***Chemistry***

**10: Liquids and Solids**

**10.6: Lattice Structures in Crystalline Solids**

75. Describe the crystal structure of iron, which crystallizes with two equivalent metal atoms in a cubic unit cell.

Solution

The structure of this low-temperature form of iron (below 910 °C) is body-centered cubic. There is one-eighth atom at each of the eight corners of the cube and one atom in the center of the cube.

77. What is the coordination number of a chromium atom in the body-centered cubic structure of chromium?

Solution

Coordination number refers to the number of nearest neighbors. A chromium atom lies at the center of a body-centered cube and has eight nearest neighbors (at the corners of the cube): four in one plane above and four in one plane below. The coordination number is therefore eight.

79. Cobalt metal crystallizes in a hexagonal closest packed structure. What is the coordination number of a cobalt atom?

Solution

Hexagonal closest packing occurs in such a way that each atom touches 12 nearest neighbors: 6 in its own layer and 3 in each adjacent layer. The coordination number is therefore 12.

81. Tungsten crystallizes in a body-centered cubic unit cell with an edge length of 3.165 Å.

(a) What is the atomic radius of tungsten in this structure?

(b) Calculate the density of tungsten.

Solution

(a) In a body-centered cubic unit cell, the metal atoms are in contact along the interior diagonal of the cube. The interior diagonal forms a right triangle with the unit cell edge and the diagonal of the face. Use the Pythagorean theorem to determine the length of the diagonal, d, on the face of the cube in terms of the edge, *e*. See the figure in Example 10.14:

d2 = e2 + e2 = 2e2

d = e

The interior diagonal of the cube is the length of four atomic radii and can be calculated again by using the Pythagorean theorem and the face diagonal and edge.

(diagonal)2 = d2 + e2

= (e) + e2

= 2e2 + e2

= 3e2

diagonal = *e* = 4*r*

radius of tungsten = (3.165 Å) = 1.370 Å;

(b) Given the body-centered cubic structure, each unit cell contains two atoms. Use the unit cell edge length to calculate the unit cell volume and the volume occupied by each atom. Multiply to obtain the molar volume and divide the atomic mass by this value to obtain density (e = edge length):

*V*(cell) = e3 = (3.165 × 10–8 cm)3 = 3.170 × 10–23 cm3

*V*(atom) = 

*V*(mol) = 1.585 × 10–23 cm3/atom × 6.022 × 1023 atoms/mol

= 9.546 cm3/mol

density = 

= 19.26 g/cm

83. Barium crystallizes in a body-centered cubic unit cell with an edge length of 5.025 Å

(a) What is the atomic radius of barium in this structure?

(b) Calculate the density of barium.

Solution

(a) In a body-centered cubic unit cell, the metal atoms are in contact along the diagonal of the cube. The diagonal of the cube forms a right triangle with the unit cell edge and the diagonal of a face. Use the Pythagorean theorem to determine the length of the diagonal, d, on the face of the cube in terms of e.

d2 = e2 + e2 = 2e2

d = e

The diagonal of the cube is the length of four atomic radii and can be calculated by again using the Pythagorean theorem:

(diagonal)2 = (4*r*)2 = (2e)2 + e2 = 16r2 = 3e2

diagonal = 4*r* = 

*r* = (5.025 Å) = 2.176 Å;

(b) Given a body-centered cubic structure, each unit cell contains two atoms. Use the unit cell edge length to calculate the unit cell volume and the volume occupied by each atom. Multiply to obtain the molar volume and divide the gram atomic weight by this value to obtain density (e = edge length):

*V* (cell) = e3 = (5.025 × 10–8 cm)3 = 1.26884 × 10–22 cm3

*V* (atom) = 1.26884 ×  = 6.3442 × 10–23 cm3

*V* (mole) = 6.3442 × 10–23 cm3 × 6.022 × 1023 atoms/mol = 38.205 cm3

*d*(Ba) = = 3.595 g/cm3

85. The density of aluminum is 2.7 g/cm3; that of silicon is 2.3 g/cm3. Explain why Si has the lower density even though it has heavier atoms.

Solution

The crystal structure of Si shows that it is less tightly packed (coordination number 4) in the solid than Al (coordination number 12).

87. Cadmium sulfide, sometimes used as a yellow pigment by artists, crystallizes with cadmium, occupying one-half of the tetrahedral holes in a closest packed array of sulfide ions. What is the formula of cadmium sulfide? Explain your answer.

Solution

In a closest-packed array, two tetrahedral holes exist for each anion. If only half the tetrahedral holes are occupied, the numbers of anions and cations are equal. The formula for cadmium sulfide is CdS.

89. What is the formula of the magnetic oxide of cobalt, used in recording tapes, that crystallizes with cobalt atoms occupying one-eighth of the tetrahedral holes and one-half of the octahedral holes in a closely packed array of oxide ions?

Solution

In a closest-packed array of oxide ions, one octahedral hole and two tetrahedral holes exist for each oxide ion. If one-half of the octahedral holes are filled, there is one Co ion for every two oxide ions. If one-eighth of the tetrahedral holes are filled, there is one Co ion for each four oxide ions. For every four oxide ions, there are two Co ions in octahedral holes and one Co in a tetrahedral hole; thus the formula is Co3O4.

91. A compound of thallium and iodine crystallizes in a simple cubic array of iodide ions with thallium ions in all of the cubic holes. What is the formula of this iodide? Explain your answer.

Solution

In a simple cubic array, only one cubic hole can be occupied be a cation for each anion in the array. The ratio of thallium to iodide must be 1:1; therefore, the formula for thallium is TlI.

93. What is the percent by mass of titanium in rutile, a mineral that contains titanium and oxygen, if structure can be described as a closest packed array of oxide ions with titanium ions in one-half of the octahedral holes? What is the oxidation number of titanium?

Solution

The ration of octahedral holes to oxygen anions is 1:1 in a closest-packed array. Only one-half of the octahedral holes are occupied. Thus, the titanium to oxygen ratio is 1:2 and the formula is TiO2. The percentage by mass of Ti in the structure is:

percent Ti = 

The oxidation number of titanium is +4 because there are two O2– ions for each Ti ion.

95. As minerals were formed from the molten magma, different ions occupied the same cites in the crystals. Lithium often occurs along with magnesium in minerals despite the difference in the charge on their ions. Suggest an explanation.

Solution

Both ions are close in size: Mg, 0.65; Li, 0.60. This similarity allows the two to interchange rather easily. The difference in charge is generally compensated by the switch of Si4+ for Al3+.

97. One of the various manganese oxides crystallizes with a cubic unit cell that contains manganese ions at the corners and in the center. Oxide ions are located at the center of each edge of the unit cell. What is the formula of the compound?

Solution

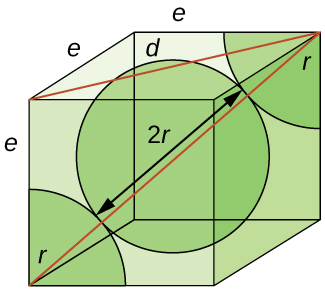
The total number of Mn ions is determined by adding the contributions from the corners and center. Mn (corners): 8 ×; Mn (center) = 1. Total Mn contribution to the unit cell = 2.

For O, there are a total of 12 edges in the cube and each ion in the edge contributes one-fourth to the unit cell. Consequently, there are 12 ×= 3 O atoms. The ratio is Mn:O = 2:3, and the formula is Mn2O3.

99. Thallium(I) iodide crystallizes with the same structure as CsCl. The edge length of the unit cell of TlI is 4.20 Å. Calculate the ionic radius of TI+. (The ionic radius of I– is 2.16 Å.)

Solution

A body-centered cube contains two atoms of radius *r* in the unit cell. The length of the face diagonal of the cube is calculated using the Pythagorean theorem:



The diagonal of the cube is 4*r*.

(4*r*)2 = d2 + e2

but d2 = e2 + e2

d2 = e2 + e2 = 2e2 = 2(4.20 Å)2 = 35.28 Å2

The diagonal of the cube is:

d2 + e2 = 35.28 + (4.20)2

= 35.28 + 17.64 = 52.92

= 7.27 Å

= 2*r*+ + 2*r*–

Since *r*– = 2.16 Å,

*r*+ = 

101. What is the spacing between crystal planes that diffract X-rays with a wavelength of 1.541 nm at an angle *θ* of 15.55° (first order reflection)?

Solution

The Bragg equation is:

*n*λ = 2*d* sin *θ*

where *d* is the spacing between planes.

*d* = 

= 2.874 Å

103. A metal with spacing between planes equal to 0.4164 nm diffracts X-rays with a wavelength of 0.2879 nm. What is the diffraction angle for the first order diffraction peak?

Solution

, so *θ* = sin–1(0.3457) = 20.2°

105. When an electron in an excited molybdenum atom falls from the L to the K shell, an X-ray is emitted. These X-rays are diffracted at an angle of 7.75°by planes with a separation of 2.64 Å. What is the difference in energy between the K shell and the L shell in molybdenum assuming a first-order diffraction?

Solution

Use the Bragg equation, where *n* = 1,



Then



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