Crystal Lattice in Two Dimensions
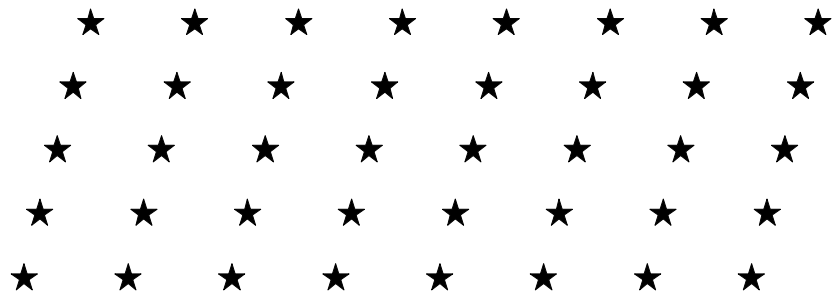
☞   A crystal consists of atoms, molecules, or ions in a pattern that repeats in three dimensions.

● The geometry of the repeating pattern of a crystal can be described in terms of a *crystal lattice*, constructed by connecting equivalent points throughout the crystal.

● To introduce basic concepts, we will consider a two-dimensional crystal lattice (properly called a *net*).
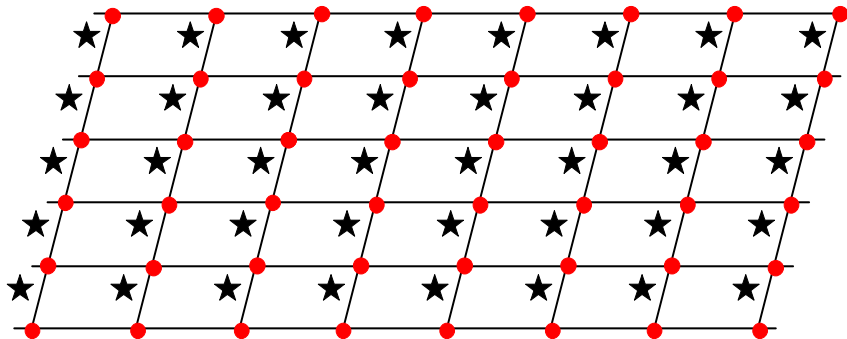
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A two dimensional "crystal"

Lattice Points

☞   A crystal lattice is constructed by connecting adjacent
    equivalent points (lattice points) throughout the crystal.
  • The environment about any lattice point is identical to the
    environment about any other lattice point.
  • The choice of reference lattice point is arbitrary.
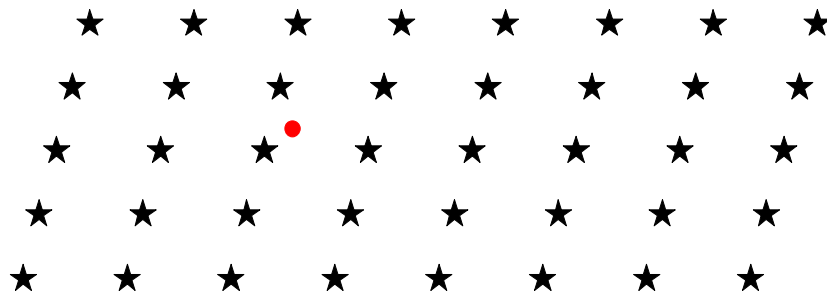

One choice of a reference point

A lattice constructed from the chosen point.

● The basic parallelogram (parallelepiped in three dimensions)
   constructed by connecting lattice points defines a *unit cell*.

Lattice Points and Unit Cells

- Because the choice of reference lattice point is arbitrary, the location of the lattice relative to the contents of the unit cell is variable.
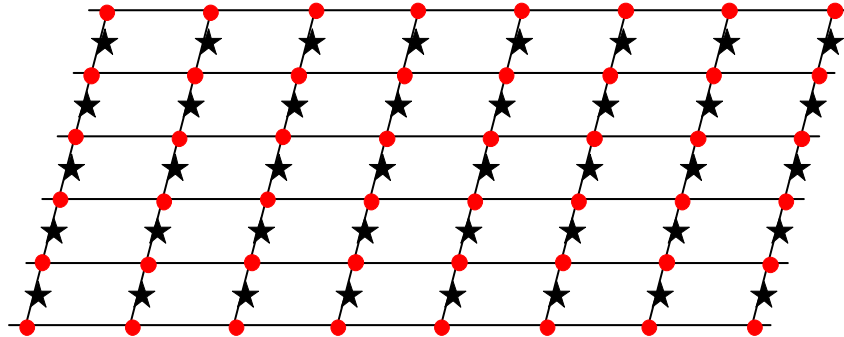

The same lattice and unit cell defined from a different reference point.

- Regardless of the reference point chosen, the unit cell contains the same number of atoms with the same geometrical arrangement. (Here, the unit cell contains one star, so $Z = 1$)

- The unit cell is the basic repeat unit from which the entire crystal can be built.

- A *primitive unit cell* contains only one lattice point.

- The unit cell is defined in terms of the lengths of the edges of the parallelepiped (a, b, c) and the three angles between these edges (α, β, γ)
  - The angle α is between b and c, the angle β is between a and c, and the angle γ is between a and b.

Alternate Lattices

☞ Any parallelepiped that connects lattice points defines a valid unit cell, and there are an infinite number of choices for drawing these.
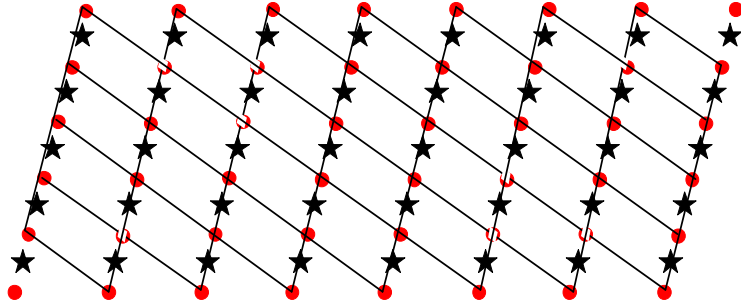
Alternate choice of unit cell for the same "crystal"

- As with the previous definition of unit cell, each unit cell contains one lattice point ($\frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} = 1$) and one "molecule" ($Z = \frac{1}{2} \bigstar + \frac{1}{2} \bigstar = 1 \bigstar$).

- Like the previous choice, this unit cell is primitive (one lattice point).

Primitive and Non-Primitive Unit Cells

● Sometimes a non-primitive cell is chosen to better show the symmetry relationships between lattice points.
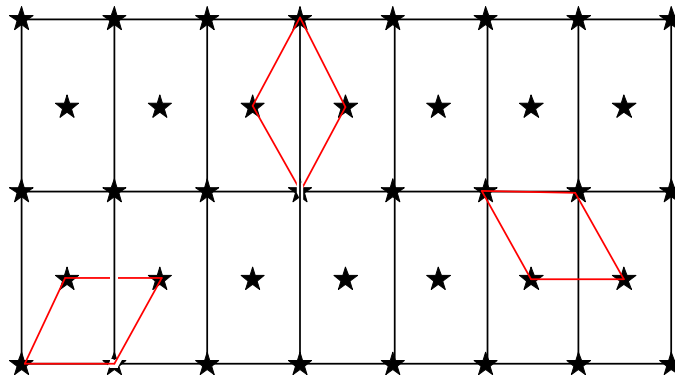
Lattice with non-primitive unit cell choice

- The chosen non-primitive unit cell has a body-centered lattice point and a net of one other lattice point from the four at the corners, which are shared among four adjacent unit cells.

- The unit cell contains two lattice points $[(4 \times ¼) + 1 = 2]$.

- Various choices of primitive unit cell, each containing one lattice point, are shown in red.

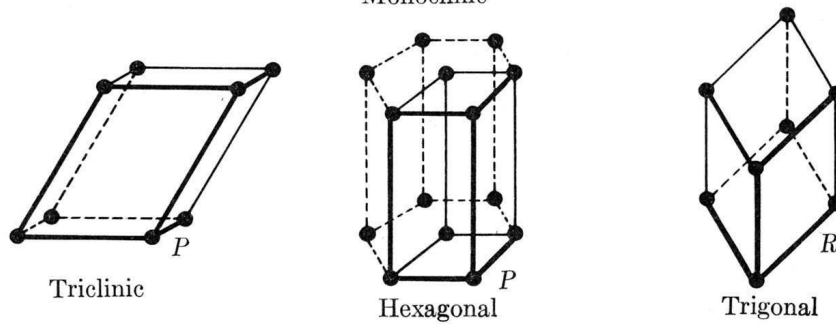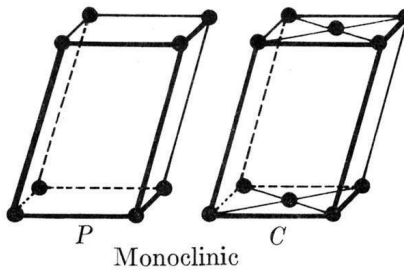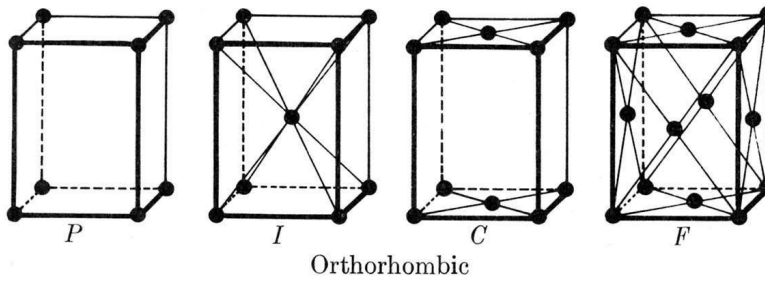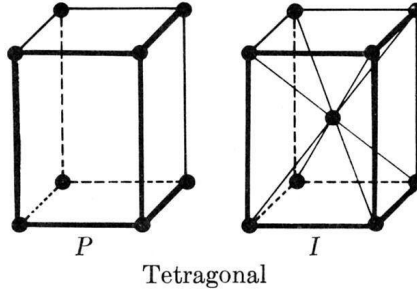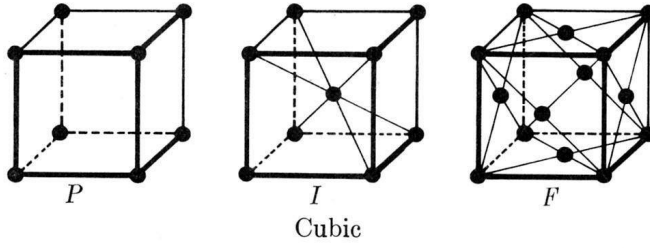- Choice of the primitive unit cell is not unique.

Crystal Systems

- By convention, lattices and unit cells of real crystals are chosen on the basis of the symmetry of the lattice points.

- On the basis of symmetry, there are seven crystal systems[1] with the following properties.

Crystal System	Restrictions
Triclinic	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$
Monoclinic	$a \neq b \neq c$; $\alpha = \gamma = 90^o$, $\beta \neq 90^o$
Orthorhombic	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90^o$
Tetragonal	$a = b \neq c$; $\alpha = \beta = \gamma = 90^o$
Trigonal	$a = b = c$; $120^o > \alpha = \beta = \gamma \neq 90^o$
Hexagonal	$a = b \neq c$; $\alpha = \beta = 90^o$, $\gamma = 120^o$
Cubic	$a = b = c$; $\alpha = \beta = \gamma = 90^o$

- Within these seven crystal systems, there can be a total of fourteen different symmetry-based lattices, called *Bravais lattices* (Auguste Bravais, 1848).

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[1]Crystallographers tend to use the term "crystal system", but the term "crystal class" is also used.

Bravais Lattices

P   I   F

Cubic

P   I

Tetragonal

P   I   C   F

Orthorhombic

P   C

Monoclinic

P

Triclinic

P

Hexagonal

R

Trigonal

Lattice Points in Bravais Lattices

- Because they are defined on the basis of symmetry, the unit cells of the Bravais lattices are not all primitive.

- The number of lattice points correlates to the symmetry designation of the Bravais lattice as *P*, *I*, *C*, *F*, or *R*.

Type	Description	Lattice Points
P	Primitive	1
I	Body-centered (Ger., *innenzentriert)*	2
C	C-centered (also, end-centered)	2
F	Face-centered	4
R	Rhombohedral	1

Example: Primitive (*P*)
   Each of the eight points at the corners is shared by eight cells
   Lattice points = $8(⅛) = 1$

Example: Body-centered (*I*)
   Each corner point is shared by eight cells
   Body-centered point is entirely in one cell
   Lattice Points = $8(⅛) + 1 = 2$

Example: Face-centered (*F*)
   Each corner point is shared by eight cells
   Each point on a face is shared by two adjacent cells
      Lattice points = $8(⅛) + 6(½) = 4$

Close-Packed Structures

- The structures of metals and some monatomic elements in the solid phase can be understood as close-packed layers of atoms, acting like hard spheres.

- In a close packed layer, each atom is surrounded by six nearest neighbor atoms.
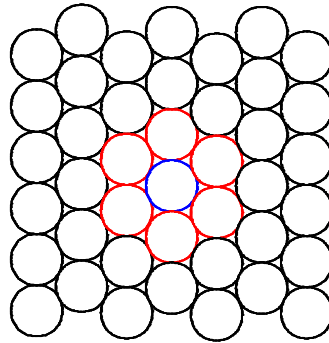
- The next layer is formed by placing it so that atoms nestle into the "dimples" of the first layer.
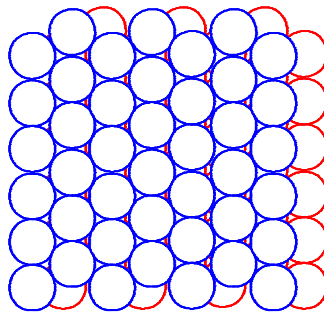
Adding the Third Layer

- If the third layer is placed over the "dimples" of the second layer in same way (here offset to the left), an A-B-C patten is achieved, which results in a cubic close-packed (ccp) structure, which is face-centered cubic (fcc).
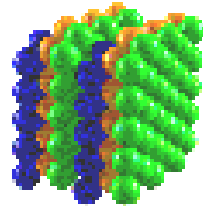
    Packing efficiency: 74.05%
    Examples: Al, Ni, Cu, Ag, Au

- If the third layer is placed to align with the first, an A-B-A pattern is achieved, which results in a hexagonal close-packed structure (hcp).
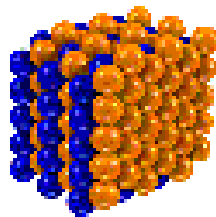
    Packing efficiency: 74.05%
    Examples: Zn, Ti, Co

☞   An excellent description of close-packed structures with graphic simulations can be found at the following web site:

  http://departments.kings.edu/chemlab/animation/clospack.html

Coordination in Close-Packed Structures

- Both ccp and hcp structures result in CN12 for every atom.

- In hcp the top three touching atoms and bottom three touching atoms are eclipsed relative to each other (D_{3h}) [below left].

- In ccp the top three touching atoms are staggered relative to the bottom three touching atoms (D_{3d}) [below right].
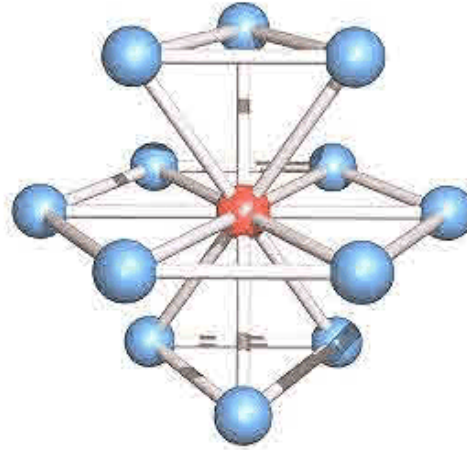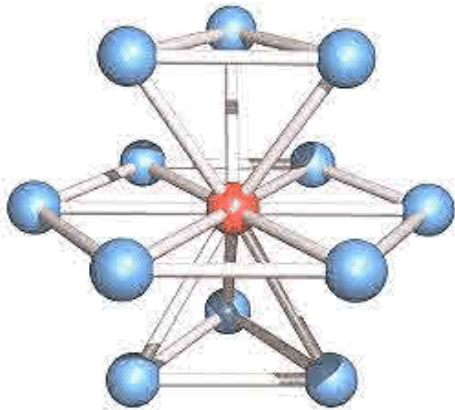
Holes in Close-Packed Structures

- Close-packed structures (either ccp or hcp) contain octahedral and tetrahedral holes (or sites).

- There is one octahedral hole for every atom and twice as many tetrahedral holes.
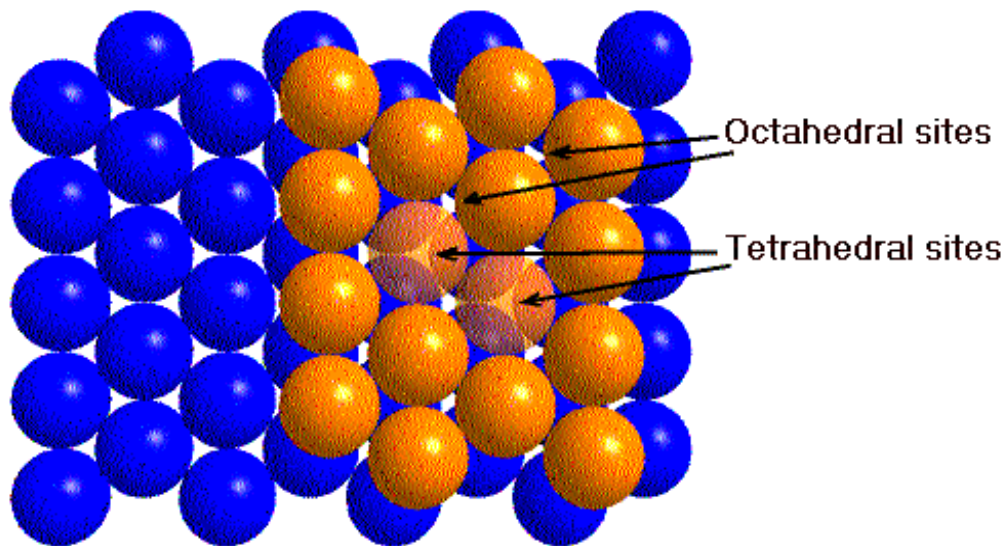
- Some ionic compound structures can be understood in terms of close-packed anions with cations occupying the holes (interstices).

- Tetrahedral holes can fit interstitial atoms with $r_{tet} \leq 0.23r$, and octahedral holes can fit interstitial atoms with $0.23r \leq r_{oct} \leq 0.41r$, where r is the radius of the close-packed atoms or ions.

Non-close-packing

● Some metals (e.g., Na, Cr, Fe, W) adopt a non-close-packing body-centered cubic structure.

● If the central hole of a simple cubic structure is expanded enough to accommodate another atom, the eight atoms at the corners of the cube will not be touching, but the central atom will touch all the corner atoms of the expanded cube. The resulting structure is body-centered cubic (bcc).
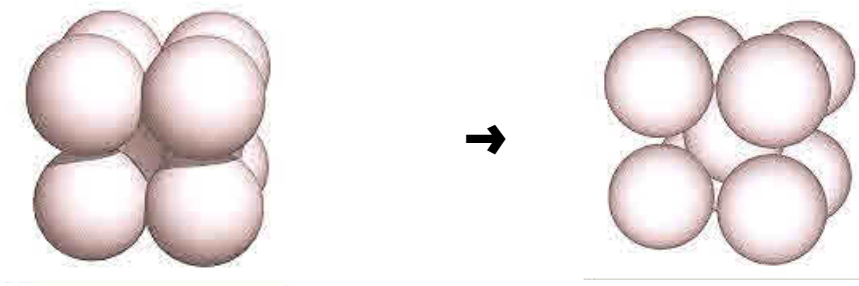
● Packing efficiency of bcc is 69.02%.

● Each atom has CN8 in bcc.

● The diagonal of the bcc cell is $4r$.

Excellent illustrations of bcc structure are available at the following web site:

http://departments.kings.edu/chemlab/animation/bcc.html

Simple Ionic Structure
NaCl

● NaCl structure can be understood as a cubic close-packed structure (ccp/fcc) of Cl^- ions (181 pm) with the Na^+ ions (102 pm) occupying the octahedral holes.
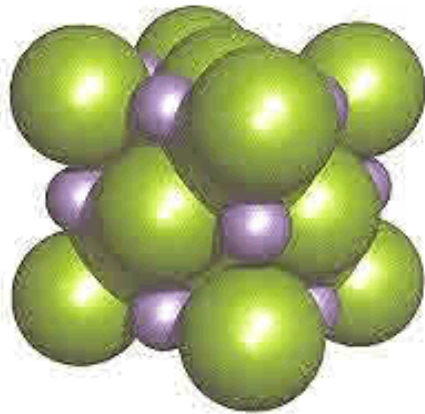
● The Na^+ ions are actually "too big" for the octahedral holes made by the Cl^- ions, but the structure is possible because the ions are compressible (i.e., not hard spheres), and the Cl^- ions need not be truly close-packed.

$$r^+/r^- = 102/181 = 0.564$$

● NaCl structure is found for all alkali halides except CsCl, CsBr, and CsI.

● In CsF the cation is actually bigger than the anion, but the structure is still NaCl-type.

$$r^+/r^- = 167/133 = 1.26$$

NaCl Unit Cell Contents

- The face-centered cubic unit cell is non-primitive (F) and contains four NaCl formula units ($Z = 4$).
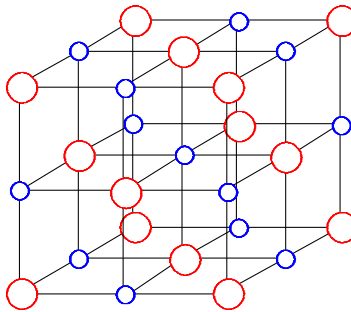
Site	Na^+	Cl^-
Center	1	0
Edges	$(12)(¼) = 3$	0
Corners	0	$(8)(⅛) = 1$
Faces	0	$(6)(½) = 3$
Total	4	4

- Both Na^+ and Cl^- ions are CN6, so the unit cell could equally be defined with Na^+ ions on the corners and a Cl^- ion at the center.

Ionic Radii

- Ionic radii are estimates, generally based on best fit for a commonly occurring ion, such as O^{2-} (e.g., Pauling).

- Ionic radii for some large anions in the presence of small cations can be obtained directly if it can be assumed that the anions are touching.

$$\tfrac{1}{2}d = r_-$$
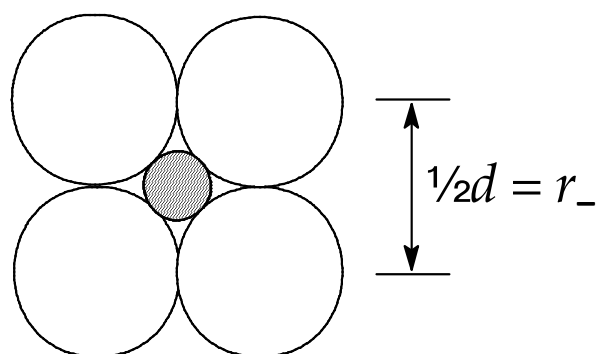
- Assuming the cation touches the anions in close-packed structures, the cation radius increases as the size of the hole increases.

- The cation hole, and hence the cation radius, increases as the coordination number increases.

- Conversely, the coordination number (CN) increases as the size of the cation increases.

- Shannon[2] tabulated ionic radii for several CN values.

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[2]R. D. Shannon, *Acta Crystallogr., A32*, 751-767 (1976).

Comparison of Some Pauling and Shannon Ionic Radii

Ion	Pauling	Shannon		
		CN4	CN6	CN8
Li^+	60	59	76	
Na^+	95	99	102	116
K^+	133	137	138	151
Rb^+	148		152	161
Cs^+	169		167	174
F^-	136	131	133	
Cl^-	181		181	
Br^-	195		194	
I^-	216		220	

- Shannon CN6 values are most often used as a set when exact coordinations are not known.

- Shannon CN6 values tend to be a little larger for cations and about the same or smaller for anions, relative to Pauling values.

- The set used is less important than using one set for comparisons (i.e., don't "mix and match")

Radius Ratio

● Most often cations are smaller than anions (except cases like KF, CsF, etc.)

● CN about a cation, to a first approximation, can be predicted on the basis of the radius ratio, r_+/r_-.

r_+/r_-	Predicted CN	Predicted Geometry
<0.15	2	linear
0.15-0.22	3	trigonal planar
0.22-0.41	4	tetrahedral
0.41-0.73	6	octahedral
>0.73	8	cubic

● Many exceptions occur, because ions are not hard spheres.

Radius Ratio Calculation Examples

Data (Shannon CN6 values)

Cation	Li^+	Na^+	K^+	Rb^+	Cs^+
r_+	76	102	138	152	167
Anion	F^-	Cl^-	Br^-	I^-	
r_-	133	181	194	220	

Examples

Salt	r_+/r_-	Predicted CN	Observed CN
NaCl	$102/181 = 0.56$	6	6
KBr	$138/194 = 0.71$	6	6
CsI	$167/220 = 0.76$	8	8
LiF	$76/133 = 0.57$	6	6
LiCl	$76/181 = 0.42$	6	6
LiI	$76/220 = 0.35$	4	6
CsF	$167/133 = 1.26$	8	6

☞ All alkali halides at room temperature have the NaCl (CN6) structure, except CsCl, CsBr, and CsI.