# Oxide crystal structures: The basics

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Photo by Tony Mastres

# This lecture

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

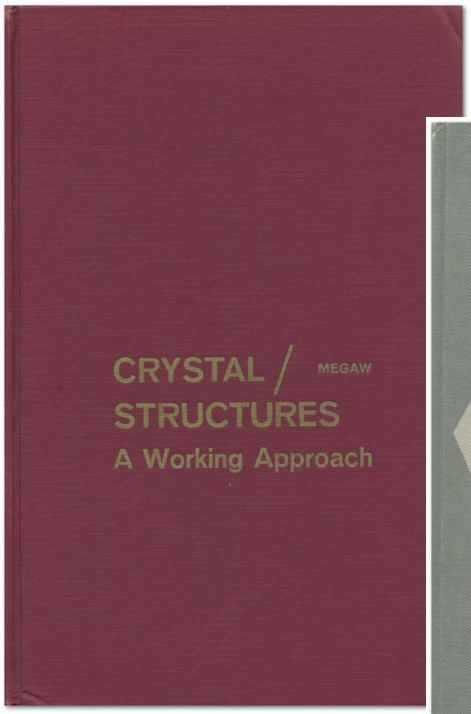
    a. Ionic radii and Pauling's rules
    b. Electrostatic valence
    c. Bond valence, and bond valence sums

*Why do certain combinations of atoms take on specific structures?*

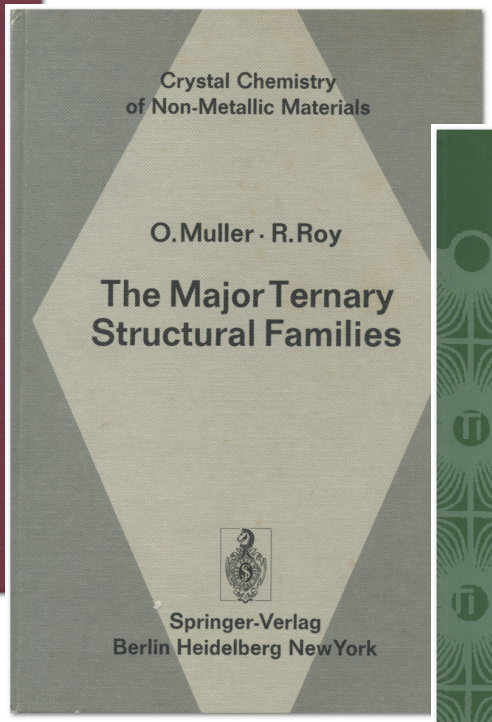
2. Counting electrons and simple electronic structures (largely avoiding transition metals)

3. $d^0$ and $s^2$ configurations.

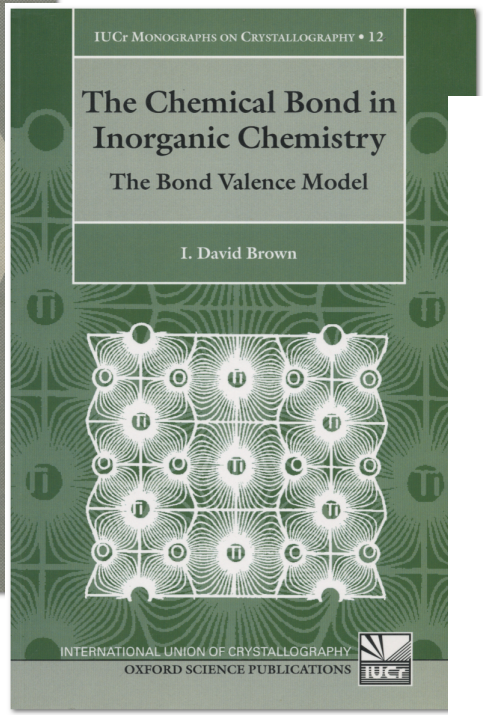
# My bookshelf



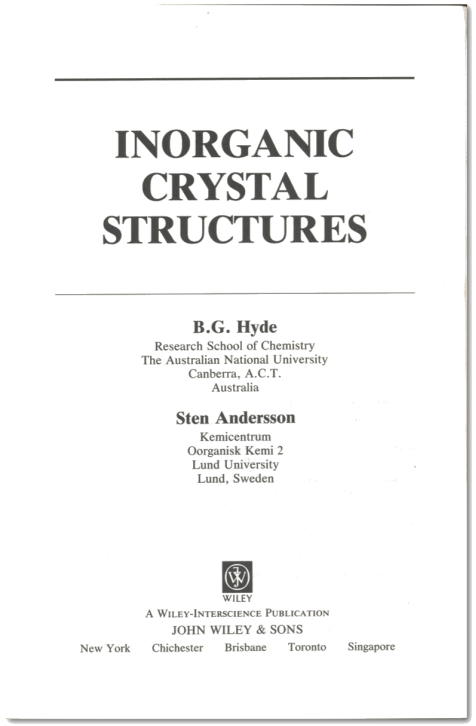

H. D. Megaw




O. Muller &
R. Roy

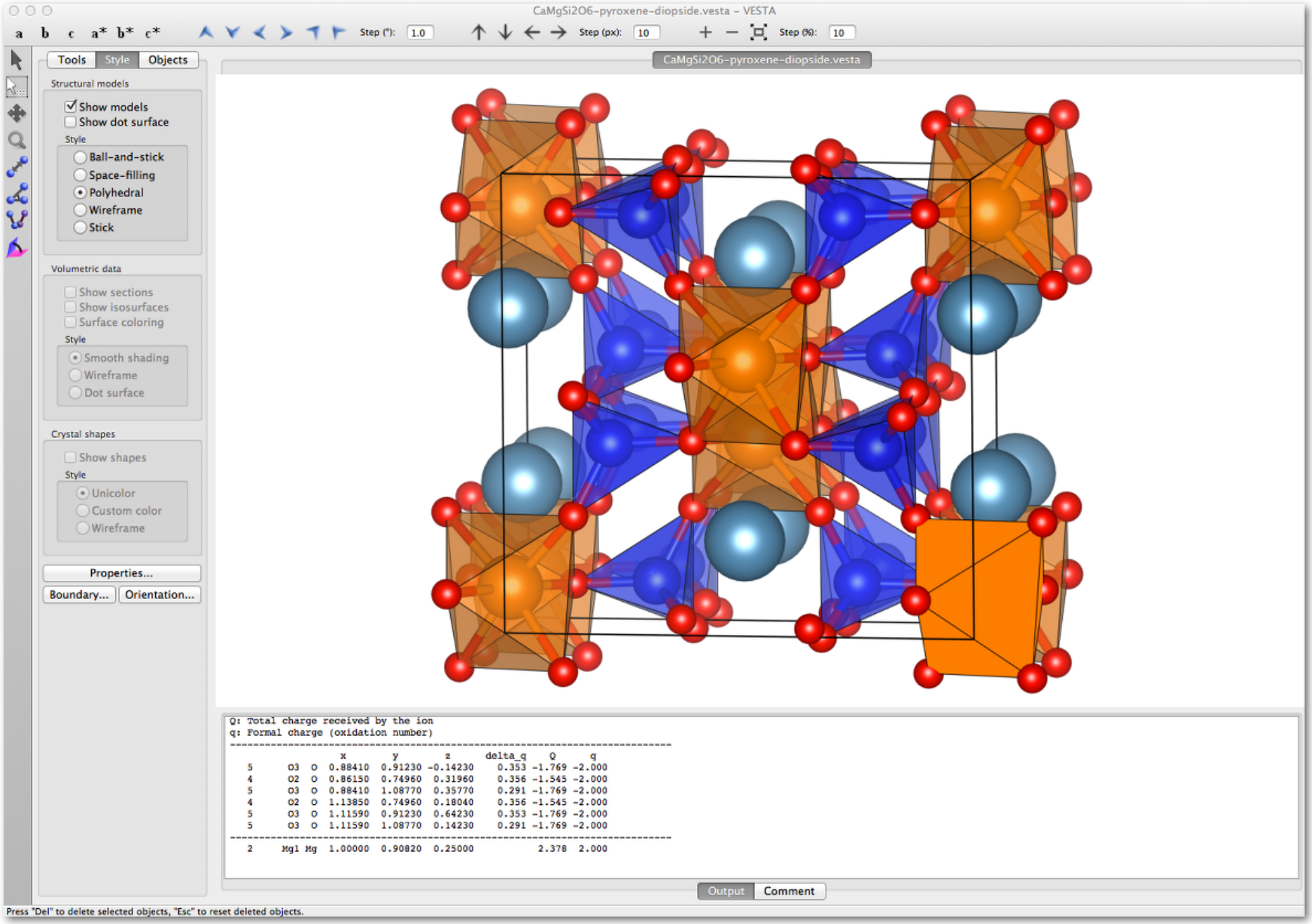



I. D. Brown




B. G. Hyde &
S. Andersson

# Software: ICSD + VESTA




K. Momma and F. 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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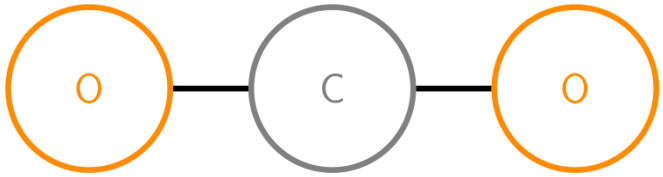
# Crystal structures of simple oxides [containing a single cation site]

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

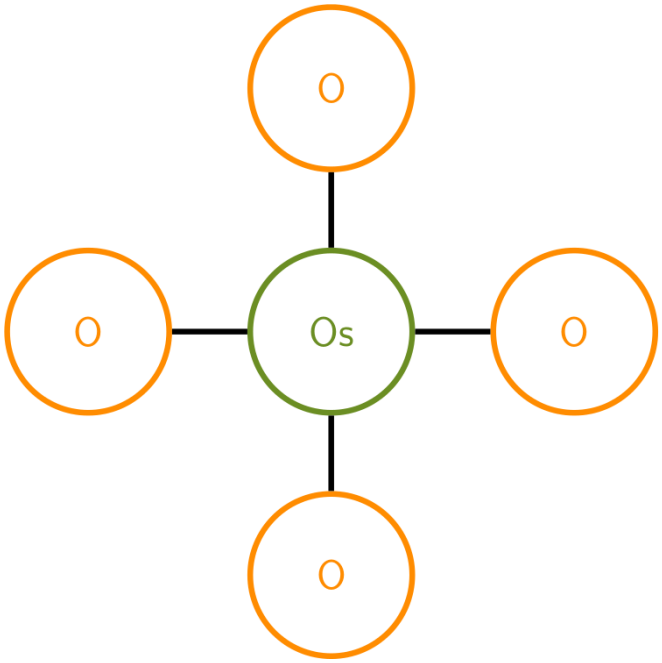
N.B.: CoO is simple, $Co_3O_4$ is not. $ZnCo_2O_4$ is certainly not !
$Co_3O_4$ and $ZnCo_2O_4$ are complex oxides.

***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

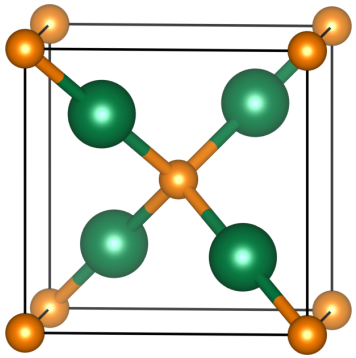


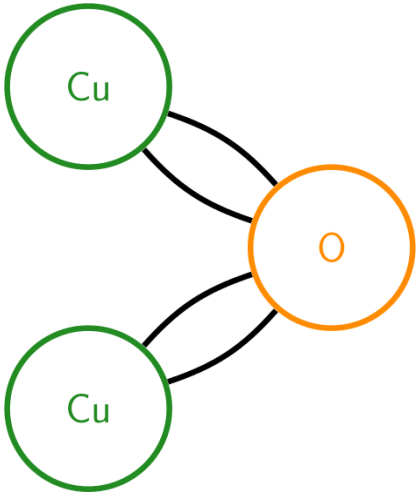

$OsO_4$: The structure comprises isolated tetrahedra (molecular). The graph is below:
Each Os connected to 4 O and each O to 1 Os



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

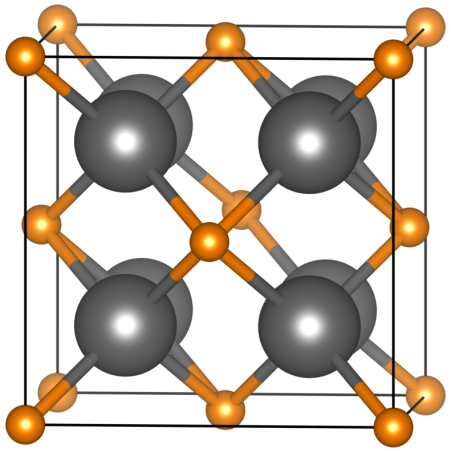
## $Cu_2O$

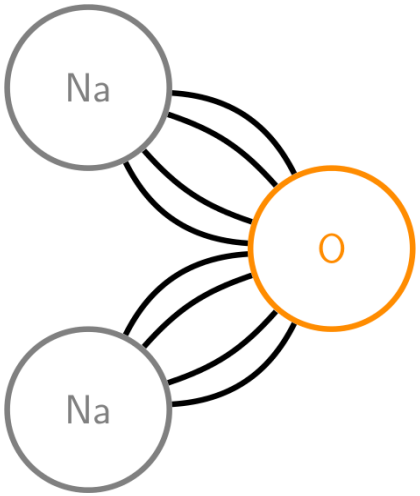





Linear coordination is unusual. Found usually in $Cu^+$ and $Ag^+$.

## $Na_2O$ (anti-fluorite)

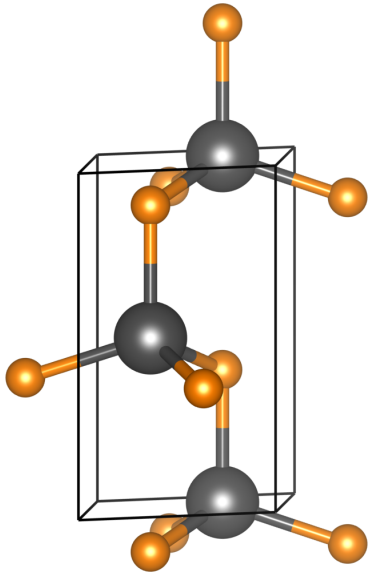


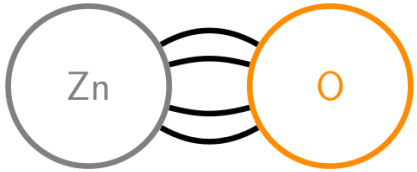



4-coordination for $Na^+$ and 8-coordination for $O^{2-}$ are unusual.

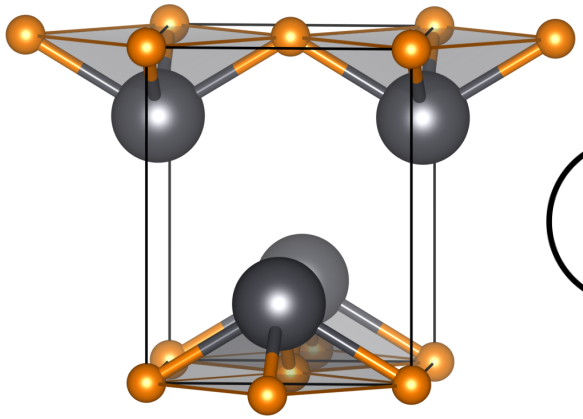
# Crystal structures of simple oxides of divalent ions: *AO*

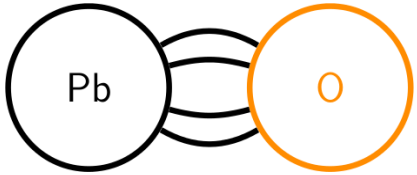
## ZnO (wurtzite), $sp^3$



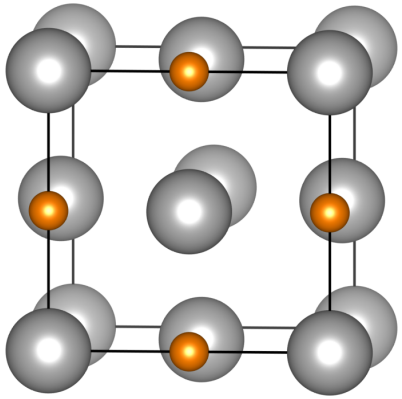


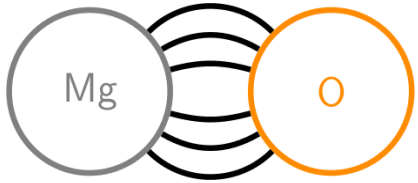

## PbO (litharge), lone pairs






## MgO (rock-salt)



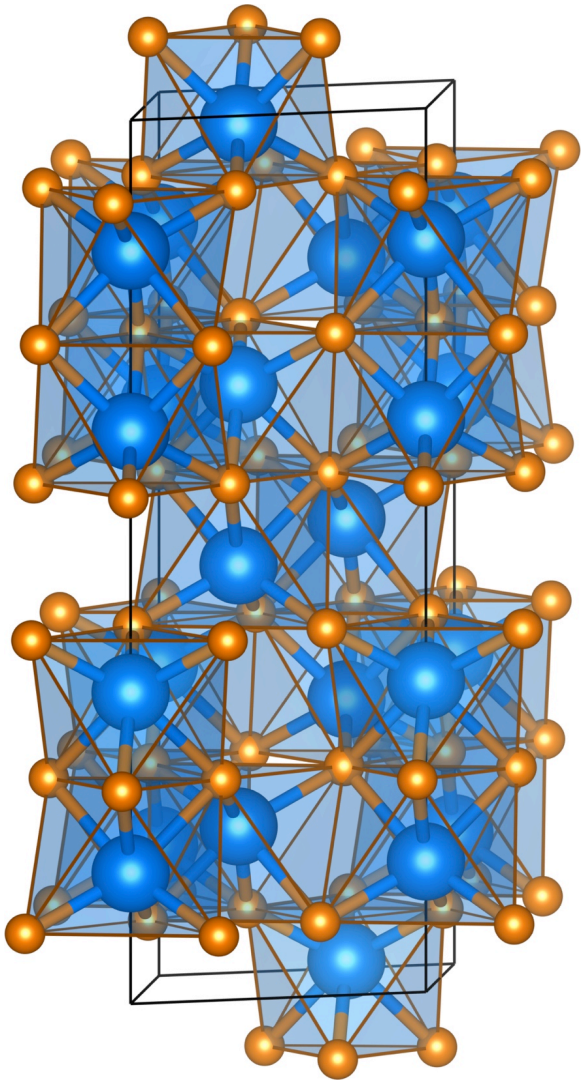


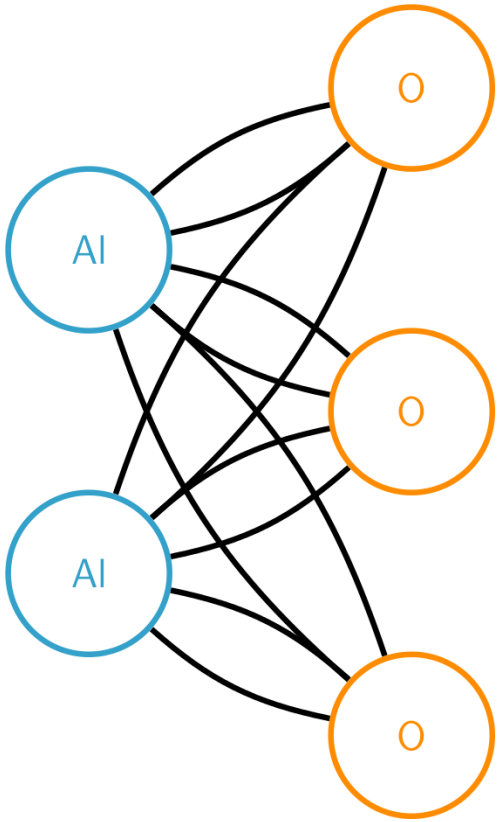

Ubiquitous for *AO* oxides including transition metals (distorted for CuO and NbO).

Insulators, metals (TiO), magnetic, …

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

$\alpha$-$Al_2O_3$ (corundum)





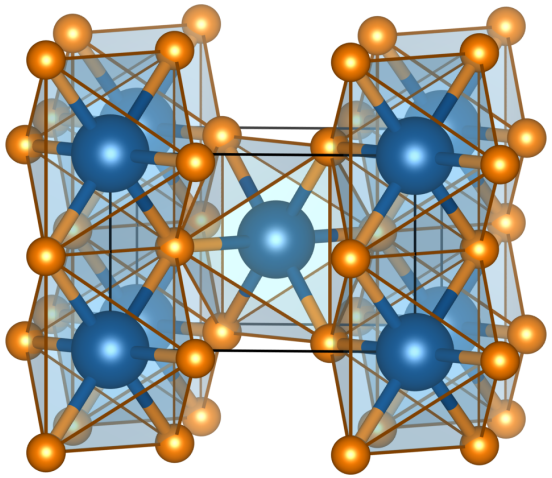

Also the structure of $Cr_2O_3$ and $Fe_2O_3$.

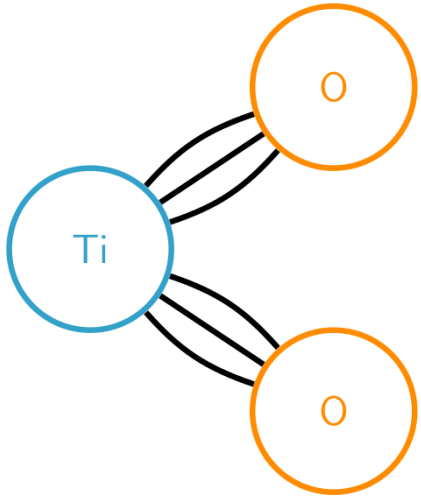
$Ga_2O_3$ does funny things.

$In_2O_3$ is different (bixbyite).

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

## $TiO_2$ (rutile)

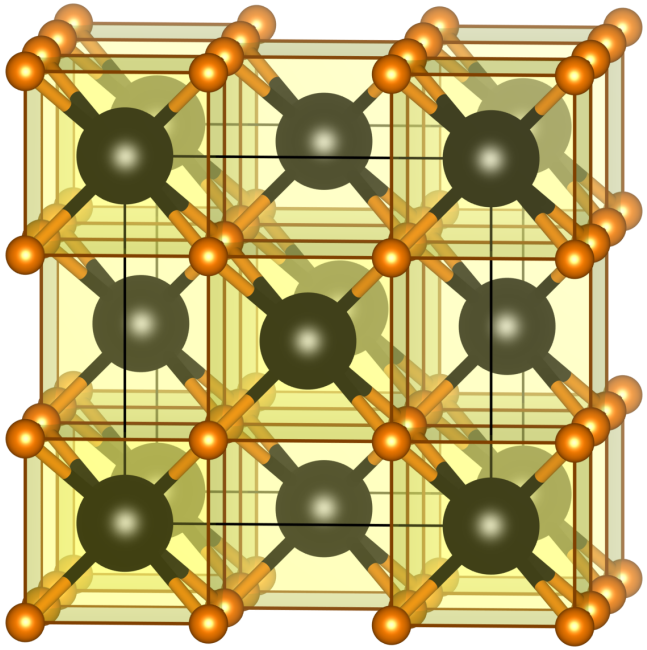


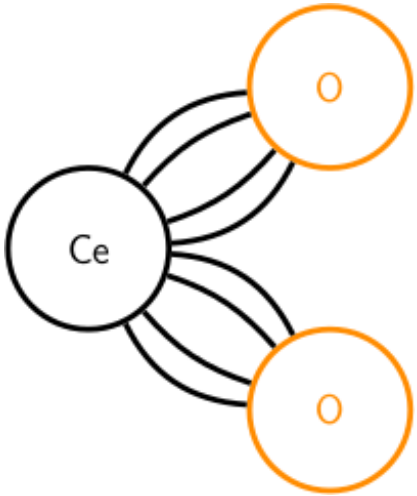



$TiO_2$ also crystallizes as anatase and brookite.

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

## $CeO_2$ (fluorite)



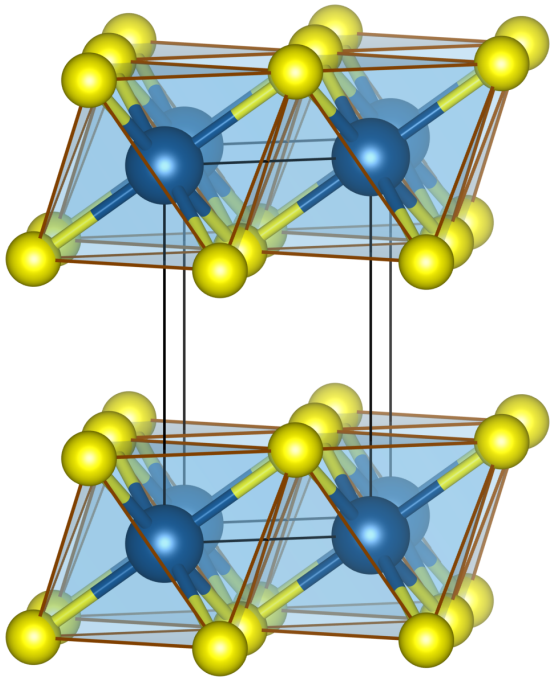



Also the structure of $ThO_2$, and of $ZrO_2$ and $HfO_2$ at elevated temperatures.

Ordered variants abound.

# Oxides versus sulfides: $TiS_2$

$2H$–$TiS_2$

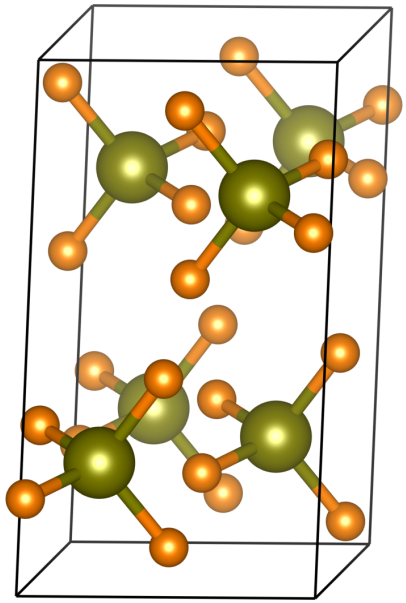


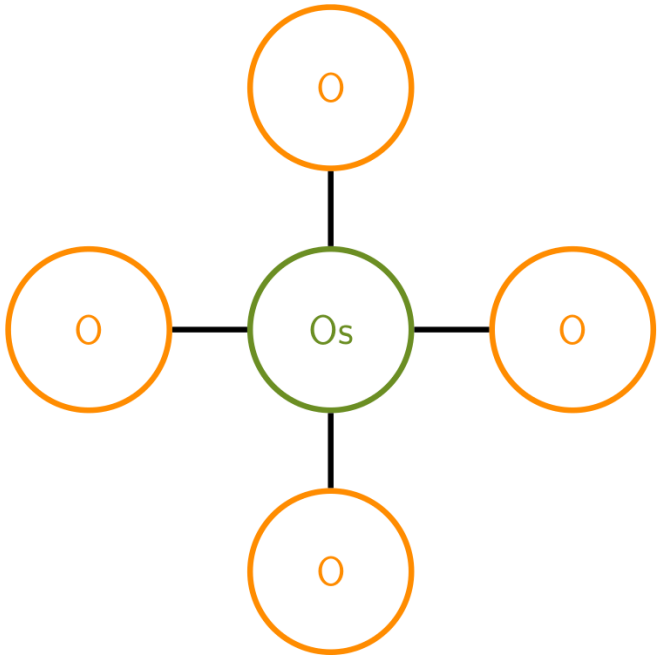
van der Waals gap (unlikely in oxides or fluorides, but occurs frequently in hydroxides)

This is the $CdI_2$ structure.

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

$OsO_4$



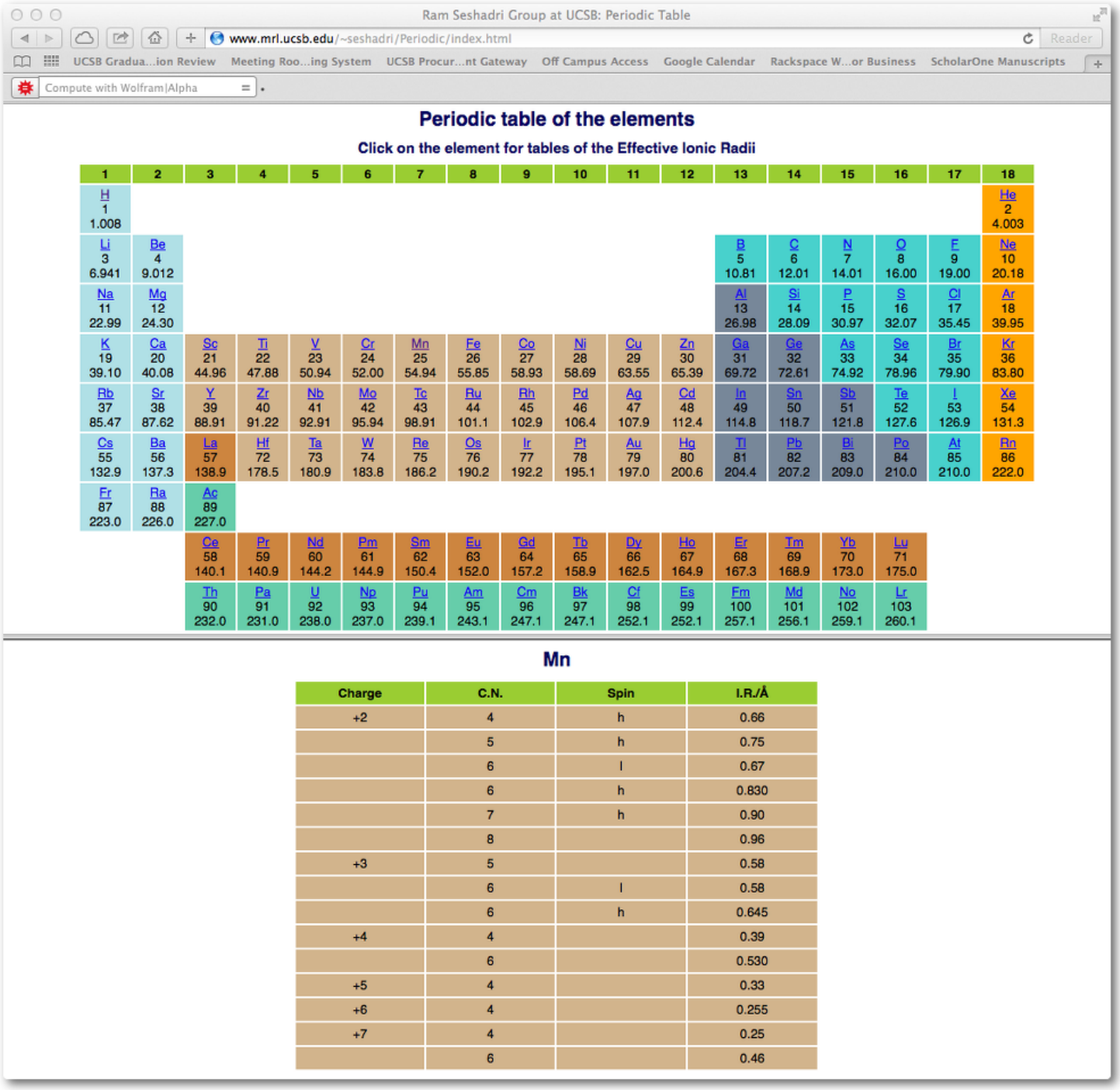


# Shannon-Prewitt (ionic) radii

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**

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

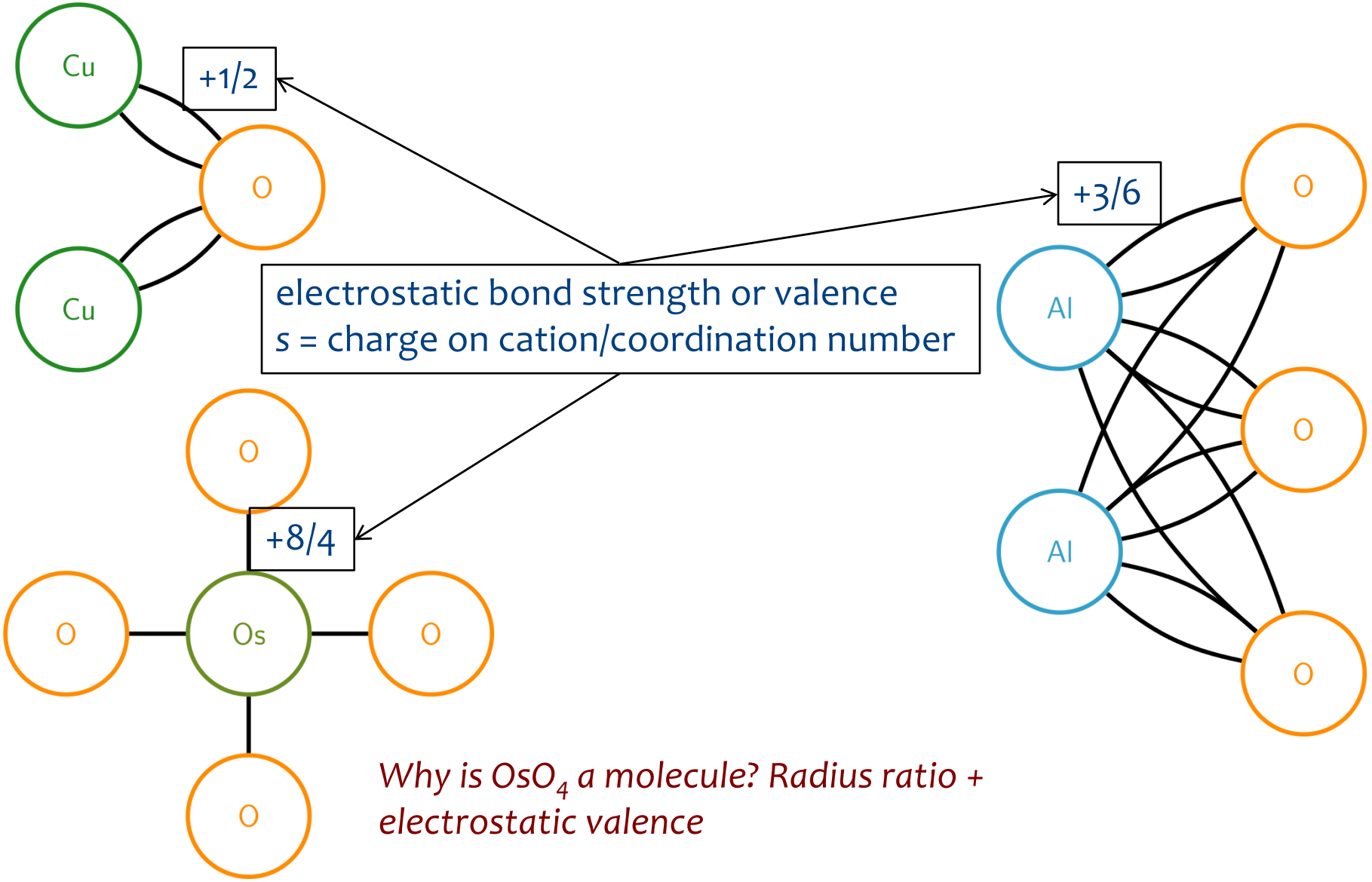
In brief: The cation-anion distance is the sum of cation and anion radii, and the number of anions around a cation (the coordination number) is a function of the radius ratio. Exemplified by $AO_2$ compounds below. MRR is the mimimum radius ratio.

| 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 |

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

# Pauling's second rule: The electrostatic valence rule

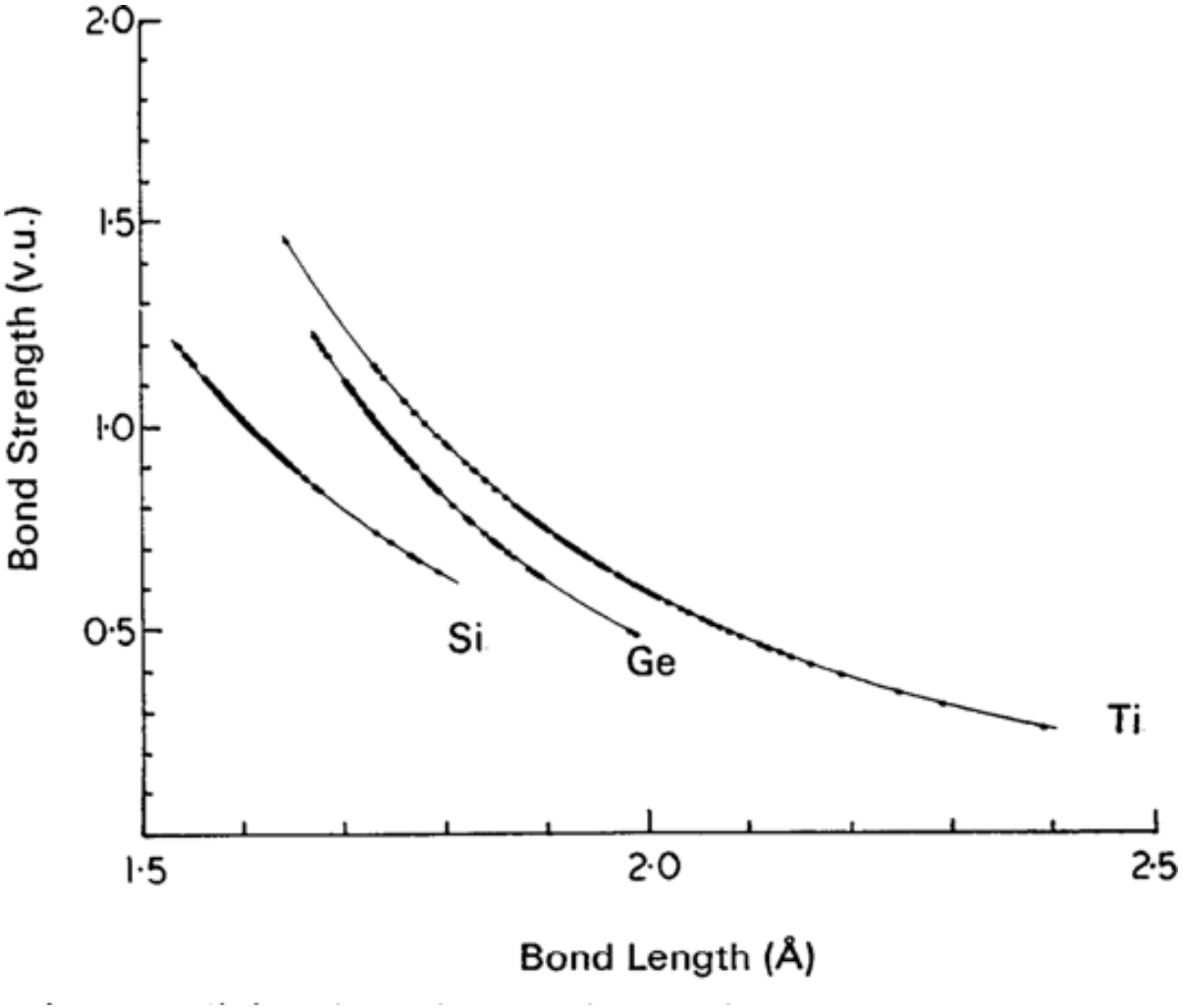
In brief: Charges going out from cations should balance anions and *vice-versa*




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

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

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*




I. D. Brown and R. D. Shannon, Empirical bond-strength-bond-length curves for oxides, *Acta Cryst.* **A29** (1973) 266–281

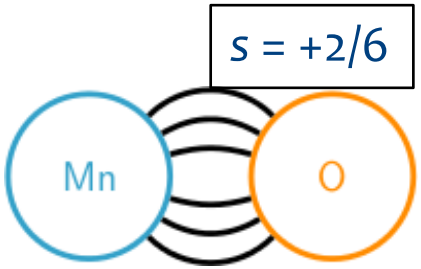
# Electrostatic valence and bond valence

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

I. D. Brown and R. D. Shannon, Empirical bond-strength-bond-length curves for oxides, *Acta Cryst.* **A29** (1973) 266–281.

# Electrostatic valence and bond valence: Parameters for Mn

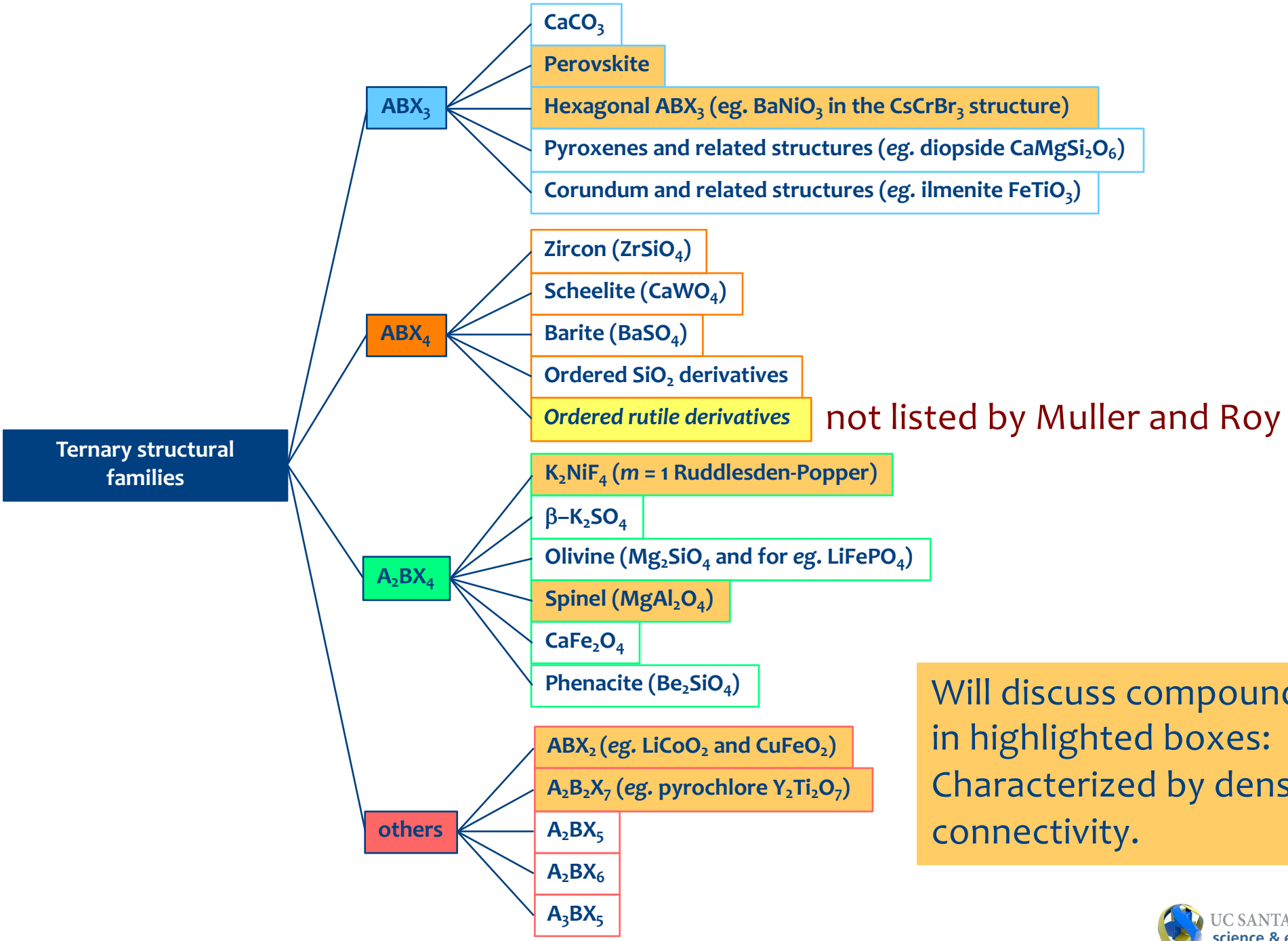
| | | | | | |
|---|---|---|---|---|---|
| Mn | 2 | O | −2 | 1.790 | 0.37 | a |
| Mn | 2 | O | −2 | 1.765 | 0.37 | j |
| Mn | 2 | S | −2 | 2.22 | 0.37 | e |
| Mn | 2 | F | −1 | 1.698 | 0.37 | a |
| Mn | 2 | Cl | −1 | 2.133 | 0.37 | a |
| Mn | 2 | Br | −1 | 2.34 | 0.37 | e |
| Mn | 2 | I | −2 | 2.52 | 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**

I. D. Brown and R. D. Shannon, Empirical bond-strength-bond-length curves for oxides, *Acta Cryst.* **A29** (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)




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

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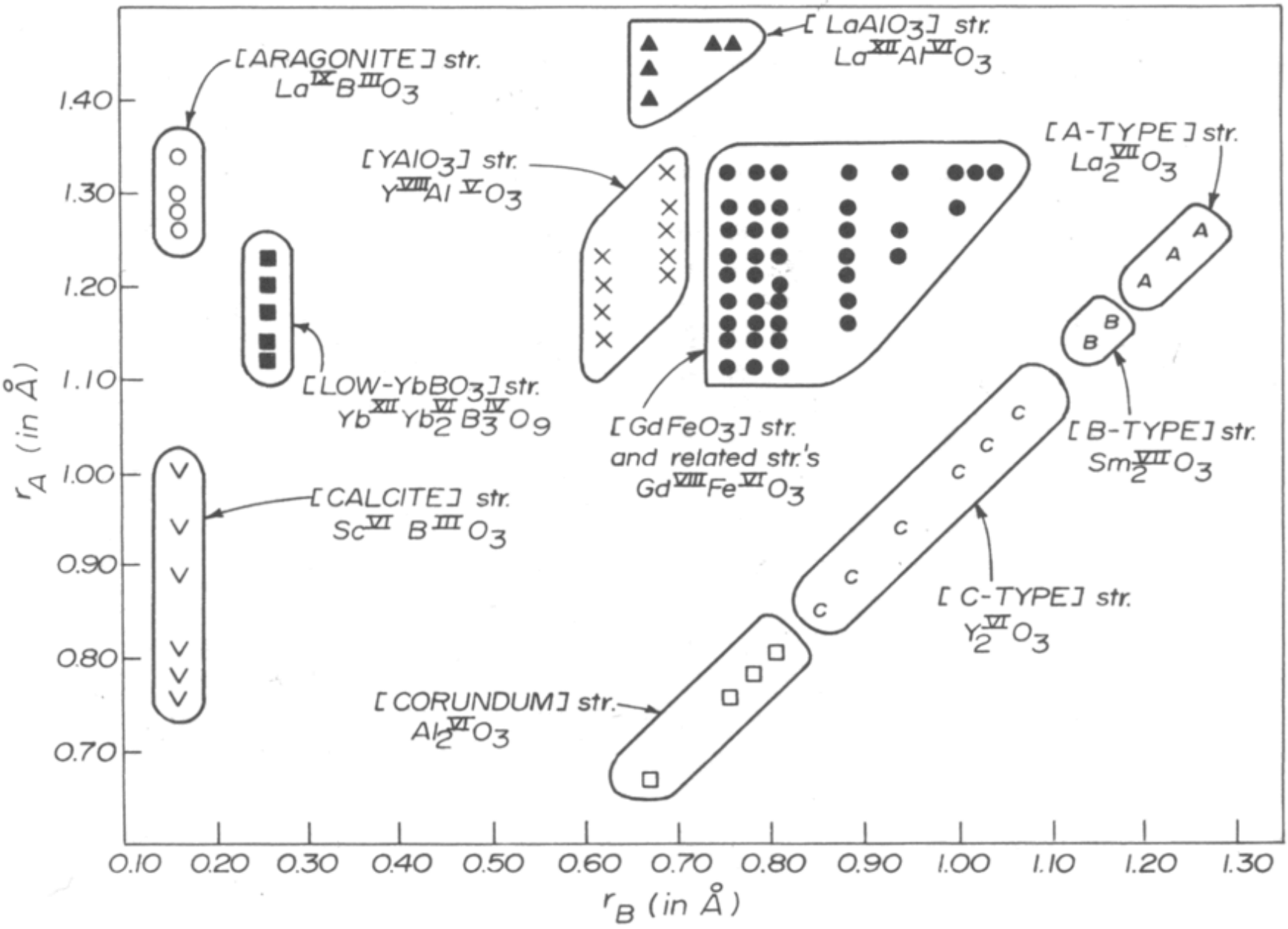
# The $ABO_3$ structure-sorting field (from Muller and Roy)




The superscripted roman numerals indicate coordination number.

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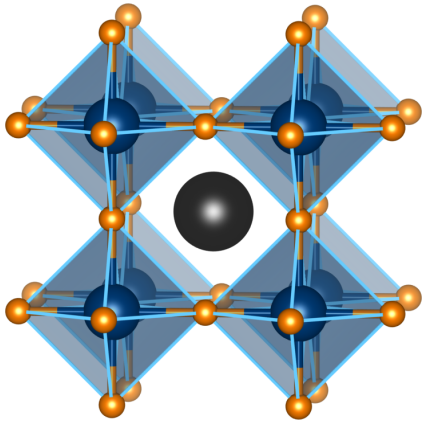
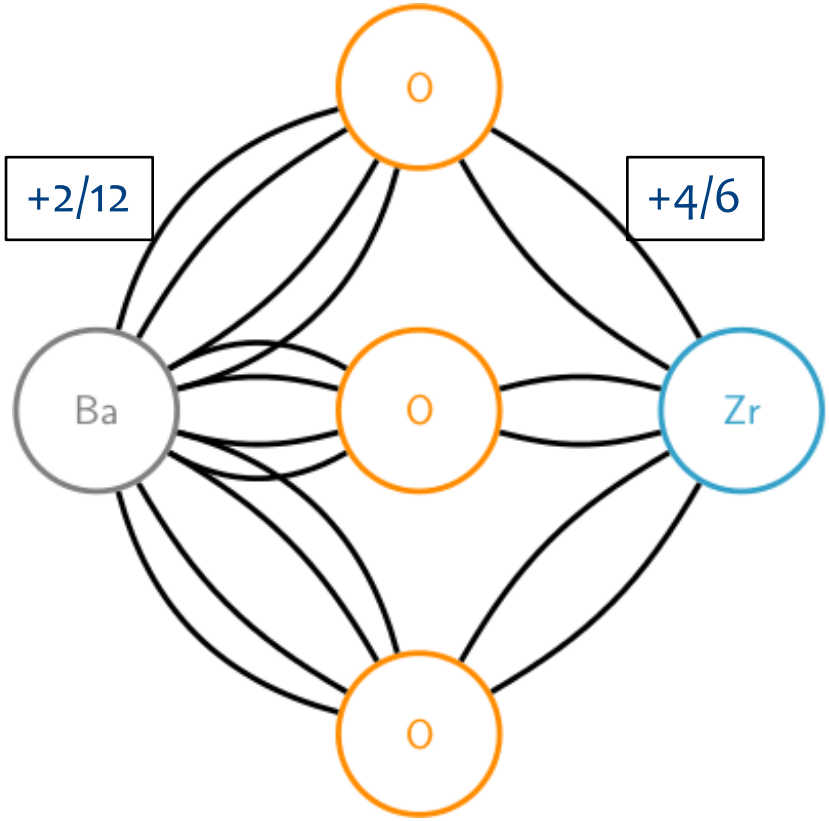
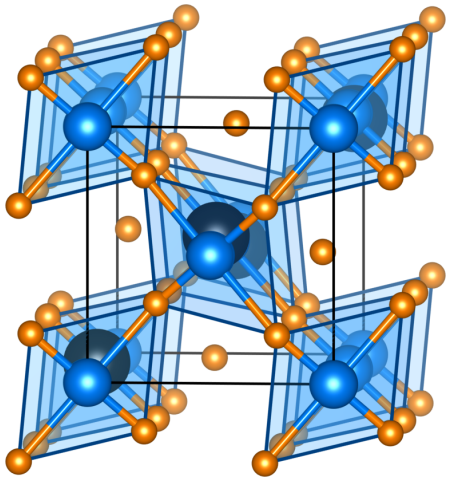
# Perovskite

$BaZrO_3$






$LaMnO_3$ *Pnma*
*(Jahn-Teller distorted)*



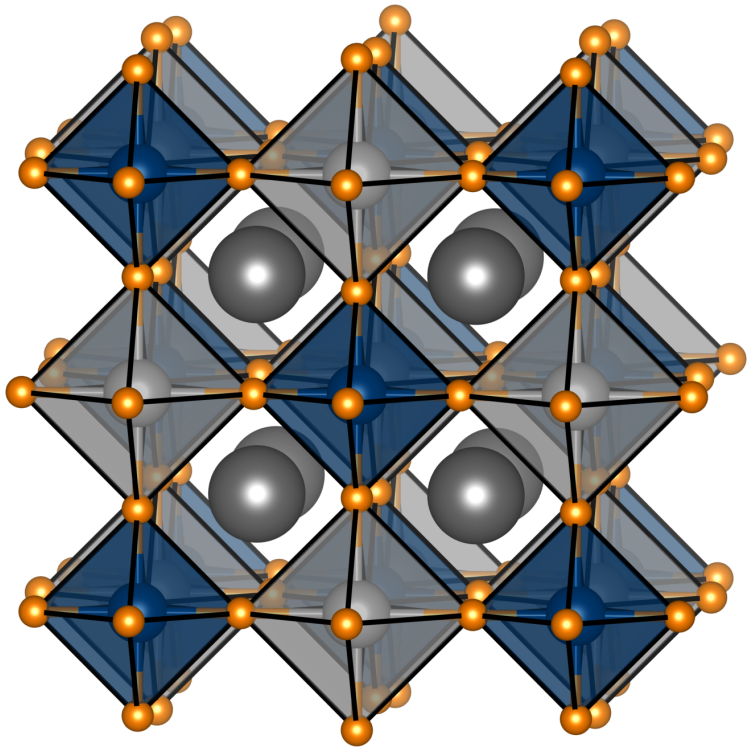
Note that the space group *Pnma* (#62) can be written in a variety of ways.

This is the most common perovskite space group.

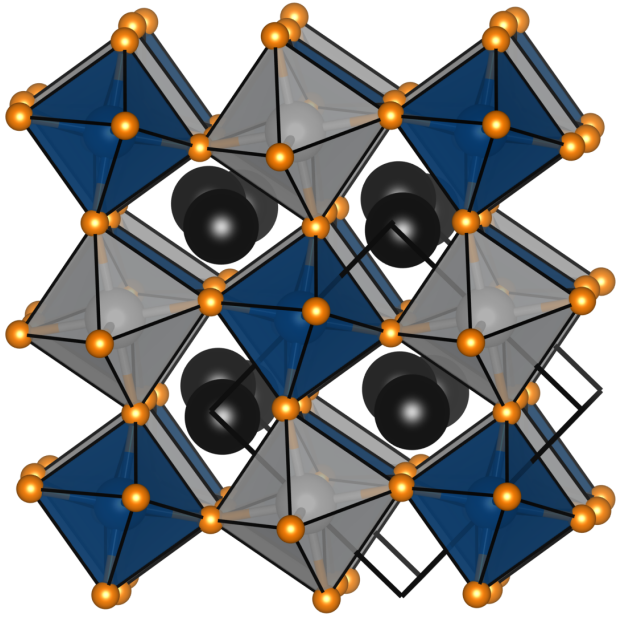
In the next so many structures, $BO_6$-polyhedra are depicted.

# Ordered double perovskites (elpasolites)

$Ba_2MgWO_6$



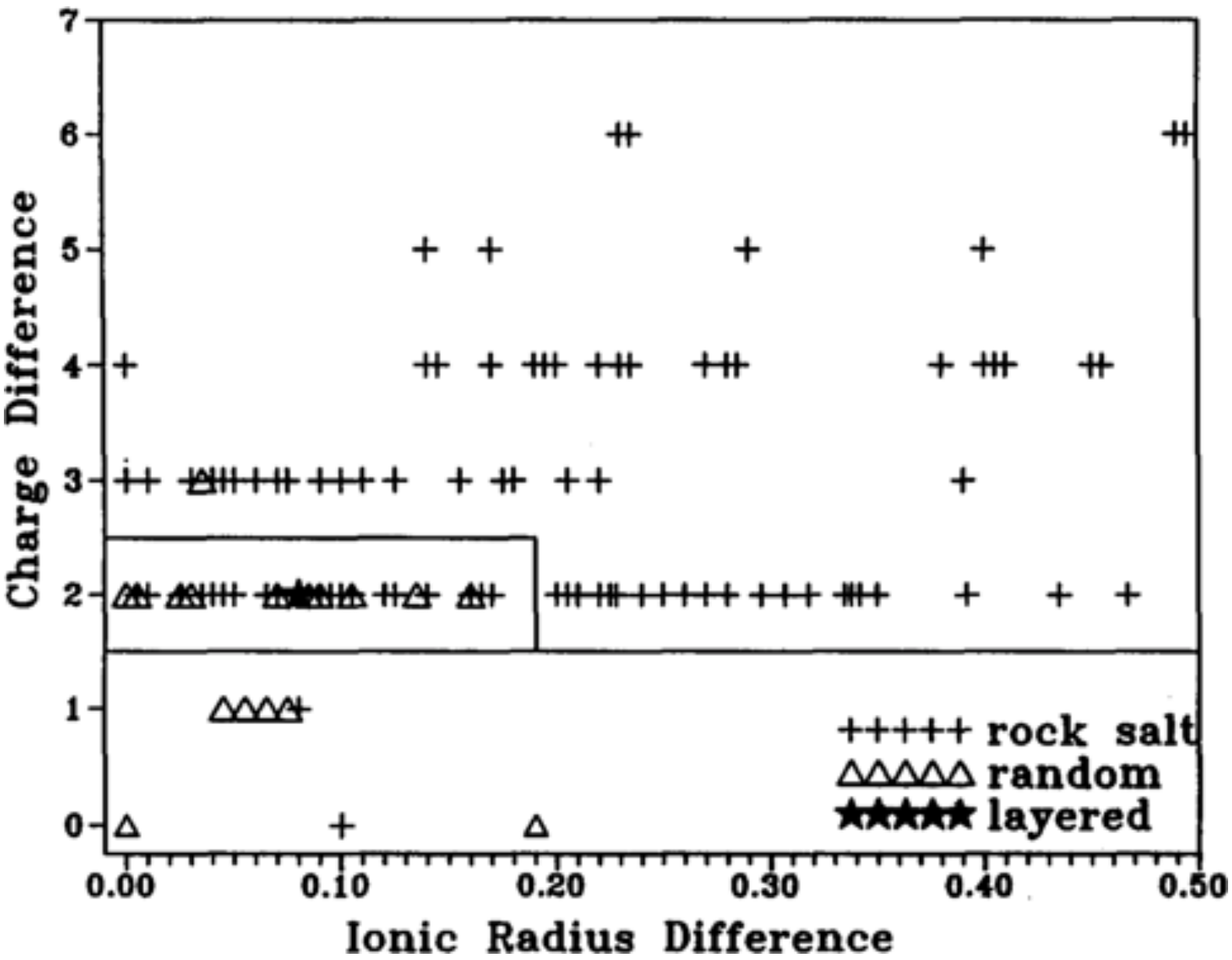
$Ca_2MgWO_6$



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

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

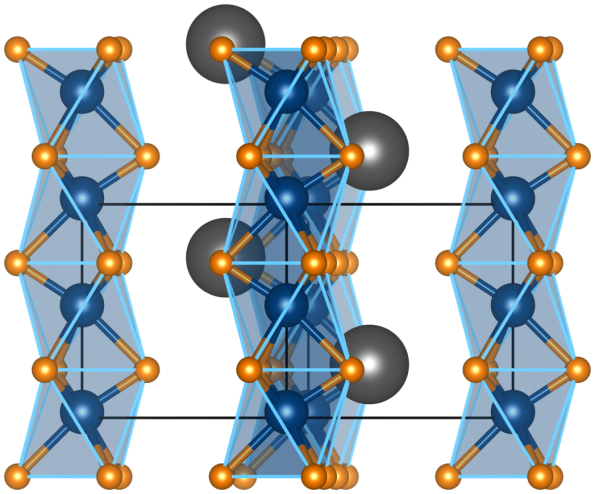
# The double perovskite field: Charge and radius



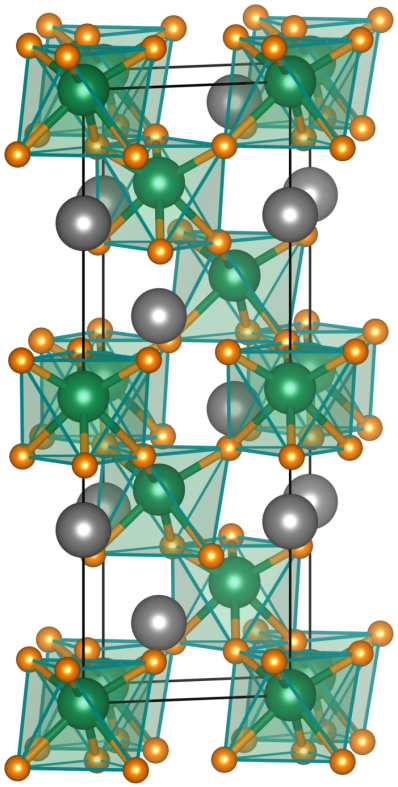

Anderson, Greenwood, and Poeppelmeier, *Prog. Solid State Chem.* **22** (1993) 197–233.

# Hexagonal $ABO_3$ structures

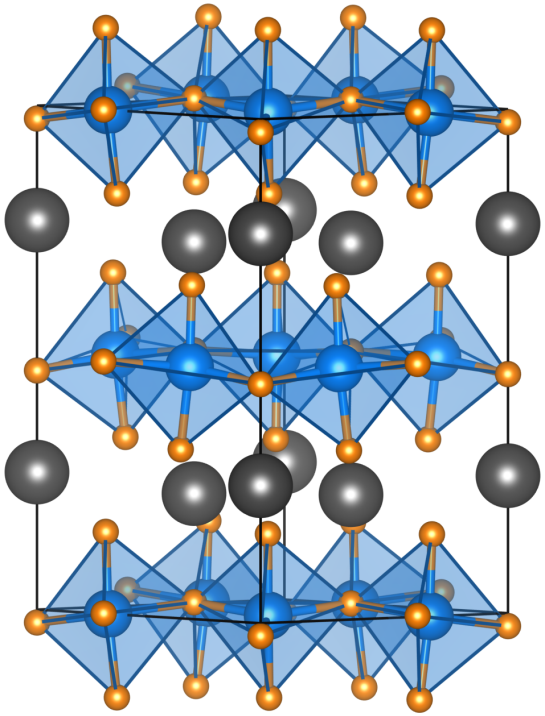
$BaNiO_3$



$LiNbO_3$ (ferroelectric $R3c$)



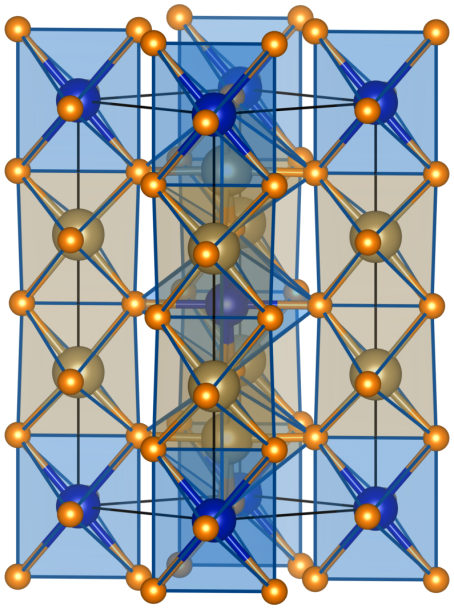
Ferroelectric $YMnO_3$ ("$YAlO_3$")



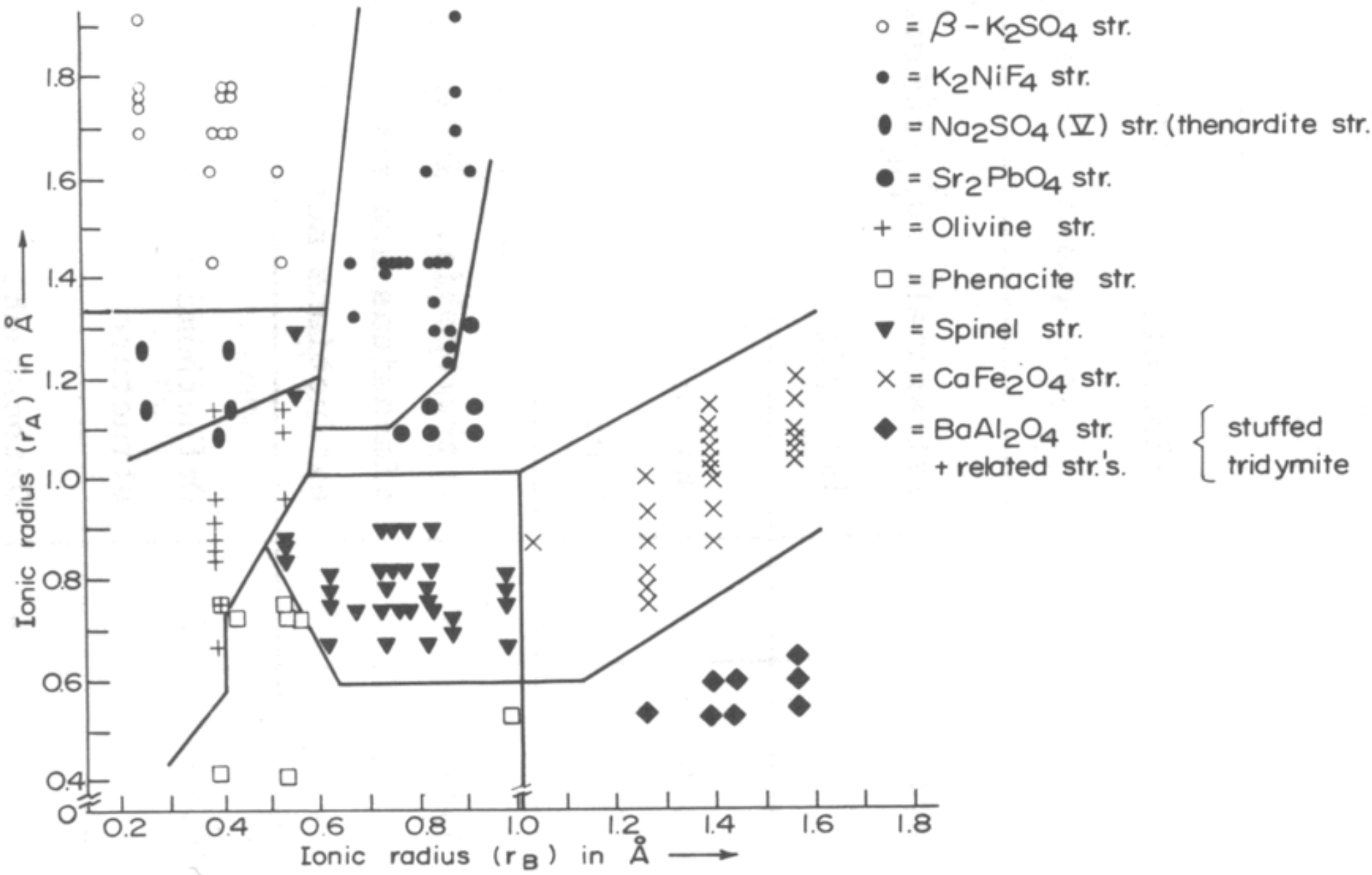
Unusual 5-fold coordination (trigonal bibyramid) of $MnO_5$

# Ordered rutiles (the trirutile)

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



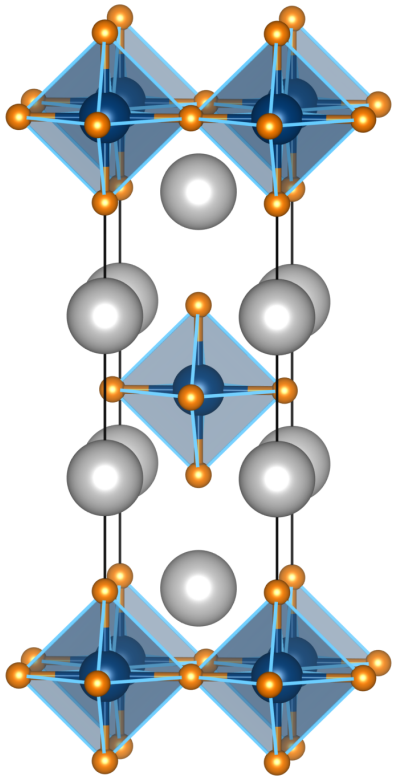
# The $A_2BO_4$ structure-sorting field (from Muller and Roy)



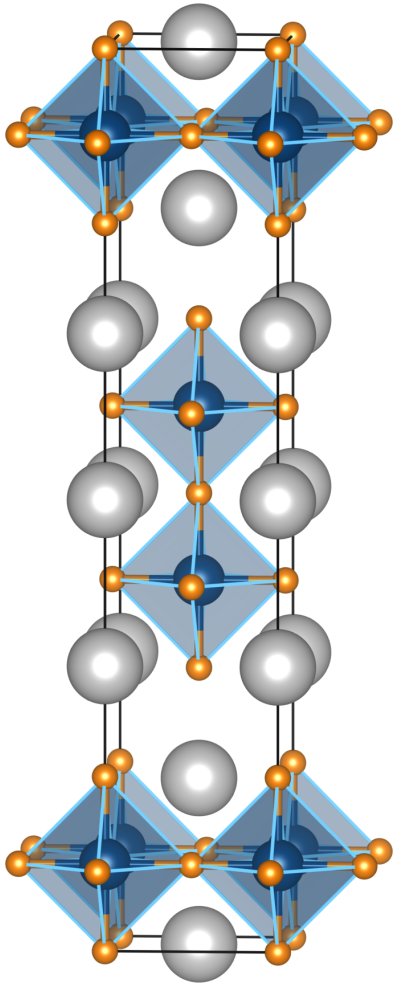

The superscripted roman numerals indicate coordination number.

# $K_2NiF_4$ and Ruddlesden-Popper ($m$ = 1, 2, 3)
General formula $[SrO][SrTiO_3]_m$

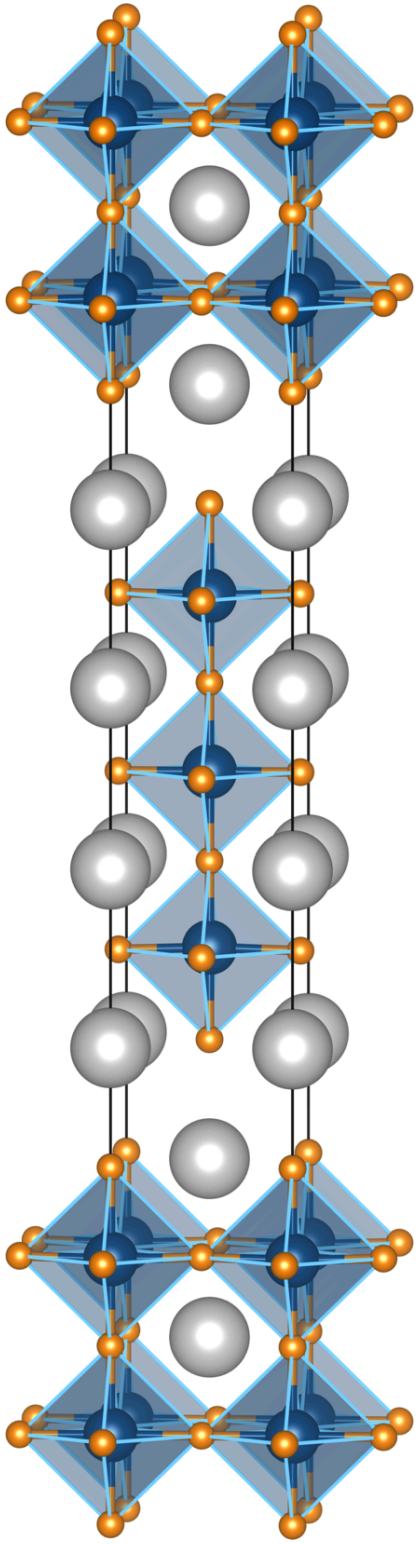
$Sr_2TiO_4$



$Sr_3Ti_2O_7$



$Sr_4Ti_3O_{10}$



$m = 3$

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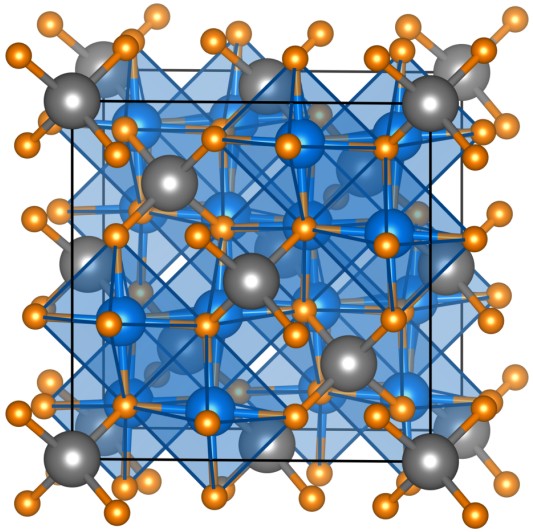
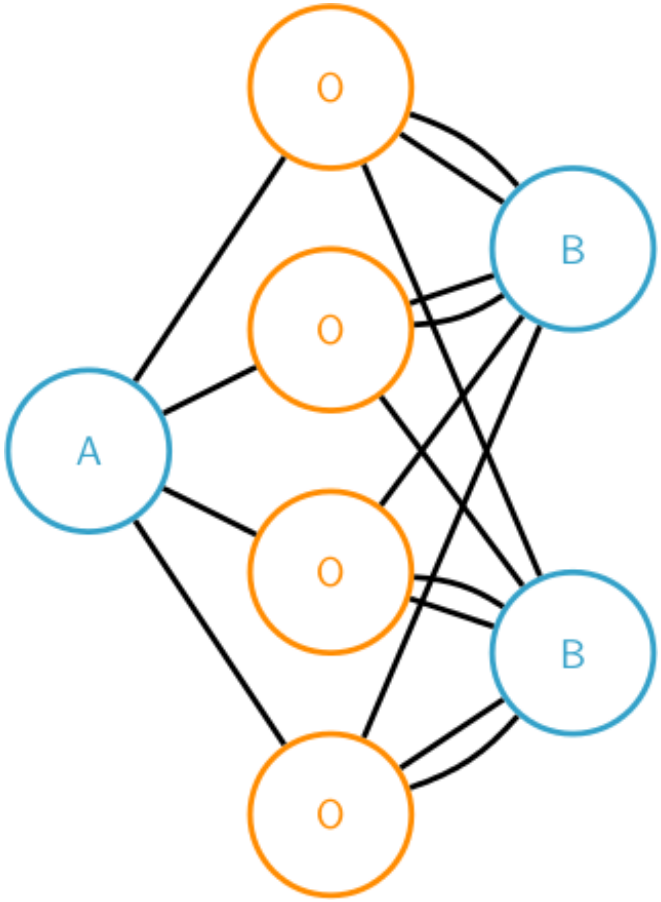
# Spinel $AB_2O_4$

$MgAl_2O_4$



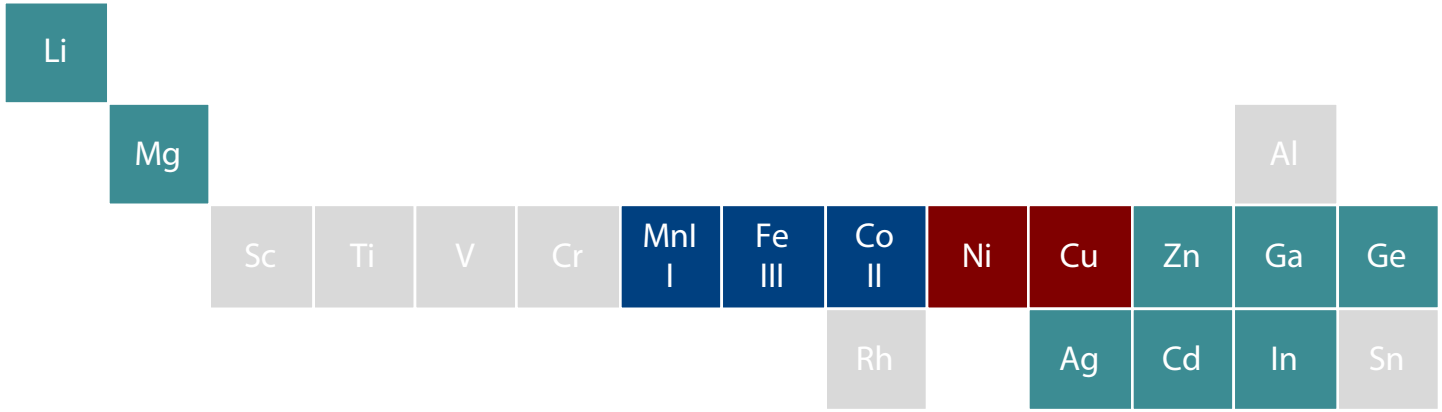



Ubiquitous structure when ions have similar sizes, around 0.6 Å.
*A* is tetrahedrally coordinated, and *B* octahedral (actually with a slight trigonal distortion).

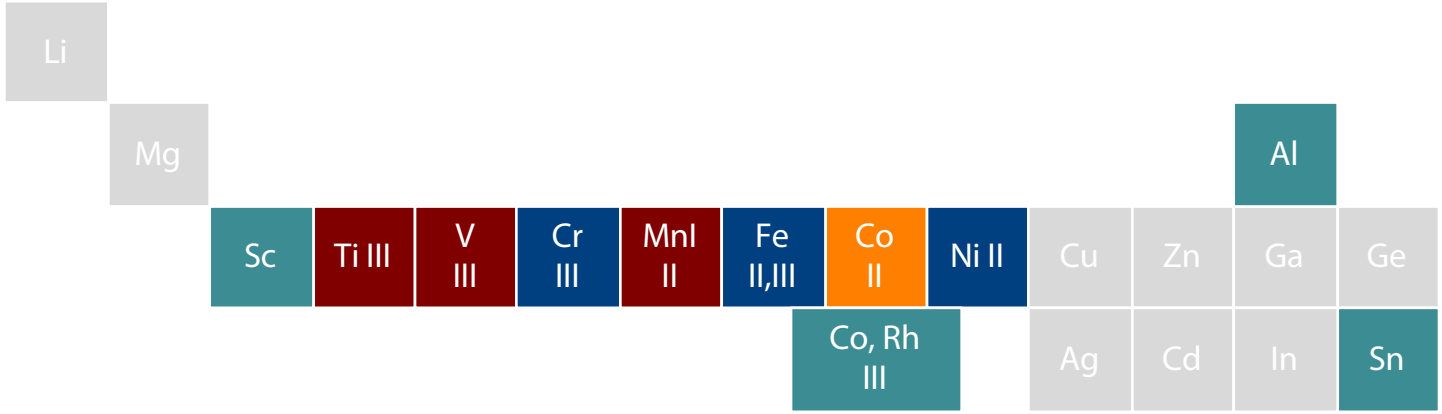
In general, lower oxidation states and smaller bandwidths than in perovskites.

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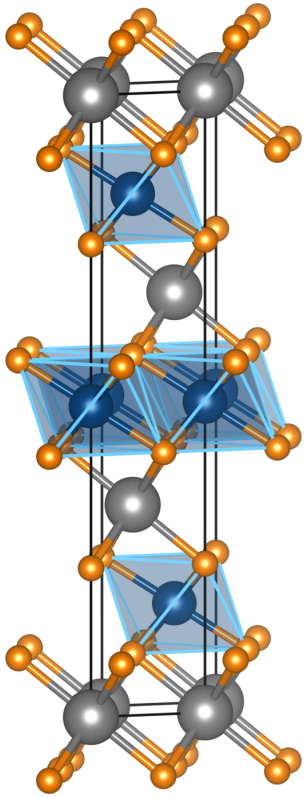
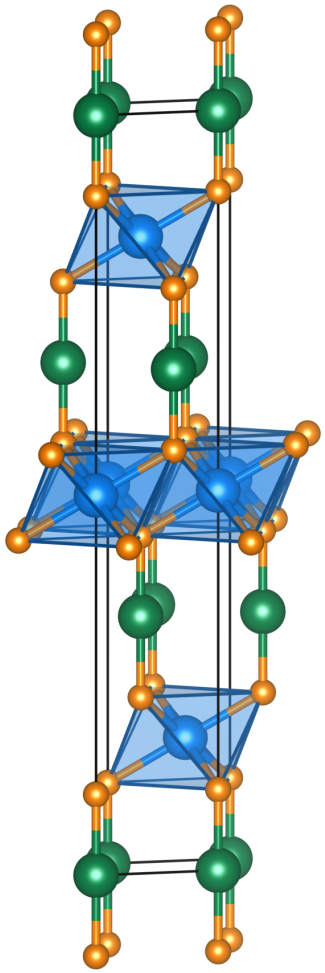
# Some $ABO_2$ structures: Highly dense in-plane, and frequently metallic

## $LiCoO_2$ (ordered rock-salt)



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

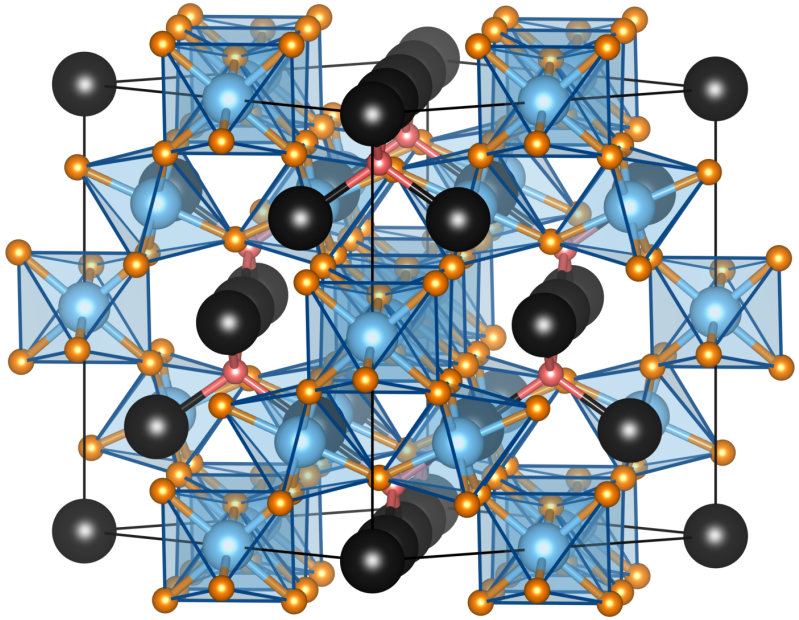
## $3R$–$CuFeO_2$ (delafossite)

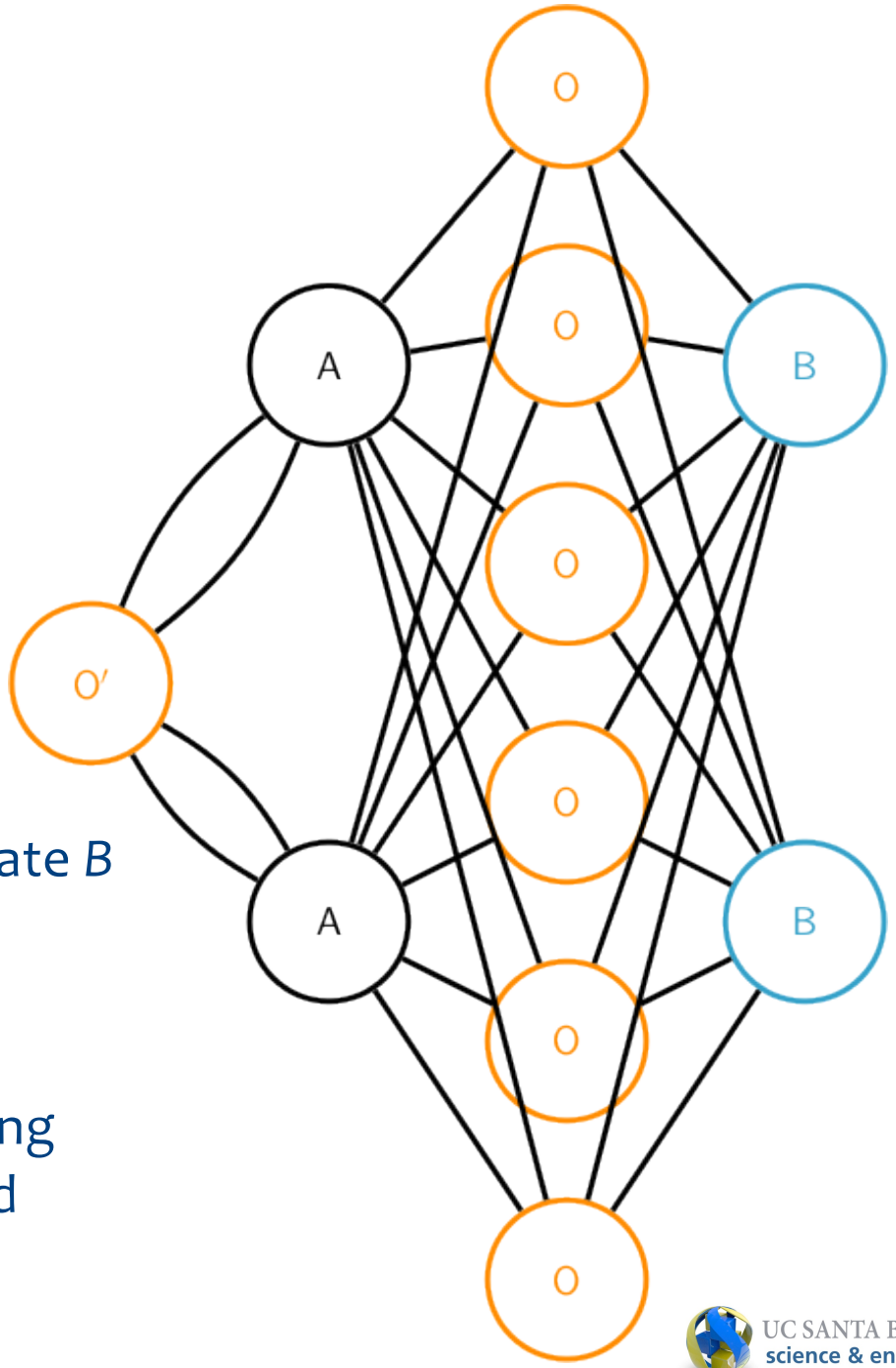


$BO_2$ ($CdI_2$) slabs separated by two-coordinate atoms, usually $Cu^+$ and $Ag^+$. Also unusually, $Pd^{1+}$ and $Pt^{1+}$.

# $A_2B_2O_7$ pyrochlore

$Y_2Ti_2O_7 = Y_2Ti_2O_6Ó$






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.


Thank you
Photo by Tony Mastres