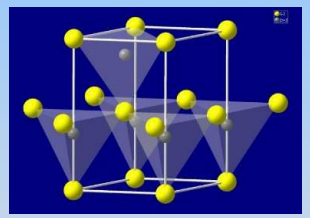
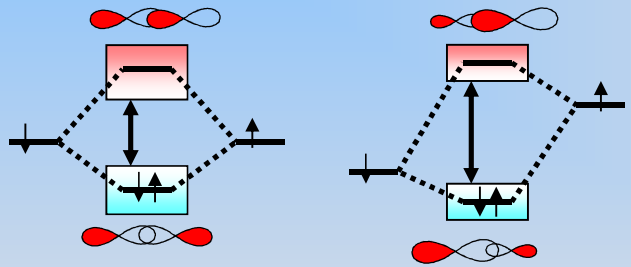
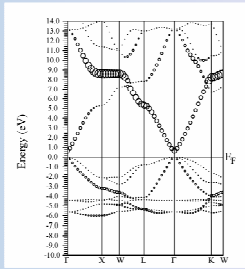
Solid State Chemistry :
composition(synthesis)/structure/electronic properties relationships. Which key parameters to design new compounds ? A panorama at dawn of the 21st century







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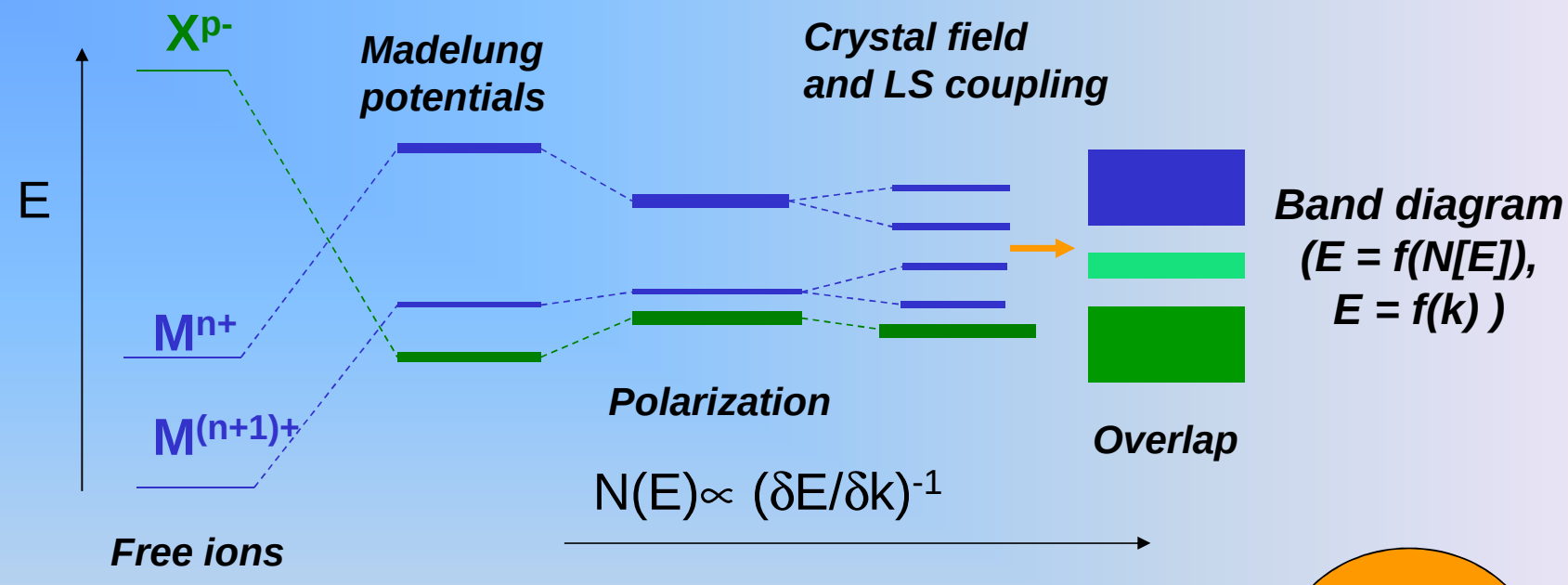
Ecole du GDR MEETIC

Matériaux, Etats ElecTroniques et Couplages non-Conventionnels

Banyuls (4-10 Fevrier 2018)

Outline



The key parameters

Ionization energies , Electronegativity, Madelung potentials, Crystal field

Polarization and Covalency

Synthesis

Structural features

Electronic properties (U, W, Δ) : insulating, semiconducting, superconducting, metallic behaviors

Pauling electronegativity χ

1929 (Rules), 1954 (Nobel Prize),
1962 (Nobel peace prize)

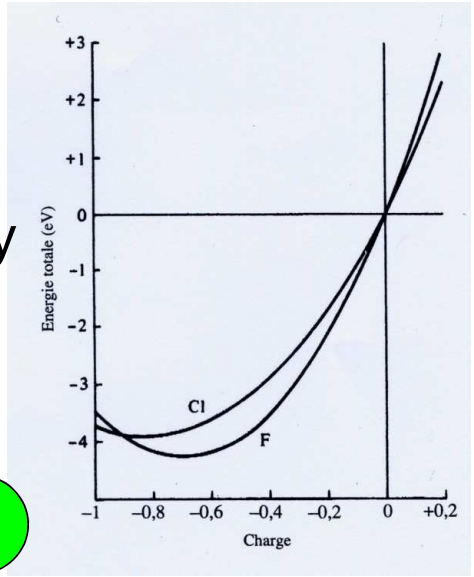
2,2 H 1																	He 2
0,98 Li 3	1,57 Be 4											2,04 B 5	2,55 C 6	3,04 N 7	3,44 O 8	3,98 F 9	Ne 10
0,93 Na 11	1,31 Mg 12											1,61 Al 13	1,9 Si 14	2,19 P 15	2,58 S 16	3,16 Cl 17	Ar 18
0,82 K 19	1 Ca 20	1,36 Sc 21	1,54 Ti 22	1,63 V 23	1,66 Cr 24	1,55 Mn 25	1,83 Fe 26	1,88 Co 27	1,91 Ni 28	1,9 Cu 29	1,65 Zn 30	1,81 Ga 31	2,01 Ge 32	2,18 As 33	2,55 Se 34	2,96 Br 35	Kr 36
0,82 Rb 37	0,95 Sr 38	1,22 Y 39	1,33 Zr 40	1,6 Nb 41	2,16 Mo 42	2,1 Tc 43	2,2 Ru 44	2,28 Rh 45	2,2 Pd 46	1,93 Ag 47	1,69 Cd 48	1,78 In 49	1,96 Sn 50	2,05 Sb 51	2,1 Te 52	2,66 I 53	Xe 54
0,79 Cs 55	0,89 Ba 56	1,1 La 57	1,3 Hf 72	1,5 Ta 73	1,7 W 74	1,9 Re 75	2,2 Os 76	2,2 Ir 77	2,2 Pt 78	2,4 Au 79	1,9 Hg 80	1,8 Tl 81	1,8 Pb 82	1,9 Bi 83	2 Po 84	2,2 At 85	Rn 86
0,7 Fr 87	0,9 Ra 88	1,1 Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	113	114	115	116	117	118

1,12 Ce 58	1,13 Pr 59	1,14 Nd 60	1,13 Pm 61	1,17 Sm 62	1,2 Eu 63	1,2 Gd 64	1,2 Tb 65	1,22 Dy 66	1,23 Ho 67	1,24 Er 68	1,25 Tm 69	1,1 Yb 70	1,27 Lu 71
1,3 Th 90	1,5 Pa 91	1,7 U 92	1,3 Np 93	1,3 Pu 94	1,3 Am 95	1,3 Cm 96	1,3 Bk 97	1,3 Cf 98	1,3 Es 99	1,3 Fm 100	1,3 Md 101	1,3 No 102	1,3 Lr 104

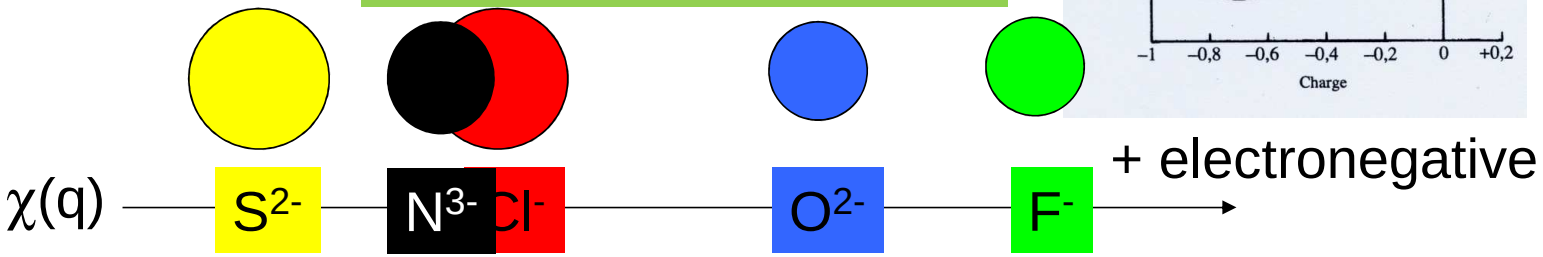
$E(q) = \alpha\, q + \beta\, q^2$ **Mulliken**-Jaffé (1935 – 1963)

$\chi(q) = \delta E(q)/\delta q = \alpha + 2\beta\, q$: Electronegativity

$\eta = \delta^2 E(q)/\delta^2 q = 2\beta$: Hardness= 1/Polarizability (Pearson)



The anions X^{p-}



Hard-Soft Acid-Base (**HSAB**) theory
Ralph Pearson (1960)

Energy

Hard acid : $H^+(1s^0)$, $Ti^{4+}(3d^0)$, K^+, Ba^{2+}, La^{3+}

Soft acid : $Fe^{2+}(3d^6)$, $Cu^+(3d^{10})$

Soft base : $H^-(1s^2)$, S^{2-}, I^-, SO_4^{2-}, CO_3^{2-}

Hard base : F^-, O^{2-}, OH^-, Cl^-, NH_3

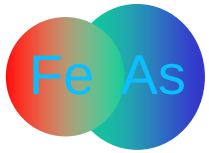
Hard-Hard or Soft-Soft AB react faster leading to stronger bonds !

Basics of structures :

in a first approximation, atoms can be treated like spheres

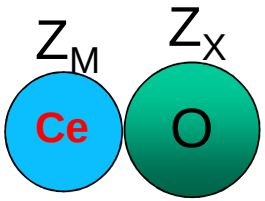
Electronic and steric effect : χ Electronegativity, Hardness ($\delta\chi/\delta q$) and Size (covalent, ionic and metallic bonding)

Covalent bonds



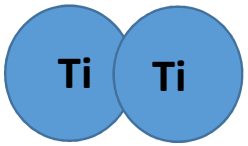
Element with high χ
Covalent radii (Quantum mechanics)

Ionic bonds



Element with various χ
Ionic radii (Shannon & Prewitt)

Metallic bonds (Alloys)

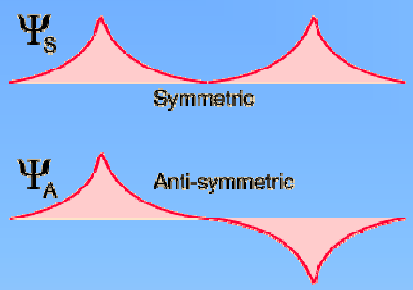


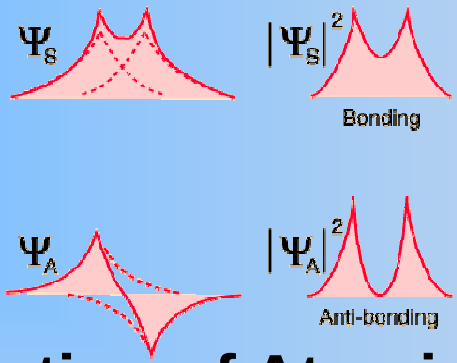
Element with low χ
(low concentration of e-)
Metallic radii (Tables, Alloys)

Charges Z_M/Z_X, polarizing power (Z_M/r_M for element with low/medium χ value) and polarizability (r_X/Z_X for element with high χ value)

Covalency and Polarization

MX Chemical bonding : generation of bonding, anti-bonding and non-bonding states/orbitals



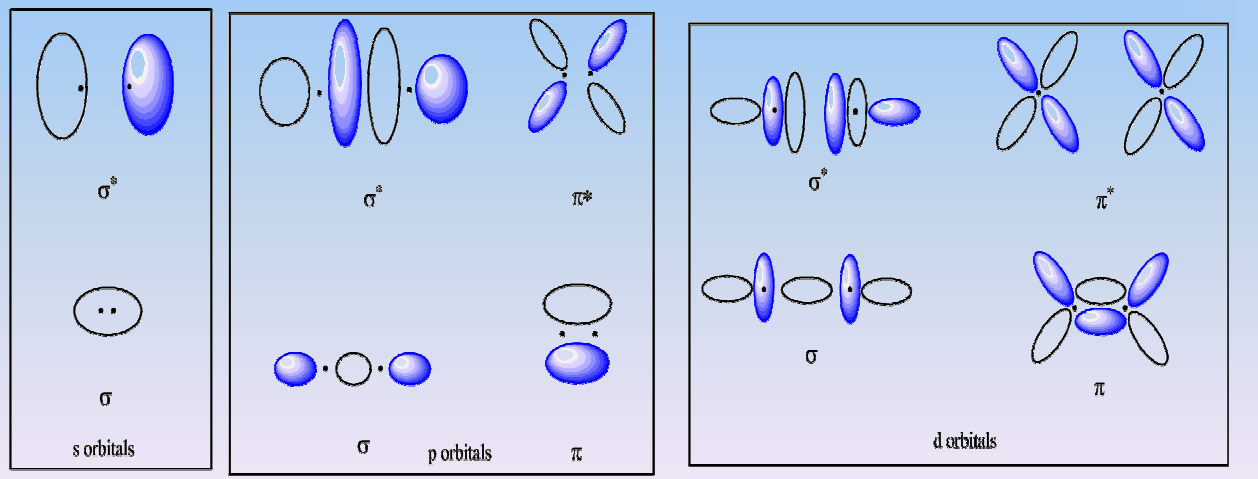


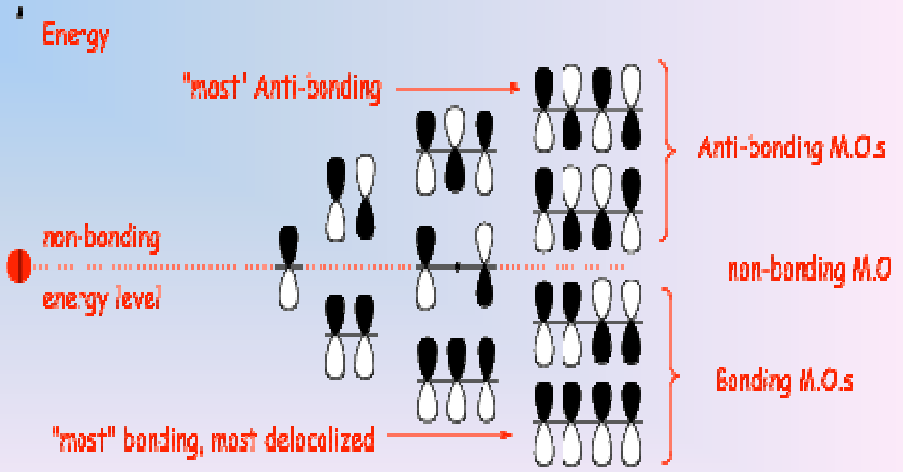
$\psi_S = a_X \psi_X + a_M \psi_M \qquad a_X > a_M$

$\psi_A = a^*_X \psi_X - a^*_M \psi_M \qquad a^*_X < a^*_M$

Linear Combination of Atomic Orbitals

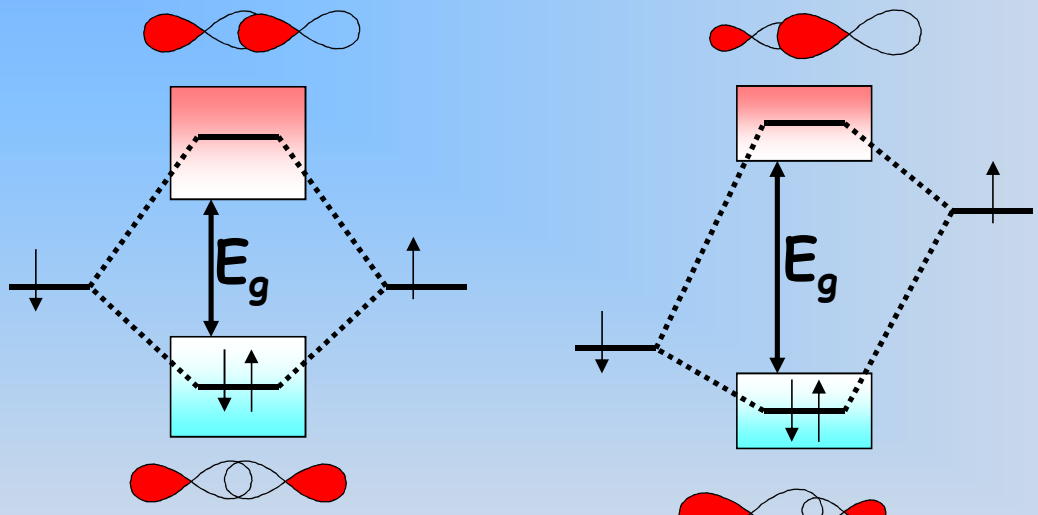
$\Delta E^*_M(A) > \Delta E_X(S)$





Polarizability (deformation of orbitals, electrical field) **of π orbitals >> σ orbitals**

Difference of (χ) electronegativity (ionicity degree) and band gap

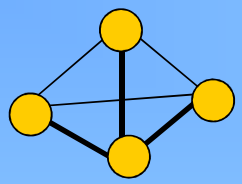


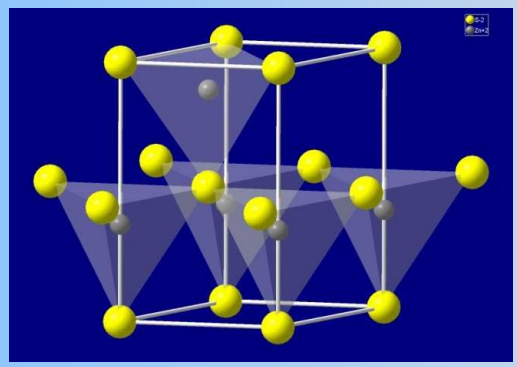
Covalent bond

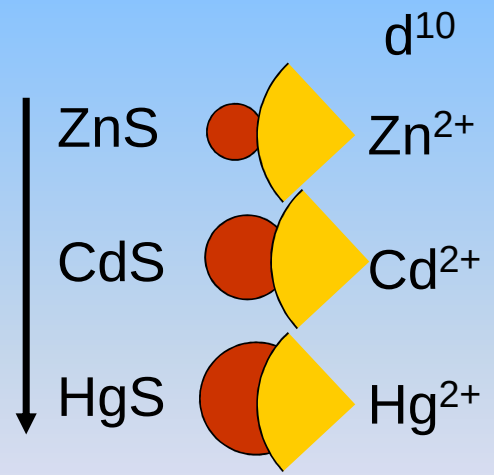
Ionic bond

$\Delta\chi \uparrow \longrightarrow E_g \uparrow$

Difference of (χ) electronegativity (ionicity degree) : refractive index and band gap : sulfides with wurtzite-type network



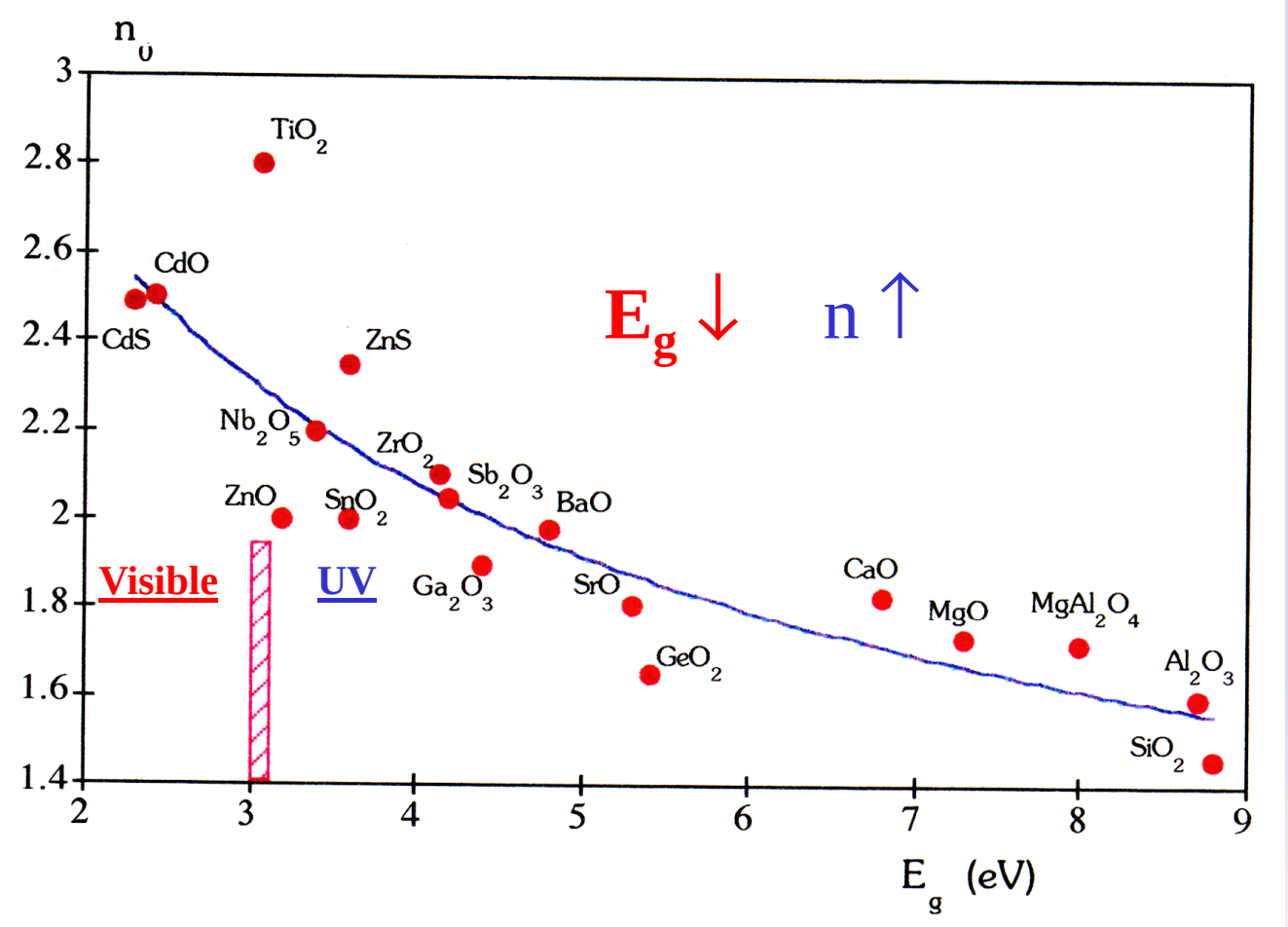




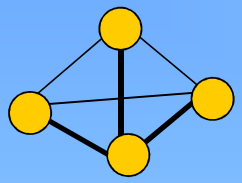
	Eg(eV)	n(500 nm)
ZnS	**3,6 eV (blanc)**	2,35
CdS	**2,4 eV (jaune)**	2,50
HgS	**2,0 eV (rouge)**	2,70

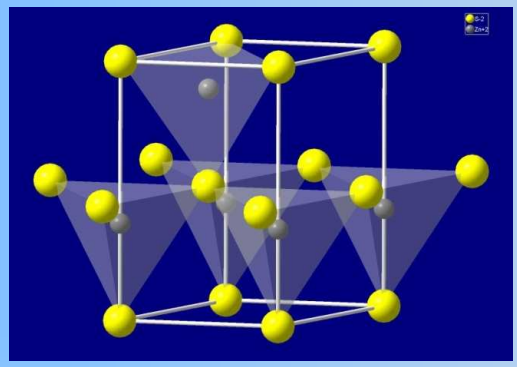
$\Delta\chi \downarrow$ e- Polarizability $\uparrow$ → Covalency $\uparrow$ → Band gap $\downarrow$ Refractive index $\uparrow$

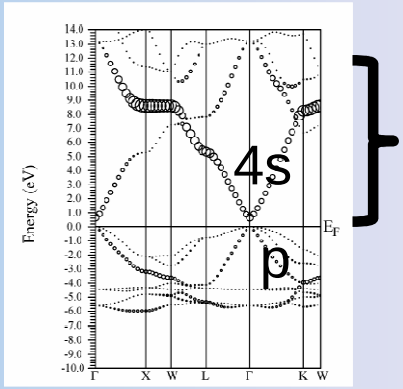
Charge Transfer band involving metal (nd^0, nd^{10}, ns^0, ns^2) in oxides/sulfides : band gap (covalency) and refractive index (e- polarizability)



From ZnO to ZnS (wurtzite) : reduction of W[σ(4s)] bandwidth and band gap ↑*







W (bandwidth) = **N(Coord Numb).b**

b ∝ **exp(-2R_{MX}/a_0)**

R_{MX} : bond distance

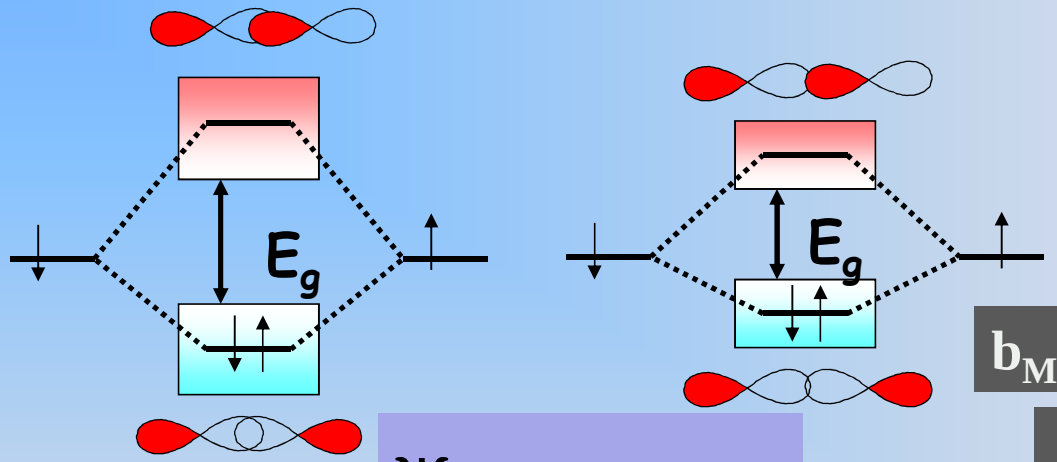
		Eg(eV)	n(500 nm)
ZnO	BC (4s-Zn)	3.2 eV	2.00
	CTB, Eg		
ZnS	BV (p-Anions)	3.6 eV	2.35

$\Delta\chi \downarrow$ Orbital expansion : 3p(S) > 2p(O)

ZnO → ZnS : W[σ*(4s)] ↓ Band gap ↑, e- Polarisability (S) ↑ (n ↑)

b_{ZnX} = < $\psi_{Zn(4s)}$ | H | $\psi_{x(p)}$ > : transfer integral

Polarisation and transfer integral : Variation of the band gap



$\Psi = a_M\Psi_M \pm a_X\ \Psi_X$

$b_{MX} = < \psi_M \mid H \mid \psi_X >$

$S = < \psi_M \mid \psi_X >$
Overlap integral

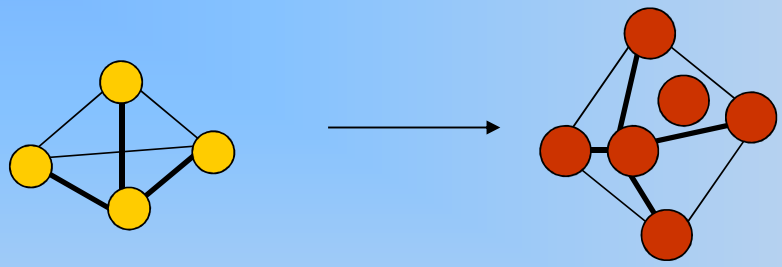
Bond Distance R_{MX} → Transfer Integral $b \propto S^2$ → E_g

$b \propto \exp(-2R_{MX}/a_0)$

W (bandwidth) = **N(Coord Numb).b**

Distance and Coordination number : polarisation, transfer integral and band gap

CdS (ZnS) **CdS (NaCl)**



Pressure (20-30 kbars)

Distance R_{MX} + Coordination Number (**N**) ↑ → Transfer Integral **b** ↘ → E_g ↘

$$W = N.b \propto N.\exp(-2R_{MX}/a_0)$$

Polarizing power of M (Z/r) ↑ → b↑

Polarization, covalency and Madelung energy in inorganic synthesis: melting point, solubility and chemical stability !

Melting point ↓ as covalency ↑ :

LiF (845°C) >LiCl (605°C) >LiBr (550°C) > LiI (449°C)

Solubility ↓ as polarizing power (Z/r) and Madelung energy ↑

LiBr > LiCl > LiI (large size I^- : low hydration energy) > LiF (stronger Madelung energy)

Hydration energy $\propto Z^2/(r_{eff} = r_{ion} + 85$ –pm-)

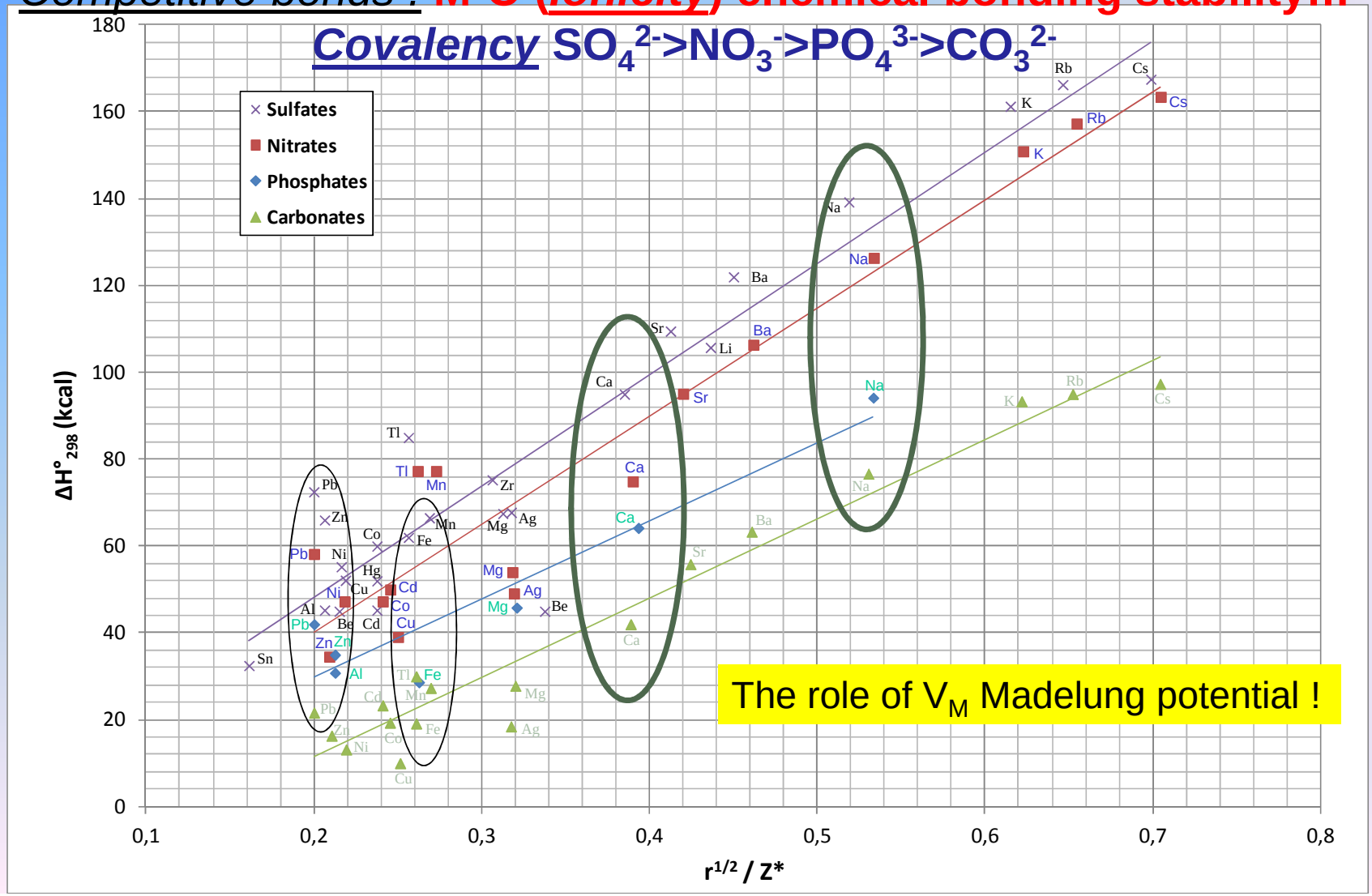
Thermal stability ($MCO_3 \rightarrow MO + CO_2$) ↑ as polarizing power ↓

$\Delta H \propto r_{ion}^{1/2} / q$

Stability/Ionicity/Polarisation of M-O bonding and *'formal'* Electronegativity of anionic groups.
Formation enthalpy (kcal/mol) : Sulfate>Nitrate->Phosphate>Carbonate

Competitive bonds : M-O (*Ionicity*) chemical bonding stability…

Covalency $SO_4^{2-}>NO_3^{-}>PO_4^{3-}>CO_3^{2-}$



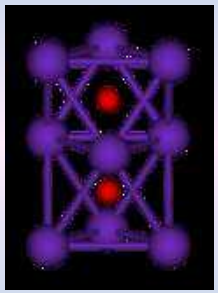
Competitive bonds and bands : the (π) non-bonding character

a) Inductive effect and competitive bonds

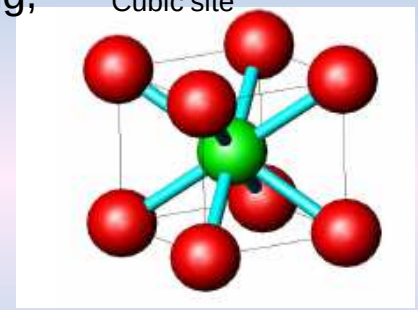
The more covalent [**Td, 4**] : SO_4^{2-} **= SiO_4^{4-} > PO_4^{3-}** … > MoO_4^{2-} > TiO_4^{4-}

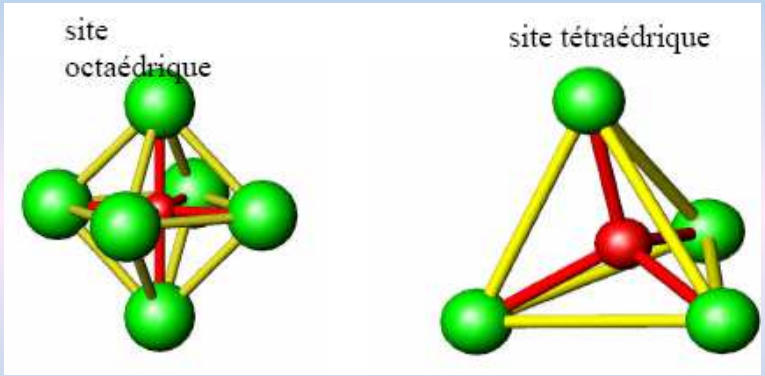
The more ionic / large size Fe^{2+} [8]-***cubes*** > Fe^{2+} [6]-***octahedra***

The stronger M-M (π) bonding,

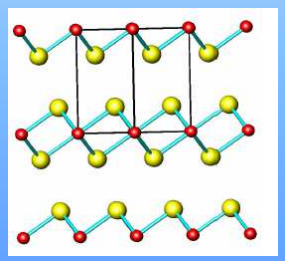


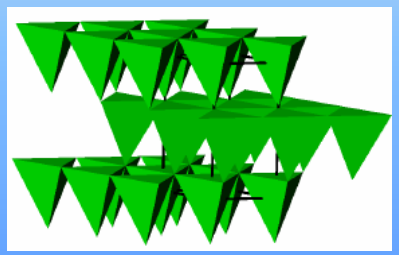
the lower M-O (σ) bonding





b) The lone pair and (π) non-bonding character : 2D networks and VdW bonds





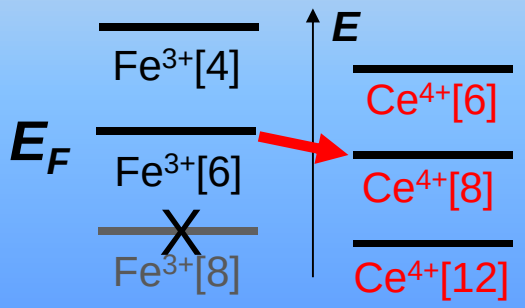
Layer structure :
Electron doublet, lone-pair, non-bonding charcter(π) and repulsive effect
Example : d^{10}, s^2 ions
Cu^{2+}, Zn^{2+}, Cd^{2+} … Sn^{2+}, Pb^{2+}, Bi^{3+}

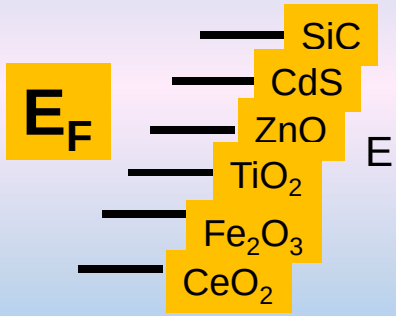
Polarisability and covalency !

Chemical bonding and reactivity of solids
Redox and Lewis acidity/basicity in the solids

M/X Coordination number [ ] (+ site symmetry)
Non-bonding character (π bonding)
M-M, M-O interactions

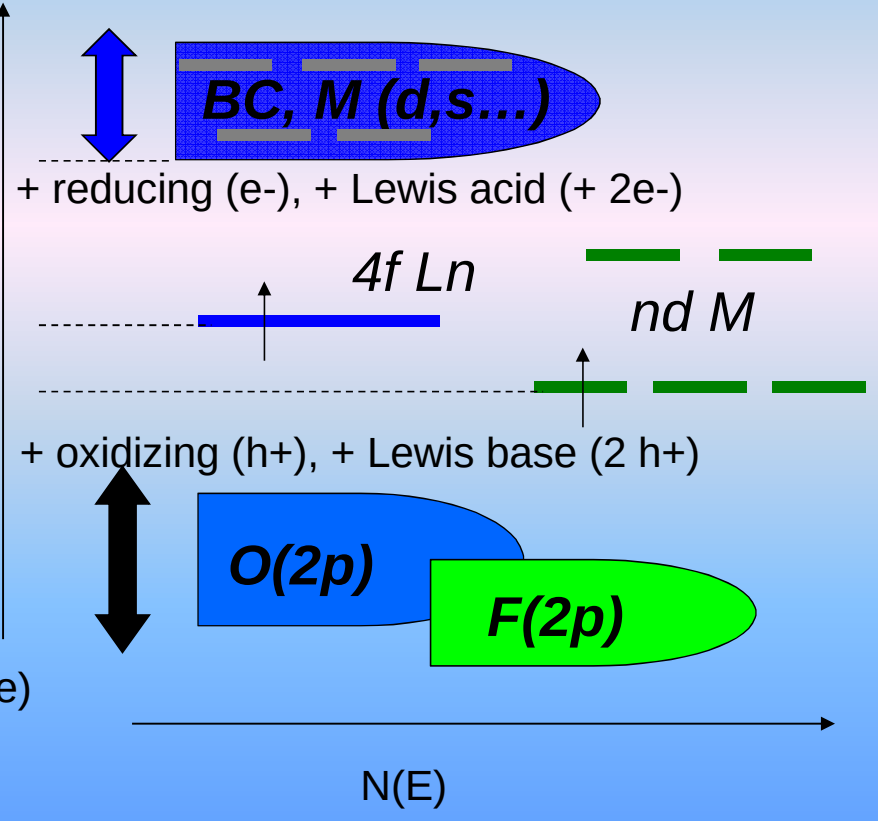
Ionization energy (I_n, M^{n+}) +
Madelung Potential (n+, R_{MX})
and redox equilibrium



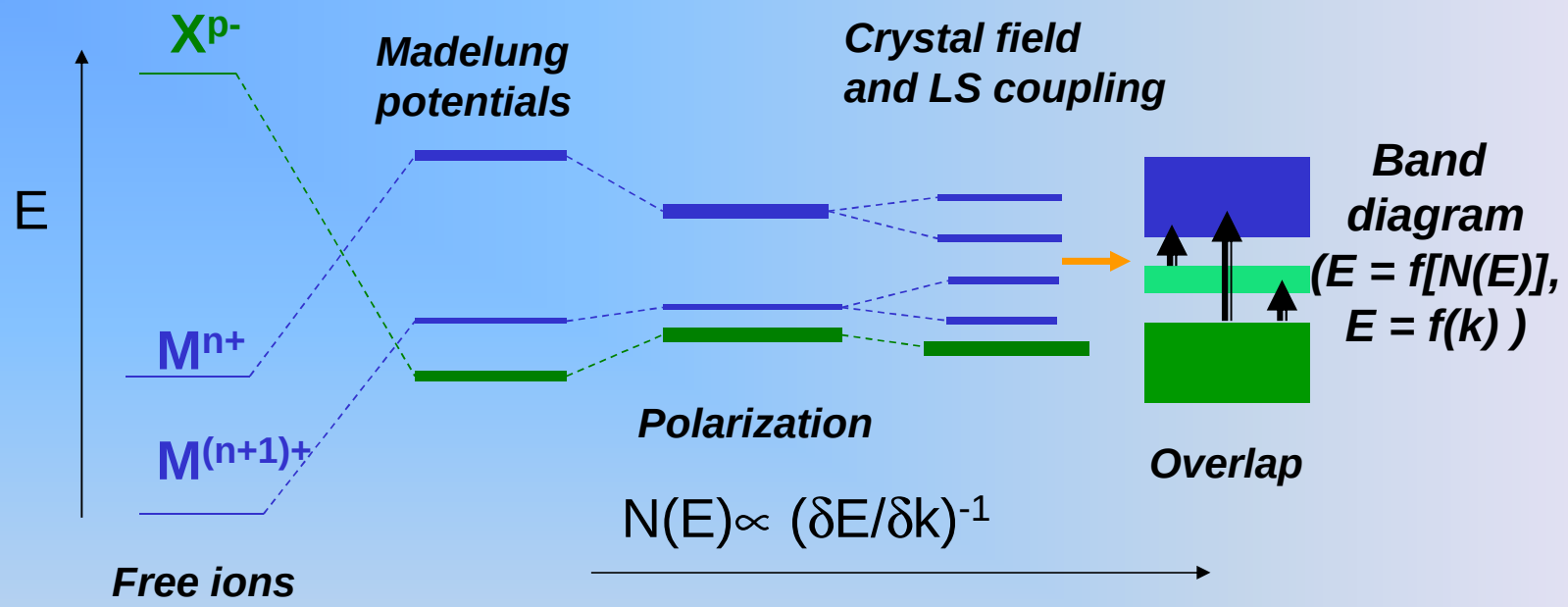


$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$ (Perovskite)

$Ti^{4+} + Fe^{2+} \leftarrow Ti^{3+} + Fe^{3+}$
(Ilmenite, [6] $FeTiO_3$)



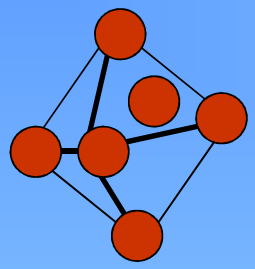
Electronic properties of solids : schematic band diagrams



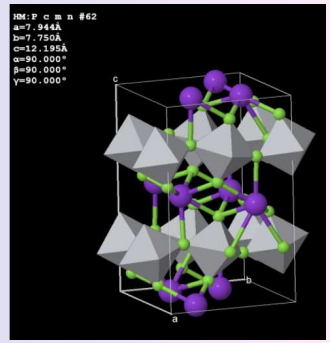
Ionization energies , Electronegativity, Madelung potentials, Crystal field

Polarization and Covalency

Electronic properties : insulating, semiconducting, superconducting, metallic behaviors



Molecular orbitals in $[TiF_6]^{3-}$ octahedra ($KTiF_4$, SG : Pcmn)



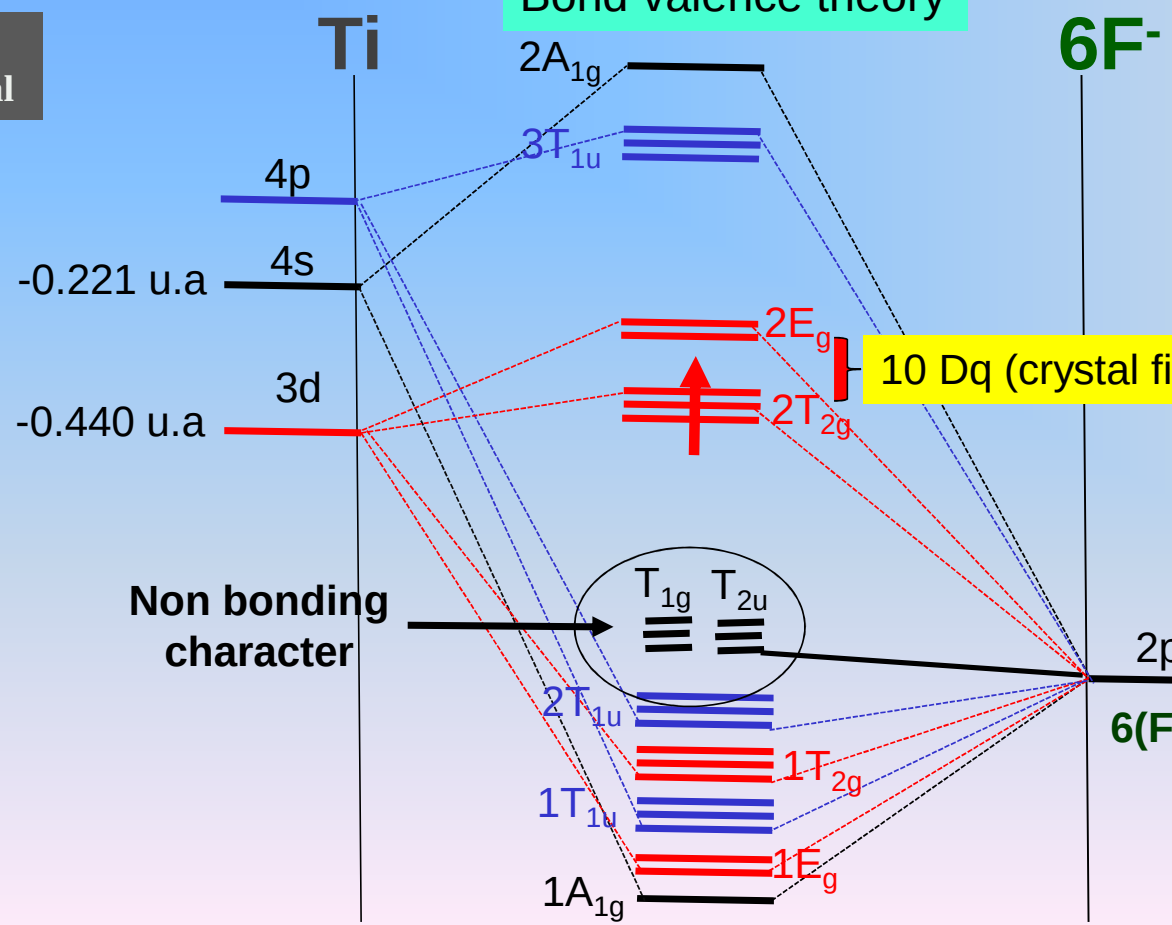
From Oh (m3m) Character Table :

Irreducible group representations : A_{1g}, E_g, T_{1u}, T_{2g}, T_{1u}, T_{2u}

Atomic orbitals : AO_{Ti} (xyz) + Comb(6) (xyz) AO_F : basis of irreducible representation

$S = \langle \psi_{Ti} | \psi_X \rangle$
Overlap integral

Bond valence theory



10 Dq (crystal field) ~ 0.05 u.a ~ 10^4 cm^{-1}

Overlap $S(\sigma, Eg) > S(\pi, T_{2g})$

10 Dq↓ as $S(\pi, T_{2g})$ ↑

Ligand π donor (I^-): 10 Dq↓

Crystal field 10 Dq **: Symmetry, Coordination Number, L (Ligand) x D (Metal = Z, n+, nd)**

C.K. Jorgensen (1971)

L Ligand field **x** **D** d (Metal) orbital splitting (cm^{-1})

π donors

I^-	0.66	H_2O	1
Br^-	0.72	NCS^-	1.02
S_2^-		$p\text{-}CH_3C_6H_4NH_2$	1.15
SCN^-	0.73	NC^-	1.15
Cl^-	0.78	CH_3NH_2	1.17
$(C_2H_5O)_2PSe^-$	0.8	$H_2NCH_2CO_2^-$	1.18
N_3^-	0.83	CH_3CN	1.22
$(C_2H_5O)_2PS_2^-$	0.83	C_5H_5N	1.23
NO_3^-	0.78–0.9	NH_3	1.25
F^-	0.9	$H_2NCH_2CH_2NH_2$	1.28
$(C_2H_5)2NCS_2^-$	0.9	$NH(CH_2CH_2NH_2)_2$	1.30
$(CH_3)_2SO$	0.91	2,2'–bipyridyl	1.33
$(NH_2)_2CO$	0.92	1,10–phenantroline	1.34
CH_3COOH	0.94	NO_2^-	1.7
C_2H_5OH	0.97	$CH_3C(CH_2CH_2O)_3P$	1.7
$(CH_3)_2NCHO$	0.98	CN^-	1.7
OH^-	0.9–0.99	CO	1.7
$C_2O_4^{2-}$	0.99		

π acceptors

3d		*4d*		*5d*	
V^{2+}	12000				
Cr^{2+}	14000				
Mn^{2+}	8000				
Fe^{2+}	10000	Ru^{2+}	20000		
Co^{2+}	9000				
Ni^{2+}	8700				
Cu^{2+}	13000				
Ti^{3+}	20300				
V^{3+}	18000				
Cr^{3+}	17400	Mo^{3+}	24600		
Mn^{3+}	21000				
Fe^{3+}	14000	Ru^{3+}	28600		
Co^{3+}	18200	Rh^{3+}	27000	Ir^{3+}	32000
Mn^{4+}	23000	Tc^{4+}	30000	Pt^{4+}	36000

The Energy Levels of d-orbitals in Crystal Fields of Different Symmetries

C.N.	Structure	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}
1	Linear[c]	5.14	−3.14	−3.14	0.57	0.57
2	Linear[c]	10.28	−6.28	−6.28	1.14	1.14
3	Trigonal[d]	−3.21	5.46	5.46	−3.86	−3.86
4	Tetrahedral	−2.67	−2.67	1.78	1.78	1.78
4	Square planar[d]	−4.28	12.28	2.28	−5.14	−5.14
5	Trigonal bipyramidal[e]	7.07	−0.82	−0.82	−2.72	−2.72
5	Square pyramidal[e]	0.86	9.14	−0.86	−4.57	−4.57
6	Octahedral	6.00	6.00	−4.00	−4.00	−4.00
6	Trigonal prismatic	0.96	−5.84	−5.84	5.36	5.36
7	Pentagonal bipyramidal	4.93	2.82	2.82	−5.28	−5.28
8	Cubic	−5.34	−5.34	3.56	3.56	3.56
8	Square antiprismatic	−5.34	−0.89	−0.89	3.56	3.56
9	$[ReH_9]^{2-}$ structure (see Fig. 12.40)	−2.25	−0.38	−0.38	1.51	1.51
12	Icosahedral	0.00	0.00	0.00	0.00	0.00

[a] Zuckerman, J. J. *J. Chem. Educ.* **1965**, *42*, 315. Krishnamurthy, R.; Schaap, W. B. *J. Chem. Educ.* **1969**, *46*, 799. Used with permission.

[b] All energies are in *Dq* units; $10Dq = \Delta_o$.

[c] Ligands lie along *z* axis.

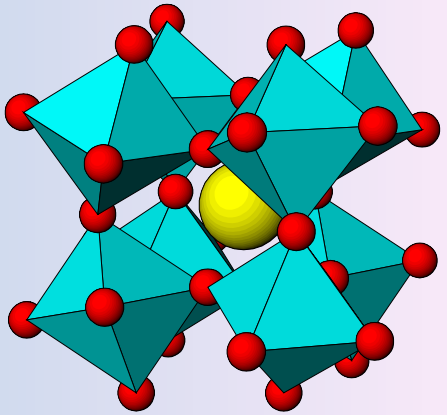
[d] Ligands lie in *xy* plane.

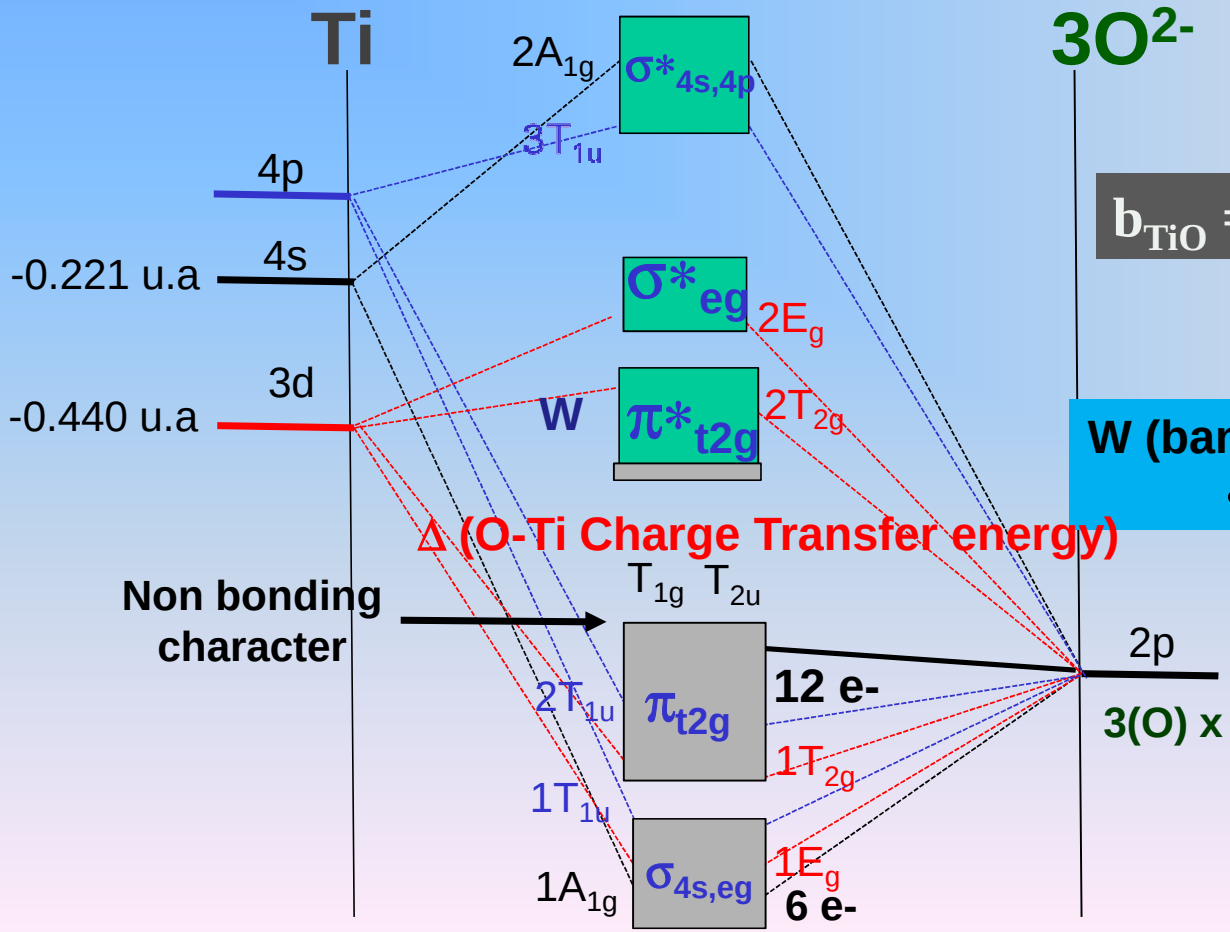
[e] Pyramid base in *xy* plane.

Band diagram of $LaTiO_3$ (Ti^{3+}-$3d^1$- SG : Pbnm)

$$\psi = a_{Ti}\,\psi_{Ti} \pm a_O\,\psi_O$$

$$S = \langle \psi_{Ti} \mid \psi_O \rangle$$





$$b_{TiO} = \langle \psi_{Ti} \mid H \mid \psi_O \rangle$$

b_{TiTi} and b_{TiO}

W (bandwidth) = N b (transfer integral) $\propto S^2_\pi$ (covalent parameter)

N : Number of neighbors

3(O) x 3 (2p) = 18 e-

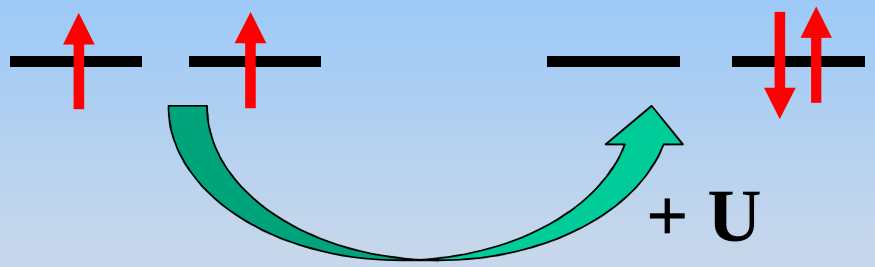
If W ↑, (b) S_π (covalency) ↑ then metallic behavior

Competition between b and U (Hubbard, intraatomic Coulomb repulsion)

Ionic model $U_{ion} = I_{n+1} - I_n - e^2/d_{M-M}$ **~ 10-20 eV**

$U < U_{ion}$ (Z^*_{eff} screening effect –Slater orbitals, b_{MX} and b_{MM} transfer integrals)

➡ **~ 1 eV**



Covalency (b_{MM}) ↑

Extension of orbitals

Goodenough (M^{n+}, Spin state, Z atomic number)

$R_c(M^{n+}) = 3.2 - 0.05n - 0.03\,(Z-Z_{Ti}) - 0.04\,S(S+1)$

$R_{MM} > R_c$: localized electrons

$R_{MM} < R_c$: collective electrons

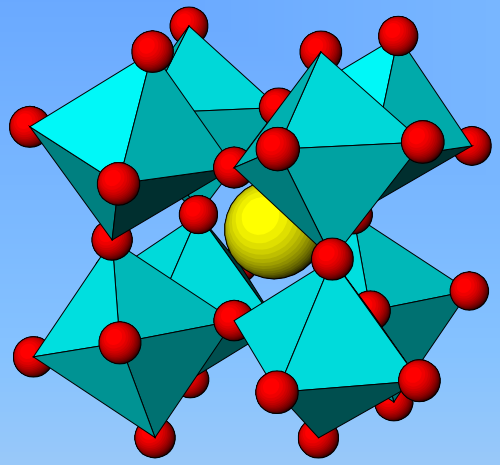
b >> U (bands, s or p electrons)

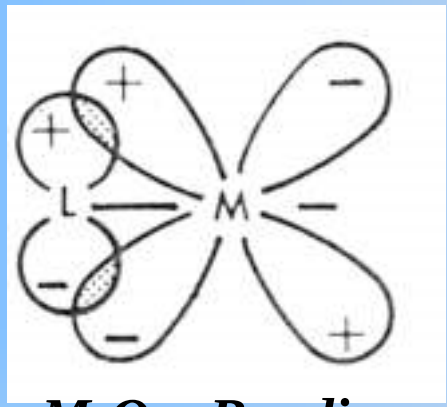
Intermediate d states

b << U (localized levels with f electrons)

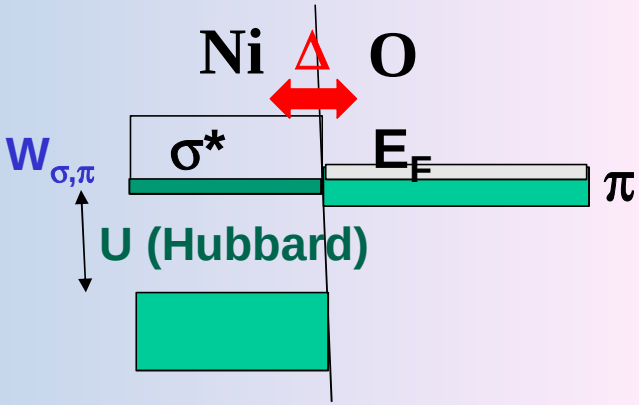
U ↓

Band diagram of $RNiO_3$ (Ni^{3+}-t_2^6 e^1- A= La, Sm)





M-O π Bonding



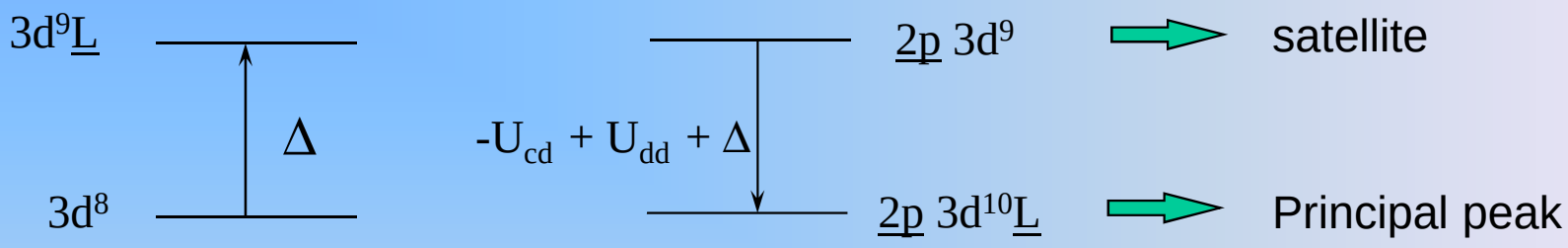
Competitive bonds between R-O and Ni-O :
(O) p_π orbital for Ni-O <=> (O) p_σ orbital for R-O

R size ↓ (acidic character ↑) : Covalency of R-O bond (pσ) ↑
W_π (Ni-O) ↓
Ni-O-Ni Angle ↓ orbital overlap (σ) ↓ ***W_σ(Ni-O) ↓***

From ***metallic behavior ($LaNiO_3$)*** to ***semiconducting behavior ($SmNiO_3$)***

Charge Transfer calculations : Cu^{3+} $L_{2,3}$ edges XAS

• Cu^{3+} $\alpha\,|3d^8\rangle + \beta\,|3d^9\underline{L}\rangle$ ⟶ $|2p^5\,3d^9\rangle + |2p^5\,3d^{10}\underline{L}\rangle$



Fondamental state Excited state

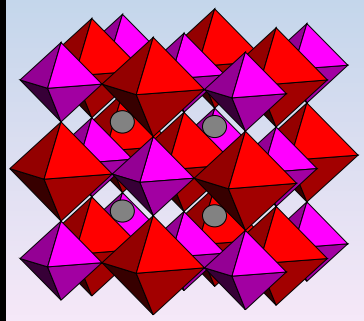


TABLE I. Energetic parameters used to calculate the energy difference between a hole on a fluorine and on a metal site.

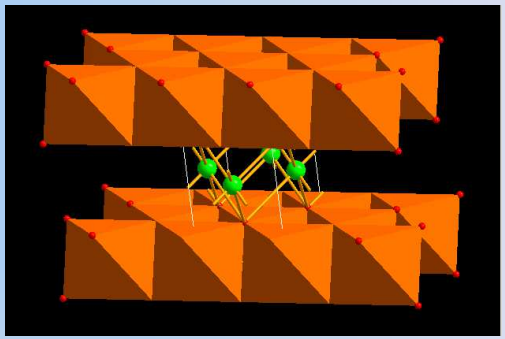
Compounds	Ionization energy (eV)	Electrostatic Madelung site potential (V)	$e\Delta V_M$ (eV)	$d_{M\text{-}F}$ (Å)	Charge-transfer energy Δ_{ion} (eV)
$KNiF_3$	18.19	22.19	33.77	2.006	4.98
$KCuF_3$	20.32	22.14	33.74	2.035	2.95
K_2NaNiF_6	35.21	30.90	43.02	1.890	−3.20
K_2NaCuF_6	36.88	30.88	43.00	1.870	−4.97

About the Cu^{3+}-X chemical bonding (X=F, O)

- Cu^{3+} : 40 % $|3d^8\rangle$ + 60 % $|3d^9\underline{L}\rangle$

  → Formal charge < 3

  → Isolated (molecular) entities $(CuF_6)^{3-}$



- fluorides vs oxides

$2p^5\ 3d^9$

$-U_{cd} + U_{dd} + \Delta =$ 6 - 7,4 eV

$2p^5\ 3d^{10}\underline{L}$

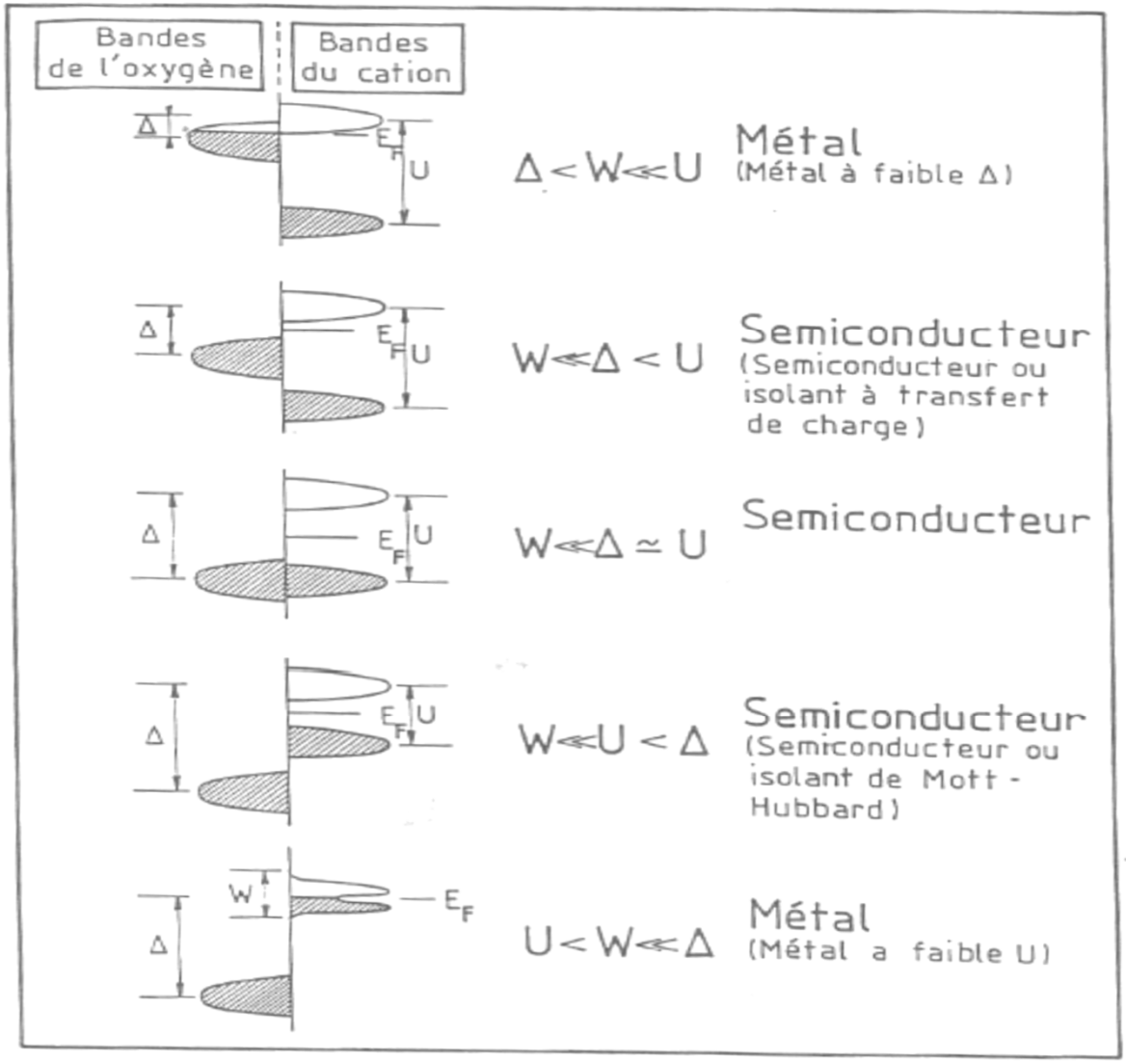
7 -10 eV : $NaCuO_2$

$\Delta < 0$: 20% $|3d^8\rangle$ + 69 % $|3d^9\underline{L}\rangle$ + 11% $|3d^{10}\underline{L}^2\rangle$

Mizokawa et al,
Phys. Rev. Lett. 67, 12, 1638 (1991)

C. De Nadaï , A. Demourgues et al. Phys Rev B.**63**, (2001) 125123,
only *40% of $3d^8$ configuration (Cu^{3+}) in $K_2NaCu^{III}F_6$*.

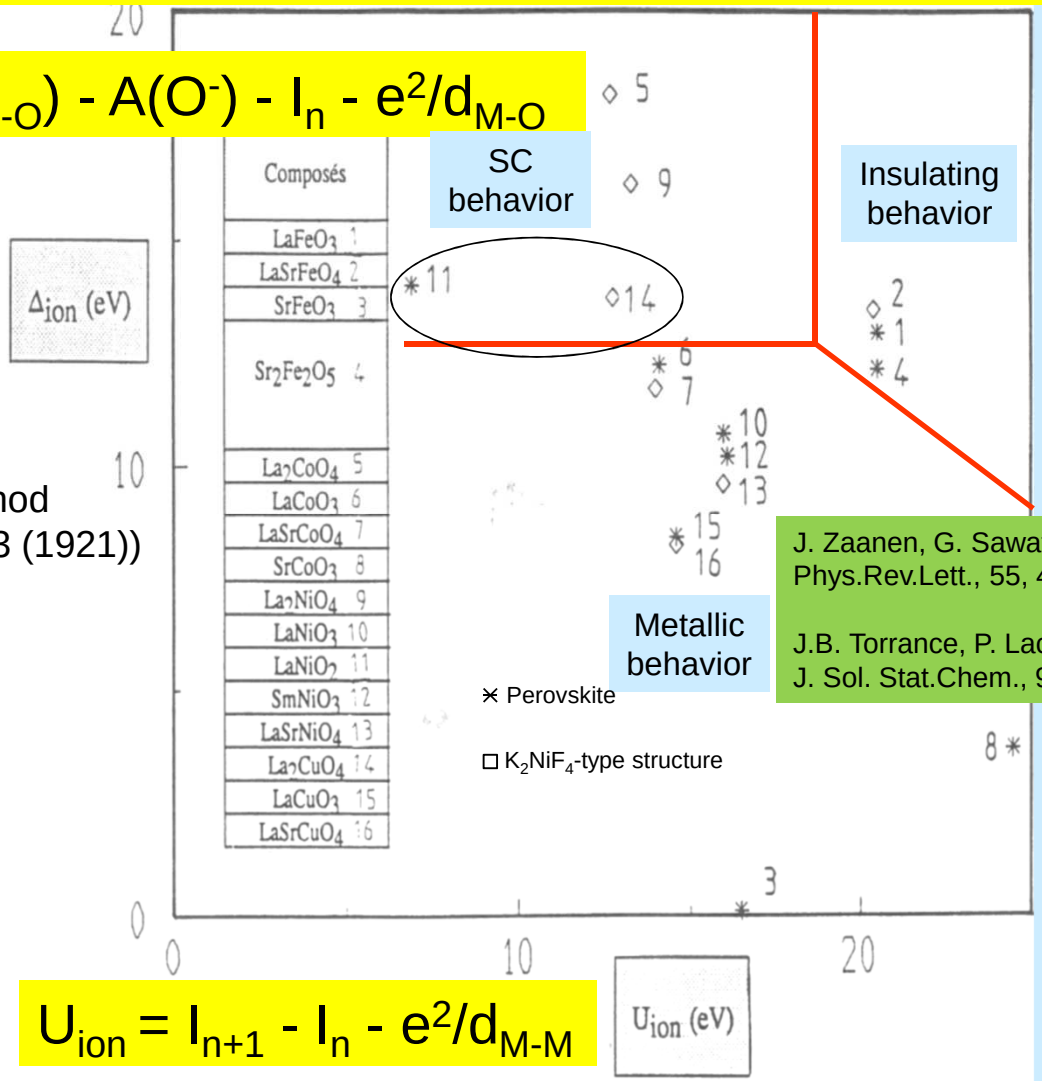
Electronic properties of oxides : band diagrams W, Δ and U



Competition between M-O charge transfer Δ_{ion} and Coulomb repulsion U_{ion}(i.e Hubbard energy) energies in oxides : a ionic view

$$\Delta_{ion} = e\,\Delta(V_{M\text{-}O}) - A(O^{-}) - I_n - e^2/d_{M\text{-}O}$$

Madelung potential difference V_M-V_O
(P.P EWALD method
Ann.Phys, 64, 253 (1921))

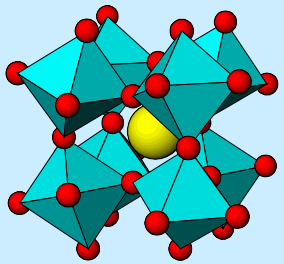


$$U_{ion} = I_{n+1} - I_n - e^2/d_{M\text{-}M}$$

Perovskite and K_2NiF_4-type (perovskite layer)

J. Zaanen, G. Sawatsky and J.W. Allen
Phys.Rev.Lett., 55, 418 (1985)

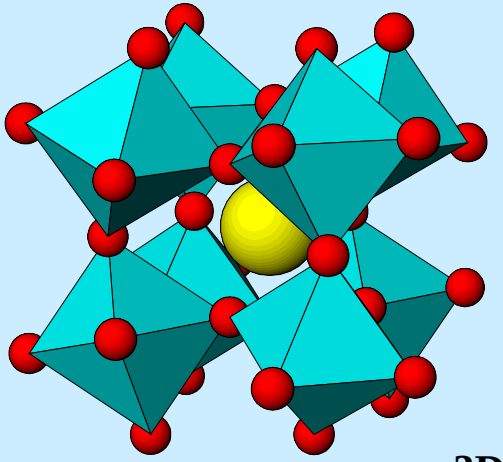
J.B. Torrance, P. Lacorre and R.M. Metzger
J. Sol. Stat.Chem., 90, 168 (1991)

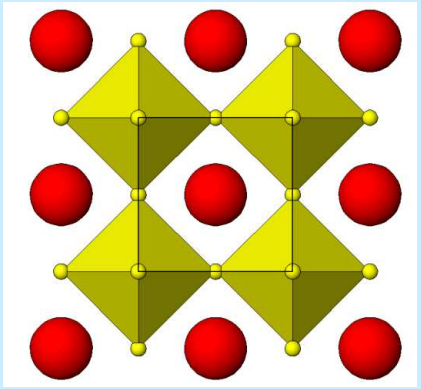


Description of crystalline networks, structural filiation:

- **Some general rules**
- **Hexagonal/Cubic Close Packed structures and Polyhedra**
- **The Pauling rules**

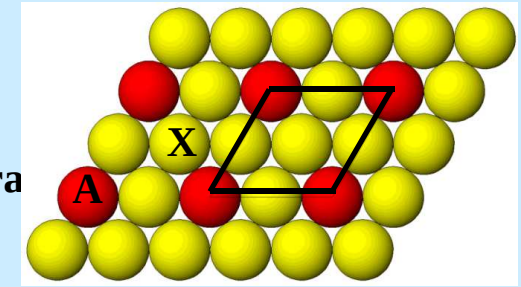
Visualization of structures : polyhedra and simple close packed structures (CCP and HCP)





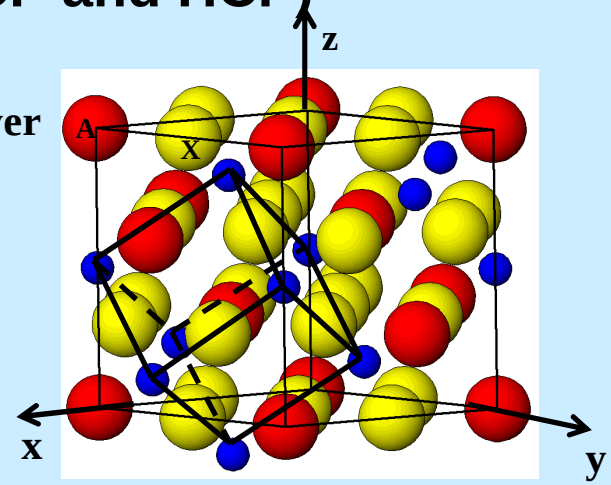
Perovskite AMX_3 (P)
3D corner sharing octahedra

z axis corresponds to $[111]_P$



AX_3 layer ($AuCu_3$ type)

AX_3 layer



Some general rules

- Projection of the structure along the shortest parameter

- Volume per formulae unit and anion number (V/ZX) to identify the compactness of the structure

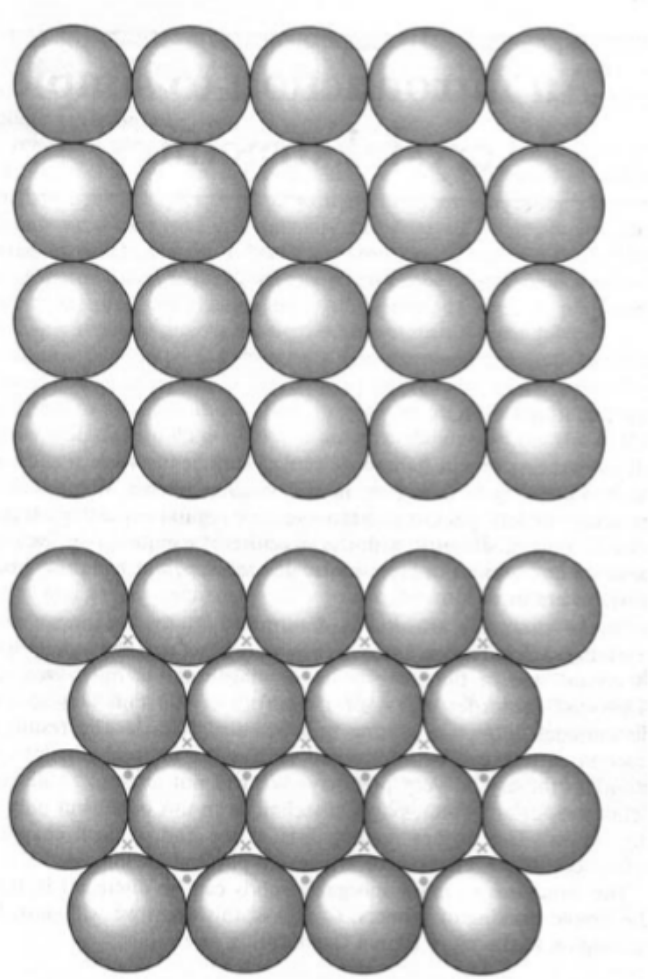
$BaTiO_3$ (V/ZX = 21.4 A^3) , $CaMnO_3$ (V/ZX = 17.3 A^3)
$LaFeO_3$ (V/ZX = 20.3 A^3), $LaNiO_3$ (V/ZX = 18.8 A^3) $SmNiO_3$ (V/ZX= 18.2 A^3)

- Search for the compact planes and the stacking mode

- Filling of holes : which environment ? Concept of polyhedra

Metal atoms → Spheres

Arrangements in 2D

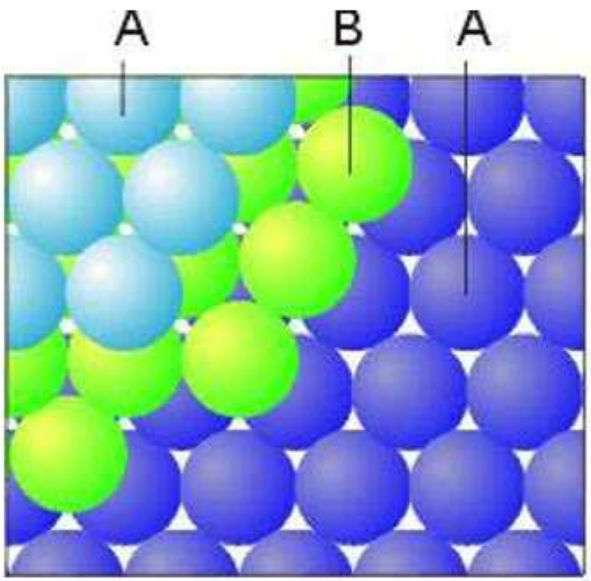


primitive (square) packing
(large holes, low space filling)

close (hexagonal) packing
(small holes, high space filling)

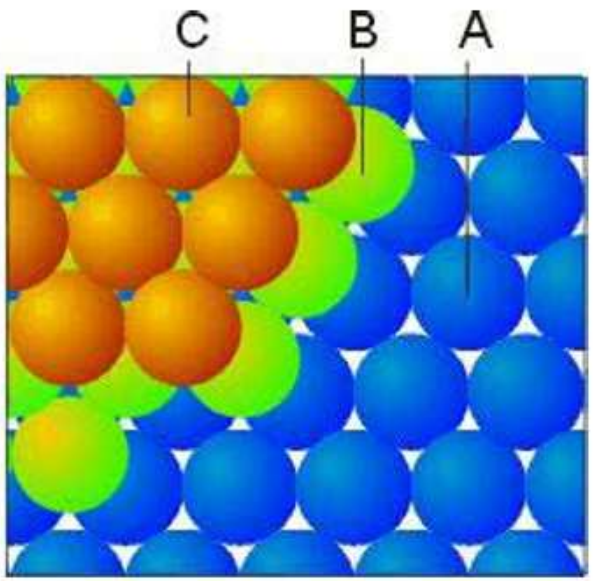
3D close packing:
different stacking sequences of close packed layers

Example 1: HCP



stacking sequence: AB

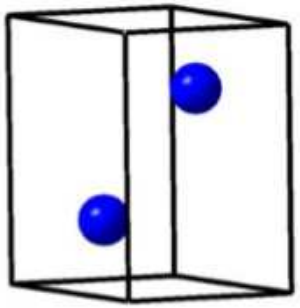
Example 2: CCP

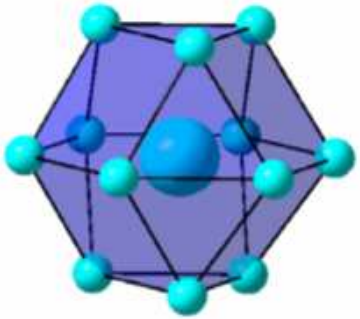


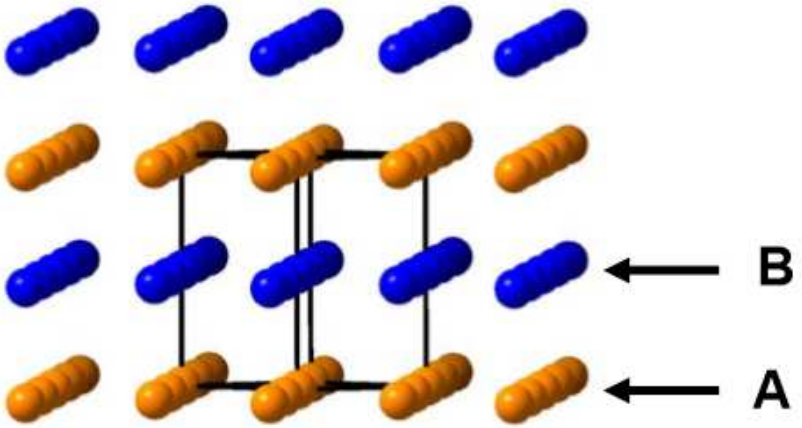
stacking sequence: ABC

HCP

(Be, Mg, Zn, Cd, Ti, Zr, Ru ...)

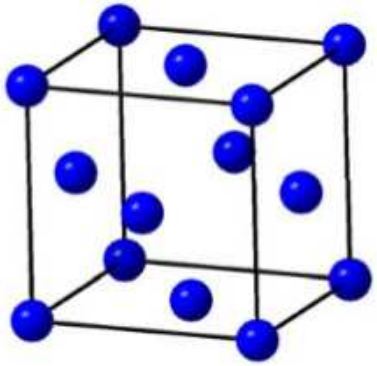


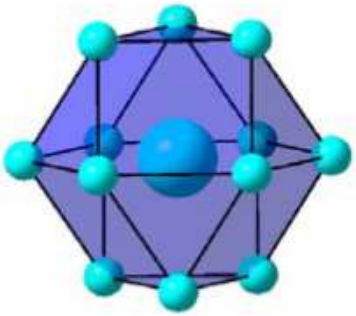


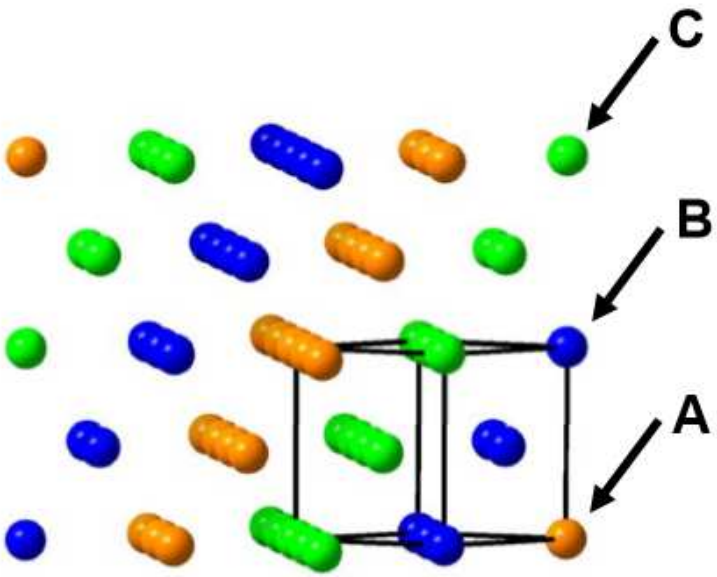


CCP

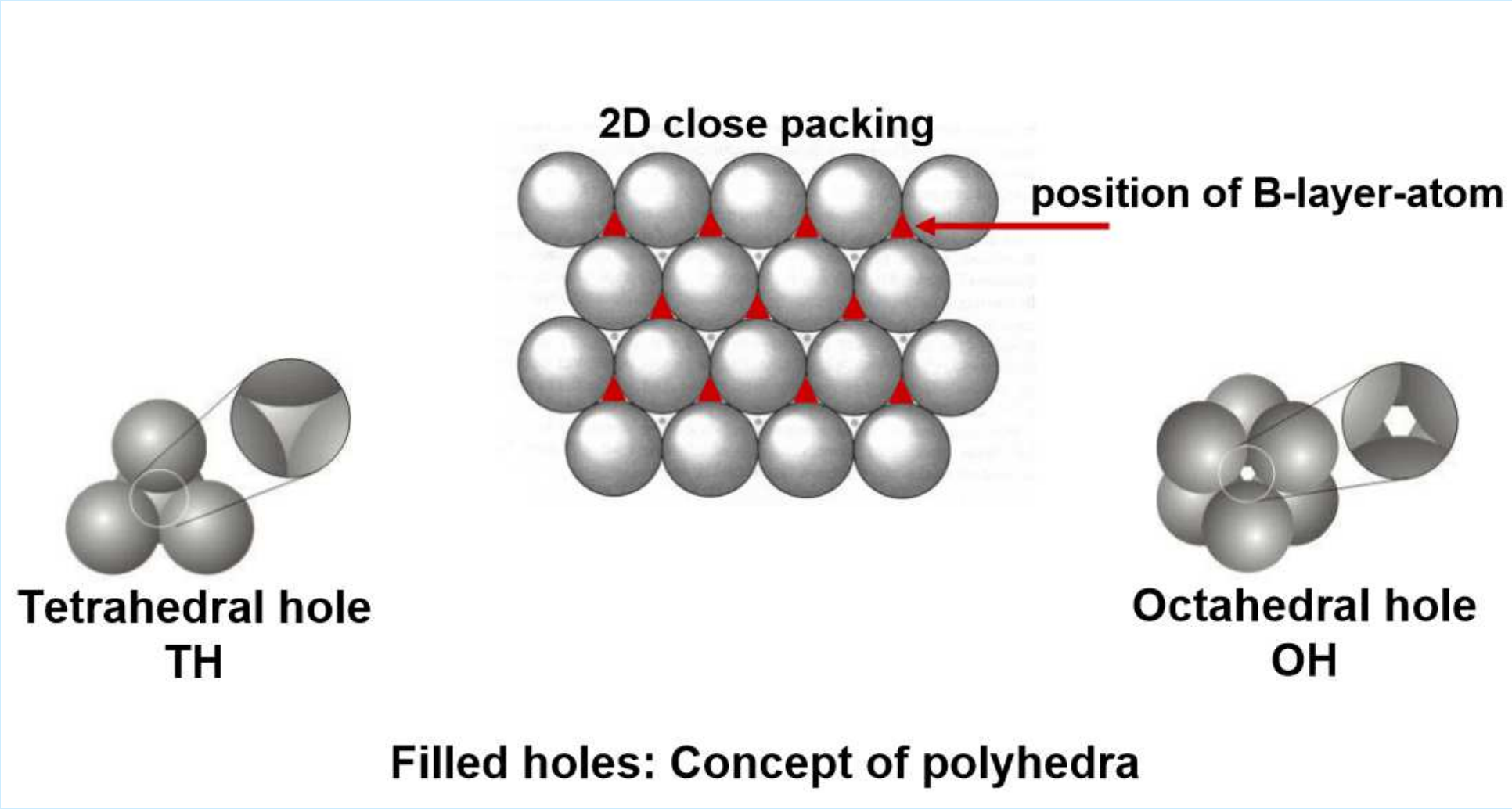
(Cu, Ag, Au, Al, Ni, Pd, Pt ...)





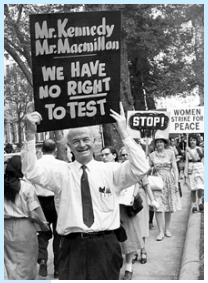


Description of the environment of holes



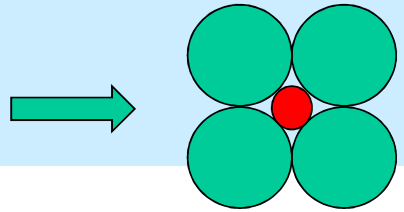
Filled holes: Concept of polyhedra

Relationship between polyhedron (Coordination Number) and cation/anion ionic size ratio

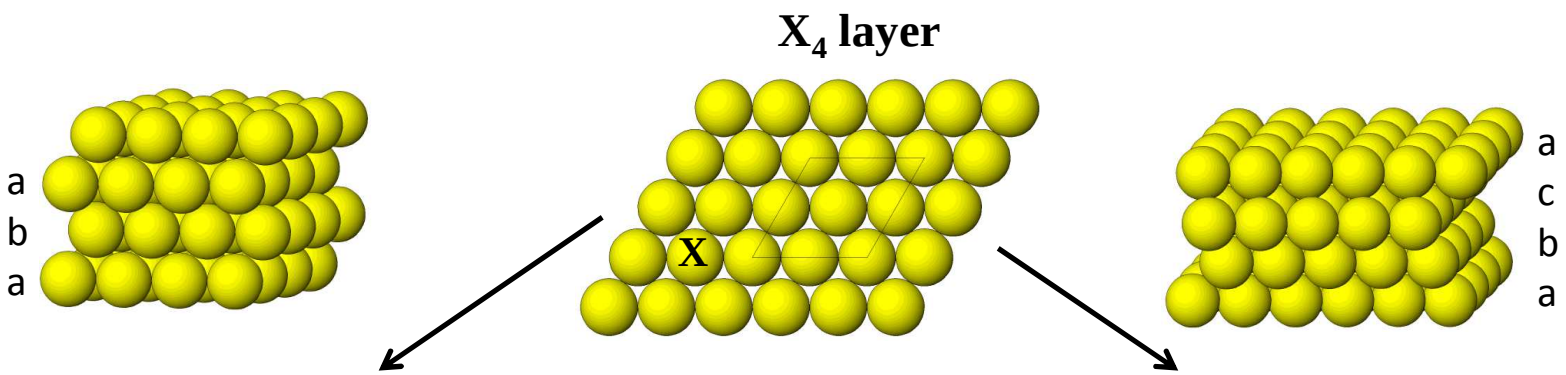


The 1st Pauling's rule

r_{cation}/r_{anion} = optimum value



coordination	anion polyhedron	radius ratios	cation
3	triangle	0.15-0.22	B in borates
4	tetrahedron	0.22-0.41	Si, Al in oxides
6	octahedron	0.41-0.73	Al, Fe, Mg, Ca in oxides
8	cube	0.73-1.00	Cs in CsCl
12	close packing (anti)cuboctahedron	1.00	metals



Hexagonal close-packing (hcp)

100% octahedra ⟷ **50% tetrahedra**

oct. + tetra.

- **NiAs**
- **Olivine $(Mg,Fe)_2SiO_4$ $LiFePO_4$**
- **Wurtzite ZnS Zincite ZnO**

50% octahedra

CdI_2 type, TiO_2 -Rutile
α–AlO(OH) α–PbO_2
Li_2ZrF_6 type

33% octahedra

β-$TiCl_3$

Cationic ordering

$LiGaO_2$
β-$NaFeO_2$,
Li_3PO_4

Cubic close-packing (ccp)

100% octahedra ⟷ **50% tetrahedra**

oct. + tetra.

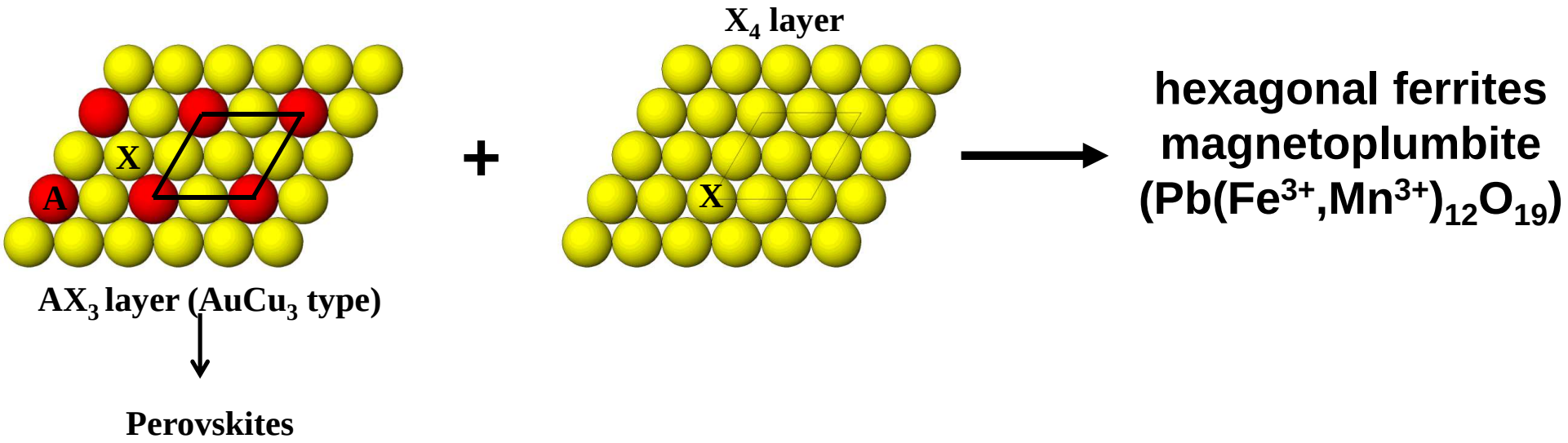
- **NaCl type**
- **spinel $ZnAl_2O_4$, β–Ga_2O_3**
- **ZnS Blende**

Cationic ordering

α–$NaFeO_2$ ($LiNiO_2$)
Li_2MO_3 (M=Mn,Ti,…)
Na_3MO_4 (M=Nb, Ta, Ru, Bi)

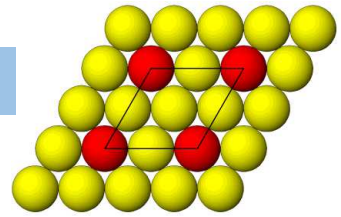
50% octahedra

$CdCl_2$, TiO_2 -Anatase


X
A
AX3 layer (AuCu3 type)
Perovskites
+
X4 layer
X
hexagonal ferrites
magnetoplumbite
(Pb(Fe3+,Mn3+)12O19)

$BaFe_{12}O_{19}$ ⟺ β-alumina

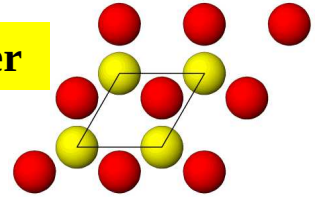
BaO_3 layer



$BaFe_{12}O_{19}$ ⟶ stacking of $[O_4]$ and $[BaO_3]$ layers along the c-axis

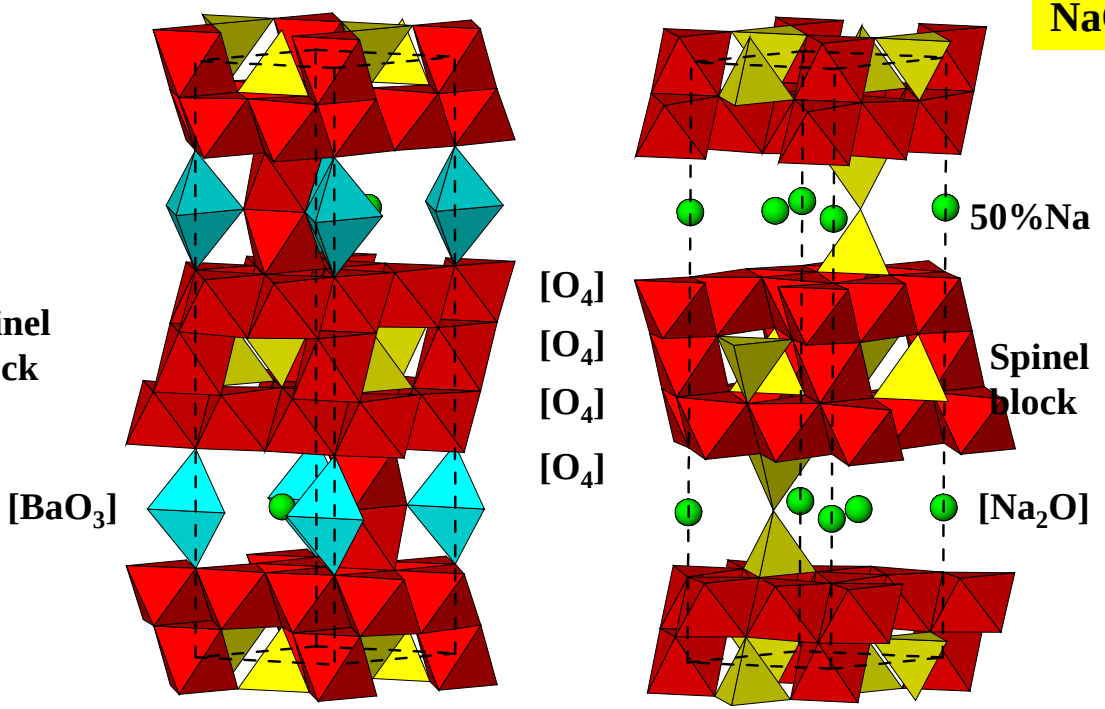
β-alumina (Na_2O, $11Al_2O_3$ = 2 $NaAl_{11}O_{17}$) ⟶ same stacking, the $[BaO_3]$ layer is replaced by a $[NaO]$ layer

NaO layer



Ferrimagnetic properties

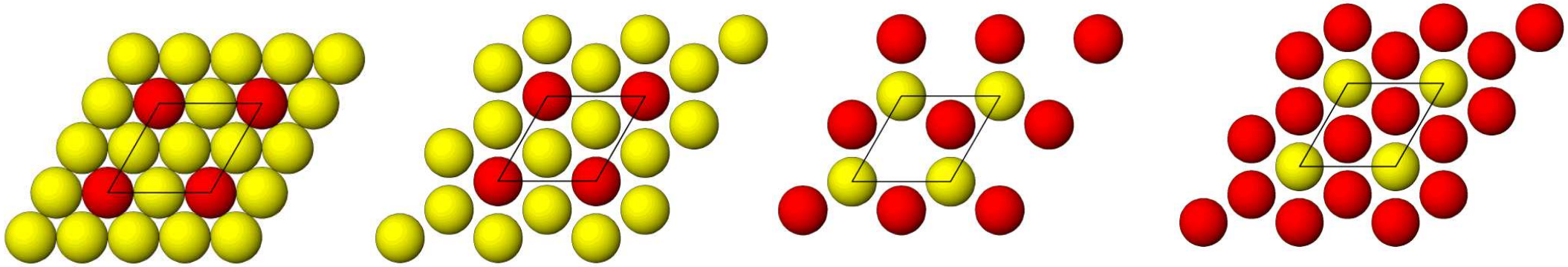
Na conductivity
Na-S Battery



$BaFe_{12}O_{19}$
$P6_3/mmc$
a = 5.80Å c=23.18Å

β-alumina
$P6_3/mmc$
a = 5.59Å c = 22.53Å

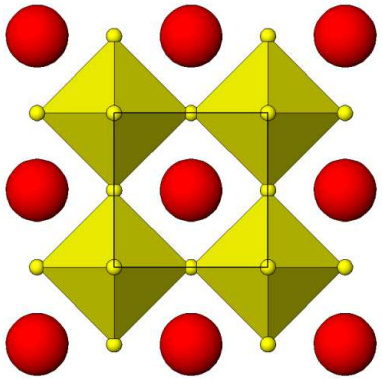
Various $[A_nX_m]$ layers for stacking



$[AX_3]$ layer **$[AX_2]$ layer** **$[AX]$ layer** **$[A_2X]$ layer**

$LaNiO_3$

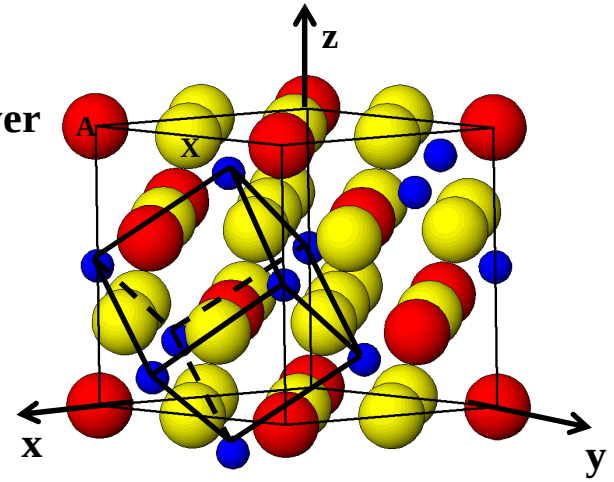
Ni^{3+} ($t_2^6e^1$)



3C polytype

Relationship between the cubic and hexagonal unit cells. z axis corresponds to[111]p

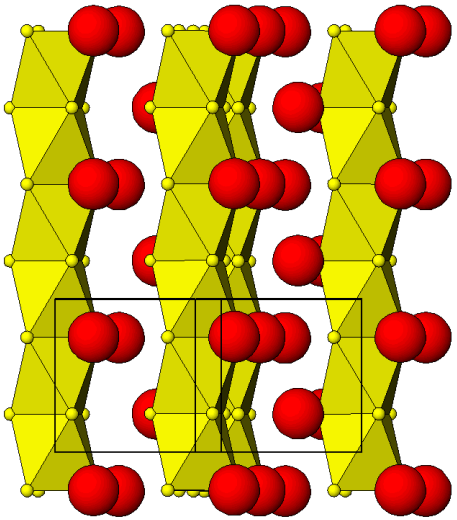
AX_3 layer



$LaNiO_3$

Ni^{4+} ($t_2^6e^0$)

$BaNiO_3$



AX_3 a layer

AX_3 b layer

AX_3 a layer

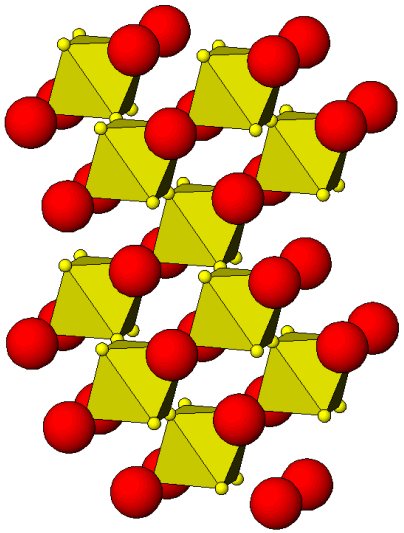
2H polytype
Chains of face sharing octahedra

AX_3 a layer

AX_3 b layer

AX_3 c layer

AX_3 a layer

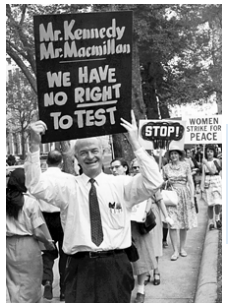


3C polytype
3D corner sharing octahedra

Volume per formulae unit and anion number (V/ZX) in various structures

Structures	V/ZX (Å)^3
TiO_2, rutile	15.6
TiO_2, anatase	17.0
TiO_2, brookite	16.0
TiO_2 (II-HP, α-PbO_2)	15.2
$ZrTiO_4$ (α-PbO_2)	16,6
$BaTiO_3$	21.4
$SiFe_2O_4$, spinel (Fe^{2+})	17.4
Fe_2SiO_4, Olivine (Fe^{2+})	19.7
Fe_3O_4, spinel (Fe^{2+}/Fe^{3+})	18.5
$BaFe_{12}O_{19}$, magnetoplumbite	18.8
$Y_3Fe_5O_{12}$, garnet	19.7
$Fe_{0.9}O$, rocksalt (Fe^{2+})	19.9
α-$NaFeO_2$, ordered rocksalt	21.2
β-$NaFeO_2$, ordered wurtzite	27.3
B-Fe_2O_3, Bixbyite (Fluorite)	17.3
α-Fe_2O_3	16.8
$LaFeO_3$	21.5
$LaSrFeO_4$	23.9
SnO_2, rutile	17.9
SnF_2(E)	22.3

Compact structure
(Sten Andersson)
V/ZX = 15-17 A^3



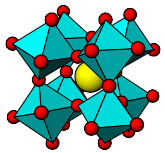
The 2nd Pauling rule : the electrostatic valence rule [v(valence)/Cn(Coordination number)]

1929 (Rules), 1954 (Nobel Prize),
1962 (Nobel peace prize)

$$\Sigma n_i(\text{cation})\, v_i/Cn_i = \text{charge (anion)}$$

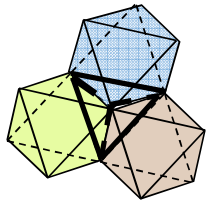
Fluorite CeO_2 : 4 x 4/8 = 2 (Cn(O) = 4, Cn(Ce) =8)

Rutile TiO_2 : 3 x 4/6 = 2 (Cn(O) =3, Cn(Ti) = 6)



Perovskite $BaTiO_3$: 4(Ba) x 2/12 + 2(Ti) x 4/6 = 2 [Cn (Ba) =12, Cn(Ti) =6, **Cn(O) = 4(Ba) + 2(Ti)**]

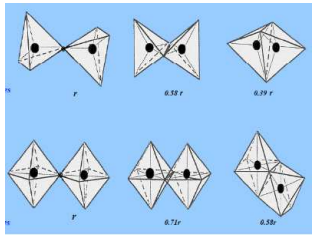
Spinel $MgAl_2O_4$: (Mg) 2/4 + 3(Al) 3/6 = 2 [Cn(Mg) =4, Cn(Al) = 6, **Cn(O) = 3 (Al) + 1 (Mg)**]



The 3rd Pauling rules : sharing of polyhedron corners > edges > faces vs stability of ionic structures

TiO_2 Rutile > TiO_2 Brookite > TiO_2 Anatase

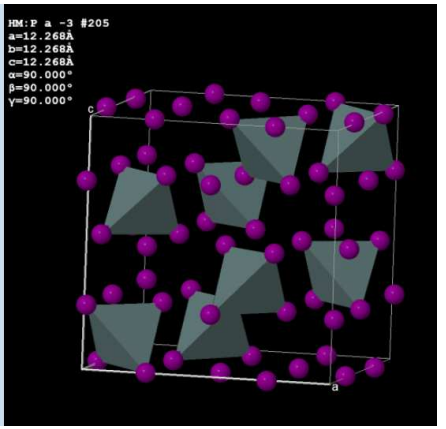
V/ZX = 15.6 A^3 < 16.0 A^3 < 17.0 A^3



The 4th Pauling rule : Crystals containing different cations

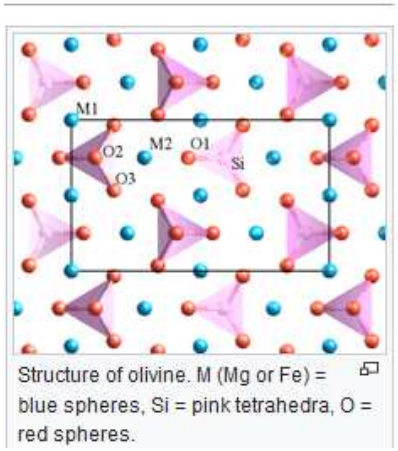
Small cations (vs anions) with high valency and low coordination
tend not to share polyhedron with one another

SnI_4 (molecular): (CCP) I^- and 1/8 Td sites ***(isolated) $(SnI_4)^0$***

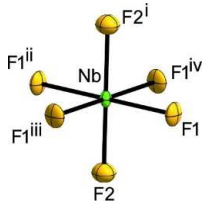


Olivine
$(Mg,Fe)_2SiO_4$

Isolated Td ***$(SiO_4)^{2-}$***



Structure of olivine. M (Mg or Fe) = blue spheres, Si = pink tetrahedra, O = red spheres.

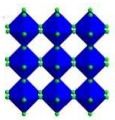


NbF_6

Corner-sharing octahedra

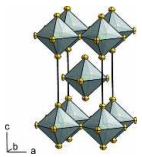
NbF_3 (3D)

6 Corners (Perovskite)



NbF_4 (2D)

4 Corners (K_2NiF_4)



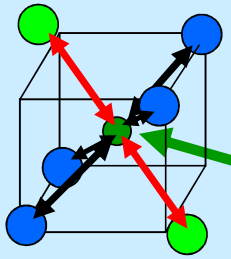
NbF_5 (0D, molecular)

2 Corners (isolated tetramers)

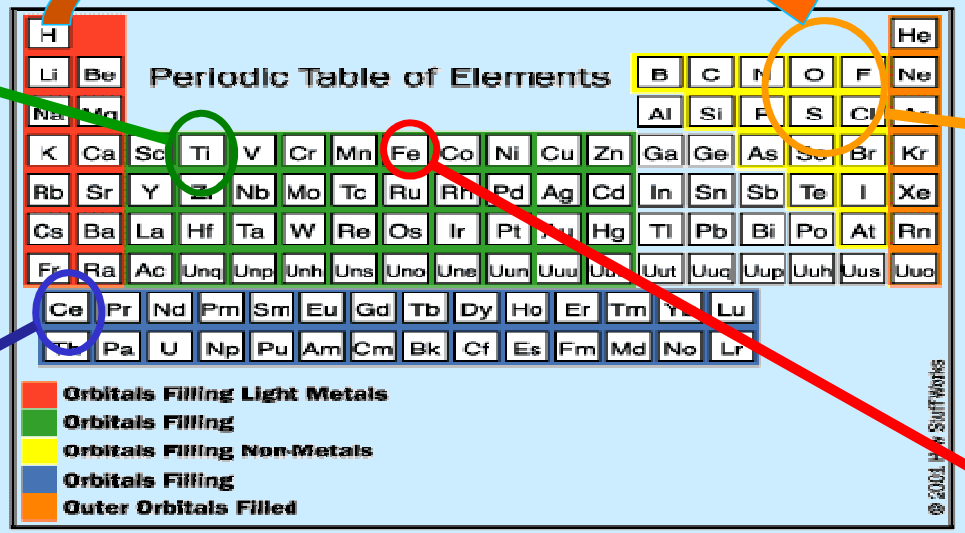
The key role of Electronegativity (χ), Charge (Z^+), Ionic radius (r_{ion}) of M^{z+} to define local electrical field = $\chi(z)/ r_{ion}$

Point group symmetry (M vs X),
Mixing empty d orbitals with filled ligand p orbitals,
Looking for non-bonding character
Lowering the band gap

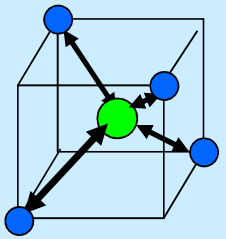
^{22}Ti
Pauling : 1.4
[Ar] $4s^2 3d^2$



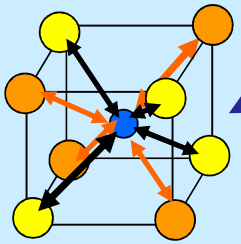
$Ti^{4+}(J=0)/Ti^{3+}(J=3/2)$



OH^-
O^{2-} F^-
S^{2-}

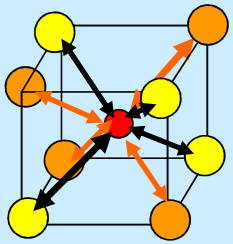


^{58}Ce
Pauling : 1.1
[Xe] $6s^2 4f^2$

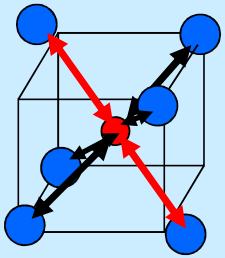


$Ce^{4+}(J=0)/Ce^{3+}(J=5/2)$

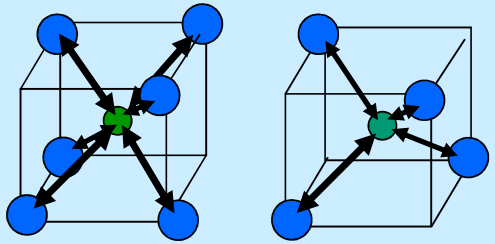
^{26}Fe
Pauling : 1.8
[Ar] $4s^2 3d^6$



Fe^{2+} ($^5T_2$)

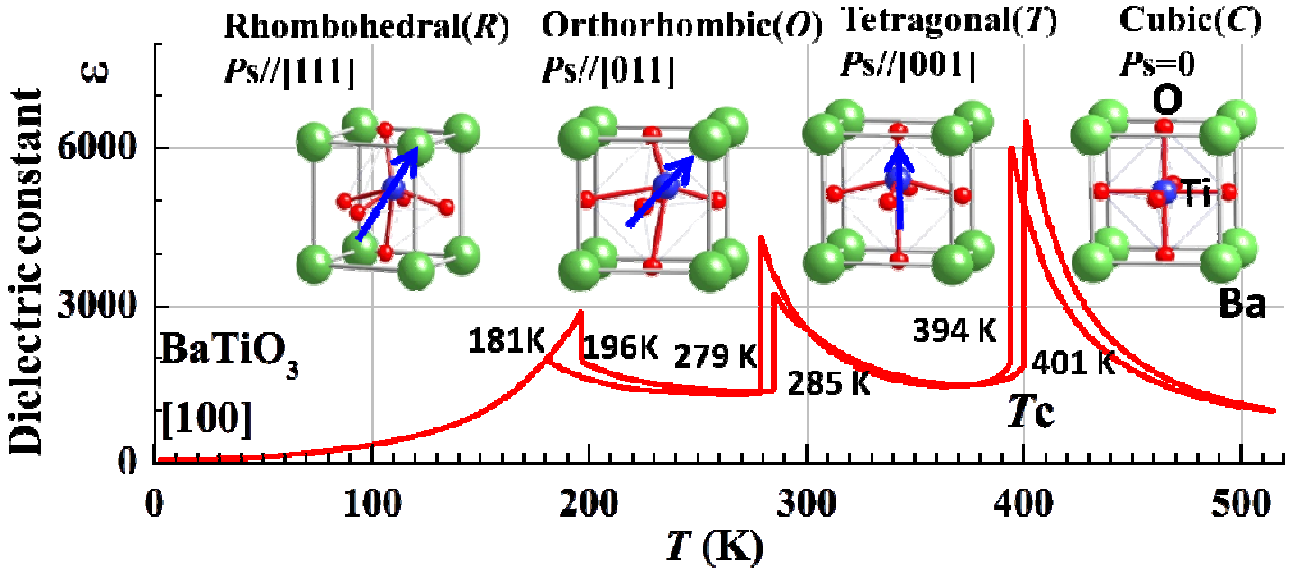


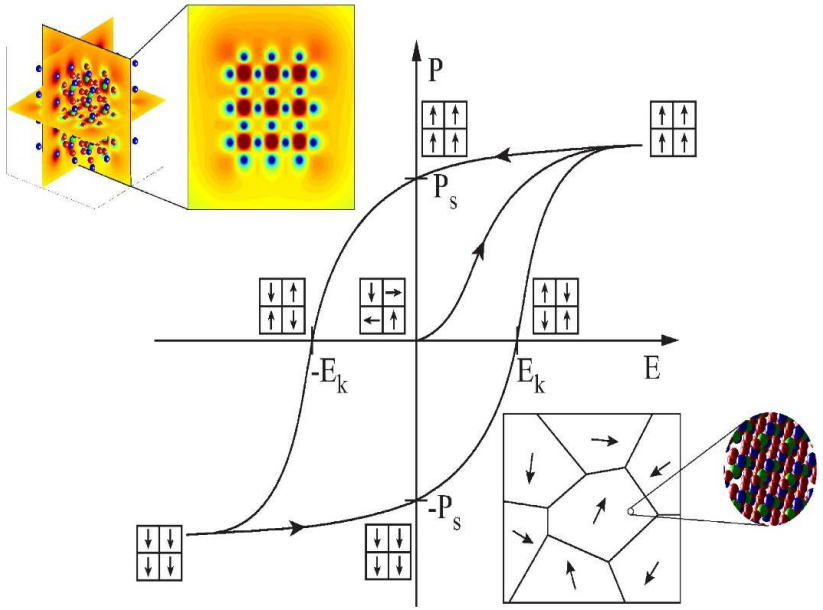
Fe^{2+} ($^5T_2$, $^1A_{1g}$)



$Fe^{3+}(^6A_1)$

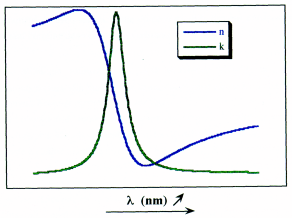
Ti-O chemical bonding and Polarization ($P = (\varepsilon-1)\,\varepsilon_0\,E$) : phase transitions and ferroelectric/piezoelectric properties of $BaTiO_3$ (capacitors, non-linear optics, …)

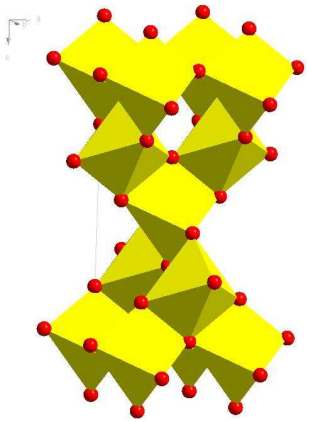




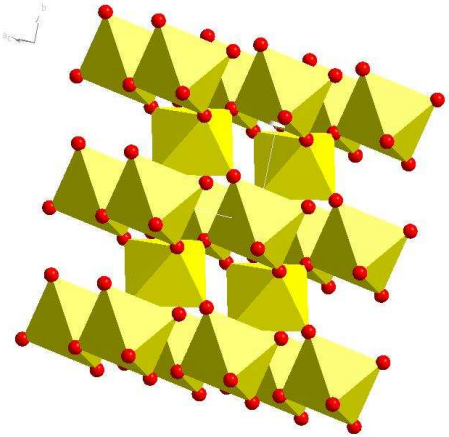
Ti-O chemical bonding, polarization P , refractive index n ($\sqrt{\varepsilon\mu}$) and absorption k

The Kramers-Kronig Relationship n(λ) ⇔ k(λ)

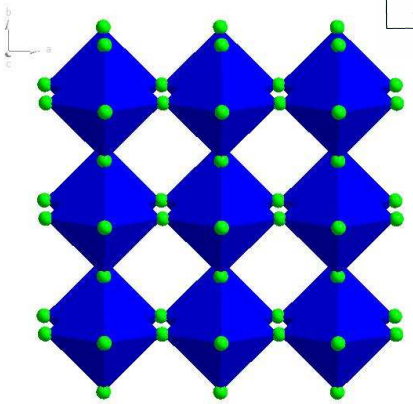




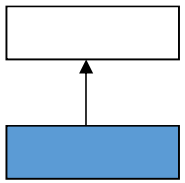
Anatase -TiO_2
Tetragonal ($I4_1/amd$)
ρ = 3.91 g/cm^{-3}
n = 2.52, Eg = 3.25 eV



Rutile -TiO_2
Tetragonal ($P4_2/mnm$)
ρ = 4.32 g/cm^{-3}
n = 2.75, Eg = 3.1 eV



ReO_3 –$Ti_{0.75}(OH)_{1.5}F_{1.5}$
Cubic (Pn-3m)
ρ = 2.65 g/cm^{-3}
n = 1.9, Eg = 3.2 eV

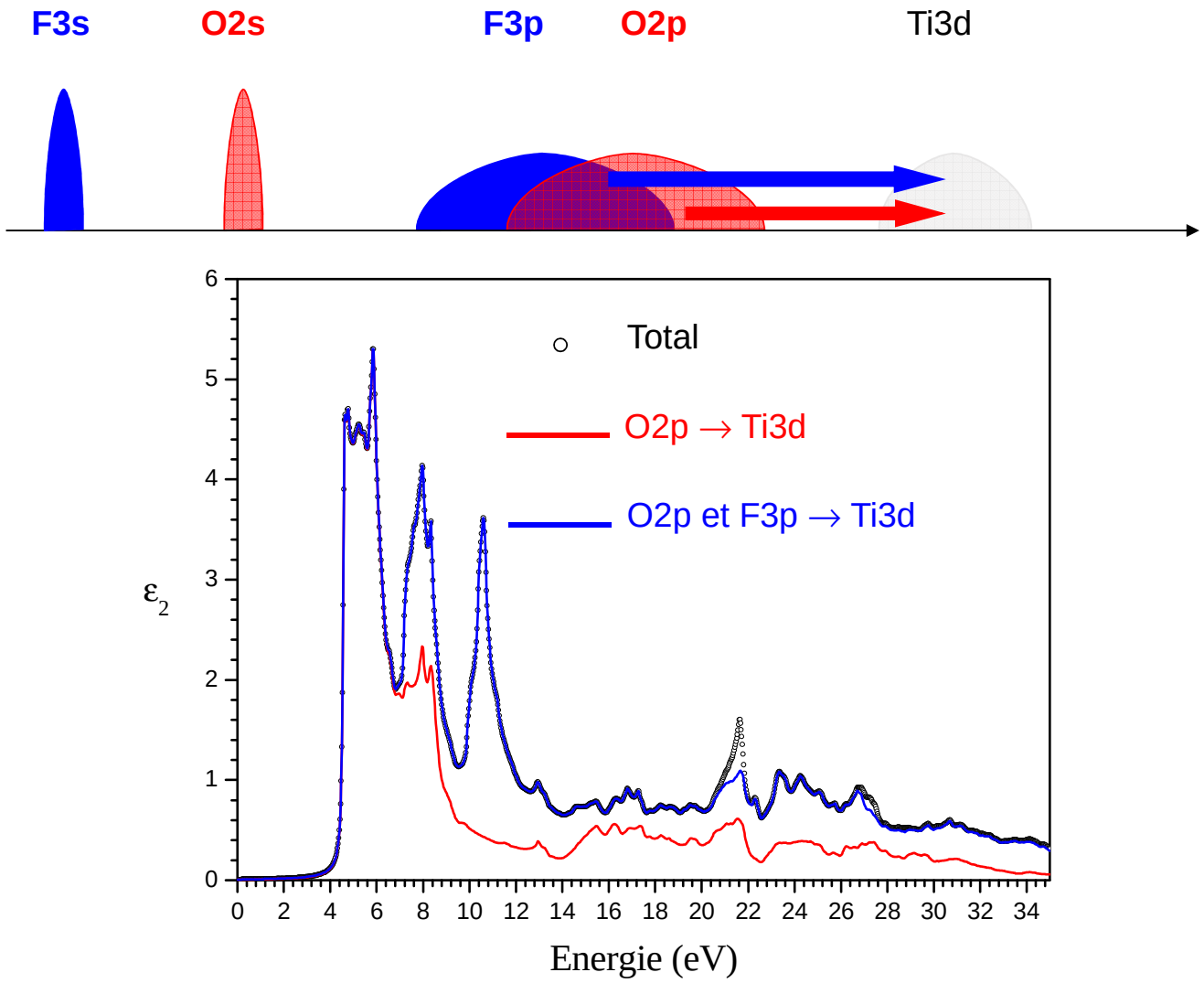


π*,Ti 3d^0

TiO_2, CTB : 3.1-3.2 eV

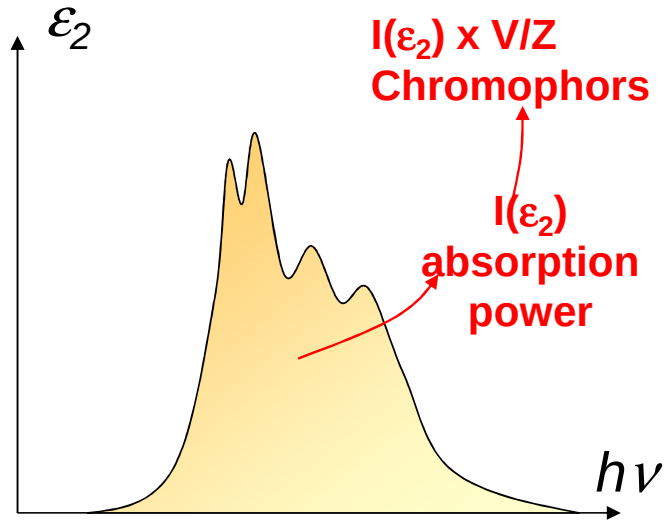
O 2p^6

Ti oxyfluoride : Density of states and dielectric function ε_2



The dielectric function in UV-Visible-NIR range

$$\varepsilon = \varepsilon_1 + i\,\varepsilon_2$$



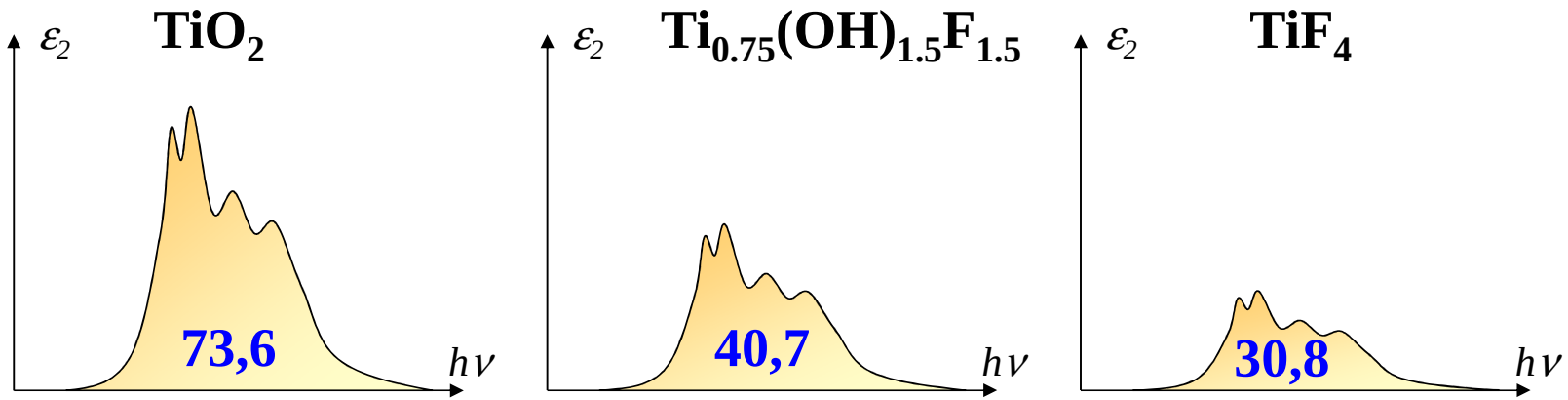
$$\varepsilon_1 = n^2 - k^2$$

$$\varepsilon_2 = 2nk$$

n (scattering) and k (absorption)

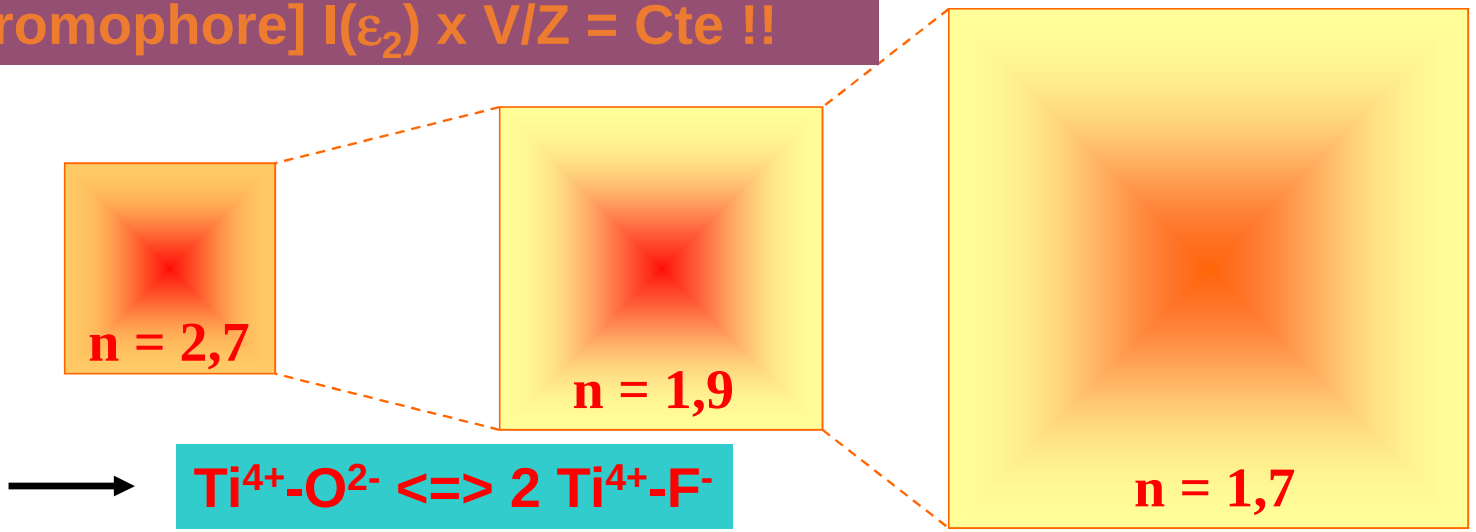
n, k = f[I(ε2)] **n, k = f[I(ε2)×V]**

Absorption and scattering power of Ti-based compounds



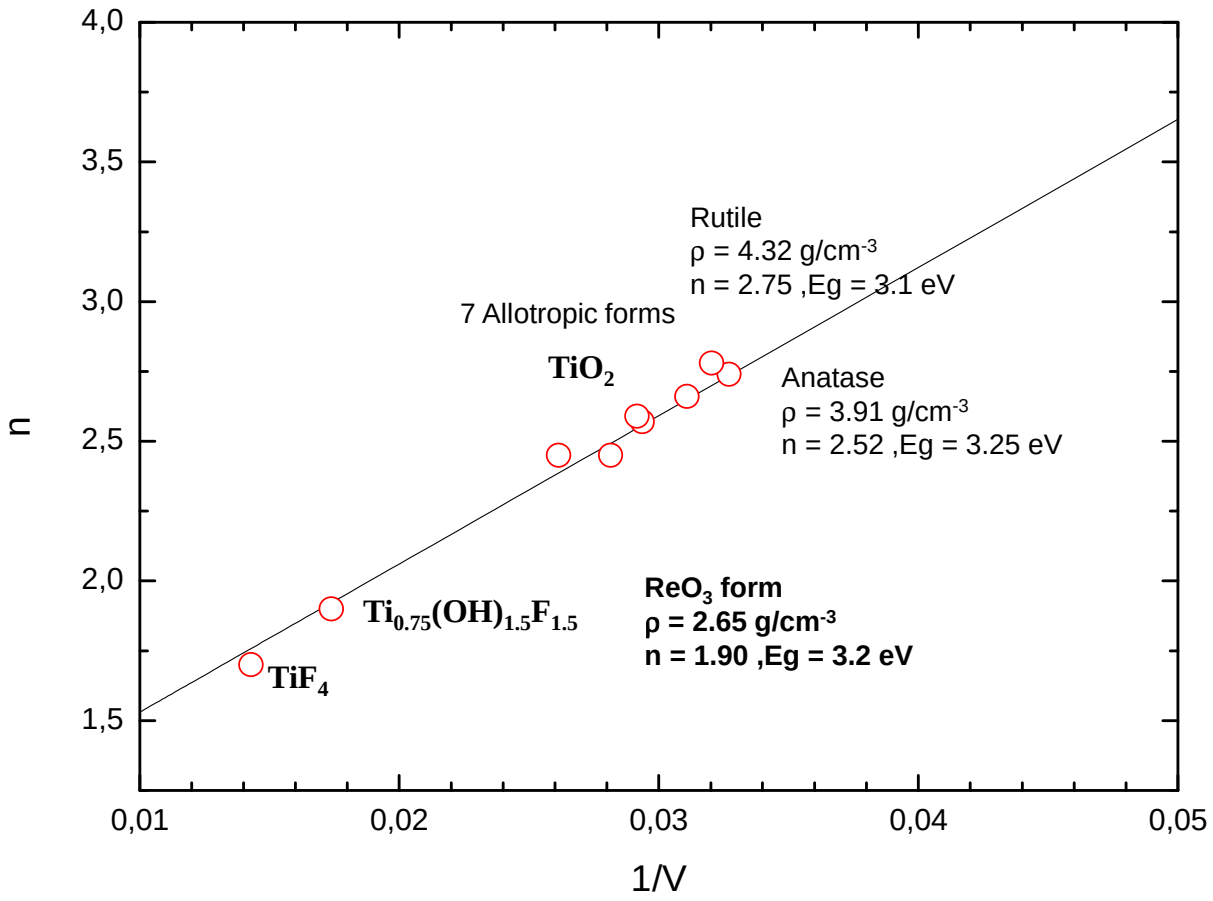
V/Z = 32,17 Å³ **V/Z = 57,51 Å³** **V/Z = 69,99 Å³**

[Chromophore] I(ε_2) x V/Z = Cte !!

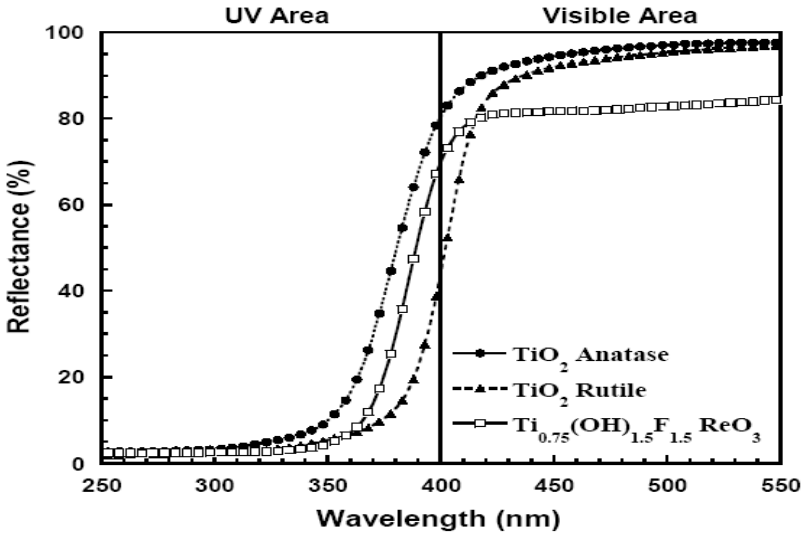


Ti^{4+}-O^{2-} <=> 2 Ti^{4+}-F^{-}

The Gladstone-Dale relationship (TiO_2) : n(550 nm) = 1+ 0.4 (Z/V)



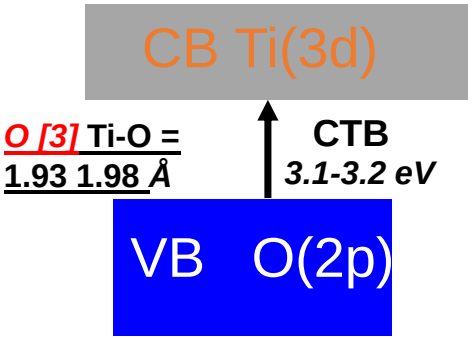
Ti-based hydroxy-fluorides with ReO_3-derived network and band gap



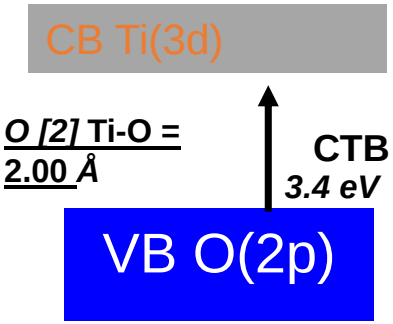
□Ti vacancies
→distorted Oh site→
Stabilization of CB Ti(3d)

χ electronegativity
$\chi[F^-] > \chi[O^{2-}] > \chi[OH^-]$

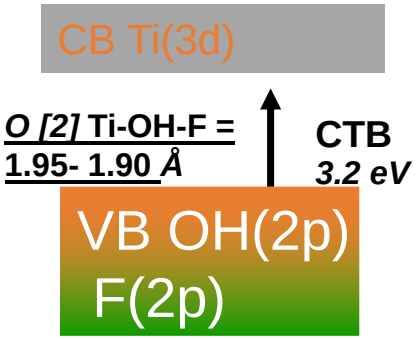
TiO_2



$BaTiO_3$

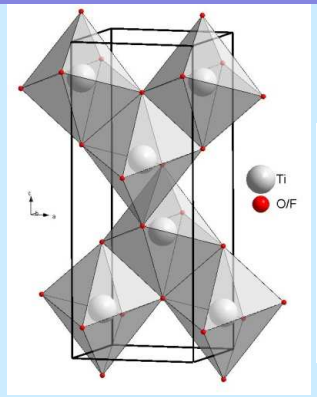


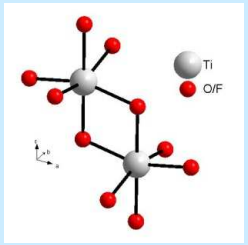
(ReO_3)
$Ti_{0.75}\square_{0.25}OH_{1.5}F_{1.5}$



A. Demourgues et al. Chem. Mater. 21, 2009, 1275-1283

Anatase-TiO_2 and orbital molecular diagram : Generation of defects and photocatalysis





Ti^{4+} (e_g)

Ti^{4+} (t_{2g})

d_{xz} d_{yz}

d_{xy}

σ* anti-bonding

π* anti-bonding

d_{xy} non-bonding

Non-bonding character of d_{xy} orbitals, 4 interactions Ti^{4+} - Ti^{4+} at 3.04 Å

d_{xy} (Ti) and p_π (O) levels with ***non-bonding character***

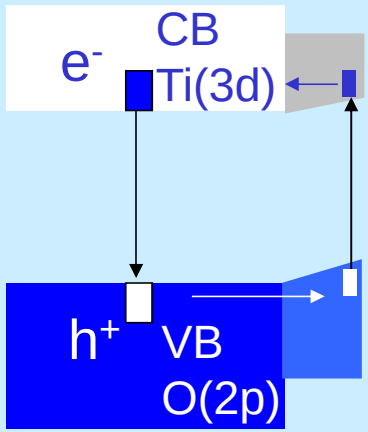
$O(p_\pi)$

$O(p_\sigma)$

p_π non-bonding

π bonding

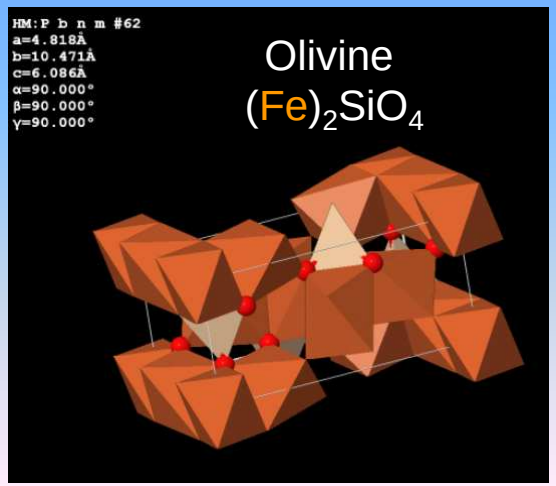
σ bonding



Bulk Surface(OH)

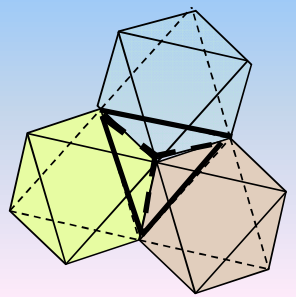
R_{Ti-Ti} = 3.04 A > R_c (Goodenough) = 3.0 A
→ Localized electrons

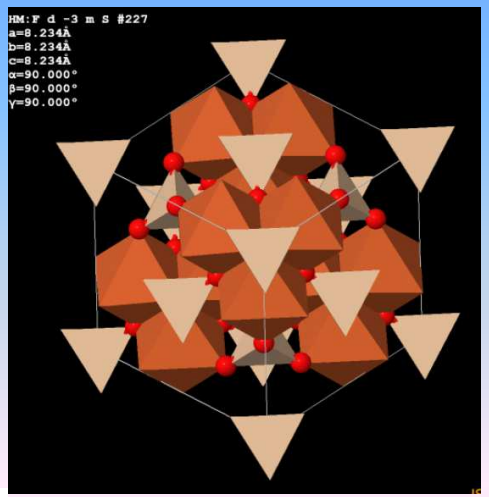
Oxides : Fe^{2+} (S=2) in cubic, octahedral sites, Fe^{3+} (S=5/2) in octahedral, tetrahedral sites and Ferrimagnetic properties



V/ZX = 19.7 A^3

Pressure, T





V/ZX = 17.4 A^3

Spinel $SiFe_2O_4$

Tc = 850 K $Fe^{3+}(Fe^{2+}, Fe^{3+})O_4$

(0 K) $J_{Td\text{-}Oh}$ = 5μ_B 4 + 5 μ_B = - 4 μ_B

Tc = 960 K $Fe^{3+}(Li_{0.5}^{+}, Fe_{1.5}^{3+})O_4$

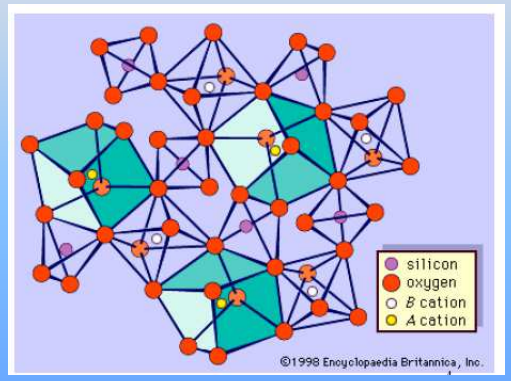
(0 K) $J_{Td\text{-}Oh}$ = 5μ_B **1.5 x** 5 μ_B = - 2.5 μ_B

$Fe^{3+}(\ _{1/3}, Fe_{5/3}^{3+})O_4$

(0 K) $J_{Td\text{-}Oh}$ = 5μ_B **5/3 x** 5 μ_B = -10/3 μ_B
- 2.5 μ_B / Fe_2O_3

$BaFe_{12}O_{19}$ = 'BaO' +

Tc = 730 K $Fe^{3+}(\ _{1/3}, Fe_{5/3}^{3+})O_4$



V/ZX = 19.7 A^3

Garnet : $Fe_3Al_2Si_3O_{12}$

$Y_3Fe^{3+}{}_2Fe^{3+}{}_3O_{12}$

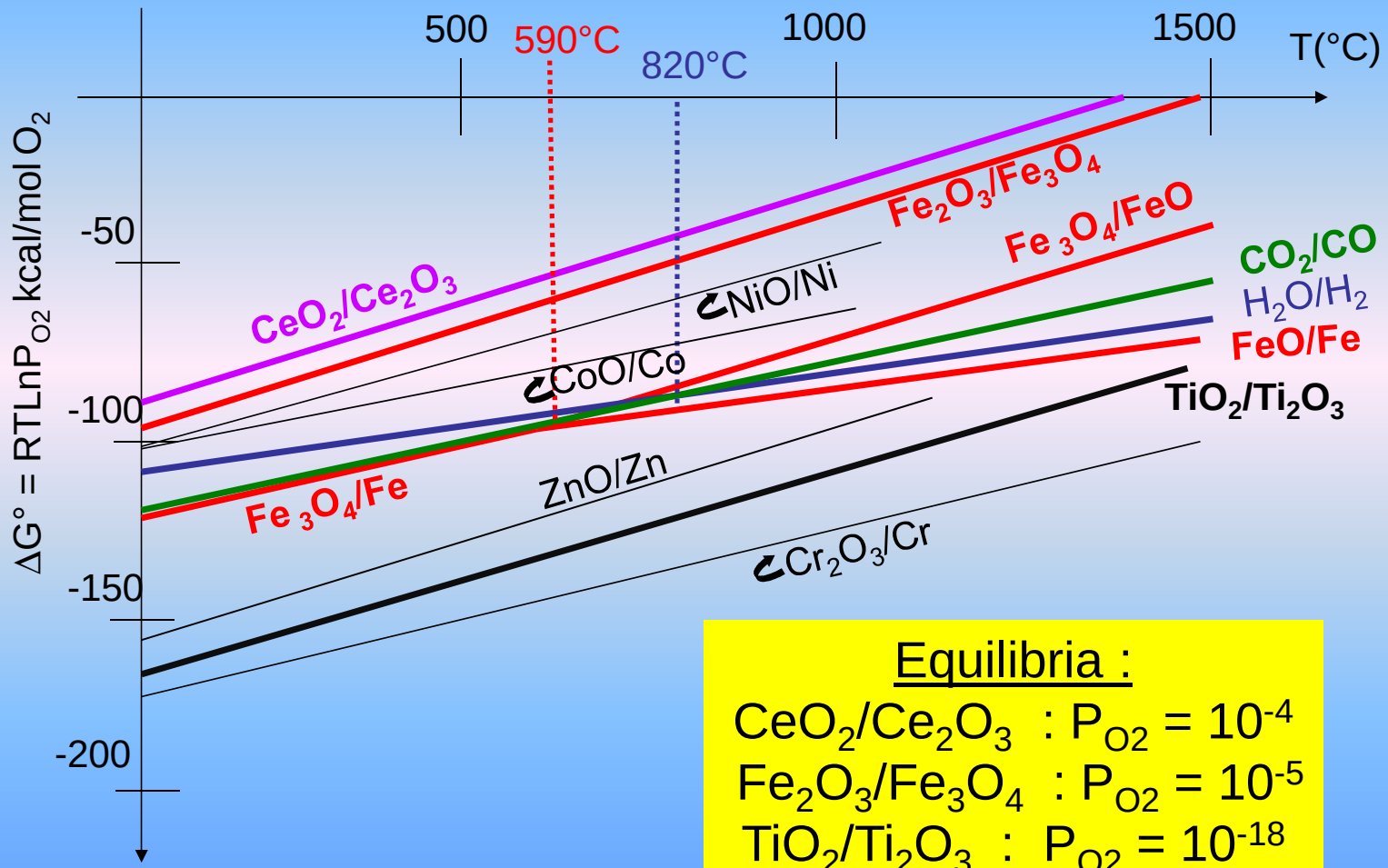
(0K) J = - 5 µB

Tc = 560 K

Ferri (Ferro) magnetic properties :
Tc ∝ -J/k x Z x 2/3 S(S+1)
: exchange integral, ***major*** $J_{Td\text{-}Oh} > J_{Oh\text{-}Oh}$,
Z : magnetic neighbors

Neel Theory and Goodenough-Kanamori rules

Ti/Fe/Ce oxides and CO_2/CO, H_2O/H_2 equilibria
Thermodynamics, Ellingham diagrams : $\Delta G° = RTLnP_{O2} = f(T)$



Equilibria :

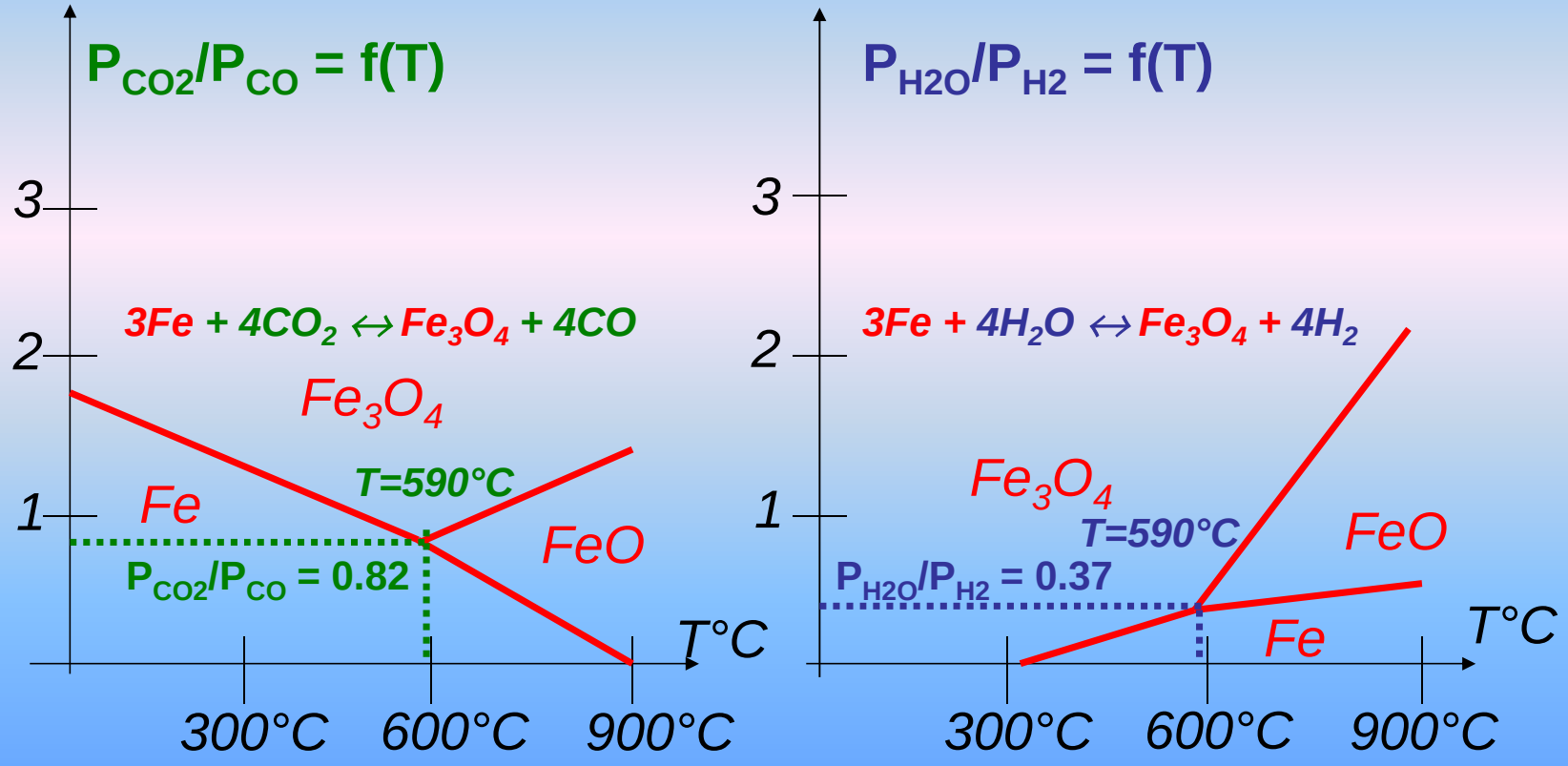
CeO_2/Ce_2O_3 : $P_{O2} = 10^{-4}$

Fe_2O_3/Fe_3O_4 : $P_{O2} = 10^{-5}$

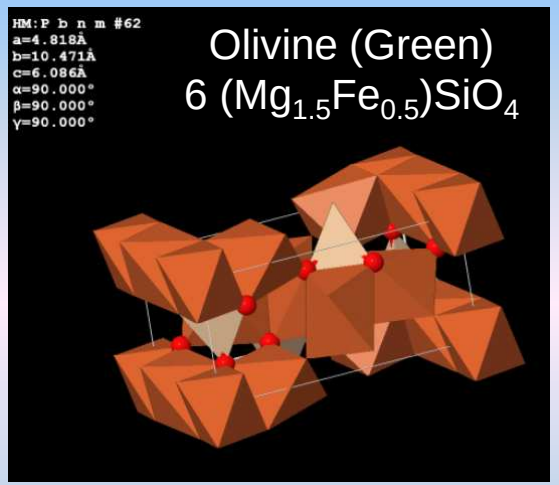
TiO_2/Ti_2O_3 : $P_{O2} = 10^{-18}$

Thermodynamics : reduction of CO_2 at T < 600°C involving metallic Fe and Fe oxides

$P_{CO2}/P_{CO} = f(T)$ and $P_{H2O}/P_{H2} = f(T)$ diagrams

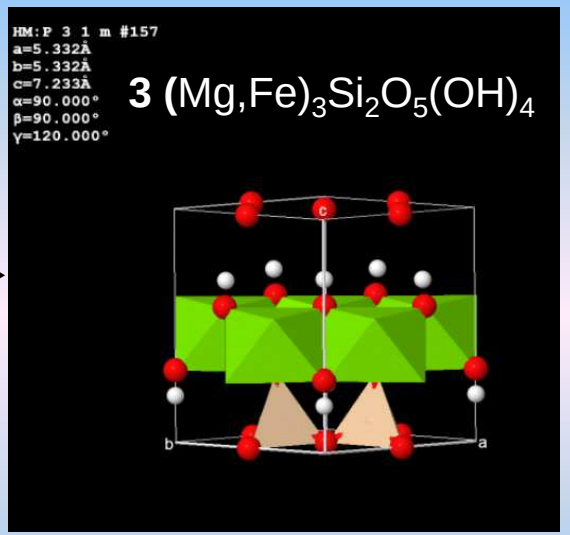


Olivine and Serpentine in deep ocean :
Fe^{2+} oxydation and production of magnetite Fe_3O_4 and hydrogen ($CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$)
(T>350°C, 200-400 bars)



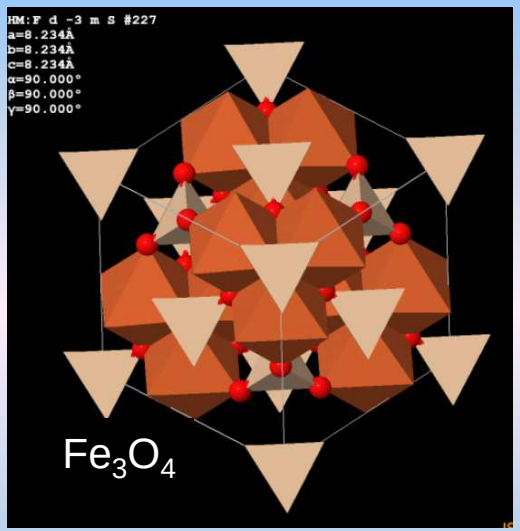
$V/ZX = 19.7\ A^3$

+ 7 H_2O →



$V/ZX = 19.8\ A^3$

(Serpentine)

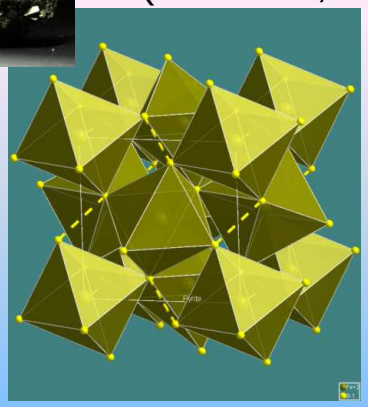


$V/ZX = 17.4\ A^3$

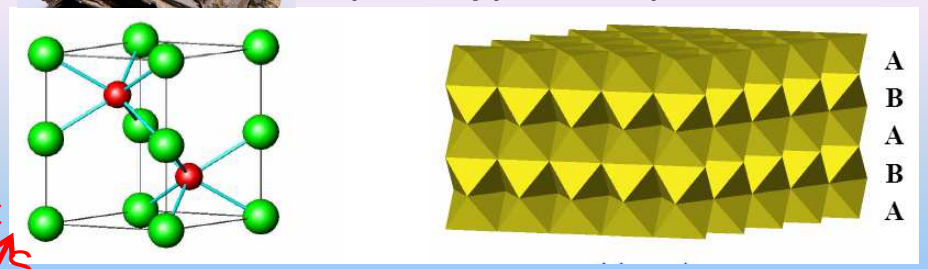
+ H_2

Geologically hydrothermal synthesis (T=400°C) of Pyrite FeS_2 and Pyrrothin FeS

FeS_2, Cubic, Pa-3
(Rocksalt, CCP)



$Fe_{1-x}S$, Hexagonal
(NiAs-type, HCP)

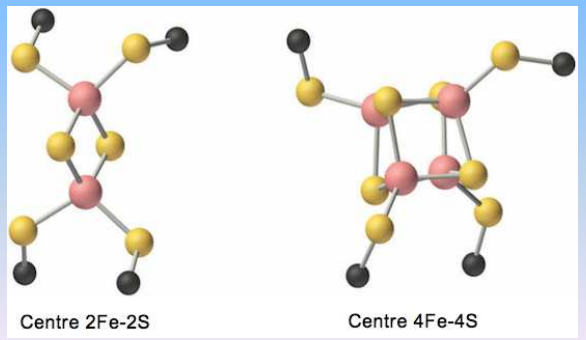


T=600°C
vacuum/S

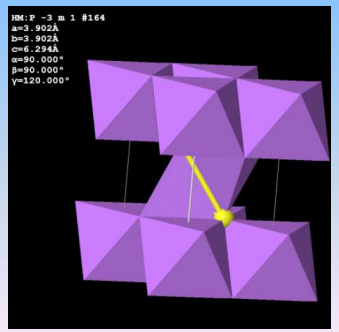
Pyrite FeS_2 (Fe^{2+}, S=0, $t_2^6e^0$, High Crystal Field)
Semi-Metal = e^- conductor

Pyrrhotine FeS (Fe^{2+}, S=2 ,$t_2^4e^2$, Low Crystal Field) = $Fe_{1-x}S$ (Fe^{2+}/Fe^{3+})
Ferrimagnetic (T<150°C)

Fe^{2+} in Td coordination $[FeS_4]$, Iron-Sulphur proteins and clusters $[Fe_nS_n]$: Redox process (ferredoxine $[Fe_4S_4]$) in mitochondria : cellular respiration !

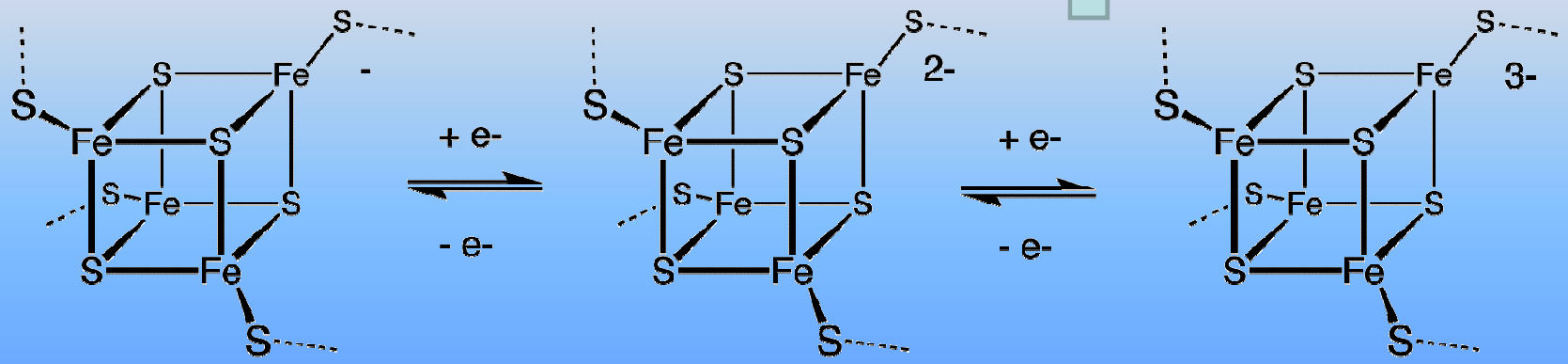


Li_2FeS_2 (Fe^{2+}) – $Li_{2-x}FeS_2$ (Fe^{2+},Fe^{3+}) : batterie Li



IMN (Nantes)
R. Brec, J. Rouxel

$2H^+ + 2\ e^- + ½\ O_2 \rightarrow H_2O\ (H^+)$: Mitochondria

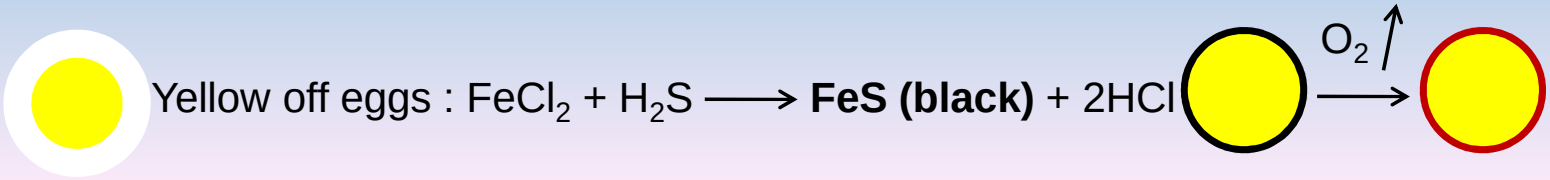


$[Fe^{2+}_3Fe^{3+}_1S^{2-}_4]^+$ $[Fe^{2+}_2Fe^{3+}_2S^{2-}_4]^{2+}$ $[Fe^{2+}_1Fe^{3+}_3S^{2-}_4]^{3+}$

Natural synthesis of pyrite and pyrrothin

Oxidation of pyrite FeS_2
and pyrrhotin FeS (under air at T=300°C)

$$2\ FeS\ (black) + 7/2\ O_2 \longrightarrow Fe_2O_3\ (red\ cinnabar) + 2SO_2$$



$$(in\ solution)\ 3Fe^{2+} + 7S^0 + 4H_2O \longrightarrow 3\mathbf{FeS_2} + SO_4^{2-} + 8H^+$$

Synthesis of pyrite FeS_2 at low temperature (N_2, glove box) :

$$FeCl_3 + 2NaHS \longrightarrow \mathbf{FeS_2} + 2NaCl + HCl + ½\ H_2$$

Stabilization of various anions around Fe !
To tune the redox/electronic/magnetic properties…

Thin Films and electronic/magnetic properties
‘$Fe^{2+}_{0.3}Fe^{3+}_{0.7}O_{0.35}N_{0.65}$’

M. Grafouté, J.M. Grenèche et al.
J. Phys: Condens. Matter 19 (2007) 226207

^{7}N
Pauling : 3.0
[He] $2s^2 2p^3$

^{8}O
Pauling : 3.5
[He] $2s^2 2p^4$

Na Battery
$NaFe^{2+}OF$
$Fe^{3+}OF$

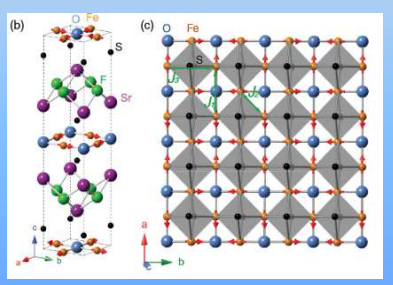
J. Zhu and D. Deng
Angew. Chem,
54 (2015), 3079

^{9}F
Pauling : 4.0
[He] $2s^2 2p^5$

^{26}Fe
Pauling : 1.8
[Ar] $4s^2 3d^6$

2D electronic/magnetic properties
$Sr_2F_2Fe^{2+}_2OS_2$

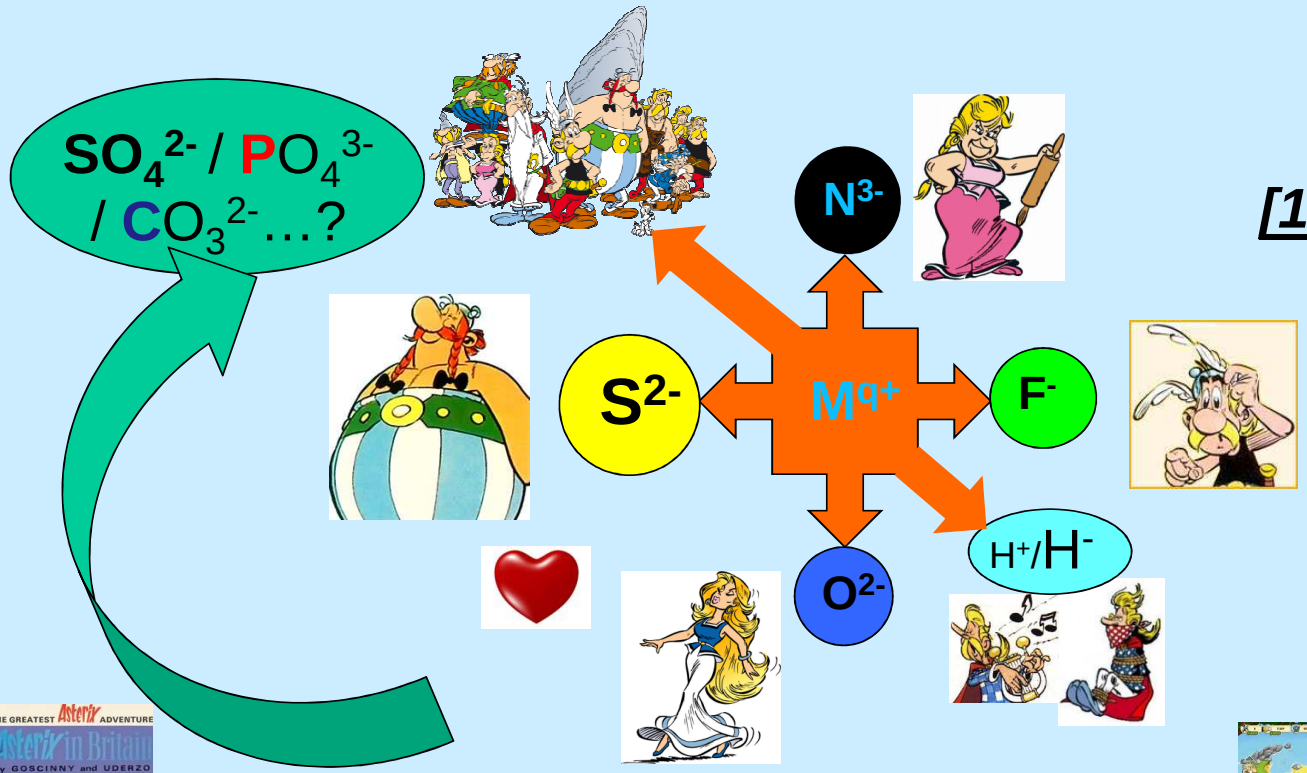
^{16}S
Pauling : 2.6
[Ne] $3s^2 3p^4$



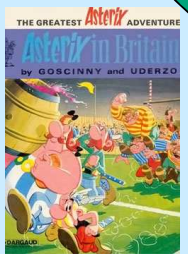
H. Kabbour, L. Cario et al.
J.A.C.S, 130 (2008) 8261

The M-X chemical bonding and the effect of mixed anions

M^{q+} : Partial density of charges and oxydation states
Point group (M^{q+} / X^{p-}), anisotropy and networks
Crystal field, Polarization, Covalency



Wednesday, the 7th ***[10:30-11:30]*** of february…



A way to tune the ionicity-covalency of the chemical bonding and consequently the electronic properties !