

## Assignment 2

Due: Tuesday, March 14

### Question #1

1. A study of crystalline sample of molybdenum hexacarbonyl,  $\text{Mo}(\text{CO})_6$ , showed to be molecular and to crystallize in the space group  $Pnma$  (No. 62). Discuss the possible locations and the symmetries of the ions if there were: (i) 8 formula units per cell (ii) 4 formula units per cell (iii) 2 formula units per cell.

*For  $Pnma$ , the symmetry matrices are:*

*Symmetry Matrices:*

- (1)  $x, y, z$
- (2)  $0.5-x, -y, 0.5+z$
- (3)  $0.5+x, 0.5-y, 0.5-z$
- (4)  $-x, 0.5+y, -z$
- (5)  $-x, -y, -z$
- (6)  $0.5+x, y, 0.5-z$
- (7)  $0.5-x, 0.5+y, 0.5+z$
- (8)  $x, 0.5-y, z$

*which indicate that there must be 8 asymmetric units in the unit cell.*

*i) If there are 8 formula units per cell, then the molecules are located at general positions  $(x,y,z)$  with 1 symmetry and each of the other positions generated by the relationships listed above. This implies that there are no restrictions on the coordinates of any of the atoms in the compound.*

*ii) If there are 4 formula units per unit cell, this implies that only  $\frac{1}{2}$  of each of the compound's atoms are found in the asymmetric unit thus the molecule must be located either on a mirror/glide plane or on an inversion center. These special positions are found at:*

*For the sites with  $m$  symmetry:*

- (1)  $x, 0.25, z$
- (2)  $-x+0.5, 0.75, z+0.5$
- (3)  $-x, 0.75, -z$
- (4)  $x+0.5, 0.25, -z+0.5$

*For the sites with  $-I$  symmetry:*

- (1)  $0, 0, 0.5$
- (2)  $0.5, 0, 0$

- (3) 0, 0.5, 0.5  
 (4) 0.5, 0.5, 0

or

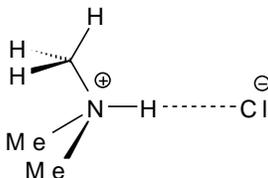
- (1) 0, 0, 0  
 (2) 0.5, 0, 0.5  
 (3) 0, 0.5, 0  
 (4) 0.5, 0.5, 0.5

Note that the complex has a structure that can accommodate either mirror or inversion symmetry and thus any of the above sets would be possible.

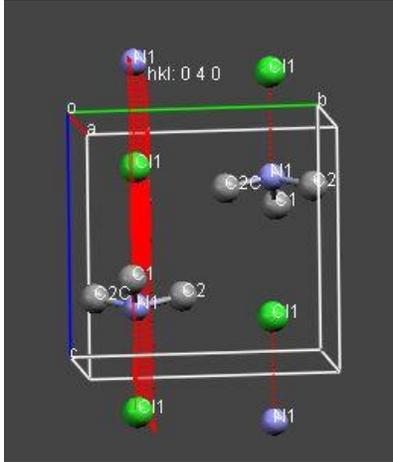
iii) If there are 2 formula units per unit cell, this implies that only  $\frac{1}{4}$  of each of the molecule's atoms are found in the asymmetric unit. Although the octahedral symmetry of the complex would allow for such a situation, the space group does NOT have any positions of high enough symmetry to produce this result so the choice of space group (or unit cell) must have been incorrect!

2.  $\text{Me}_3\text{NHCl}$  crystallizes in a monoclinic centrosymmetric space group, with  $a = 6.09$ ,  $b = 7.03$ ,  $c = 7.03$  Å,  $\beta = 95.73$  and  $Z = 2$ . The only limiting condition is  $0k0$   $k = 2n$ . What is the space group? Comment on the probable positions of (a) Cl (b) C (c) N (d) H atoms.

The systematic absence indicates the presence of only a  $2_1$  along  $b$ , so the space group could either be  $P2_1$  or  $P2_1/m$ . Since  $P2_1$  is not centrosymmetric, the space group must be  $P2_1/m$ . For  $P2_1/m$ , there are 4 asymmetric units per unit cell so since  $Z = 2$ , only half of the cation and anion will be present in the asymmetric unit. As in question 1, there are several choices of positions having either  $-1$  or  $m$  symmetry, however, in this case, the cation ( $\text{Me}_3\text{NH}$ ) can not conform to  $-1$  symmetry so it must be located on a mirror plane. This implies that the cationic fragment pictured below:



Thus two H atoms (one on N the other on the methyl group on the  $m$ ), the N and one C atom must be on the  $m$  plane. While the position of the Cl atom is not required to be on the  $m$  plane (since Cl could also sit on a position with  $-1$  symmetry), because we are Chemists who know about the importance of H-bonding, we would predict that the Cl atom is likely to be found in the  $m$  plane as well, although not necessarily in the position that I have drawn in the picture. The other H atoms and C atoms are related to an equivalent atom by the  $m$  plane. The real locations of the atoms in the unit cell are shown below:



3. Calcium (Ca) crystallizes in a cubic space group with  $a = 5.56 \text{ \AA}$  and we observe a reflection corresponding to a d-spacing of  $1.85 \text{ \AA}$ . What families of planes ( $hkl$ ) could contribute to this reflection?

For a cubic system:  $d = (a^2/(h^2 + k^2 + l^2))^{1/2}$  thus  $(h^2 + k^2 + l^2) = (a/d)^2$

$(a/d)^2 = (5.56 \text{ \AA}/1.85 \text{ \AA})^2 = (3)^2 = 9$ , thus the families of planes that can contribute to this reflection must have:

$(h^2 + k^2 + l^2) = 9$ . So the possible planes are:  $(\pm 1 \pm 2 \pm 2)$ ,  $(\pm 2 \pm 1 \pm 2)$ ,  $(\pm 2 \pm 2 \pm 1)$ ,  $(\pm 3 \pm 0 \pm 0)$ ,  $(\pm 0 \pm 3 \pm 0)$ , and  $(\pm 0 \pm 0 \pm 3)$ . These are readily summarized  $\{122\}$ ,  $\{212\}$ ,  $\{221\}$ ,  $\{300\}$ ,  $\{030\}$ ,  $\{003\}$ : note that the cubic symmetry actually relates all of the  $\{221\}$  families and all of the  $\{300\}$  families so there are really only two independent families of planes, but I only wanted you to show me that any planes with the appropriate  $hkl$  values would contribute.

4. The default setting for the analysis software on the powder X-ray diffractometer lists peaks by their d-spacing instead of by their diffraction angle. Explain why d-spacing is a more useful default using a plane from Ca as an example.

The reason that the default setting of the software lists peaks by d-spacing instead of by diffraction angle is because d-spacing is an inherent property of the crystal and it will not change from one experiment to another. The diffraction angle is dependent on the wavelength of the X-radiation used, as indicated by Bragg's law:

$$\lambda = 2d \sin \theta$$

Planes with a d-spacing of  $1.85 \text{ \AA}$  will have a diffraction angle of  $11.07^\circ$  if we use  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and they will have a diffraction angle of  $24.63^\circ$  if we use  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). It is therefore much easier to compare data collected under different conditions if they are reported in terms of d-spacings. In effect, this is a way to standardize the data obtained from diffraction experiments.

5. For a primitive cubic lattice composed of only one type of atom:

- (a) What are the positions of each of the atoms in the unit cell (using the standard setting with positions in fractional coordinates)?

In a primitive unit cell, the atom locations are only at the corners, thus the positions are:  $(0,0,0)$ ,  $(1,0,0)$ ,  $(0,1,0)$ ,  $(0,0,1)$ ,  $(1,1,0)$ ,  $(1,0,1)$ ,  $(0,1,1)$ ,  $(1,1,1)$

(b) What fraction of each atom is contained within the unit cell?

The fraction of each atom contained within the unit cell is  $1/8$ .

(c) Using the information from (a) and (b), calculate the value of a general structure factor,  $F(hkl)$ , for this structure in terms of the atomic scattering factor  $f_{atom}$ . Remember that:  $\exp(i\theta) = \cos(\theta) + i\sin(\theta)$ .

$$F(hkl) = \sum f_{atom} \exp[2\pi i(hx_j + ky_j + lz_j)]$$

Filling in the values for all the  $(x,y,z)$  coordinates for the summation gives:

$$F(hkl) = 1/8 f_{atom} \{ \exp[2\pi i(0)] + \exp[2\pi i(h)] + \exp[2\pi i(k)] + \exp[2\pi i(l)] + \exp[2\pi i(h+k)] + \exp[2\pi i(h+l)] + \exp[2\pi i(k+l)] + \exp[2\pi i(h+k+l)] \}$$

Since  $\exp[2\pi i(n)] = \cos[2\pi(n)] + i\sin[2\pi(n)]$ , and  $n$  must be an integer in this case (making the  $i\sin$  term = 0),  $\exp[2\pi i(n)] = \cos[2\pi(n)] = 1$ . Thus:

$$F(hkl) = 1/8 f_{atom} \{ 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 \}$$

$$F(hkl) = f_{atom}$$

(d) Comment on the importance/utility of your result in part (c).

While there are many possible answers to (d), from a practical standpoint, this means that you only have to calculate the structure factor for the atom at the origin to account for the contribution that would arise from each of the atoms at the corners of the cell. Another important aspect is the simplification that arises from not having imaginary components to consider, etc.

(e) Calculate the general structure factor for a face-centered cubic lattice.

In an FCC unit cell, there are atoms located at the corners (as in the primitive cell in part a), thus the positions are:

$(0,0,0)$ ,  $(1,0,0)$ ,  $(0,1,0)$ ,  $(0,0,1)$ ,  $(1,1,0)$ ,  $(1,0,1)$ ,  $(0,1,1)$ ,  $(1,1,1)$  and we have already determined that this leads to:  $F(hkl) = f_{atom}$

In addition, there are atoms located in the center of each face:

$(0,0.5,0.5)$ ,  $(0.5,0,0.5)$ ,  $(0.5,0.5,0)$ ,  $(1,0.5,0.5)$ ,  $(0.5,1,0.5)$ ,  $(0.5,0.5,1)$  and there is  $1/2$  of each atom contained within the unit cell. This is equivalent to having whole atoms located at  $(0,0.5,0.5)$ ,  $(0.5,0,0.5)$ ,  $(0.5,0.5,0)$  thus the total summation is:

$$F(hkl) = f_{atom} + f_{atom} \{ \exp[2\pi i(h/2 + k/2)] + \exp[2\pi i(h/2 + l/2)] + \exp[2\pi i(k/2 + l/2)] \}$$

Again,  $h$ ,  $k$  and  $l$  must be integers. If  $h$ ,  $k$  and  $l$  are all even or all odd, the summation becomes:

$$F(hkl) = f_{atom} + f_{atom} \{1 + 1 + 1\}$$

$$F(hkl) = 4 f_{atom}$$

If two of  $h$ ,  $k$  or  $l$  are even and the other one is odd, or if two are odd and the other one is even, then the summation becomes:

$$F(hkl) = f_{atom} + f_{atom} \{1 - 1 - 1\} \quad (\text{i.e. two of the terms must be } -1 \text{ because } \exp(n\pi i) = (-1)^n)$$

$$F(hkl) = 0$$

This is the reason for the systematic absence conditions found in a face centered lattice.

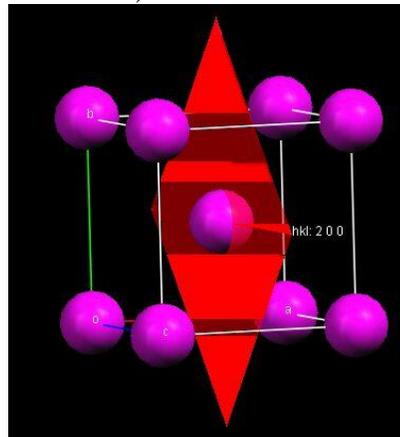
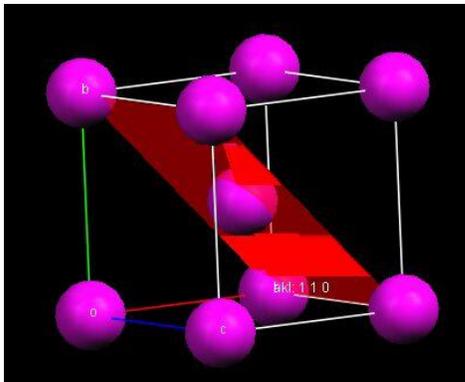
6. Tantalum (Ta) crystallizes in a cubic space group with  $a = 3.3013 \text{ \AA}$ . Reflections for the following families of planes are observed:

$(110)$ ,  $(200)$ ,  $(211)$ ,  $(220)$ ,  $(310)$ ,  $(222)$ ,  $(321)$ ,  $(400)$ ,  $(411)$ ,  $(420)$ ,  $(332)$ ,  $(431)$

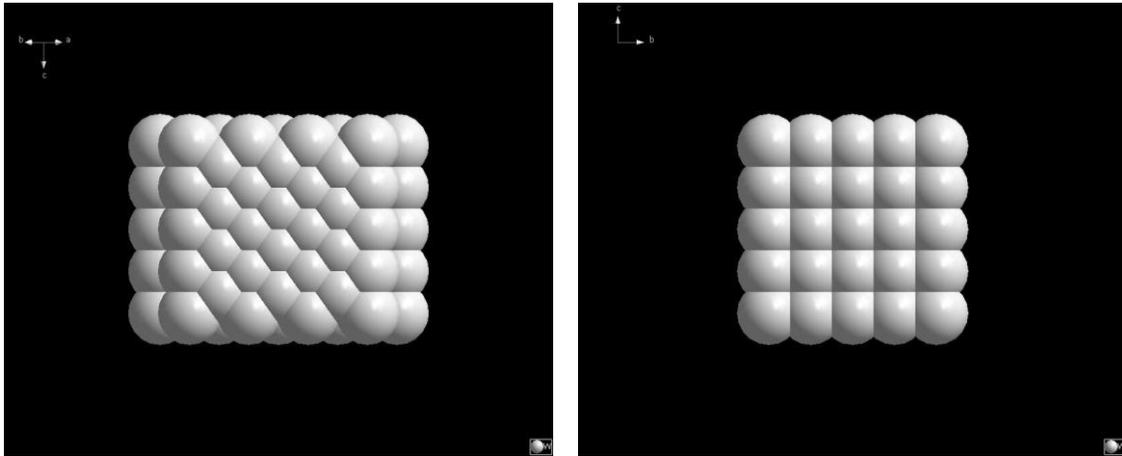
(a) What type of cubic lattice do these data imply?

Since the  $hkl$  values are not all odd or all even for a given reflection, a face-centered cubic cell is not possible. These data are consistent with a body-centered lattice (while a primitive lattice is not excluded, one would have expected to see additional reflections such as  $(100)$ ,  $(111)$ , etc. for a primitive lattice).

(b) Which reflection  $(110)$  or  $(200)$  should be more intense? (note: just draw one representative plane for each  $(hkl)$  to help you make your decision)



From these drawings it is clear that the  $(110)$  planes contain 1.5 atoms per unit cell (for a plane with an area of  $(3.3013\text{\AA})^2 \cdot (1 \cdot 2^{1/2})$ ) whereas the  $(200)$  planes only contain one atom per unit cell (for a plane with an area of  $(3.3013\text{\AA})^2$ ), thus one would predict that the  $(110)$  planes will be more intense because there will be more electrons per unit area in those planes available to scatter the X-rays. The space filling models below show that the density of atoms in the  $(110)$  planes is actually more than the density of atoms in the  $(200)$  planes.



(c) Determine the structure factors for the  $(110)$  and  $(200)$  planes. Note that the atomic scattering factors in units of electrons are:  $f_{Ta}(110) = 57$ ;  $f_{Ta}(200) = 50$ .

Using the simplification you determined in question 5, you only have to use the coordinates  $(0,0,0)$  and  $(0.5,0.5,0.5)$  for these calculations. Note that, when  $n$  is an integer,  $\exp(n\pi i) = (-1)^n$ , and likewise  $\cos(\pi n) = (-1)^n$ , if you prefer to figure it out that way so:

$$F(hkl) = \sum f_{atom} \exp[2\pi i(hx_j + ky_j + lz_j)]$$

Filling in the values for all the  $(x,y,z)$  coordinates for the summation gives:

$$F(110) = f_{Ta(110)} \{ \exp[2\pi i(0)] + \exp[2\pi i((1)(0.5) + (1)(0.5) + (0)(0.5))] \} = 2 f_{Ta(110)}$$

$$F(110) = 2(57) = 114$$

Likewise,

$$F(200) = f_{Ta(200)} \{ \exp[2\pi i(0)] + \exp[2\pi i((2)(0.5) + (0)(0.5) + (0)(0.5))] \} = 2 f_{Ta(200)}$$

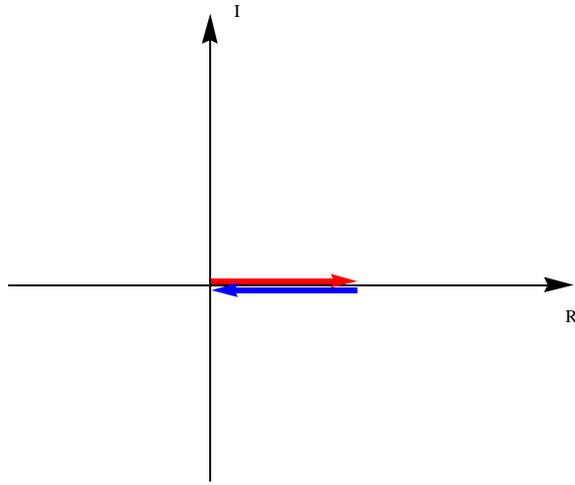
$$F(200) = 2(50) = 100$$

(d) Determine the structure factor for the  $(111)$  plane if  $f_{Ta}(111) = 54$ . Draw an Argand diagram to illustrate your result.

$$F(111) = f_{Ta(111)} \{ \exp[2\pi i(0)] + \exp[2\pi i((1)(0.5) + (1)(0.5) + (1)(0.5))] \} = f_{Ta(111)} \{ 1 + \exp[3\pi i] \}$$

$$F(111) = f_{Ta(111)} \{ 1 - 1 \} = 0$$

*This indicates that (111) must be systematically absent from the diffraction pattern, as we would expect for an I-centered cubic cell! The Argand diagram would just consist of two vectors on the real axis that cancel each other and the resultant vector has 0 magnitude.*



7. Determine the final magnitude  $|F|$  and phase  $\alpha$  obtained by the addition of the following atomic scattering factors (or waves) and draw an approximate Argand diagram to illustrate the process:

$f_j$	$\phi_j(^{\circ})$
33	45
9	120
7	140
7	-10
7	180
6	-90
1	-110
1	-100
1	-105

Here is the spreadsheet I used to add the vectors together:

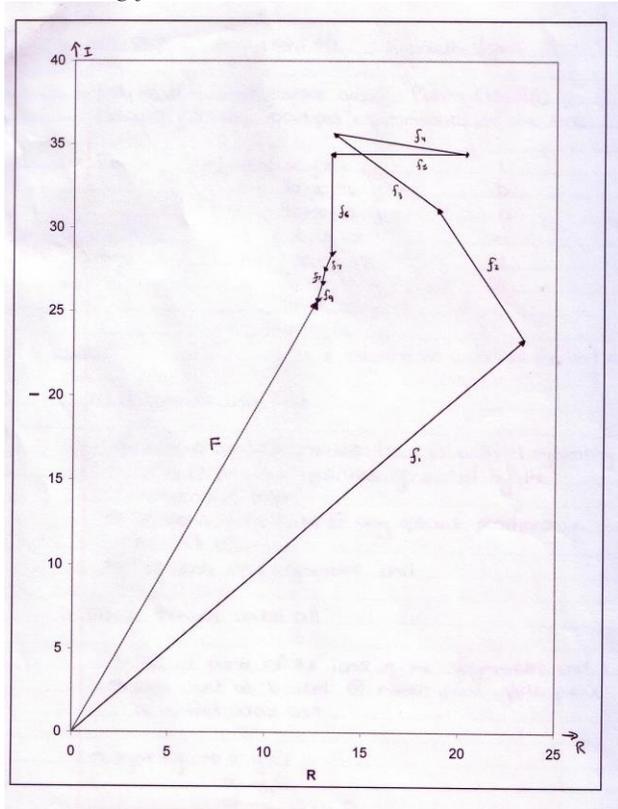
$f_j$	degrees	radians	A	B
33	45	0.785398	<b>23.33452</b>	<b>23.33452</b>
9	120	2.094395	<b>-4.5</b>	<b>7.794229</b>
7	140	2.443461	<b>-5.36231</b>	<b>4.499513</b>
7	-10	-0.17453	<b>6.893654</b>	<b>-1.21554</b>
7	180	3.141593	<b>-7</b>	<b>8.58E-16</b>
6	-90	-1.5708	<b>3.68E-16</b>	<b>-6</b>
1	-110	-1.91986	<b>-0.34202</b>	<b>-0.93969</b>
1	-100	-1.74533	<b>-0.17365</b>	<b>-0.98481</b>
1	-105	-1.8326	<b>-0.25882</b>	<b>-0.96593</b>

Resultant	A	B
	<b>12.59138</b>	<b>25.5223</b>

	F	alpha	
F	28.45928	1.112484	radians
<b>F</b>	<b>28.45928</b>	<b>63.74066</b>	degrees

The resultant vector has a magnitude of 28.46 and a phase angle of 63.74°. The Argand diagram showing the addition of the component scattering factor vectors to give the resultant structure factor vector is shown below (courtesy of a former student).

Argand Diagram which illustrates the determination of the final magnitude and phase for the atomic scattering factors listed above.



Comment briefly on the phase you have calculated.

The most important thing to notice is that the phase of the resultant vector is **similar** to the phase of the heavy atom. In other words, the phase of the resultant vector is predominantly determined by the phase of the largest component vector (which must arise from the heaviest atom) if there is only one very heavy atom. This is the basis of the Patterson method and it shows how locating the position/phase of a heavy atom provides a good starting point for solution and refinement.