# Oxide crystal structures and electron counts: The basics


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Photo by Tony Mastres

# This lecture

1. Brief description of oxide crystal structures (simple and complex)

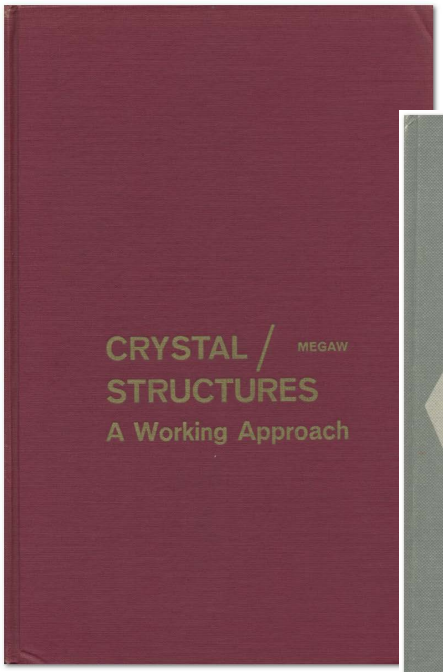
    a. Ionic radii and Pauling's rules
    b. Electrostatic valence
    c. Bond valence, and bond valence sums

    Why do certain combinations of atoms take on specific structures?

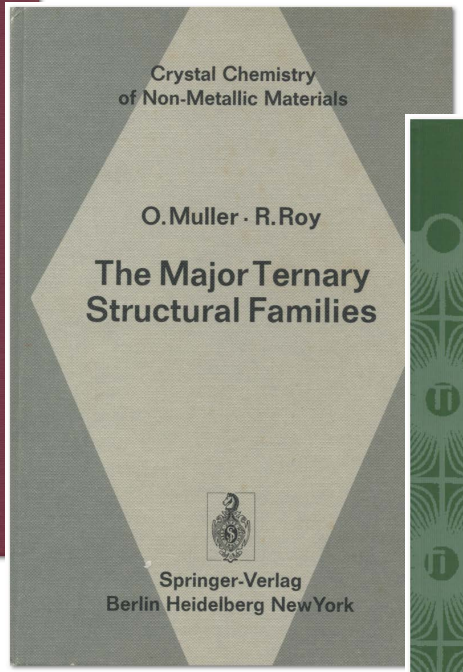
2. Counting electrons and simple electronic structures (largely avoiding transition metals)

3. Trends in the transition metals

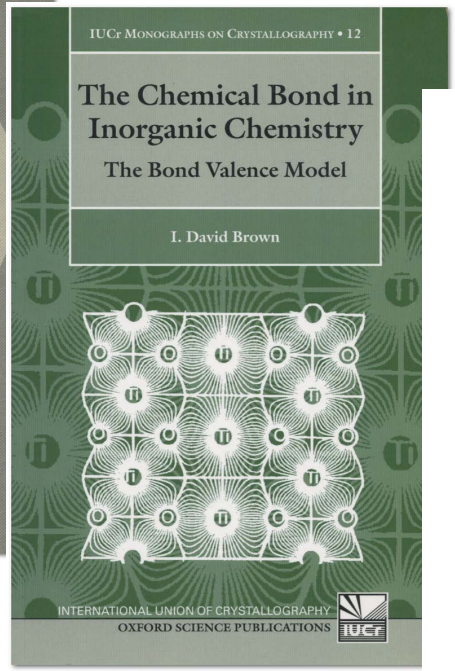
# My bookshelf



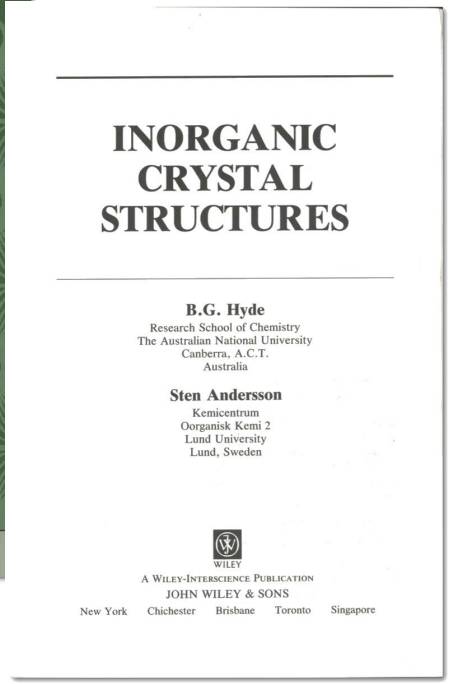

H. D. Megaw




O. Muller &
R. Roy

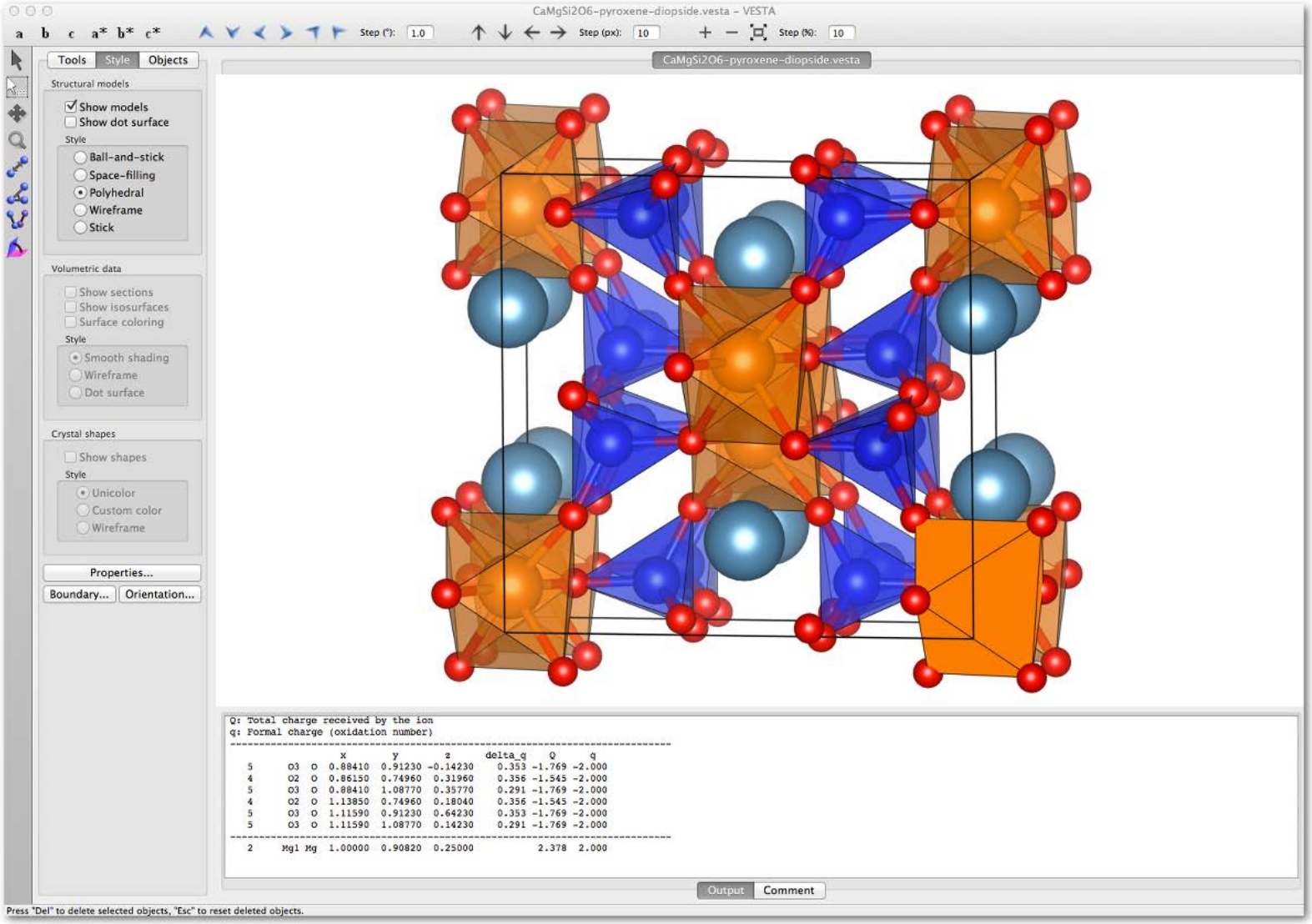



I. D. Brown




B. G. Hyde &
S. Andersson

# Software: ICSD + VESTA




Momma , Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Cryst*. **44** (2011) 1272–1276. [doi:10.1107/S0021889811038970]

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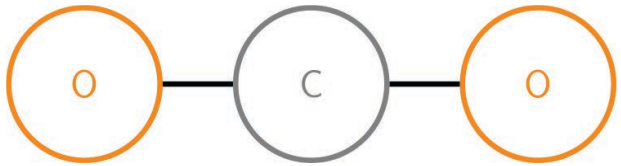
# Crystal structures of simple oxides [containing a single cation site]

# Crystal structures of simple oxides [containing a single cation site]

N.B.: CoO is simple, $Co_3O_4$ is not. $ZnCo_2O_4$ is certainly not !
$Co_3O_4$ and $ZnCo_2O_4$ are complex oxides.

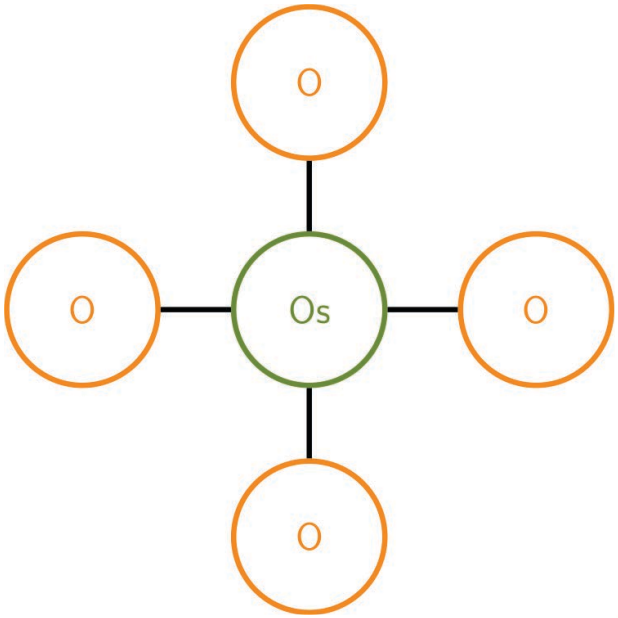
Graphs of connectivity in crystals: Atoms are nodes and edges (the lines that connect nodes) indicate short (near-neighbor) distances.

$CO_2$: The molecular structure is O=C=O. The graph is:
Each C connected to 2 O, each O connected to a 1 C



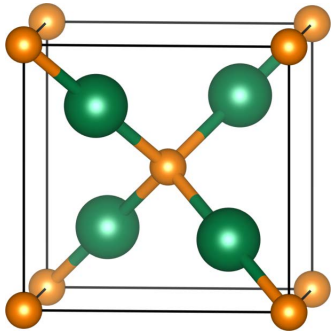

$OsO_4$: The structure comprises isolated tetrahedra (molecular). The graph is below:
Each Os connected to 4 O and each O to 1 Os

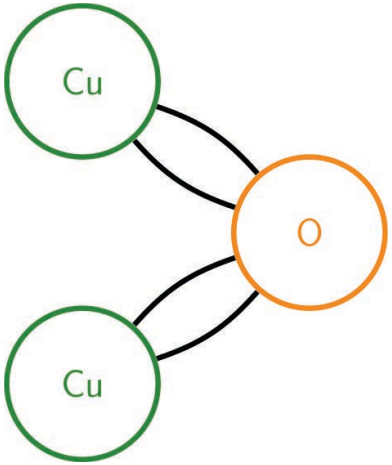
LaTeX and Ti*k*Z for the structural graphs



# Crystal structures of simple oxides of monovalent ions: $A_2O$

## $Cu_2O$

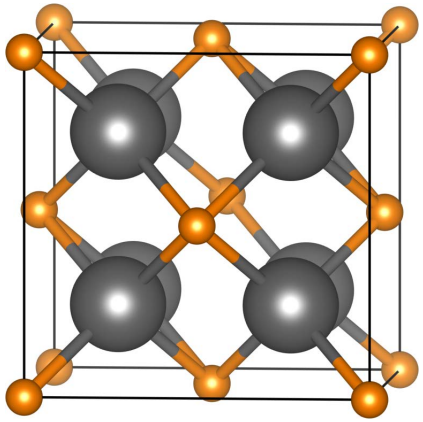


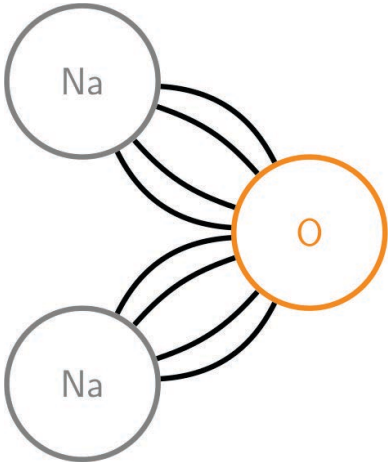



Linear coordination is unusual. Found usually in $Cu^+$ and $Ag^+$.

*All structures in this presentation are drawn to the same relative scale.*

## $Na_2O$ (anti-fluorite)

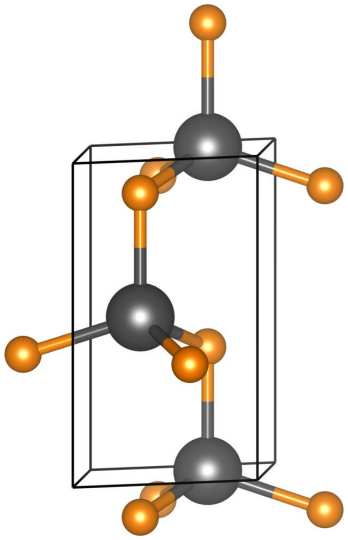


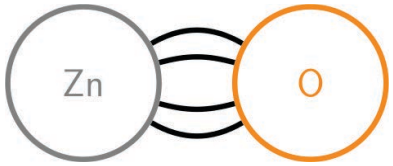



4-coordination for $Na^+$ and 8-coordination for $O^{2-}$ are unusual.

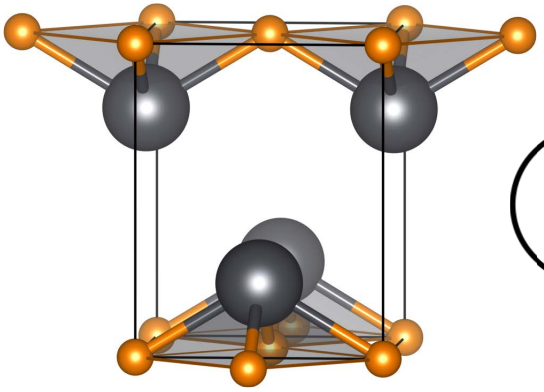
# Crystal structures of simple oxides of divalent ions: *AO*

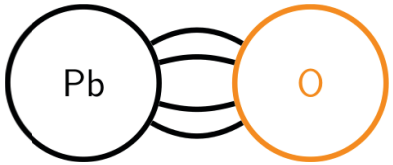
## ZnO (wurtzite), $sp^3$



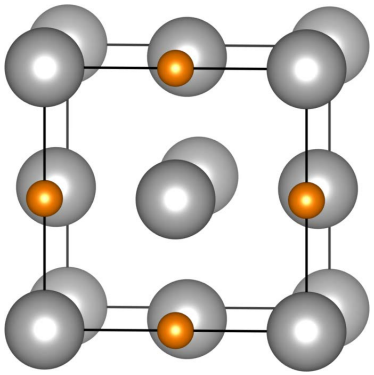


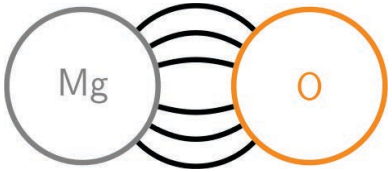

## PbO (litharge), lone pairs






## MgO (rock-salt)



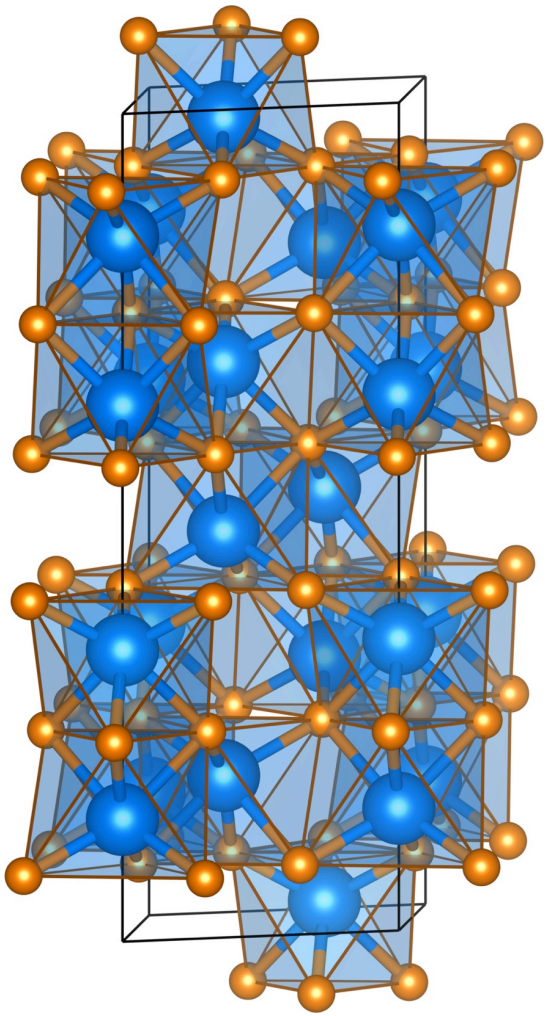


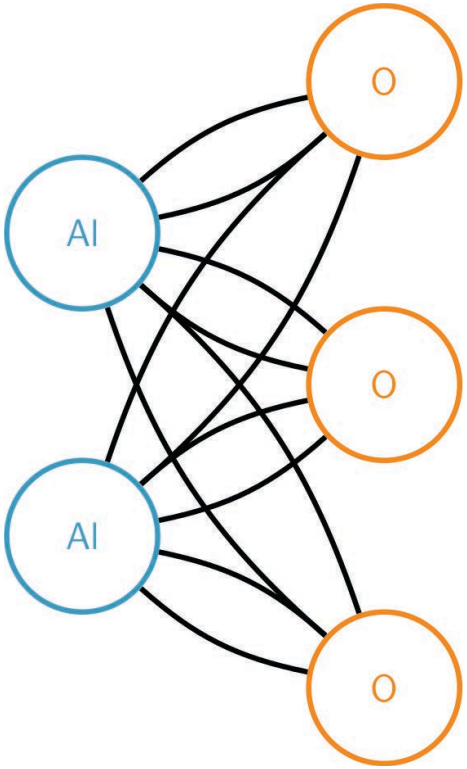

Ubiquitous for AO oxides including transition metals (distorted for CuO and NbO).

Insulators, metals (TiO), magnetic, …

# Crystal structures of simple oxides. $Al_2O_3$ as an example of a sesquioxide

$\alpha$-$Al_2O_3$ (corundum)





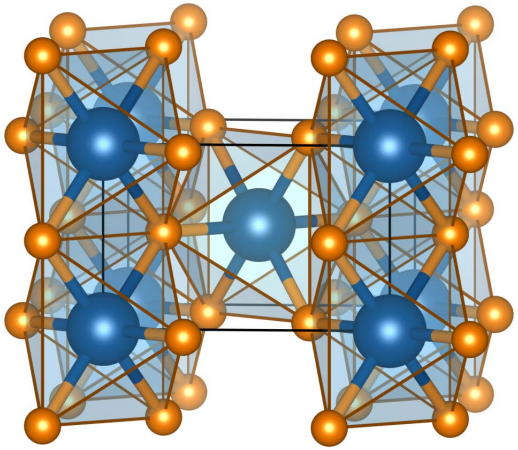

Also the structure of $Cr_2O_3$ and $Fe_2O_3$.

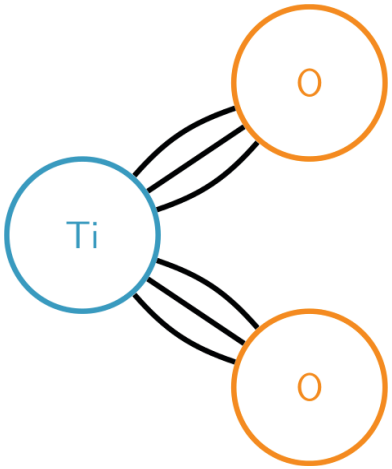
$Ga_2O_3$ does funny things.

$In_2O_3$ is different (bixbyite).

# Crystal structures of simple oxides of tetravalent ions: $AO_2$

## $TiO_2$ (rutile)

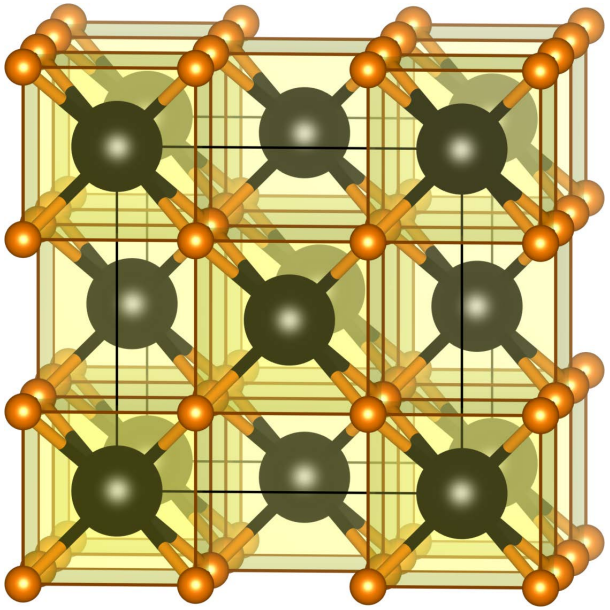


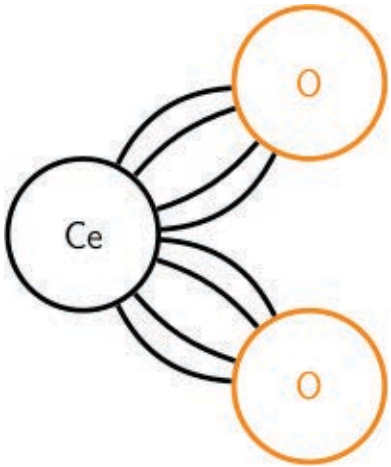



$TiO_2$ also crystallizes as anatase and brookite.

$SiO_2$ takes on this structure, and can be quenched to it, (stishovite) under pressure.

## $CeO_2$ (fluorite)



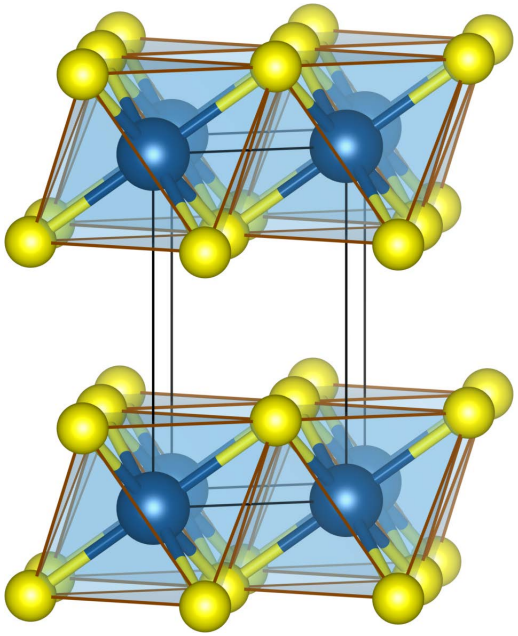



Also the structure of $ThO_2$, and of $ZrO_2$ and $HfO_2$ at elevated temperatures.

Ordered variants abound.

# Oxides versus sulfides: $TiS_2$

$2H–TiS_2$

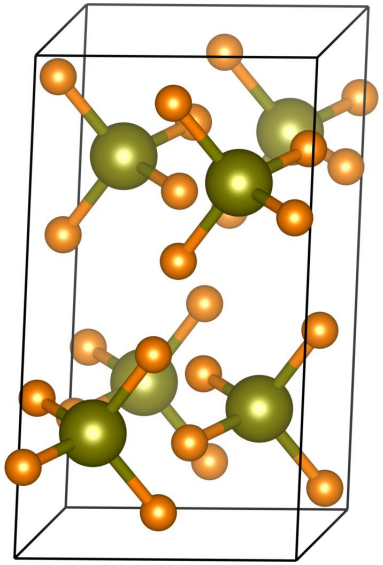


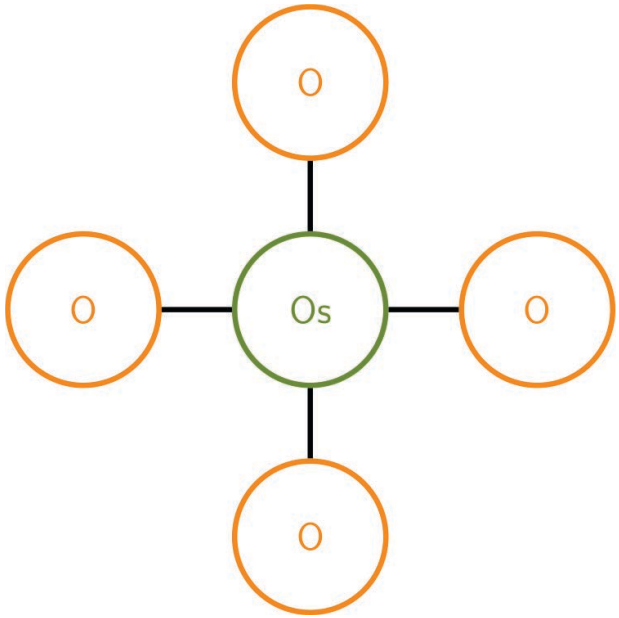
van der Waals gap (unlikely in oxides or fluorides, but occurs frequently in hydroxides)

This is the $CdI_2$ structure.

# Crystal structures of an oxide with an octavalent ion: $OsO_4$

$OsO_4$



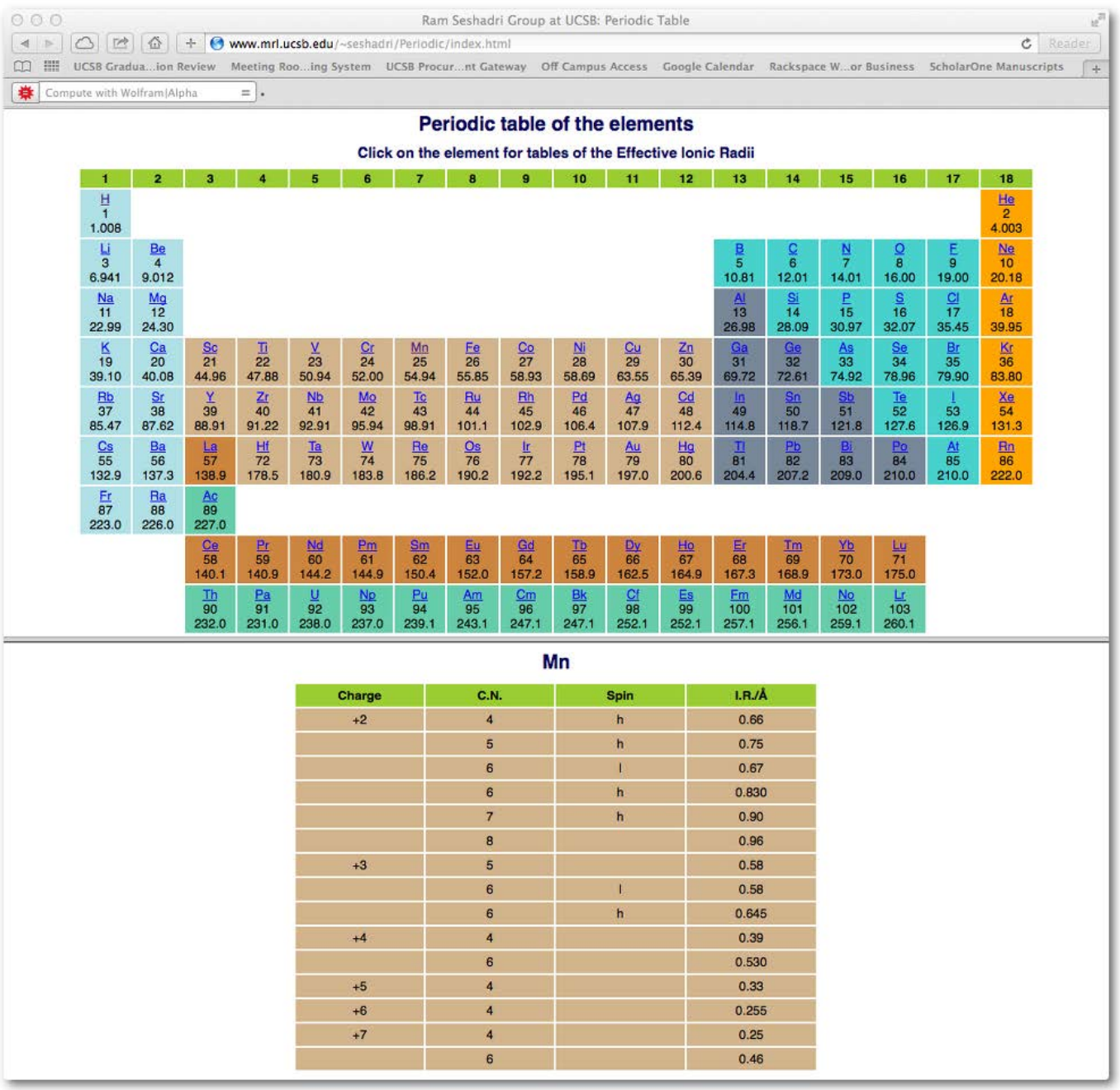


# Shannon-Prewitt effective ionic radii

Radii assigned by systematically examining cation-anion pairs in oxides, fluorides etc.

May not work for other kinds of compounds

Be sensitive to coordination number and spin state




**www.mrl.ucsb.edu/~seshadri/Periodic/index.html**

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# Ionic radii and Pauling's first rule (the radius ratio rule)

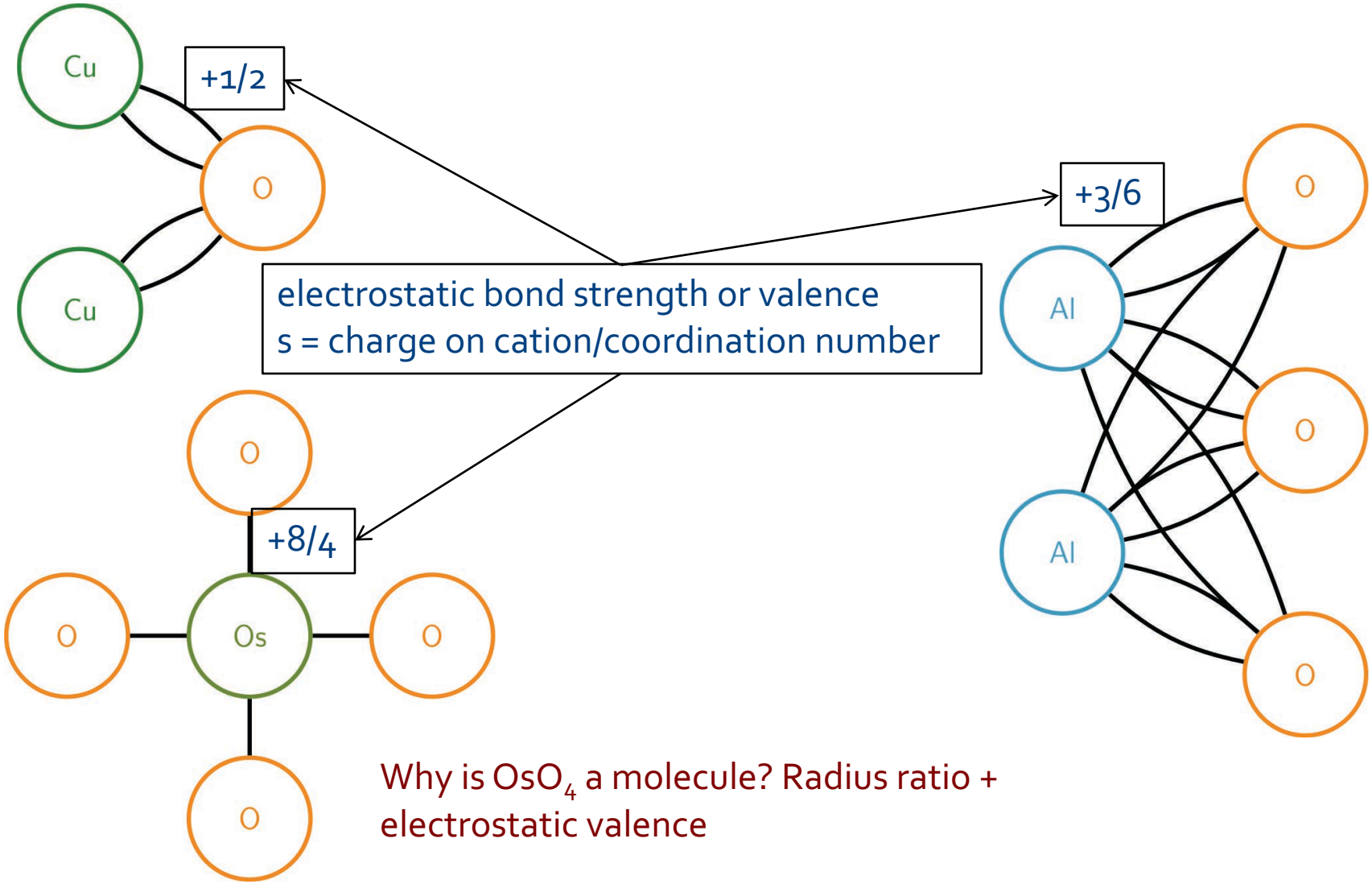
In brief: The cation-anion distance is the sum of cation and anion radii, and the number of anions around a cation (the coordination number) is a function of the radius ratio. Exemplified by $AO_2$ compounds below. MRR is the mimimum radius ratio.

| Compound | $r_C$ (Å) | $r_C + r_O$ (Å) | $r_C/r_O$ | Coordination | MRR |
|---|---|---|---|---|---|
| $CO_2$ | $-0.19(?)$ | 1.16 (exp.) | ? | 2 | |
| $SiO_2$ | 0.26 | 1.61 | 0.19 | 4 | 0.225 |
| $TiO_2$ | 0.605 | 1.955 | 0.45 | 6 | 0.414 |
| $CeO_2$ | 0.97 | 2.32 | 0.72 | 8 | 0.732 |

Pauling, The Nature of the Chemical Bond, 3rd Edn.
Cornell University Press, Ithaca 1960

# Pauling's second rule: The electrostatic valence rule

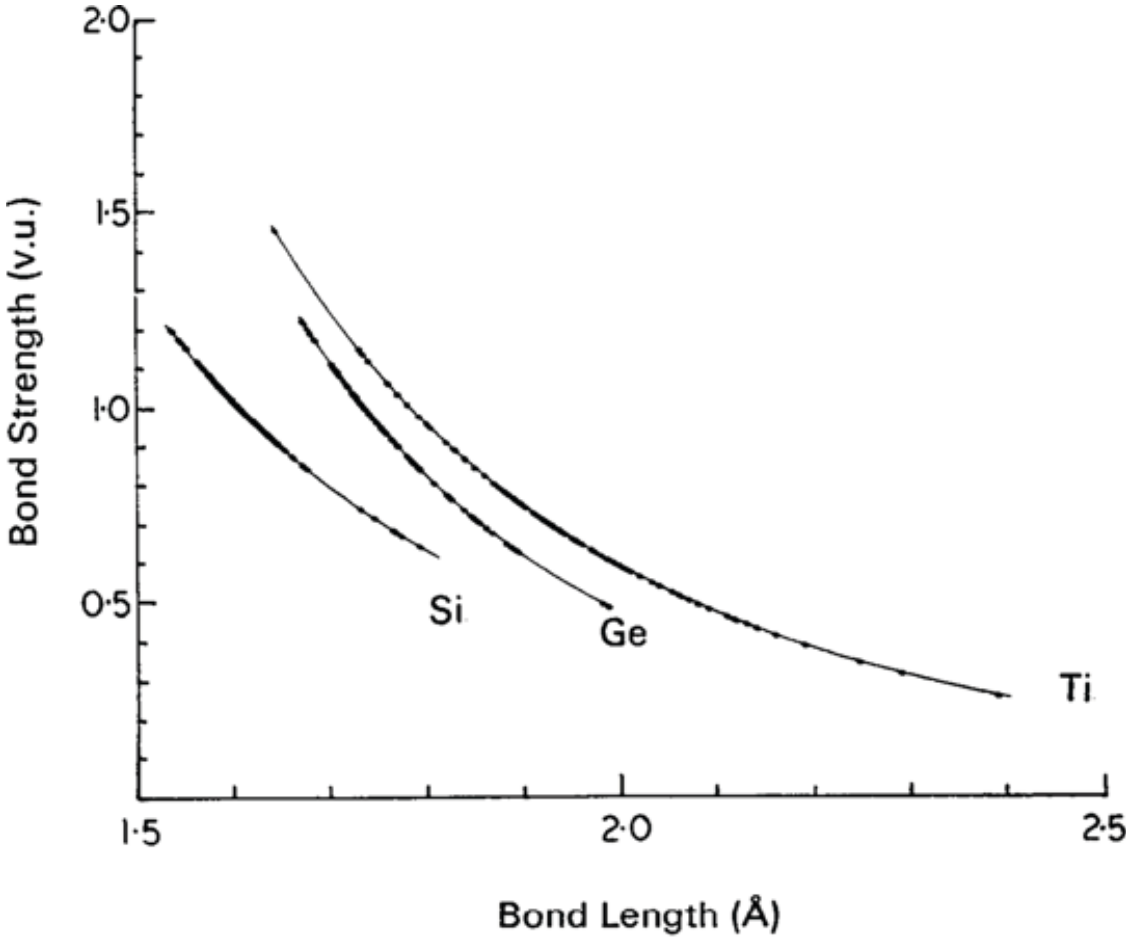
In brief: Charges going out from cations should balance anions and vice-versa




Why is $OsO_4$ a molecule? Radius ratio + electrostatic valence

# Electrostatic valence and bond valence

Pauling, and later Brown and Shannon, noted that the Pauling bond strength (the electrostatic valence) correlates very well with distance for many oxides: Short bonds (distances) correpond to strong bonds and vice-versa




Brown, Shannon, Empirical bond-strength-bond-length curves for oxides, *Acta Cryst. A* **29** (1973) 266–281

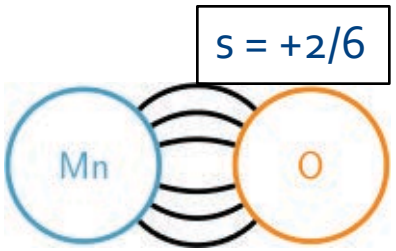
# Electrostatic valence and bond valence

The modern bond valence relationship:

$$s = \exp\left(\frac{R_0 - R}{B}\right)$$

Where s is the strength of the bond, $R$ is the cation to anion distance, and $R_0$ and $B \approx 0.37$ Å are parametrized for the specific ion pair.

When all s are calculated: $\sum_{\mathrm{CN}} s =$ valence of the ion




For $Mn^{2+}$–$O^{2-}$, $R_0 = 1.790$ Å, $B = 0.37$ Å.

This means $R = 2.20$ Å.
experiment: 2.22 Å

Brown, Shannon, Empirical bond-strength-bond-length curves for oxides, *Acta Cryst. A* **29** (1973) 266–281

# Electrostatic valence and bond valence: Parameters for Mn

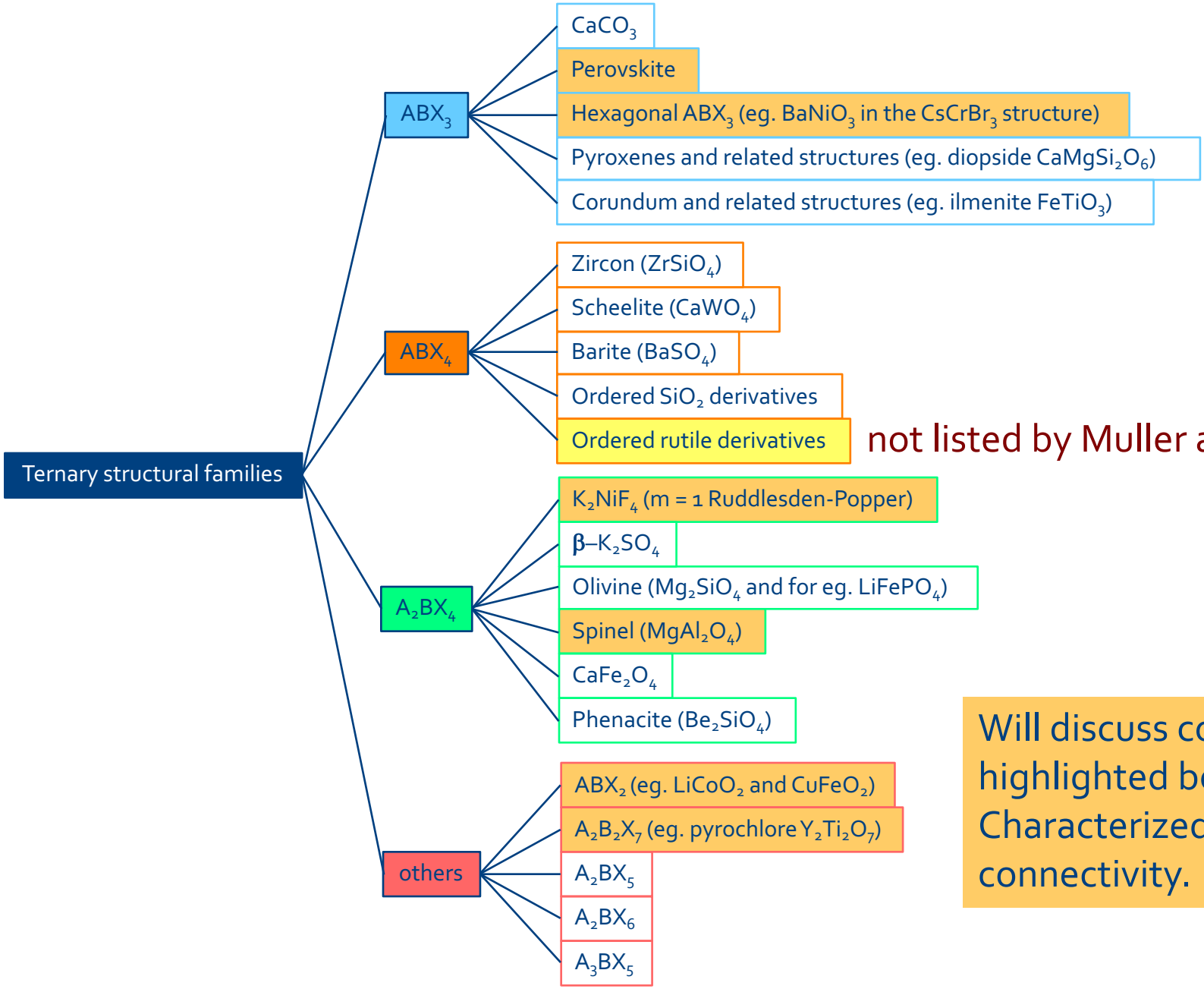
| | | | | | |
|---|---|---|---|---|---|
| Mn | 2 | O | −2 | 1.790 | 0.37 | a |
| Mn | 2 | O | −2 | 1.765 | 0.37 | j |
| Mn | 2 | S | −2 | 2.22 | 0.37 | e |
| Mn | 2 | F | −1 | 1.698 | 0.37 | a |
| Mn | 2 | Cl | −1 | 2.133 | 0.37 | a |
| Mn | 2 | Br | −1 | 2.34 | 0.37 | e |
| Mn | 2 | I | −2 | 2.52 | 0.37 | e |
| Mn | 2 | N | −3 | 1.849 | 0.37 | j |
| Mn | 2 | N | −3 | 1.65 | 0.35 | e |
| Mn | 3 | O | −2 | 1.760 | 0.37 | a |
| Mn | 3 | O | −2 | 1.732 | 0.37 | j |
| Mn | 3 | F | −1 | 1.66 | 0.37 | b |
| Mn | 3 | Cl | −1 | 2.14 | 0.37 | b |
| Mn | 3 | N | −3 | 1.837 | 0.37 | j |
| Mn | 4 | O | −2 | 1.753 | 0.37 | a |
| Mn | 4 | O | −2 | 1.750 | 0.37 | j |
| Mn | 4 | F | −1 | 1.71 | 0.37 | b |
| Mn | 4 | F | −1 | 1.63 | 0.37 | e |
| Mn | 4 | Cl | −1 | 2.13 | 0.37 | b |
| Mn | 4 | N | −3 | 1.822 | 0.37 | j |
| Mn | 6 | O | −2 | 1.79 | 0.37 | e |
| Mn | 7 | O | −2 | 1.827 | 0.37 | e |
| Mn | 7 | O | −2 | 1.79 | 0.37 | b |
| Mn | 7 | F | −1 | 1.72 | 0.37 | b |
| Mn | 7 | Cl | −1 | 2.17 | 0.37 | b |

**bvsparm.cif**

Brown, Shannon, Empirical bond-strength-bond-length curves for oxides, *Acta Cryst. A* **29** (1973) 266–281

# Crystal structures of some complex oxides [containing two or more cation sites]

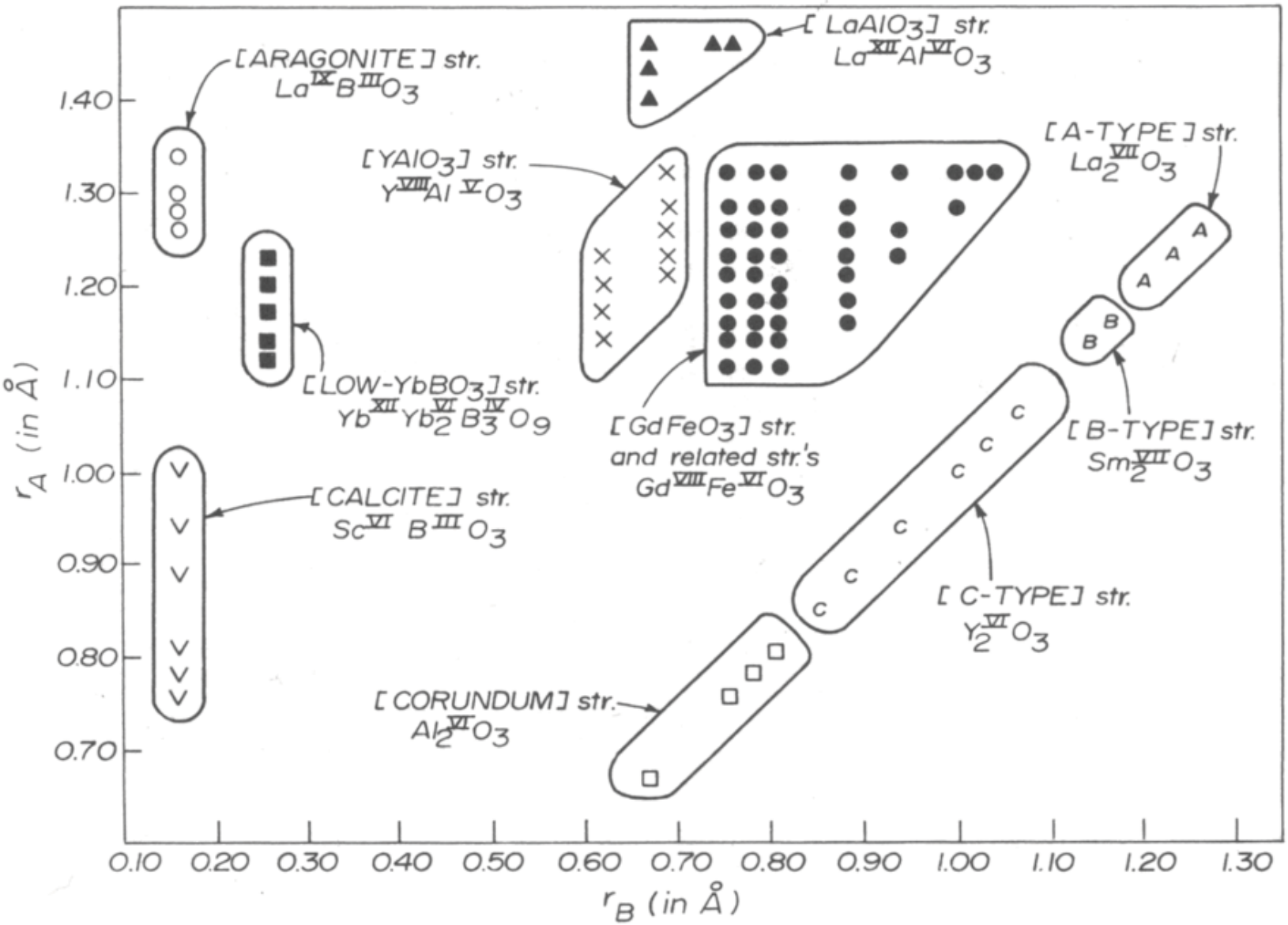
# The major ternary structural families (Muller and Roy, page 3, redrawn and modified)




not listed by Muller and Roy

Will discuss compounds in highlighted boxes: Characterized by dense connectivity.

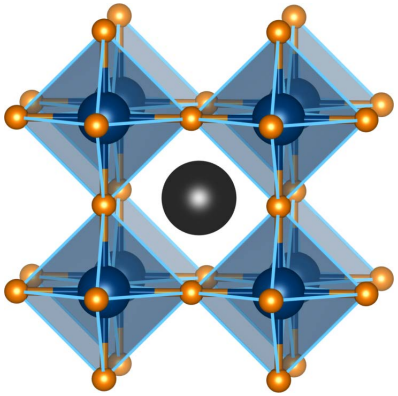
# The $ABO_3$ structure-sorting field (from Muller and Roy)

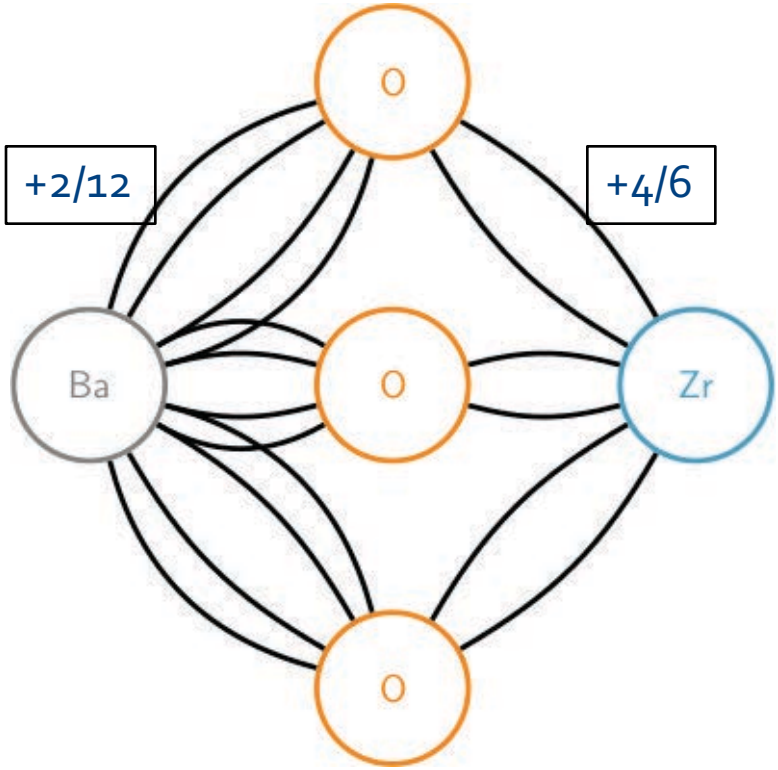



The superscripted roman numerals indicate coordination number.

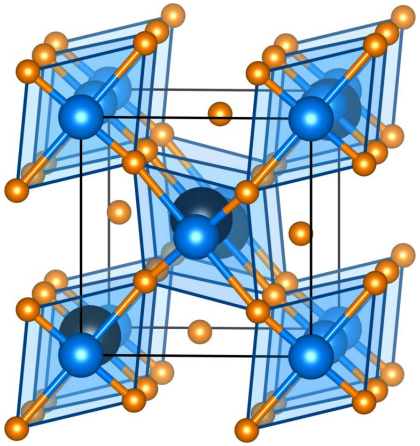
# Perovskite

$BaZrO_3$






$LaMnO_3$ Pnma
(Jahn-Teller distorted)



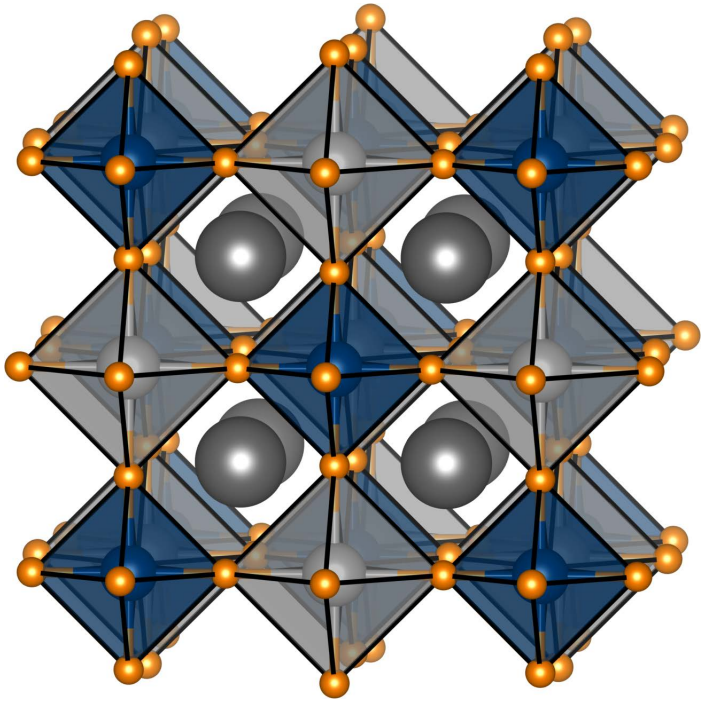
Note that the space group *Pnma* (#62) can be written in a variety of ways.

This is the most common perovskite space group.

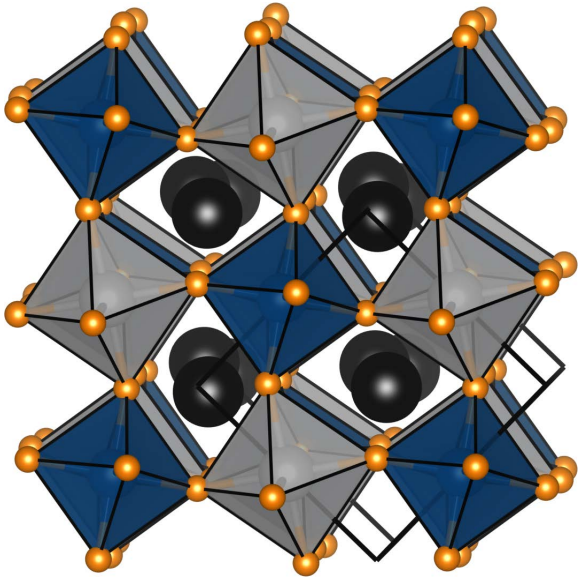
In the next so many structures, $BO_6$-polyhedra are depicted.

# Ordered double perovskites (elpasolites)

$Ba_2MgWO_6$



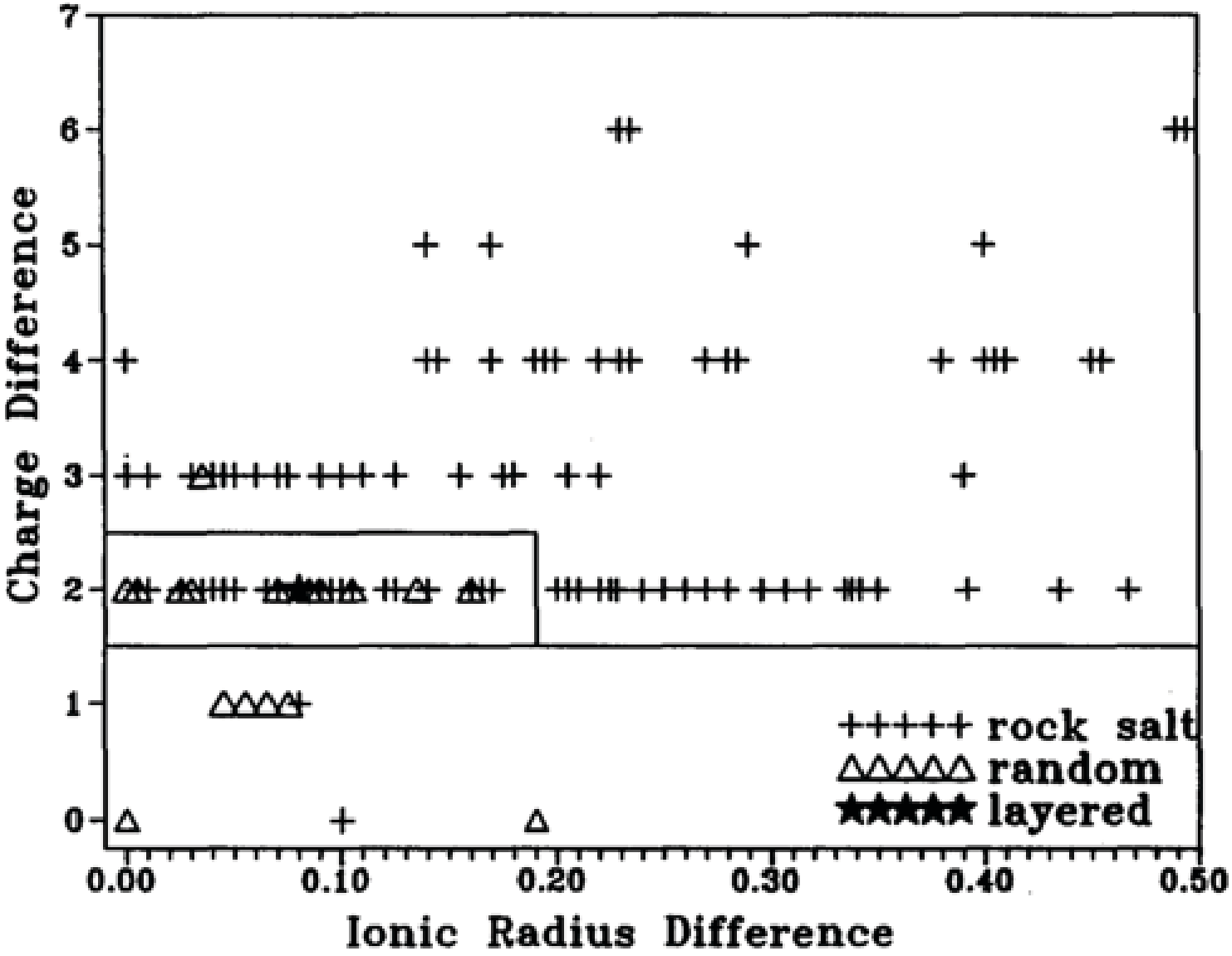
$Ca_2MgWO_6$



Rock-salt like ordering of dissimilar octahedra. Space group same as rock-salt: *Fm*–3*m*

Smaller A-ions associated with tilting as in simple perovskites.

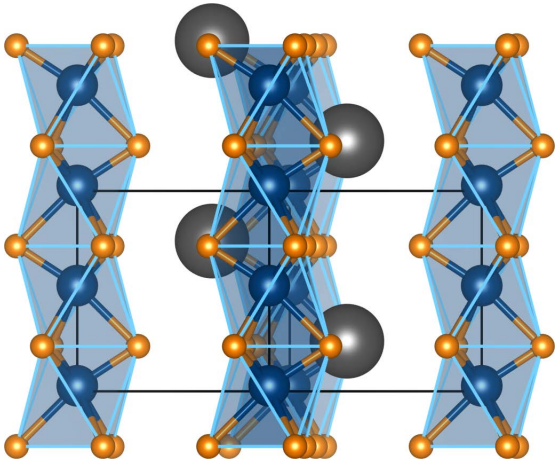
# The double perovskite field: Charge and radius



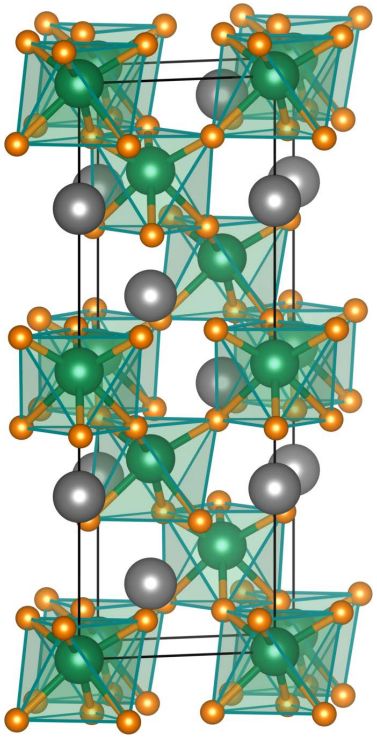

Anderson, Greenwood, Poeppelmeier, *Prog. Solid State Chem*. **22** (1993) 197–233.

# Hexagonal $ABO_3$ structures

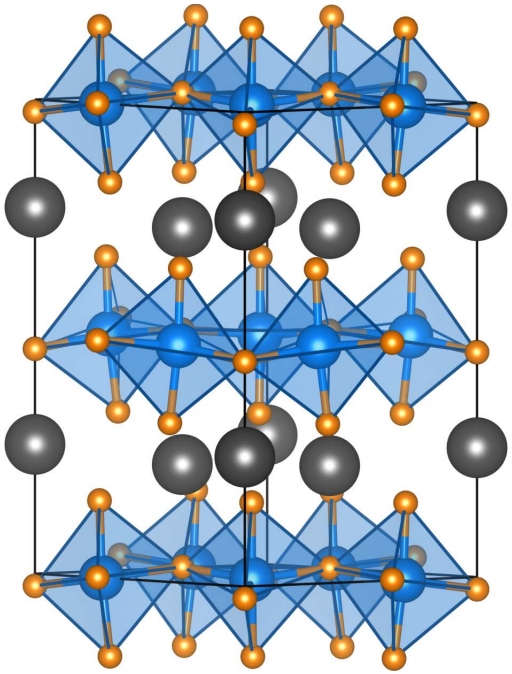
$BaNiO_3$



$LiNbO_3$ (ferroelectric $R3c$)



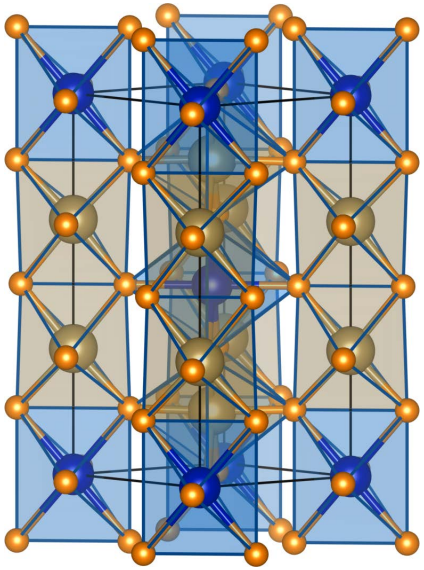
Ferroelectric $YMnO_3$ ("$YAlO_3$")



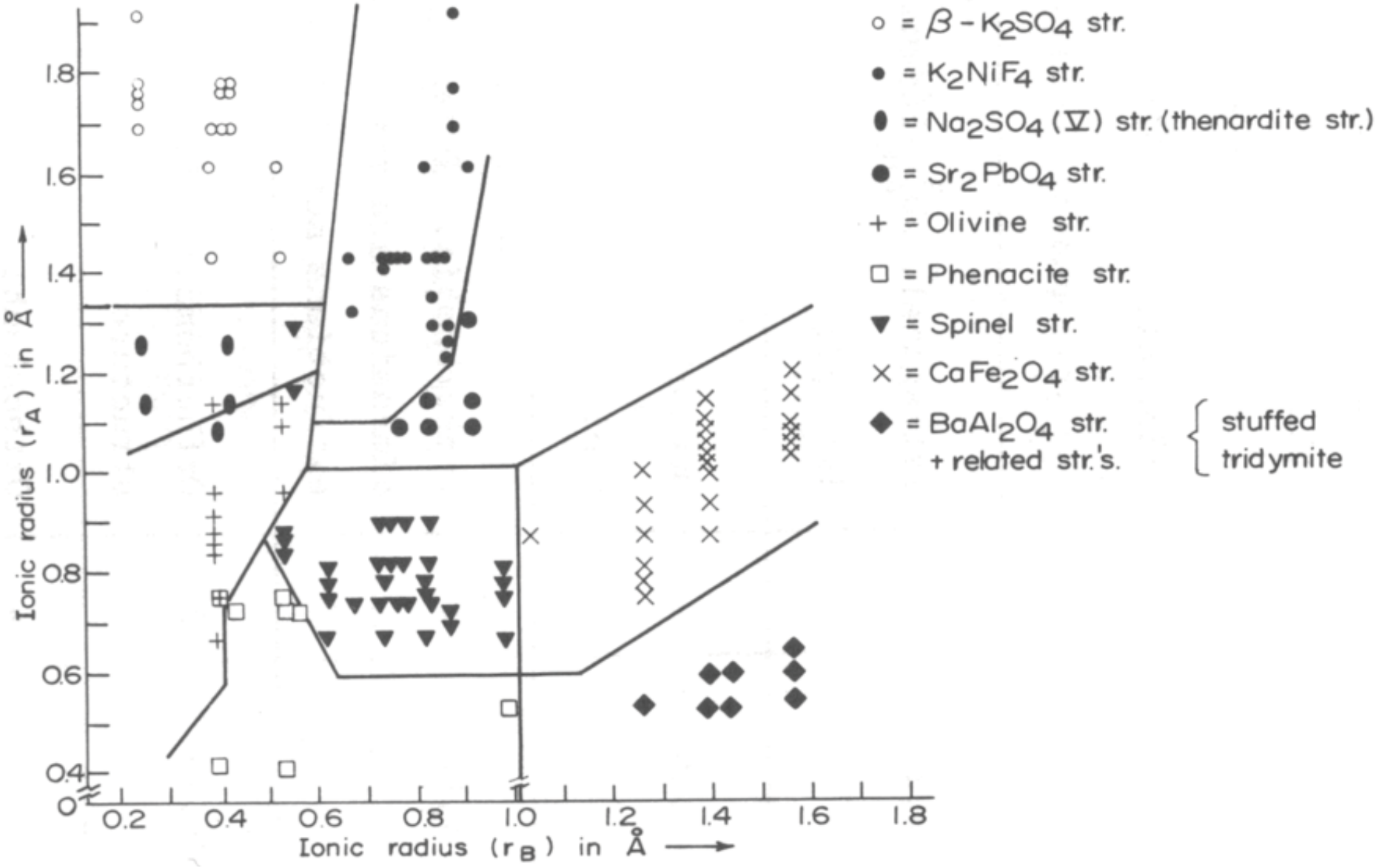
Unusual 5-fold coordination (trigonal bibyramid) of $MnO_5$

# Ordered rutiles (the trirutile)

$CoTa_2O_6$: $3 \times TiO_2 = Ti_3O_6$; $3 \times Ti^{4+} = Co^{2+} + 2 \times Ta^{5+}$



# The $A_2BO_4$ structure-sorting field (from Muller and Roy)

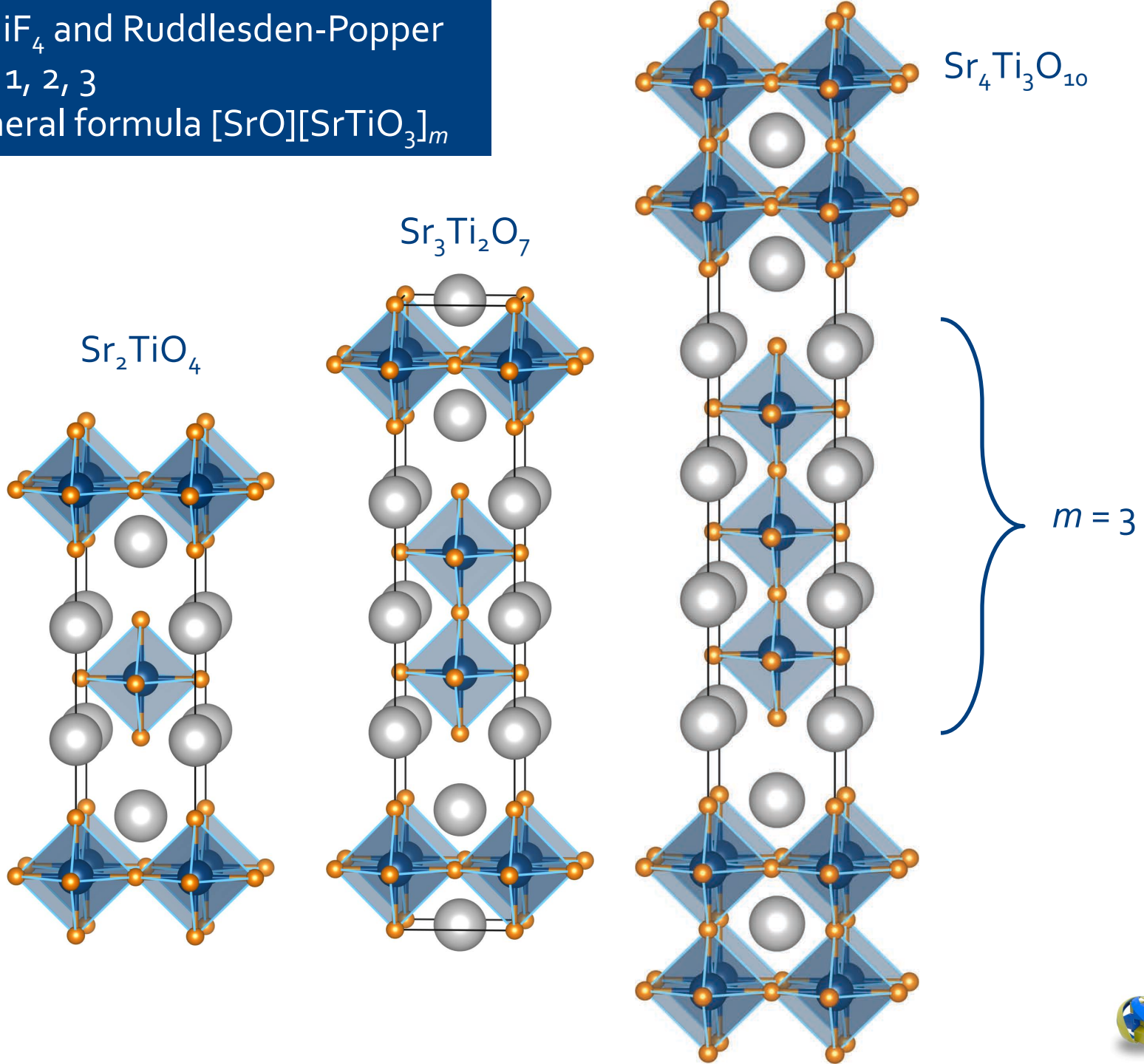



The superscripted roman numerals indicate coordination number.

# $K_2NiF_4$ and Ruddlesden-Popper

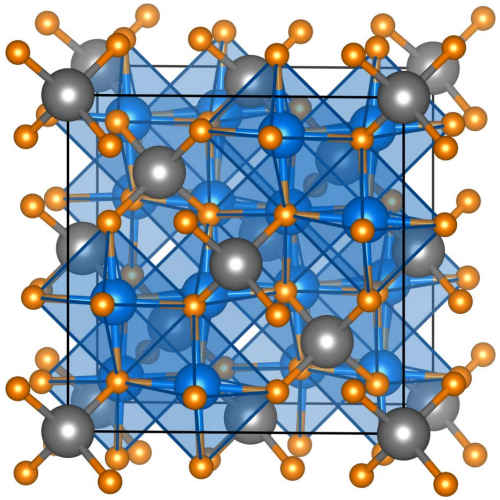
$m$ = 1, 2, 3

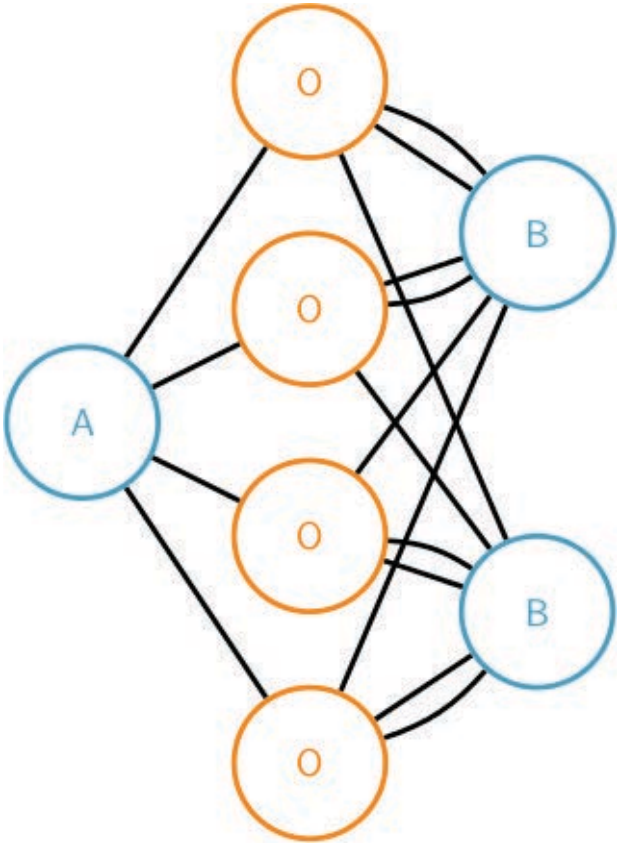
General formula $[SrO][SrTiO_3]_m$



# Spinel $AB_2O_4$

$MgAl_2O_4$



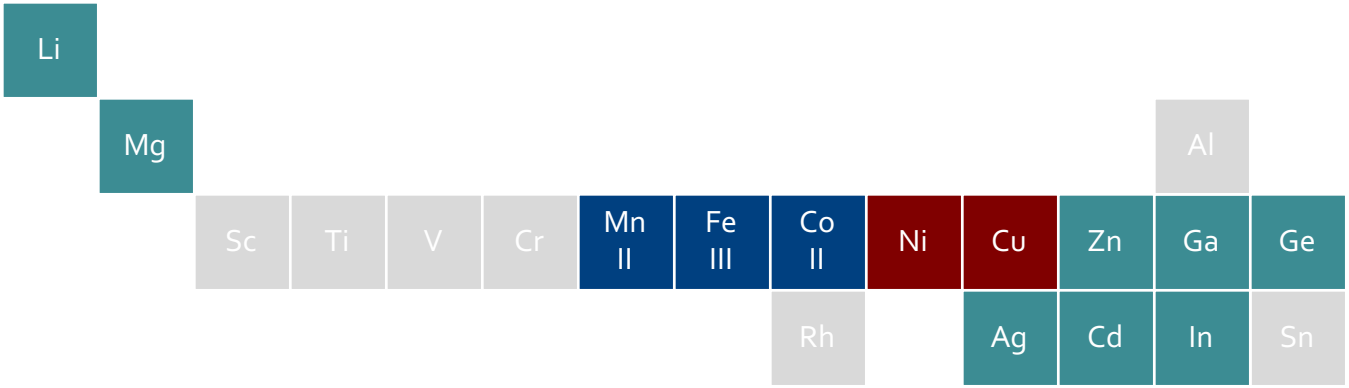



Ubiquitous structure when ions have similar sizes, around 0.6 Å.
*A* is tetrahedrally coordinated, and *B* octahedral (actually with a slight trigonal distortion).

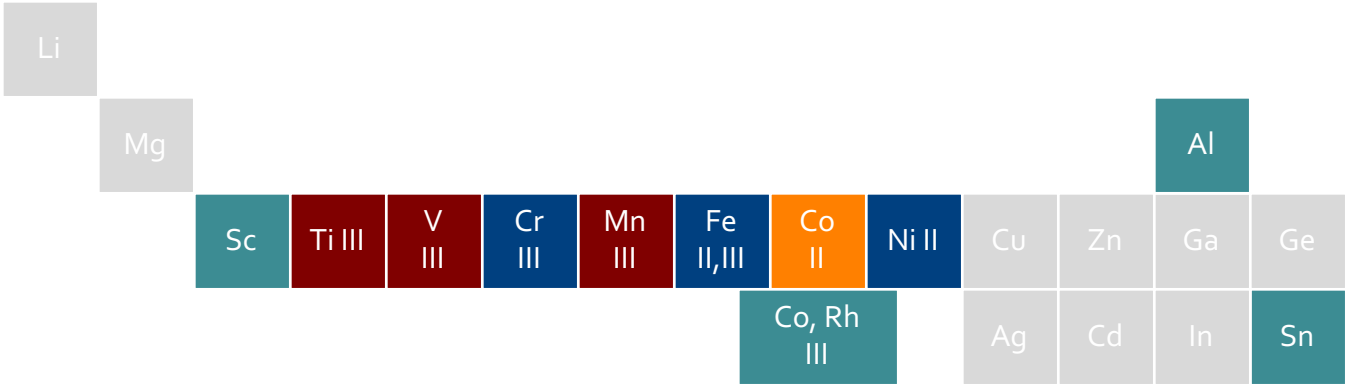
In general, lower oxidation states and smaller bandwidths than in perovskites.

# Spinel $AB_2O_4$

ions on the *A* site




ions on the *B* site




A,B Jahn-Teller active

A,B Diamagnetic

Co II High single-ion anisotropy

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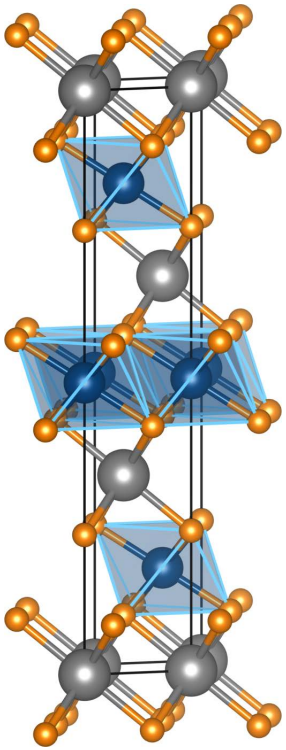
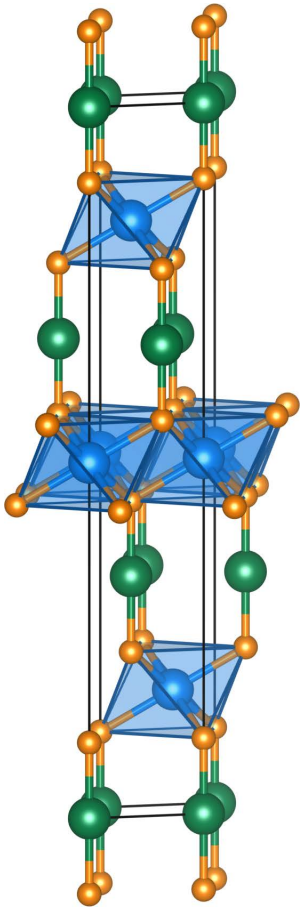
# Some $ABO_2$ structures: Highly dense in-plane, and frequently metallic

## $LiCoO_2$ (ordered rock-salt)



111-ordered with alternating octahedral $LiO_6$ and $CoO_6$ stacking

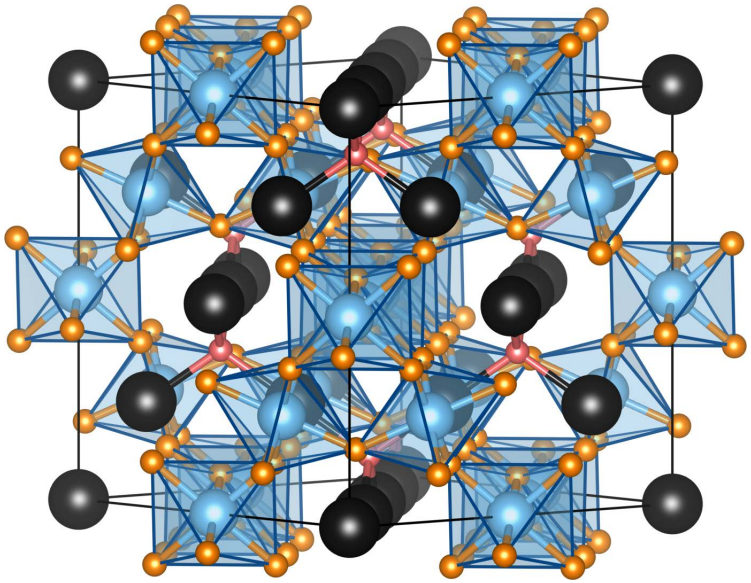
## $3R–CuFeO_2$ (delafossite)

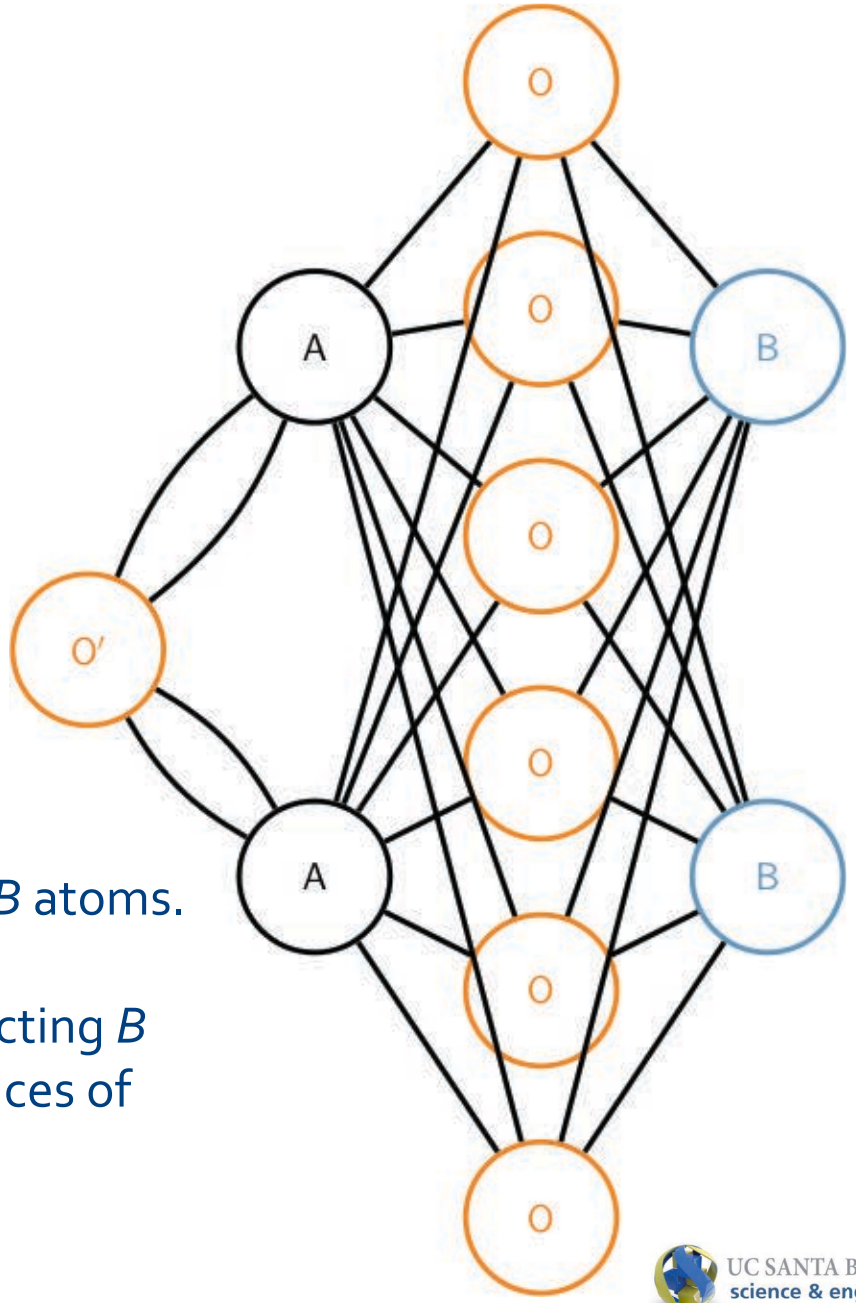


$BO_2$ ($CdI_2$) slabs separated by two-coordinate atoms, usually $Cu^+$ and $Ag^+$. Also unusually, $Pd^{1+}$ and $Pt^{1+}$.

# $A_2B_2O_7$ pyrochlore

$Y_2Ti_2O_7 = Y_2Ti_2O_6O'$





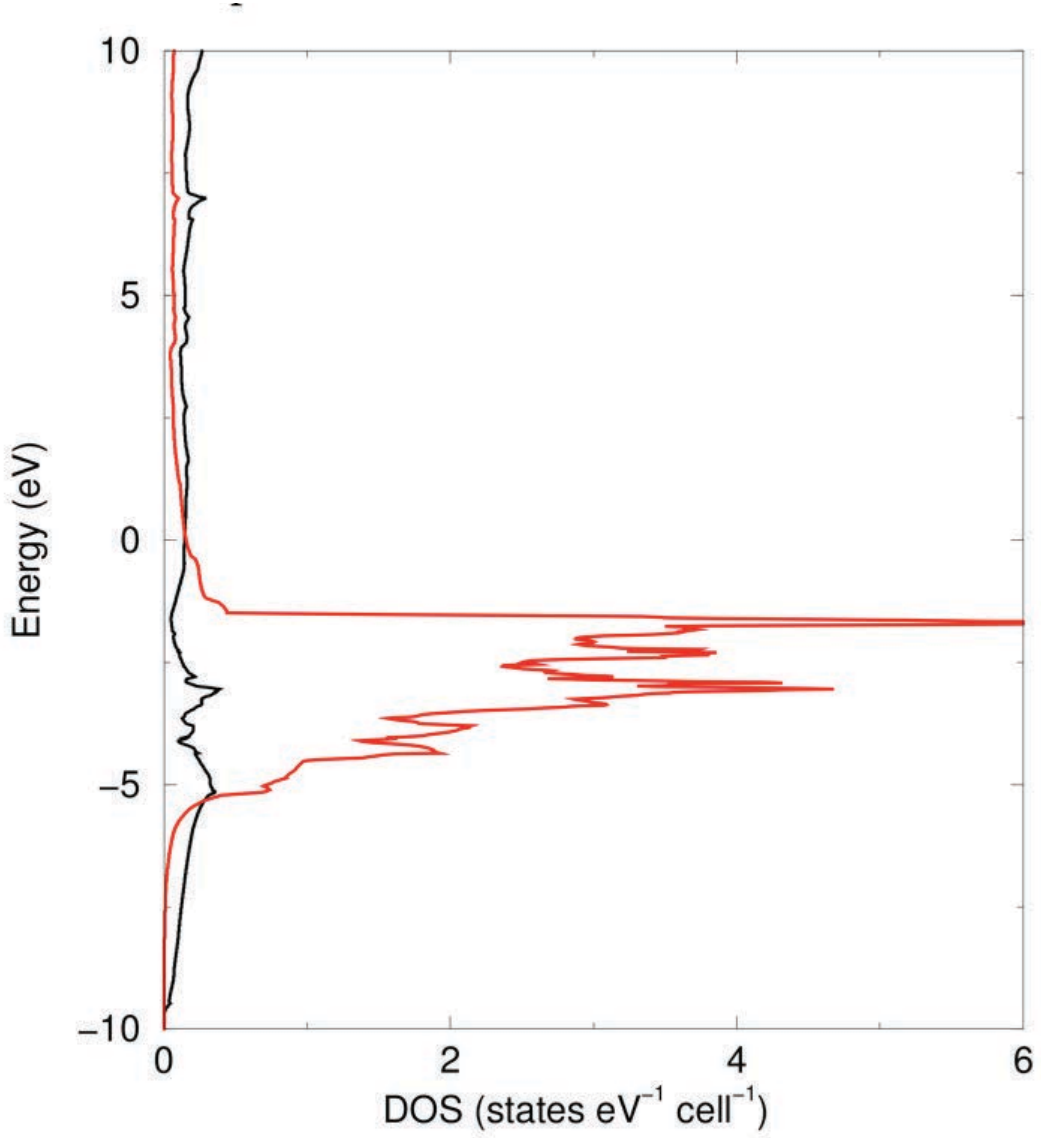

6+2-coordinate *A* atoms and 6-coordinate *B* atoms.

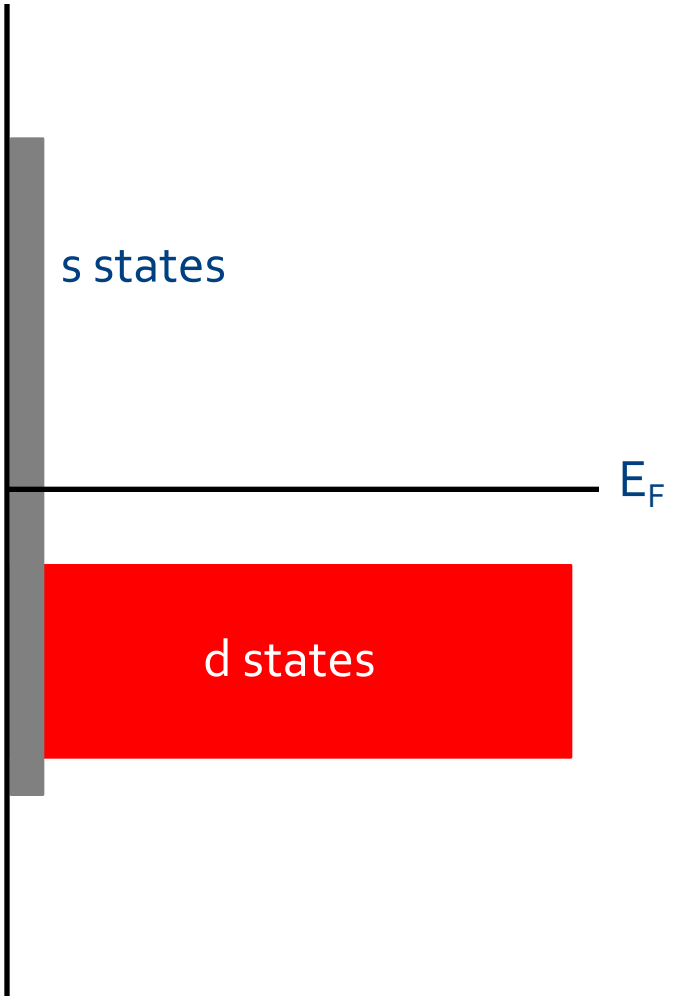
Separately, just connecting *A* or just connecting *B* yields two interpenetrating pyrochlore lattices of corner-connected tetrahedra.

# Counting electrons

# Some "real" electronic structures: Cu

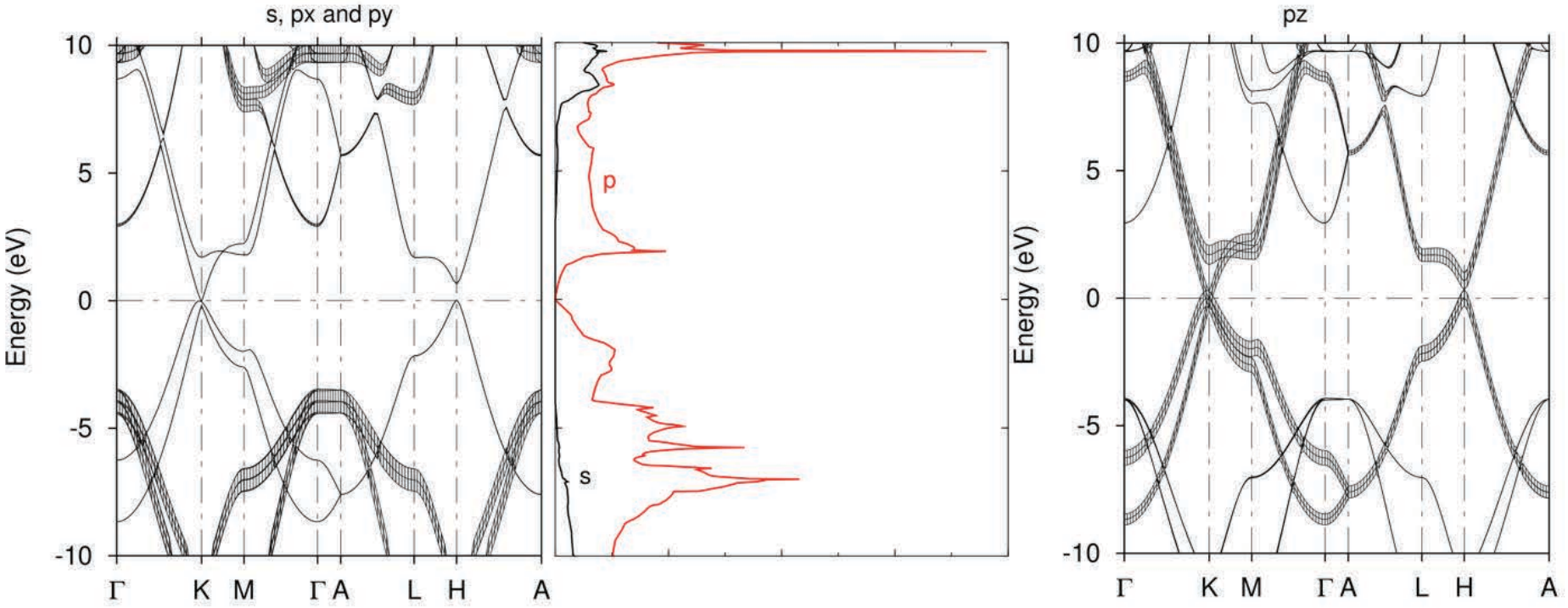
Cu is a metal with s states (black) at $E_F$. The red d states are close on hand and this is why Cu has a characteristic color that Ag does not.



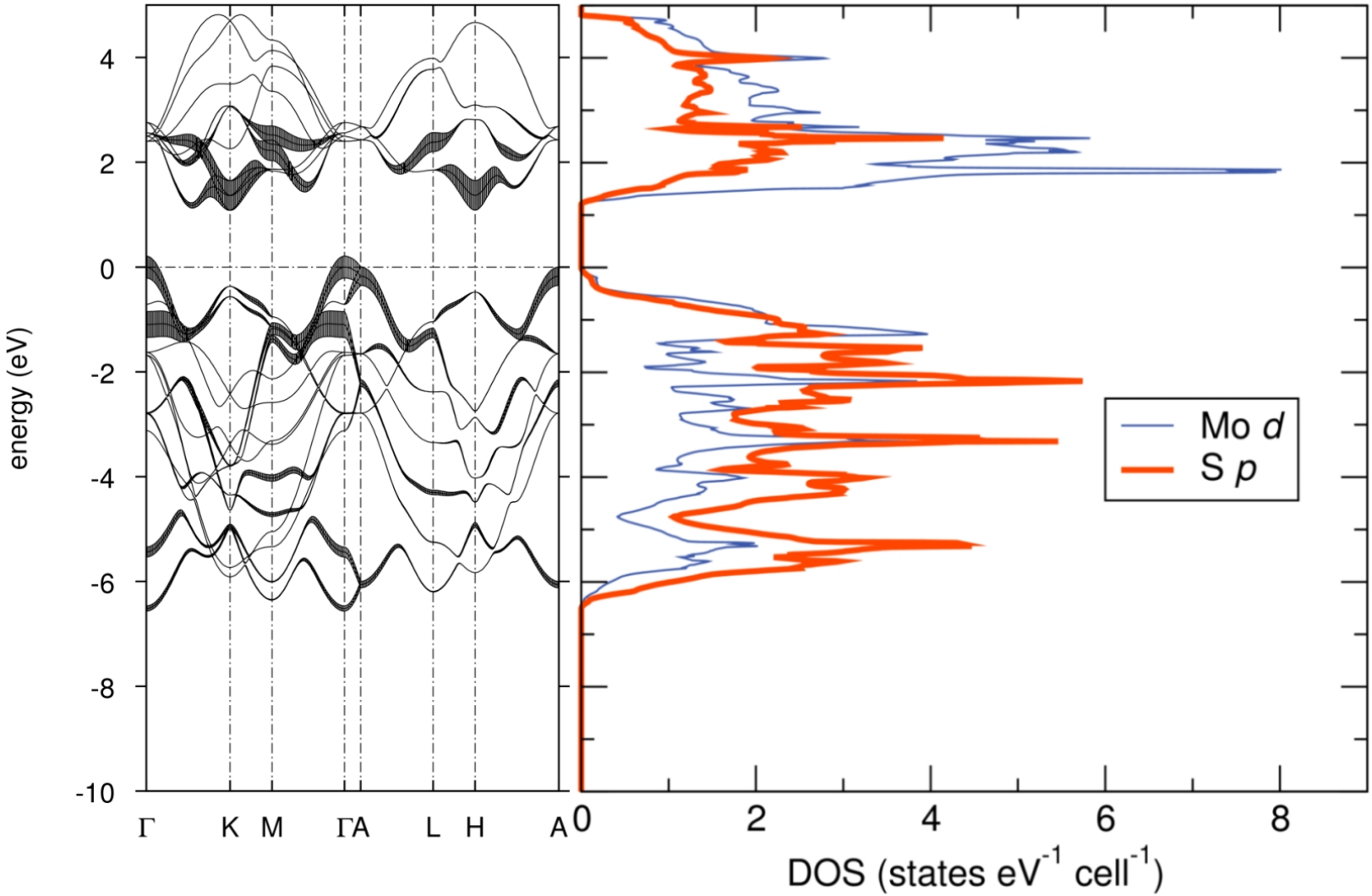
# Some "real" electronic structures: Graphite (a semi-metal)

The valence band and the conduction band just touch each other. Also, note the distinct difference in the electronic structure of the σ and π networks.

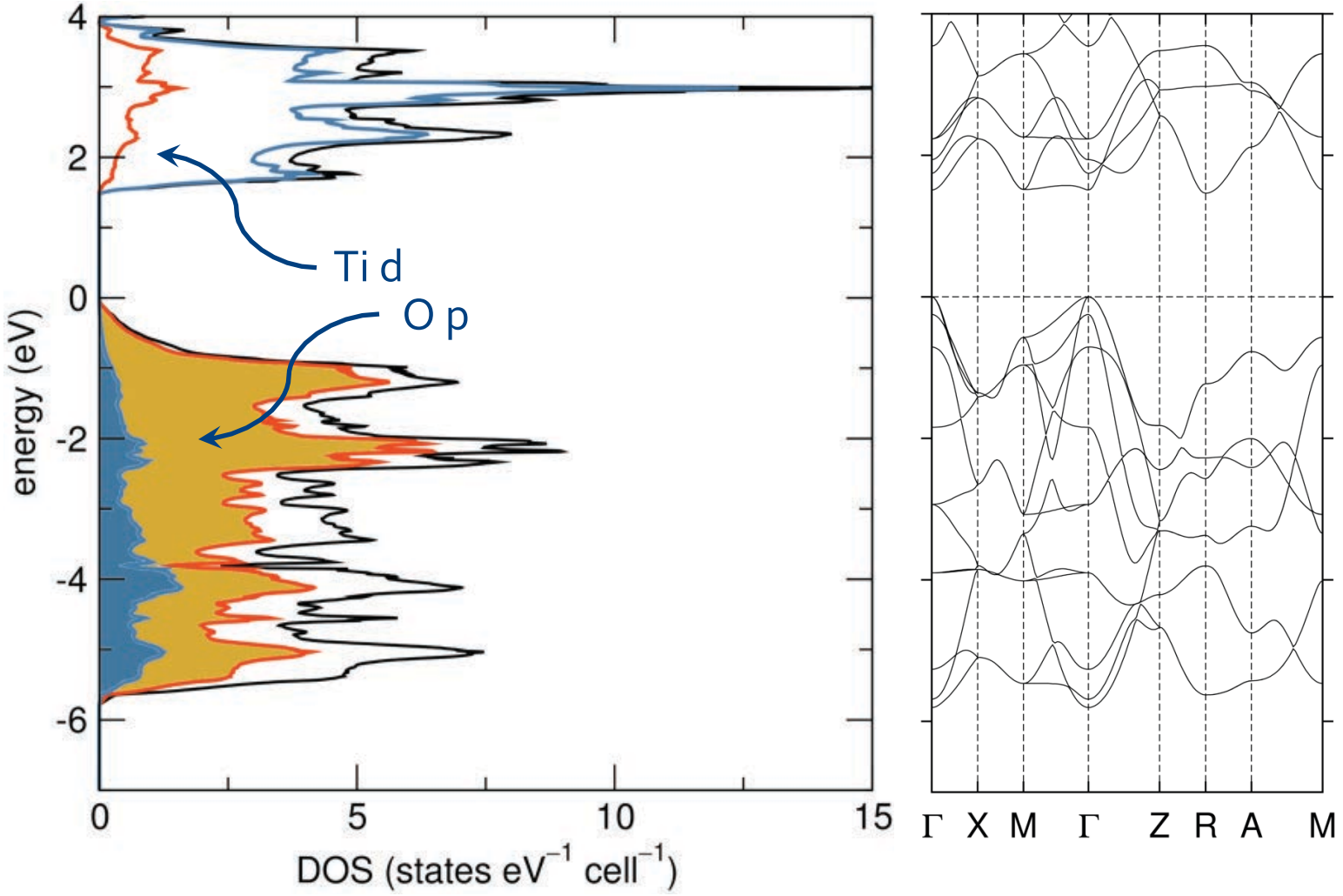


# Some "real" electronic structures: $MoS_2$ a $d^2$ semiconductor

$MoS_6$ prisms allow a crystal-field gap between the filled $d_{z^2}$ and the rest of the d states. Structure matters !

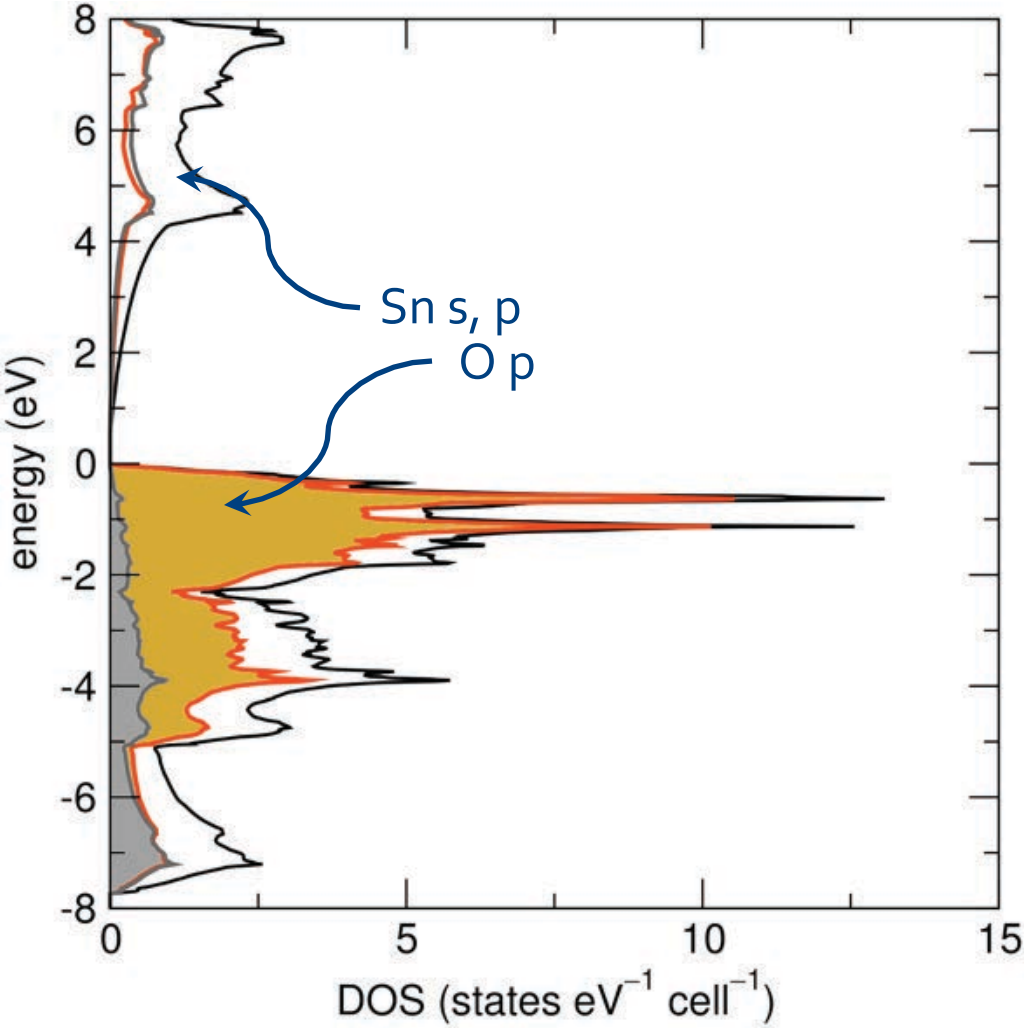


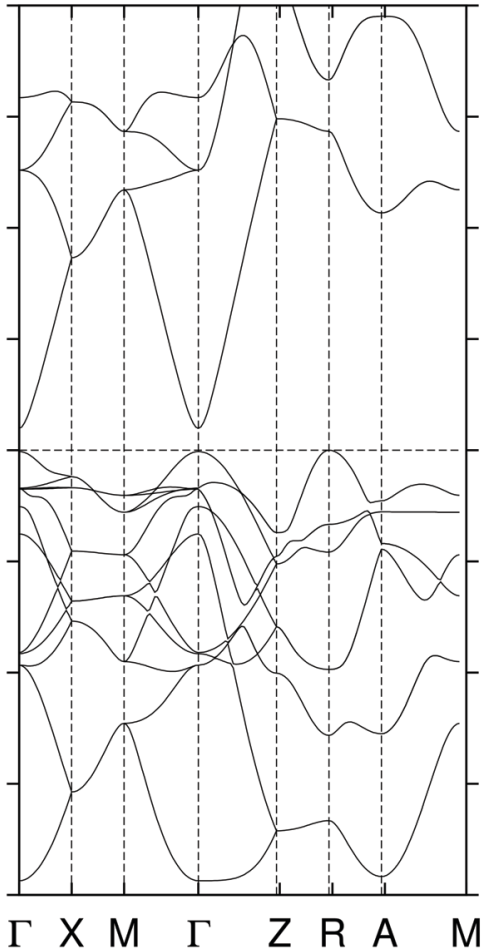
# Counting electrons in $TiO_2$: Assign as $Ti^{4+}$ and $O^{2-}$




Insulator, not so easy to dope.

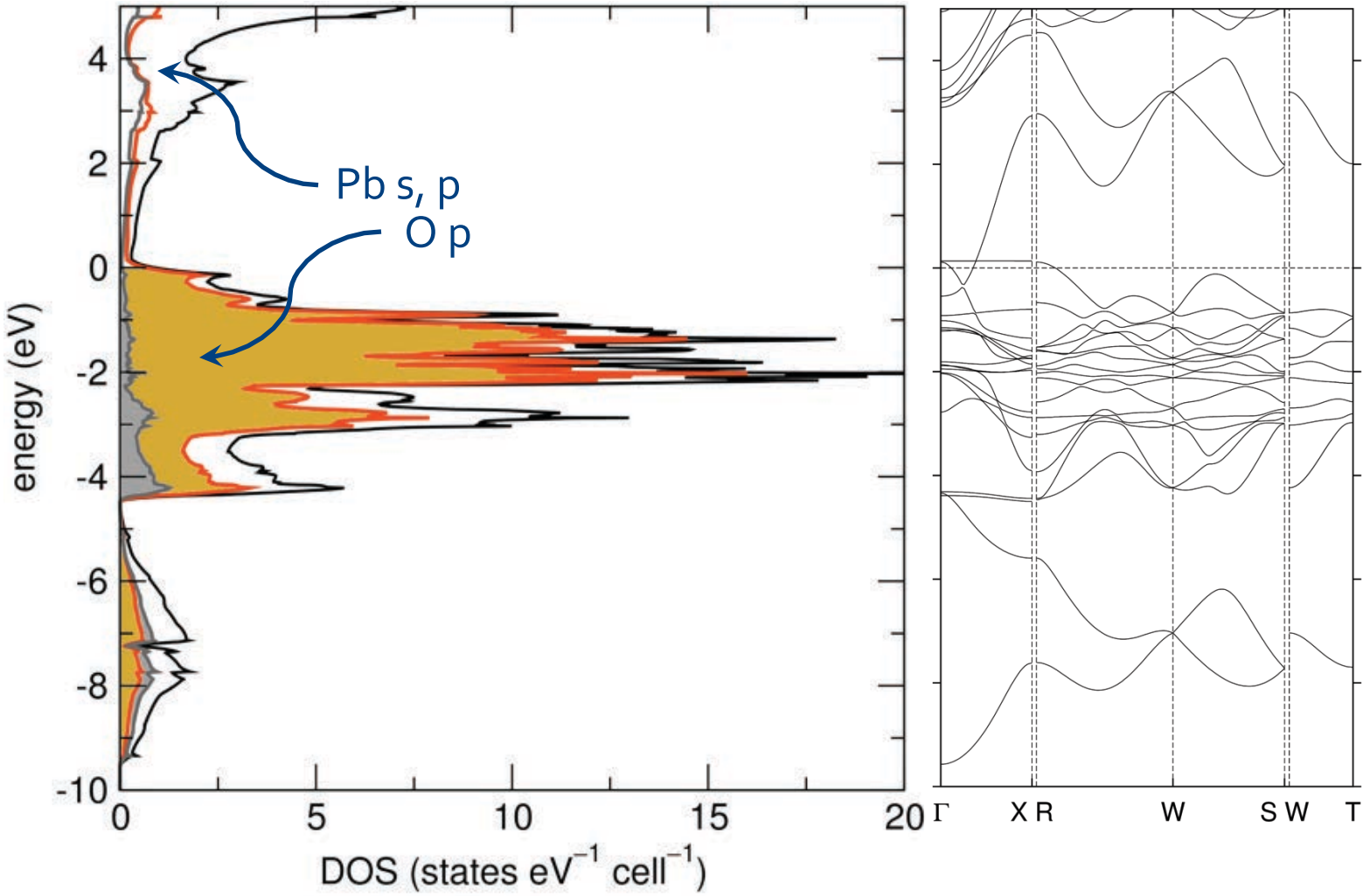
# Counting electrons in $SnO_2$: Assign as $Sn^{4+}$ and $O^{2-}$ (more covalent than $TiO_2$)




Insulator, easier to dope (TCOs).

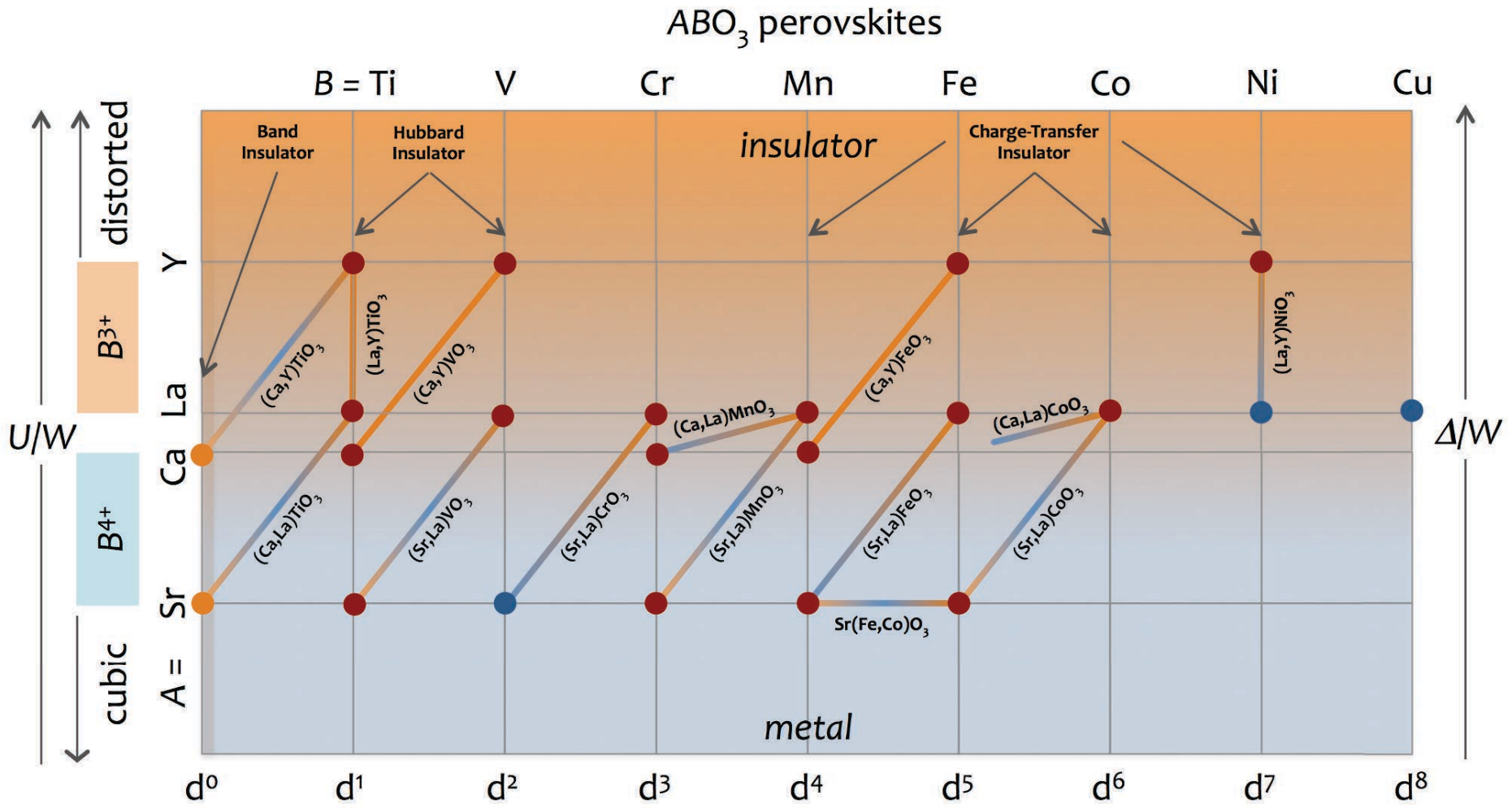
# Counting electrons in $BaPbO_3$: Assign as $Pb^{4+}$ and $O^{2-}$. An unexpected semi-metal




Equivalent $Sn^{4+}$ compounds are insulating.

# Transition metal compounds: Trends in energetics and insulator-to-metal transitions

# The 3d transition metal perovskite oxides: Doping and oxidation

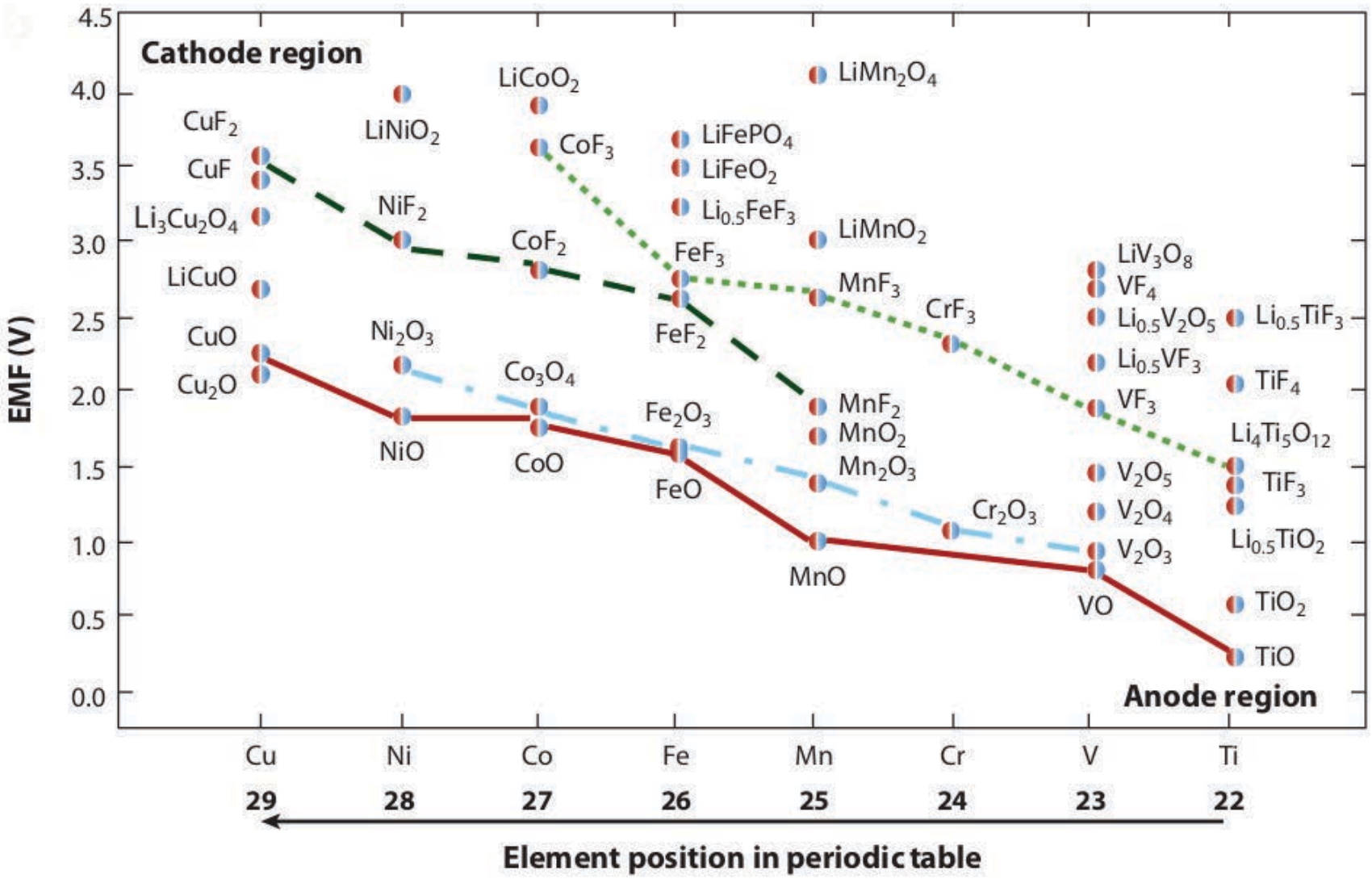



Note the trends from left to right, and as the oxidation state is changed.

Modified from Fujimori, Electronic structure of metallic oxides: band-gap closure and valence control, *J. Phys. Chem. Solids* **53** (1992) 1595–1602.

# The 3d transition metals: Energetics in Li-ion batteries

The transition metal d and anion p levels manifest in Li-battery electrochemistry.




Hayner, Zhao, Kung, *Annu. Rev. Chem. Biomolec. Eng.* **3** (2012) 445–471.

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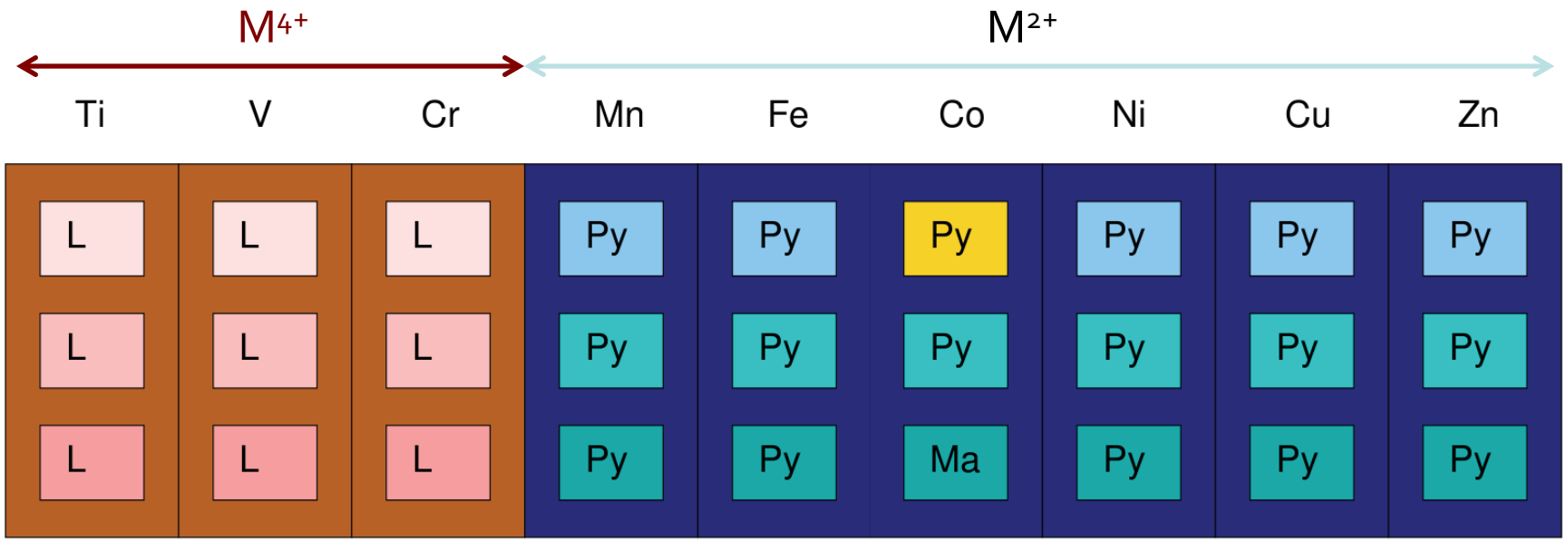
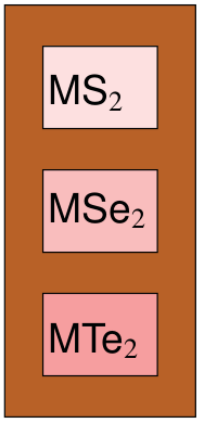
# The transition metal dichalcogenides: Redox competition



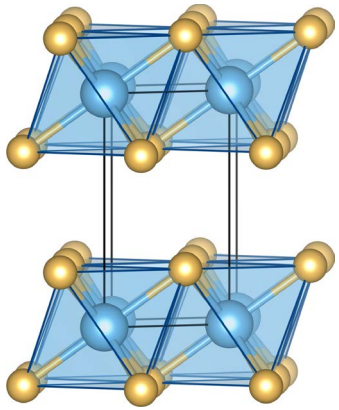



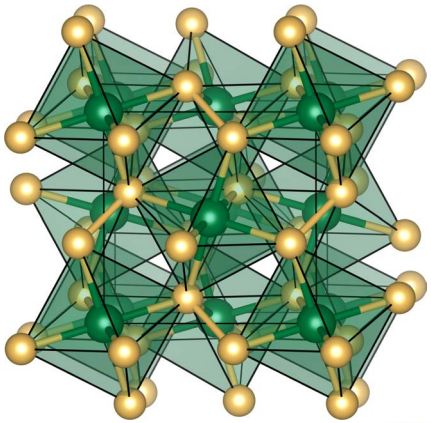

Py = pyrite

Ma = marcasite

L = layered

Py ferromagnetic





Ideas of Goodenough, Rouxel and others


Thank you
Photo by Tony Mastres