Oxide crystal structures and electron counts: The basics

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Materials 218/ Chemistry 277 Class 1, Winter 2016

Photo by Tony Mastres

This lecture

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

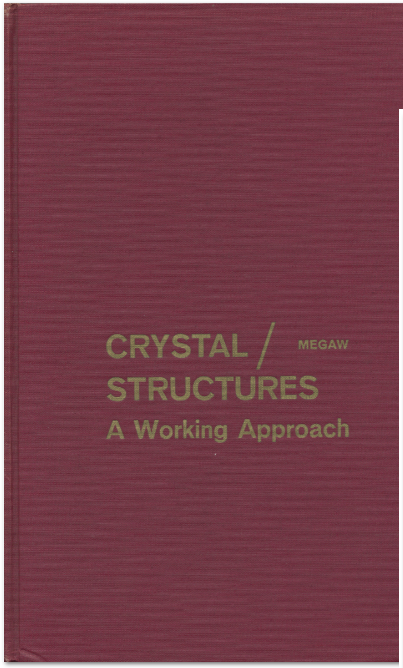
    a. Ionic radii and Pauling's rules
    b. Electrostatic valence
    c. Bond valence, and bond valence sums

Why do certain combinations of atoms take on specific structures?

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

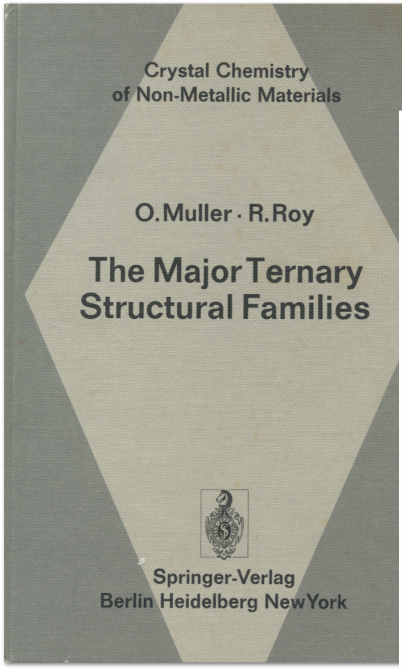
3. d^0 and s^2 configurations.

My bookshelf



CRYSTAL / STRUCTURES
A Working Approach
MEGAW

H. D. Megaw



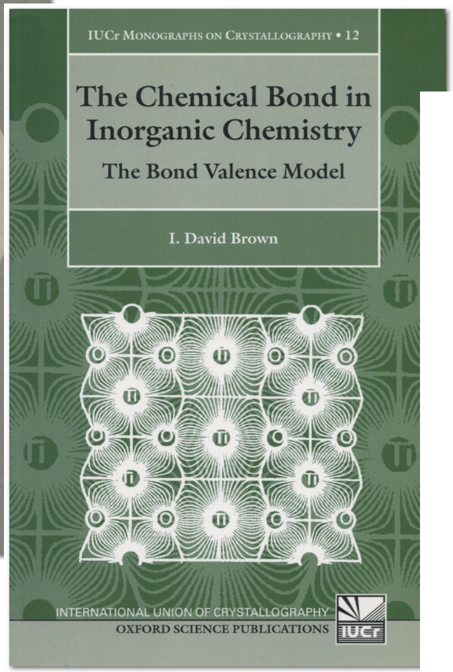
Crystal Chemistry
of Non-Metallic Materials

O. Muller · R. Roy

The Major Ternary Structural Families

Springer-Verlag
Berlin Heidelberg NewYork

O. Muller &
R. Roy



IUCr Monographs on Crystallography • 12

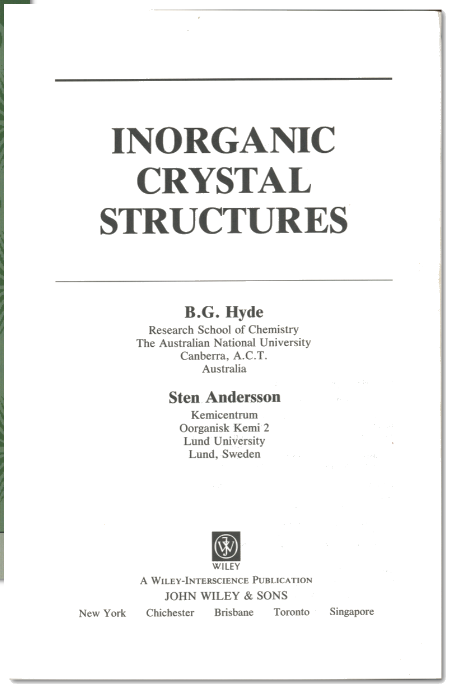
The Chemical Bond in Inorganic Chemistry

The Bond Valence Model

I. David Brown

INTERNATIONAL UNION OF CRYSTALLOGRAPHY
OXFORD SCIENCE PUBLICATIONS

I. D. Brown



INORGANIC CRYSTAL STRUCTURES

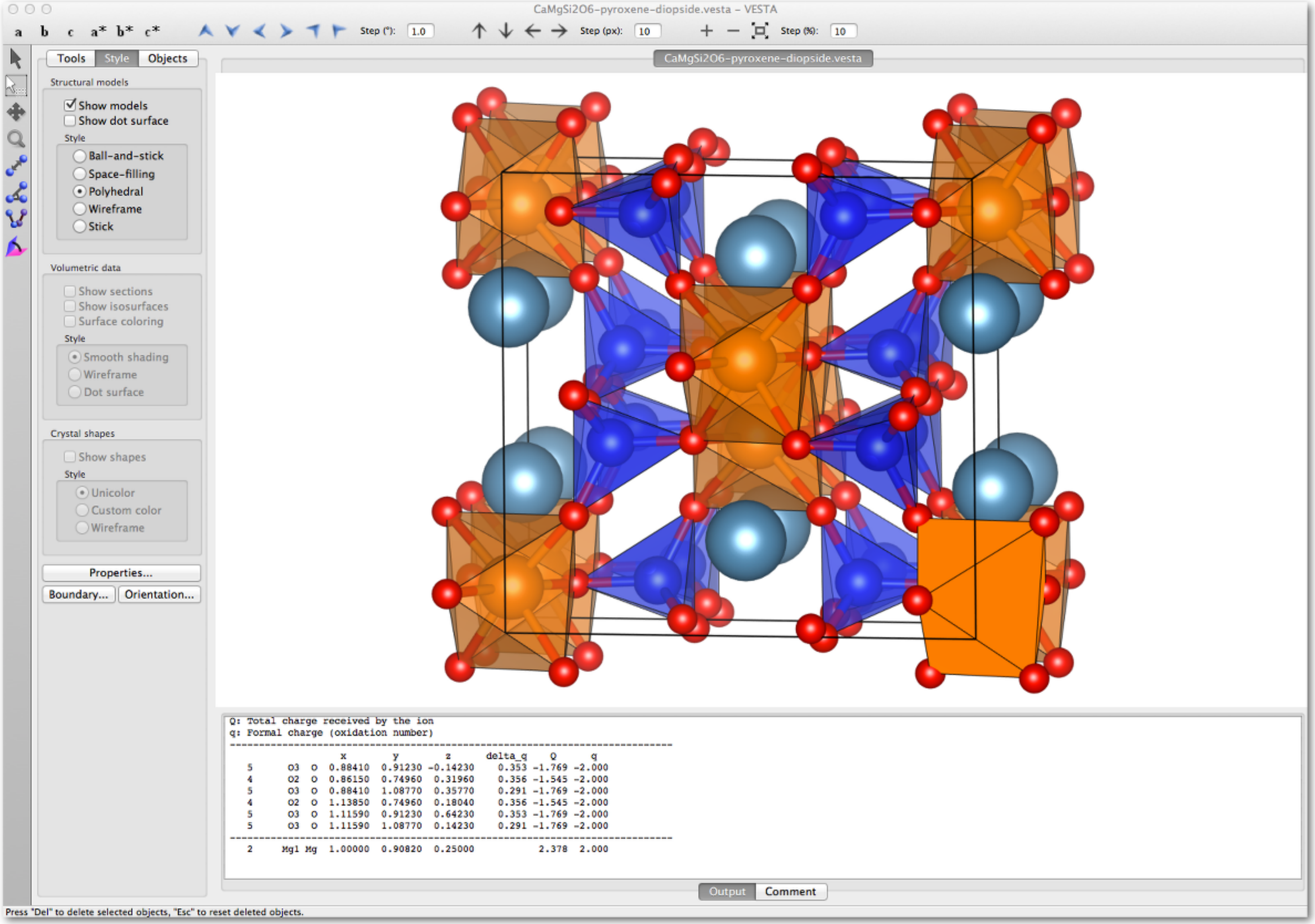
B.G. Hyde
Research School of Chemistry
The Australian National University
Canberra, A.C.T.
Australia

Sten Andersson
Kemicentrum
Oorganisk Kemi 2
Lund University
Lund, Sweden

WILEY
A Wiley-Interscience Publication
JOHN WILEY & SONS
New York Chichester Brisbane Toronto Singapore

B. G. Hyde &
S. Andersson

Software: ICSD + VESTA



CaMgSi2O6-pyroxene-diopside.vesta – VESTA

Step (°): 1.0

Step (px): 10

Step (%): 10

Structural models

☑ Show models
☐ Show dot surface

Style

○ Ball-and-stick
○ Space-filling
● Polyhedral
○ Wireframe
○ Stick

Volumetric data

☐ Show sections
☐ Show isosurfaces
☐ Surface coloring

Style

● Smooth shading
○ Wireframe
○ Dot surface

Crystal shapes

☐ Show shapes

Style

● Unicolor
○ Custom color
○ Wireframe

```
Q: Total charge received by the ion
q: Formal charge (oxidation number)
-----------------------------------------------------------------------------
                     x         y         z      delta_q     Q       q
  5      O3   O  0.88410   0.91230 -0.14230    0.353 -1.769 -2.000
  4      O2   O  0.86150   0.74960  0.31960    0.356 -1.545 -2.000
  5      O3   O  0.88410   1.08770  0.35770    0.291 -1.769 -2.000
  4      O2   O  1.13850   0.74960  0.18040    0.356 -1.545 -2.000
  5      O3   O  1.11590   0.91230  0.64230    0.353 -1.769 -2.000
  5      O3   O  1.11590   1.08770  0.14230    0.291 -1.769 -2.000
-----------------------------------------------------------------------------
  2     Mg1 Mg  1.00000   0.90820  0.25000             2.378  2.000
```

Press "Del" to delete selected objects, "Esc" to reset deleted objects.

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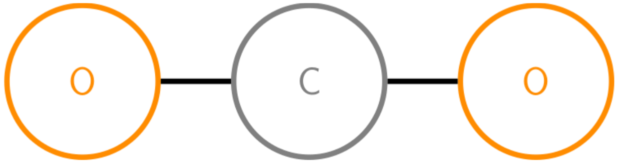
Crystal structures of simple oxides [containing a single cation site]

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

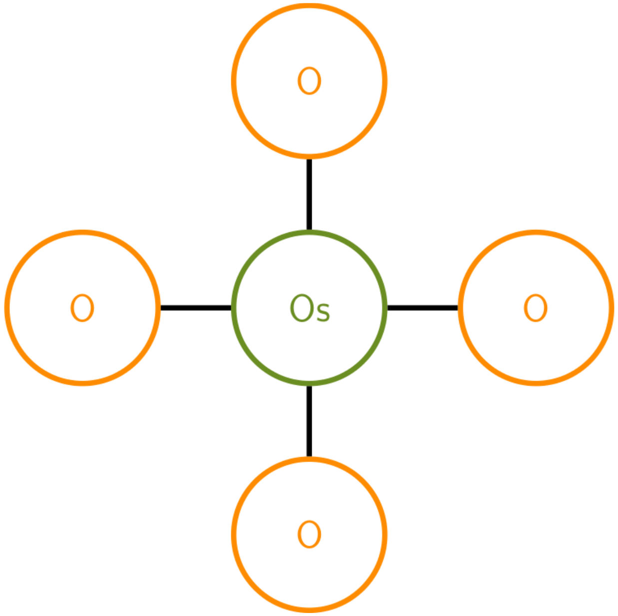
N.B.: CoO is simple, Co_3O_4 is not. $ZnCo_2O_4$ is certainly not !
Co_3O_4 and $ZnCo_2O_4$ are complex oxides.

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



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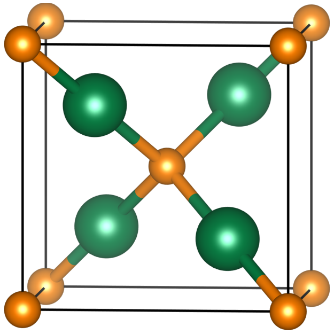
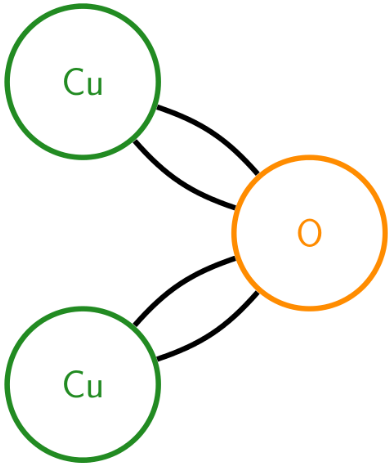
Crystal structures of simple oxides of monovalent ions: A_2O

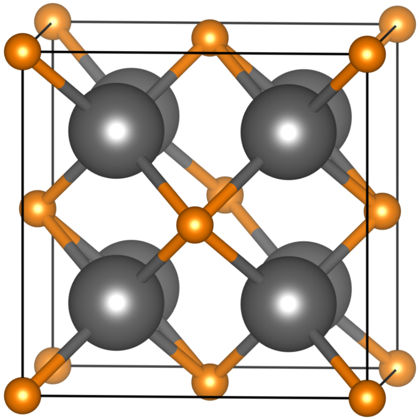
Cu_2O

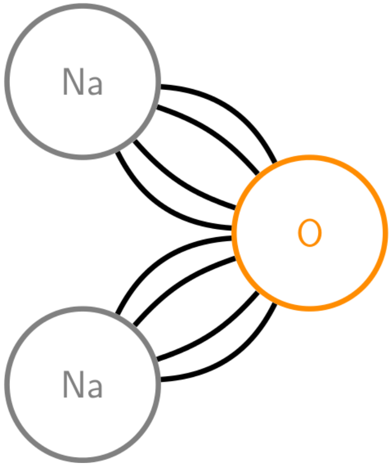




Linear coordination is unusual. Found usually in Cu^+ and Ag^+.

Na_2O (anti-fluorite)

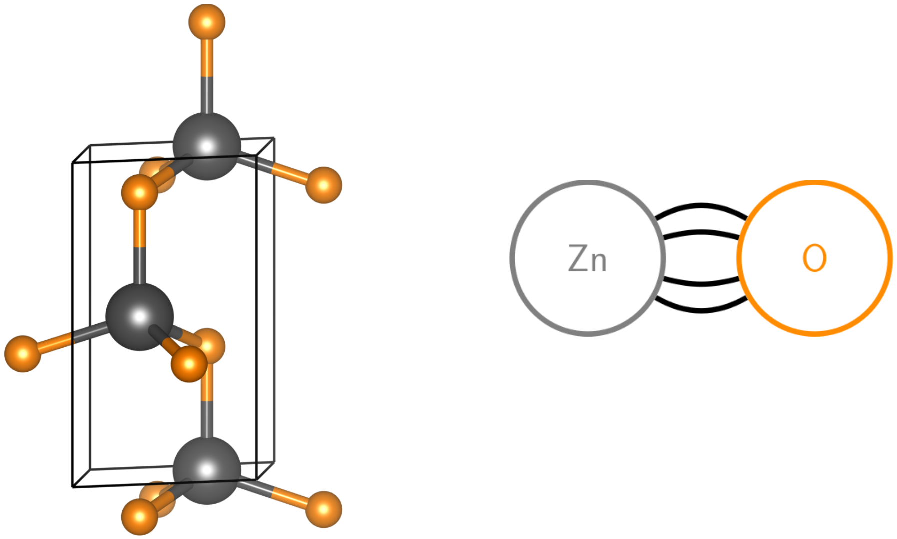




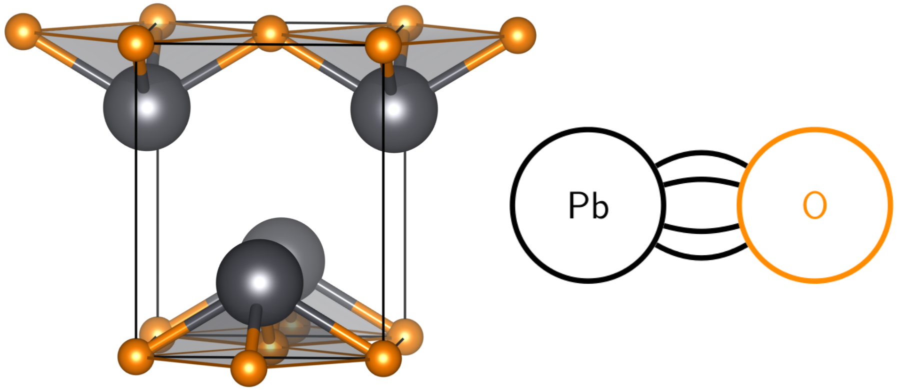
4-coordination for Na^+ and 8-coordination for O^{2-} are unusual.

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

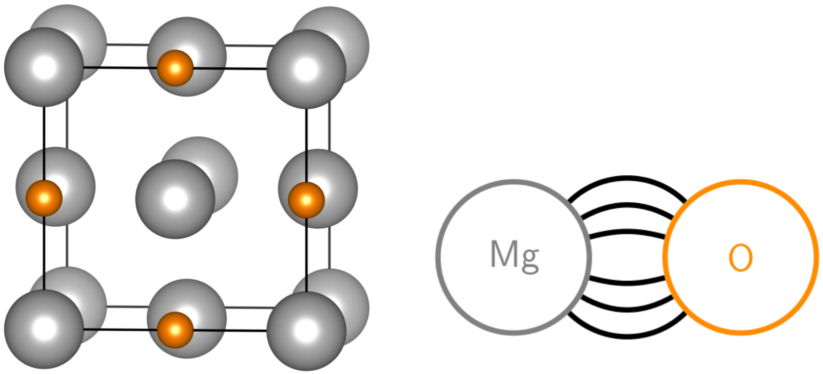
ZnO (wurtzite), sp^3



PbO (litharge), lone pairs



MgO (rock-salt)

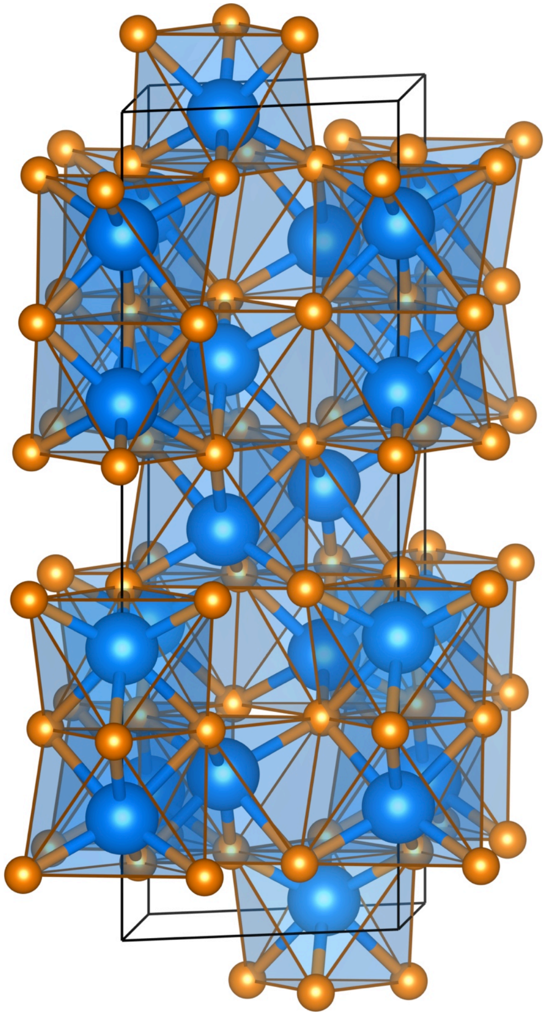


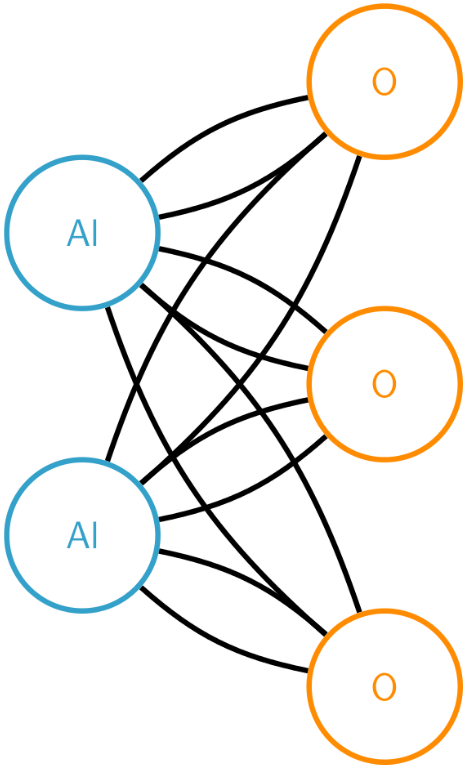
Ubiquitous for *AO* oxides including transition metals (distorted for CuO and NbO).

Insulators, metals (TiO), magnetic, …

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

α-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).

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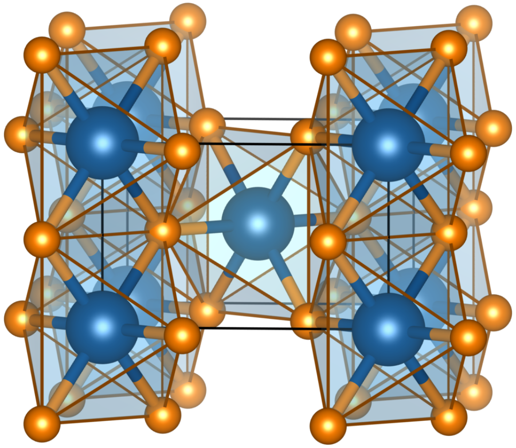
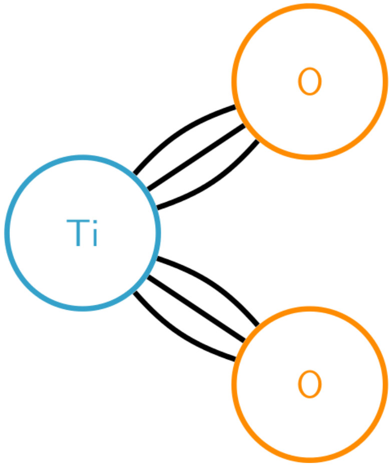
Crystal structures of simple oxides of tetravalent ions: AO_2

TiO_2 (rutile)

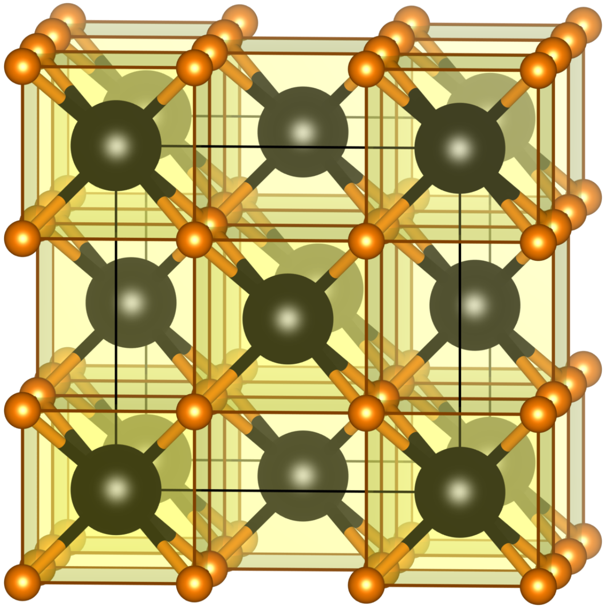


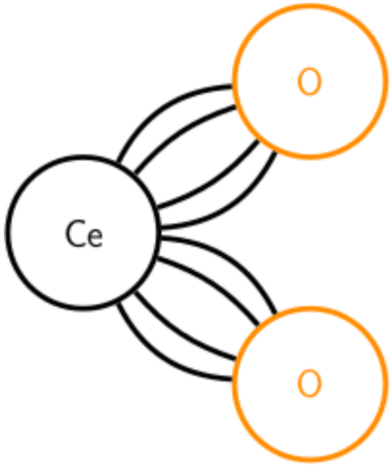


TiO_2 also crystallizes as anatase and brookite.

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

CeO_2 (fluorite)



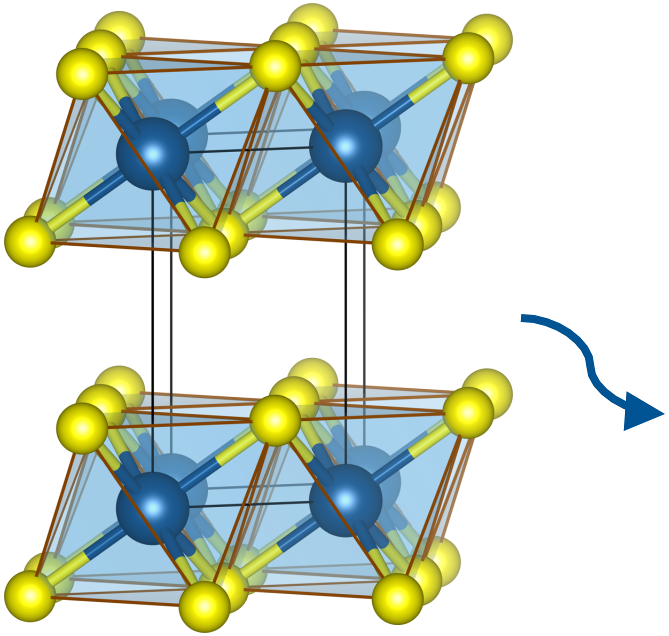


Also the structure of ThO_2, and of ZrO_2 and HfO_2 at elevated temperatures.

Ordered variants abound.

Oxides versus sulfides: TiS_2

2*H*–TiS_2

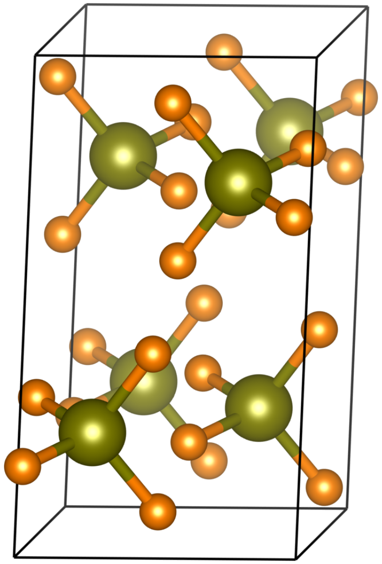


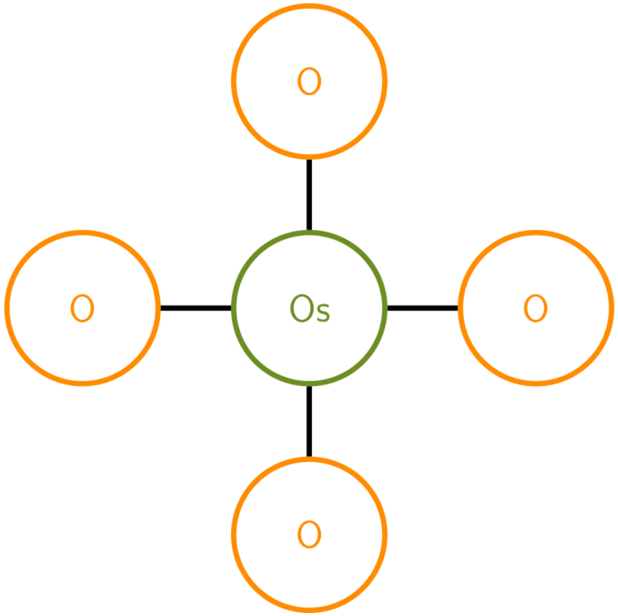
van der Waals gap (unlikely in oxides or fluorides, but occurs frequently in hydroxides)

This is the CdI_2 structure.

Crystal structures of an oxide with an octavalent ion: OsO_4

OsO_4





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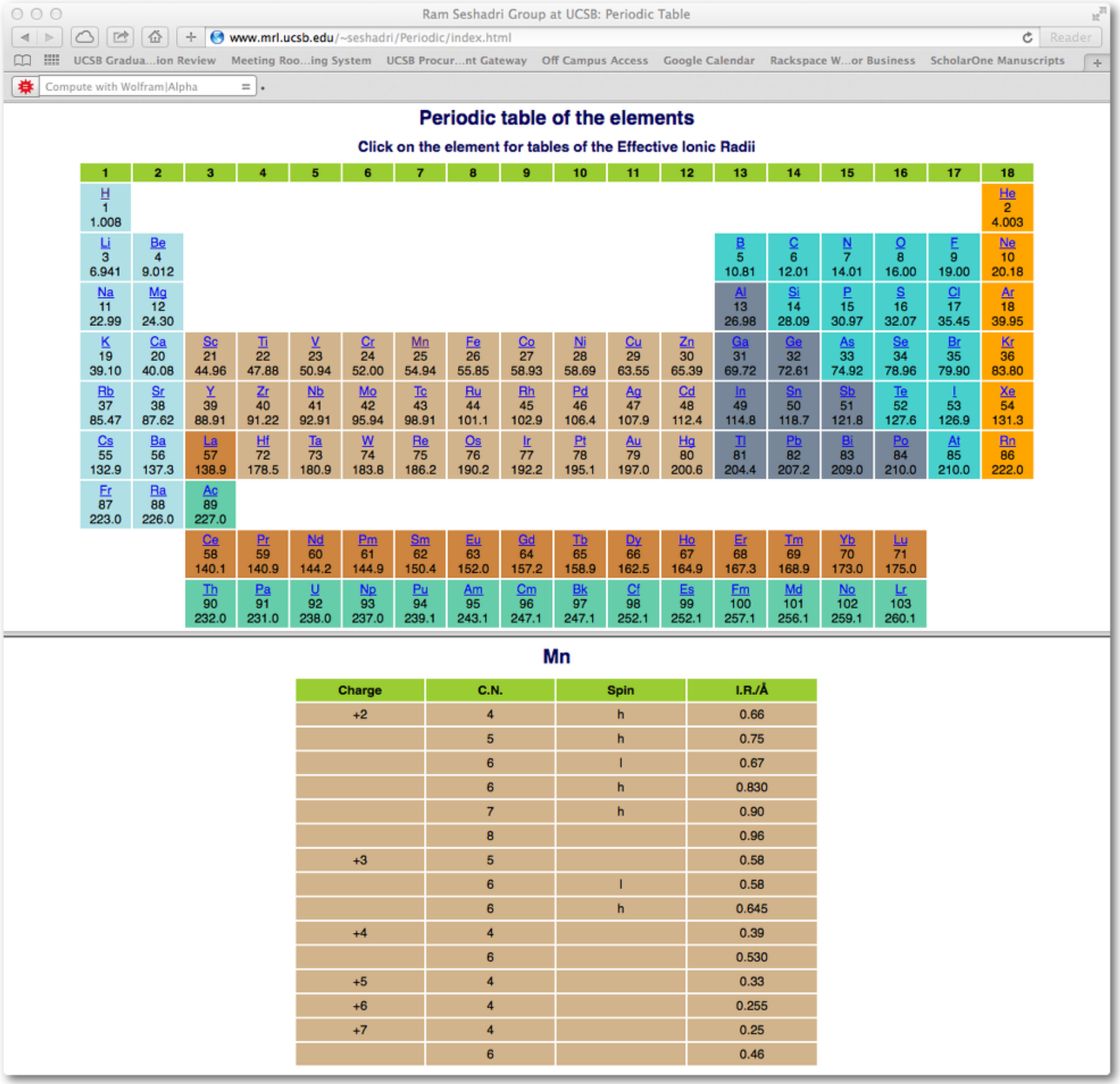
Shannon-Prewitt (ionic) radii

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



Periodic table of the elements

Click on the element for tables of the Effective Ionic Radii

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 1 1.008																	He 2 4.003
Li 3 6.941	Be 4 9.012											B 5 10.81	C 6 12.01	N 7 14.01	O 8 16.00	F 9 19.00	Ne 10 20.18
Na 11 22.99	Mg 12 24.30											Al 13 26.98	Si 14 28.09	P 15 30.97	S 16 32.07	Cl 17 35.45	Ar 18 39.95
K 19 39.10	Ca 20 40.08	Sc 21 44.96	Ti 22 47.88	V 23 50.94	Cr 24 52.00	Mn 25 54.94	Fe 26 55.85	Co 27 58.93	Ni 28 58.69	Cu 29 63.55	Zn 30 65.39	Ga 31 69.72	Ge 32 72.61	As 33 74.92	Se 34 78.96	Br 35 79.90	Kr 36 83.80
Rb 37 85.47	Sr 38 87.62	Y 39 88.91	Zr 40 91.22	Nb 41 92.91	Mo 42 95.94	Tc 43 98.91	Ru 44 101.1	Rh 45 102.9	Pd 46 106.4	Ag 47 107.9	Cd 48 112.4	In 49 114.8	Sn 50 118.7	Sb 51 121.8	Te 52 127.6	I 53 126.9	Xe 54 131.3
Cs 55 132.9	Ba 56 137.3	La 57 138.9	Hf 72 178.5	Ta 73 180.9	W 74 183.8	Re 75 186.2	Os 76 190.2	Ir 77 192.2	Pt 78 195.1	Au 79 197.0	Hg 80 200.6	Tl 81 204.4	Pb 82 207.2	Bi 83 209.0	Po 84 210.0	At 85 210.0	Rn 86 222.0
Fr 87 223.0	Ra 88 226.0	Ac 89 227.0															
		Ce 58 140.1	Pr 59 140.9	Nd 60 144.2	Pm 61 144.9	Sm 62 150.4	Eu 63 152.0	Gd 64 157.2	Tb 65 158.9	Dy 66 162.5	Ho 67 164.9	Er 68 167.3	Tm 69 168.9	Yb 70 173.0	Lu 71 175.0		
		Th 90 232.0	Pa 91 231.0	U 92 238.0	Np 93 237.0	Pu 94 239.1	Am 95 243.1	Cm 96 247.1	Bk 97 247.1	Cf 98 252.1	Es 99 252.1	Fm 100 257.1	Md 101 256.1	No 102 259.1	Lr 103 260.1		

Mn

Charge	C.N.	Spin	I.R./Å
+2	4	h	0.66
	5	h	0.75
	6	l	0.67
	6	h	0.830
	7	h	0.90
	8		0.96
+3	5		0.58
	6	l	0.58
	6	h	0.645
+4	4		0.39
	6		0.530
+5	4		0.33
+6	4		0.255
+7	4		0.25
	6		0.46

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

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

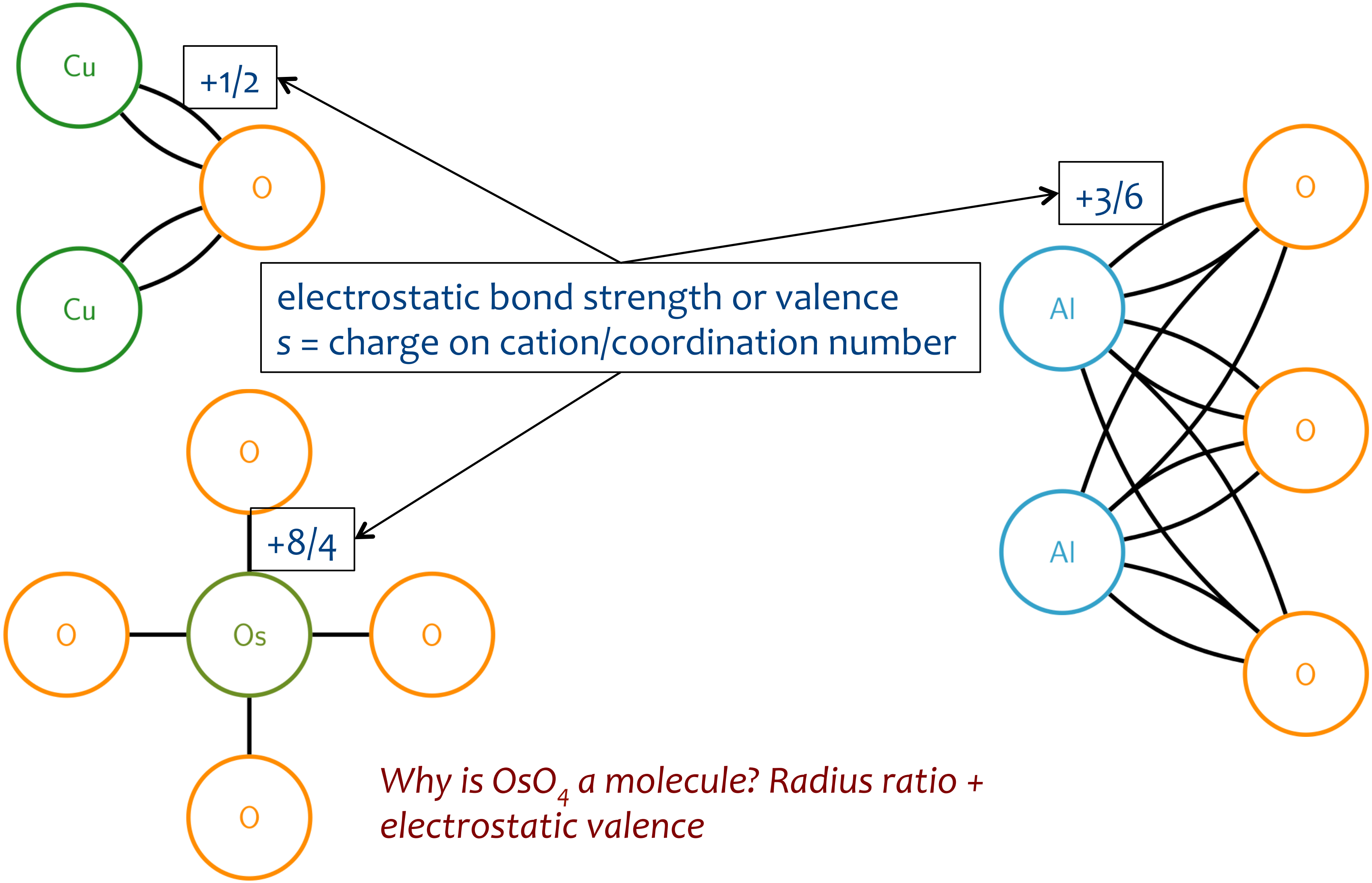
In brief: The cation-anion distance is the sum of cation and anion radii, and the number of anions around a cation (the coordination number) is a function of the radius ratio. Exemplified by AO_2 compounds below. MRR is the mimimum radius ratio.

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*



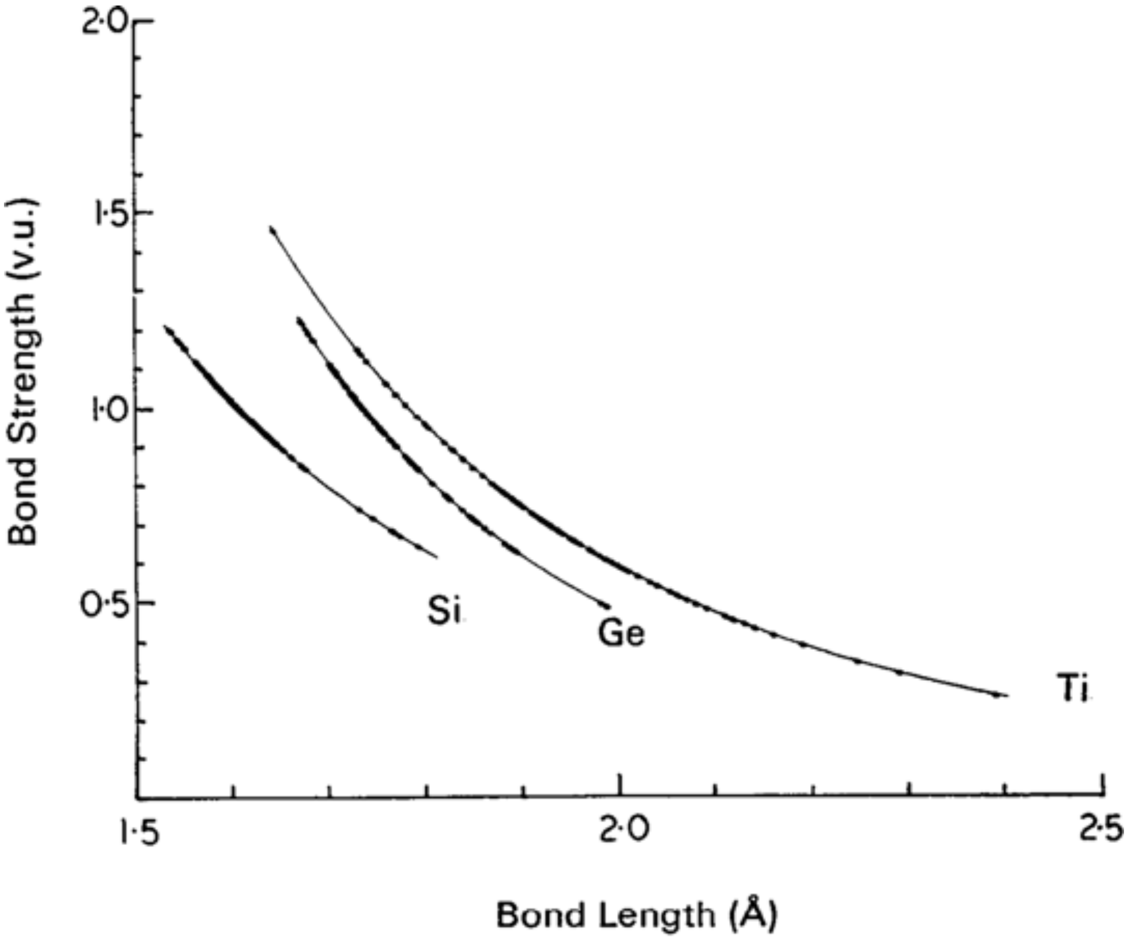
electrostatic bond strength or valence
s = charge on cation/coordination number

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

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*



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

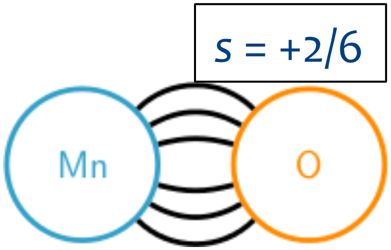
Electrostatic valence and bond valence

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

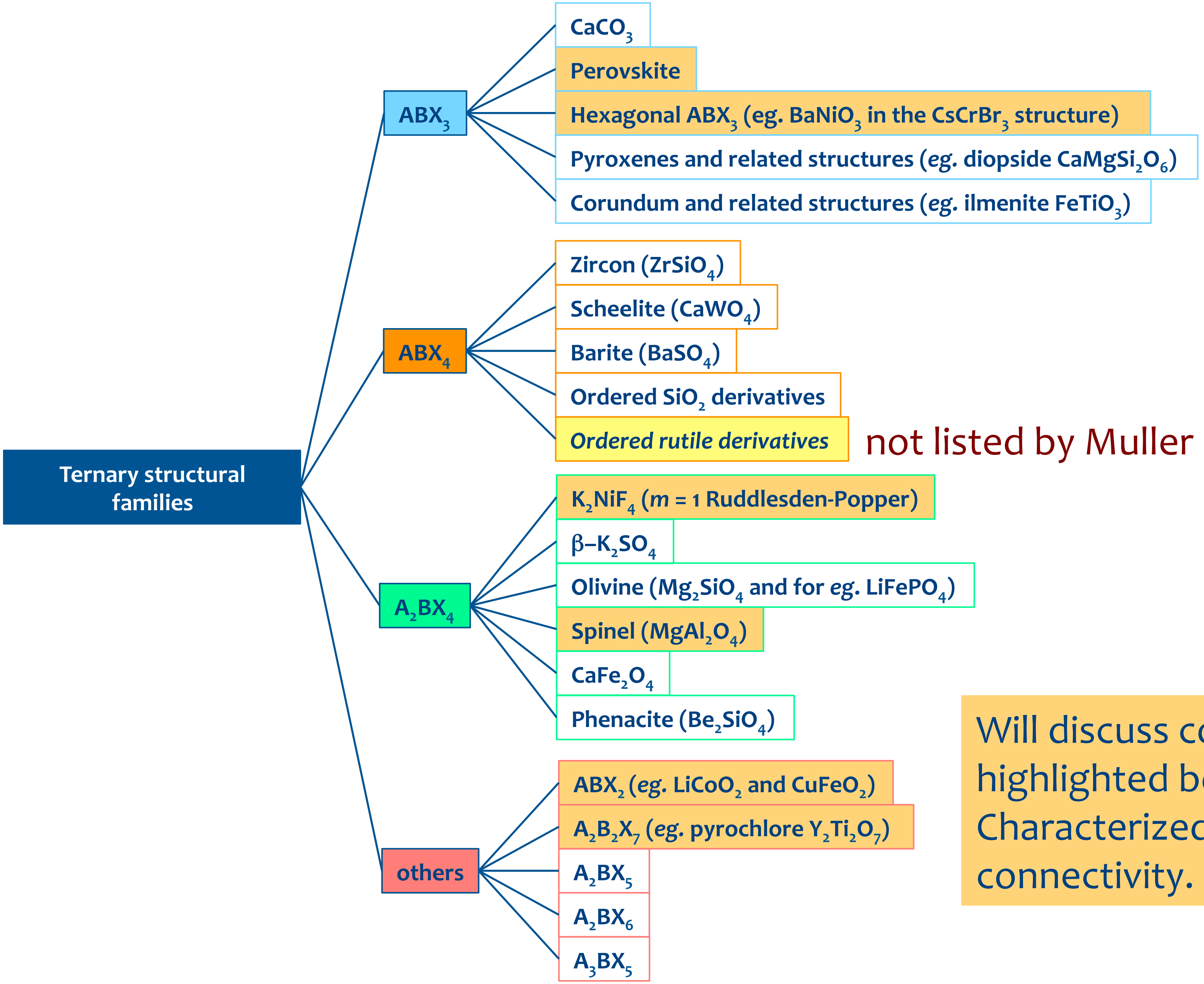
```
Mn 2   O  -2    1.790    0.37     a
Mn 2   O  -2    1.765    0.37     j
Mn 2   S  -2    2.22     0.37     e
Mn 2   F  -1    1.698    0.37     a
Mn 2   Cl -1    2.133    0.37     a
Mn 2   Br -1    2.34     0.37     e
Mn 2   I  -2    2.52     0.37     e
Mn 2   N  -3    1.849    0.37     j
Mn 2   N  -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)

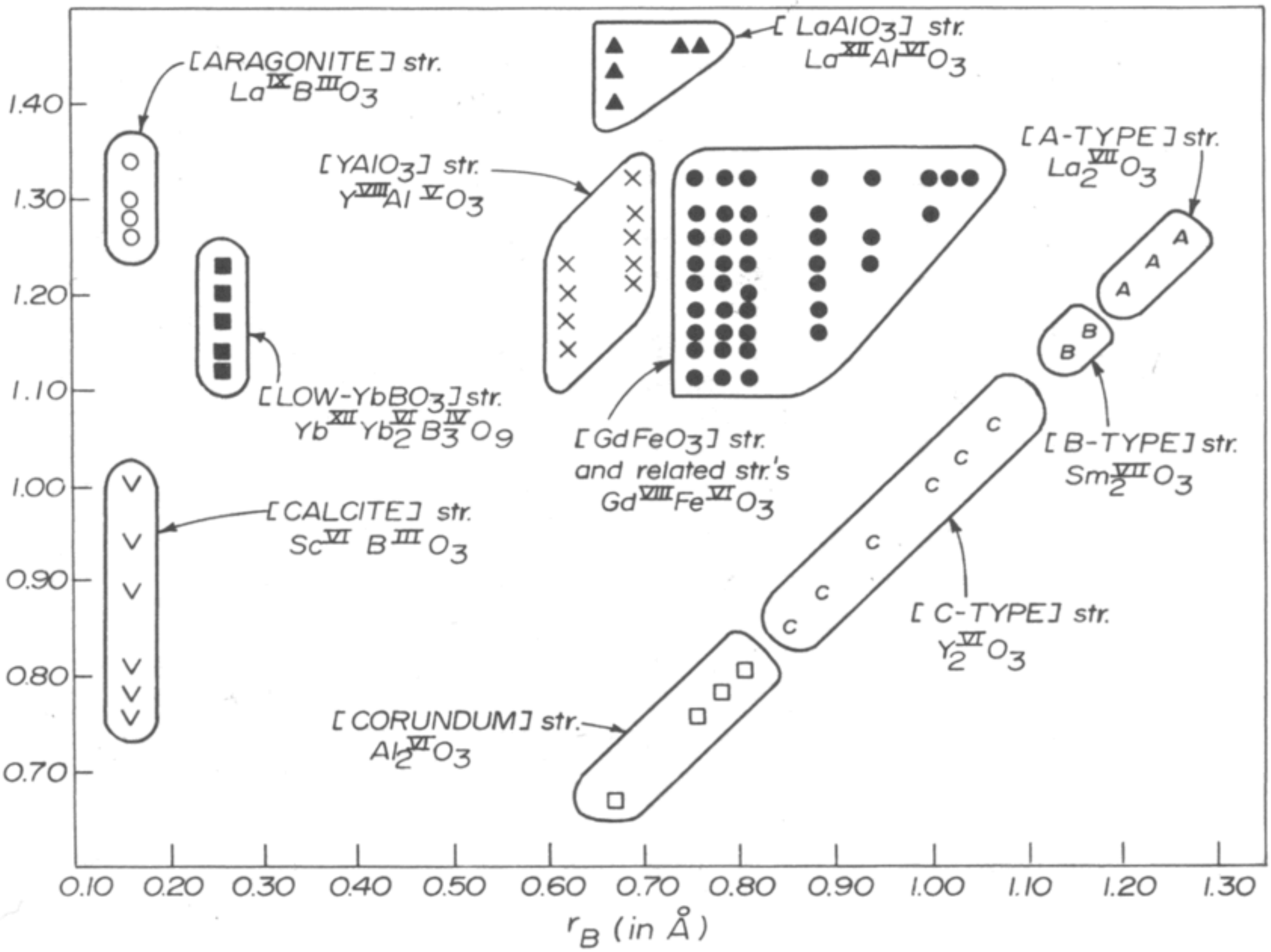


- **Ternary structural families**
  - **ABX_3**
    - $CaCO_3$
    - Perovskite
    - Hexagonal ABX_3 (eg. $BaNiO_3$ in the $CsCrBr_3$ structure)
    - Pyroxenes and related structures (*eg*. diopside $CaMgSi_2O_6$)
    - Corundum and related structures (*eg*. ilmenite $FeTiO_3$)
  - **ABX_4**
    - Zircon ($ZrSiO_4$)
    - Scheelite ($CaWO_4$)
    - Barite ($BaSO_4$)
    - Ordered SiO_2 derivatives
    - *Ordered rutile derivatives*
  - **A_2BX_4**
    - K_2NiF_4 (m = 1 Ruddlesden-Popper)
    - β–K_2SO_4
    - Olivine (Mg_2SiO_4 and for *eg*. $LiFePO_4$)
    - Spinel ($MgAl_2O_4$)
    - $CaFe_2O_4$
    - Phenacite (Be_2SiO_4)
  - **others**
    - ABX_2 (*eg*. $LiCoO_2$ and $CuFeO_2$)
    - $A_2B_2X_7$ (*eg*. pyrochlore $Y_2Ti_2O_7$)
    - A_2BX_5
    - A_2BX_6
    - A_3BX_5

not listed by Muller and Roy

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

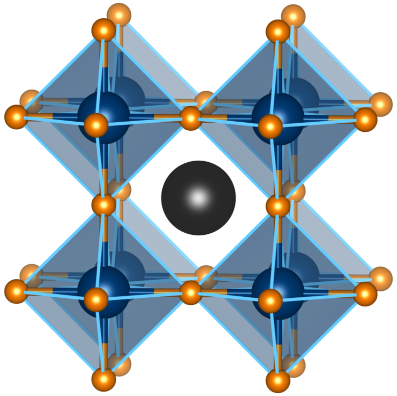
The ABO_3 structure-sorting field (from Muller and Roy)

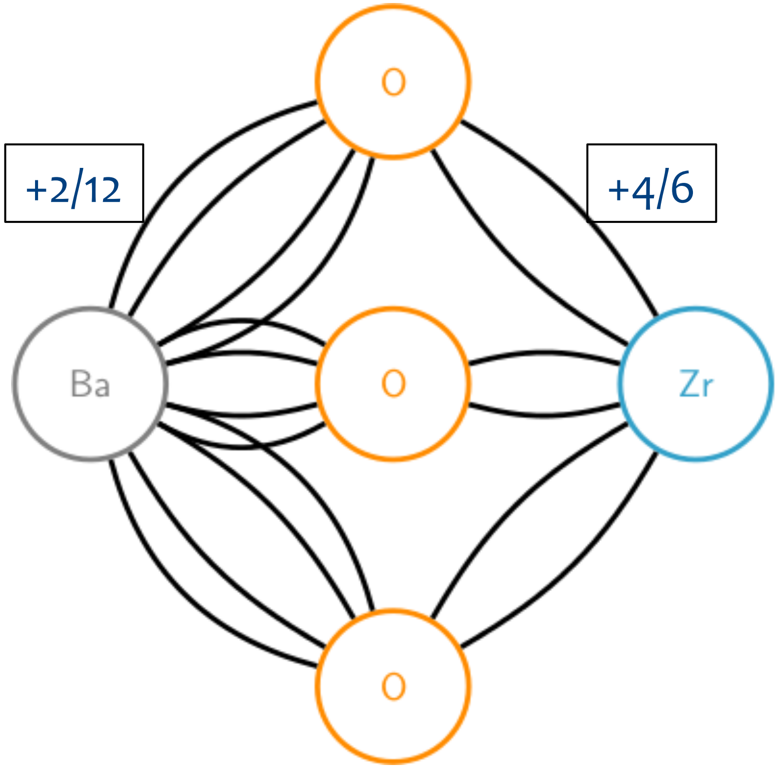


The superscripted roman numerals indicate coordination number.

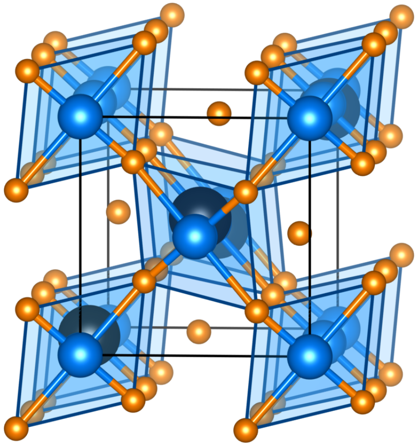
Perovskite

$BaZrO_3$





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



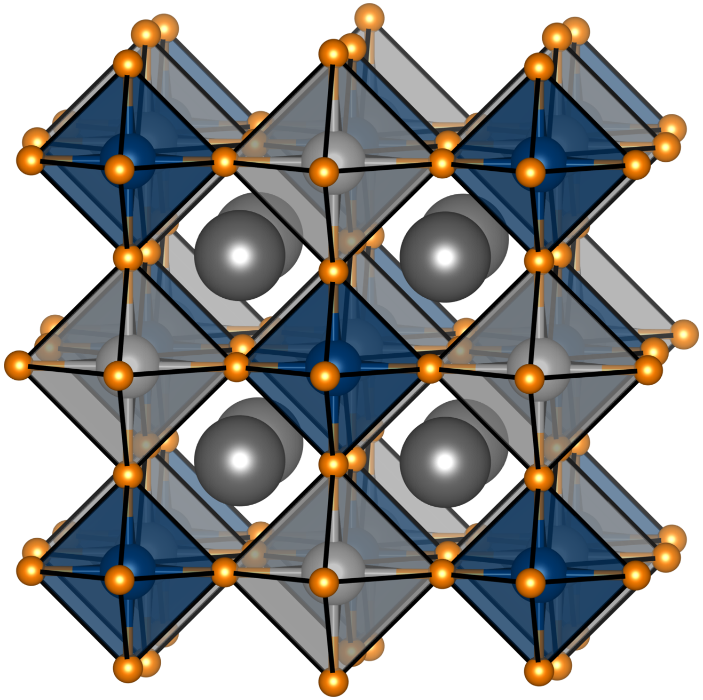
Note that the space group *Pnma* (#62) can be written in a variety of ways.

This is the most common perovskite space group.

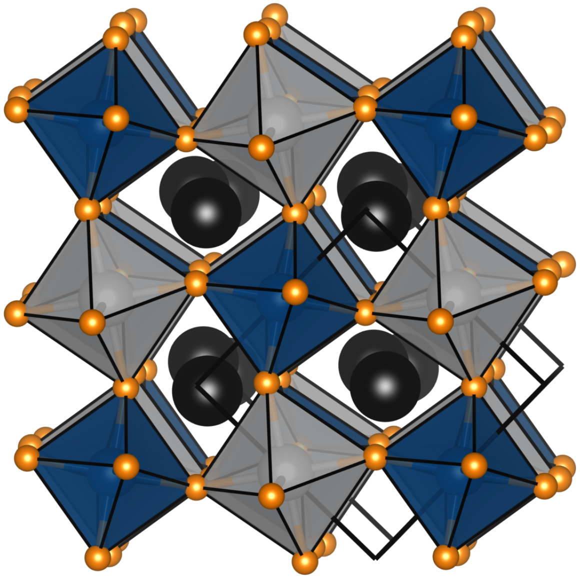
In the next so many structures, BO_6-polyhedra are depicted.

Ordered double perovskites (elpasolites)

Ba_2MgWO_6



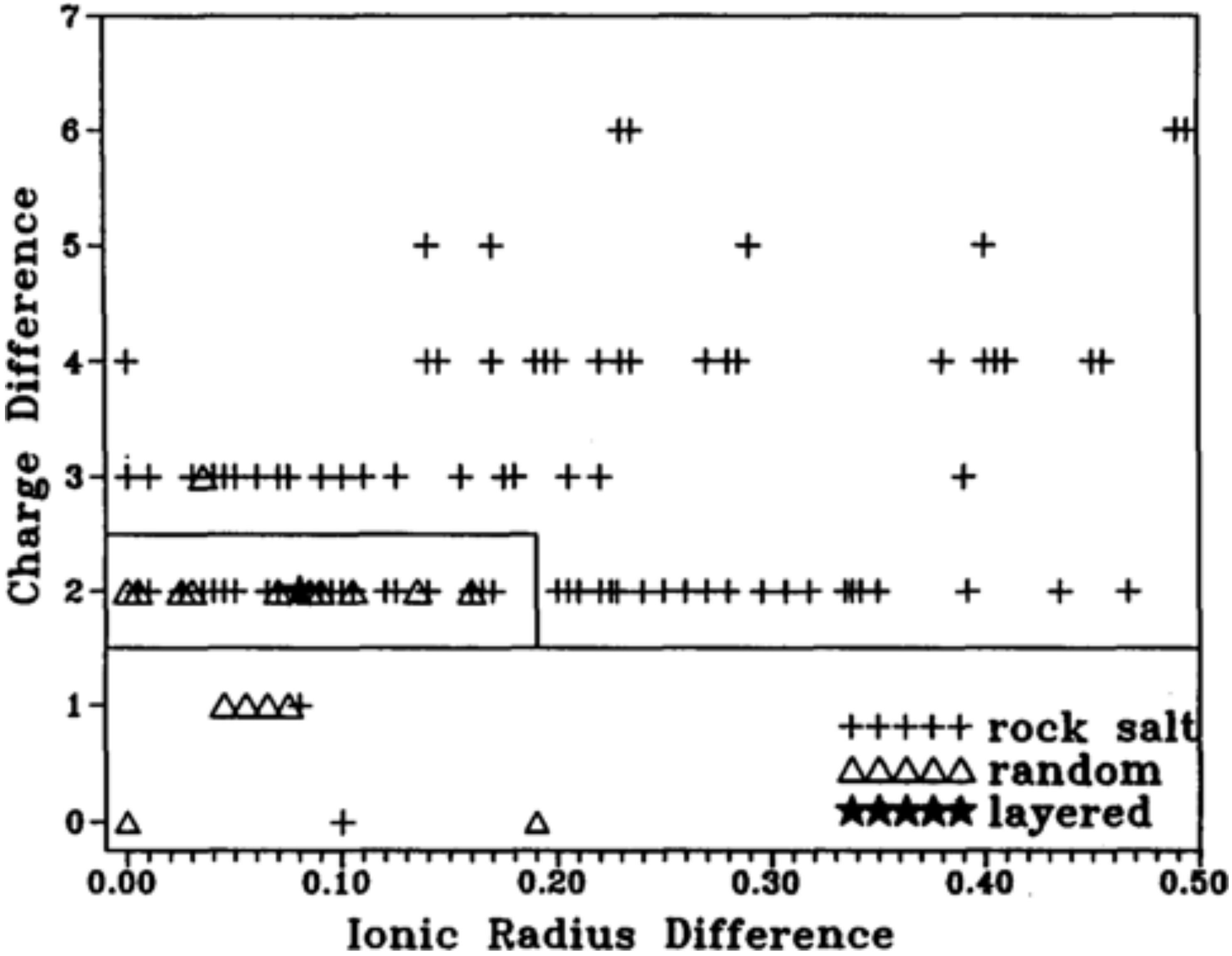
Ca_2MgWO_6



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

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

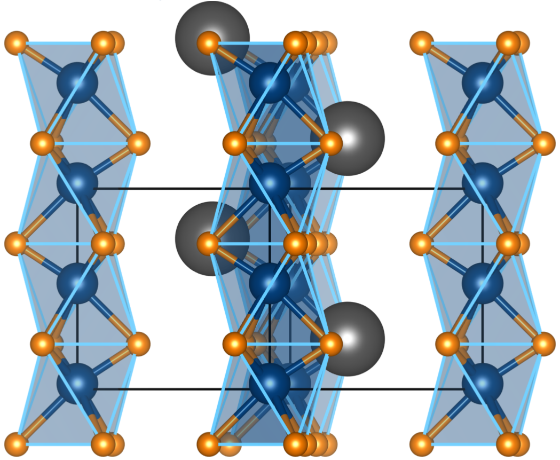
The double perovskite field: Charge and radius



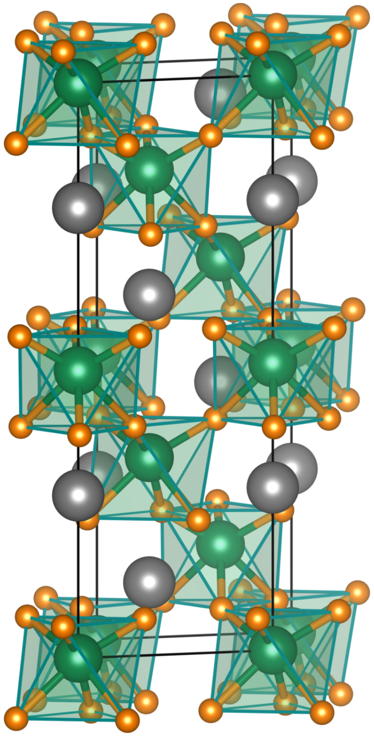
Anderson, Greenwood, and Poeppelmeier, *Prog. Solid State Chem.* **22** (1993) 197–233.

Hexagonal ABO_3 structures

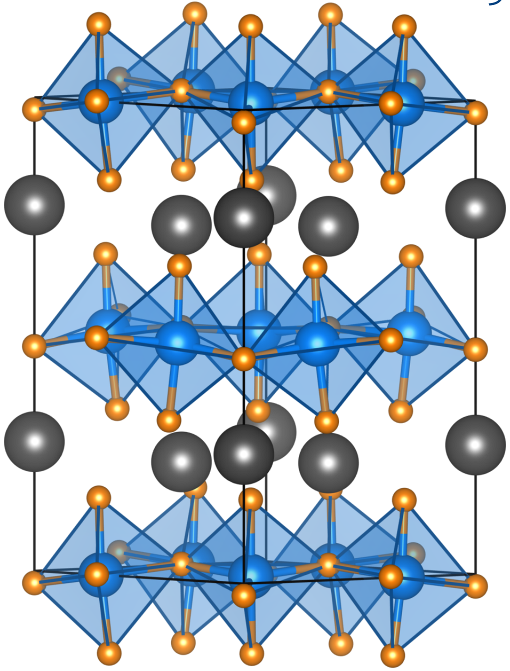
$BaNiO_3$



$LiNbO_3$ (ferroelectric $R3c$)



Ferroelectric $YMnO_3$ (“$YAlO_3$”)



Unusual 5-fold coordination (trigonal bibyramid) of MnO_5

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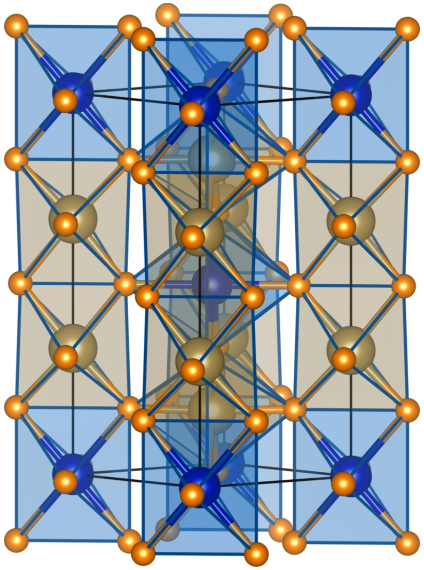
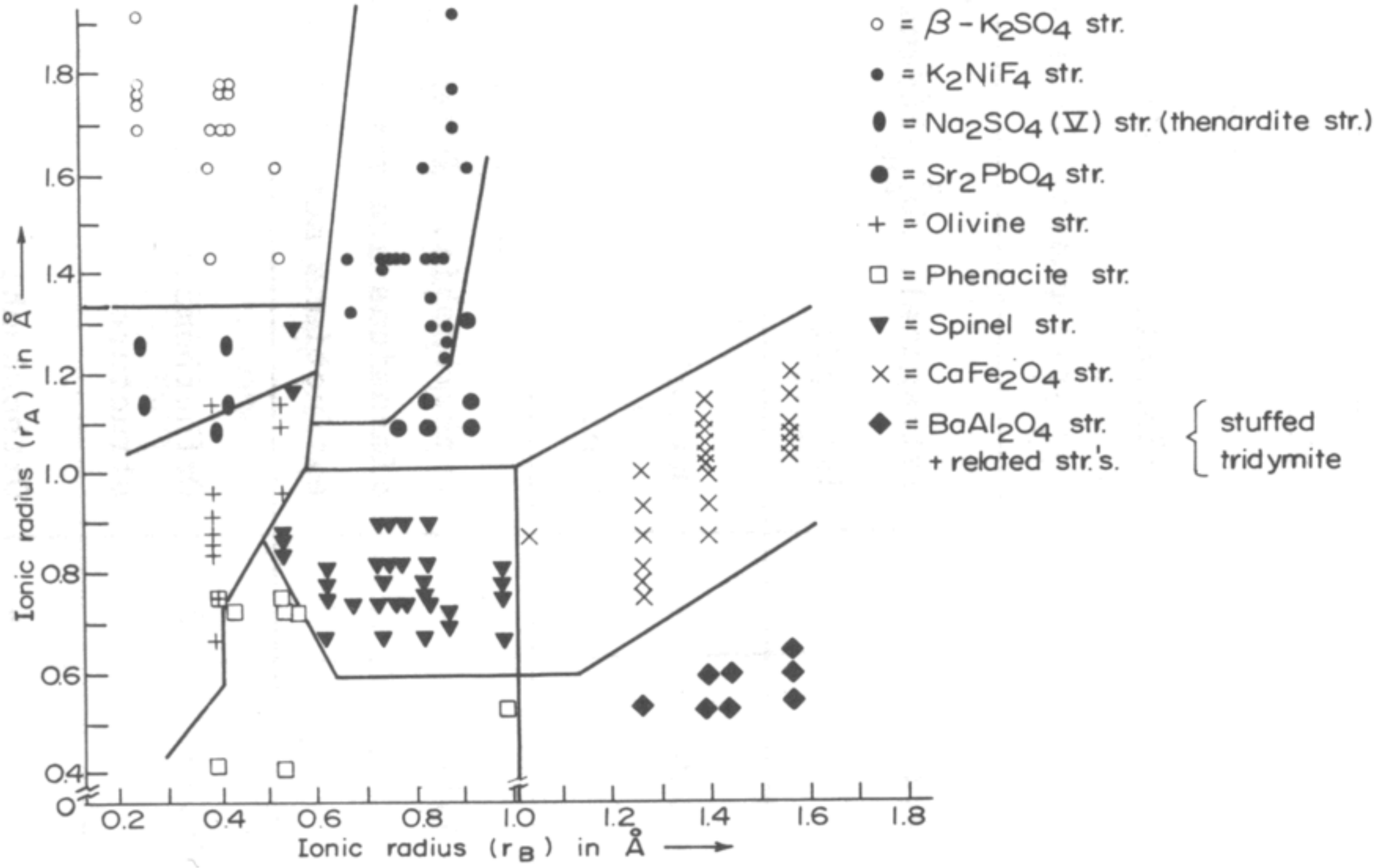
Ordered rutiles (the trirutile)

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



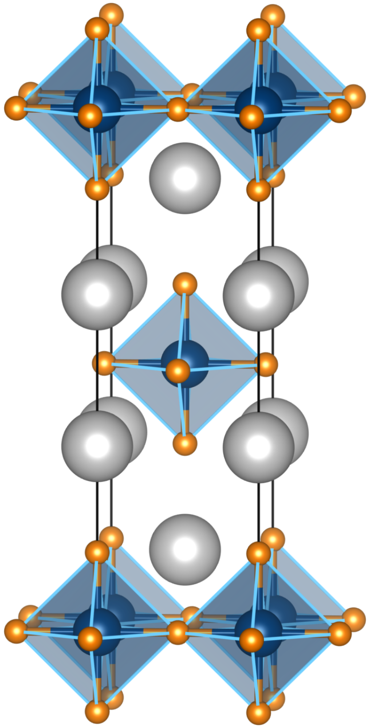
The A_2BO_4 structure-sorting field (from Muller and Roy)



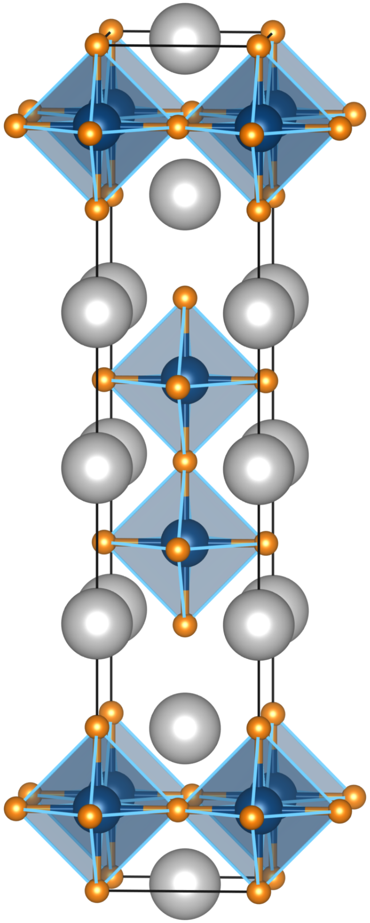
The superscripted roman numerals indicate coordination number.

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

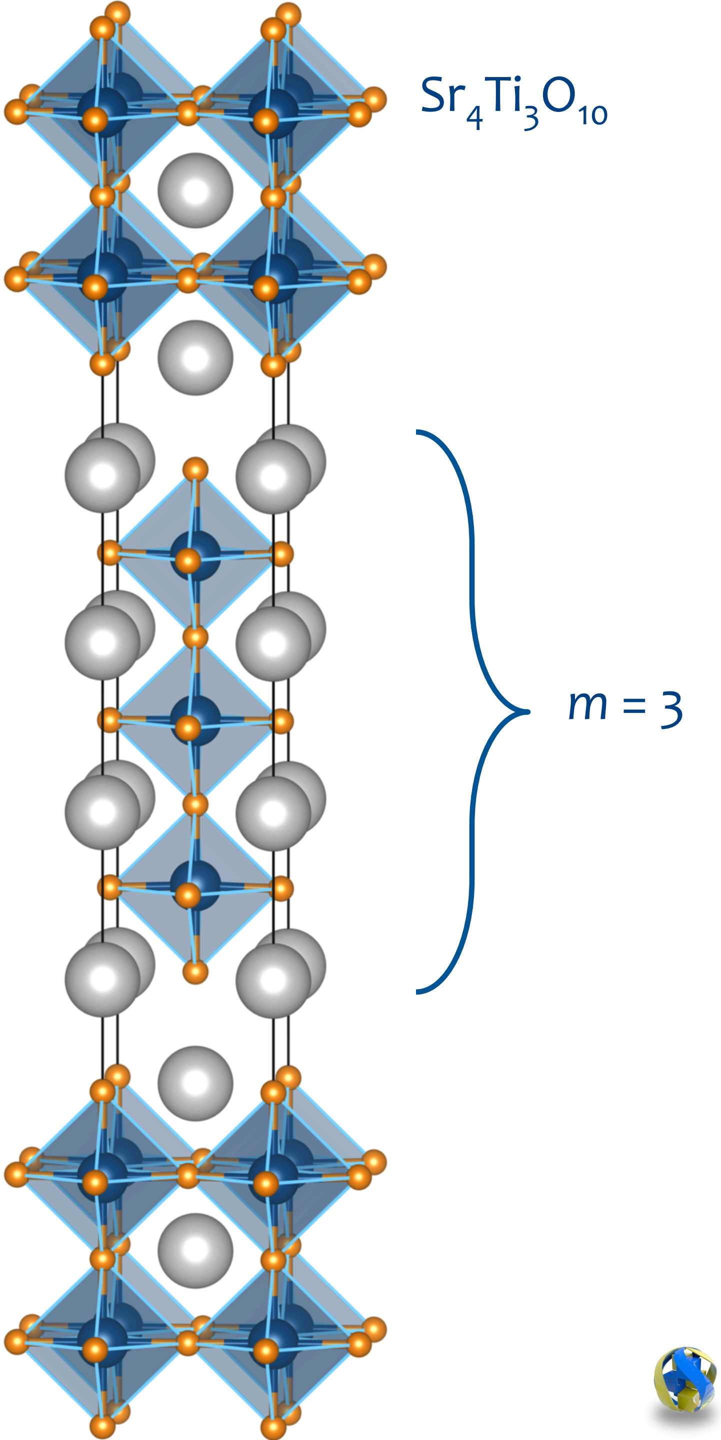
Sr_2TiO_4



$Sr_3Ti_2O_7$

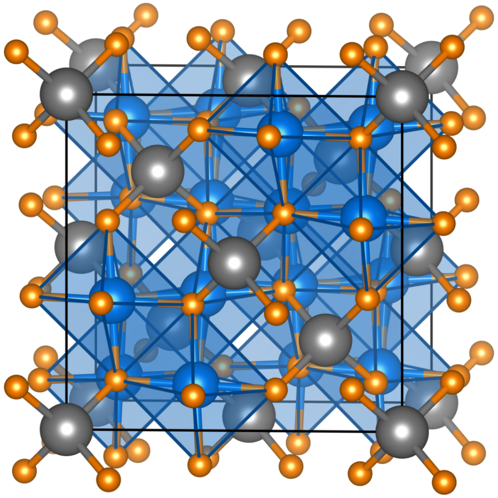


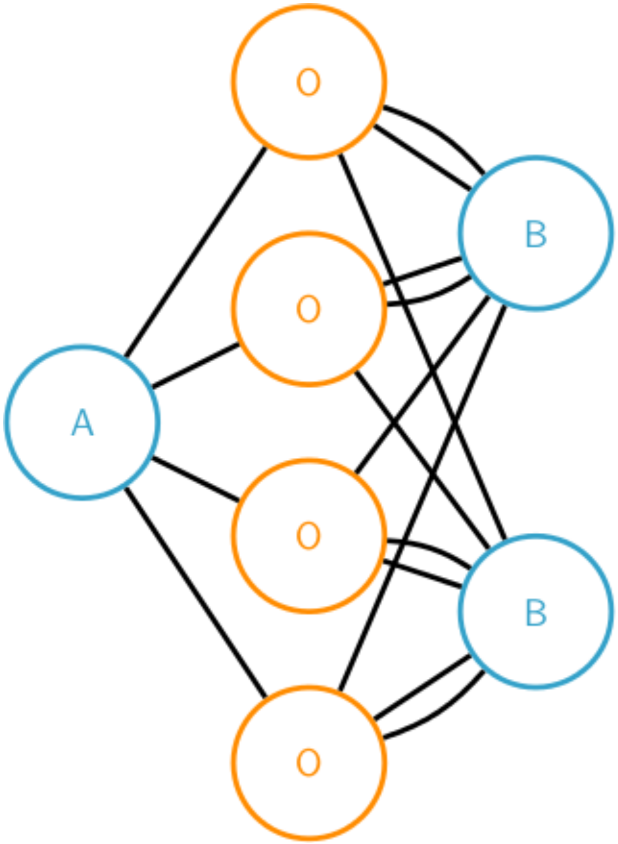
$Sr_4Ti_3O_{10}$



Spinel AB_2O_4

$MgAl_2O_4$



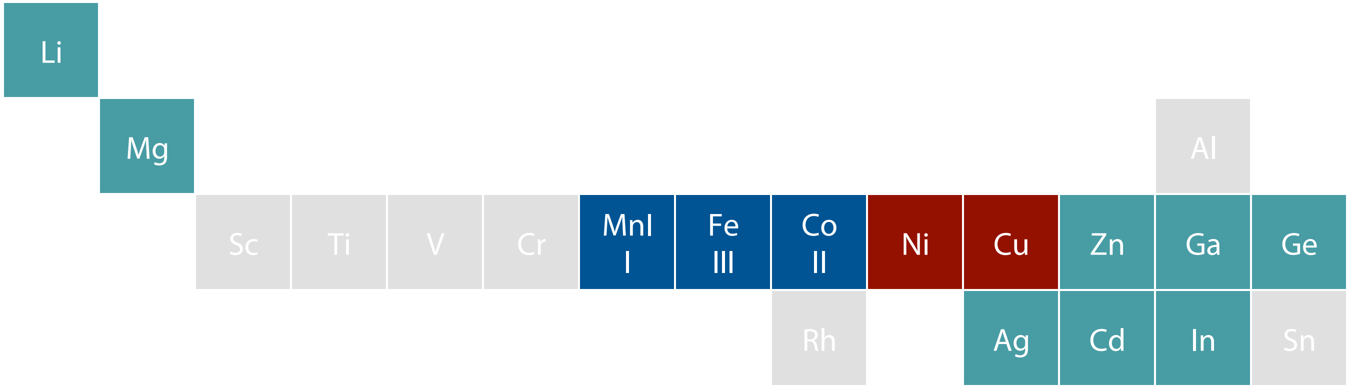


Ubiquitous structure when ions have similar sizes, around 0.6 Å.
A is tetrahedrally coordinated, and *B* octahedral (actually with a slight trigonal distortion).

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

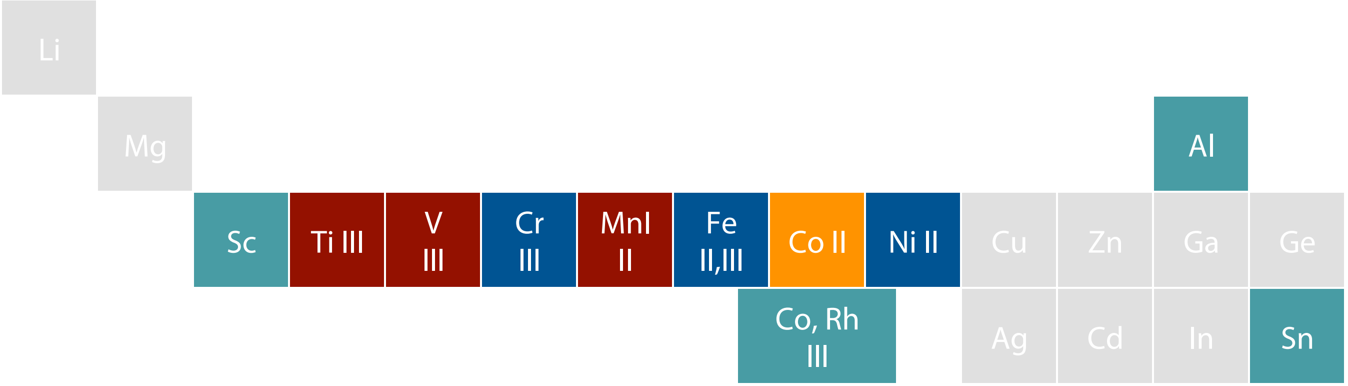
Spinel AB_2O_4

ions on the *A* site



Li													
	Mg											Al	
		Sc	Ti	V	Cr	Mn II	Fe III	Co II	Ni	Cu	Zn	Ga	Ge
								Rh		Ag	Cd	In	Sn

ions on the *B* site



Li													
	Mg											Al	
		Sc	Ti III	V III	Cr III	Mn III	Fe II,III	Co II	Ni II	Cu	Zn	Ga	Ge
								Co, Rh III		Ag	Cd	In	Sn

A,B	Jahn-Teller active
A,B	Diamagnetic
Co II	High single-ion anisotropy

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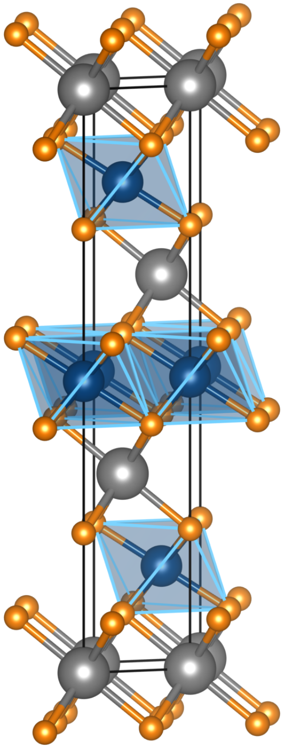
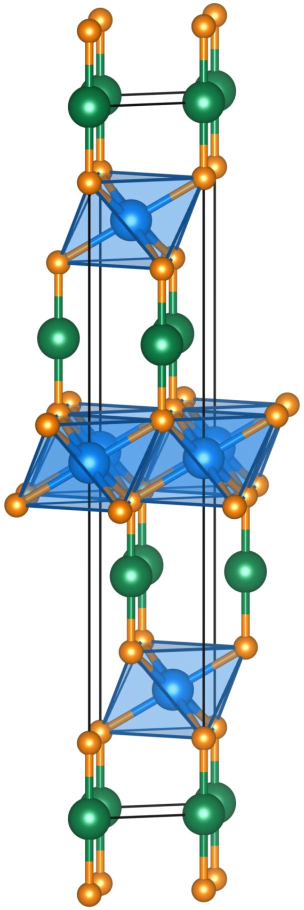
Some *ABO*$_2$ structures: Highly dense in-plane, and frequently metallic

LiCoO$_2$ (ordered rock-salt)



111-ordered with alternating octahedral LiO$_6$ and CoO$_6$ stacking

3*R*–CuFeO$_2$ (delafossite)



*B*O$_2$ (CdI$_2$) slabs separated by two-coordinate atoms, usually Cu$^+$ and Ag$^+$. Also unusually, Pd^{1+} and Pt^{1+}.

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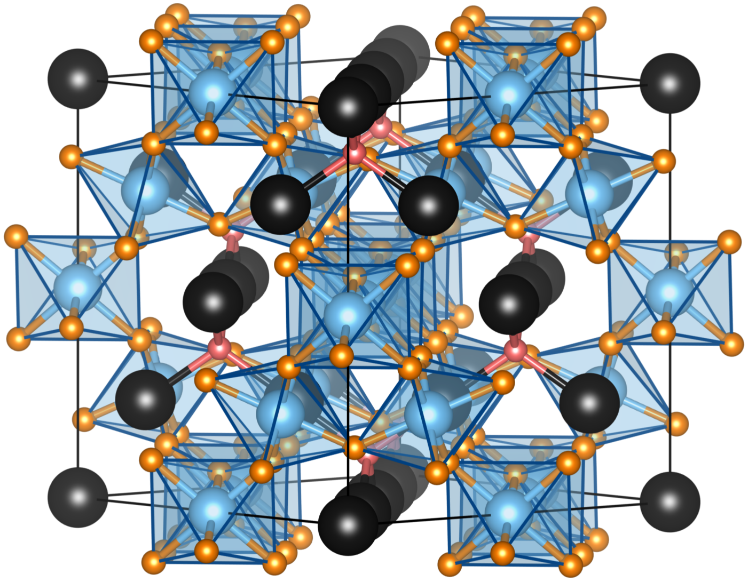
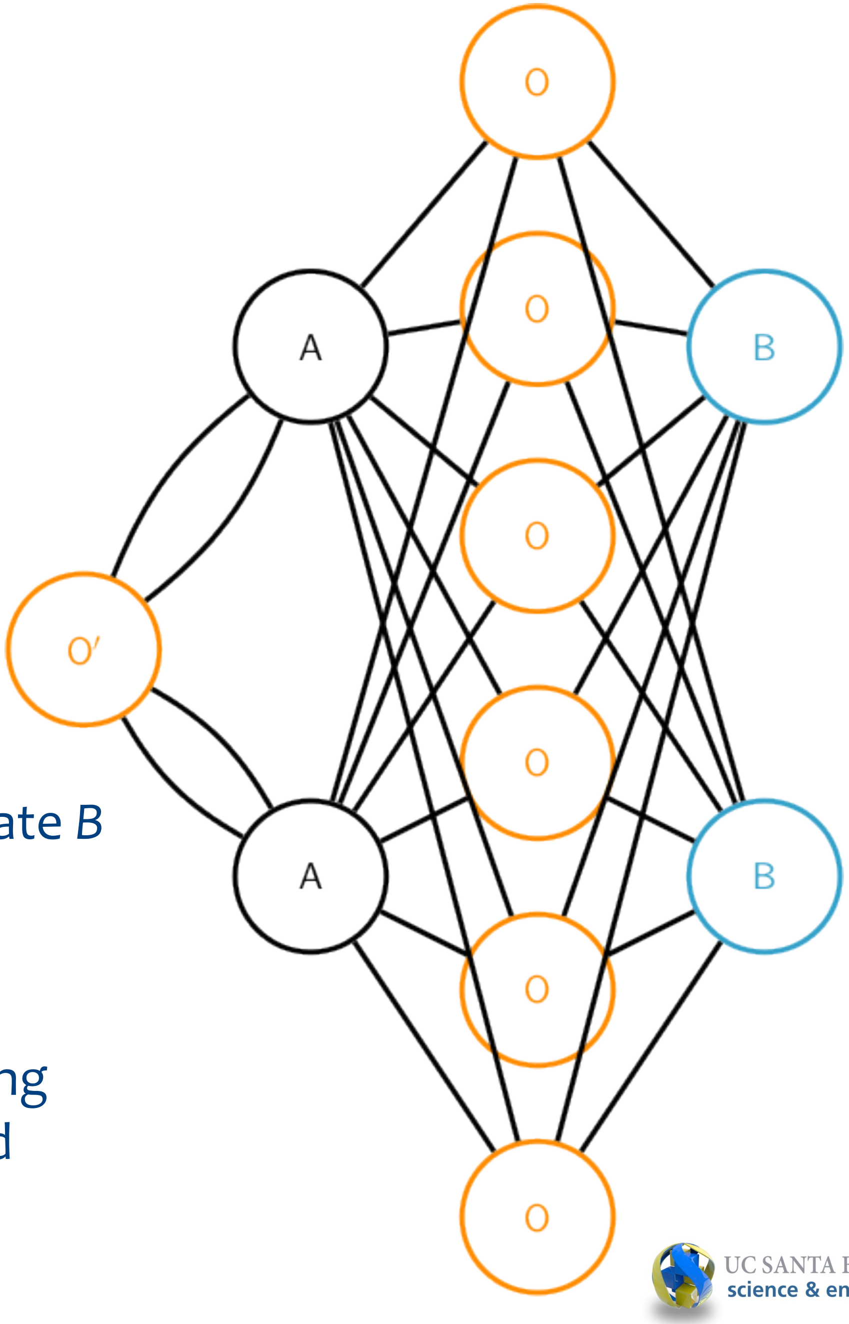
$A_2B_2O_7$ pyrochlore

$Y_2Ti_2O_7 = Y_2Ti_2O_6O'$



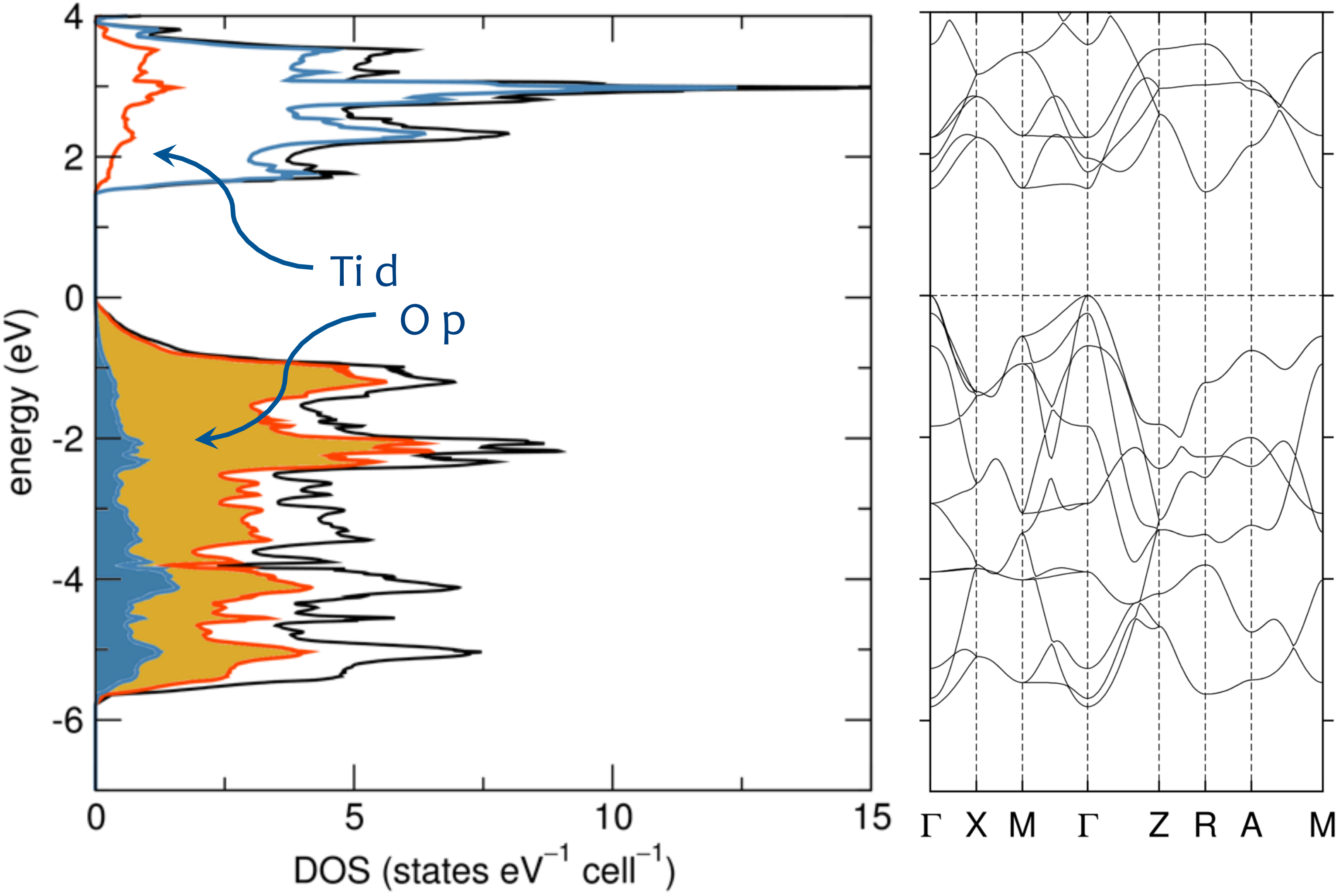


6+2-coordinate *A* atoms and 6-coordinate *B* atoms.

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

Counting electrons

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

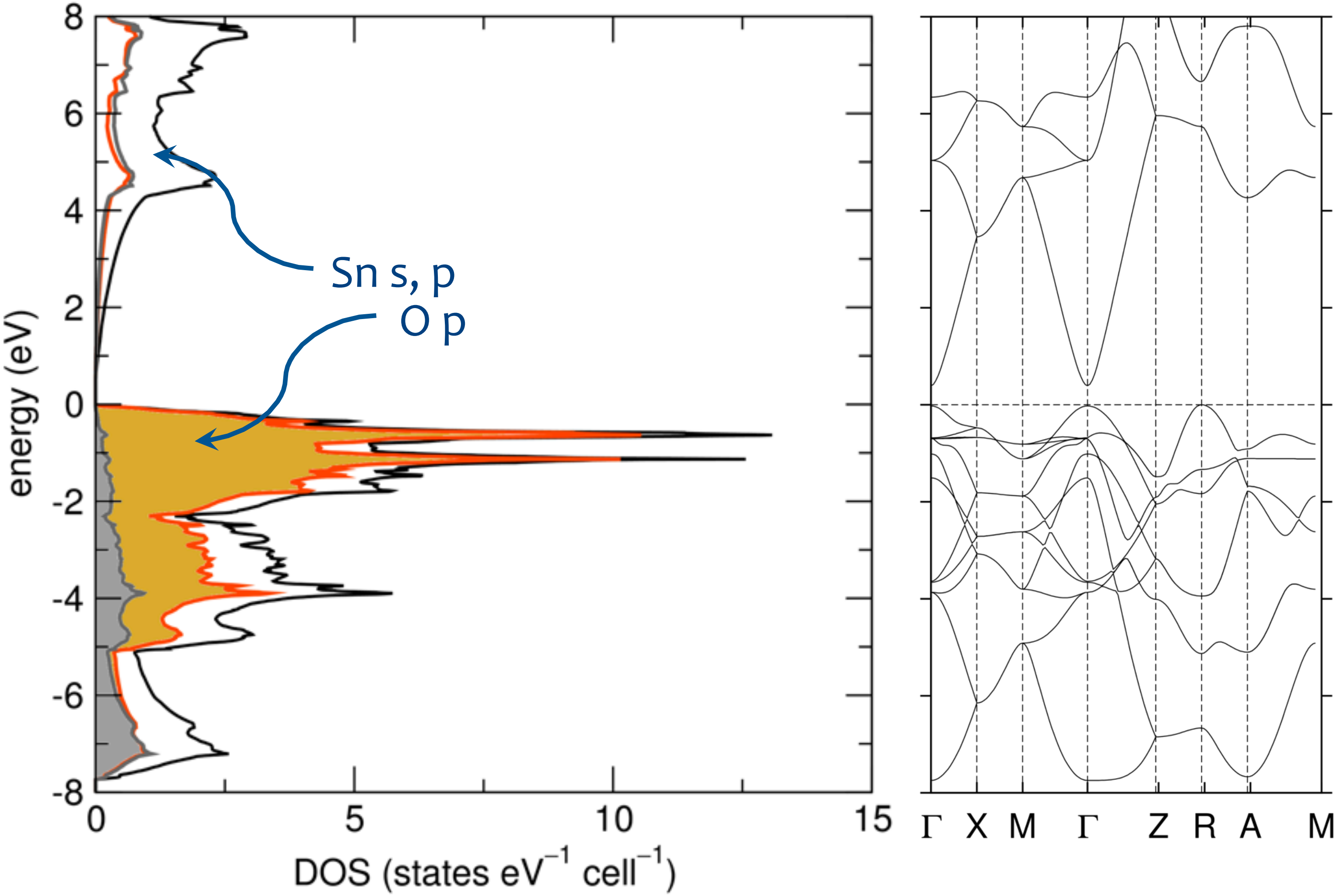


Ti d

O p

Insulator, not so easy to dope.

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

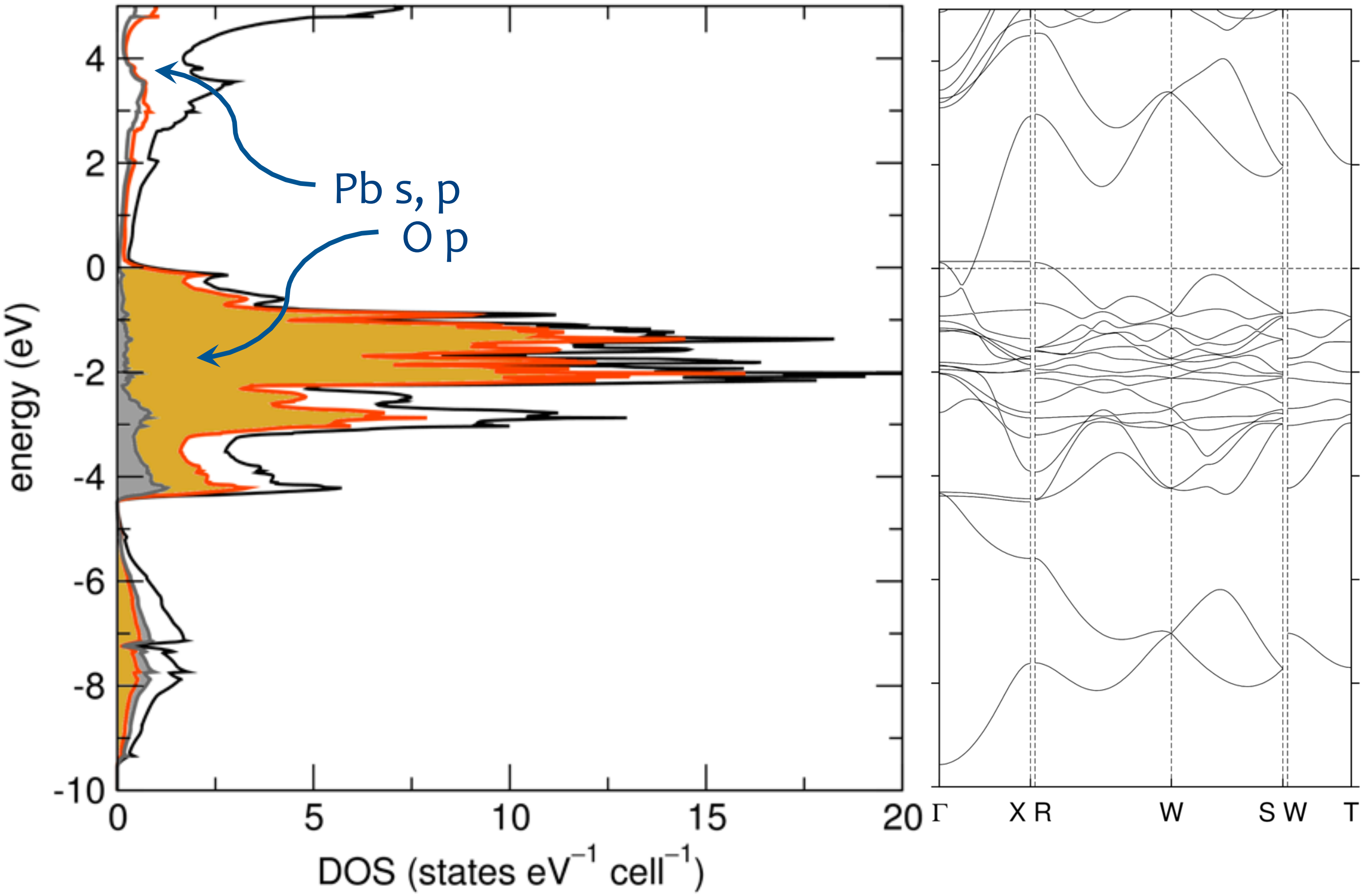


Sn s, p

O p

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.

d^0 and s^2 systems: Second-Order Jahn-Teller (SOJT) effects

d^0 and s^2 systems: Second-Order Jahn-Teller (SOJT) effects

Expand the vibronic Hamiltonian in terms of a normal coordinate Q :

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)}Q + \frac{1}{2}\mathcal{H}^{(2)}Q^2 + \ldots$$

where:

$$\mathcal{H}^{(1)} = (\partial\mathcal{H}/\partial Q)_{Q=0}; \mathcal{H}^{(2)} = (\partial^2\mathcal{H}/\partial Q^2)_{Q=0}$$

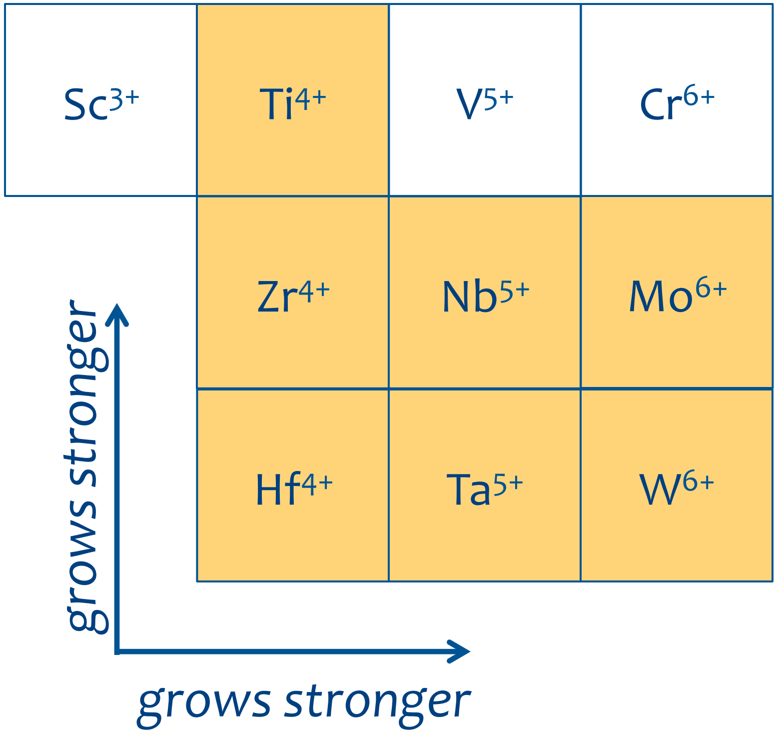
resulting in:

$$E = E^{(0)} + \underbrace{\langle 0|\, \mathcal{H}^{(1)}\, |0\rangle\, Q}_{\text{1st order (J–T)}} + \underbrace{\frac{1}{2}\left[\langle 0|\, \mathcal{H}^{(2)}\, |0\rangle - 2\sum_n \frac{\langle 0|\, \mathcal{H}^{(1)}\, |n\rangle^2}{E^{(n)} - E^{(0)}}\right] Q^2}_{\text{SOJT}} + \ldots$$

Rondinelli, Eidelson, Spaldin, *Phys. Rev. B.* **79** (2009) 205119(1–N)

d^0 systems

Seen in early transition metal oxides in their highest oxidation state. Effects strengthens with smaller ions and higher charge (*ie*. with higher covalency):

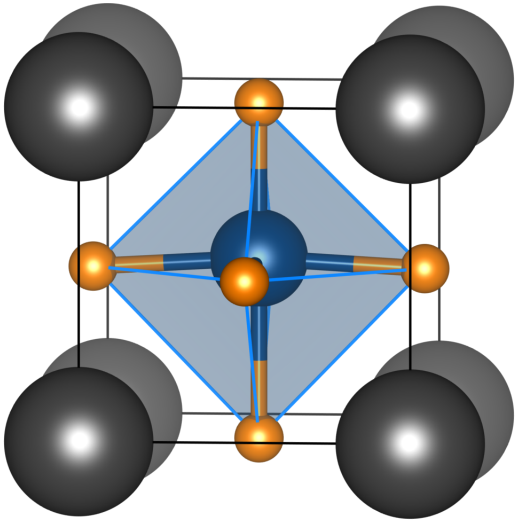


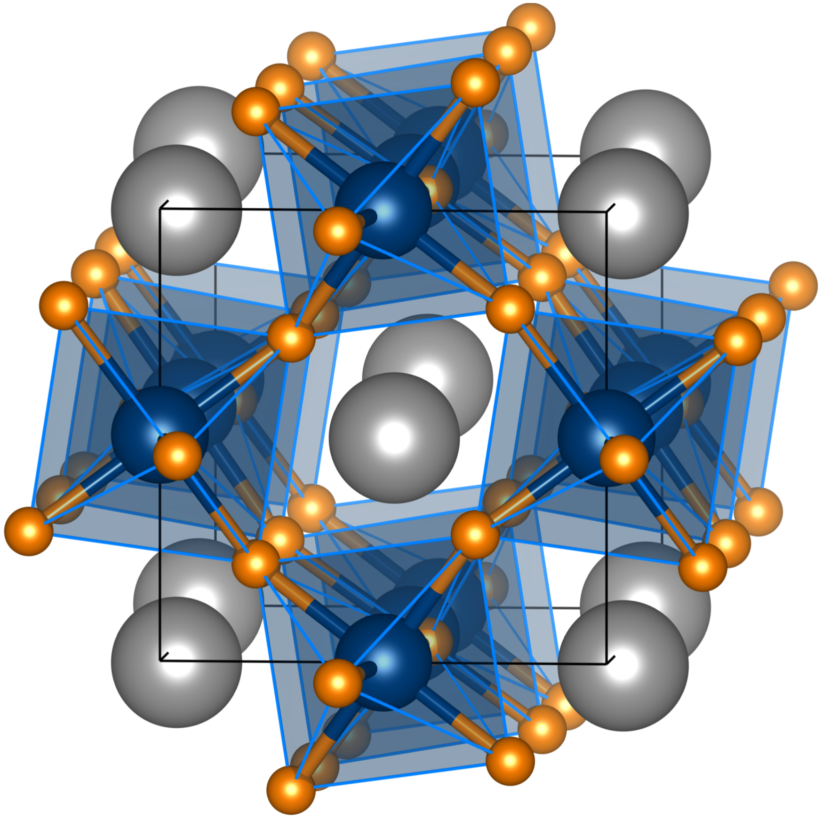
Sc^{3+}	Ti^{4+}	V^{5+}	Cr^{6+}
	Zr^{4+}	Nb^{5+}	Mo^{6+}
	Hf^{4+}	Ta^{5+}	W^{6+}

Both JT and SOJT result in distortions, but the latter results in off-centering as well (*ie*. creates a local dipole).

d⁰ systems

Countercations (other cations) play a role in determining distortion:





*P*4*mm* $BaTiO_3$ at room temperature with distorted TiO_6 octahedra.

Pnma $CaTiO_3$ at room temperature with tilting and rotation, but relatively undistorted TiO_6 octahedra.

s^2 systems: Lone pairs

Cation centered lone pairs – the important cations (note the valence is 2 below the group valence):

	1+	**2+**	**3+**	**4+**	**5+**	**6+**
$3d^{10}\ 4s^2$	Ga	Ge	As	Se	Br	
$4d^{10}\ 5s^2$	In	Sn	Sb	Te	I	Xe
$5d^{10}\ 6s^2$	Tl	Pb	Bi	Po		

The sub-valent state is particularly important in the last row.

s^2 systems: Lone pairs

Hyde and Andersson, *Inorganic Crystal Structures*, Wiley (1988):

In many crystalline solids with cation-centered lone pairs, the lone pair occupies the same volume as an oxide or fluoride ion. However the cation-lone pair distances (in Å) is much shorter than typical cation-anion distances:

	1+	**2+**	**3+**	**4+**	**5+**	**6+**
$3d^{10}$ $4s^2$	Ga 0.95	Ge 1.05	As 1.26	Se 1.22	Br 1.47	
$4d^{10}$ $5s^2$	In 0.86	Sn 0.95	Sb 1.06	Te 1.25	I 1.23	Xe 1.49
$5d^{10}$ $6s^2$	Tl 0.69	Pb 0.86	Bi 0.98	Po 1.06		

Polyhedra of anions and lone pairs must have off-centric cations.

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s^2 systems: Lone pairs

Cation-centered lone pairs (often with Pb^{2+} as the central cation, but also Sn^{2+} and Bi^{3+}) are important for applications requiring off-centered polyhedra and their associated dipoles:

- Ferroelectric and piezoelectric materials, actuators
- High-refractive index materials (lead crystal)
- Ionic conductors
- Multiferroic materials
- Non-linear optical materials
- Phosphors
- Semiconductor/semimetal to insulator transitions

s^2 systems: Lone pairs

Visualization: DFT based on the Stuttgart TB-LMTO-ASA program
[O. K. Andersen, O. Jepsen *etc.*]

Electron localization functions (ELFs): An orbital independent measure of electron localization based on the pair probability of electrons [Becke, Edgecombe *J. Chem. Phys.* **92** (1990) 5397; Silvi, Savin, *Nature* **371** (1994) 683.]

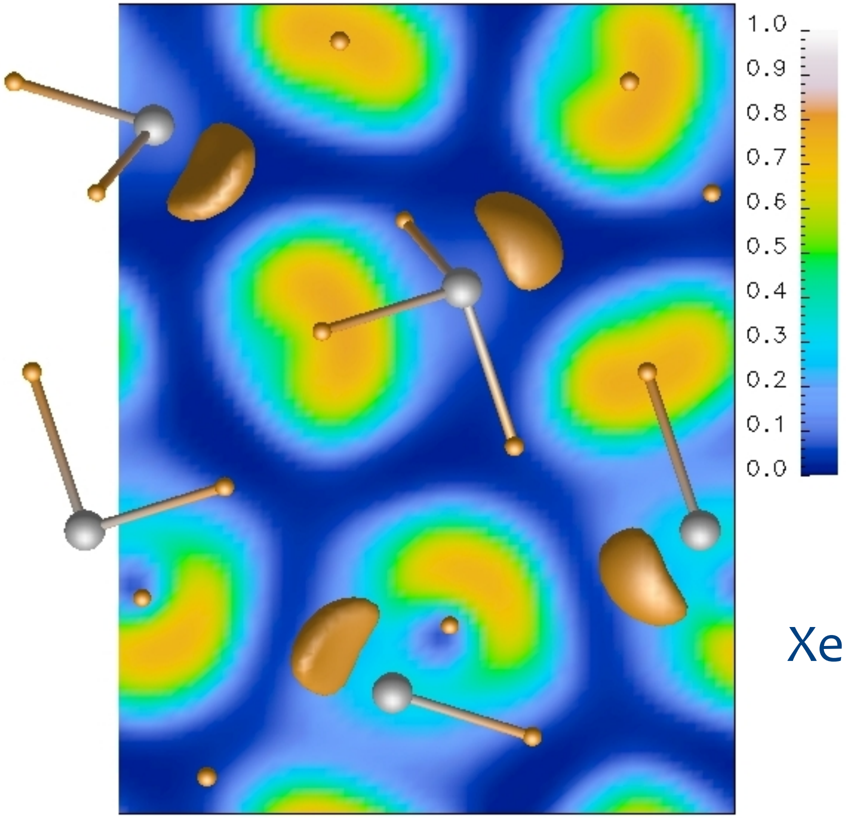
$$\mathrm{ELF} = \frac{1}{1+\left(\dfrac{D}{D_H}\right)^2} \qquad \in (0,1)$$

with

$$D = \frac{1}{2}\sum_i |\nabla\phi_i|^2 - \frac{1}{8}\frac{|\nabla\rho|^2}{\rho}$$

and

$$D_H = \frac{3}{10}(3\pi^2)^{5/3}\rho^{5/3}$$

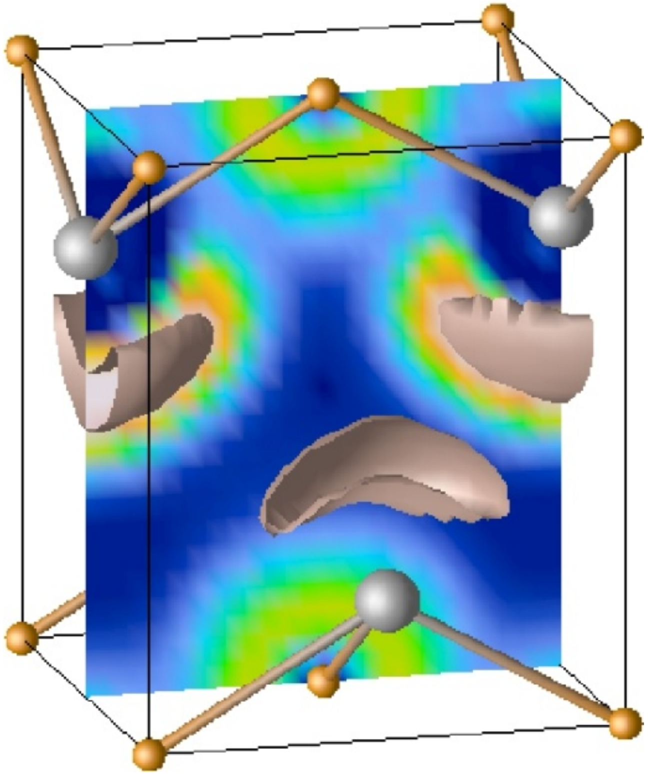


XeO_3

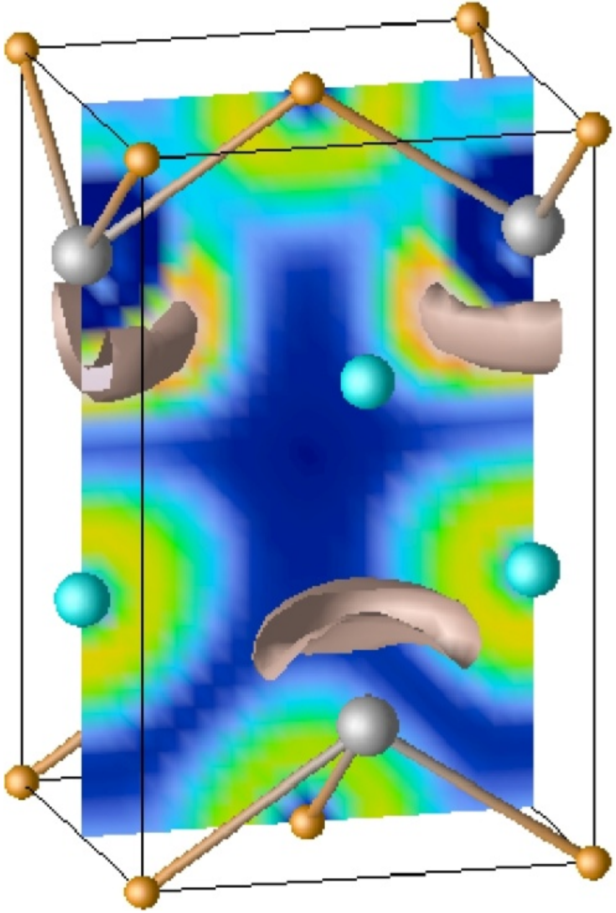
The electron density ρ does not reveal lone pairs.

s^2 systems: Lone pairs

α-PbO



BiOF



Lone pairs typically visualized with ELF values between 0.65 and 0.9

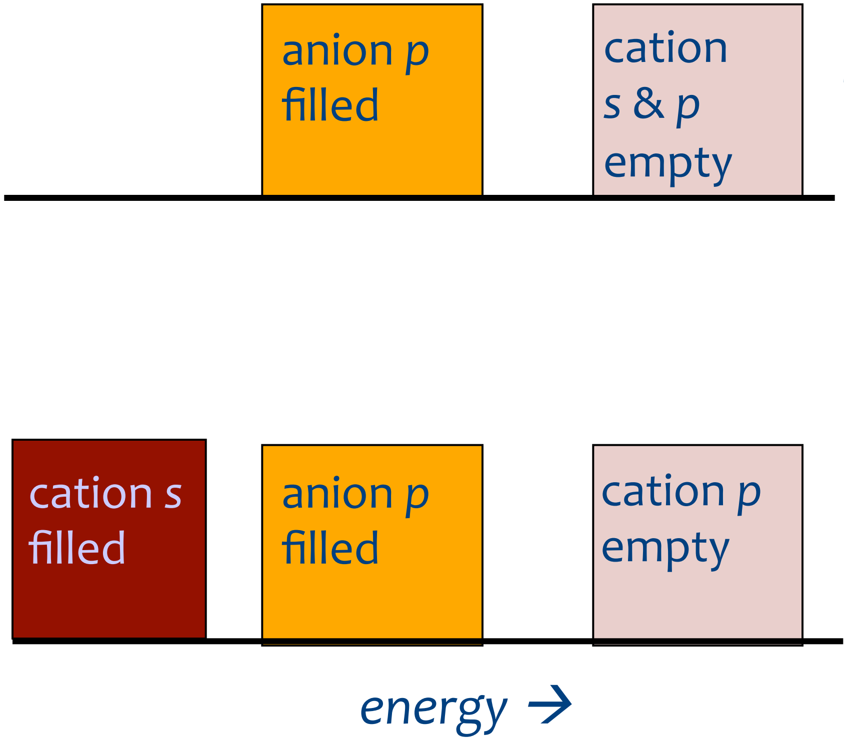
Raulot, Baldinozzi, Seshadri, Cortona, *Solid State Sciences* **4** (2002) 467; Seshadri, *Proc. Indian Acad. Sci. (Chem. Sci.)* **113** (2001) 487.

s^2 systems: Lone pairs

Composition of the lone pair

Orgel (1959): The lone pair cannot have purely *s* character when it is *stereochemically* active; it must admix with *p.*

Bersuker (1984): Filled anion *p* states must play a role.



anion *p* filled

cation *s* & *p* empty

typical oxide (BaO)

cation *s* filled

anion *p* filled

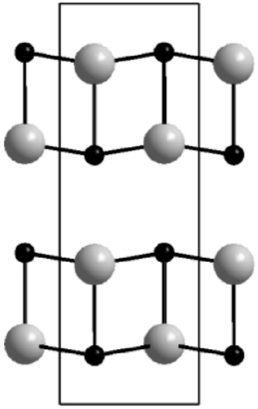
cation *p* empty

lone pair oxide (PbO)

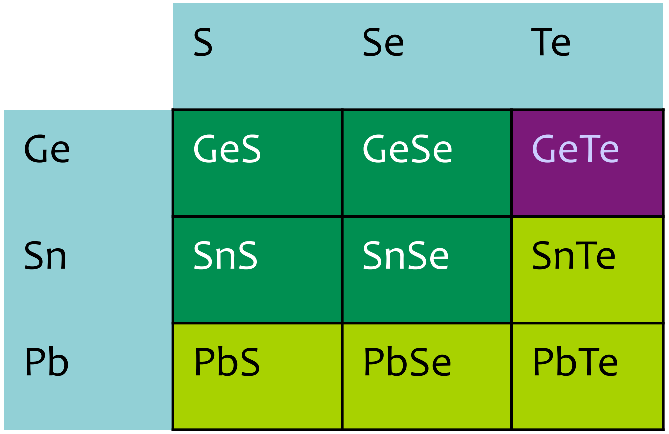
energy →

s^2 systems: Lone pairs

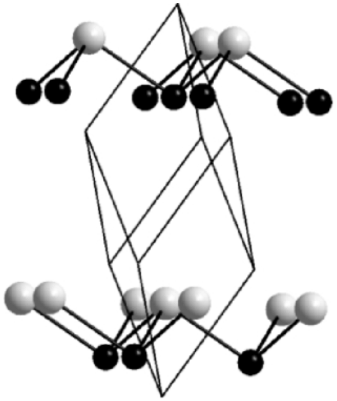
A lone pair sorted structural field AQ (IV-VI semiconductors): The lone pair is not always active!



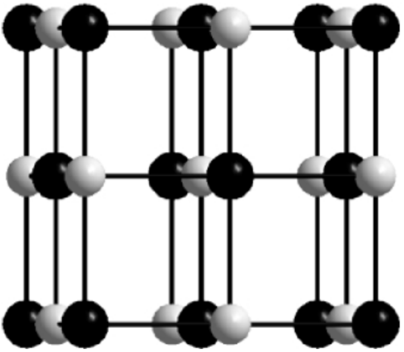
massicot



	S	Se	Te
Ge	GeS	GeSe	GeTe
Sn	SnS	SnSe	SnTe
Pb	PbS	PbSe	PbTe

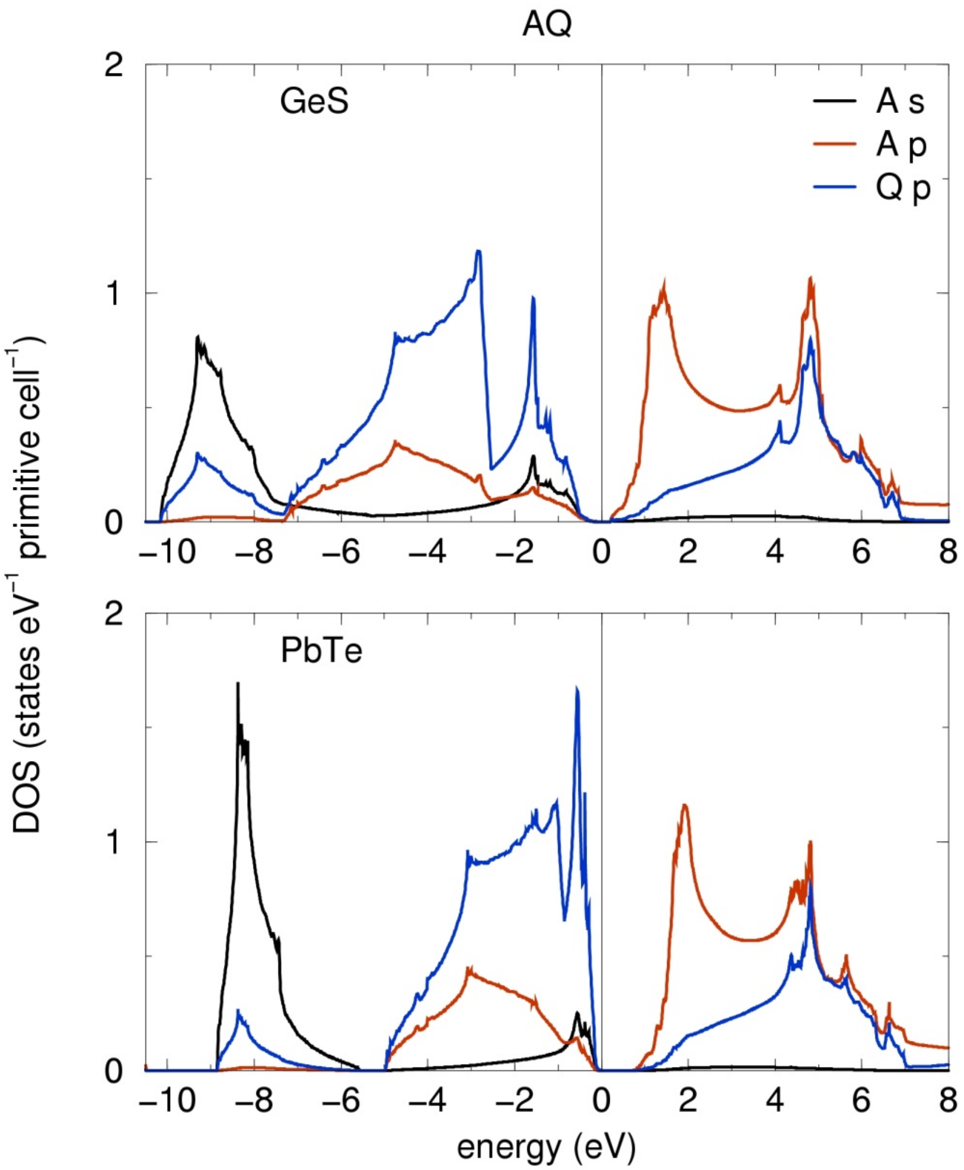


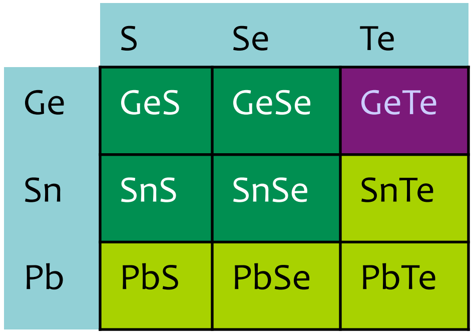
arsenic (polar)



rock salt

s^2 systems: Lone pairs





	S	Se	Te
Ge	GeS	GeSe	GeTe
Sn	SnS	SnSe	SnTe
Pb	PbS	PbSe	PbTe

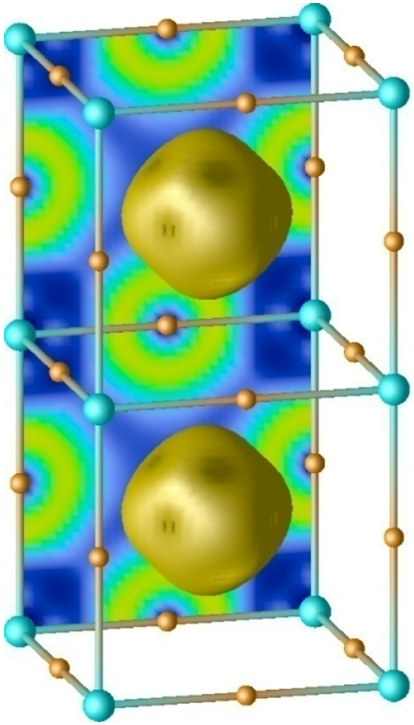
When the lone pair is stereochemically active (as in GeS), cation *s* states are broader and are better mixed with anion *p* states. The mixing is intermediated by empty cation *p*.

Cation *s* states are narrow and largely unmixed with anion *p* in cases when the lone pair is not stereochemically active (*cf.* the inert pair effect).

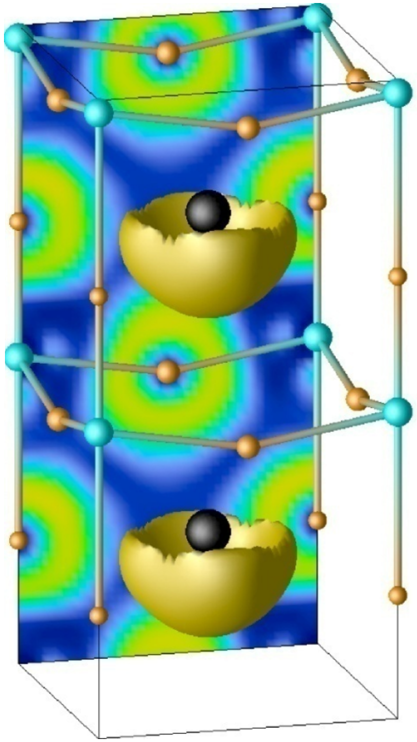
Waghmare, Spaldin, Kandpal, Seshadri, *Phys. Rev. B.* **67** (2003) 125111.

s^2 systems: Lone pairs driving ferroelectricity

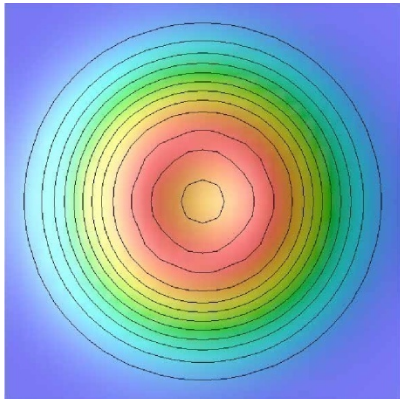
The expression of cooperative stereochemical activity of the lone pair plays an important role in the development of polar behavior.



$PbTiO_3$ above
766 K
Pm-3m



$PbTiO_3$ below
766 K
P4mm



Even above the phase transition, the Pb^{2+} ion (here, in in Pb_2NbYbO_6) is not really where it is supposed to be.

Baldinozzi, Raulot, Seshadri, *MRS Symp. Proc.* **718** (2002) D12.7.1.

Seshadri, *Proc. Indian Acad. Sci. (Chem. Sci.)* **113** (2001) 487.

Thank you

Photo by Tony Mastres