Lesson 12—Working with Space Groups

- How to convert a space group to a point group
- Adding the translational elements
- Calculating the coordinates of the symmetry operations
- Cell transformations

Homework

- Is there anything wrong with the proposed space group Pbac? If so what.
- Is there a difference between 2_1 and 6_3? If so what is it.

Working with Space Groups

- I find it easiest to begin by reducing the space group to a point group.
- This is done by removing all the translational symmetry elements (i.e. Fractions like ½)
- Then try to identify what the symmetry operation is from the operation
- Look up $P2_1/c$

x,y,z; -x,1/2+y,1/2-z; -x-y-z; x,1/2-y,1/2+z

- Note the cell is centric.
- The fourth coordinates are the second operated on by the inversion center
  - -x goes to x
  - 1/2+y goes to -1/2-y but since -1/2 = ½ it becomes 1/2-y
  - 1/2-z becomes 1/2+z
- When symmetry is entered into SHELX operations related by inversion are omitted

x,y,z; -x,1/2+y,1/2-z; -x-y-z; x,1/2-y,1/2+z

- x,y,z contains no translation and is 1
- -x,+y,-z is 2 along b
- -x,-y,-z is -1 (one bar)
- x,-y,z is m perpendicular to b
- The Shöenflies symbol then is C2h

x,y,z; -x,1/2+y,1/2-z; -x-y-z; x,1/2-y,1/2+z

- Since this Space Group is $P2_1/c$ it can be concluded
  - The 2 must become 2_1—there must be a translation of ½ along b with the rotation
  - The m must become c – there must be a translation of ½ along c with the mirror perpendicular to b

x,y,z; -x,1/2+y,1/2-z; -x-y-z; x,1/2-y,1/2+z

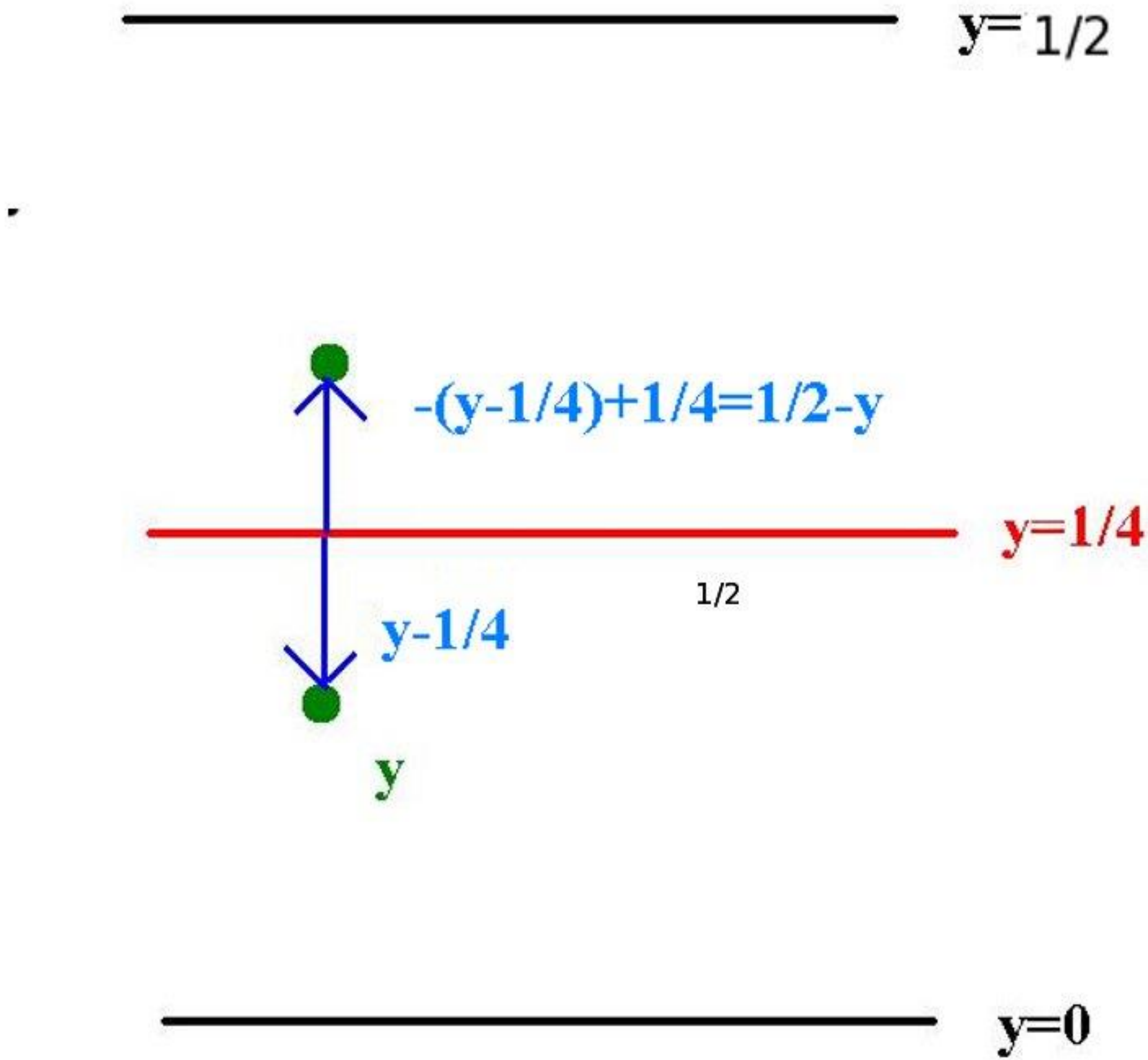
- So the second operation becomes
  - -x,1/2+y,-z
- The fourth operation becomes
  - x,-y,1/2+z
- These do not match the operations for the space group! What is wrong?

A New Wrinkle

In point group symmetry all the symmetry operations must pass through the origin!

In space group symmetry the operations do NOT have to intersect each other or the origin.

For example the plane that is the xz mirror can be at y=1/4!



y= 1/2
-(y-1/4)+1/4=1/2-y
y=1/4
1/2
y-1/4
y
y=0

Offset Symmetry Element

- For an element passing offset in -x by 1/n then the operation will produce a value 1/(2*n)- x
- Thus if the screw axis is offset in z by ¼ it produces -x,1/2+y,1/2-z
- Similarly if the glide plane is at y= 1/4 then it produces x,1/2-y,1/2+z

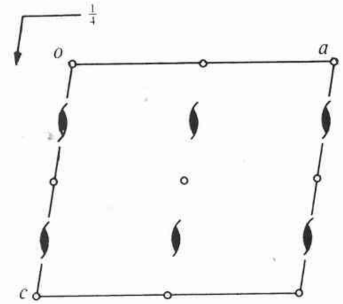
x,y,z; -x,1/2+y,1/2-z; -x-y-z; x,1/2-y,1/2+z

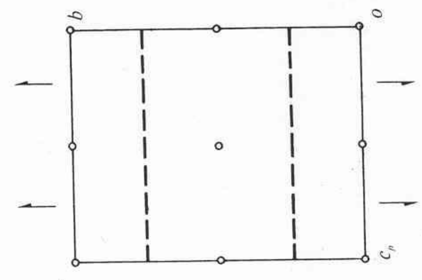
- So we can now explain the entire P21/c operations
- x,y,z is 1
- -x,1/2+y,1/2-z is a 2_1 which intersects the xz plane at (0,0,1/4)
- -x,-y,-z is -1
- x,1/2-y,1/2+z is a c glide where the plane of the mirror is xz and is displaced ¼ along y.

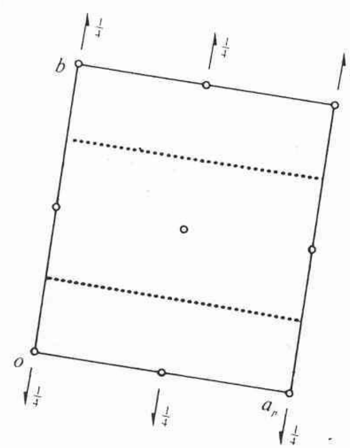
$P\,2_1/c$ C_{2h}^{5} $2/m$ Monoclinic

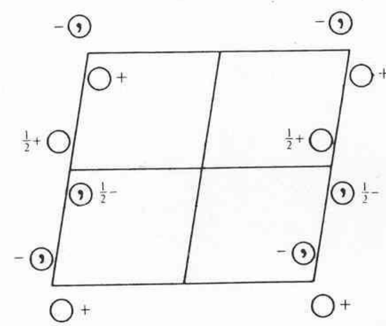
No. 14 $P\,1\,2_1/c\,1$ Patterson symmetry $P\,1\,2/m\,1$

UNIQUE AXIS b, CELL CHOICE 1









Origin at $\bar{1}$

Asymmetric unit $0 \leq x \leq 1;\ \ 0 \leq y \leq \frac{1}{4};\ \ 0 \leq z \leq 1$

Symmetry operations

(1) 1 (2) $2(0,\frac{1}{2},0)\ \ 0,y,\frac{1}{4}$ (3) $\bar{1}\ \ 0,0,0$ (4) $c\ \ x,\frac{1}{4},z$

Types of Space Groups

Centric—containing an inversion center.

Accentric – not containing an inversion center

Polar – not containing inversion, mirrors, glides, or improper rotations. Enantiomorphic!

The origin for a unit cell is defined by the symmetry elements.

Some high symmetry space groups have different “settings” where the origin is defined at different symmetry sites. We will always use the setting where the origin is defined at an inversion center in a symmetric cell.

Standard Axes

For tetragonal, trigonal, hexagonal, and cubic cells the order of the axes is determined.

For triclinic cells the current standard for the angles is they all be acute or obtuse but not a mixture. Usually $a<b<c$.

For monoclinic and orthorhombic cells the order for the axes is that required to produce a standard space group (you do not know the space group until after data collect)

Pnma vs $Pna2_1$

For monoclinic cells the β angle should be greater than 90°

At Purdue we will only work with standard space groups!!

Cell Transformations

- An cell can be transformed into another setting by a transformation matrix
- The transformation is contained in a 3x3 matrix which when multiplied into a,b,c gives the new a',b',c'.

Some comments on Transformations

- Swapping any two axis changes the handedness of the cell.
- A cyclic rotation (abc becomes bca or the reverse cab) maintains handedness.
- Multiplying an axis by -1 changes the angles involving that axis to 180º-angle and the handedness Has no effect on 90º angles.
- The determinat of the transformation is the volume of the new cell. If it is negative then the handedness has changed!

The Simplest Transformation

- This is the case when axes must be swapped
- In monoclinic it is because after determining the space group a and c must be swapped.
- Note since this will switch the handedness one axis must be made negative.
- To keep β obtuse must be b
- 0 0 1
0 -1 0
1 0 0

Effects of a transformation on the H-M Name

- Swapping axes effects both the order of the indices and the glide plane designations.
- Example—Take Pcab and swap a and b
  - Since this changes the handedness must also make an axis negative (for orthorhombic can be any axis)
  - Making an axis negative has no effect on the symmetry operations or the H-M name.
  - 0 1 0
  - 1 0 0
  - 0 0 -1

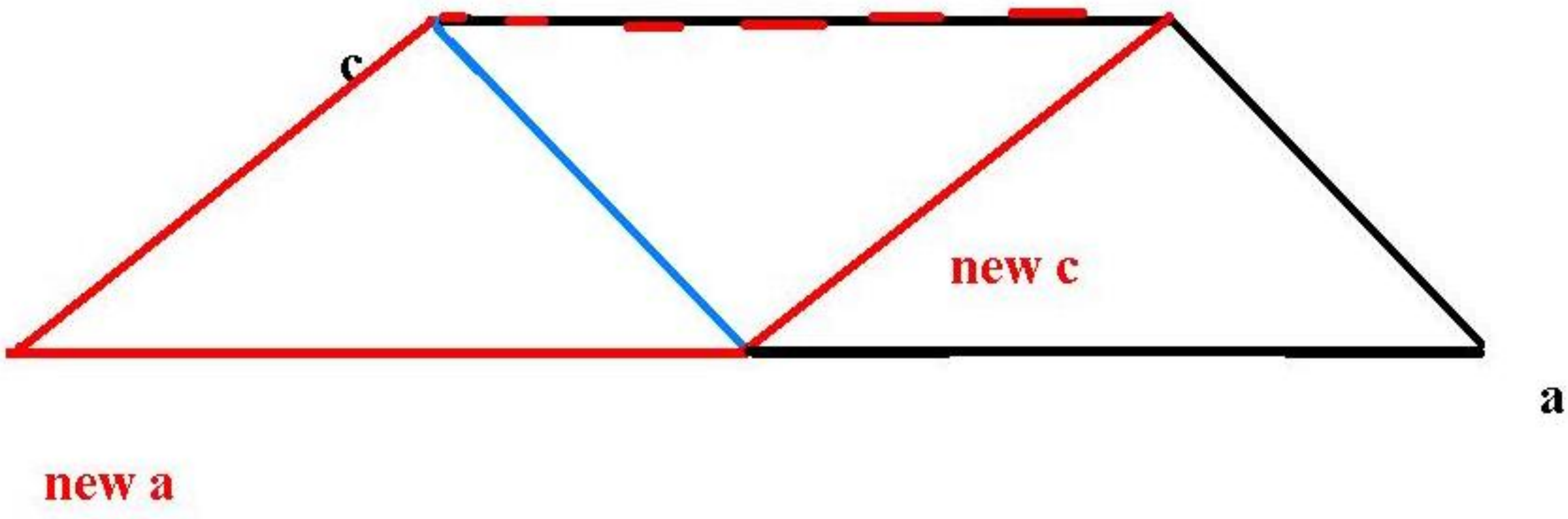
Pcab

- This means a → b; b → a; and c → -c (or just c)
- So the new first position in the name is the old second one which is a. However, a is now b so the new name begins Pb__
- The second position is the old first position. Since c is not changed the new name is Pbc_
- The third position does not move but the b becomes a.
- The new name is Pbca.

More involved Transformations

- If any row has more than one non-zero number than the transformation is more complex.
- There is no easy way to determine the new axes lengths or the new cell angles. This is beyond the scope of this course.
- There is one common such transformation—sort of

The one non-standard cell commonly used is $P2_1/n$ which is derived from $P2_1/c$



The blue line is the glide plane which is along c in $P2_1/c$ but along the diagonal in $P2_1/n$. The new cell coordinates will be more orthogonal but cannot be simply calculated.

$P2_1/n$

- Generally when a monoclinic cell in $P2_1/c$ is indexed there are three possibilities involving a and c.
- 1. The axes are correct as indexed.
- 2. The a axis is actually c and vice versa and will have to be transformed.
- 3. The cell constants are for $P2_1/n$ and we will use this as a standard cell even though it can be transformed to $P2_1/c$

Symmetry in Reciprocal Space

Since there is a one-to-one correspondence between real and reciprocal space then symmetry in real space should be observed in reciprocal space.

In reciprocal space all symmetry operations must pass through the origin so the offsets can be ignored!

Symmetry Ignoring Translations

While there is an effect of translation observed in reciprocal space it only effects reflections located on the translation element.

For the moment we will ignore translation.

Translation will give rise to systematic presences which will allow for determination of space group.

Equivalent Data

In $P2_1/c$ the symmetry elements are x,y,z; -x,y+1/2,-z+1/2; -x,-y,-z; x,-y+1/2;z+1/2

Ignoring translation: x,y,z; -x,y,-z, -x,-y,-z, x,-y,z

There must be a 1:1 correlation between xyz and hkl

Equivalent Data in $P2_1/c$

x,y,z means h,k,l
-x,y,-z means -h,k,-l
-x,-y,-z means -h,-k,-l
x,-y,z means h,-k,l

Since the four positions are equivalent then the four hkl sets are equivalent

h,k,l=-h,k,-l=-h,-k,-l=h,-k,l

That is data for $P2_1/c$ must have the same intensity relationships.

Amount of Data Needed

There are 8 octants of data possible

hkl -hkl h-kl hk-l -h-kl -hk-l h-k-l -h-k-l

Since 4 are equivalent in $P2_1/c$, only two unique octants need to be collected.

This greatly decreases data collection time

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 $Pna2_1$