

# La modélisation appliquée aux matériaux en chimie du solide : *de l'étude de la structure à celle des propriétés*

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FRANCE



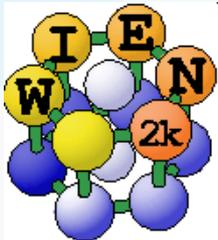
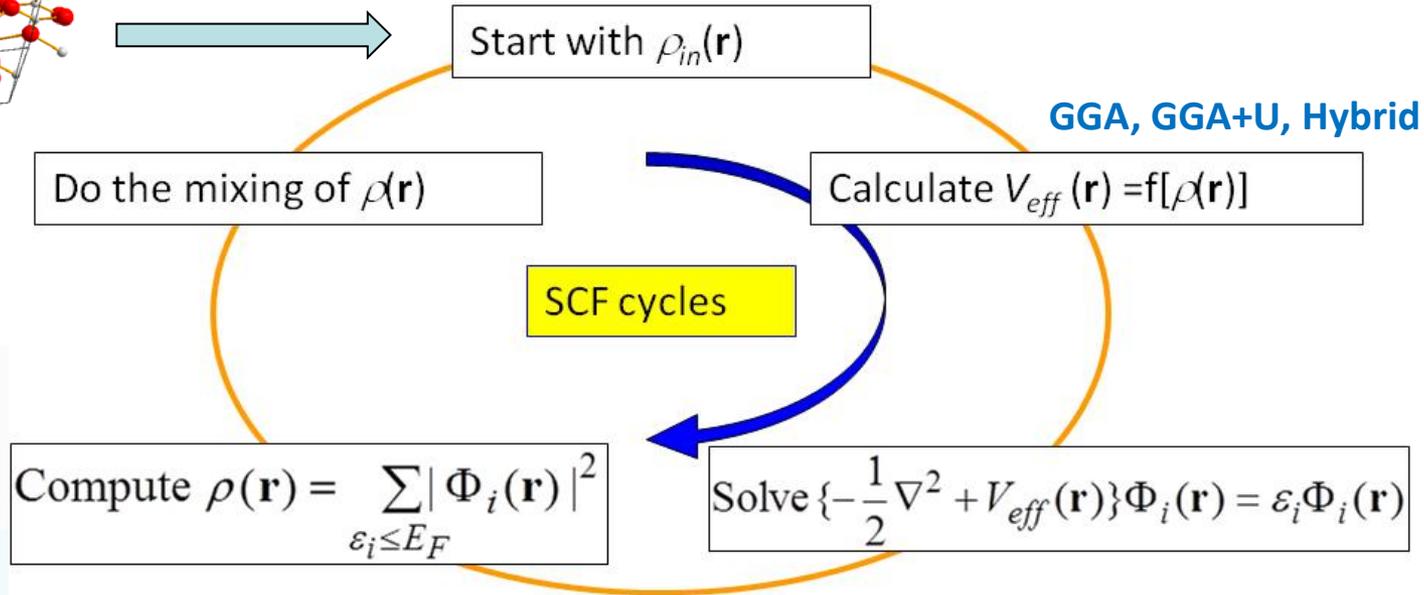
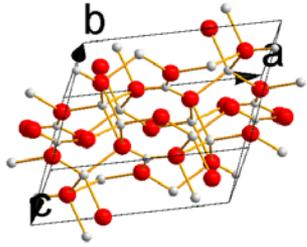
# Plan de l'exposé

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- ❖ La modélisation DFT : comment et pourquoi ?
- ❖ Exemples d'applications
  - aspects structuraux
  - densité de charge et de spin
  - structure électronique
  - *au-delà de OK, vers la prédiction...*
- ❖ Codes et moyens de calculs
- ❖ La communauté, les réseaux

# La modélisation DFT : comment et pourquoi ?

## DFT : la procédure auto-cohérente

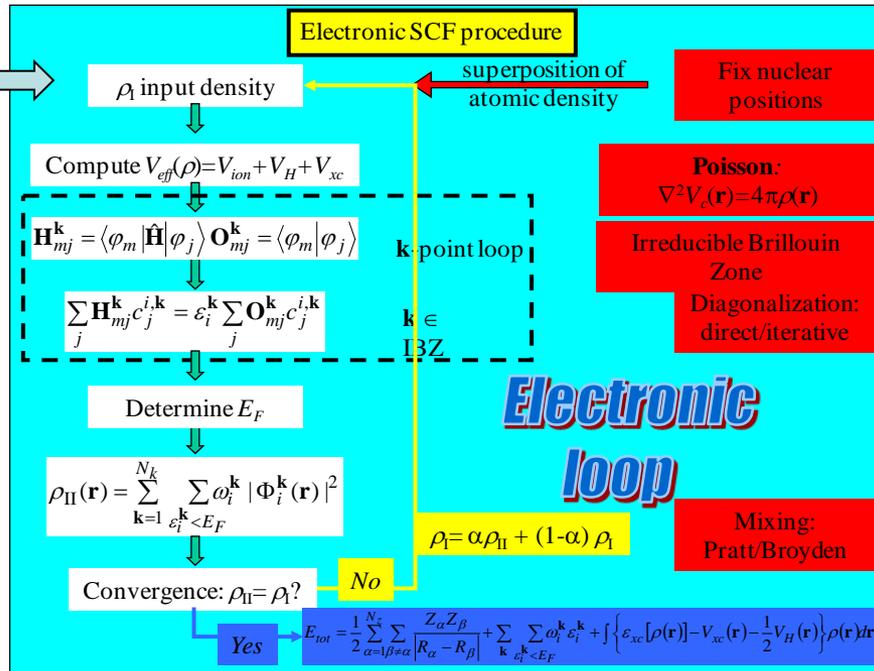
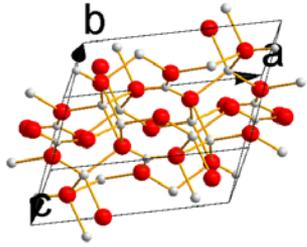


CASTEP



# La modélisation DFT : comment et pourquoi ?

## DFT : énergie totale, forces et optimisation



Apply atomic displacements

Calculate  $\Delta \mathbf{R}_I$  atomic displacements

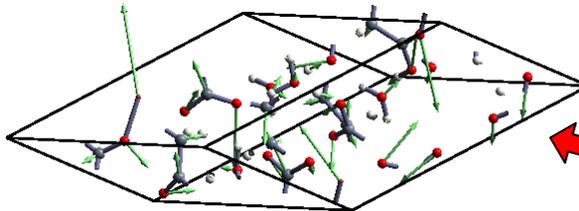
**Ionic loop**

Calculations of forces

$F_I \neq 0$

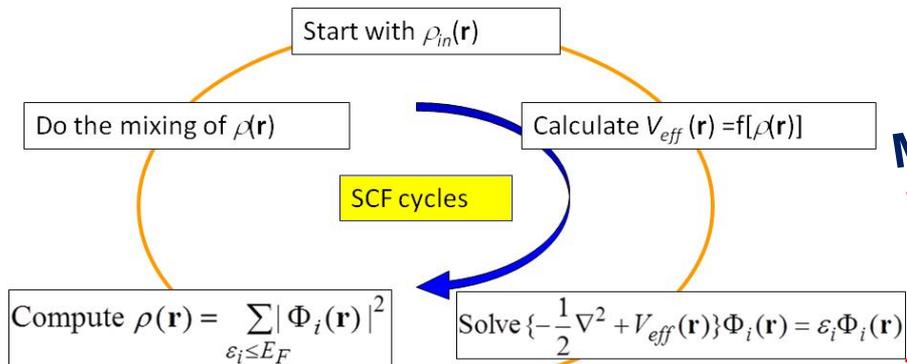
$F_I \approx 0$

Structure is relaxed



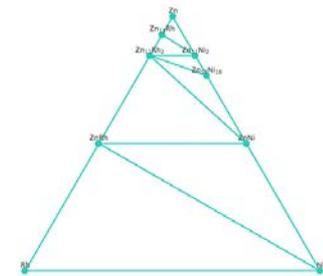
# La modélisation DFT : comment et pourquoi ?

## DFT : énergie totale, forces et optimisation

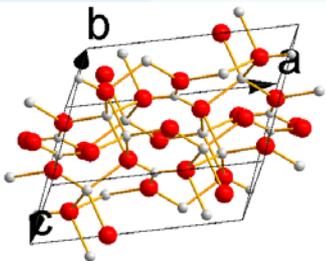


**Material Project**

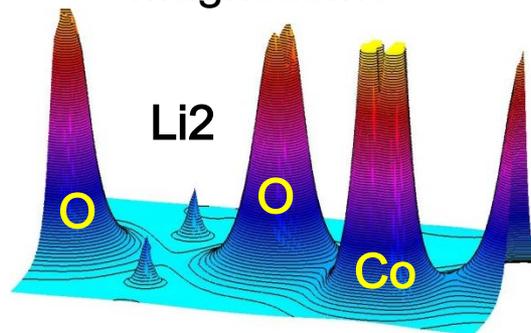
**Prédiction**  
Diagramme de phase  
Diagramme ternaire



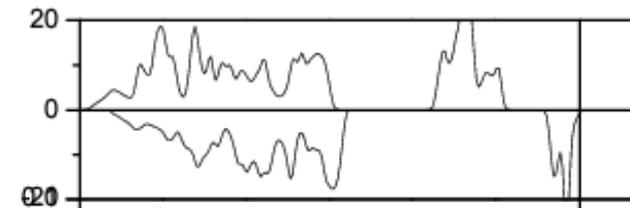
**Structure/Energie Totale**  
Optimisation  
Stabilité de phase



**Densité (charge, spin)**  
RMN, Mössbauer  
Magnétisme



**Structure électronique**  
XAS, EELS, XPS, Optic

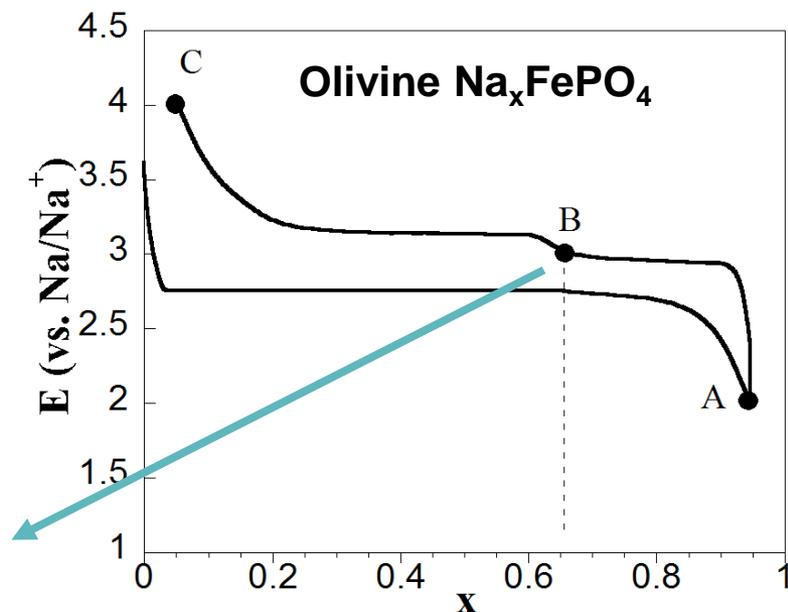
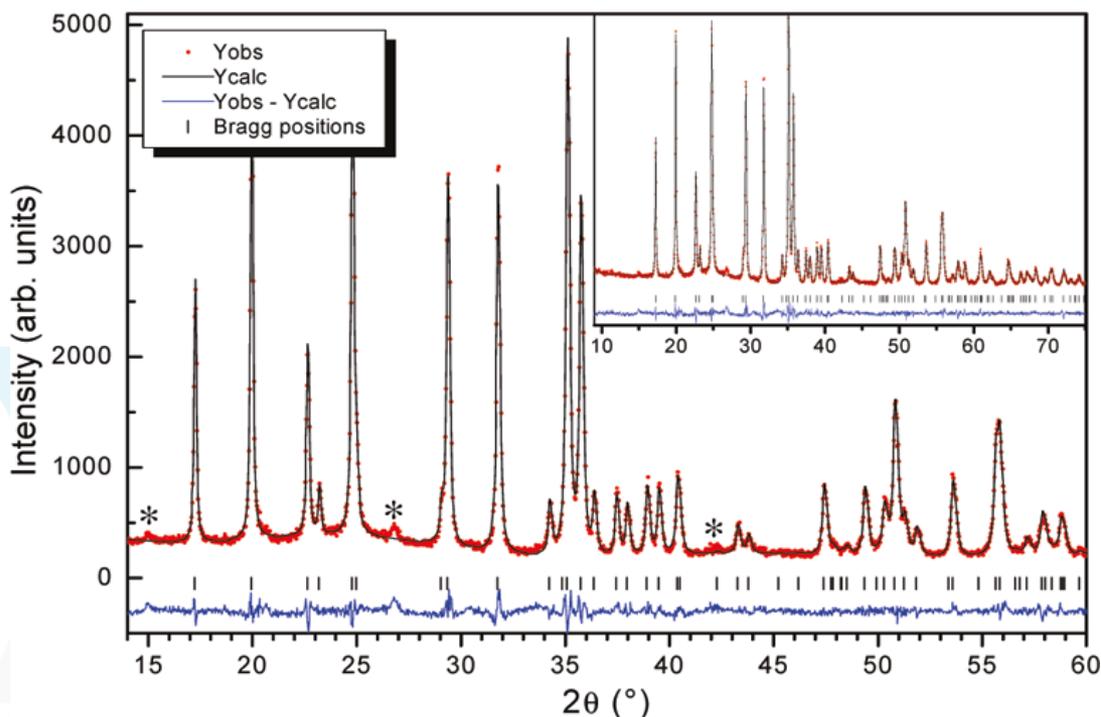


# Exemples d'applications

## Aspects structuraux, énergie totale, stabilité de phase

### Le système $A_x\text{FePO}_4$ ( $A = \text{Li}, \text{Na}$ )

Moreau *et al.* *Chem. Mater.* 2010, 22, 4126–4128.



$\text{Na}_{2/3}\text{FePO}_4$ : average cell

Space Group: Pnma, Z = 4

a = 10.2886(7) Å

b = 6.0822(4) Å

c = 4.9372(4) Å

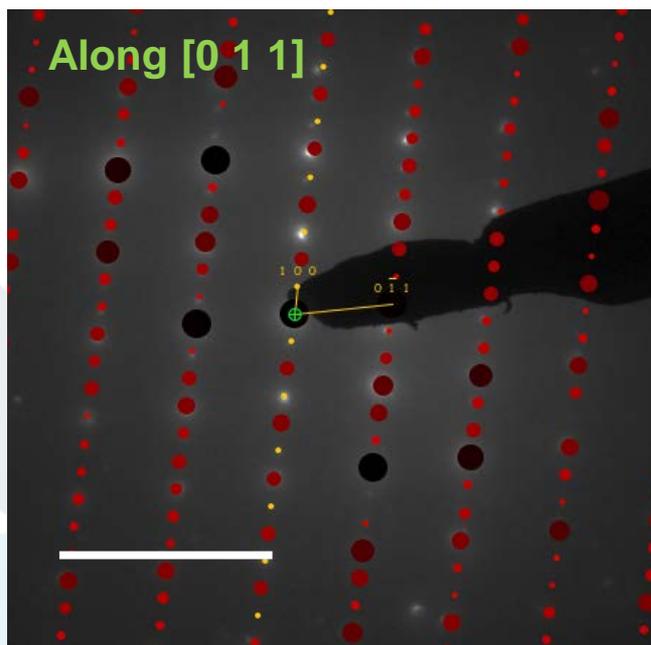
V = 308.95(4) Å<sup>3</sup>

$\tau(\text{Na}) = 0.71(2)$

# Exemples d'applications

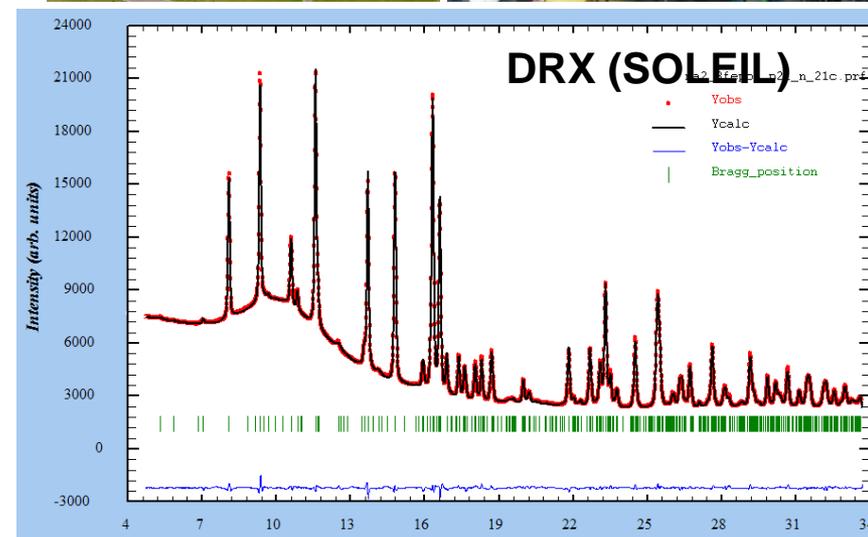
## Aspects structuraux, énergie totale, stabilité de phase

### Résolution de la structure de $\text{Na}_{2/3}\text{FePO}_4$



**Supercell (x3)**  
**P2<sub>1</sub>/n**

$a = 18.25 \text{ \AA}$   
 $b = 4.94 \text{ \AA}, \beta = 120.7^\circ$   
 $c = 11.96 \text{ \AA}$   
 $V = 926 \text{ \AA}^3 \quad Z = 12$



# Exemples d'applications

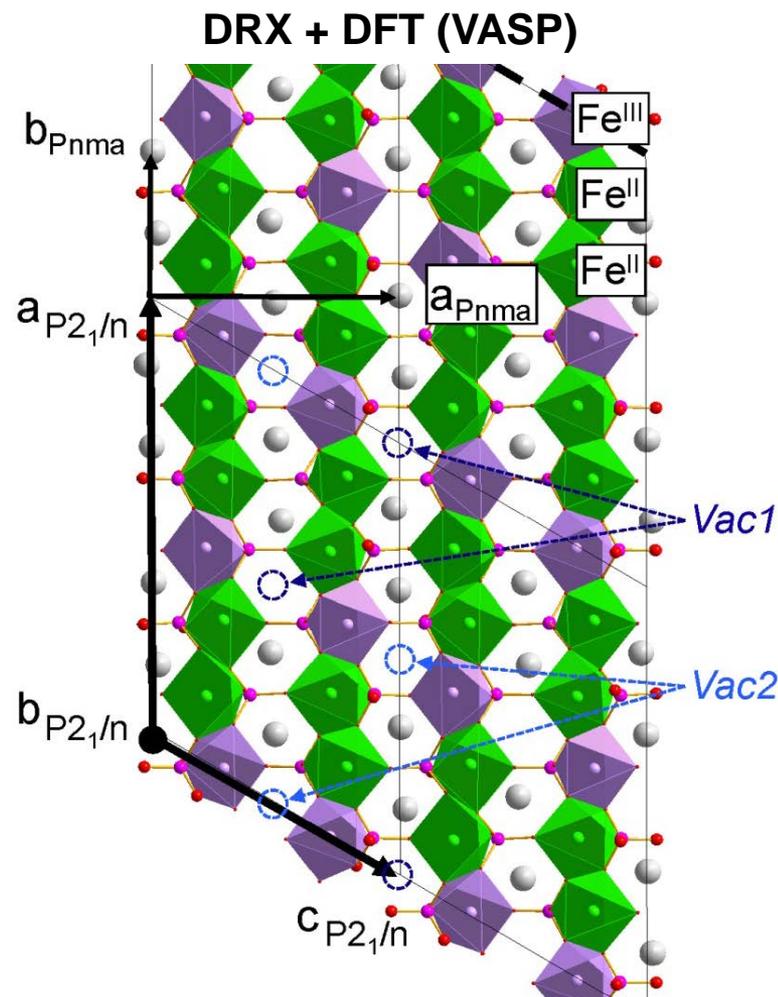
## Aspects structuraux, énergie totale, stabilité de phase

### Résolution de la structure de $\text{Na}_{2/3}\text{FePO}_4$

Boucher *et al.* *JACS* 2014, 136, 9144–9157.

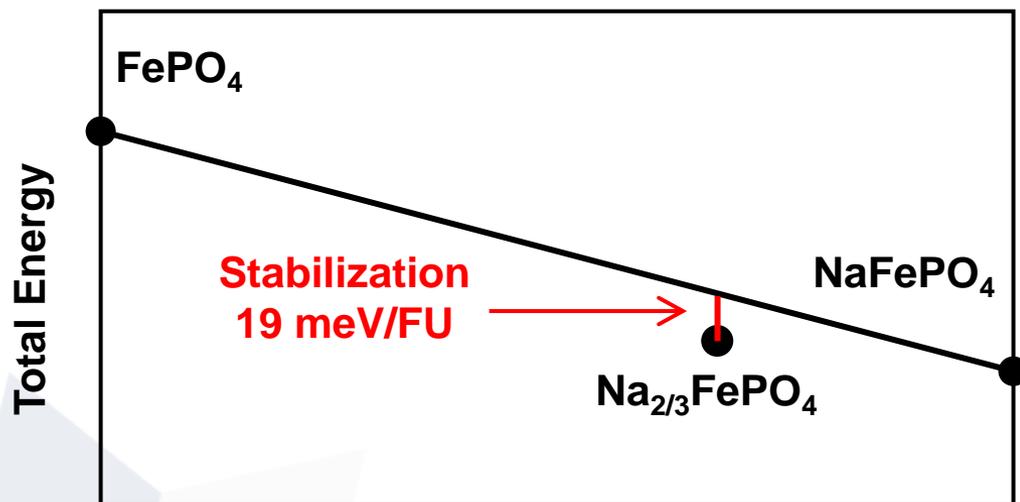
VASP, Structural optimization  
Ferromagnetic ordering, GGA+U

Atom	Valence bond DRX	Valence bond DFT
Fe1	2.014	2.007
Fe2	2.906	3.015
Fe3	2.041	2.010
Na1	1.012	0.989
Na2	1.002	0.993
P1	5.073	4.972
P2	5.012	5.001
P3	4.94	5.014



# Exemples d'applications

Aspects structuraux, énergie totale, stabilité de phase

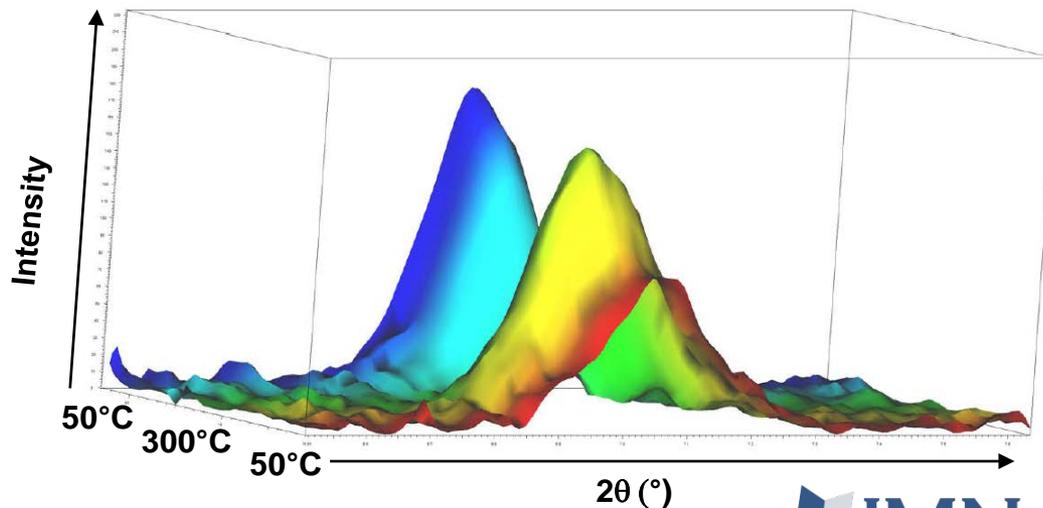


## Phase stability

Comparison Na<sub>2/3</sub>FePO<sub>4</sub>  
vs. 1/3 FePO<sub>4</sub> + 2/3 NaFePO<sub>4</sub>  
(VASP program, GGA+U)

## Order/disorder transition

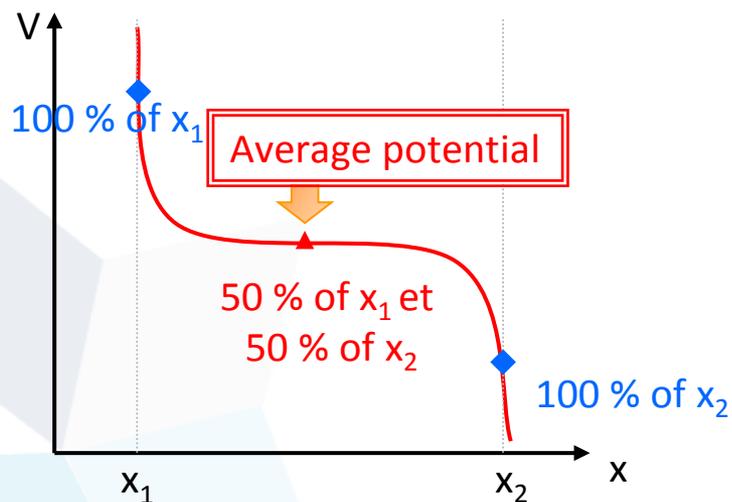
Intensity variation of a  
superstructure peak vs.  
temperature



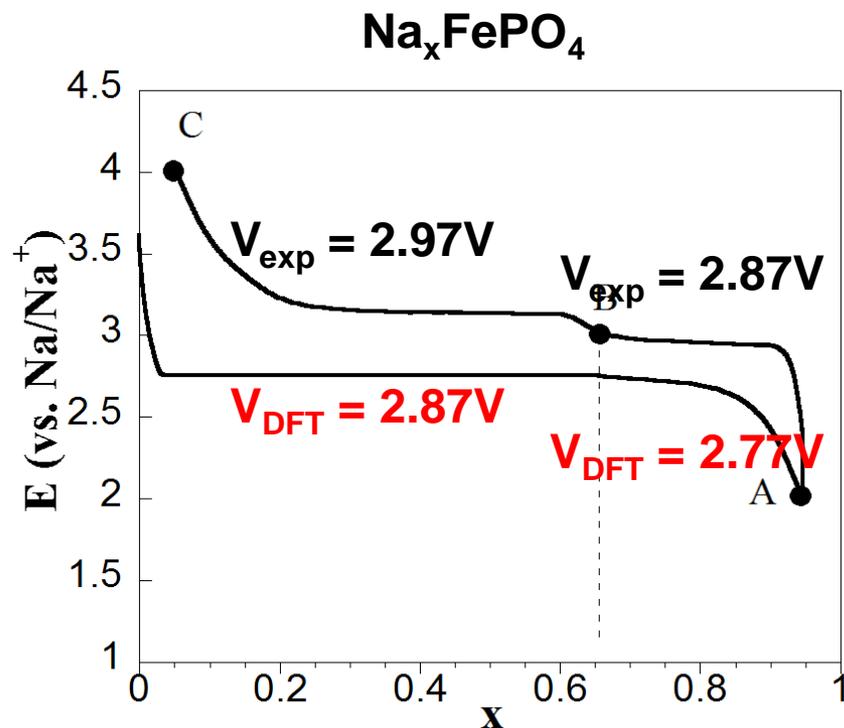
# Exemples d'applications

## Aspects structuraux, énergie totale, stabilité de phase

### Potentiel de batteries



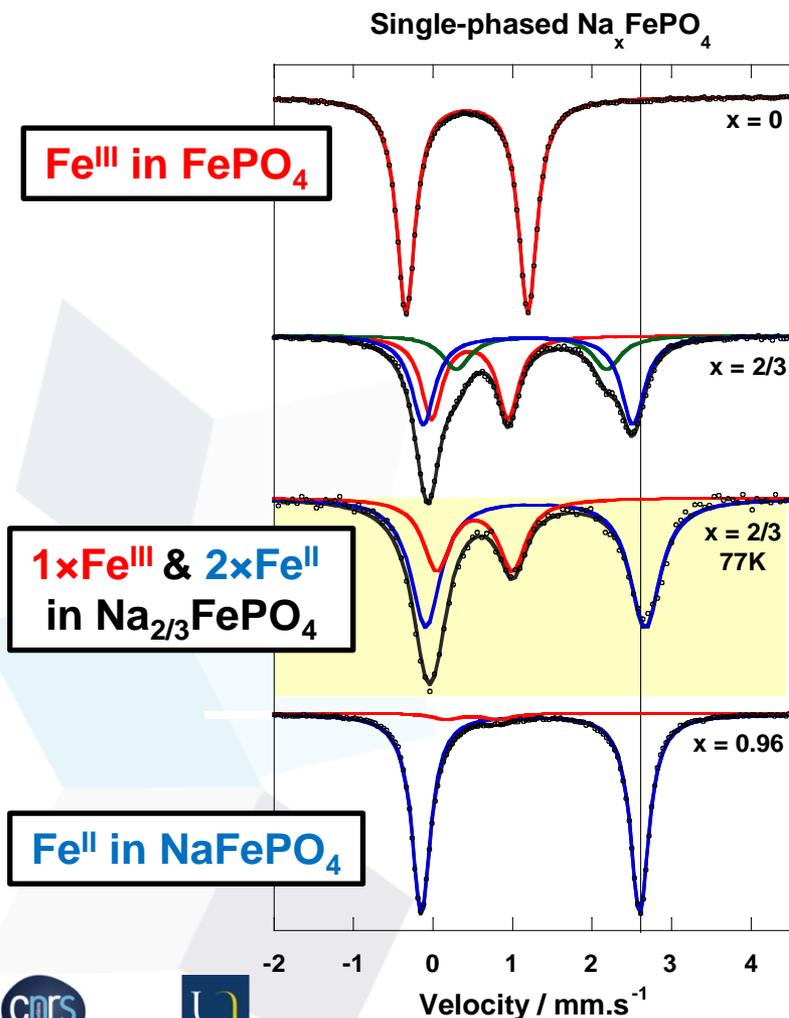
$$V(x) = \frac{-[E_{\text{Na}_{x_2}\text{FePO}_4} - E_{\text{Na}_{x_1}\text{FePO}_4} - (x_2 - x_1)E_{\text{Na}}]}{(x_2 - x_1)F}$$



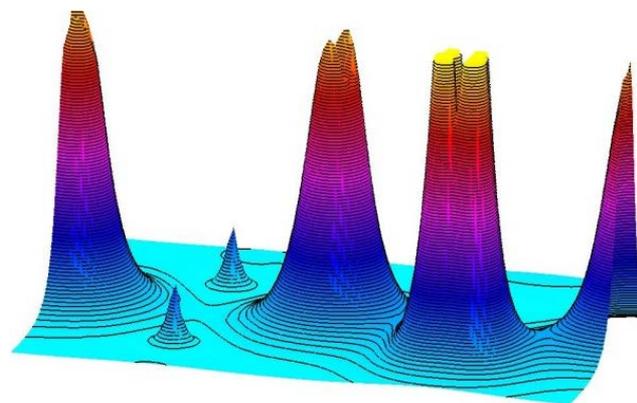
# Exemples d'applications

## Densité de charge et de spin

### Paramètres Mössbauer



### Densité électronique $\rho(r)$



**Isomer Shift :**

$$\text{IS} \propto \rho_0(r)$$

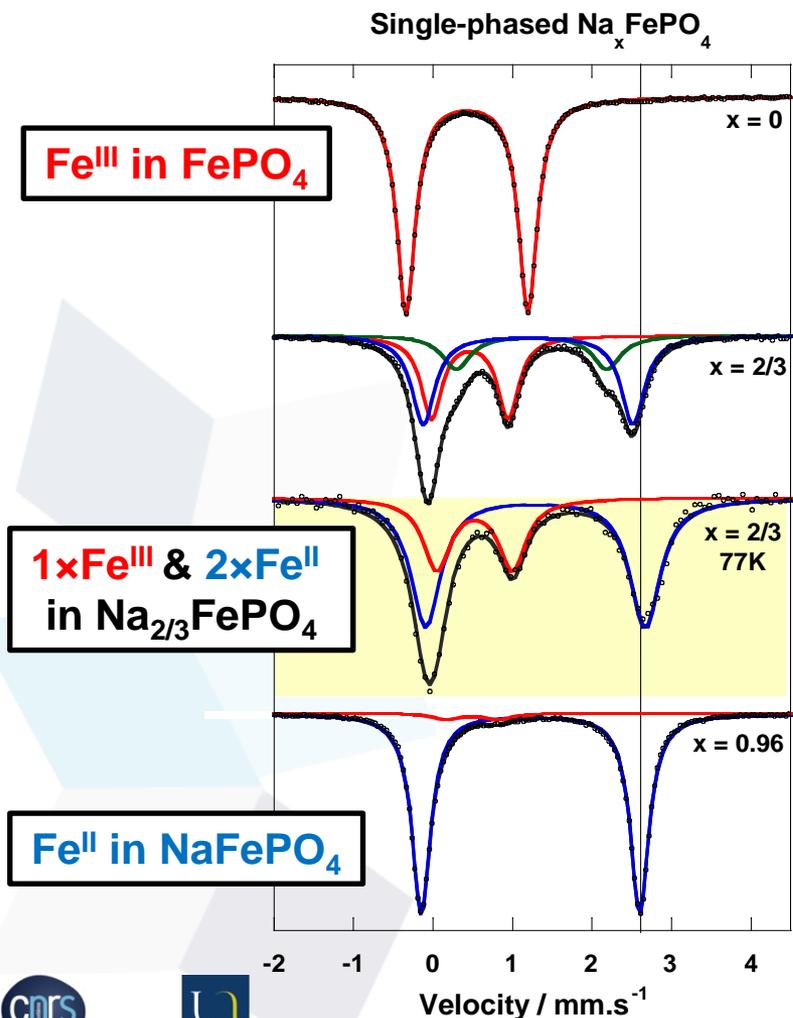
**Quadrupol Splitting :**

$$\Delta(\text{QS}) \propto \text{EFG}(\rho(r))$$

# Exemples d'applications

## Densité de charge et de spin

### Paramètres Mössbauer



### DFT modeling with WIEN2k (GGA +U)

	QS (Exp)	QS (Calc.)	IS (Exp.)	IS (Calc.)
<b>Fe<sup>III</sup> in FePO<sub>4</sub></b>	<b>1.54</b>	1.48	<b>0.43</b>	0.55
<b>Fe<sup>III</sup> (Fe2) in Na<sub>2/3</sub>FePO<sub>4</sub> (77K)</b>	<b>0.92</b>	0.79	<b>0.41</b>	0.63
<b>Fe<sup>II</sup> (Fe1) in Na<sub>2/3</sub>FePO<sub>4</sub> (77K)</b>	<b>2.47</b>	2.42	<b>1.21</b>	1.28
<b>Fe<sup>II</sup> (Fe3) in Na<sub>2/3</sub>FePO<sub>4</sub> (77K)</b>	<b>2.87</b>	2.57	<b>1.25</b>	1.29
<b>Fe<sup>II</sup> in Na<sub>1</sub>FePO<sub>4</sub></b>	<b>2.78</b>	2.55	<b>1.23</b>	1.31

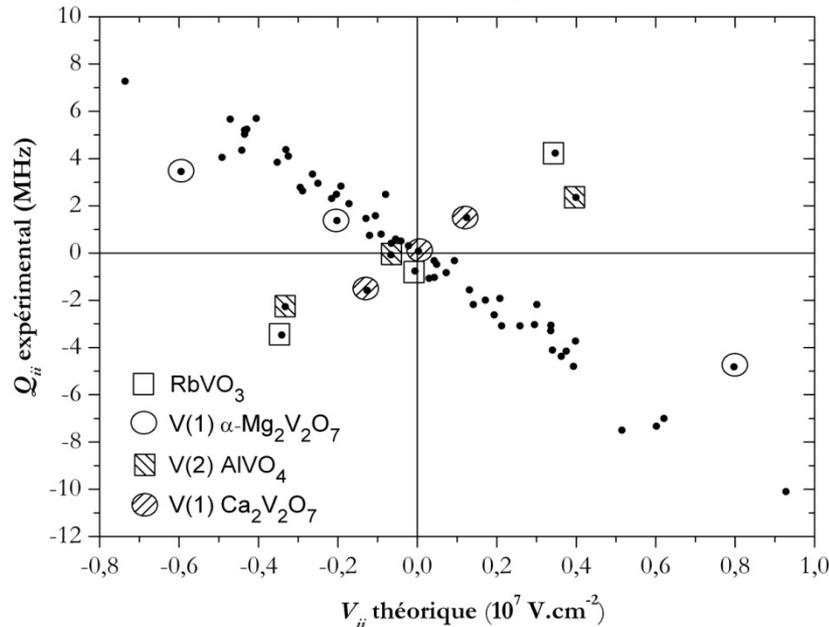
# Exemples d'applications

## Densité de charge et de spin

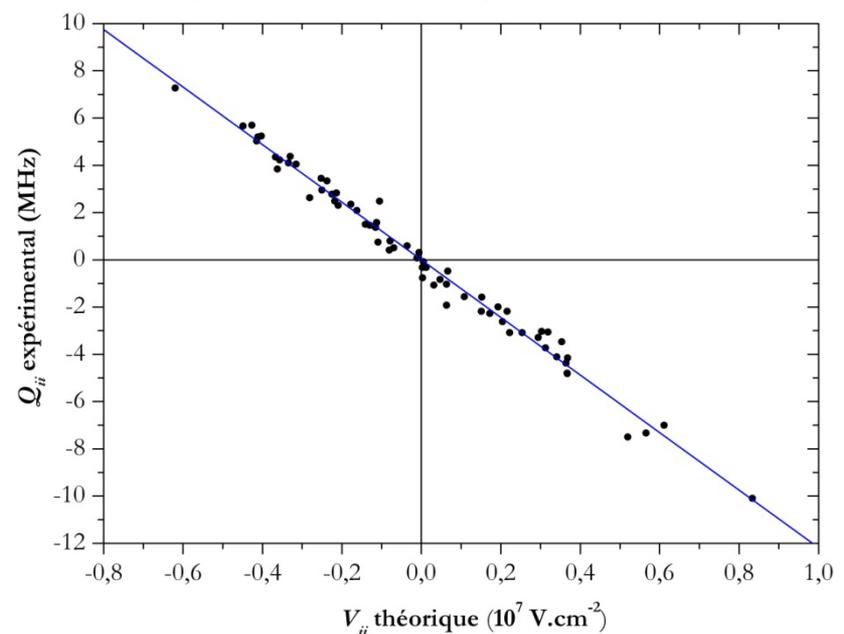
### Paramètres RMN : gradient de champ électrique

Truflandier PhD thesis (2007).

$^{51}\text{V}$ (EFG) : structures expérimentales



$^{51}\text{V}$ (EFG) : structures optimisées (DFT)



### Interaction Quadripolaire

$$Q_{ij} \propto \text{EFG}(\rho(r))$$

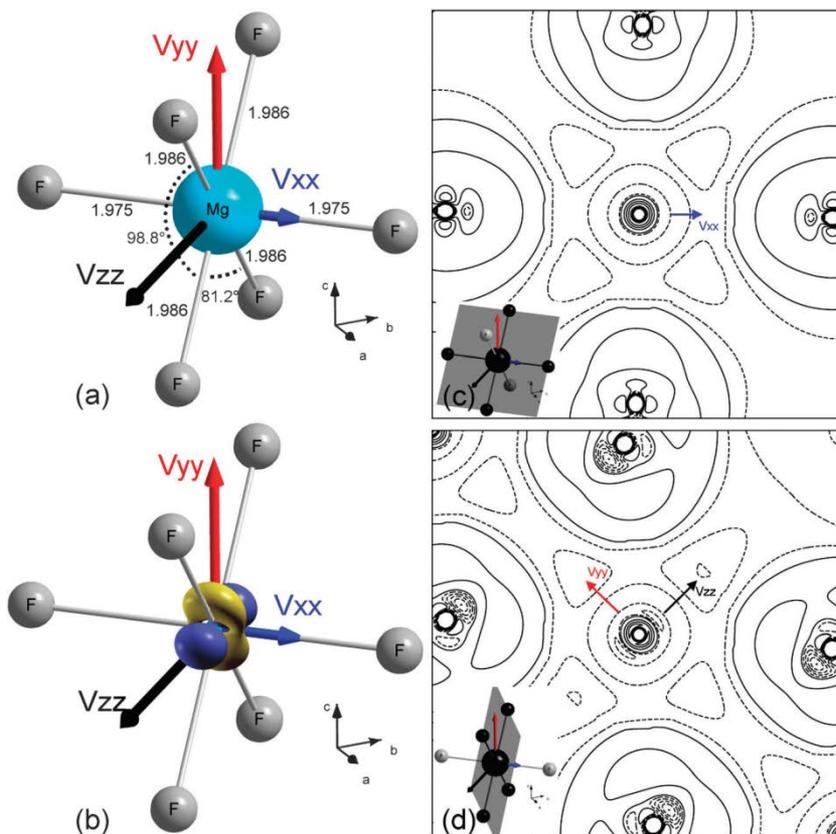
# Exemples d'applications

## Densité de charge et de spin

### Paramètres RMN : gradient de champ électrique

Sadoc *et al.* PCCP 2011, 13, 18539–18550.

$^{25}\text{Mg}(\text{EFG})$  :  $\text{MgF}_2$  structure optimisée (DFT)

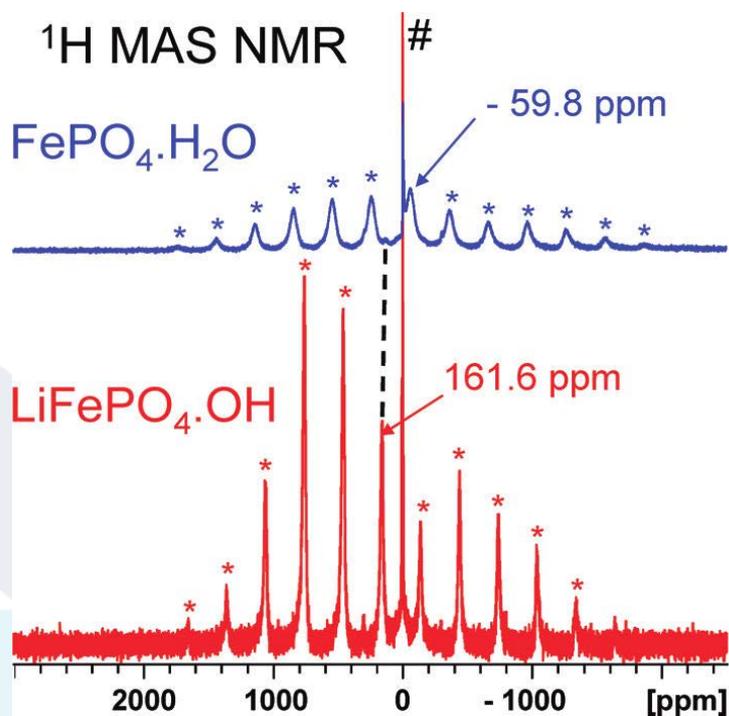


→ Orientation du tenseur EFG

# Exemples d'applications

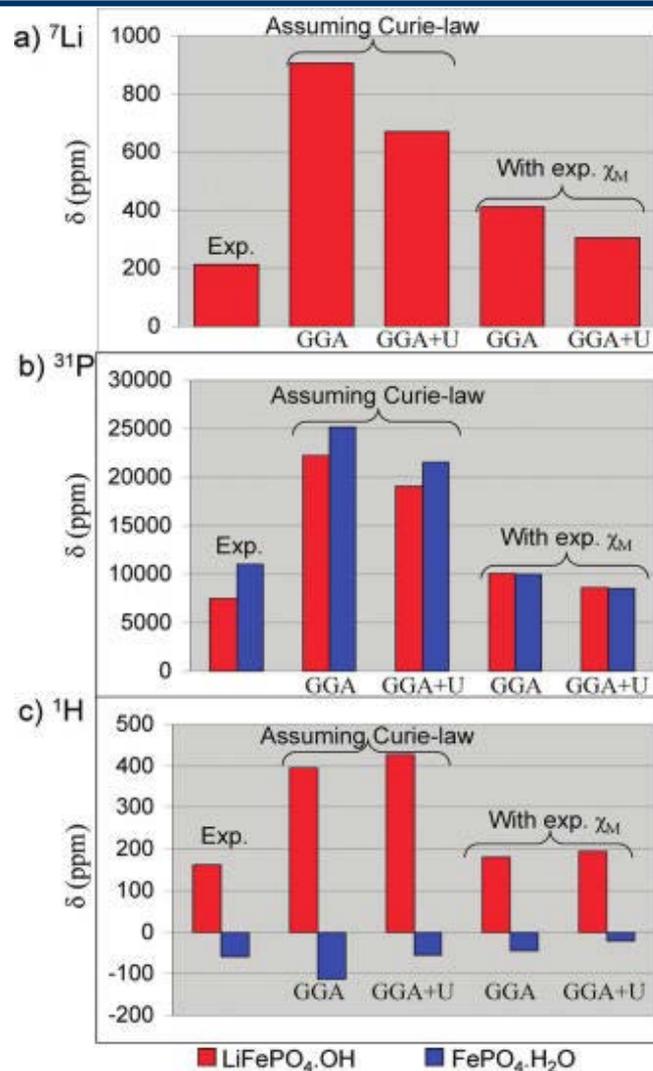
## Densité de charge et de spin

### Paramètres RMN : contact de Fermi



$$\delta^A_{iso}(T) = \frac{1}{3S} \rho^A(0) \chi_M(T)$$

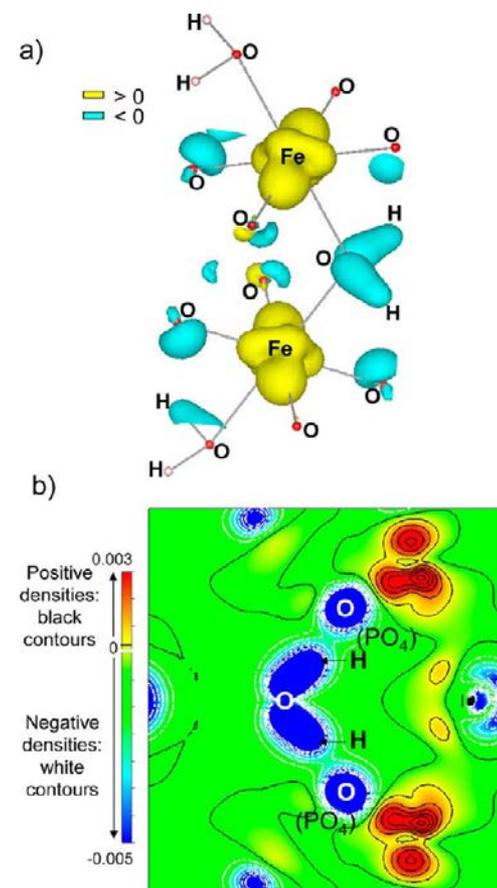
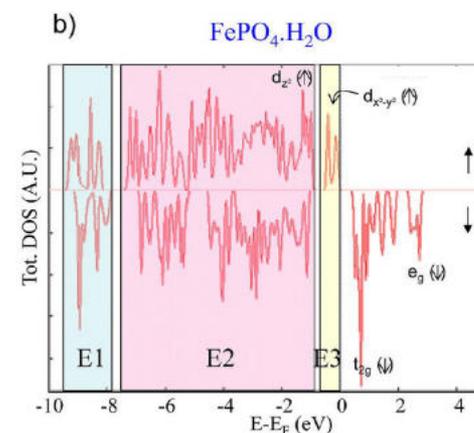
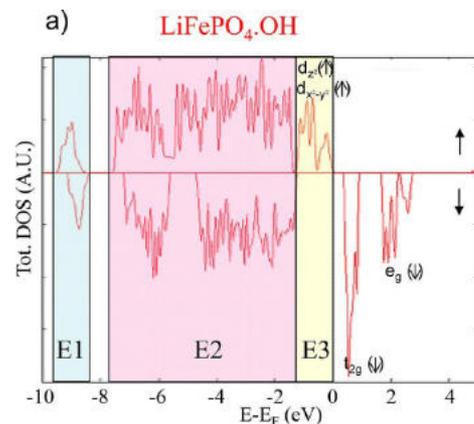
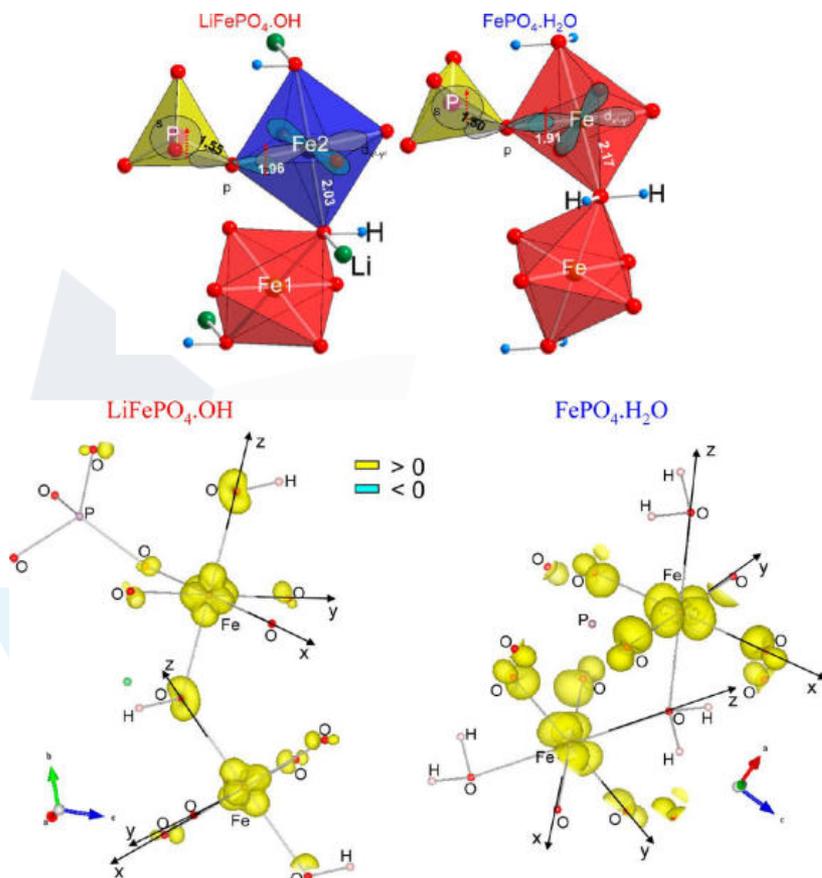
Castets et al. *J. Phys. Chem. C* 2011, 115, 16234–16241.



# Exemples d'applications

## Densité de charge et de spin

### Paramètres RMN : contact de Fermi



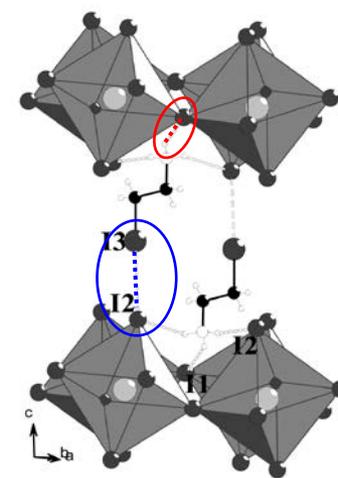
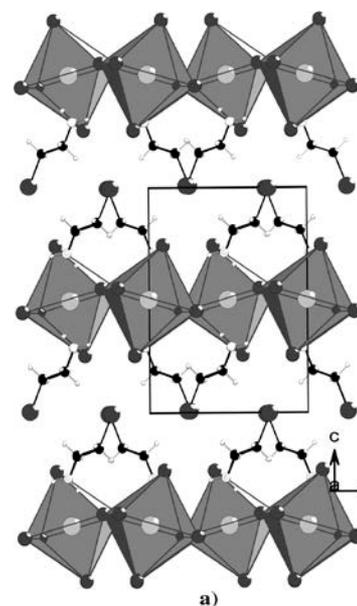
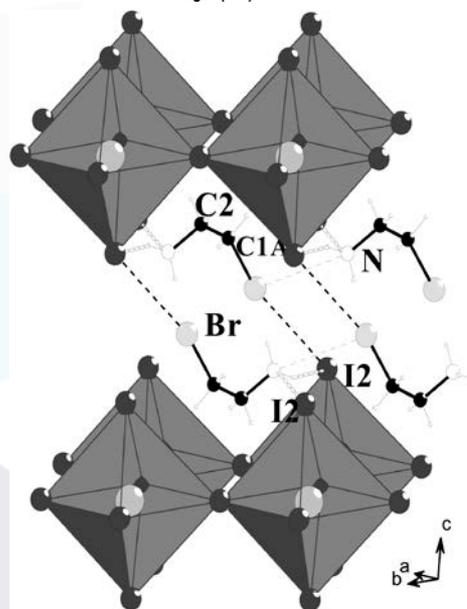
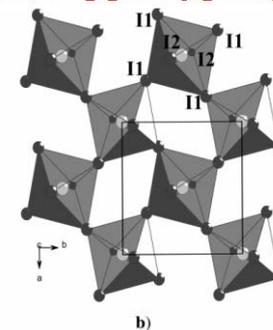
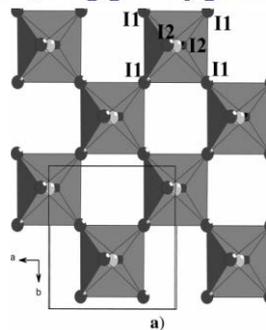
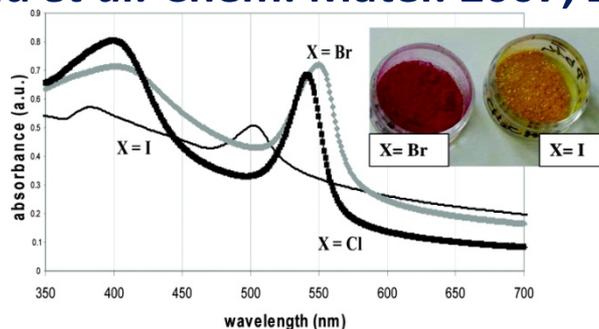
Castets et al. *J. Phys. Chem. C* 2011, 115, 16234–16241.

# Exemples d'applications

## Structure électronique

### Etude de Perovskites Hybrides

Sourisseau *et al.* Chem. Mater. 2007, 19, 600

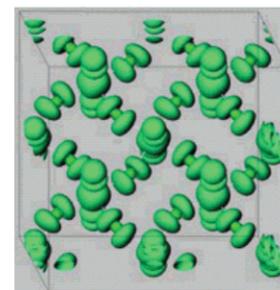
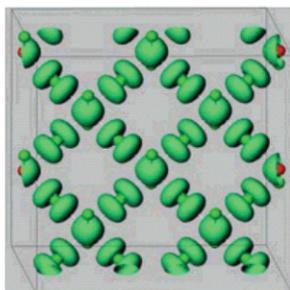
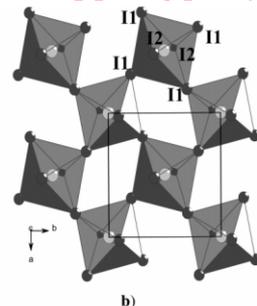
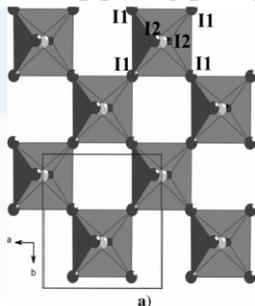
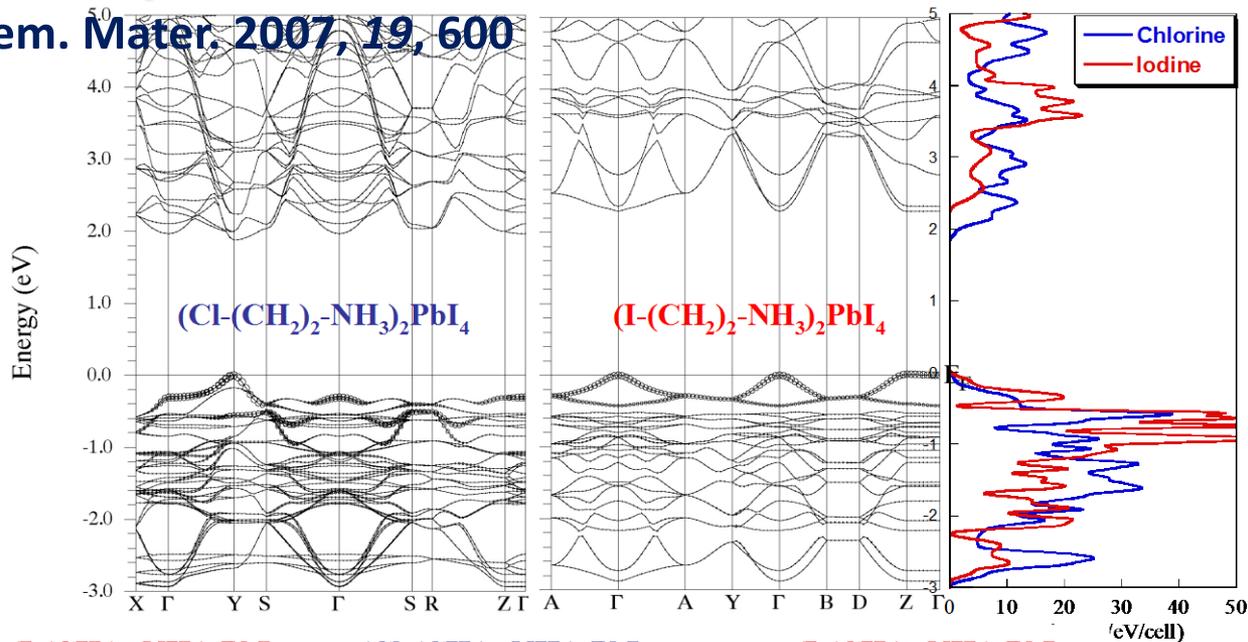
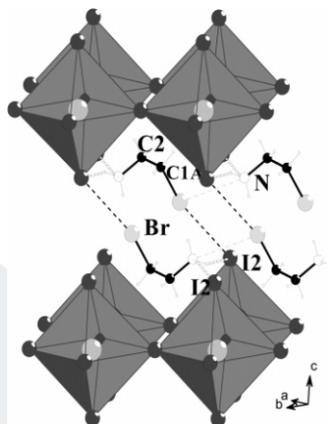


# Exemples d'applications

## Structure électronique

### Etude de Perovskites Hybrides

Sourisseau *et al.* Chem. Mater. 2007, 19, 600

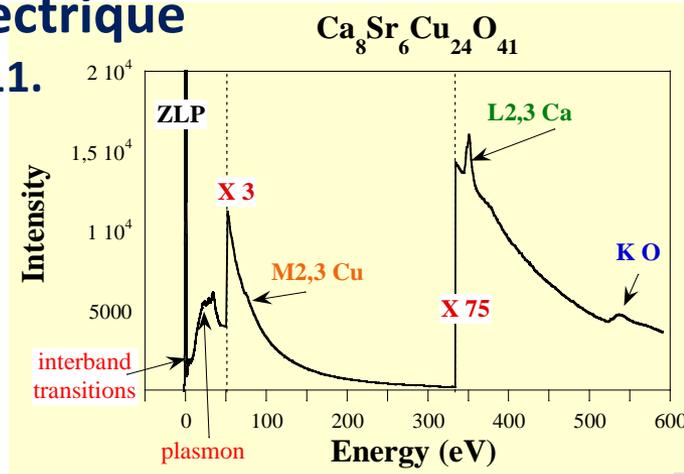


# Exemples d'applications

## Structure électronique

### Spectres EELS Fonction diélectrique

Moreau *et al.* APL 2009, 14, 123111.



Optic  
(no LFE)

Calculation of all matrix elements between  
valence band and conduction band

$$M_{i,j} = \langle \varphi_c^k | p^i | \varphi_v^k \rangle \langle \varphi_v^k | p^j | \varphi_c^k \rangle$$

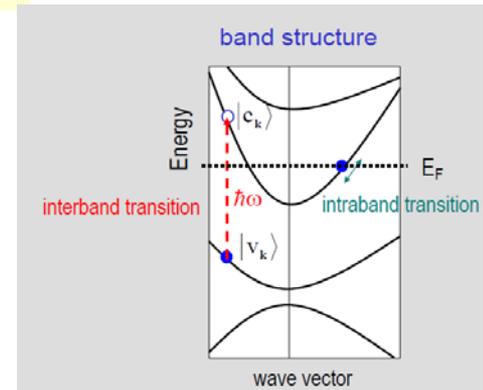
$$\Rightarrow \epsilon_2(0, \omega)$$

Kramers-Kronig transformation

$$\Rightarrow \epsilon_1(0, \omega)$$

Evaluation of the Energy loss function

$$\Rightarrow \frac{d^2 \sigma}{d\Omega dE} \propto \text{Im} \left[ \frac{-1}{\epsilon(0, \omega)} \right]$$



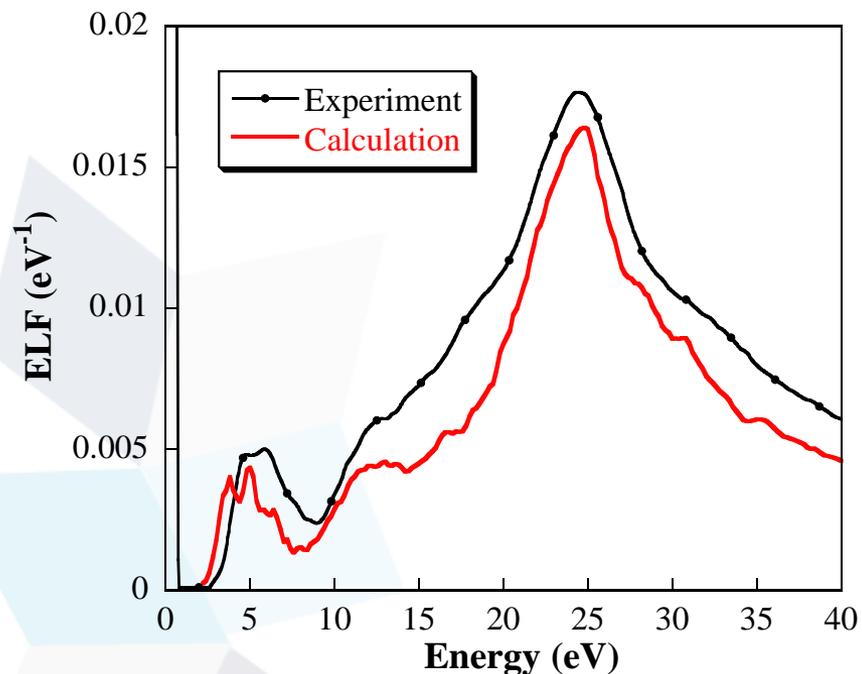
# Exemples d'applications

## Structure électronique

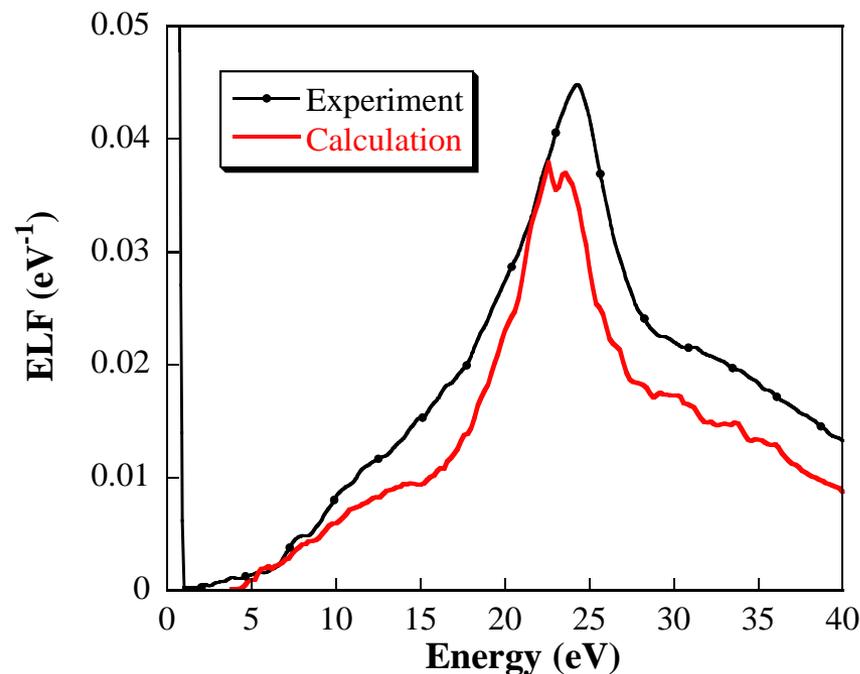
### Spectres EELS Fonction diélectrique

Moreau *et al.* APL 2009, 14, 123111.

$\text{FePO}_4$



$\text{LiFePO}_4$



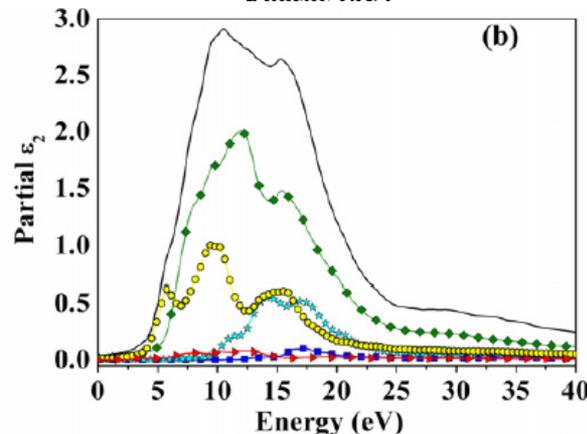
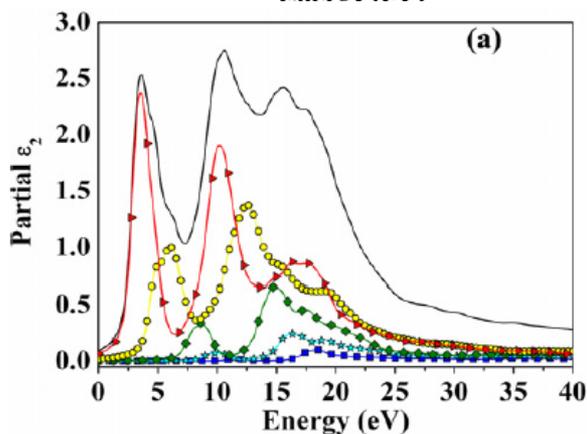
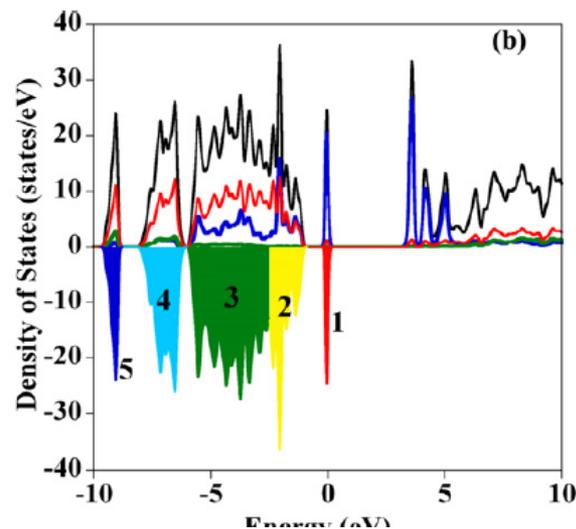
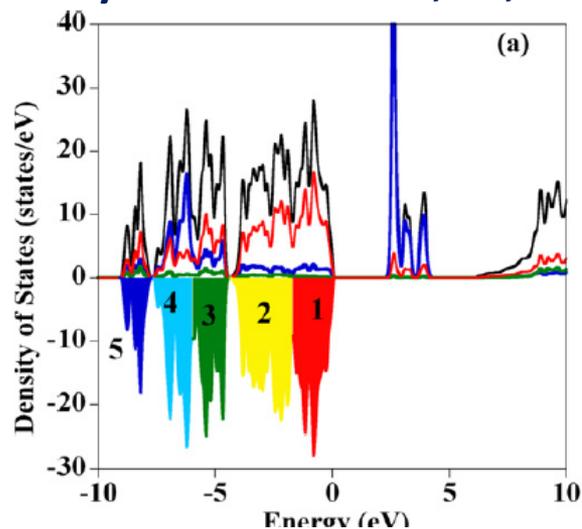
$V_{\text{xc}}$ : GGA+U with  $U=4.3$  eV  
Spin polarized / Anti-ferromagnetic order

ANF 2015 Chimie du Solide – Caen du 23-25 Novembre

# Exemples d'applications

## Structure électronique

Spectres EELS Fonction diélectrique  
Kinyanjui *et al.* J. Phys. Chem. C 2009, 22, 275501.



# Exemples d'applications

## Structure électronique

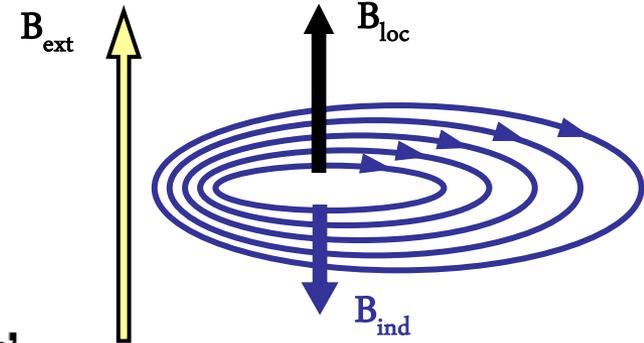
### Paramètres RMN : écrantage et déplacement chimique

Yates, J. R. and Pickard, C. J. **Computations of Magnetic Resonance Parameters for Crystalline Systems: Principles**

Encyclopedia of Magnetic Resonance, 2008, 1-9

$$\sigma_{s,\alpha\beta} = \frac{\partial B_{s,\alpha}^{ind}}{\partial B_{\beta}^{ext}}$$

$$\mathbf{B}^{ind}(\mathbf{r}) = \frac{\mu_0}{4\pi} \int d^3r' \mathbf{j}(\mathbf{r}') \times \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3}$$



DFPT = Density functional perturbation theory

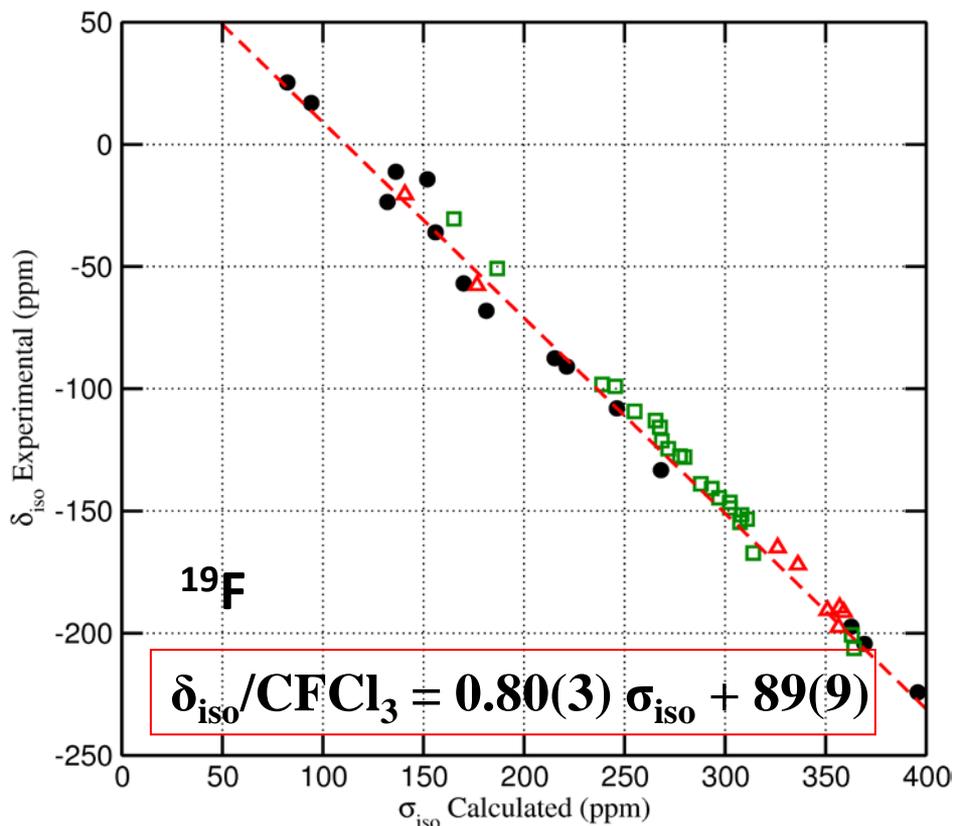
$$\mathbf{j}^{(1)}(\mathbf{r}') = 2 \sum_o \left[ \langle \Psi_o^{(0)} | \mathbf{J}^p(\mathbf{r}') | \Psi_o^{(1)} \rangle + \langle \Psi_o^{(1)} | \mathbf{J}^p(\mathbf{r}') | \Psi_o^{(0)} \rangle \right] + 2 \sum_o \langle \Psi_o^{(0)} | \mathbf{J}^d(\mathbf{r}') | \Psi_o^{(0)} \rangle$$

# Exemples d'applications

## Structure électronique

### Paramètres RMN : écrantage et déplacement chimique

Sadoc *et al.* PCCP 2011, 13, 18539–18550.



# Exemples d'applications

## Structure électronique

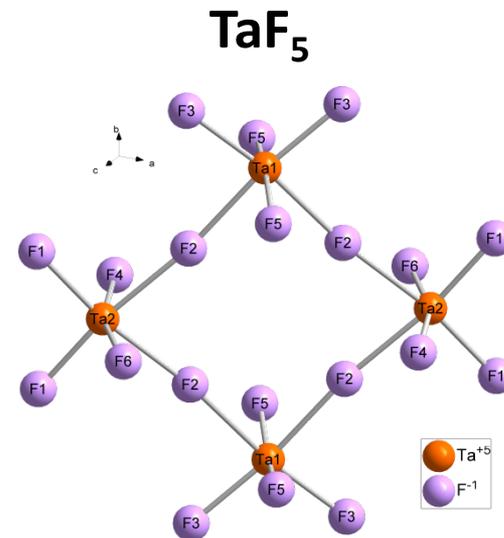
Paramètres RMN : écrantage et déplacement chimique  
 Biswal *et al.* JSSC 2013, 207, 208–217.

$$\delta_{\text{iso}}/\text{CFCl}_3 = 0.80(3) \sigma_{\text{iso}} + 89(9)$$

NMR experiment

NMR simulation

$\delta_{\text{iso}}$ (ppm)	Multiplicity	Assignment	$\sigma_{\text{iso}}$ (ppm)	$\delta_{\text{iso}}$ (ppm)	Assign.
-70.1	4	F2	210.7	-75.4	F2
106.4	2	F4, F6	10.0	90.1	F4
121.9	4	F1, F3, F5	-31.7	124.5	F5
136.3	2	F4, F6	-43.4	134.2	F6
168.6	4	F1, F3, F5	-86.1	169.4	F1
175.9	4	F1, F3, F5	-89.4	172.1	F3



# Codes et moyens de calculs

## Quelques statistiques de publications sur 5 ans (France)



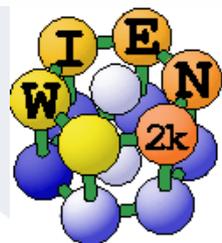
180 publications/an

- Energie/Surface
- Bordeaux, Lille, Montpellier, Nantes



70 publications/an (Physiciens)

- Surface, Optic, RMN
- Jussieu (UPMC)



40 publications/an (Physiciens)

- Spectro, Magnétisme, Lanthanides
- Nantes, Toulouse, Bordeaux

30 publications/an

- AIMD
- Strasbourg

CPMD

16 publications/an

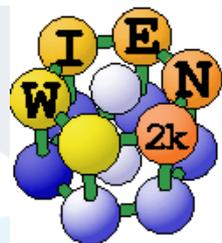
- RMN
- Orléans, Versailles, Rennes, Nantes

CASTEP



# Codes et moyens de calculs

## Disponibilités des codes



Centre Nationaux	Mésocentres	Grappes locales
++	++	++
++	++	++
(+)	+	++
++	++	+
(+)	+	++

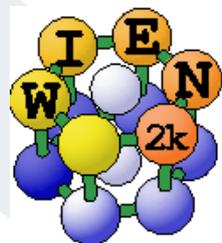
# La communauté, les réseaux

## Des modélisateurs proches des développeurs



### Relations avec G. Kresse

- Nancy, Nantes
- VASP workshop (2012/2016)



### Relations avec P. Blaha/K. Schwarz

- Nantes, Rennes
- WIEN2k workshop (2010/2014)

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### Relations avec J. Yates/C. Pickard Rennes, Orléans, UPMC



# La communauté, les réseaux

## Les modélisateurs entre eux et avec les autres ?

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### → Des structures pour fédérer les modélisateurs

- ✓ RFCT
- ✓ GDR (DFT++, REST)
- ✓ *et pour les modélisateurs de la 15 ?*

### → Comment renforcer le lien entre modélisateurs et expérimentateurs ?

- ✓ Workshop (CECAM Zurich 2013 : RMN et RPE)
- ✓ Formations aux calculs via des écoles (Nantes 2007 : RMN)

### → Rencontres autour de la modélisation pour les matériaux (ICAMM)

- ✓ ICAMM 2016 + VASP Workshop : Rennes/Nantes (Sept. 2016)

# La modélisation en chimie du solide

## Ce dont je n'ai pas parlé !

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### → Au-delà de 0K : Dynamique Moléculaire

- ✓ Conductivité ionique (ions  $\text{Li}^+$ ,  $\text{O}^{2-}$ )
- ✓ Transitions de phase
- ✓ Description des matériaux amorphes (verres chalcogénés)

### → Problématique des défauts

- ✓ Génération des structures
- ✓ Thermodynamique

### → Etude des interfaces

- ✓ Interfaces solide/solide
- ✓ Interfaces solide/molécule

### → Prédiction de structure : « **structure from scratch !** »

- ✓ The Materials Project (G. Ceder & K. Persson)
- ✓ USPEX (A. R. Oganov)

International Symposium on  
**STRUCTURE-PROPERTY RELATIONSHIPS IN SOLID STATE MATERIALS**



 **NANTES**

**SPSSM-2016**

from July 1<sup>st</sup> to 6<sup>th</sup> - Nantes, France

[spssm2016.sciencesconf.org](http://spssm2016.sciencesconf.org)



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infos sur le site [spssm2016.sciencesconf.org](http://spssm2016.sciencesconf.org)



ANF 2015 Chimie du Solide – Caen du 23-25 Novembre

