Set 4:

Theme: Sphere packing and simple structures

The description of the symmetry of dense packed structures is given in the compendium. This should be revised by going through the examples of the compendium. By this, one will obtain an understanding of terms such as dense packed directions, dense packed planes, unit cells, atom coordinates, Bravais lattice, point symmetry operations, screw axis and space group (symbol). For metal structures, the metal atoms form the packing sphere. There are some cases of phases where small atoms fill holes between dense packed layers, e.g. the Ti-group (Ti, Zr, Hf) is known to dissolve relatively large amounts of hydrogen, carbon, nitrogen and oxygen by interstitial positions. Viz. statistically distributed over a large number of tetrahedra and/or octahedra holes. These holes are largest for the big d-elements and occur for hcp and ccp phases (not to the same extent for bcc!). From hcp and ccp packing of anion spheres (which will form the packing spheres) one can derive the simple NaCl-, NiAs-, würtsitt-, zinkblende-, and antifluorit type structures by that the cations fill 100% if the octahedral holes or 50% of the tetrahedral holes. For CdI_2 and $CdCl_2$ type structures, 50% of the octahedral holes are filled – in a systematically way.

Task 1:

The simplest structures derived from the sphere packing model (se above) is based on that all the packing spheres are of the <u>same</u> kind (ideally of same size, non-compressible and without interactions). In this task we shall consider a more complicated structure type. It is noted as perovskite type and is derived by the sphere packing model by that one applies two different types of packing spheres (X and Y).

1.1.   The ratio of the X and Y spheres are 1:3. The spheres are of equal size and together form dense sphere packing within a two dimensional layer. The distribution of X and Y spheres are systematic. The two-dimensional unit cell has the relations $a = b$, $\gamma = 120°$. The coordinates for the X-sphere are (0,0), for Y (0,1/2) and (1/2,0) and (1/2,1/2). Draw a XY_3 layer and mark the unit cell.

1.2.   You shall now make a three-dimensional dense sphere packing from the XY_3 layers. When XY_3 layers are stacked on top of each other, either in the form of …AB… or …ABC… packing, holes are formed, among others octahedral holes. How many octahedral holes are there in a three dimensional structure of XY_3 units? (Hint: consider a …AB… packing of identical spheres.)

1.3.   Since the 2D-layers do not contain identical spheres, one must make a choice when the layers are stacked. Place the next layer such that an X-sphere goes in the depression between three Y-spheres in the layer below. Consider then what kind of environments (with respect to X and Y) the octahedral holes have (consider all of the octahedra holes for XY_3, confer 1.2.)

1.4.   Let the X spheres be cations and the Y spheres be anions. In the octahedral holes one shall now place other cations, M. However, only some of the octahedral holes are suitable (of electronically reasons). Which holes are filled and how many are there pr. Y (anion) sphere?

1.5.   Consider then a …ABC… packing of XY_3 layers with M in the suitable octahedraholes. Give the coordinates (x,y,z) for the three M atoms in a …ABC… stacking sequence (make a unit cell based on the two-dimensional with the c-axis as origin in one A-layer.).

1.6.   Assume that the X and Y atoms has a diameter of 2.70 Å. Calculate the size of

the octahedrahole. What is the ratio between the diameter of the octahedrehole and a packing sphere?

1.7. Consider the ions Na^+, Nb^{5+} and O^{2-} with ionic radii's of respectively 1.30, 0.78 and 1.40 Å. How would you ascribe these ions to the spheres X, Y and M?

1.8. The structure type you have reached is noted as Perovskite type. You have considered the unit cell from a hexagonal cell. The structure can however be described with the cubic system by setting M in (1/2,1/2,1/2), X in (0,0,0) and Y in (1/2,1/2,0), (0,1/2,1/2) and (1/2,0,1/2). Draw the unit cell. How many formula units does the cell contain? Is the belonging Bravais lattice primitive or centered?

1.9. The ReO_3 type structure is closely related to the perovskite type, however it lack the X atoms. Describe the ReO_3 structure from connection of coordination polyhedra (Hint: draw many unit cells in projection of the e.g. ab-plane).

1.10. Based on the knowledge of the coordination relationships for the cations in the perovskite type structure (X is included in dense packed layers of anions, M in octahedral holes), calculate the coordination numbers for oxygen.

The perovskite type phase has got important physical and chemical properties. They can be ion conducting, ferroelastic, permanent magnets, superconductors, take part in fuel cells or be heterogeneous catalysts.

Task 2:

In this task we shall consider what holes that appears in dense packing of spheres, and consider simple structure types derived from the sphere packing model.
Consider first a hcp sphere packing (…AB…) of identical spheres (X).

2.1. What types of holes occur for hexagonal sphere packing? Sketch the corresponding coordination polyhedra. Which holes can be filled at the same time?

2.2. What structure types have (a) all octahedral holes filled, (b) half of the tetrahedral holes filled?

2.3. Which structure type do you get if each second layer (along the c-axis) of octahedral holes between A and B packing layers are filled with atoms? What composition will a compound with this structure type have? Describe the bonding relations for this structure type.

2.4. The structure of $ScCl_3$ is related to the $CdCl_2$ type structure. This is made by that within each layer of filled octahedral holes in the $CdCl_2$ type structure, 1/3 of the holes are systematically empty. Sketch such a layer with 1/3 empty and 2/3 full octahedraholes.

2.5. Describe the Cs_2O structure with basis in the CdI_2 type structure.

2.6. Consider the NiAs-type structure. What will the composition be altered to if all trigonal bipyramidal holes are filled in addition to the octahedral holes?

2.7. What type of point symmetry does (a) Ni and (b) As feel if you only consider the nearest neighbors in the NiAs type structure? (Hint: draw the coordination polyhedras, for instance as projection on the ab-plane).

2.8. For hcp based structure types a deviation from the ideal c/a ratio ($\sqrt{8/3} = 1.631$) is often observed. Why are these deviations larger for NiAs-type phases than for pure metals and würtsitt-type phases which all have hcp packing?