Name ____

Chemistry 208 X-ray Crystallography

Midterm Exam #1 February 18, 2009

Total 100 points

1. (20 points) Below you will find a periodic array you have seen before.

   a) Use a ruler and a pencil to outline a unit cell. Define the axes. [4 points]

Indicated on array. Other options are possible – any choice should be rectangular and possess the same dimensions. Axes will be defined as x[horizontal] and y[vertical].

   b) Explain your choice of origin in both directions. Is this a primitive cell? [4 points]

This unit cell places the glide planes at x = (0 or ½), and possesses the symmetry of the lattice. Alternative choices exist, but the one presented is the one that happens to match the space group table for this plane group and has the most pleasant placement of the glide planes. The cell is primitive.

   c) Identify the symmetry operations within this unit cell. [4 points]

Two glide planes exist, marked on the unit cell as dashed lines. One is represented by the line (0, y) and the other as (1/2, y).

   d) Using modulo 1 arithmetic, describe the symmetry elements as [x, y] → [new position]. [4 points]

The first mirror plane (0,y) will take the point (x,y) to (-x, y+1/2).
The second mirror plane (1/2, y) will take the point (x,y) to (1-x, y+1/2).
Because (1-x)=(-x+1), and we are in modulo 1 arithmetic, these operations both take (x,y) to (-x, y+1/2).

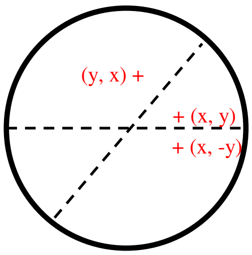
e) Either using the results in d) or by inspection, write out the products of the symmetry elements. [4 points]

A multiplication table for this plane group is quite trivial – the product of the two glides moves a point (x,y) to (x+1, y+1), which is simply related by translation.

PLATE 12

2. (21 points)

a) Show, using a stereographic projection, that a vertical mirror plane perpendicular to the y axis takes x,y to x,-y. [7 points]



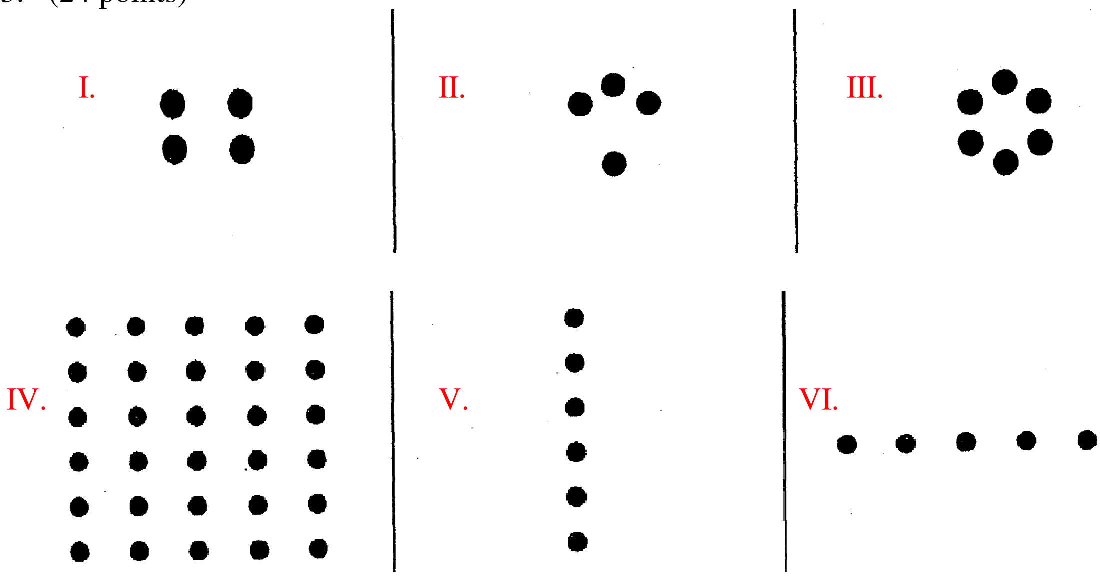
b) Show, on the same stereographic projection, that a mirror plane bisecting the x and y axes takes x,y to y,x. [7 points]

The mirror plane bisecting the axes is along the diagonal.

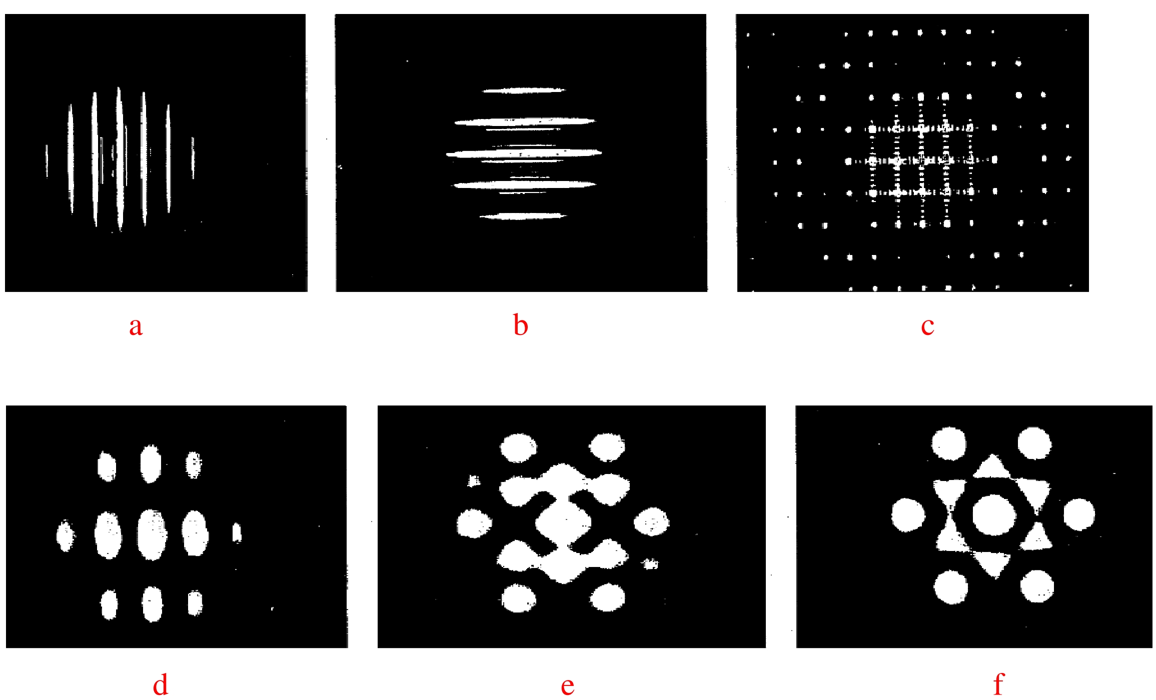
c) Finally, show using both the stereographic projection and the algebraic combination of the two symmetry elements in a) and b) (in that order!) what one operation results from this combination. Must it be proper or improper? [7 points]

Algebraically, it should be clear that the composition of these elements gives (-y, x). This is equivalent to a four-fold rotation. As the composition of two improper operations, we would expect this operation to be proper – which is also consistent with an axis of rotation. Therefore, this is a ***proper*** operation.

3. (24 points)



Correlate the above diffraction gratings with their diffraction patterns, below. *<u>Provide clear justification for each choice.</u>* [4 points each.]



Id. The rectangular symmetry, along with the large, blotty spots, suggest that d is the best choice for this lattice.

IIe. Posessing only mirror symmetry in the lattice, the 'almost' 6-fold symmetry seen here is basically an illusion created by the inversion center always found in the diffraction pattern.

IIIf. The 6-fold symmetry is a giveaway here. No other lattice has the right symmetry.

IVc. The complete lattice gives sharp, clearly defined diffraction spots with the correct symmetry.

Vb. A vertical grating will create diffraction lines in the vertical dimension, with horizontal smearing.

VIa. A horizontal grating will create diffraction lines in the horizontal dimension, with vertical smearing.

4. (15 points)

Your crystal shows mmm Laue symmetry and the general requirement that h+k+*l* be even, which indicates body centering. You consider the space groups I222 (#23), $I2_12_12_1$ (#24), Imm2 (#44) Immm (#71). [attached at end of exam]

a) For each of these groups, which symmetry elements present in the lattice should generate systematic absences?[10 points]

Space Group	I222	$I2_12_12_1$	Imm2	Immm
Symmetry Elements	2_1 axes, body centering	2_1 axes, body centering	2_1 axes, glide planes, body centering	2_1 axes, glide planes, body centering

b) Mindful of the different symmetry elements you highlighted in a), can you choose among these based on your diffraction data? Explain your reasoning ***thoroughly***. [5 points]

Each of these space groups possesses identical Laue symmetry and identical systematic absences. You will be unable to make any distinction by simply examining the space group tables.

Though the absence-generating elements are not identical between the groups, the body-centering condition will mask all of the 'lesser' elements of symmetry which might give clues as to the space group of your crystal. Specifically, it should be clear that the screw-axis generated absences (i.e, h00:h=2n+1) are masked by the glide generated absences (i.e., h0l: h=2n+1), which are in turn masked by the body-centering absences (i.e., hkl: h+k+l=2n+1).

5. (20 points) A diamond (d) glide involves translating ¼ in two directions of the crystal and reflection across the third direction.

a) For an atom at the origin show that this generates an identical atom at ¼,¼,0 if the glide plane is perpendicular to z and passes through the origin. [6 points]

Reflection across the plane perpendicular to z will take (x, y, z) to (x, y, -z). For the origin, this does nothing. The translation will then take the origin to (¼, ¼, 0).

b) For a structure factor $F_{h,k,l}$ what is the phase shift (degrees or radians or cycles) of the scattering by these two atoms? [8 points]

The phase shift in cycles (1 cycle = 2π radians = 360^o) is given by:
$\delta_j = hx + ky + lz$.
$\delta_j = h(¼) + k(¼) + l(0)$.
$\delta_j = h/4 + k/4$

c) Using an Argand diagram sketch the phase shift for the following Miller indices: 1,0,0; 1,1,0; 1,0,1; 4,0,0 [8 points, 2 points each]

Plugging these (h,k,l) values into our answer from b), we obtain shifts of ¼, ½, ¼, and 1 cycle. These are represented on an Argand diagram (Cartesian coordinates with a real[x] and imaginary[y] axes) as vectors (of equal length F_{hkl}) with angles of π (180^o), $\pi/2$(90^o), π(180^o), and 2π(0 or 360^o).