# Class 1: Simple structures
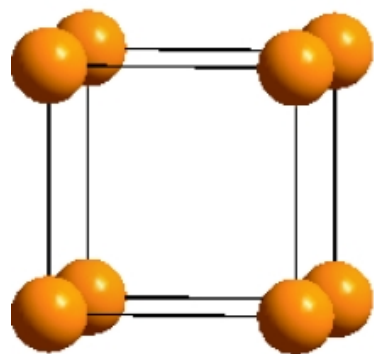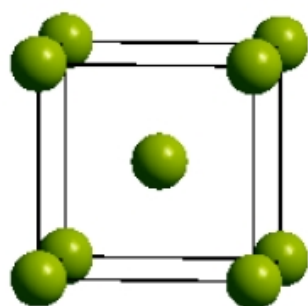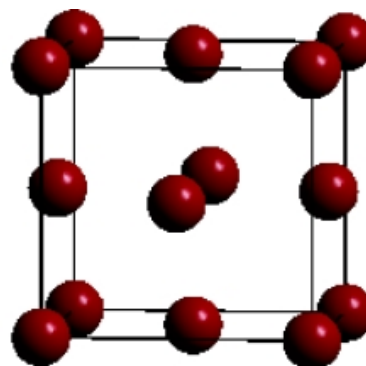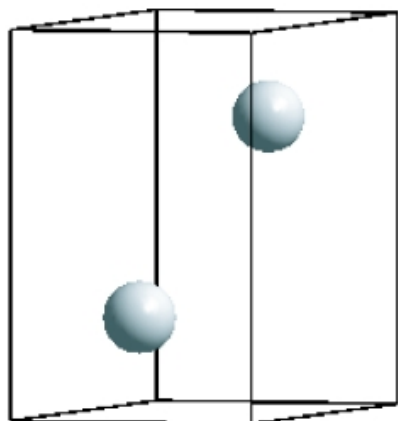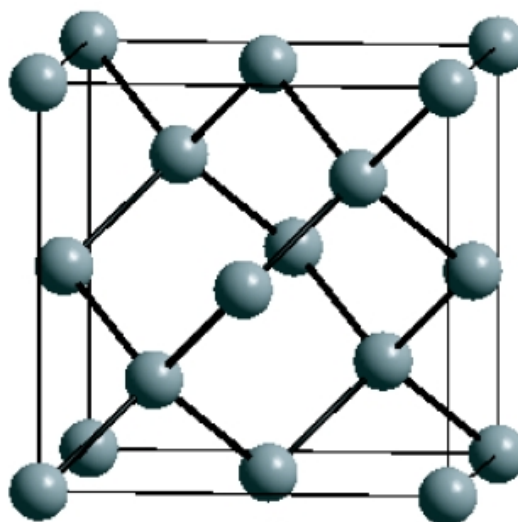


α-Po

α-Fe

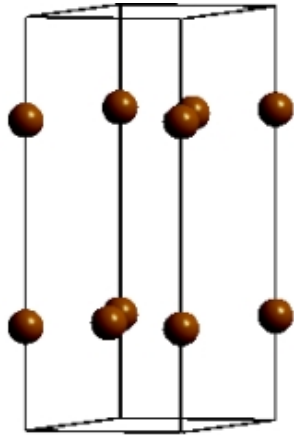Cu

Mg

Si

C (graphite)
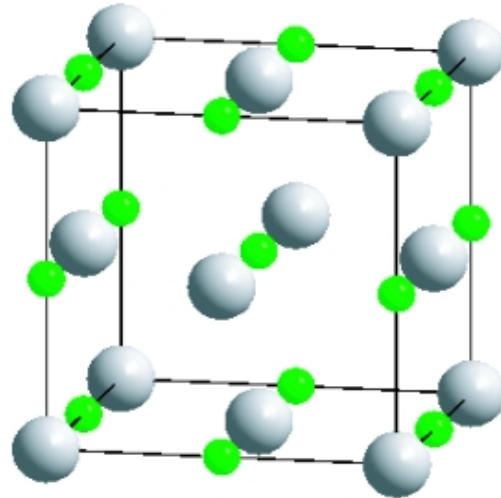
NaCl
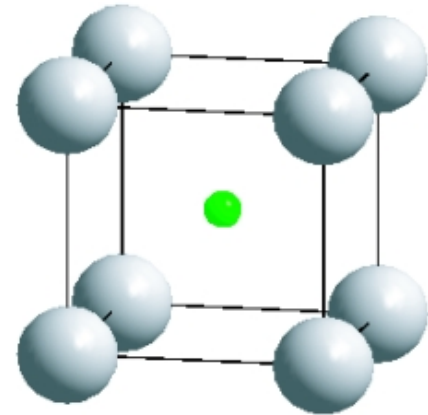
CsCl

Use of the International Tables:
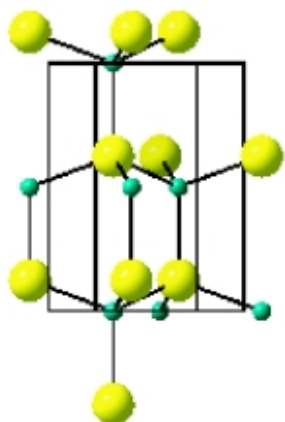The example of space group *Fd-3m* (No. 227)

Origin Choice 1 (at -1/8, -1/8, -1/8)
Coordinates: (0,0,0)+ (0,1/2,1/2)+ (1/2,0,1/2)+ (1/2,1/2,0)+

| 16 | d | -3m | 5/8,5/8,5/8 | 3/8,7/8,1/8 | … |
| 8 | a | -43m | 0,0,0 | 3/4,1/4,3/4 | |

Structure of Diamond Si: *Fd-3m* Si at 0,0,0 *a* = 5.43042 Å

ZnS wurtzite

ZnS zinc blende
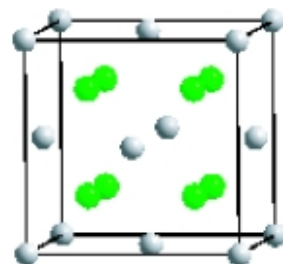
NiAs

Fluorite
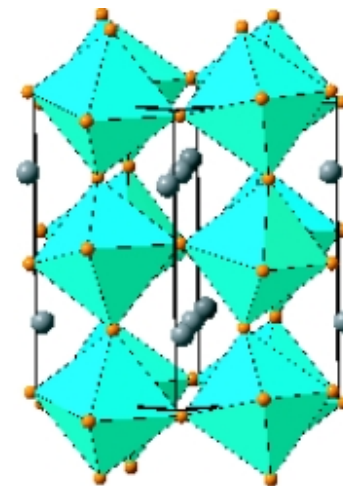
Perovskite
CaTiO₃
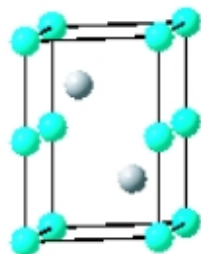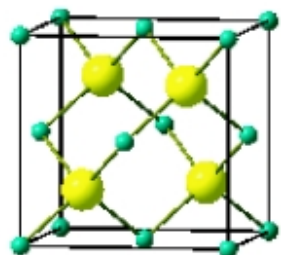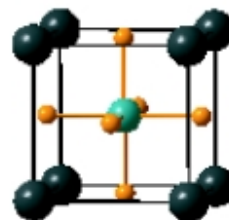
cubic perovskite (BaSnO₃)

Stabilization of ionic crystals:

$$-N_A \sum \frac{q_1 q_2 e^2}{4\pi\varepsilon_0 r_{ij}}$$

ionic, also: $E_c = -A N_A q_1 q_2 \frac{e^2}{4\pi\varepsilon_0 R}$

$$-N_A \sum B_{ij} \exp(-\alpha_{ij} r_{ij})$$ repulsion

$$+N_A \sum C_{ij} r_{ij}^{-6}$$ dispersion

$$-2N_A \frac{1}{2} h v_{max}$$ zero point

*Madelung constants:*
$A$ = 1.76267 (CsCl)
$A$ = 1.74756 (NaCl)
$A$ = 1.64132 (wurtzite)
$A$ = 1.63805 (blende)

Paulings rules (approximately):

1. *Coordination Polyhedra:* … of anions fromed around cations. Cation-anion distances are determined by the sum of the radii, and corrdination number by the radius ratio.
2. *Electrostatic valence rule:* In a stable ionic structure, the valence (ionic charge) of each anion with changed sign is exactly equal to the sum of the electrostatic bond strengths to it from adjacent cations. The electrostatic bond strength is defined as ratio of charge on cation to its coordination number.
3. *Linking of polyhedra:* The presence of shared edges and especially of shared faces decreases stability. The effect is large for cations with high charge and low coordination number.
4.  *Sharing of anions:* Polyhedra around cations with high charge and low coordination number tend not to share features.
5. *Parsimony:* Structures tend to be simple

Paulings electrostatic valence rule disregards distance between atoms. Distance is particularly important when there is more than one cation in the structure. Pauling's rules can be found in *J. Am. Chem. Soc.* 51 (1929) 1010.

Brown [The Chemical Bond in Inorganic Chemistry etc.] has (with others) suggested an extension of electrostatic valence by noting that the bond valence usually obeys a simple relation with distance:

$$S_{ij} = \exp[(R_0 - R_{ij})/B] \text{ and } S_{ij} = (R_{ij}/R_0)^{-N}$$

Where $S_{ij}$ is the bond valence of the bond between i and j, and $R_{ij}$ is the distance. $B$, $R_0$ and $N$ are chosen from crystallographic data so that the bond valence sum is equal to the formal valence.

The Bond Valence Sum is simply the sum of all bond valences to an atom: $V_i = \Sigma_j \, S_{ij}$

In this class, we will examine the use of the bond valence calculator, *valence*, from I. D. Brown, and also SPuDs from Lufaso and Woodward.

We will also discuss a few publications on *ab-initio* structure prediction: Pannetier et al. *Nature* 346 (1990) 343; Schon and Jansen, *Angew. Chem. Int. Edn.* 35 (1996) 1304; Jansen, *Angew. Chem. Int. Edn.* 41 (2002) 3746.