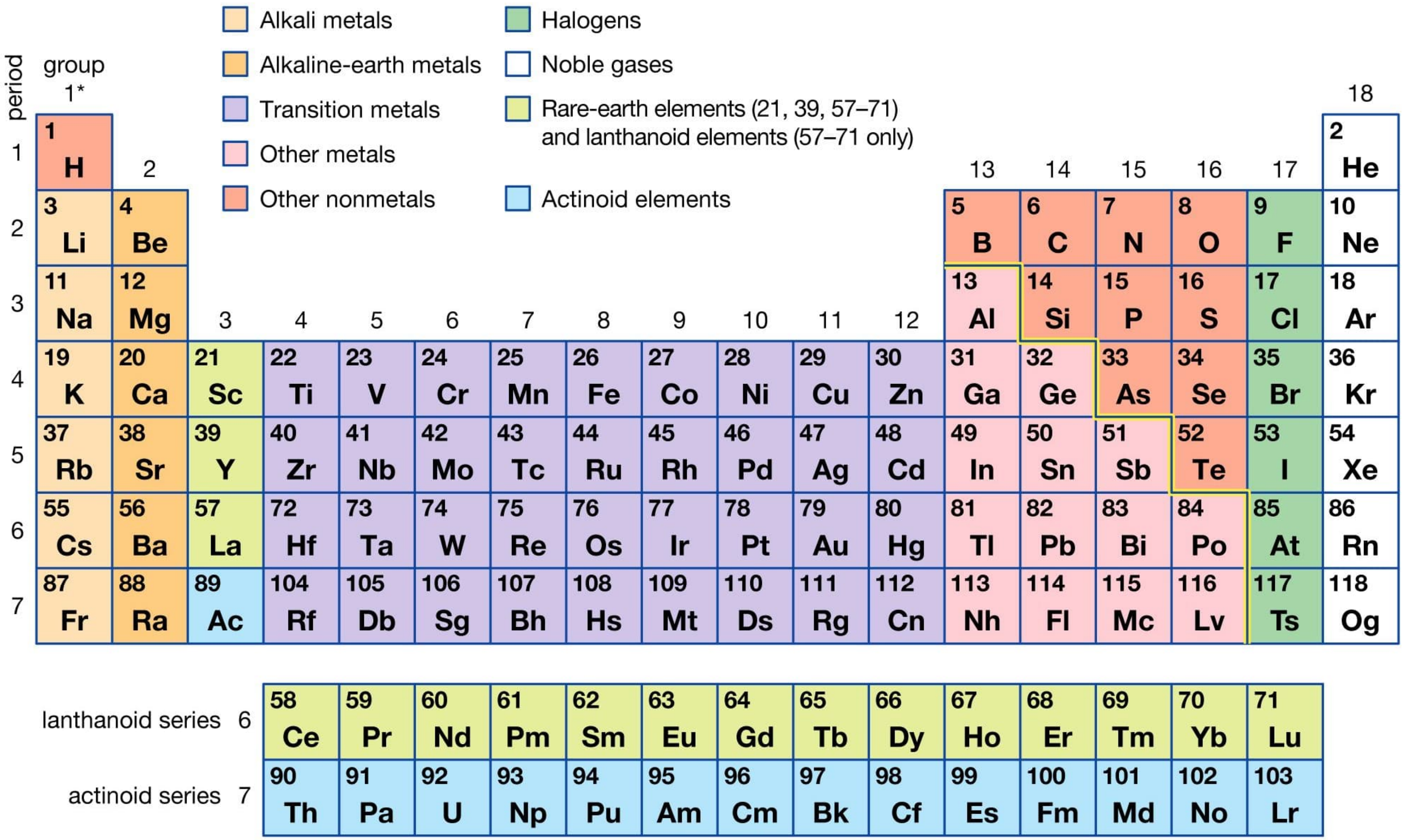
SCHEDULE

	Date		Topic
1.	Wed	28.02.	Lec-1: Introduction
2.	Mon	04.03.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Mon	04.03.	EXERCISE 1
4.	Wed	06.03.	Lec-3: Crystal Chemistry & BVS
5.	Fri	08.03.	Lec-4: Symmetry & Point Groups
6.	Mon	11.03.	EXERCISE 2
7.	Wed	20.03.	Lec-5: Crystallography & Space Groups (Linda)
8.	Fri	22.03.	Lec-6: XRD & Reciprocal lattice (Linda)
9.	Mon	25.03.	EXERCISE 3 (Linda)
10.	Thu	04.04.	Lec-7: Rietveld (Linda)
11.	Fri	05.04.	EXERCISE 4: Rietveld (Linda)
	Mon	08.04.	EXERCISE 4: Rietveld (Linda)
12.	Thu	11.04.	Lec-8: ND & GI-XRD
13.	Fri	12.04.	Lec-9: XRR (Topias)
14.	Mon	15.04.	EXERCISE 5: XRR (Topias)
	Wed	17.04.	EXERCISE 5: XRR (Topias)
15.	Mon	22.04.	Lec-10: Synchrotron radiation & XAS & EXAFS
16.	Wed	24.04.	Mössbauer (to 25.10)
17.	Fri	26.04.	EXERCISE 6
18.	Mon	29.04.	Seminars:
19.	Fri	03.05.	Seminars:
20.	Mon	06.05.	ADDITIONAL DISCUSSION/QUESTION POSSIBILITY

INSTRUCTIONS for SEMINAR PRESENTATION

- Topics: **XPS, IR, Raman, HRTEM, ED, EELS, SEM, AFM**
- Seminar presentation is mandatory
- Given individually or in a group of two students
- Evaluated in the scale: 10 ~ 20 points
- Presentation is given in English, and the slides will be put up in MyCourses afterwards
- Presentation: 25+5 minutes
- Rough content of the presentation:
    - principle of the technique(s)
    - type of information gained
    - interpretation of the measured data
    - pros & cons
    - **two to four research examples**
      (you will be given some relevant research papers for an example)

Periodic table of the elements



Alkali metals
Alkaline-earth metals
Transition metals
Other metals
Other nonmetals
Halogens
Noble gases
Rare-earth elements (21, 39, 57–71) and lanthanoid elements (57–71 only)
Actinoid elements

period	group 1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H**																	2 **He**
2	3 **Li**	4 **Be**											5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**
3	11 **Na**	12 **Mg**											13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	18 **Ar**
4	19 **K**	20 **Ca**	21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**
5	37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**
6	55 **Cs**	56 **Ba**	57 **La**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**
7	87 **Fr**	88 **Ra**	89 **Ac**	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Ds**	111 **Rg**	112 **Cn**	113 **Nh**	114 **Fl**	115 **Mc**	116 **Lv**	117 **Ts**	118 **Og**

lanthanoid series 6	58 **Ce**	59 **Pr**	60 **Nd**	61 **Pm**	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**	71 **Lu**
actinoid series 7	90 **Th**	91 **Pa**	92 **U**	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**	103 **Lr**

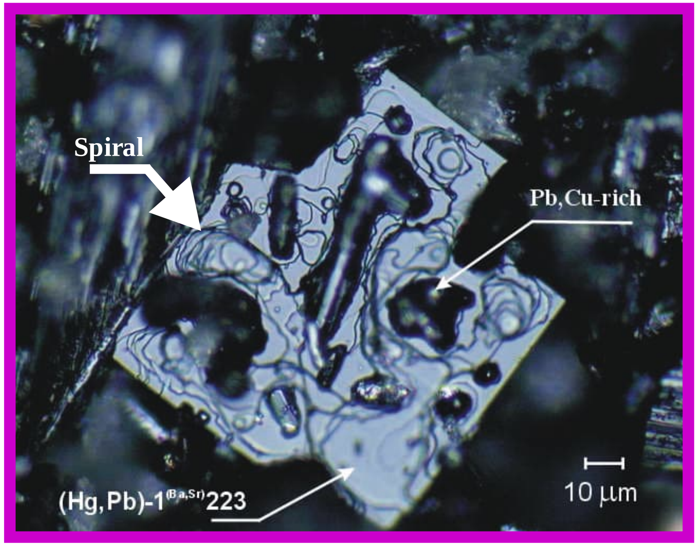
*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

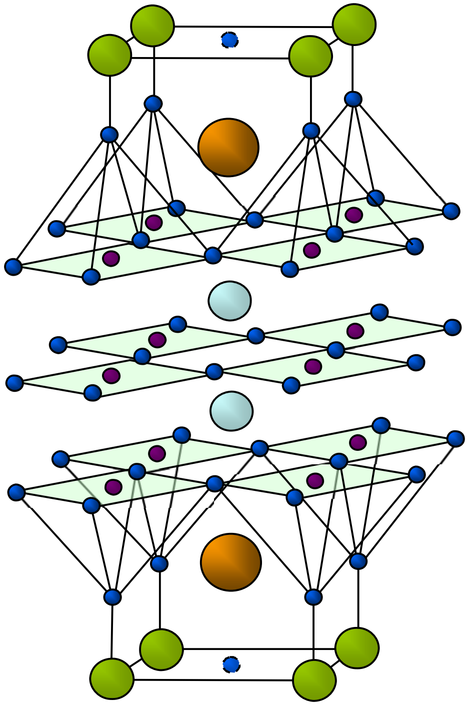
LECTURE 2: CRYSTAL CHEMISTRY - 1

- **Unit-cell composition:**
  atomic coordinates, multiplicities & occupancies
- **Ionic radius:**
  dependence on V (valence) & CN (coordination number)
- **Tolerance factor concept:**
  prediction of stability, distortions & redox behaviour

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





WHAT WE LIKE TO KNOW ABOUT THE CRYSTAL STRUCTURE

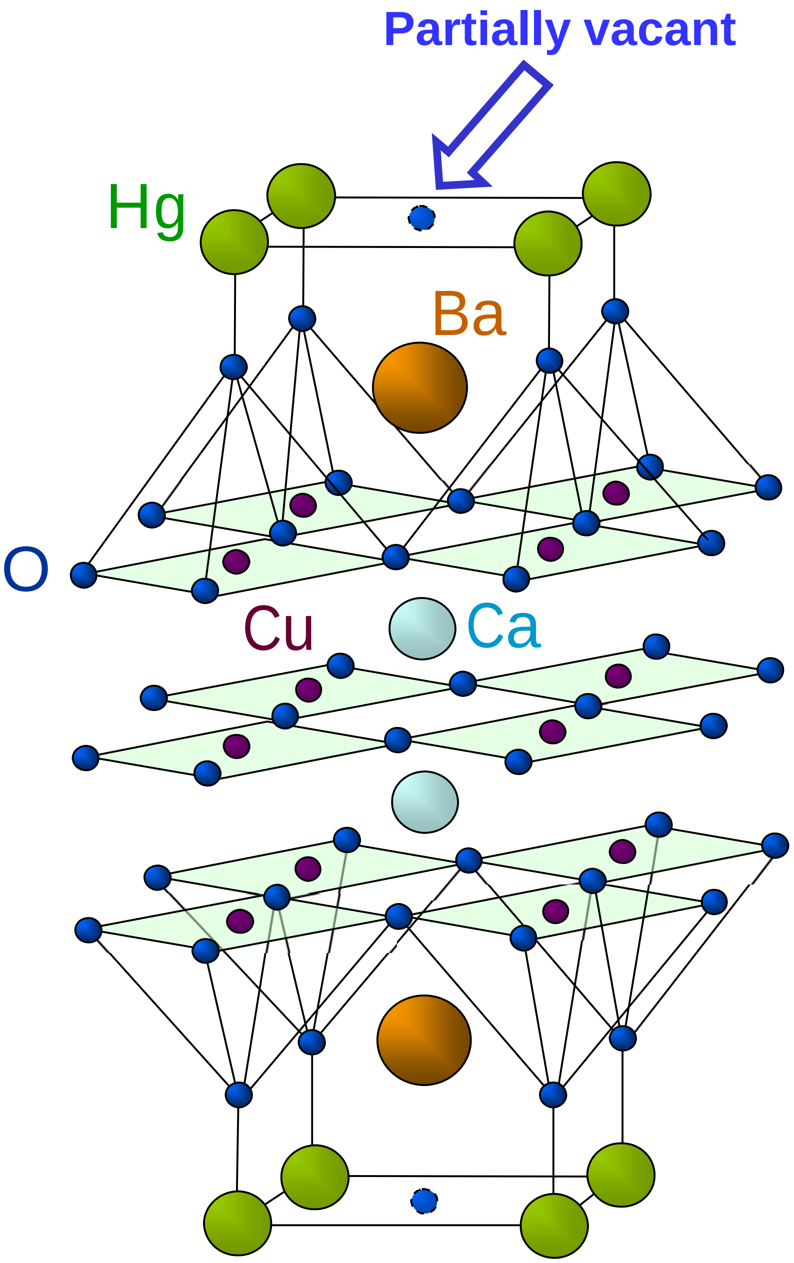
CRYSTALLOGRAPHY

- **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.**

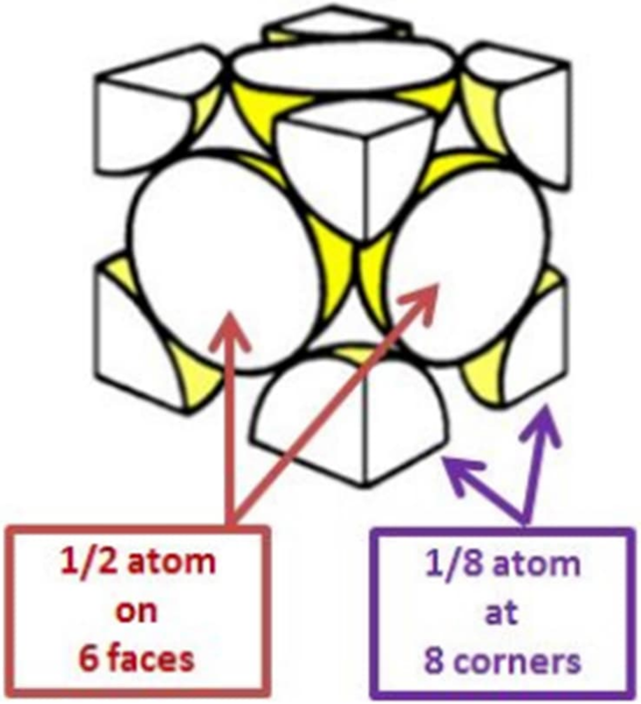
This lecture is of crystal chemistry !



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**



How the atoms are located in the structure depends on:

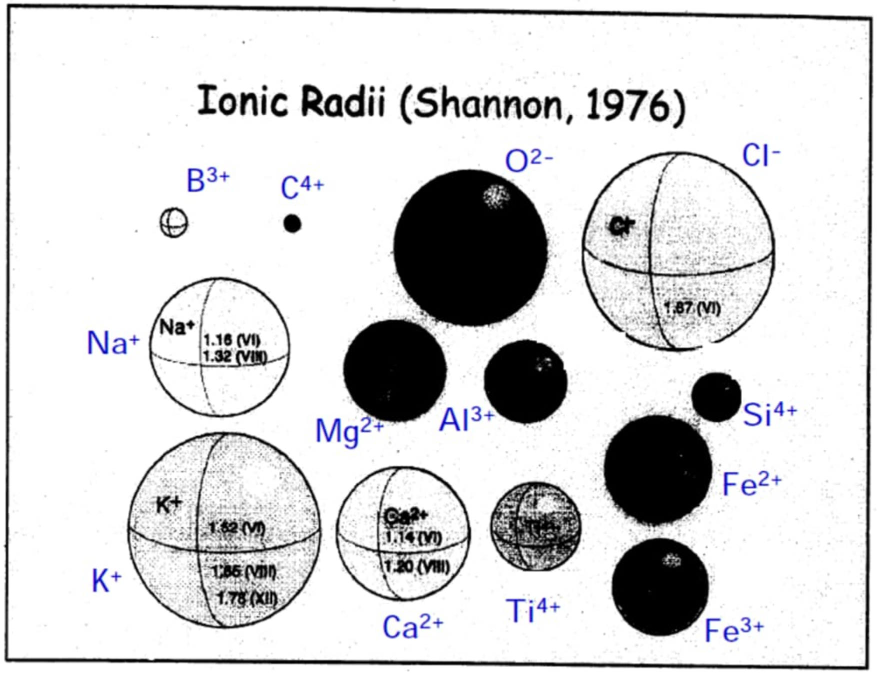
- **relative sizes of atoms/ions**
- **charges (oxidation states) of ions**
- **nature of chemical bonds (involvement of different orbitals)**

NEXT WE BRIEFLY RECALL & DISCUSS:

- Ion size (ionic radius) and how it affects the structure

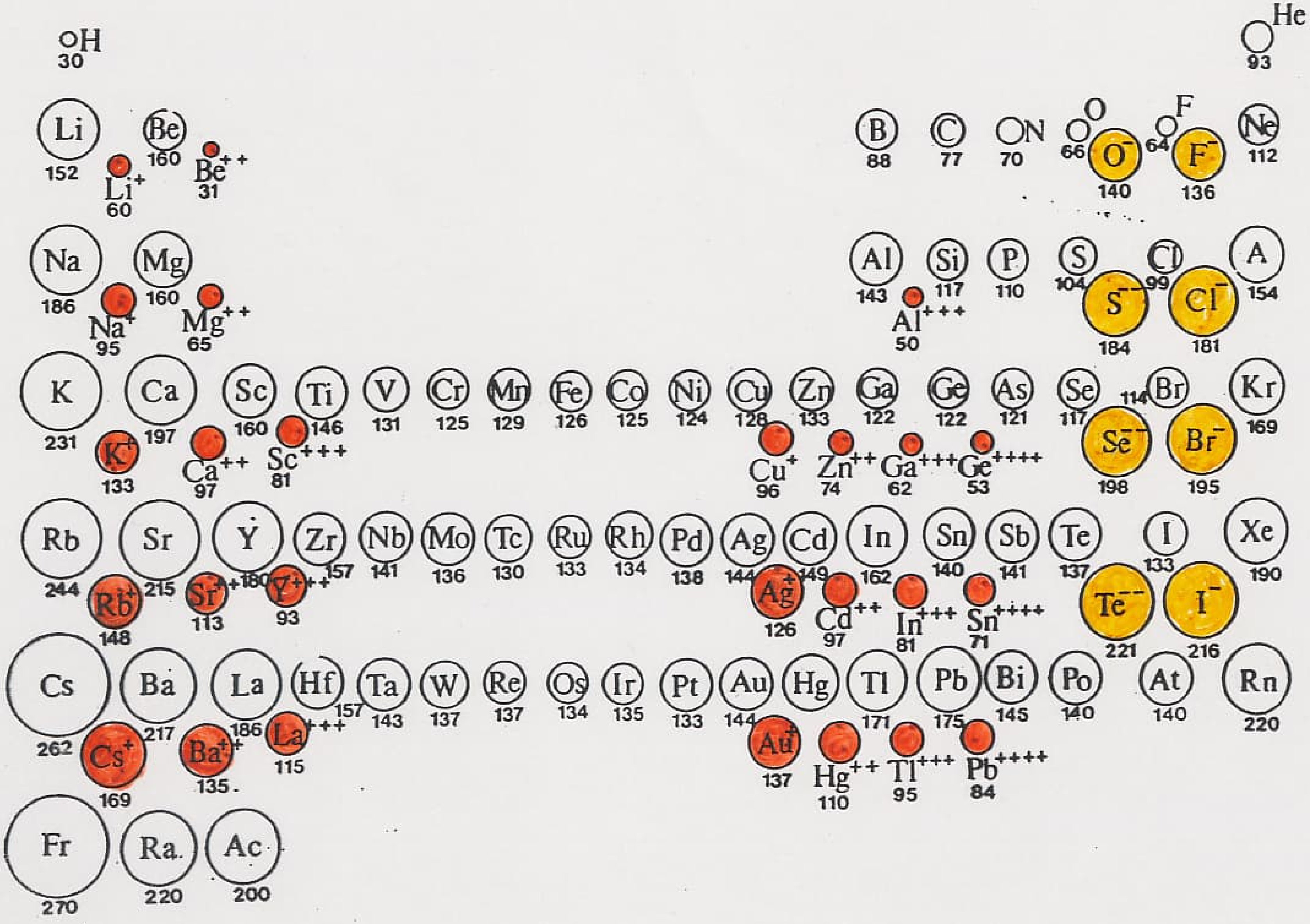
IONIC RADIUS

- **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 - 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
Be 160
Li$^+$ 60
Be^{++} 31
B 88
C 77
N 70
O 66
O$^-$ 140
F 64
F$^-$ 136
Ne 112
Na 186
Mg 160
Na$^+$ 95
Mg^{++} 65
Al 143
Si 117
P 110
S 104
Cl 99
A 154
Al^{+++} 50
S^{--} 184
Cl$^-$ 181
K 231
Ca 197
Sc 160
Ti 146
V 131
Cr 125
Mn 129
Fe 126
Co 125
Ni 124
Cu 128
Zn 133
Ga 122
Ge 122
As 121
Se 117
Br 114
Kr 169
K$^+$ 133
Ca^{++} 97
Sc^{+++} 81
Cu$^+$ 96
Zn^{++} 74
Ga^{+++} 62
Ge^{++++} 53
Se^{--} 198
Br$^-$ 195
Rb 244
Sr 215
Y 180
Zr 157
Nb 141
Mo 136
Tc 130
Ru 133
Rh 134
Pd 138
Ag 144
Cd 149
In 162
Sn 140
Sb 141
Te 137
I 133
Xe 190
Rb$^+$ 148
Sr^{++} 113
Y^{+++} 93
Ag$^+$ 126
Cd^{++} 97
In^{+++} 81
Sn^{++++} 71
Te^{--} 221
I$^-$ 216
Cs 262
Ba 217
La 186
Hf 157
Ta 143
W 137
Re 137
Os 134
Ir 135
Pt 133
Au 144
Hg
Tl 171
Pb 175
Bi 145
Po 140
At 140
Rn 220
Cs$^+$ 169
Ba^{++} 135
La^{+++} 115
Au$^+$ 137
Hg^{++} 110
Tl^{+++} 95
Pb^{++++} 84
Fr 270
Ra 220
Ac 200

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

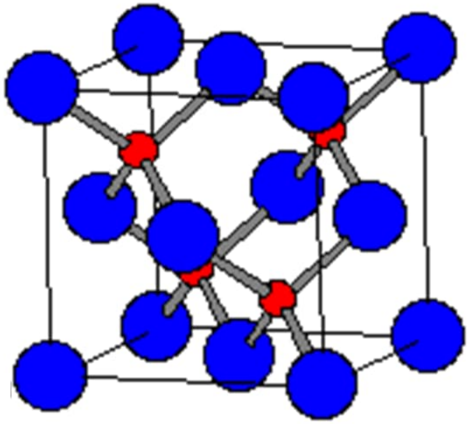
Pauling's Rule for binary AB compounds

$r_C / r_A < 0.155$	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

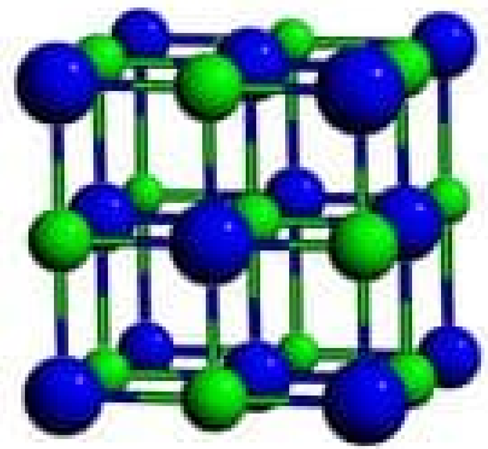
QUESTION: what are the coordination numbers (CN) in ZnS, NaCl and CsCl ?

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

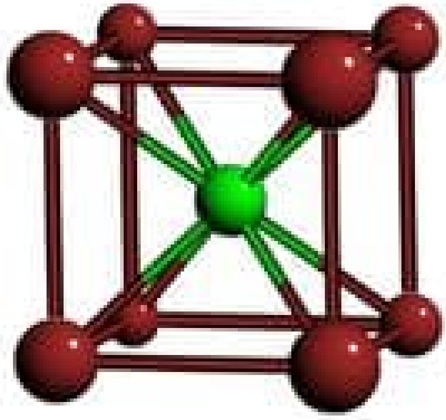
Prof P.D. Battle



ZnS



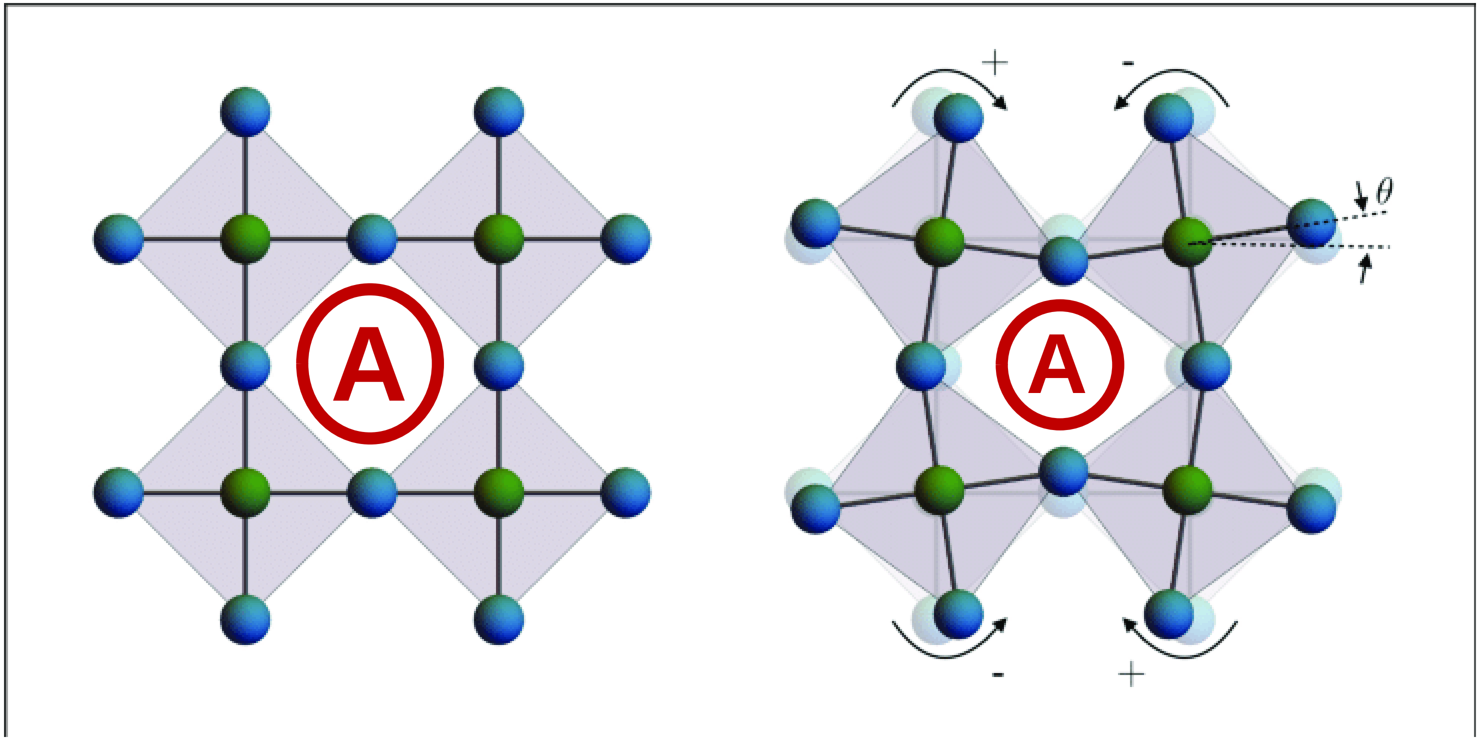
NaCl



CsCl

COMMON EXAMPLE OF DISTORTIONS in ABO_3

- For the better A/B ionic radius match, oxygen atoms often move from their ideal positions such that the **BO_6 octahedra** e.g. get **tilted**
- There are many other ways for oxygen atoms to get displaced
- These **distortions affect many properties** (magnetic, ferroelectric, etc.)



Victor Moritz Goldschmidt
(1888-1947)

Another approach:
TOLERANCE FACTOR (t)

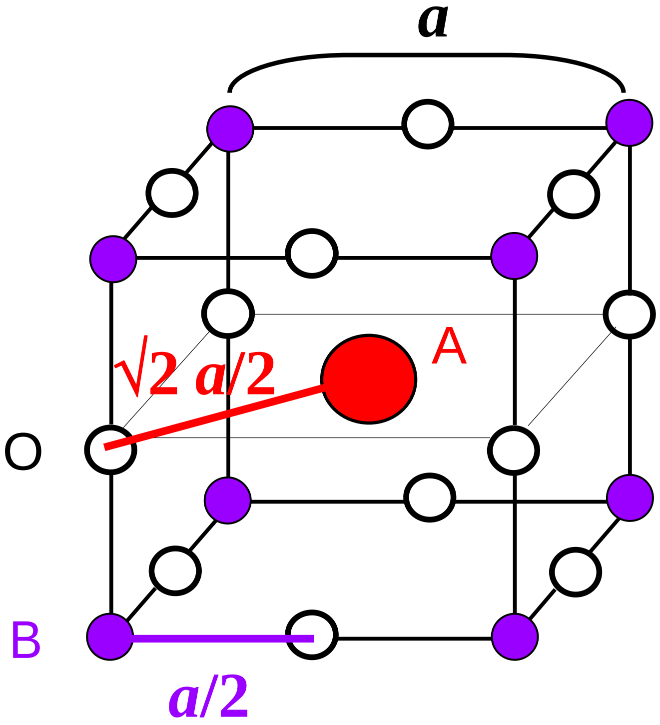
- **1926 Goldschmidt**

  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

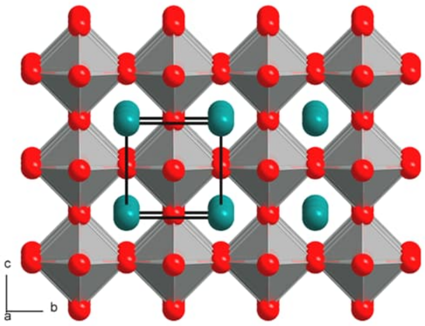
$$t = \frac{(r_A + r_O)}{\sqrt{2}\,(r_B + r_O)}$$



$t = 1$: ideal matching (0.80 < t < 1.05 possible)

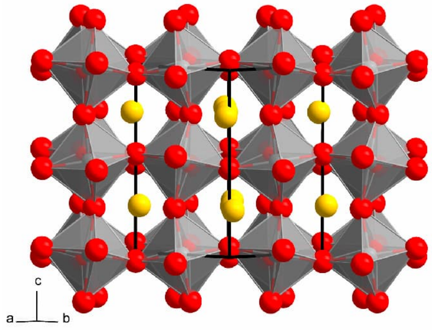
$t < 1$: A is too small → changes in oxygen position

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



$t = 1$

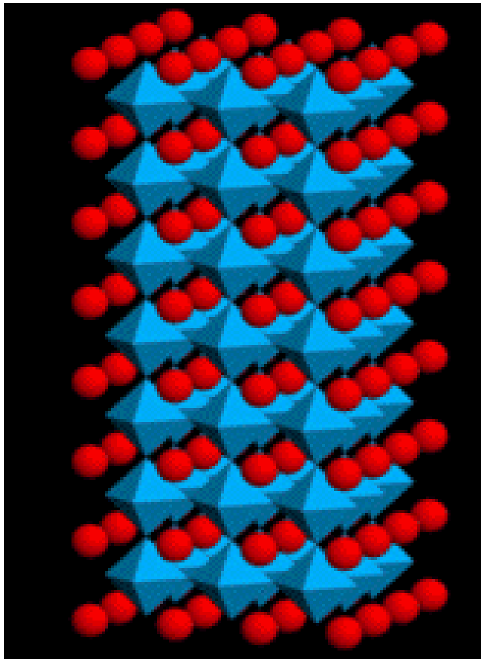
$t < 1$



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

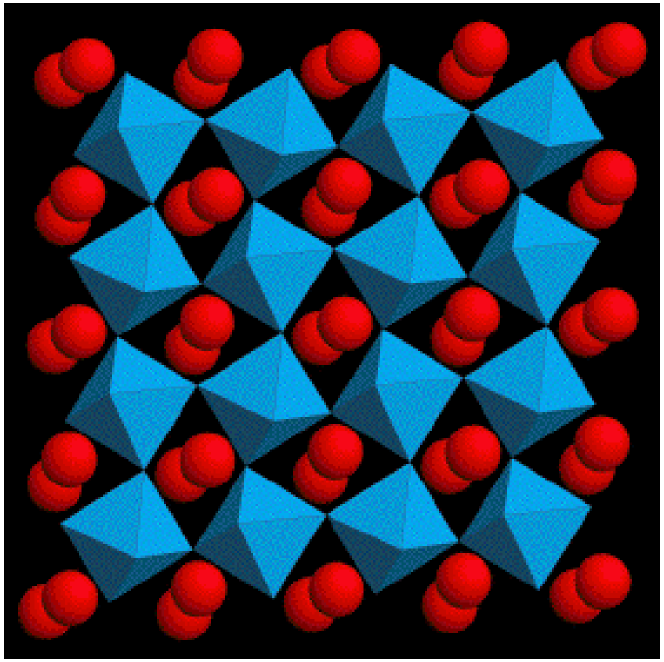
NOTE:
Oxygen vacancies can be random or ordered (as below)

$t = 1$



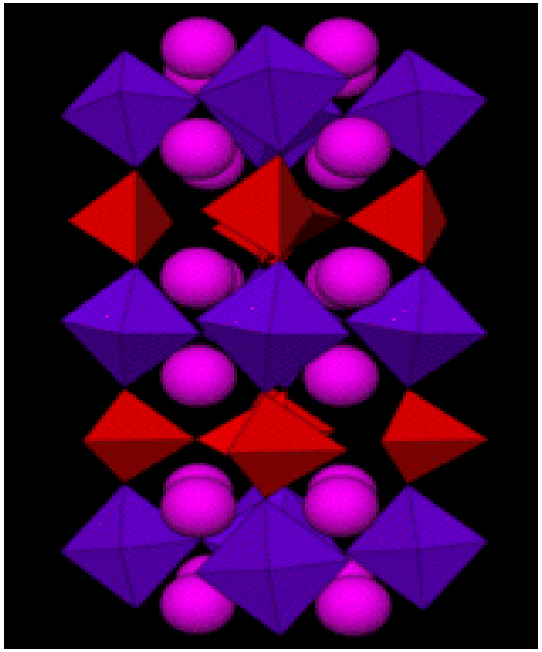
IDEAL

$t < 1$



Changes in atomic positions

$t > 1$



Oxygen deficiency

HYPOTHETICAL EXAMPLE: Ferromagnetic (Ba/Sr/Ca)BO_3

- Ferromagnetic transition temperature (T_C) highest when strong B-O-B interactions: short bond length and non-tilted bonding
- LEFT: with the largest **A = Ba** cation, ideal perovskite structure, **B-O-B** bond angle 180 °C, but **B-O** bond length long → **T_C = 320 K**
- MIDDLE: with the intermediate-sized **A = Sr** cation, ideal perovskite structure, **B-O-B** bond angle 180 °C, and **B-O** bond length shorter → **T_C = 400 K**
- RIGHT: with the smallest **A = Ca** cation, tilted perovskite structure, **B-O** bond length short, but the **B-O-B** bond angle < 180 °C → **T_C = 370 K**