Chapter 16.   Solids

16.1. Crystal Lattices

Crystals consist of atoms or molecules bound tightly into regular lattices. Atoms (noble gases and metals) and simple covalent molecules form the simplest solids with structures predictable from the solid geometry of packed spheres. Ionic solids pack smaller ions into the holes between the larger ions. Network covalent solids can be crystalline with structure determined by three-dimensional directional covalent bonds, or random where ambiguities in bonds to neighbors occur.

The most dense packing is called **close packing** and consists of layers of atoms at the apices of a network of hexagons. Each layer is shifted with respect to the adjacent layer to bring the layers close together, resulting in two kinds of spaces, or *holes* in the lattice, *tetrahedral* and *octahedral*, named for the geometric figure of the surrounding atoms. Simple atoms like noble gas atoms solidify in close-packed arrangement. The larger ion in ionic solids may also close-pack, with the smaller ion fitting in the tetrahedral or octahedral holes, depending on the ratio of the ionic radii. *There are as many octahedral holes as close-packed sites, but only half as many tetrahedral holes as close-packed sites.* The occupancy of the holes is therefore dependent on both the relative sizes of the ions and the stoichiometry of the crystal. The following algorithm classifies the structure of crystalline solids.

Crystal Structure Algorithm

Purpose: To determine the structure of a solid substance.

Procedure:

1. Classify the substance as simple (noble gas, metal or simple covalent), co-valent network or ionic. Atomic substances pack in closest-packing structure. Covalent network substances pack in lattice structures reflecting the directional character of the covalent bonding.

2. If ionic, determine the sizes of the ions.

   a) If the ratio of ionic radii is less than 0.414, the larger ion is close-packed and the smaller ion fits into tetrahedral holes.

   b) If the ratio of ionic radii is between 0.414 and 0.732, the larger ion is close-packed and the smaller ion fits into octahedral holes.

   c) If the ratio of ionic radii is between 0.732 and 1.0, the lattice consists of interlocking simple cubes, with each ion fitting in the simple cubic hole of the other.

Example 16.1 Discuss the crystalline lattice of table salt.

1. NaCl is ionic.

2. The ratio of ionic radii is $r(Na^+)/r(Cl^-) = 97/181 = 0.54$. Therefore the solid structure consists of close-packed chloride ions with sodium ions in the octahedral holes.

The fraction of space occupied by the atoms in a solid measures the **packing efficiency**, which may be calculated in terms of the smallest repetitive unit of the solid, called the **unit cell**, according to the following formula:

$$\text{packing efficiency} = \frac{V_{\text{occupied}}}{V_{\text{total}}} = \frac{(\text{atoms/cell})(\text{volume/atom})}{(\text{volume/cell})} \qquad (16.1)$$

where atoms/cell is the effective number of atoms in a unit cell (sum of all pieces of atoms), volume/atom is the atomic volume, and volume/cell is the volume of a unit cell. The simplest unit cells are the *simple cubic (SC) unit cell*, with eight atoms at the corners of a cube, the *body-centered (BCC) unit cell*, with eight atoms at the corners and one at the center of a cube, and the *face-centered (FCC) cubic unit cell*, with atoms at each corner and face of a simple cube. The FCC is a close-packed structure. Solid geometry applies to solids. Refer to Section 3.9 for a short review. The volume/atom for spherical atoms is just the volume of a sphere of radius equal to the radius of the atom.

Example 16.2 Calculate the packing efficiency of a body-centered cubic unit cell.

1. A BCC unit cell has 8(1/8) atoms on the corners and one in the center, for a total of 2 effective atoms per unit cell.

2. The volume per atom is $(4/3)\pi r^3$, where r is the radius of the atom.

3. The volume of a cubic unit cell is just the cube of the edge length of the unit cell. To use this quantity in Eq. (16.1), it is necessary to relate the edge length of the unit cell with the radius of the atoms in the cell. The relation is best derived from a space model of eight spheres on the corners of a cube surrounding a central sphere. The spheres on the corners have to move apart to make room for the central sphere (of the same radius), so they don't touch. A straight-line path through the *diagonal* of the cube connects the central sphere to two corner spheres and passes through the points where the spheres make contact. Solid geometry tells us that the length of the diagonal of a cube is √3 times the length of the edge (e).[1] Since the diagonal of the cube passes through four atomic radii, √3e = 4r, and the volume of the unit cell is $e^3 = (4r/\sqrt{3})^3$.

4. Combining the above ratios into Eq. (16.1) gives

$$\text{packing efficiency} = \frac{[2][(4/3)\pi r^3]}{(4r/\sqrt{3})^3} = \sqrt{3}\,\frac{\pi}{8} = 0.68017476$$

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[1] See Fig. 3.6. This relationship can be obtained by two successive applications of the Pythagorean theorem to the right triangles formed first by two edges of the cube (of length e) and a diagonal of a face (of length f), and then formed by an edge, the diagonal of the face and the diagonal of the cube (of length d): $f^2 = e^2 + e^2$, and $d^2 = f^2 + e^2 = 3\,e^2$.

X-rays have wavelengths comparable to the size of unit cells and produce diffraction patterns on passing through crystals from which lattice spacing and atomic radii may be derived. For a given wavelength of x-ray light, λ, constructive interference (bright light) is produced between beams of light reflected from adjacent layers in a crystal at certain angles of reflection, θ, dependent on the the spacing between layers of the lattice, a, according to the *Bragg formula*,

$$2 \, e \, \sin(\theta) = n \, \lambda \qquad (16.2)$$

where n is a positive integer, called the *order* of refraction, and θ has units of degrees.

The lattice spacing may be combined with the density of the crystal to derive the unit cell packing. Expressing the density first in macroscopic variables, then in microscopic variables produces the formula:

$$D = \frac{m}{V} = \frac{\text{(mass/atom) (atoms/cell)}}{\text{(volume/cell)}} = \frac{AM \text{ (atoms/cell)}}{N_A e^3}, \qquad (16.3)$$

where AM is atomic mass in g/mol, N_A is Avogadro's number, and e is the lattice spacing. X-ray data may be combined with density measurements to estimate the radii of atoms, as the following procedure explains.

Crystal Atom Radius Algorithm

Purpose: To determine the radius of an atom in an atomic crystal.

Procedure:

1. Determine the lattice spacing from the x-ray reflection angle for a given wavelength, according to Eq. (16.2).

2. Use Eq. (16.3) to determine the number of effective atoms per unit cell from the lattice spacing, atomic mass and density of the crystal. SC, BCC and FCC unit cells have 1, 2 and 4 atoms/cell, respectively.

3. From the lattice spacing and geometry of the unit cell, determine the atomic radius. For SC, $r = e/2$, for BCC, $r = \sqrt{3}e/4$, for FCC, $r = \sqrt{2}e/4$, where e is the unit cell edge length and r is the atomic radius. It may be assumed that the lattice spacing and unit cell edge length are the same.

Example 16.3 Calculate the radius of a sodium atom from the experimental observation that X-rays of wavelength 149.3 pm are reflected at an angle of 10° in first order (n = 1).

1. From the data and Eq. (16.2), the lattice spacing e = 430 pm. $e = \dfrac{(1)(149.3)}{(2)\sin(10°)}$

2. The density of metallic sodium is 0.97 g/cc, and the atomic mass is 23.0. Rearranging Eq. (16.3) to solve for (atoms/cell), the given data yields 2.0 atoms/cell. This corresponds to the packing in a BCC unit cell.

3. Since $r = \sqrt{3}e/4$ for BCC, assuming e = 430 pm yields r = 186 pm.

If the cell type is known, the atomic radius can be found directly from the density using Eq. 16.3.

Example 16.4 Calculate the radius of an neon atom from the experimental density of 1.444 g/cc.

Assuming that noble gases are close-packed in a FCC lattice, the number of atoms per unit cell is 4. From the data and Eq. (16.3), the lattice spacing may be deduced:

$$e = (\frac{AM \text{ x atoms/cell}}{D \text{ x } N_A})^{1/3}$$

$$e = (\frac{20.179 \text{ g/mol x 4 atoms/cell}}{1.444 \text{ g/cm}^3 \text{ x } 6.022 \times 10^{23} \text{ atoms/mol}})^{1/3} = 4.528 \times 10^{-8} \text{cm} = 452.8 \text{ pm}$$

This is close to the experimental lattice spacing from x-ray analysis of 445.5 pm, confirming that Ne indeed does pack in the most efficient way.

Since r = √2e/4 for FCC and e = 452.8 pm, r = 160 pm.

16.2. Lattice Energy

The energy required to separate all the species (atoms, molecules or ions) at the lattice sites in a crystal to infinity is called the **crystal lattice energy** (LE) of the crystal. In 1923 Max Born applied the first law of thermodynamics to obtain experimental values of crystal lattice energies (LE). The direct heat of formation of a solid substance is equal to the heat of an indirect path passing through separated particles (atoms or ions).
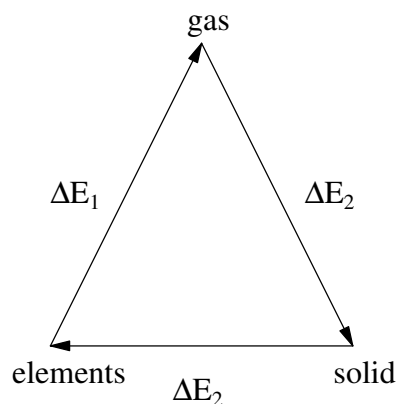
Fig. 16.1 Born Cycle

The arrows indicate the directions from initial to final states. Applying Eq. (10.4) to the cycle leads to

$$\Delta E_{\text{cycle}} = \Delta E_1 + \Delta E_2 + \Delta E_3 = 0$$

ΔE_1 can be obtained experimentally from sublimation energies, bond energies (and ionization potentials and electron affinities for ionic crystals)

$$\Delta E_1 = \Delta E_{sublimation} + BE + IP + EA$$

ΔE_3 is the negative of energy of formation of the crystal from the elements. It too can be obtained experimentally (Chapter 13). ΔE_2 is the *negative* of the lattice energy, which may be deduced from the experimentally measured quantities. Thus, solving for the lattice energy of a metal-nonmetal (MN) ionic crystal,

$$\tilde{LE}(MN) = \Delta \tilde{E}_{sublimation}(M) + \tilde{BE}(N) + \tilde{IP}(M) + \tilde{EA}(N) - \Delta \tilde{E}_f(MN) \qquad 16.5$$

Example 16.5 Determine the experimental lattice energy of NaCl.

The sublimation energy of sodium metal is 107 kJ/mol, the ionization energy of gaseous sodium is 496 kJ/mol, the bond dissociation energy of gaseous dichlorine is 243 kJ/mol of molecules (Table 8.1), or 243/2 kJ/mol of atoms, the electron affinity of gaseous atomic chlorine is −348 kJ/mol, and the heat of formation of crystalline sodium chloride is −411 kJ/mol. Putting this information into Eq. (16.9) gives

$$\tilde{LE}(NaCl) = \Delta \tilde{E}_{sublimation}(Na) + \tilde{BE}(Cl_2)/2 + \tilde{IP}(Na) + \tilde{EA}(Cl) - \Delta \tilde{E}_f(NaCl)$$

$$\tilde{LE}(NaCl) = 107 + 243/2 + 496 - 348 + 411 = 788 \text{ kJ/mol}$$

Lattice energy is a measure of the bonding strength in the solid and is closely related to the interparticle binding energy. To make a connection between the energy of the entire lattice and the individual interparticle bond energies, it is necessary to recognize that the particles are packed closely and interact with significantly with neighbors beyond the nearest neighbors. The total interaction energy is the accumulation of all the interactions at the sites of increasing distance from a given site. This generates a series (with alternating signs for attractions to opposite charged nearest neighbors, repulsions for like charged next neighbors, etc.) which converges because interaction energies fall off with increasing distance (Eq. (8.5)). The total energy is proportional to an individual pair energy through the series, called the *Madelung constant*. Madelung constants depend on the geometry of the lattice, but are small numbers greater than unity. The connection between total lattice energy and bond energy provides a way to calculate lattice energies from bond energies.

Example 16.6 Estimate the lattice energy of NaCl, given the lattice spacing from X-ray analysis is 282 pm and the Madelung constant is 1.747558.

Since NaCl is essentially ionic, we can assume at first that the total binding potential energy in the lattice is due to the Coulombic attraction of the two ions at their lattice separation (282 pm) multiplied by the Madelung constant for all neighboring interactions. The total ionic attraction is then given by Coulomb's Law, Eq. (4.9), with charge q = 1 for both Na^+ and Cl^-, e equal to the charge on the electron, 1.518919×10^{-14} $(Jm)^{1/2}$, k equal to the Madelung constant, and R_e equal to the ion separation.

$$LE = \frac{q^2 e^2 k}{R_e}$$

$$LE = \frac{(1.518919 \times 10^{-14} \ (Jm)^{1/2})^2 (1.747558)}{282 \ pm} \left(\frac{10^{12} \ pm}{1 \ m}\right)\left(\frac{6.022 \times 10^{23} \ molecules}{1 \ mol}\right)\left(\frac{1 \ kJ}{10^3 \ J}\right) = 861 \ kJ/mol$$

A strictly ionic model ignores the repulsive contribution to the total potential energy. The Mie potential (Eq. (8.5)) takes both attraction and repulsion into account, and should give a more accurate estimate of the lattice energy. From the footnote to Eq (8.5), we see that

$$D_e = \frac{B}{R_e^n} \left(1 - \frac{1}{m}\right)$$

where $LE = D_e$, B is the Coulombic potential coefficient $q^2 e^2 k$, and n = 1. The $1 - \frac{1}{m}$ term corrects the attractive potential for repulsion. Taking m = 12, a common value for repulsive interactions, corrects the lattice energy for NaCl to 789 kJ/mol.

Note that the simple ionic model for solids requires knowledge only of the lattice spacing to estimate the lattice energy. Lattice spacing can in turn be estimated by adding ionic radii. For example, $r(Na^+) + r(Cl^-) = 97 + 181 = 278$ pm, close to the X-ray value of 282 pm.[2] Hence, useful information about a large number of solids can be obtained from a relatively small table of radii.

Table 16.1 illustrates trends in lattice energies due to size and charge. (Values are experimental except the alkai oxides are estimated theoretically. Values may have uncertainities of a few kJ/mol.) The table is blocked into groups by charge which clearly show higher

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[2] The diatomic radii in Table 8.1, where $R_e(NaCl) = 236$ pm, are for gas molecules, not solids.

charge produces higher lattice binding energy. Within each block lattice energy decreases with increasing size for both positive and negative ions.

Table 16.1 Lattice Energies (kJ/mol)

	H^-	F^-	Cl^-	Br^-	I^-	OH^-	O^{2-}	CO_3^{2-}	SO_4^{2-}
Li^+	920	1036	853	807	757	1039	2799	2269	2142
Na^+	808	923	786	747	704	900	2841	2030	1938
K^+	714	821	715	682	649	804	2238	1858	1796
Rb^+	685	785	689	660	630	773	2163	1795	1748
Cs^+	694	740	659	631	604	724	_	1702	1658
Be^{2+}	3295	3505	3020	2914	2800	3629	4293	_	_
Mg^{2+}	2706	2957	2526	2440	2327	3006	3795	3122	_
Ca^{2+}	2394	2630	2258	2176	2074	2645	3414	2810	2480
Sr^{2+}	2253	2492	2156	2075	1963	2483	3217	2688	2484
Ba^{2+}	2121	2352	2056	1985	1877	2239	3029	2554	2378
Cu^{2+}							4135	3327	2166
Al^{3+}	5924	5215	5492	5361	5218	5627	15916	_	_

Lattice energies can be used to determine experimental values of bonding energies since they equal the sum of sublimation from crystal to gas molecules and dissociation of the gas molecules.

$$LE(crystal) = \Delta E_{sublimation}(crystal) + \Delta E_{bond}(molecule) \qquad (16.6)$$

Example 16.7 Estimate the dissociation energy of gaseous NaCl to its ions.

We will apply Eq. (16.6), using the lattice energy obtained from Example 16.4 and the experimental value of the sublimation energy of NaCl, 234 kJ/mol.

$$\Delta E_{bond}(molecule) = LE(crystal) - \Delta E_{sublimation}(crystal) = 788 - 234 = 554 \text{ kJ/mol}$$

Another estimate adds to the value of the bond dissociation energy (to neutral atoms) in Table 8.1 the sum of the ionization potential of Na and the electron affinity of Cl, 412 + 496 − 348 = 560 kJ/mol.

Summary

    The solid state is dominated by order, the gas state is dominated by chaos. Each of these extreme conditions can be put to advantage in developing practical models to describe the behavior of collections of molecules. In solids, the molecules are relatively fixed and solid geometry may be employed to determine crystal structures, atomic radii and packing efficiencies. Simple bonding models provide semiquantitative values for the properties of solids.

SOLID STATE EXERCISES

1. Describe the structure of glass, SiO_2.
2. Find the size of an argon atom from the density of the solid, 1.65 g/cc.
3. Determine the lattice energy of LiF from the sublimation energy of lithium metal, 158 kJ/mol, the ionization energy of gaseous lithium, 520 kJ/mol, the bond dissociation energy of gaseous difluorine, 159 kJ/mol of molecules, the electron affinity of gaseous atomic fluorine, −333 kJ/mol, and the heat of formation of crystalline LiF, −614 kJ/mol.
4. Estimate the lattice energy of LiF, given the ionic radii $r(Li^+) = 68$ pm and $r(F^-) = 133$ pm.

SOLID STATE EXERCISE HINTS

1. Crystalline quartz and amorphous glass are two known forms of silica. The radius of Si = 41 pm, that of O = 140 pm.
2. Ar is close packed.
3. Follow Example 16.4.
4. Assume m = 12.