



OX

THE SOLID STATE

B. HOLES & IONIC COMPOUNDS

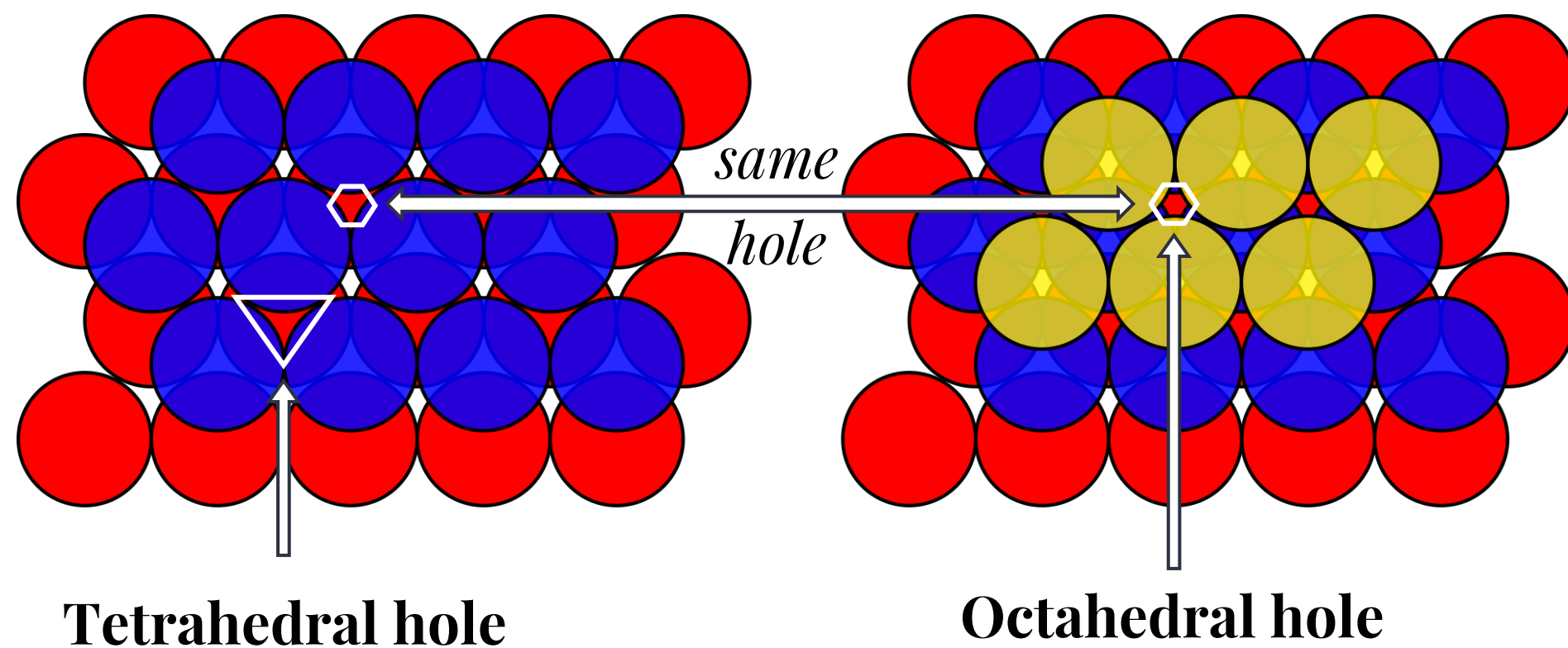
HOLES

Objective: *Understand the two types of holes (tetrahedral and octahedral) in ccp*



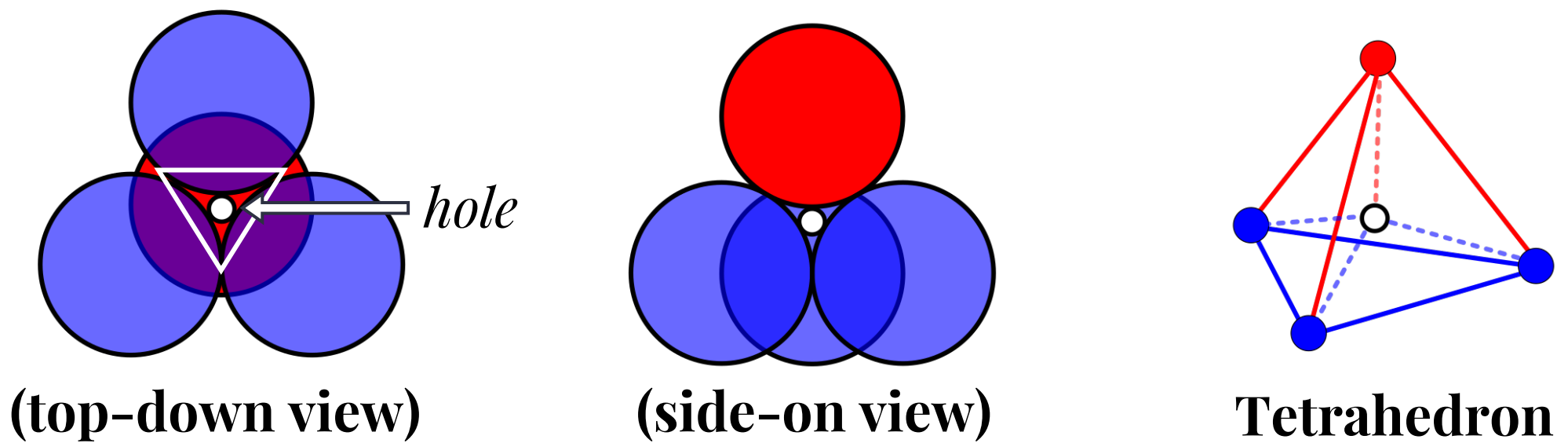
Even in the most efficient and densest packing arrangements (ccp or hcp), there will exist voids where the spherical atoms do not touch. We call these spaces holes or interstices.

In particular, for ccp (or fcc unit cells) there are two types of holes: tetrahedral holes and octahedral holes, as shown in the diagram below.

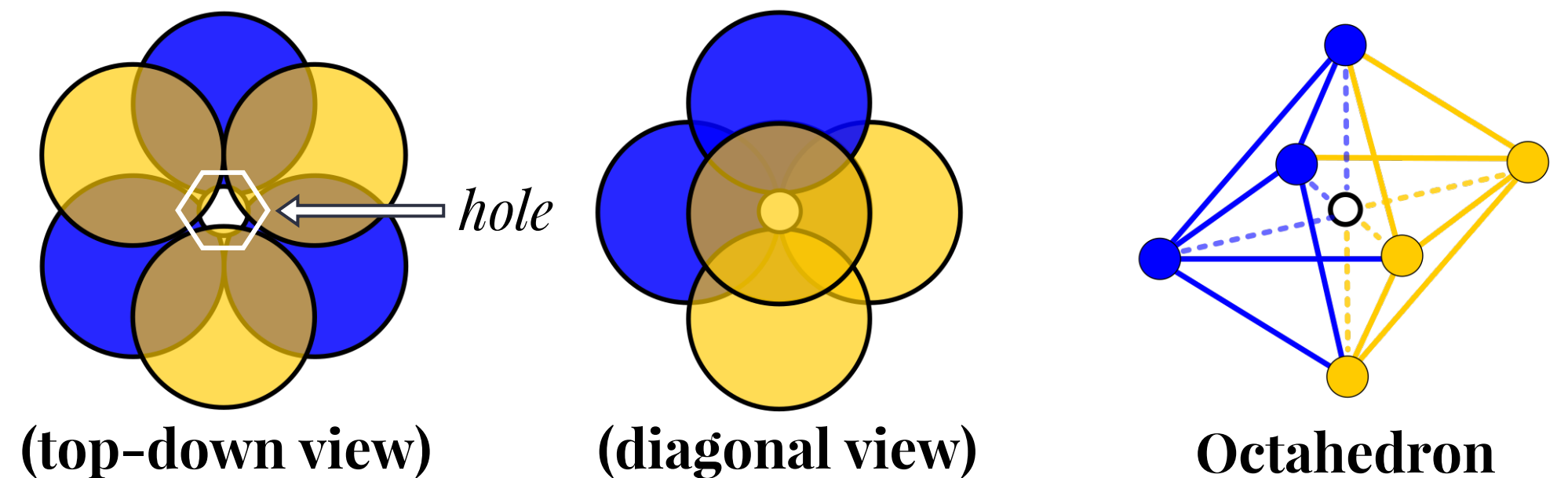


Why are the holes named as such?

Tetrahedral Hole. If we imagine placing a small sphere inside the tetrahedral hole, that sphere (the hole) would have a steric number $SN = 4$ and a tetrahedral geometry.



Octahedral Hole. If we imagine placing a small sphere inside the octahedral hole, that sphere (the hole) would have a steric number $SN = 6$ and octahedral geometry.



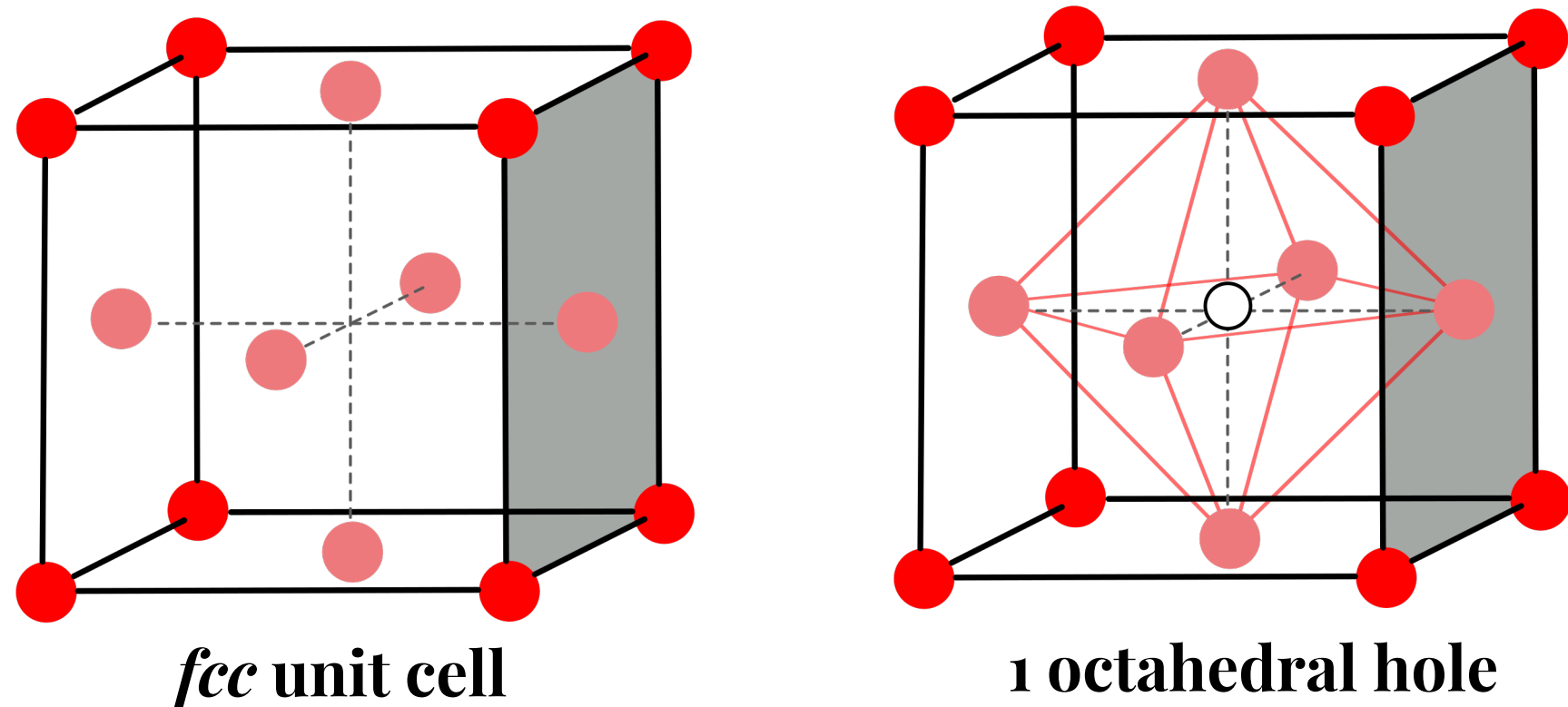
FCC UNIT CELL: HOLES

Objective: *Understand the location and number of tetrahedral and octahedral holes in a fcc unit cell*



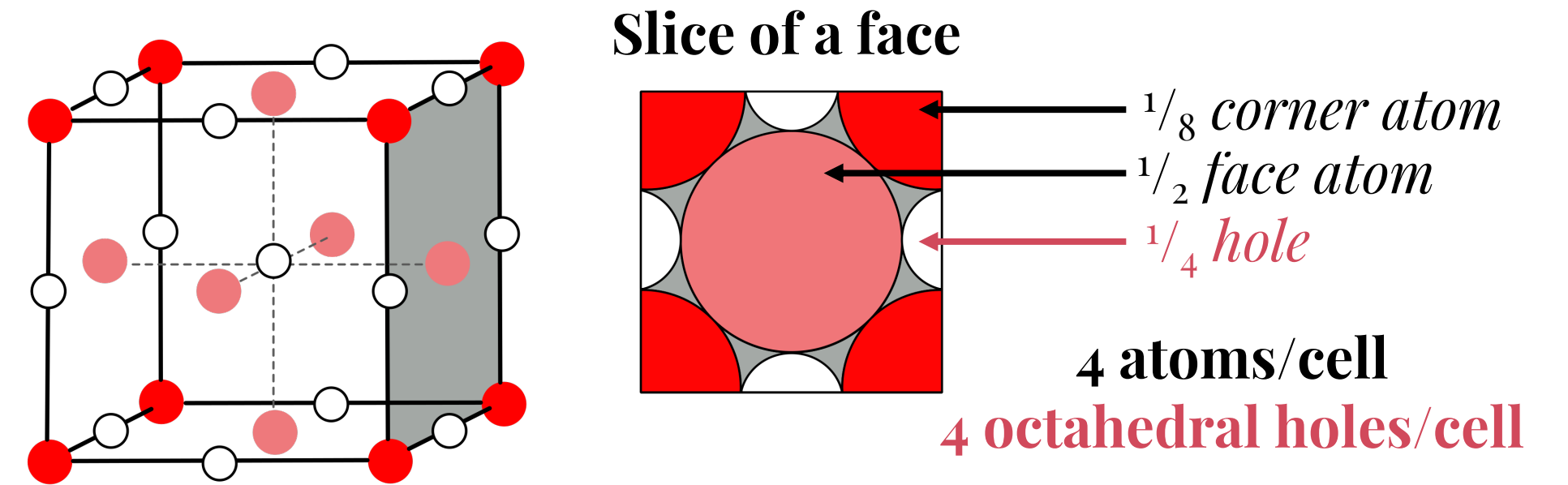
Since the unit cell is the smallest repeating unit, it would be more useful to understand the locations and number of tetrahedral and octahedral holes inside a fcc unit cell.

Consider the fcc unit cell below. The easiest hole to locate is the octahedral hole that is positioned directly at the body-center of the cube (note octahedron formed about hole).



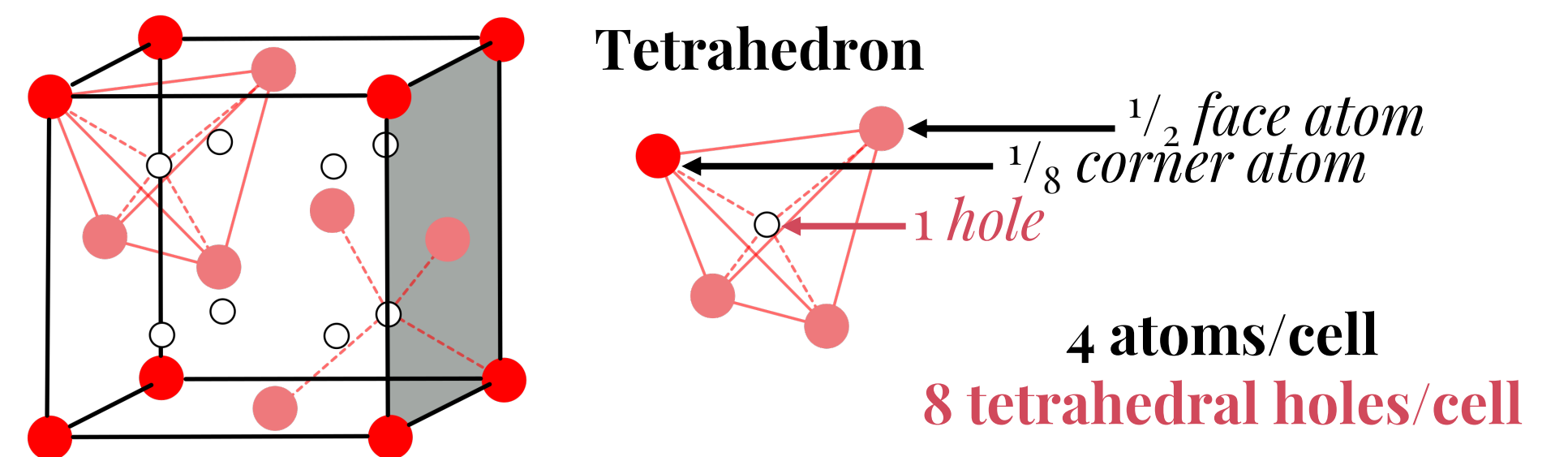
There are actually 12 more octahedral holes in a fcc unit cell, but these are fractional holes that exist along the edges of the cube—only $\frac{1}{4}$ of the hole exists *inside* the cube.

$$\text{Octahedral holes per fcc cell} = 1 \text{ hole} + \frac{1}{4} \times 12 \text{ holes} = 4 \text{ holes}$$



In a fcc unit cell, there are also eight tetrahedral holes, each fully *inside* the cube. The diagram shows two tetrahedrons, one for the upper left hole and one for the lower right hole.

$$\text{Tetrahedral holes per fcc cell} = 8 \text{ holes}$$

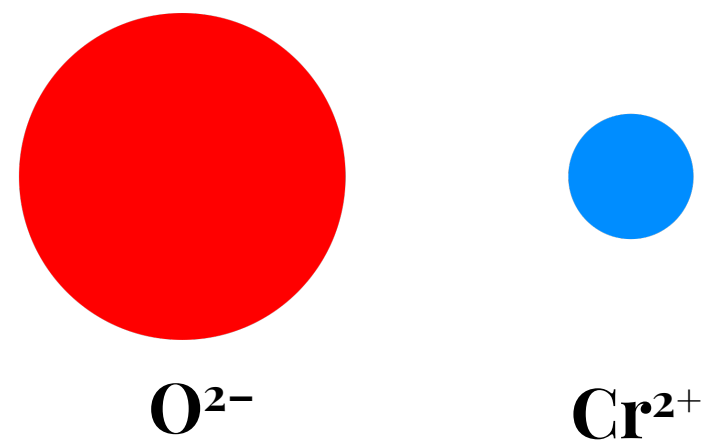


IONIC COMPOUNDS I

Objective: *Understand the structure of ionic compounds*

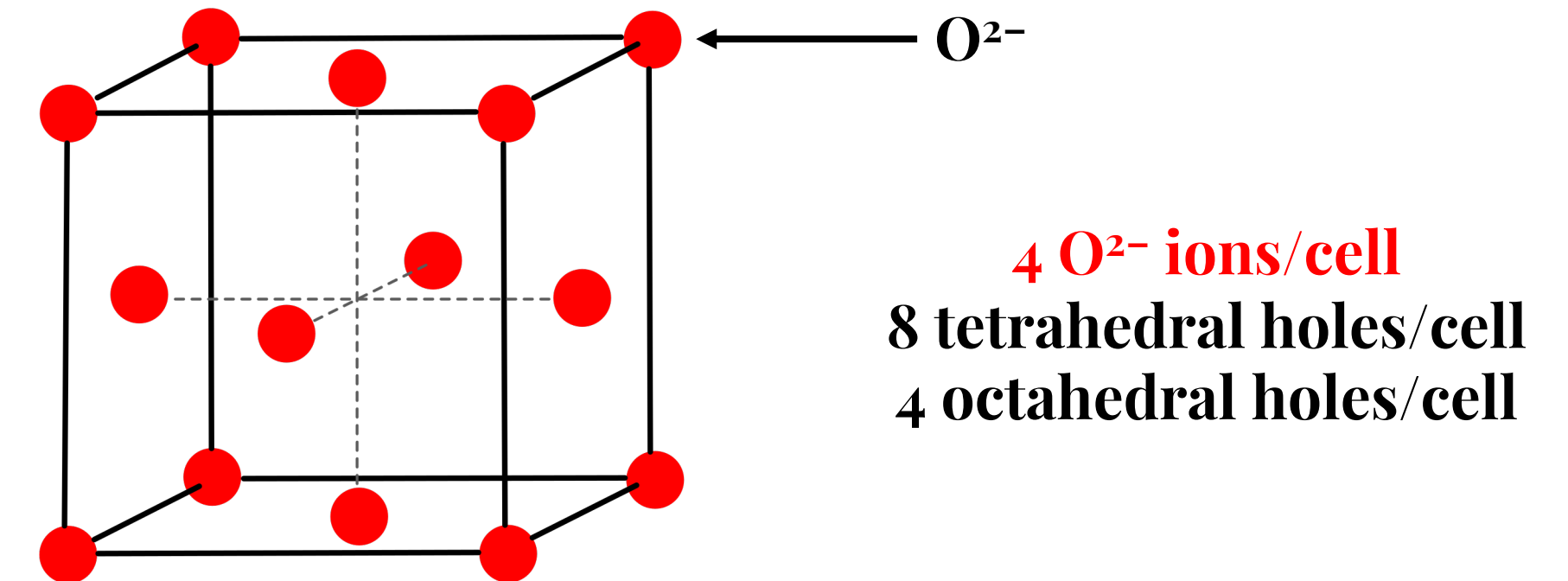


Consider the ionic compound chromium(II) oxide (CrO). How does the structure of this solid look like? Because the compound is ionic, we must consider the two ions, Cr^{2+} and O^{2-} , and treat them as hard-spheres. Now, how would these two types of spheres pack?

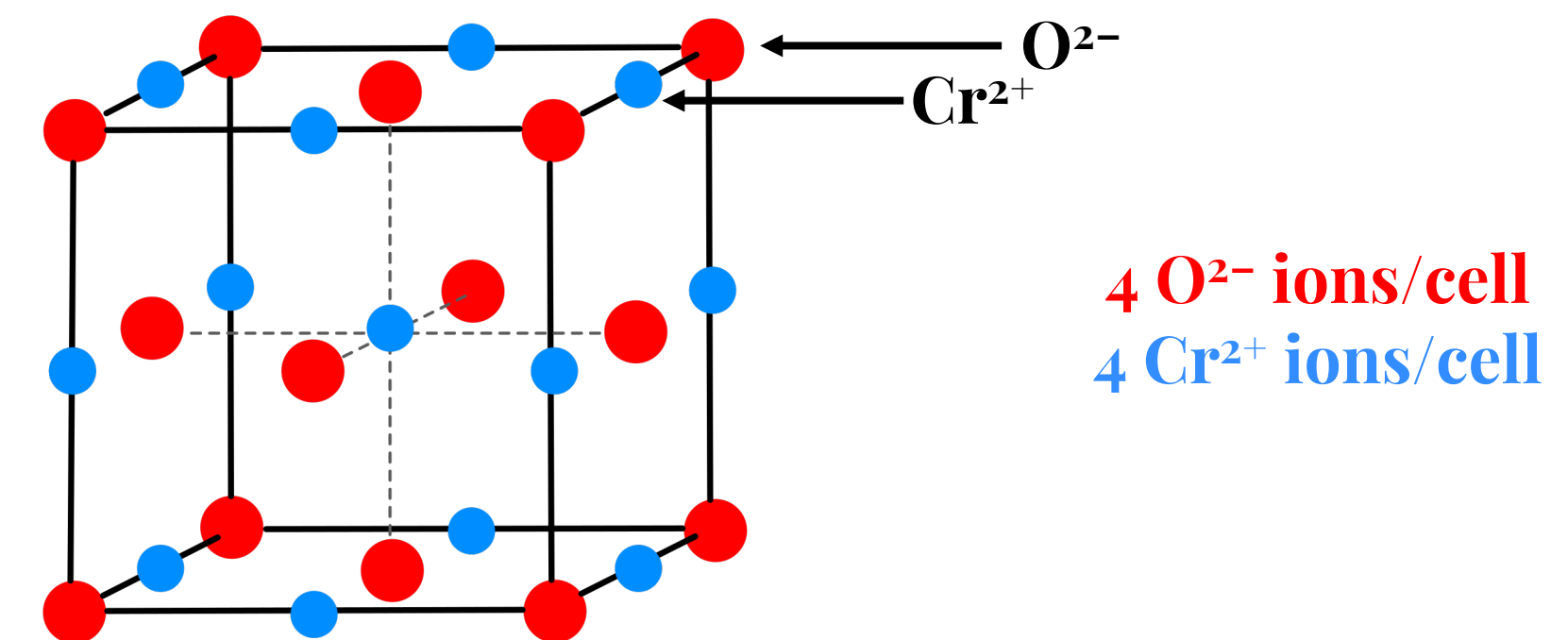


As you may recall, the ionic radii of anions is much larger than the ionic radii of cations; hence, O^{2-} is larger than Cr^{2+} . Generally, the *larger* ion (the anion) informs the type of unit cell. In this case, the O^{2-} ions pack in a *fcc* unit cell.

If the oxide anion form a *fcc* lattice, then we have the following unit cell composed of four O^{2-} anions.



As cations are generally *smaller* in radii, they typically occupy the holes in the lattice. In this case, the Cr^{2+} cations will occupy *all* of the octahedral holes in the O^{2-} *fcc* unit cell to give a $\text{Cr}^{2+}:\text{O}^{2-}$ ratio of 1:1 as dictated by charge balance.



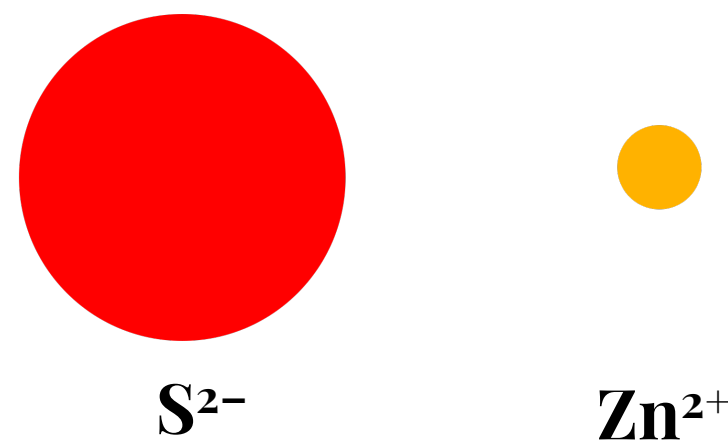
IONIC COMPOUNDS II

Objective: *Understand the structure of ionic compounds*



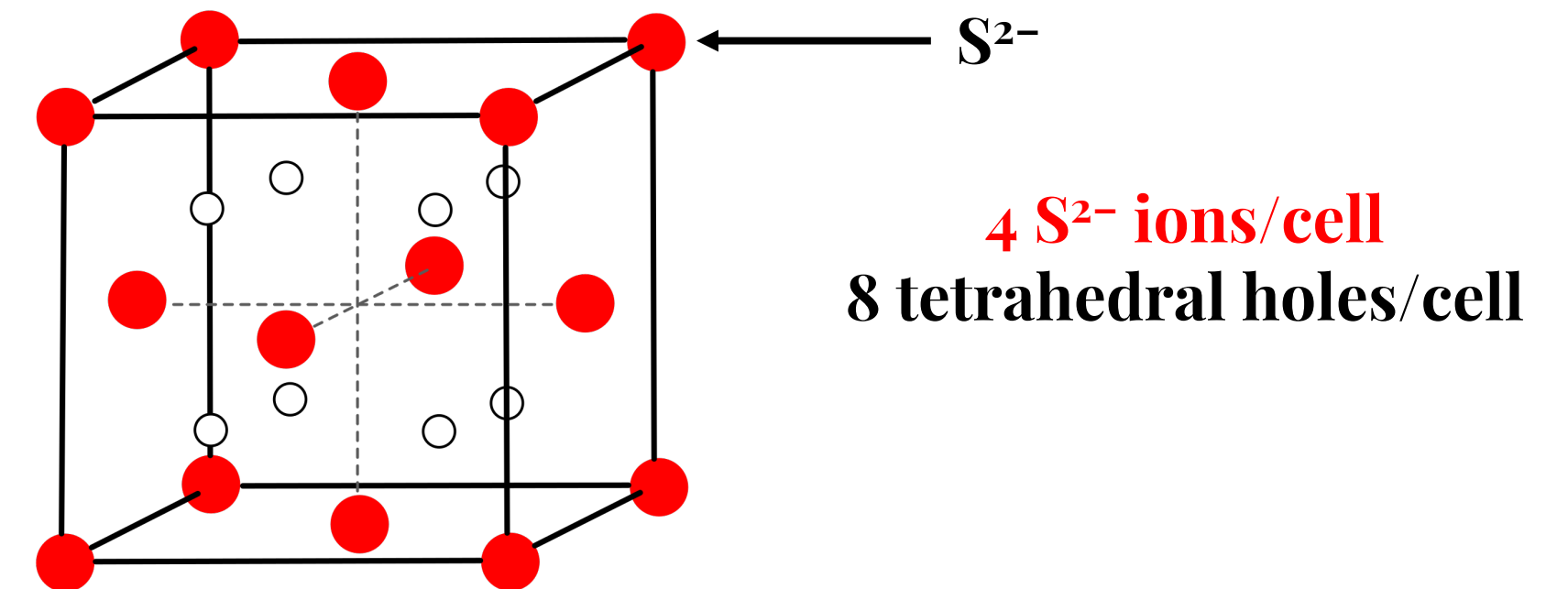
What about a different ionic compound? Surely, we need not always fill the octahedral holes and need not always fill *all* of the holes in a unit cell.

Let us consider now zinc sulfide (ZnS), which is composed of the Zn^{2+} cation and the S^{2-} anion.

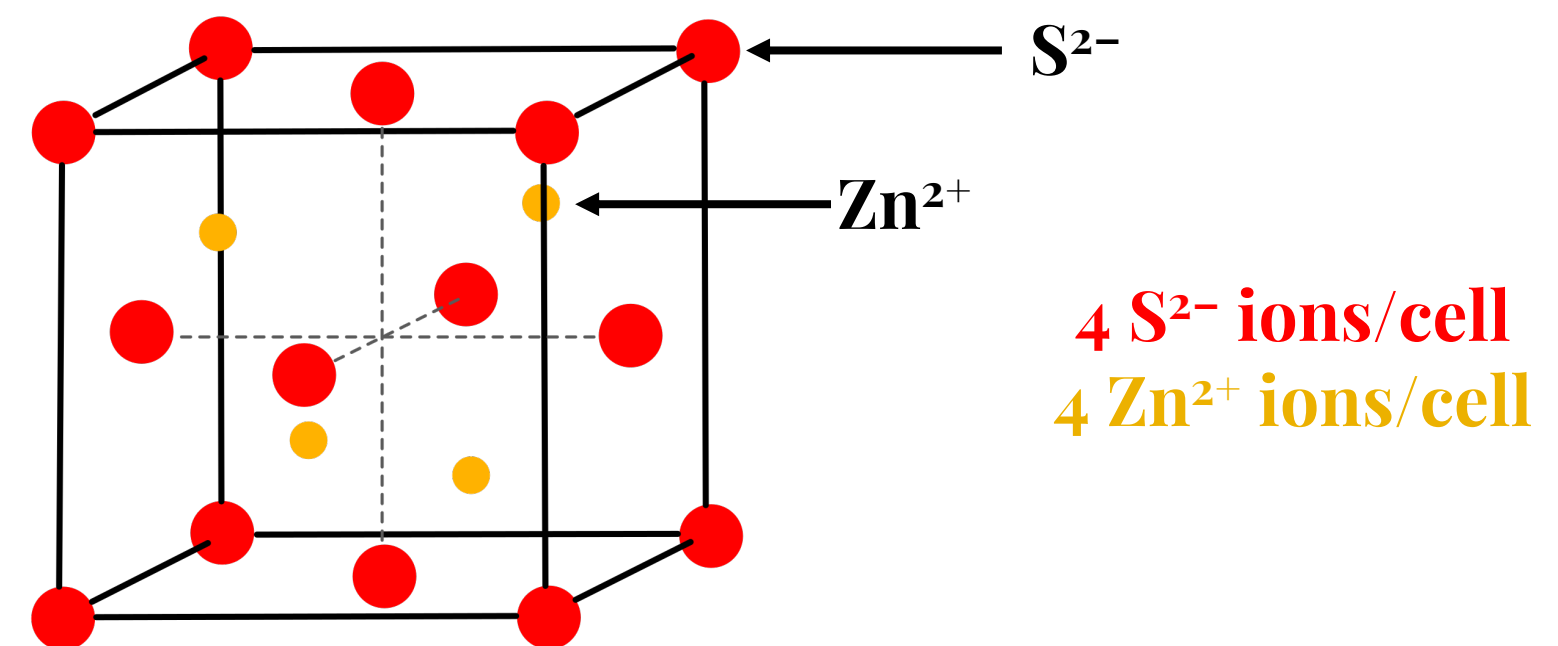


Again, the larger anion (S^{2-}) informs the general lattice, which is *fcc* for sulfide as well. We need then consider which and how many holes the Zn^{2+} cations will occupy.

Generally, the tetrahedral holes are smaller than the octahedral holes. As such, the Zn^{2+} cations will prefer to occupy the octahedral holes.



However, if we occupied all eight tetrahedral holes with Z^{2+} , the ratio of $\text{Zn}^{2+}:\text{S}^{2-}$ would be 2:1, which does not agree with charge balance. So, for ZnS, the Zn^{2+} cations only occupy *half* the tetrahedral holes (shown below) to give a 1:1 ratio.



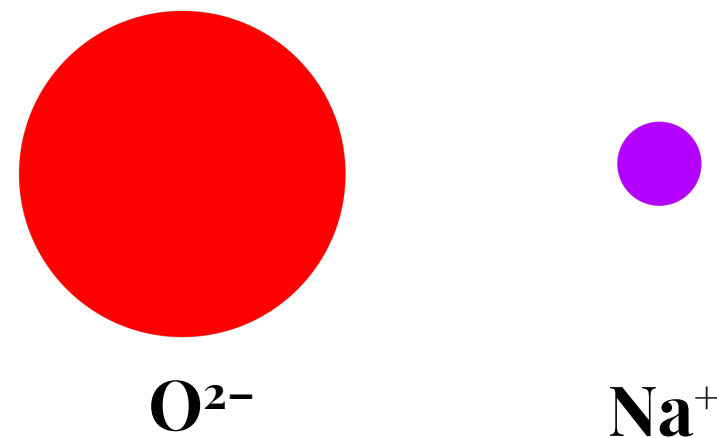
IONIC COMPOUNDS III

Objective: *Understand the structure of ionic compounds*



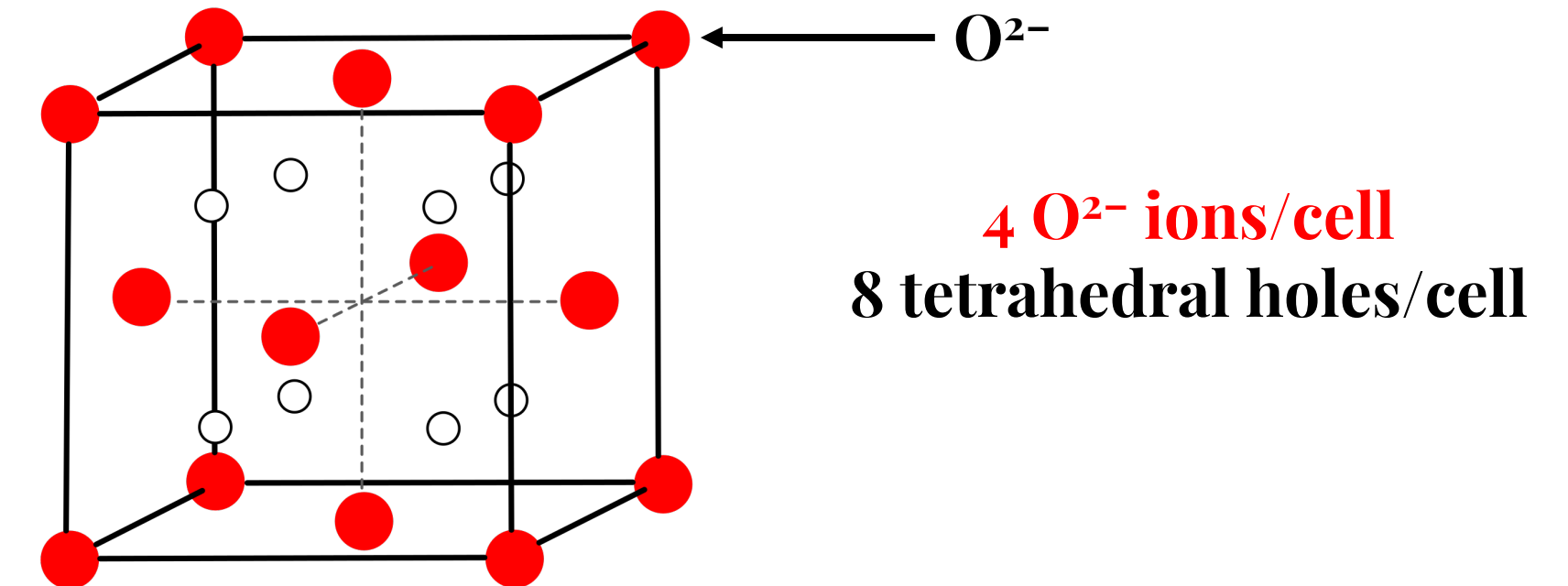
In some compounds, it is possible to fill all eight of the tetrahedral holes.

Take, for example, the ionic compound sodium oxide (Na_2O), which is composed of the Na^+ cation and the O^{2-} anion.



The larger anion (O^{2-}) informs the general lattice, which is *fcc* for oxide anions. We need then consider which and how many holes the Na^+ cations will occupy.

Again, we start with the *fcc* O^{2-} unit cell with the eight tetrahedral holes.



If the Na^+ cations occupied all of the octahedral holes or half the tetrahedral holes, like in the case of ZnS , we would get a formula of NaO for sodium oxide, which is incorrect. So, for Na_2O , the Na^+ cations occupy *all* of the eight tetrahedral holes (shown below) to give a 2:1 $\text{Na}^+:\text{O}^{2-}$ ratio.

