

LECTURE 2: CRYSTAL CHEMISTRY

- Learn to "read" different types of crystal structure representations
- Concepts of coordination number (CN) and coordination polyhedron (= spatial arrangement of nearest-neighbour atoms)
- Ionic radius: dependence on CN and valence (V)
- Tolerance factor concept and utilization
- Bond-valence-sum (BVS) concept and utilization

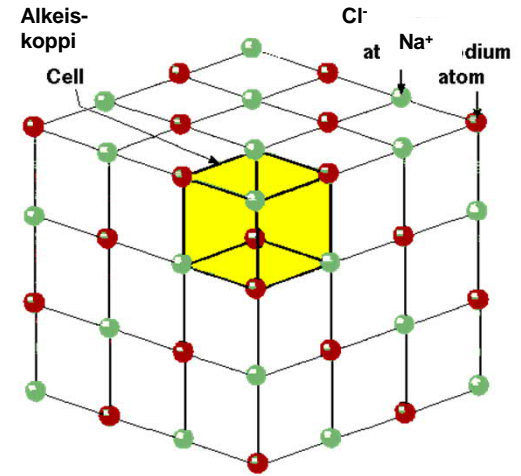
EXAMPLES of "everyday" crystals/structures



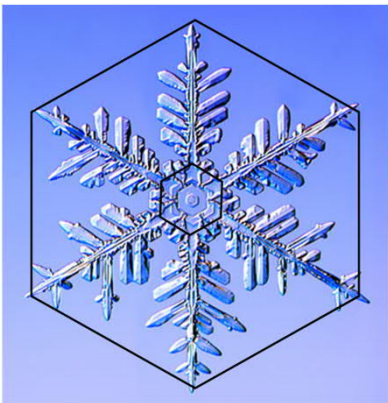
Rock salt (NaCl)



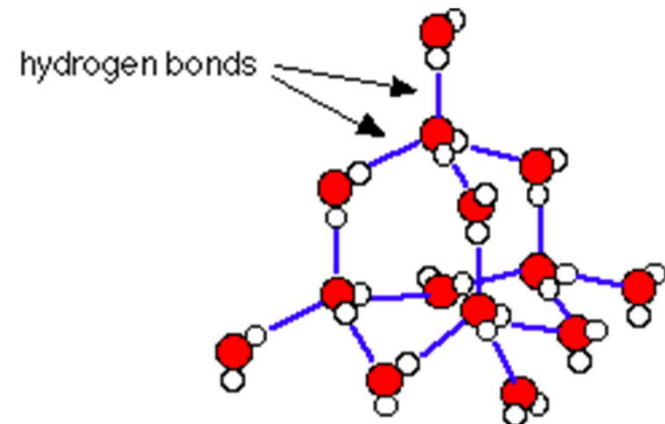
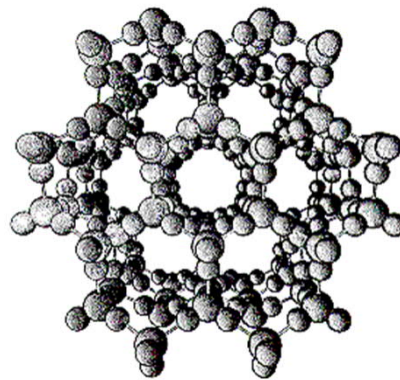
NaCl single crystal



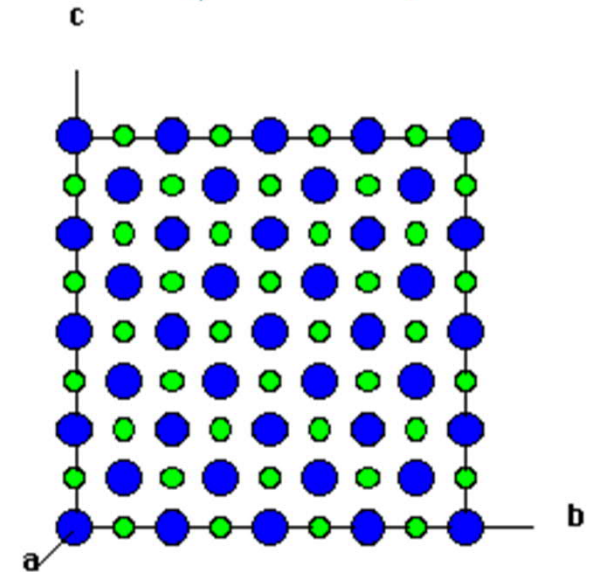
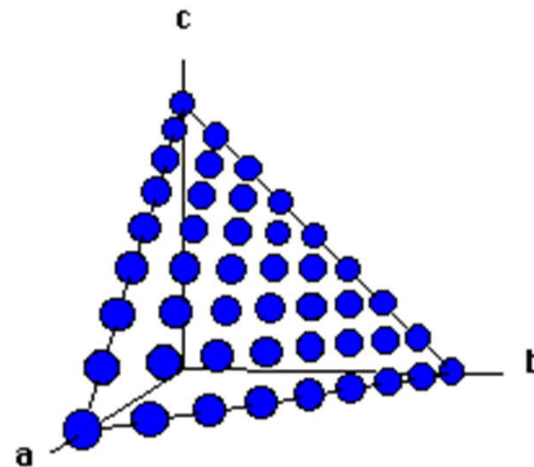
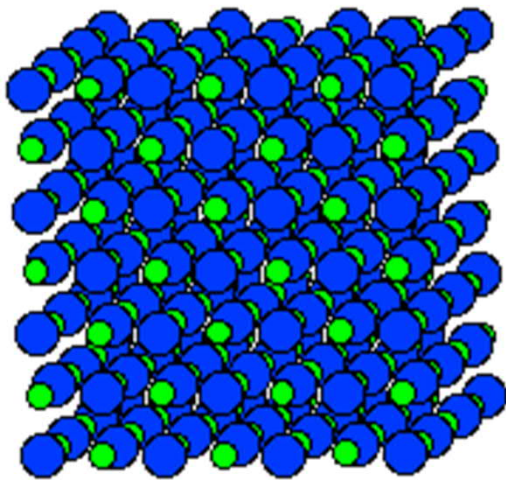
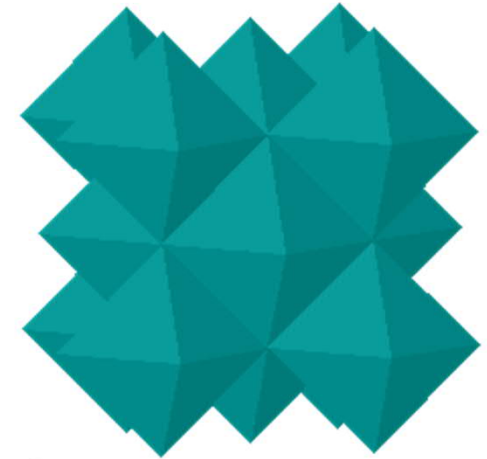
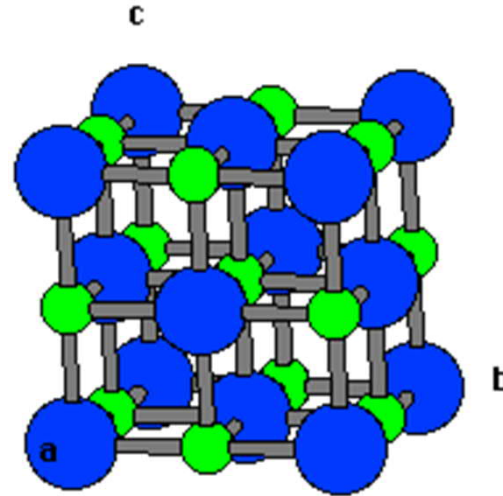
Cubic crystal structure:
high symmetry, ionic bonds
→ extremely stable

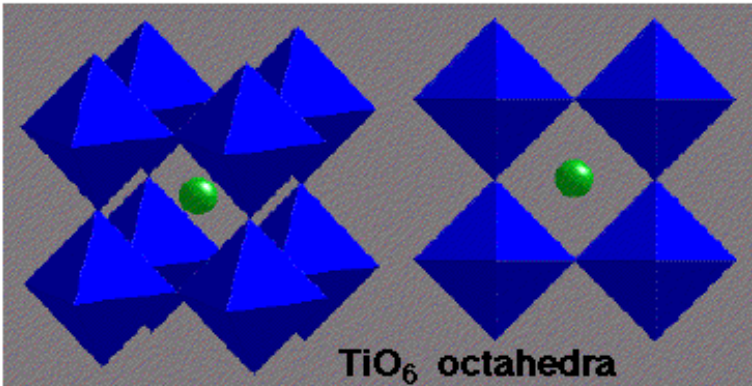


Snow flake:
hexagonal



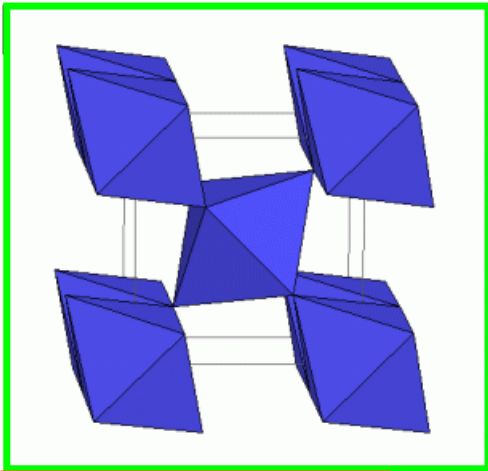
The same (NaCl) crystal structure can be presented in multiple ways



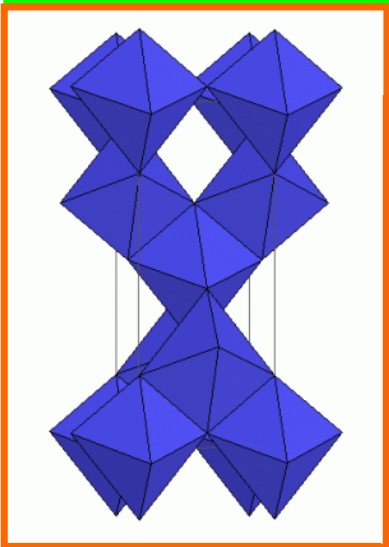
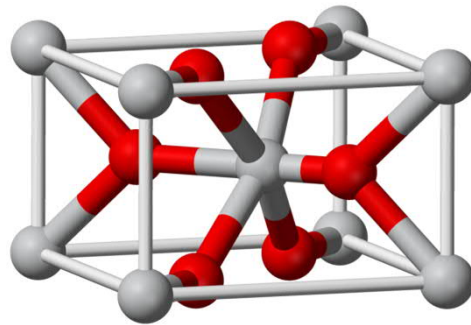


PEROVSKITE CaTiO₃

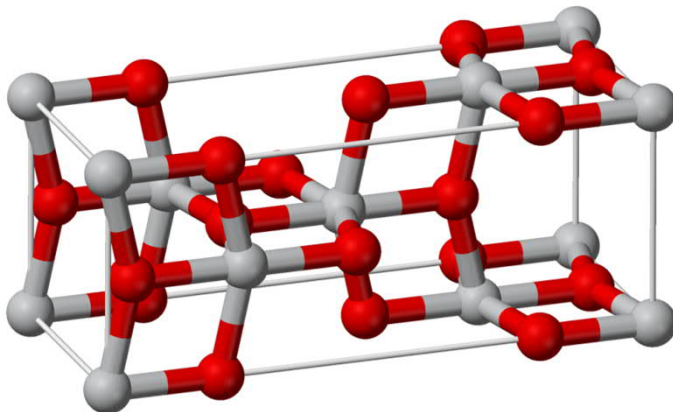
Other Examples of common crystal structures



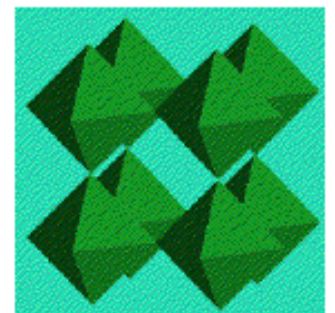
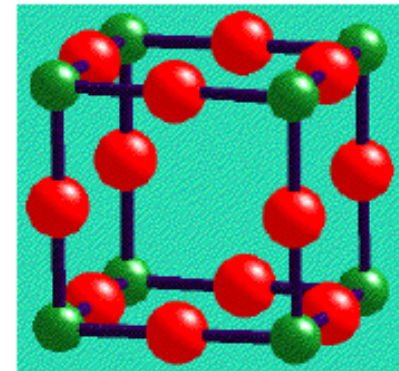
RUTILE TiO₂



ANATASE TiO₂

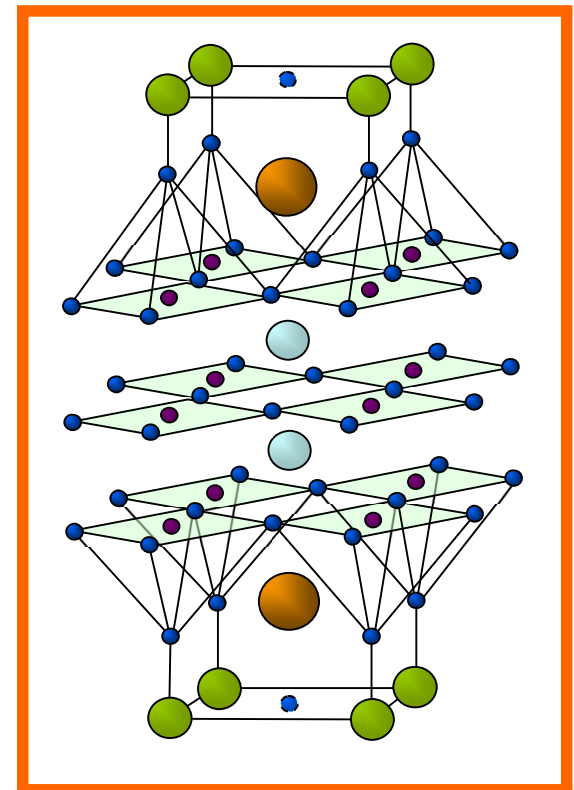
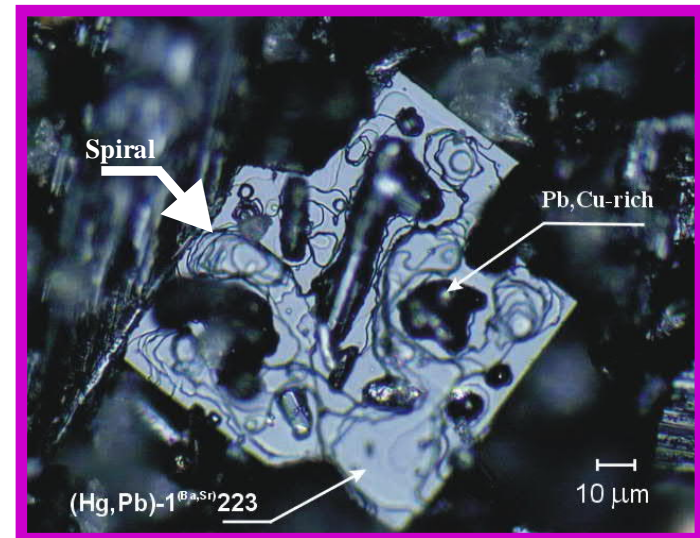


ReO₃



CRYSTAL

- Regularity of small building units in crystalline solids was predicted already in 17th century based on the beautifully symmetric shapes of macroscopic crystals
- Experimentally this was verified in 1912 by showing that crystals work as 3D diffraction gratings for X-rays (with wavelength of the same order as the distances of atoms in crystals)
- Interatomic distances in crystals are of **Ångström-scale: $1 \text{ \AA} = 10^{-10} \text{ m} = 0.1 \text{ nm}$**
- On the right, the tiny crystal (grown from flux by my students) is a single crystal of the record-high T_c (135 K) $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-\delta}$ superconductor; crystal structure shown below



WHAT WE LIKE TO KNOW ABOUT THE CRYSTAL STRUCTURE

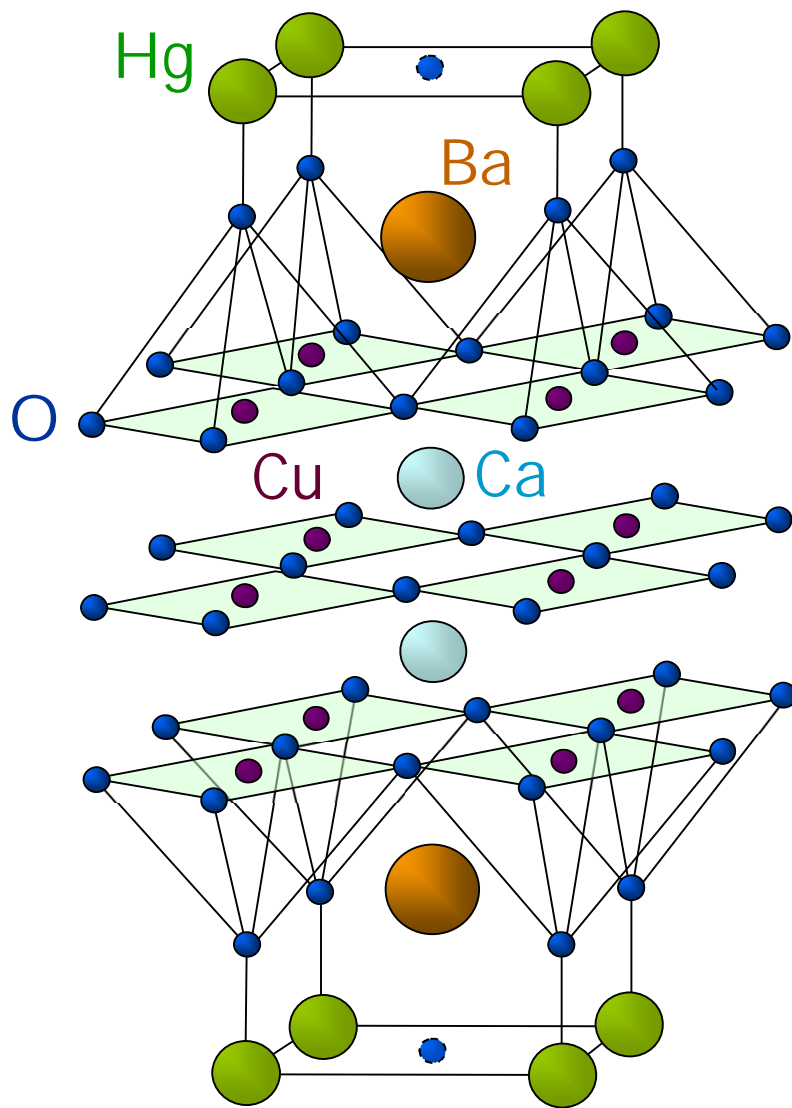
CRYSTALLOGRAPHY

- unit cell
- lattice parameters
- symmetry
- space group
- number of formula units in unit cell
- etc.

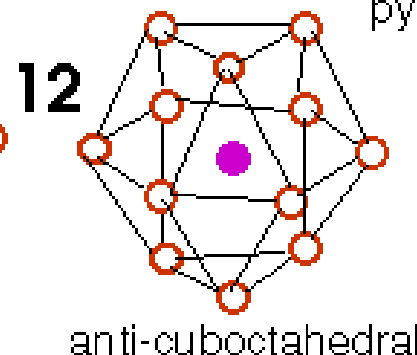
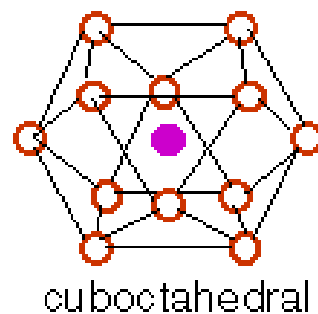
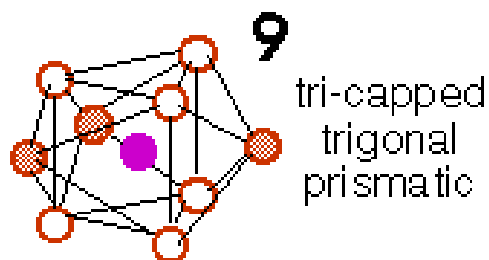
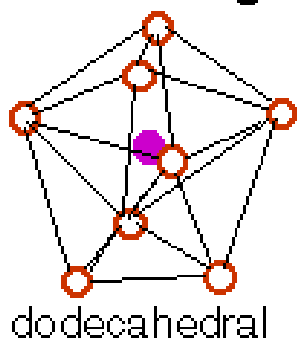
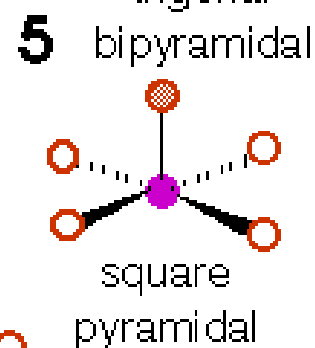
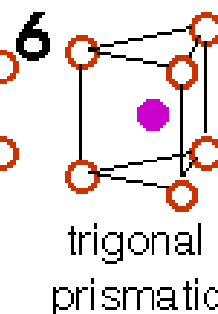
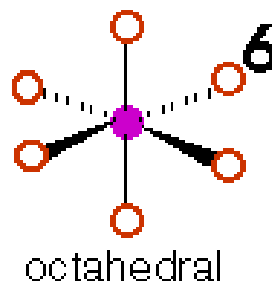
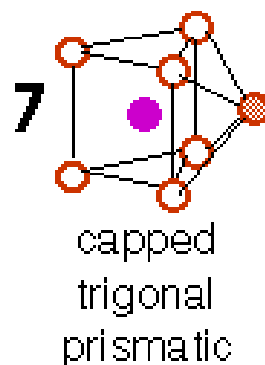
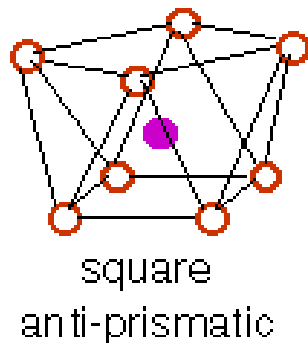
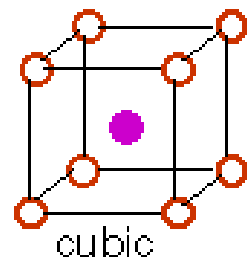
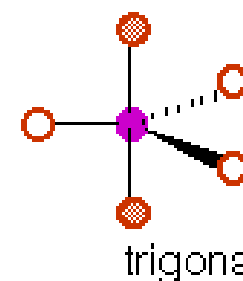
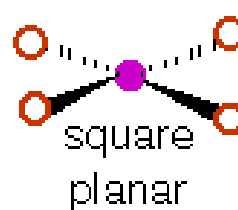
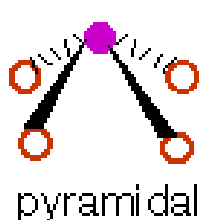
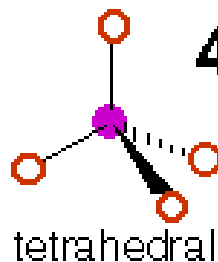
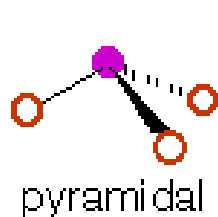
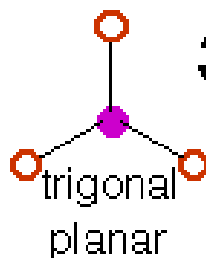
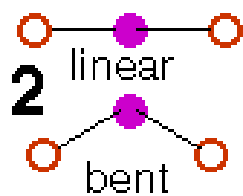
CRYSTAL CHEMISTRY

- coordination numbers
- coordination polyhedra
- bond lengths/angles
- occupation factors
- etc.

This lecture is of **crystal chemistry** !

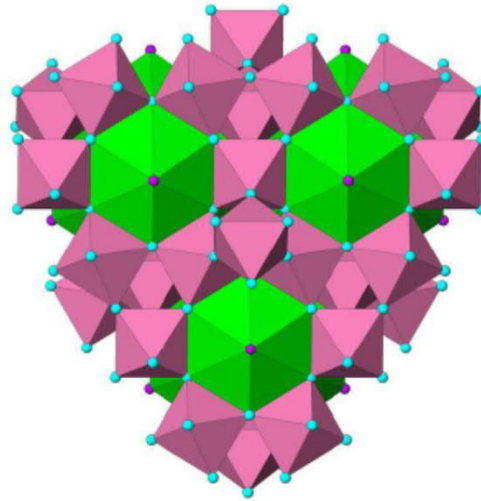
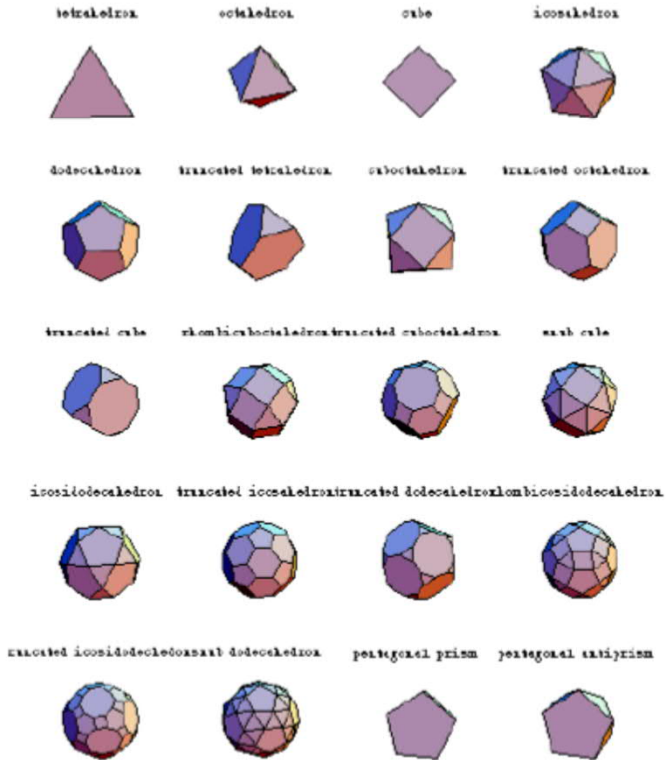


EXAMPLES OF COORDINATION NUMBERS/POLYHEDRA

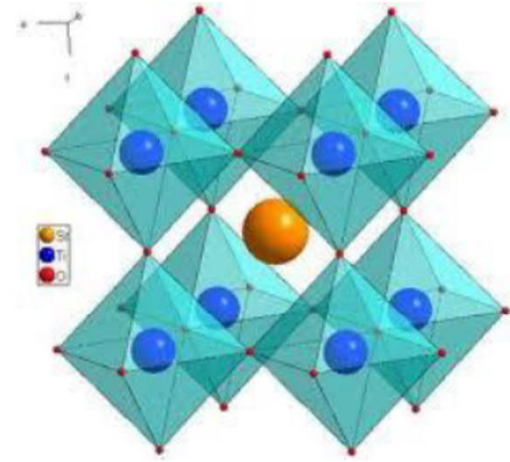


Polyhedra

Generally metal in centre and oxide or halide at vertices



Pyrochlore



Perovskite

How the atoms are located in the structure depends on:

- relative sizes of atoms/ions
- charges (oxidation states) of ions
- nature of chemical bonds (involvement of different orbitals)

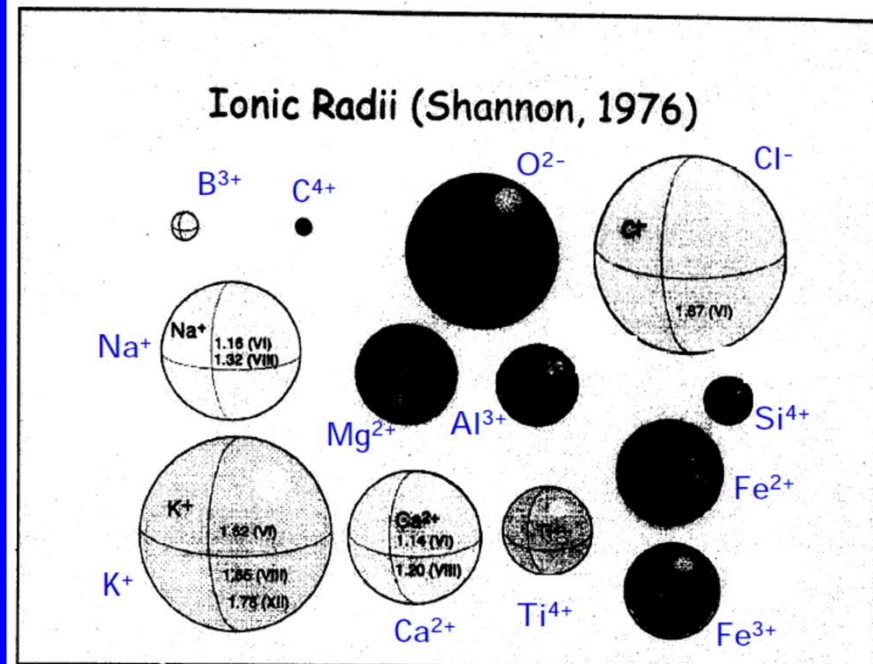
NEXT WE START THE DISCUSSION ON:

- Ion size (ionic radius) and how it affects the structure
- Relationship: valence *versus* bonding
(bond lengths & coordination number/sphere)

Theorists are always predicting new structures that we (experimentalists) can't make. But we keep making structures they can't predict.

IONIC RADIUS

- It is not possible to measure ionic radius values directly
- The values are estimated (using statistical techniques) for each ion from a large experimental data set for bond lengths between many pairs of two different elements in different (ionic) compounds
- These are tabulated; there are several different ionic radius tables; the most commonly used one is: R.D. Shannon, Acta Cryst. A 32, 751 (1976)
- There are relatively large differences in ionic radii among different ions
- For the same element, ionic radius depends on the oxidation state and coordination number



Ionic Radii - Notable Trends

- The radius increases as you move down a column.
 - $\text{Al}^{3+} = 0.675 \text{ \AA}$, $\text{Ga}^{3+} = 0.760 \text{ \AA}$, $\text{In}^{3+} = 0.940 \text{ \AA}$, $\text{Tl}^{3+} = 1.025 \text{ \AA}$
- The radius decreases as you move across a period.
 - $\text{La}^{3+} = 1.172 \text{ \AA}$, $\text{Nd}^{3+} = 1.123 \text{ \AA}$, $\text{Gd}^{3+} = 1.078 \text{ \AA}$, $\text{Lu}^{3+} = 1.001 \text{ \AA}$
- The 4d & 5d metals have similar radii due to the lanthanide contraction.
 - $\text{Nb}^{5+} = 0.78 \text{ \AA}$, $\text{Ta}^{5+} = 0.78 \text{ \AA}$, $\text{Pd}^{4+} = 0.755 \text{ \AA}$, $\text{Pt}^{4+} = 0.765 \text{ \AA}$
- The cation radius decreases as you increase the oxidation state.
 - $\text{Mn}^{2+} = 0.810 \text{ \AA}$, $\text{Mn}^{3+} = 0.785 \text{ \AA}$, $\text{Mn}^{4+} = 0.670 \text{ \AA}$
- The radius increases as the coordination number increases.
 - Sr^{2+} : CN=6 \rightarrow 1.32 \AA , CN=8 \rightarrow 1.40 \AA ,
CN=10 \rightarrow 1.50 \AA , CN=12 \rightarrow 1.58 \AA

Linus Pauling was the first to predict crystal structures based on relative (cation versus anion) ionic radii

Pauling's Rule for binary AB compounds

$$r_C/r_A < 0.155$$

$$\text{CN} = 2$$

$$0.155 < r_C/r_A < 0.225$$

$$\text{CN} = 3$$

$$0.225 < r_C/r_A < 0.414$$

$$\text{CN} = 4$$

$$0.414 < r_C/r_A < 0.732$$

$$\text{CN} = 6$$

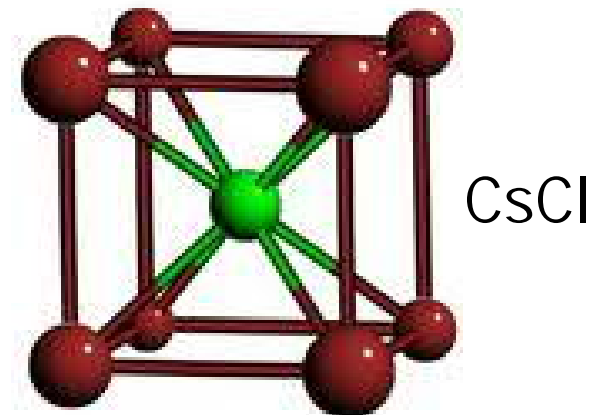
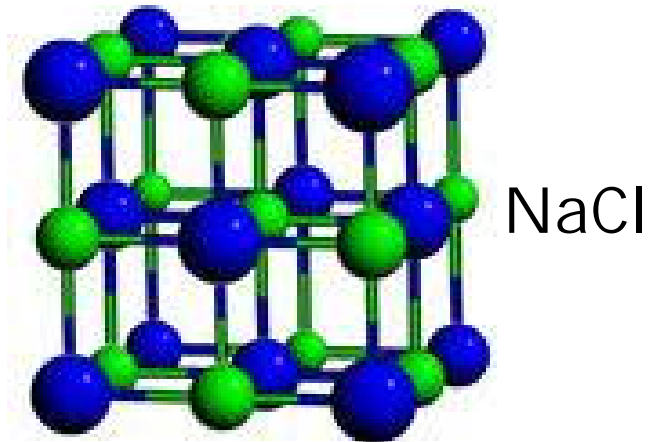
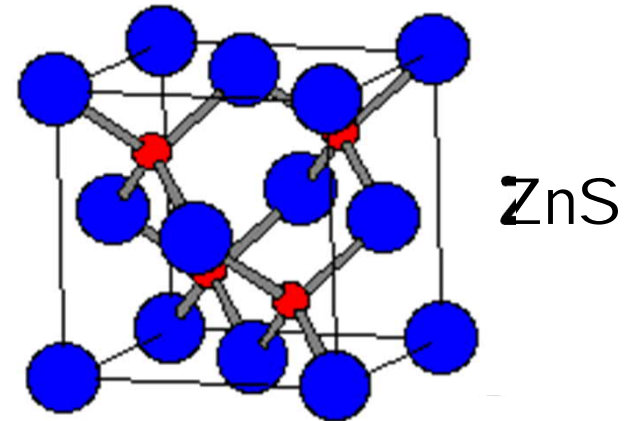
$$0.732 < r_C/r_A < 1.00$$

$$\text{CN} = 8$$

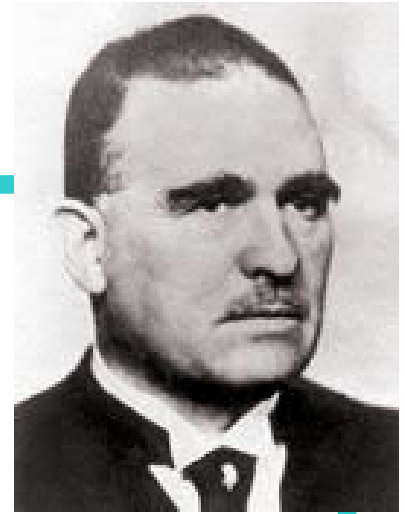
$$r_C/r_A > 1.00$$

$$\text{CN} = 12$$

QUESTION: what are the coordination numbers (CN) in ZnS, NaCl and CsCl ?



Victor Moritz Goldschmidt
(1888-1947)



Another approach:

TOLERANCE FACTOR (t)

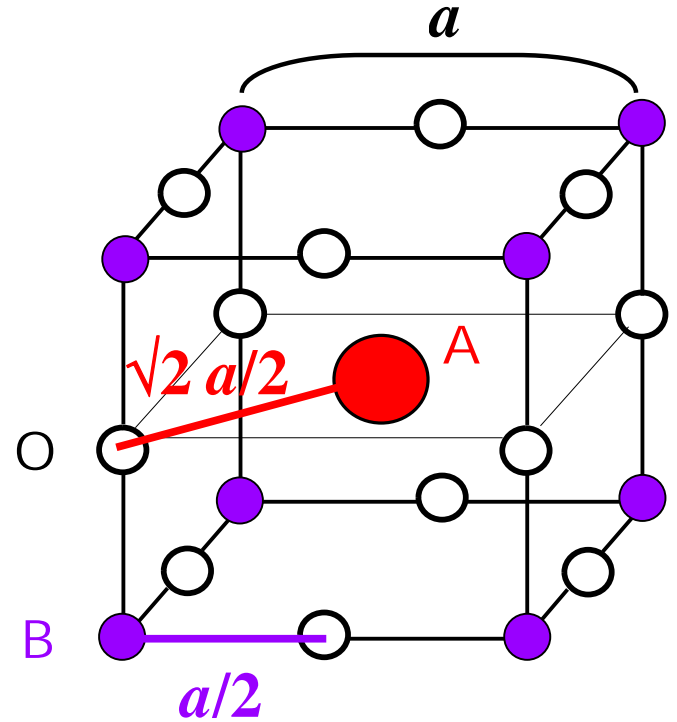
- **1926 Goldschmidt**

V.M. Goldschmidt , “Geochemische Verteilungsgesetze der Elemente”,
Skrifter Norske Videnskaps-Akad, Oslo, I. Mat-Naturr. K1 (1926)

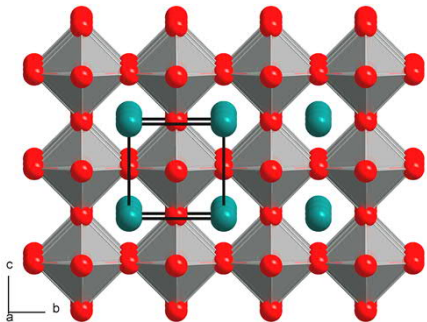
- **t : measure for the degree of mismatch between two different atomic layers: at $t = 1$, perfect match**
- **Calculated from preferred bond lengths**
- **Preferred bond lengths are estimated from ionic radii (Shannon)**
- **Developed first for the perovskite structure, later extended to other structures as well**
- **To understand the stability of the structures and the creation of different distortions/defects (e.g. oxygen vacancies)**

Tolerance factor for ABO_3 perovskite

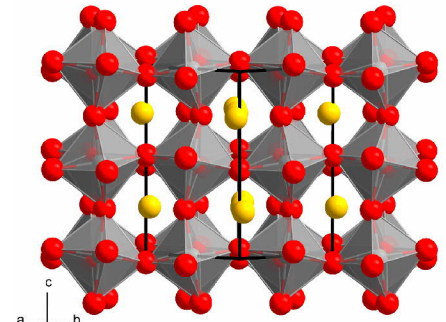
$$t = \frac{(r_A + r_O)}{\sqrt{2} (r_B + r_O)}$$



- $t = 1$: ideal matching (0.80 < t < 1.05 possible)
- $t < 1$: A is too small \rightarrow changes in oxygen position
- $t > 1$: B is too small \rightarrow B is reduced \rightarrow oxygen vacancies



$t = 1$

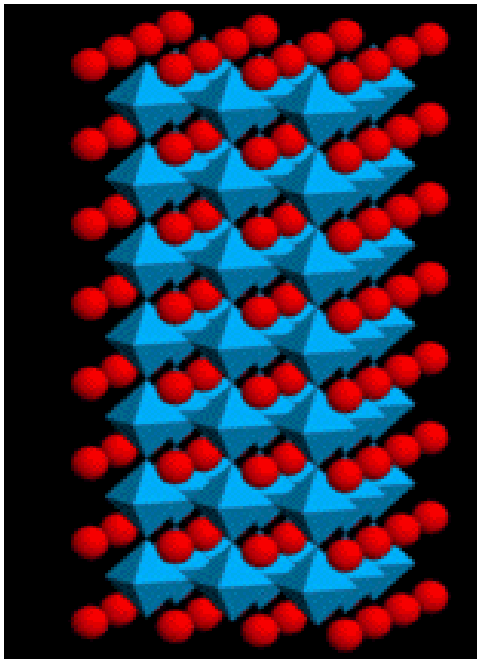


$t < 1$

$$t = \frac{(r_A + r_O)}{\sqrt{2} (r_B + r_O)}$$

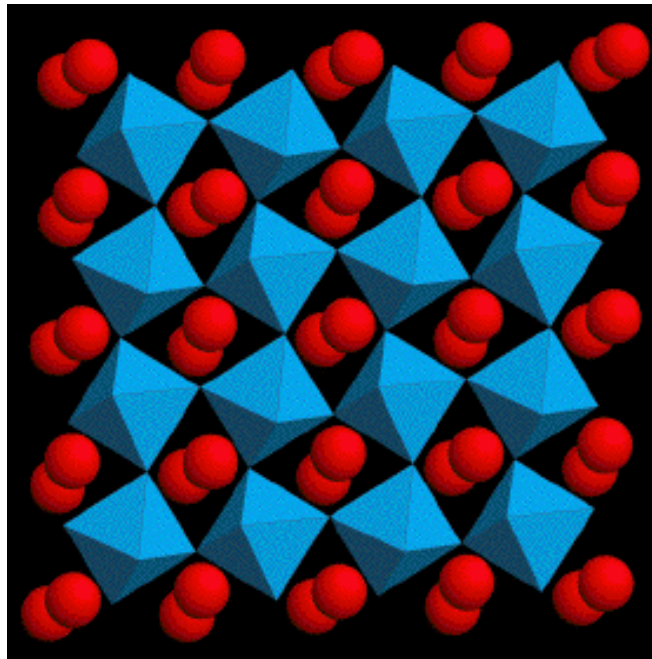
NOTE:
Oxygen vacancies
can be random or
ordered (as below)

$t = 1$



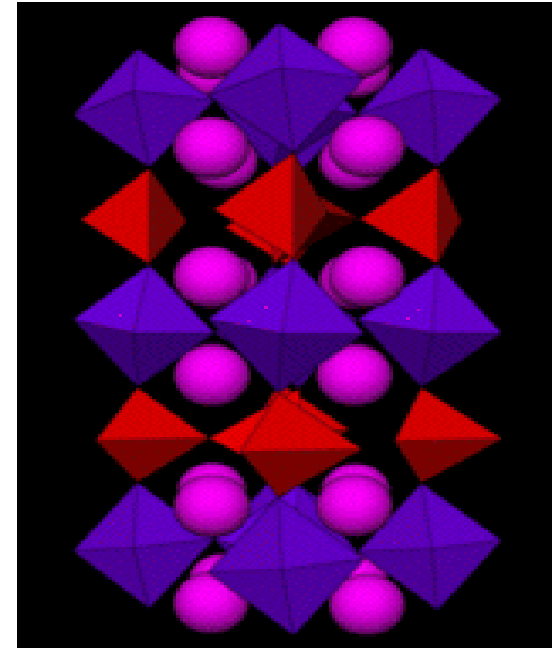
IDEAL

$t < 1$



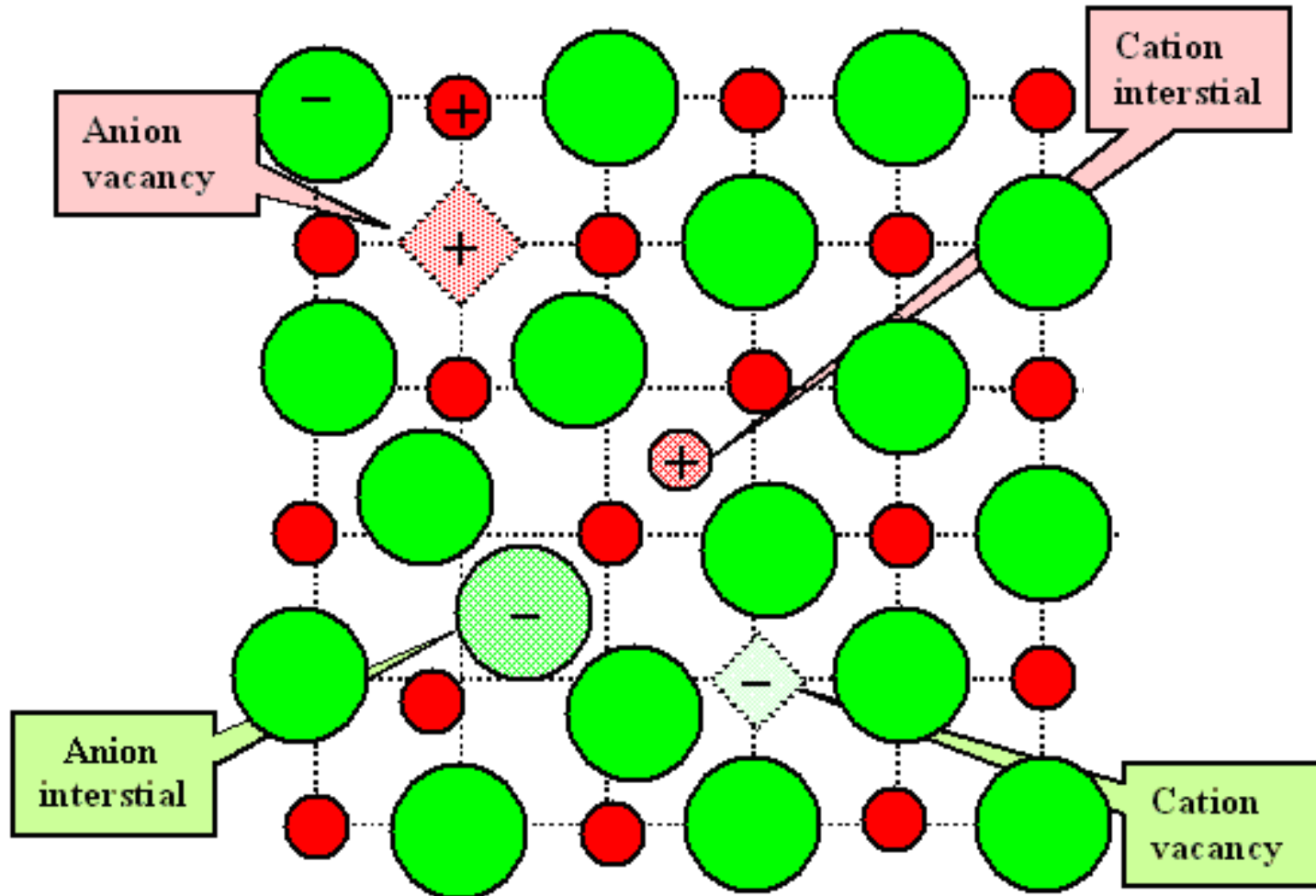
**Changes in
atomic positions**

$t > 1$



**Oxygen
deficiency**

PRACTICAL CRYSTALS ARE RARELY IDEAL, BUT CONTAIN DIFFERENT DEFECTS



FOR METAL OXIDES, defects are usually discussed in terms of oxygen nonstoichiometry

(1) Interstitial oxygen atoms



(2) Cation vacancies



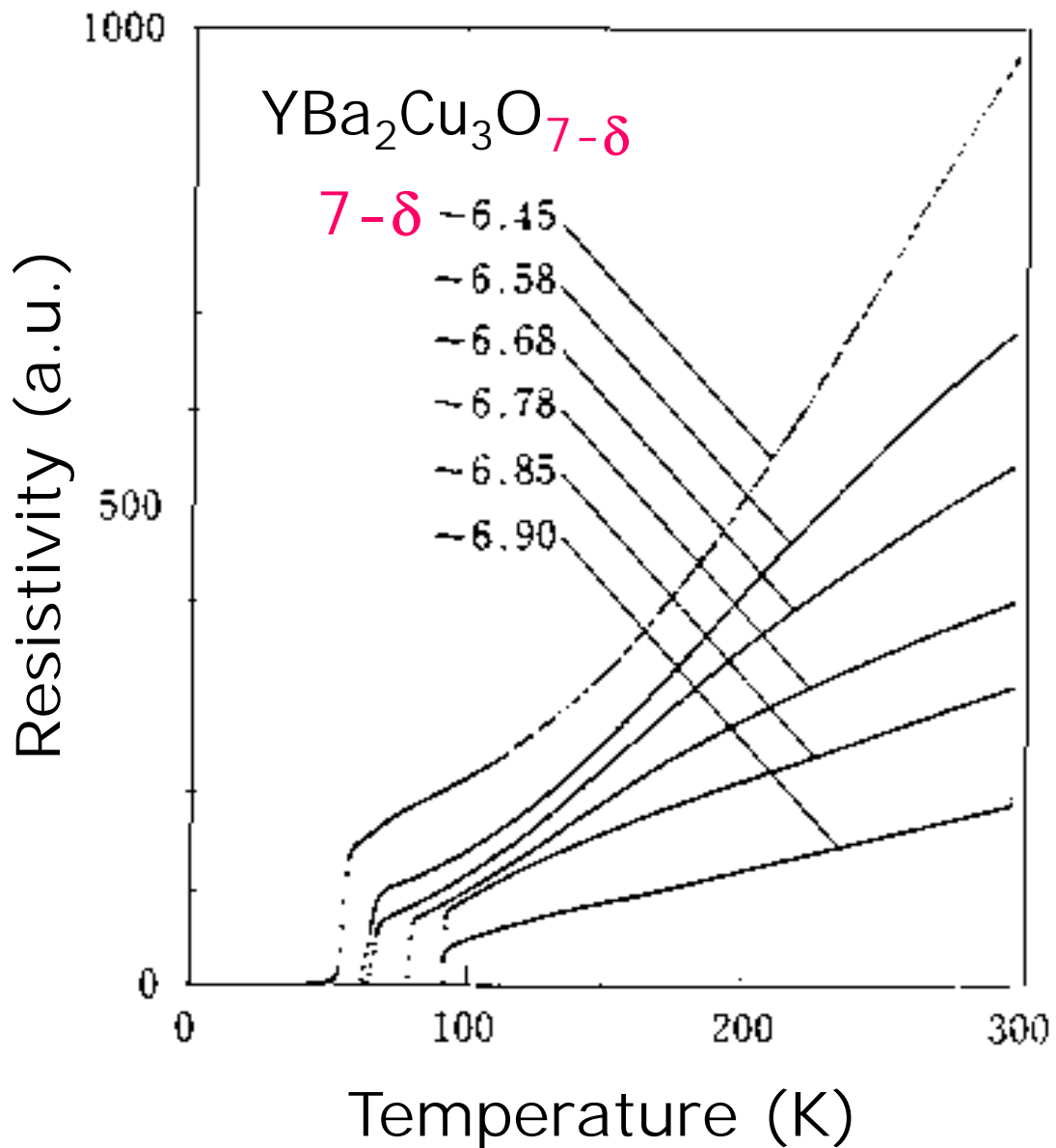
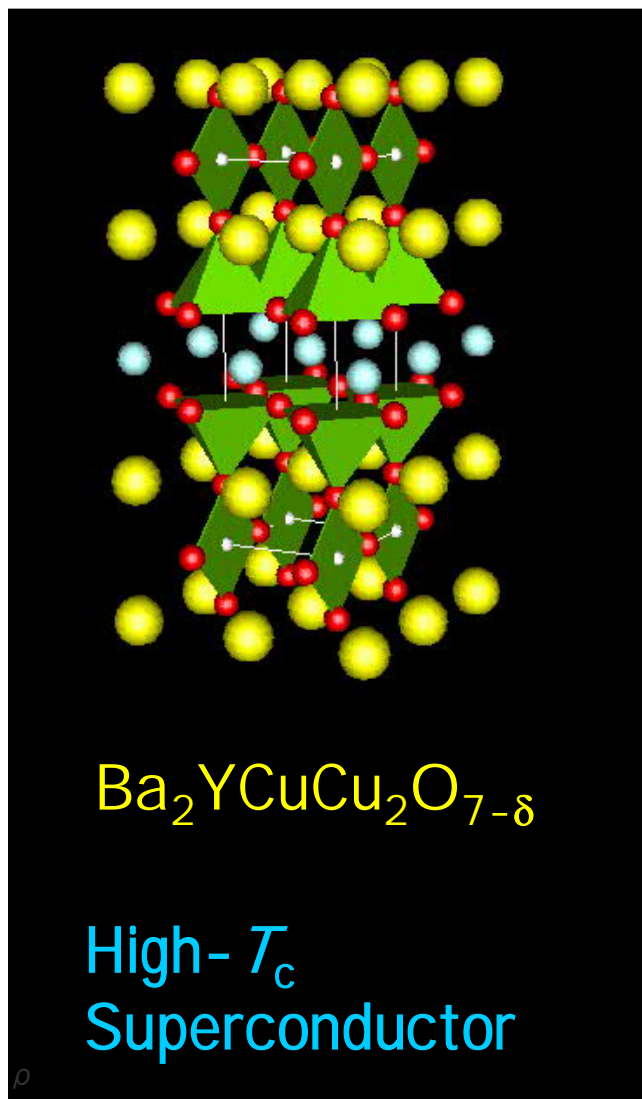
(3) Oxygen vacancies



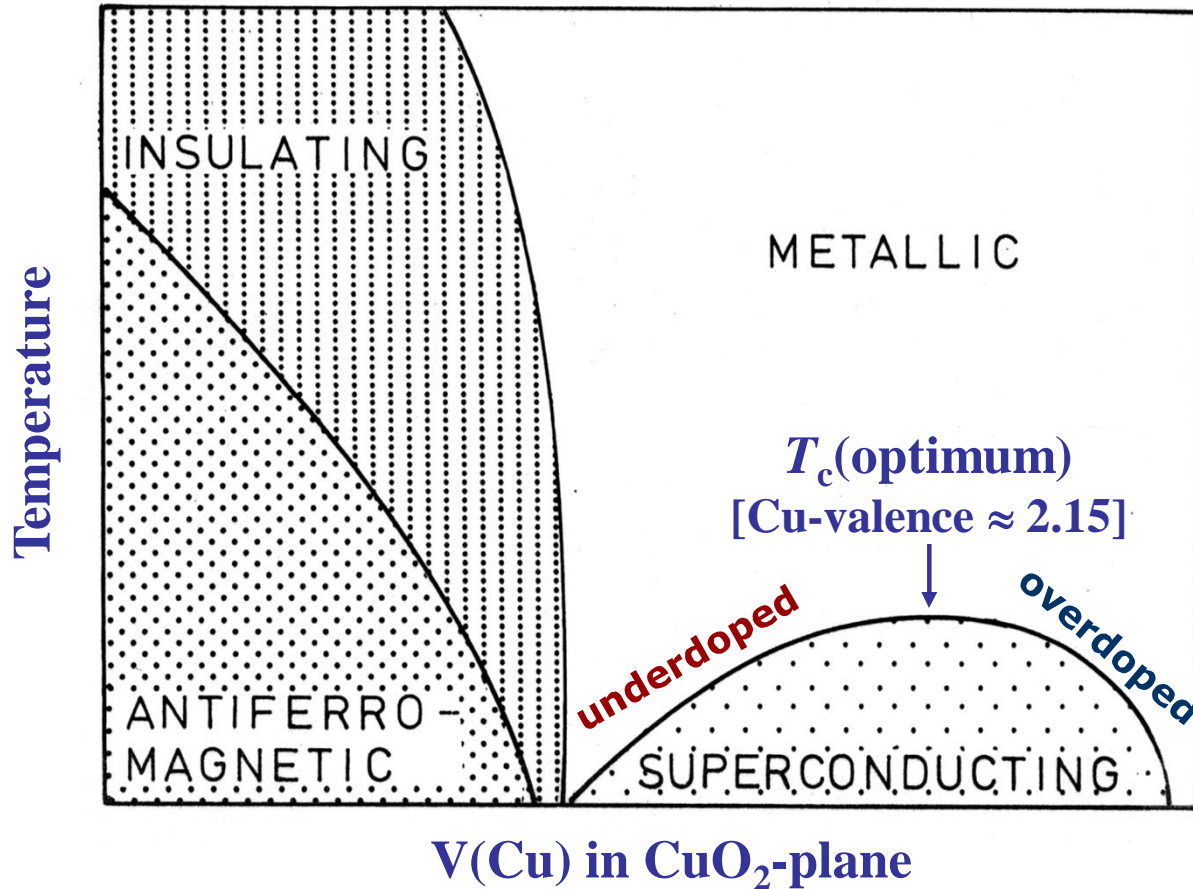
(4) Interstitial cations



$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (or $\text{Ba}_2\text{YCu(1)Cu(2)}_2\text{O}_{7-\delta}$ to more properly reflect the structure) is a notorious example of the huge impact of oxygen (non)stoichiometry



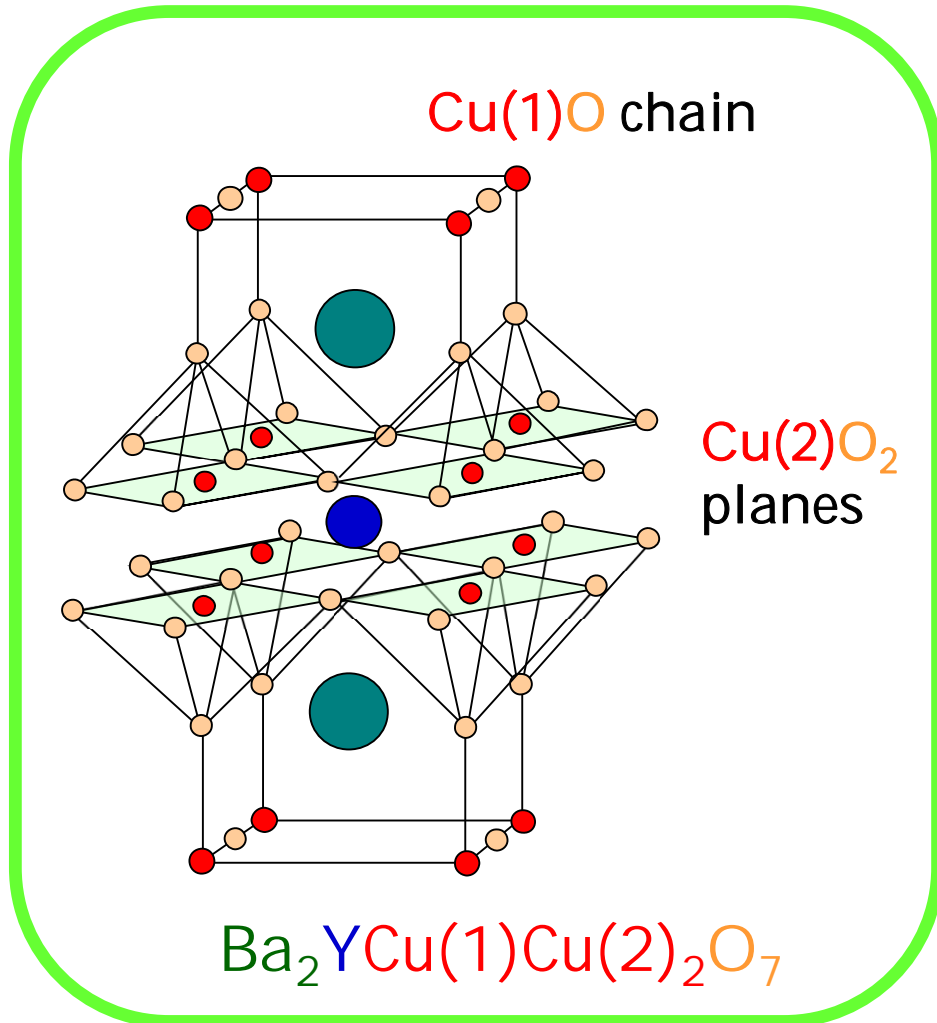
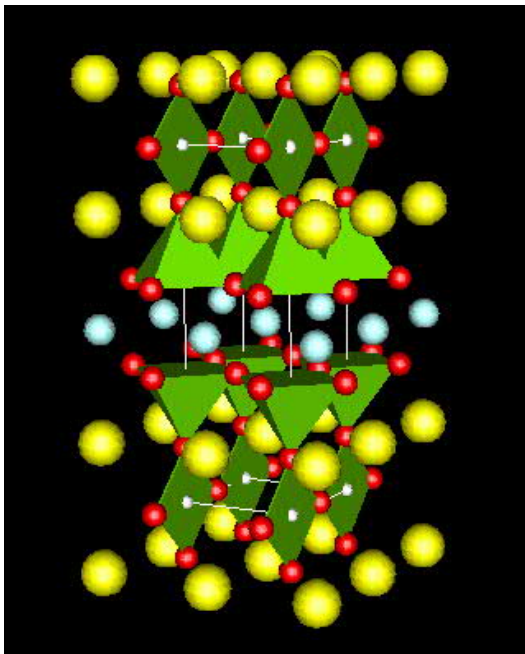
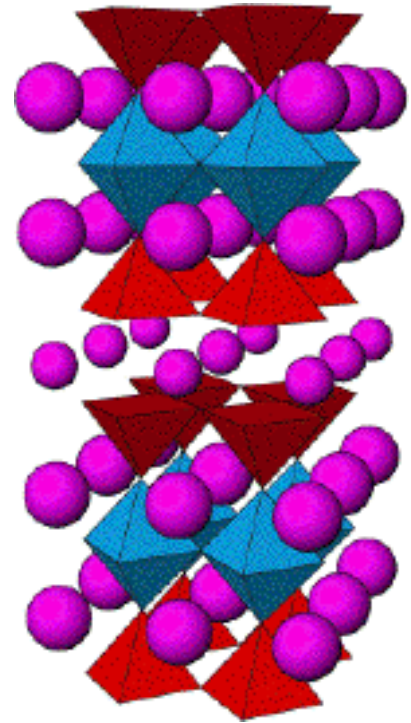
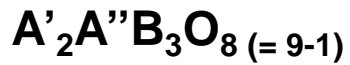
Phase Diagram of High- T_c Superconductors



Oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ controls the valence state of copper, and thereby the superconductivity (T_c value)

Illustration how the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure is derived from the perovskite structure through cation ordering and ordered oxygen vacancies

A-site ordered &
oxygen-vacancy ordered
TRIPLE PEROVSKITE



BVS (Bond Valence Sum)

Correlation between bond length(s) and valence value

Empirical but highly useful tool for:

- Estimation of actual/mixed valence values (also site-specific)
- Evaluation of the feasibility of crystal structures
- Prediction of bond distances (viz. predictions based on ionic radii):
$$d_{ij} = R_{ij}^0 - 0.37 \times \ln s_{ij}$$

(can handle unsymmetrical coordination environments)
- Identification of bonding instabilities
- Location of light atoms (H, Li, etc.) that are hard to find by XRD, by examining the valences of the surrounding atoms

BOND-VALENCE-SUM (BVS)

C-C	1.54 Å
C=C	1.33 Å
C≡C	1.20 Å

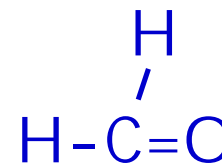
- Organic compounds:

- the valence of each bond takes an integer value
- the bond order (single, double or triple) correlates with the bond length (the higher the order, the shorter the bond)
- each atom possesses a valence that equals to the number of bonds it forms

- FOR EXAMPLE: formaldehyde HCHO

Bonds: 2 x C-H, 1 x C=O

Valences: C : 4, O : 2, H : 1



- Inorganic compounds:

- bonds do not adopt integer valences only
- FOR EXAMPLE: Al is trivalent in all its compounds but exists commonly in either tetrahedral or octahedral coordination

Bond-Valence-Sum (BVS) Calculation

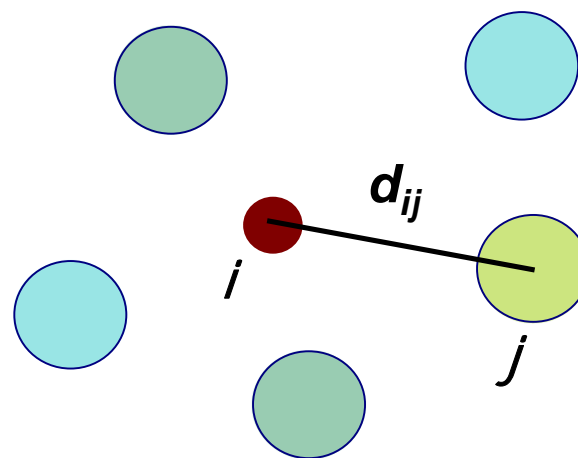
- Quantitative relation between the bond valence and the bond length
- Bond valence can be fractional & Neighbours may be unequivalent
- The shorter the bond, the stronger it is, and the larger the s_{ij} is

- Empirical equation:

$$s_{ij} = \exp[(R_{ij}^0 - d_{ij})/0.37]$$

$$V_i = \pm \sum s_{ij}$$

- R_{ij}^0 values tabulated
(for various i-j combinations)

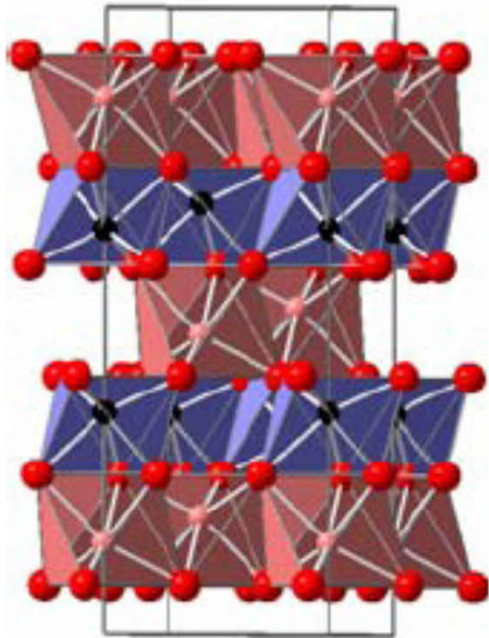


1. I.D. Brown, *Chem. Soc. Reviews* **7**, 359-376 (1978).
2. I.D. Brown, "The chemical bond in inorganic chemistry: the bond valence model" Oxford Univ. Press, New York (2002).
3. Brown & Altermatt, *Acta Cryst. B* **41**, 244-247 (1985).
4. Brese & O'Keefe, *Acta Cryst. B* **47**, 192-197 (1991).
5. O'Keefe, *Acta Cryst. A* **46**, 138-142 (1990).

$$s_{ij} = \exp \left[\frac{(R_{ij}^0 - d_{ij})}{0.37} \right]$$

$$V_i = \pm \sum_j s_{ij}$$

FeTiO₃ (Ilmenite)



Bond Distances

$$\text{Fe-O} = 3 \times 2.07, 3 \times 2.20$$

$$\text{Ti-O} = 3 \times 1.88, 3 \times 2.09$$

Bond Valence Sums

$$\text{Fe} = 3 \times 0.40 + 3 \times 0.28 = 2.04$$

$$\text{Ti} = 3 \times 0.84 + 3 \times 0.48 = 3.96$$

$$\text{O} = 0.40 + 0.28 + 0.84 + 0.48 = 2.00$$

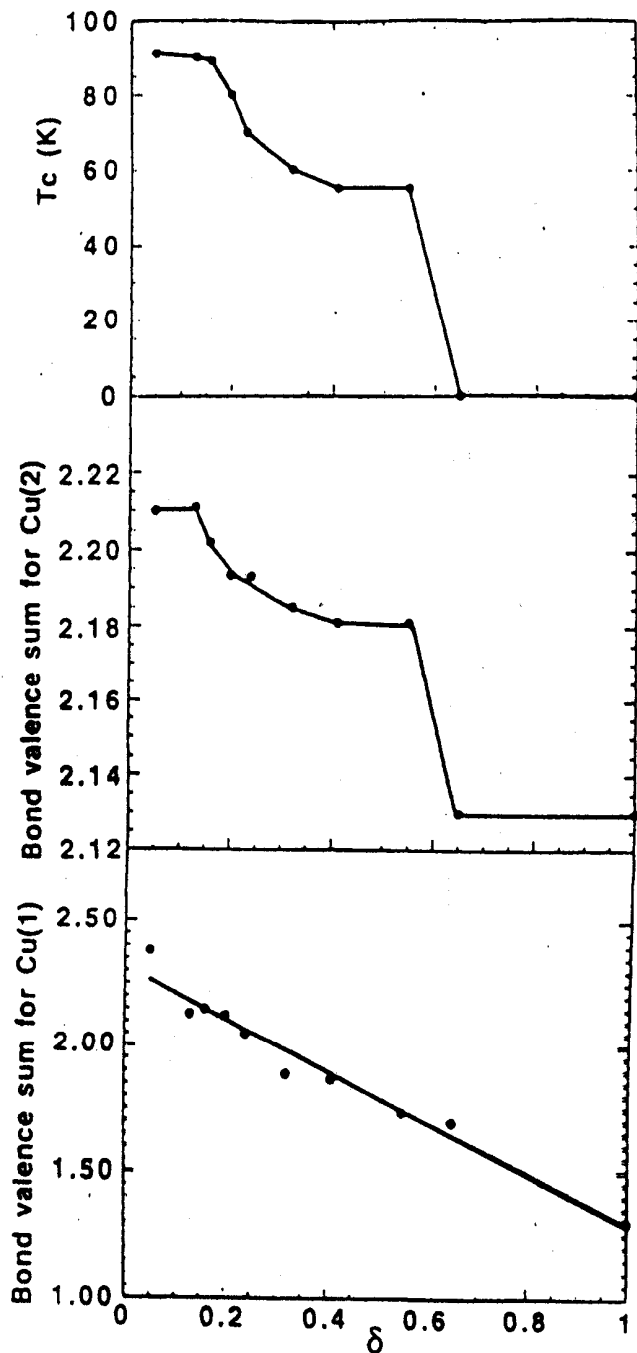
BVS calculation confirms that Fe occupies the larger (red) octahedra and Ti the smaller (blue) octahedra in ilmenite structure



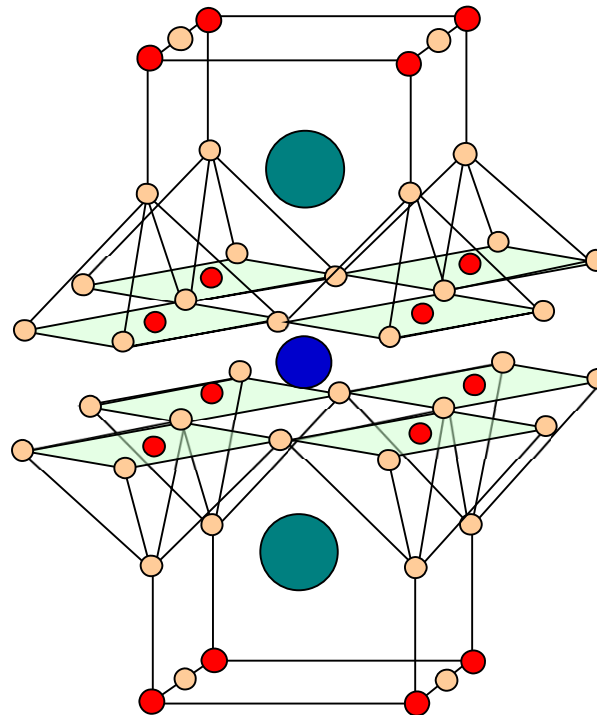
COPPER OXIDES

Compound	CN(Cu)	Cu-O bonds	$V_{\text{nom}}(\text{Cu})$	BVS : V_{Cu}
Cu_2O	2	2 x 1.849	+I	+1.02
CuO	4	2 x 1.951 2 x 1.961	+II	+1.89
Sr_2CuO_3	4	2 x 1.958 2 x 1.967	+II	+1.86
KCuO_2	4	2 x 1.815 2 x 1.832	+III	+3.11
LaCuO_3	6	6 x 1.952	+III	+3.29
$\text{LaCuO}_{2.5}$	5	2 x 1.941 2 x 1.966 1 x 2.285	+II	+2.10

R^0 : $\text{Cu}^+-\text{O}^{2-}$ 1.600 Å, $\text{Cu}^{2+}-\text{O}^{2-}$ 1.679 Å, $\text{Cu}^{3+}-\text{O}^{2-}$ 1.730 Å



Cu(1)O chain



Cu(2)O₂ planes



BVS calculation shows that with decreasing oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ the valence state of both Cu(1) and Cu(2) decrease. Most importantly, the trend in Cu(2) valence follows the trend in T_c , indicating the valence of Cu(2) is important for the superconductivity.