



Exercises

Review Questions

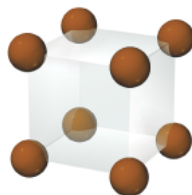
1. What is graphene? Why is graphene unique?
2. Explain the basic principles involved in X-ray crystallography. Include Bragg's law in your explanation.
3. What is a crystalline lattice? How is the lattice represented with the unit cell?
4. Make a drawing of each unit cell: simple cubic, body-centered cubic, and face-centered cubic.
5. For each of the cubic cells in the previous problem, give the coordination number, edge length in terms of r , and number of atoms per unit cell.
6. What is the difference between hexagonal closest packing and cubic closest packing? What are the unit cells for each of these structures?
7. What are the three basic types of solids and the composite units of each? What types of forces hold each type of solid together?
8. What are the three categories of atomic solids?
9. What kinds of forces hold each of the three basic categories of atomic solids together?
10. What is a polymorph?
11. In an ionic compound, how are the relative sizes of the cation and anion related to the coordination number of the crystal structure?
12. Show how the cesium chloride, sodium chloride, and zinc blende unit cells each contain a cation-to-anion ratio of 1:1.
13. Show how the fluorite structure accommodates a cation-to-anion ratio of 1:2.
14. Name and describe the different allotropes of carbon.
15. What are silicates? What is quartz?
16. What is the definition of a *ceramic*? What are the three categories of ceramics?
17. List the major and minor components of Portland cement. What is the difference between the hardening process of Portland cement and the hardening process of clays?
18. How is concrete made from Portland cement? What advantage does concrete have for building compared to the construction methods that predated the development of concrete?
19. Describe what happens on the molecular level when silica is heated and then cooled to make glass.
20. Describe the difference between vitreous silica and soda-lime glass. What are some advantages and disadvantages of each of these types of glass?
21. In band theory of bonding for solids, what is a *band*? What is the difference between the *valence band* and the *conduction band*?
22. In band theory of bonding for solids, what is a band gap? How does the band gap differ in metals, semiconductors, and insulators?
23. Explain how doping can increase the conductivity of a semiconductor. What is the difference between an n-type semiconductor and a p-type semiconductor?
24. What is the trend in the size of the band gap as you move down the column of the group 4A elements?
25. What is a polymer? What is the difference between a polymer and a copolymer?
26. How do an addition polymer and a condensation polymer differ from each other?

Problems by Topic

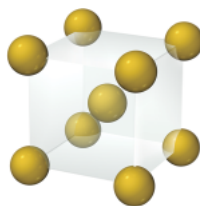
*Note: Answers to all odd-numbered problems can be found in **Appendix III**. Exercises in the Problems by Topic section are paired, with each odd-numbered problem followed by a similar even-numbered problem. Exercises in the Cumulative Problems section are also paired but more loosely. Because of their nature, Challenge Problems and Conceptual Problems are unpaired.*

Types of Solids and Their Structures

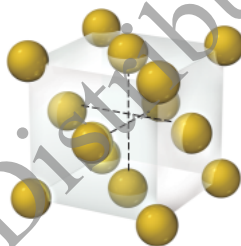
27. An X-ray beam with $\lambda = 154 \text{ pm}$ incident on the surface of a crystal produced a maximum reflection at an angle of $\theta = 28.3^\circ$. Assuming $n = 1$, calculate the separation between layers of atoms in the crystal.
28. An X-ray beam of unknown wavelength is diffracted from a NaCl surface. If the interplanar distance in the crystal is 286 pm and the angle of maximum reflection is found to be 7.23° , what is the wavelength of the X-ray beam? (Assume $n = 1$.)
29. Determine the number of atoms per unit cell for each metal.
- Polonium



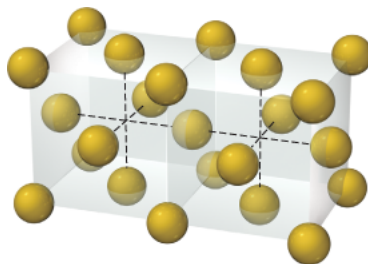
- Tungsten



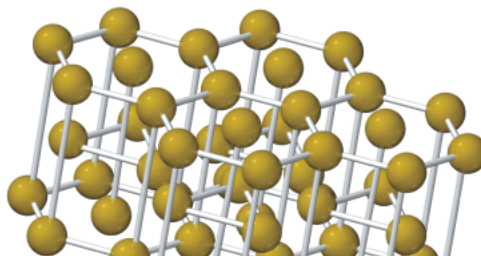
- Nickel

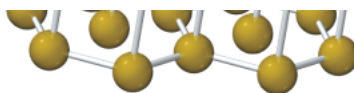


30. Determine the coordination number for each structure.
- Gold

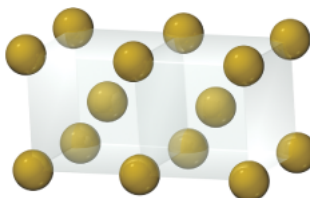


- Ruthenium

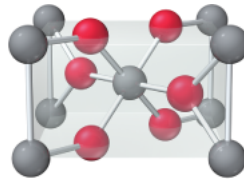




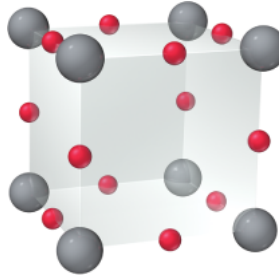
c. Chromium



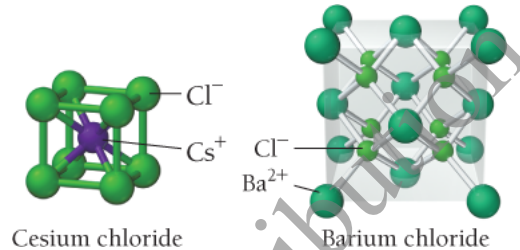
31. Calculate the packing efficiency of the body-centered cubic unit cell. Show your work.
32. Calculate the packing efficiency of the face-centered cubic unit cell. Show your work.
33. Platinum crystallizes with the face-centered cubic unit cell. The radius of a platinum atom is 139 pm. Calculate the edge length of the unit cell and the density of platinum in g/cm^3 .
34. Molybdenum crystallizes with the body-centered unit cell. The radius of a molybdenum atom is 136 pm. Calculate the edge length of the unit cell and the density of molybdenum.
35. Rhodium has a density of $12.41 \text{ g}/\text{cm}^3$ and crystallizes with the face-centered cubic unit cell. Calculate the radius of a rhodium atom.
36. Barium has a density of $3.59 \text{ g}/\text{cm}^3$ and crystallizes with the body-centered cubic unit cell. Calculate the radius of a barium atom.
37. Polonium crystallizes with a simple cubic structure. It has a density of $9.3 \text{ g}/\text{cm}^3$, a radius of 167 pm, and a molar mass of 209 g/mol. Use these data to calculate Avogadro's number (the number of atoms in one mole).
38. Palladium crystallizes with a face-centered cubic structure. It has a density of $12.0 \text{ g}/\text{cm}^3$, a radius of 138 pm, and a molar mass of 106.42 g/mol. Use these data to calculate Avogadro's number.
39. Identify each solid as molecular, ionic, or atomic.
 - a. $\text{Ar}(s)$
 - b. $\text{H}_2\text{O}(s)$
 - c. $\text{K}_2\text{O}(s)$
 - d. $\text{Fe}(s)$
40. Identify each solid as molecular, ionic, or atomic.
 - a. $\text{CaCl}_2(s)$
 - b. $\text{CO}_2(s)$
 - c. $\text{Ni}(s)$
 - d. $\text{I}_2(s)$
41. Which solid has the highest melting point? Why?
 $\text{Ar}(s), \text{CCl}_4(s), \text{LiCl}(s), \text{CH}_3\text{OH}(s)$
42. Which solid has the highest melting point? Why?
 $\text{C}(s, \text{diamond}), \text{Kr}(s), \text{NaCl}(s), \text{H}_2\text{O}(s)$
43. Which solid in each pair has the higher melting point and why?
 - a. $\text{TiO}_2(s)$ or $\text{HOOH}(s)$
 - b. $\text{CCl}_4(s)$ or $\text{SiCl}_4(s)$
 - c. $\text{Kr}(s)$ or $\text{Xe}(s)$
 - d. $\text{NaCl}(s)$ or $\text{CaO}(s)$
44. Which solid in each pair has the higher melting point and why?
 - a. $\text{Fe}(s)$ or $\text{CCl}_4(s)$
 - b. $\text{KCl}(s)$ or $\text{HCl}(s)$
 - c. $\text{Ti}(s)$ or $\text{Ne}(s)$
 - d. $\text{H}_2\text{O}(s)$ or $\text{H}_2\text{S}(s)$
45. An oxide of titanium crystallizes with the unit cell shown here (titanium = gray; oxygen = red). What is the formula of the oxide?



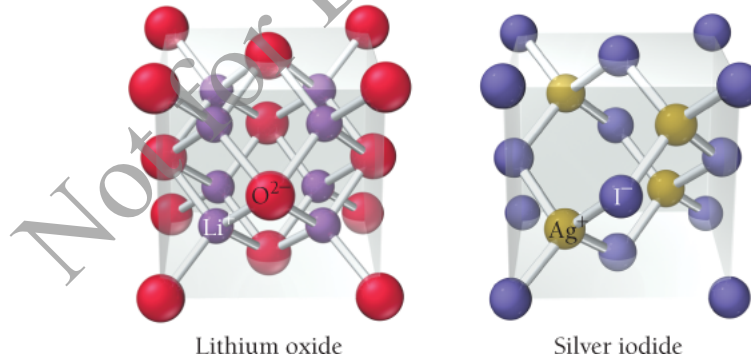
46. An oxide of rhenium crystallizes with the unit cell shown here (rhenium = gray; oxygen = red). What is the formula of the oxide?



47. The unit cells for cesium chloride and barium(II) chloride are shown here. Show that the ratio of cations to anions in each unit cell corresponds to the ratio of cations to anions in the formula of each compound.



48. The unit cells for lithium oxide and silver iodide are shown at the top of the next column. Show that the ratio of cations to anions in each unit cell corresponds to the ratio of cations to anions in the formula of each compound.



49. Identify the structure of each of the two unit cells shown in Problem 47 as the rock salt structure, zinc blende structure, fluorite structure, antifluorite structure, or none of these.
50. Identify the structure of each of the two unit cells shown in Problem 48 as the rock salt structure, zinc blende structure, fluorite structure, antifluorite structure, or none of these.
51. Consider the rock salt structure in Figure 12.13. What type of structure would result if all the anions were somehow removed, leaving only one type of atom?
52. Consider the zinc blende structure in Figure 12.14. What type of structure would result if the remaining tetrahedral sites in the unit cell were also filled with cations?

Ceramics, Cement, and Glass

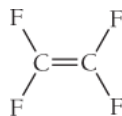
53. Classify each of the following as a component of a silicate ceramic, an oxide ceramic, or a nonoxide ceramic.
- B_4C
 - Mg_2SiO_4
 - $MoSi_2$
54. Classify each of the following as a component of a silicate ceramic, an oxide ceramic, or a nonoxide ceramic.
- TiB_2
 - ZrO_2
 - $NaAlSi_3O_8$
55. What are the name and formula of the compound commonly used in the manufacture of glass to reduce its tendency to crack or shatter under thermal shock?
56. What are the name and formula of the compound commonly used in the manufacture of glass to increase the index of refraction?
57. One of the key components in the manufacture of Portland cement is Ca_3SiO_5 , a compound that is obtained by firing the reactants in a kiln at 1400–1500 °C. Assign an oxidation state to each element in this compound.
58. Replacement of aluminum ions in kaolinite with magnesium ions yields a compound with the formula $Mg_3Si_2O_5(OH)_4$. Assign an oxidation state to each element in this compound.

Semiconductors and Band Theory

59. Which solid would you expect to have little or no band gap?
- $Zn(s)$
 - $Si(s)$
 - $As(s)$
60. Which solid would you expect to have the largest band gap?
- $As(s)$
 - $Sb(s)$
 - $Bi(s)$
61. How many molecular orbitals are present in the conduction band of a lithium crystal with a mass of 11.2 g?
62. How many molecular orbitals are present in the valence band of a sodium crystal with a mass of 5.45 g?
63. A substance has a band gap of 6.9 eV at 273 K. Is this substance best classified as an insulator, a semiconductor, or a metal?
64. A substance has a band gap of 0.85 eV at 273 K. Is this substance best classified as an insulator, a semiconductor, or a metal?
65. Indicate if each solid forms an n-type or a p-type semiconductor.
- germanium doped with gallium
 - silicon doped with arsenic
66. Indicate if each solid forms an n-type or a p-type semiconductor.
- silicon doped with gallium
 - germanium doped with antimony
67. Does a photon of red light with a frequency of 4.29×10^{14} Hz have sufficient energy to promote an electron from the valence band to the conduction band in a sample of silicon (the band gap in silicon is 1.11 eV)?
68. Which wavelength of light (in nm) is emitted if an electron moves from the conduction band to the valence band in a sample of diamond (diamond has a band gap of 5.5 eV)?

Polymers

69. Teflon is an addition polymer formed from the monomer shown here. Draw the structure of the polymer.

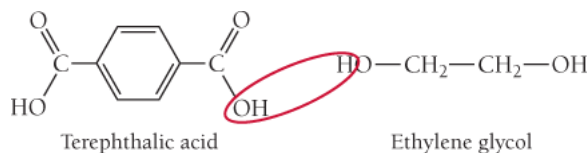


70. Saran, the polymer used to make saran wrap, is an addition polymer formed from two monomers—vinylidene chloride and vinyl chloride. Draw the structure of the polymer. (*Hint: The monomers alternate.*)

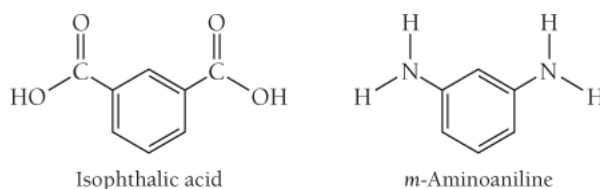




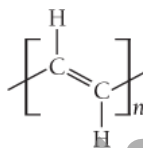
71. One kind of polyester is a condensation copolymer formed from terephthalic acid and ethylene glycol. Draw the structure of the dimer. [Hint: Water (circled) is eliminated when the bond between the monomers forms.]



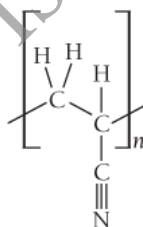
72. Nomex, a condensation copolymer used by firefighters because of its flame-resistant properties, forms from isophthalic acid and *m*-aminoaniline. Draw the structure of the dimer. (Hint: Water is eliminated when the bond between the monomers forms.)



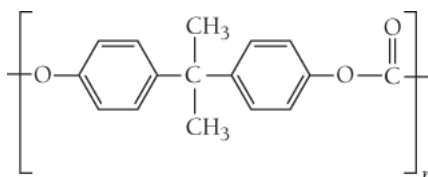
73. Polyacetylene is an addition polymer with the structure shown here. Draw the structure of the monomer.



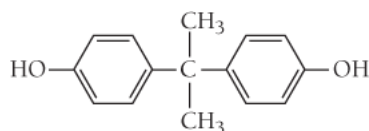
74. Polyacrylonitrile (PAN) is an addition polymer with the structure shown here. Draw the structure of the monomer.



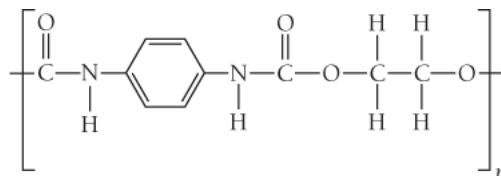
75. The polycarbonate Lexan is a condensation polymer and has the structure shown here:



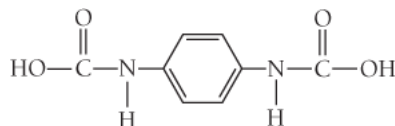
Assuming this polymer was formed from the monomer shown here plus another monomer, provide a structure of the other monomer that would be required to form Lexan.



76. Consider the following condensation polymer with the structure shown here:

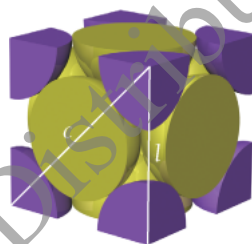


Assuming this polymer was formed from the monomer shown here plus another monomer, provide a structure of the other monomer that would be required to form this polymer.



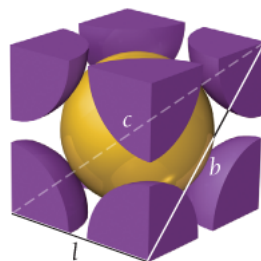
Cumulative Problems

77. Silver iodide crystallizes in the zinc blende structure. The separation between nearest-neighbor cations and anions is approximately 325 pm, and the melting point is 558 °C. Cesium chloride, by contrast, crystallizes in the structure shown in [Figure 12.12](#). Even though the separation between nearest-neighbor cations and anions is greater (348 pm), the melting point of cesium chloride is higher (645 °C). Explain.
78. Copper iodide crystallizes in the zinc blende structure. The separation between nearest-neighbor cations and anions is approximately 311 pm, and the melting point is 606 °C. Potassium chloride, by contrast, crystallizes in the rock salt structure. Even though the separation between nearest-neighbor cations and anions is greater (319 pm), the melting point of potassium chloride is higher (776 °C). Explain.
79. Consider the face-centered cubic structure shown here:



- What is the length of the line (labeled c) that runs diagonally across one of the faces of the cube in terms of r (the atomic radius)?
- Use the answer to part a and the Pythagorean theorem to derive the expression for the edge length (l) in terms of r .

80. Consider the body-centered cubic structure shown here:



- What is the length of the line (labeled c) that runs from one corner of the cube diagonally through the center of the cube to the other corner in terms of r (the atomic radius)?
- Use the Pythagorean theorem to derive an expression for the length of the line (labeled b) that runs diagonally across one of the faces of the cube in terms of the edge length (l).
- Use the answer to parts a and b along with the Pythagorean theorem to derive the expression for the edge length (l) in terms of r .

81. The volume of a unit cell of diamond is 0.0454 nm^3 , and the density of diamond is 3.52 g/cm^3 . Find the number of carbon atoms in a unit cell of diamond.
82. The density of an unknown metal is 12.3 g/cm^3 , and its atomic radius is 0.134 nm . It has a face-centered cubic lattice. Find the atomic mass of this metal.
83. An unknown metal is found to have a density of 7.8747 g/cm^3 and to crystallize in a body-centered cubic lattice. The edge of the unit cell is 0.28664 nm . Calculate the atomic mass of the metal.
84. When spheres of radius r are packed in a body-centered cubic arrangement, they occupy 68.0% of the available volume. Use the fraction of occupied volume to calculate the value of a , the length of the edge of the cube, in terms of r .
85. Potassium chloride crystallizes in the rock salt structure. Estimate the density of potassium chloride using the ionic radii provided in [Chapter 3](#).
86. Calculate the fraction of empty space in cubic closest packing to five significant figures.
87. A tetrahedral site in a closest-packed lattice is formed by four spheres at the corners of a regular tetrahedron. This is equivalent to placing the spheres at alternate corners of a cube. In such a closest-packed arrangement, the spheres are in contact, and if the spheres have a radius r , the diagonal of the face of the cube is $2r$. The tetrahedral hole is inside the middle of the cube. Find first the length of the body diagonal of this cube and then the radius of the tetrahedral hole.
88. X-ray diffractometers often use metals that have had their core electrons excited as a source of X-rays. Consider the $2p \rightarrow 1s$ transition for copper, which is called the $K\alpha$ transition. Calculate the wavelength of X-rays (in Å) given off by the $K\alpha$ transition if the energy given off by a mole of copper atoms is $7.77 \times 10^5 \text{ kJ}$.
89. Why is it necessary to use the $K\alpha$ transition ($2p \rightarrow 1s$) in copper (see [Problem 88](#)) to generate X-rays? Why not use, for example, the $4s \rightarrow 3p$ transition?
90. In certain cases where X-ray diffraction is unsuitable for determining the structure of a crystal, *neutron diffraction* can be used. Instead of X-rays, a beam of neutrons is used to analyze the sample. Calculate the velocity of a beam of neutrons with a wavelength of 2.00 Å .

Challenge Problems

91. The structure of the addition polymer polypropylene is shown in [Table 12.2](#).
- Draw the structure of the monomer.
 - Show how an alternate version of the polypropylene polymer (with a different arrangement) could be formed from the monomer you found in part a.
92. Perovskite is a compound with a cubic unit cell and has a strontium atom at the center of the cell, titanium atoms at the corners of the unit cell, and oxygen atoms at the centers of each edge of the unit cell.
- What is the formula of perovskite?
 - What is the coordination number of strontium in the perovskite structure?
 - If the edge length of the unit cell is 3.905 Å , calculate the density of perovskite in g/cm^3 .
93. A compound with the formula Rb_3C_{60} has been shown to demonstrate superconductivity below 30.0 K . Given that the C_{60} molecules have a face-centered cubic arrangement, which of the tetrahedral and octahedral sites are occupied by Rb atoms?
94. Despite Dalton's laws, it is now known that many ionic compounds do not always contain atoms in small integer ratios. For example, a sample of iron(II) oxide may, in fact, contain a significant amount of Fe^{3+} in addition to Fe^{2+} . This is an example of a *nonstoichiometric* compound. A sample of iron(II) oxide is found to be 75.65% iron by mass. Determine the percentage of Fe^{3+} ions in the sample.

Conceptual Problems

95. During the glass manufacturing process, the liquid must be cooled relatively quickly to form the glass. Why?
96. Why are X-rays used for crystallography? Why not use some other, more accessible type of electromagnetic radiation such as ultraviolet light?
97. Compare the crystal structure of diamond (C) and zinc blende (ZnS). What are the key similarities and differences between the two structures?
98. In X-ray crystallography, a small amount of oil is often used to mount the crystal sample on a glass fiber. Explain why neither the oil nor the glass fiber interferes with the diffraction pattern of the crystal.
99. Which is not likely to lead to an increase in electrical conductivity?

- a. increasing the temperature of a semiconductor
- b. choosing a semiconductor with a smaller band gap
- c. doping the semiconductor
- d. All of the above would likely lead to an increase in electrical conductivity.

Questions for Group Work

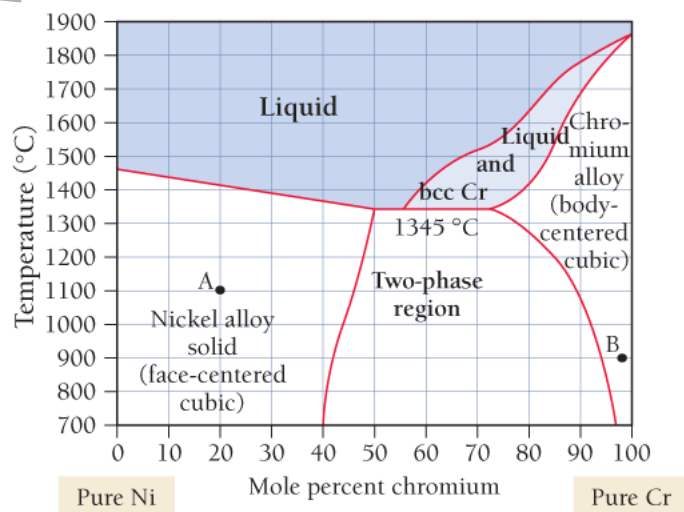
Active Classroom Learning

Discuss these questions with the group and record your consensus answer.

100. Have each group member select one of the cubic crystalline lattices. Learn everything you can about your lattice, and present it to the group.
101. Using group members to play the role of atoms or molecules, demonstrate the main structural features of the following categories of crystalline solids: molecular solid, ionic solid, nonbonded solid, metallic solid, and network covalent solid. Clearly identify what each individual represents and how you are representing various interactions between particles (e.g., covalent bond, ionic bond, etc.).
102. List the questions you would need to ask in order to classify a solid into one of the categories of crystalline solids (molecular solid, ionic solid, nonbonded solid, metallic solid, and network covalent solid). In what sequence is it best to ask them? (*Hint:* You may need a branching decision tree.) Once you have agreed on a good set of questions, have each group member choose a substance from the chapter, and have the other group members ask the questions from the list in turn until the correct classification is reached. Group members may agree to edit the list if they discover ways to improve it while using it.
103. Have each group member select and study a material from [Section 12.7](#) on ceramics, cement, and glass. Take turns describing your material to the group, and see if group members can identify the type of material based on your description (without consulting the text).
104. Describe how a common object or toy (e.g., a train, building blocks, or beads on a string) could represent the structure of a polymer. Describe how you can represent the following terms using your model: monomer, dimer, addition polymer, condensation polymer, branching.

Data Interpretation and Analysis

105. An *alloy* is a metallic mixture composed of two or more elements. As is the case in all mixtures, the relative amounts of the elements in an alloy can vary. In some cases, the components of an alloy can have different crystal structures. For example, a nickel-chromium alloy consists of nickel, which has a face-centered cubic structure, and chromium, which has a body-centered cubic structure. Which structure does the alloy adopt? It depends on the relative compositions. The phase diagrams for alloys such as these reveal the structure as a function of the alloy composition. For example, the nickel and chromium phase diagram from 700 °C to 1900° is shown here:



Ni-Cr Phase Diagram

Notice that the diagram has two different solid phases: face-centered cubic and body-centered cubic. From pure nickel (0 mol % chromium) to about 40–50 mol % chromium, the structure is face-centered cubic. In this structure, Cr atoms substitute for Ni atoms in the face-centered cubic structure of nickel. However, when an amount of chromium beyond a certain percentage (which depends on temperature) is added, that structure is no longer stable. At the other end of the diagram, from pure chromium to about 75% chromium (depending on temperature), the structure is body-centered cubic, with nickel substituting into the body-centered cubic structure of the chromium. The region in between the two phases is called the *two-phase region*. At these compositions, the two phases (nickel-rich face-centered cubic and chromium-rich body-centered cubic) exist together (the solution is not homogeneous in this region). Use the phase diagram to answer the following questions.

- What is the relative composition of the mixture at point A? At what temperature does a solid mixture having this composition melt?
- Is it possible to have a homogeneous solid mixture that is 50% Ni and 50% Cr? If so, what crystalline structure would it have?
- What is the relative composition at point B? What is the crystalline structure at point B?
- At what temperature does the solid present at point B begin to melt?

Answers to Conceptual Connections

Cc 12.1 ☐ The face-centered cubic unit cell has four atoms per unit cell.

Cc 12.2 ☐ (a) MgO is an ionic solid, which means that the forces holding the solid together are strong ionic bonds. The other two substances are I₂(s), a molecular solid, and Kr(s), a nonbonding atomic solid. These two

solids are held together by dispersion forces and will therefore have much lower melting points.

Cc 12.3 ☐ (c) The zinc blende structure occurs in ionic compounds with a one-to-one cation-to-anion ratio in which the cation is much smaller than the anion.

Cc 12.4 ☐ An increase in pressure favors the denser phase, in this case diamond.

Cc 12.5 ☐ (a) Since indium has three valence electrons and germanium has four, the presence of indium would introduce holes into the valence band, resulting in a p-type semiconductor.

Not for Distribution

Not for Distribution

Not for Distribution