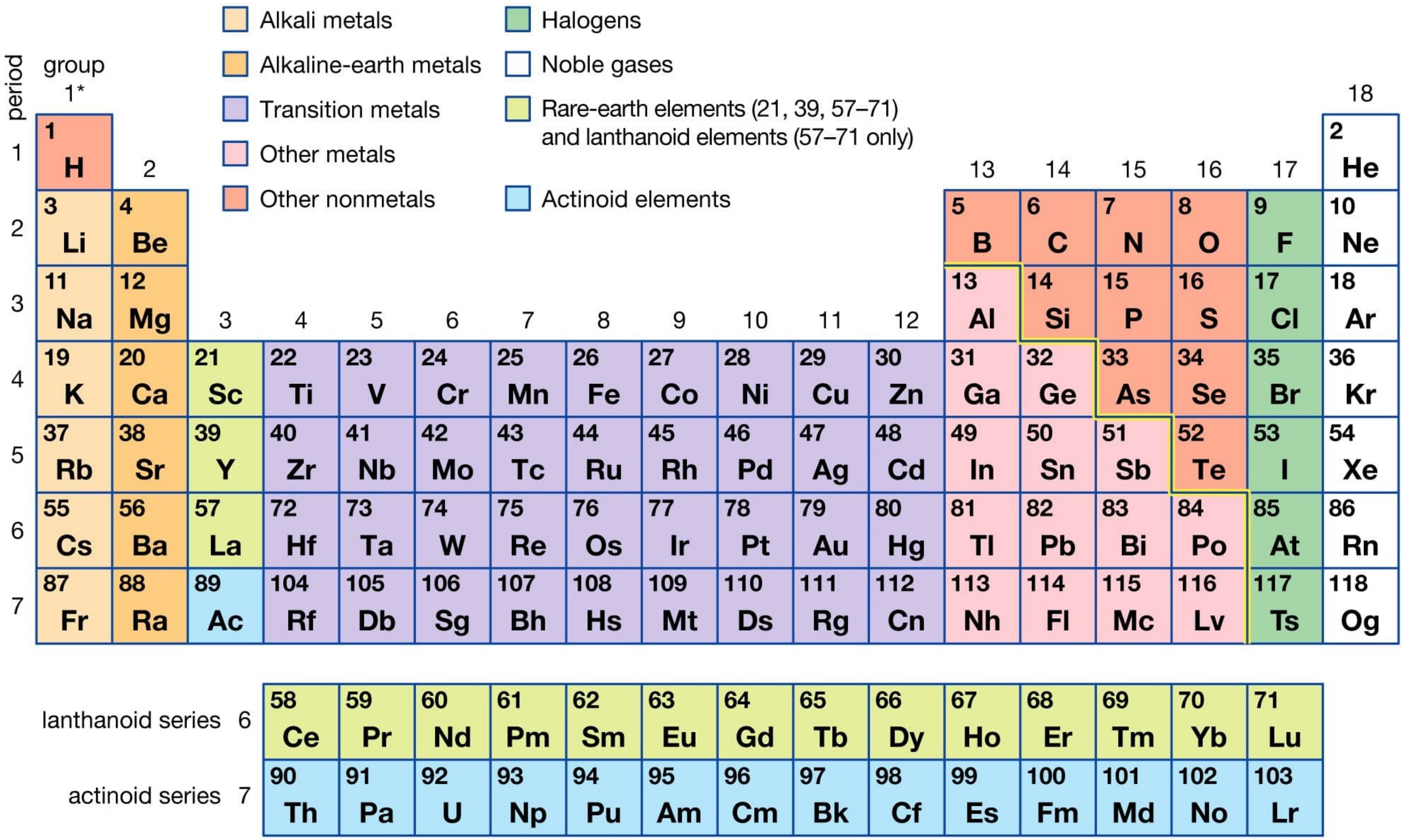
SCHEDULE

	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

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 3: CRYSTAL CHEMISTRY & BVS

- **Correlations between: Ionic radius (r), Coordination number (CN), Bond distance (d) & Valence state (V)**
- **Bond Valence Sum (BVS): quantitative measure for the correlation**
- **Pauling’s second rule was a ”simple-minded” but important first step for the BVS concept**
- **Also, recall what we discussed in the previous lecture on the Tolerance Parameter concept**

BOND & VALENCE

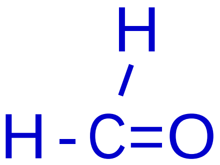
C-C 1.54 Å
C=C 1.33 Å
C≡C 1.20 Å

ORGANIC COMPOUNDS

- Bonds (mostly) have integer valence values: Single, Double or Triple
- Correlation between Bond order & Bond length: the higher the order, the shorter the bond
- Each atom in on organic molecule has a valence value that equals to the number of bonds it forms
- FOR EXAMPLE: formaldehyde HCHO

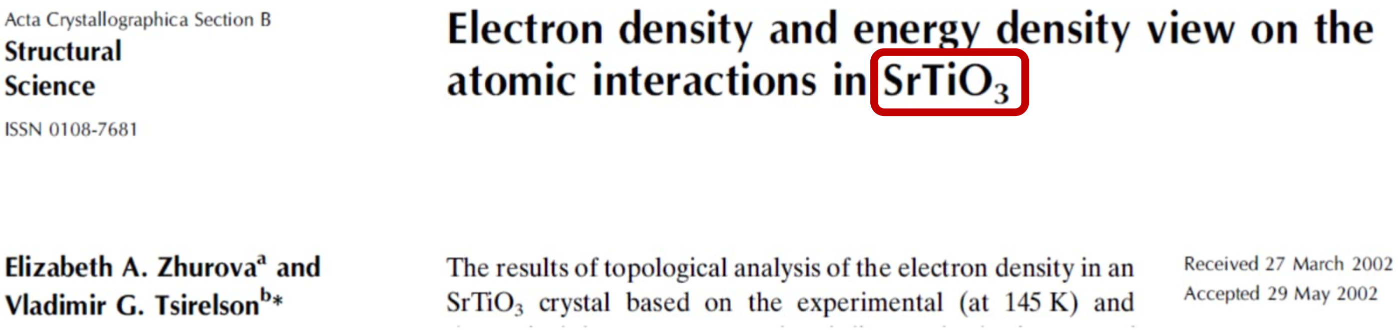
Bonds: 2 x C-H, 1 x C=O

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



INORGANIC COMPOUNDS

- Bonds do not adopt integer valence values only
- FOR EXAMPLE: Aluminum is trivalent in all its compounds but exists commonly in octahedral (or tetrahedral) coordination



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Electron density and energy density view on the atomic interactions in $SrTiO_3$

Elizabeth A. Zhurova[a] and Vladimir G. Tsirelson[b]*

The results of topological analysis of the electron density in an $SrTiO_3$ crystal based on the experimental (at 145 K) and

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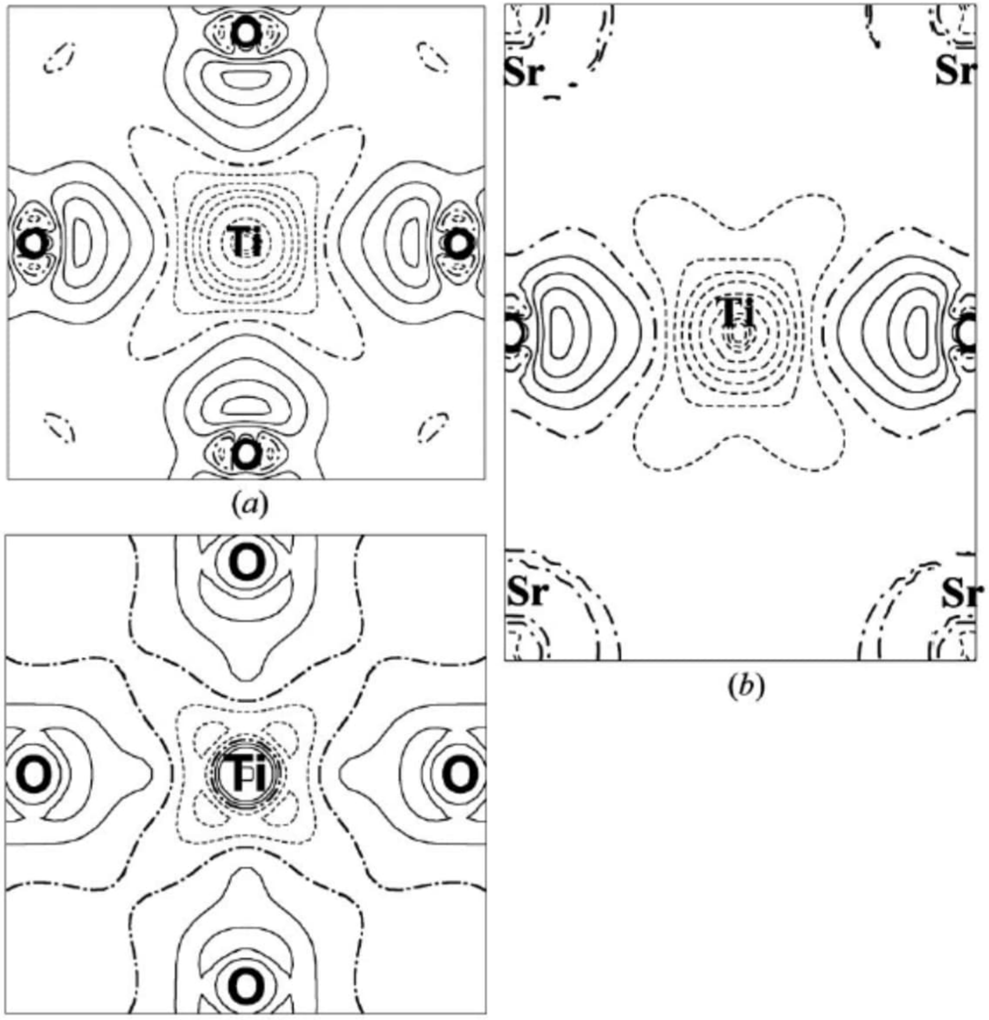
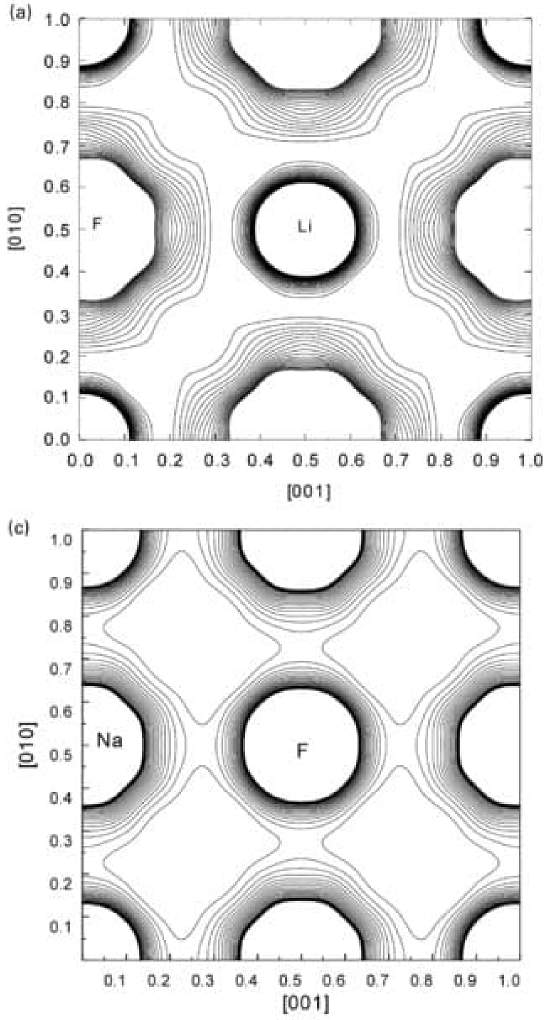


(*a*)

(*b*)

(*c*)



PAULING's SECOND RULE (Valence-Sum-Rule)

- **Valence sum of an atom is equal to the sum of bond valences (BVs) around it**
- **Valence sum of an atom is equal to its oxidation state (OS)**

EXAMPLE-1: Perovskite $CaTiO_3$

OS(Ti) = +4 & CN(Ti) = 6, hence BV(Ti-O) = 4/6 = 0.67

OS(Ca) = +2 & CN(Ca) = 12, hence BV(Ca-O) = 2/12 = 0.167

→ since OS(O) = -2 = - (2 x 0.67 + 4 x 0.167), CN(O) = 6

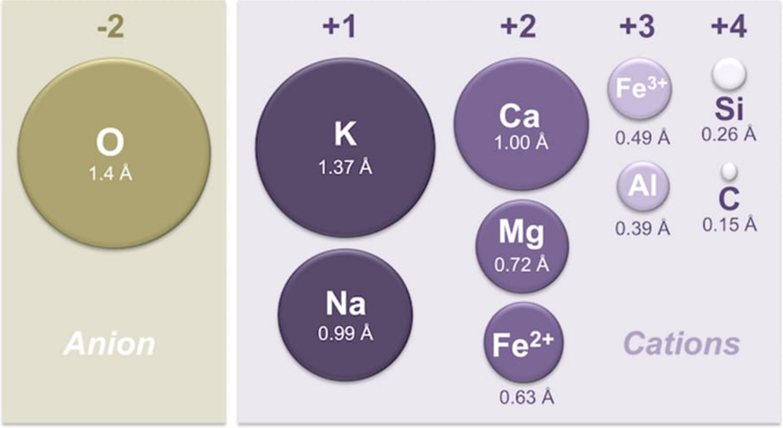
EXAMPLE-1: Rutile TiO_2

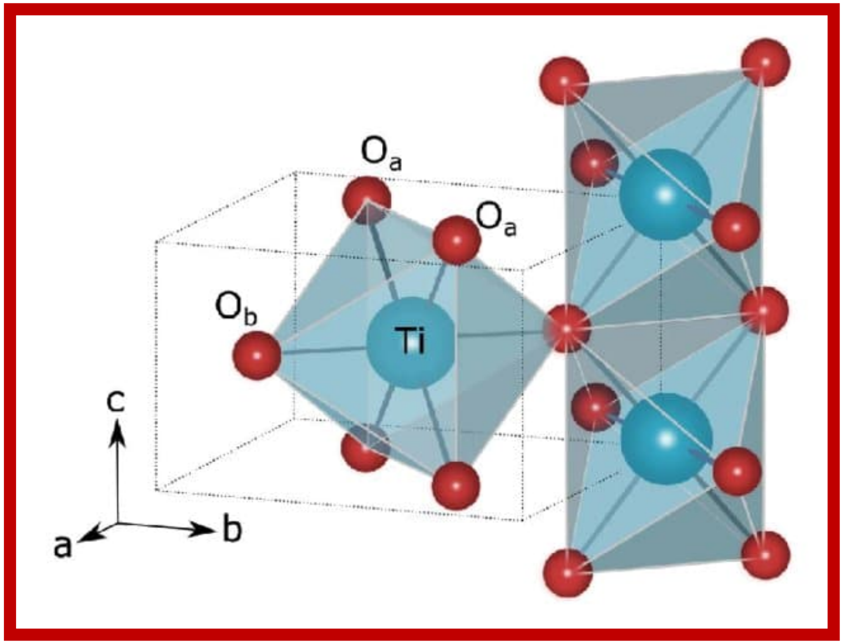
OS(Ti) = +4 & CN(Ti) = 6, hence BV(Ti-O) = 4/6 = 0.67

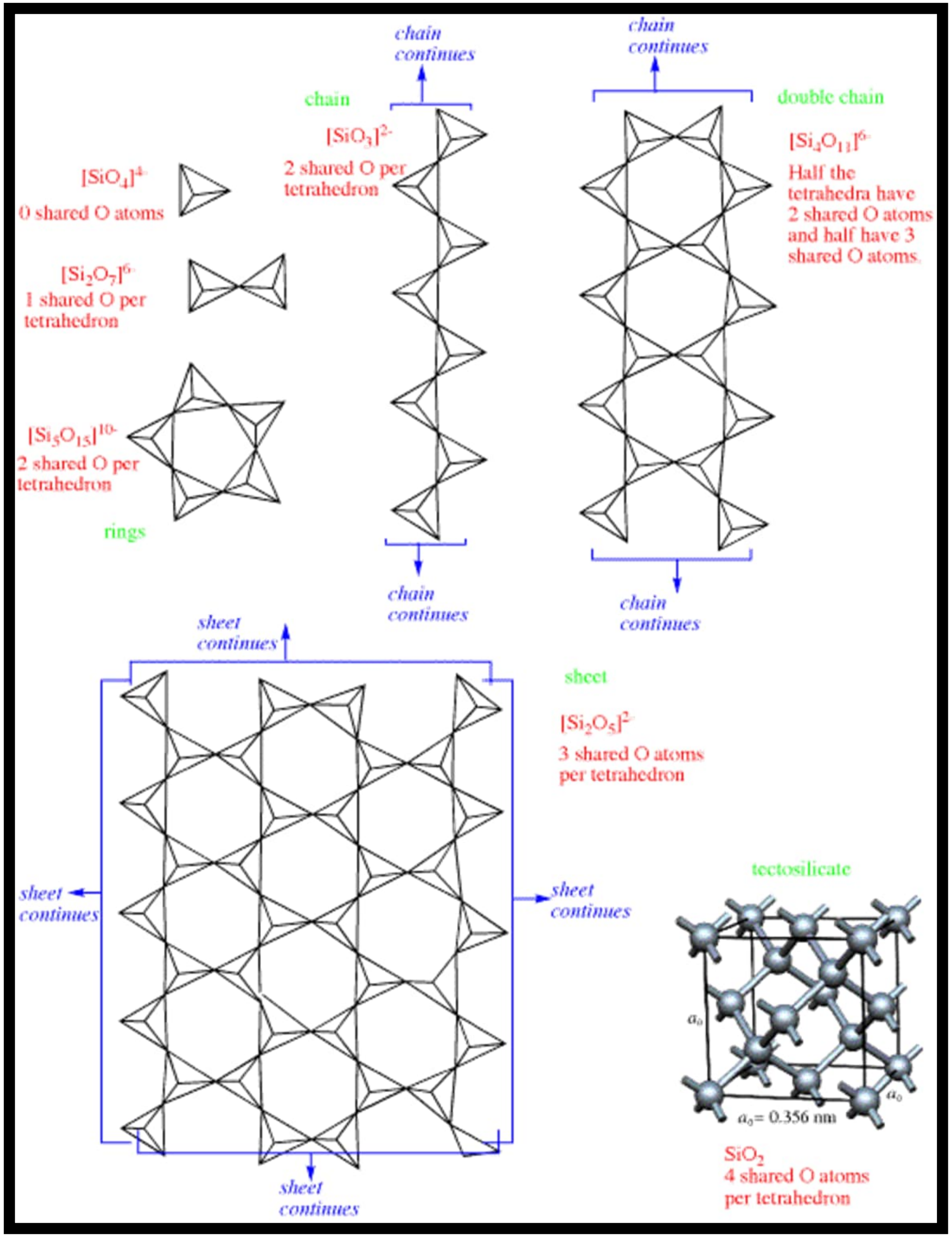
→ since OS(O) = -2 = - (3 x 0.67), CN(O) = 3

EXAMPLE-3: Silicate minerals consist of SiO_4 tetrahedra. Silicon has the oxidation state of +4, and CN = 4, hence each Si-O bond valence is 4/4 = 1. Since oxygen valence is -2, each oxygen can make only two bonds to Si atoms. Hence, in silicates the SiO_4 tetrahedra can only share corners (not e.g. edges)

- **NOTE: stability of crystals decrease when the polyhedra share edges**


-2
O
1.4 Å
Anion
+1
K
1.37 Å
Na
0.99 Å
+2
Ca
1.00 Å
Mg
0.72 Å
Fe^{2+}
0.63 Å
+3
Fe^{3+}
0.49 Å
Al
0.39 Å
+4
Si
0.26 Å
C
0.15 Å
Cations


O_a
O_a
O_b
Ti
c
a
b


$[SiO_4]^{4-}$
0 shared O atoms
$[Si_2O_7]^{6-}$
1 shared O per tetrahedron
$[Si_5O_{15}]^{10-}$
2 shared O per tetrahedron
rings
chain continues
chain
$[SiO_3]^{2-}$
2 shared O per tetrahedron
chain continues
chain continues
double chain
$[Si_4O_{11}]^{6-}$
Half the tetrahedra have 2 shared O atoms and half have 3 shared O atoms.
chain continues
sheet continues
sheet
$[Si_2O_5]^{2-}$
3 shared O atoms per tetrahedron
sheet continues
sheet continues
sheet continues
tectosilicate
a_0
a_0
a_0 = 0.356 nm
SiO_2
4 shared O atoms per tetrahedron

Linus Pauling (1901–1994)

- American chemist, biochemist and peace activist, graduated from **Oregon State University**
- One of the founders of quantum chemistry: contributions to chemical bonding, electronegativity, orbital hybridization, molecular biology, protein structure, X-ray crystallography
- **Nobel Prize in Chemistry in 1954, Nobel Peace Prize in 1962**

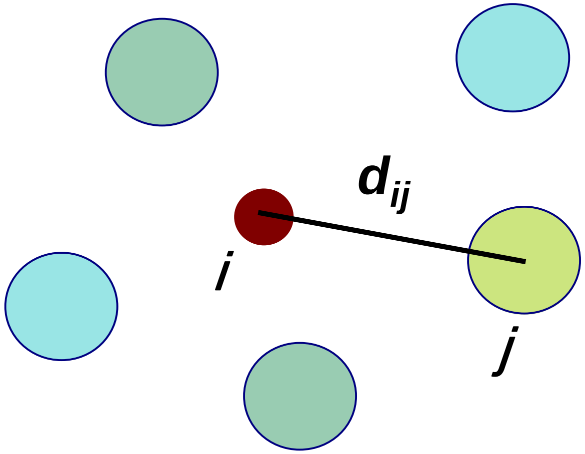
Bond-Valence-Sum (BVS) Calculation

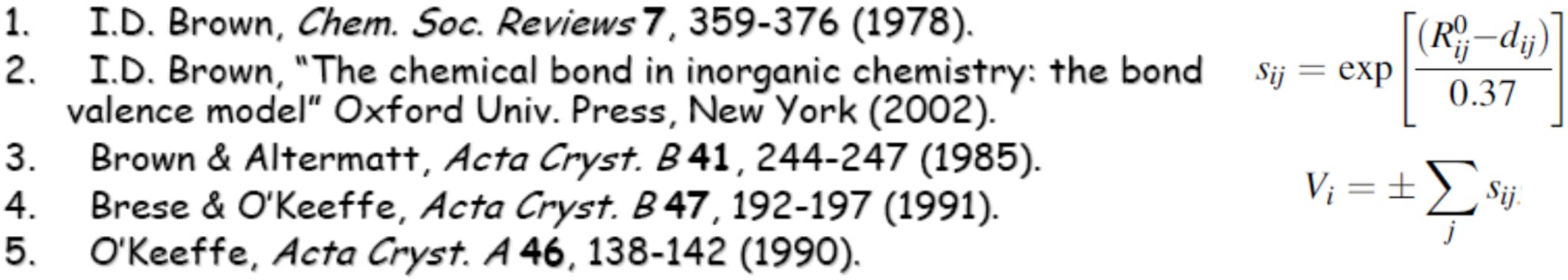
- **Quantitative relation between the bond valence and the bond length**
- **Bond valence can be fractional & Neighbours may be unequivalent**
- **The shorter the bond, the stronger it is, and the larger the s_{ij} is**
- **Empirical equation:**

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

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

- **R^0_{ij} values tabulated**
  (for various i-j combinations)



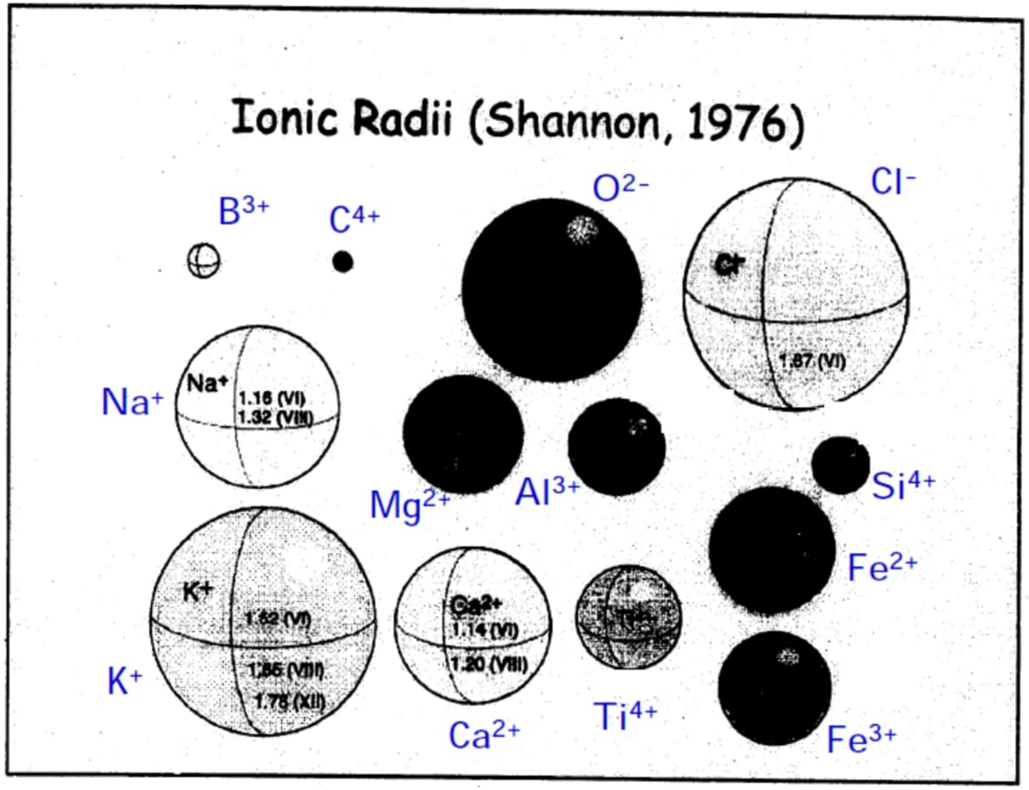

1. I.D. Brown, *Chem. Soc. Reviews* **7**, 359-376 (1978).
2. I.D. Brown, "The chemical bond in inorganic chemistry: the bond valence model" Oxford Univ. Press, New York (2002).
3. Brown & Altermatt, *Acta Cryst. B* **41**, 244-247 (1985).
4. Brese & O'Keeffe, *Acta Cryst. B* **47**, 192-197 (1991).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

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

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

Examples of R^0 Values

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



Ca^{2+} - O^{2-}	1.933
Sr^{2+} - O^{2-}	2.118
Ba^{2+} - O^{2-}	2.265
Fe^{2+} - O^{2-}	1.734
Fe^{3+} - O^{2-}	1.759
Cu^{+} - O^{2-}	1.60
Cu^{2+} - O^{2-}	1.679
Cu^{3+} - O^{2-}	1.73
Cu^{2+} - S^{2-}	2.054
Cu^{3+} - Cl^{-}	1.979
Cu^{3+} - F^{-}	1.58

COPPER OXIDES

Compound	CN(Cu)	Cu-O bonds	V_{nom}(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
$LaCuO_{2.5}$	5	2 x 1.941 2 x 1.966 1 x 2.285	+II	+2.10

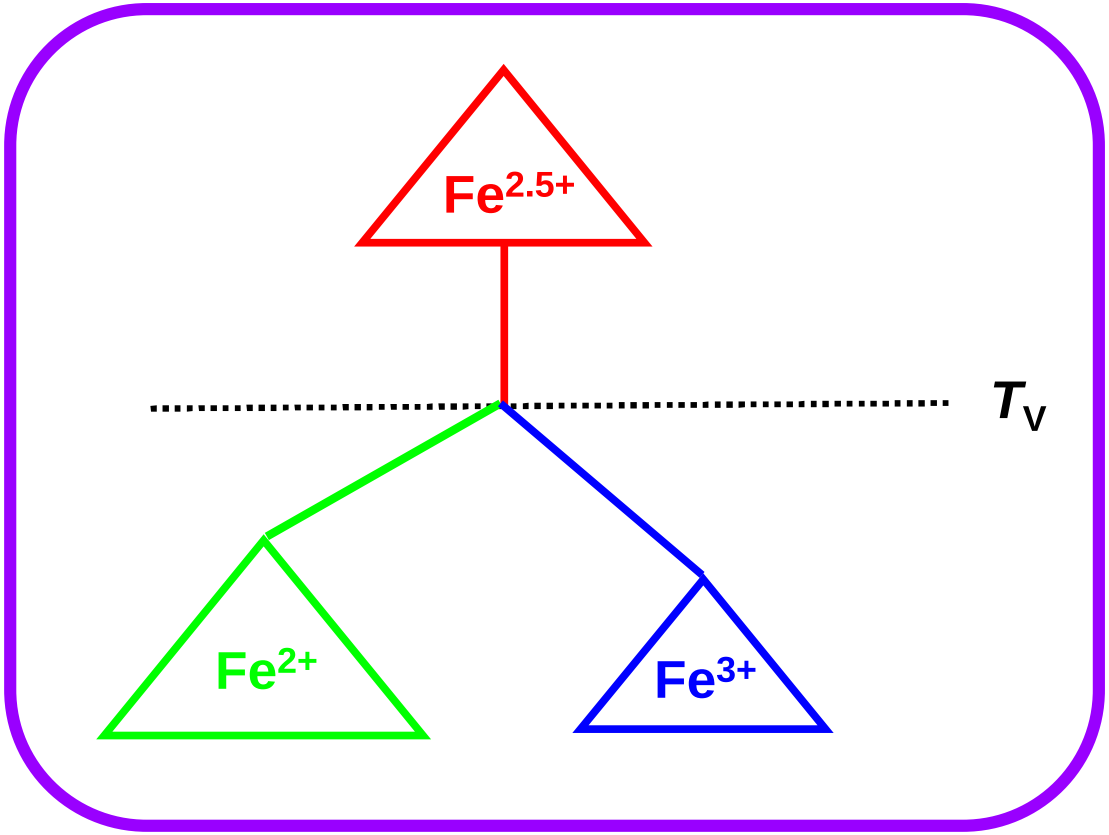
R^0: Cu^+-O^{2-} 1.600 Å, Cu^{2+}-O^{2-} 1.679 Å, Cu^{3+}-O^{2-} 1.730 Å

BVS (Bond Valence Sum)

- Empirical but highly useful tool !!!
- Validation of crystal structure determination results
- ”Inspecting” crystal structures (e.g. to find bonding instabilities)
- Location of light atoms (H, Li, etc.) that are hard to find by XRD, by examining the valences of the surrounding atoms
- Prediction of bond distances: $d_{ij} = R^0_{ij} - 0.37 \times \ln s_{ij}$
  (can handle unsymmetrical coordination environments)
- Prediction/design of new materials/structures (for synthesis efforts); c.f. Tolerance parameter
- Determining the charge distribution between two (or multiple) different sites of the same element in the same crystal structure
- Reasoning/prediction of structural distortions → important e.g. for ferroelectrics, piezoelectrics and magnetics

https://journals.iucr.org/b/issues/2015/05/00/yb5007/

Mixed Valency: e.g. Verwey Transition



Material Design

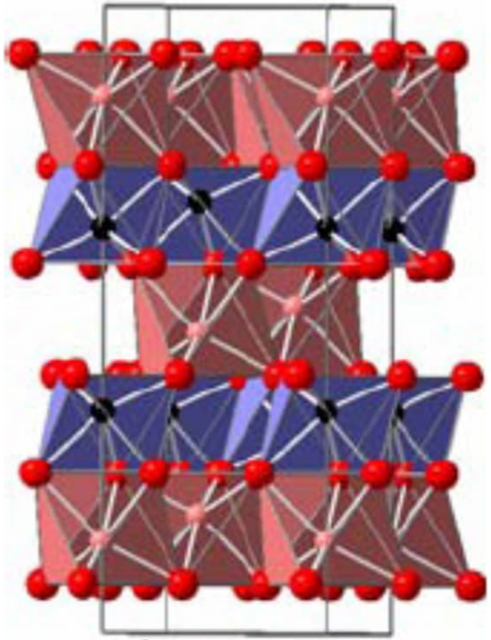
YOU CAN SEE from the BVS EQUATION:

Distorting the environment around an atom by lengthening some bonds and shortening others while holding the average bond length constant
→ Increase in the BVS

YOU CAN PREDICT for your NEW MATERIAL:

Distortion around a certain (transition metal) atom, is likely to occur if the atom is located on a crystal site that is too large (BVS too small);
In such a case the distortion would increase the BVS towards the ideal value.

$FeTiO_3$ (Ilmenite)



Bond Distances

Fe-O = 3×2.07, 3×2.20

Ti-O = 3×1.88, 3×2.09

Bond Valence Sums

Fe = 3×0.40 + 3×0.28 = **2.04** → Fe^{2+}

Ti = 3×0.84 + 3×0.48 = **3.96** → Ti^{4+}

O = 0.40 + 0.28 + 0.84 + 0.48 = **2.00**

ILMENITE STRUCTURE

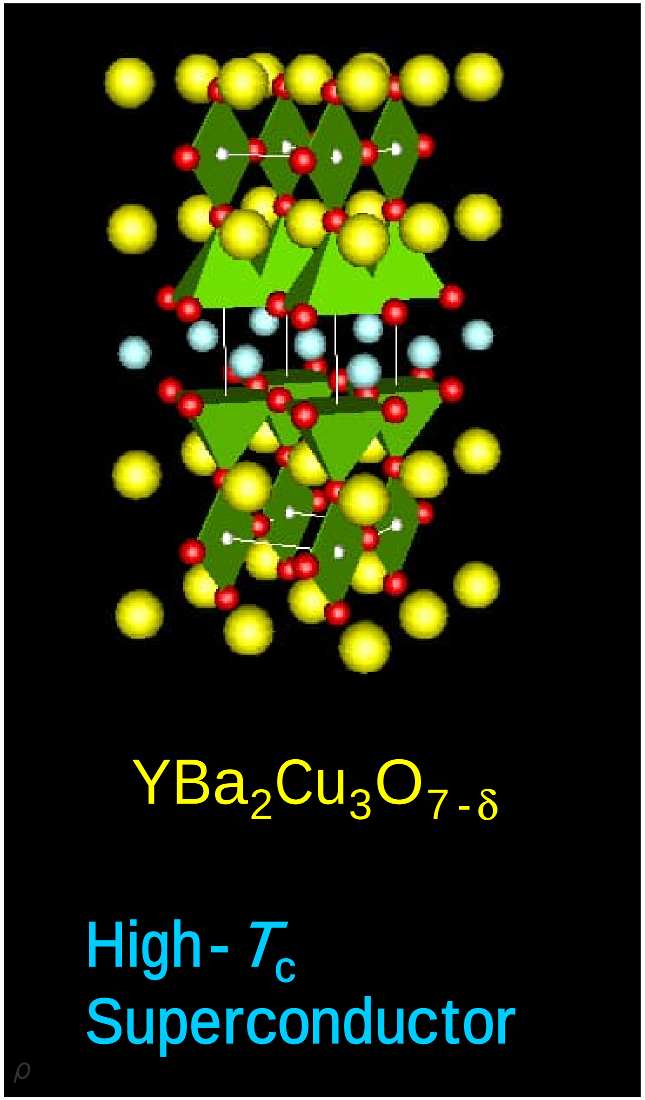
- Consists of Fe^{2+} and Ti^{4+} ions, both located within oxygen octahedra

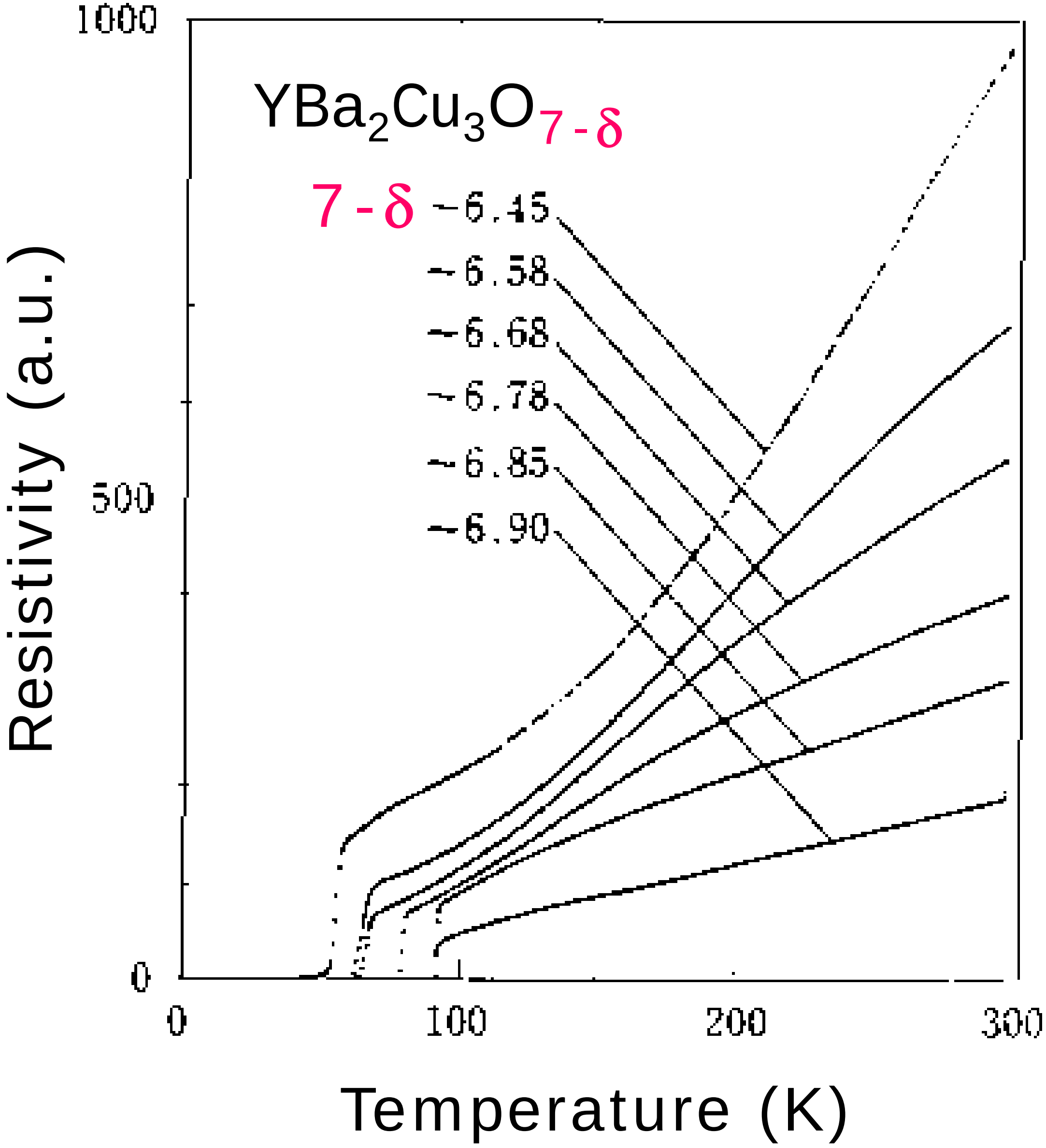
- XRD analysis can not directly tell us whether the Fe^{2+} ions are within the smaller and the Ti^{4+} ions within the larger octahedra, or vice versa

- BVS calculation confirms that:
Fe occupies larger (red) octahedra &
Ti occupies smaller (blue) octahedra

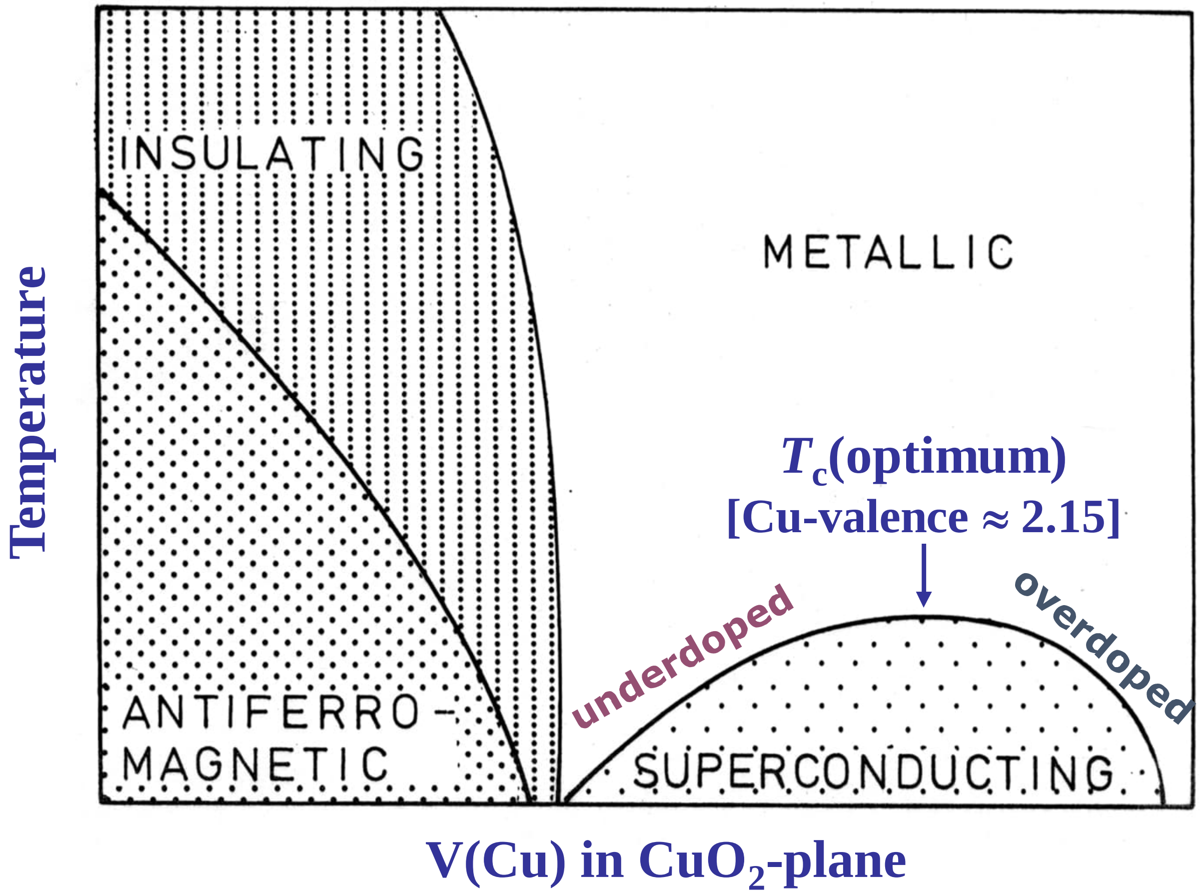
$YBa_2Cu_3O_{7-\delta}$ SUPERCONDUCTOR:

Oxygen (non)stoichiometry controls superconductivity properties





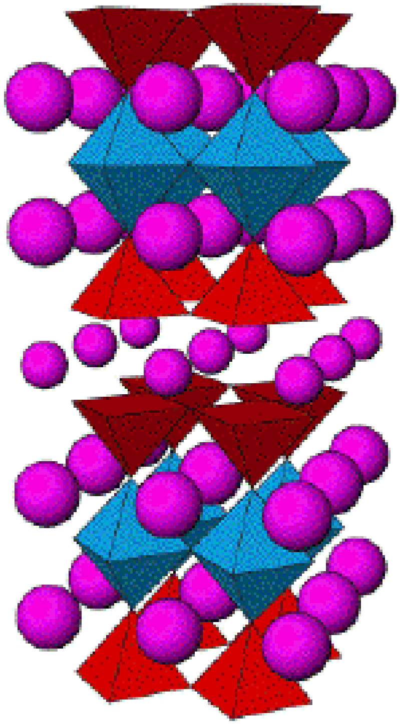
Phase Diagram of High-T_c Superconductors

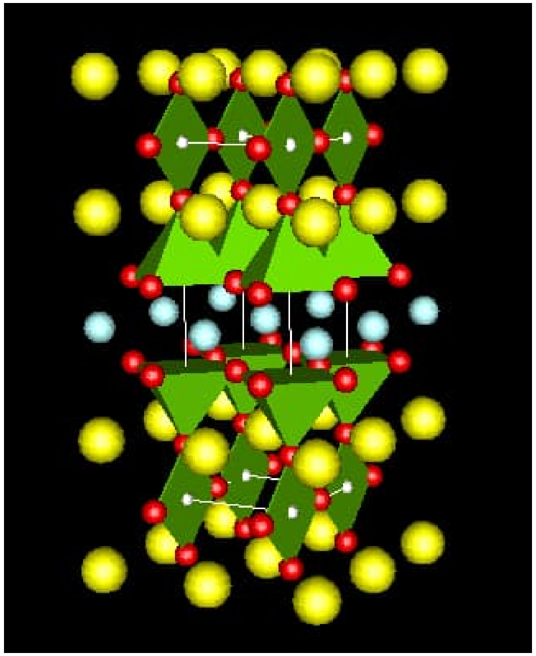


Oxygen content in $YBa_2Cu_3O_{7-\delta}$ controls the valence state of copper, and thereby the superconductivity (Tc value)

Illustration how the $YBa_2Cu_3O_{7-\delta}$ structure is derived from the perovskite ABO_3 structure through cation ordering and ordered oxygen vacancies

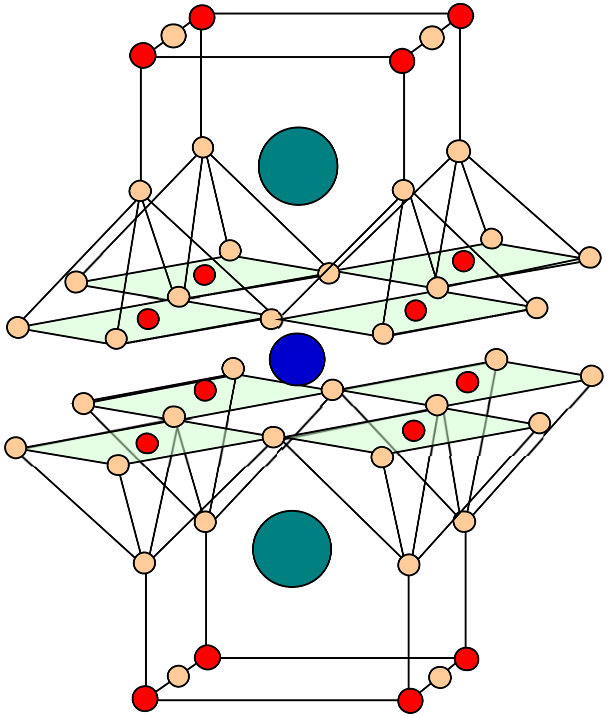
A-site ordered &
oxygen-vacancy ordered
TRIPLE PEROVSKITE
$A'A''_2B_3O_{8}$ (= 9-1)





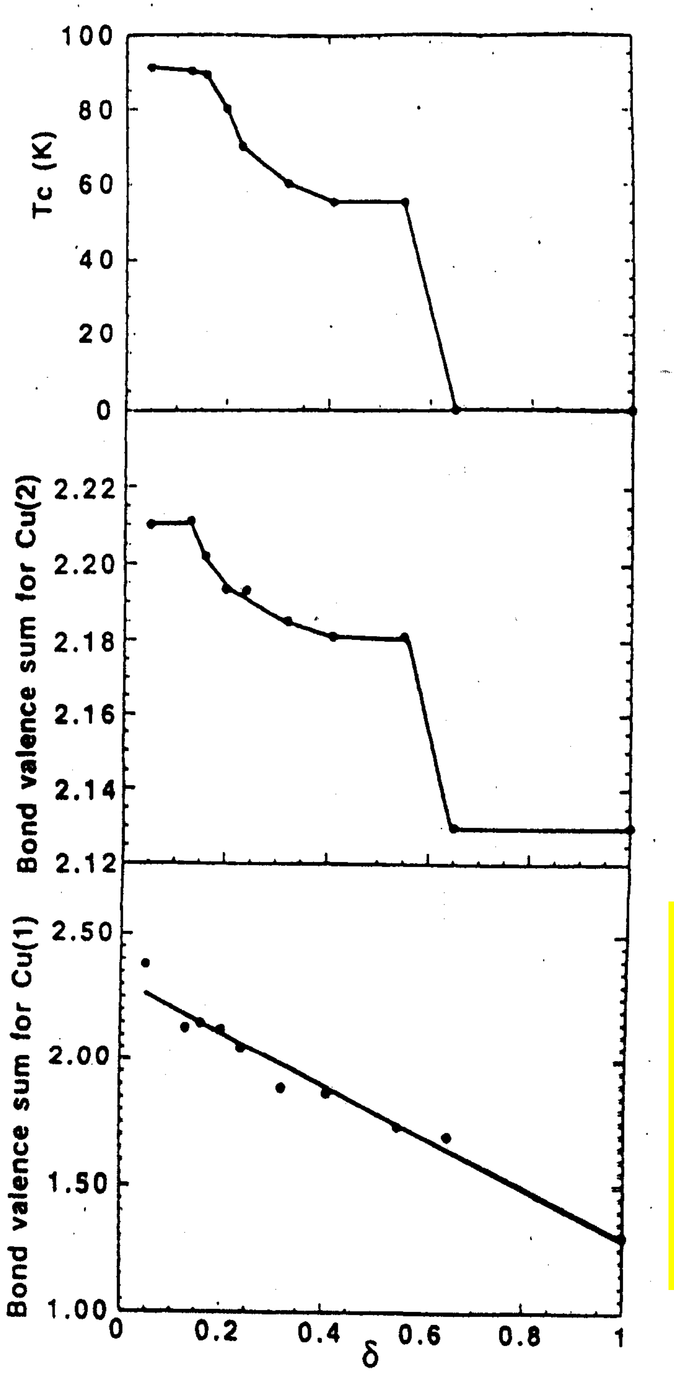
$YBa_2Cu_{(1)}Cu_{(2)2}O_7$ (= 9-2)

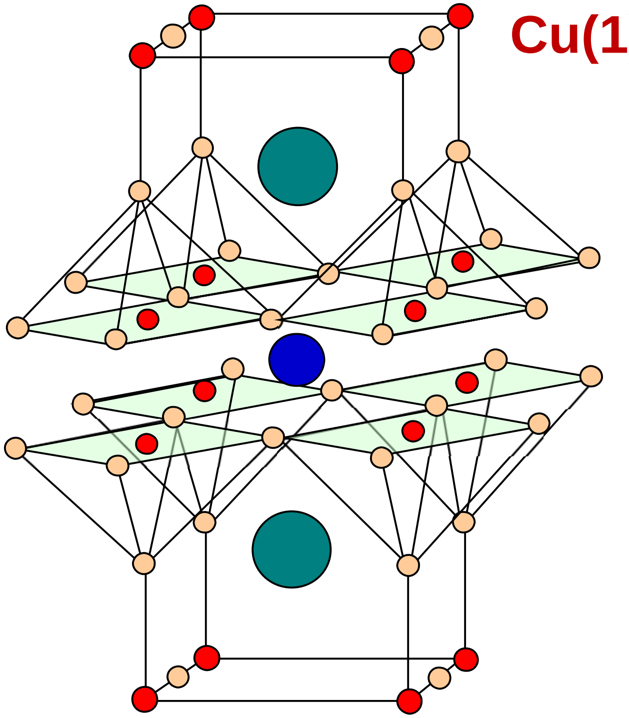
Cu(1)O chain



$Cu(2)O_2$ planes

$YBa_2Cu(1)Cu(2)_2O_7$





$Cu(1)O_{1-\delta}$ chain

$Cu(2)O_2$ planes

$YBa_2Cu(1)Cu(2)_2O_{7-\delta}$

BVS calculation shows:

- **Oxygen content decreases**
  → both V[Cu(1)] & V[Cu(2)] decrease
- **Same trend for V[Cu(2)] & T_c value**
  → V[Cu(2)] controls superconductivity

R.J. Cava et al., Physica C 165, 419 (1990).