

- 1) Indicate which species below (if either) will have a larger atomic scattering factor ( $f_j$ ), and provide a short rationale for your choice.
- a)  $\text{Ca}^{2+}$  or  $\text{Sr}^{2+}$  ( $\text{Sr}^0$  will have another full shell of electrons, and a *much* larger structure factor.)
  - b)  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  (Nuclear charge is conserved here – the extra electron on  $\text{Fe}^{2+}$  should give it a greater factor. As a practical matter, however, the difference is small – structure factors are not considered to vary with oxidation state and a single factor is used for any instance of a particular atom.)
  - c)  $\text{Mg}^{2+}$  or  $\text{Na}^+$  (As these two are isoelectronic, the larger nuclear charge of  $\text{Mg}^{2+}$  should hold the electrons more tightly.  $\text{Mg}^{2+}$  will have the greater structure factor.)
  - d)  $^{12}\text{C}$  or  $^{13}\text{C}$  (Neither should be higher. Nuclear mass should be completely irrelevant.)
- 2) For each of the reflection conditions (due to systematic absences) listed below, indicate the symmetry element indicated. Provide proof that this element of lattice symmetry provides the indicated systematic absences (Massa 6.6.2 can provide a model if these directions are unclear).

a)  $h00, h = 2n+1$ .

This indicates a  $2_1$  screw axis in the  $a$  direction. From the general position which I will call atom **A**, at  $(x,y,z)$ , this symmetry operation generates a symmetry-related atom at **B**, with coordinates  $(x + \frac{1}{2}, -y, -z)$ . We can describe the phases of each of these atoms according to the  $\delta = \mathbf{h} \cdot \mathbf{r}$  formula (where  $\delta$  is the phase shift in cycles).

$$\delta_A = hx + ky + lz$$

$$\delta_B = h(x + \frac{1}{2}) + k(-y) + l(-z)$$

In order to generate systematic absences, these atoms will need to be in phase. Specifically, this can be described as the relationship:

$$\delta_B - \delta_A = n$$

Substitution of the prior equations gives:

$$h(x + \frac{1}{2}) + k(-y) + l(-z) - hx - ky - lz = n$$
$$\frac{h}{2} - 2ky - 2lz = n$$

As a result, systematic absences will only occur where  $k = l = 0$ , which is the  $h00$  plane. Within that plane, this equation becomes:

$$\frac{h}{2} = n$$

Multiplying this equation by 2 gives the reflection condition.

b)  $0k0$ ,  $k = 4n$ .

This is the absence condition for a four-fold screw axis ( $4_n$ ) along b. While there will be four atoms per unit cell, we need only consider two – if these two interfere destructively, the next two will as well. (The third atom will be exactly in phase with the first, and the fourth with the second.) Thus, we construct two atoms **A** and **B** as above, which will have positions  $(x,y,z)$  and  $(-z, y + 1/4, x)$ , and write the constructive interference condition as above:

$$\begin{aligned} h(-z) + k\left(y + \frac{1}{4}\right) + l(x) - hx - ky - lz &= n \\ -hz + \frac{k}{4} + lx - hx - lz &= n \end{aligned}$$

Again, establishing systematic conditions requires that the  $h = l = 0$ , or that we only look to the  $0k0$  plane. The above relationship simplifies to:

$$\frac{k}{4} = n$$

Multiplication by 4 gives the reflection condition  $0k0$ :  $k = 4n$ .

c)  $hk0$ ,  $k = 2n$ .

This is the condition for a b glide perpendicular to c. Atoms **A** and **B** will be  $(x,y,z)$  and  $(x, y + 1/2, -z)$ . Therefore, our constructive interference condition is:

$$\begin{aligned} h(x) + k\left(y + \frac{1}{2}\right) + l(-z) - hx - ky - lz &= n \\ \frac{k}{2} - 2lz &= n \end{aligned}$$

Here, we need only  $l = 0$ , which is the  $hk0$  plane. This simplifies our equation to:

$$\frac{k}{2} = n$$

Which gives the reflection condition  $hk0$ :  $k = 2n$ .

d)  $hkl$ ,  $h + k = 2n$ .

This is the reflection condition for  $[\ ]$ . We generate **A** and **B** with coordinates  $(x,y,z)$  and  $(x + 1/2, y + 1/2, z)$ :

$$\begin{aligned} h\left(x + \frac{1}{2}\right) + k\left(y + \frac{1}{2}\right) + l(z) - hx - ky - lz &= n \\ \frac{h}{2} + \frac{k}{2} &= n \end{aligned}$$

Multiplication by 2 gives the general condition  $hkl$ :  $h + k = 2n$ .

3) The X-ray diffraction intensities for MgO and NaF have *extremely* low intensities for all  $hkl$  *except*  $h, k, l$  all even. Explain. Which compound should have these faint spots be brighter, and why?

$\text{Mg}^{2+}$ ,  $\text{O}^{2-}$ ,  $\text{Na}^+$ , and  $\text{F}^-$  all have 10 electrons so their scattering factors ( $f_j$ ) are very similar. Both compounds face-centered have cubic lattices and since both atoms in the lattice scatter the x-rays similarly, to a first approximation, the crystal diffracts much like a cubic crystal with half of the unit cell length ( $a/2$ ). Although the atoms have similar scattering factors, they are not exactly the same. Thus, while the F-centering requires  $h, k, l$  all even or all odd, the odd values will be very weak (as if  $a^*$ ,  $b^*$ , and  $c^*$  were all halved).

The difference in scattering factors will be more pronounced for MgO than for NaF because the difference in nuclear charge is 4, instead of 2. These almost-absences will be somewhat brighter for MgO as a result.

4) The compound  $\text{Ir}[\text{PPh}_2\text{Me}]_4\text{BF}_4$  [Clark, Skelton & Waters (1975). *J. Organomet. Chem.* 85, 375-394] was reported to crystallize in the space group  $C2/c$  with the cell constants [ $a = 36.805$ ,  $b = 22.93$ ,  $c = 21.676$ ,  $\beta = 121.41^\circ$ ,  $Z=12$ ]. It can alternatively be described with the alternate cell choice of  $R\bar{3}c$ . The transformation matrix which accomplishes this is:

$$\begin{pmatrix} 0 & 1 & 0 \\ \frac{1}{2} & \frac{1}{2} & 1 \\ 1 & 0 & -1 \end{pmatrix}$$

a) Write the equations which describe the new cell vectors in terms of the  $C2/c$  lattice vectors.

The matrix given defines the following set of equations relating the original monoclinic cell lattice vectors ( $a_m, b_m, c_m$ ) to the rhombohedral cell lattice vectors ( $a_r, b_r, c_r$ ).

$$\vec{a}_r = -\vec{b}_m$$

$$\vec{b}_r = \frac{1}{2}\vec{a}_m + \frac{1}{2}\vec{b}_m + \vec{c}_m$$

$$\vec{c}_r = \vec{a}_m - \vec{c}_m$$

As a result,  $a_r = 22.93$ .

b) Does the new space group ( $R\bar{3}c$ ) have systematic absences which did not appear in the prior space group? Are there systematic absences from  $C2/c$  which disappear? How do you explain these changes (i.e. how can systematic absences appear/disappear when the diffraction pattern has not?)

Both of these space groups have the following elements of symmetry which generate glide planes:

C-face centering ( $hkl$ ,  $h+k=2n$ ) and c-glide are present in both space groups, producing the same systematic absences. (In the hexagonal cell, the c-axis is the unique axis – and is always face-centered). Examining the space group tables, you will see that these absences are tabulated quite differently in the two space groups, but the elements of lattice symmetry which produce absences are identical between the two space groups.

- 5) The compound  $U(C_8H_8)_2$  shows  $2/m$  symmetry in its diffraction photographs and the systematic conditions:  $h0l$ ,  $h+l=2n$ ;  $0k0$ ,  $k=2n$ . The cell constants are  $a = 7.084$ ,  $b = 8.715$ ,  $c = 10.631 \text{ \AA}$ , and  $\beta = 98.75^\circ$ . A density of 2.0 to 2.5 would be reasonable for a compound with this chemical formula.
- Calculate the volume and the number of molecules per unit cell.
  - Identify the symmetry operations which are implied by the systematic absences.
  - Name the space group based on your answer to (b). [Identify any other symmetry operations for the space group which do not appear in your answer to (a).]
  - Is there any symmetry imposed on the molecule? If so, what does this imply about the structure, especially the relative orientations of the  $C_8H_8$  rings?
  - Calculate the closest uranium to uranium distance within the cell.
  - All of the diffraction maxima which correspond to  $h+k+l=2n+1$  are very weak, often to the point of not being observable. Explain.

- (a). Uranocene  $U(C_8H_8)_2$ :  $a = 7.084$ ,  $b = 8.715$ ,  $c = 10.631$ ,  $\beta = 98.75^\circ$

$$V = (\det \mathbf{M})^{1/2} \quad \mathbf{M} = \begin{pmatrix} \vec{a} \cdot \vec{a} & \vec{a} \cdot \vec{b} & \vec{a} \cdot \vec{c} \\ \vec{b} \cdot \vec{a} & \vec{b} \cdot \vec{b} & \vec{b} \cdot \vec{c} \\ \vec{c} \cdot \vec{a} & \vec{c} \cdot \vec{b} & \vec{c} \cdot \vec{c} \end{pmatrix}$$

$$\alpha = \gamma = 90^\circ \Rightarrow \vec{a} \cdot \vec{b} = \vec{b} \cdot \vec{c} = 0$$

$$\beta = 98.75^\circ \Rightarrow \vec{a} \cdot \vec{c} = \vec{c} \cdot \vec{a} = (a)(c)\cos 98.75 = -11.456 \text{ \AA}$$

$$\det \mathbf{M} = \begin{pmatrix} 50.183 & 0 & -11.456 \\ 0 & 75.951 & 0 \\ -11.456 & 0 & 113.02 \end{pmatrix} = 4.208 \times 10^5 \text{ \AA}^6 \Rightarrow 648.69 \text{ \AA}^3$$

The formula weight of uranocene is  $446.327 \text{ g/mol} = 0.60226 \frac{V\rho}{Z}$  (see PS#2 key)

$$\text{With } \rho \approx 2.25 \text{ g: } Z = 0.60226 \left( \frac{(648.69)(2.25)}{446.327} \right) = 1.97 \Rightarrow Z = 2$$

- (b).  $h0l : h+l=2n \Rightarrow n\text{-glide } \perp \text{ to } b$   
 $0k0 : k=2n \Rightarrow 2_1 \text{ along } b$

- (c). Space group:  $P2_1/n$

(d). Since  $Z = 2$ , the uranium atom must lie on an inversion center which imposes inversion symmetry on the molecule. This requires the rings to be eclipsed (carbons aligned) rather than staggered.

(e). Placing the first uranium at 000 puts the second uranium at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$   
The distance is:

$$d\vec{x} = (1/2, 1/2, 1/2)$$

$$[(d\vec{x})^T \cdot \mathbf{M} \cdot (d\vec{x})]^{1/2} = \text{distance} = 7.353\text{\AA}$$

(f). The scattering from the uranium (92 electrons) dominates the diffraction. Since the first uranium is at (0,0,0) and the second uranium is at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , the cell is body centered if we neglect the carbon atoms.