Lesson 13

- How the reciprocal cell appears in reciprocal space.
- How the non-translational symmetry elements appear in real space
- How translational symmetry element appear in real space

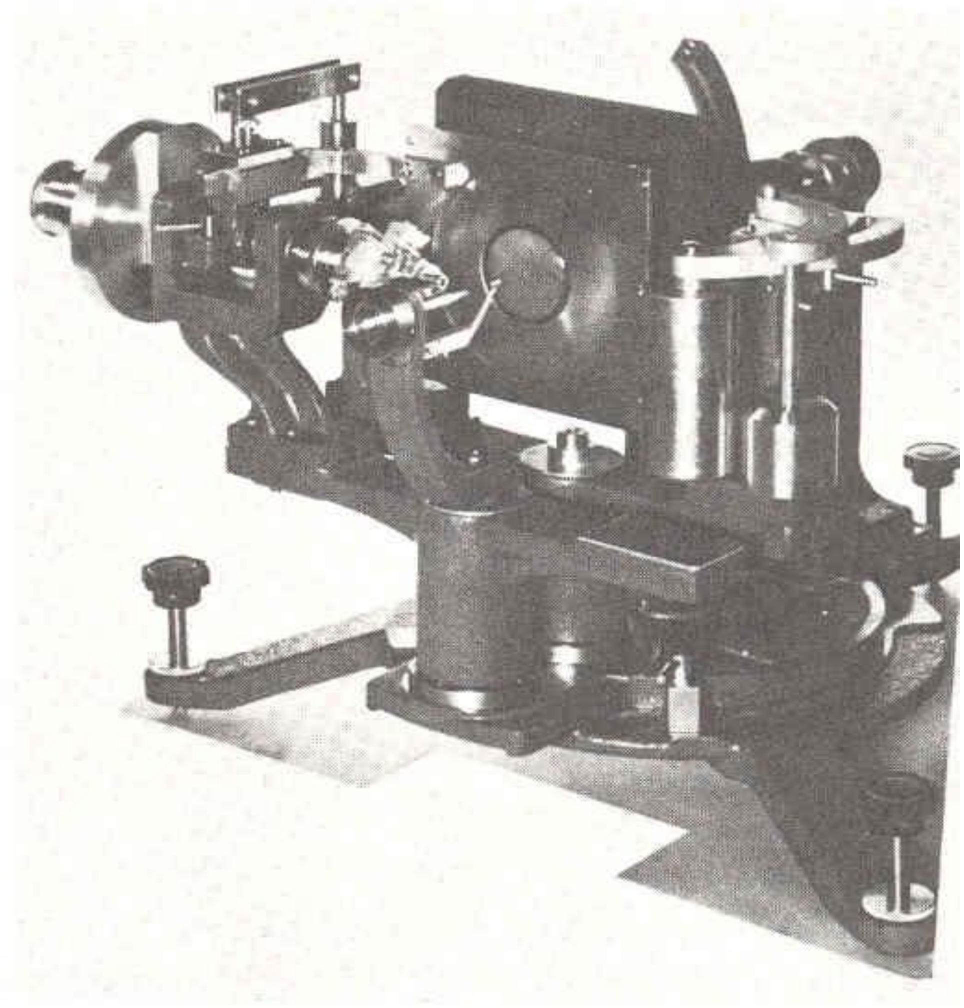
HOMEWORK

- Calculate the correct transformation matrix for going from $P2_1/c$ to $P2_1/n$ in the drawing given in the lecture.
- Analyze the space group $Pna2_1$ and state what operation each coordinate set represents and the coordinates for the axis or plane.
- Determine the equivalent hkl's for $Pna2_1$

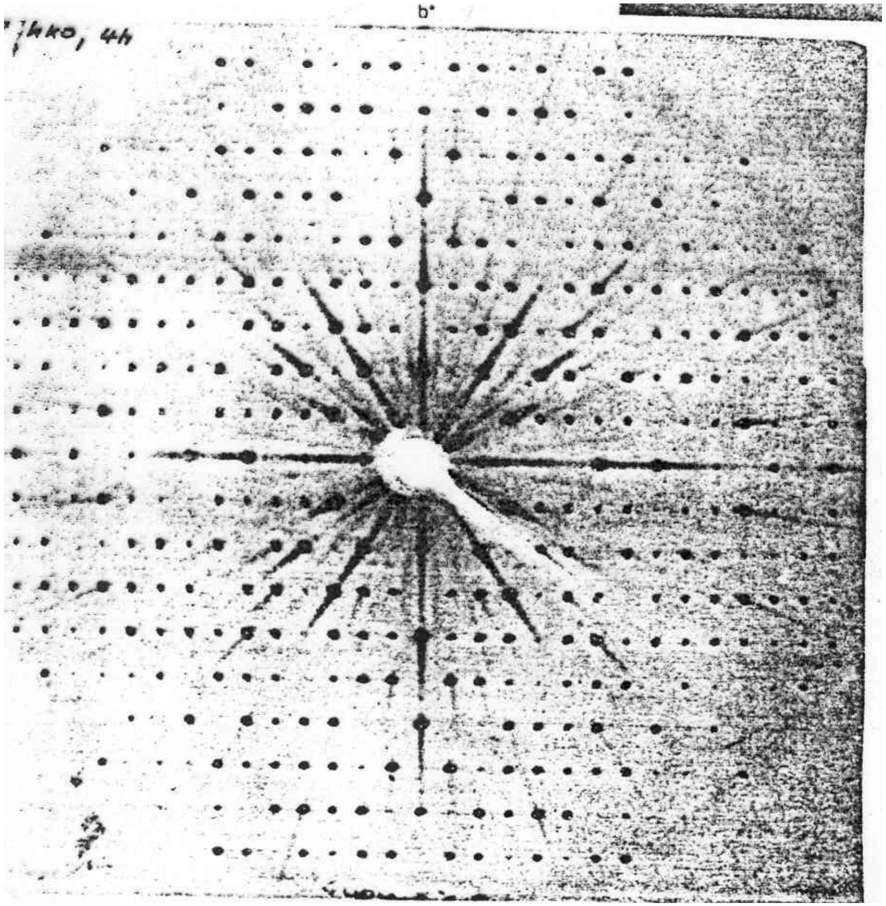
Reciprocal Space

- In order to look at reciprocal space we need a way to view it.
- Ideally the appearance will be a two dimensional grid.
- To simplify matters the grid will be perpendicular to a reciprocal vector
- Such views are call precession photos.

The Burger Precession Camera



A Precession Photo

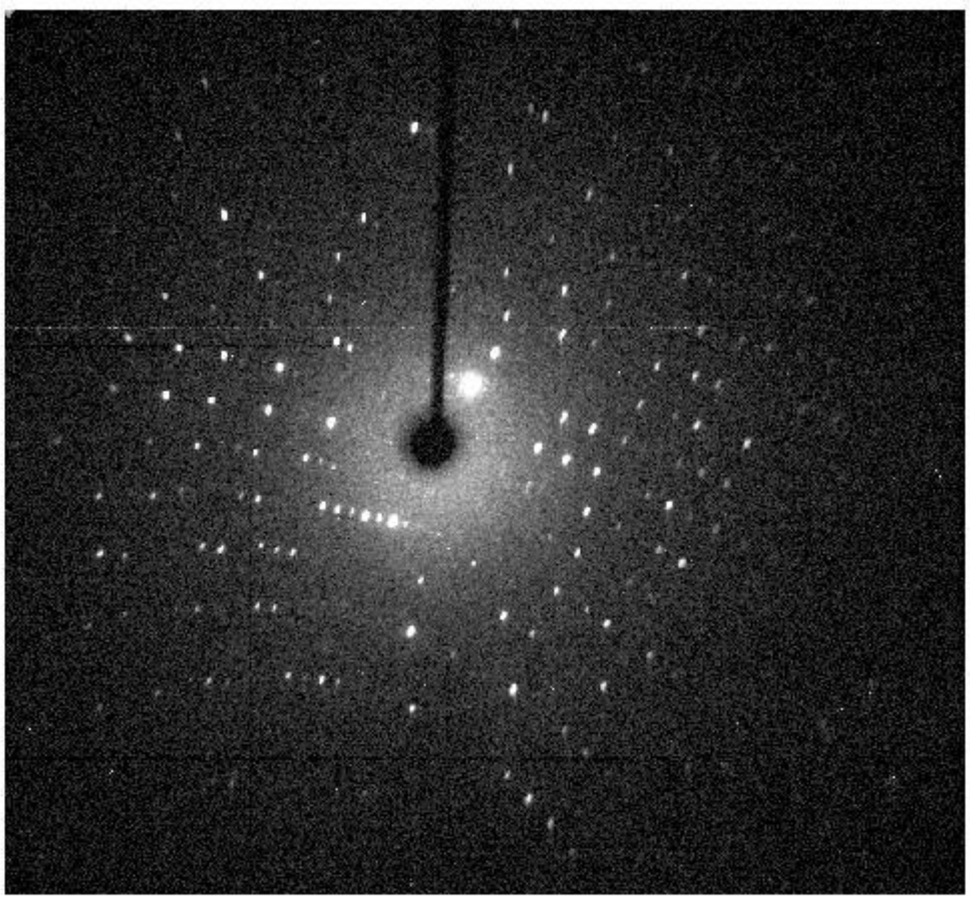


This is looking down the c-axis
Note the main axes are perpendicular

Problems with the Precession Camera

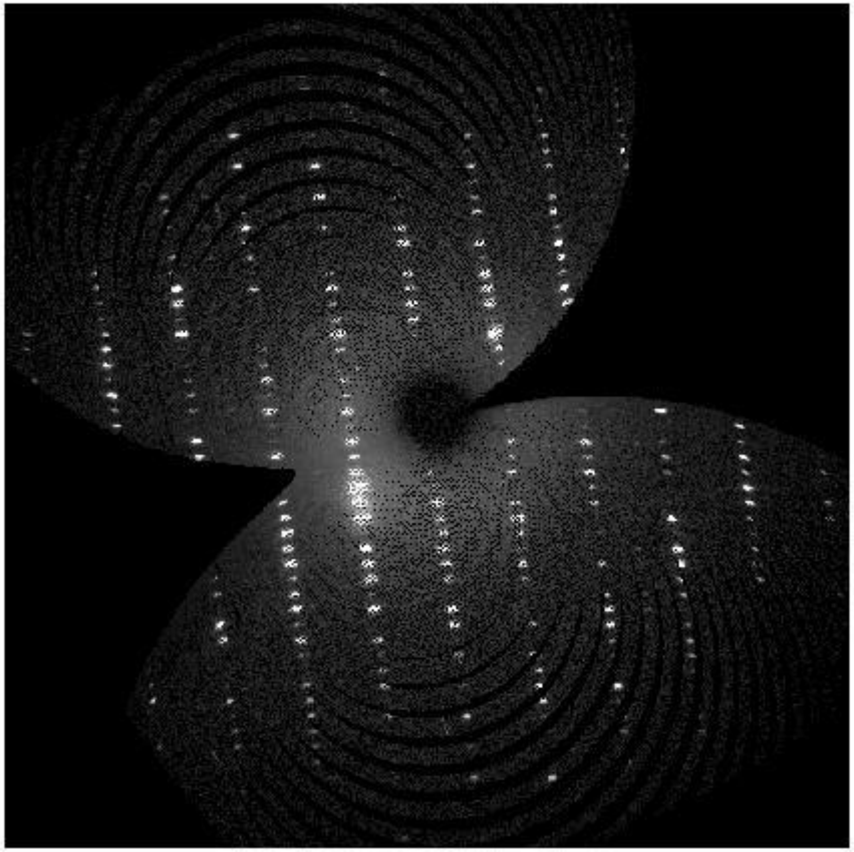
- It is very painful to align the crystal as it needs to rotate around a reciprocal axis.
- The pictures take several days to expose.
- Can only see two axes in the photo-- to get a picture on the third the crystal must be remounted and re-aligned.

A random Frame



- No easily observed pattern
- Taken with a ccd detector-- sort of a digital camera
- However, if we know the unit cell and its orientation, the pixels that would be in a precession photo can be calculated.
- Generate a synthetic precession photo from a large collection of frames.

A Calculated Precession Photo



This is the h0l plane of a monoclinic crystal

Note one axis is horizontal and the other makes an angle of β* with it

Since the horizontal separation is larger than the vertical it means the horizontal reciprocal axis is larger than the vertical or the horizontal real axis is smaller than the vertical

The black circle in the center is the beam stop

The black regions are areas where no pixels were collected.

How do symmetry operations effect reciprocal space

Here we are talking about the observed data.

- Not surprisingly the symmetry elements appear in the intensity pattern and not the arrangement of the spots.

Symmetry and Data

- The Fourier transform will convert glide planes to mirrors and screw axes to rotation axes.
- The fact that the symmetry operation does not run through the origin will be lost in Reciprocal space.
- The effect of translation will be observed in missing classes of reflections.

A word about x-ray data.

- The x-ray data is very simple containing the hkl of the reflection, the intensity, and the estimated standard deviation of the intensity (σ)
- Since measuring x-ray intensity is a type of radiation counting there is an error in the observed value.
- In general intensities that are less than 3σ in intensity can at first be considered unreliable.
- Sometimes some human judgement is needed.

An actual data set

2	-1	12	4.40	1.10
-2	1	-12	2.20	1.10
2	-1	13	0.50	1.00
-2	1	-13	-0.90	1.60
2	-1	14	2.60	1.00
2	-1	15	22.30	2.70
-2	0	15	14.90	2.10
2	0	-14	2.00	1.60
-2	0	14	1.70	0.90
2	0	-13	23.50	3.00
-2	0	13	22.70	2.70
2	0	-12	3.90	1.30
-2	0	12	5.10	1.10
2	0	-11	6.90	1.30
-2	0	11	8.10	1.30
2	0	-10	76.30	5.30
-2	0	10	84.10	4.70
2	0	-9	46.20	4.60
-2	0	9	48.50	3.20
2	0	-8	7.50	2.30
-2	0	8	8.30	1.00
2	0	-7	4.20	0.80
-2	0	7	3.70	0.70
2	0	-6	1.00	0.50
-2	0	6	1.10	0.40
2	0	-5	22.50	2.00
-2	0	5	22.30	1.60
-2	0	4	23.60	1.70
2	0	-4	26.10	1.40
2	0	-3	33.10	2.40
2	0	-2	36.60	2.00
-2	0	3	35.70	2.30
2	0	-1	334.20	12.90
-2	0	2	36.70	2.10
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

An example

- Lets consider $P2_1/c$ ignoring translation.
- There is a mirror (glide plane) perpendicular to b which takes xyz to x-yz
- Therefore reflections with hkl and h-kl should have the same intensity
- Similarly the 2-fold creates -xy-z and means hkl and -hk-l should have the same intensity.
- The Patterson symmetry in the International Tables is the symmetry of the data.

A comment on Inversion

- The existence of an inversion center will make hkl and -h-k-l equivalent.
- Even when there is not an inversion center this is almost true
- This is Friedel's law which says $I_{hkl} \approx I_{-h-k-l}$
- For centric cells the approximate sign can be replace by an equal sign.

The Octant of Data

- All the data possible from a crystal is called a sphere of data.
- It consists of the eight octants which have one of the eight possible sign arrangements of hkl   hk-l h-kl -hkl -h-kl -hk-l h-k-l -h-k-l
- If Friedel's law is obeyed only need 4 octants because the other four are related by symmetry i.e. hkl=-h-k-l
- Data that is hkl and -h-k-l are called Friedel pairs

For $P2_1/c$

- Since four octants are related by symmetry $I_{hkl} = I_{-hk-l} = I_{h-kl} = I_{-h-k-l}$
- Only need two octants for complete data coverage.
- If more than one unique octant is collected the data are not independent and are said to be redundant data.
- The redundant data can be averaged so only unique data is used.

Laue Groups

- If to a first approximation it is assumed that Friedel's law applies than all the monoclinic space groups have the same equivalent reflections.(an aside-- crystallographers call their data reflections even though it has nothing to do with reflection)
- The symmetry of this pattern is called the Laue group.
- All the monoclinic cells belong to the Laue group 2/m

Table 3.4 Equivalent data for diffraction groups

Diffraction group (with related chiral group)	Conditions as for	Additional conditions for $I(hkl) \equiv$	Additional conditions for $I(\overline{hkl}) \equiv$	Multiplicity of centrosymmetric general data
$\bar{1}$ (1)	–	–	–	2
$2/m$ (2)	$\bar{1}$ (1)	$I(\bar{h}k\bar{l})$	$I(h\bar{k}l)$	4
mmm (222)	$2/m$ (2)	$I(h\overline{kl})$, $I(\overline{hk}l)$	$I(\bar{h}kl)$, $I(hk\bar{l})$	8
$4/m$ (4)	$\bar{1}$ (1)	$I(\overline{hk}l)$, $I(\bar{k}hl)$, $I(k\bar{h}l)$	$I(hk\bar{l})$, $I(k\overline{hl})$, $I(\bar{k}h\bar{l})$	8
$4/mmm$ (422)	$4/m$ (4)	$I(\bar{h}k\bar{l})$, $I(h\overline{kl})$, $I(\overline{khl})$, $I(kh\bar{l})$	$I(\bar{h}kl)$, $I(h\bar{k}l)$, $I(khl)$, $I(\overline{kh}l)$	16
$\bar{3}$ (3)	$\bar{1}$ (1)	$I(kil)$, $I(ihl)$,	$I(\overline{kil})$, $I(\overline{ihl})$*	6
$\bar{3}m1$ (321)	$\bar{3}$ (3)	$I(\overline{khl})$, $I(\overline{hil})$, $I(\overline{ikl})$	$I(hil)$, $I(khl)$, $I(ikl)$	12
$\bar{3}1m$ (312)	$\bar{3}$ (3)	$I(kh\bar{l})$, $I(hi\bar{l})$, $I(ik\bar{l})$	$I(\overline{kh}l)$, $I(\overline{hi}l)$, $I(\overline{ik}l)$	12
$6/m$ (6)	$\bar{3}$ (3)	$I(\overline{hk}l)$, $I(\overline{ki}l)$, $I(\overline{ih}l)$	$I(hk\bar{l})$, $I(ih\bar{l})$, $I(ki\bar{l})$	12
$6/mmm$ (622)	$6/m$ (6)	$I(\overline{khl})$, $I(\overline{hil})$, $I(\overline{ikl})$	$I(hil)$, $I(khl)$, $I(ikl)$	
		$I(kh\bar{l})$, $I(hi\bar{l})$, $I(ik\bar{l})$	$I(\overline{kh}l)$, $I(\overline{hi}l)$, $I(\overline{ik}l)$	24
$m\bar{3}$ (23)	mmm (222)	$I(klh)$, $I(k\overline{lh})$, $I(\bar{k}l\bar{h})$, $I(\overline{kl}h)$	$I(\overline{klh})$, $I(k\bar{l}h)$, $I(\bar{k}lh)$, $I(kl\bar{h})$	
		$I(lhk)$, $I(l\overline{hk})$, $I(\bar{l}h\bar{k})$, $I(\overline{lh}k)$	$I(\overline{lhk})$, $I(\bar{l}hk)$, $I(l\bar{h}k)$, $I(lh\bar{k})$	24
$m\bar{3}m$ (432)	$m\bar{3}$ (23)	$I(l\bar{k}h)$, $I(lk\bar{h})$, $I(\overline{lkh})$, $I(\bar{l}kh)$	$I(lkh)$, $I(l\overline{kh})$, $I(\bar{l}k\bar{h})$, $I(\overline{lk}h)$	
		$I(\overline{khl})$, $I(\bar{k}hl)$, $I(kh\bar{l})$, $I(k\bar{h}l)$	$I(khl)$, $I(\bar{k}h\bar{l})$, $I(\overline{kh}l)$, $I(k\overline{hl})$	
		$I(\overline{hlk})$, $I(\bar{h}lk)$, $I(h\bar{l}k)$, $I(hl\bar{k})$	$I(hlk)$, $I(\overline{hl}k)$, $I(\bar{h}l\bar{k})$, $I(h\overline{lk})$	48

*In trigonal and hexagonal crystals, $i = -h - k$.

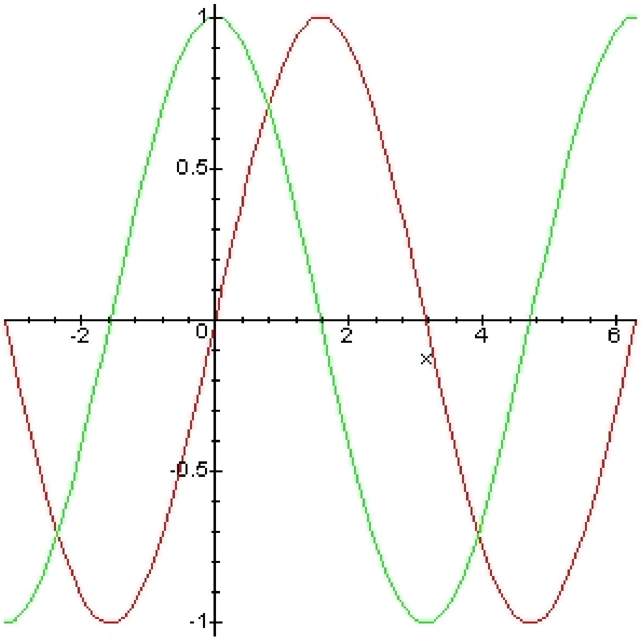
The Effect of Translation in the Reciprocal Lattice

- Translation will cause some set of reflections to have zero intensity
- These missing reflections are called systematic absences.
- The remaining reflections in the set are called systematic presences.
- Working with translation in reciprocal space, the symmetry offsets can be ignored. They are removed by the Fourier transform!

A new meaning for hkl

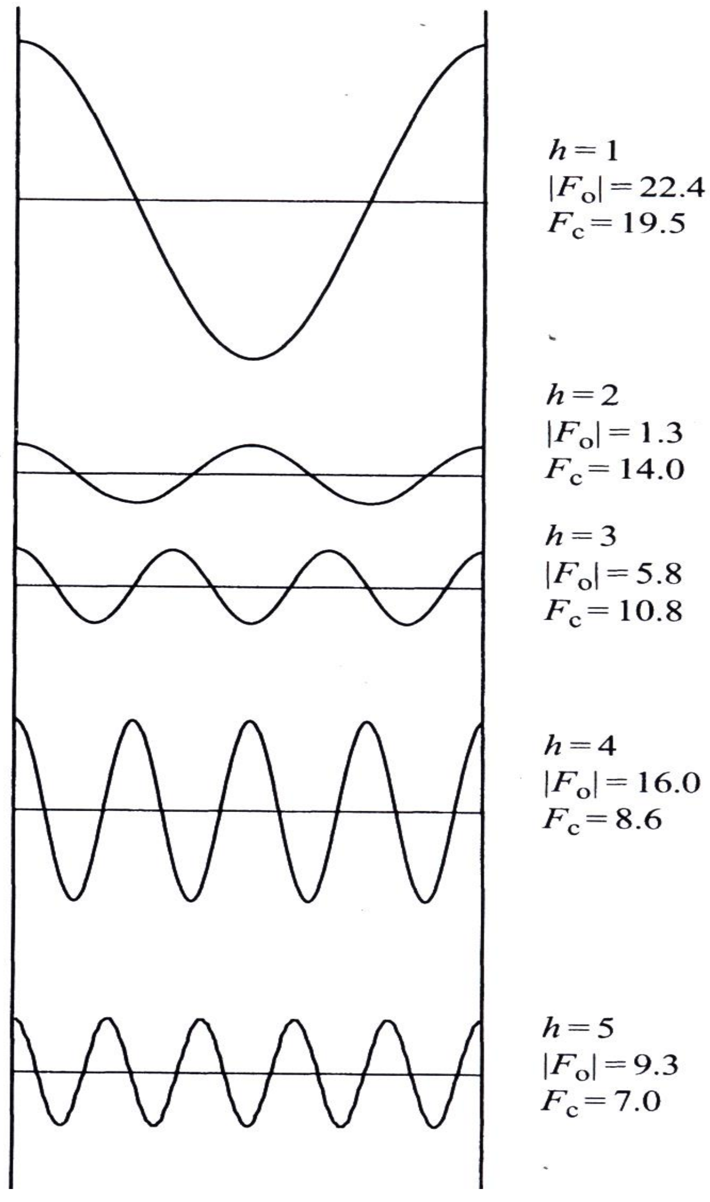
- The indices hkl are overloaded with meanings
  - They define the crystal faces
  - They define the Bragg planes
  - They index a vector on the reciprocal axis
- A new meaning—hkl represent a Fourier component –hkl are the direction and wavelength of a wave.

Lets look at a 1-d case



The symmetry of the wave must obey the symmetry of the crystal. If there is a center of inversion at x=0 then only the cosine wave is allowed.

A 1-d Centered Cell



Lets Imagine a 1-d Centered Cell

- This means that x=1/2 is equivalent to x=0 by translation.
- Obviously this is ridiculous in 1-d as it is just a cell that is twice as long as it needs to be.
- However, this is a thought exercise and we can play with it.

The Result

- Whenever h is odd the wave will not be the same at x=1/2 and x=0
- Thus by symmetry all the h=2n+1 spots will be systematically absent.
- All the h=2n spots will be present
- Note if we made x=1/3 equivalent then only h=3n spots would be present.

Centering

- Centering is applied to every point.
- For c centering for every point x,y,z there is an equivalent point a 1/2+x,1/2+y,z.
- The presence for c centering is hkl,h+k=2n
- For a centering k+l=2n
- For b centering h+l=2n
- For i centering h+k+l=2n
- For f centering a and b and c

Apply to screw axis

- If a point is exactly on the screw axis then it will only be translated since the rotation will not move it at all
- For $P2_1/c$ the rotation is along b so a point at x=0 y=anything z=0 is on the screw axis (remember we do not need to consider the offset)
- Thus 0,y,0 and 0,y+½,0 must be the same.
- Thus in reciprocal space for 0,k,0 the point only has ½ cell translation resulting in the presence 0,k,0 k=2n

In general

- For a d dimensional screw axis
  - If along c then 0,0,l l=dn (i.e. For a 3 fold 3n Since the handedness of the 3 fold does not survive the Fourier transform this is also true for 3_2).
  - If along a then h,0,0 h=dn
- For a 63 since the translation involves 3/6 or ½ the cell the presences are 2n not 6n

For a Glide Plane

- If the point sits in the plane of the mirror then it only undergoes translation.
- For the c-glide in P21/c the mirror is x,0,z (ignoring the offset) and the translation is along c resulting in h,0,l l=2n
- For the n-glide the translation is along the diagonal moving to x=1/2+x, z=1/2+z so the presence is h,0,l h+l=2n
- A point not in the plane does not undergo a simple translation so there is no general presences.

Note

- The intensities of systematic absences will not be exactly zero!
- First look at reflections where $I > 3\sigma(I)$
- Look for a pattern of weak vs strong.
- In some cases must guess based on common versus uncommon space groups.
- We will use the programs xprep and absen to determine space groups.