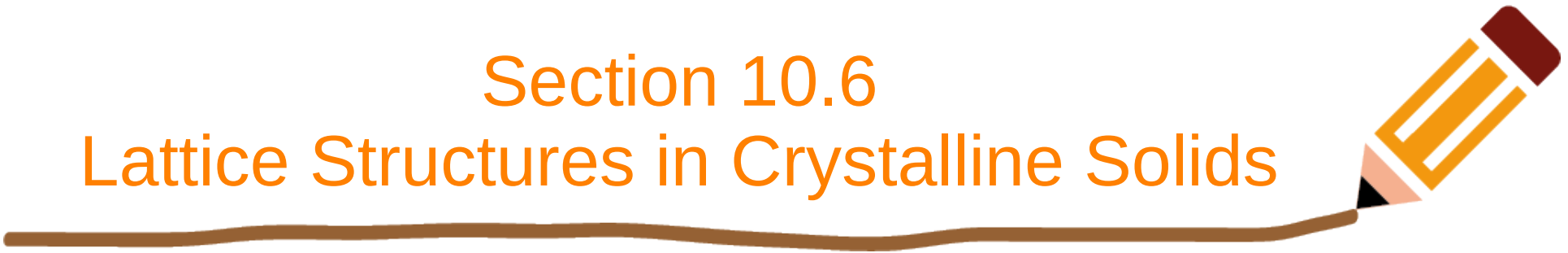
Section 10.6
Lattice Structures in Crystalline Solids



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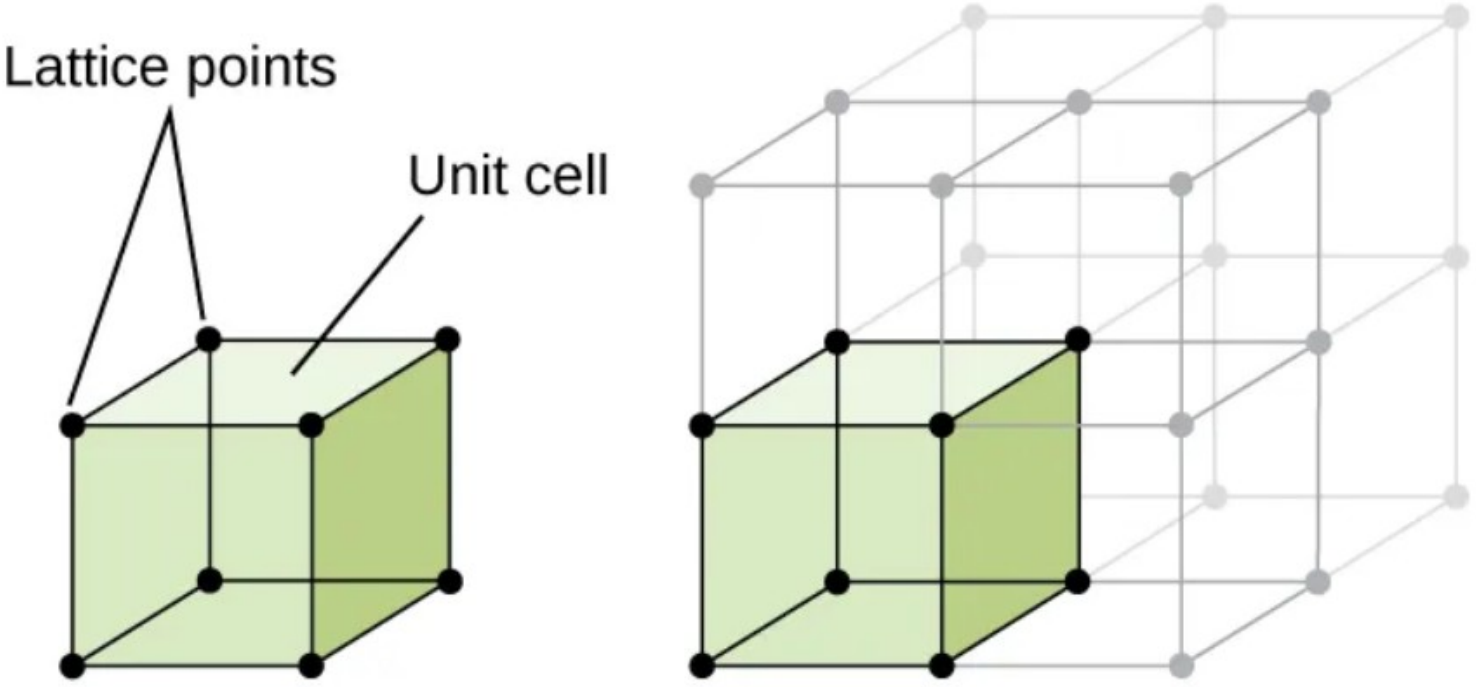
Learning Objectives

- Describe the arrangement of atoms and ions in crystalline structures
- Compute ionic radii using unit cell dimensions
- Explain the use of X-ray diffraction measurements in determining crystalline structures

Unit Cells

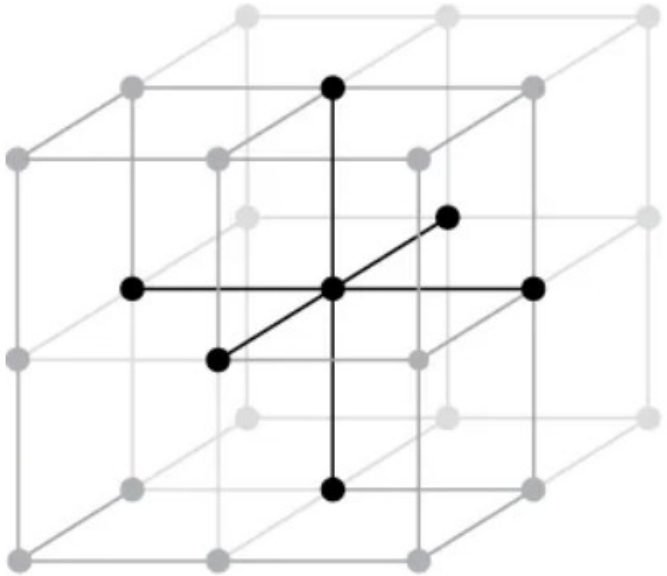
- Crystalline solids are closely packed atoms in a repeating pattern.
- The **unit cell** consists of lattice points that represent the locations of atoms or ions.
- The unit cell is the smallest repeating unit of the overall structure.
- Elements and compounds that crystallize with the same unit cell structure are called **Isomorphous**.

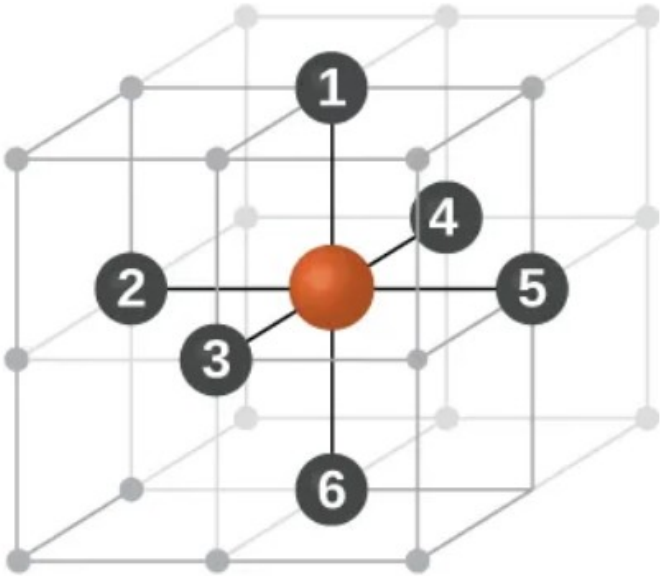
Unit Cells



Coordination Number

- The number of other particles that each particle in a crystalline solid contacts is known as its **Coordination Number**.



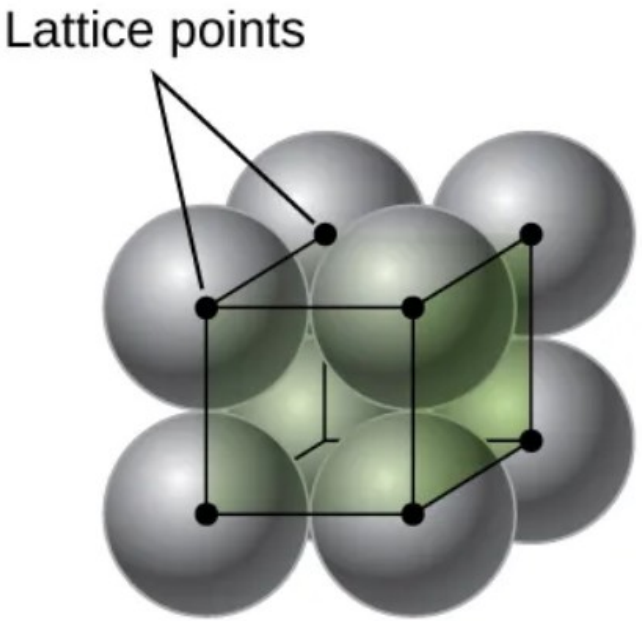


Structures of Metals

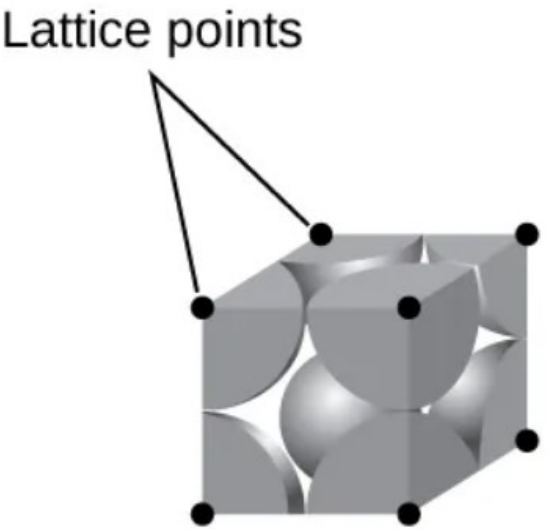
Simple Cubic Structure

- **Simple Cubic Unit Cells** have the atoms lying on the corners of a cube.
- This is an inefficient method of packing atoms. Only about 52% of the overall volume of the unit cell is filled.
- This arrangement has a coordination number of six. Each cell only holds one atom.

Simple Cubic Unit Cell



Simple cubic lattice cell

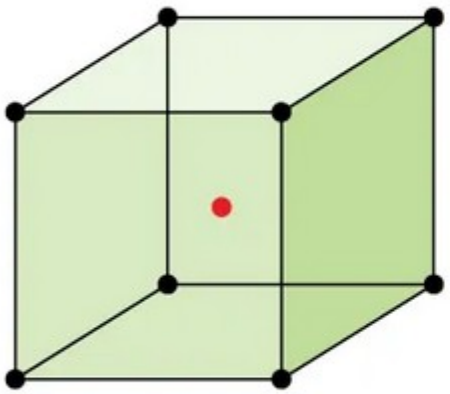


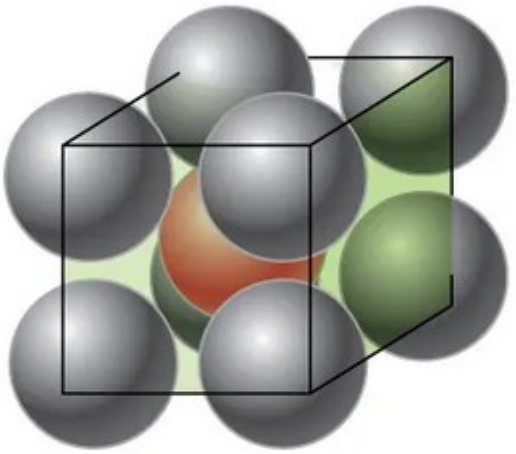
8 corners

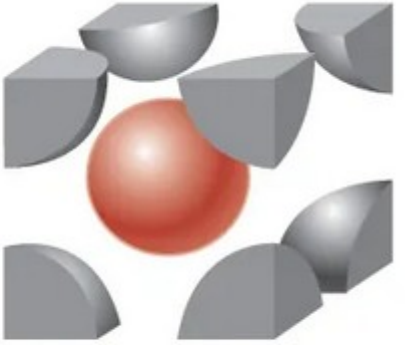
Body-Centered Cubic Structure

- **Body-Centered Cubic (BCC) Solids** have atoms at each corner and an atom in the center.
- BCC solids have a coordination number of eight.
- Each unit cell contains two atoms.
- 68% of the unit cell’s volume is filled.

Body-centered Cubic Unit Cell



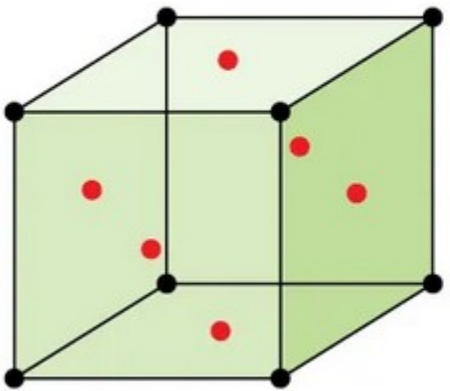


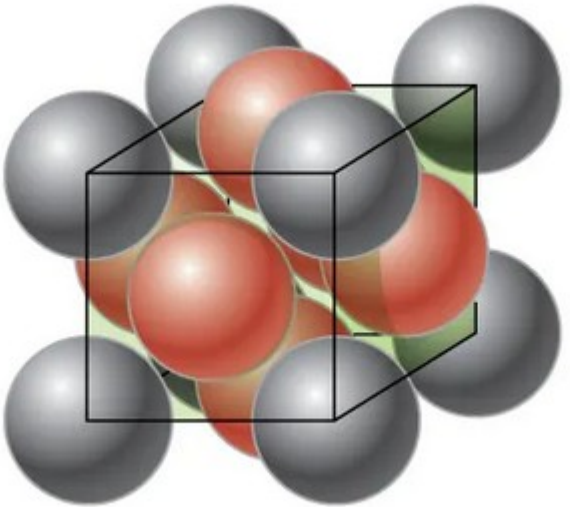


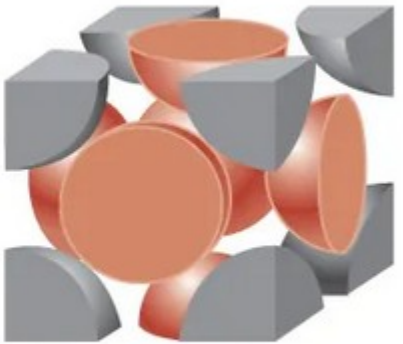
Face-Centered Cubic Structure

- **Face-Centered Cubic (FCC) Solid** has a cubic unit cell with atoms at all of the corners and at the centers of each face.
- This structure is also called **Cubic Closest Packing (CCP).**
- They have a coordination number of twelve.
- Each Unit cell contains four atoms.
- FCC arrangements pack the cells as efficiently as possible. 74% of the volume is filled.

Face-Centered Unit Cell

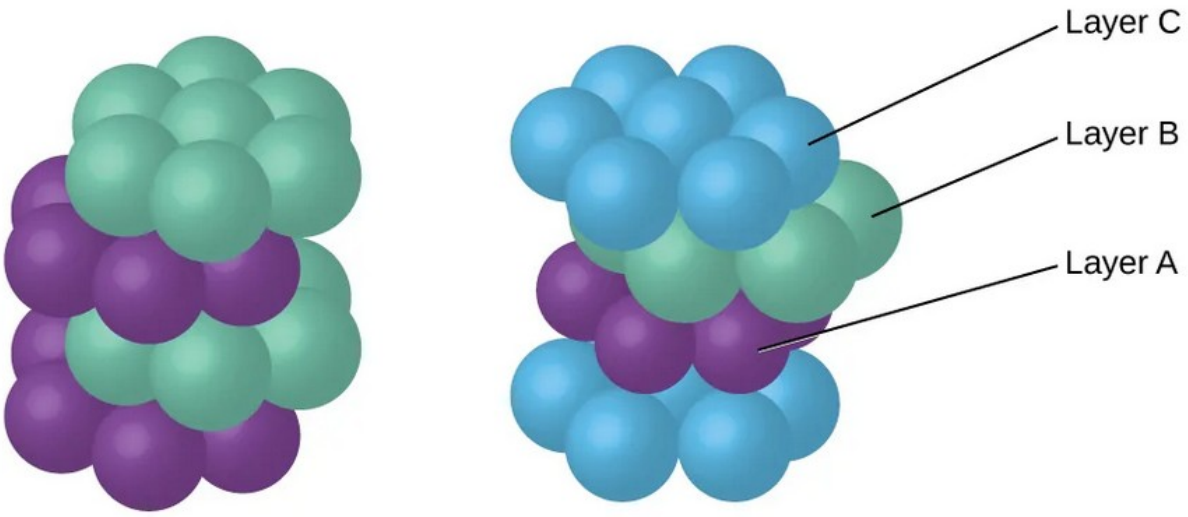






Hexagonal Closest Structure

- **Hexagonal Closest Packing (HCP)** consist of repeating layers of hexagonally arranged atoms.

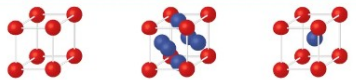
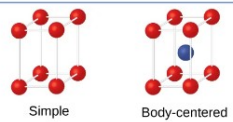
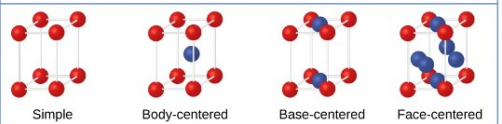
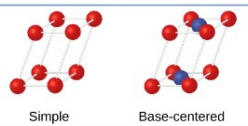
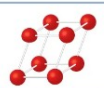
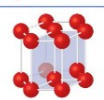
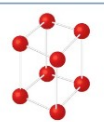


Hexagonal closest packed

Cubic closest packed

Other Lattice Systems

- There are seven different lattice systems, some of which have more than one type of lattice, for a total of fourteen different unit cells.

System/Axes/Angles	Unit Cells
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	
Hexagonal $a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$	
Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	

Structures of Ionic Crystals

Ionic Crystal Structure

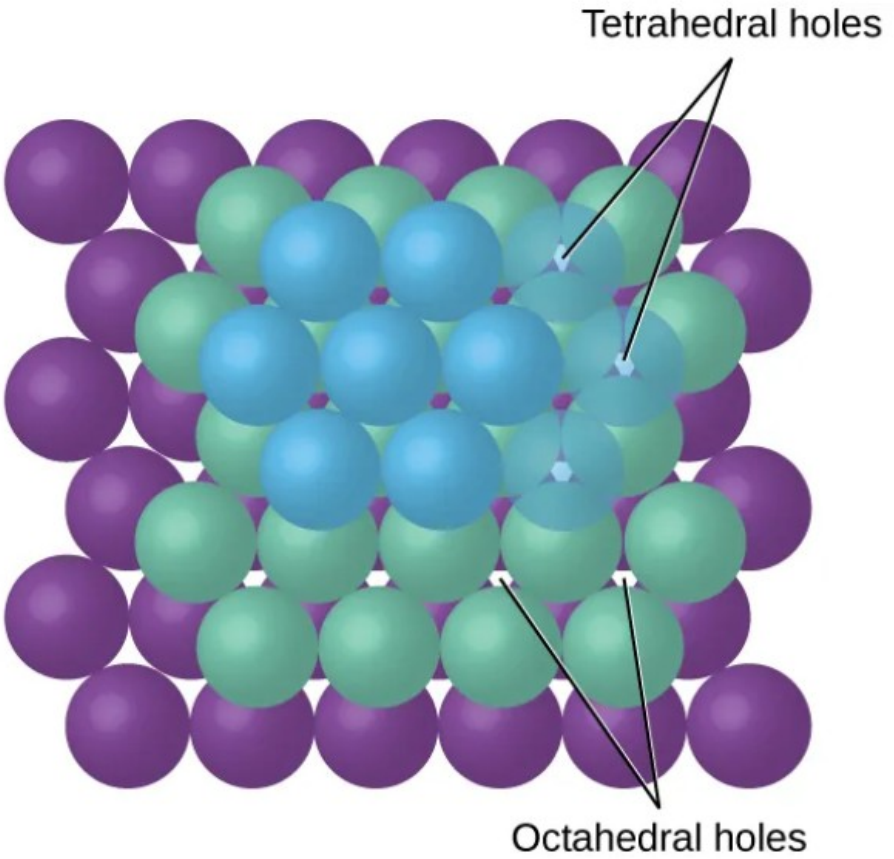
- The packing of ions into a crystal structure is more complex than the packing of metal atoms that are the same size.
- Stable structures for ionic compounds result when
  - Ions of one charge are surrounded by as many ions as possible of the opposite charge
  - Cations and anions are in contact with each other.
- Structures are determined by two principal factors
  - Relative sizes of the ions
  - Ratio of the numbers of positive and negative ions in the compound.

Simple Ionic Structures

- Larger anions are arranged in a closest-packed array.
- Smaller cations commonly occupy one of two types of **holes (or interstices)** between the anions.
- **Tetrahedral Holes** are found at the center of four atoms and are smaller.
- **Octahedral Holes** are found at the center of six atoms and are larger.

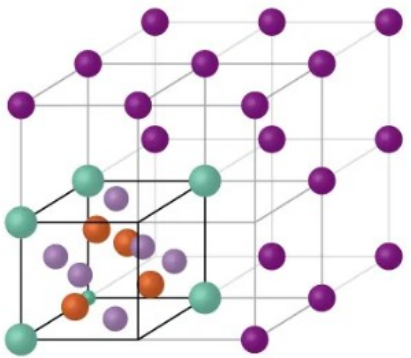
Ionic Holes

- Relatively small cations occupy tetrahedral holes, and larger cations occupy octahedral holes.



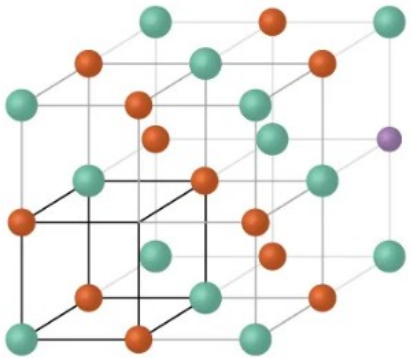
Cubic Holes

- If the cations are too large to fit into the octahedral holes, the anions may adopt a more open structure, such as a simple cubic array. The larger cations can then occupy the larger cubic holes made possible by the more open spacing.



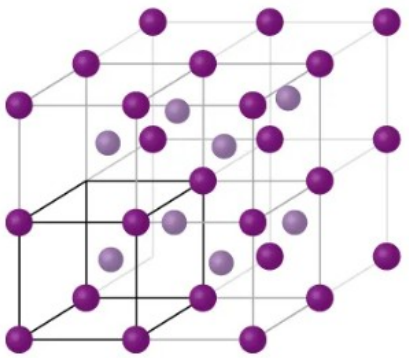
Tetrahedral hole

Cation radius is about 22.5 to 41.4% of the anion radius



Octahedral hole

Cation radius is about 41.4 to 73.2% of the anion radius

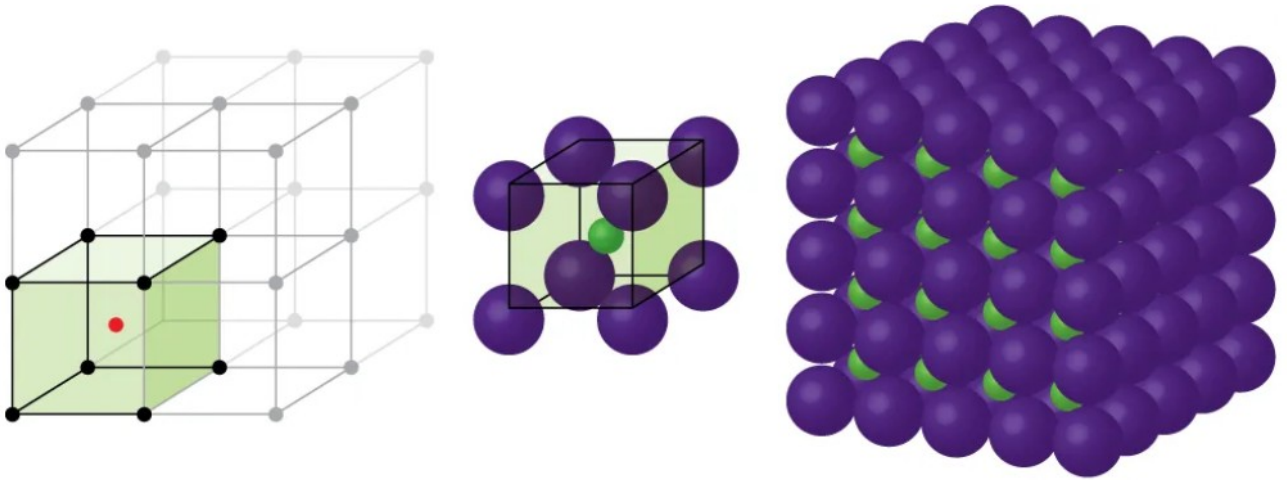


Cubic hole

Cation radius is about 73.2 to 100% of the anion radius

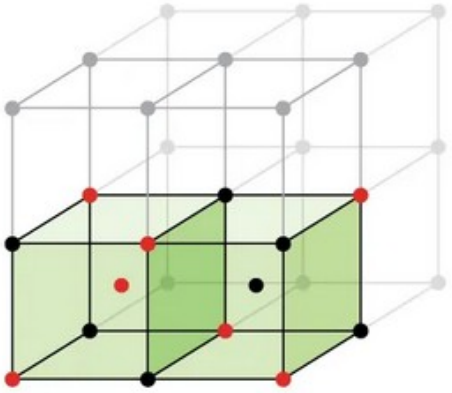
Unit Cells of Ionic Compounds

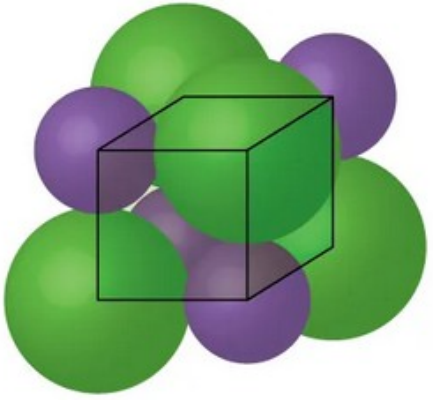
- When an ionic compound is composed of cations and anions of similar size in a 1:1 ratio, it typically forms a simple cubic structure.

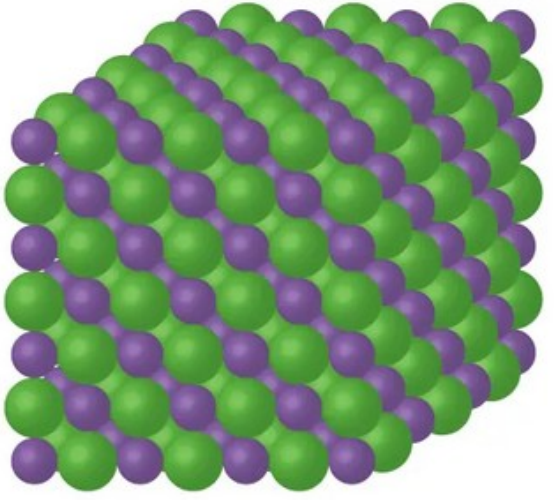


Unit Cells of Ionic Compounds

- When an ionic compound is composed of a 1:1 ratio of cations and anions that differ significantly in size, it typically crystallizes with an FCC unit cell.

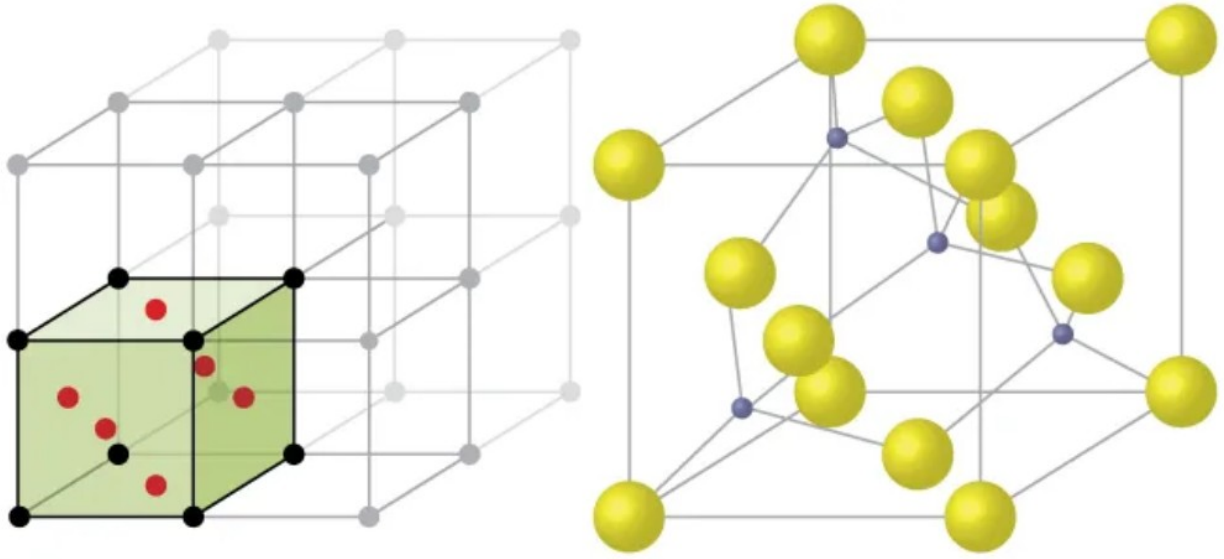






Tetrahedral Holes

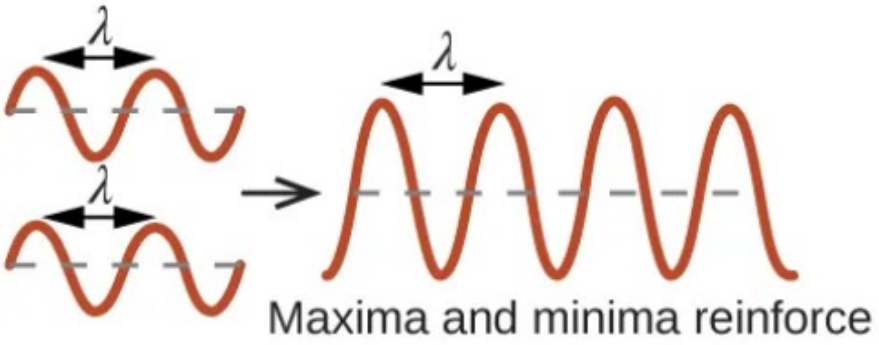
- ZnS forms an FCC unit cell with sulfide ions at the lattice points and much smaller zinc ions occupying half of the tetrahedral holes in the structure.



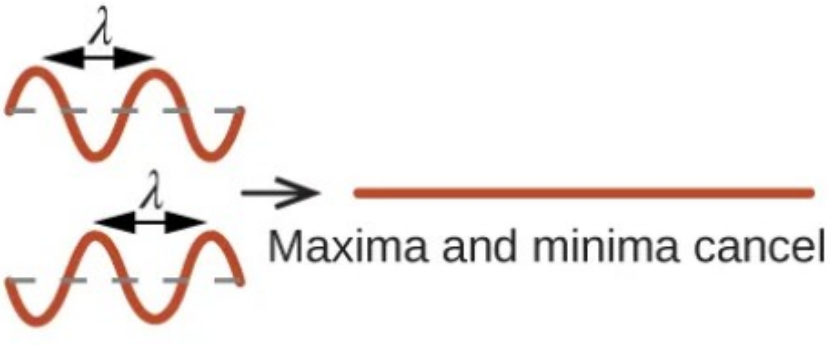
X-Ray Crystallography

- **X-Ray Crystallography** is a method of determining the crystal structure of a solid by analyzing the diffraction pattern of xrays.
- **Diffraction** is the change in the direction of travel experienced by an electromagnetic wave when it encounters a physical barrier whose dimensions are comparable to those of the wavelength of the light.
- **Interference** is a process by which the waves combine to yield either an increase or a decrease in amplitude depending upon the phase of the two waves.

Constructive vs. Destructive



Constructive interface



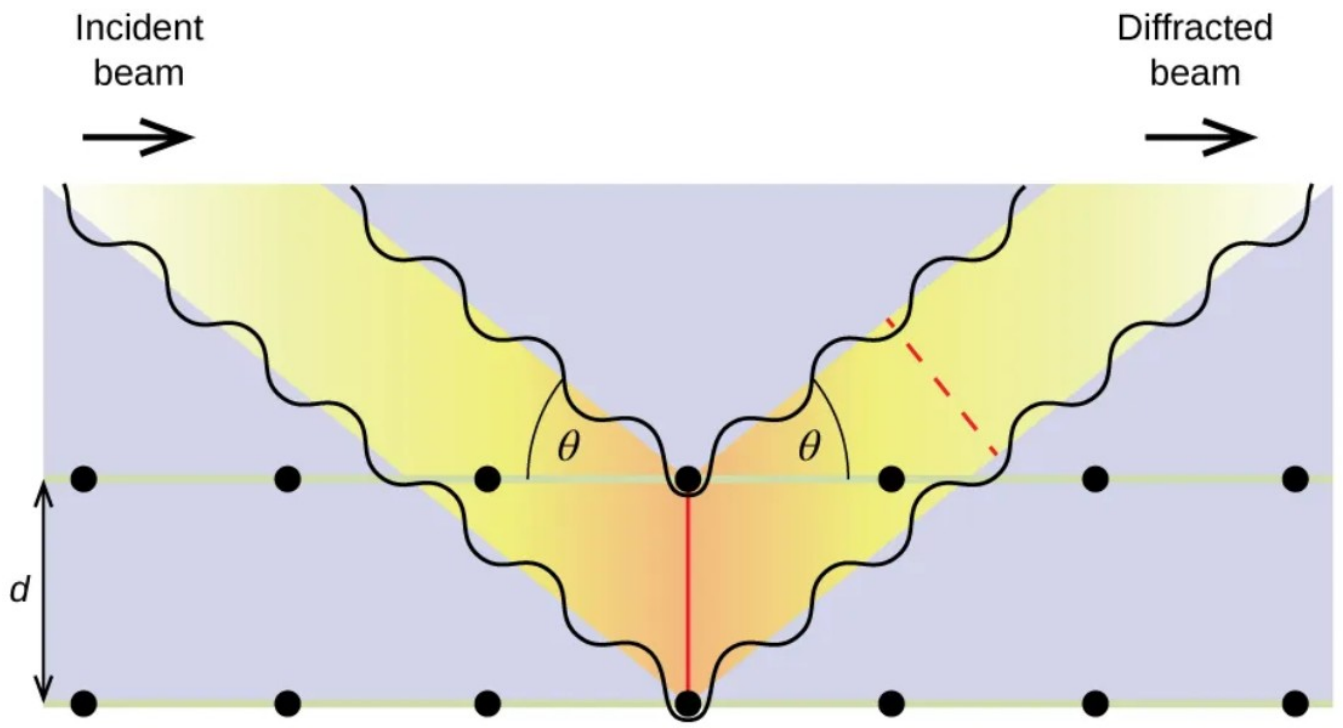
Destructive interface

Bragg Equation

- When X-rays of a certain wavelength, λ, are scattered by atoms in adjacent crystal planes separated by a distance, d, they may undergo constructive interference when the difference between the distances traveled by the two waves prior to their combination is an integer factor, n, of the wavelength.

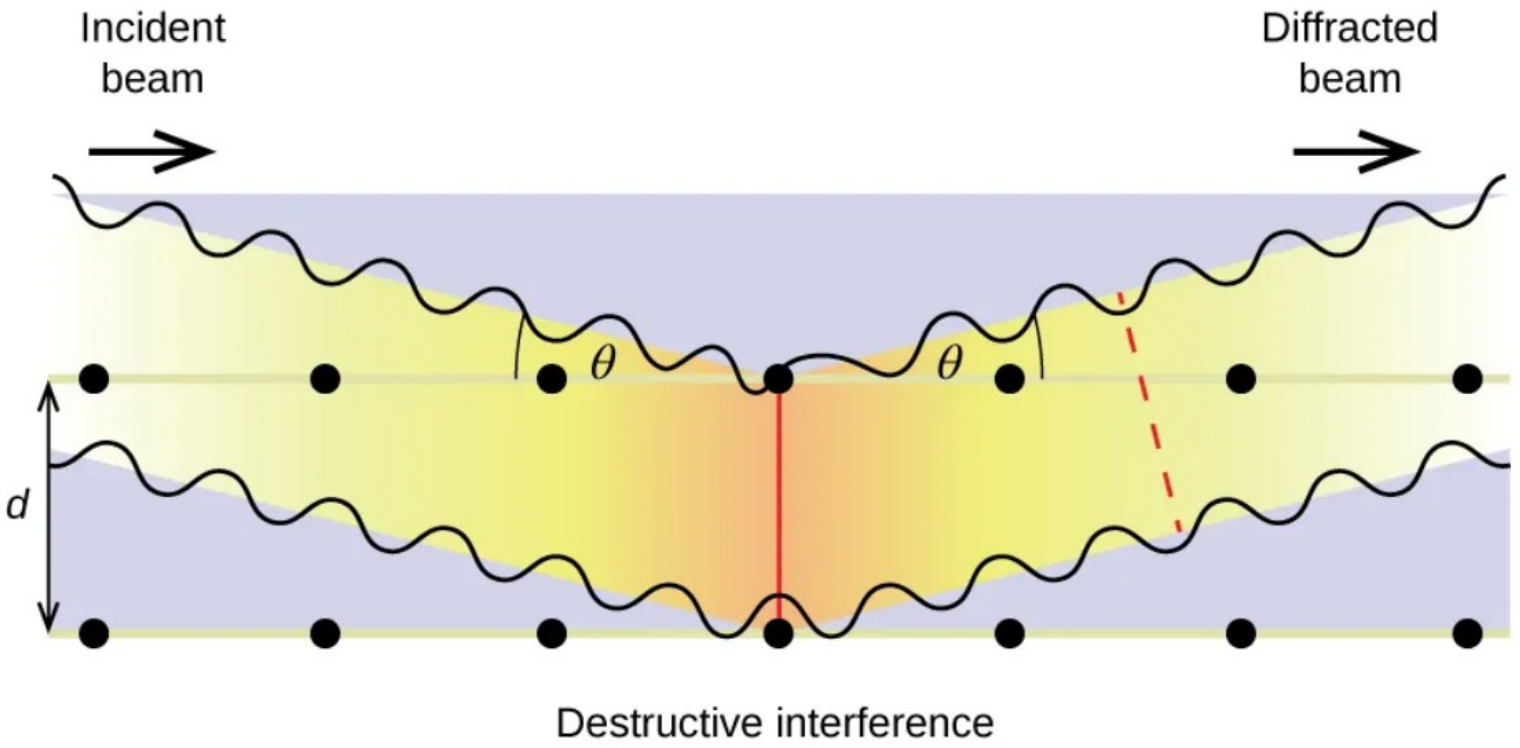
$$n\lambda = 2d\sin\theta$$

Constructive Interference



Constructive interference

Destructive Interference



X-Ray Diffractometer