# **Chapter 2** Bonding in Solids

Crystalline materials exhibit the complete spectrum of bond types: ionic, covalent, van der Waals, metallic.

- \* In salts of complex anions, e.g. Li<sub>2</sub>SO<sub>4</sub> have both ionic and covalent bonds.
- \* Commonly, bonds are a blend of different types, e.g. TiO is ionic/metallic; CdI<sub>2</sub> is ionic/covalent/van der Waals
- \* <u>In discussing structures, it is convenient</u> to ignore temporarily the complexities of mixed bond types and to <u>treat bonds as though they</u> were purely ionic.
- *Ionic bonding* structure with high symmetry and coordination number as high as possible, such that the electrostatic attractive force is maximized. Alkali and alkaline earth elements usually form ionic structures (Be is an exception), especially in combination with small electronegative anions such as  $O^{2-}$  and  $F^{-}$ .
- Covalent bonding— highly directional bonds irrespective of other atoms that are present, and CN is usually small. Covalent structure occur with (a) small atoms with high valence which, in the cationic state, would be highly <u>polarizing 具極化能力</u>, e.g.  $B^{3+}$ ,  $Si^{4+}$ ,  $P^{4+}$ ,  $S^{4+}$ , etc.; (b) large atoms which in the anionic state are highly polarizable 易被極化但不丟電子, e.g.  $\Gamma$ ,  $S^{2-}$ .

Most non-molecular materials have mixed ionic and covalent bonding:

- \* Ionicity = percentage of ionic character in the bond
- \* Transition metal compounds: the occurrence of metallic bonding

### 2.1 Ionic bonding

Purely ionic bonding rarely occurs. Even NaCl and CaO have some partial covalent character. The degree of covalent bonding increases with valence and ions with a net charge greater than +1 or -1 are unlikely to exist. While NaCl is reasonably represented as Na<sup>+</sup>Cl<sup>-</sup>, TiC (which has the NaCl structure) certainly does not contain Ti<sup>4+</sup> and C<sup>4-</sup> ions. So, ionic bonding is simply useful as a starting point for describing structures which have considerable covalent bonding.

## 2.2 Ions and ionic radii

Definitive information on the sizes of ions is important for discussing crystal structure. The long-established tables of Pauling, Goldschmidt and others are thought to be serious in error; more recent Shannon and Prewitt: cations are larger and anions smaller than previously thought.

Pauling radii of Na<sup>+</sup> and F = 0.98 and 1.36 Å

Shannon and Prewitt, 1.14-1.30 Å for Na<sup>+</sup> and 1.19 Å for F<sup>-</sup>.

High quality XRD advances the ionic radius estimation and gives maps of the distribution of electron density throughout crystals. Fig. 2.1 shows the electron density contour map of LiF ((100) plane). Fig. 2.2 shows the variation of electron density with distance along the line that connects adjacent  $\text{Li}^+$  and F<sup>-</sup> ions. Conclusions drawn:

- (a) Ions are essentially spherical
- (b)Two parts for ions: a center core with concentrated electron density and an <u>outer sphere of influence</u> containing very little electron density

(c)Assignment of radii to ions is difficult. Between adjacent cations and anions, the electron density passes through a broad, shallow minimum. Fig. 2.2, the Pauling and Goldschmidt radii for Li<sup>+</sup> and the electron density minimum are marked, with values ranging from 0.60 to 0.92 Å.



Fig. 2.1 Electron density contour map of LiF (rock salt structure): a section through part of the unit cell face. The electron density (electrons Å<sup>-3</sup>) is constant along each of the contour lines. (From Krug, Witte and Wolfel, Zeit. Phys. Chem., Frankfurt, 4, 36, 1955)



Ions cannot be regarded as hard spheres with a clear defined radius. The electron density decreases roughly exponentially with increasing radius.

The outer sphere of influence is quite elastic and flexible, in order to explain the variation of ionic radii with CN and environment. Because most electron density is concentrated close to the nuclei of ions, most of the total volume in a crystal is essentially free space.

Shannon and Prewitt give two sets of radii: one is based on  $r_{O2-} = 1.40$  Å and is similar to Pauling, Goldschmidt; the other is based on  $r_{F-} = 1.19$  Å ( $r_{O2-} = 1.26$  Å) and is related to the values determined by X-ray diffraction. Fig. 2.3 shows cation radii as a function of CN (based on  $r_{F-} = 1.19$  Å) and the trends are:



- (a) For the s- and p-block elements, radii increase with atomic number for any vertical groups, e.g, octahedrally coordinated alkali ions.
- (**b**) For isoelectronic series of cations, radii decrease with increasing charge, e.g. Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup> and Si<sup>4+</sup>.
- (c) For any element, the cation radius decreases with increasing oxidation state, e.g. V<sup>2+</sup>, V<sup>3+</sup>, V<sup>4+</sup>, V<sup>5+</sup>.
- (d) For any element, the cation radius increases with increasing CN.

- (e) In the 'lanthanide (稀土元素 57-81) contraction", ions with the same charge but increasing atomic number show a reduction in size (due to ineffective shielding of the nuclear charge by the d and, especially, f electrons 這些軌域的電子易 delocalized, large atomic no. 的正核反而易吸引 anions), e.g. octahedral radii La<sup>3+</sup> (1.20 Å) ... Eu<sup>3+</sup>(1.09 Å) ... Lu<sup>3+</sup>(0.99 Å). Similar effects occur across some series of transition metal ions.
- (f) The radius of a transition metal ion is smaller than that of the corresponding main group ions for the reason (e), e.g. octahedral radii, Rb<sup>+</sup>(1.63Å) and Ag<sup>+</sup>(1.29Å) or Ca<sup>2+</sup>(1.14Å) and Zn<sup>2+</sup>(0.89Å).
- (g) diagonal pairs of elements in the periodic table have similar ionic size due to effects (a) and (b), e.g. Li<sup>+</sup>(0.88Å) and Mg<sup>2+</sup>(0.86Å).

Note: highly charged ions are unlikely to exist; they have their positive charge reduced by polarization of the anion and consequent partial covalent bonding.

#### 2.3 Ionic structures–general principles

- (a) Ions are charged, elastic and polarizable spheres.
- (b) Structures are held together by electrostatic forces; cations are surrounded by anions and vice versa.
- (c) CNs are as high as possible under the condition that the central ion maintains contacts with its neighboring ions of opposite charge.
- (d) Next nearest neighbor interactions are of the anion-anion and cation-cation type and are repulsive. Like ions arrange themselves to be as far apart as possible → high symmetry and a maximized volume.
- (e) Local electroneutrality prevails; the valence of an ion is equal to the

sum of the electrostatic bond strengths between it and adjacent ions.

Point (a): size varies with CN  $\rightarrow$  elastic; polarizable when departures from purely ionic bonding occurs (Fig. 2.1, a small distortion from spherical shape of the Li ions  $\rightarrow$  a small amount of covalent bond). Ionic bond 的定義是 cation and anion 均為 spherical.

Points (b)–(d) imply a 3D array of point charges for ionic crystals. The net coulombic energy should be considered; Coulombic's law:

$$F = \frac{(Z_{+}e)(Z_{-}e)}{r^{2}}$$
(2.1)

where F is the force between two ions of charge  $Z_+e$  and  $Z_-e$ , separated by distance r.

Point (d) reflects that reducing repulsion between like ions, with constraints of minimized cation-anion distance and maximized CN, leads to regular and highly symmetrical arrays of ions which tend to have maximized volume.

Point (e) is Pauling's electrostatic valence rule  $(2^{nd} \text{ of Pauling's for ionic crystals})$ . The charge of an anion must be balanced by an equal and opposite charge on the immediately surrounding cations. For a cation  $M^{m+}$  surrounded by n anions,  $X^{x-}$ , the electrostatic bond strength (ebs) of the cation-anion bonds:

$$ebs = \frac{m}{n}$$
(2.2)

Pauling's second rule  $\rightarrow$  ebs sum of all cations =  $\sum \frac{m}{n} = x$  (2.3)

Example:

(a) spinel,  $MgAl_2O_4$ , contains octahedral  $Al^{3+}$  and tetrahedral  $Mg^{2+}$ ; each

O is surrounded by three Al<sup>3+</sup> and one Mg<sup>2+</sup>. (octahedral, M/X =1/1, MX<sub>6</sub> and XM<sub>6</sub> for 100% occupancy, half octahedral sites by Al,  $\therefore$  (6× $\frac{1}{2}$ )Al ions surround O atom; tetrahedral (T+,T.), M/X = 2/1, MX<sub>4</sub> and XM<sub>8</sub> for 100% occupancy,  $\frac{1}{8}$  of tetra. sites by Mg,  $\therefore 8 \times \frac{1}{8}$  Mg ions surround O)

Mg<sup>2+</sup>, ebs = 
$$2/4 = 1/2$$
;  
Al<sup>3+</sup>, ebs =  $3/6 = 1/2$   
 $\Sigma$ ebs( $3$ Al<sup>3+</sup> + 1 Mg<sup>2+</sup>) = 2 in agreement with the charge of oxygen

(b) three SiO<sub>4</sub> tetrahedra cannot share a common corner in silicate structures.

Si<sup>4+</sup>, ebs = 4/4 =1. Three tetrahedra for a corner O  $\rightarrow \Sigma$ ebs = 3, unacceptable for oxygen.

Table 2.1: cations with their formal charge, CN and ebs.

Cation	Coordination number(s)	ebs
Li <sup>+</sup>	4, 6	$\frac{1}{4}, \frac{1}{6}$
Na <sup>+</sup>	6,8	$\frac{1}{6}, \frac{1}{8}$
Be <sup>2+</sup>	3,4	$\frac{2}{3}, \frac{1}{2}$
$Mg^{2+}$	4,6	$\frac{1}{2}, \frac{1}{3}$
$Ca^{2+}$	8	
$Zn^{2+}$	4	$\frac{1}{2}$
$Al^{3+}$	4,6	$\frac{3}{4}, \frac{1}{2}$
Cr <sup>3+</sup>	6	$\frac{1}{2}$
Si <sup>4+</sup>	4	1
Ge <sup>4+</sup>	4,6	$1, \frac{2}{3}$
$Ti^{4+}$	6	213
$Th^{4+}$	8	1

Allowed	Example	Unallowed
2SiO4tet.	Silica	$> 2SiO_4$ tet.
$1MgO_4$ tet. + $3AlO_6$ oct.	Spinel	3AlO4tet.
1SiO4tet. + 3MgO6oct.	Olivine	1SiO4tet. + 2AlO4tet
8LiO₄tet.	Li <sub>2</sub> O	4TiO <sub>6</sub> oct.
$2TiO_6oct. + 4CaO_{12}dod.$	Perovskite	
3TiO6oct.	Rutile	

 Table 2.2
 Allowed and unallowed combinations of corner-sharing oxide polyhedra

Table 2.2: allowed and unallowed combinations of polyhedra about  $O^{2-}$ .

Pauling' 3<sup>rd</sup> rule (chap. 1): Shared edges and faces decrease the stability of a structure, particularly for cations of high valence and small coordination number.

Pauling' 1<sup>st</sup> rule: A polyhedron is formed about each cation; the M-X distances are determined by the radius sum; the CN of the cation is determined by the radius ratio.

### 2.4 The radius ratio rule

The radius ratio rule: the ionic structures adopted depend on the relative sizes of the ions; useful qualitatively. Two guidelines: (a) a cation must be in contact with anionic neighbors, giving a lower limit to the size; (b)

neighboring anions may or may not be in contact.



Fig. 2.4 Radius ratio calculation for octahedral coordination

Minimum radius for an octahedral cation site, CN = 6 (Fig. 2.4):

$$\begin{aligned} (2r_x)^2 + (2r_x)^2 &= \left[2(r_M + r_x)\right]^2 \\ 2r_x \sqrt{2} &= 2(r_M + r_x) \\ r_M / r_x &= \sqrt{2} \quad -1 = 0.414 \end{aligned}$$

Radius ratio < 0.414, the cation is too small for an octahedral site, should occupy a site of smaller CN. For radius ratios > 0.414, the cation would push the anions apart and this happens increasingly up to a ratio of 0.732.

Minimum radius for CN = 8 (Fig. 1.31, CsCl). 2  $(r_M + r_x)$  = cube body diagonal  $a = 2r_x$   $2(r_M + r_x) = 2r_x\sqrt{3}$  $r_M/r_x = \sqrt{3} -1 = 0.732$ 

Minimum radius for CN = 4 (Figs. 1.18 and 21)

2  $r_x = \text{face diagonal}$   $(2r_x)^2 + (\sqrt{2} r_x)^2 = [2(r_M + r_x)]^2$  $r_M/r_x = 0.225$ 

Table 2.3 summarizes the minimum radius ratios. The radius ratio rules are successful in predicting <u>trends</u> in CN and structure type. Radius ratios depend very much on which table of ionic radii is consulted. For larger cations, Cs, r+/r- > 1, and it is more realistic to consider the inverse ratio, r-/r+ (e.g. CsF).

Coordination	Minimum $r_{\rm M}: r_{\rm x}$	
Linear, 2		
Trigonal, 3		0.155
Tetrahedral, 4		0.225
Octahedral, 6		0.414
Cubic, 8		0.732
Dodecahedral, 12		1.000

A more convincing example (Table 2.4) of general formula MX<sub>2</sub>, with possible structure types silica (CN=4), rutile (CN=6) and fluorite (CN=8). 此圖較 Fig. 2.3 實用性大 The radius ratios are calculated from Fig. 2.3 (using  $r_{O2-} = 1.26$ Å). An example: GeO<sub>2</sub> is <u>polymorphic</u> and has both silica and rutile structures; the ratio for tetrahedral coordination is <u>borderline</u> between the values for CN = 4 and 6.

Oxide	Calculated radius ratio*		Observed structure type	
CO <sub>2</sub>	~ 0.1	(CN = 2)	Molecular	(CN = 2)
$SiO_2$	0.32	(CN = 4)	Silica	(CN = 4)
GeO <sub>2</sub>	$\left\{ \begin{array}{c} 0.43\\ 0.54 \end{array} \right.$	(CN = 4) (CN = 6)	{ Silica Rutile	(CN = 4) $(CN = 6)$
TiO <sub>2</sub>	0.59	(CN = 6)	Rutile	(CN = 6)
$SnO_2$	0.66	(CN = 6)	Rutile	(CN = 6)
PbO <sub>2</sub>	0.73	(CN = 6)	Rutile	(CN = 6)
HfO <sub>2</sub>	$\left\{ \begin{array}{c} 0.68 \\ 0.77 \end{array} \right.$	(CN = 6) (CN = 8)	Fluorite	(CN = 8)
CeO <sub>2</sub>	$\left\{ \begin{array}{c} 0.75\\ 0.88 \end{array} \right.$	(CN = 6) (CN = 8)	Fluorite	(CN = 8)
$ThO_2$	0.95	(CN = 8)	Fluorite	(CN = 8)

Table 2.4 Structures and radius ratios of oxides, MO<sub>2</sub>

\* Since cation radii vary with CN, Fig. 2.3, radius ratios may be calculated for different CNs. The CNs used here are shown in parentheses. Calculations are based on  $r_{o^{2-}} = 1.26$  Å.

### 2.5 Borderline radius ratios and distorted structures

 $GeO_2$  has a borderline radius ratio and also exhibits polymorphism (polymorphs have CN = 4 and 6, but CN = 5 do not occur).

In other borderline cases, distorted polyhedral and/or CNs of 5 are observed.  $V^{5+}$  (r ratio = 0.39 for CN = 4, 0.54 for CN = 6) has one polymorph of V<sub>2</sub>O<sub>5</sub> which is a distortion of octahedral; five V–O = 1.5–2.0Å and the sixth 2.8 Å; the coordination is square pyramidal. It appears that V<sup>5+</sup> is rather small to occupy an octahedral site.

Similar distortions occur between CNs = 6 and 8; example:  $ZrO_2$ .

When a cation is only slightly too small, the regular CN is maintained but the cation may rattle or displace. Example:  $PbTiO_3$  (r ratio for Ti = 0.59 for CN = 6), Ti is diplaced with an electric field (ferroelectricity).