

12.5: The Structures of Ionic Solids

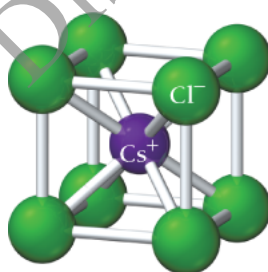
Many ionic solids have crystalline structures that are closely related to unit cells that we examined in [Section 12.3](#). However, because ionic compounds necessarily contain both cations and anions, their structures must accommodate two different types of ions. In an ionic solid, the cations and anions attract one another. The coordination number of the unit cell represents the number of close cation–anion interactions. Because these interactions lower potential energy, the crystal structure of a particular ionic compound is the structure that maximizes the coordination number while accommodating both charge neutrality (each unit cell must be charge neutral) and the different sizes of the cations and anions that compose the particular compound. In general, the more similar the radii of the cation and the anion, the higher the coordination number.

Cesium chloride (CsCl) is a good example of an ionic compound with cations and anions of similar size (Cs^+ radius = 167 pm; Cl^- radius = 181 pm). In the cesium chloride structure, the chloride ions occupy the lattice sites of a simple cubic cell and one cesium ion lies in the very center of the cell, as shown in [Figure 12.12](#). (In this figure and in subsequent figures of ionic crystal structures, the different-colored spheres represent different ions.) The coordination number for cesium chloride is 8, meaning that each cesium ion is in direct contact with eight chloride ions (and vice versa). The cesium chloride unit cell contains one chloride anion ($8 \times \frac{1}{8} = 1$) and one cesium cation for a ratio of Cs to Cl of 1:1, as the formula for the compound indicates. (Note that complete chloride ions are shown in [Figure 12.12](#), even though only $\frac{1}{8}$ of each ion is in the unit cell.) Calcium sulfide (CaS) has the same structure as cesium chloride.

Figure 12.12 Cesium Chloride Unit Cell

The different-colored spheres in this figure represent the different ions in the compound.

Cesium chloride (CsCl)



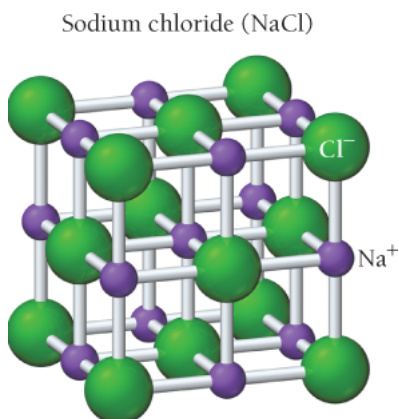
The crystal structure of sodium chloride must accommodate the more disproportionate sizes of Na^+ (radius = 97 pm) and Cl^- (radius = 181 pm). If ion size were the only consideration, the larger chloride anion could theoretically fit many of the smaller sodium cations around it, but charge neutrality requires that each sodium cation be surrounded by an equal number of chloride anions. Therefore, the coordination number is limited by the number of chloride anions that can fit around the relatively small sodium cation.

The sodium chloride structure that minimizes the energy is shown in [Figure 12.13](#) and has a coordination number of 6 (each chloride anion is surrounded by six sodium cations and vice versa). We can visualize this structure, called the *rock salt* structure, as chloride anions occupying the lattice sites of a face-centered cubic structure, with the smaller sodium cations occupying the holes between the anions. (Alternatively, we can visualize this structure as the *sodium cations* occupying the lattice sites of a face-centered cubic structure with the *larger chloride anions* occupying the spaces between the cations.) Each unit cell contains four chloride anions $\left[\left(8 \times \frac{1}{8} = 1 \right) + \left(6 \times \frac{1}{2} = 3 \right) = 4 \right]$ and four sodium cations $\left[\left(12 \times \frac{1}{4} = 3 \right) + 1 = 4 \right]$, resulting in a ratio of 1:1, as the formula of the compound specifies. Other compounds exhibiting the sodium chloride structure include LiF, KCl,

KBr , AgCl , MgO , and CaO .

Figure 12.13 Sodium Chloride Unit Cell

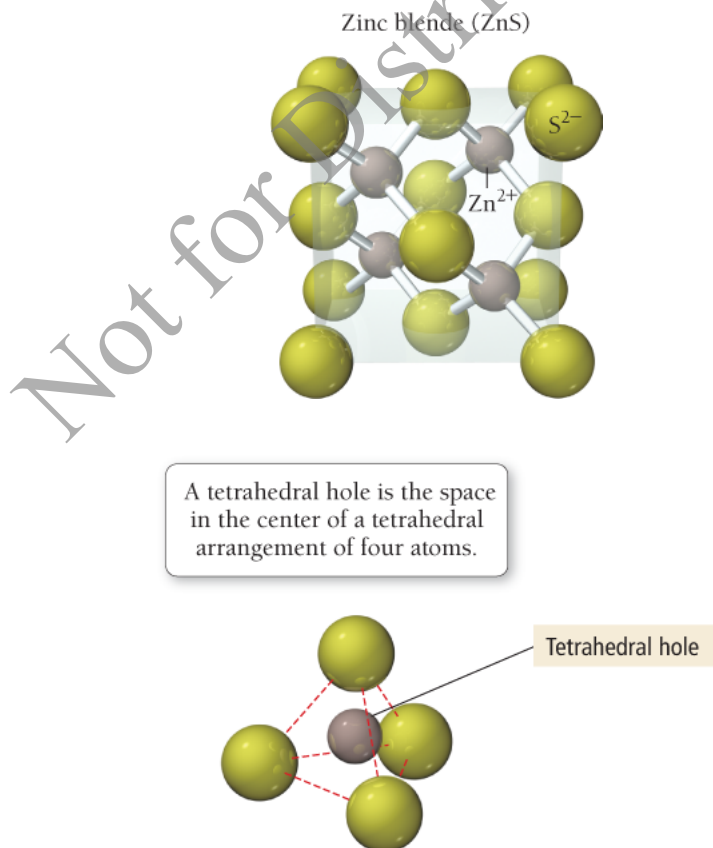
The different-colored spheres in this figure represent the different ions in the compound.



When there is a greater disproportion between the sizes of the cations and anions in a compound, a coordination number of even 6 is physically impossible. For example, in ZnS (Zn^{2+} radius = 74 pm; S^{2-} radius = 184 pm) the crystal structure, shown in Figure 12.14, has a coordination number of only 4. We can visualize this structure, called the *zinc blende* structure, as sulfide anions occupying the lattice sites of a face-centered cubic structure, with the smaller zinc cations occupying four of the eight tetrahedral holes located directly beneath each corner atom. A tetrahedral hole is the empty space that lies in the center of a tetrahedral arrangement of four atoms, as shown in the figure below.

Figure 12.14 Zinc Sulfide (Zinc Blende) Unit Cell

The different-colored spheres in this figure represent the different ions in the compound.



Each unit cell contains four sulfide anions $\left[\left(8 \times \frac{1}{8} \right) + \left(6 \times \frac{1}{2} \right) = 4 \right]$ and four zinc cations (each of the four

L \ o / \ 4 / J

zinc cations is completely contained within the unit cell), resulting in a ratio of 1:1, just as the formula of the compound indicates. Other compounds that exhibit the zinc blende structure include CuCl, AgI, and CdS.

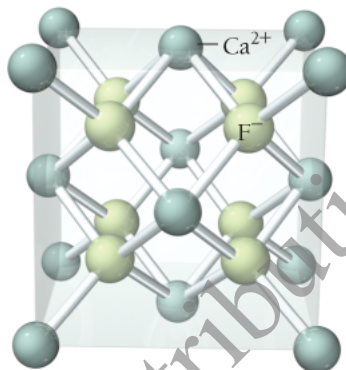
When the ratio of cations to anions is not 1:1, the crystal structure must accommodate the unequal number of cations and anions. Many compounds that contain a cation-to-anion ratio of 1:2 adopt the *fluorite* (CaF_2) structure shown in Figure 12.15. We can visualize this structure as calcium cations occupying the lattice sites of a face-centered cubic structure, with the larger fluoride anions occupying all eight of the tetrahedral holes located directly beneath each corner atom. Each unit cell contains four calcium cations

$\left[\left(8 \times \frac{1}{8} \right) + \left(6 \times \frac{1}{2} \right) = 4 \right]$ and eight fluoride anions (each of the eight fluoride anions is completely contained within the unit cell), resulting in a cation-to-anion ratio of 1:2, as the formula of the compound indicates. Other compounds exhibiting the fluorite structure include PbF_2 , SrF_2 , and BaCl_2 . Compounds with a cation-to-anion ratio of 2:1 often exhibit the *antifluorite* structure, in which the anions occupy the lattice sites of a face-centered cubic structure and the cations occupy the tetrahedral holes beneath each corner atom.

Figure 12.15 Calcium Fluoride Unit Cell

The different-colored spheres in this figure represent the different ions in the compound.

Calcium fluoride (CaF_2)



Conceptual Connection 12.3 Ionic Crystalline Solid Unit Cells

Interactive

Not for Distribution