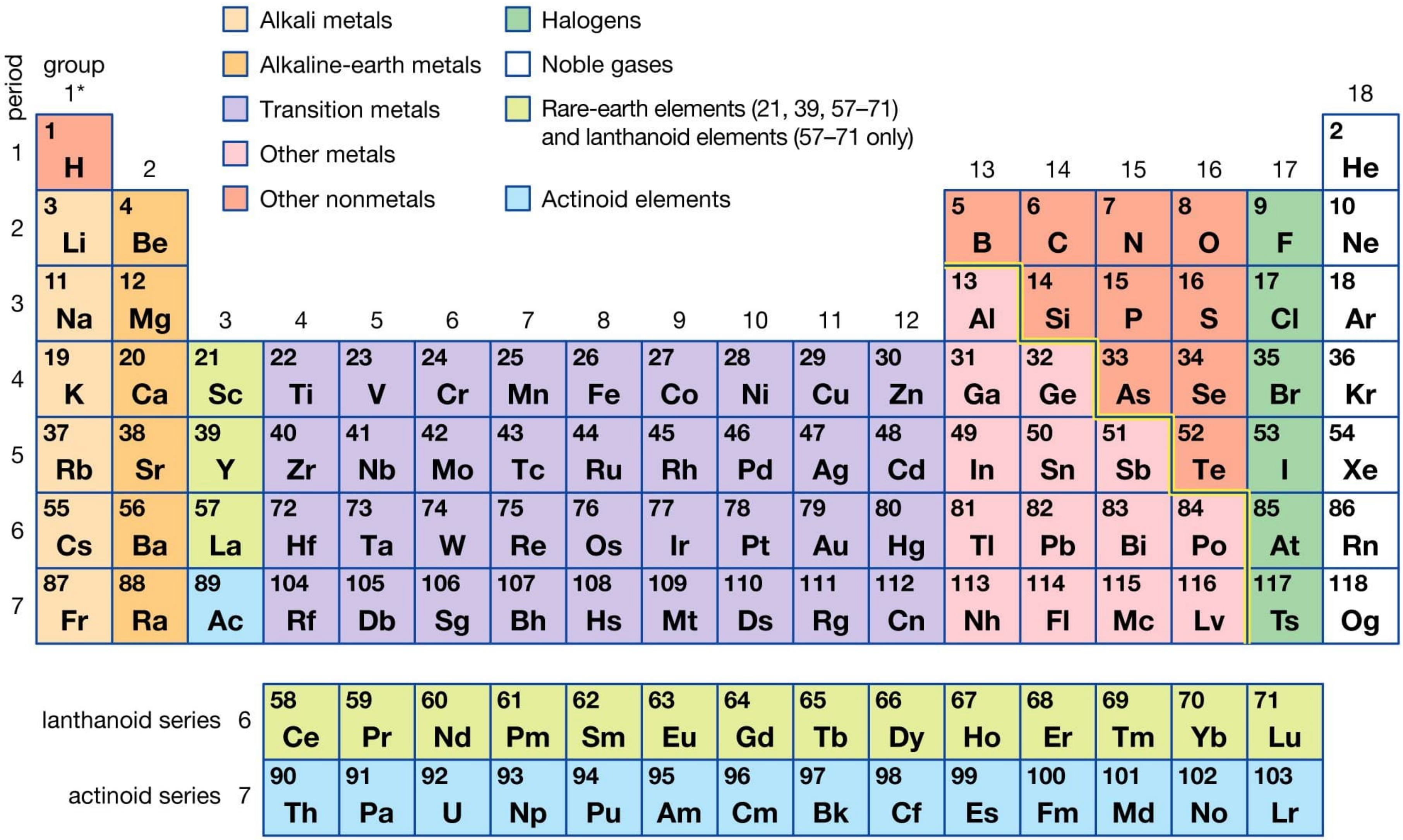
SCHEDULE

	Date		Topic
1.	Wed	01.03.	Lec-1: Introduction
2.	Mon	06.03.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Mon	06.03.	EXERCISE 1
4.	Wed	08.03.	Lec-3: Crystal Chemistry & BVS
5.	Fri	10.03.	Lec-4: Symmetry & Point Groups
6.	Mon	13.03.	EXERCISE 2
7.	Wed	15.03.	Lec-5: Crystallography & Space Groups (Linda)
8.	Fri	17.03.	Lec-6: XRD & Reciprocal lattice (Linda)
9.	Mon	20.03.	EXERCISE 3 (Linda)
10.	Fri	31.03.	Lec-7: Rietveld (Linda)
11.	Mon	03.04	EXERCISE 4: Rietveld (Linda)
12.	Wed	12.04.	Lec-8: ND & GI-XRD
13.	Fri	14.04.	Lec-9: XRR (Topias)
14.	Mon	17.04.	EXERCISE 5: XRR (Topias)
15.	Wed	19.04.	Lec-10: Synchrotron radiation & XAS & EXAFS
16.	Fri	21.04.	Mössbauer
17.	Fri	21.04.	EXERCISE 6
18.	Thu	27.04.	Seminars: XPS, FTIR, Raman
19.	Fri	28.04.	Seminars: ED, HRTEM, SEM, AFM

EXAM

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 BVS concept**
- **Also, recall what we discussed in the previous lecture on the Tolerance parameter concept**

BOND & VALENCE

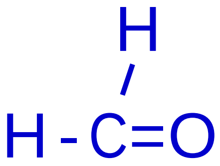
C-C 1.54 Å
C=C 1.33 Å
C≡C 1.20 Å

ORGANIC COMPOUNDS

- **Bonds tend to adopt integer valence values: bond order is single, double or triple**
- **Bond order correlates with the 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 either tetrahedral or octahedral coordination**

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

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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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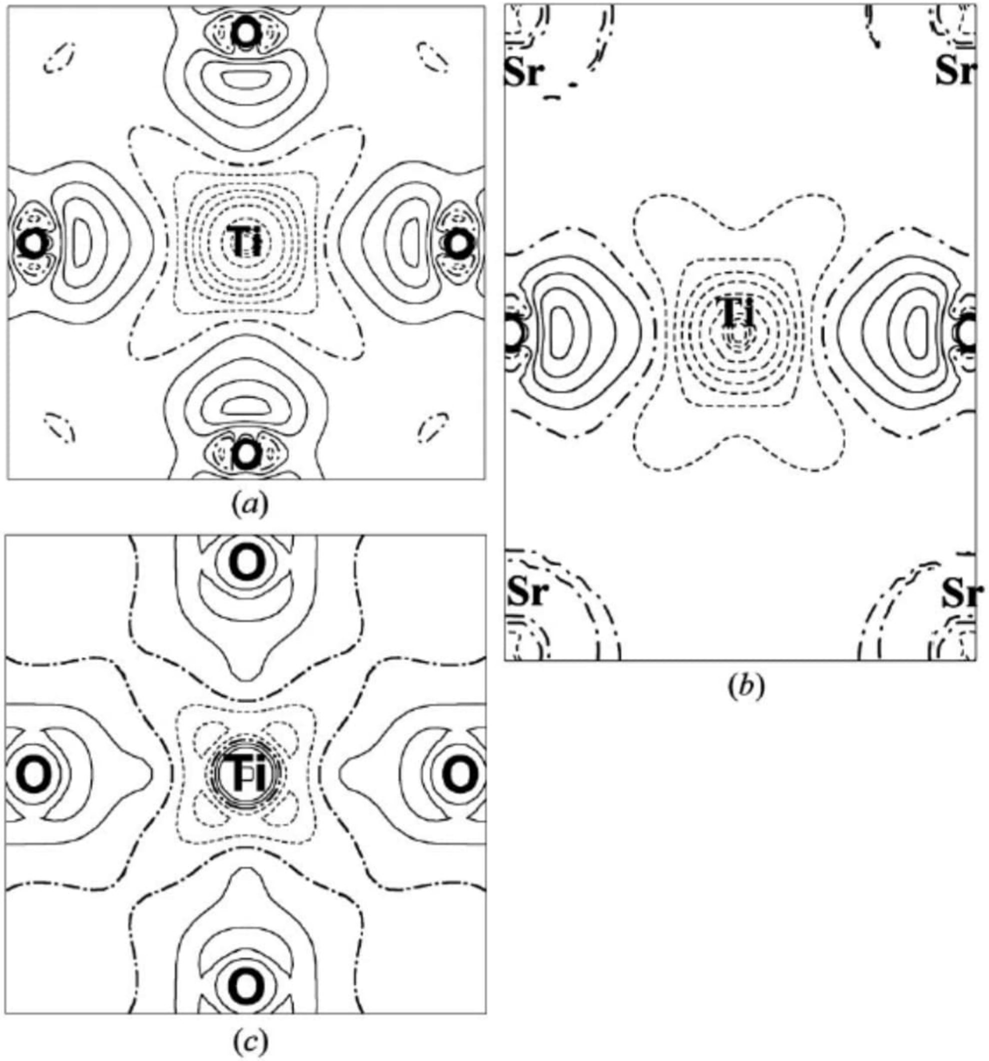
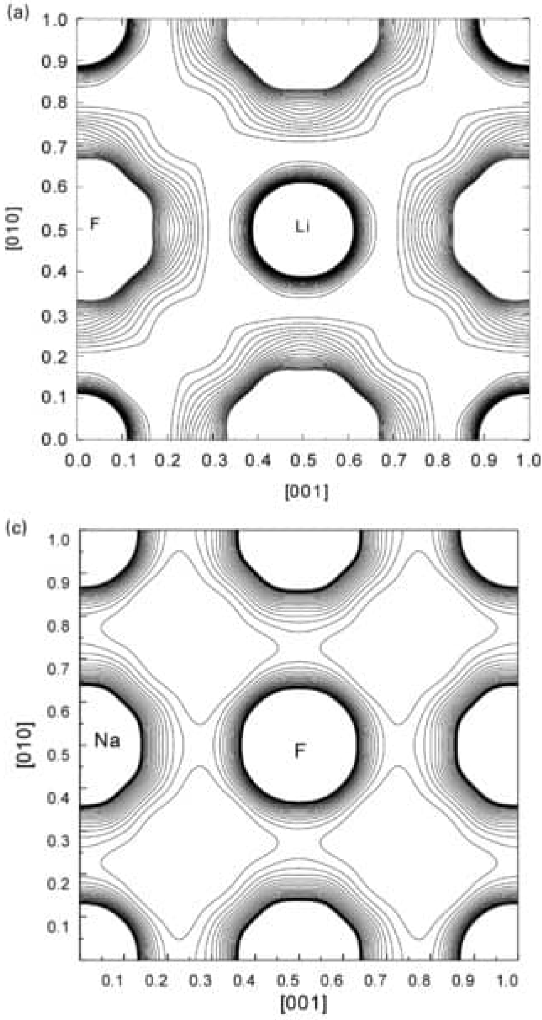


(*a*)

(*b*)

(*c*)



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

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

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

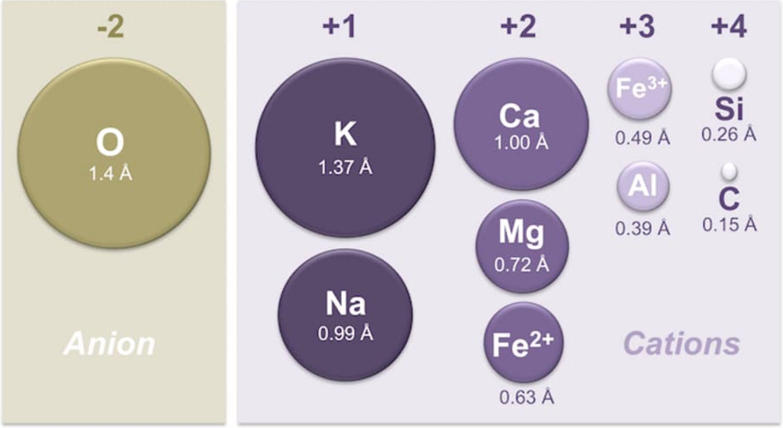
EXAMPLE-1: Rutile TiO_2

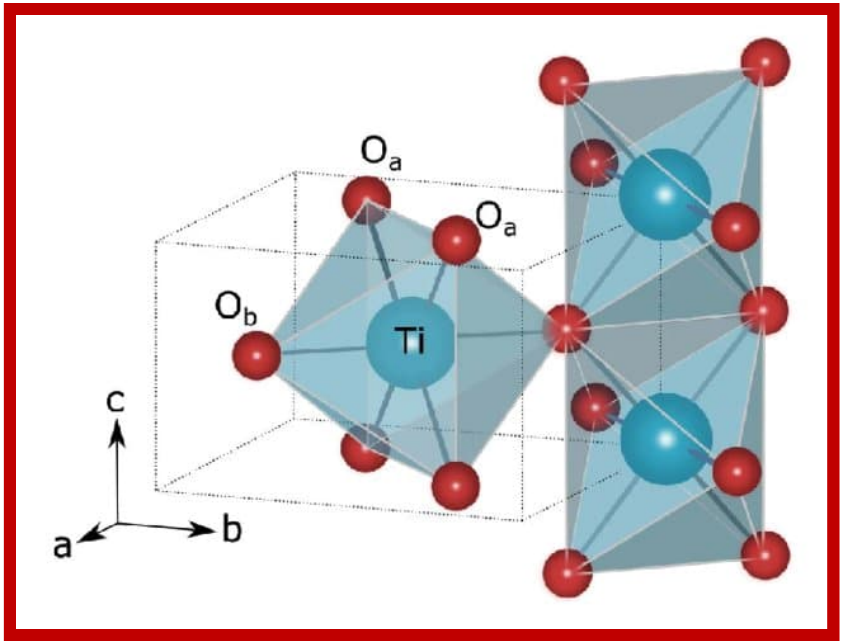
OS(Ti) = +4 & CN(Ti) = 6, hence BV(Ti-O) = 4/6 = 0.67

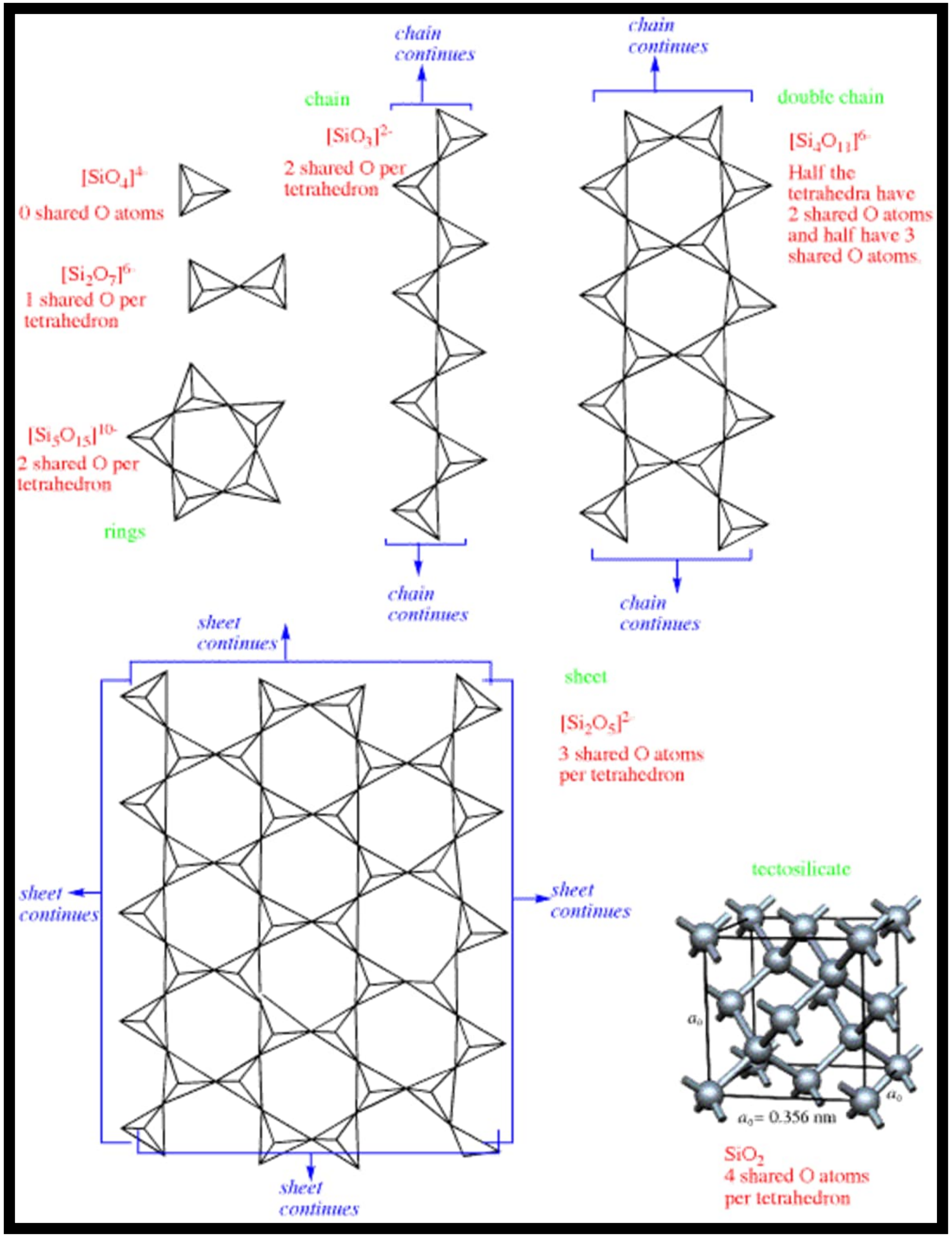
→ since OS(O) = -2 = - (3 x 0.67), CN(O) = 3

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 polyhedral 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


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

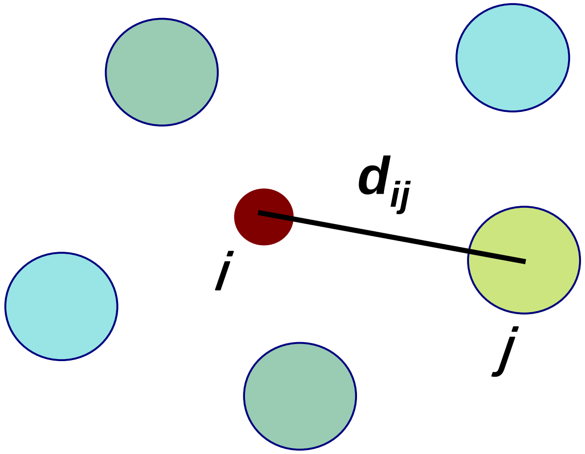
Bond-Valence-Sum (BVS) Calculation

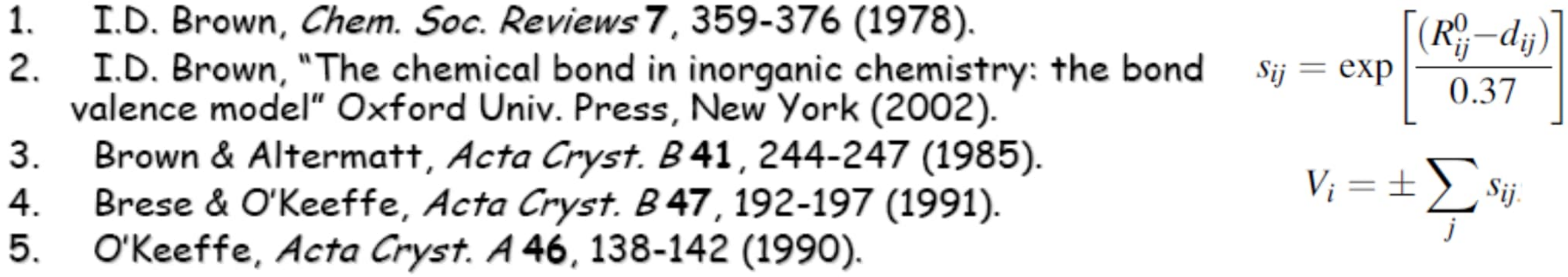
- Quantitative relation between the bond valence and the bond length
- Bond valence can be fractional & Neighbours may be unequivalent
- The shorter the bond, the stronger it is, and the larger the s_{ij} is
- Empirical equation:

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

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

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



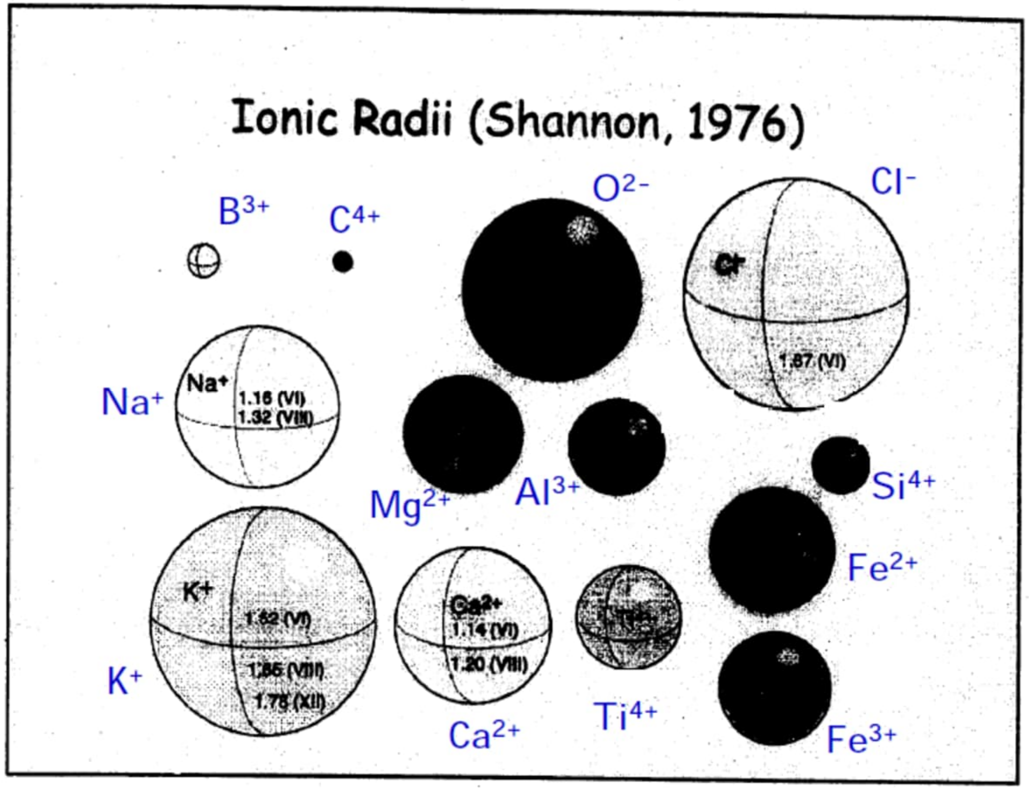


1. I.D. Brown, *Chem. Soc. Reviews* **7**, 359-376 (1978).
2. I.D. Brown, "The chemical bond in inorganic chemistry: the bond valence model" Oxford Univ. Press, New York (2002).
3. Brown & Altermatt, *Acta Cryst. B* **41**, 244-247 (1985).
4. Brese & O'Keeffe, *Acta Cryst. B* **47**, 192-197 (1991).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



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

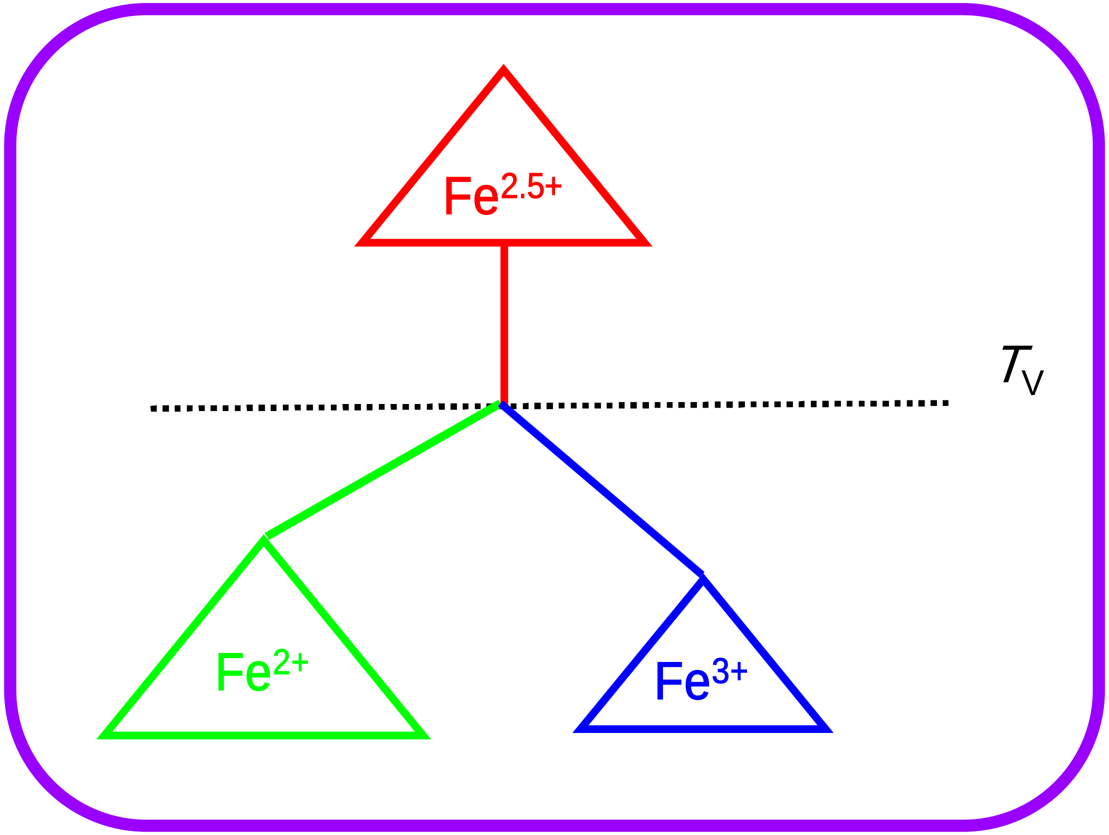
BVS (Bond Valence Sum)

- **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/

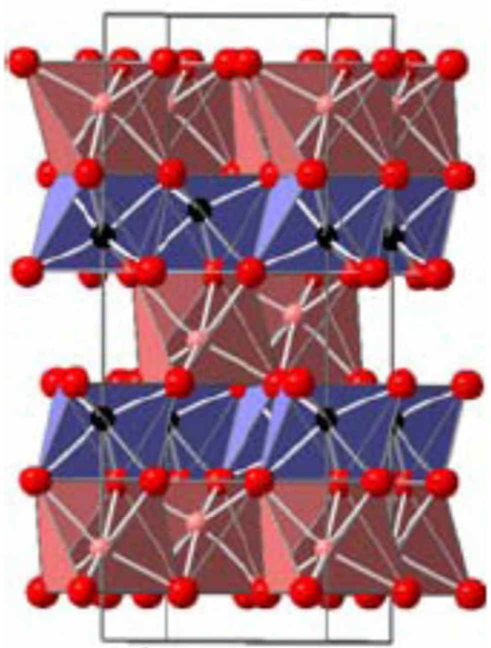
Verwey Transition



Distorting the environment of an atom by lengthening some bonds and shortening others while holding the average bond length constant, results in an increase in the bond valence sum

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**

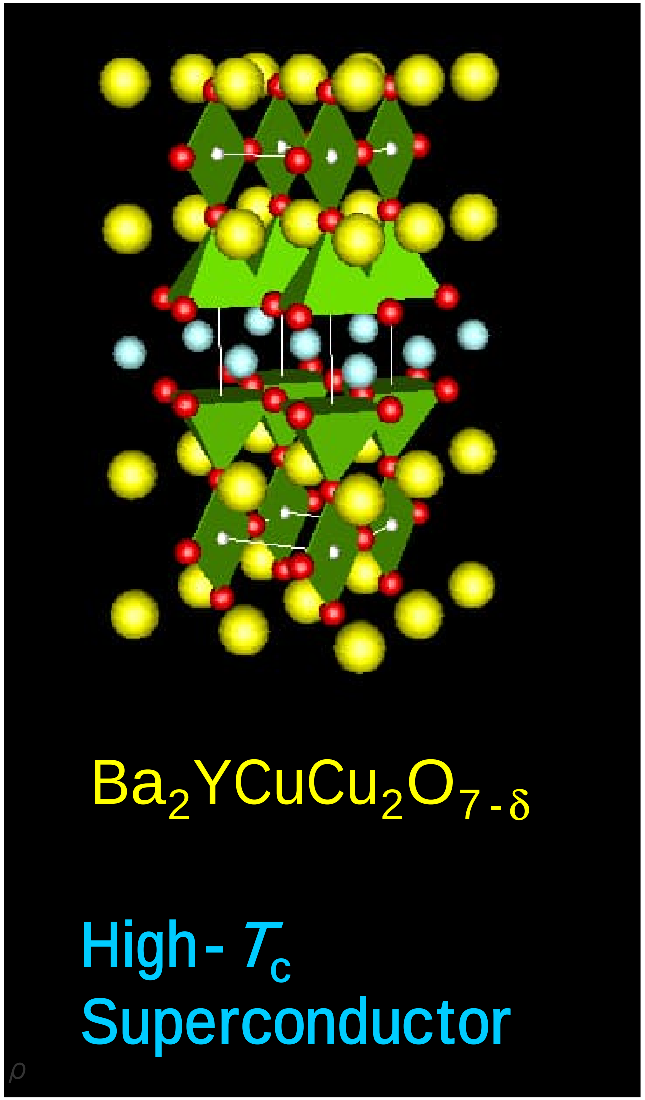
BVS calculation confirms that:

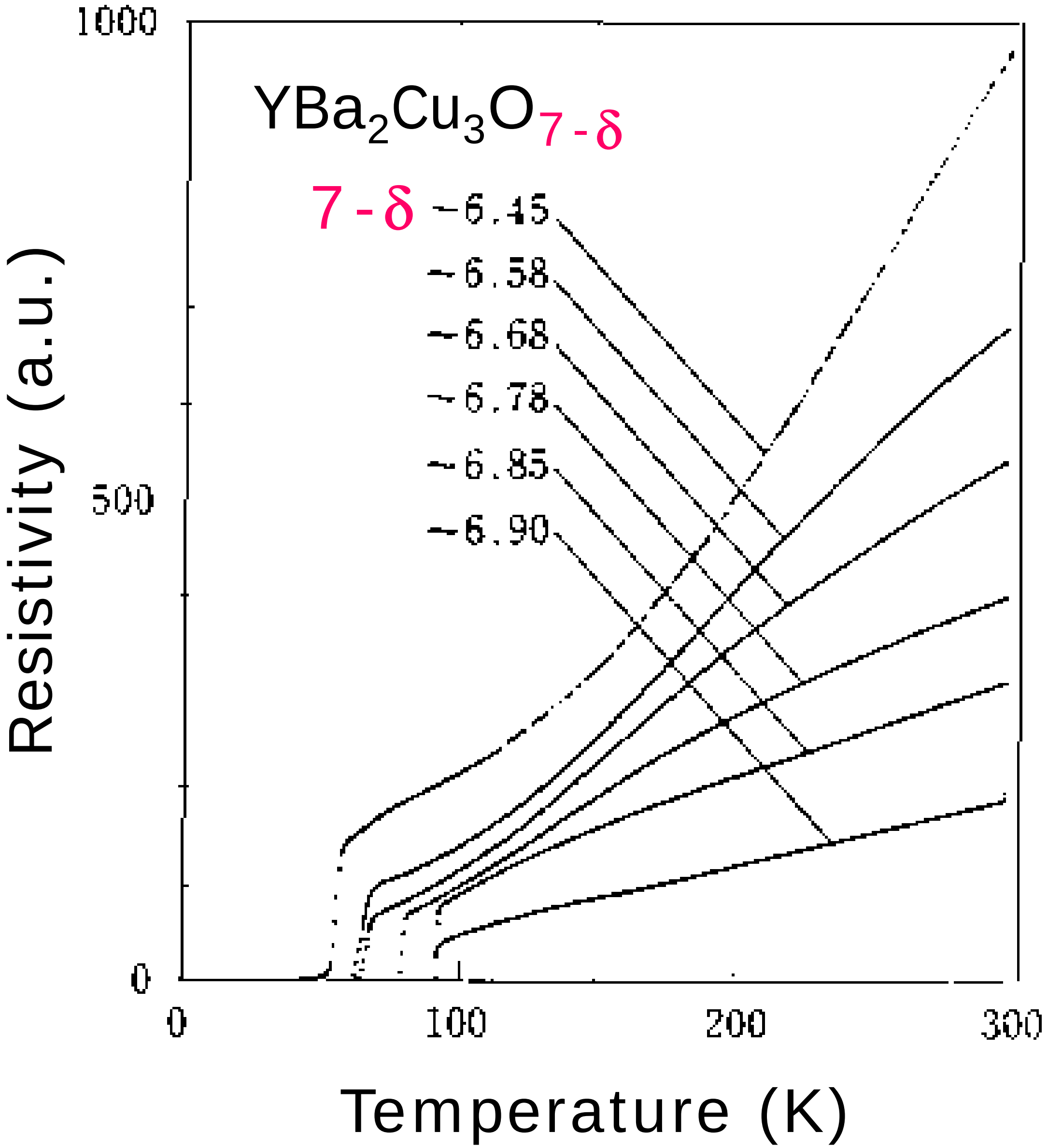
Fe occupies the larger (red) octahedra

& Ti the smaller (blue) octahedra

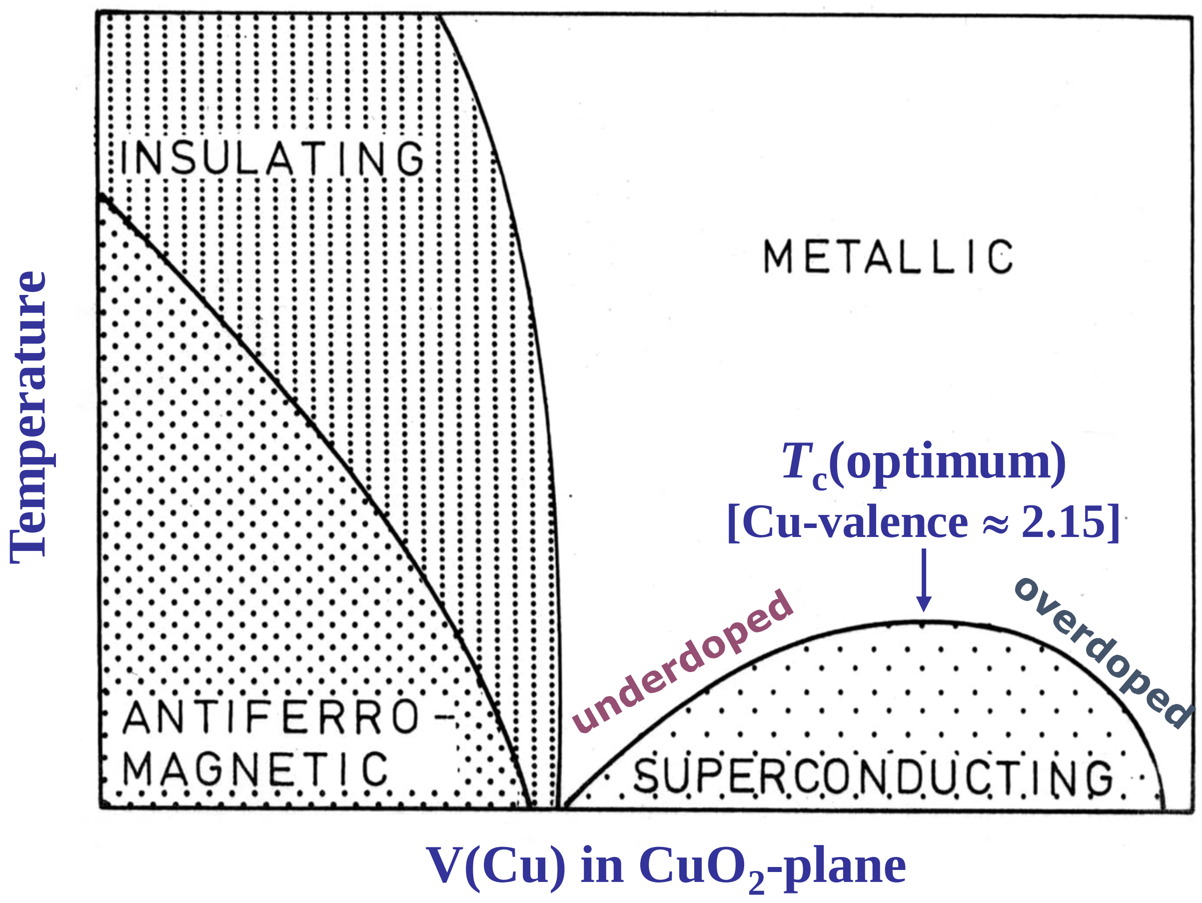
in the Ilmenite structure

$YBa_2Cu_3O_{7-\delta}$ (or $Ba_2YCu(1)Cu(2)_2O_{7-\delta}$ 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

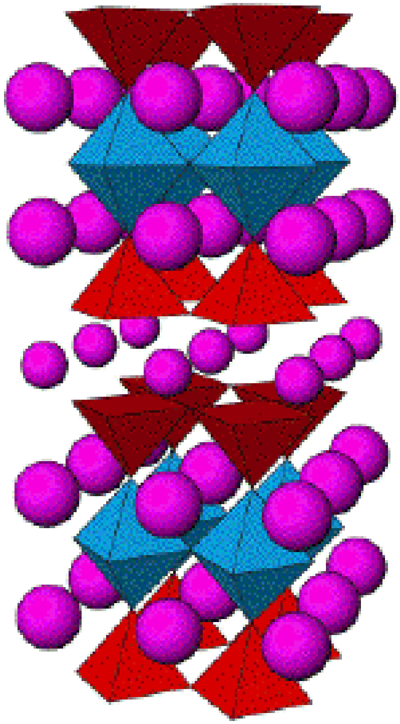


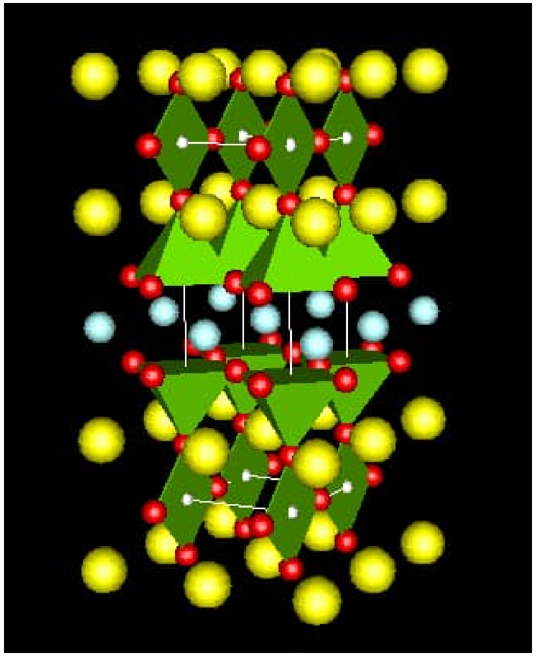
T_c(optimum)
[Cu-valence ≈ 2.15]

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

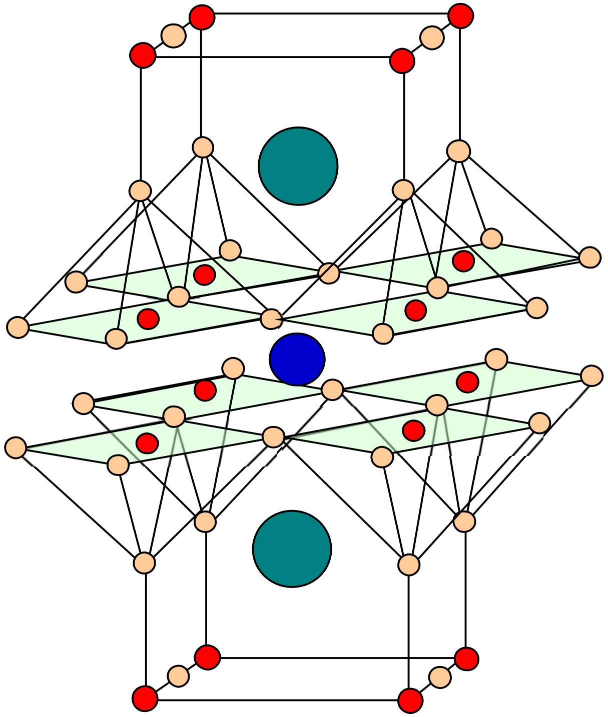
Illustration how the $YBa_2Cu_3O_{7-\delta}$ structure is derived from the perovskite structure through cation ordering and ordered oxygen vacancies

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

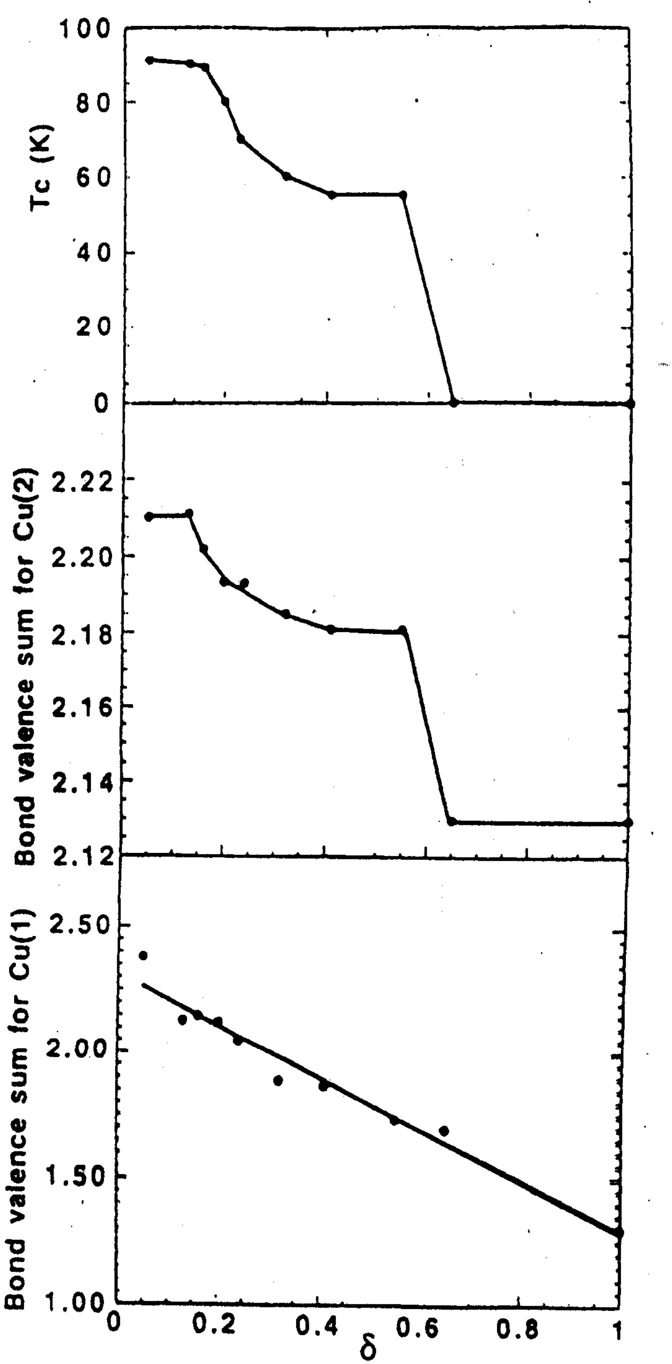




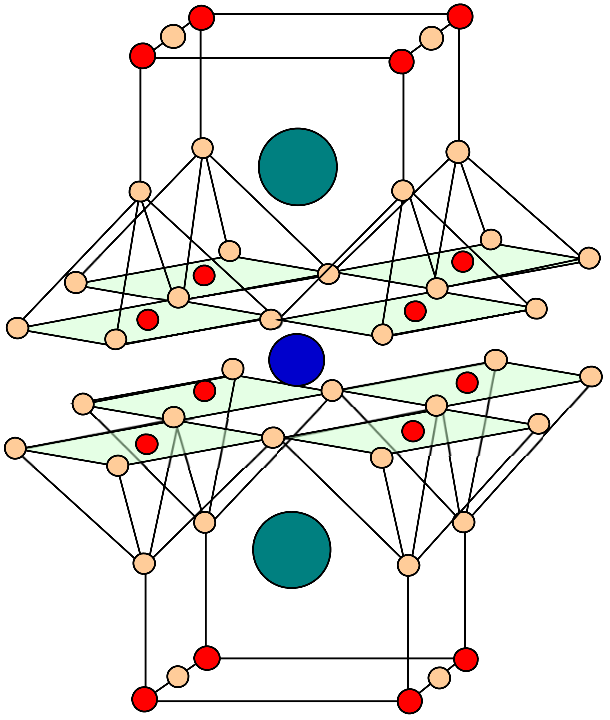
$Ba_2YCu_{(1)}Cu_{(2)_2}O_7$ (= 9-2)



$Ba_2YCu(1)Cu(2)_2O_7$



$Cu(1)O$ chain



$Cu(2)O_2$ planes

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

BVS calculation shows that with decreasing oxygen content in $YBa_2Cu_3O_{7-\delta}$ the valence state of bot 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.

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