



UNIVERSITÉ DE NANTES

**INSTITUT DES MATERIAUX JEAN ROUXEL**  
**IMN UMR CNRS 6502 - Université de Nantes**



# Grandes classes de composés à propriétés électroniques remarquables

Des composés connus  
à la recherche de nouveaux composés.

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Ecole MICO  
Grenoble 29 Mai 2014

# *Plan*

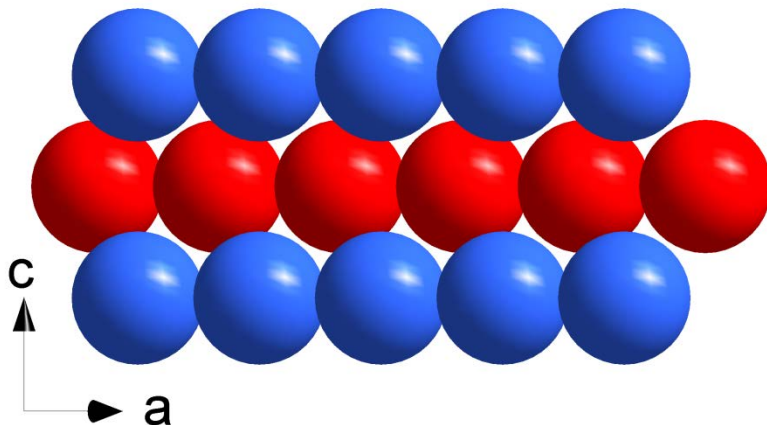
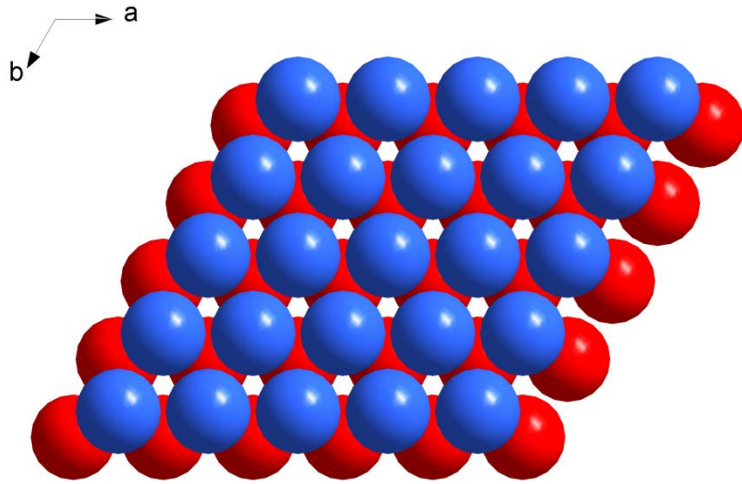
## **Partie 1 : Structures et propriétés des grandes classes de composés connus**

- 1. principaux types structuraux**
- 2. Oxydes de métaux de transition**
- 3. Chalcogénures de métaux de transition**

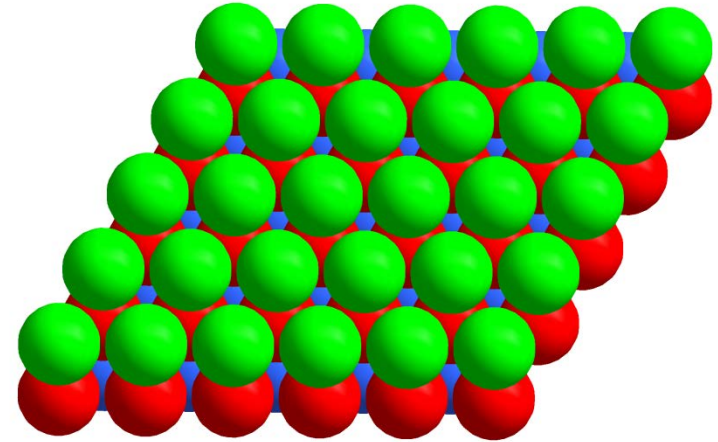
## **Partie 2 : Recherche de nouveaux composés inorganiques**

- 1. Synthèse et recherche exploratoire de nouveaux composés**
- 2. Outils de rationalisation en chimie inorganique**
- 3. Conception raisonnée de nouveaux composés inorganiques**

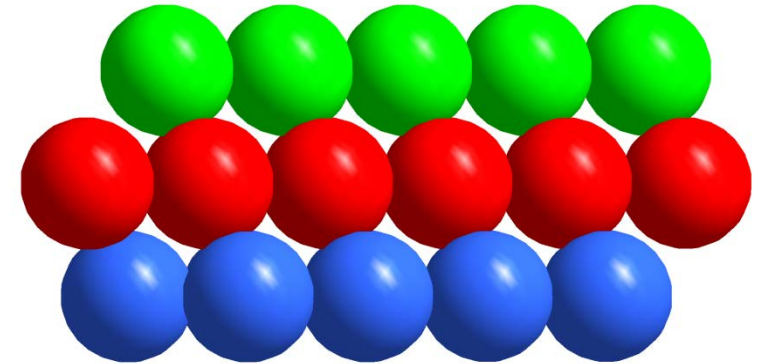
# *La nature à horreur du vide : empilements compacts*



Hexagonal Compact (HC)  
ABAB....

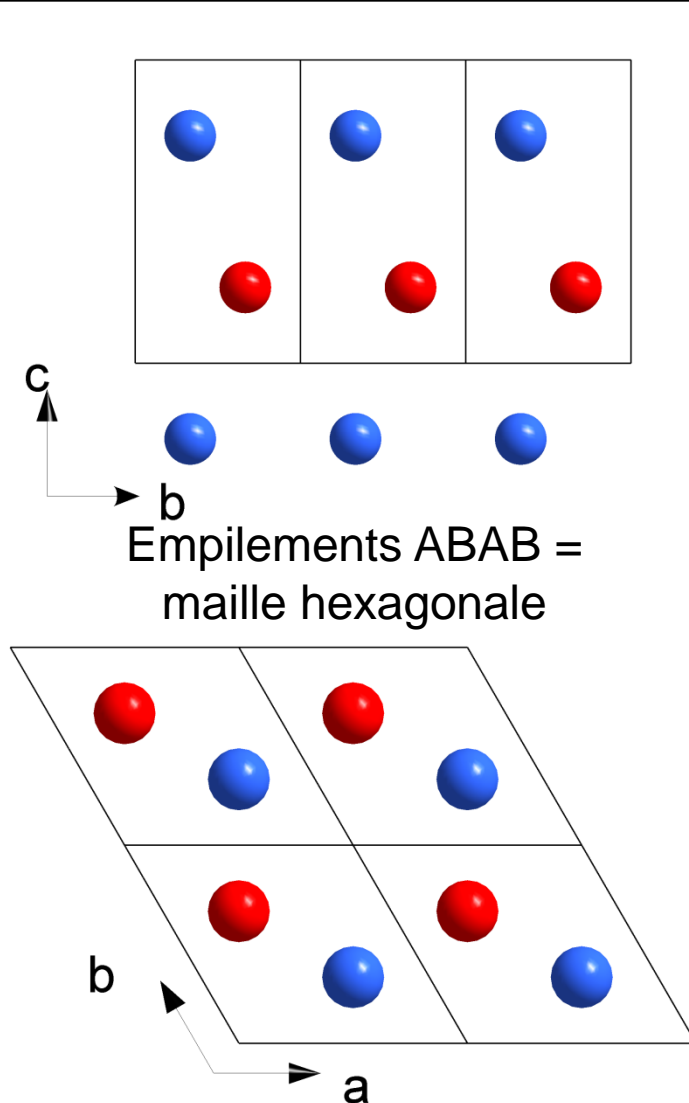


A C  
B  
A

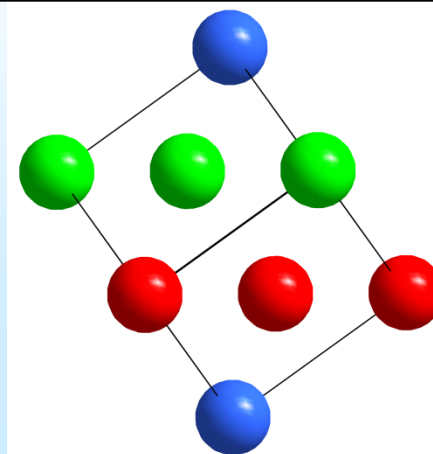


Cubique Faces Centrées (CFC)  
ABCABC....

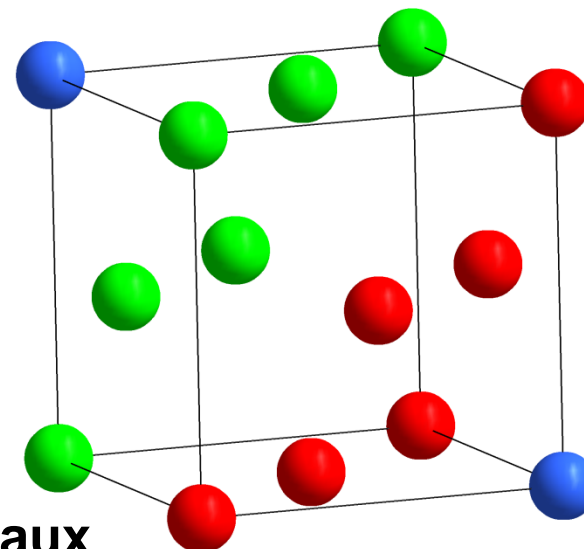
# La nature à horreur du vide : empilements compacts



Structure des métaux

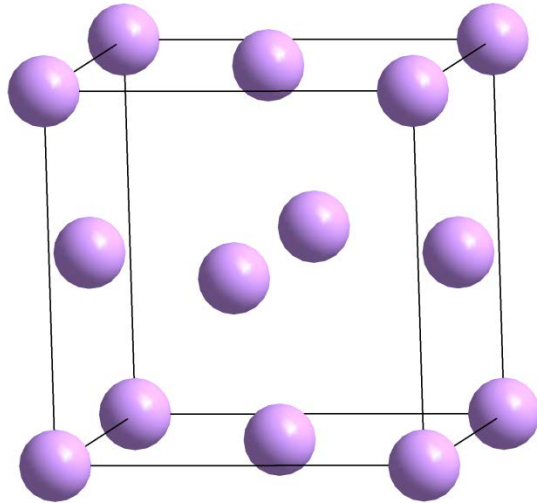
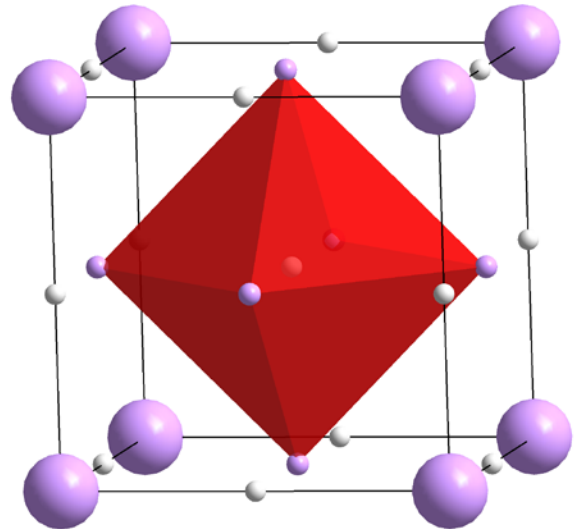
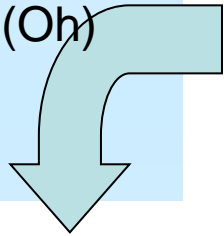


Empilements ABCABC =  
maille cubique face centrée



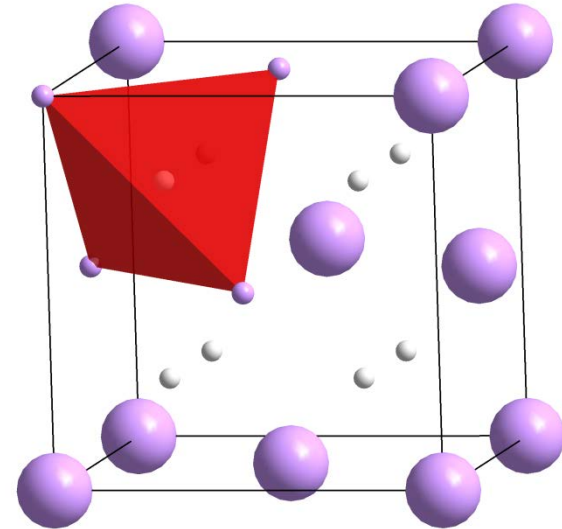
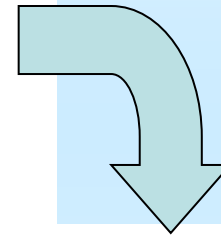
# Structures simples : remplissage des empilements CFC et HC

4 sites  
octaédriques (Oh)  
vides / maille

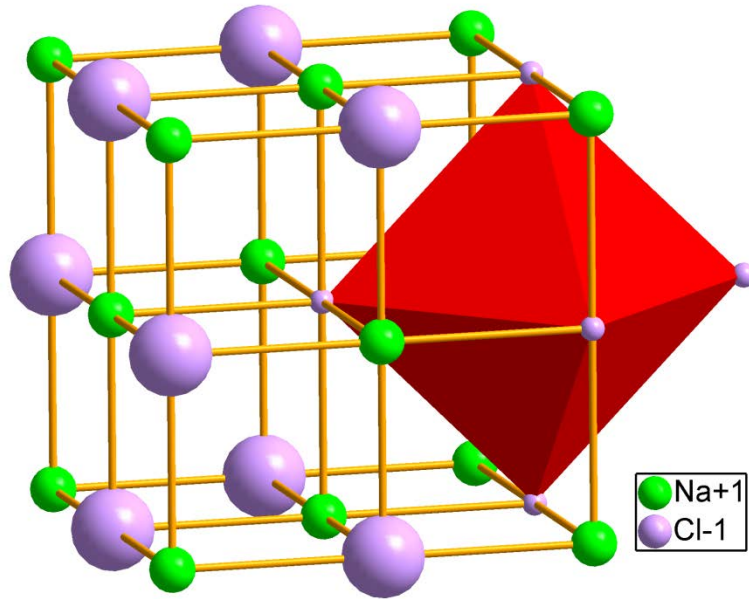


Empilement  
Cubique Faces Centrées  
CFC 4 atomes / maille

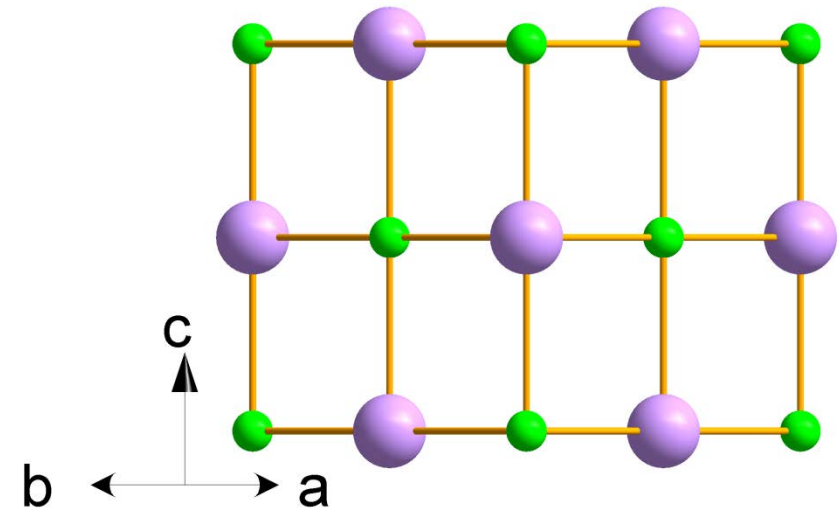
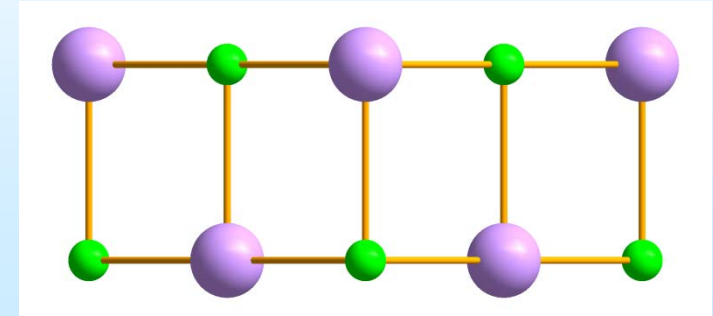
8 sites  
tétraédriques (Td)  
vides / maille



# Structure type NaCl : remplissage de tous les sites octaédriques



Structure  
des oxydes d'alcalino terreux AeO  
Ae= Mg, Ca, Sr, Ba  
Des oxydes d'éléments de transition MO  
M= Mn , Fe, Co, Ni  
Des sulfures de terres rares LnS  
Ln = La, Ce ...

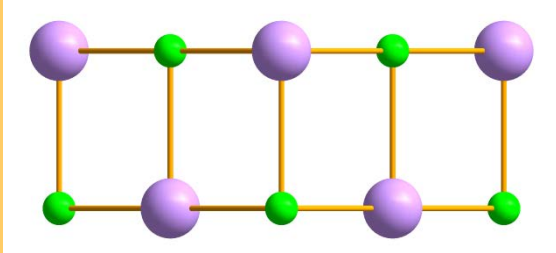


Projection selon 110



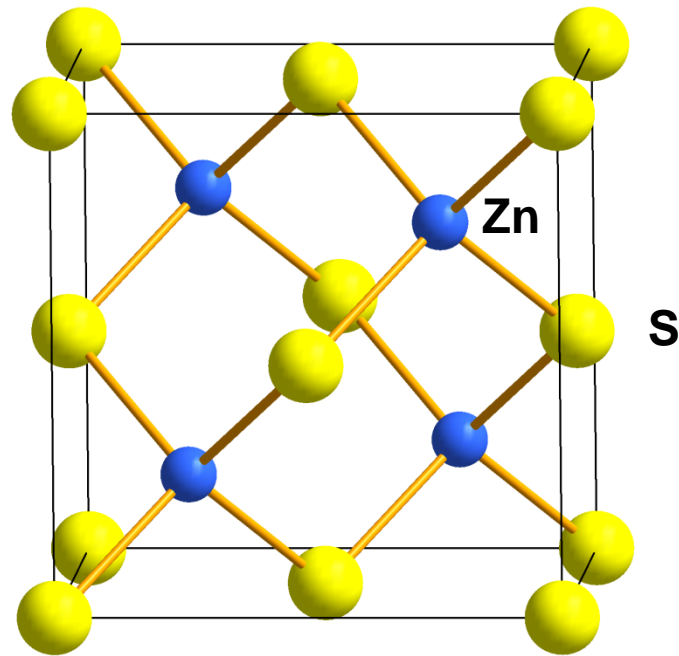
**CFC**

**NaCl**

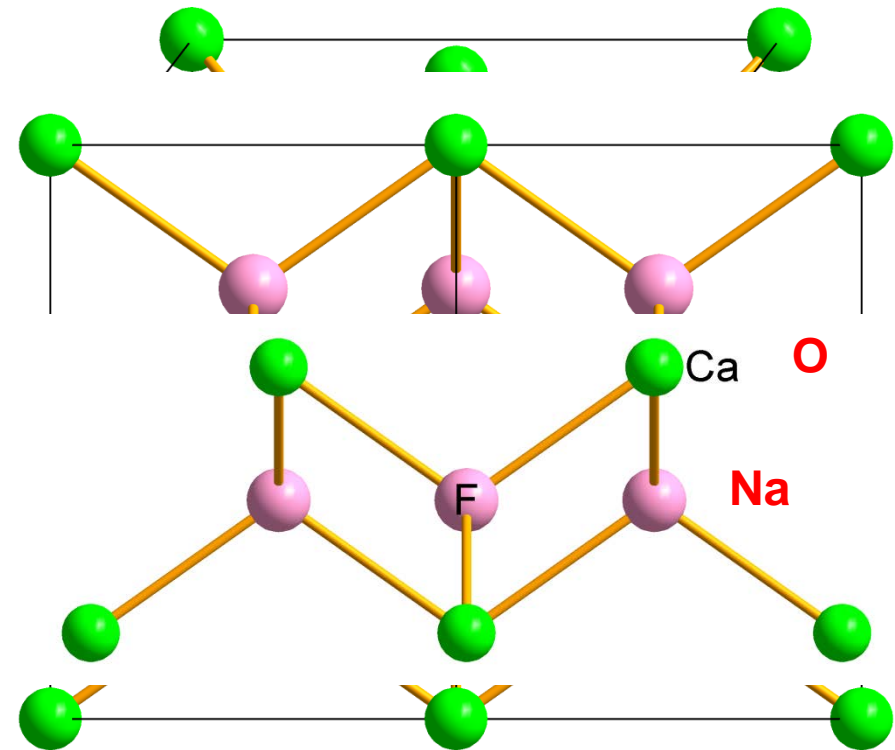


# Remplissage des sites Tétraédriques

Un site tétraédrique sur deux :  
Structure type ZnS sphalérite



Tous les sites tétraédriques :  
Structure type fluorine  $\text{CaF}_2$  et  
anti fluorine  $\text{Na}_2\text{O}$

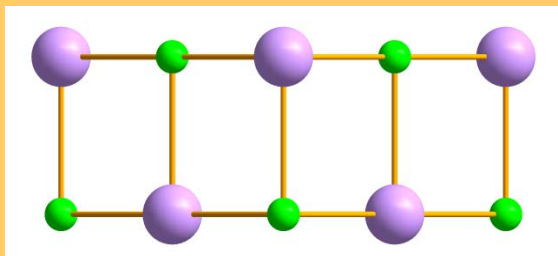




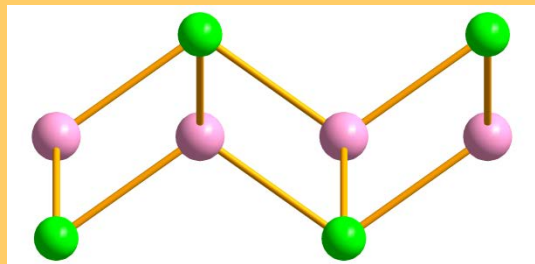


**CFC**

**NaCl**

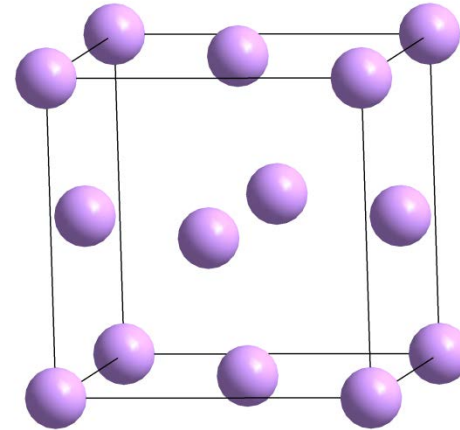
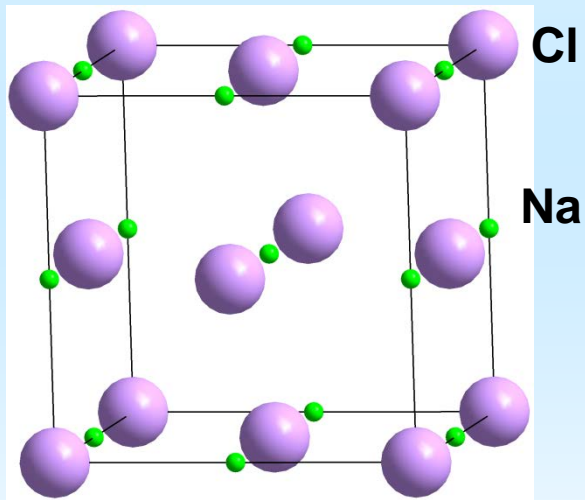


**Fluorine**

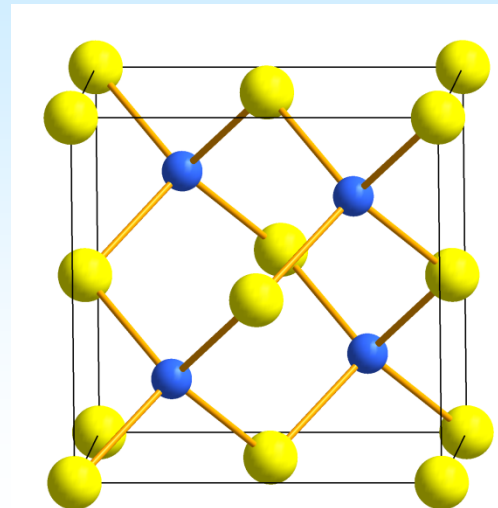


# Types structuraux dérivant du CFC

NaCl :  
tous les sites Oh

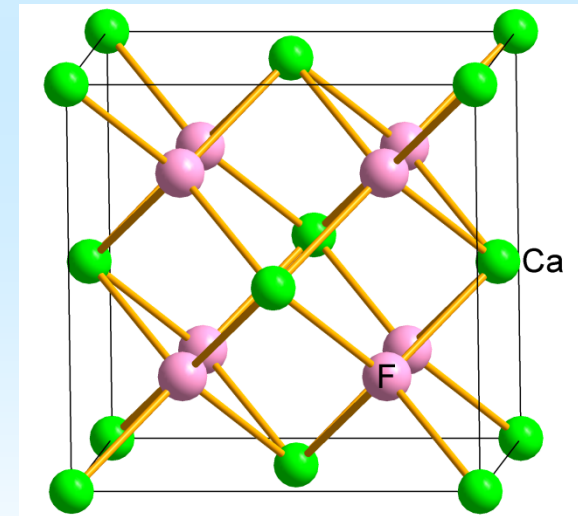


ZnS :  
1/2 des sites Td

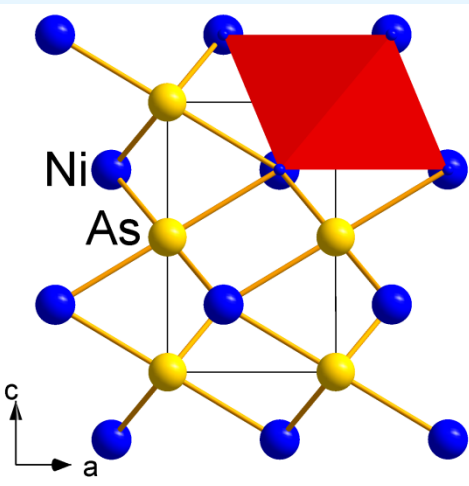


CFC

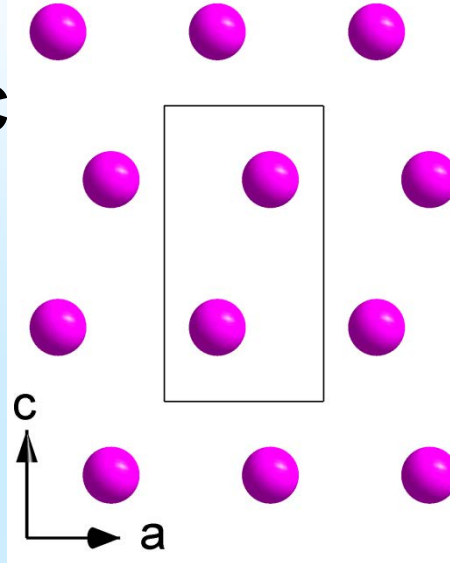
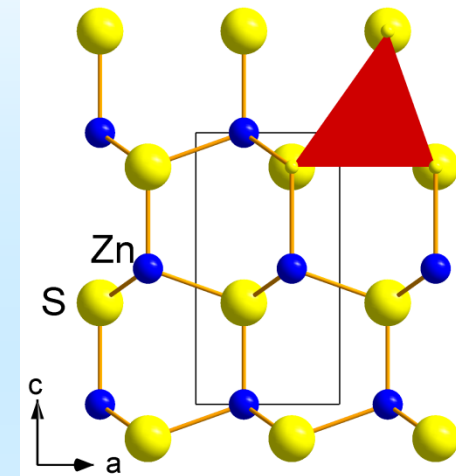
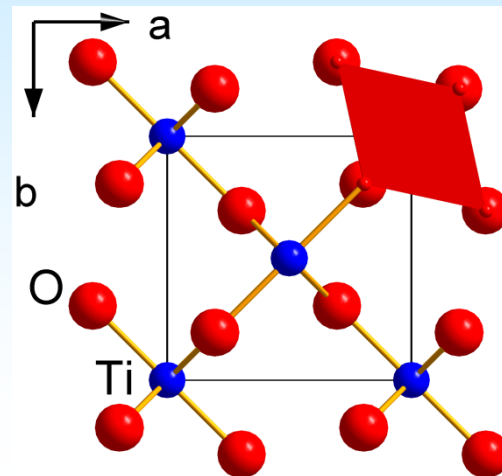
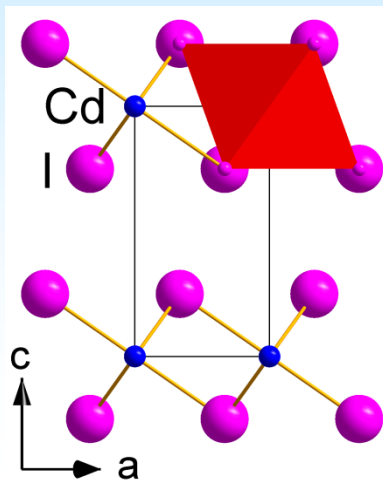
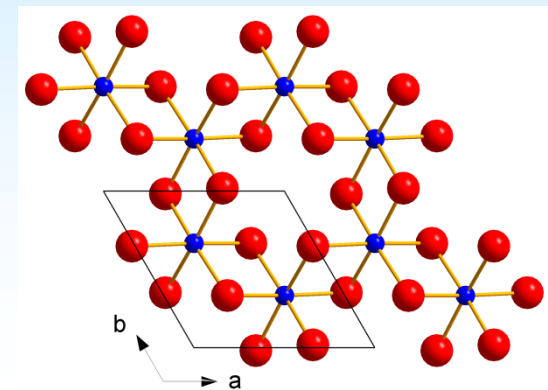
CaF<sub>2</sub> et Na<sub>2</sub>O :  
tous les sites Td



## Types structuraux dérivant du HC

NiAs :  
tous les sites Oh

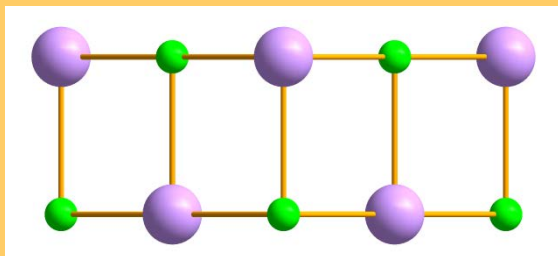
HC

ZnS Wurtzite:  
 $\frac{1}{2}$  des sites TdCdI<sub>2</sub> et TiO<sub>2</sub>:  $\frac{1}{2}$  des sites OhAl<sub>2</sub>O<sub>3</sub> Corindon :  $\frac{2}{3}$   
des sites Oh

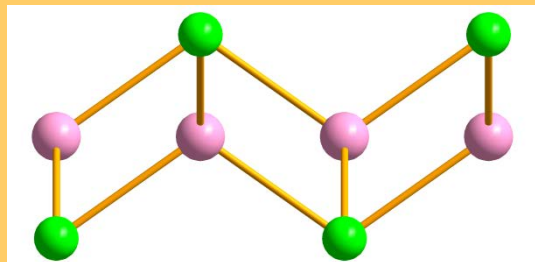


**CFC**

**NaCl**

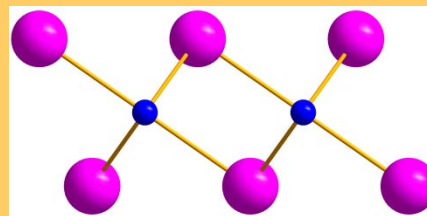


**Fluorine**



**HC**

**CdI<sub>2</sub>**



# Rationalisation des types structuraux : Degrés d'oxydation et composition

Le degré d'oxydation (D.O.), caractérise l'état électronique d'une espèce chimique par rapport à l'état élémentaire neutre servant de référence (D.O. = 0).

D.O.  
+1 +2

D.O.  
-2 -1

hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
		D.O. +2 à +6																					
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
cesium 55 Cs 132.91	barium 56 Ba 137.33	lanthanum 57 La 138.91	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]						
francium 87 Fr [223]	radium 88 Ra [226]	actinium 89 Ac [227]	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununium 110 Uun [271]	ununium 111 Uuu [272]	ununium 112 Uub [277]	ununquadium 114 Uuq [289]										

Ni<sup>2+</sup>O<sup>2-</sup>  
structure MX 1:1  
NaCl

Ti<sup>4+</sup>(O<sup>2-</sup>)<sub>2</sub>  
structure MX<sub>2</sub> 1:2  
Rutile

\* Lanthanide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
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\*\* Actinide series

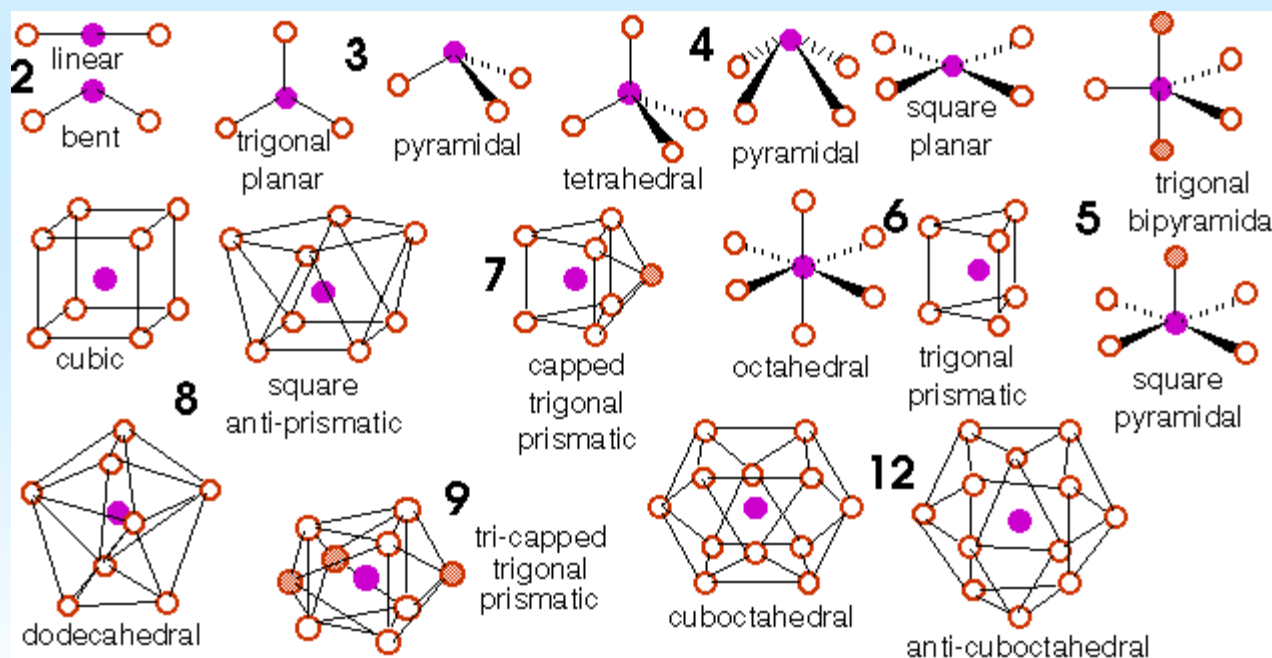
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]
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Pour un composé donné la somme des D.O. est nulle → fixe la composition  
→ impact sur la structure

# Rationalisation des types structuraux :

## Rayons ioniques et principaux polyèdres de coordination

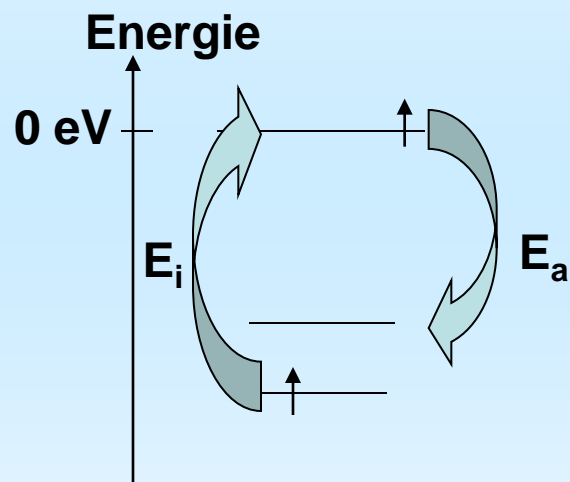
### Petits rayons ioniques Métaux de transition



**Gros rayons ioniques**  
**Terres Rares, métaux alcalino terreux**

# Rationalisation des types structuraux : électronégativité et diagrammes de structure

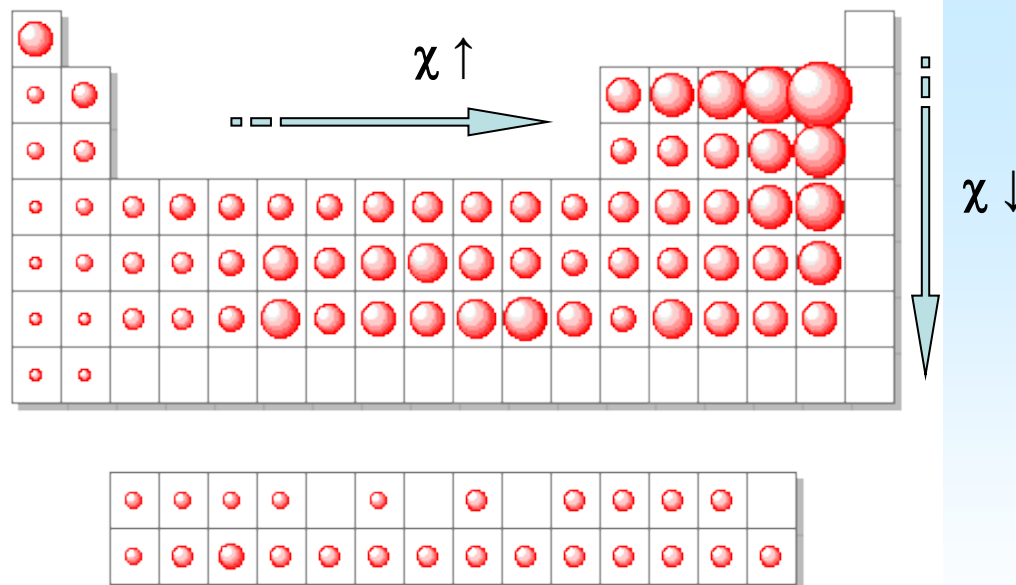
L'électronégativité est une grandeur relative qui traduit la plus ou moins grande aptitude d'un atome à attirer les électrons de la liaison chimique qui le lie à un autre atome



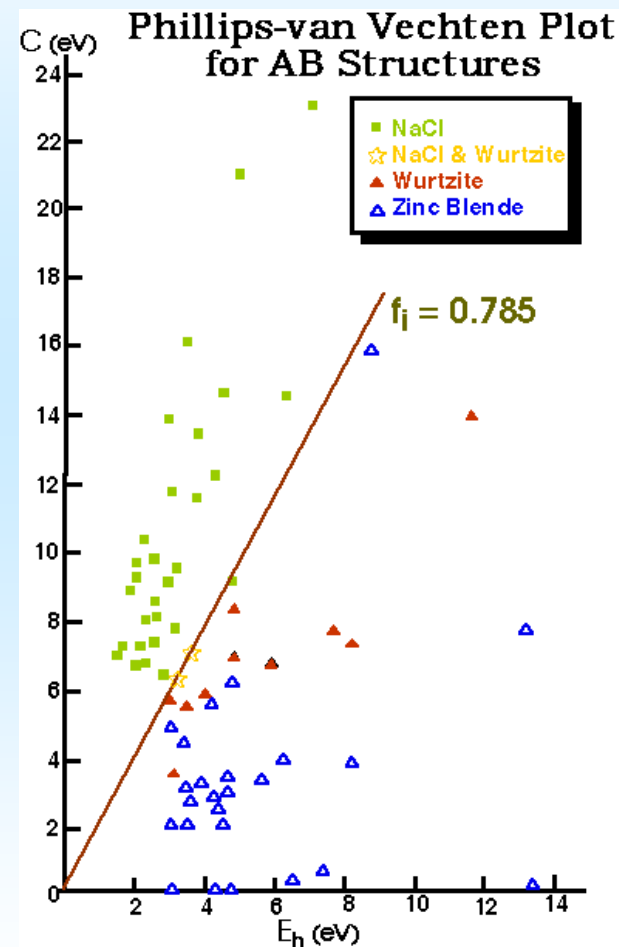
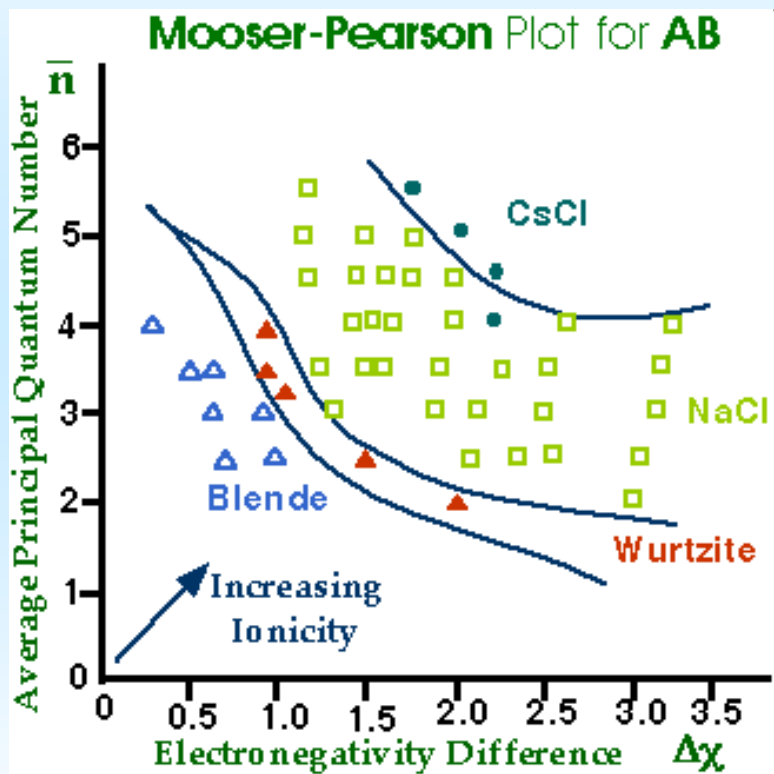
$$\chi(A) = \frac{1}{2} (E_i(A) + E_a(A))$$

**Définition de Mulliken**

Electronegativités (Pauling) représentées selon la taille de sphères



# Rationalisation des types structuraux : électronégativité et diagrammes de structure



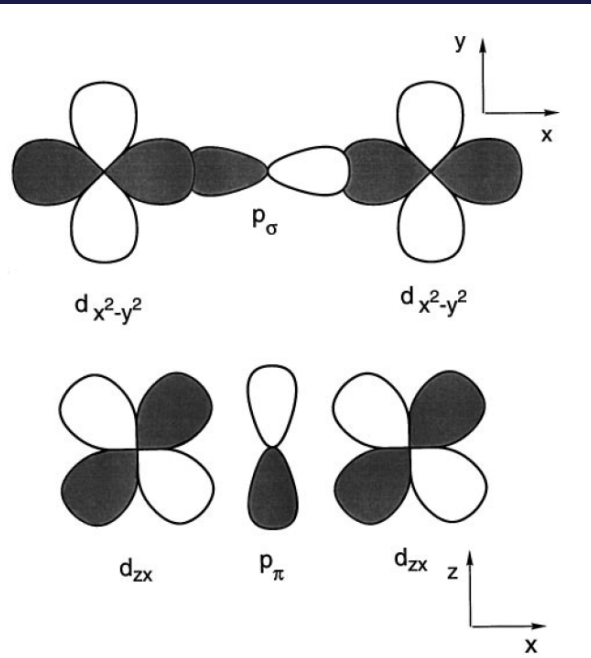
HH et AB  
Isoélect.

$$E_g(AB) = E_h(HH) + iC$$

Le type structural adopté dépend du rapport des rayons ioniques  
et de la différence d'électronégativité

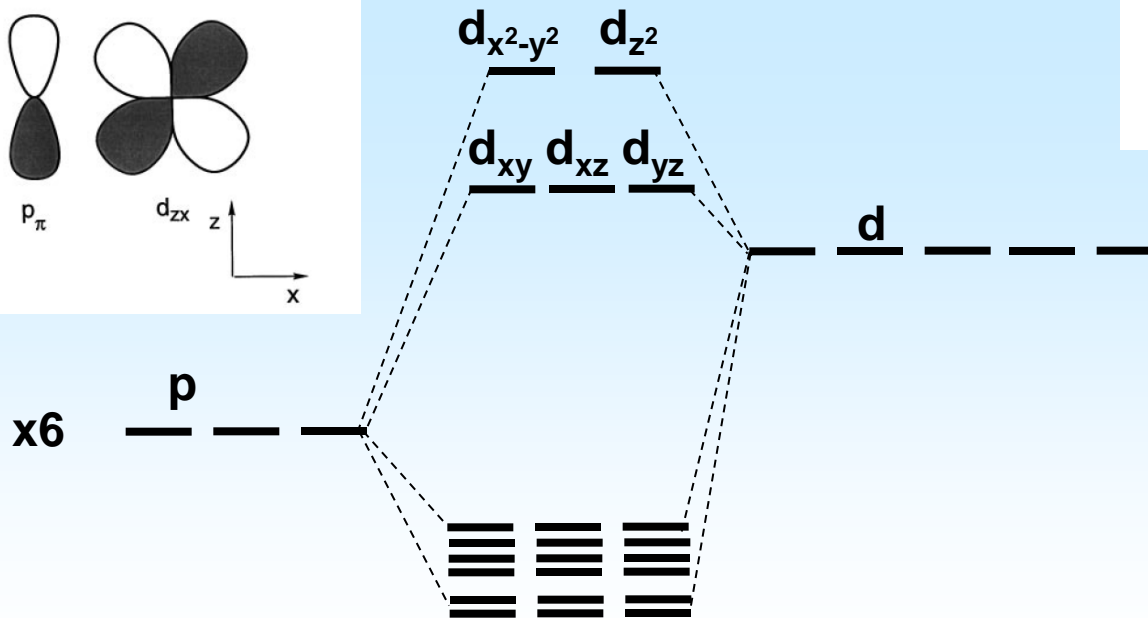
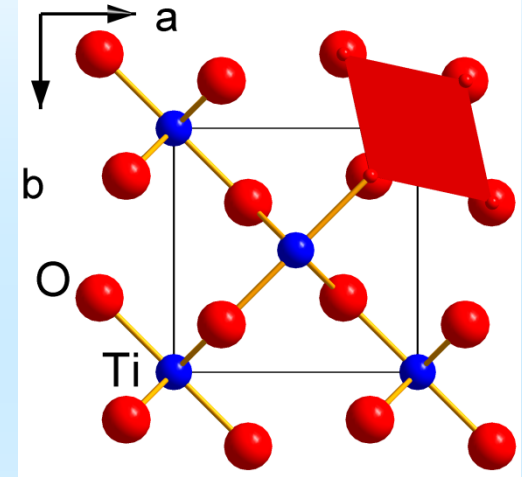


# Oxydes binaires : relation structure – structure de bandes - propriétés

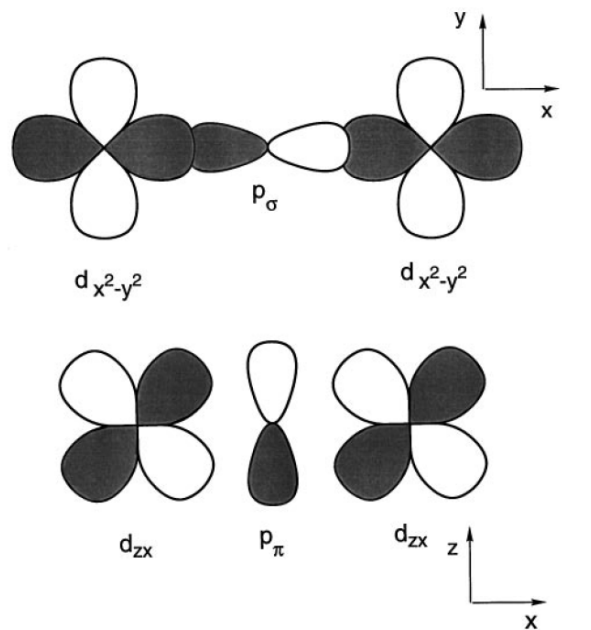


## $\text{TiO}_2$ Structure Rutile

$\text{Ti}^{4+}(\text{O}^{2-})_2$  donc  $d^0$



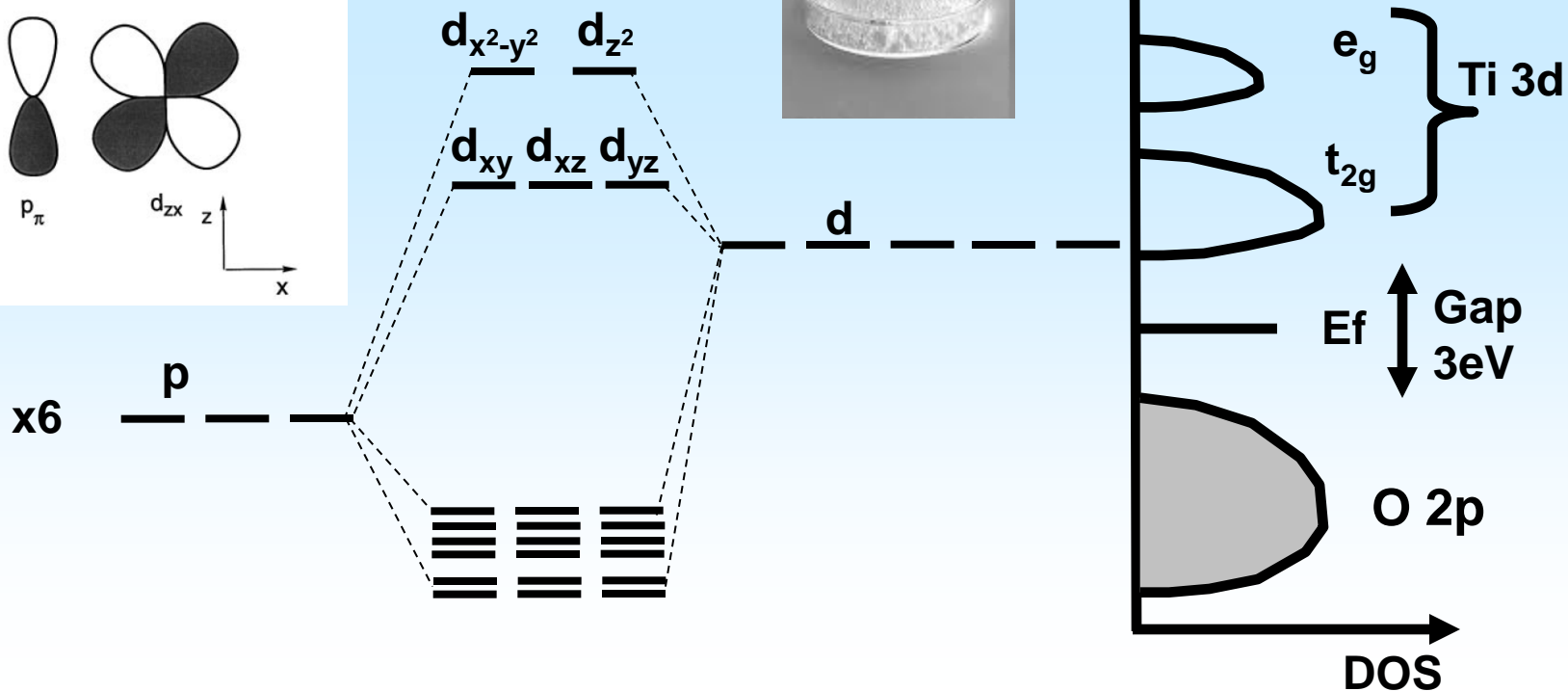
# Oxydes binaires : relation structure – structure de bandes - propriétés



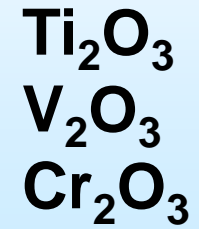
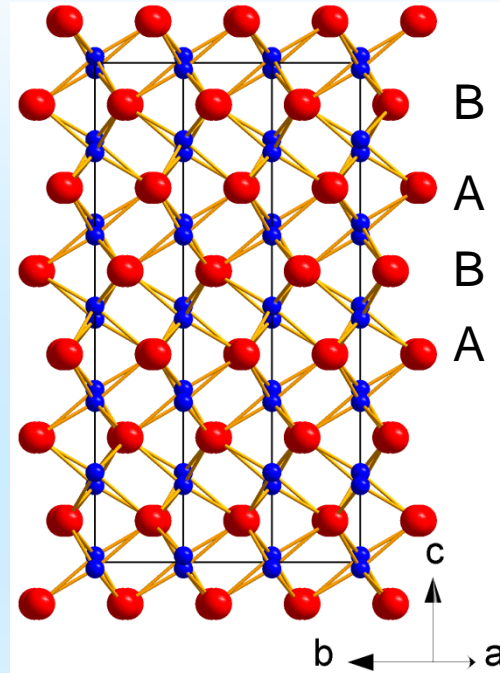
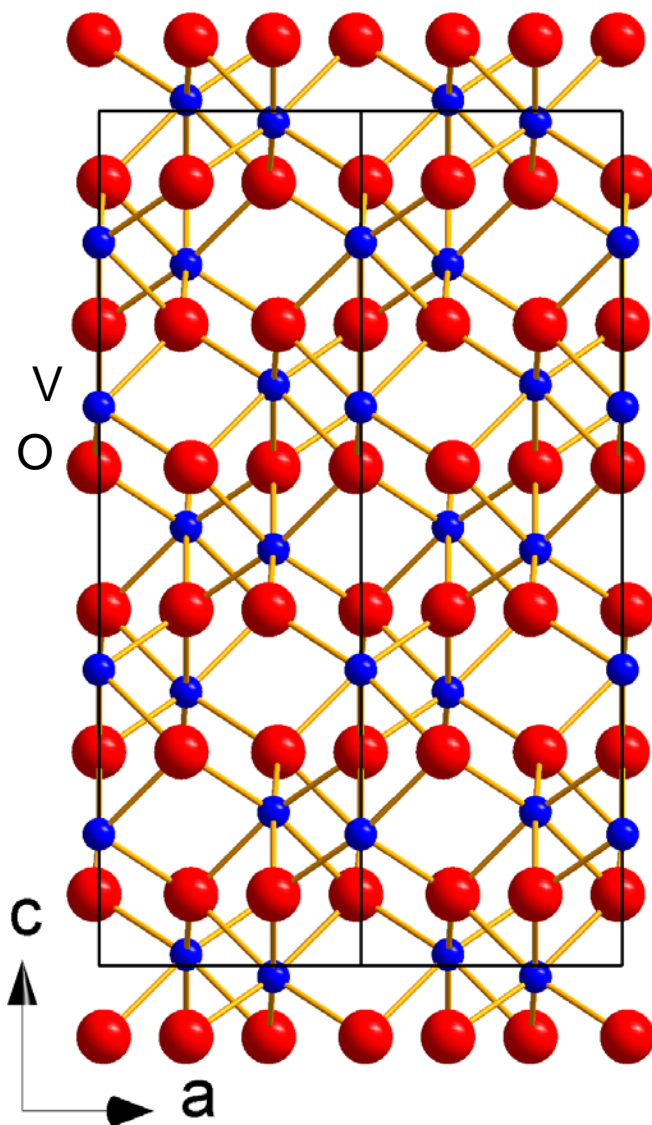
## $\text{TiO}_2$ Structure Rutile

$\text{Ti}^{4+}(\text{O}^{2-})_2$  donc  $d^0$

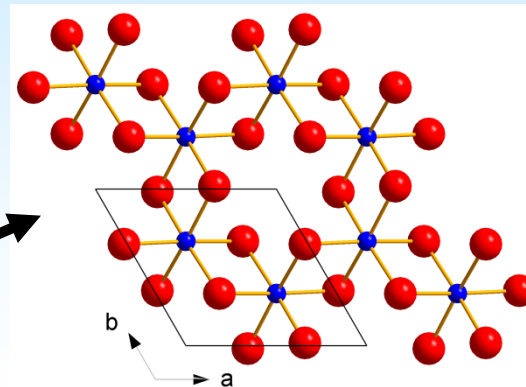
Isolant de bande  
Transparent dans le visible



# Les oxydes à structure corindon $M_2O_3$

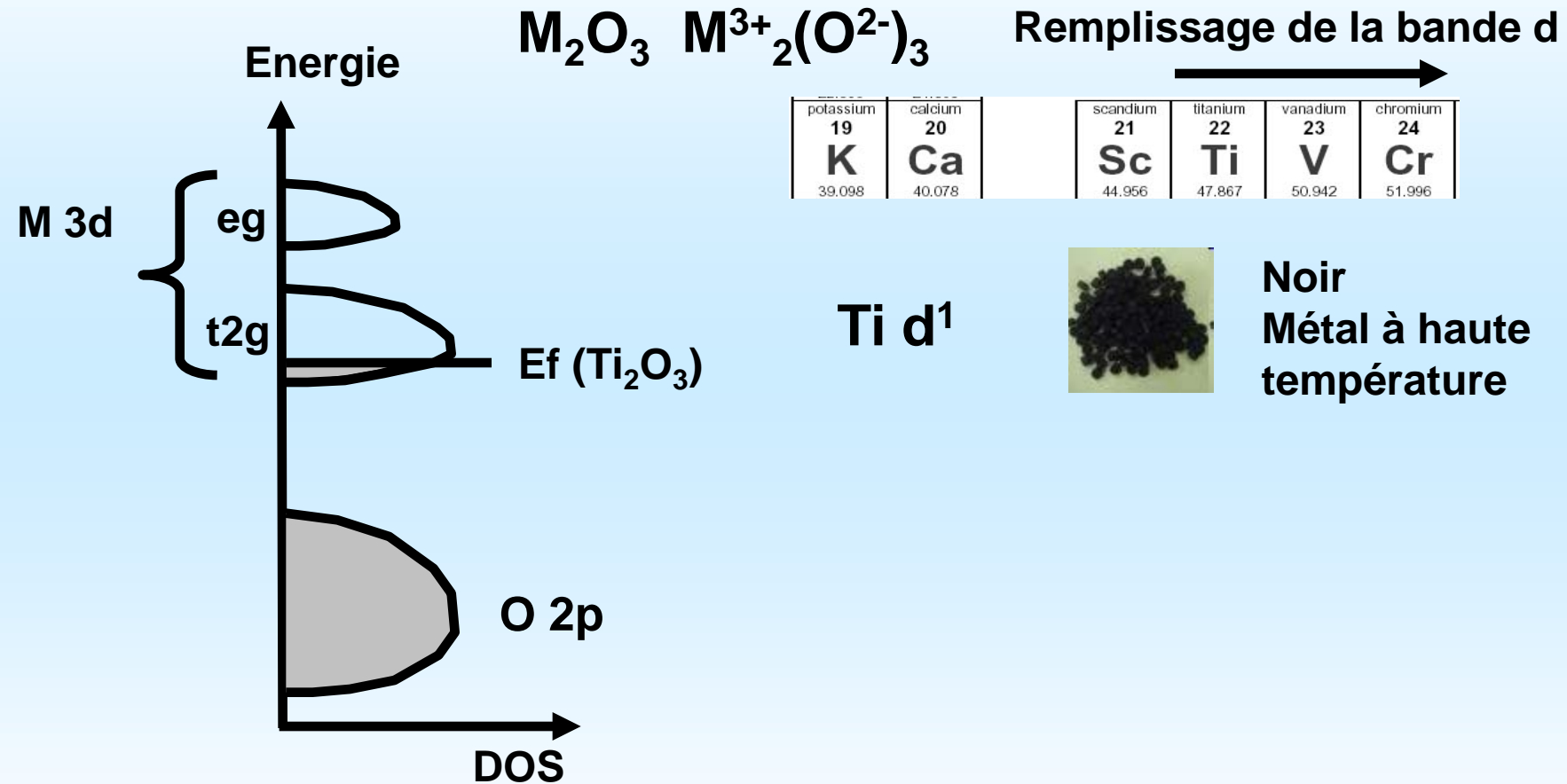


Projection  
selon  $-2 -1 0$

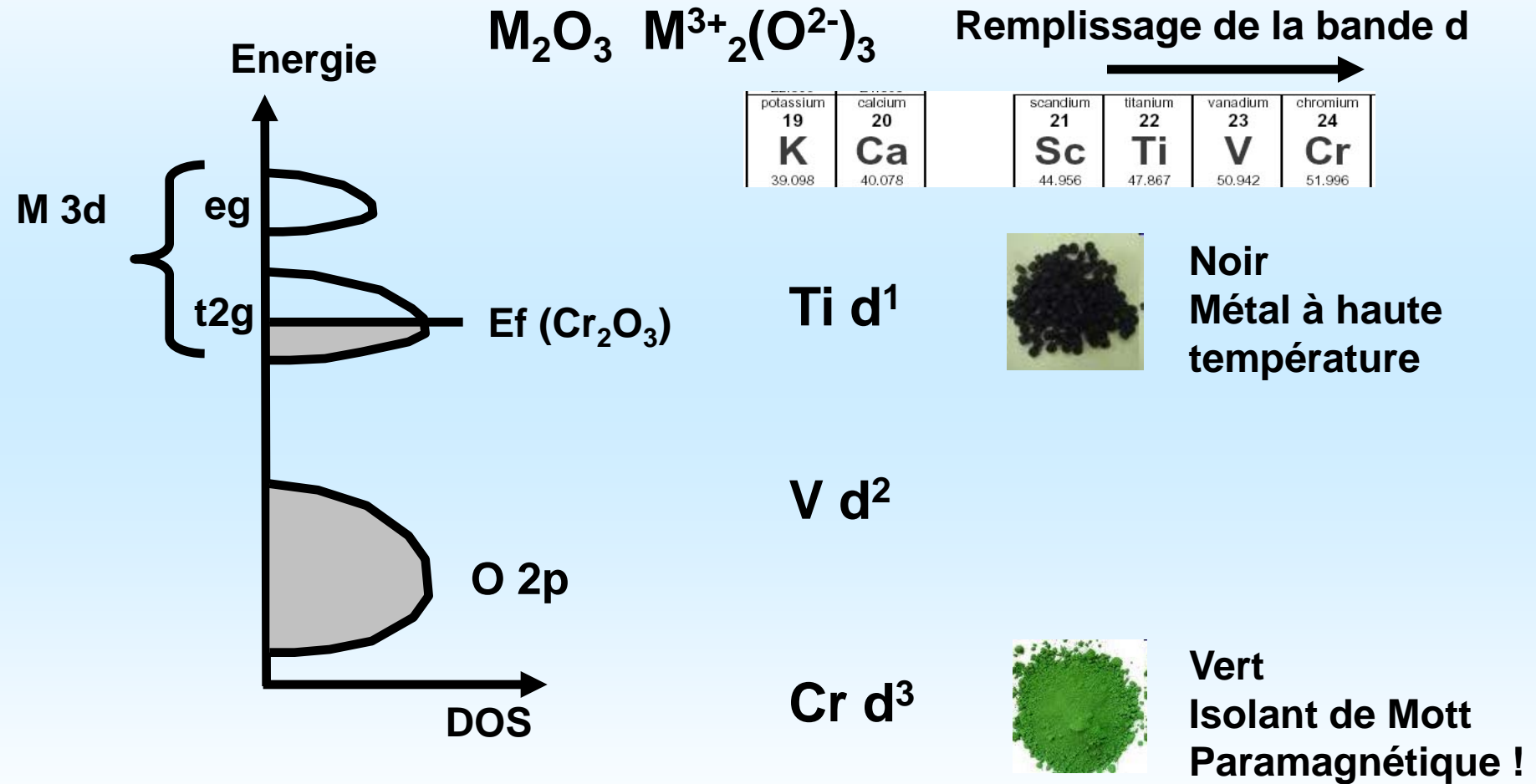


Projection  
selon  $0 0 -1$

# Les oxydes à structure corindon $M_2O_3$

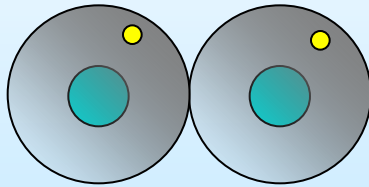


# Les oxydes à structure corindon $M_2O_3$

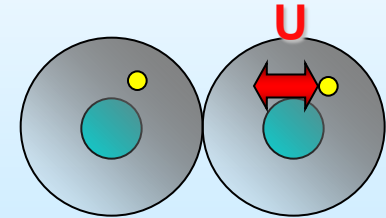
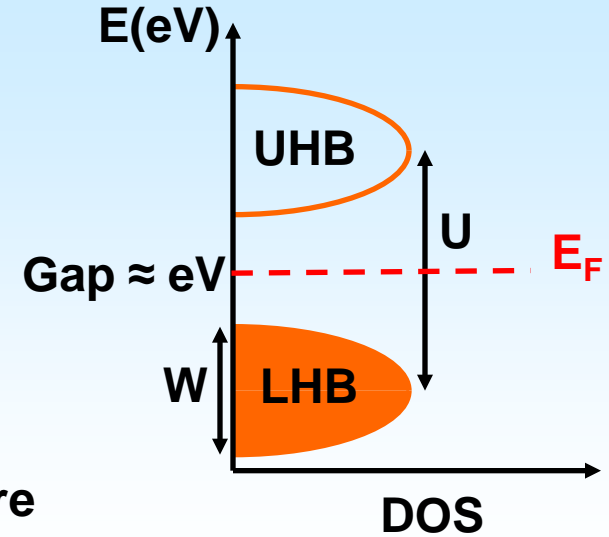
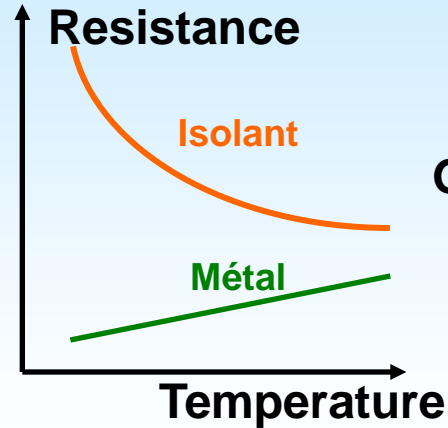
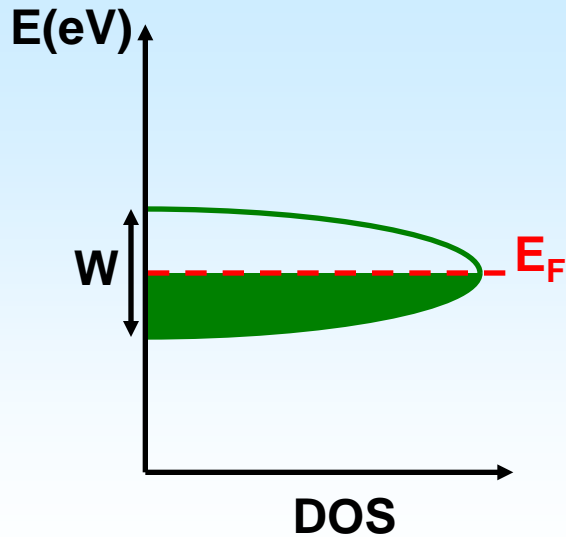


# Isolant de Mott : définition

## Métal

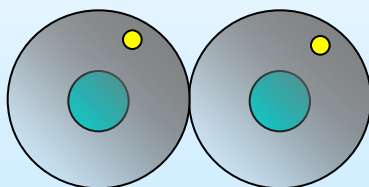

 $U \ll W$ 

## Isolant de Mott


 $U \gg W$ 


# Isolant de Mott : définition

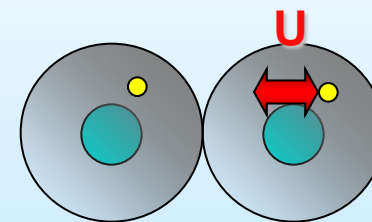
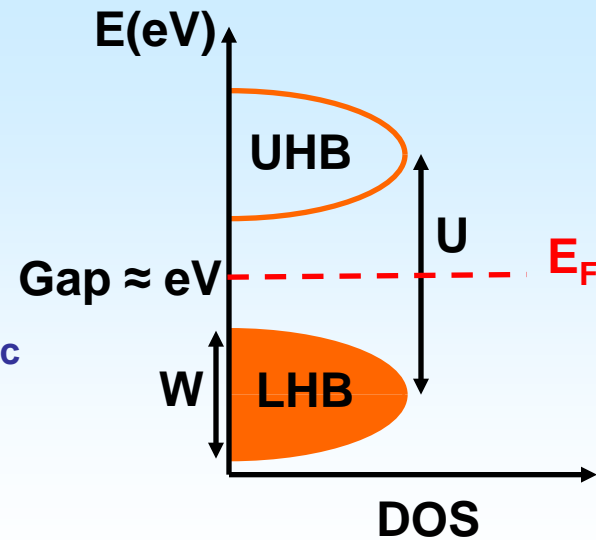
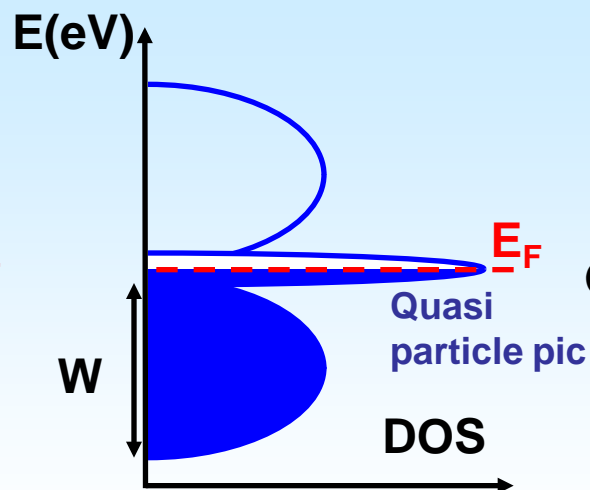
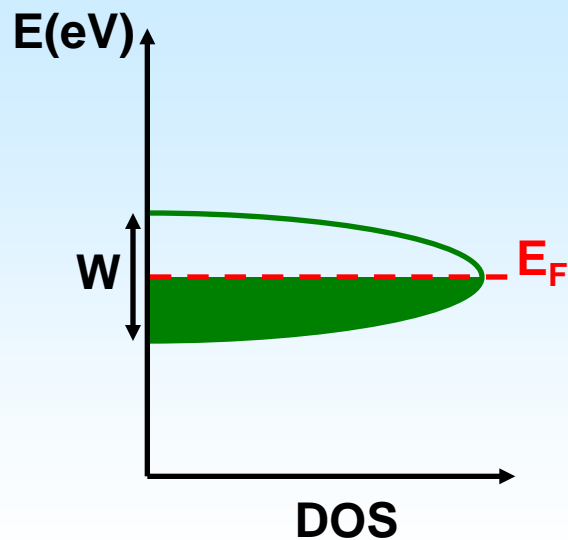
## Métal


 $U \ll W$ 

## Métal Corrélé

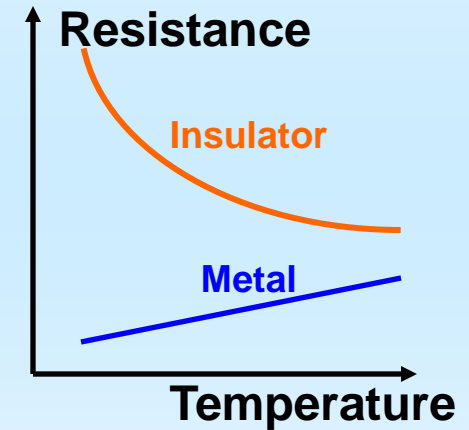
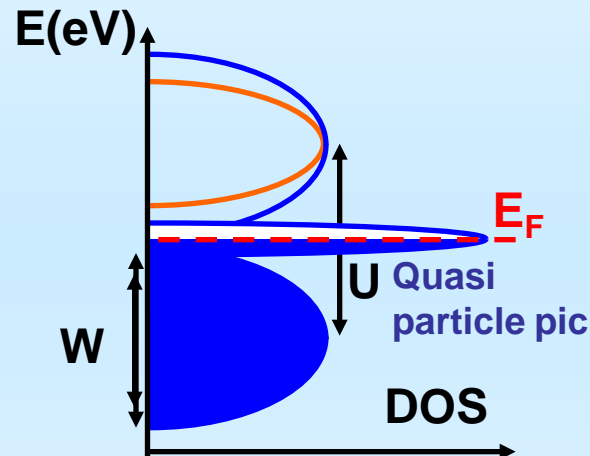
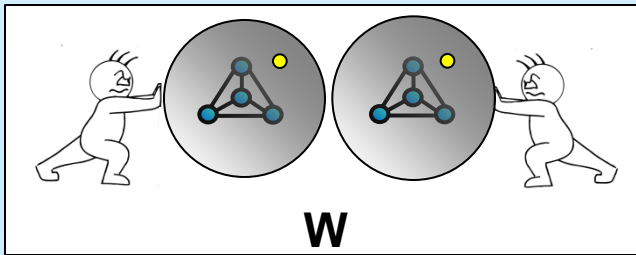
 $U \sim W$ 

## Isolant de Mott


 $U \gg W$ 


# Transition Isolant Métal de Mott pilotée par la largeur de bande

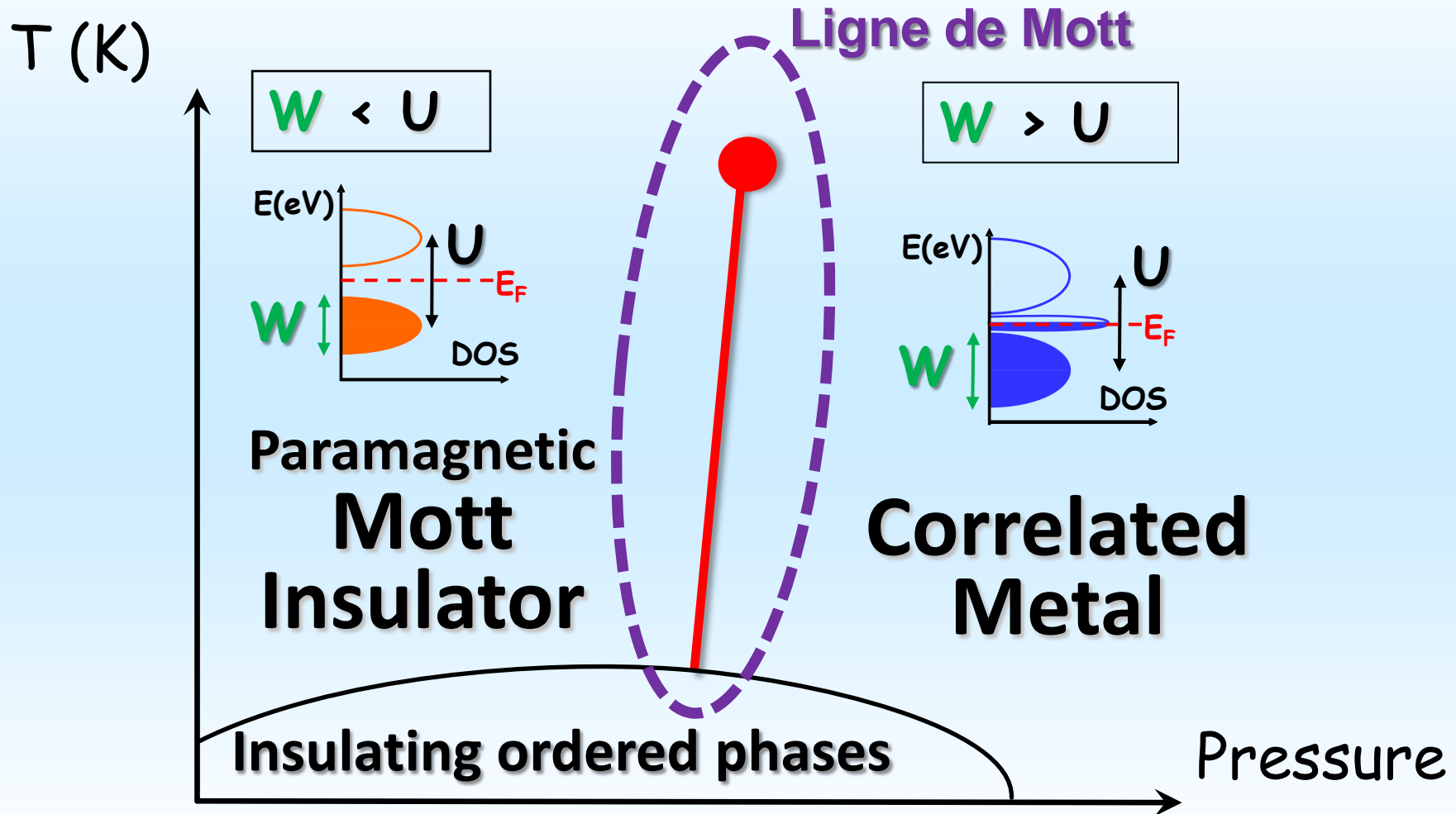
## Pression



Exotic properties at the (Mott) insulator to metal transition



# Diagramme de phase universel des isolants de Mott



\*Dynamical Mean-Field Theory(DMFT).

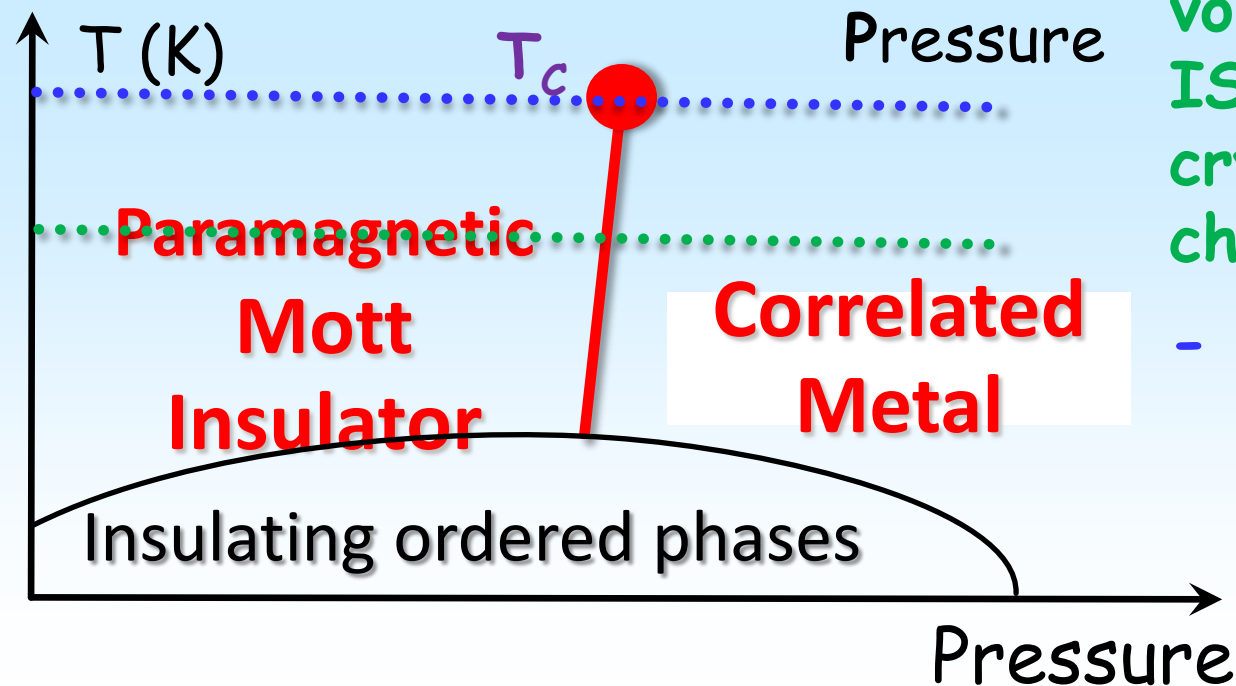
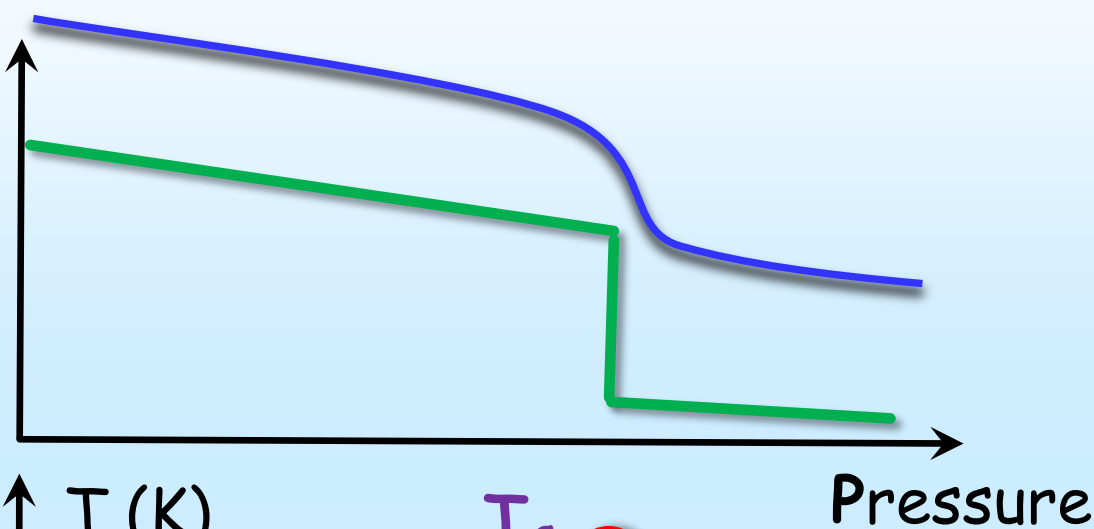
See e.g. Kotliar & Vollhardt, Physics Today 57, 53 (2004)

# A first kind of Mott MIT: bandwidth-controlled

1- Mott MIT Physics

2- Mott memories

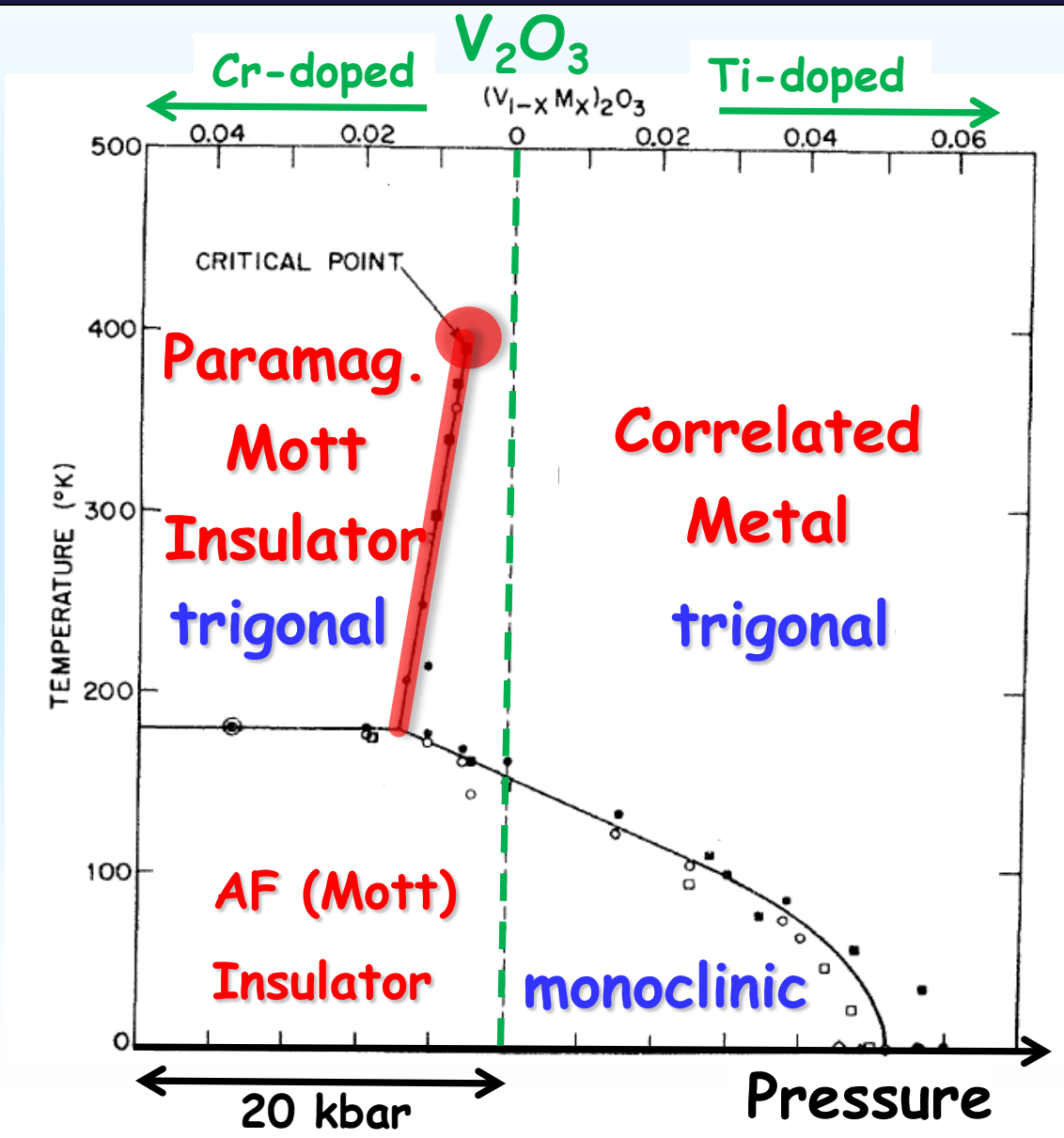
Unit cell volume



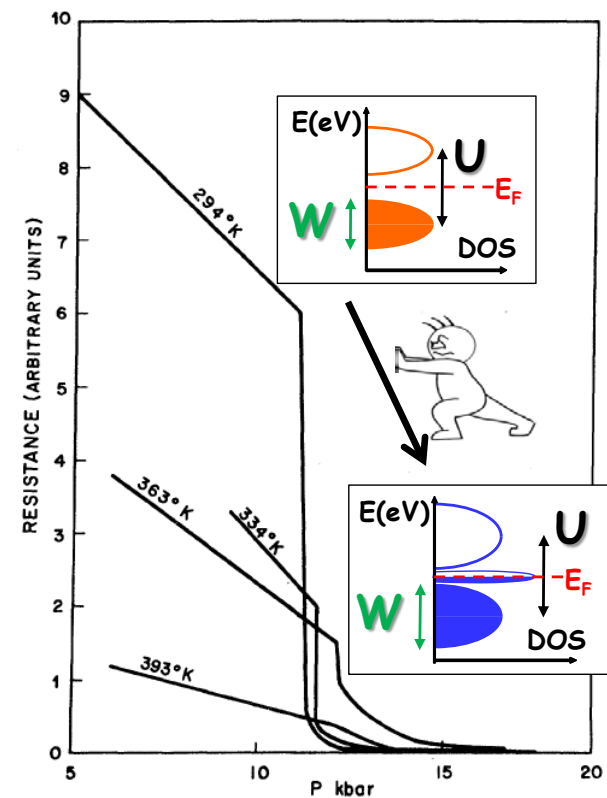
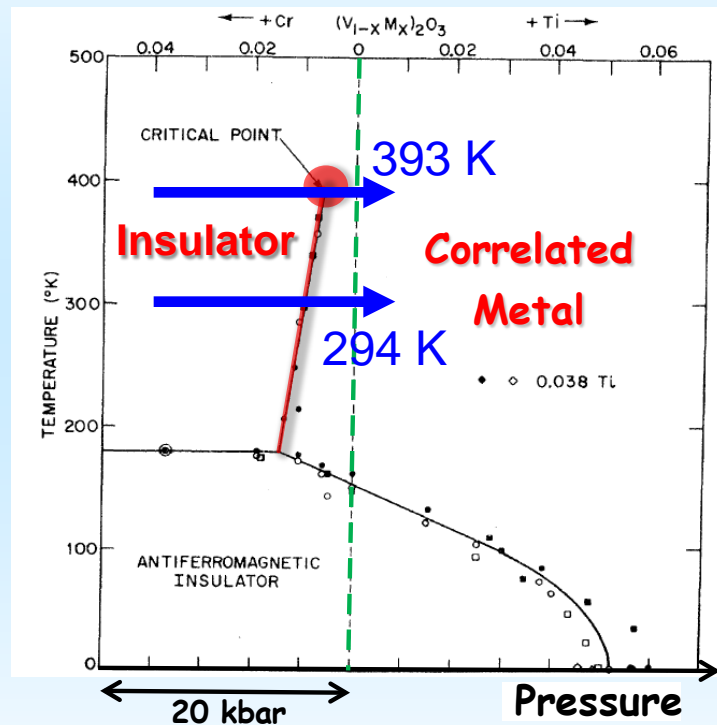
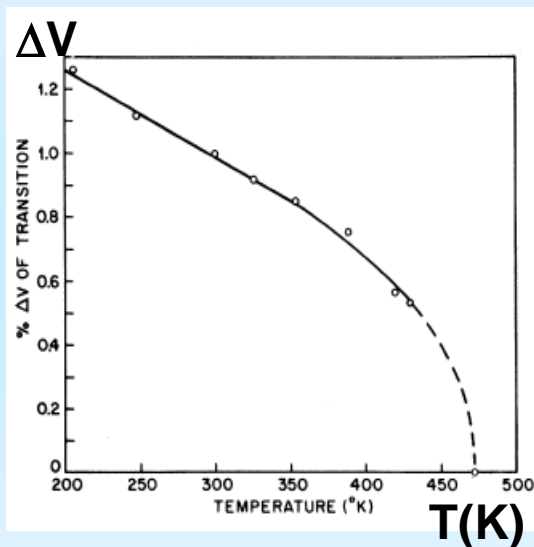
## Mott MIT line :

- Transition line with a critical endpoint at  $T=T_c$  ( $\approx 0.02W$ )
- 1<sup>st</sup> order for  $T < T_c$ : volume collapse BUT **ISOSTRUCTURAL** (no crystallographic change)
- 2<sup>nd</sup> order at  $T=T_c$

# L'isolant de Mott canonique V<sub>2</sub>O<sub>3</sub>



# Isolant de Mott canonique $V_2O_3$ : transition isolant métal pilotée par largeur de bande



PHYSICAL REVIEW B

VOLUME 7, NUMBER 5

1 MARCH 1973

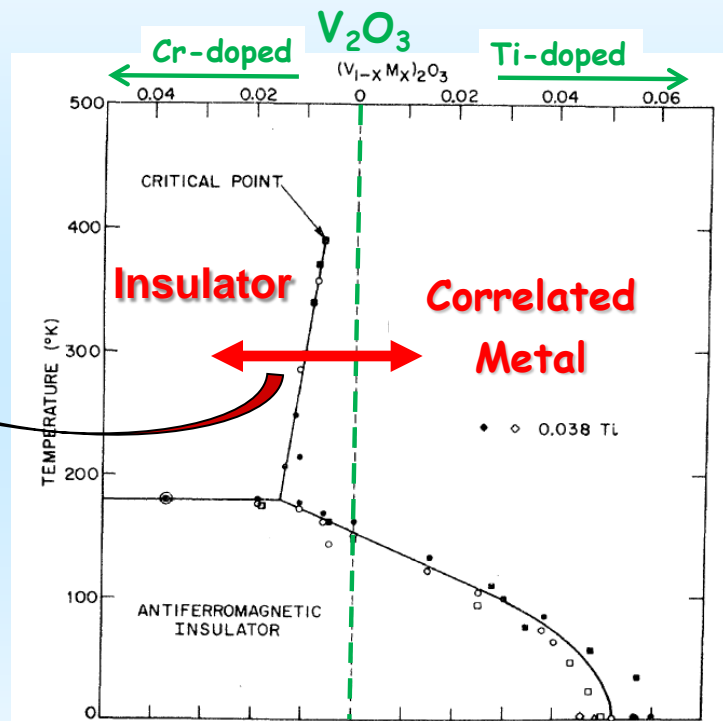
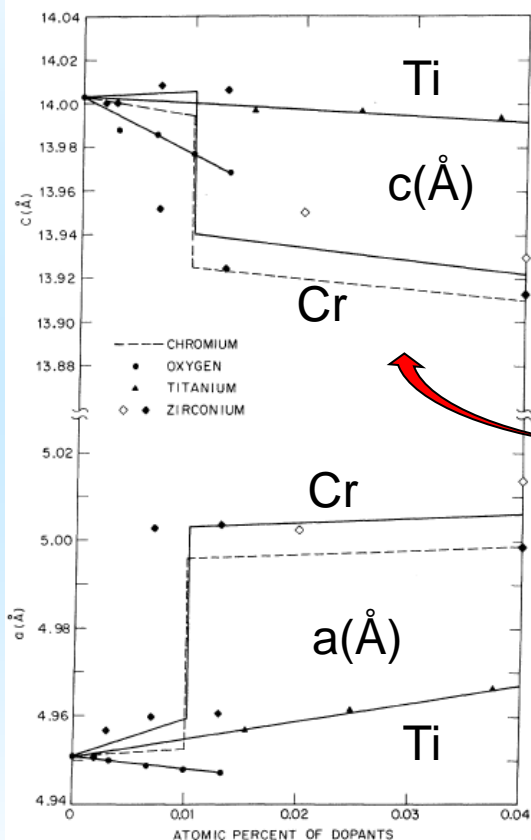
## Metal-Insulator Transitions in Pure and Doped $V_2O_3$

D. B. McWhan, A. Menth\*, J. P. Remeika, W. F. Brinkman, and T. M. Rice

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 31 January 1972)

# $V_2O_3$ transition isolant métal pilotée par la largeur de bande



Rayon ionique ↓

titanium	vanadium	chromium
22	23	24
<b>Ti</b>	<b>V</b>	<b>Cr</b>
47.867	50.942	51.996

Pression chimique  
=  
Pression physique



PHYSICAL REVIEW B

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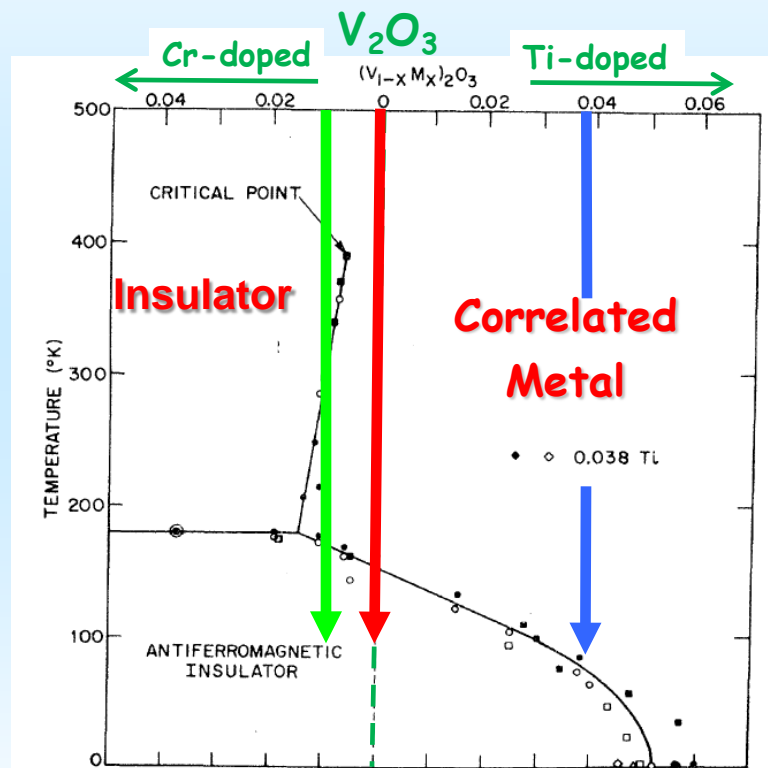
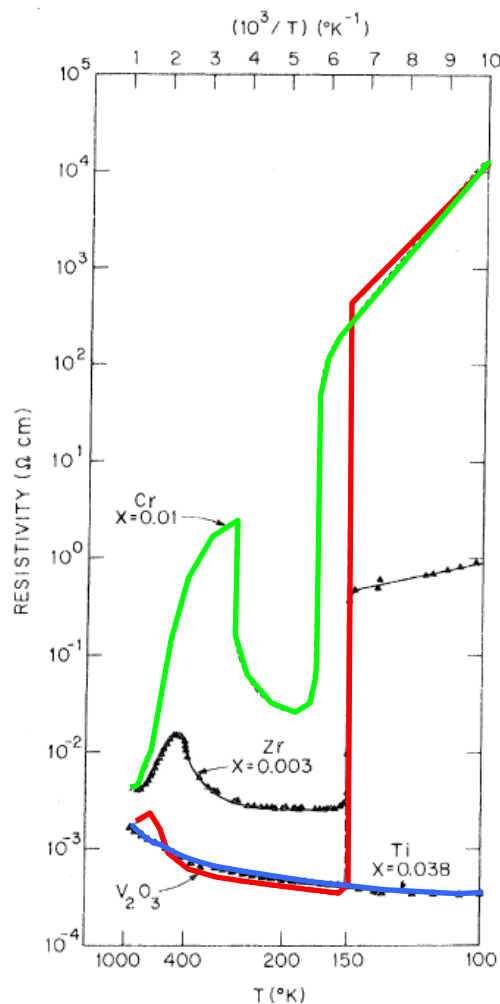
1 MARCH 1973

## Metal-Insulator Transitions in Pure and Doped $V_2O_3$

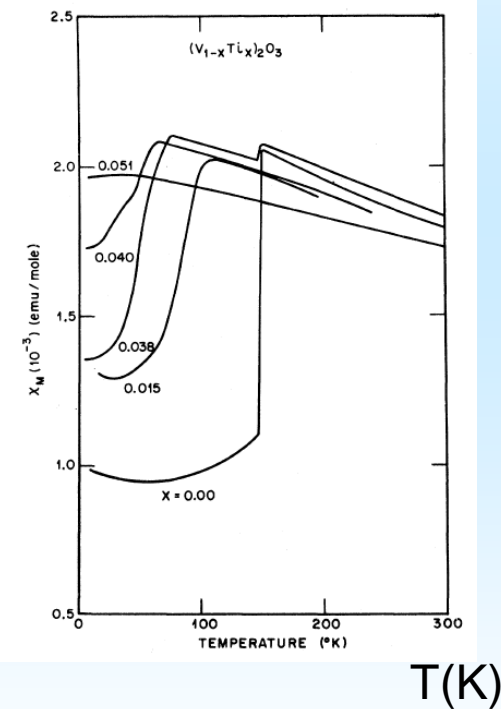
D. B. McWhan, A. Menth\*, J. P. Remeika, W. F. Brinkman, and T. M. Rice  
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 31 January 1972)

# $V_2O_3$ transition isolant métal pilotée par un changement de phase



$\chi$  ( $10^{-3} \text{ emu/mol}$ )



PHYSICAL REVIEW B

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1 MARCH 1973

## Metal-Insulator Transitions in Pure and Doped $V_2O_3$

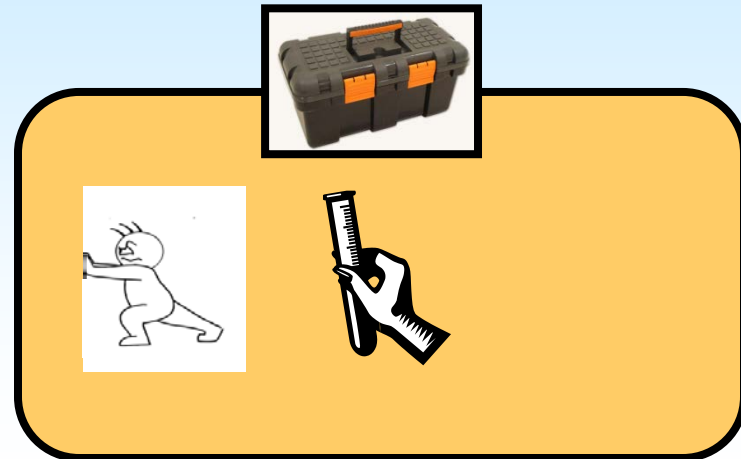
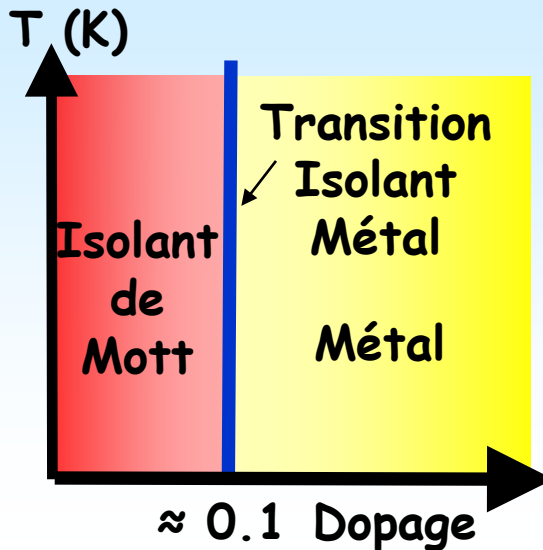
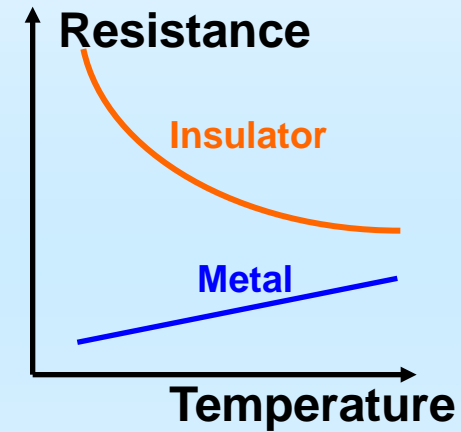
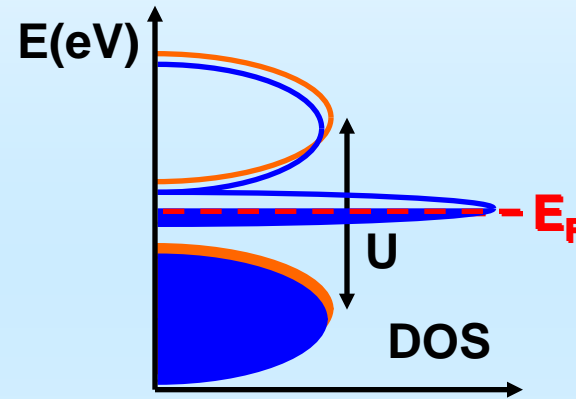
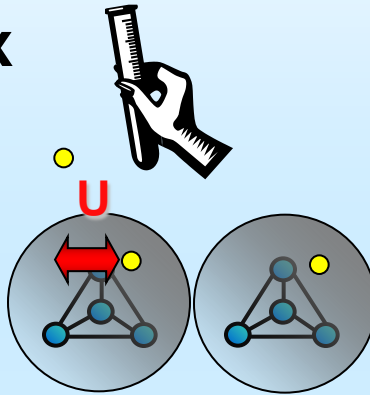
D. B. McWhan, A. Menth\*, J. P. Remeika, W. F. Brinkman, and T. M. Rice

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

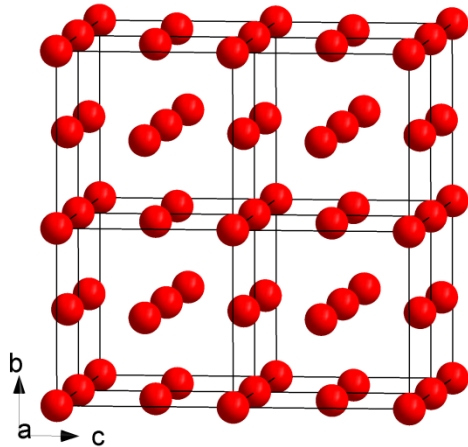
(Received 31 January 1972)

# Transition Isolant Métal de Mott pilotée par le remplissage électronique

Dopage x

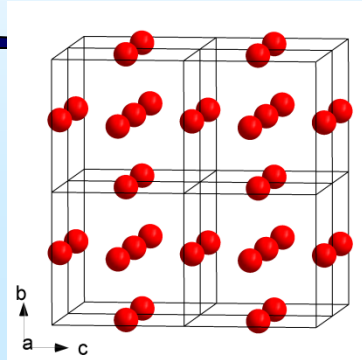


# Oxydes mixtes $ABO_3$ à structure pérovskite

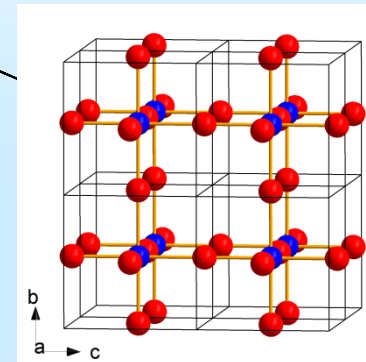


CFC oxygène

Suppression  
 $\frac{1}{4}$  O (sommets)



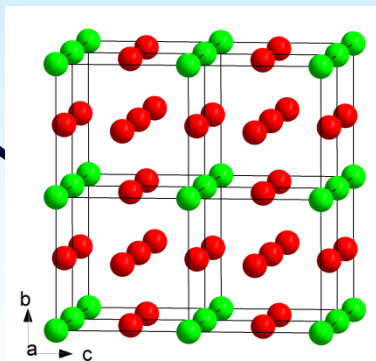
Remplissage  
 $\frac{1}{4}$  site Oh



Type  
 $ReO_3$

Remplissage  
site cubique

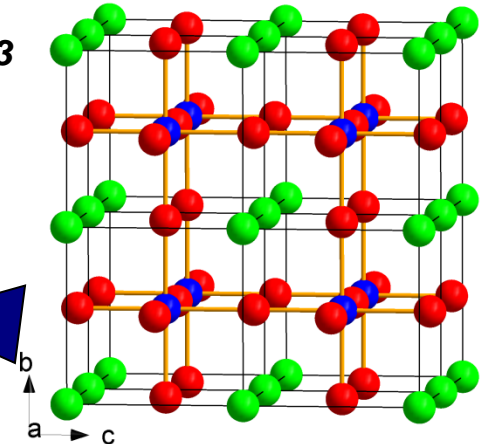
remplacement  
 $\frac{1}{4}$  O par A



CFC mixte  $AO_3$

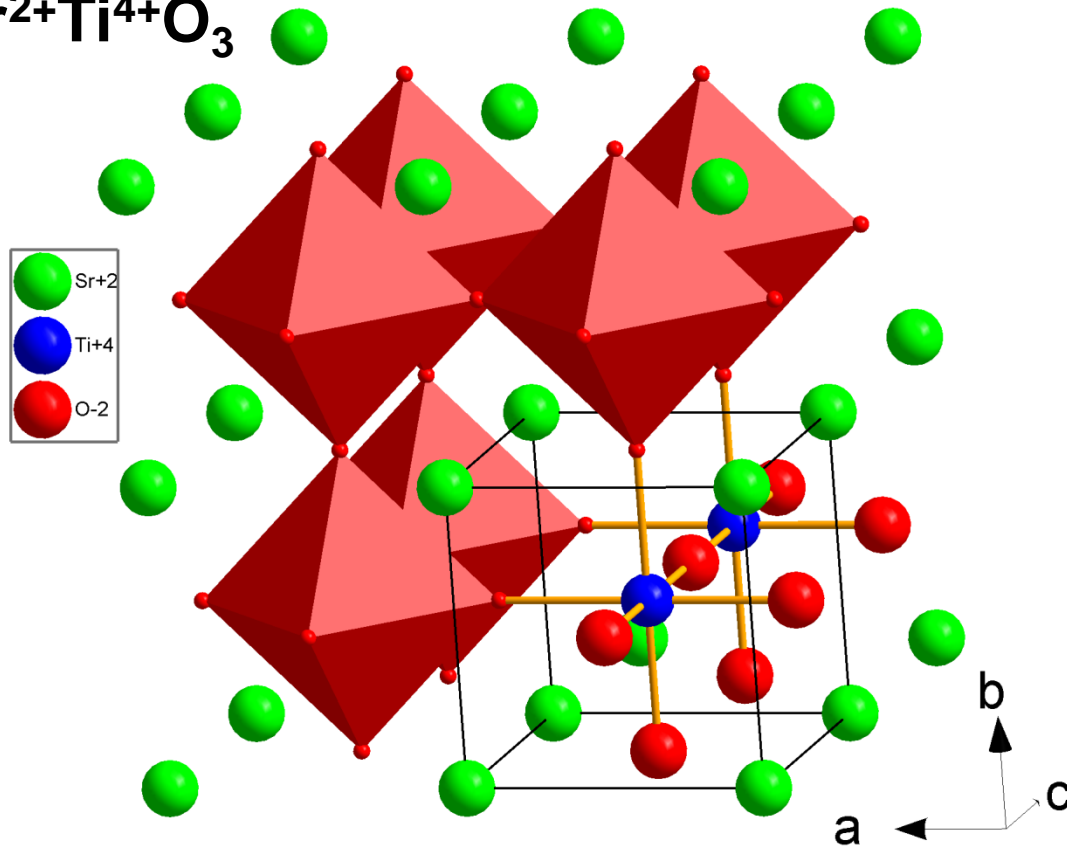
Remplissage  
 $\frac{1}{4}$  site Oh

Pérovskite  
 $ABO_3$

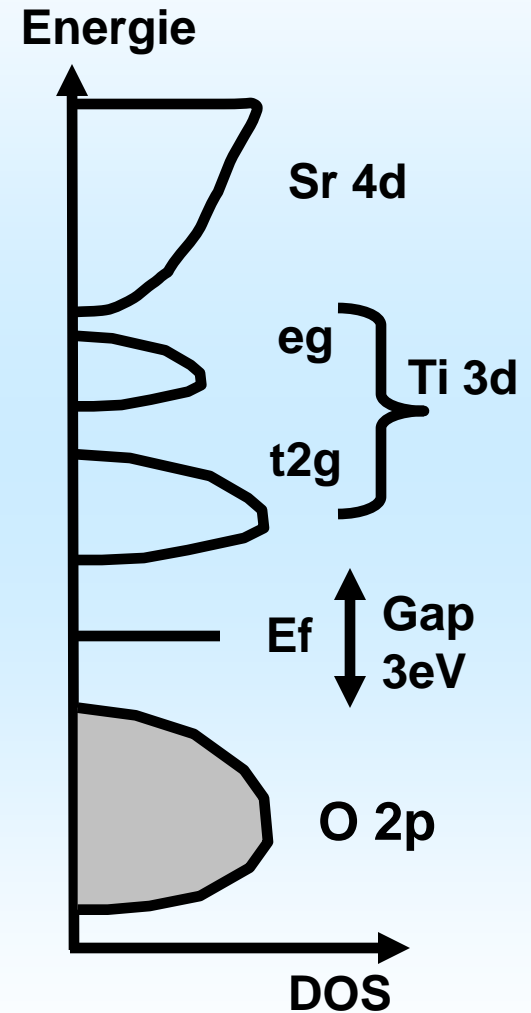




# Oxydes mixtes $ABO_3$ à structure pérovskite



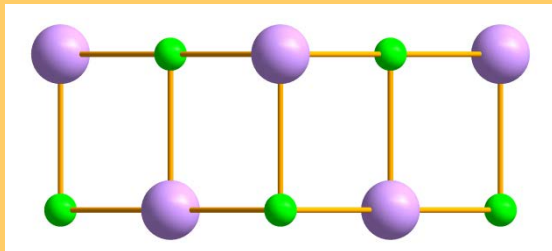
Structure de beaucoup d'oxydes mixtes avec  
 A = alcalino terreux ou terres rares  
 B = éléments de transition



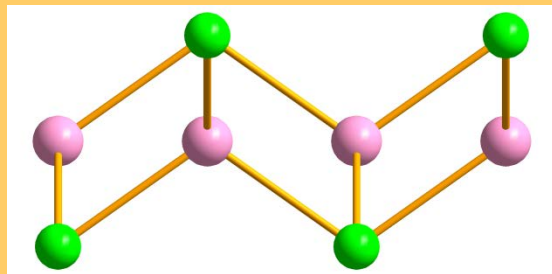
Isolant de bande



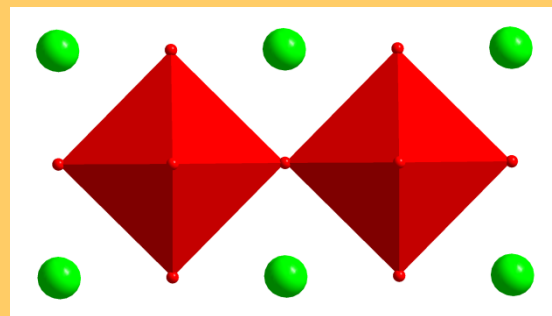
**NaCl**



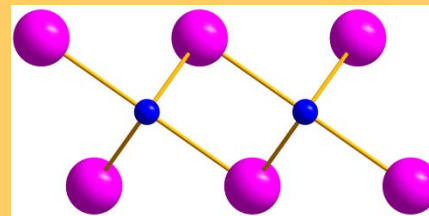
**Fluorine**



**Perovskite**



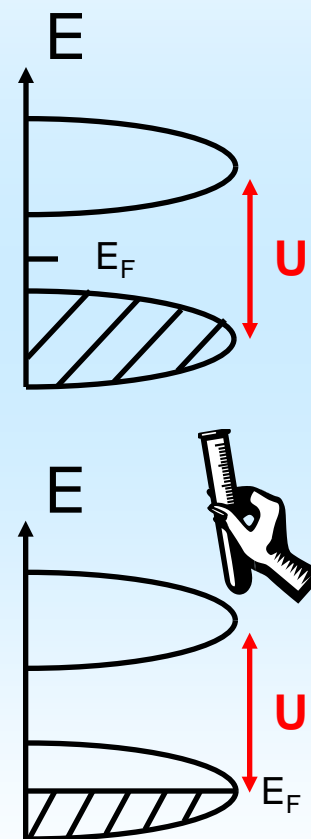
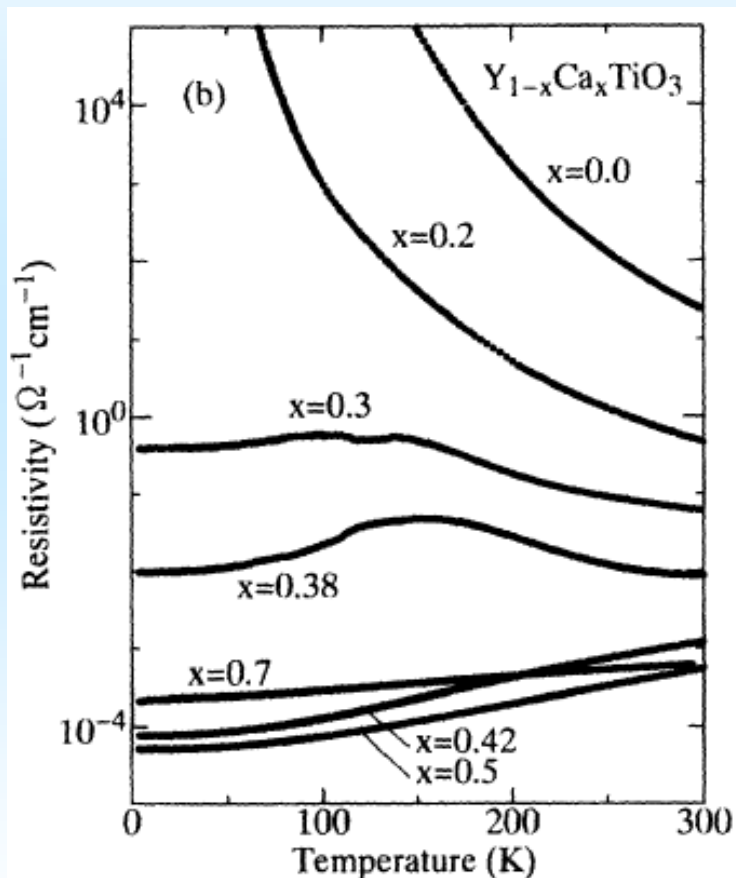
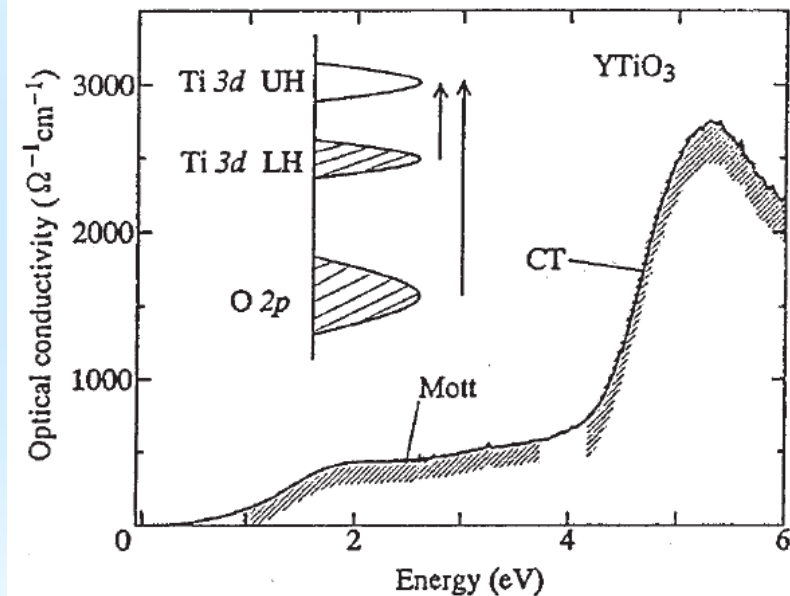
**HC**



**CdI<sub>2</sub>**

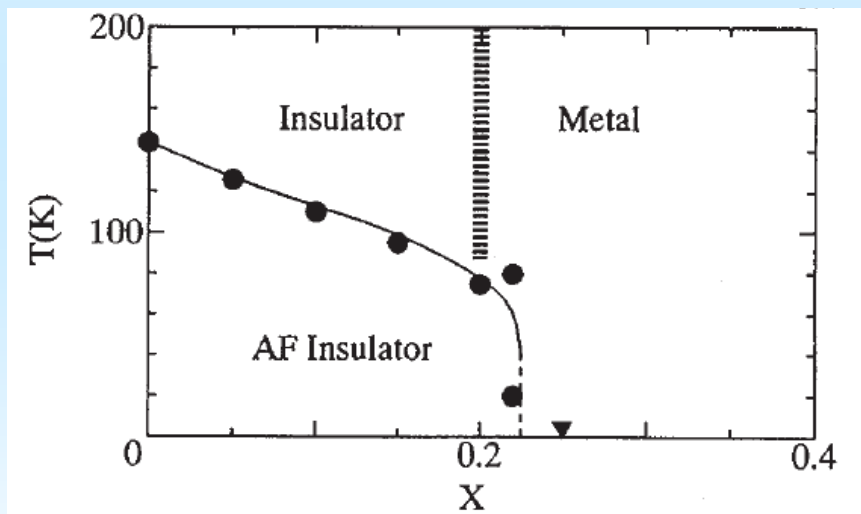
# Transition Isolant métal contrôlée par le remplissage dans la série $Y_{1-x}Ca_xTiO_3$ à structure pérovskite

$Y^{3+}Ti^{3+}O_3$

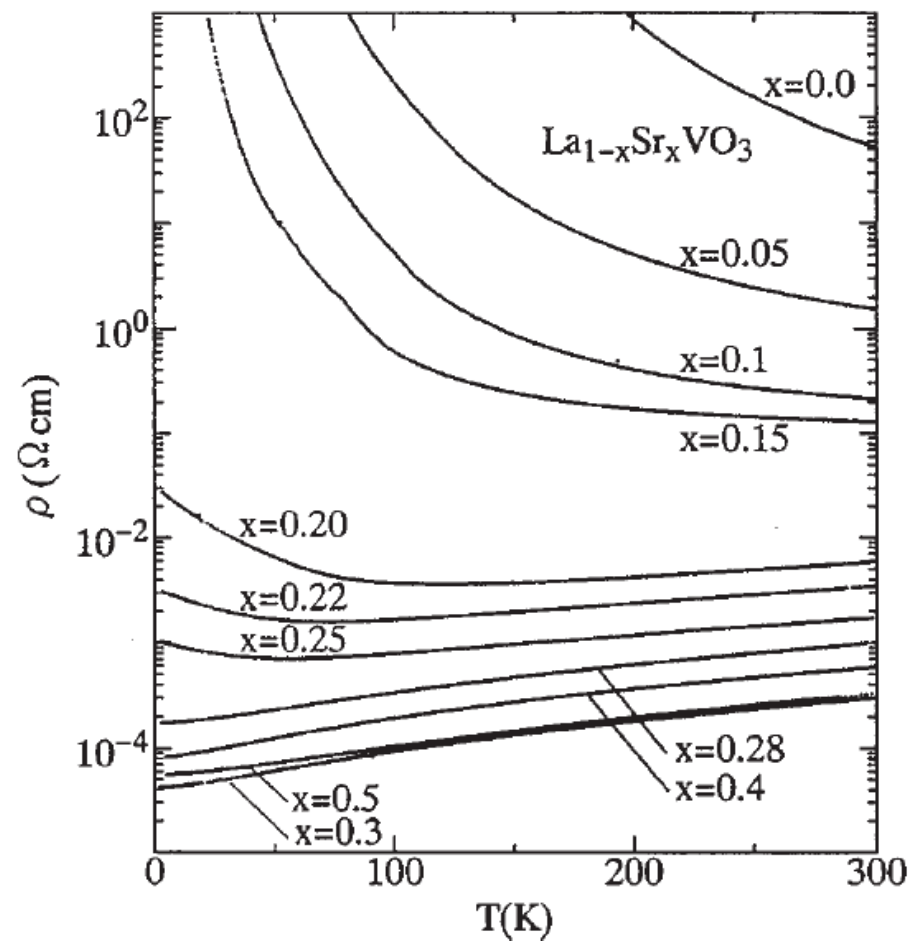


Substitution  $Y^{3+}$  par  $Ca^{2+}$  = dopage trou

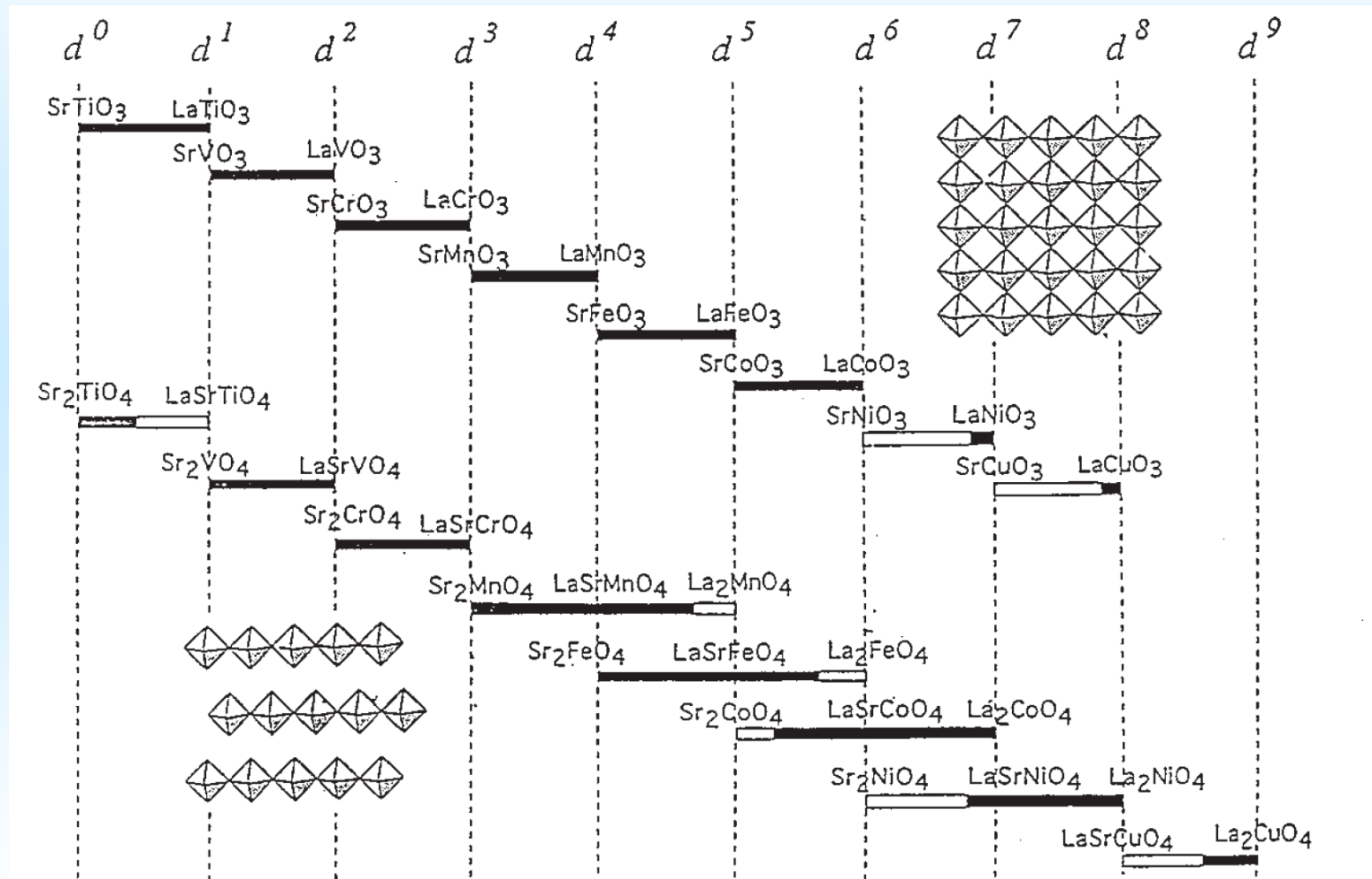
# Transition Isolant métal contrôlée par le remplissage dans les pérovskites $La_{1-x}Sr_xVO_3$



**Même chose dans les  
pérovskites au Vanadium**



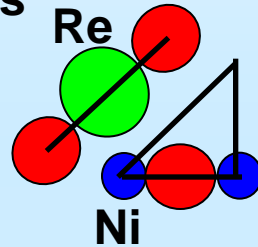
# Control du remplissage dans les pérovskites



# Transition Isolant métal contrôlée par la largeur de bande dans les pérovskites $ReNiO_3$ ( $Re = \text{terres rares}$ )

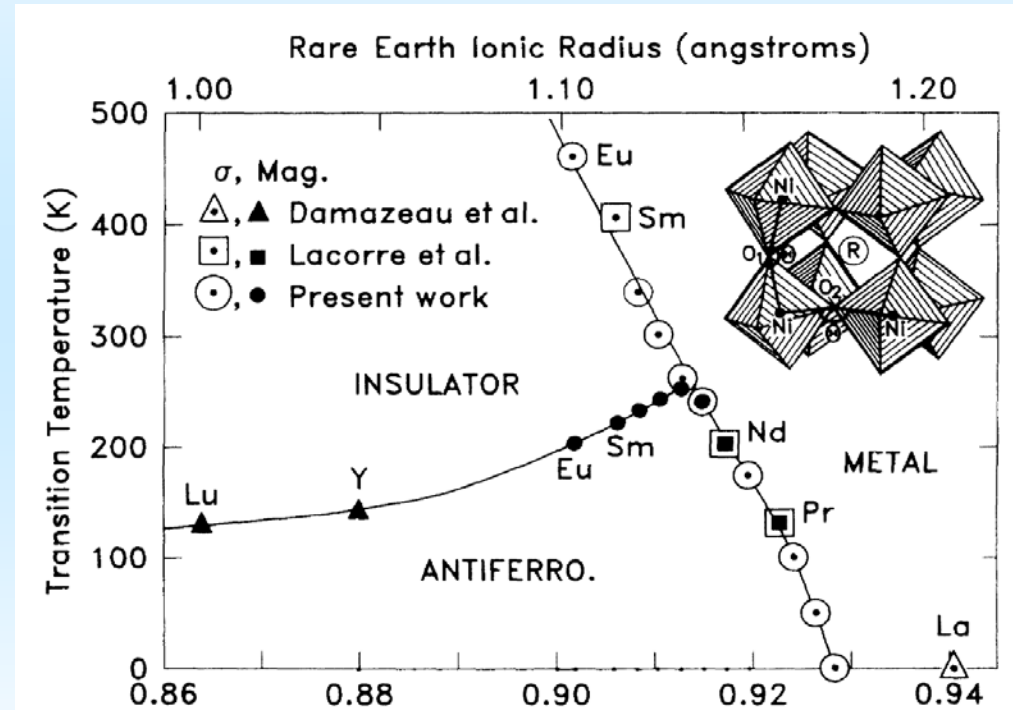
Facteur de tolérance des pérovskites  $ABO_3$  :

$$f = (r_A + r_O) / \sqrt{2}(r_B + r_O)$$



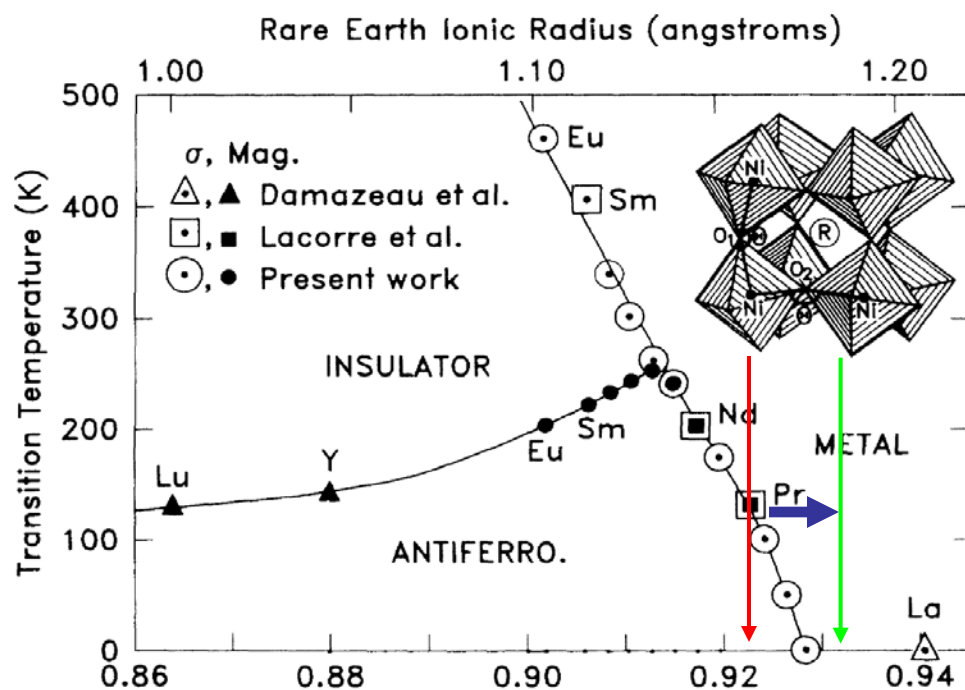
Si  $f \approx 1$  pérovskite cubique

Si  $f < 1$  ( $r_A$  trop petit) transition vers pérovskite orthorhombique  $GdFeO_3$

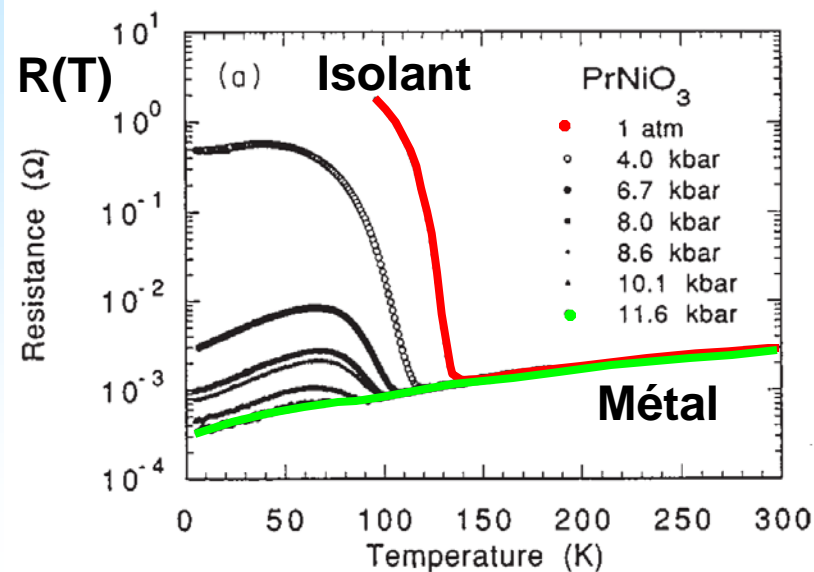
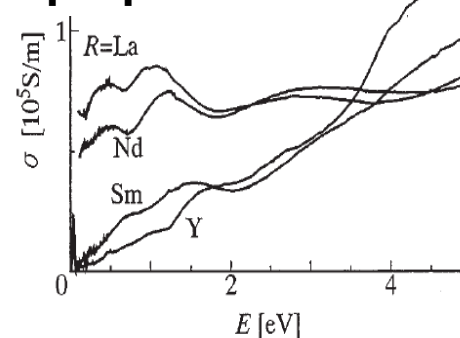


La distorsion permet de jouer sur la largeur de bande  $\rightarrow$  TMI

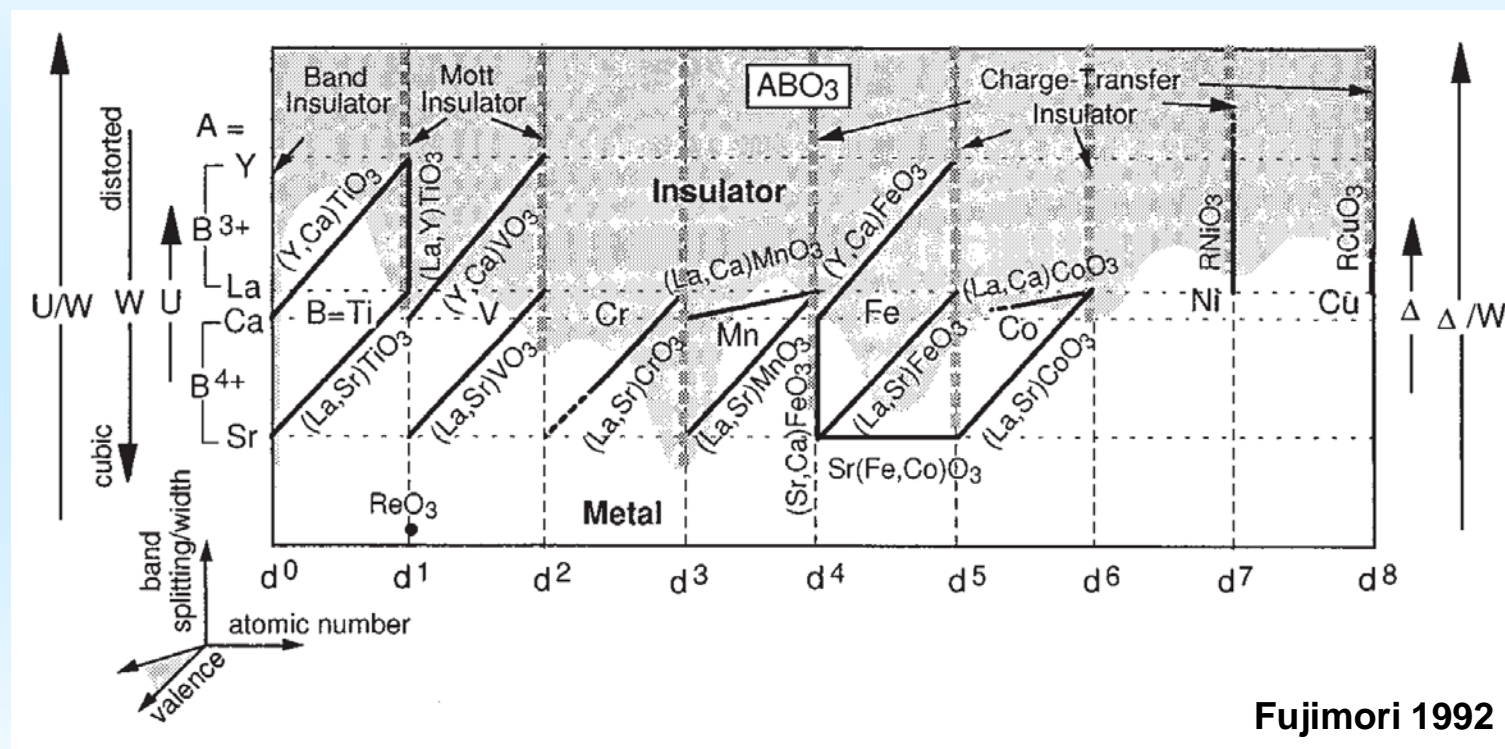
# Transition Isolant métal contrôlée par la largeur de bande dans les pérovskites $ReNiO_3$ ( $Re =$ terres rares)



## Conductivité optique



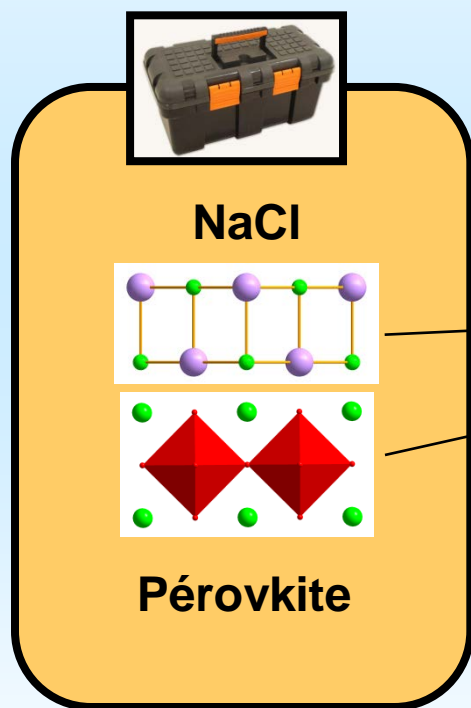
# Transition Isolant métal contrôlée par la largeur de bande dans les pérovskites $ReNiO_3$ ( $Re =$ terres rares)



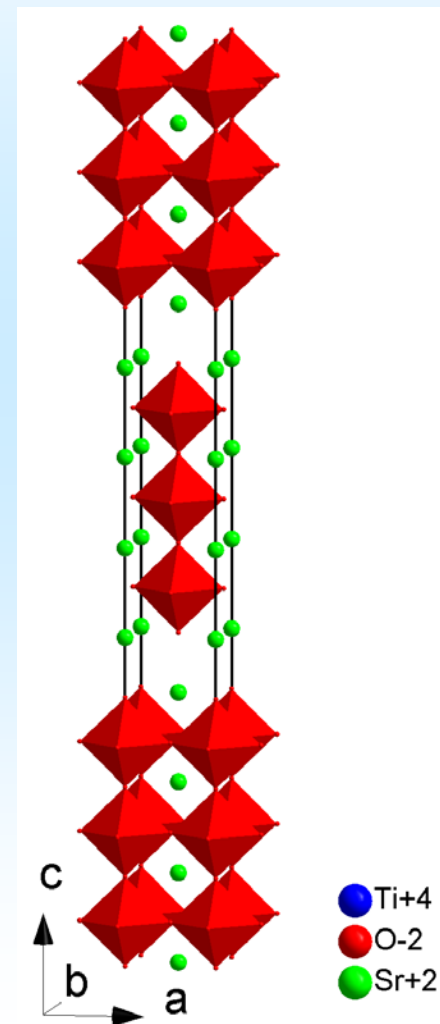
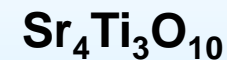
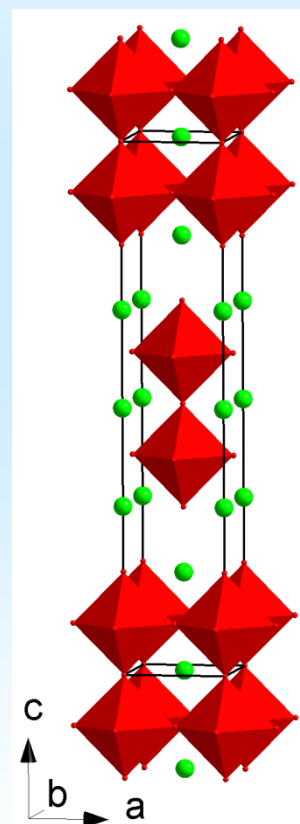
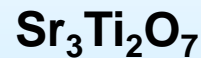
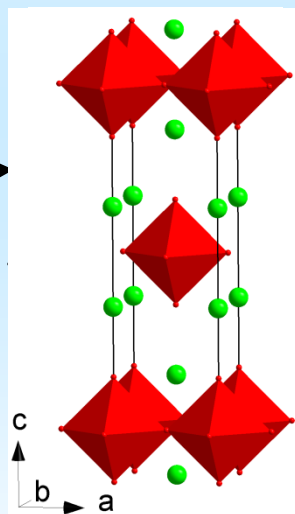
Rationalisation TMI dans pérovskites



# La série d'homologue Ruddlesden-Popper

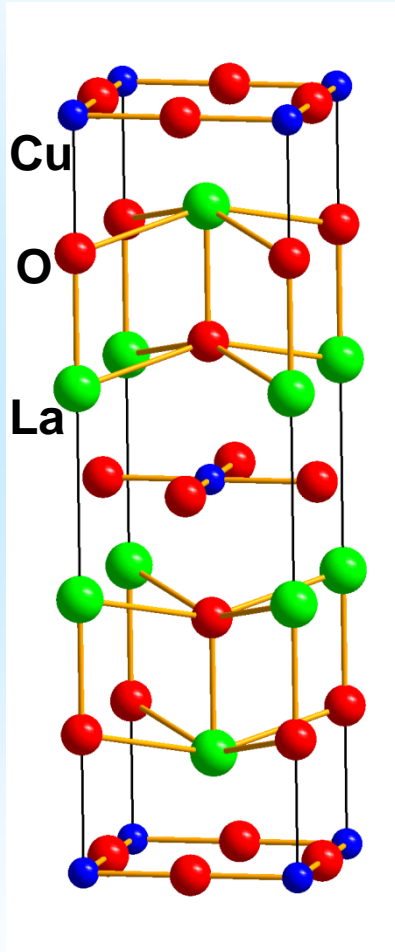


Intercroissance de feuillets  
types NaCl et Pérovskite



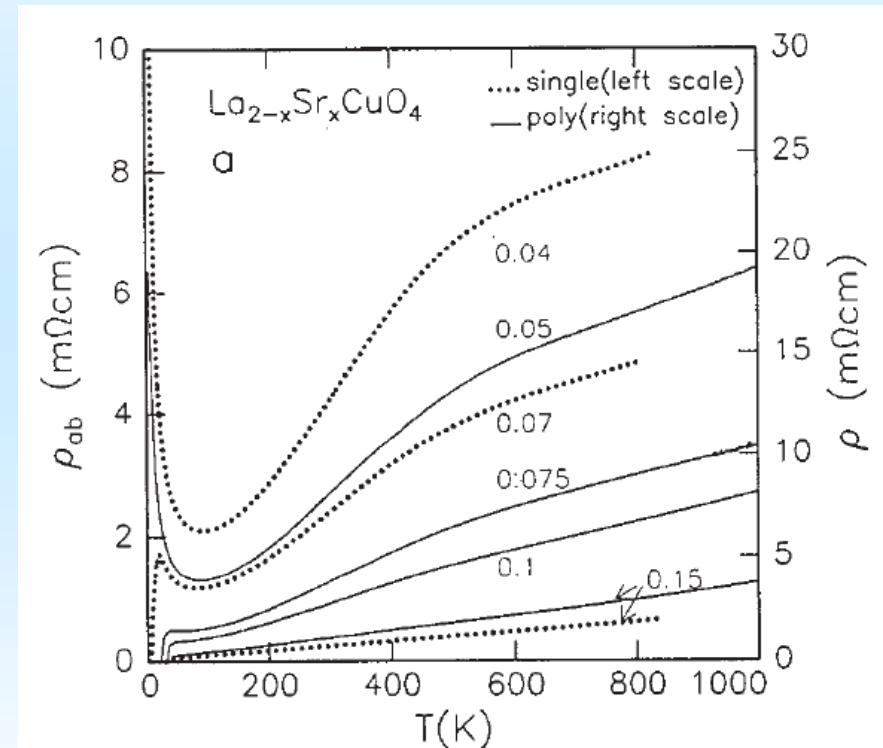
Formulation générale  $\text{A}_{n+1}\text{M}_n\text{O}_{3n+1}$

# Les cuprates supraconducteurs



$\text{La}_2\text{Cu}^{2+}\text{O}_4$   
Phase RP  $n=1$   
Isolant de Mott

TMI par dopage trou



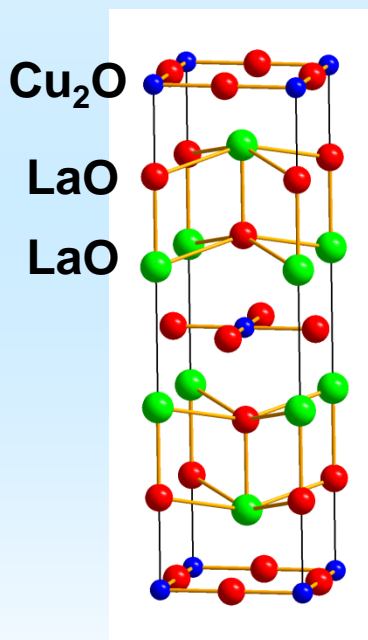
Supra !  $T_c \approx 40\text{K}$

1986 Bednorz et Müller supraconductivité dans le composé  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$   
*Z. Physik B*, 64, 189 (1986)

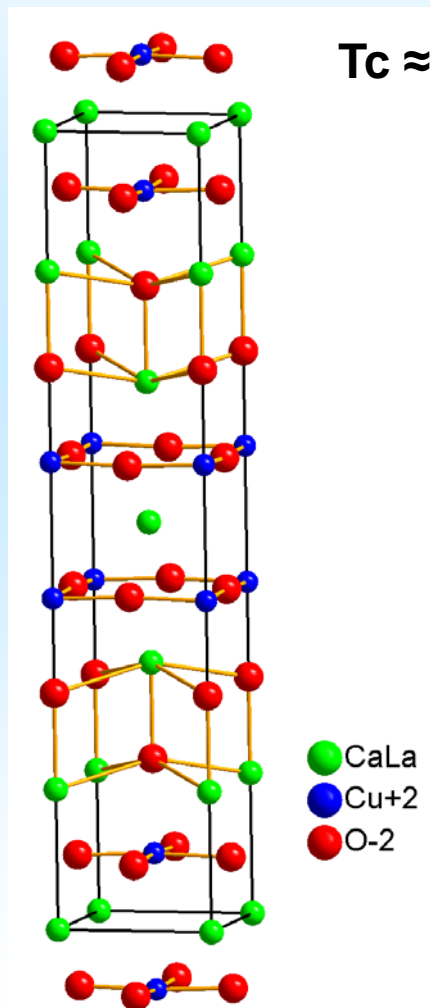
# Les HTc cuprates supraconducteurs

$\text{La}_{2-x}\text{Ca}_x\text{Cu}_2\text{O}_6$  Phase RP n=2

$\text{La}_2\text{CuO}_4$   
Phase RP n=1

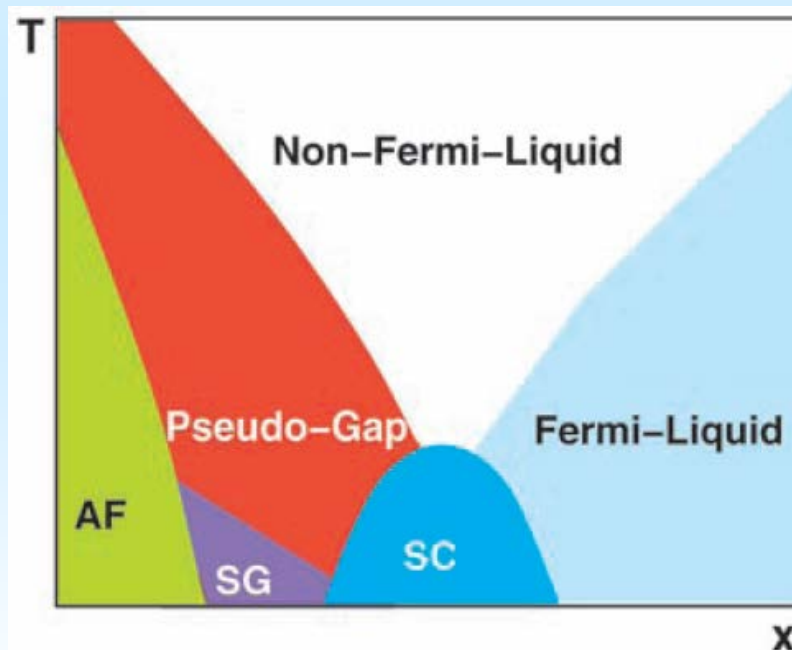


$T_c \approx 40\text{K}$



Cava et al. Nature 345, 602 (1990)

Diagramme de phase générique

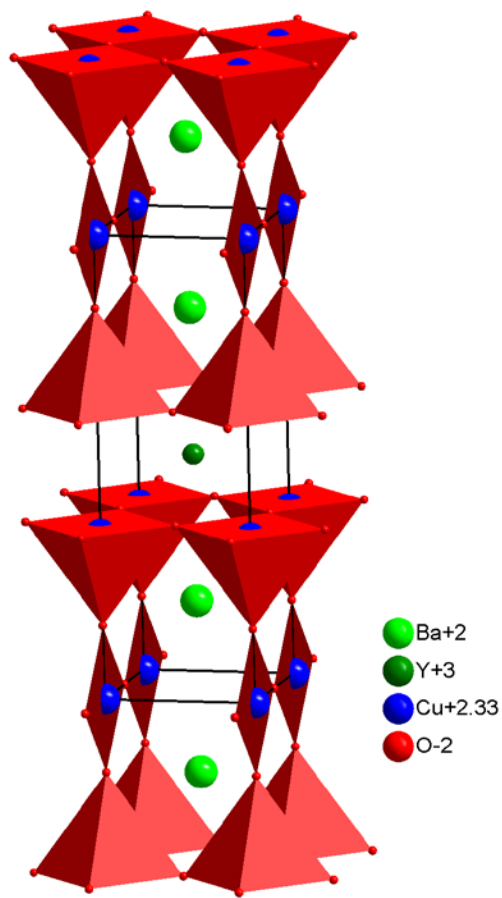


Plan  $\text{CuO}_2$  dopé  $\approx 0.2$  trou  
= HTc supraconductivité

Relation « structure propriétés »

# Les HTc cuprates supraconducteurs

## Ba<sub>2</sub>YCu<sub>3</sub>O<sub>7</sub> Pérovskite déficiente en O



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PHYSICAL REVIEW LETTERS

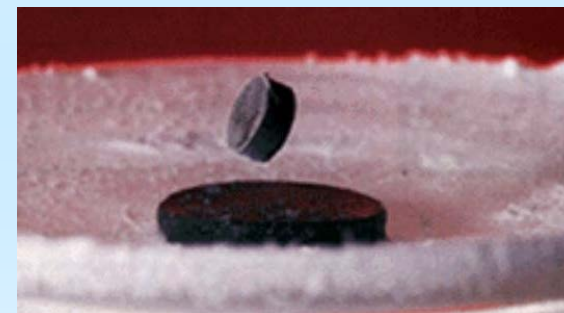
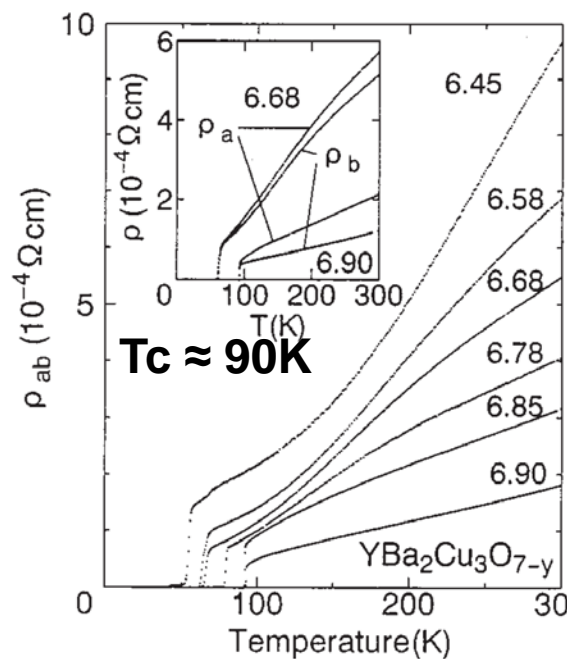
20 APRIL 1987

### Bulk Superconductivity at 91 K in Single-Phase Oxygen-Deficient Perovskite Ba<sub>2</sub>YCu<sub>3</sub>O<sub>9-δ</sub>

R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika,  
E. A. Rietman, S. Zahurak, and G. P. Espinosa

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 5 March 1987)



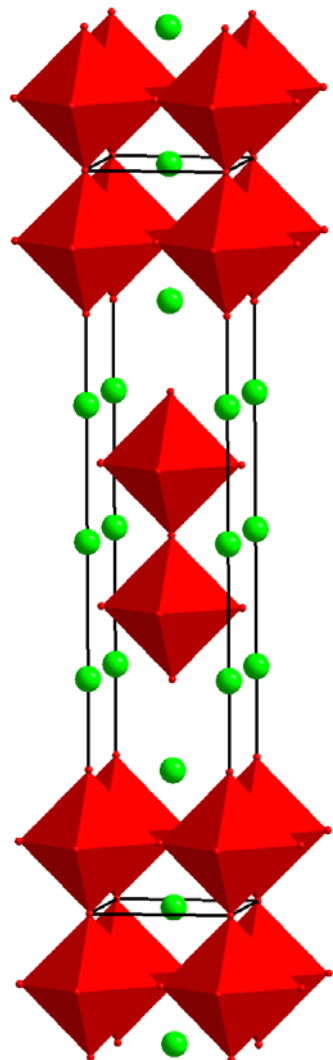
Et puis  
Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> T<sub>c</sub> = 85 K ....

*Nature* 363, 56 - 58 (06 May 1993)

**Superconductivity above 130 K in  
Hg-Ba-Ca-Cu-O**

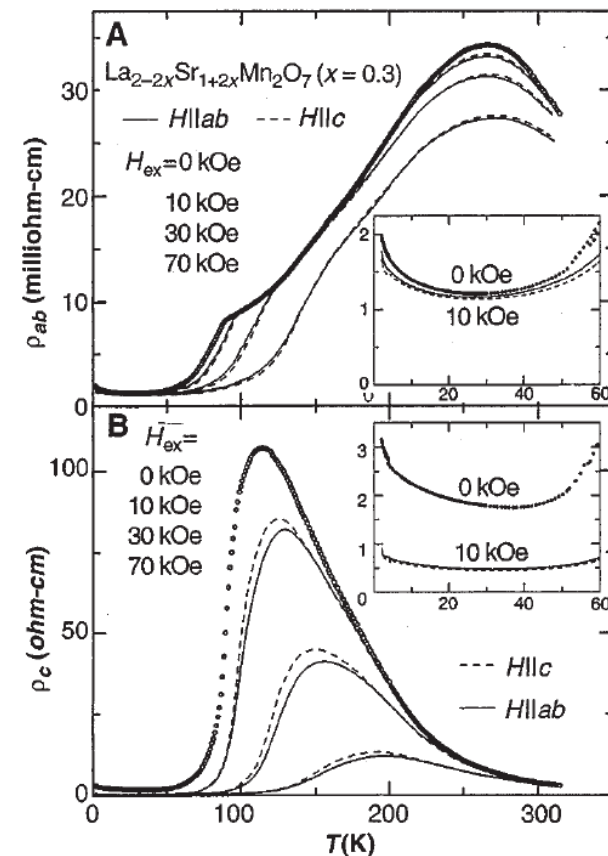
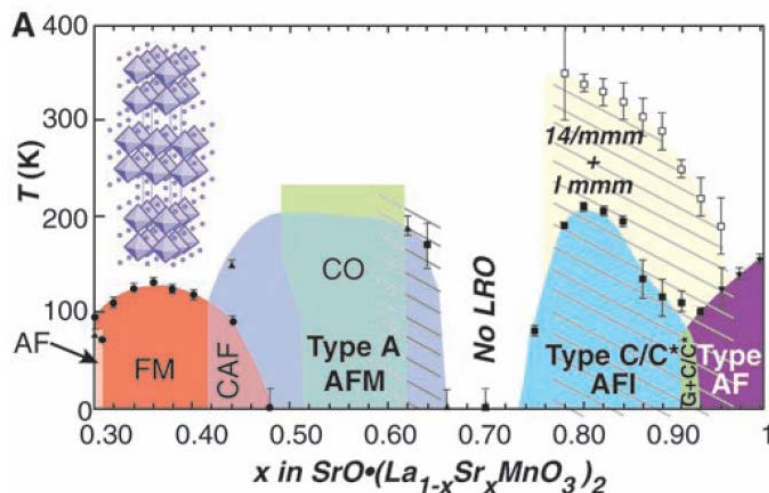
A. Schilling, M. Cantoni, J. D. Guo & H. R. Ott

# Autres phases Ruddlesden Popper : les manganites



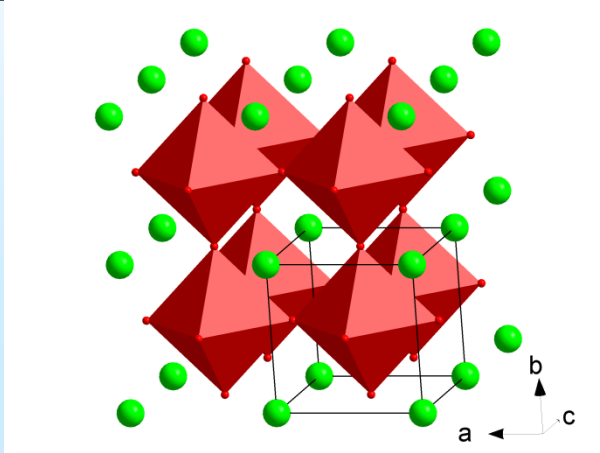
Phase RP n=2  
 $\text{La}_{2-x}\text{Sr}_{1+x}\text{Mn}_2\text{O}_7$  ( $\text{Mn}^{3+}$ )  
 Isolant de Mott pour  $x=0$

Dopage  $\rightarrow$   $\text{Mn}^{4+}$   
 Transition Isolant Métal  
 Magnétorésistance colossale

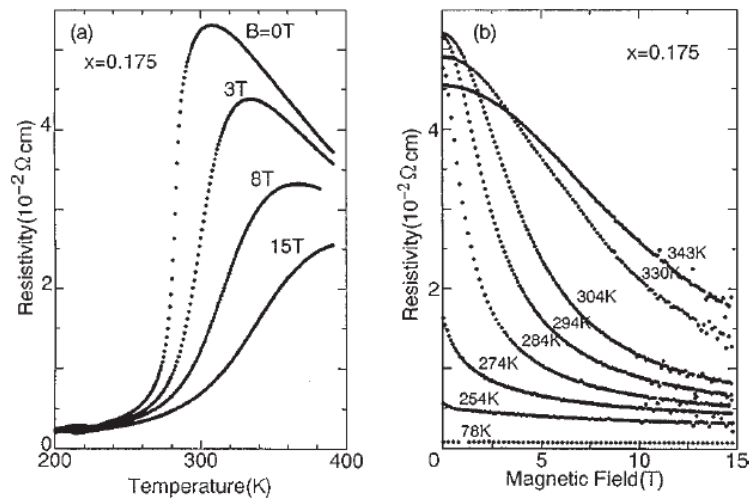


Couplage entre degrés de liberté de charge de spin et orbitaux

# Magnétorésistance négative Colossale : Pérovskite $La_{1-x}Sr_xMnO_3$

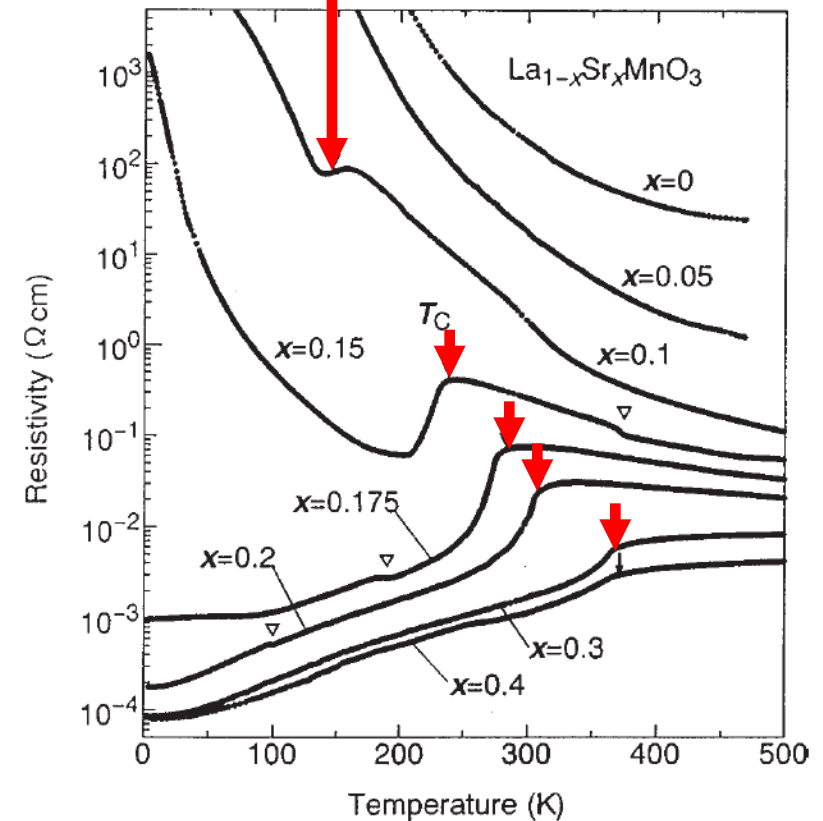


## Magnétorésistance négative



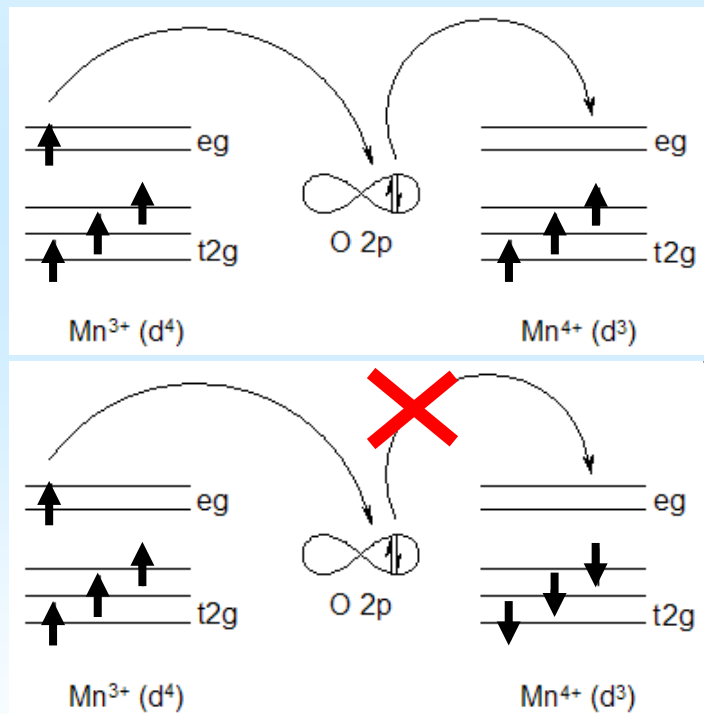
TMI par dopage trou

**Ordre  
Ferromagnétique**



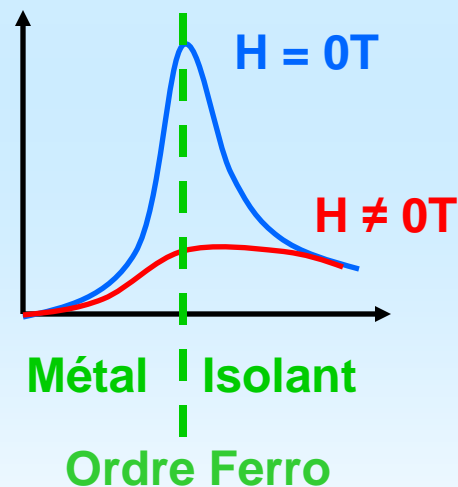
# Magnétorésistance négative Colossale : mécanisme de double échange

Règle de Hund les électrons  $e_g$   
induisent une interaction ferromagnétique

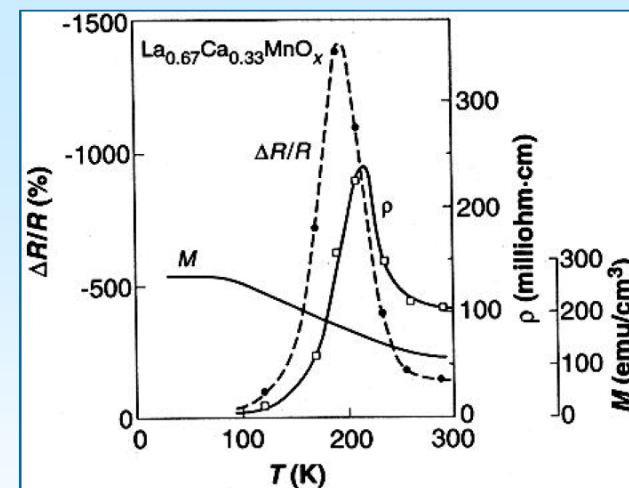


Valence mixte  $Mn^{3+}/Mn^{4+}$

Résistance



MagnétoRésistance



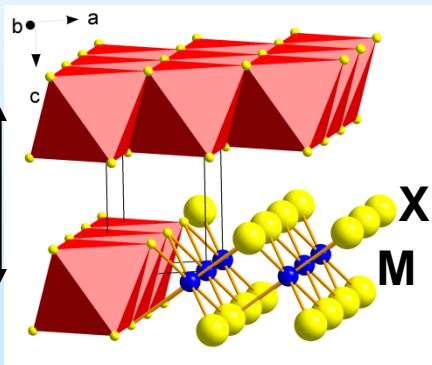
Science 15 April 1994:

Thousandfold Change in Resistivity in  
Magnetoresistive La-Ca-Mn-O Films

S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and Chen

# Dichalcogénures d'éléments de transition $MX_2$

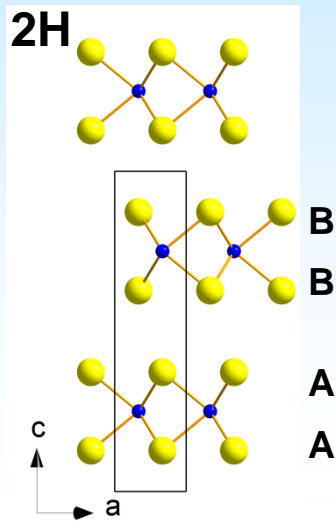
## Structures lamellaires



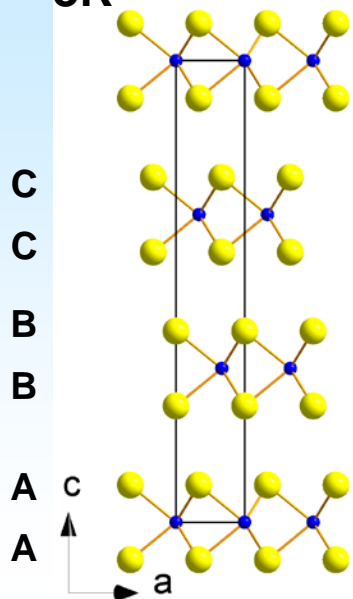
$CdI_2$



ou  $MoS_2$

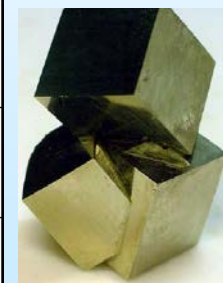


3R

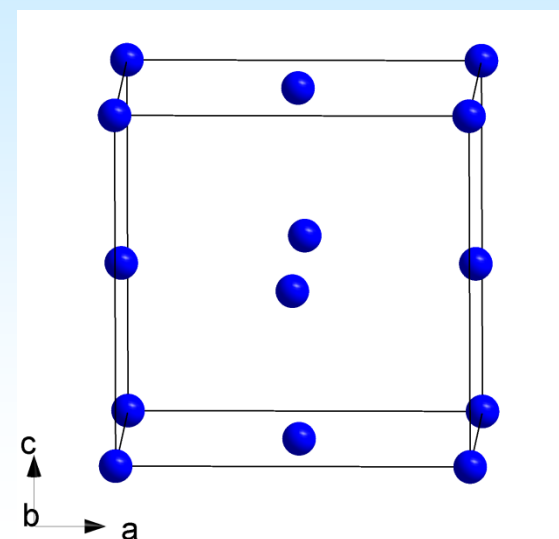


## Structures 3D

titanium 22 <b>Ti</b> 47.867	vanadium 23 <b>V</b> 50.942	chromium 24 <b>Cr</b> 51.996	manganese 25 <b>Mn</b> 54.938	iron 26 <b>Fe</b> 55.845	cobalt 27 <b>Co</b> 58.933	nickel 28 <b>Ni</b> 58.693	copper 29 <b>Cu</b> 63.546
zirconium 40 <b>Zr</b> 91.224	niobium 41 <b>Nb</b> 92.906	molybdenum 42 <b>Mo</b> 95.94	technetium 43 <b>Tc</b> [98]	ruthenium 44 <b>Ru</b> 101.07	rhodium 45 <b>Rh</b> 102.91	palladium 46 <b>Pd</b> 106.42	silver 47 <b>Ag</b> 107.87
hafnium 72 <b>Hf</b> 178.49	tantalum 73 <b>Ta</b> 180.95	tungsten 74 <b>W</b> 183.84	rhenium 75 <b>Re</b> 186.21	osmium 76 <b>Os</b> 190.23	iridium 77 <b>Ir</b> 192.22	platinum 78 <b>Pt</b> 195.08	gold 79 <b>Au</b> 196.97



Pyrite ou marcassite





# $TX_2$ un cas de compétition redox à l'état solide

titanium 22 <b>Ti</b> 47,867	vanadium 23 <b>V</b> 50,942	chromium 24 <b>Cr</b> 51,996	manganese 25 <b>Mn</b> 54,938	iron 26 <b>Fe</b> 55,845	cobalt 27 <b>Co</b> 58,933	nickel 28 <b>Ni</b> 58,693	copper 29 <b>Cu</b> 63,546
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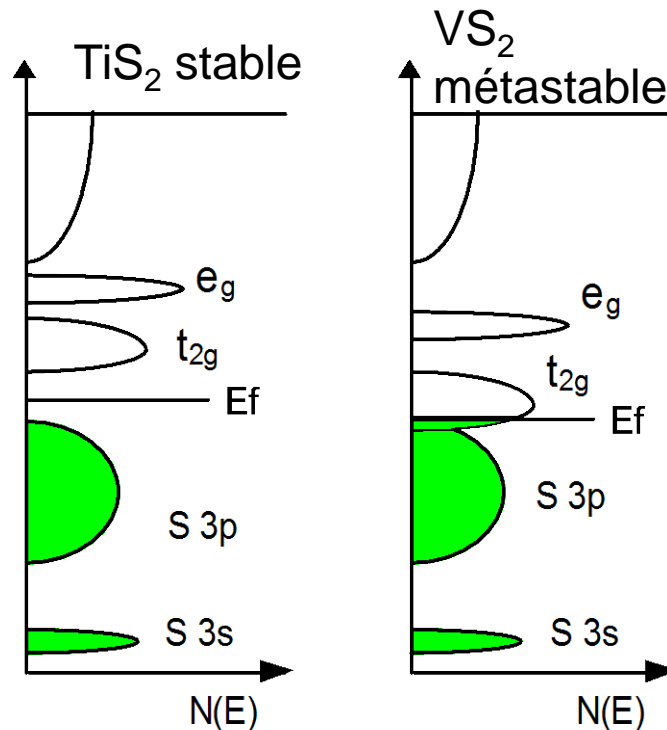
Abaissement des niveaux d

$Ti^{4+}(S^{2-})_2$

$M^{4+}$

$M^{3+}$

$M^{2+}$

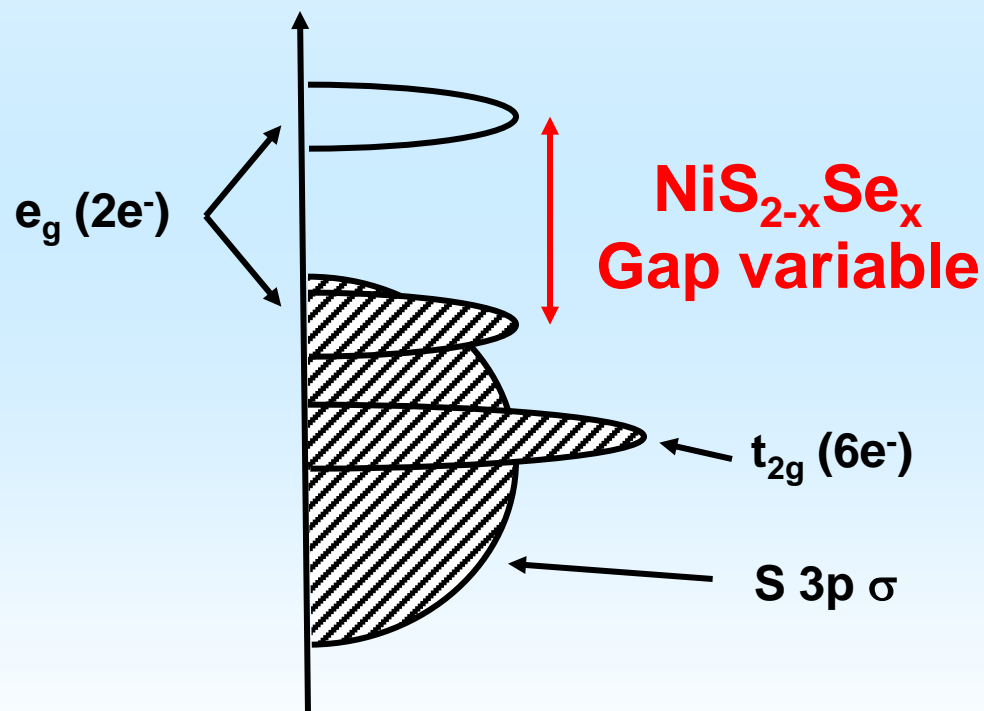
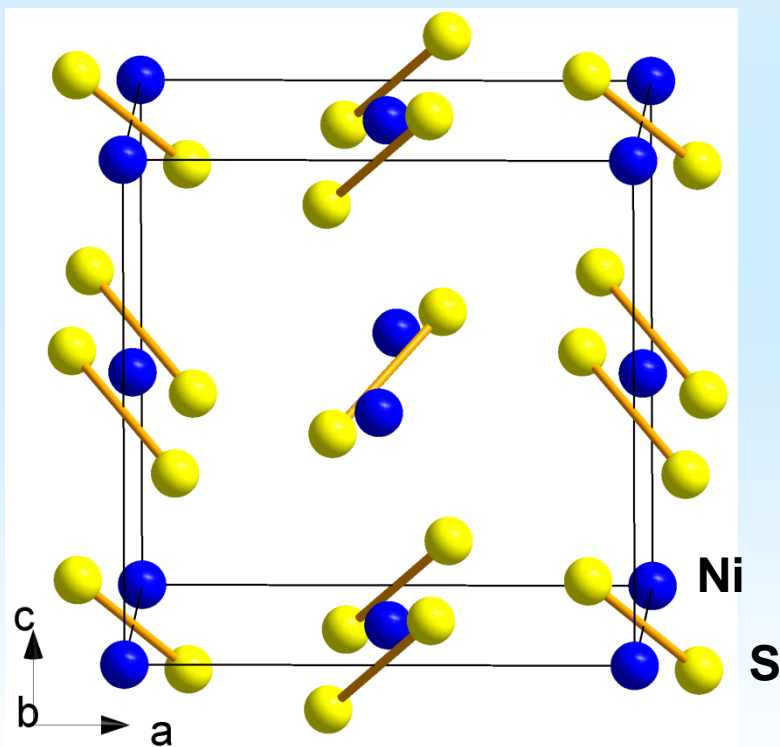


$M^{4+}$  instable  $\rightarrow$   $M^{2+}$  oxydation du soufre et formation de paires  $(S_2)^{2-}$

# La transition de Mott dans $\text{NiS}_{2-x}\text{Se}_x$

Structure pyrite (cubique)

$\text{NiS}_2$  Isolant Mott – gap  $\sim 0.5\text{eV}$

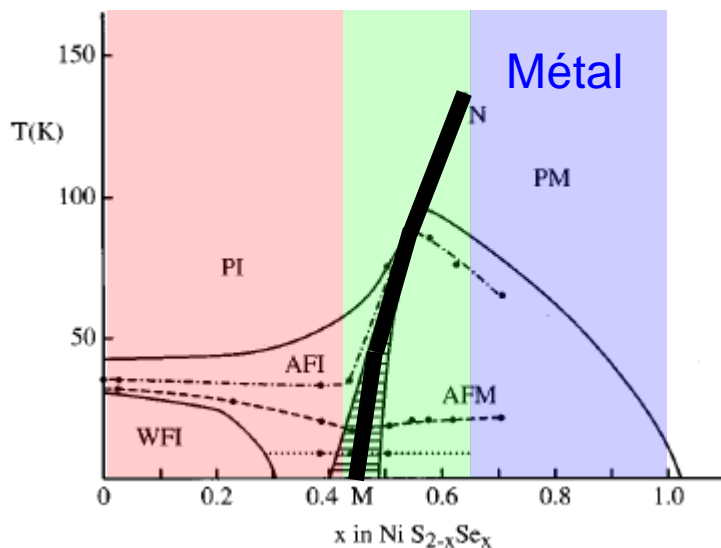


$\text{NiSe}_2$  métal

# La transition de Mott dans $\text{NiS}_{2-x}\text{Se}_x$

Honig and Spalek., Chem. Mater. 10, 2910 (1998)

Diagramme  
phase et  
résistivité :



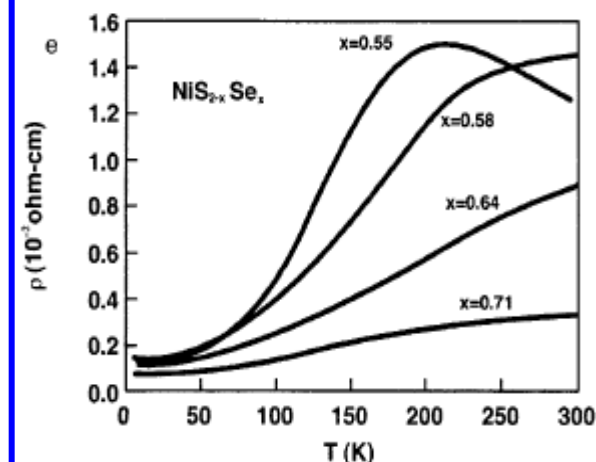
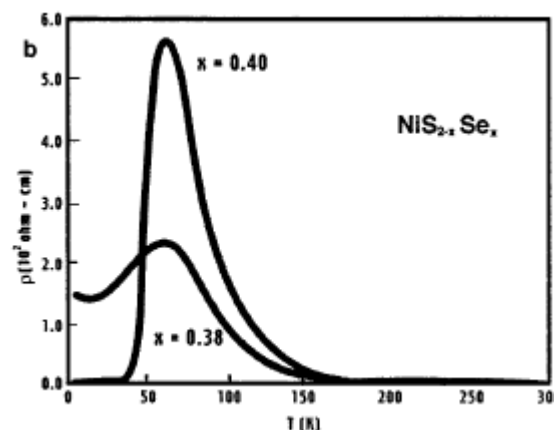
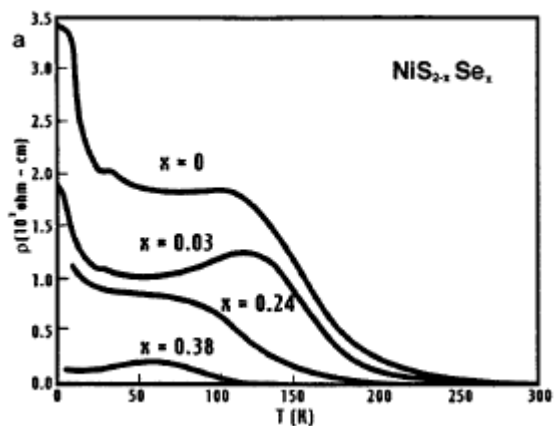
Pression chimique  
ou physique



Isolant

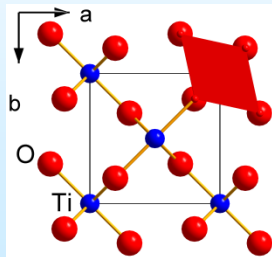
Transition de Mott

Métal

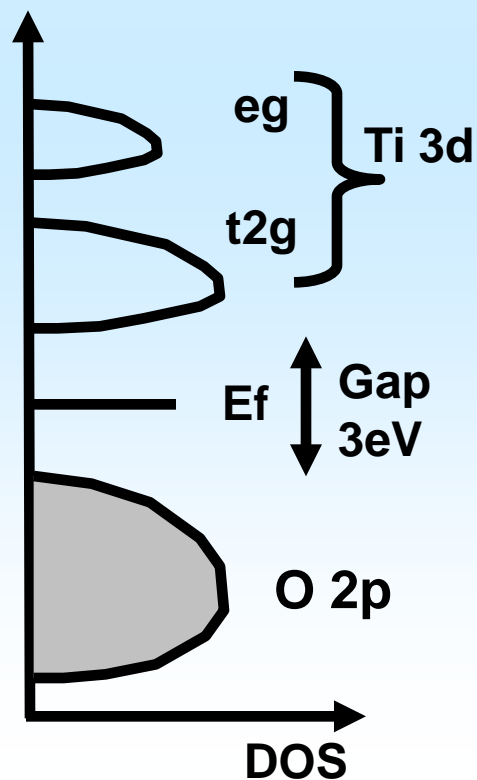


# Série $TiX_2$ ( $X=S, Se, Te$ ) : transition isolant semi-métal

$TiO_2$   
Rutile

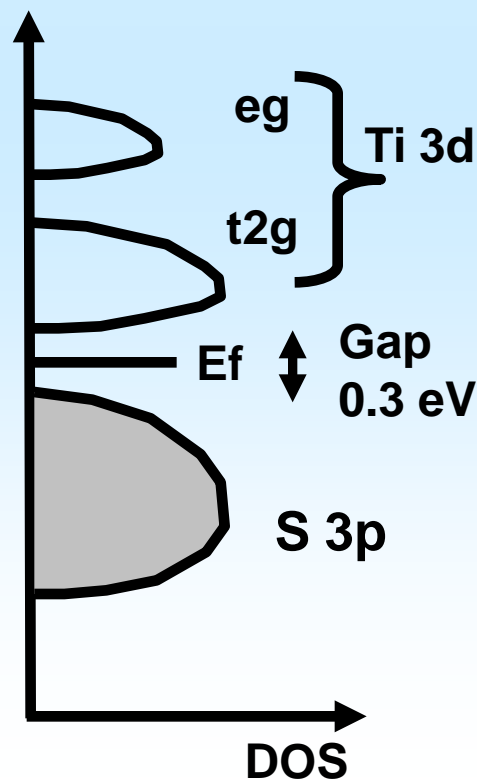


Energie



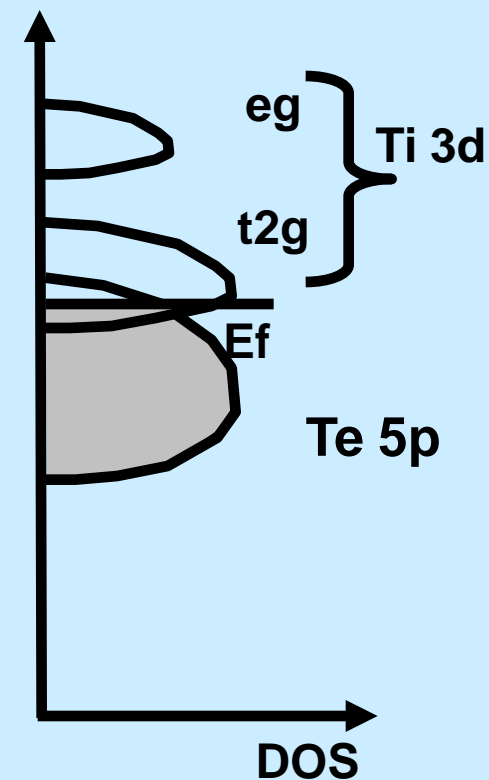
$TiS_2$  semi-  
conducteur

Energie



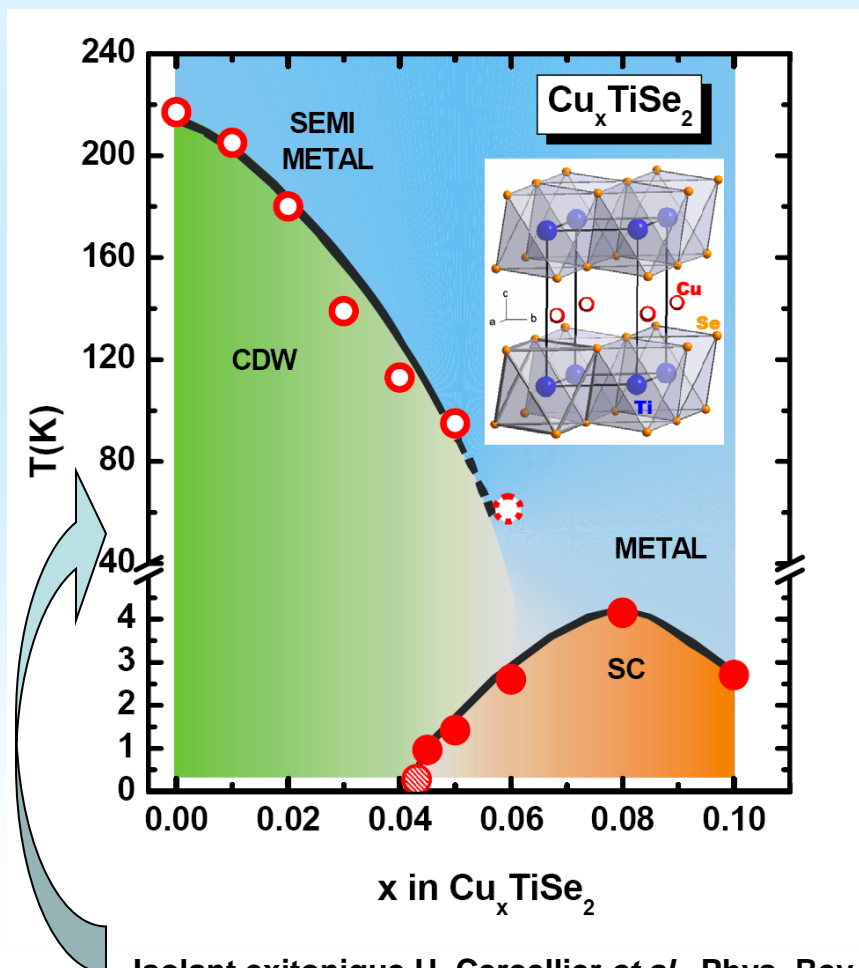
$TiSe_2$   $TiTe_2$   
semi-Métaux

Energie

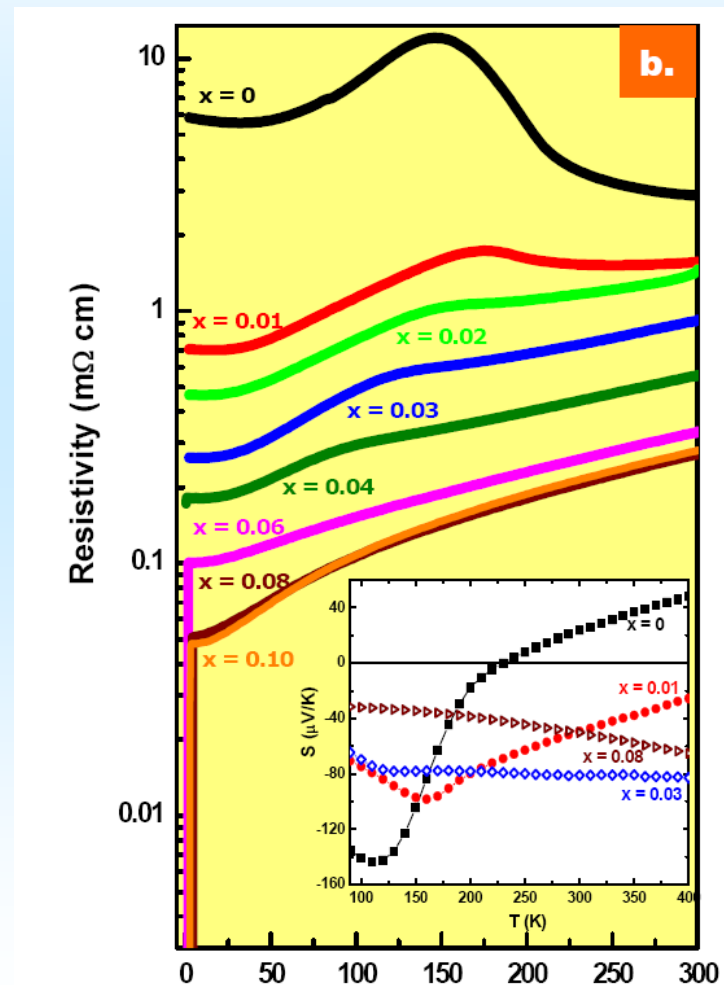


# $TiSe_2$ ( $X=S, Se, Te$ ) : Coexistence onde de densité de charges et supraconductivité

Cava et al. Nature Physics 2, 544 - 550 (2006)

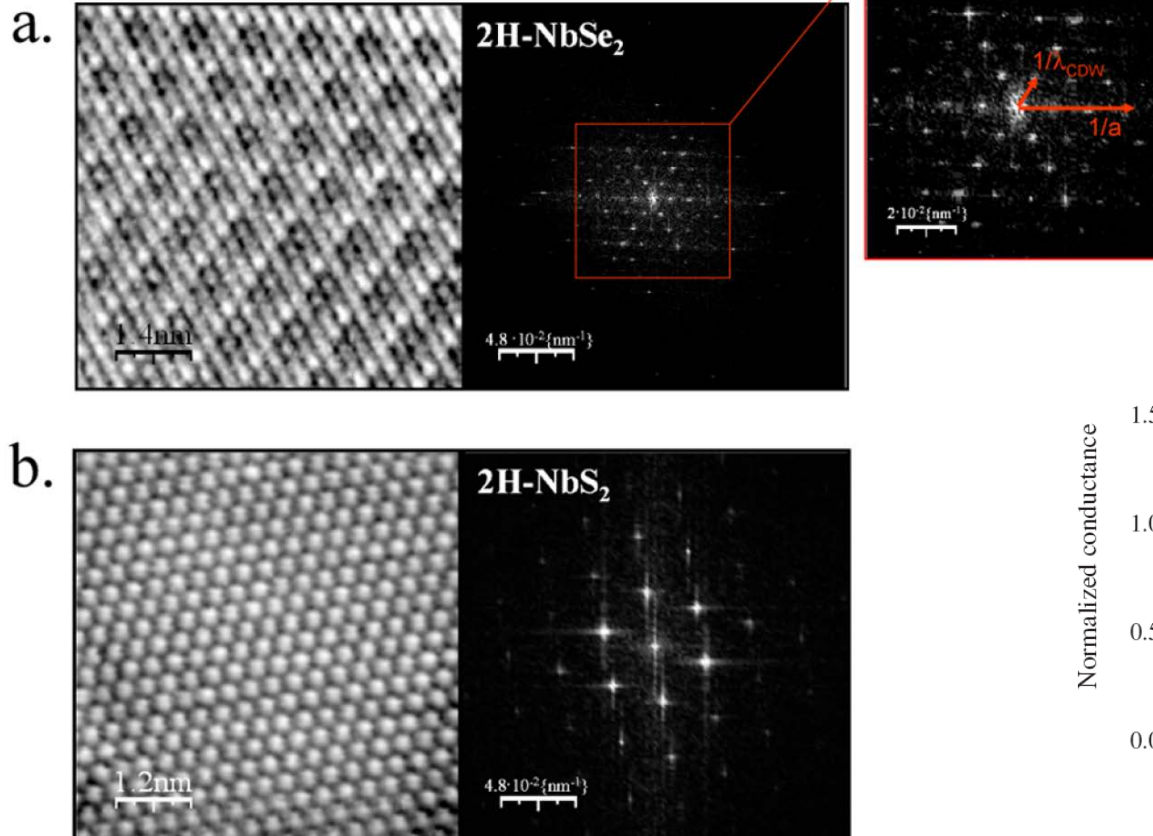


Isolant excitonique H. Cercellier *et al.*, Phys. Rev. Lett. 99, 146403 (2007)

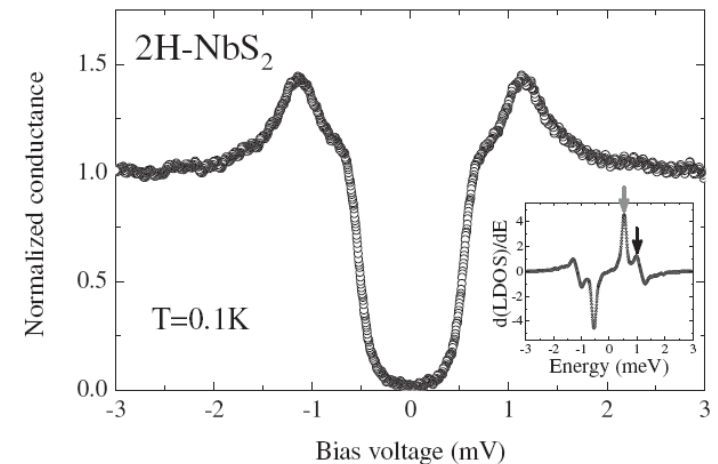


# $2H-NbX_2$ ( $X=S, Se$ ) : onde de densité de charges et supraconductivité non conventionnelle

STM

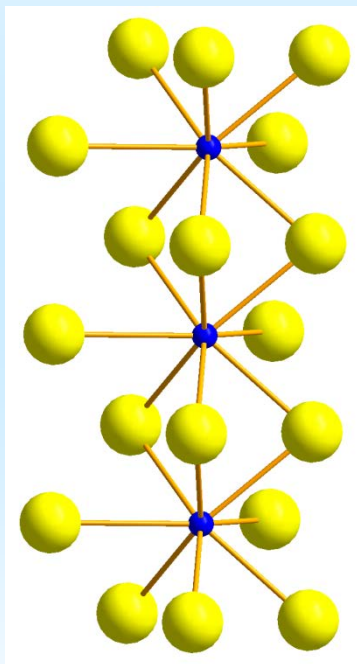


Supra à deux gaps ?

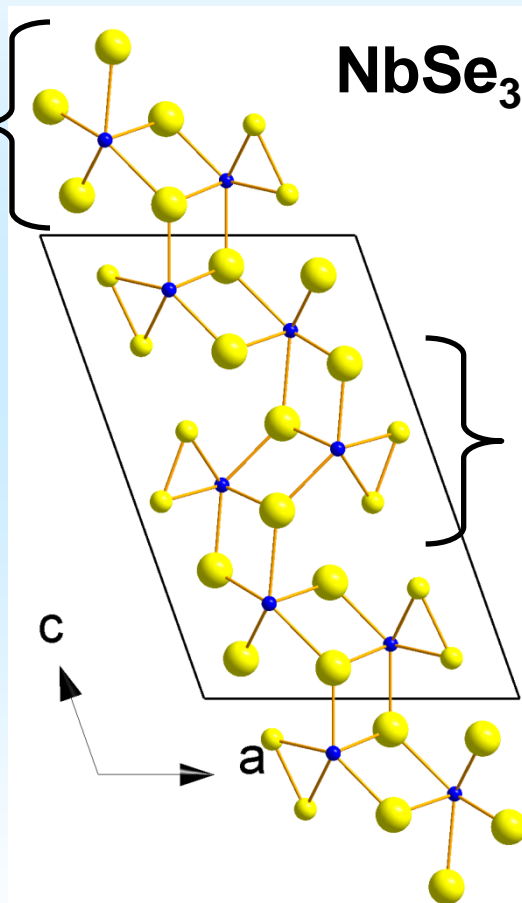


# Les phases 1D $NbSe_3$ , $TaS_3$ et $(TaSe_4)_3I$ : onde de densité de charges et non linéarités

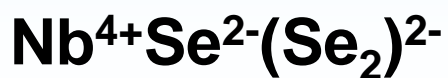
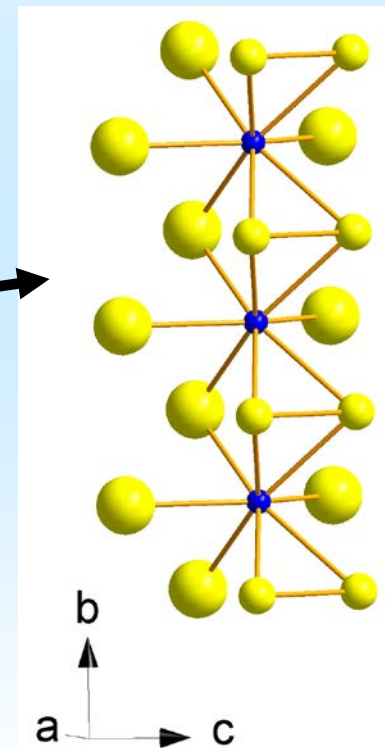
Chaîne sans paires  
de soufre



$NbSe_3$



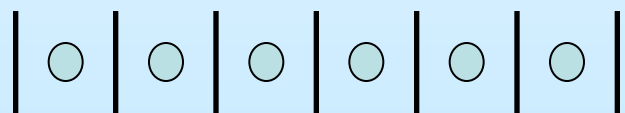
Chaîne avec paires  
De soufre



Chaines métalliques  
bandes demi-remplies

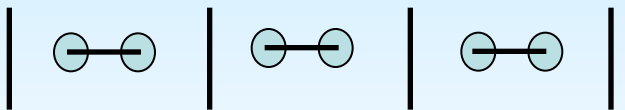
# Onde de densité de charges et non linéarités

La chaîne métallique demie remplie :  
instabilité de Peierls



a

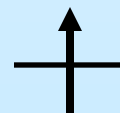
Dimèrisation



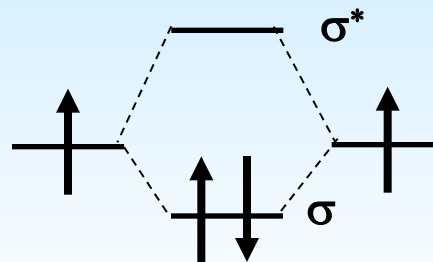
2 a

Maille

1 orbitale  
 $\frac{1}{2}$  remplie

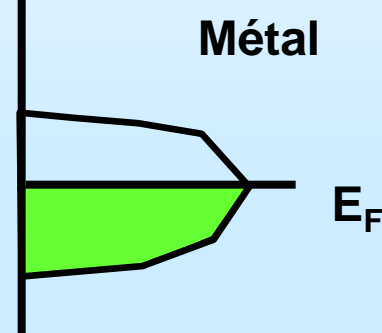


2 Orbitales  
 $\frac{1}{2}$  remplie



Formation  
d'une orbitale  
moléculaire

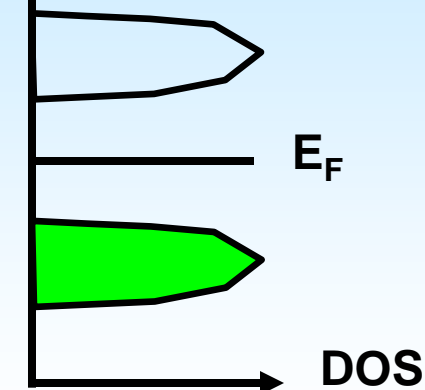
E Solide



Métal

$E_F$

E Solide



Isolant

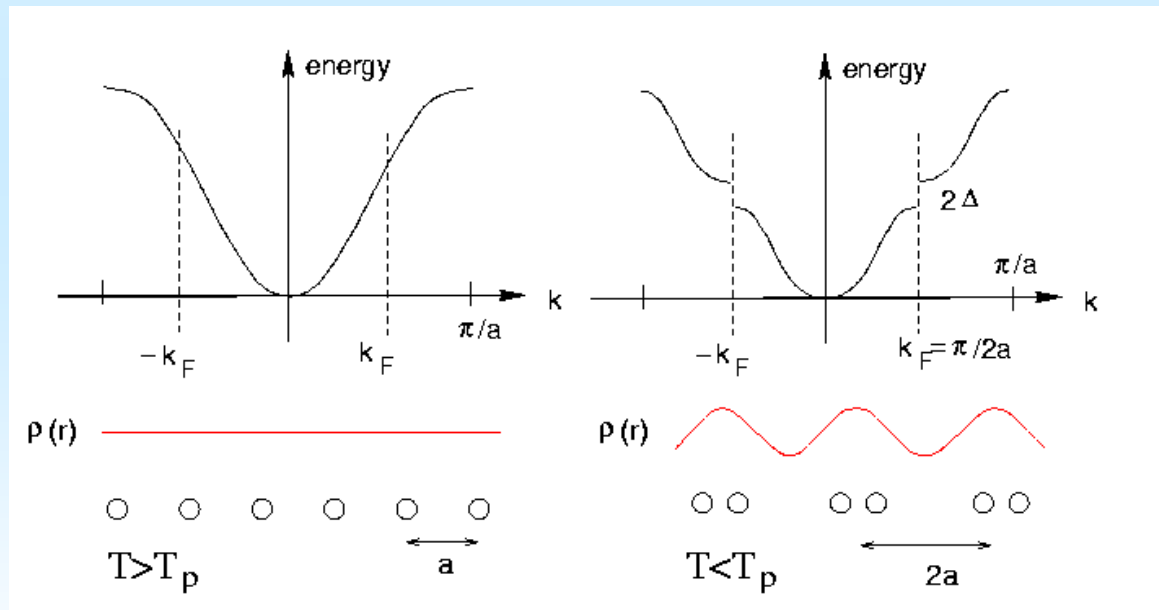
$E_F$

DOS



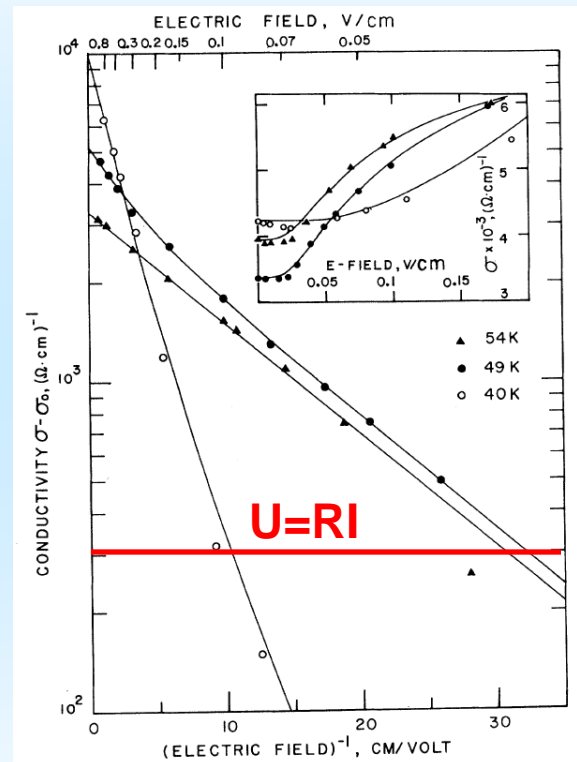
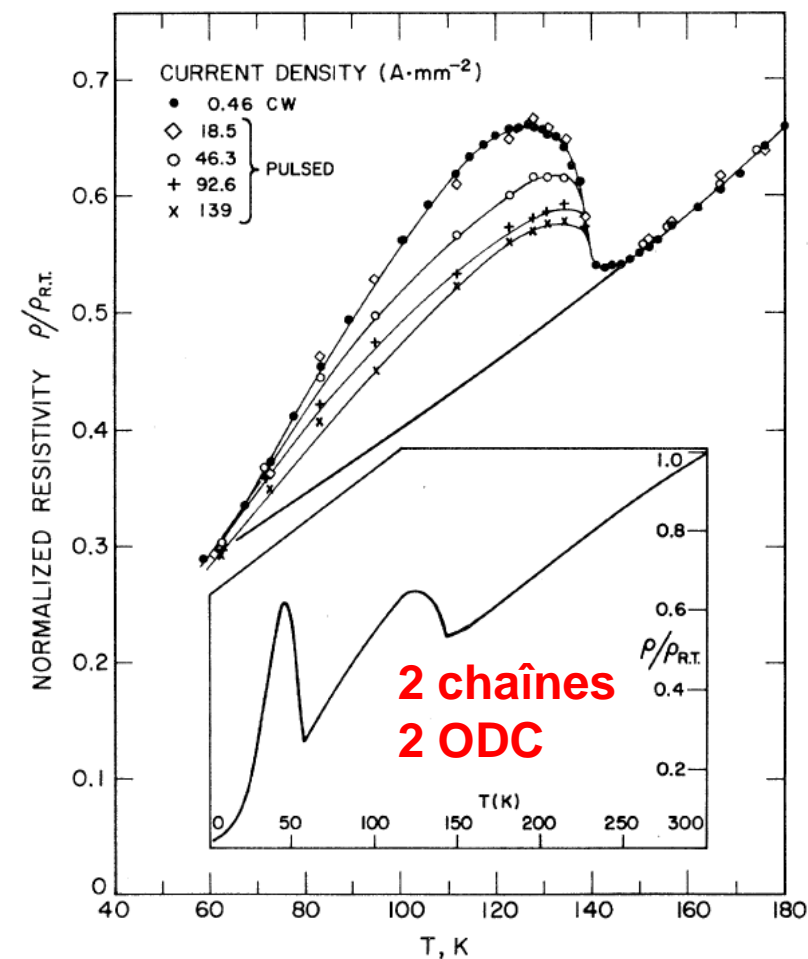
# onde de densité de charges et non linéarités

La chaîne métallique demie remplie :  
instabilité de Pierls



# $NbSe_3$ :

## onde de densité de charges et non linéarités



**Déviaton à la loi d'Ohm**  
**Décrochage de l'onde de densité de charge**

Electric Field Breakdown of Charge-Density-Wave-Induced Anomalies in  $NbSe_3$  †

P. Monceau,\* N. P. Ong, and A. M. Portis  
Department of Physics, University of California, Berkeley, California 94720

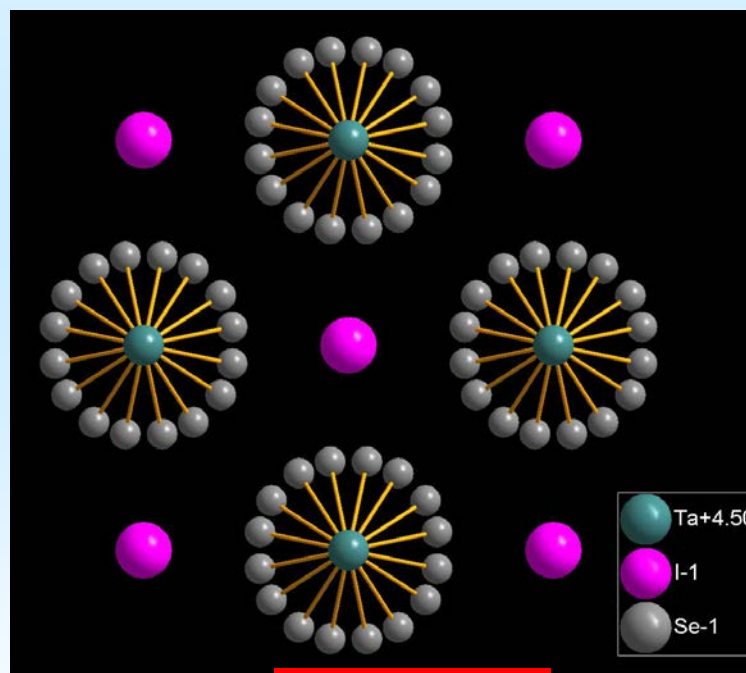
PRL 37, 602 (1976)

and

A. Meerschaut and J. Rouxel  
Laboratoire de Chimie Minérale A, 44037 Nantes Cedex, France  
(Received 1 June 1976)

# Autres conducteurs unidimensionnels ...

Composés inorganiques quasi-1D :



P. Gressier, L. Guemas, A. Meerschaut,  
*Acta Cryst. B* 38 (1982) 2877

Collaboration  
IMN – CRTBT

Phases 1D oxydes à ODC : Bronzes de Molybdène K<sub>0.3</sub>MoO<sub>3</sub> ... voir livre Claire Schlenker  
low dimensional electronic properties of molybdenum bronzes and oxides.

## *Conclusion*

- *Les grandes classes de composés ont des structures dérivant d'empilements simples*
- *Il existe une relation étroite entre la structure et les propriétés*
- *Des propriétés remarquables naissent :*
  - *à la proximité de la transition isolant métal de Mott*
  - *dans les composés de basse dimensionnalité*



UNIVERSITÉ DE NANTES

**INSTITUT DES MATERIAUX JEAN ROUXEL**  
**IMN UMR CNRS 6502 - Université de Nantes**



# Grandes classes de composés à propriétés électroniques remarquables

## 2. recherche de nouveaux composés

**Laurent Cario**

*Institut des Matériaux Jean Rouxel, Nantes (France)*

*Laurent.cario@cnrs-imn.fr*

# *Plan*

## **Partie 1 : Structures et propriétés des grandes classes de composés connus**

- 1. principaux types structuraux**
- 2. Oxydes de métaux de transition**
- 3. Chalcogénures de métaux de transition**

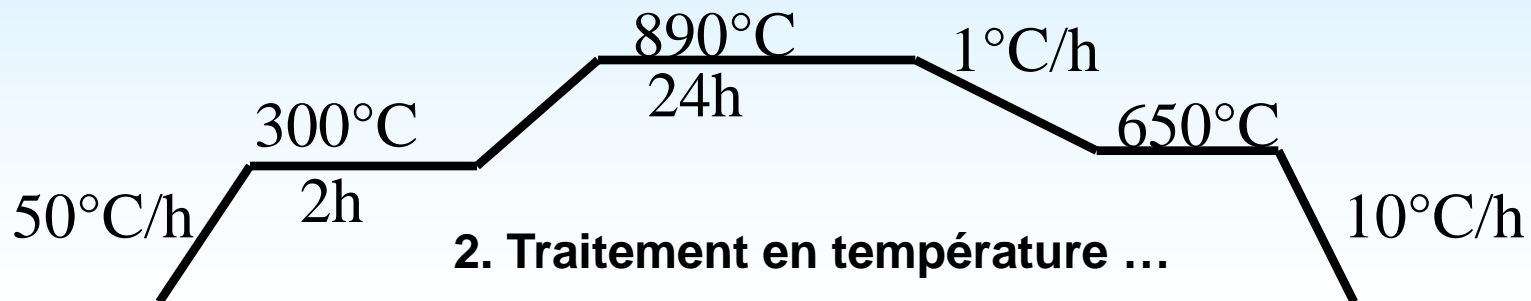
## **Partie 2 : Recherche de nouveaux composés inorganiques**

- 1. Synthèse et recherche exploratoire de nouveaux composés**
- 2. Outils de rationalisation en chimie inorganique**
- 3. Conception raisonnée de nouveaux composés inorganiques**

# *Comment synthétiser une céramique ?*

## **Synthèse par voie haute température**

**1. Mélange des précurseurs : éléments, composés binaires ...**



**3. Purification : rebroyage, pastillage, chauffage ...**

# Comment faire croître des cristaux ?

## 1. Méthode de transport en phase vapeur:

Iode, Chlore ...



Gradient de T

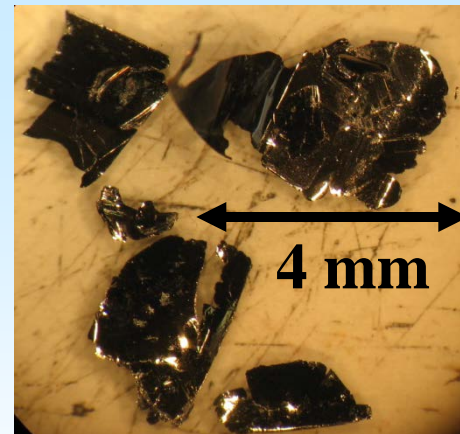
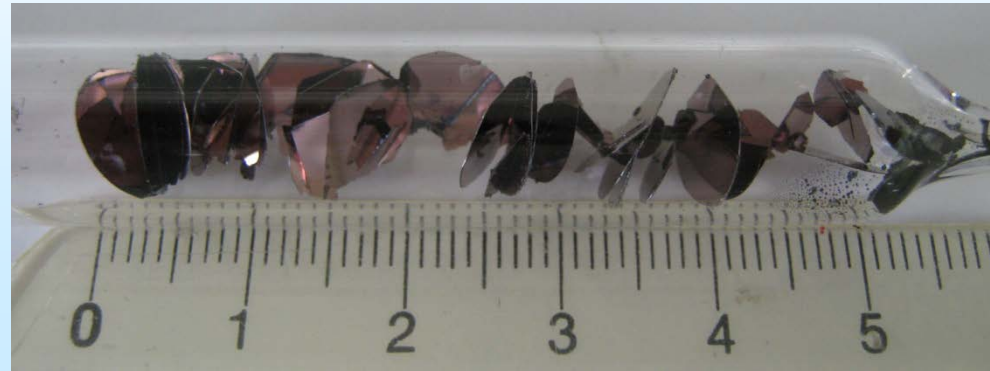


cristaux

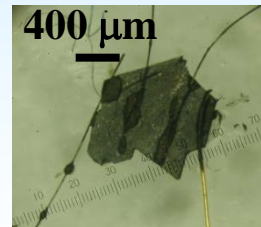
Poudre de  
départ +  
iode

Tube de quartz  
sous vide

Cristaux de  $\text{TiSe}_2$  @ S. Salmon



Cristaux de  
 $(\text{LaS})_{1.193}\text{VS}_2$



## 2. Méthode des flux :

**Croissance dans un bain solubilisant partiellement le composé**

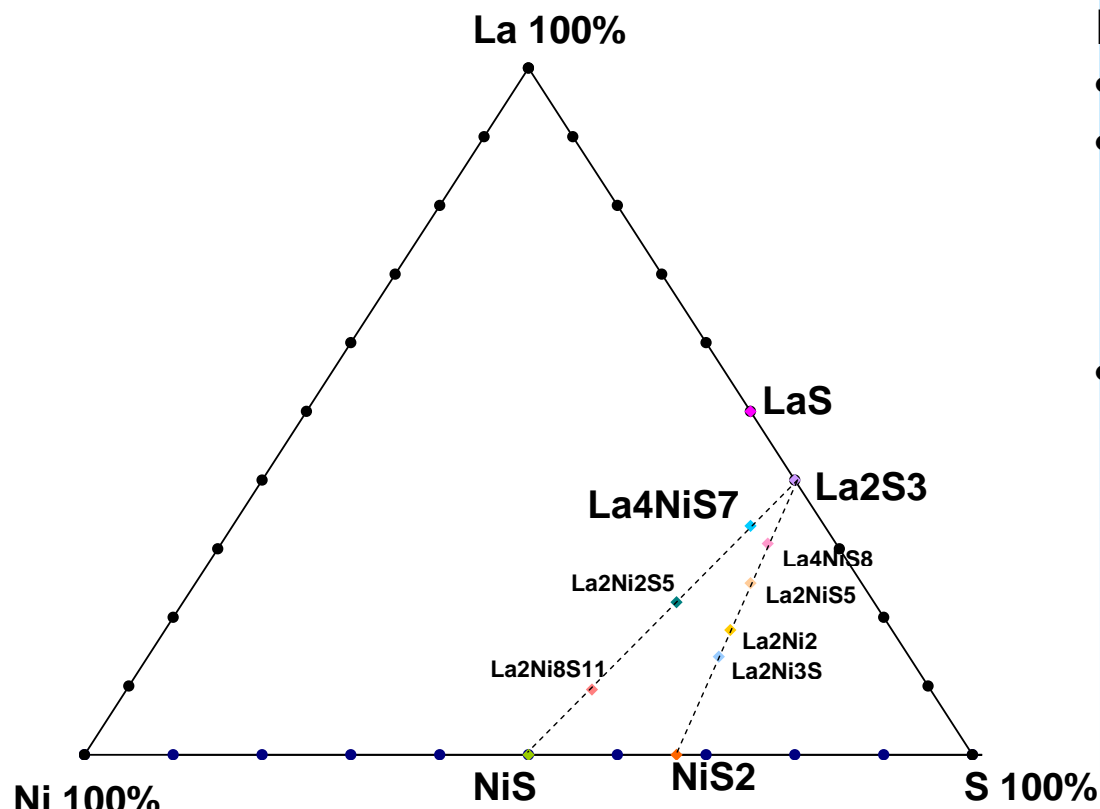
Ex :  $\text{LiVO}_2$  (flux  $\text{LiBO}_2$ ) : valence  $\text{V}^{3+} \Rightarrow$  stable pour  $p\text{O}_2 \approx 10\text{-}20$  atm vers  $850^\circ\text{C}$



# Comment faire des nouveaux composés ?

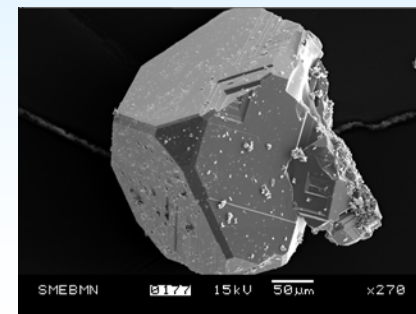
## 1 – exploration systématique

Pour composés ternaires :  
Espace des compositions à 3 dimensions  
+ choix de la température de synthèse ....



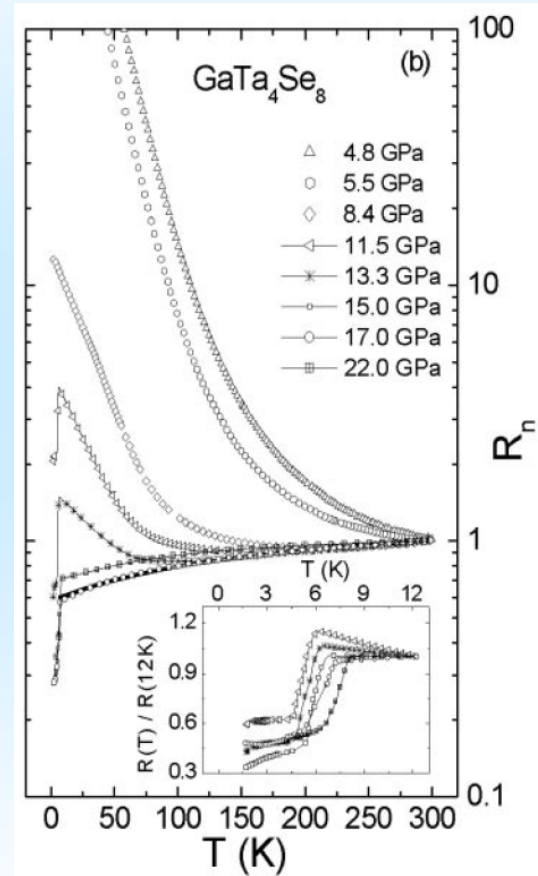
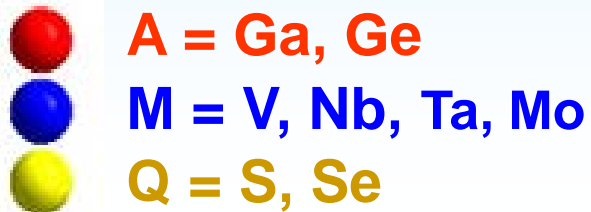
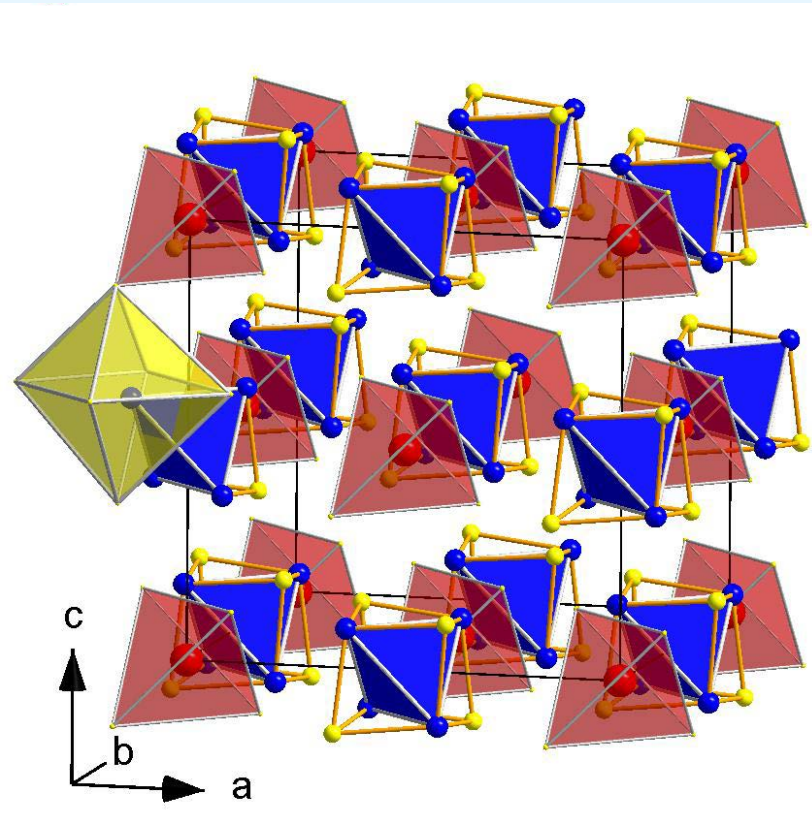
Démarche :

- Synthèse
- détection de phases nouvelles :
  - DRX,
  - Analyses chimiques (SEM)
  - MET
- Synthèse de cristaux des phases repérées : étude structurale



# Comment faire des nouveaux composés ?

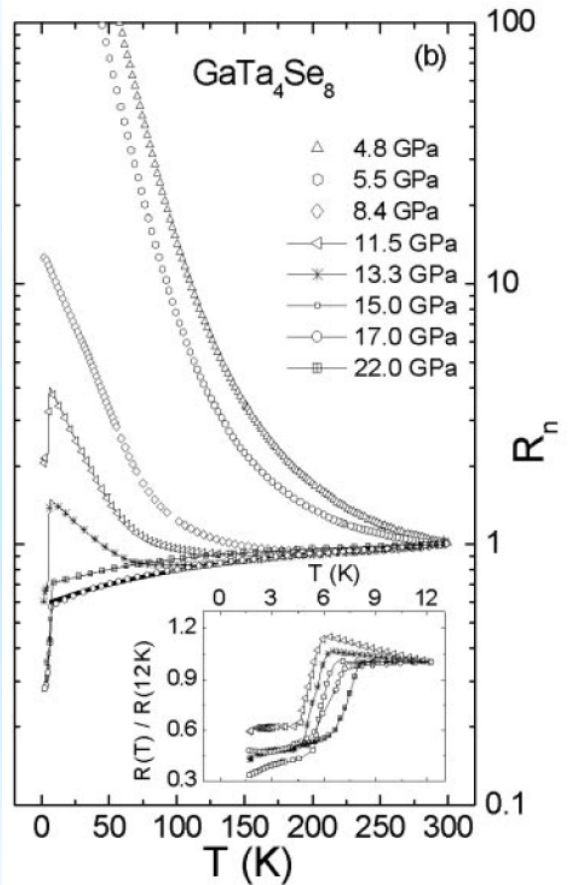
## 2 – exploration ciblée



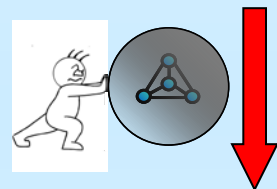
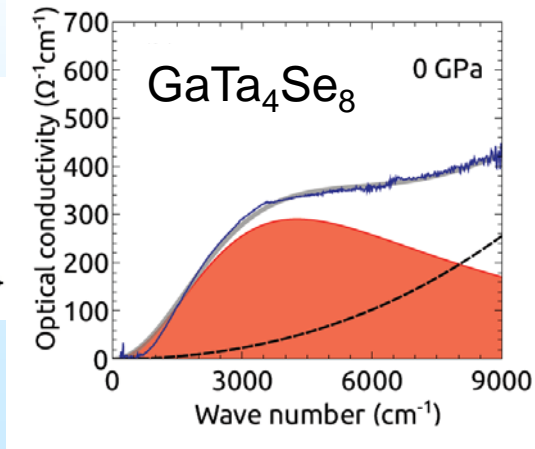
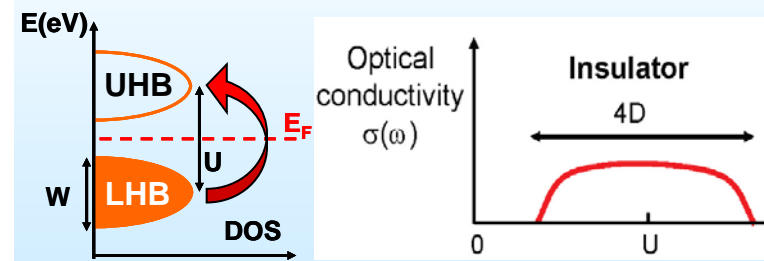
Abd-Elmeguid et al.  
*Phys. Rev. Lett.*  
**93**, 126403 (2004)

**AM<sub>4</sub>Q<sub>8</sub> : isolants de Mott ?**

# TMI contrôlée par la largeur de bande dans les $AM_4Q_8$

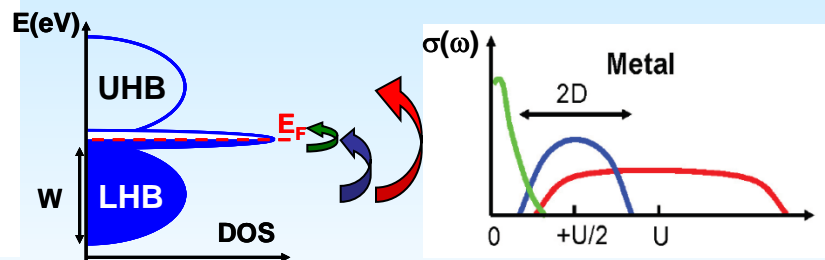


## Mott Insulator

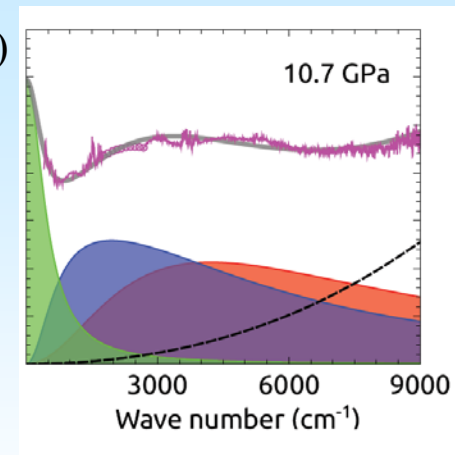


Pressure

## Correlated Metal



$\sigma(\omega)$



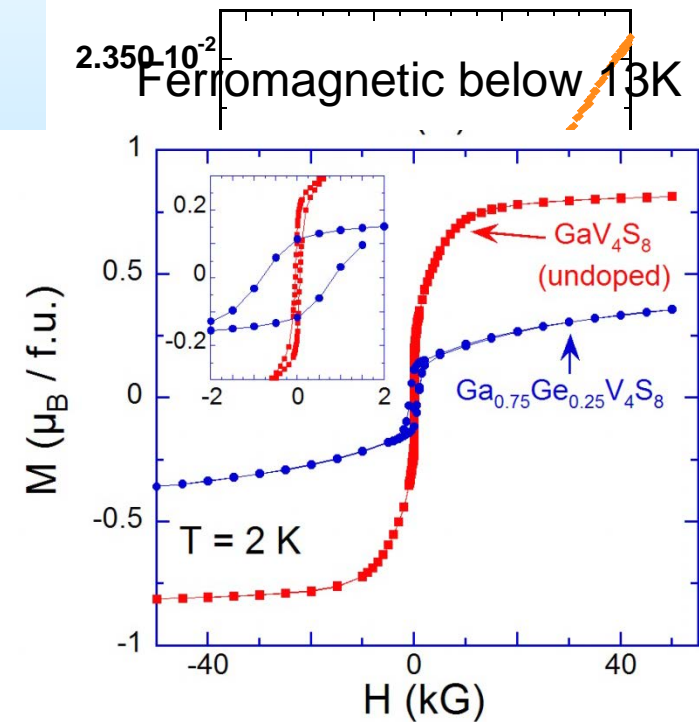
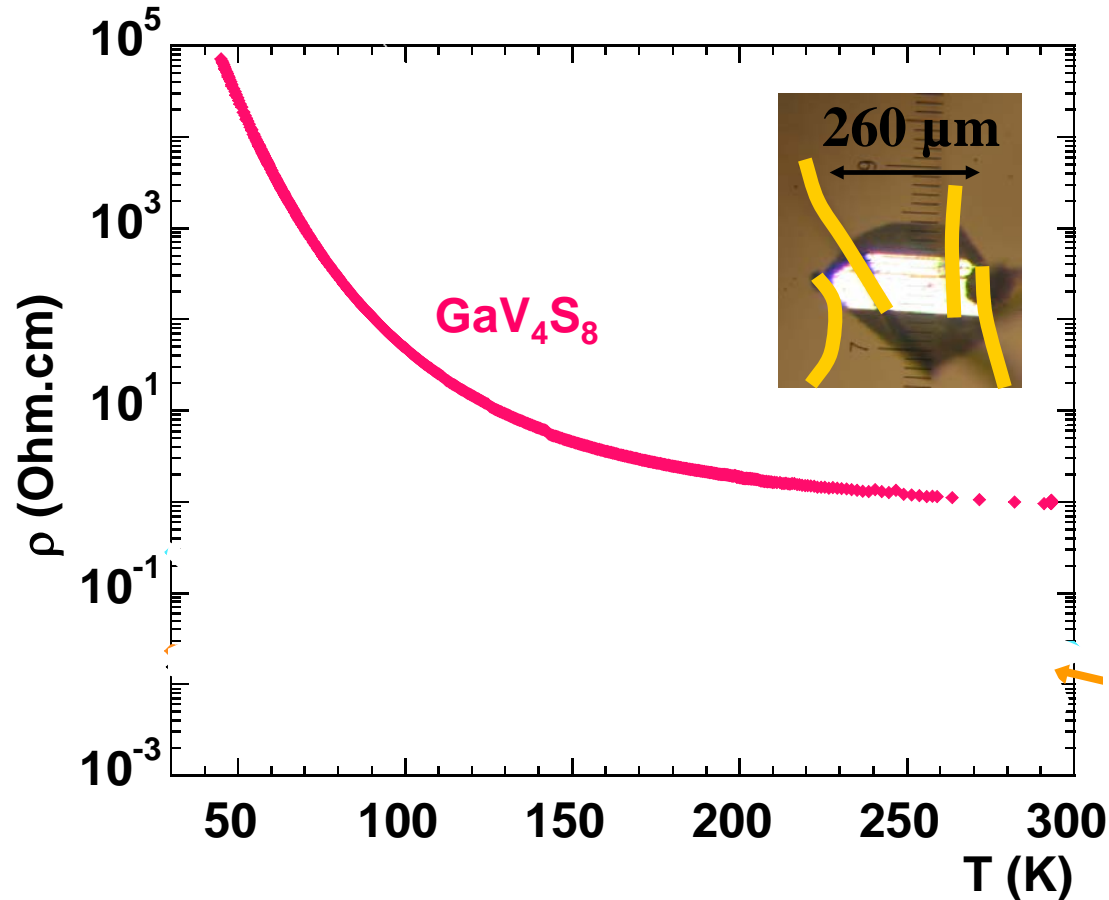
Abd-Elmeguid et al.,  
Phys. Rev. Lett. **93**, 126403 (2004)

R. Pocha et al.,  
J. Am. Chem. Soc. **127**, 8732 (2005)

Vinh Ta Phuoc et al. *Phys Rev Let.* **110**, 037401 (2013)

**Mott insulator - metal transition under pressure**

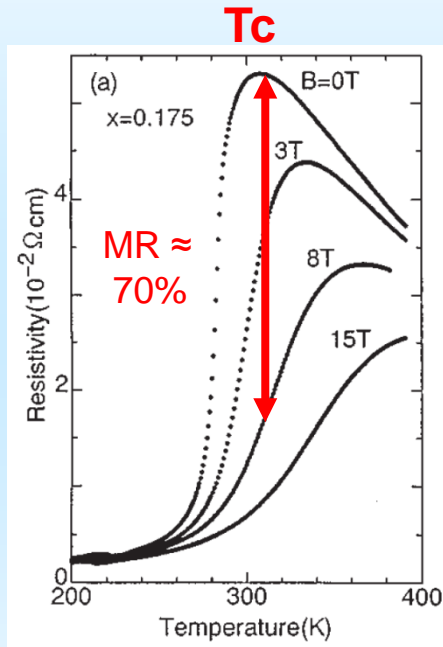
*Exploration ciblée (chimie du petit x) :*  
*recherche TMI contrôlée par le dopage dans  $\text{Ga}_{1-x}\text{Ge}_x\text{V}_4\text{S}_8$*



**$\text{Ga}_{1-x}\text{Ge}_x\text{V}_4\text{S}_8$  a Mott transition in a Ferromagnetic system**

# Recherche de nouvelles propriétés

## Manganites



→ negative CMR

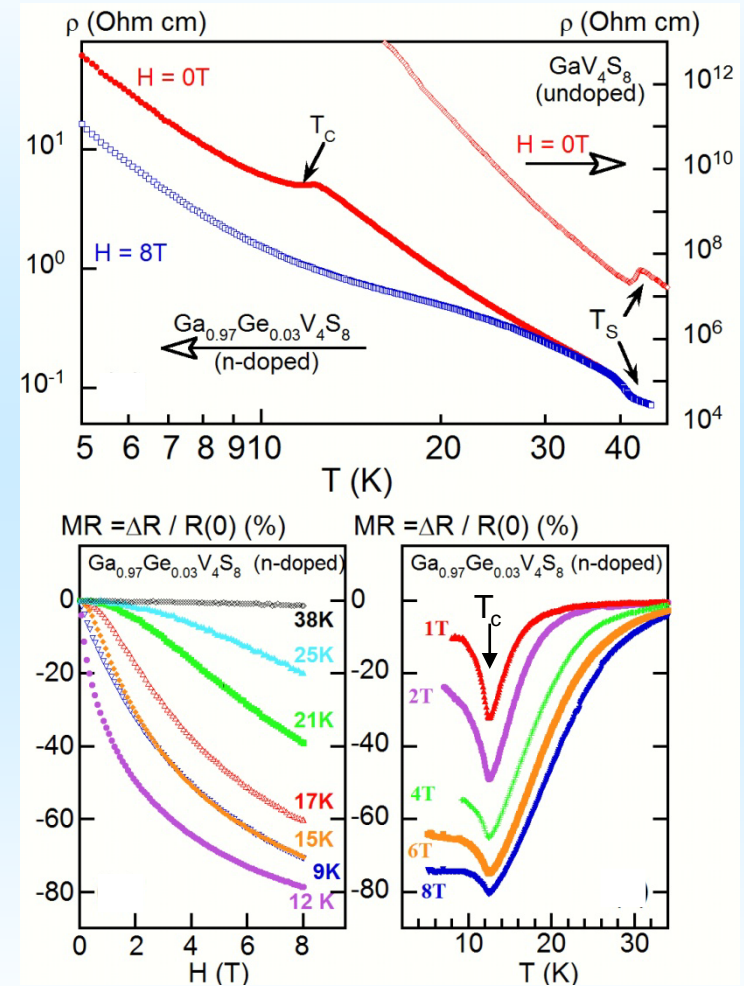
$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $x=0.175$ ) crystal

Tokura *et al.*,

J. Phys. Soc. Jpn. **63**, 3931 (1994)

## Ge-doped $\text{GaV}_4\text{S}_8$

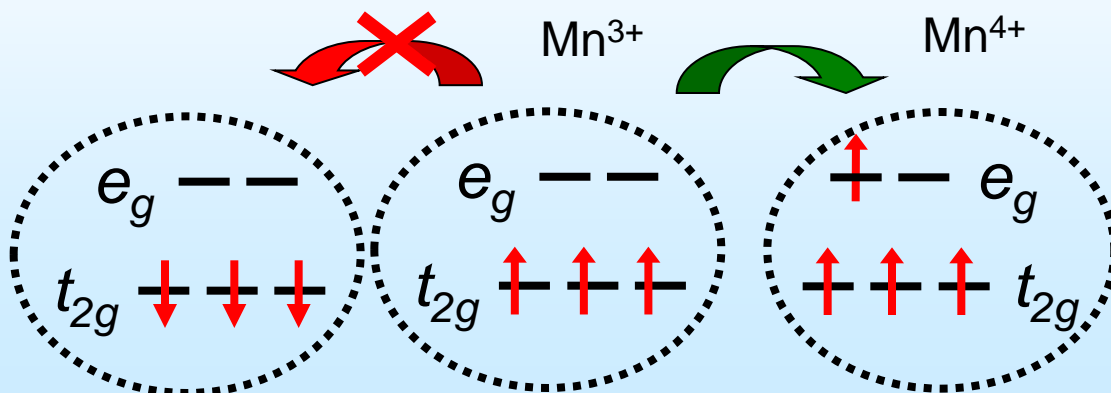
E. Janod *et al.*  
Submitted



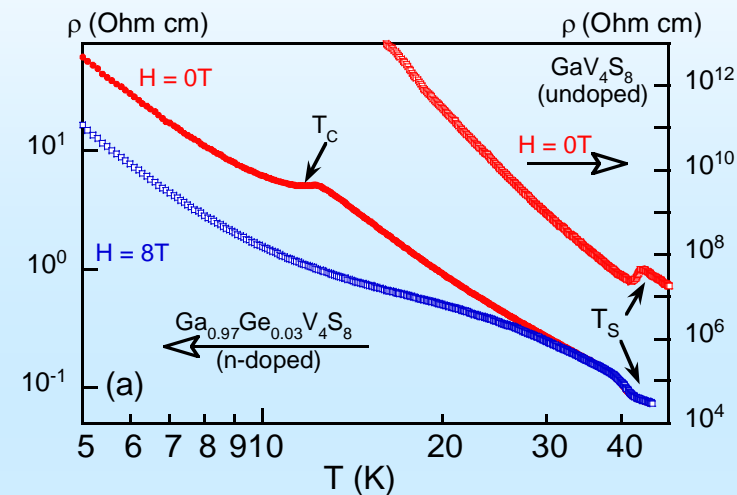
$\text{Ga}_{1-x}\text{Ge}_x\text{V}_4\text{S}_8$  un nouveau système CMR

# Recherche de nouvelles propriétés

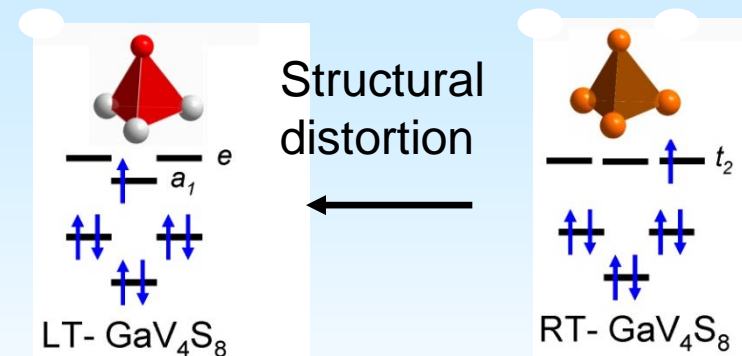
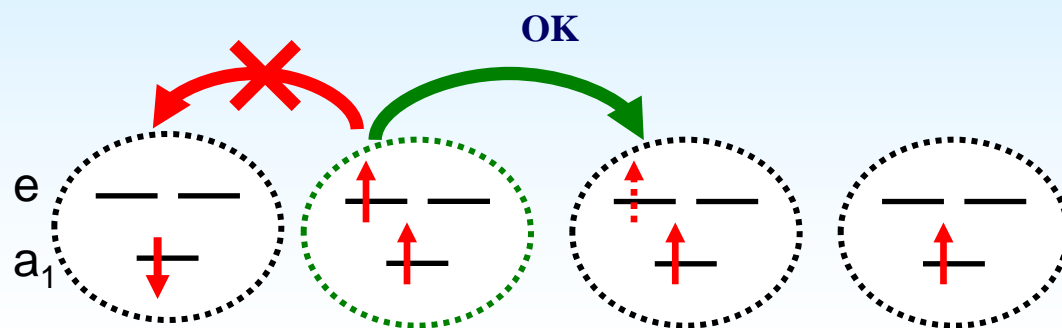
## Manganites



## Ge-doped GaV<sub>4</sub>S<sub>8</sub>



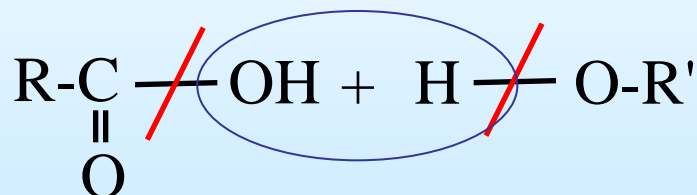
**GaV<sub>4</sub>S<sub>8</sub> n-doped**  
**→ negative CMR**



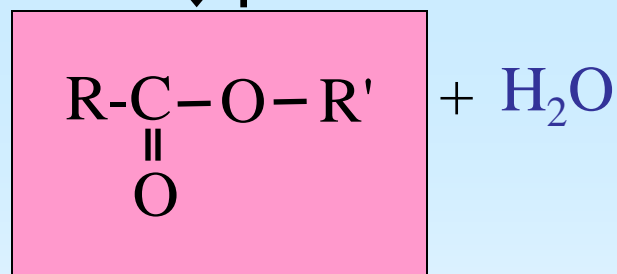
H. Müller, W. Kockelmann  
 and Dirk Johrendt,  
*Chem. Mater.* **2006**, 18, 2174.

# Nouveaux composés organiques : conception et rétro-synthèse

Rétro-synthèse



Contrôle de la structure



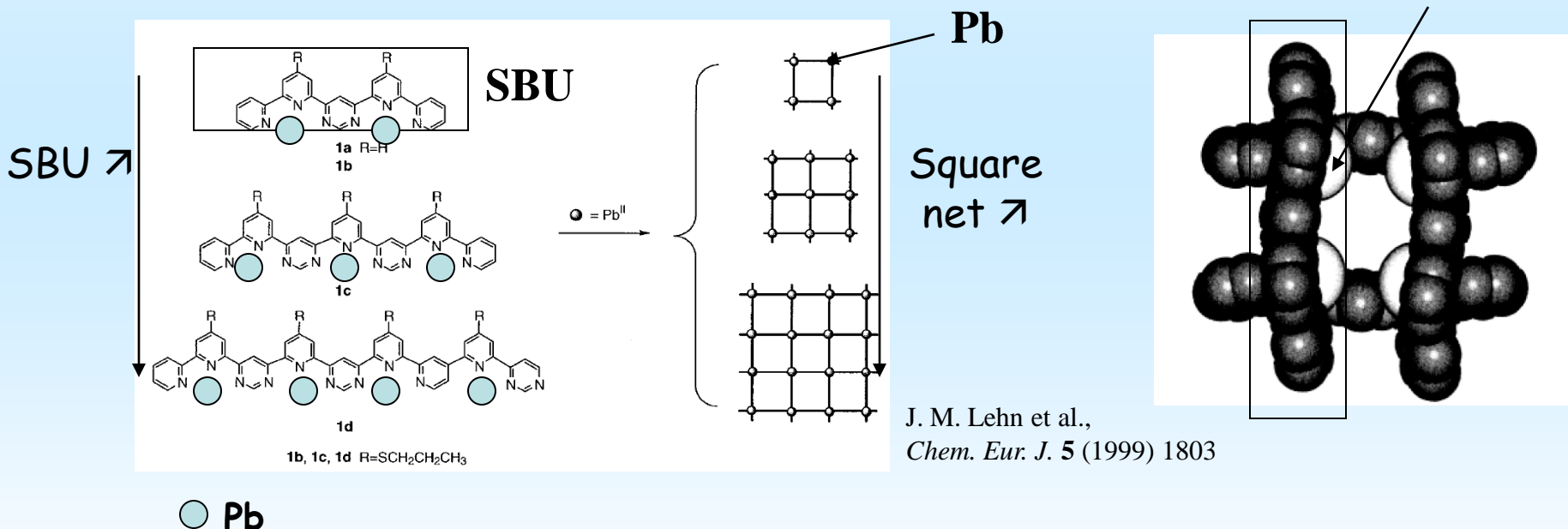
Contrôle des propriétés

Fonctionnalisation

# Composés supramoléculaires et concept de SBU

« SBU » Secondary Building Units

Assembly of SBU = supramolecular compound



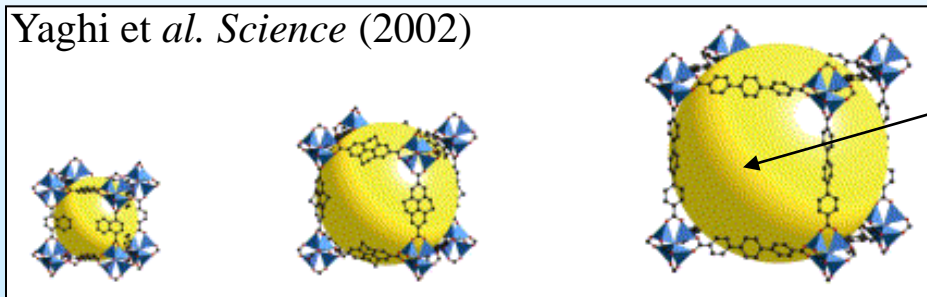
*Supramolecular compounds can be designed by auto-assembling Secondary Building Units (SBU).*



# Composés hybrides : liés des SBU inorganiques

- « MOF » METAL OXIDE FRAMEWORK compounds

Yaghi et al. *Science* (2002)

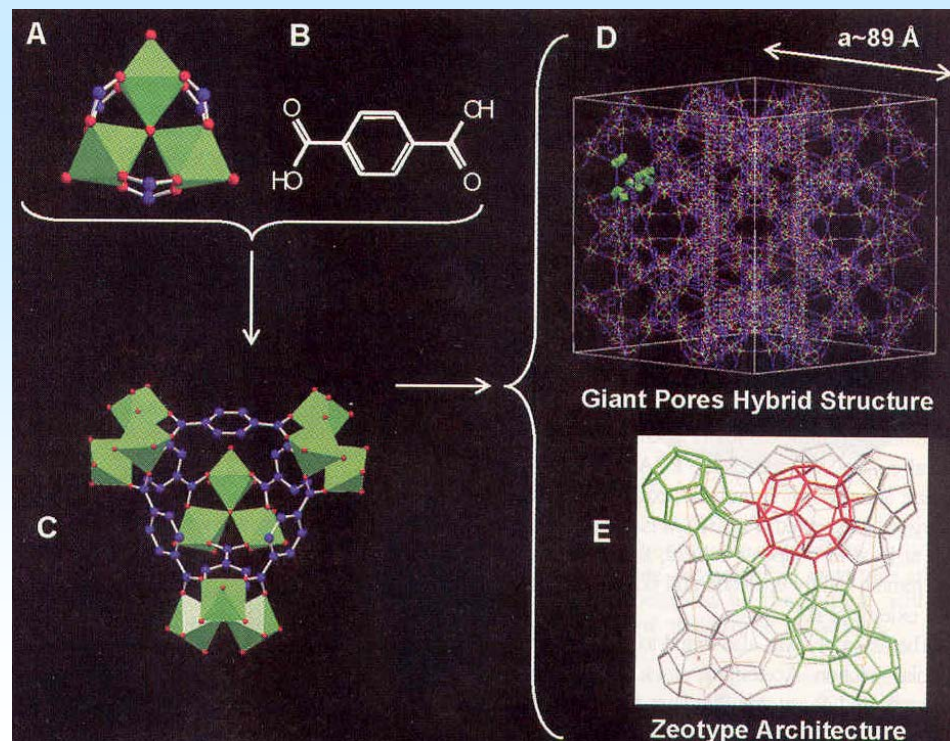


Pore size tuned with the  
organic linker

- « MOF » with giant pores

→ MIL101

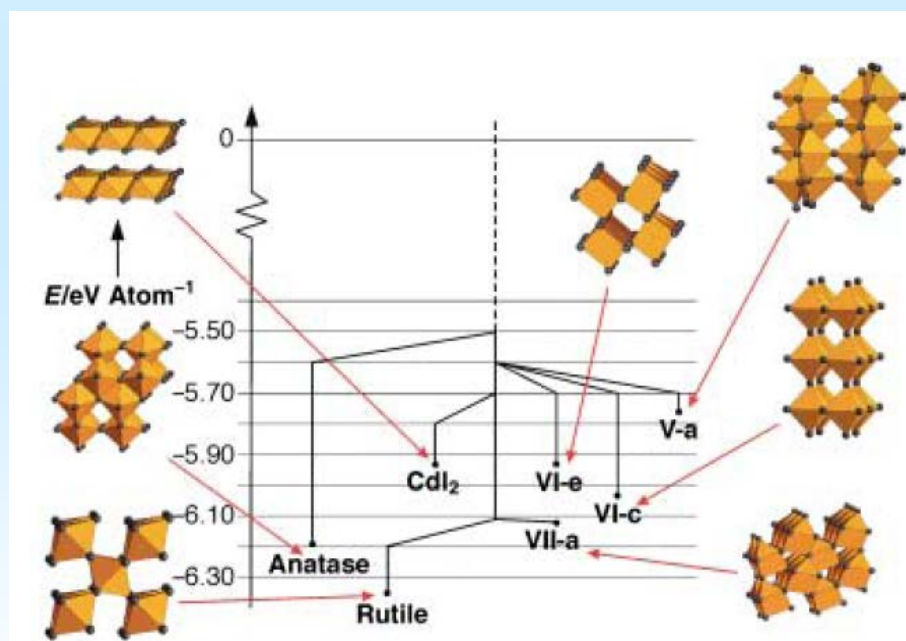
Férey et al. *Science* (2005)



# Composés inorganiques

## 1- prédiction des structures

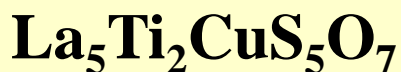
Exploration of the energy landscape of  $\text{MgF}_2$



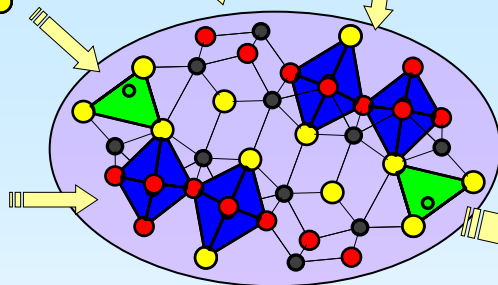
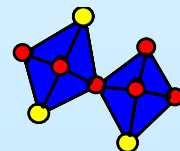
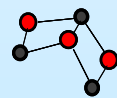
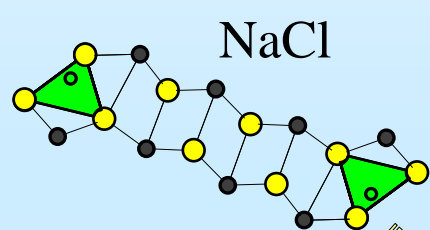
J. C. Schoen and M. Jansen, *Angew. Chem. Int. Ed.* **35** (1996) 1286 ;  
M. Jansen, *Angew. chem. Int. Ed.* **41** (2002) 3746.

## Composés inorganiques

## 2 – description modulaire et série d'homologues



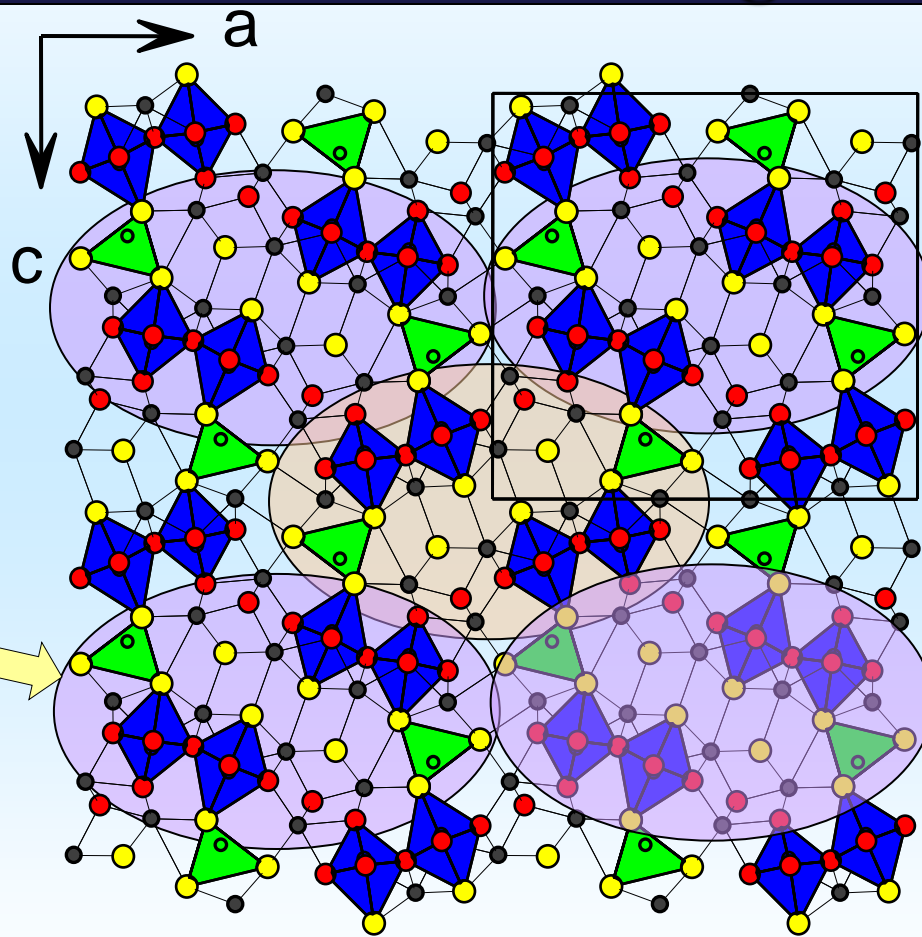
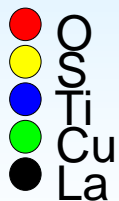
NaCl



Pérovskite



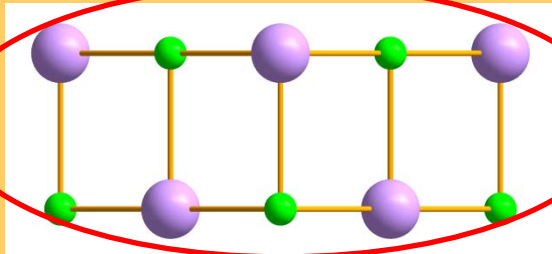
Anti-fluorite



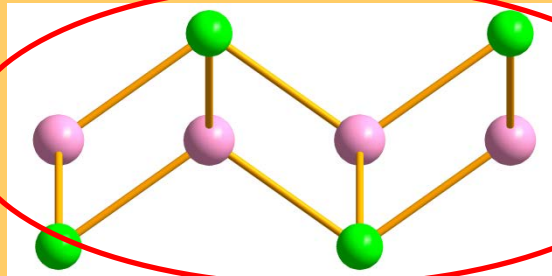
The structure can be built from  
three types of modules



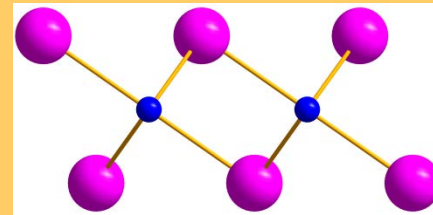
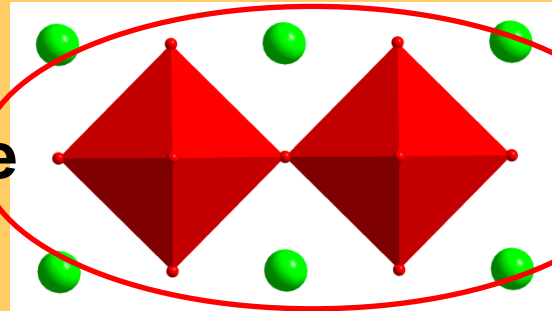
**NaCl**



**Fluorine**



**Pérovskite**



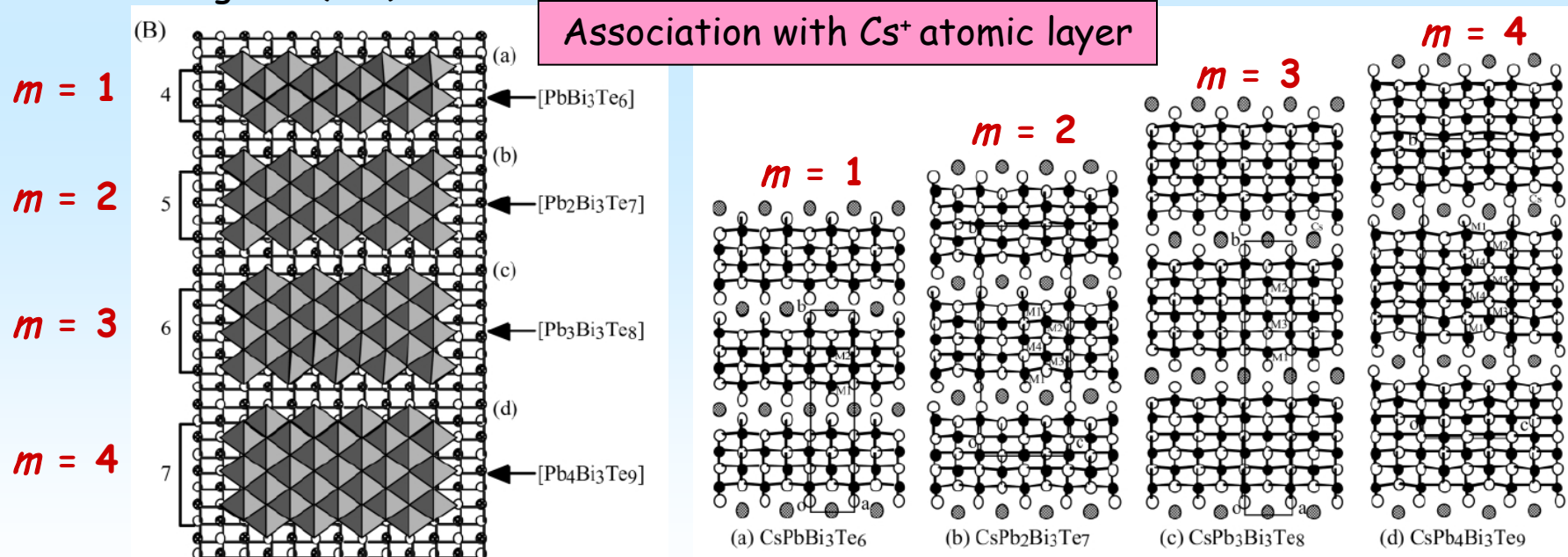
**CdI<sub>2</sub>**

# Composés inorganiques

## 2 – description modulaire et série d'homologues

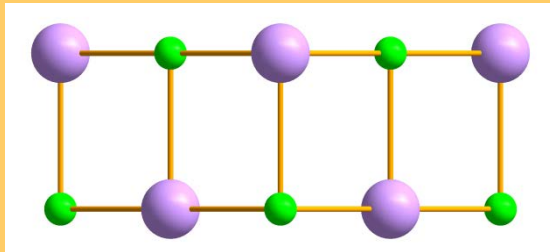
homologous series  $\text{CsPb}_m\text{Bi}_3\text{Te}_{5+m}$   
Obtained from PbTe type modules

PbTe structure (NaCl type)  
along the (110) direction

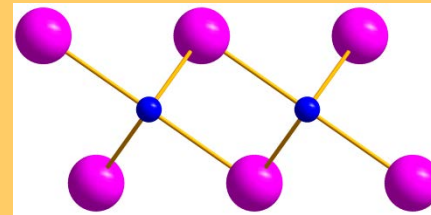




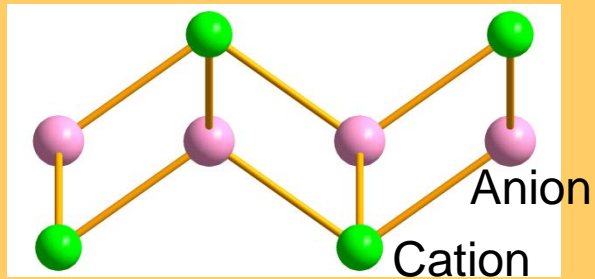
**NaCl**



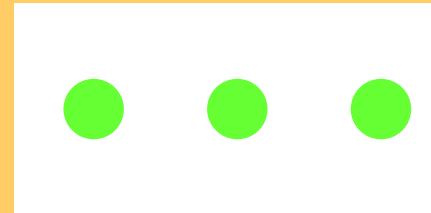
**CdI<sub>2</sub>**



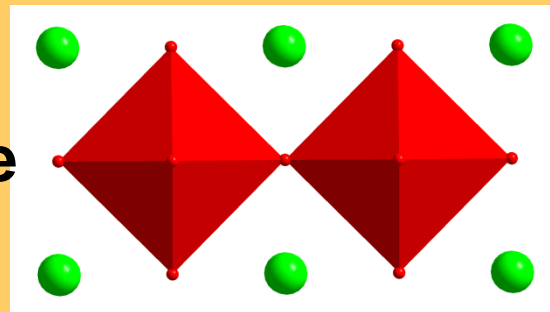
**Fluorine**



**Feuillet atomique**



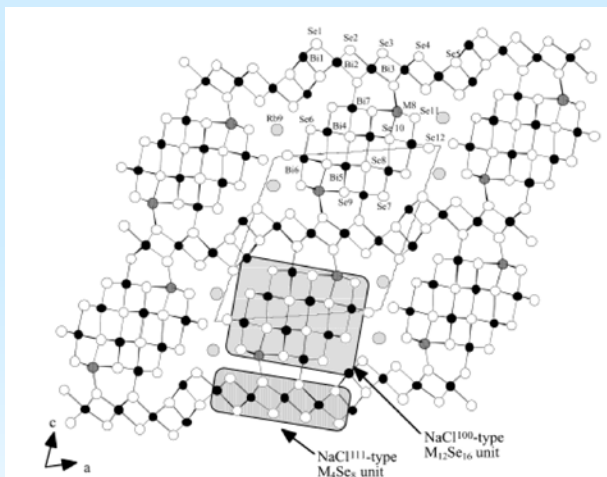
**Pérovskite**



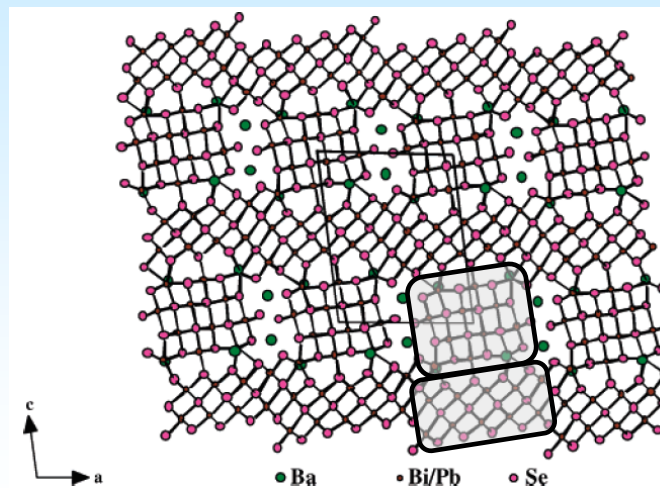
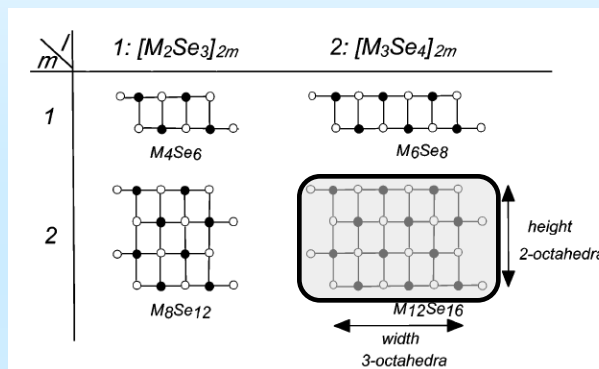
## Composés inorganiques

## 2 – description modulaire et série d'homologues

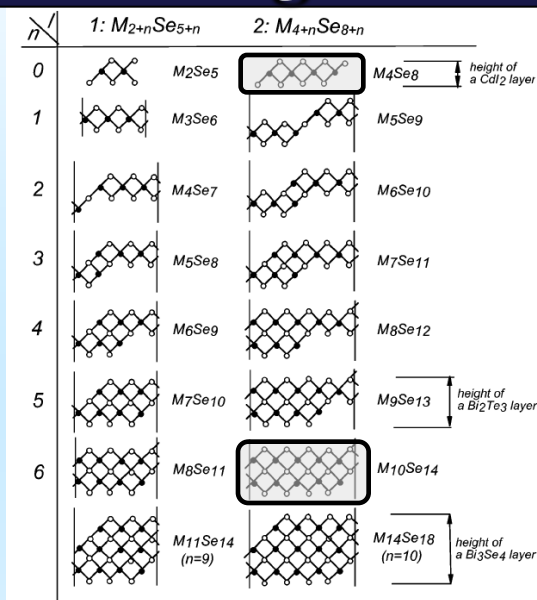
Megaséries  $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{2l+n}Se_{2+3l+n}]$



$RbSnBi_7Se_{12}$  ( $m=2$ ,  $l=2$ ,  $n=0$ )



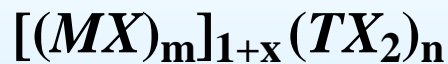
$Ba_{2+x}Pb_{4-x}Bi_6Se_{15}$  ( $l=2$ ,  $m=2$ ,  $n=6$ ).



A. Mrotzek and M. G. Kanatzidis, *Acc. Chem. Res.* **36** (2003) 111.

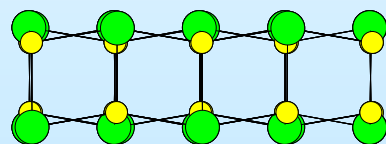
# Les phases misfits : série d'homologues 2D

A. Meerschaut (ed.),  
Materials Science Forum, 100-101 (1992)

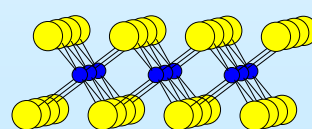
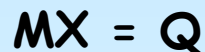


M = Sn, Sb, Pb, Bi, Rare Earths  
T = Ti, V, Cr, Nb, Ta ; X = S, Se

2D Modules

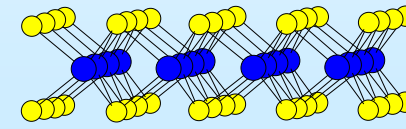
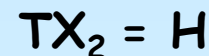


● M ● X



● T (Ti, V, Cr)

● X

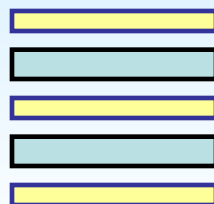


● T (Nb, Ta)

Different sequence types mQ/nH m = 1, 1.5, 2 and n = 1, 2 or 3



2Q/1H



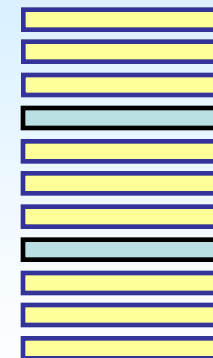
1.5Q/1H



1Q/1H



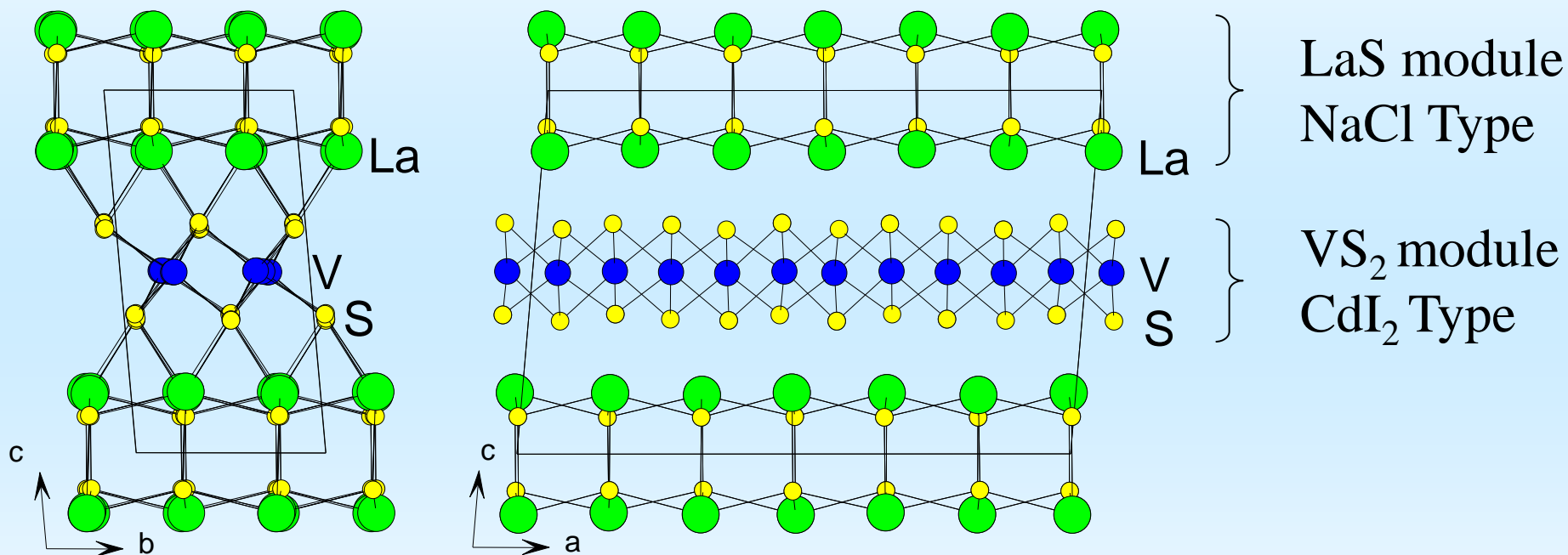
1Q/2H



1Q/3H

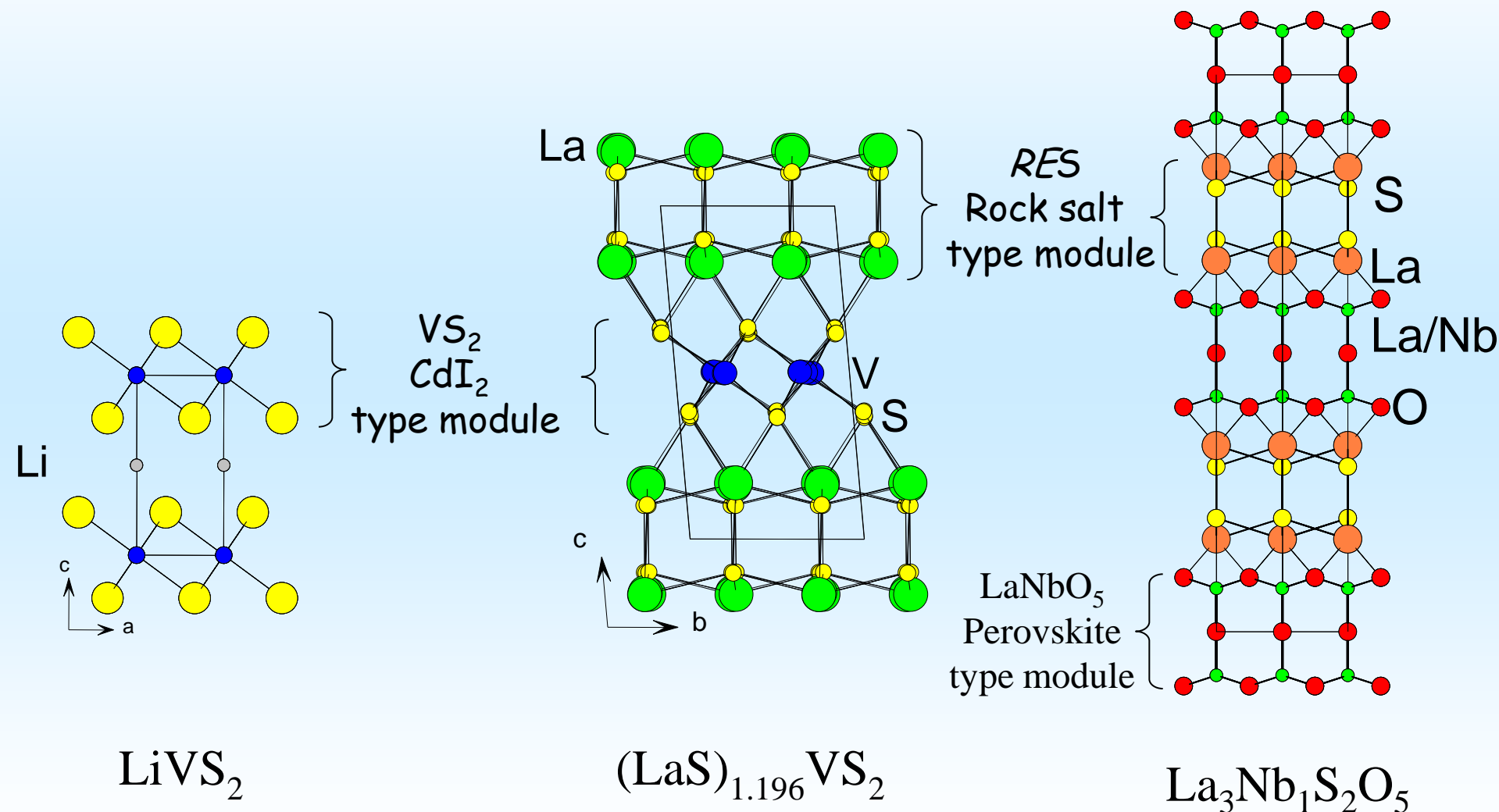


# La série d'homologues misfits 2D : Structure incommensurable de $(LaS)_{1.196}VS_2$

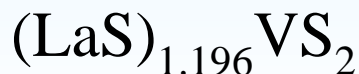


Triclinic (3+1)D Superspace Group  $X\bar{1}(\alpha\beta\gamma)$  with pseudo C centering

# Modules 2D et environnements chimiques



van Laar, B. Ijdo, D.J.W.  
JSSC 1971

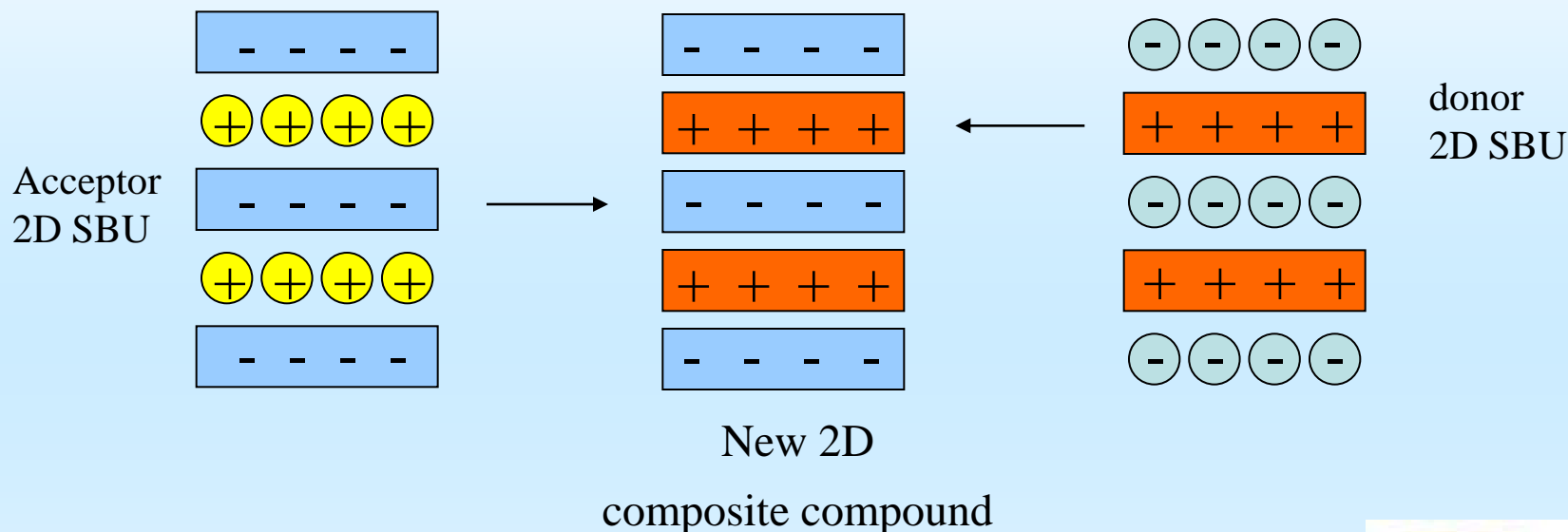


L. Cario et al.  
Mater. Res. Bul. 40 (2005) 125



L. Cario et al.  
Inorg. Chem. 46, 9584 (2007)

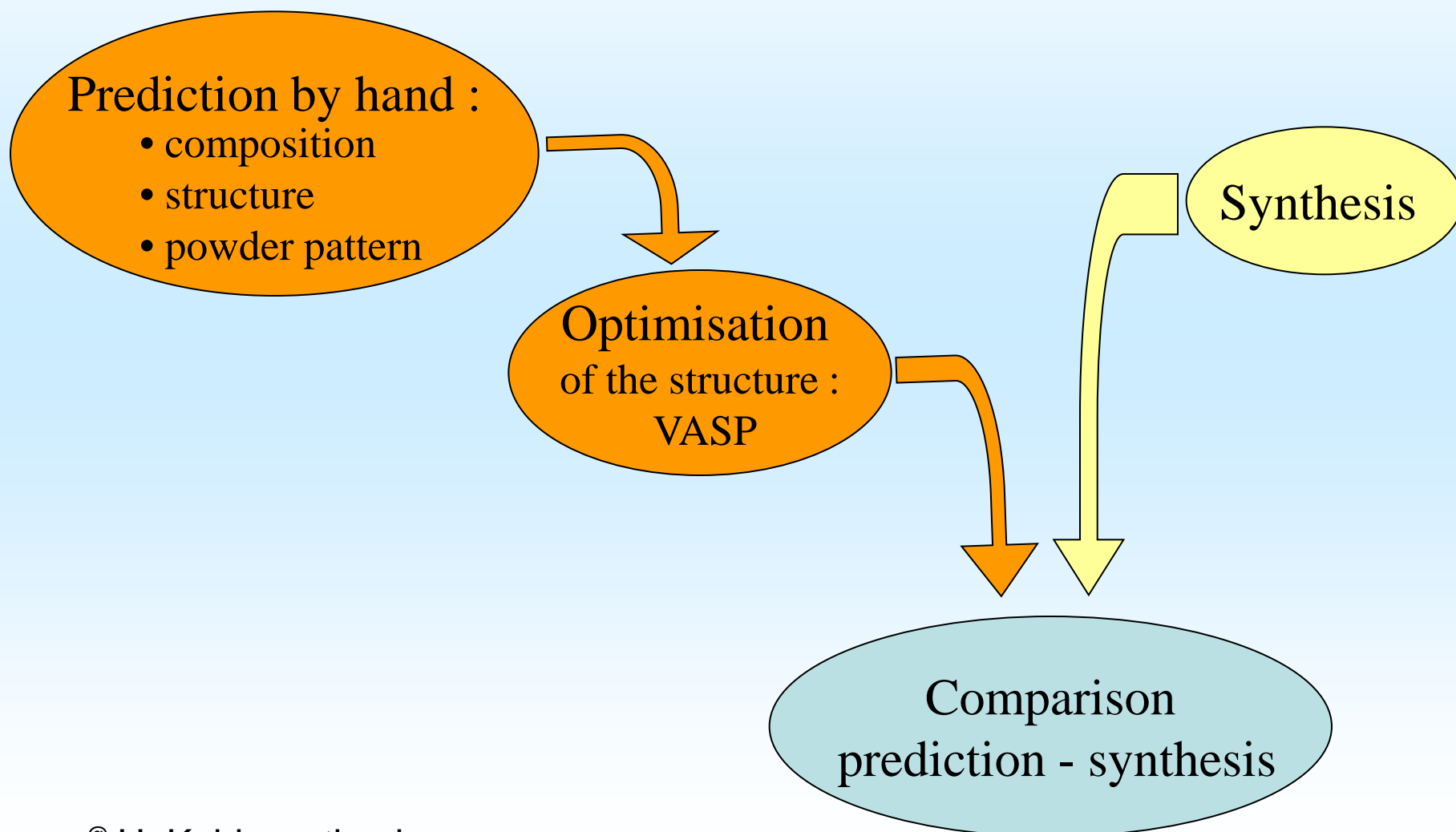
# Concevoir un nouveau composé à structure composite lamellaire : un lego chimique ?



- layers = secondary building units
- Similar in-plane parameters
- Electronic transfer
- Redox competition between cations

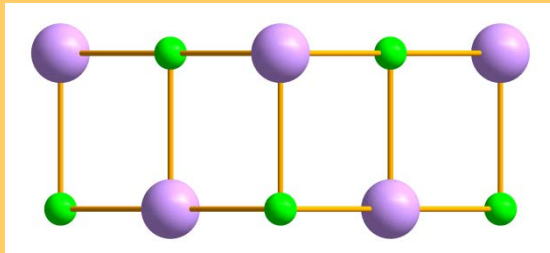


# Concevoir un nouveau composé à structure composite lamellaire : un lego chimique ?

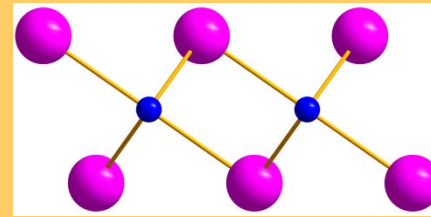




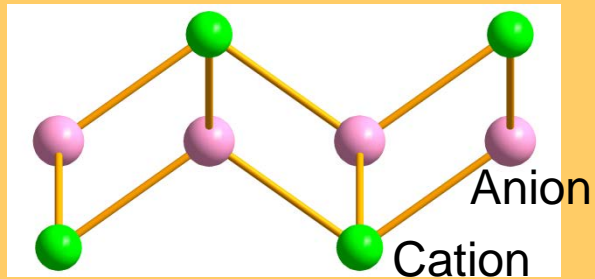
**NaCl**



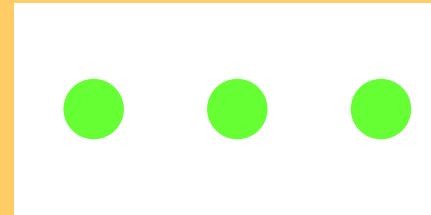
**CdI<sub>2</sub>**



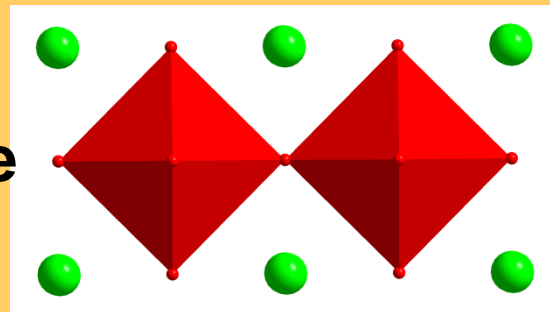
**Fluorine**



**Feuillet atomique**

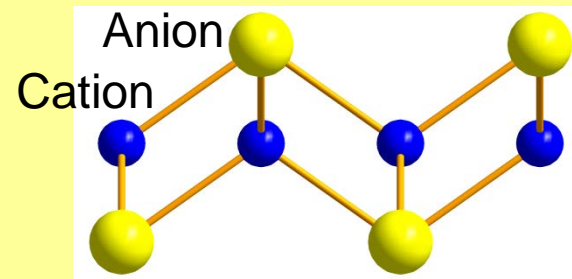
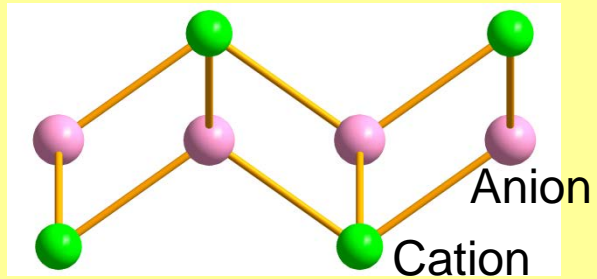


**Pérovskite**



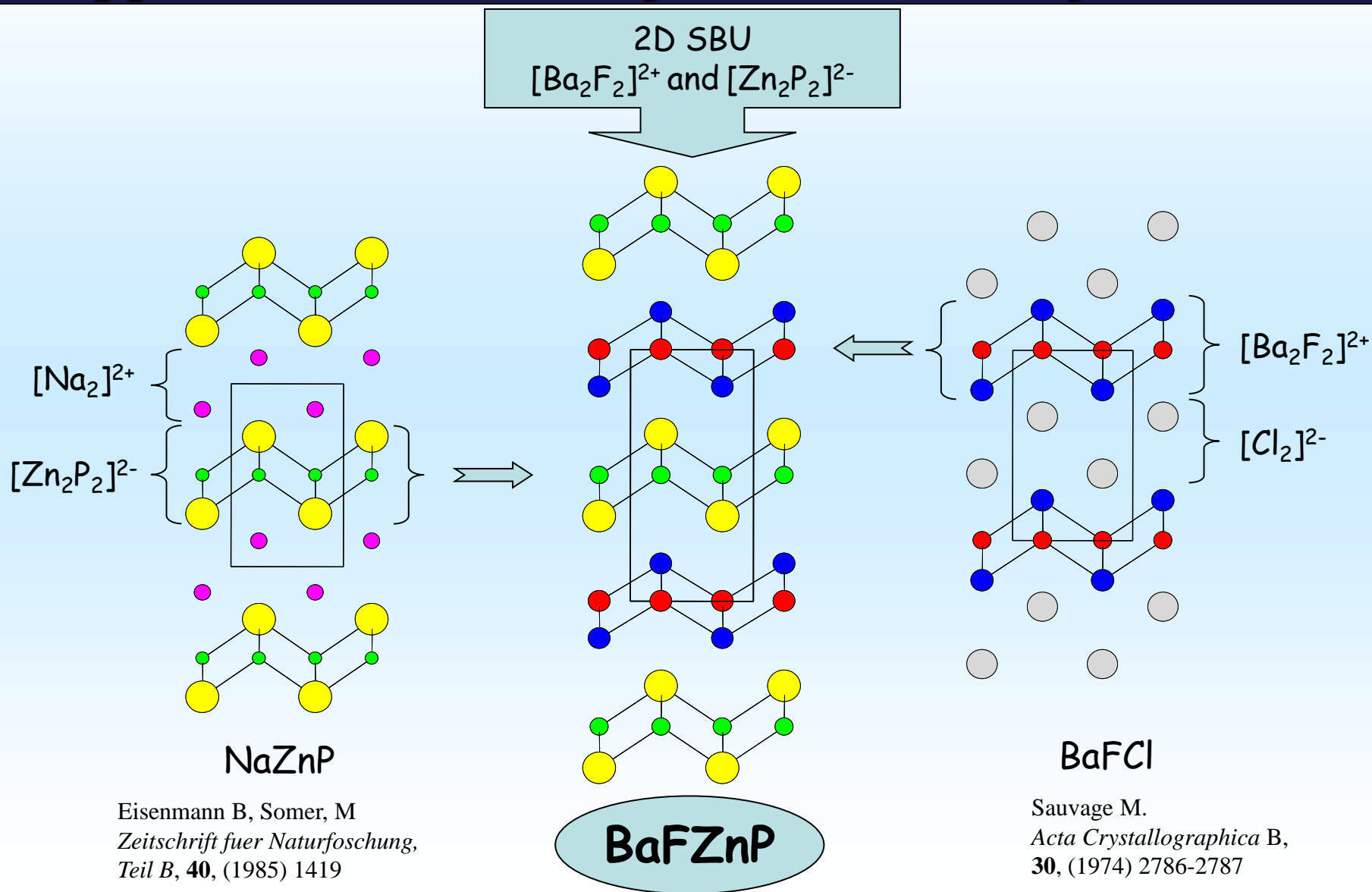


**Fluorine**

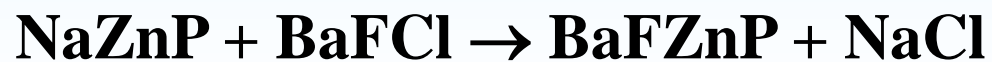
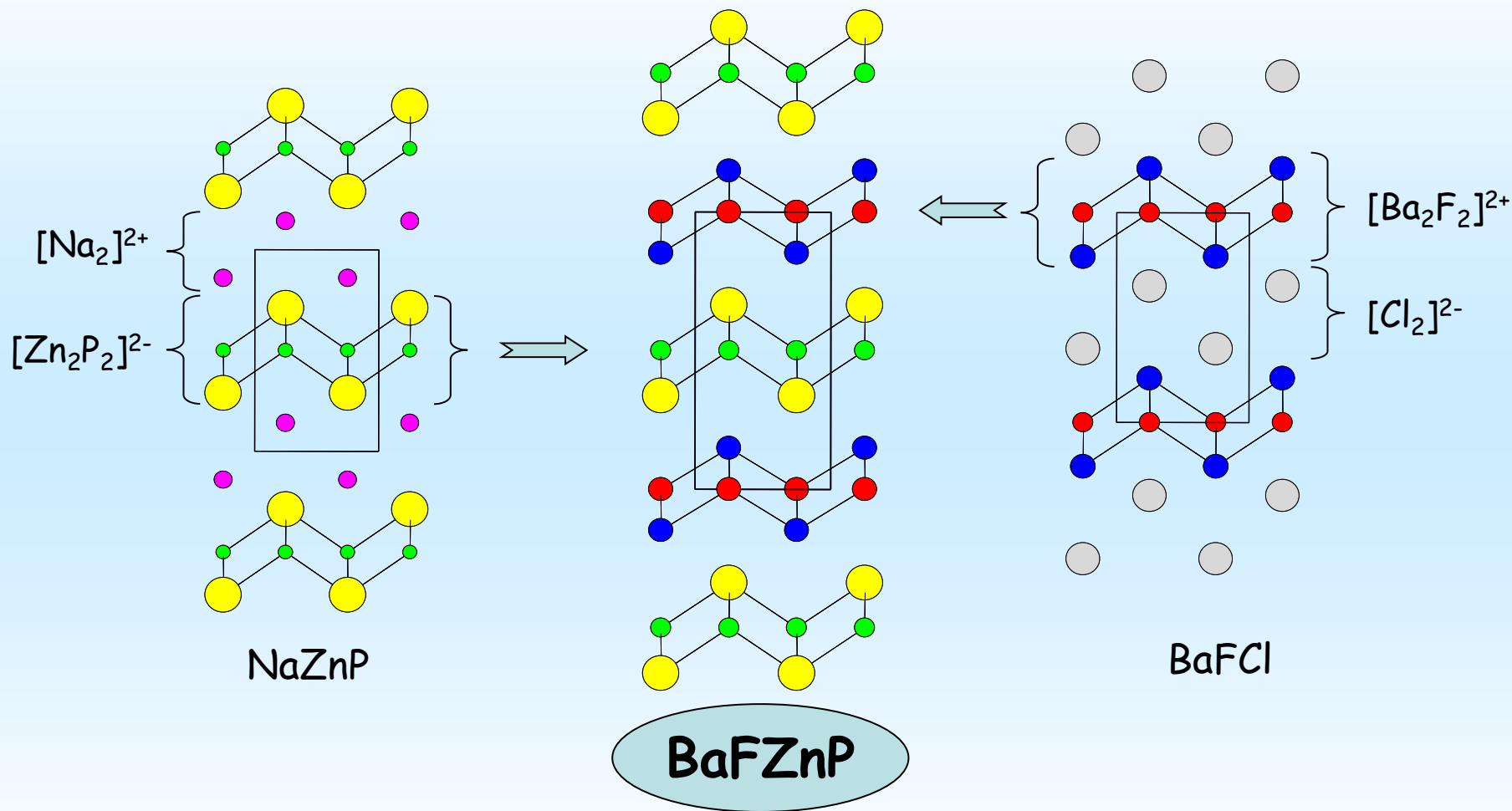


**Anti-Fluorine**

# Application aux blocs fluorines et antifuorines



# Application aux blocs fluorines et antifuorines



$$\Delta_r G = -26,0 \text{ kJ.mol}^{-1}$$

Optimized structure  
with VASP

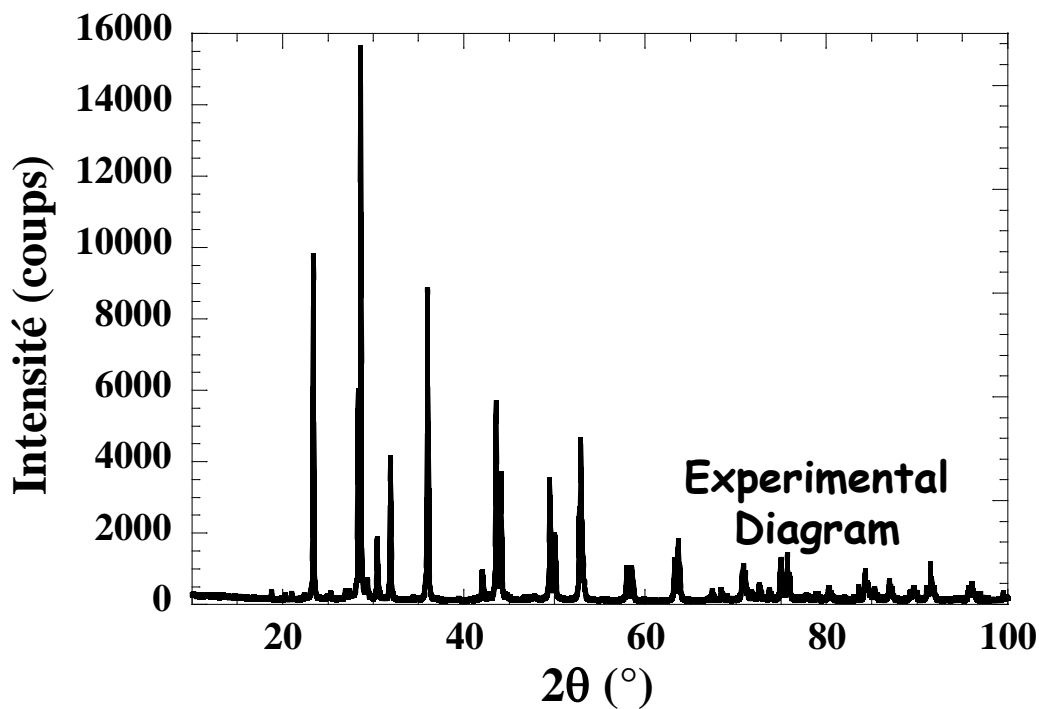


# Synthèse du composé $BaFZnP$

## Synthesis

→ Metathesis (600 °C) → NaCl + new phase

→ HT ceramic (900 °C) → new phase



# Affinement structural du composé BaFZnP

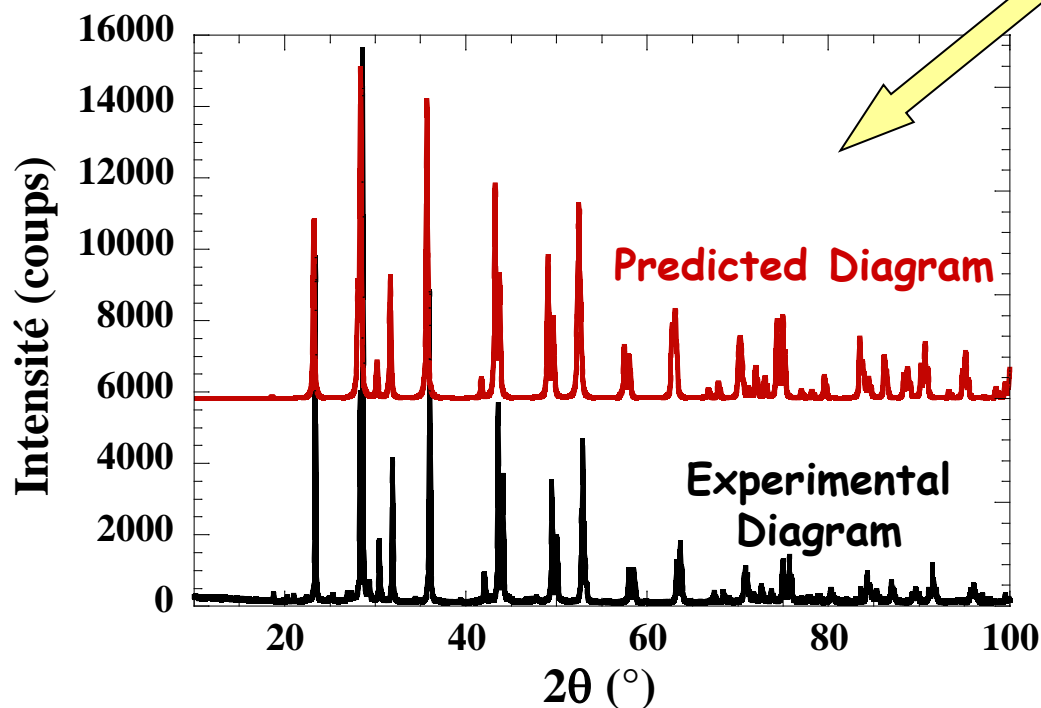
Optimised (VASP)

I4/nmm

$a=4.1625\text{\AA}$   $\neq$  (0.2%)

$c=9.4842\text{\AA}$   $\neq$  (0.3%)

Predicted  
Structure

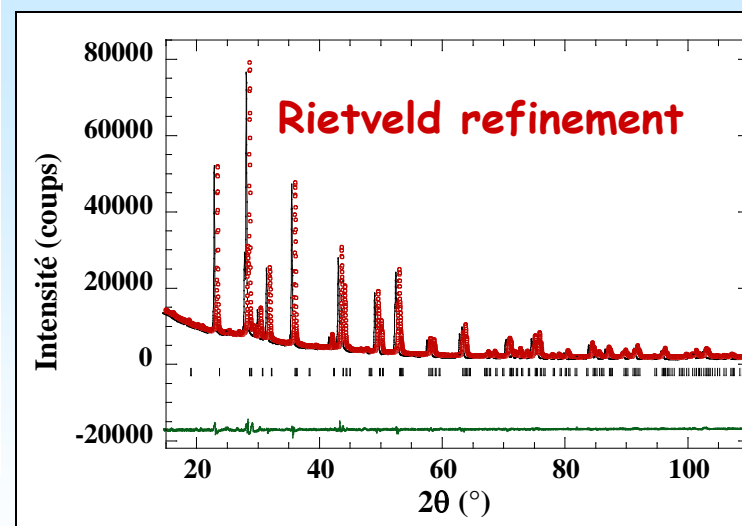


Refined structure

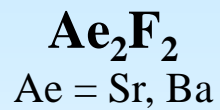
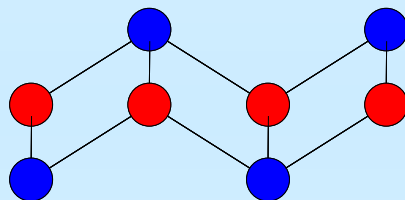
I4/nmm

$a=4.1564(1)\text{\AA}$

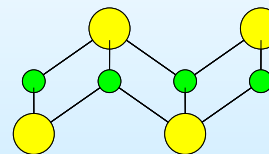
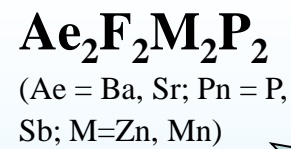
$c=9.4574(1)\text{\AA}$



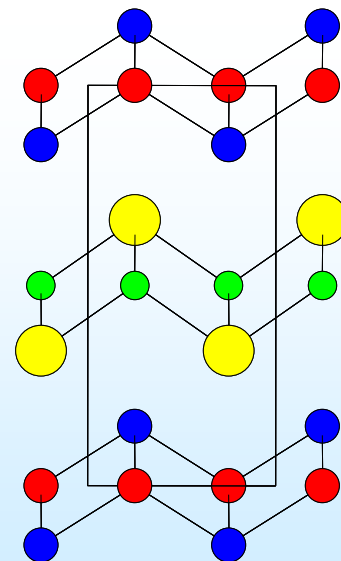
$$R_{\text{Bragg}} = 2,05 \%$$



L. Cario; H. Kabbour  
and A. Meerschaut  
*Chem. Mat.* **17**, 234 (2005)

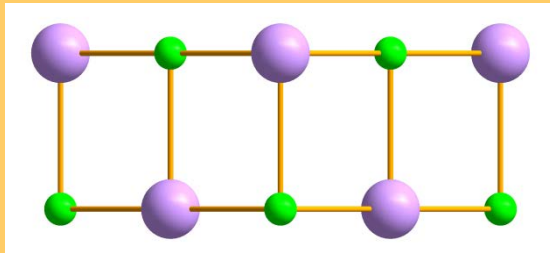


H. Kabbour, L. Cario and F. Boucher,  
*J. Mater. Chem.*  
**15**, 3525 (2005).

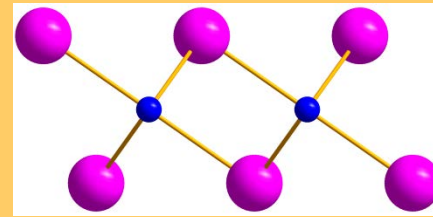




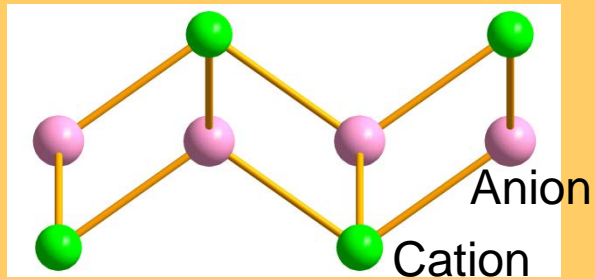
**NaCl**



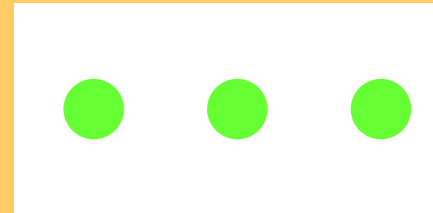
**CdI<sub>2</sub>**



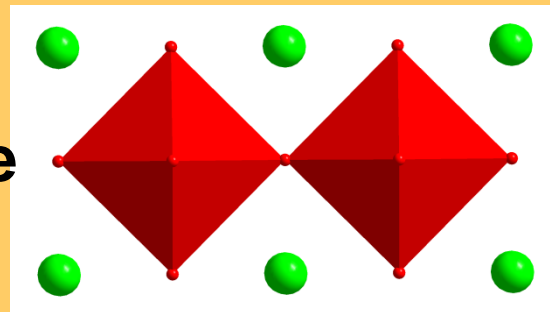
**Fluorine**



**Feuillet atomique**

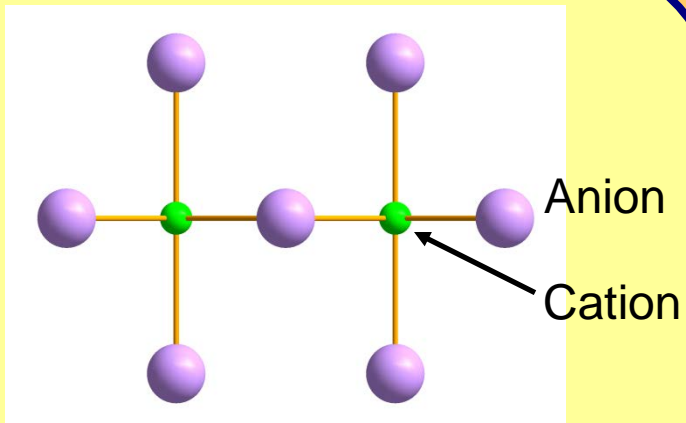


**Pérovskite**

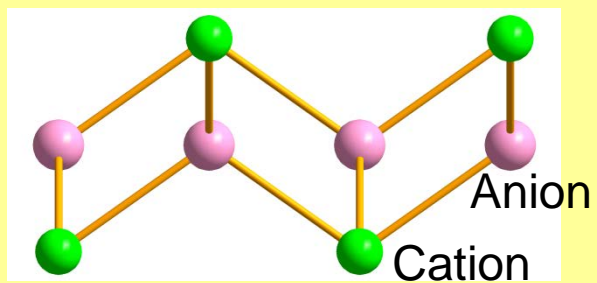




**NaCl**

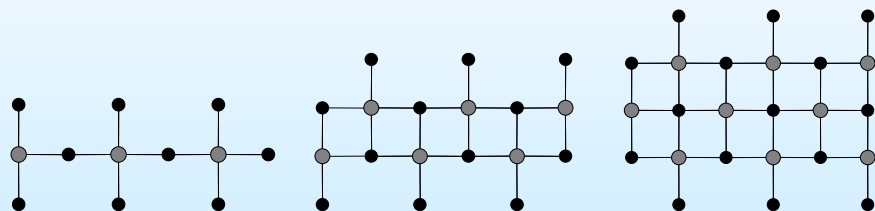


**Fluorine**



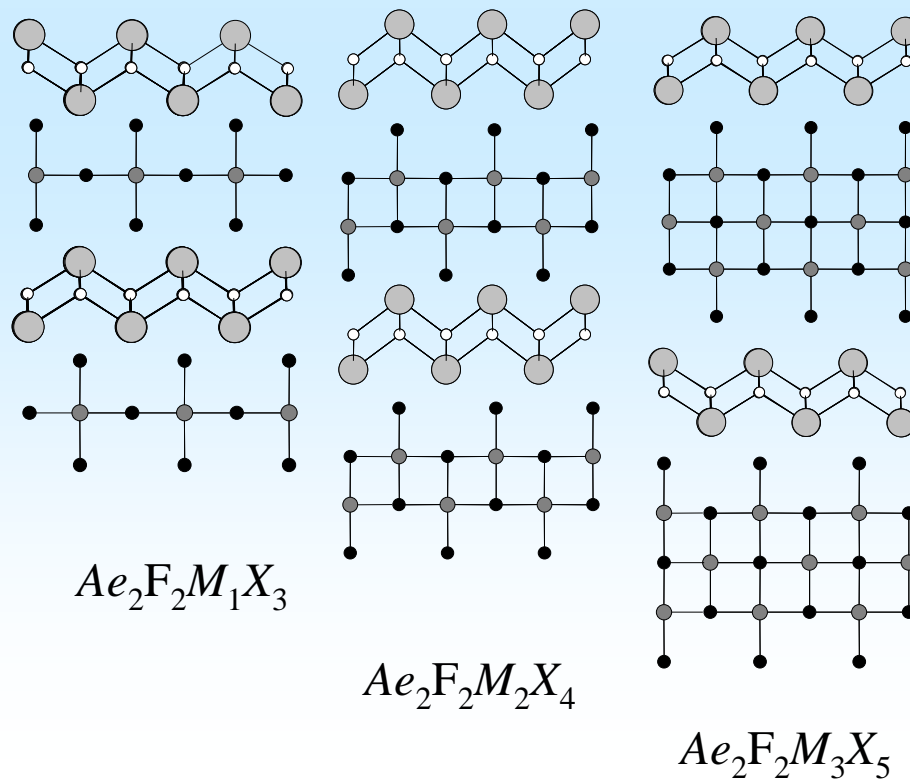
# Application aux blocs fluorine et NaCl

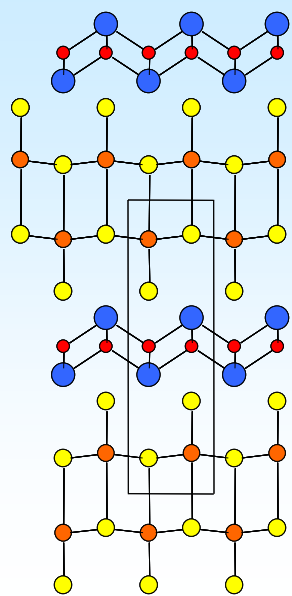
Coupe (110)  $\rightarrow$  blocs  $^{(110)}\text{NaCl} \rightarrow$  blocs à 3, 4 ou 5 couches d'anions



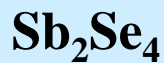
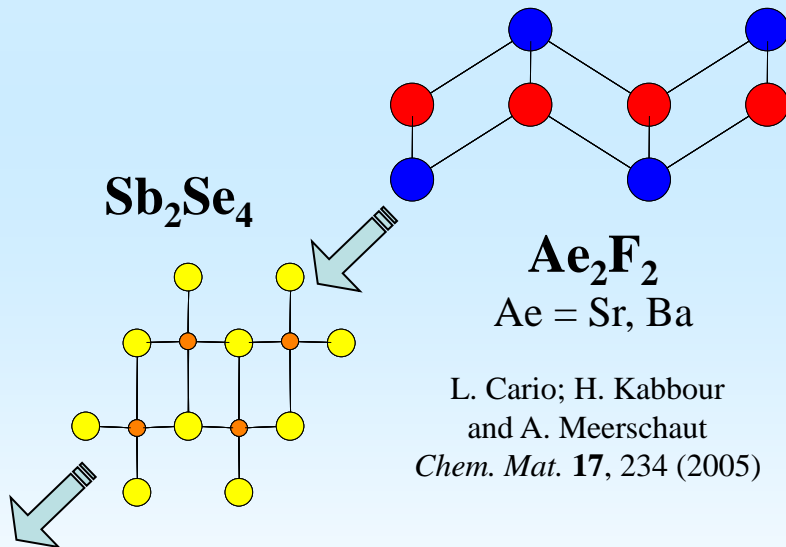
Associé au bloc  
fluorine  $[\text{Ae}_2\text{F}_2]$

Série homologue  $\text{Ae}_2\text{F}_2\text{M}_{1+n}\text{X}_{3+n}$

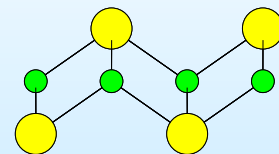




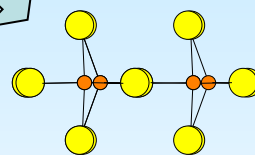
H. Kabbour, and L. Cario  
*Inorg. Chem.* **45**, 2713 (2006).



(Ae = Ba, Sr; Pn = P,  
Sb; M=Zn, Mn)

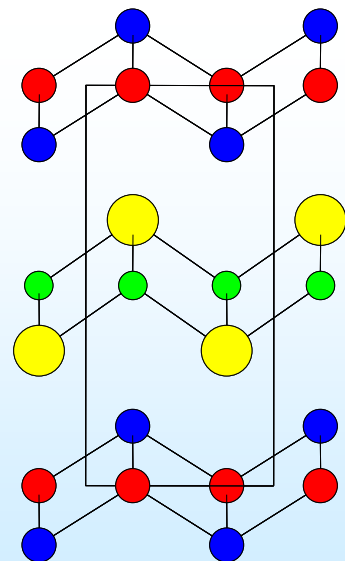
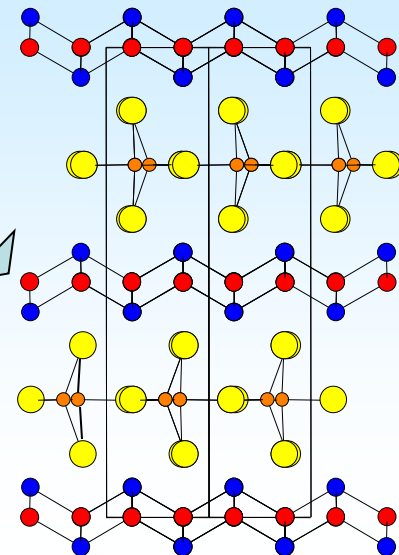


H. Kabbour, L. Cario and F. Boucher,  
*J. Mater. Chem.*  
**15**, 3525 (2005).



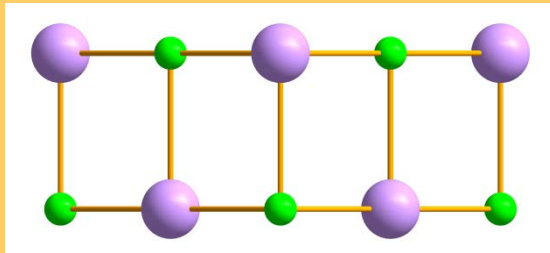
(Ae = Ba, Sr;  
X = S, Se)

H. Kabbour, L. Cario, M. Danot  
and A. Meerschaut  
*Inorg. Chem.* **45**, 917 (2006).

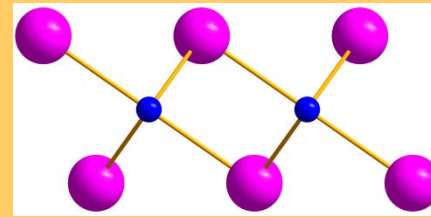




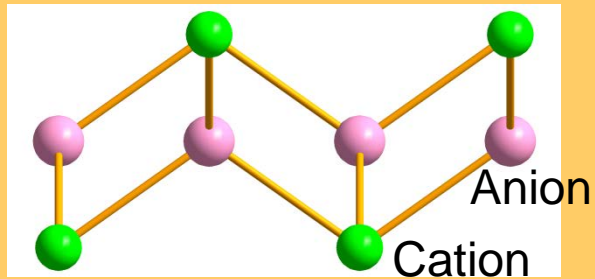
**NaCl**



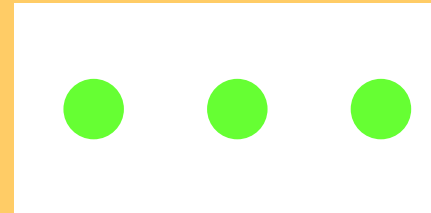
**CdI<sub>2</sub>**



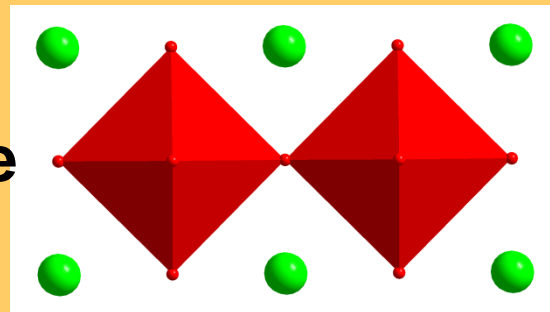
**Fluorine**



**Feuillet atomique**



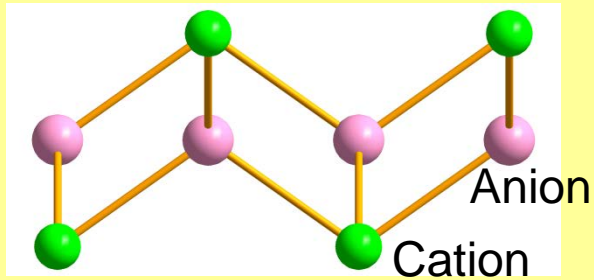
**Pérovskite**



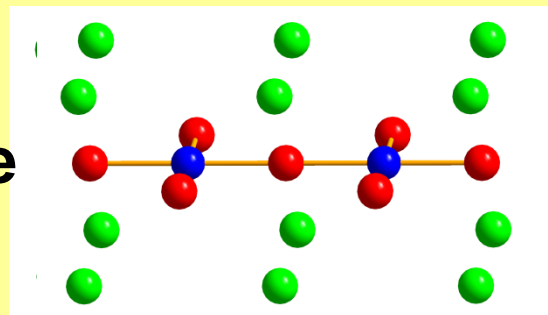




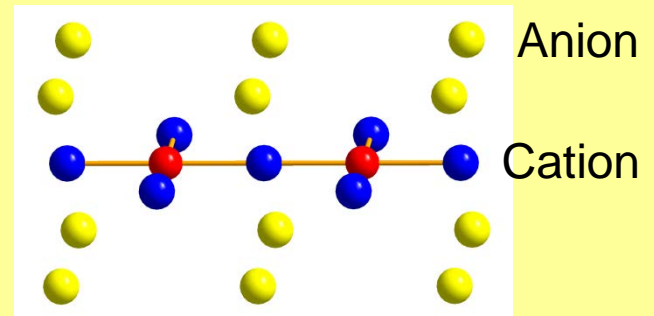
**Fluorine**



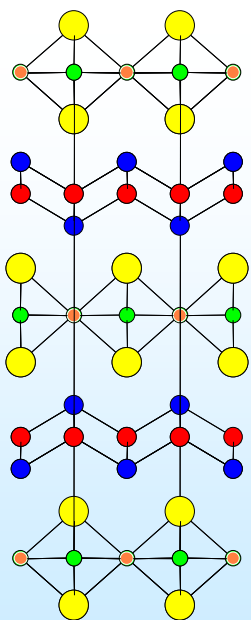
**Pérovskite**



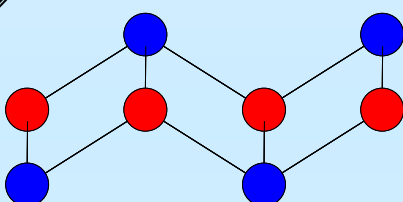
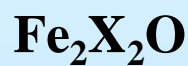
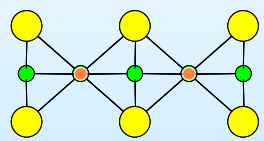
Plan CuO<sub>2</sub>



Plan anti-CuO<sub>2</sub>



(Ae = Ba, Sr; X = S, Se)

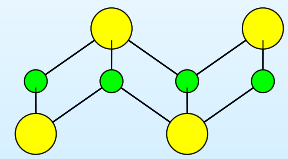
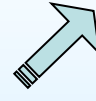


Ae = Sr, Ba

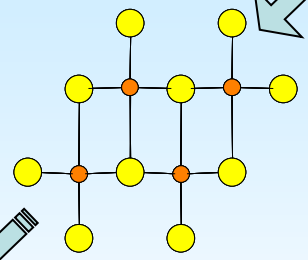
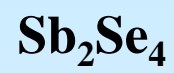
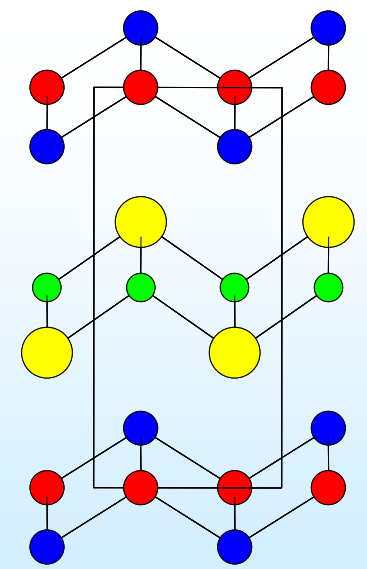
L. Cario; H. Kabbour  
and A. Meerschaut  
*Chem. Mat.* **17**, 234 (2005)



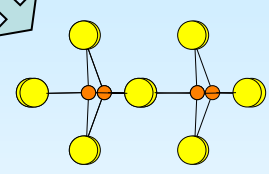
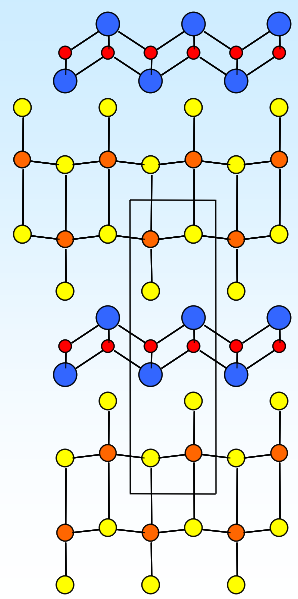
(Ae = Ba, Sr; Pn = P,  
Sb; M=Zn, Mn)



H. Kabbour, L. Cario and F. Boucher,  
*J. Mater. Chem.*  
**15**, 3525 (2005).

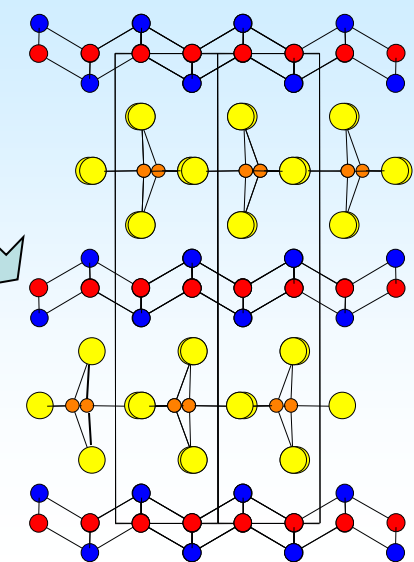


H. Kabbour, and L. Cario  
*Inorg. Chem.* **45**, 2713 (2006).

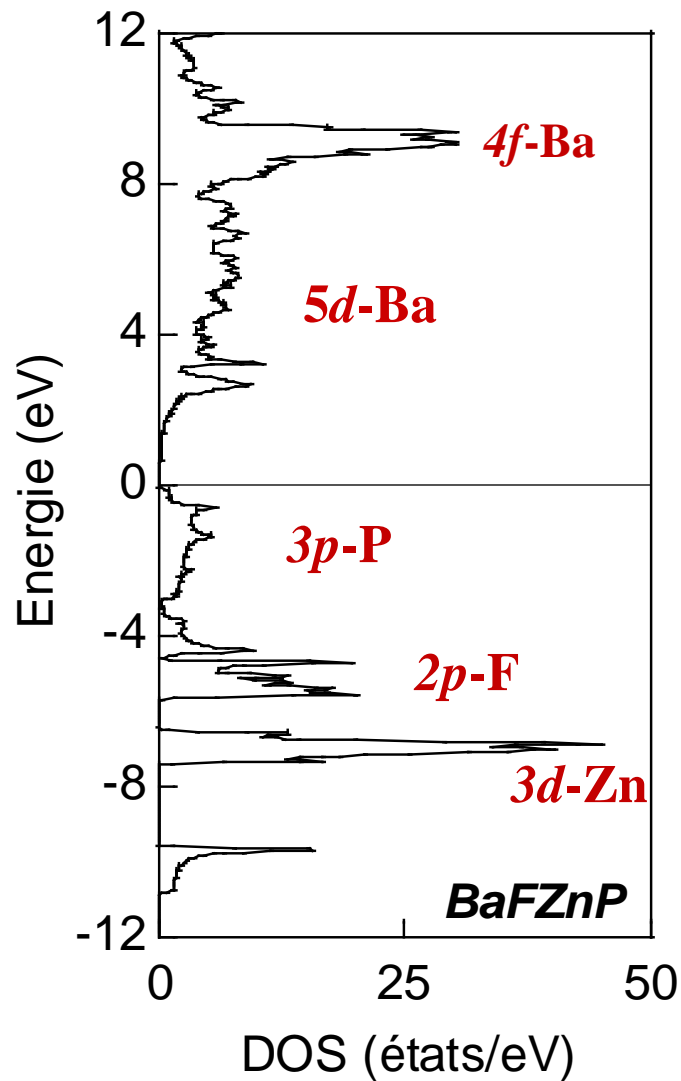


(Ae = Ba, Sr;  
X = S, Se)

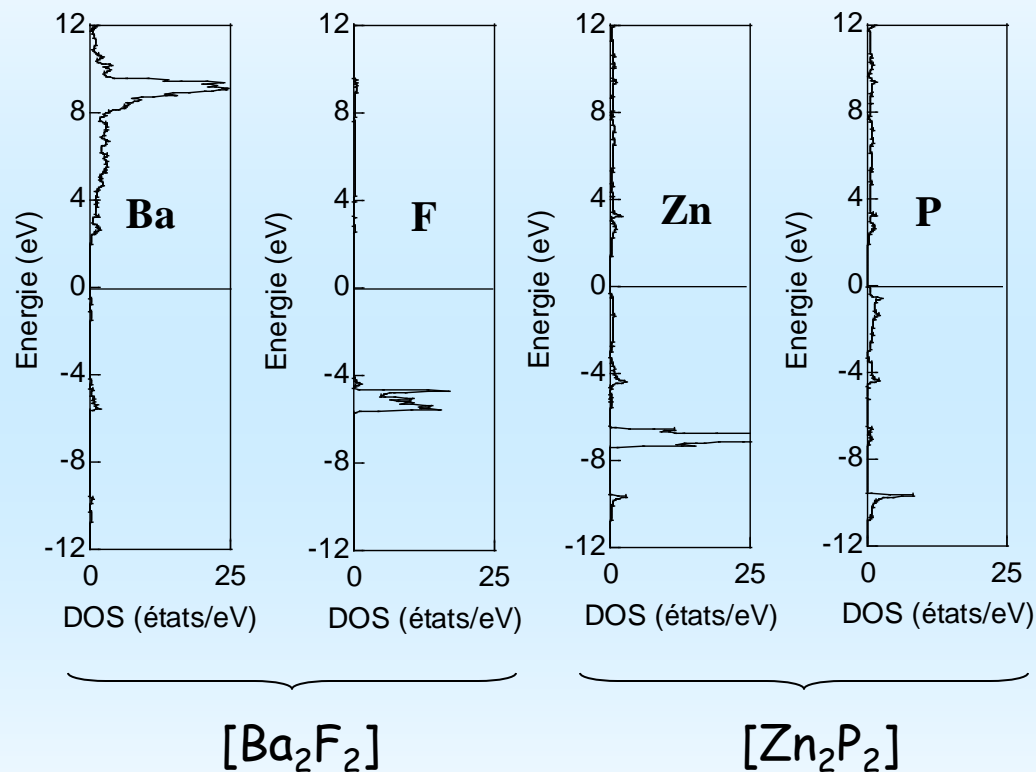
H. Kabbour, L. Cario, M. Danot  
and A. Meerschaut  
*Inorg. Chem.* **45**, 917 (2006).



# Stabilité des SBU 2D : calculs de structure de bandes

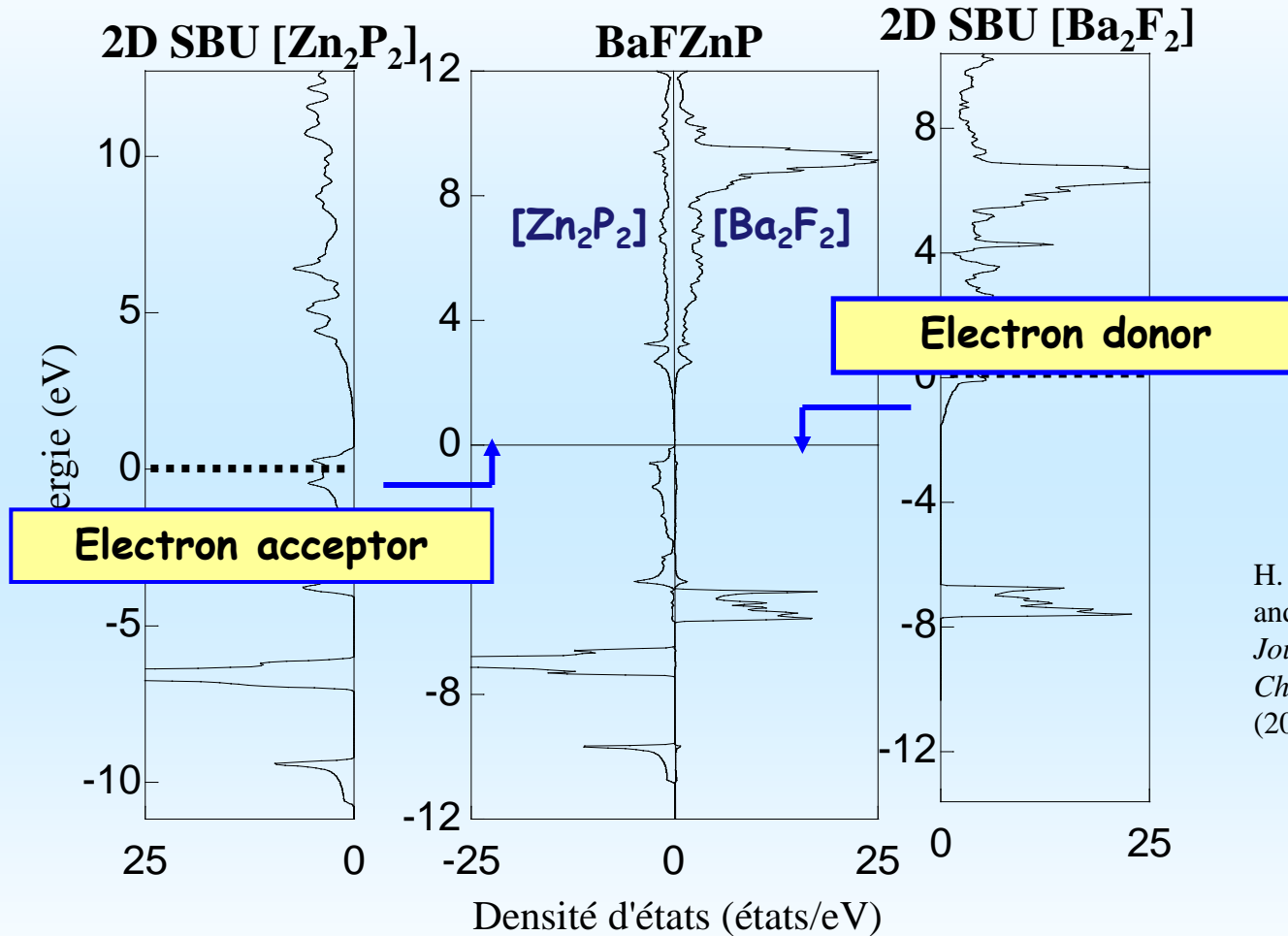


projected DOS on each atoms



projected DOS on each SBU

# Stabilité des SBU 2D : calculs de structure de bandes

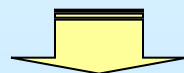


H. Kabbour, L. Cario  
and F. Boucher,  
*Journal of Material  
Chemistry*, **15**, 3525  
(2005).

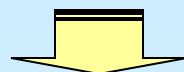
2D SBU when assembled together could keep not only their structural features, but also their electronic structures.

# *Stabilité des SBU 2D : calculs de structure de bandes*

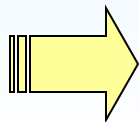
**DOS of the SBU are weakly  
affected by each others**



**2D Secondary Building Units = Secondary Electronic Units**



**Stability of the SBU  
Enable their  
Assembly**

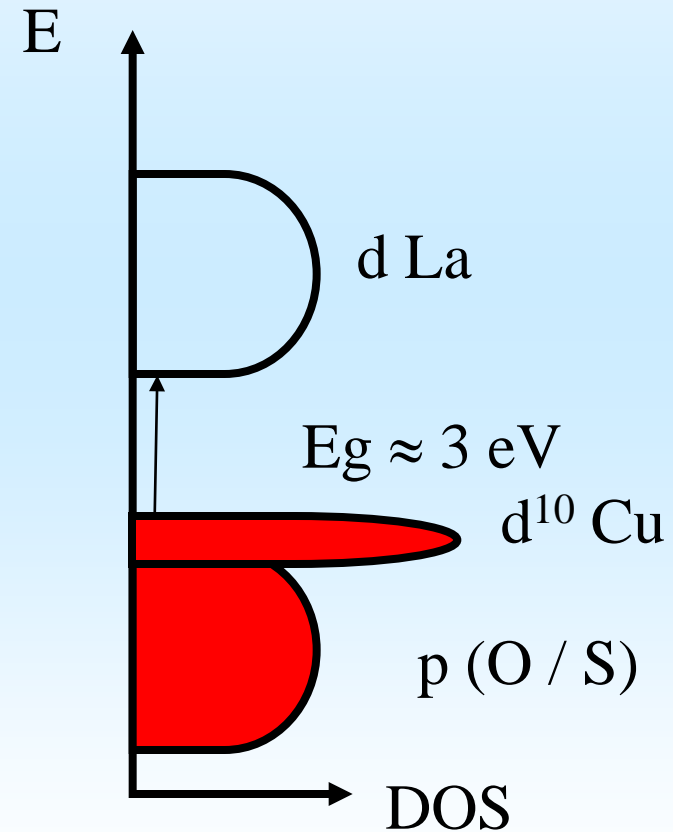
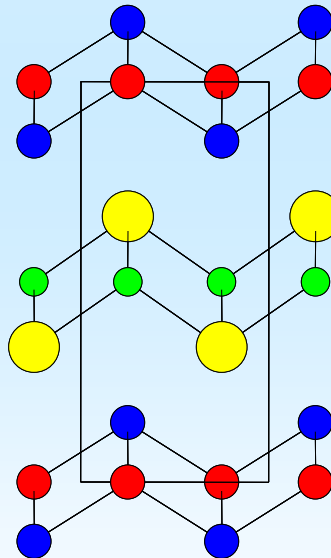
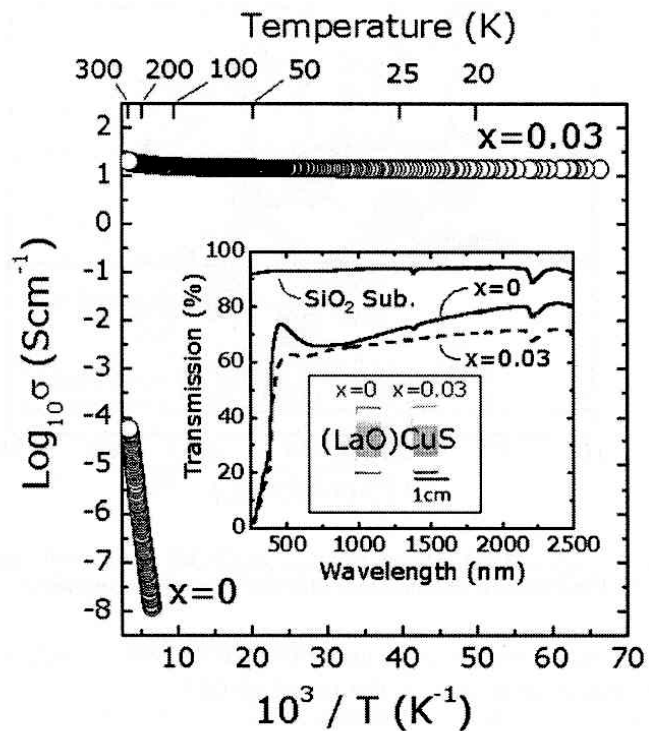


**Do 2D SBU keep their properties ?  
Can we design compounds with targeted properties ?**

# Conception d'un nouveau conducteur transparent de type p

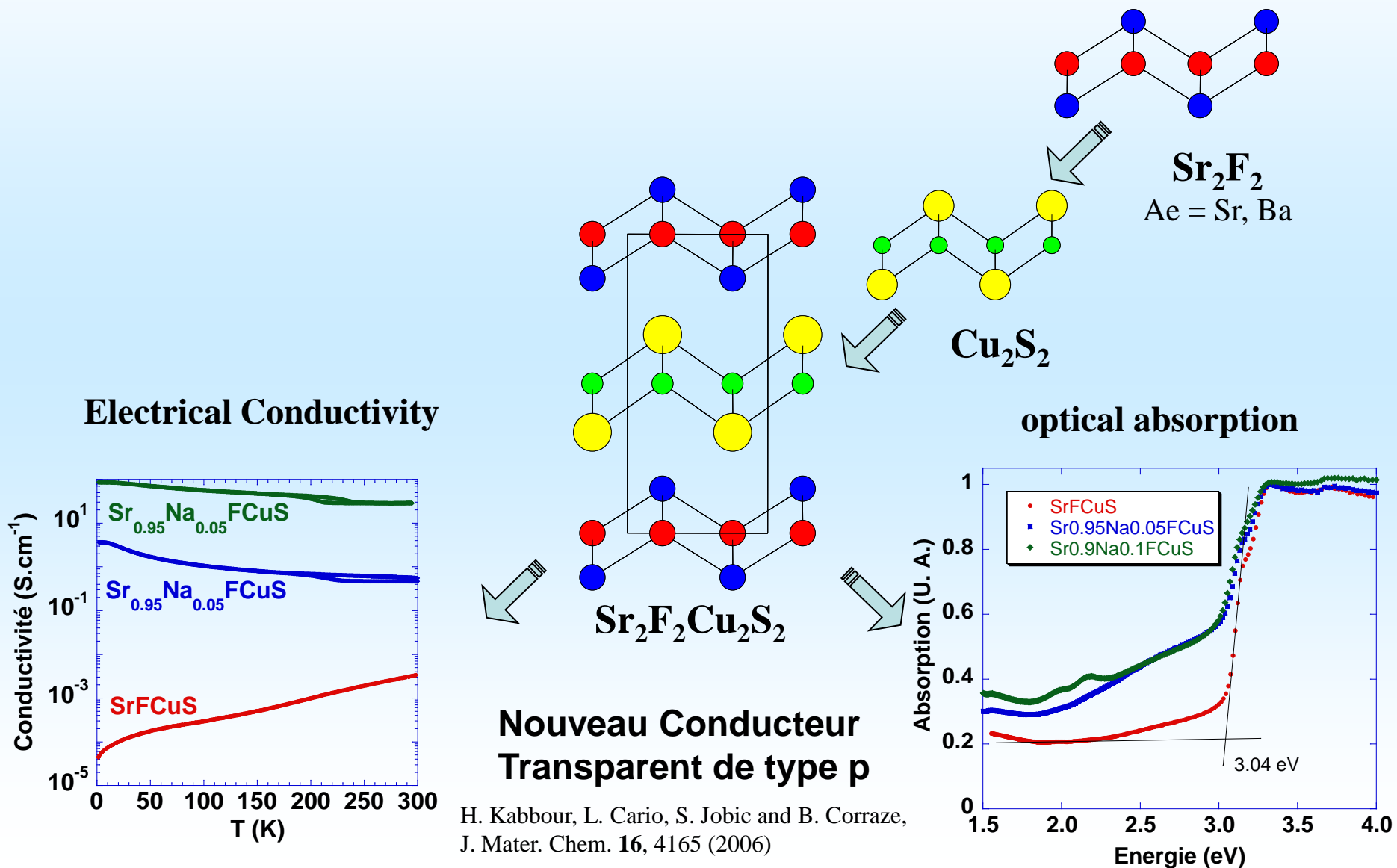
## ➤ p-type Transparent Conductors : LnCuOS gap $\approx 3$ eV ; $\sigma \approx 10$ S.cm<sup>-1</sup>

Hiramatsu et al. *Thin solid films* 411, 125-128 (2002)



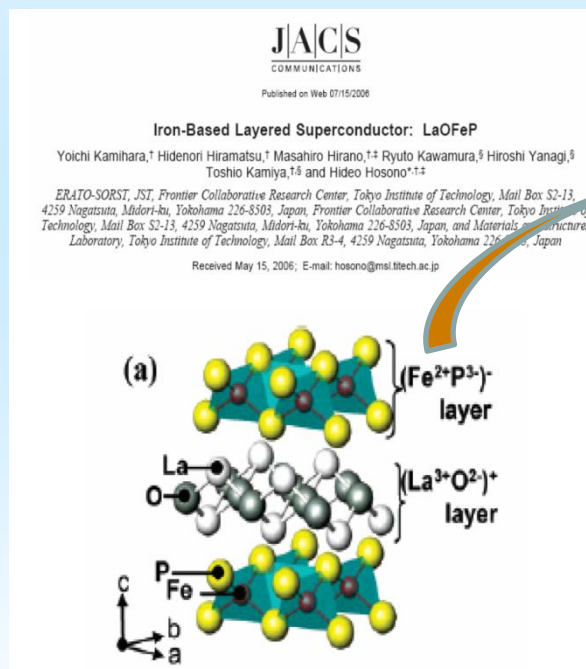
D'après Inoue et al., *Phys. Rev. B* 64, 254211 (2001)

# *SrFCuS* : nouveau conducteur transparent de type p

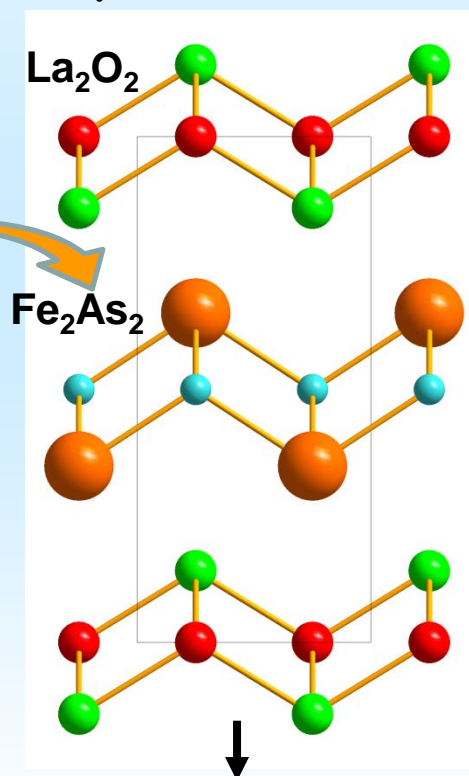


# Supraconductivité dans les plans FeAs

2006 :  $\text{LaO}_{1-x}\text{F}_x\text{FeP}$   
superconductivity at 3.6 K  
Hosono et al. JACS 2008



2008 : découverte de  
supraconductivité haut  $T_c$  dans  
les plans FeAs

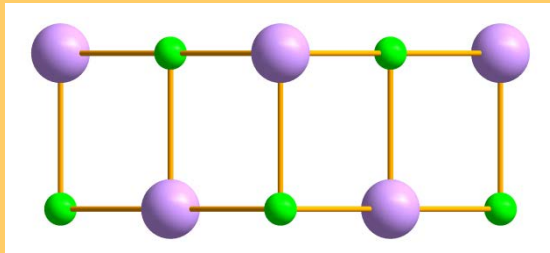


$\text{LaO}_{1-x}\text{F}_x\text{FeAs}$   $T_c = 26$  K  
Hosono et al. JACS 2008

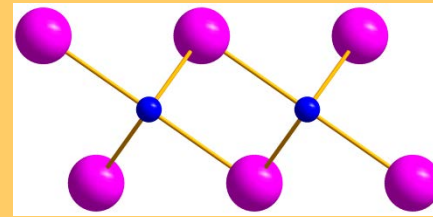




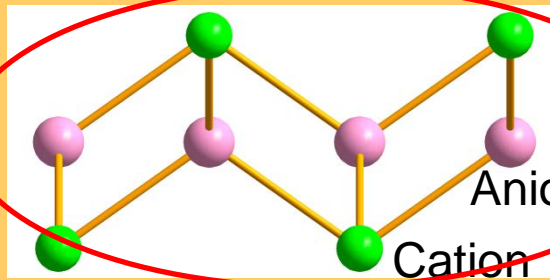
**NaCl**



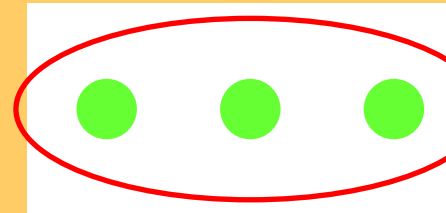
**CdI<sub>2</sub>**



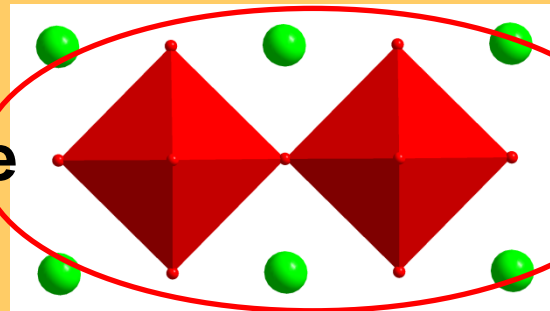
**Fluorine**



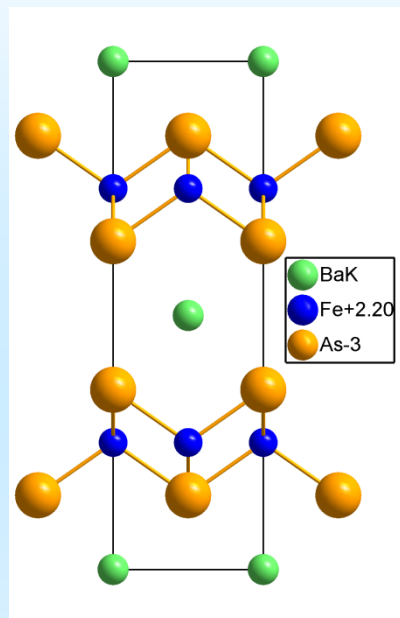
**Feuillet atomique**



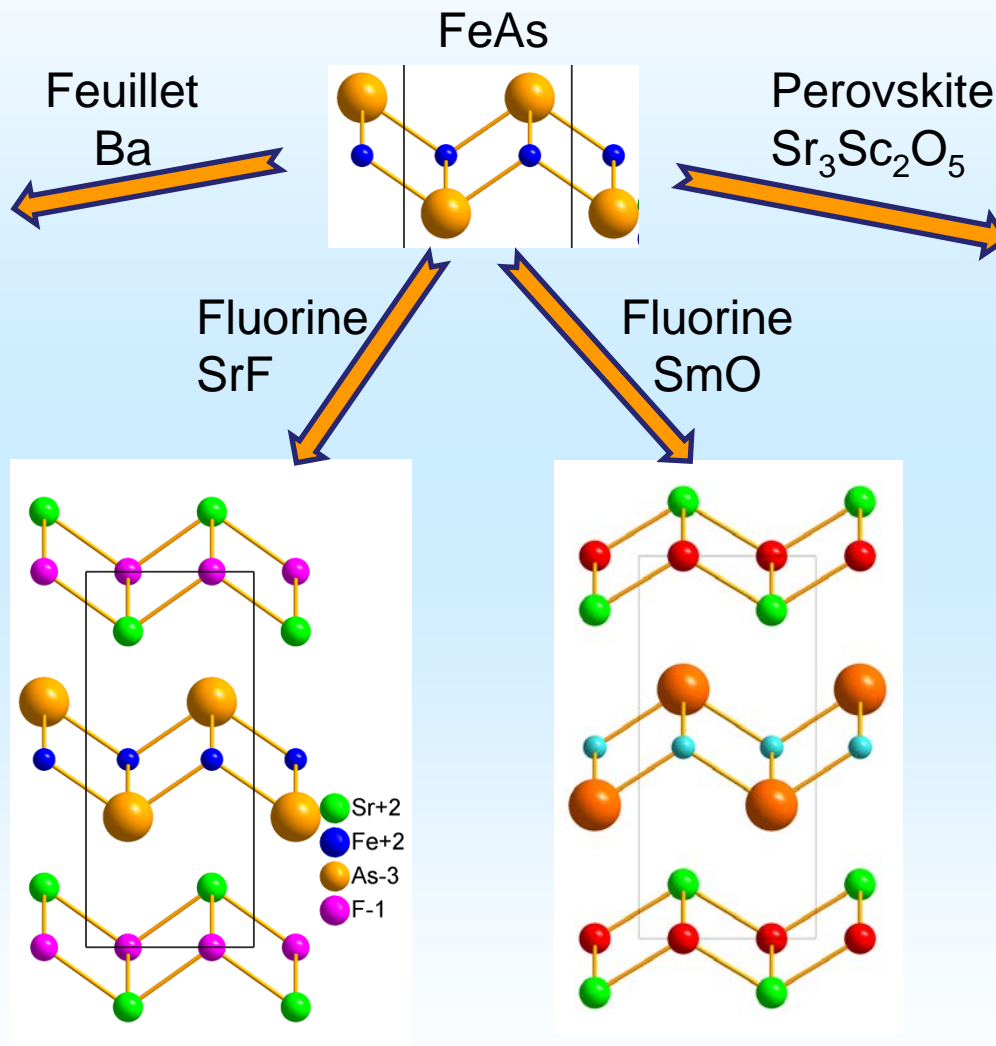
**Pérovskite**



# Recherche de nouveaux Supra à plans FeAs

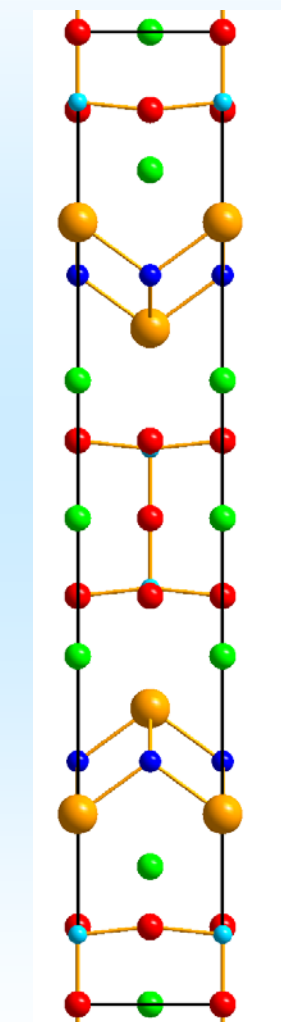


$\text{BaFe}_2\text{As}_2\text{Tc} = 38\text{K}$   
 Jorhendt et al. 2008



$\text{Sr}_{1-x}\text{Sm}_x\text{FFeAs}$  Tc=56K  
 Hosono et al. 2008

$\text{SmO}_{1-x}\text{F}_x\text{FeAs}$  Tc=56K  
 Chen et al. 2008



$\text{Sr}_3\text{Sc}_2\text{O}_5\text{Fe}_2\text{As}_2$   
 Zhu et al. 2008

## *Conclusion*

- Il est difficile de prédire les structures stables des matériaux inorganiques*
- Il est possible de jouer avec les empilements déjà connus pour concevoir des composés de manière raisonnée*
- Les relations structures-propriétés dans des empilements connus permettent de cibler des propriétés dans de nouveaux composés contenant ces empilements*
- Par contre il reste difficile de prédire les propriétés de nouveaux empilements !*