MATRL 218/CHEM277: Assignment 3

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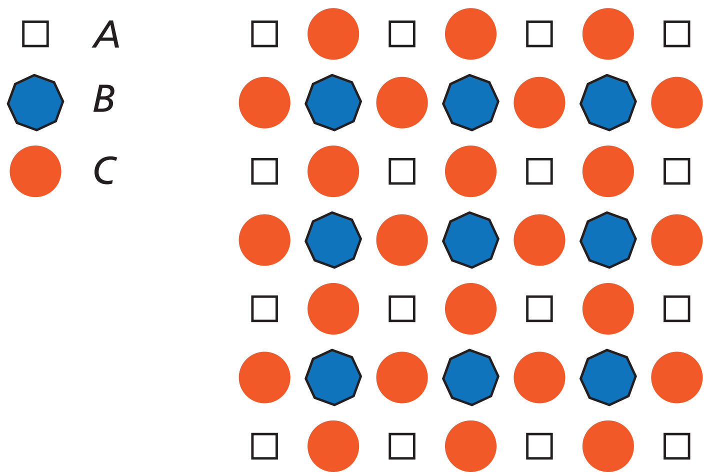
1. The accompanying figure shows a two dimensional crystal structure formed by A, B, and C atoms.



   (a) What is the formula of the compound ?
   (b) Identify the mirrors and rotation axes at the different atom sites.
   (c) Outline the unit cell.
   (d) What is the centering in the crystal ?
   (e) Can you suggest the name of the plane group.
   (f) Provide the complete minimal crystal structure description in terms of the plane group, cell parameters and the atom positions.

2. The compound OsAl has the following structure: SG = $Pm\bar{3}m$, $a = 3.00$ Å, Os at (1/2,1/2,1/2) and Al at (0,0,0).

   (a) Sketch the structure as sections, and within a cube.
   (b) What is this structure type called ?
   (c) $OsAl_2$ is formed by successively stacking OsAl cubes, but every new stack is created from the old one by adding (1/2, 1/2, $\approx$1.5) Sketch $OsAl_2$ as sections after generating its coordinates. Is $OsAl_2$ cubic ? What are the cell parameters?
   (d) Can you guess the space group of $OsAl_2$?
   (e) Can you guess how Os_2Al_3 is built up ?

3. Superconductivity was recently (2008) discovered in iron arsenides. Since then, several other iron containing superconducting compounds with related structures have also been found, including the off-stoichimetric compound $Fe_{1+\delta}Se$. The structure of $Fe_{1.06}Se$ crystallizes in the $P4/nmm$ space group (129), with iron in the $2a$ Wyckoff position (3/4,1/4,0), and selenium in the $2c$ Wyckoff position (1/4,1/4,0.2669). The unit cell dimensions are $a = 3.7747$ Å, $c = 5.5229$ Å. Use VESTA to draw this structure. hint: the space group has two origins, try using origin 2; iron's nearest neighbors should be further than 2 Å away.

   (a) Describe the coordination around Fe (number and disposition of Se neighbors and the distances).

   (b) What kind of polyhedral linking is observed?

   (c) The superconducting behavior is incredibly sensitive to the compound stoichiometry. If iron does not fully occupy the lattice site, and is only there 98.7% of the time (occupancy = 0.987), the using this information, what is the composition in the unit cell?

   (d) Based on the unit cell, what is the structural formula of the compound, assuming one selenium per formula unit? How does it compare to the chemical stoichiometry, $Fe_{1.06}Se$?

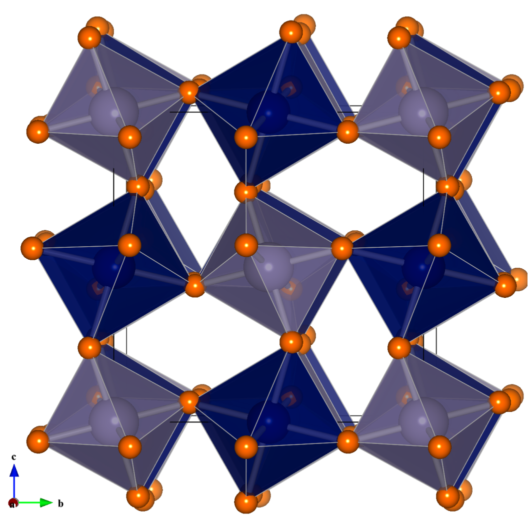
4. Sketch the ideal perovskite ABO_3 structure with A atoms at the corners of the cell and the B atom in the middle. What are the coordinates of A, B and O ? Remember to provide the minimal, crystallographic description. How many nearest neighbors do A, B, and O each have?

5. The mineral Wickmanite (connectivity shown below) has corner-sharing octahedra of $Mn^{2+}O_6$ and $Sn^{4+}O_6$ with Mn^{2+}-O and Sn^{4+}-O bond lengths of 2.15 Å and 2.02 Å, respectively.

   Using the exponential bond-valence-sum relationship,

$$s = \exp\left(\frac{R - R_0}{B}\right),$$

   and the tabulated values for R_0 and B, calculate the bond valence sums (BVS) for Mn(II), Sn(IV), and O? What do the BVS tell you about the composition of the compound (hint: is this an oxide)?



6. Use VESTA to draw all of the binary and ternary structures discussed in class.