# Problems

7.1 Determine the point groups of the following unit cells:
  a. Face-centered cubic
  b. Body-centered tetragonal
  c. CsCl (Figure 7.7)
  d. Diamond (Figure 7.6)
  e. Nickel arsenide (Figure 7.10)

7.2 Show that atoms occupy only 52.4% of the total volume in a primitive cubic structure in which all the atoms are identical.

7.3 Show that a sphere of radius $0.73r$, where r is the radius of the corner atoms, will fit in the center of a primitive cubic structure.

7.4 **a.** Show that spheres occupy 74.0% of the total volume in a face-centered cubic structure in which all atoms are identical.
  b. What percent of the total volume is occupied by spheres in a body-centered cube in which all atoms are identical?

7.5 Using the diagrams of unit cells shown below, count the number of atoms at each type of position (corner, edge, face, internal) and each atom's fraction in the unit cell to determine the formulas (M_mX_n) of the compounds represented. Open circles represent cations, and closed circles represent anions.
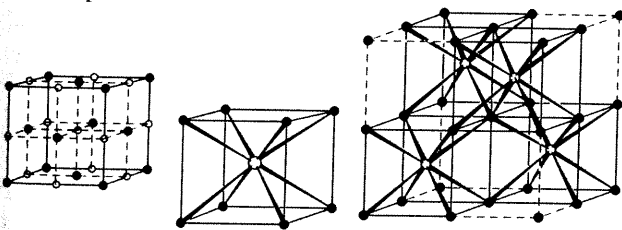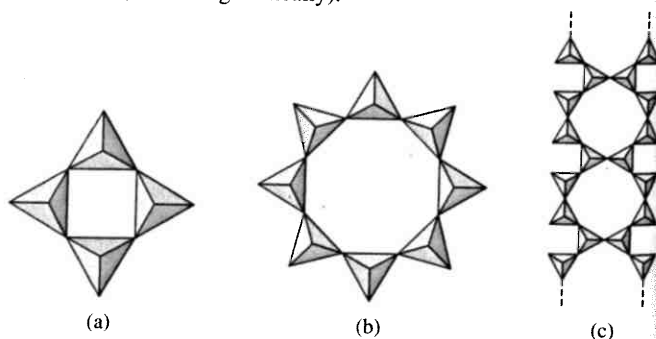

7.6 LiBr has a density of 3.464 g/cm³ and the NaCl crystal structure. Calculate the interionic distance, and compare your answer with the value from the sum of the ionic radii found in Appendix B-1.

7.7 Compare the CsCl and CaF_2 lattices, particularly their coordination numbers.

7.8 Show that the zinc blende structure can be described as having zinc and sulfide ions each in face-centered lattices, merged so that each ion is in a tetrahedral hole of the other lattice.

7.9 Graphite has a layered structure, with each layer made up of six-membered rings of carbon fused with other similar rings on all sides. The Lewis structure shows alternating single and double bonds. Diamond is an insulator, and graphite is a moderately good conductor. Explain these facts in terms of the bonding in each. (Conductance of graphite is significantly lower than metals but is higher than most nonmetals.) What behavior would you predict for carbon nanotubes, the cylindrical form of fullerenes?

7.10 What experimental evidence is there for the model of alkali halides as consisting of positive and negative ions?

7.11 Mercury(I) chloride and all other Hg(I) salts are diamagnetic. Explain how this can be true. You may want to check the molecular formulas of these compounds.

7.12 **a.** Formation of anions from neutral atoms results in an increase in size, but formation of cations from neutral atoms results in a decrease in size. What causes these changes?
  b. The oxide ion and the fluoride ion both have the same electronic structure, but the oxide ion is larger. Why?

7.13 Calculate the radius ratios for the alkali halides. Which fit the radius ratio rules, and which violate them? (See L. C. Nathan, *J. Chem. Educ.*, **1985**, *62*, 215.)

7.14 Comment on the trends in the following values for interionic distances (pm):

LiF	201	NaF	231	AgF	246
LiCl	257	NaCl	281	AgCl	277
LiBr	275	NaBr	298	AgBr	288

7.15 Calculate the electron affinity of Cl from the following data for NaCl, and compare your result with the value in Appendix B-1: Cl_2 bond energy = 239 kJ/mol; $\Delta H_f(NaCl) = -413$ kJ/mol; $\Delta H_{sub}(Na) = 109$ kJ/mol; $IE(Na) = 5.14$ eV; and $r_+ + r_- = 281$ pm.

7.16 CaO is harder and has a higher melting point than KF, and MgO is harder and has a higher melting point than CaF_2. CaO, KF, and MgO have the NaCl structure. Explain these differences.

7.17 Calculate the lattice energies of the hypothetical compounds $NaCl_2$ and MgCl, assuming that the Mg^+ and Na^+ ions and the Na^{2+} and Mg^{2+} ions have the same radii. How do these results explain the compounds that are found experimentally? Use the following data in the calculation: Second ionization energies ($M^+ \longrightarrow M^{2+} + e^-$): Na, 4562 kJ/mol; Mg, 1451 kJ/mol; enthalpy of formation: NaCl, –411 kJ/mol; $MgCl_2$, –642 kJ/mol.

7.18 Use the Born–Haber cycle to calculate the enthalpy of formation of KBr, which crystallizes in the NaCl lattice. Use these data in the calculation: $\Delta H_{vap}(Br_2) = 29.8$ kJ/mol; Br_2 bond energy = 190.2 kJ/mol; and $\Delta H_{sub}(K) = 79$ kJ/mol.

7.19 Use the Born–Haber cycle to calculate the enthalpy of formation of MgO, which crystallizes in the NaCl lattice. Use these data in the calculation: O_2 bond energy = 494 kJ/mol; $\Delta H_{sub}(Mg) = 37$ kJ/mol. Second ionization energy of Mg = 1451 kJ/mol; second electron affinity of O = –744 kJ/mol.

7.20 Using crystal radii from Appendix B-1, calculate the lattice energy for PbS, which crystallizes in the NaCl structure. Compare the results with the Born–Haber cycle values obtained using the ionization energies and the following data for enthalpies of formation. Remember that enthalpies of formation are calculated beginning with the elements in their standard states. Use these data: ΔH_f; $S^{2-}(g)$, 535 kJ/mol;

Pb(g), 196 kJ/mol; PbS, −98 kJ/mol. The second ionization energy of Pb = 15.03 eV.

7.21 In addition to the doping described in this chapter, n-type semiconductors can be formed by increasing the amount of metal in ZnO or TiO_2, and p-type semiconductors can be formed by increasing the amount of nonmetal in Cu_2S, CuI, or ZnO. Explain how this is possible.

7.22 Explain how Cooper pairs can exist in superconducting materials, even though electrons repel each other.

7.23 Referring to other references if necessary, explain how zeolites that contain sodium ions can be used to soften water.

7.24 CaC_2 is an insulating ionic crystal. However, $Y_2Br_2C_2$, which can be described as containing C_2^{4-} ions, is metallic in two dimensions and becomes superconducting at 5 K. Describe the possible electronic structure of C_2^{4-}. In the crystal, monoclinic crystal symmetry leads to distortion of the Y_6 surrounding structure. How might this change the electronic structure of the ion? (See A. Simon, *Angew. Chem., Int. Ed.*, **1997**, *36*, 1788.)

7.25 Gallium arsenide is used in LEDs that emit red light. Would gallium nitride be expected to emit higher or lower energy light than gallium arsenide? How might such a process (emission of light from gallium nitride) be useful?

7.26 A series of ZnSe quantum dots was prepared of a range of sizes, with diameters from approximately 1.5 to 4.5 nm, and the photoluminescence emission spectra were recorded. Were the lowest energy emission bands produced by the largest or smallest quantum dots? Explain. (See V. V. Nikesh, A. D. Lad, S. Kimura, S. Nozaki, S. Mahamuni, *J. Appl. Phys.*, **2006**, *100*, 113520.)

7.27 Medical studies on applications of quantum dots are progressing rapidly. Using appropriate search tools, such as Web of Science and SciFinder, find and briefly describe medical applications of quantum dots other than those mentioned in this chapter. Cite the references you consult.

7.28 The correlation between the size of quantum dots (QDs) and their emission spectra motivates the development of methodology to prepare QDs with specific sizes. The size of CdS QDs can be controlled by employing the reaction of *L*-cysteine and CS_2 as a source of S^{2-} (in the form of H_2S) for combination with Cd^{2+}. The *R*-2-thiotetrahydrothiazole-4-carboxylic acid formed in these reactions further modulates QD size by binding to the QD surface, effectively stabilizing it towards further growth. Which *L*-cysteine/Cd^{2+} molar ratio affords the smallest CdS quantum dots? Which *L*-cysteine/Cd^{2+} molar ratio affords CdS quantum dots that absorb UV-vis radiation of highest energy? (Y.-M. Mo, Y. Tang, F. Gao, J. Yang, Y.-M. Zhang, *Ind. Eng. Chem. Res.*, **2012**, 2012, 51, 5995.)

7.29 A variety of sulfide precursors can be used to prepare CdS QDs, including thiourea (A. Aboulaich, D. Billaud, M. Abyan, L. Balan, J.-J. Gaumet, G. Medjadhi, J. Ghanbaja, R. Schneider, *ACS Appl. Mater. Interfaces*, **2012**, *4*, 2561).

Provide a reaction scheme and describe the reaction conditions employed to prepare 3-mercaptopropionic acid-capped CdS QDs. What reaction time is optimum to achieve the highest energy emission obtained when these QDs are excited with UV radiation? What is the primary influence of the reaction time on the size of these QDs?

7.30 "Digestive ripening" is a technique used for narrowing quantum dot size distributions. The properties of water-soluble CdSe and CdTe QDs change during the ripening process (M. Kalita, S. Cingarapu, S. Roy, S. C. Park, D. Higgins, R. Janlowiak, V. Chikan, K. J. Klabunde, S. H. Bossmann, *Inorg. Chem.*, **2012**, *51*, 4521). What two methods did these chemists employ to assess whether their CdSe or CdTe QDs were larger after digestive ripening? Which quantum dots were larger, and how did the data support this claim?

7.31 The superconductivity of a binary barium germanide, $BaGe_3$, has been established (H. Fukuoka, Y. Tomomitsu, K. Inumaru, *Inorg. Chem.*, **2011**, *50*, 6372). What data were used to determine that $BaGe_3$ was metallic, and what observation prompted the assignment of the 4.0 K critical temperature? Density of states (DOS) calculations help assess orbital contributions to superconductor band structure. Which orbitals contribute the most to the conduction band of $BaGe_3$? Which orbitals contribute most near the $BaGe_3$ Fermi level?

7.32 Understanding connections between "structure and function" is a traditional chemical pursuit, and similar correlations are emerging in the field of FeAs superconductors. A correlation between the a-axis lattice constant and T_c has been noted in both LnFeAsO-based (Ln = lanthanide element) and perovskite-based FeAs superconductors (P. M. Shirage, K. Kikou, C.-H. Lee, H. Kito, H. Eisaki, A. Iyo, *J. Am. Chem. Soc.*, **2011**, *133*, 9630). For LnFeAsO-based materials, what is the optimum a-axis lattice constant that results in the highest T_c? How do the T_c values vary on the basis of the identity of Ln? Do these T_c values exhibit a periodic trend? Explain. For perovskite-based (As) materials, what is the predicted a-axis lattice constant upper limit above which superconductivity would not be expected at any temperature?

7.33 Determine the formulas of the following silicates (c is a chain, extending vertically).

(a) (b) (c)