Lecture 7:   Systematic Absences

The reason that we have focussed on crystal symmetry for the last four lectures is that symmetry is going to help us to simplify the interpretation of crystallographic experiments. The crux of this lecture is to understand how the various symmetry elements — Bravais lattice, translational symmetry and point symmetry — affect diffraction patterns. What we are leading towards is being able to use the symmetry of an observed diffraction pattern in reciprocal space to deduce the symmetry about the crystal in real space.

We begin by making two simple but important observations.

(i) The structure factors at reciprocal space vectors $\mathbf{Q}$ and $-\mathbf{Q}$ are in fact complex conjugates; *i.e.* $F(hkl) = F^*(\bar{h}\bar{k}\bar{l})$. This result, known as "Friedel's law", means that the corresponding diffraction intensities are equal: $I(hkl) = I(\bar{h}\bar{k}\bar{l})$. Importantly, the diffraction pattern of a crystal is necessarily centrosymmetric irrespective of whether or not the crystal itself has a centre of symmetry.

(ii) The point symmetry of an object is preserved in its diffraction pattern. As a simple example, let us imagine that we have a system that possesses a 2-fold axis parallel to z, running through the origin. Then we can divide all the atoms in our system into three groups. The first group contains all those atoms that lie on the axis itself, and we know that these will have coordinates $(0, 0, z)$. We then divide the remaining atoms into two equal groups such that each atom in one group will be mapped onto an atom in the second group by the 2-fold axis. That is, for each atom at (x, y, z), we know that there is an equivalent atom at $(-x, -y, z)$, and we place one atom in our second group, and one atom in our third group. Taking an arbitrary point in reciprocal space (h, k, l), we will show that the Fourier component at this point is the same as that at $(-h, -k, l)$, and hence the diffraction pattern will also contain a 2-fold axis, this time lying perpendicular to $\mathbf{c}^*$.

$$F(hkl) \;=\; \sum_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)] \tag{1}$$

$$= \sum_{j\in\text{group1}} f_j \exp[2\pi i(lz_j)] + \sum_{j\in\text{group2}} f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$
$$+ \sum_{j\in\text{group3}} f_j \exp[2\pi i(-hx_j - ky_j + lz_j)] \tag{2}$$

$$= \sum_{j\in\text{group1}} f_j \exp[2\pi i(lz_j)] + \sum_{j\in\text{group2}} f_j \exp[2\pi i((-h)x_j + (-k)y_j + lz_j)]$$
$$+ \sum_{j\in\text{group3}} f_j \exp[2\pi i(-(-h)x_j - (-k)y_j + lz_j)] \tag{3}$$

$$= F(\bar{h}\bar{k}l) \tag{4}$$

(here, the notation $(\bar{h}\bar{k}l)$ is shorthand for $(-h, -k, l)$).

Taken together, these two results mean that **the point group of a diffraction pattern is the centrosymmetric parent of the point group of the crystal**.The point group of a diffraction pattern is usually called the "Laue class" of the diffraction pattern; the relationship between Laue classes and point groups is shown in the table below.

Crystal system	Laue class	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	$\bar{3}$	3	$\bar{3}$		
	$\bar{3}m$	32	$3m$	$\bar{3}m$	
Tetragonal	$4/m$	4	$\bar{4}$	$4/m$	
	$4/mmm$	422	$4mm$	$\bar{4}2m$	$4/mmm$
Hexagonal	$6/m$	6	$\bar{6}$	$6/m$	
	$6/mmm$	622	$6mm$	$\bar{6}m2$	$6/mmm$
Cubic	$m3$	23	$m3$		
	$m\bar{3}m$	432	$\bar{4}3m$	$m\bar{3}m$	

You should be able to convince yourself that the diffraction pattern for a crystal in $I4_1cd$ will have $4/mmm$ point symmetry; likewise, that of a crystal in $P6_2$ will have $6/m$ point symmetry.

Having established the effect of point symmetry on the diffraction pattern, we now proceed to show that the translational symmetry elements do not affect the symmetry of the diffraction pattern *per se*, but do result in what we call "systematic absences" — the absence of any diffraction intensity at specific sets of reciprocal lattice points.

The first type of systematic absences we will address are those that arise due to lattice centering. Let us consider a face-centred lattice (presumably of orthorhombic or cubic lattice symmetry, but this doesn't matter). What we know is that for each atom j in the unit cell at (x_j, y_j, z_j) there are corresponding atoms j', j'' and j''' at $(x_j, y_j + \frac{1}{2}, z_j + \frac{1}{2})$, $(x_j + \frac{1}{2}, y_j, z_j + \frac{1}{2})$ and $(x_j + \frac{1}{2}, y_j + \frac{1}{2}, z_j)$, respectively. Consequently, we can split our scattering equations into four parts:

$$
\begin{aligned}
F(hkl) \;=\; & \sum_j f_j \Big\{ \exp[2\pi i(hx_j + ky_j + lz_j)] \\
& + \exp[2\pi i(hx_j + k\{y_j + \tfrac{1}{2}\} + l\{z_j + \tfrac{1}{2}\})] \\
& + \exp[2\pi i(h\{x_j + \tfrac{1}{2}\} + ky_j + l\{z_j + \tfrac{1}{2}\})] \\
& + \exp[2\pi i(h\{x_j + \tfrac{1}{2}\} + k\{y_j + \tfrac{1}{2}\} + lz_j)] \Big\}
\end{aligned}
\tag{5}
$$

On factorising we obtain

$$
\begin{aligned}
F(hkl) \;=\; & \big\{ 1 + \exp[\pi i(k + l)] + \exp[\pi i(h + l)] + \exp[\pi i(h + k)] \big\} \\
& \times \sum_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)]
\end{aligned}
\tag{6}
$$

It is not difficult (and a good exercise) to show that the prefactor is zero for all h, k, l except whenever the three indices are all even or are all odd (when it equals four). This means that for a face centred crystal we do not expect to observe any intensity for *e.g.* the (100), (321), ... reflections. Let us use this result to visualise reciprocal space for a face-centred lattice:
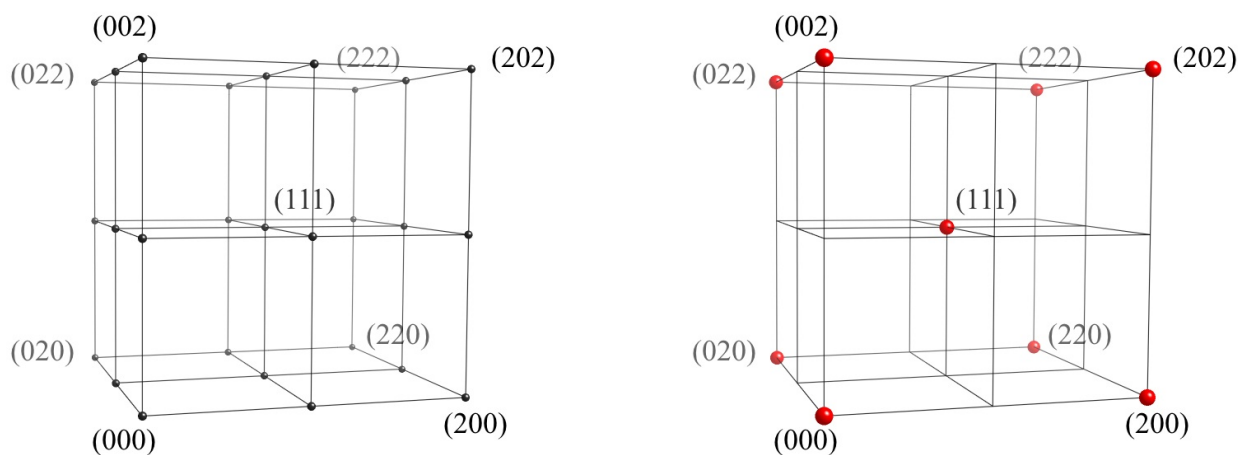
What we find is that the reciprocal lattice of a face-centred cubic lattice is itself a body-centred cubic lattice in reciprocal space, a result that we met in Lecture 1. It is a good

exercise to check that the reverse also holds true; that is, to confirm that a body-centred lattice is face-centred in reciprocal space. Consequently, the centering of a diffraction pattern we observe experimentally will tell us what particular type of centering exists in real space. This enables us to start determining the space group for our crystal.

The other two translational symmetry operations, namely screw axes and glide planes, also give rise to systematic absences. The mathematics involved is very similar, if a little tedious. We cover some representative derivations here only really to explain from where these results arise; what is important is only that the absences occur, and that we know how to recognise and interpret these in a diffraction pattern.

Let us address quickly the mathematics for screw axes, and we will use as our example a crystal that contains a 2_1 screw axis parallel to $\mathbf{b}$. This will have the effect of replicating each atom j, originally at (x_j, y_j, z_j), at $(-x_j, \frac{1}{2} + y_j, -z_j)$. The structure factor is then given as

$$F(hkl) = \sum_j f_j \big\{ \exp[2\pi i(hx_j + ky_j + lz_j)] + \exp[2\pi i(-hx_j + k\{\tfrac{1}{2} + y_j\} - lz_j)] \big\}. \quad (7)$$

What we do is to consider the intensity at reciprocal lattice points of the type $(0k0)$:

$$
\begin{aligned}
F(0k0) \quad &= \quad \sum_j f_j \big\{ \exp(2\pi i k y_j) + \exp[2\pi i k(\tfrac{1}{2} + y_j)] \big\} & (8) \\[2mm]
&= \quad [1 + (-1)^k] \sum_j f_j \exp(2\pi i k y_j) & (9) \\[2mm]
\left\{
\begin{aligned}
&= \quad 0 \text{ if } k = 2n + 1 \quad (\text{odd}) \\
&\neq \quad 0 \text{ if } k = 2n \quad (\text{even})
\end{aligned}
\right. \,, && (10)
\end{aligned}
$$

where n is an integer. What this tells us is that $(0k0)$ reflections with odd values of k will not be observed: a new set of "systematic absences" that we should be able to observe in a diffraction pattern. Similar systematic absences would arise from screw axes along other directions.

For completeness we will cover a similar calculation for glide planes. This time our example will be a c-glide perpendicular to $\mathbf{b}$. This will replicate each atom j, originally at (x_j, y_j, z_j), at $(x_j, -y_j, \frac{1}{2} + z_j)$. Writing out the structure factor explicitly we obtain

$$F(hkl) = \sum_j f_j \big\{ \exp[2\pi i(hx_j + ky_j + lz_j)] + \exp[2\pi i(hx_j - ky_j + l\{\tfrac{1}{2} + z_j\})] \big\}. \quad (11)$$

Now, for $(h0l)$ reflections we have

$$F(h0l) \quad = \quad \sum_j f_j \big\{ \exp[2\pi i(hx_j + lz_j)] + \exp[2\pi i(hx_j + l\{\tfrac{1}{2} + z_j\})] \big\} \tag{12}$$

$$= \quad [1 + (-1)^l] \sum_j f_j \exp[2\pi i(hx_j + lz_j)] \tag{13}$$

$$\begin{cases} = & 0 \text{ if } l = 2n + 1 \quad (\text{odd}) \\ \neq & 0 \text{ if } l = 2n \quad (\text{even}) \end{cases}, \tag{14}$$

where again n is an integer. Similar systematic absences arise from glide planes involving other directions.

We can summarise these three types of systematic absences in three separate tables.

Conditions due to lattice centering:

Centering	Reflection condition	Reflections involved
I	$h + k + l = 2n$	
F	h, k, l all even or all odd	
A	$k + l = 2n$	
B	$h + l = 2n$	all reflections
C	$h + k = 2n$	
R (obverse)	$-h + k + l = 3n$	
R (reverse)	$h - k + l = 2n$	

Conditions due to the existence of screw axes:

Screw axis	Reflection condition	Reflections involved
2_1	h, k or $l = 2n$	
$4_2, 6_3$	$l = 2n$	$h00$ for axis $\parallel \mathbf{a}$
$3_1, 3_2, 6_2, 6_4$	$l = 3n$	$0k0$ for axis $\parallel \mathbf{b}$
$4_1, 4_3$	$l = 4n$	$00l$ for axis $\parallel \mathbf{c}$
$6_1, 6_5$	$l = 6n$	

Conditions due to the existence of glide planes (*n.b.* this list is not comprehensive for the d-glides):

Glide plane	Reflection condition	Reflections involved
a	$h = 2n$	
b	$k = 2n$	$0kl$ for plane $\perp \mathbf{a}$
c	$l = 2n$	$h0l$ for plane $\perp \mathbf{b}$
n	$h + k,\ k + l$ or $h + l = 2n$	$hk0$ for plane $\perp \mathbf{c}$
d	$h + k,\ k + l$ or $h + l = 4n$	

More important than all this book-keeping is the ability to interpret systematic absences within a diffraction pattern. In order to build up our expertise here what we are going to do is to consider some simplified reflection diagrams. These are illustrations that show what reflections we expect to see in a diffraction pattern (without worrying about the actual intensities). We will only deal with orthorhombic crystals, for which we will encounter three separate planes in reciprocal space — one perpendicular to each of the three crystal axes.

$$(0kl)$$

l

k
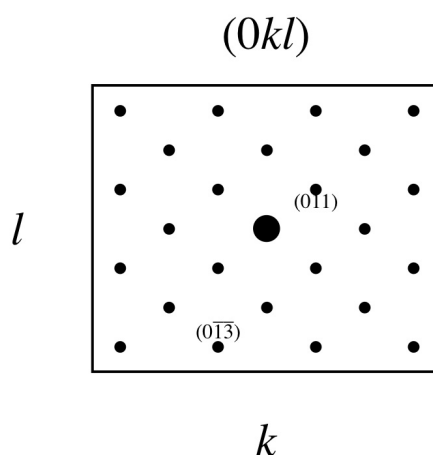
Let us consider the orthorhombic space group $Pnma$. Because we are dealing with a primitive lattice, we do not expect any absences due to lattice centering. Again, we work systematically, dealing first with the n-glide, which we know lies perpendicular to $\mathbf{a}$. Looking through our table above we see that this this will give rise to absences in the $(0kl)$ reciprocal plane whenever $k + l$ is odd. To represent this we sketch a reflection diagram for the $(0kl)$ plane (above). The central reflection, which is shown as a larger circle, corresponds to (000); k indexes the horizontal axis and l the vertical axis. We draw in smaller circles wherever we expect to see reflections: in this case whenever $k + l$ is even. Two representative points are labelled — (011) and $(0\bar{1}\bar{3})$.

Working systematically we consider the next character in the space group symbol: the m, which tells us we have mirror planes perpendicular to $\mathbf{b}$. There are no systematic absences associated with mirror planes, so we might initially draw a reflection diagram for the $(h0l)$ plane as overleaf. **This is not yet quite correct, and we will see why shortly**.

$(h0l)$

h

l
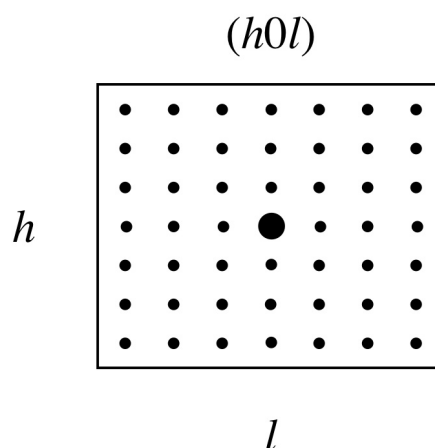
The last character in the space group symbol tells us that we have an a-glide perpendicular to $\mathbf{c}$. Again, consulting our table of reflection conditions, we see that this predicts reflections for the $(hk0)$ plane will only be observed whenever h is even. Transferring this to a reflection diagram, we obtain the following initial guess.

$(hk0)$

k

h
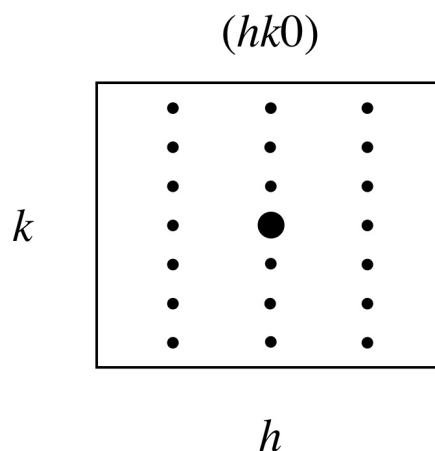
The final — and very important — step is to check for consistency along the three axes $(h00), (0k0), (00l)$. Considering the systematic absences we found for the $(0kl)$ plane, for example, we see that we expect reflections along $(0k0)$ and $(00l)$ only when k or l are even. But this is not yet reflected in the diagrams for $(hk0)$ and $(h0l)$ planes. Similarly, the a-glide absences on $(hk0)$ tell us that we will observe $(h00)$ reflections only when h is even; again we need to represent this on the $(h0l)$ diagram. Putting all this information together, we arrive at the set of reflection diagrams shown on the next page.

It is worth reiterating that the crystal itself does not "know" which axis is which, so the labels themselves are somewhat arbitrary. Here we can label the axes because we are starting from the particular space group symbol $Pnma$. However, if we were to undertake the reverse process — that is, to recover the space group symbol from the scattering

patterns — then we would end up with different, but equivalent, space group symbols for each possible choice of axes. Note that the International Tables only list unique space groups.

$(hk0)$ $\qquad\qquad$ $(h0l)$ $\qquad\qquad$ $(0kl)$
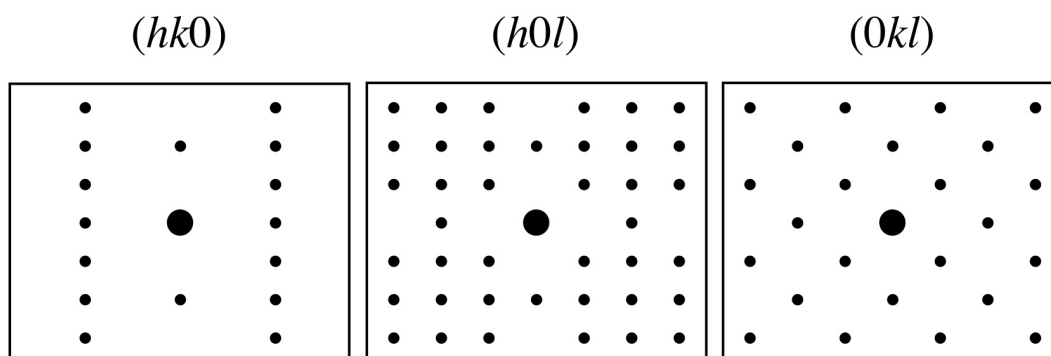
We are going to finish this lecture with a quick discussion of systematic absences in powder diffraction patterns. Because in a powder diffraction experiment we have many small crystallites oriented in all possible directions, what happens is that all of reciprocal space is effectively projected onto a single axis. We can't resolve any directions within reciprocal space but we can still determine magnitudes. An example of a powder diffraction pattern for a face-centred cubic material is shown below. The important point here is to illustrate that we can still see systematic absences; in this case, for example, we could say with confidence that the material is face-centred cubic. The situation becomes more complex for orthorhombic systems, and it may be that not all systematic absences can be determined in this way.