4. Structures of Simple Solids

4.1 Structures of metals

The familiar properties of metals stem from the metallic bonding and delocalization of electrons throughout the solid. Metals are malleable (easily deformed when pressure is applied), ductile (able to be drawn into a wire) because the electrons can adjust rapidly to relocation of metal atom nuclei and there is no directionality in the bonding. In the solid, metal atoms can be represented by hard spheres and the structure is the outcome of stacking these spheres densely together.

4.1.1 Close-packed structures

Close-packed structures (ABA / hexagonal close-packing (hcp) or ABC / cubic close-packing (ccp)) are observed in metals (see Figures 29 and 30):

![Figure 29](image1.png)

(a) The third layer reproduces the first, giving ABA structures. (b) The third layer lies above the gaps in the first layer, giving ABC structure. (see also Figure 30)

The unoccupied space in a close-packed structure amount to 26% of the total volume (can be calculated from Figure 31). Properties of metals, such as the calculated density, can be obtained by the molar mass and lattice parameter (= length of the side of the cube).

Which of the close-packed structures, hcp or ccp (Figure 31), a metal adopts depends on the details of the electronic structure of its atoms, the extent of interaction between the second-nearest neighbors, etc. Cobalt is an example that shows complex polytypism: cobalt is ccp above 500°C but undergoes transition when cooled. The layers stack in a complex repetition (e.g., ABACBAB...).

**Exercise 1:** Calculate the density of gold with a ccp (ABC) structure. Molar mass \( M = 196.97 \text{ g mol}^{-1} \), lattice parameter (length of the side of the cube) = 0.409 nm

**Exercise 2:** Calculate the metallic radius of Osmium. Molar mass \( M = 190.2 \text{ g mol}^{-1} \), density = 22.6 g cm\(^{-3}\) (highest of all the elements, used as weighting material in fishing equipment)

4.1.2 Nonclose-packed structures

Not all the metals have structures based on
close-packing (Figure 31). Even metals that are close-packed may undergo phase-transition to a less closely packed structure when they are heated and the atoms undergo large-amplitude vibrations.

One commonly adopted arrangement is known as the body-centered cubic (bcc) structure (Figure 32a), in which a sphere is at the center of a cube with spheres at each corner. The coordination number is 8. Although a bcc structure is less closely packed than the ccp and hcp structures (coordination number = 12), the difference is not so great. Alkali metals adopt bcc structures because not only s electrons but also p electrons, whose orbitals are anisotropic, are involved in the metallic bonding.

Exercise 3: Calculate the amount of occupied space in a bcc structure.

The least common metallic structure is the primitive cubic structure (Figure 32b), in which spheres are located at the corner of a cube. The coordination number is 6. One form of polonium is the only example.

4.2 Structures of ionic solids

Ionic solids such as NaCl and KNO₃ are often recognized by their brittleness because the electrons made available by the cation are localized on a neighboring anion instead of a mobile electron sea as in the case of metals. The structures of ionic solids is based on the “ionic model”, which treats the solid as an assembly of oppositely charged hard spheres that interact by nondirectional electrostatic forces (Coulomb forces).

4.2.1 CsCl structure

Cesium chloride structure is shown in Figure 33. This structure can be viewed as two interlocking primitive cubic cells, one of Cs⁺ and the other of Cl⁻. The coordination number of both types of ions is 8, which is the highest in ionic solids. The radii of the ions are similar in CsCl structures. CsI and CsBr also take this structure.

4.2.2 NaCl structure

Sodium chloride structure or the rock-salt structure is shown in Figure 34. This structure can be viewed as two interlocking ccp cells (spheres exist at each vertex of the cube and at each center of the plane (face)), one of Na⁺ and the other of Cl⁻. An alternative view is that the larger anions (Cl⁻) take the ccp array and the smaller cations (Na⁺) occupy the octahedral holes in the ccp array. This structure is most common in ionic solids and is called the face-centered cubic lattice (fcp). The coordination number of both types of ions is 6. The cations are smaller than the anions in rock-salt structures. AgCl, KI, and LiF also take the fcp structure.
4.2.3 Zinc-blende structure

Zinc-blende structure is shown in Figure 35. Like the rock-salt structures, the larger anions take the ccp array ($S^2^-$) while the much smaller cations (Zn$^{2+}$) occupy the tetrahedral holes. The coordination number of both types of ions is 4.

4.2.4 Wurtzite structure

Wurtzite structure is shown in Figure 36. Wurtzite is another polymorph of zinc sulfide. It differs from the zinc-blende structure in being derived from an hcp array rather than the ccp array of larger anions. The coordination number of both types of ions is 4. ZnO, AgI, and SiC also take the Wurtzite structure.

4.2.5 Correlation between the radius ratio $r_{\text{cation}} / r_{\text{anion}}$ and the crystal structure

The minimum radius ratio that can support a given coordination number is calculated by considering the geometrical problem of packing together spheres of different sizes. It is argued that, if the radius falls below the minimum given, then ions of oppositely charged will not be in contact and ions of same charge will touch. Then, a lower coordination number becomes favorable.

Another way of looking at this argument is that as the radius of the cation increases, more anions can pack around it, giving a larger number of energetically favorable Coulomb interactions. A cation radius between $0.225r$ and $0.414r$ ($r$: radius of anion) can occupy a tetrahedral hole in the ccp arrays of anions (= zinc-blende or Wurtzite structures). However, once the radius of a cation reaches $0.414r$, the occupation of a octahedral hole becomes favorable (= rock-salt structure). If the radius of a cation reaches $0.732r$, the octahedral hole can no longer be occupied and the the CsCl structure becomes favorable.

Figure 35 (a) Zinc-blende structure and its (b) projection.

Figure 36 (a) Wurtzite structure and its (b) projection.

Figure 37 The local structures of ionic solids used to calculate the radius ratio. Left: 8-coordination (CsCl structure), middle: 6-coordination (rock-salt structure), right: 4-coordination (the two ZnS structures).

Figure 38. Correlation between radius ratio, crystal structure, and Coulomb energy.