

Structure of Solids - Bonding in solids

Lecture 10

CHM 637

Chemistry & Physics of Materials

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Lecture Plan

- General expectations
- Bonding in elemental solids
- Bonding in compound crystals

Bonding in elemental solids

Van der Waals bonding

Predominant among atoms with filled shells.

Induced dipole - induced dipole interactions originating from quantum fluctuations of electron density.

$$U(r) = -\frac{C}{r^6}$$

Weak and short ranged. Usually an empirical repulsive term is added to account for P.E.P related effects at very short range.

$$U(r) = \frac{B}{r^{12}} - \frac{C}{r^6} = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad \text{Lennard-Jones potential}$$

Bonding in elemental solids

Van der Waals bonding

Interaction is isotropic. Therefore close-packed structures result.

E.g. inert gases have F.C.C. structure

Bonding in compound solids

Ionic bonding

For many compound solids the bonding between component atoms (usually a metal and a non-metal) can be described by a complete transfer of electron between them.

This gives rise to cations and anions in the crystal.

The crystal is then stabilised by balancing the attractive Coulomb interaction between cations and anions with the repulsive interaction between like charges.

This results in an ionic crystal.

Bonding in compound solids

Ionic bonding

Of course, in reality charge transfer is never complete and there is always some covalent nature.

Bond A-B	$ \chi_A - \chi_B $
Cs-F	3.19
Na-Cl	2.23
H-F	1.78
Fe-O	1.61
Si-O	1.54
Zn-S	0.93
C-H	0.35

Group → Pauling Electronegativity Scale

$$|\chi_A - \chi_B| = \left\{ D_0(AB) - \frac{1}{2} [D_0(AA) + D_0(BB)] \right\}^{\frac{1}{2}}$$

$\chi_F = 3.98$

Period ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
			*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27
			**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3

Bonding in compound solids

Ionic bonding

Of course, in reality charge transfer is never complete and there is always some covalent nature.

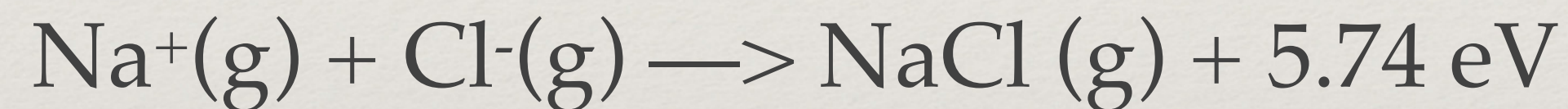
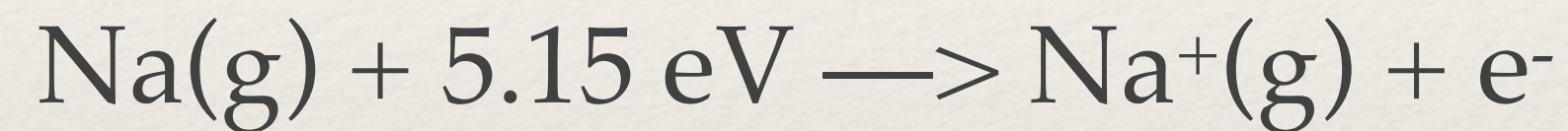
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- Polarity of bond can be assessed by the electronegativity difference.
- This is just a qualitative measure and offers no clear cut definition of ionic or covalent bond.
- Cannot differentiate between covalent and metallic bonding.
- Actual character requires quantum mechanical calculations.

Bonding in compound solids

Energetics of Ionic bonding

Thermodynamics of formation of ionic solid.

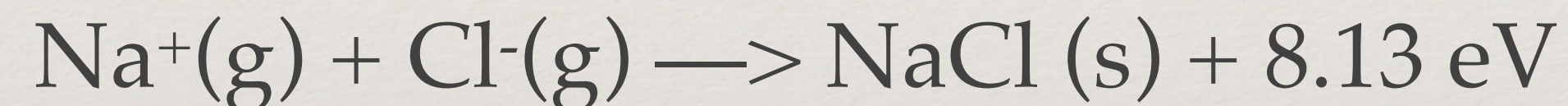


Formation of a NaCl molecule is exothermic.

Bonding in compound solids

Energetics of Ionic bonding

Thermodynamics of formation of ionic solid.



Formation of a NaCl solid is also exothermic. Even more so than just the molecule.
=> Cohesion as a solid is more energetically beneficial.

Where does this extra stabilization in solid state coming from?

Bonding in compound solids

Energetics of Ionic bonding

Assuming complete transfer we can model ionic solids as periodically arranged cations and anions. This allows us to compute the potential energy due to electrostatic interactions alone.

$$U = \frac{e^2}{4\pi\epsilon_0} \left(\frac{N}{2} \sum_{i \neq j}^n \frac{z_i z_j}{|\vec{s}_i - \vec{s}_j|} + \frac{N}{2} \sum_{\vec{R} \neq 0} \sum_{i,j}^n \frac{z_i z_j}{|\vec{R} + \vec{s}_i - \vec{s}_j|} \right)$$

$z_i e =$ charge on i^{th} ion
 $s_i =$ position of i^{th} ion in unit cell
 $R =$ lattice vector
 $n =$ no. of atoms in a unit cell
 $N =$ no. of unit cells

$$= -NA \frac{e^2}{4\pi\epsilon_0 d}$$

A is the Madelung constant.

For a binary ionic crystal with N ion pairs and d is the separation of the n-n pair.

Bonding in compound solids

Energetics of Ionic bonding

Madelung constant is purely geometrical (positive) factor decided by the lattice type.

Crystal type	<i>A</i>
CsCl	1.7627
NaCl	1.7476
ZnS (blende)	1.6381

For the same A-B distance we expect CsCl structure to be more stable.

Actual ion-ion interaction is better modelled by

$$V(r) = \frac{B}{r^m} - \frac{z_c z_a e^2}{4\pi\epsilon_0 r}$$

Where *B*, *m* are empirical parameters

Bonding in compound solids

Energetics of Ionic bonding

The stabilisation is improved by minimising repulsive interactions and maximising attractive interactions.

This can be achieved by bringing together unlike charges while keeping like charges apart. i.e. by maximising coordination number.

Clearly distances cannot be reduced beyond a point. This will decide the equilibrium lattice parameter.

This also means that we can associate some “sizes” with the interacting ions.

Bonding in compound solids

Favourable radius ratios

We assume that

(a) cations surround themselves with as many anions as possible

(b) Cations and anions touch each other.

(c) Anions do not overlap

=> Cation-anion distance = $a = r_a + r_c$

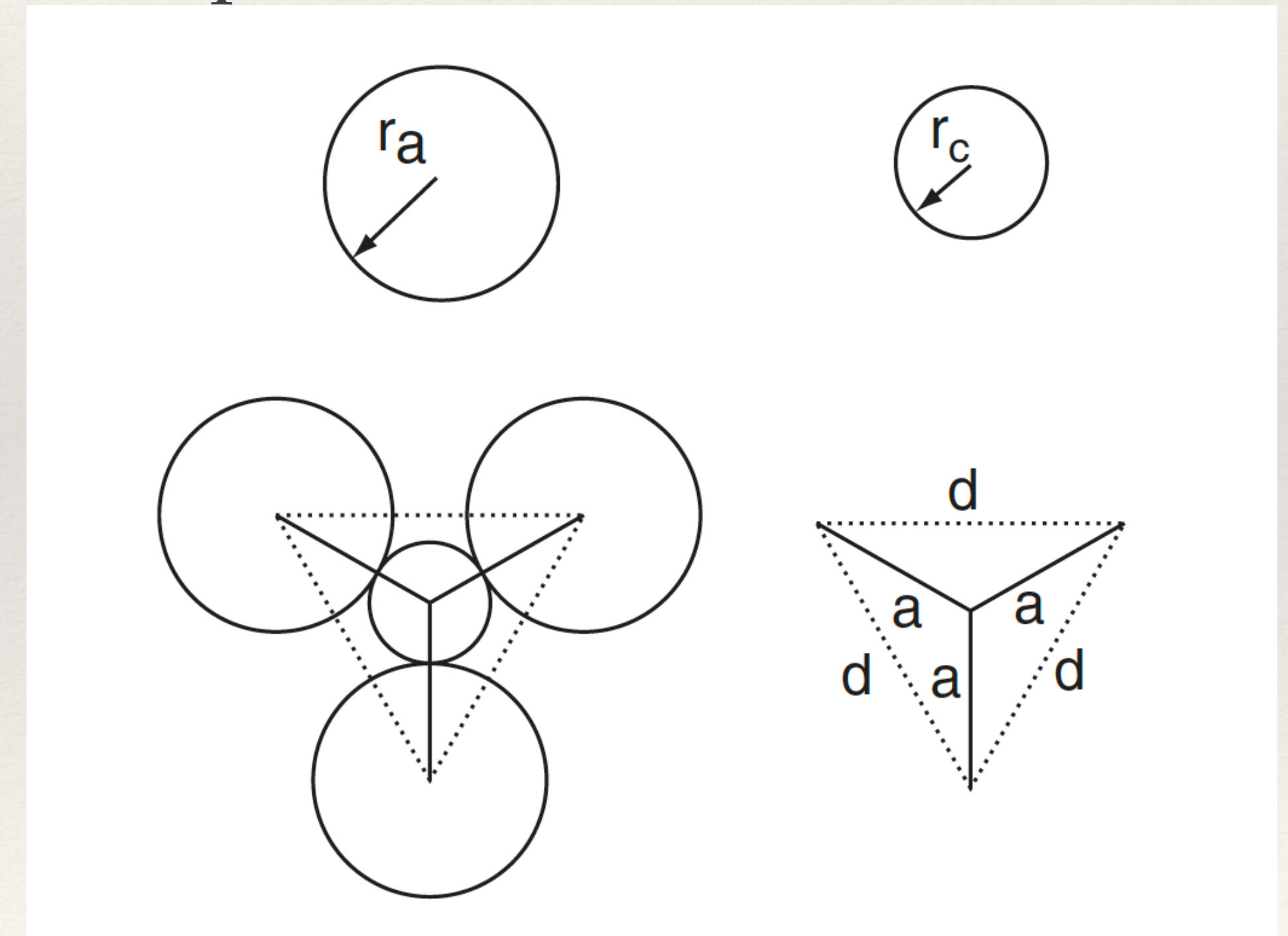
Anion-anion distance = $d \geq 2 r_a$

Example, triangular coordination

$$d = a\sqrt{3}$$

$$(r_c + r_a)\sqrt{3} \geq 2r_a$$

$$\implies R = \frac{r_c}{r_a} \geq \frac{2}{\sqrt{3}} - 1 \approx 0.1547$$



Bonding in compound solids

Favourable radius ratios

Similarly for tetrahedral coordination

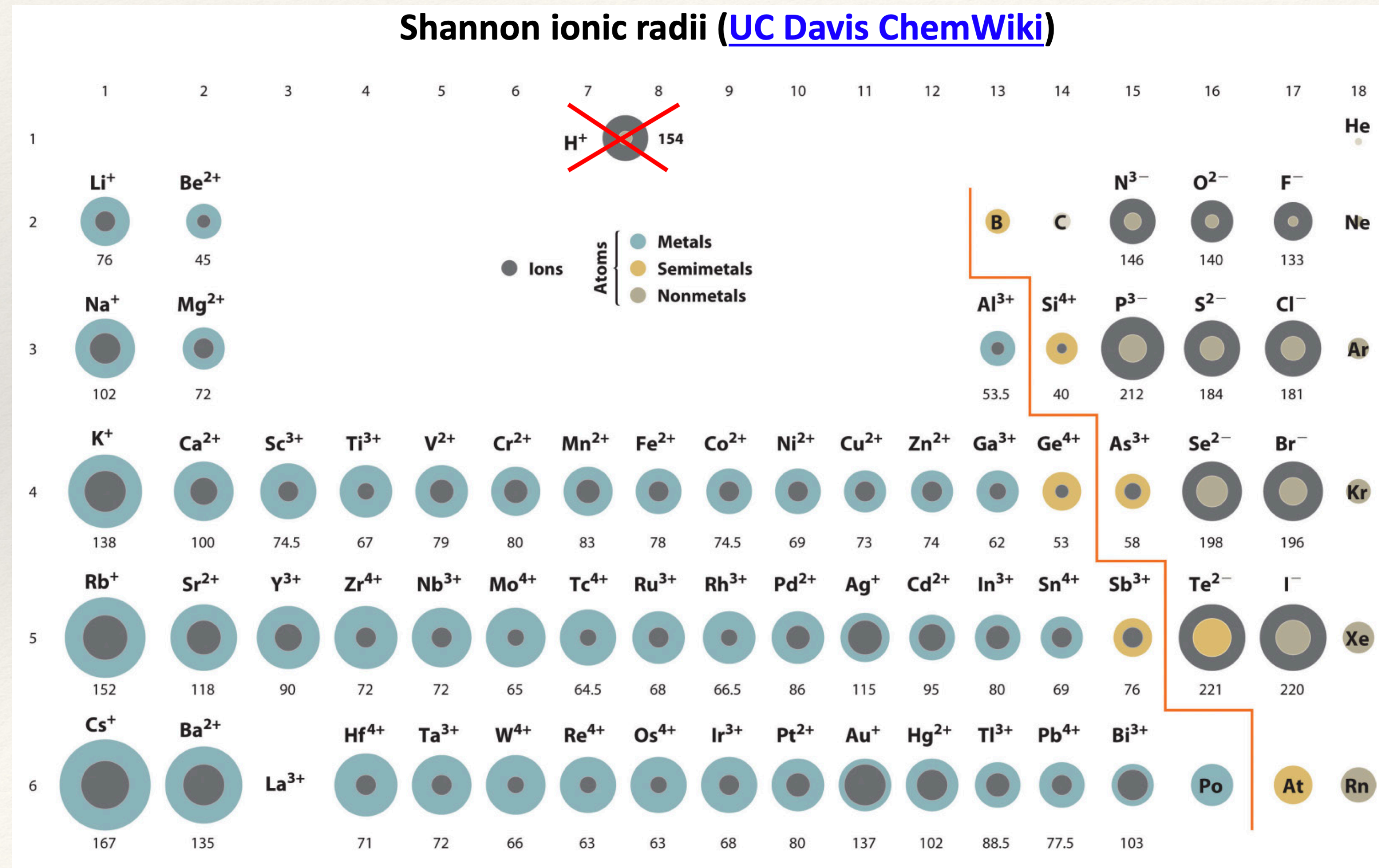
$$d = a\sqrt{\frac{8}{3}} \implies R \geq \sqrt{\frac{3}{2}} - 1 \approx 0.2247$$

Local Atomic Bonding Unit	Range of Allowed Radius Ratios r_c/r_a (Cation/Anion)	Examples (r_c/r_a)
A-B ₈ (cube)	1-0.732	CsCl (0.92)
A-B ₆ (octahedron)	0.732-0.414	NaCl (0.54)
A-B ₄ (tetrahedron)	0.414-0.225	ZnS (0.40)
A-B ₃ (triangle or pyramid)	0.225-0.155	B ₂ O ₃ (0.17), BN (0.13)
A-B ₂ (link or bridge)	<0.155	

Source: Gersten and Smith

Bonding in compound solids

Favourable radius ratios



Ionic Radii (in pm units) of the most common ionic states of the s-, p-, and d-block elements. **Gray** circles indicate the sizes of the ions shown; **colored** circles indicate the sizes of the neutral atoms. Source: R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Cryst.* **1976**, *32*, 751. Full radii data available at:

<http://abulafia.mt.ic.ac.uk/shannon/ptable.php>

Bonding in compound solids

Favourable radius ratios

Predictions don't always work.

Alkali Chloride	r_c/r_a^a	Crystal Structure	
		Predicted ^b	Observed
LiCl	0.38	Cubic ZnS or hexagonal ZnS (A-B ₄)	NaCl (A-B ₆)
NaCl	0.54	NaCl (A-B ₆)	NaCl (A-B ₆)
KCl	0.73	NaCl (A-B ₆)	NaCl (A-B ₆)
RbCl	0.81	CsCl (A-B ₈)	NaCl (A-B ₆)
CsCl	0.92	CsCl (A-B ₈)	CsCl (A-B ₈)

^aDetermined using radii presented in Table 2.4; data from L. H. Ahrens, *Geochim. Cosmochim. Acta*, **2**, 158 (1952).

^bPredictions based on criteria presented in Table 2.3.

Assuming purely ionic interactions may not be correct.

Errors might also arise from uncertainties in ionic radii.

Real crystals will have mixed ionic-covalent character.