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

EXAM: Friday, Oct. 29th, 2021

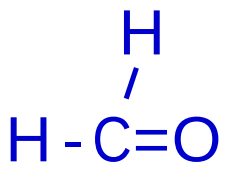
LECTURE 3: CRYSTAL CHEMISTRY & BVS

- **Correlations between:**
  Coordination Number (CN), Bond Distance (d) & Valence State (V)
- **Bond Valence Sum (BVS): quantitative measure for the correlation**

BOND & VALENCE

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

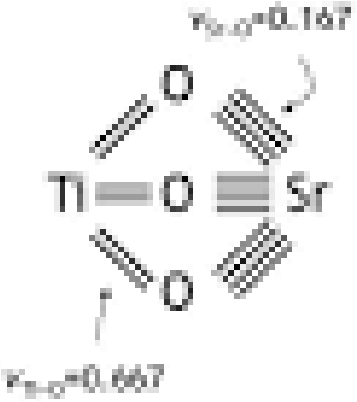
Pauling's Second Rule

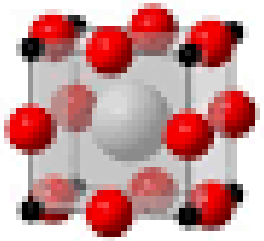
Valence sum rule

$$v_i = \sum_j v_{ij}$$

The valence sum v_i of an atom is equal to the sum of bond valences v_{ij} around it

The valence sum of each atom, v_i, should be equal to the oxidation state of the atom





Sr = 12(0.167) = 2

Ti = 6(0.667) = 4

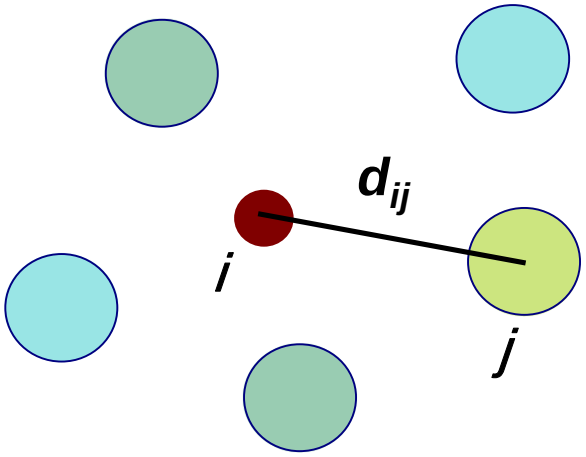
O = 2(0.667)+4(0.167) = 2

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)

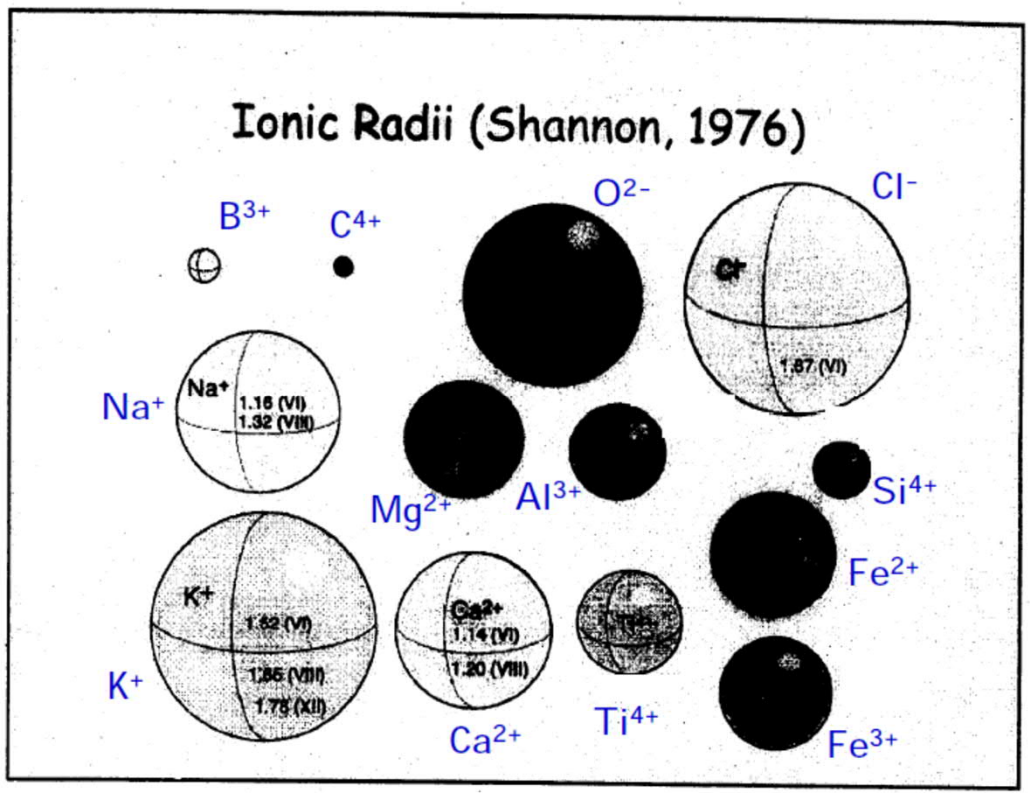


1. I.D. Brown, *Chem. Soc. Reviews* **7**, 359-376 (1978).
2. I.D. Brown, "The chemical bond in inorganic chemistry: the bond valence model" Oxford Univ. Press, New York (2002).
3. Brown & Altermatt, *Acta Cryst. B* **41**, 244-247 (1985).
4. Brese & O'Keeffe, *Acta Cryst. B* **47**, 192-197 (1991).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

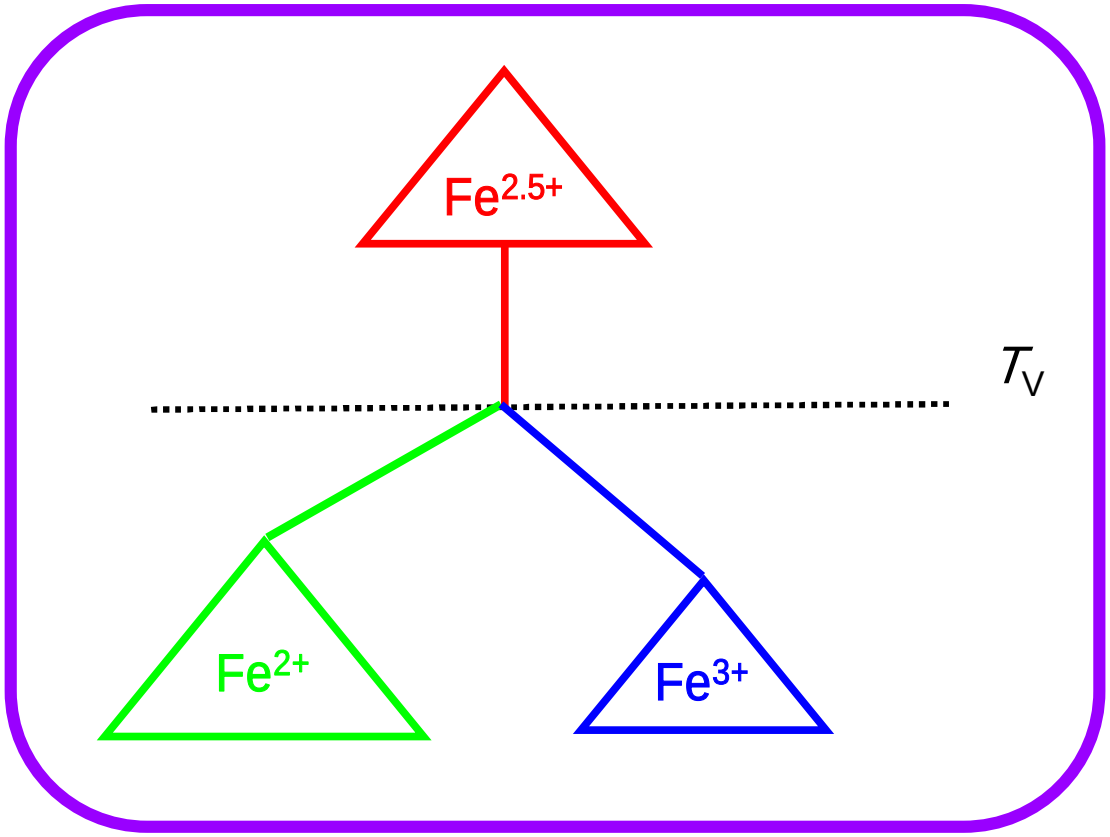
R^0: Cu^{+}-O^{2-} 1.600 Å, Cu^{2+}-O^{2-} 1.679 Å, Cu^{3+}-O^{2-} 1.730 Å

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**
- **Predicting/designing new materials/structures (for synthesis efforts)**
- **Prediction of bond distances: $d_{ij} = R^0_{ij} - 0.37 \times \ln s_{ij}$ (can handle unsymmetrical coordination environments)**
- **Determining the charge distribution between two (or multiple) different sites of the same element**
- **Reasoning/prediction of structural distortions → important e.g. for ferroelectrics**

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

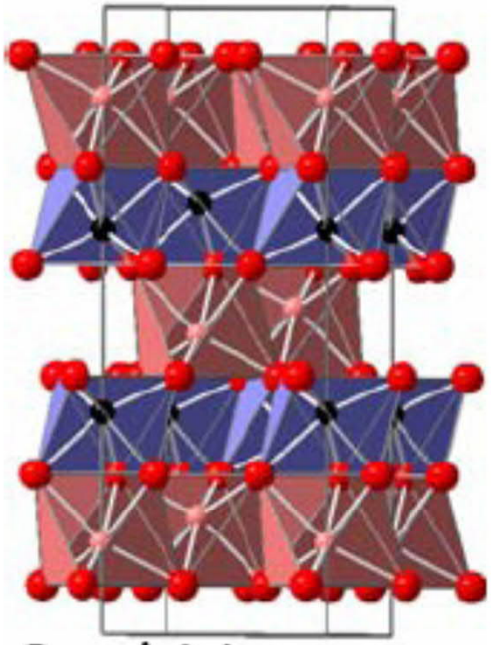
Verwey Transition



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

To achieve distortion around a certain (transition metal) atom,
this atom should be placed in a cavity that is too large (BVS too small);
In such a case its environment will most probably distort to 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**

Ti = 3×0.84 + 3×0.48 = **3.96**

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

Fe^{2+}

Ti^{4+}

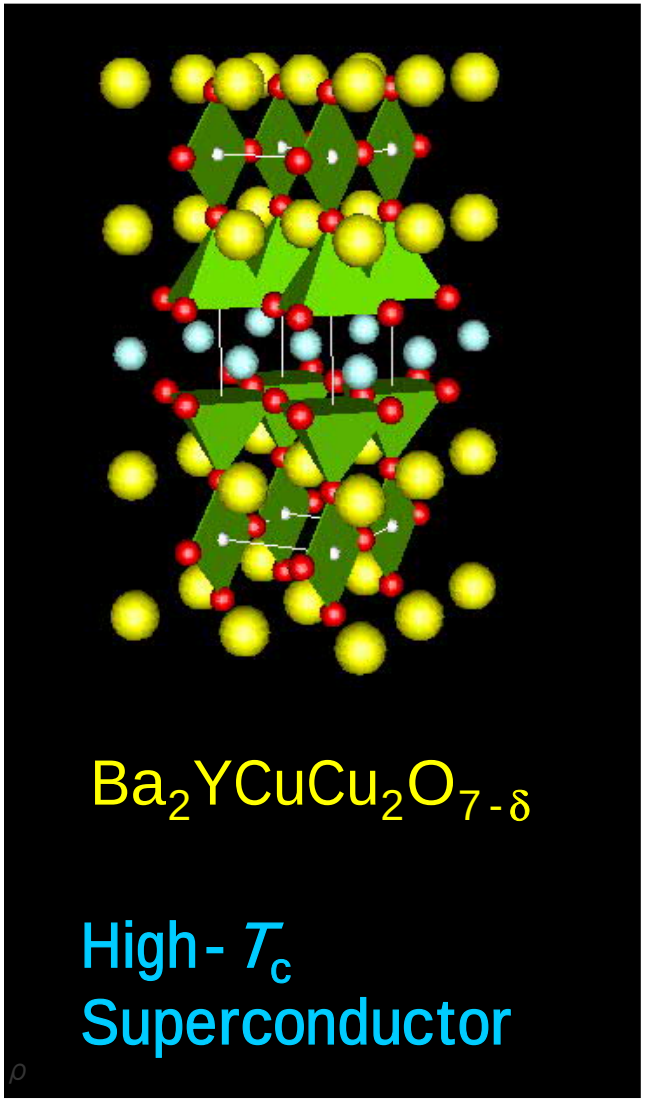
BVS calculation confirms that:

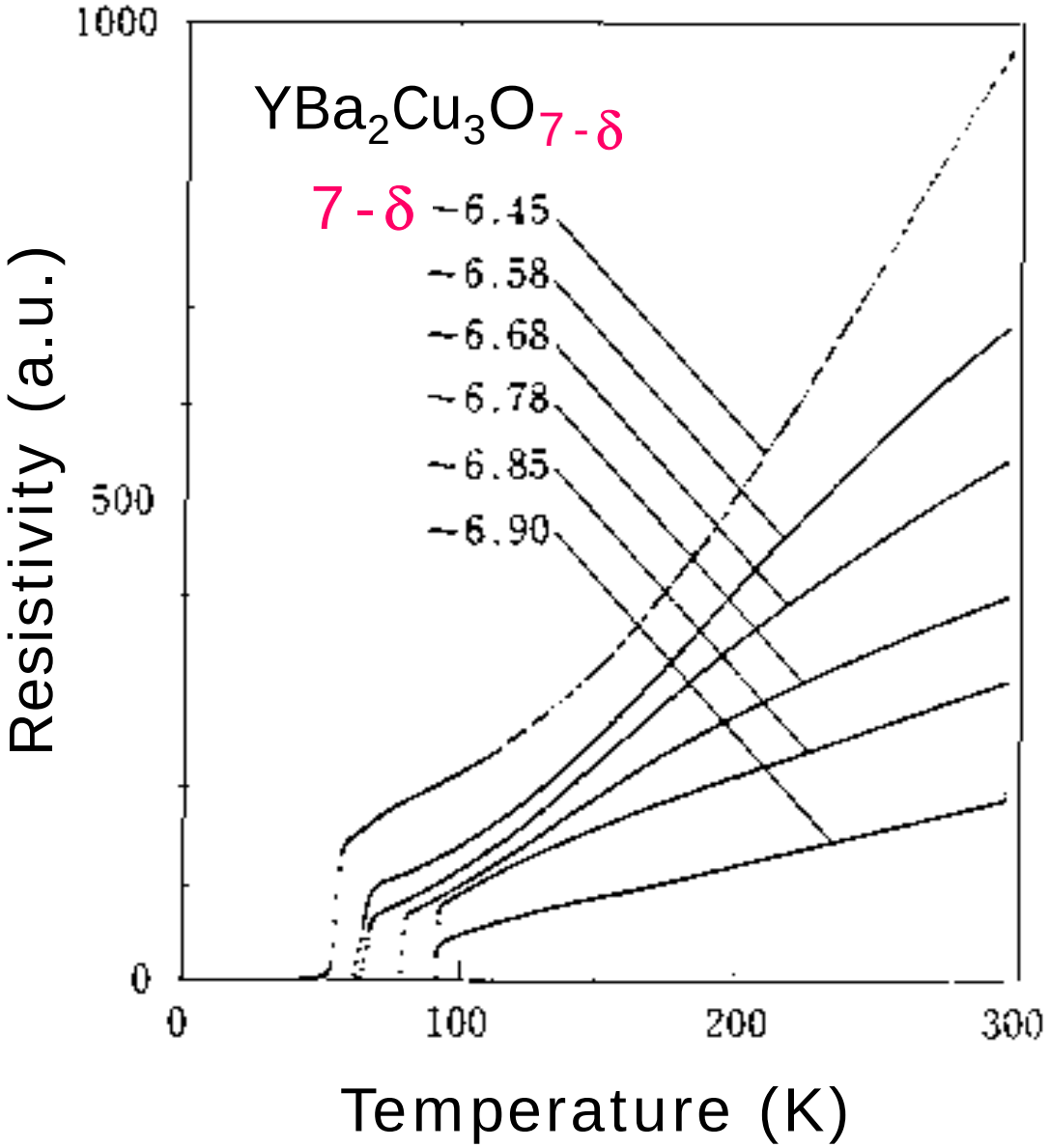
Fe occupies the larger (red) octahedra

& Ti the smaller (blue) octahedra

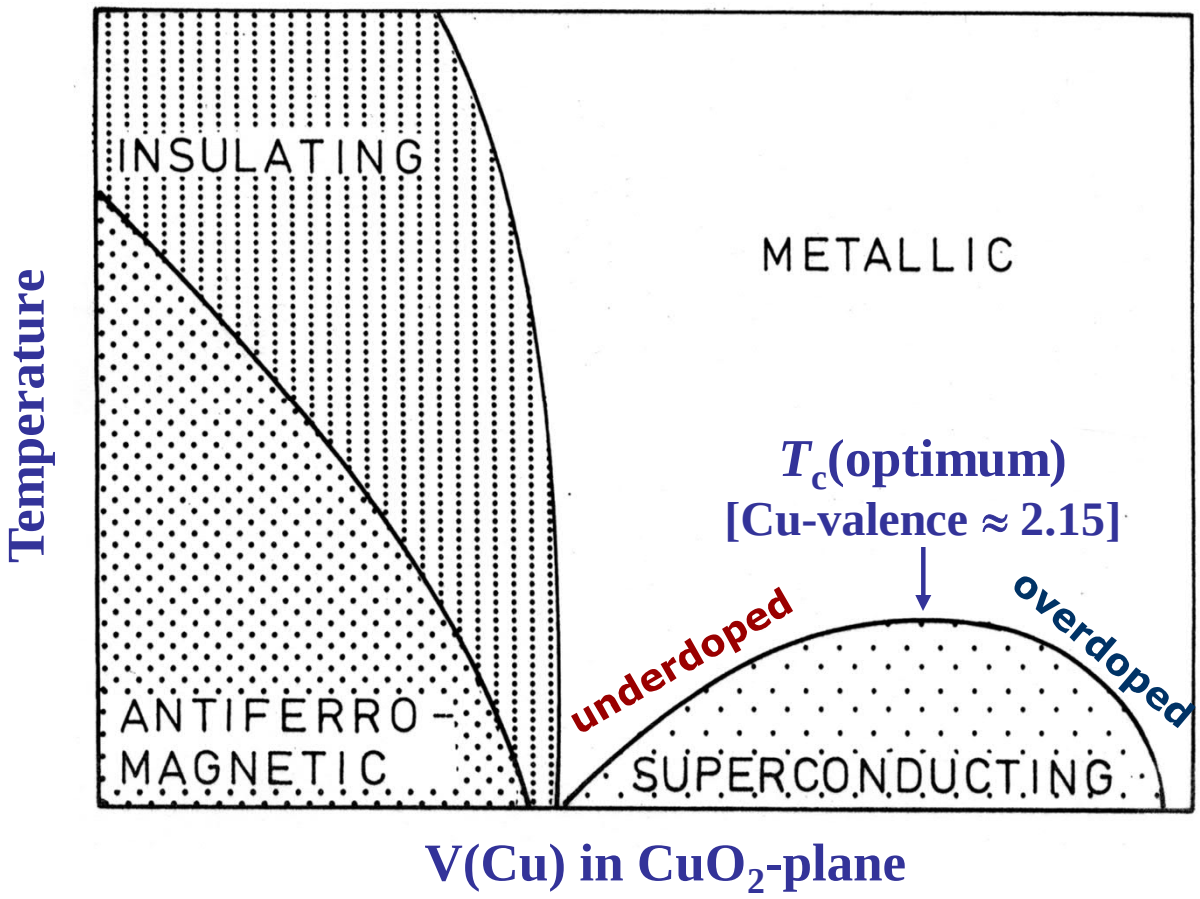
in the Ilmenite structure

$YBa_2Cu_3O_{7-\delta}$ (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





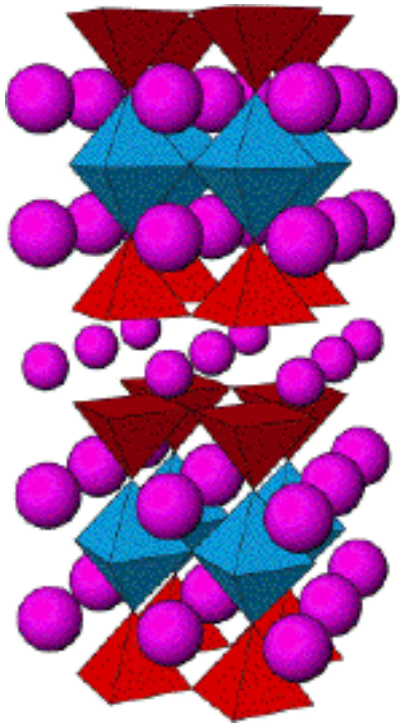
Phase Diagram of High-T_c Superconductors

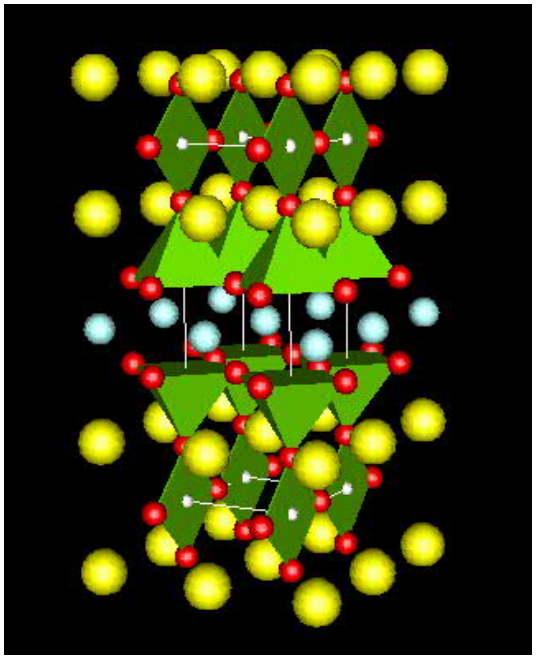


Oxygen content in $YBa_2Cu_3O_{7-\delta}$ controls the valence state of copper, and thereby the superconductivity (Tc value)

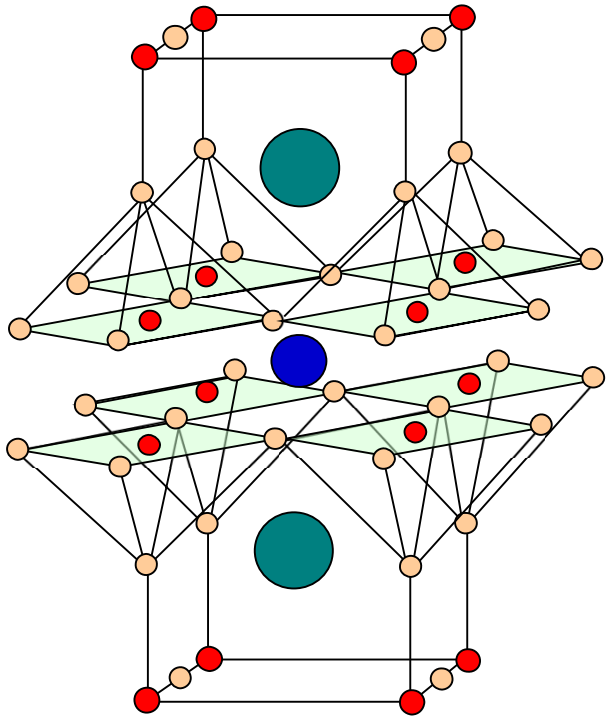
Illustration how the $YBa_2Cu_3O_{7-\delta}$ structure is derived from the perovskite structure through cation ordering and ordered oxygen vacancies

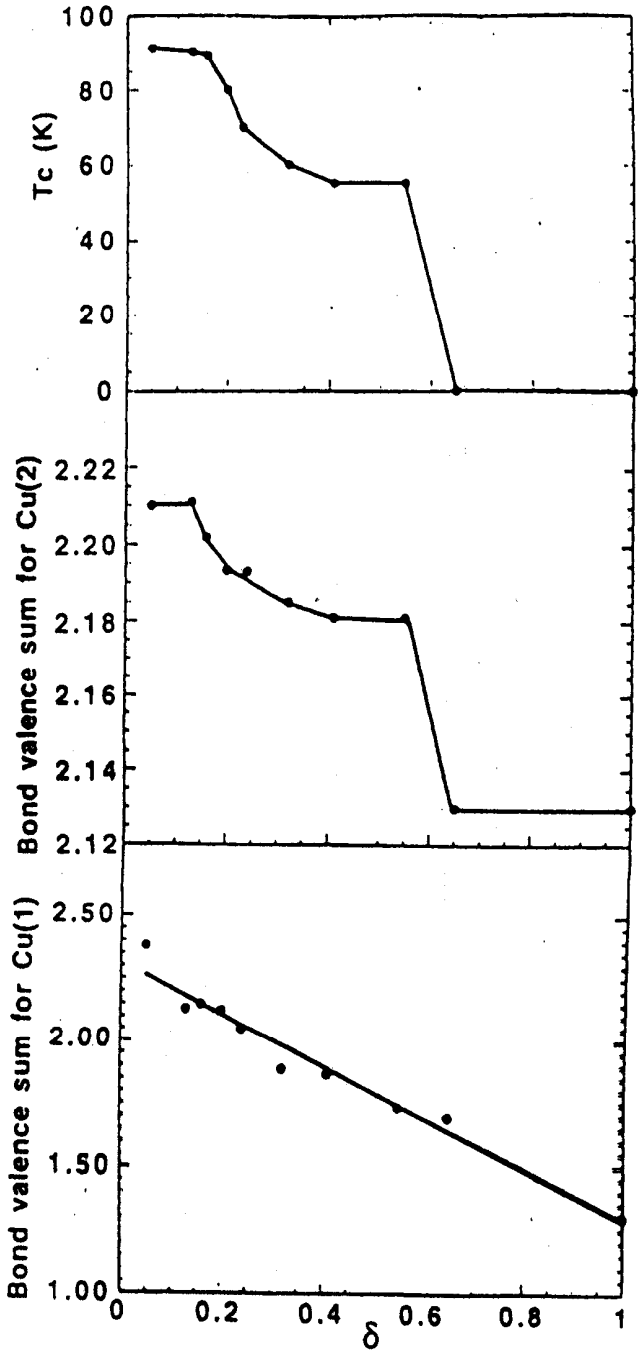
A-site ordered &
oxygen-vacancy ordered
TRIPLE PEROVSKITE
$A'_2A''B_3O_8$ (= 9-1)

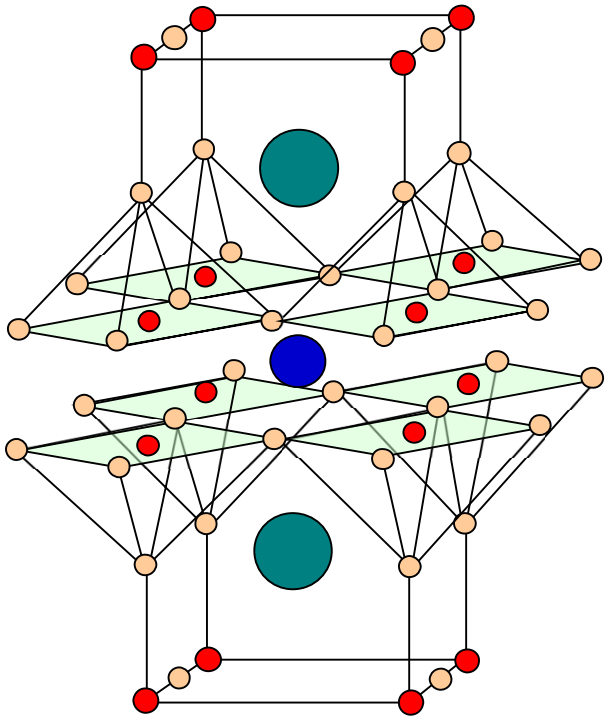




$Ba_2YCu_{(1)}Cu_{(2)_2}O_7$ (= 9-2)







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).