Supplemental Problems for Chapter 10

1) One overarching trend in atomic structures is that as the coordination number increases, the interatomic separation increases. Using the appropriate equations, answer the following questions.
(i) Can this trend be demonstrated using the 6-12 potential for van der Waals bonding, including only nearest neighbor interactions?
(ii) Can this trend be demonstrated using the 6-12 potential for van der Waals bonding, including long range interactions?
(iii) Can this trend be demonstrated using the ionic bonding model?
(iv) Can this trend be demonstrated using the free electron model?
(v) Can this trend be demonstrated using the bond valence principle?

Review Question

The structure of the mineral Goethite is described in the table below. When the crystal structure is studied by x-ray diffraction, the H positions cannot be identified. So, for the purposes of this exercise, we will take this compound to be FeO_2.

The structure of Goethite FeO(OH), Iron oxyhydroxide

Formula unit	FeO(OH), *Goethite*
Space group:	Pbnm
Cell dimensions:	a = 4.54 Å b = 10.0 Å c = 3.03 Å
Cell contents:	4 formula units per cell
Atomic positions:	all atoms in (4c) ±(x, y, 1/4) and ±(1/2-x, y+1/2, 1/4)
	Fe coords x = -0.0451, y = 0.1446
	O(1) coords x = 0.2880, y = -0.1989
	O(2) coords x = -0.1970, y = -0.0532

(i) 10% Explain why the H positions cannot be determined from X-ray diffraction patterns of this compound.

(ii) 10% Specify the Bravais lattice of this compound, the point group, and sketch the general positions in the point group.

(iii) 10% How are the O atoms packed in this structure? (specify ccp, hcp, bcc, or none of the above) Note, a workspace for sketching the structure is provided on the last page.

(iv) 5% What is the polyhedral arrangement of the O surrounding the Fe atoms?

(v) 5% Compare the Goethite structure to similar a prototype structure or structures that you know. How is it similar and how does it differ?

(vi) 10% At elevated temperatures, Goethite decomposes by evolving H_2O to form a new compound with the stoichiometry Fe_2O_3. There are two polymorphs: α-Fe_2O_3 has the corundum structure (hcp O with Fe in 2/3 of the octahedral sites) and γ-Fe_2O_3 has a spinel related structure (ccp O with Fe distributed in the tetrahedral and octahedral sites). Which polymorph does Goethite form when it decomposes? Explain the reasons for your answer.

(vii) 15% There are symmetry operators in this space group that create systematic absences in the diffraction pattern. List these operators, define their actions, and the absences that they cause.

(viii) 15% Explain how you would use measurements of the intensities of diffracted x-ray beams to determine the x and y parameters. Include appropriate equations.

(ix) 20% Low temperature dehydration reactions, such as the decomposition of FeO(OH) to form Fe_2O_3, usually yield extremely small crystals, with nanometer scale dimensions. Because of the small size of the nanocrystals, their electronic energy levels are different from those in bulk crystals and, because of this, properties sometimes differ. Explain, within the framework of a quantitative bonding model, how the electronic energy levels are influenced by the crystal size.