of this particular course, but what is important is that by observing these differences we can actually identify the absolute configuration of a given molecule in the crystal. So, when we discuss this structure determination protocol and the absolute configuration at that particular time we will

spend a little extra time to see how these Bijvoet difference as they are called the difference between I_{hkl} and I_{-h-k-l} refer to as Bijvoet differences.

The presence of the Bijvoet differences can be utilized to determine the absolute structure of an organic molecule. In fact, it can also be used to determine this structure of large proteins. Again due to this anomalous dispersion effect because what the net effect will be is you can guess is the fact that your scattering factor F versus $(\sin\theta)/\lambda$ does not know how to behave, because they only when the atoms go out of the k shell and generate that wavelength you will have this F versus $(\sin\theta)/\lambda$ behavior associated with a atom, but now the atom is also vibrating with the same frequency.

So, the problem is now it will therefore, completely absorb the radiation which is coming in and let out something else and that something else is what we have measured as the intensity and therefore, that information can be used so the your scattering factor get modified. This scattering factor is which is real. so for will also become imaginary.

So, we will have a component of f . So, what was f which was a real quantity? Now f becomes $f_0 + \Delta f'$ (a real component on the on the organ diagram) + $i \Delta f''$.

We will have a slide illustrating this detail and how to do the absolute configurations from anomalous dispersion when we discuss the structure determination aspect. So, at this moment we end up with eleven Laue classes. So, in a nut shell we have a data we have a crystal we have sent in the X-ray beam and now we want to collect the data and when we collect the data we look at the intensities and these intensities.

Now can be analyzed with respect to systematic absences and the systematic absences will tell us this space group the diffraction apart from that is also now essentially obeying the Friedel's law in most of the cases in general. And because of the fact that it obeys the Friedel's law, the number of point group symmetry is will reduce because we will get only the centro symmetric information in an X-ray diffraction pattern. So, we will get therefore, the eleven Laue classes.

So, the eleven Laue classes are essentially shown here and the scattering therefore, is essentially this. So, the diffraction pattern of your $h k l$ reflections which you get will be always with respect to the center of symmetry. In addition the fact that we have higher symmetry elements in monoclinic orthorhombic trigonal tetragonal as we go higher and

higher in symmetry for example, because of the fact that b axis is unique and we have a 2 by m symmetry in the data the h k l reflections will be equal to -h -k -l and also if you have a h -k l reflection it will also be equal to h k l.

Therefore, there will be other equivalences which will develop and therefore, the symmetry that is contained inside the data set will also sort of tell us which crystal system the data will correspond to and that is something which we will see in a next slide in the coming class. So, essentially therefore, we have covered the various aspects of space groups, the reason why I am repeating it again and again is because this is the crucial step and we should not miss any of these points.

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Systematic absences due to translational elements

Consider 'a' glide through the origin parallel to (001)
 $x y z \rightarrow \frac{1}{2}x y -z$

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

$$= \sum_1^{\frac{1}{2}N} f_n \exp 2\pi i(hx_n + ky_n) \{ \exp 2\pi i lz_n + \exp 2\pi i(\frac{1}{2}h - lz_n) \}$$

Which becomes when $l = 0$

$$F(hk0) = \sum_1^{\frac{1}{2}N} f_n \exp 2\pi i(hx_n + ky_n) \{ 1 + \exp \pi i h \}$$

$$= \sum_1^{\frac{1}{2}N} f_n \exp 2\pi i(hx_n + ky_n) \{ 1 + (-1)^h \}$$

$$= 0 \quad \text{for } h = 2n+1.$$

And therefore, let me go through it once suppose you consider an a glide we have these systematic absences when l is equal to 0.

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Symmetry elements		Set of reflections	Conditions
Glide-plane (100)	b c n d	$0kl$	$k = 2n$ $l = 2n$ $k + l = 2n$ $k + l = 4n$
Glide-plane (010)	a c n d	$h0l$	$h = 2n$ $l = 2n$ $h + l = 2n$ $h + l = 4n$
Glide-plane (110)	c b n d	hhl	$l = 2n$ $h = 2n$ $h + l = 2n$ $2h + l = 4n$

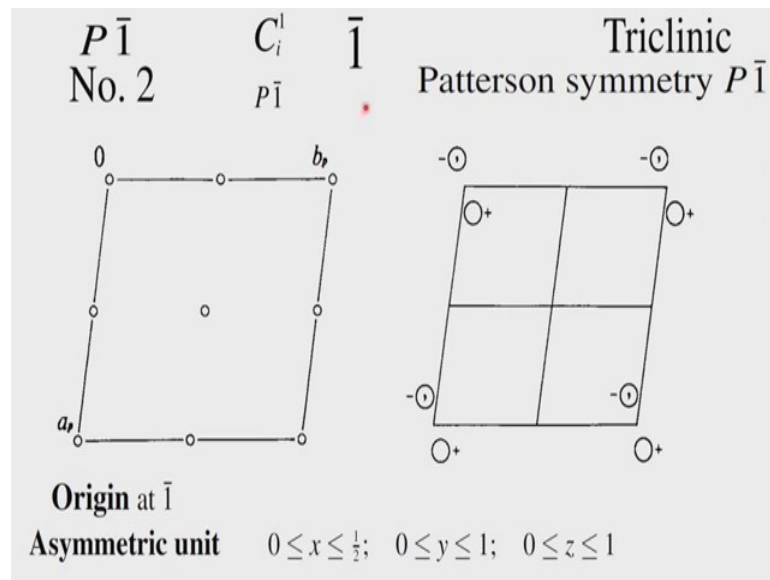
We will end up with this list where we have the conditions to be satisfied for a glide plane parallel to 1 0 0. Glide plane parallel to 0 1 0 these are the conditions to be followed glide plane parallel to 1 1 0 these are these systematic presences.

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Symmetry elements		Set of reflections	Conditions
Screw-axis a	$2_1, 4_2$ $4_1, 4_3$	$h00$	$h = 2n$ $h = 4n$
Screw-axis b	$2_1, 4_2$ $4_1, 4_3$	$0k0$	$k = 2n$ $k = 4n$
Screw-axis [110]	2_1	$hh0$	$h = 2n$

Similarly, in case we have the screw axis symmetry we see these conditions coming up.

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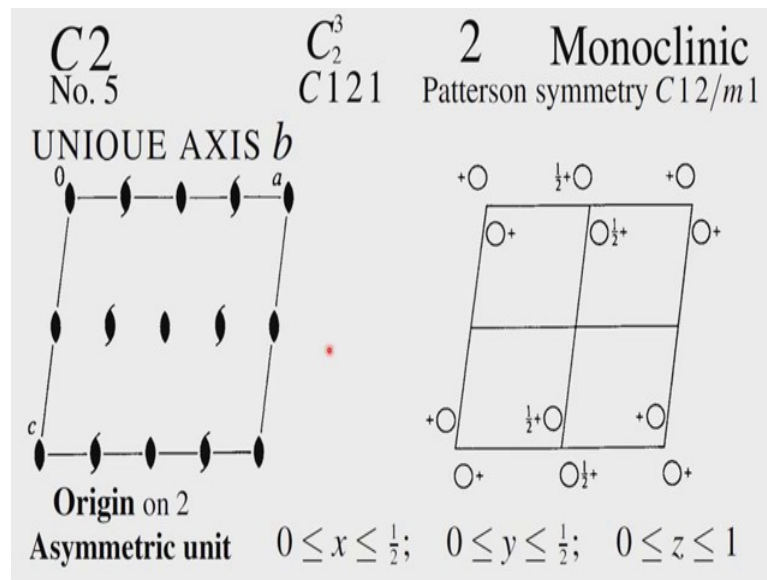
And then we have analyzed this with respect to individual space groups.

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Positions			Coordinates	$(0,0,0)+$ $(\frac{1}{2}, \frac{1}{2}, 0)+$	Reflection conditions
Multiplicity, Wyckoff letter, Site symmetry					
4	<i>c</i>	1	(1) x, y, z	(2) \bar{x}, y, \bar{z}	General: $hkl : h + k = 2n$ $h0l : h = 2n$ $0kl : k = 2n$ $hk0 : h + k = 2n$ $0k0 : k = 2n$ $h00 : h = 2n$ Special: no extra conditions
2	<i>b</i>	2	$0, y, \frac{1}{2}$		
2	<i>a</i>	2	$0, y, 0$		

The conditions which come up as in general reflections take the precedence over the conditions which come from special reflections in this particular example of C_2 there is no such worry.

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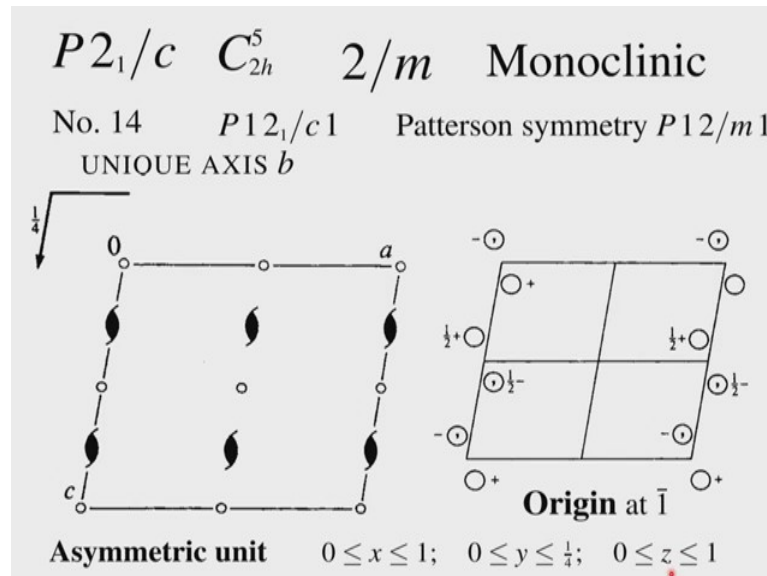
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Positions Multiplicity, Wyckoff letter, Site symmetry	Coordinates	Reflection conditions
4 e $\bar{1}$	(1) x, y, z (2) $\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$ (3) $\bar{x}, \bar{y}, \bar{z}$ (4) $x, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$	General: $h0l : l = 2n$ $0k0 : k = 2n$ $00l : l = 2n$
2 d $\bar{1}$	$\frac{1}{2}, 0, \frac{1}{2}$ $\frac{1}{2}, \frac{1}{2}, 0$	Special: $hkl : k + l = 2n$
2 c $\bar{1}$	$0, 0, \frac{1}{2}$ $0, \frac{1}{2}, 0$	$hkl : k + l = 2n$
2 b $\bar{1}$	$\frac{1}{2}, 0, 0$ $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$hkl : k + l = 2n$
2 a $\bar{1}$	$0, 0, 0$ $0, \frac{1}{2}, \frac{1}{2}$	$hkl : k + l = 2n$

But when we go to something like $P2_1/c$ you see as though this is a glide plane additional to the existing glide plane. It is not that way to be interpreted. In fact, this is the hkl . So, it looks as though it is a centered lattice. So, this gives you the information that it is the a centered lattice and that is because if you look at now the positions of the atoms in the unit cell the positions of the atoms in the unit cell mimic a centered lattice they are still in $P2_1/c$.

So, to determine the space group uniquely one has to refer to the general systematic absences, and suppose you have recorded a data and then only these absences come in, this is a point which we should now discuss. Suppose I record a data and that data gives me only this condition what is your conclusion? Your conclusion is very complicated now.

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Because your crystal system is $P2_1/c$, you determine the $a, b, c, \alpha, \beta, \gamma$ by the distribution of the d_{hkl} values, you found out the $a, b, c, \alpha, \beta, \gamma$ we are going to find out in the next set of classes exactly the methodology which is used because I thought that instead of describing it at this particular position. It is better we describe it with respect to the experiment you perform because, now the logistics will be from here on to go to the actual experiment which we perform.

So, we will take the crystal we will take the sample we will grow the crystal examine the crystal put it on the machine and then the machine collects the data. So, what I thought would be that with respect to the machine we will now see how things move, because that is what we are practically going to use in the rest of your crystallographic adventure. You are not going to use any of these things which we have learnt, but whatever we have learnt is going to be extraordinarily useful when we want to do the experiments. Otherwise we will do the experiment blindly and it can always lead to the wrong direction.

So, as I mentioned earlier in one of the classes that Jack Dentist says that a chemist makes the compound and puts it in a dark room he does not know where it is. And the crystallographer comes into the room and switches the light on and then you will see where it is and that is that's how it is and therefore, what you have to therefore do is to see that we get an idea of the way in which the systematic absences come up.

So, coming back to the question which I have asked which I have posted I get an indication that this system is $P2_1/c$, but I get systematic absences corresponding to a centered lattice. So, what do I conclude? Do I conclude that my $P2_1/c$ is wrong and say this is now a centered monoclinic system which is quite possible to have what is your conclusion? The conclusion will be that we had to look at always the general reflections. But then the general reflections are also not shown only these are shown. So, what is the conclusion? The conclusion is that if we have these special conditions that are coming up. The special conditions that are coming up is because of the atoms being in very very special positions. It is not coming up because the unit cell is this.

This is where the confusion comes, see for example if this is a compound which is crystallizing with all these atoms in these positions. Let's say any of these positions. Let's say the molecules are associated with 000, 01/20 now what is very interesting is only if and only if the atom is sitting at these positions you will have this if it is an atom. If it is a molecule only the molecule's center of symmetry will sit there and the center of symmetry of the molecule need not have any atom. Okay?

The molecule there may be one atom in the molecule which may sit for example, it could be an organometallic compound the metal atom may sit at this position, but the fact that the other atoms are sitting in other general positions will not give you only these will come only if the atoms are in these positions, but we are dealing with molecules we are dealing with compounds we are dealing with complexes.

So, in such situations we will straight away get these. So, only if there is an atom which crystallizes, in the space group $P2_1/c$ with which is sitting at 0 0 0, you will get this systematic absence. So, if there is if there is an organic metallic compound for which you have collected the data and you try to solve the structure by $P2_1/c$ you will have difficulties. You will have difficulties because the phase which you are going to determine is dominated by the heavy atom position and therefore, then you will have

some difficulties to overcome and that is something which is very special to very few compounds. So, we will not discuss that's beyond the purview of this particular course.

However you should remember that if the conditions are such that we do get atoms that are present in these positions, you will also have these indicated in the general reflections

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Positions Multiplicity, Wyckoff letter, Site symmetry	Coordinates		Reflection conditions
8 c 1	(1) x, y, z	(2) $\bar{x} + \frac{1}{2}, \bar{y}, z + \frac{1}{2}$	General: $0kl : k = 2n$ $h0l : l = 2n$ $hk0 : h = 2n$ $h00 : h = 2n$ $0k0 : k = 2n$ $00l : l = 2n$ Special: $hkl : h + k, h + l, k + l = 2n^*$ $hkl : h + k, h + l, k + l = 2n$
	(5) $\bar{x}, \bar{y}, \bar{z}$	(6) $x + \frac{1}{2}, y, \bar{z} + \frac{1}{2}$	
4 b $\bar{1}$	(3) $\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$	(4) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z}$	
	(7) $x, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$	(8) $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, z$	
4 b $\bar{1}$	$0, 0, \frac{1}{2}$	$\frac{1}{2}, 0, 0$	
	$0, \frac{1}{2}, 0$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	
4 a $\bar{1}$	$0, 0, 0$	$\frac{1}{2}, 0, \frac{1}{2}$	
	$0, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, 0$	

So, the same logic we extended to $2_12_12_1$ and in particular $Pbca$ where we get an absence equivalent of a F centered lattice and therefore, we see that we have the following information we have this space group information, we have the Friedel's law information we have the intensity data that is collected and we know that the diffraction is essentially belonging to eleven Laue classes. So, what we do next? What we do next is we have now the entire grammar book written up. We have all the necessary information which is required to do a diffraction experiment.

So, it is at this stage we can go ahead and do the diffraction experiment which we will do. So, the next step would be to do the diffraction experiment, grow the crystal to start with check the crystal for diffraction quality, put it on the machine and then get the diffraction data and one once we have the diffraction data collected using a counter of different kinds we can use CCD various kinds of machines to find out the intensity that comes in the form of a reciprocal lattice point reflection and that particular intensity is and the position of hkl will allow us to determine the geometry, and also the structure of the given material.

So, that will be the next step. So, we now have reached the stage which is the milestone of understanding the symmetry and structure in the solid state the next one is therefore, where we apply? Obviously, we apply to determine the structures. So, to determine the structures we now have a situation where we have to now get to the compounds. So, get to the chemistry of it, get to the actual experiment the idea of this course is not to describe the experiment in detail even though we need the experimental results to gain go and understand the symmetry and structure in the solid state. So, we will get some basics of the experiments, we will also find out that the major issue as we have always been discussing is the so-called phase problem the experiment is giving us only the magnitude of the structure factor and we need the structure factor to do the Fourier transform to get the electron density so; that means, we need the phase information.

We also know very in a passing discussing that if we use intensity of $h k l$ the Fourier transform of that will give us what is known as a Patterson function which essentially gives us a vector map of the distance between each atom to the other. So, we get a inter atomic vector display on the three dimensional projection and that will have some special properties obviously, which we have to examine. So, the logic therefore, is now we will go find out how the collect the data and so on.

Accumulate the data analyze the data put the data on an absolute scale because whether you collect the data in Bangalore or Timbuctoo or somewhere in synchrotron radiation the crystal or the material is still the same and therefore, you should get the structure of the material you do not care what radiation you are using what diffractometer you are using what kind of scaling is there in that and so on.

What you want is to put the whole thing on a common scale which is the absolute scale. The absolute scale come from the fact that we can you see the scattering is done by the electron density right, inside the crystal. So, it does not matter the electron density is what matters is the total electron density, the total electron density does all these scattering experiment.

So, based on that idea the total number of electrons matter. So, if you now consider the total number of electrons in the crystal system that is the one way with respect to which we do this scale and that is something which we will consider in the next class.