SCHEDULE

	Date		Topic
1.	Tue	14.09.	Lec-1: Introduction
2.	Fri	17.09.	**Lec-2: Crystal Chemistry & Tolerance parameter**
3.	Fri	17.09.	EXERCISE 1
4.	Tue	21.09.	Lec-3: Crystal chemistry & BVS
5.	Fri	24.09.	Lec-4: Symmetry & Point Groups
6.	Fri	24.09.	EXERCISE 2
7.	Tue	28.10.	Lec-4: Crystallography & Space Groups
8.	Fri	01.10.	Lec-5: XRD & Reciprocal lattice
9.	Fri	01.10.	EXERCISE 3
10.	Tue	05.10.	Lec-6: ND & GI-XRD
11.	Fri	08.10.	Lec-7: Rietveld
12.	Fri	08.10	. EXERCISE 4: Rietveld
13.	Tue	12.10.	Lec-8: Synchrotron rad. & XAS & RIXS
14.	Fri	15.10.	EXAFS & Mössbauer
15.	Fri	15.10.	EXERCISE 5
16.	Tue	19.10.	Seminars: XPS, FTIR, Raman, ED, HRTEM, SEM, AFM
17.	Fri	19.10.	Lec-12: XRR
18.	Fri	22.10.	EXERCISE 6: XRR

COURSE START:
Tue 14.09. at 12.15
in Zoom

**EXAM:
Fri Oct. 29, 2021**

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)**
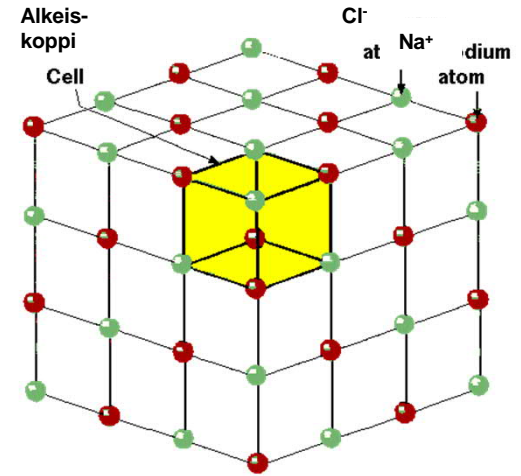
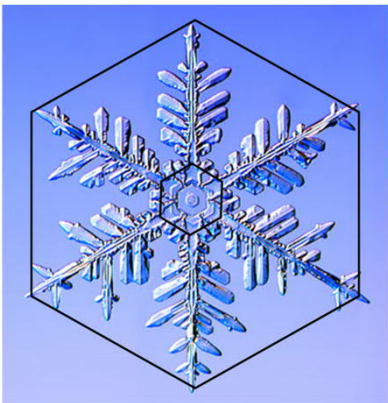- **Tolerance factor concept and utilization**

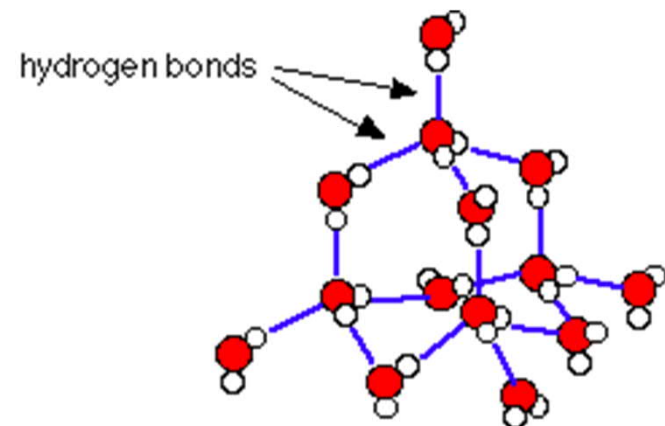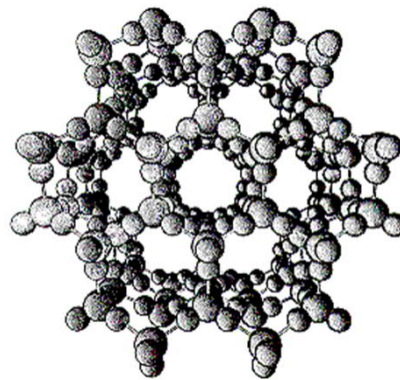# EXAMPLES of "everyday" crystals/structures

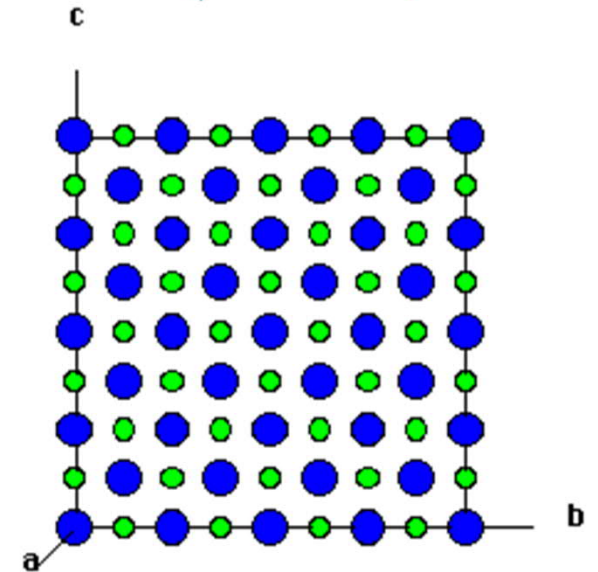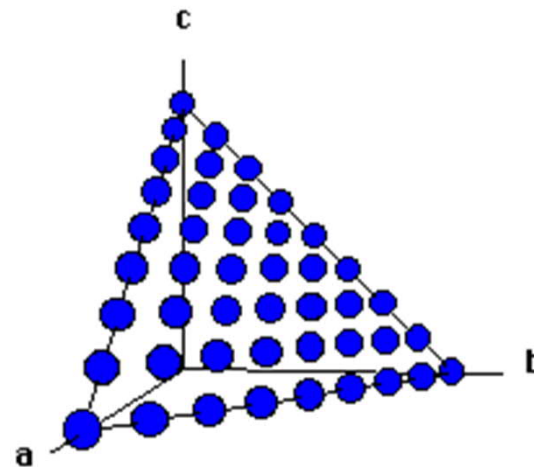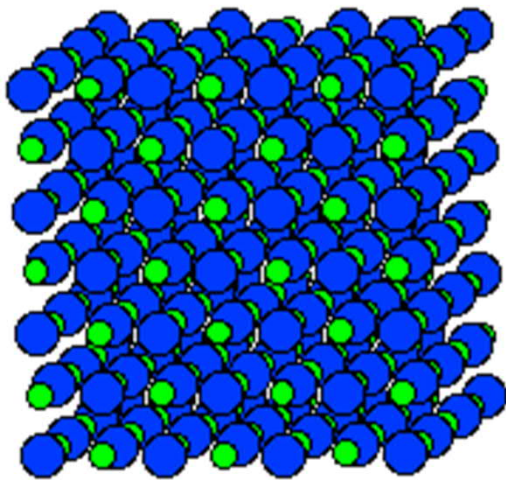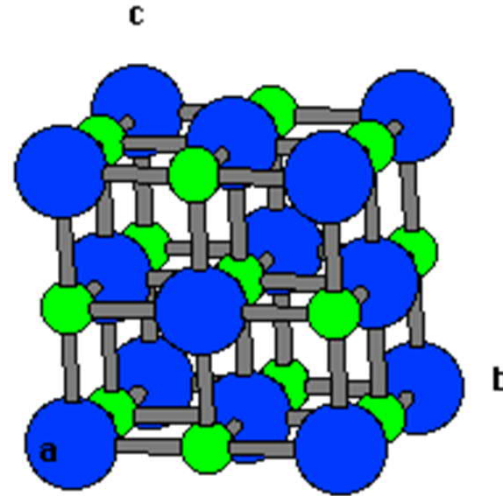Rock salt (NaCl)

NaCl single crystal

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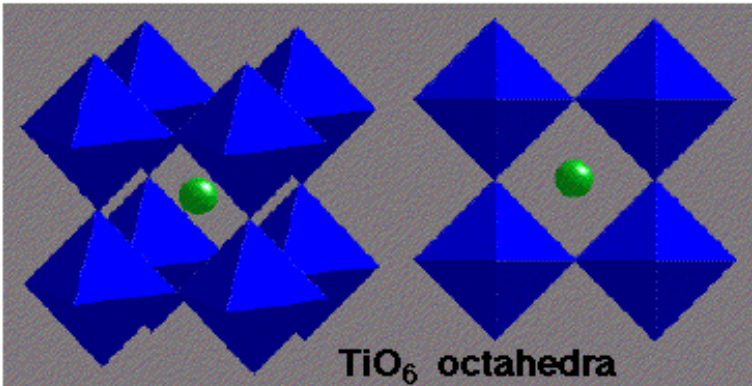high symmetry, ionic bonds
→ extremely stable

Snow flake:
hexagonal

hydrogen bonds

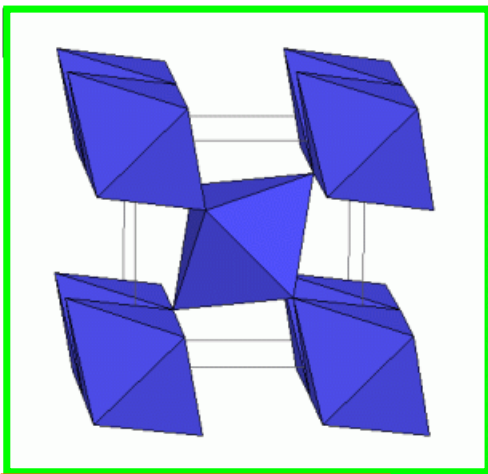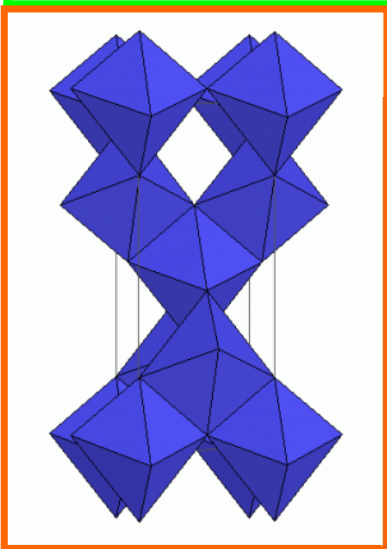# The same (NaCl) crystal structure can be presented in multiple ways

PEROVSKITE CaTiO$_3$

TiO$_6$ octahedra
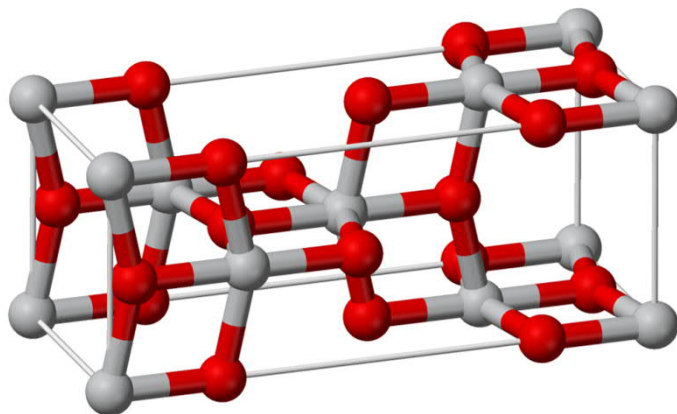
Other Examples
of common crystal structures

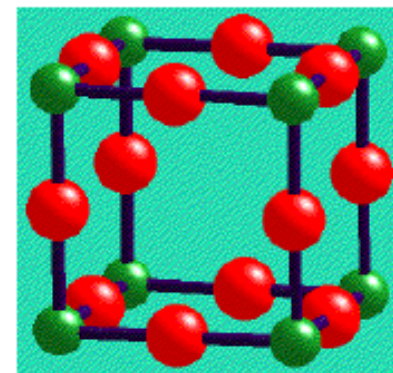RUTILE TiO$_2$
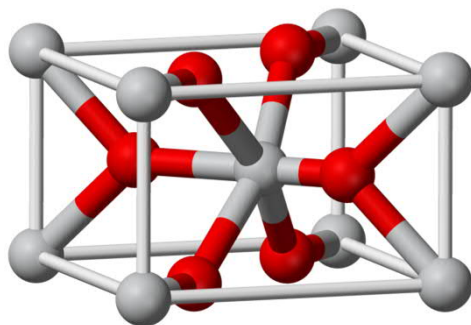
ANATASE TiO$_2$

ReO$_3$
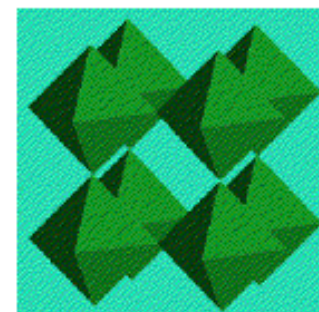
CRYSTAL

- **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: $1 \text{ Å} = 10^{-10} \text{ m} = 0.1 \text{ nm}$**

- **On the right, the tiny crystal (grown from flux by my students) is a single crystal of the record-high T_c (135 K) Hg-Ba-Ca-Cu-O superconductor; crystal structure shown below**

Spiral

Pb,Cu-rich

(Hg,Pb)-1$^{(Ba,Sn)}$223

10 μm
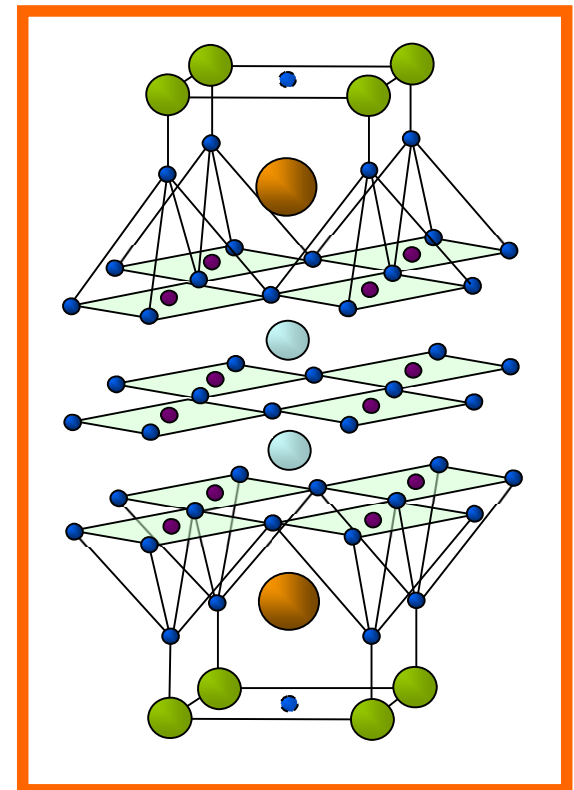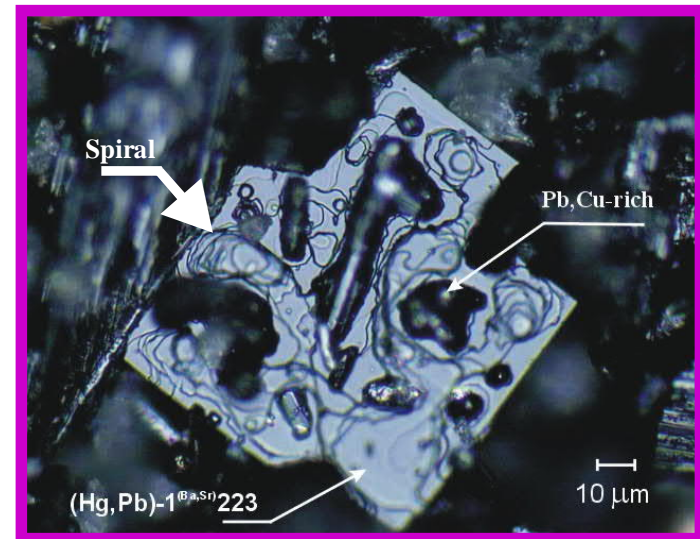
WHAT WE LIKE TO KNOW ABOUT THE CRYSTAL STRUCTURE

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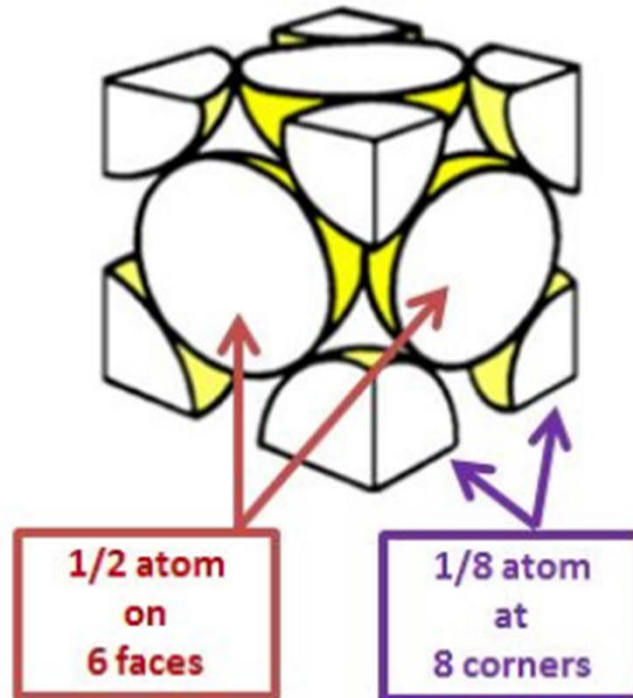- **etc.**

CRYSTAL CHEMISTRY
- **coordination numbers**
- **coordination polyhedra**
- **bond lengths/angles**
- **occupancy factors**
- **etc.**

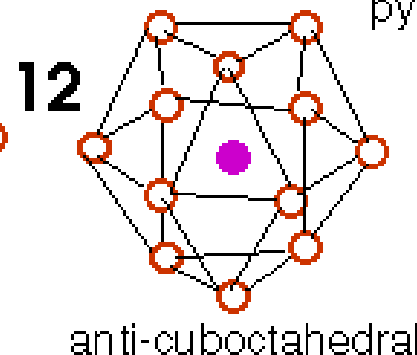**This lecture is of crystal chemistry !**

Partially vacant

Hg

Ba

O

Cu   Ca

Hg–Ba–Ca–Cu–O
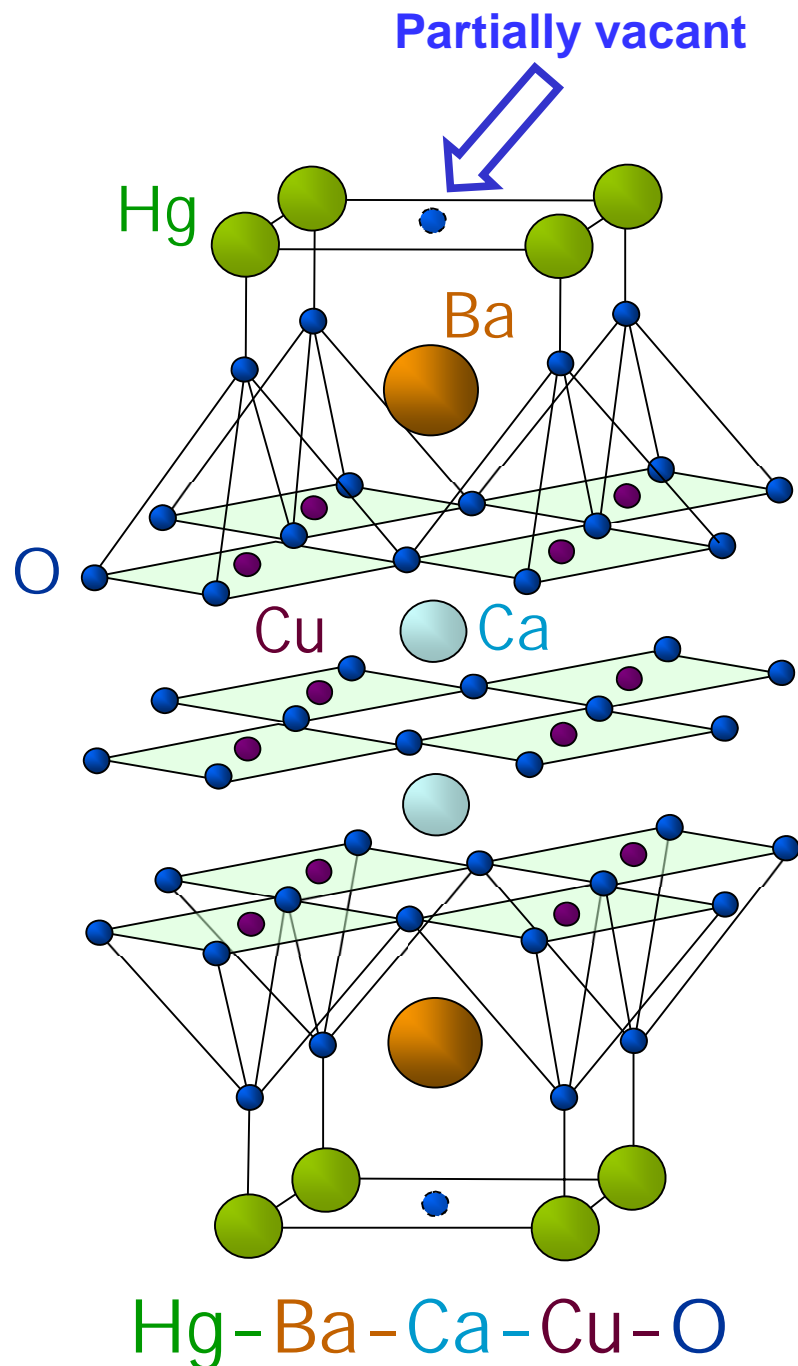
NUMBER of ATOMS in UNIT CELL

- **atom inside unit cell: belongs only to one unit cell → 1**
- **atom on unit cell face: belongs to two unit cells → 0.5**
- **atom on unit cell edge: belongs to four unit cells → 0.25**
- **atom on unit cell corner: belongs to eight unit cells → 0.125**

1/2 atom on 6 faces

1/8 atom at 8 corners

EXAMPLES OF COORDINATION NUMBERS/POLYHEDRA

2
linear
bent

3
trigonal planar
pyramidal

4
tetrahedral
pyramidal
square planar

5
trigonal bipyramidal
square pyramidal

cubic
square anti-prismatic

7
capped trigonal prismatic

6
octahedral
trigonal prismatic

8
dodecahedral

9
tri-capped trigonal prismatic

12
cuboctahedral
anti-cuboctahedral
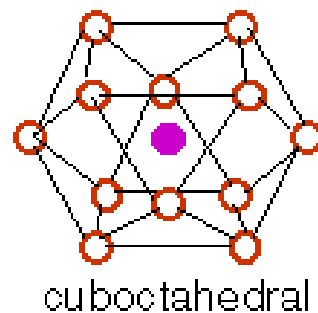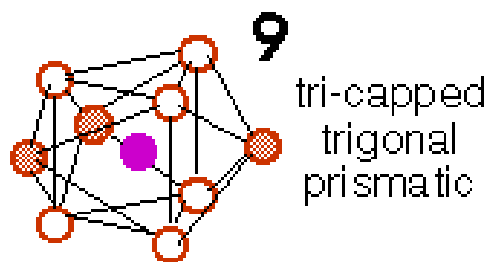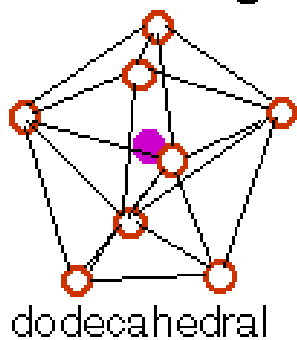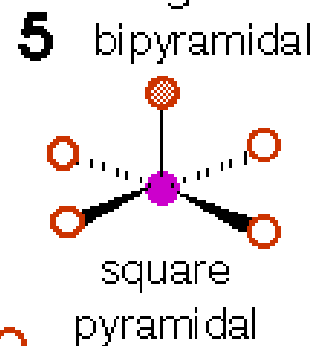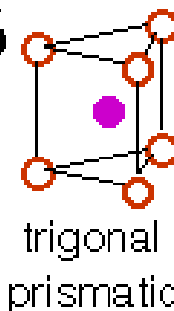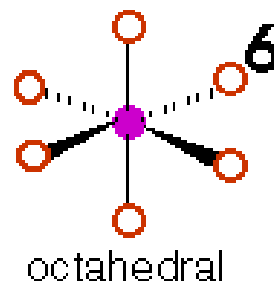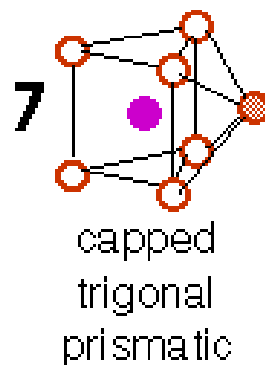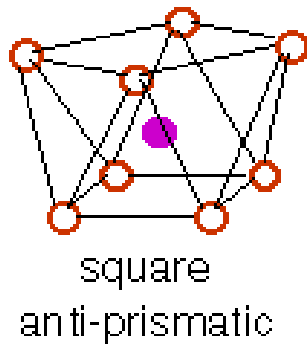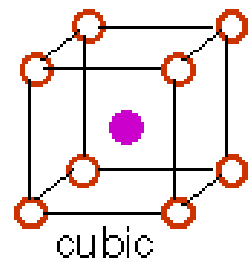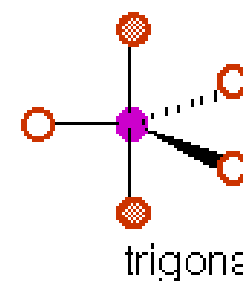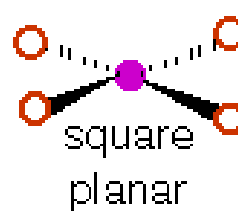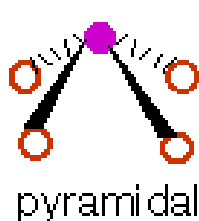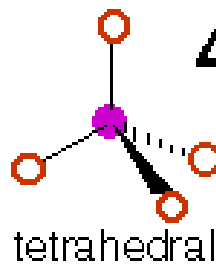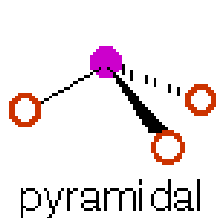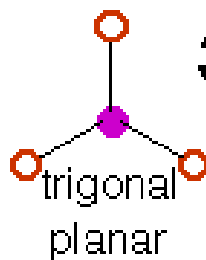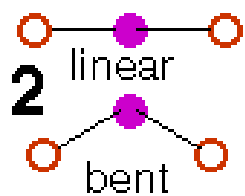
Polyhedra

Generally metal in centre and oxide or halide at vertices
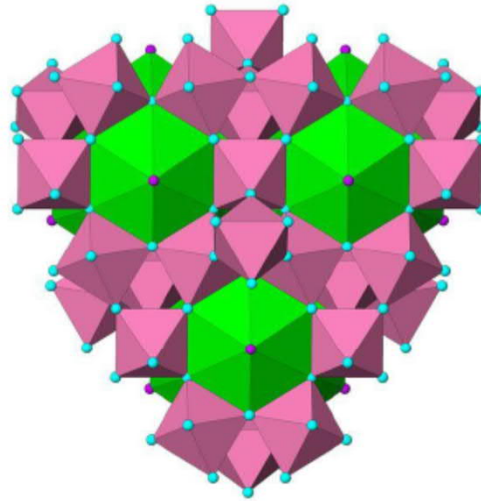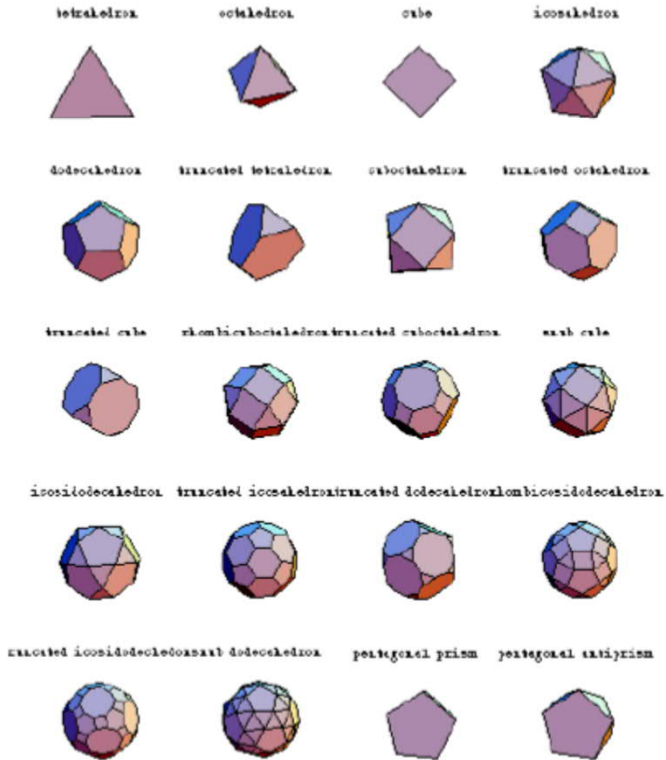
Pyrochlore
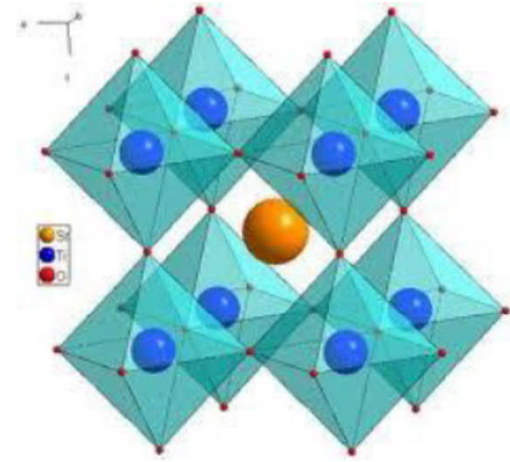
Perovskite

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**

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

Prof P.D. Battle

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 diffrences in ionic radii among different ions**

- **For the same element, ionic radius depends on the oxidation state and coordination number**

Ionic Radii (Shannon, 1976)
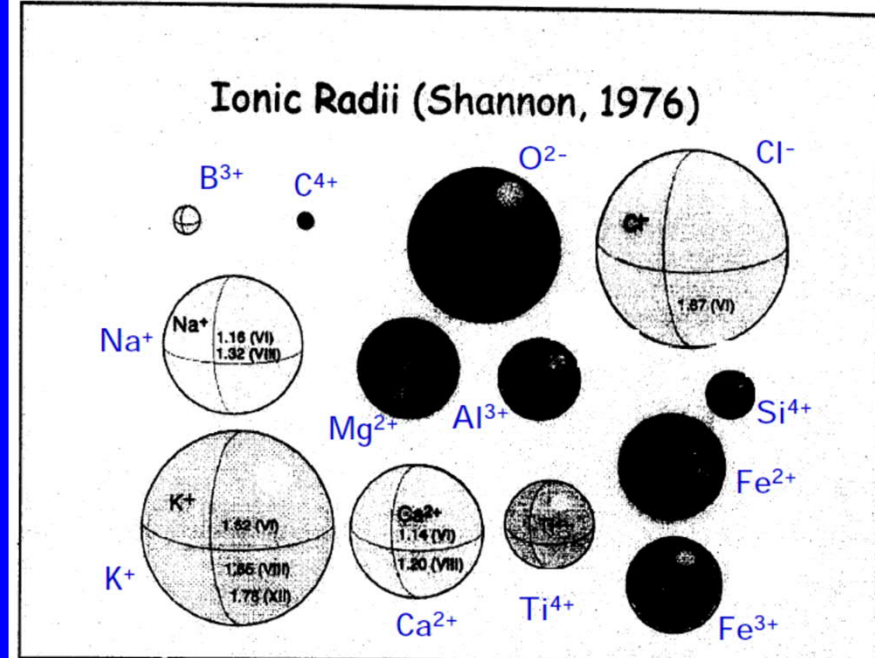
Ionic Radii – Notable Trends

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

H
30

He
93

Li
152
Li⁺
60

Be
160
Be⁺⁺
31

B
88

C
77

N
70

O
66
O⁻⁻
140

F
64
F⁻
136

Ne
112

Na
186
Na⁺
95

Mg
160
Mg⁺⁺
65

Al
143
Al⁺⁺⁺
50

Si
117

P
110

S
104
S⁻⁻
184

Cl
99
Cl⁻
181

A
154

K
231
K⁺
133

Ca
197
Ca⁺⁺
97

Sc
160
Sc⁺⁺⁺
81

Ti
146

V
131

Cr
125

Mn
129

Fe
126

Co
125

Ni
124

Cu
128
Cu⁺
96

Zn
133
Zn⁺⁺
74

Ga
122
Ga⁺⁺⁺
62

Ge
122
Ge⁺⁺⁺⁺
53

As
121

Se
117
Se⁻⁻
198

Br
114
Br⁻
195

Kr
169

Rb
244
Rb⁺
148

Sr
215
Sr⁺⁺
113

Y
180
Y⁺⁺⁺
93

Zr
157

Nb
141

Mo
136

Tc
130

Ru
133

Rh
134

Pd
138

Ag
144
Ag⁺
126

Cd
149
Cd⁺⁺
97

In
162
In⁺⁺⁺
81

Sn
140
Sn⁺⁺⁺⁺
71

Sb
141

Te
137
Te⁻⁻
221

I
133
I⁻
216

Xe
190

Cs
262
Cs⁺
169

Ba
217
Ba⁺⁺
135

La
186
La⁺⁺⁺
115

Hf
157

Ta
143

W
137

Re
137

Os
134

Ir
135

Pt
133

Au
144
Au⁺
137

Hg
171
Hg⁺⁺
110

Tl
171
Tl⁺⁺⁺
95

Pb
175
Pb⁺⁺⁺⁺
84

Bi
145

Po
140

At
140

Rn
220

Fr
270

Ra
220

Ac
200

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

ZnS

Pauling's Rule for binary AB compounds

$r_C/r_A < 0.155$ CN = 2
$0.155 < r_C/r_A < 0.225$ CN = 3
$0.225 < r_C/r_A < 0.414$ CN = 4
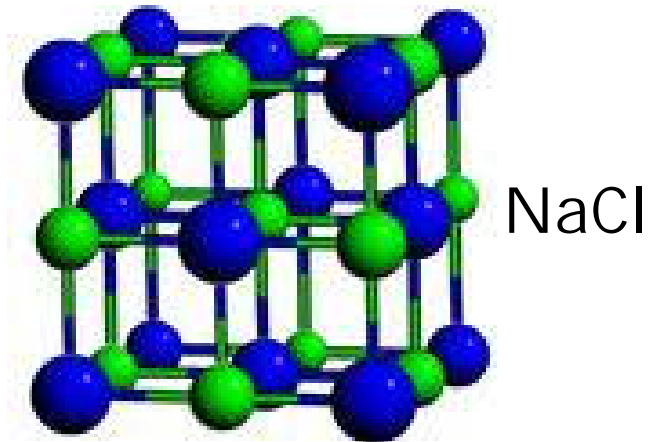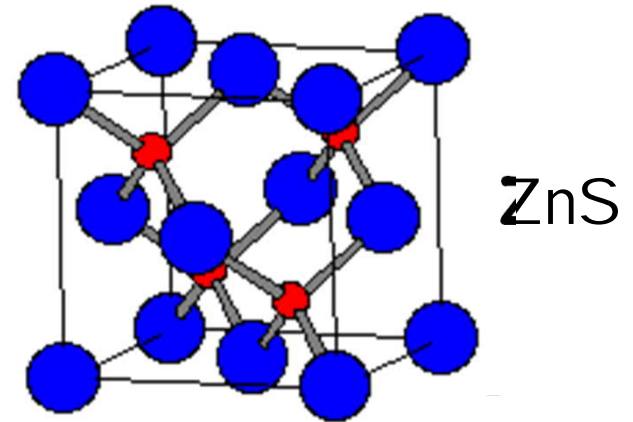$0.414 < r_C/r_A < 0.732$ CN = 6
$0.732 < r_C/r_A < 1.00$ CN = 8
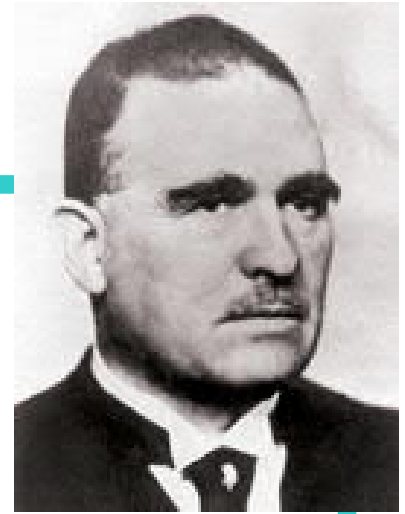$r_C/r_A > 1.00$ CN = 12

NaCl

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


CsCl
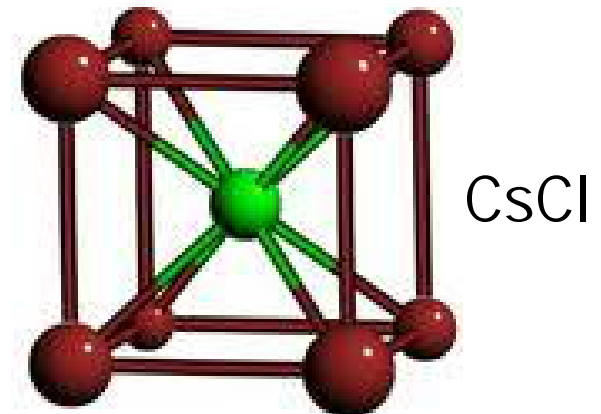
Victor Moritz Goldschmidt (1888-1947)

# Another approach:
TOLERANCE FACTOR (t)

- **1926 Goldschmidt**

  V.M. Goldschmidt , "Geochemische Vertailungsgesetze 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)**
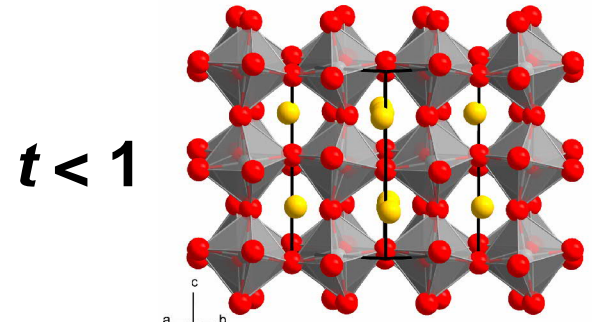
Tolerance factor for ABO_3 perovskite

$$t = \frac{(r_A + r_O)}{\sqrt{2}\,(r_B + r_O)}$$
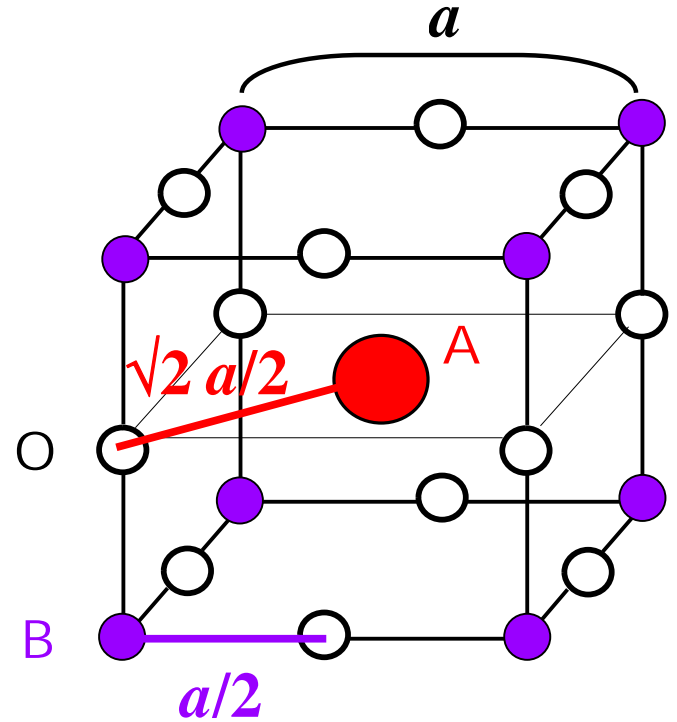
$t = 1$:   ideal matching   (0.80 < t < 1.05 possible)

$t < 1$:   A is too small $\rightarrow$ changes in oxygen position

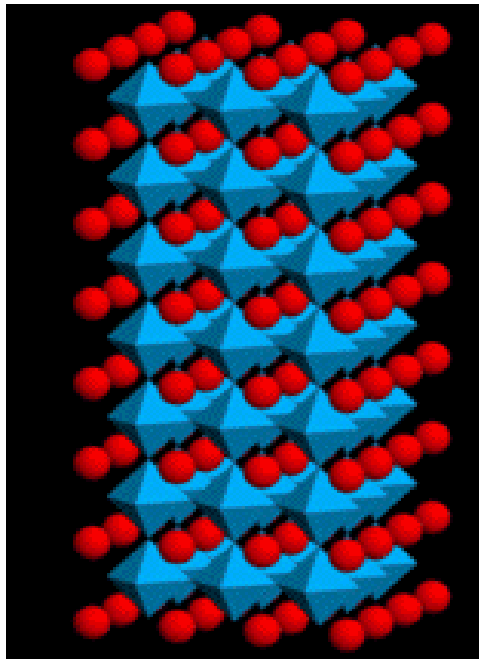$t > 1$:   B is too small $\rightarrow$ B is reduced $\rightarrow$ oxygen vacancies
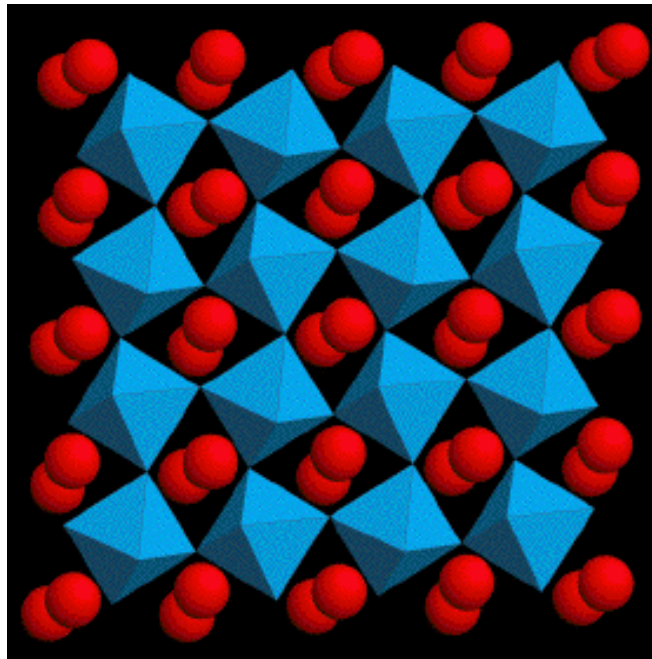

$t = 1$

$t < 1$
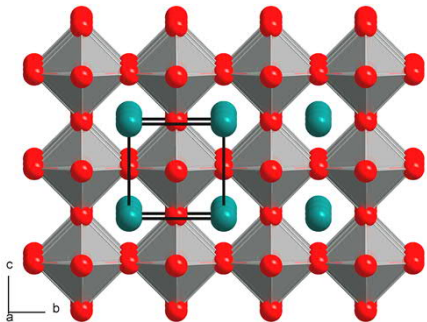
$$t = \frac{(r_A + r_O)}{\sqrt{2}\ (r_B + r_O)}$$

$t = 1$

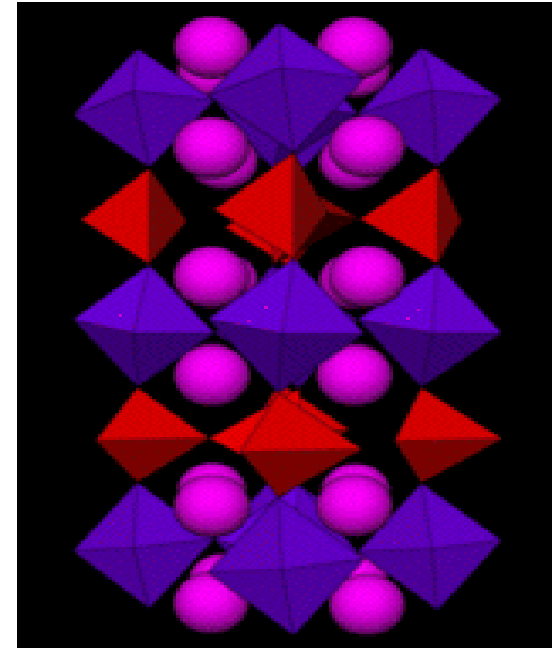

IDEAL

$t < 1$

Changes in atomic positions

$t > 1$

Oxygen deficiency

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

(1) **Interstitial oxygen atoms**

   - **$La_2CuO_{4+\delta}$**

(2) **Cation vacancies**

   -   **$La_{1-x}Mn_{1-x}O_3$**

(3) **Oxygen vacancies**

   -   **$YBa_2Cu_3O_{7-\delta}$**

(4) **Interstitial cations**

   -   **$Zn_{1+x}O$**

Cation interstial

Anion vacancy

Cation interstial

Added AB

Anion interstial

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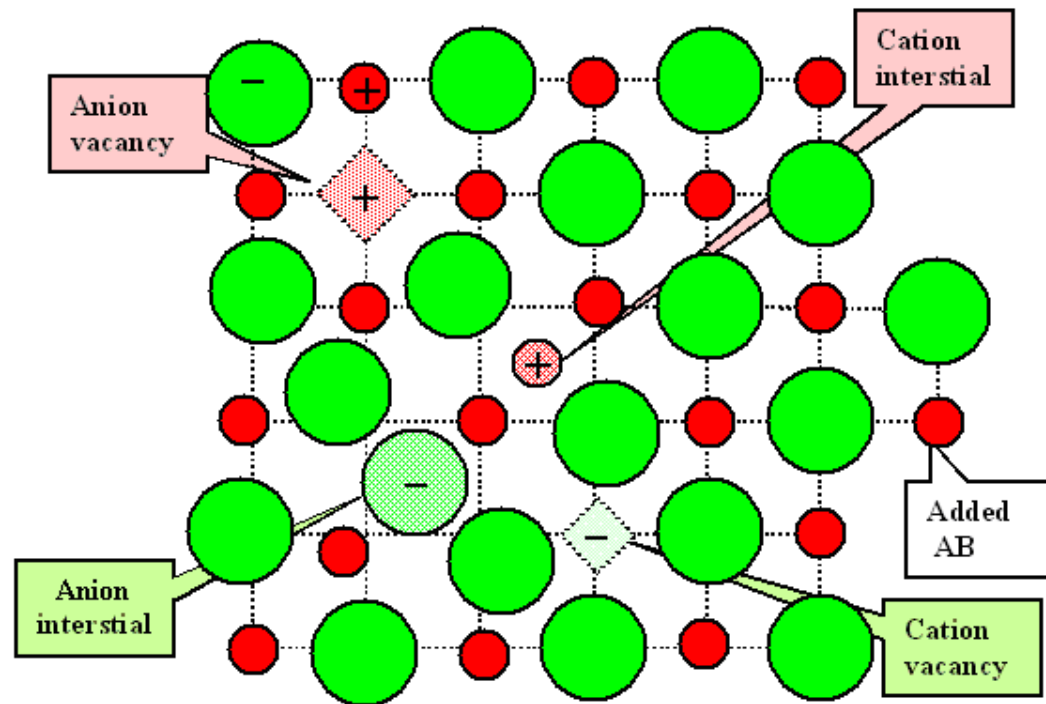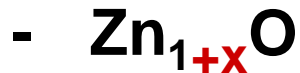
YBa$_2$Cu$_3$O$_{7-\delta}$ (or Ba$_2$YCu(1)Cu(2)$_2$O$_{7-\delta}$ to more properly reflect the structure) is a notorious example of the huge impact of oxygen (non)stoichiometry

Ba$_2$YCuCu$_2$O$_{7-\delta}$

High- T_c
Superconductor

YBa$_2$Cu$_3$O$_{7-\delta}$

$7-\delta$ ~6.45
~6.58
~6.68
~6.78
~6.85
~6.90

Resistivity (a.u.)

Temperature (K)
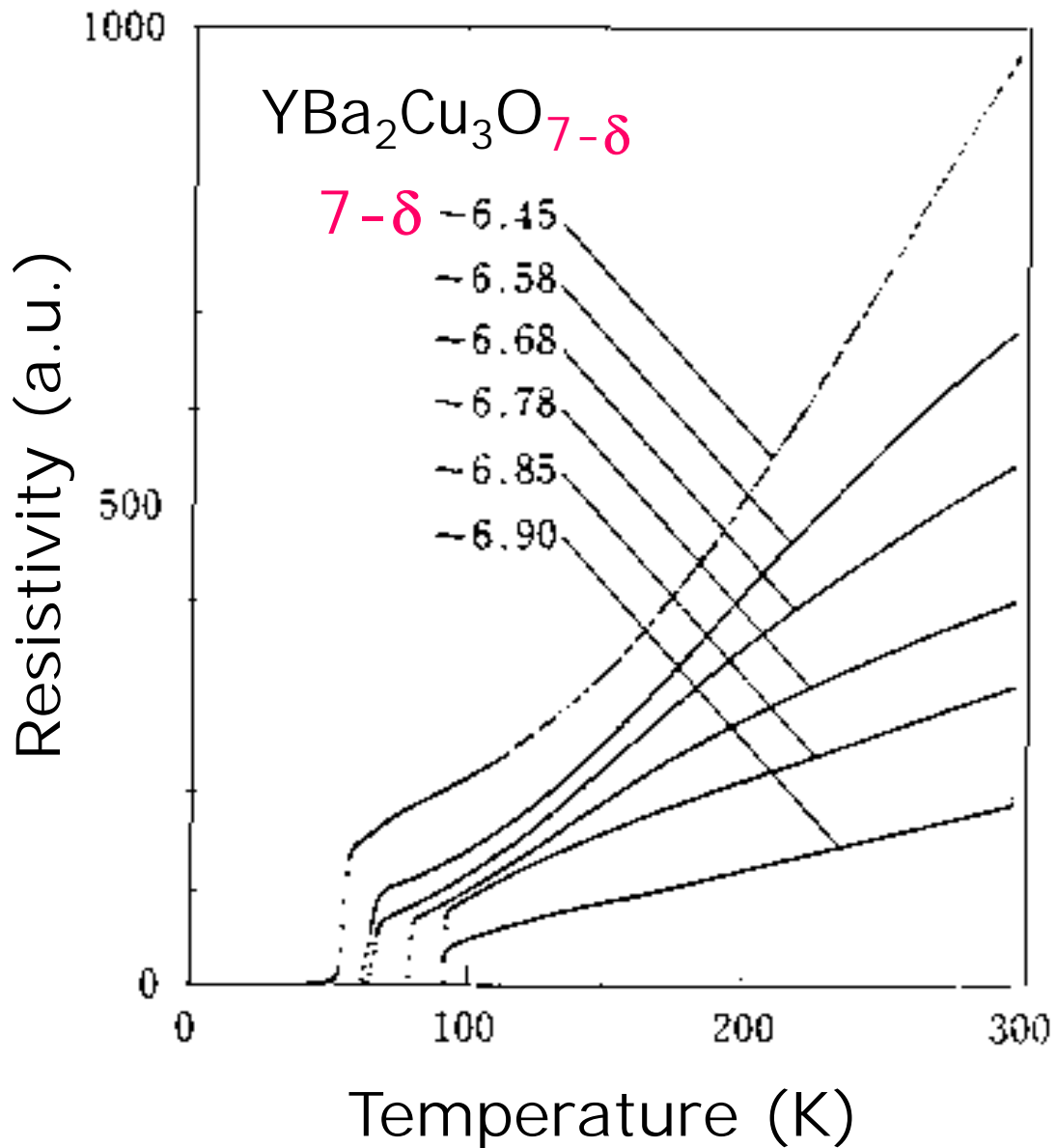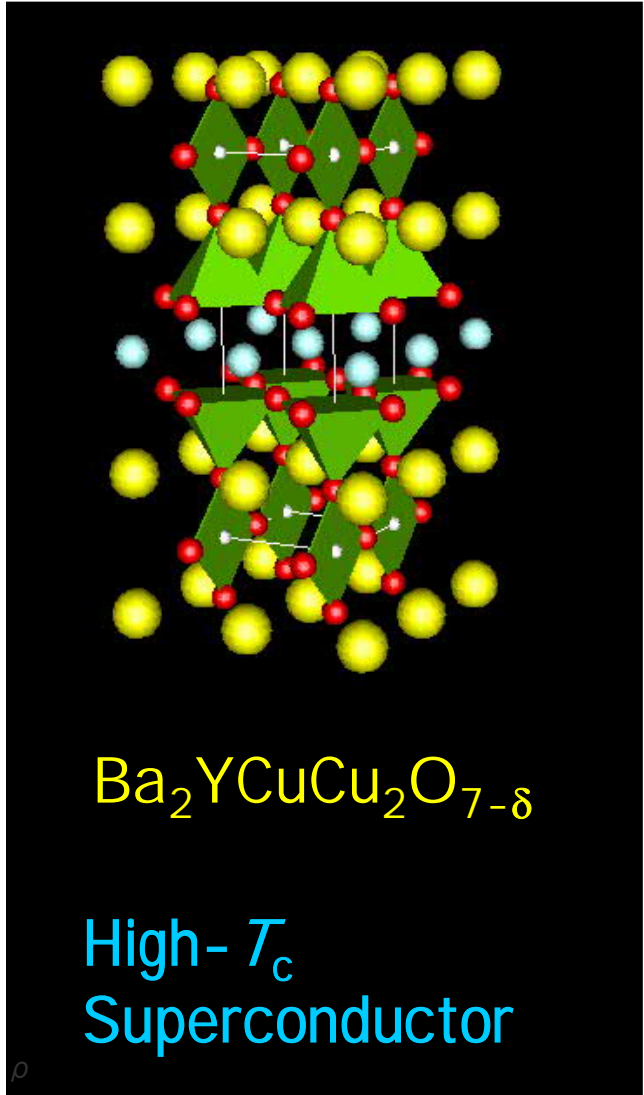
Phase Diagram of High-T$_c$ Superconductors
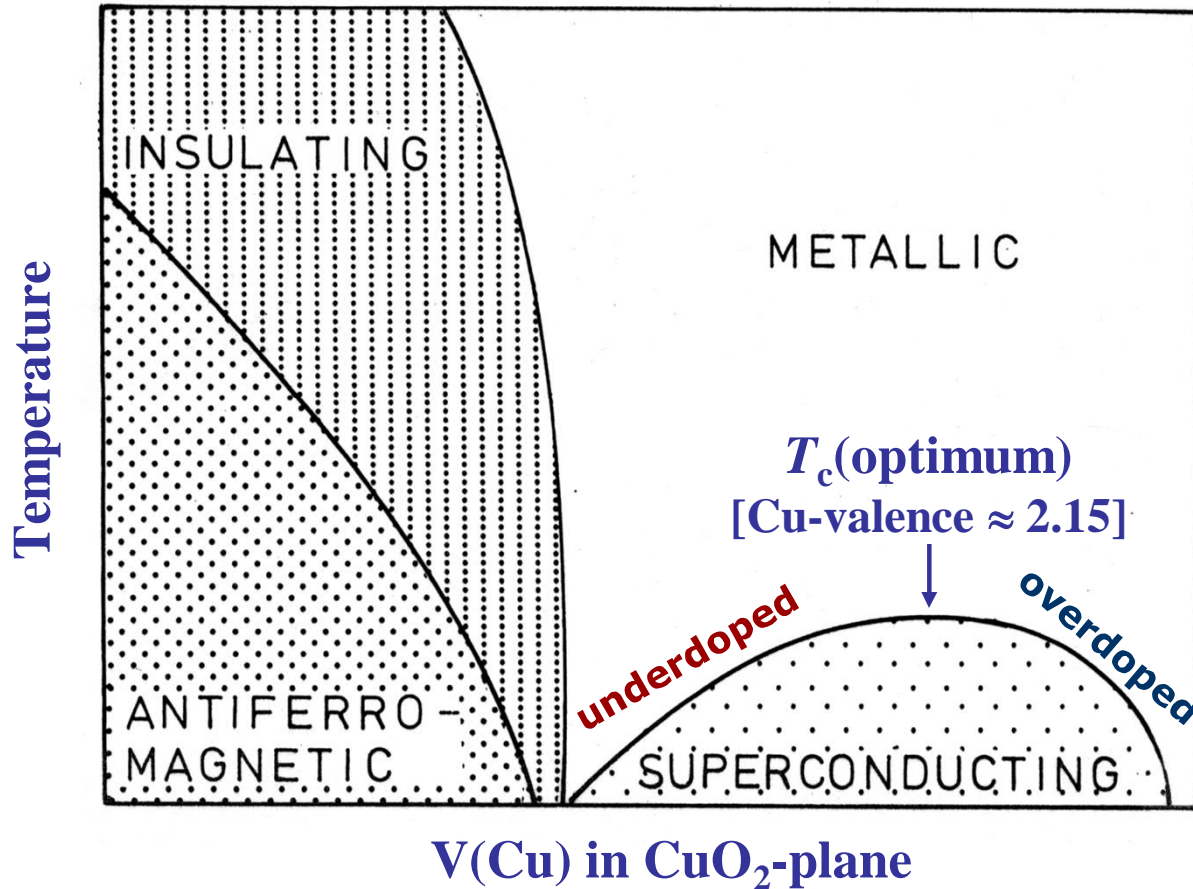
Oxygen content in YBa$_2$Cu$_3$O$_{7-\delta}$ controls the valence state of copper, and thereby the superconductivity (Tc value)

Illustration how the $YBa_2Cu_3O_{7-\delta}$ structure is derived from the perovskite structure through cation ordering and ordered oxygen vacancies

A-site ordered & oxygen-vacancy ordered TRIPLE PEROVSKITE $A'_2A''B_3O_{8\ (=\ 9-1)}$

$Ba_2YCu(1)Cu(2)_2O_{7\ (=\ 9-2)}$

Cu(1)O chain

$Cu(2)O_2$ planes

$Ba_2YCu(1)Cu(2)_2O_7$