

Le Chrome dans tous ses états (électroniques et magnétiques)

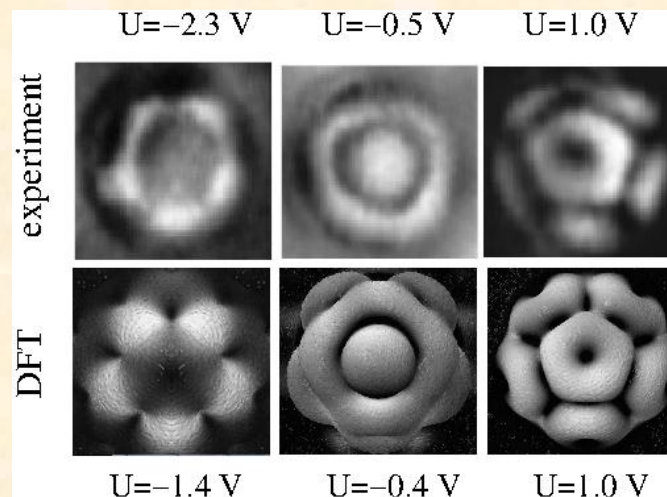
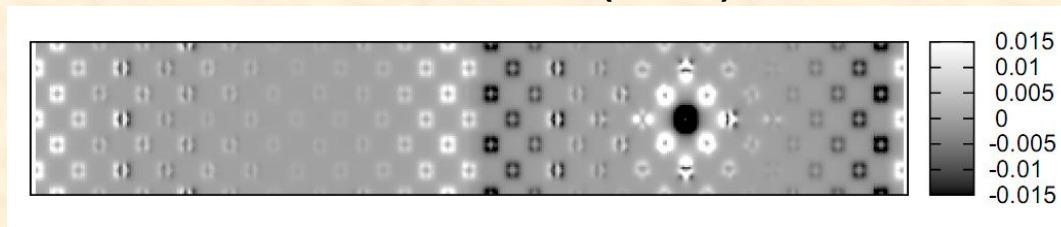
Cyrille Barreteau (SPCSI)

Alexander Smogunov (SPCSI)

Parwana Habibi (SPCSI)

Chu Chun Fu (SRMP)

Romain Soulairol (SRMP)

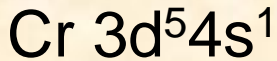


Service de Physique et Chimie des Surfaces et Interfaces (**SPSCI**)

Service de Recherche en Métallurgie Physique (**SRMP**)

Pourquoi s'intéresser au Chrome?

Élément assez répandu sur terre



	1A 1																	8A 18
Core	1 H $1s^1$	2A 2											3A 13	4A 14	5A 15	6A 16	7A 17	2 He $1s^2$
[He]	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$
[Ne]	11 Na $3s^1$	12 Mg $3s^2$	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8 9 10			1B 11	2B 12	13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$
[Ar]	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$	31 Ga $3d^{10} 4s^2 4p^1$	32 Ge $3d^{10} 4s^2 4p^2$	33 As $3d^{10} 4s^2 4p^3$	34 Se $3d^{10} 4s^2 4p^4$	35 Br $3d^{10} 4s^2 4p^5$	36 Kr $3d^{10} 4s^2 4p^6$
[Kr]	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^2$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$	49 In $4d^{10} 5s^2 5p^1$	50 Sn $4d^{10} 5s^2 5p^2$	51 Sb $4d^{10} 5s^2 5p^3$	52 Te $4d^{10} 5s^2 5p^4$	53 I $4d^{10} 5s^2 5p^5$	54 Xe $4d^{10} 5s^2 5p^6$
[Xe]	55 Cs $6s^1$	56 Ba $6s^2$	71 Lu $4f^{14} 5d^1 6s^2$	72 Hf $4f^{14} 5d^2 6s^2$	73 Ta $4f^{14} 5d^3 6s^2$	74 W $4f^{14} 5d^4 6s^2$	75 Re $4f^{14} 5d^5 6s^2$	76 Os $4f^{14} 5d^6 6s^2$	77 Ir $4f^{14} 5d^7 6s^2$	78 Pt $4f^{14} 5d^9 6s^1$	79 Au $4f^{14} 5d^{10} 6s^1$	80 Hg $4f^{14} 5d^{10} 6s^2$	81 Tl $4f^{14} 5d^{10} 6s^2 6p^1$	82 Pb $4f^{14} 5d^{10} 6s^2 6p^2$	83 Bi $4f^{14} 5d^{10} 6s^2 6p^3$	84 Po $4f^{14} 5d^{10} 6s^2 6p^4$	85 At $4f^{14} 5d^{10} 6s^2 6p^5$	86 Rn $4f^{14} 5d^{10} 6s^2 6p^6$
[Rn]	87 Fr $7s^1$	88 Ra $7s^2$	103 Lr $5f^{14} 6d^1 7s^2$	104 Rf $5f^{14} 6d^2 7s^2$	105 Db $5f^{14} 6d^3 7s^2$	106 Sg $5f^{14} 6d^4 7s^2$	107 Bh $5f^{14} 6d^5 7s^2$	108 Hs $5f^{14} 6d^6 7s^2$	109 Mt $5f^{14} 6d^7 7s^2$	110	111	112		114		116		
[Xe]	Lanthanide series		57 La $5d^1 6s^2$	58 Ce $4f^1 5d^1 6s^2$	59 Pr $4f^3 6s^2$	60 Nd $4f^7 6s^2$	61 Pm $4f^5 6s^2$	62 Sm $4f^6 6s^2$	63 Eu $4f^7 6s^2$	64 Gd $4f^7 5d^1 6s^2$	65 Tb $4f^9 6s^2$	66 Dy $4f^{10} 6s^2$	67 Ho $4f^{11} 6s^2$	68 Er $4f^{12} 6s^2$	69 Tm $4f^{13} 6s^2$	70 Yb $4f^{14} 6s^2$		
[Rn]	Actinide series		89 Ac $6d^1 7s^2$	90 Th $6d^2 7s^2$	91 Pa $5f^2 6d^1 7s^2$	92 U $5f^3 6d^1 7s^2$	93 Np $5f^4 6d^1 7s^2$	94 Pu $5f^6 7s^2$	95 Am $5f^7 7s^2$	96 Cm $5f^7 6d^1 7s^2$	97 Bk $5f^9 7s^2$	98 Cf $5f^{10} 7s^2$	99 Es $5f^{11} 7s^2$	100 Fm $5f^{12} 7s^2$	101 Md $5f^{13} 7s^2$	102 No $5f^{14} 7s^2$		
			Metals		Metalloids		Nonmetals											

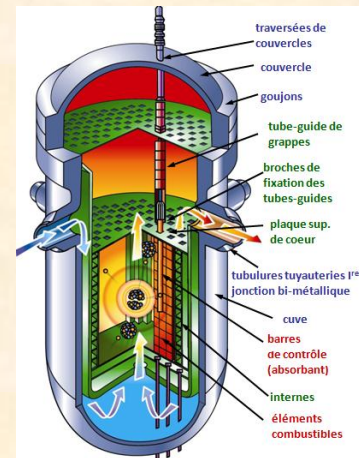
Pourquoi s'intéresser au Chrome?

Nombreuses applications en métallurgie

Chromage: meilleure
résistance à la corrosion

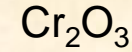
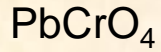


Matériau de structure envisagé pour les futurs
réacteurs (fission, fusion)



Pourquoi s'intéresser au Chrome?

Pigment

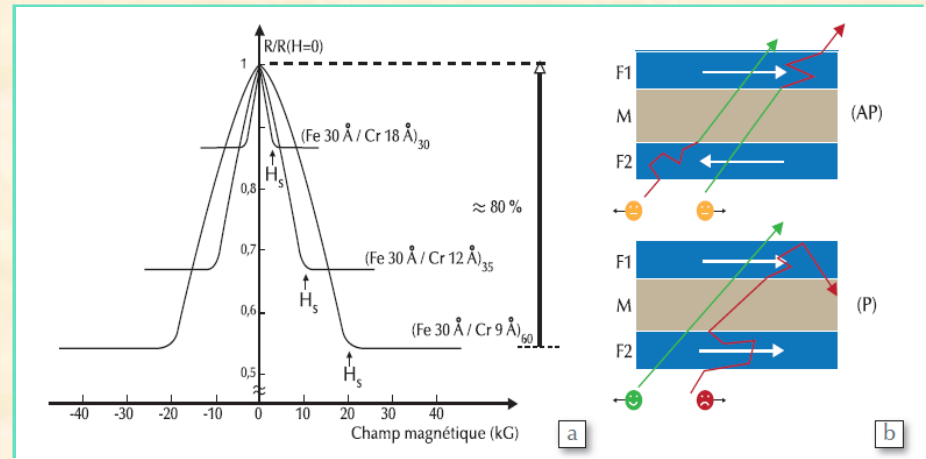


Stockage de l'information



Les bonnes vieilles cassettes

Matériau historique de la spintronique



Magnéto-Résistance Géante: GMR PRL 61, 2472 (1988)

Pourquoi s'intéresser au Chrome?

Parce que c'est joli

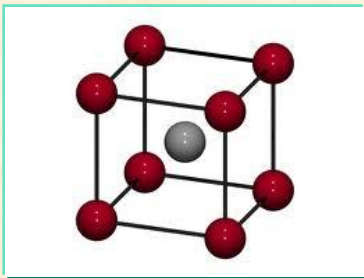
Rubis



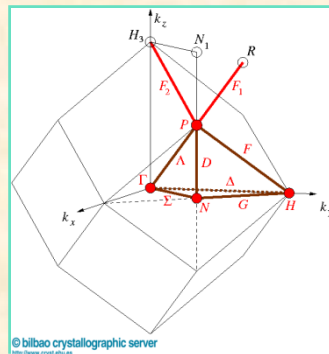
Pourquoi que je vis
Parce que c'est joli
Boris Vian

Couleur liée au Cr^{3+}

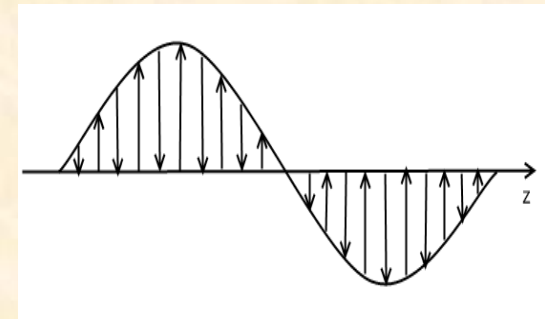
Structure cristalllographique très simple



Cubique centré



Propriétés magnétiques complexes



Onde de spin

MAIS

Susceptibilité magnétique

$$\vec{M} = \underline{\underline{\chi}} \vec{H}$$

Plus généralement

$$\delta \vec{m}(\vec{r}) = \int \chi(\vec{r}, \vec{r}') \delta \vec{H}(\vec{r}') d\vec{r}'$$

Excitation périodique

$$\delta \vec{H}(\vec{r}) = \delta H \sum_n (\cos(q \cdot \vec{R}_n), \sin(q \cdot \vec{R}_n), 0)$$

$$\begin{cases} x = r \sin \theta \cos \phi \\ y = r \sin \theta \sin \phi \\ z = r \cos \theta \end{cases} \quad \theta = \frac{\pi}{2}$$

$$\delta \vec{m}(\vec{q}) = \chi(\vec{q}) \delta \vec{H}(\vec{q})$$

Quelques rappels de magnétisme

Susceptibilité magnétique d'un système sans interaction électronique

$$\chi_0(\vec{q})$$

Susceptibilité magnétique d'un système avec interaction électronique

$$\chi(\vec{q}) = \frac{\chi_0(\vec{q})}{1 - I\chi_0(\vec{q})} \quad I: \text{paramètre de Stoner}$$

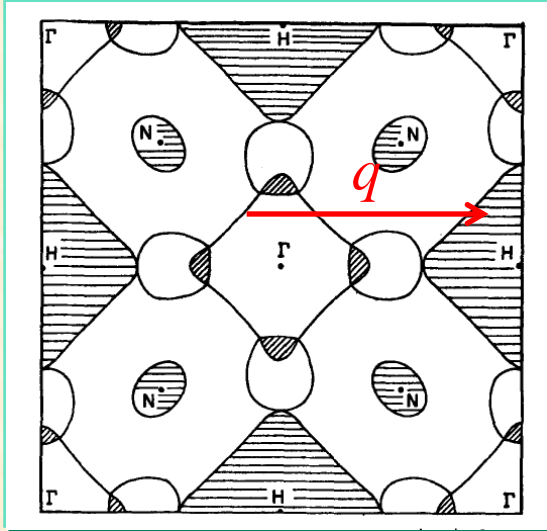
perturbation statique \rightarrow Critère de Stoner

$$\chi(0) = \frac{\chi_0(0)}{1 - I\chi_0(0)} \quad \chi_0(0) = D(E_F)$$

$$ID(E_F) \geq 1 \quad D(E_F): \text{Densité d'état au niveau de Fermi}$$

Cas général \rightarrow critère de Stoner généralisé

$$I\chi_0(q) \geq 1$$



$$\chi_0(\vec{q}) = \sum_{\vec{k}, \mu\nu} \frac{[f(\varepsilon_{\vec{k},\nu}) - f(\varepsilon_{\vec{k}-\vec{q},\mu})]}{\varepsilon_{\vec{k},\nu} - \varepsilon_{\vec{k}-\vec{q},\mu}} \left| \langle \vec{k}, \nu | e^{iq \cdot r} | \vec{k} - \vec{q}, \mu \rangle \right|^2$$

Emboitement (nesting) de la surface de Fermi

$$\vec{q} = \frac{2\pi}{a} (0, 0, 1) = H$$

Ordre antiferromagnétique

$$M(R=0) = M_0 \quad M(a(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})) = \cos(\pi)M_0 = -M_0$$

$$\vec{q} = \frac{2\pi}{a} (0, 0, q_z)$$

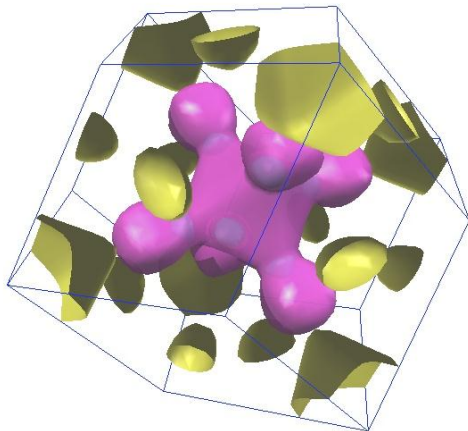
Onde de spin

$$R_n = \frac{a}{2} (x, y, n) \quad M(R_n) = M_0 \cos(q_z \pi n)$$

$$q_z = 0.952 \approx 0.95 = \frac{19}{20}$$

Période= $N = 40$

Cr



Ab-initio: PWscf & Siesta

PWscf: Ondes planes+pseudopotentiels



Précis mais lourd numériquement

Siesta: Base localisée+pseudopotentiels



Moins précis mais efficace numériquement

Liaisons fortes magnétiques

$$H = H_0 + H_{mag} + H_{LCN}$$

- H_0 : Hamiltonien liaisons fortes spd non magnétique
- H_{mag} : Hamiltonien de Stoner

$$H_{mag} = -\frac{1}{2} \sum_{i\lambda} I_{i\lambda} \vec{m}_{i\lambda} \cdot \vec{\sigma}$$

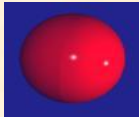
- H_{LCN} : Hamiltonien de neutralité de charge

$$H_{LCN} = \sum_{i\lambda} U_{LCN} (n_i - n_i^0) |i\lambda\rangle \langle i\lambda| + \sum_{i\lambda \in d} U_d (n_{i,d} - n_{i,d}^0) |i\lambda\rangle \langle i\lambda|$$

Détermination des paramètres

$$H_0 = \sum_{ij\lambda\mu} |i\lambda\rangle \langle i\lambda| H |j\mu\rangle \langle j\mu|$$

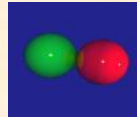
i : atom
 λ : orbitale



$\lambda = s$



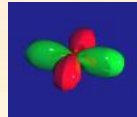
p_x



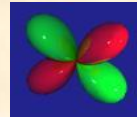
p_y



p_z



d_{xy}



d_{xz}



d_{yz}



$d_{x^2-y^2}$



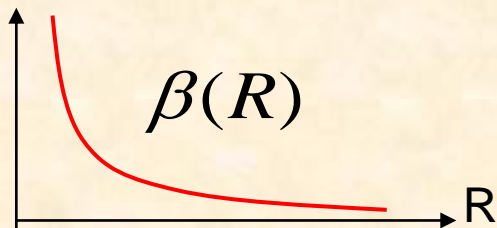
$d_{3z^2-r^2}$

Intégrale de saut

$$\beta_{ij}^{\lambda\mu} = \langle i\lambda | H | j\mu \rangle$$

Termes diagonaux

$$\varepsilon_{i\lambda} = \langle i\lambda | H | i\lambda \rangle$$

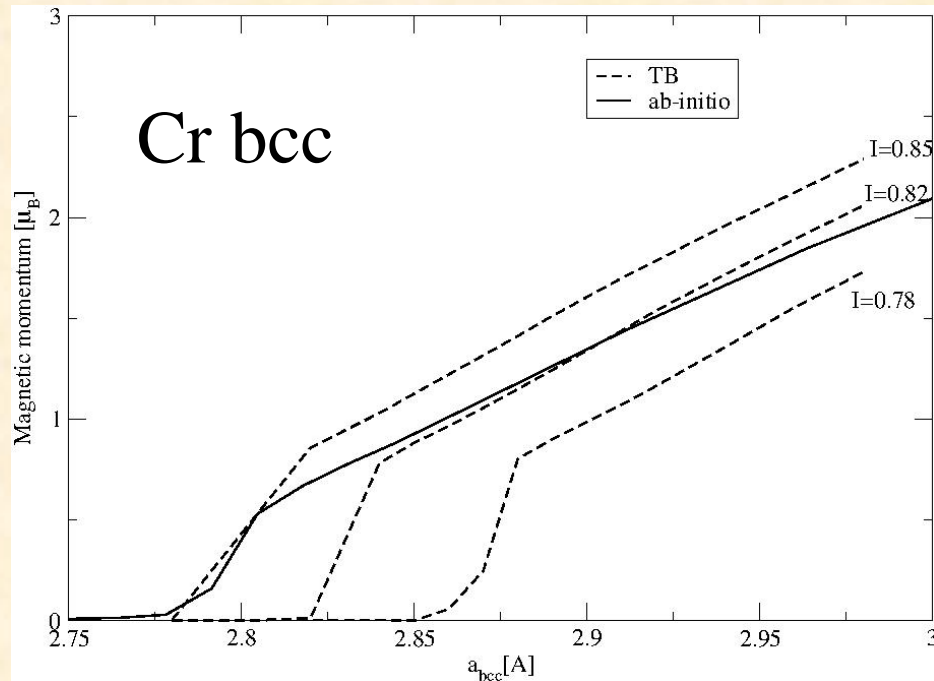


Ajustement sur des structures
de bandes et courbes de cohésion
Ab-initio non magnétiques

Détermination des paramètres

- H_{mag} : paramètre de Stoner I ajusté pour reproduire les courbes ab-initio $M(d)$

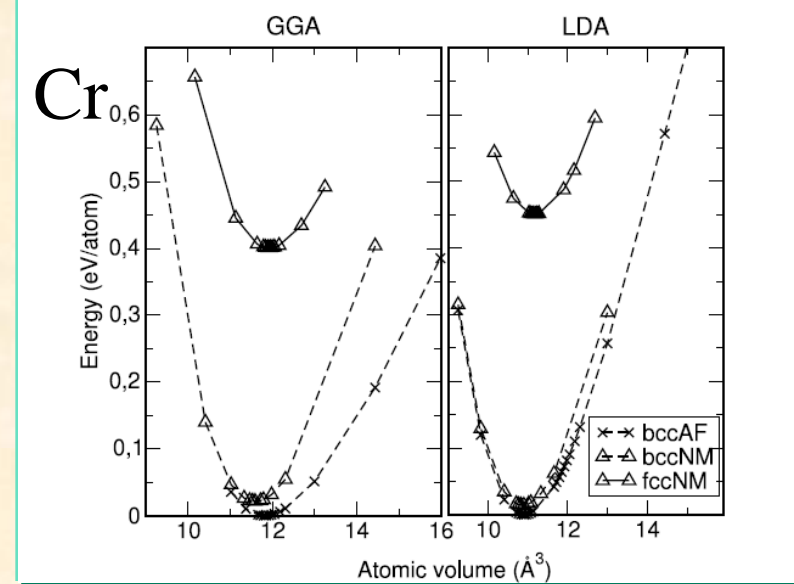
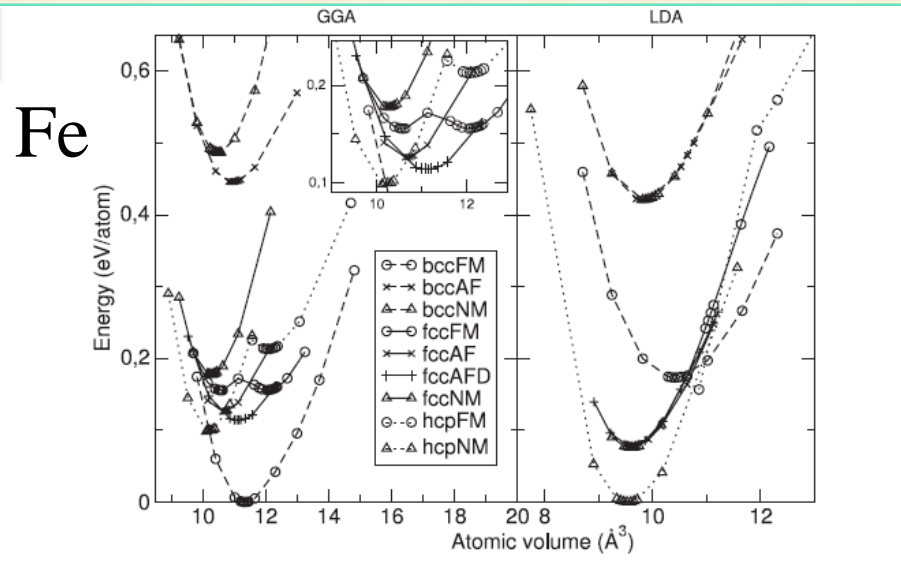
$$H_{\text{mag}} = -\frac{1}{2} \sum_{i\lambda} I_{i\lambda} \vec{m}_{i\lambda} \cdot \vec{\sigma}$$



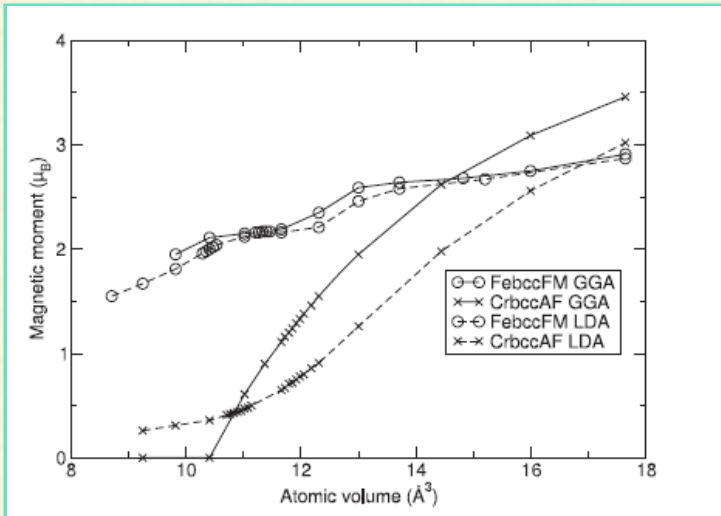
$$I = 0.82eV$$

Effet de la fonctionnelle: LDA vs GGA (PWscf PAW)

E(d)



M(d)

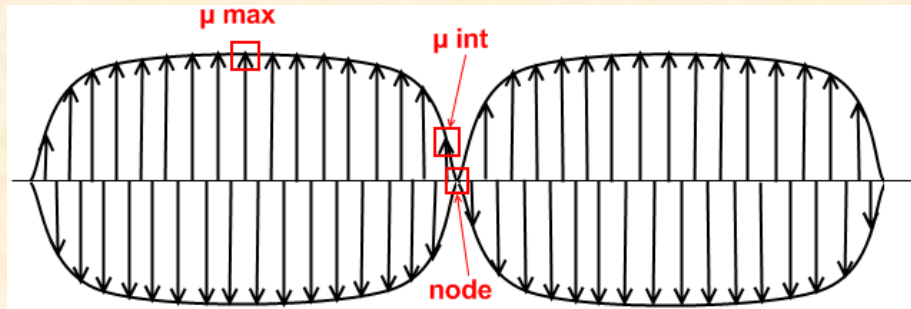
**GGA nécessaire**

(encore un effet du paramètre de maille)

Mais moment trop fort

$$|M_{th}| \sim 1.2 \mu_B \quad |M_{exp}| \sim 0.6 \mu_B$$

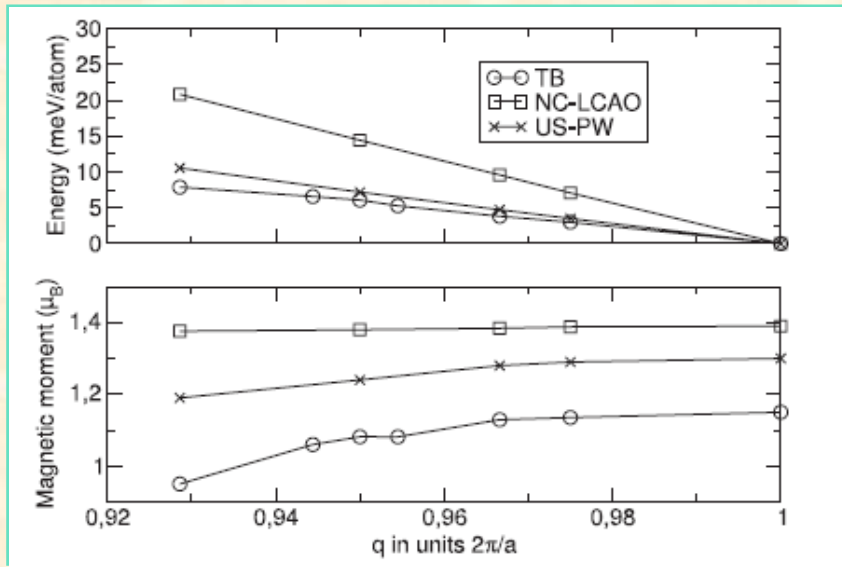
L'état fondamental de Cr: SDW??



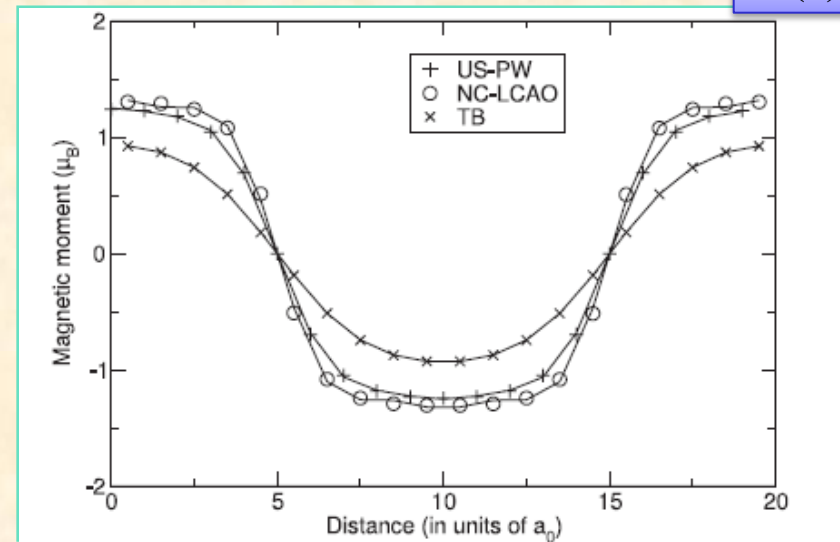
$$\mu = \mu_0 \cdot \cos(\mathbf{q} \cdot \mathbf{R})$$

L'onde de spin n'est jamais stabilisée!

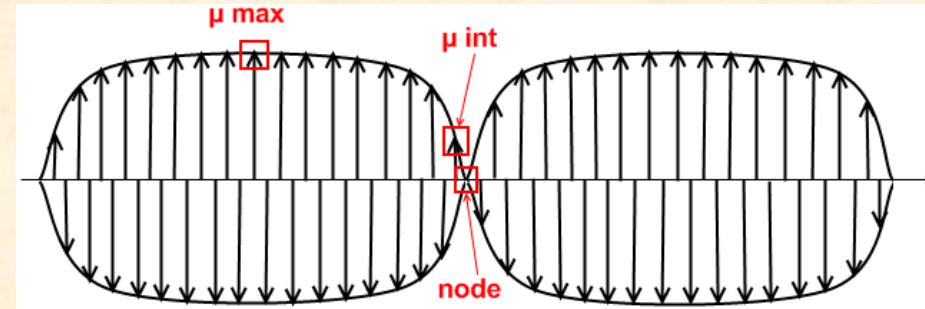
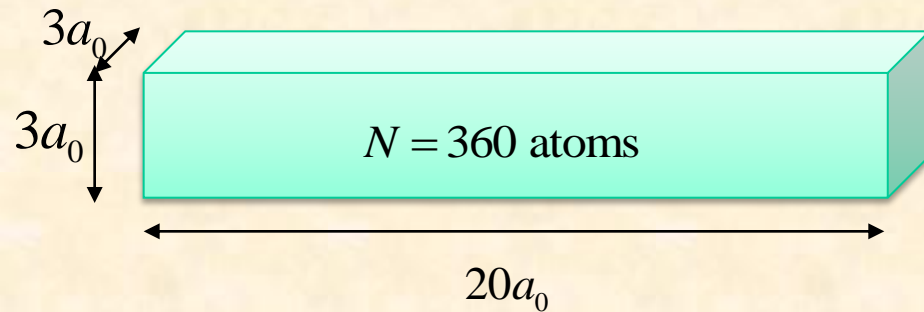
$\Delta E(\mathbf{q})$



$M(z)$



C.C Fu, R/ Soulaïrol



$$E_V^f(\text{Cr}) = E(n-1)\text{Cr},V - \frac{(n-1)}{n} E(n\text{Cr})$$

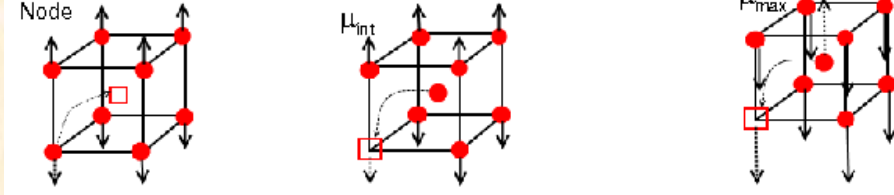
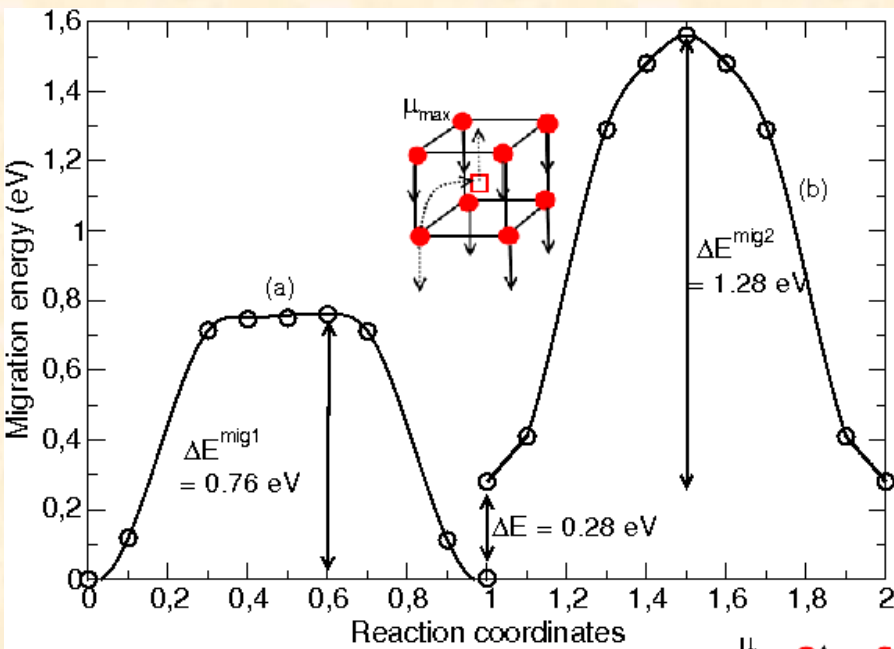
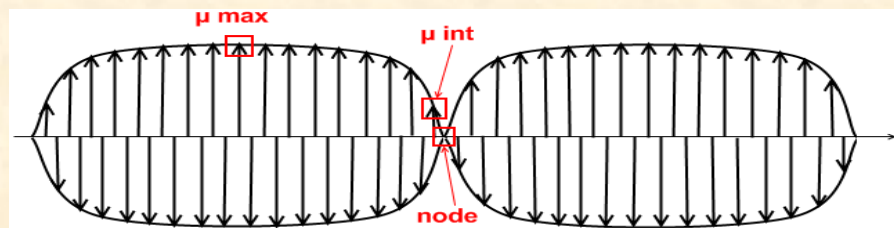
Position lacune	AF	NM	SDW-nœud	SDW- site inter.	SDW- site max.	Exp.*
E_L^f (eV)	2.41	2.32	2.09	2.10	2.38	2.0

SIESTA

* Landolt-Börnstein, PAS experiments (1985)

L'énergie de formation est plus faible dans un nœud

Energie de migration des lacunes dans Cr SDW



Cr	AF	NM	SDW-site μ_{max}	SDW-nœud
E_{mig} (eV)	1.32	0.82	1.28	0.76

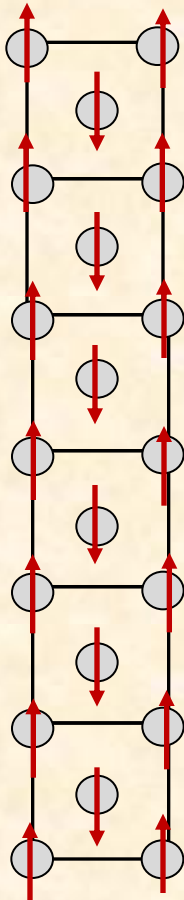
Plus facile de migrer dans les plans nœaux

Anisotropie de migration des lacunes

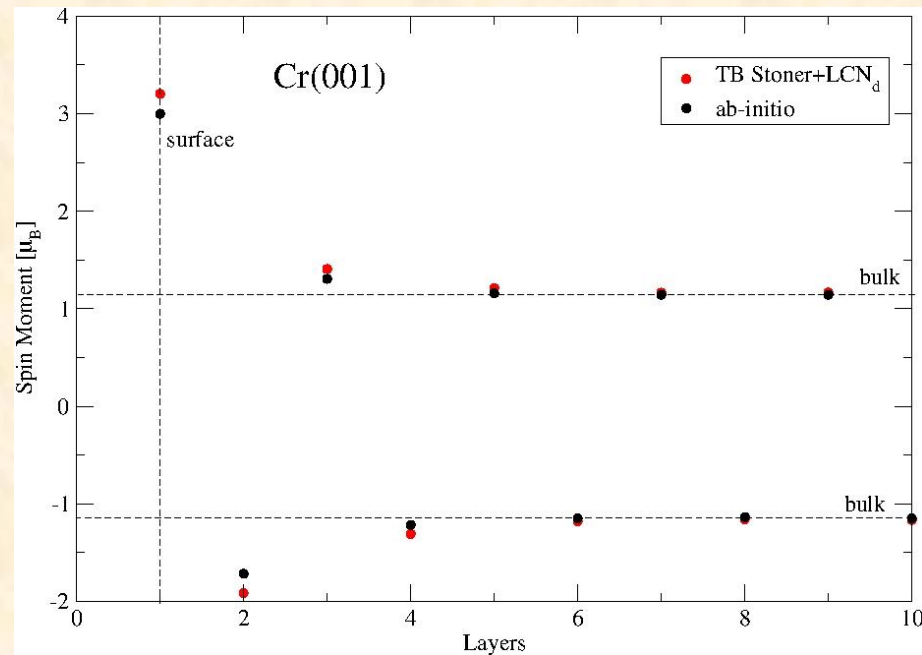
PRB 83, 214103 (2011)

Surface de Cr(001)

La surface Cr(001) simple (AF)



Le slab de N plans atomiques AF



$$\left| M_{surf}^{100} \right| \sim 3\mu_B$$

Energie de Surface

Cr(001)/Cr(110)

$$\gamma_{surf} = \frac{1}{2A} [E(Cr_N, 2surf) - E(Cr_N)] \quad [\text{J/m}^2]$$

$$E(Cr_N) = NE_{bulk}$$

Cr	AF	NM
Relaxée		
(100)	3.37	4.20
(110)	3.44	3.64
Non Relaxée		
(100)	3.38	4.34
(110)	3.44	3.71

La surface Cr(100) AF est plus stable que la Cr(110) AF

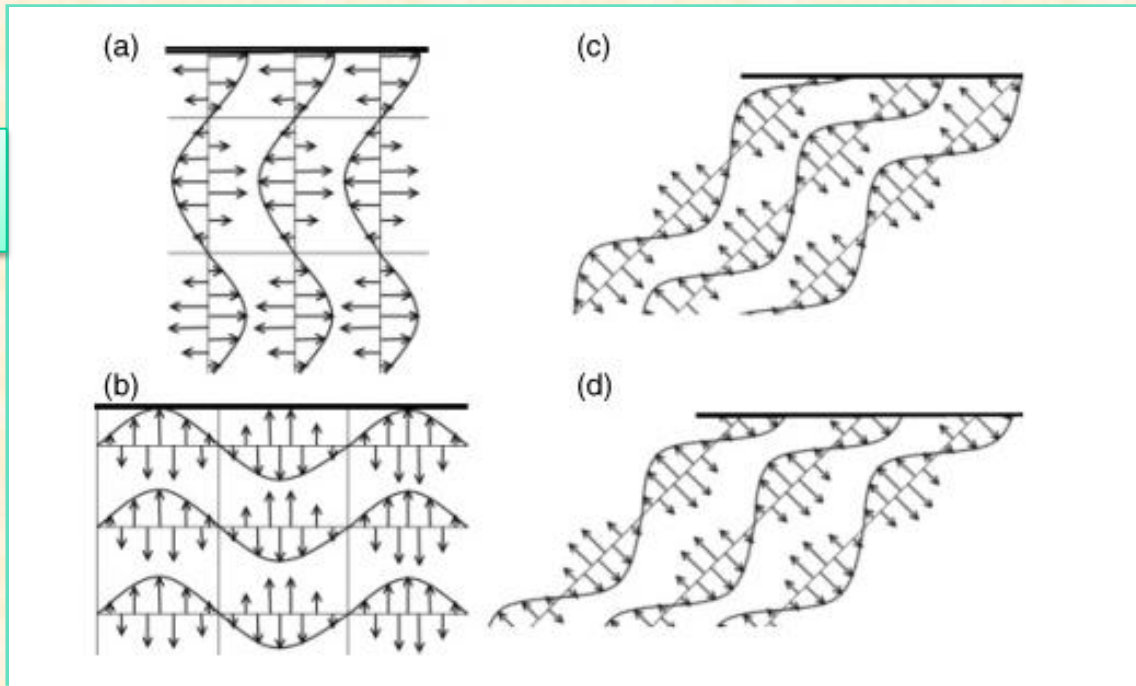
Effet du magnétisme de surface

$$|M_{surf}^{100}| > |M_{surf}^{110}|$$

Surfaces et onde de spin

out of plane
(001)

In plane
(110)

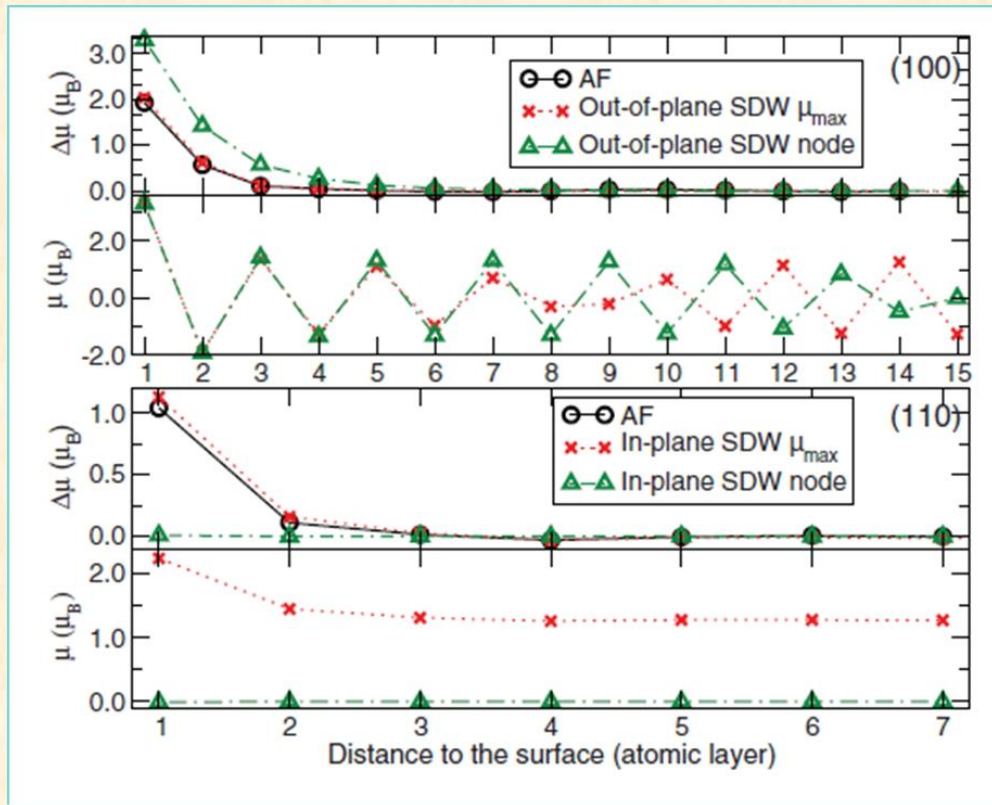


coherent
out of plane
(110)

incoherent
out of plane
(110)

Onde de spin et surface

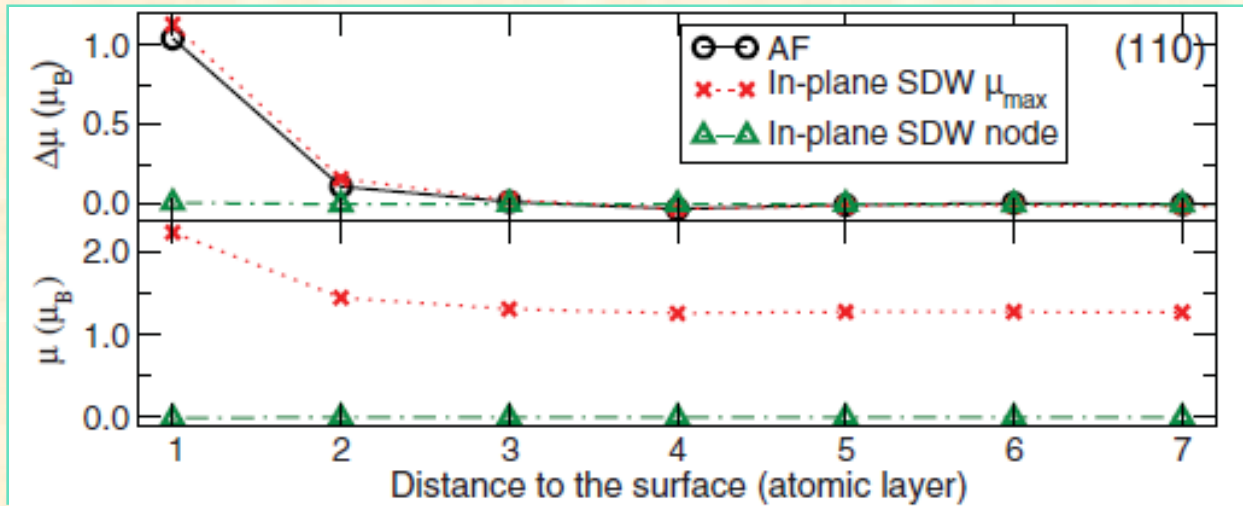
Cr(001)



Le moment à la surface est toujours exacerbé et proche du cas AF

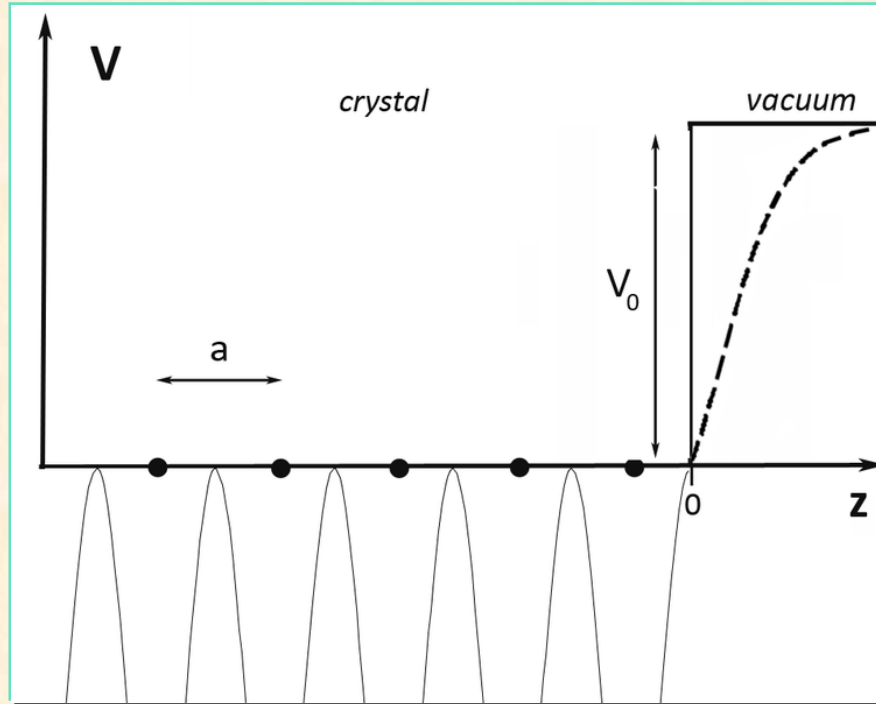
Onde de spin et surface

Cr(110)

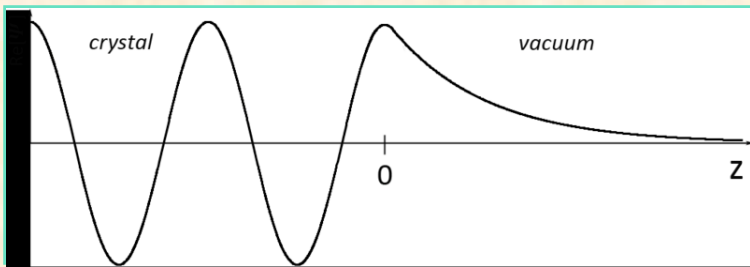


Assez faible perturbation de l'ordre magnétique

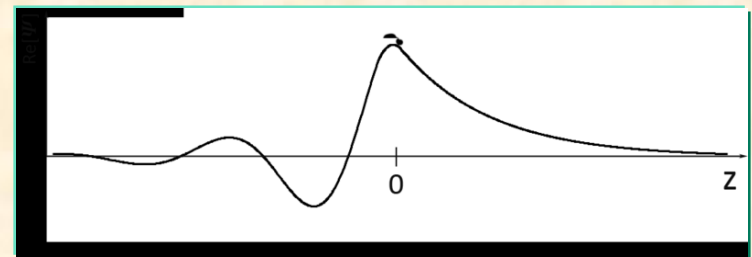
Structure électronique de surface



Etat de volume

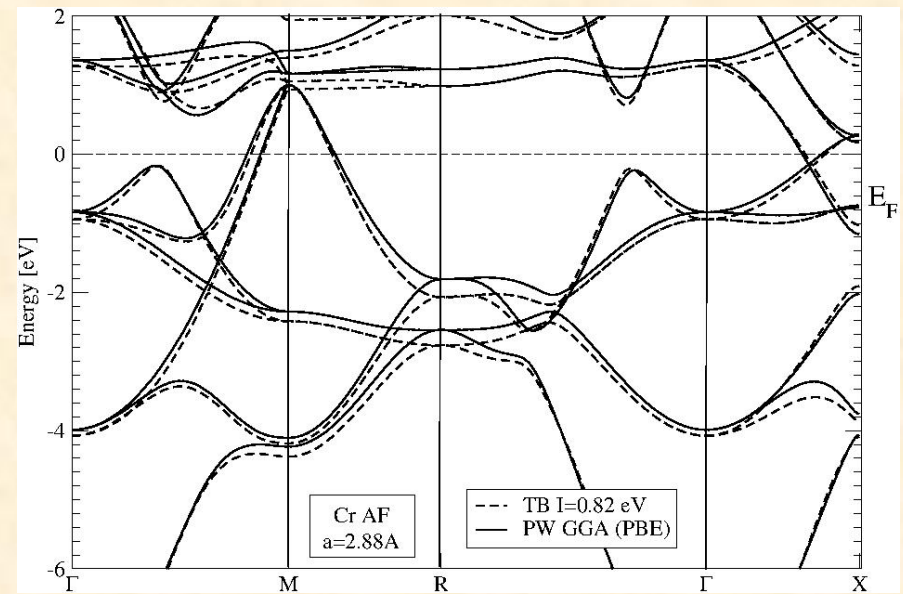
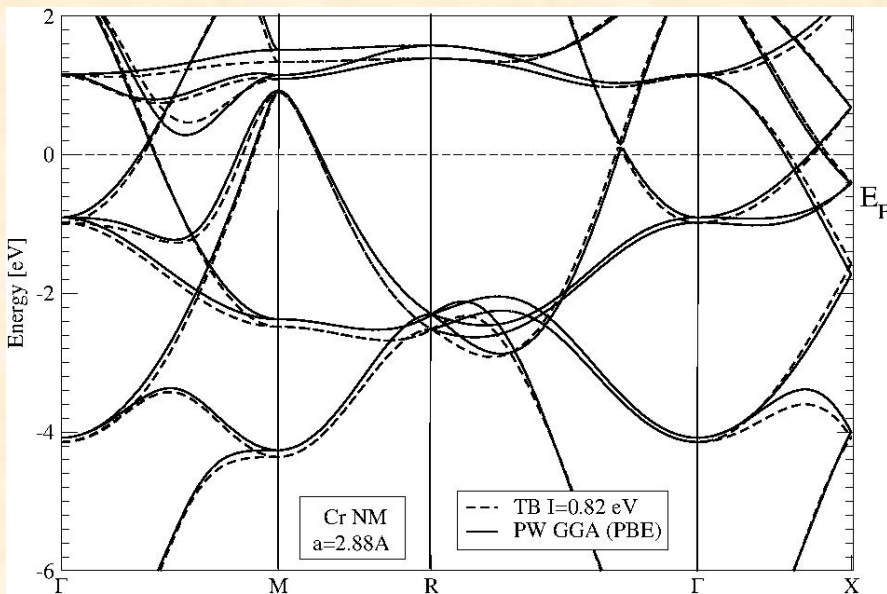
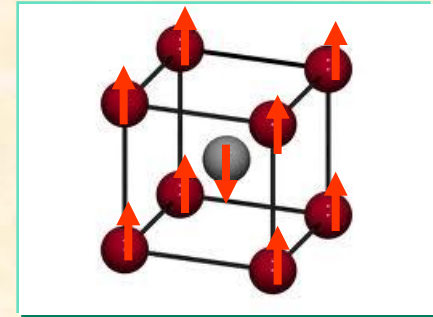
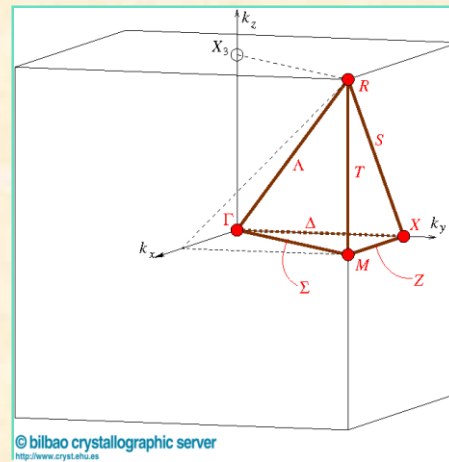
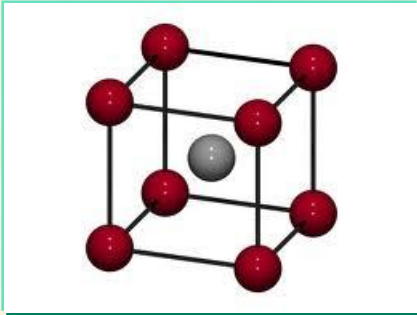


Etat de surface



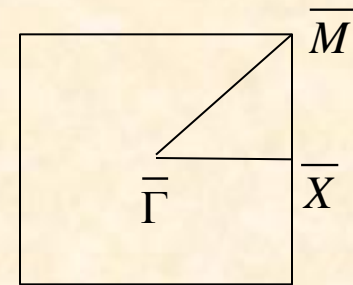
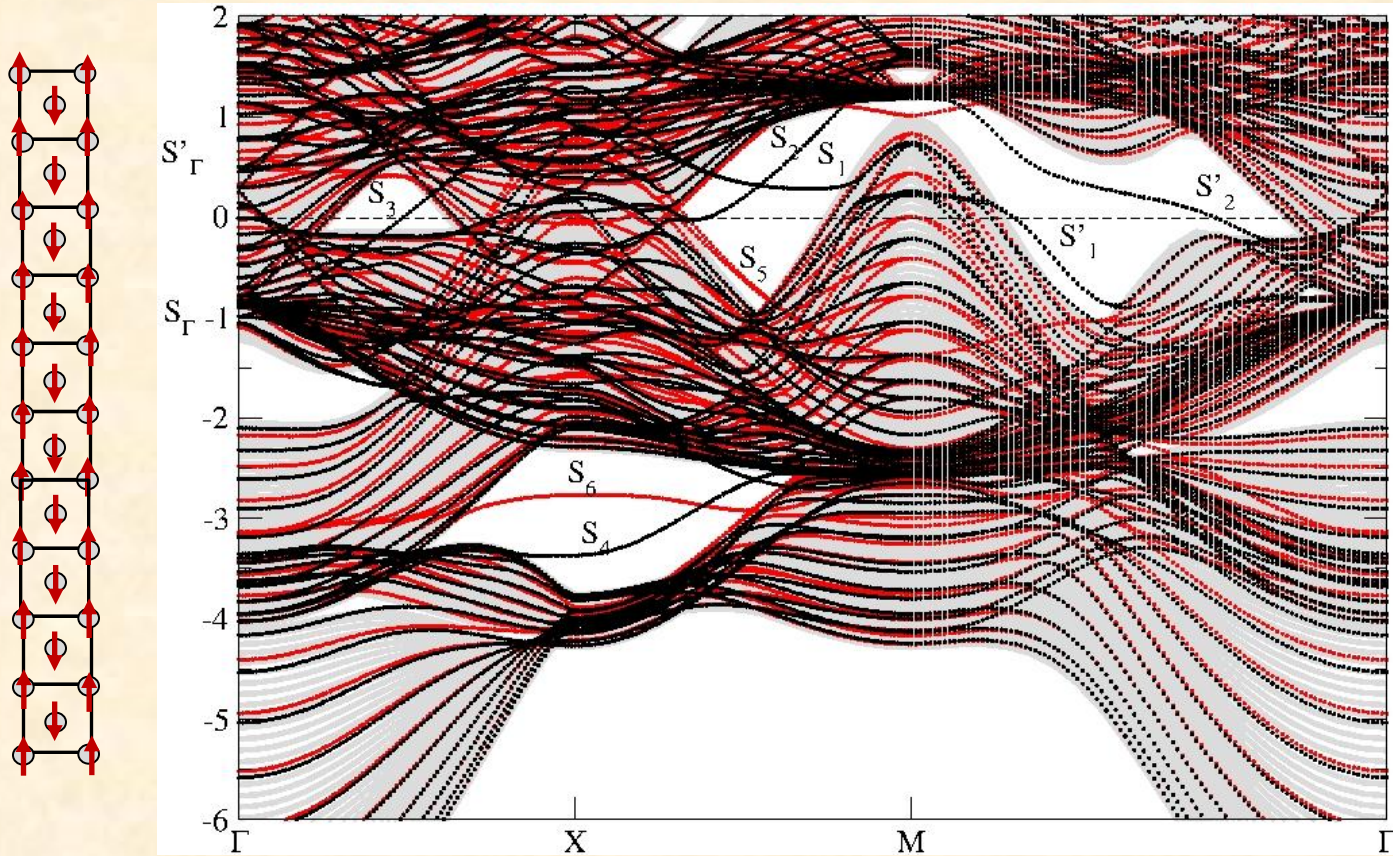
Structure de bandes de volume

Crbcc NM vs Crbcc AF



Structure de bandes de surface

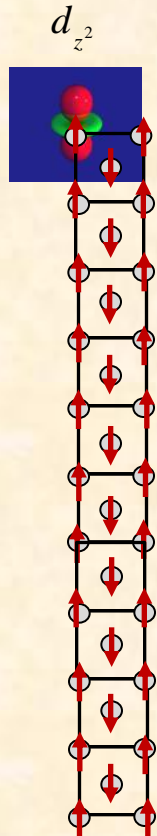
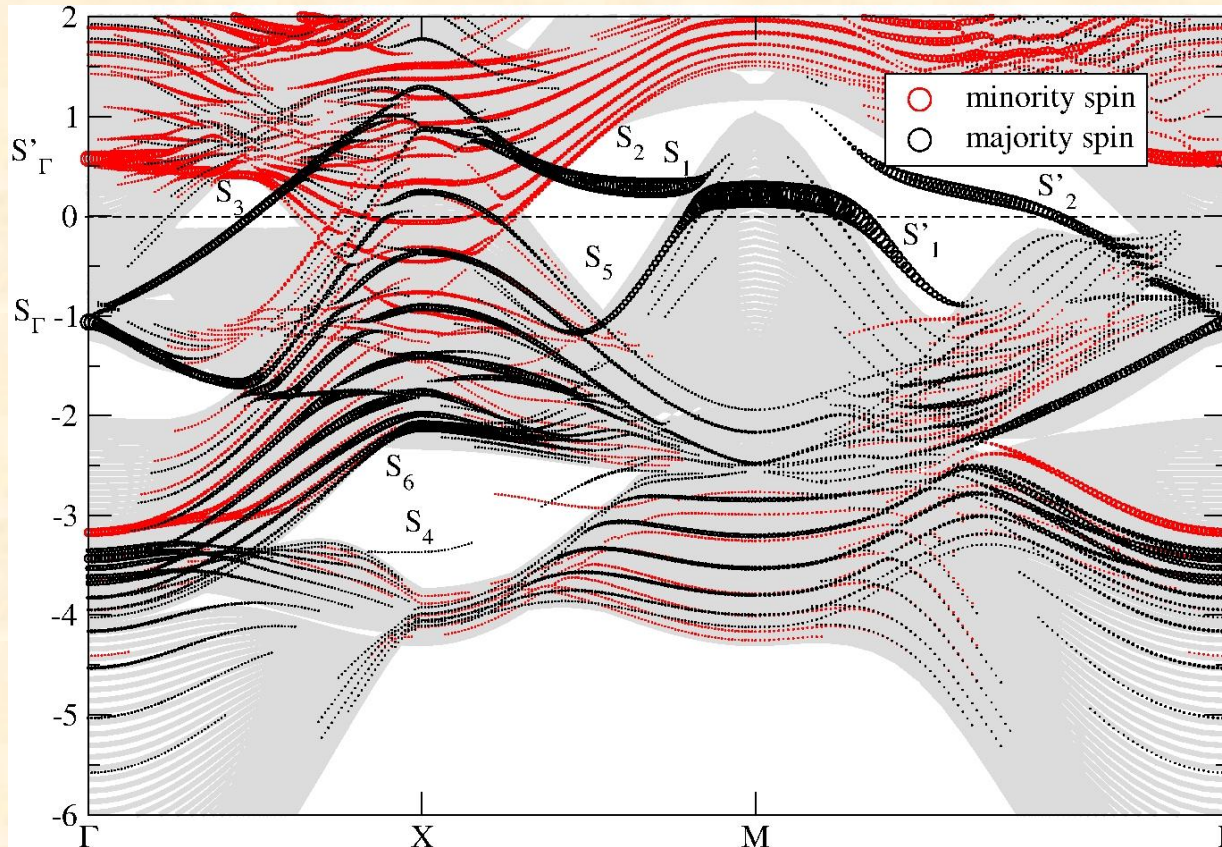
Cr(001) AF
(slab de 21 couches)



Structure de bandes de surface

Cr(001) AF

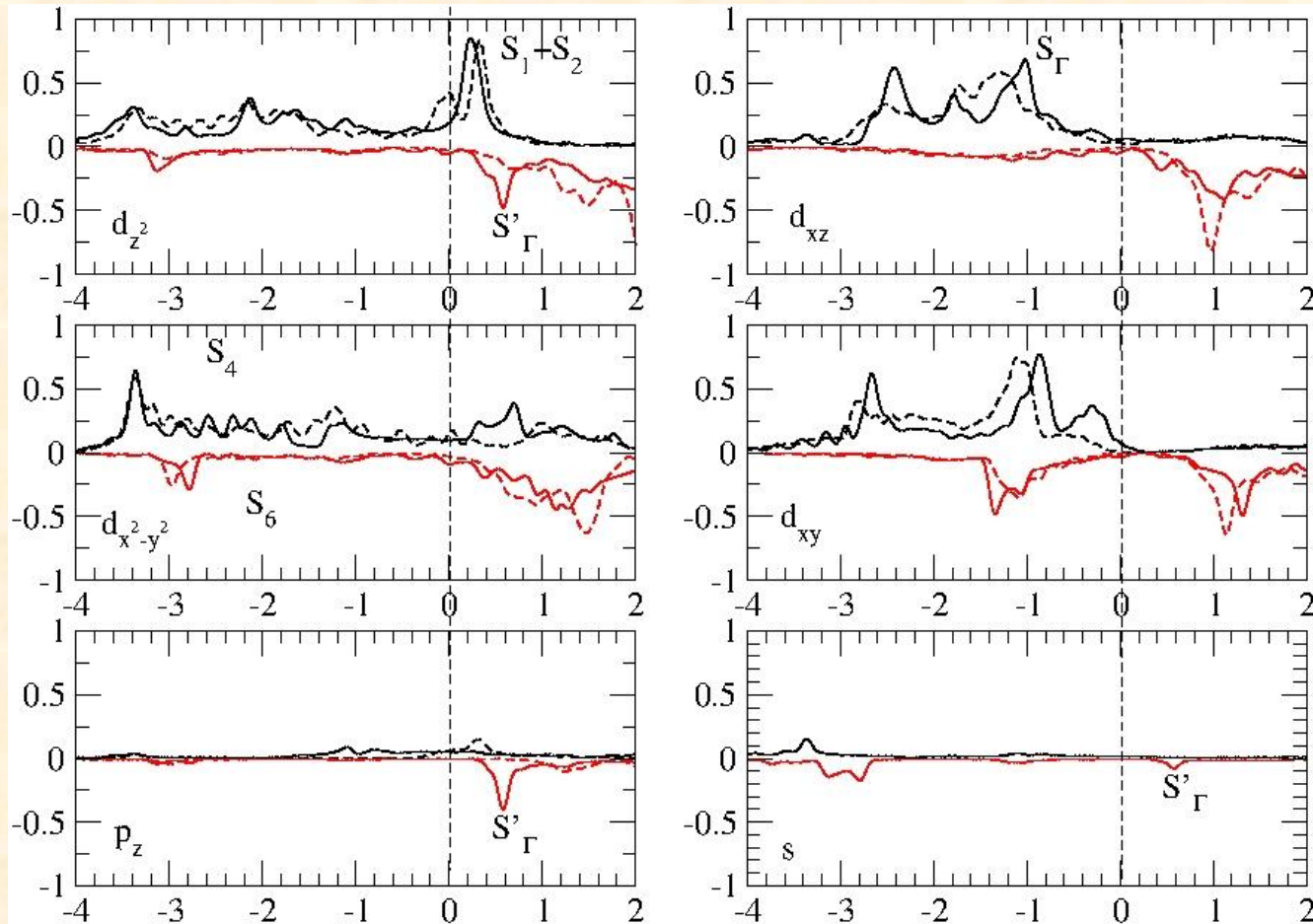
Analyse de la symétrie des états de surface



Densité d'état à la surface (001)

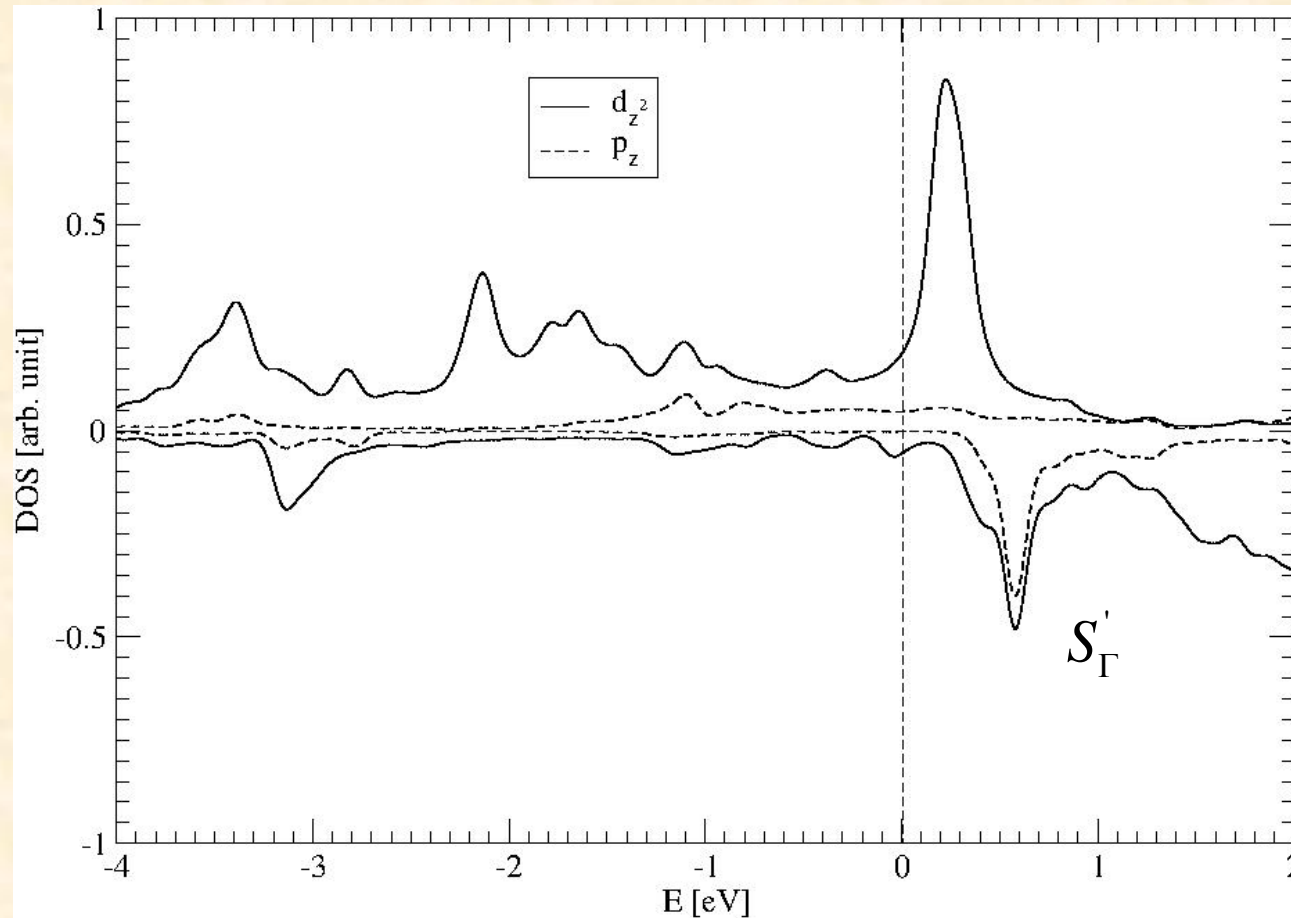
$$D_{i,\lambda}(E) = \sum_{\alpha,k} |\langle i, \lambda | \alpha, k \rangle|^2 \delta(E - \varepsilon_{\alpha}(k))$$

Projection sur les orbitales des atomes de surface



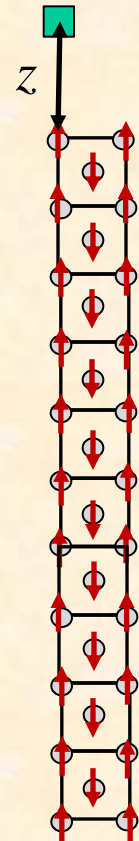
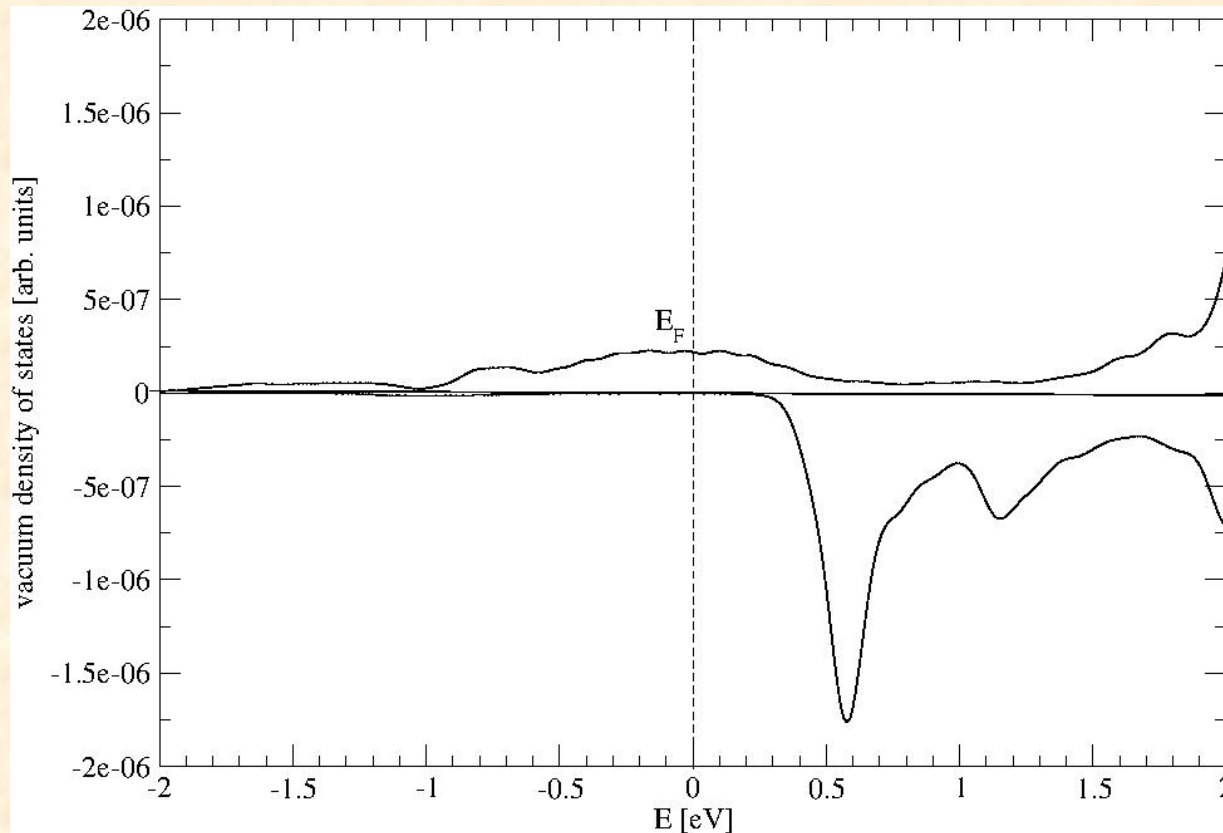
Densité d'état à la surface (001)

Projection sur les orbitales p_z et d_z^2 des atomes de surface



Densité d'état au dessus de la surface (001)

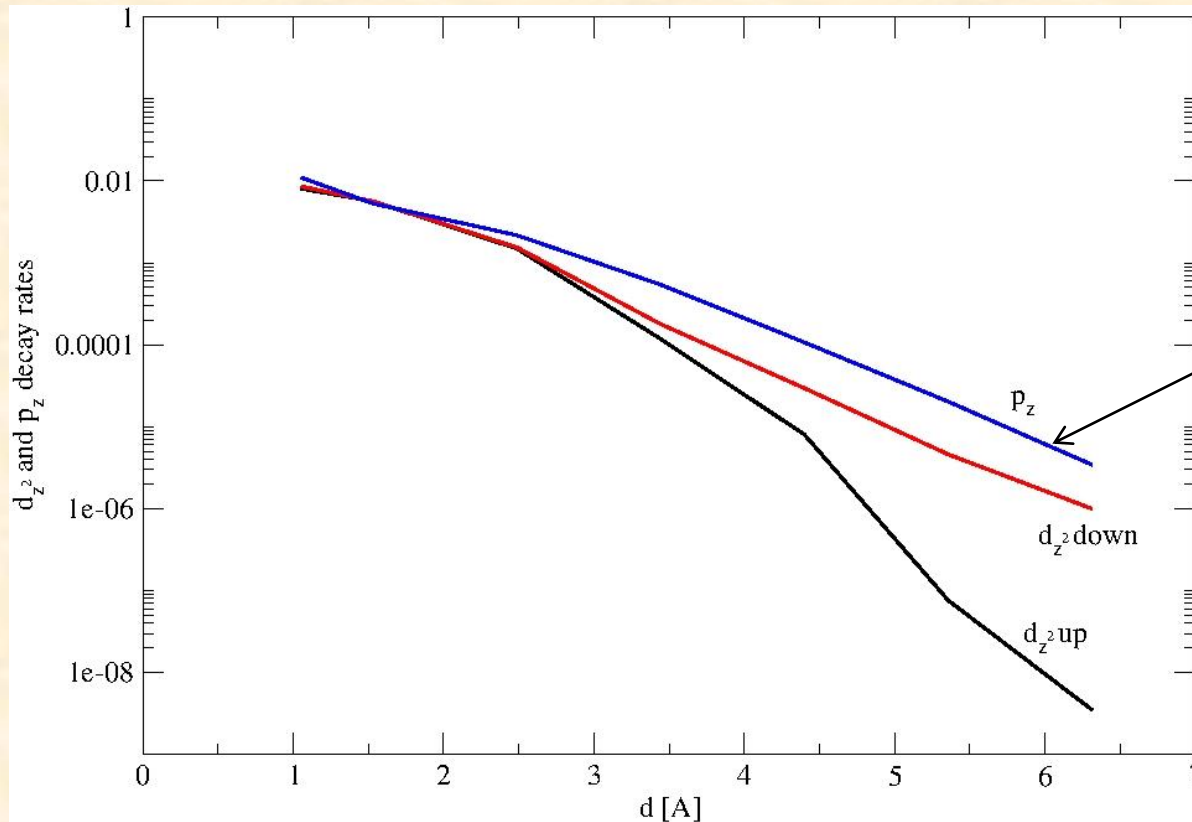
$$D(E, z) = \sum_{\alpha, k} |\Psi_{\alpha, k}(z)|^2 \delta(E - \varepsilon_{\alpha}(k))$$



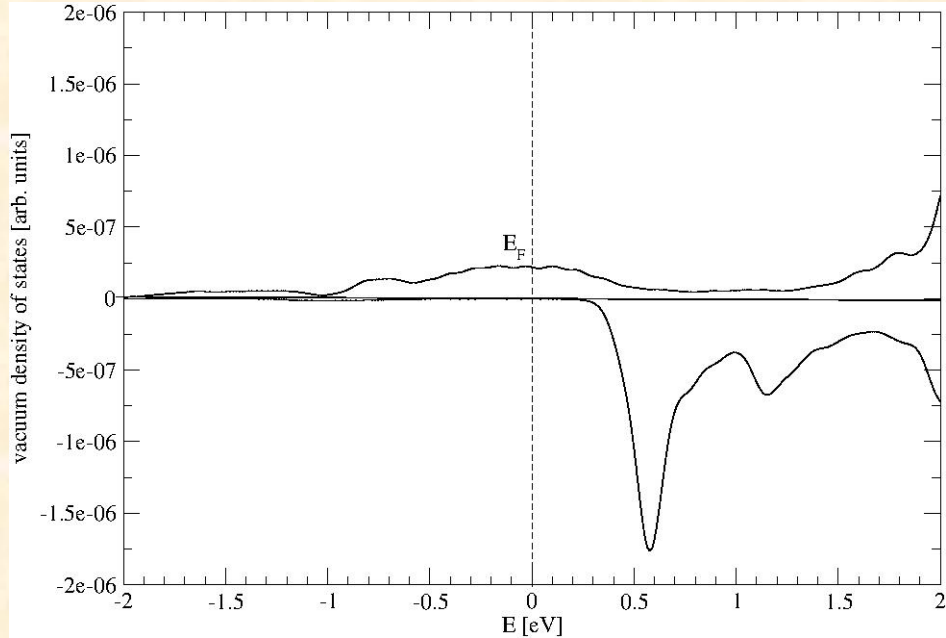
Cr(001)

Décroissance des états de surfaces dans le vide

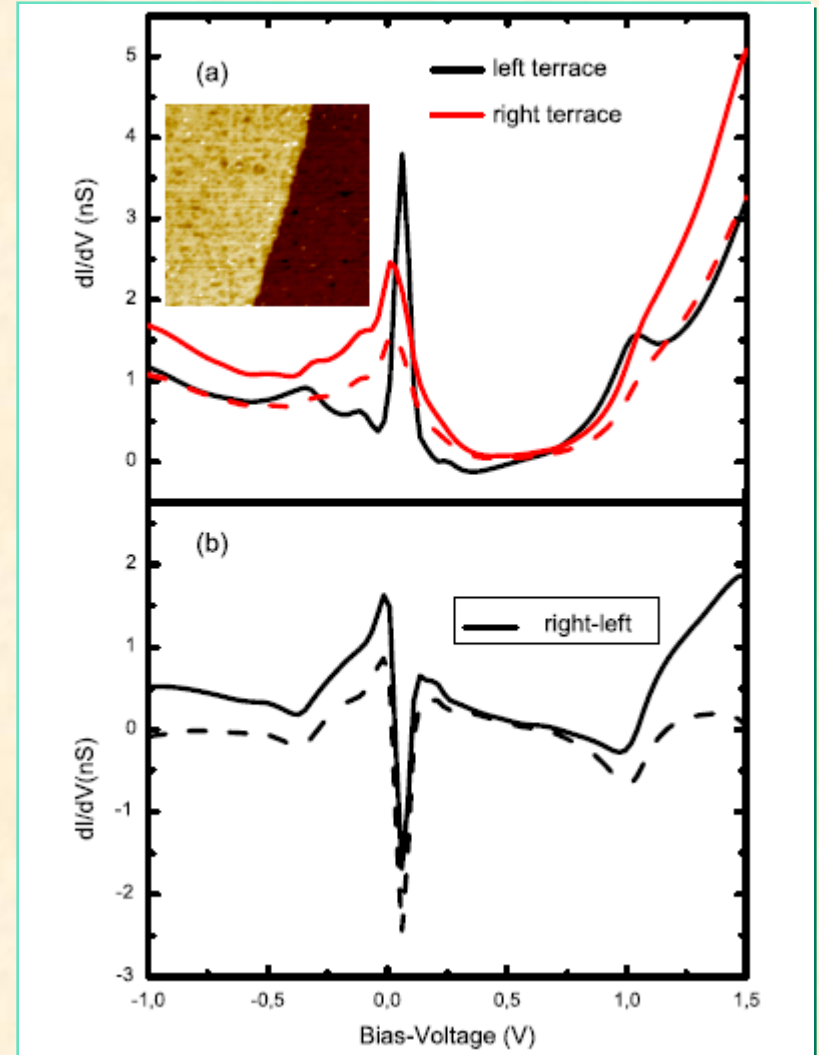
$$D_{\sigma}(E, z) = \alpha_{p_z}(z) D_{p_z}(E) + \alpha_{d_z^2}(z) D_{d_z^2}(E)$$



Présence d'un pic étroit mais position décalée....

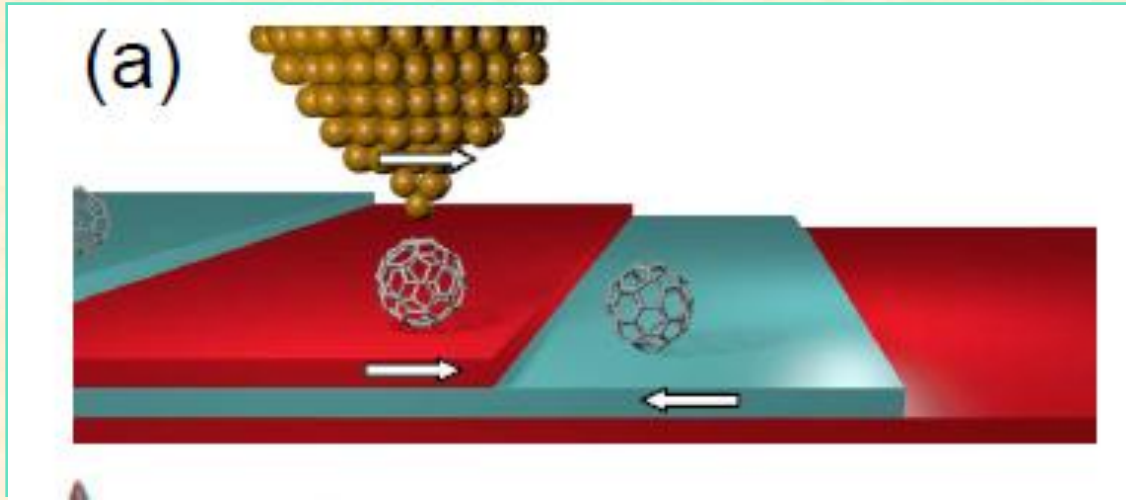


Cela provient probablement
de la surestimation du moment
de surface



C60/Cr(001)

Spin-polarized STM (SP-STM)



Mode topographique

$$I(z(x, y), U = cte) = cte \Rightarrow z(x, y)$$

Mode spectroscopique

$$G = \frac{dI}{dU}(U)$$

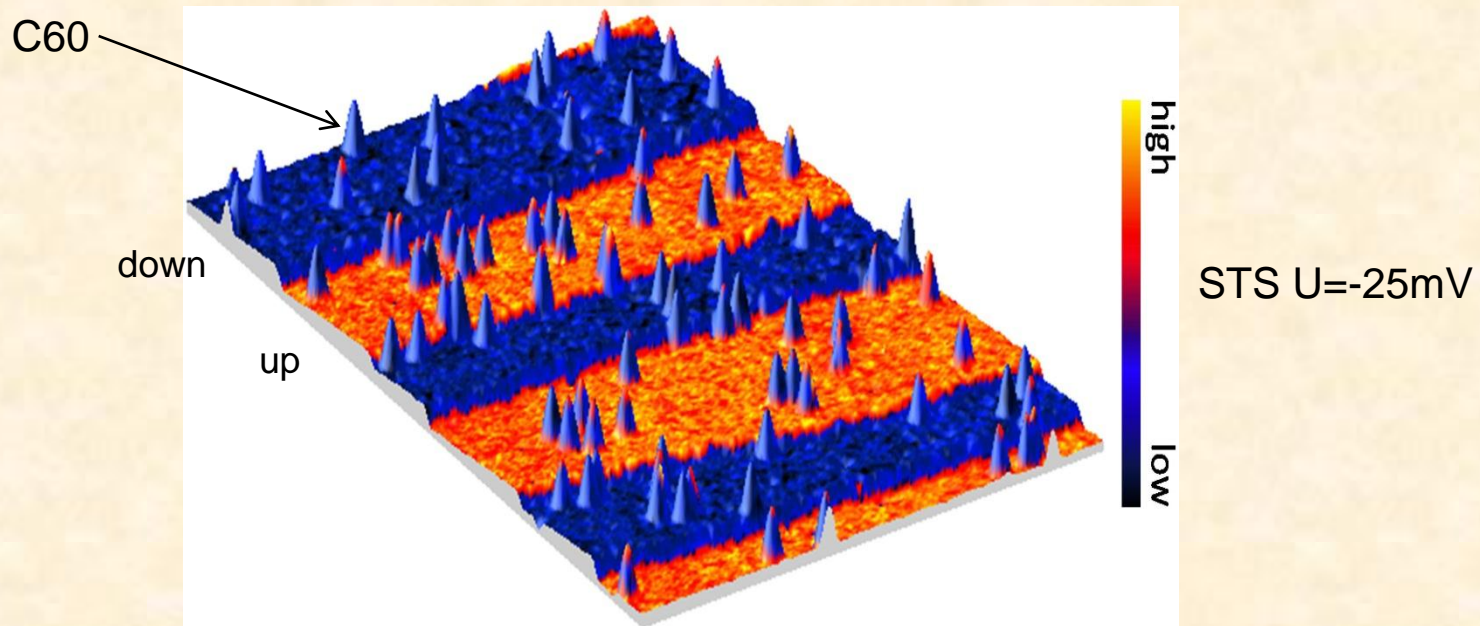
$z(x, y)$ fixé

V. Repain, J. Lagoute, L. Kawahara
Université Paris-Diderot

C60/Cr(001)

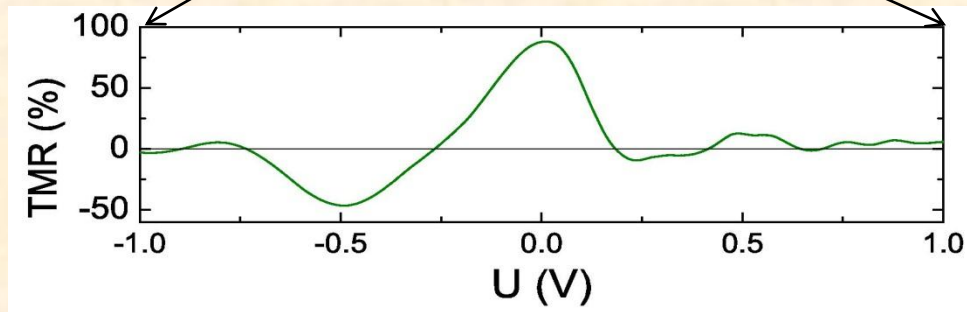
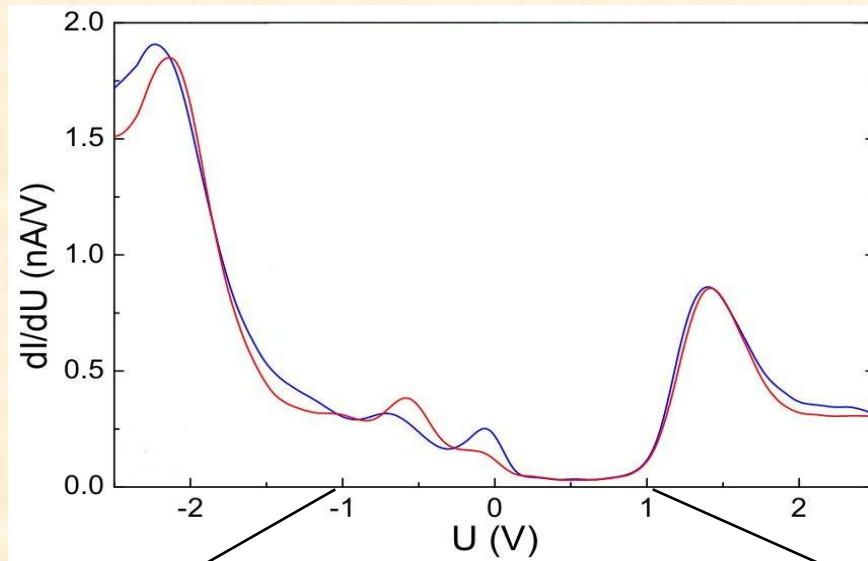
Mode topographique:

$$U_{bias} = 1V \quad I = 300pA$$



C60/Cr(001)

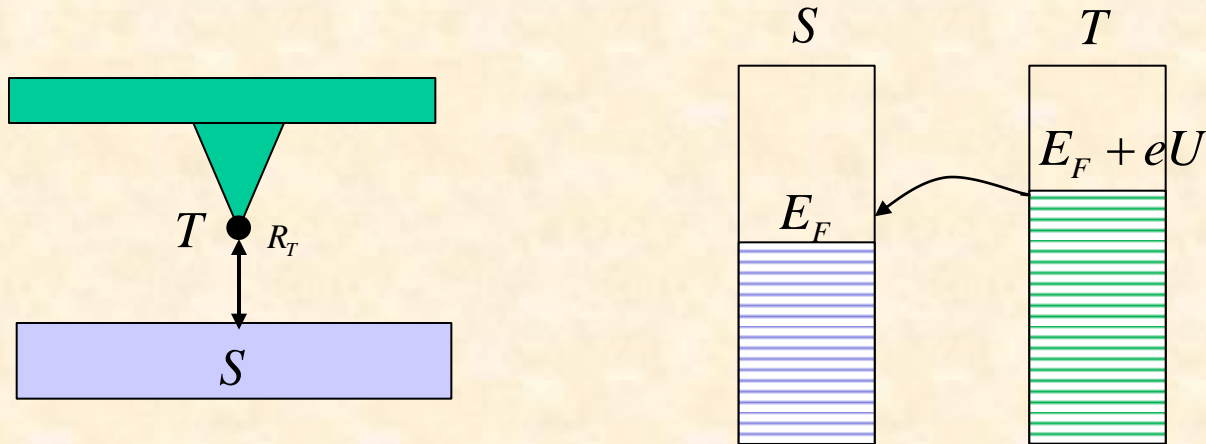
Mode spectroscopique STS



$$TMR = \frac{G_{up} - G_{down}}{G_{down}} \times 100\%$$

C60/Cr(001)

courant tunnel: approximation de Tersoff-Hamann



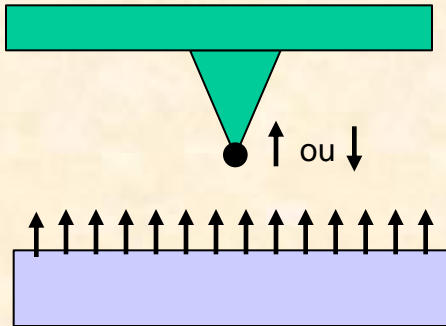
$$I_t(U) \sim D_T \int_{E_F}^{E_F + eU} D_S(E, R_T) dE \quad D_T(E) \sim cte$$

$$G = \frac{dI}{dU} \sim D_T D_S(E_F + eU, R_T)$$

$$D(E_F + eU, R_T) = \sum_{\alpha, k} |\Psi_{\alpha, k}(R_T)|^2 \delta(E_F + eU - \varepsilon_{\alpha}(k))$$

Courant tunnel polarisé en spin

$$G = \frac{dI}{dU} \sim \sum_{\sigma} D_T^{\sigma} D_S^{\sigma} (E_F + eU, R_T)$$



Pointe polarisée « complètement »

$$D_T^{\uparrow} = 0 \quad D_T^{\downarrow} \neq 0$$

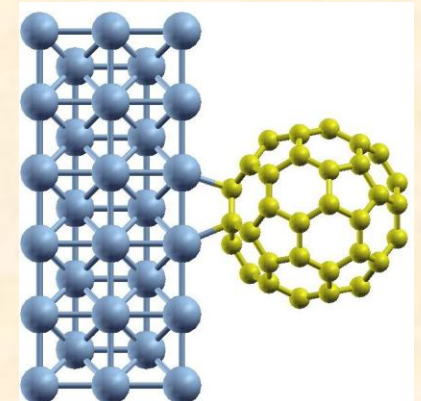
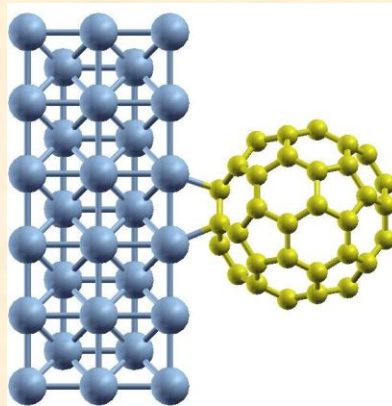
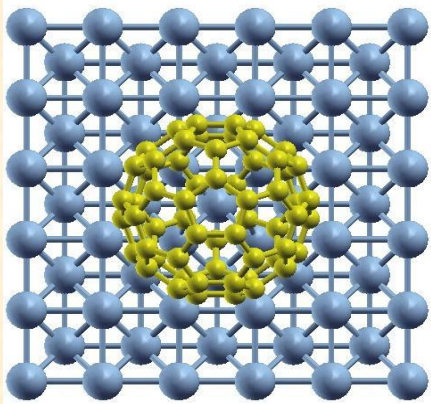
(ou inversement si la pointe et l'échantillon ont des aimantation opposées)

$$G \sim D_S^{\uparrow\downarrow} (E_F + eU, R_T)$$

Calculs ab-initio

- *ab initio* Quantum-ESPRESSO

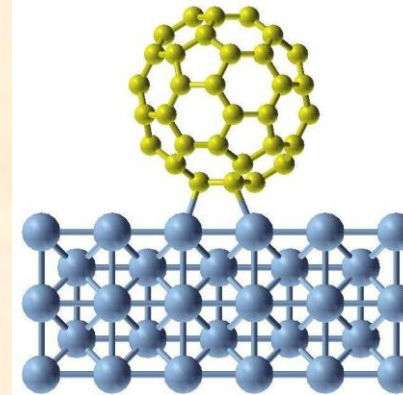
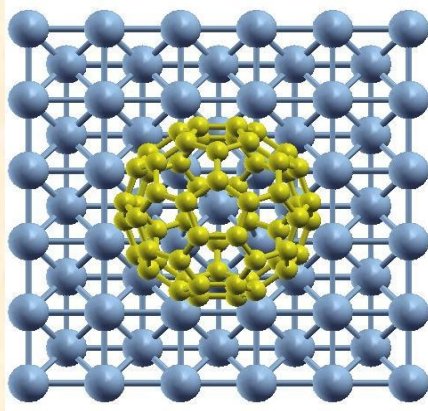
- Density Functional Theory (DFT);
- Ondes planes;
- pseudopotentiels ultrasoft;

Super-cellule

A. Smogunov

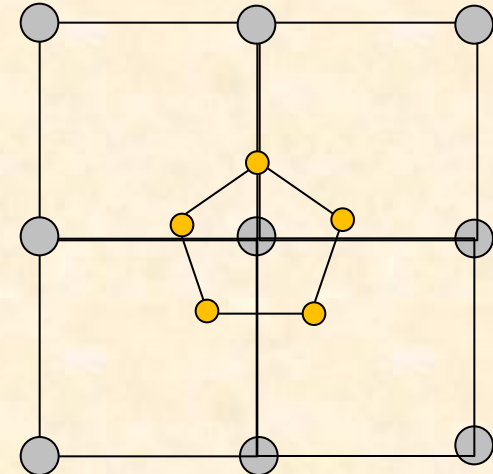
C60/Cr(001)

La relaxation atomique

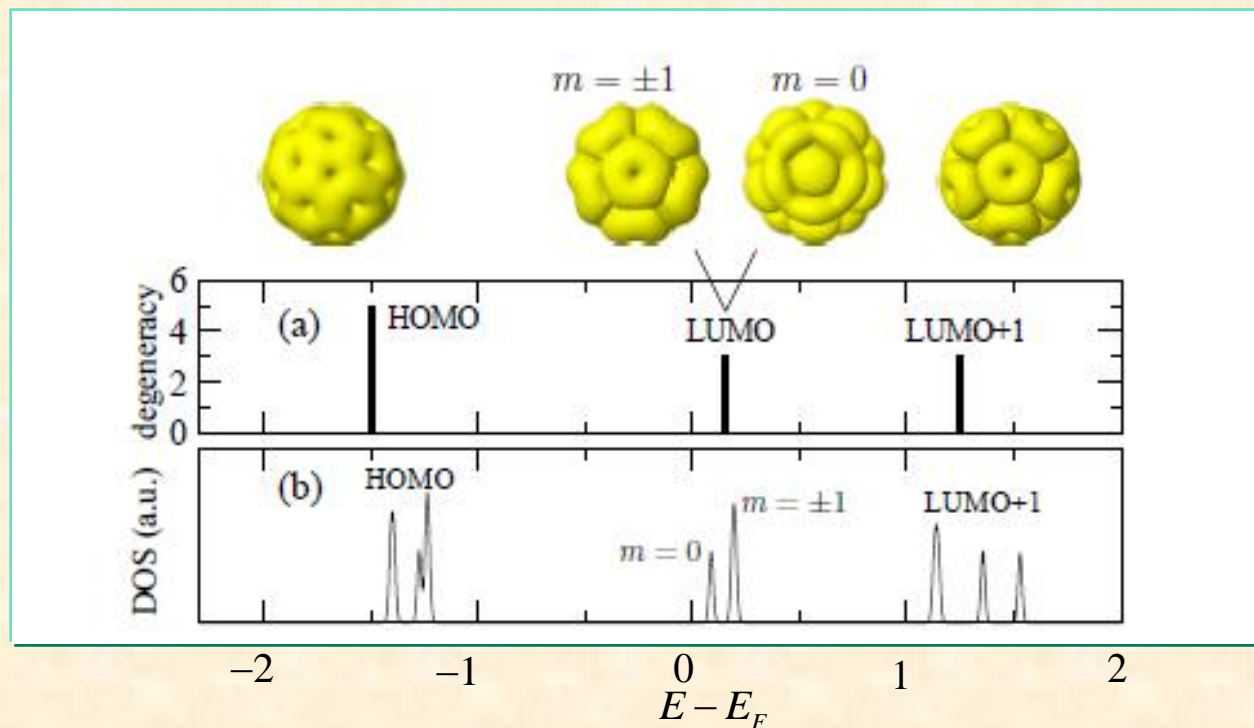


Position la plus stable:
centre du pentagone « on top »
pentagone reste « à plat »
léger aplatissement de la molécule

Petite anecdote:
C60/Cr(001) non magnétique est instable
car reconstruction de Cr(001)!!!
Comme Mo(001) et W(001)



C60 isolé



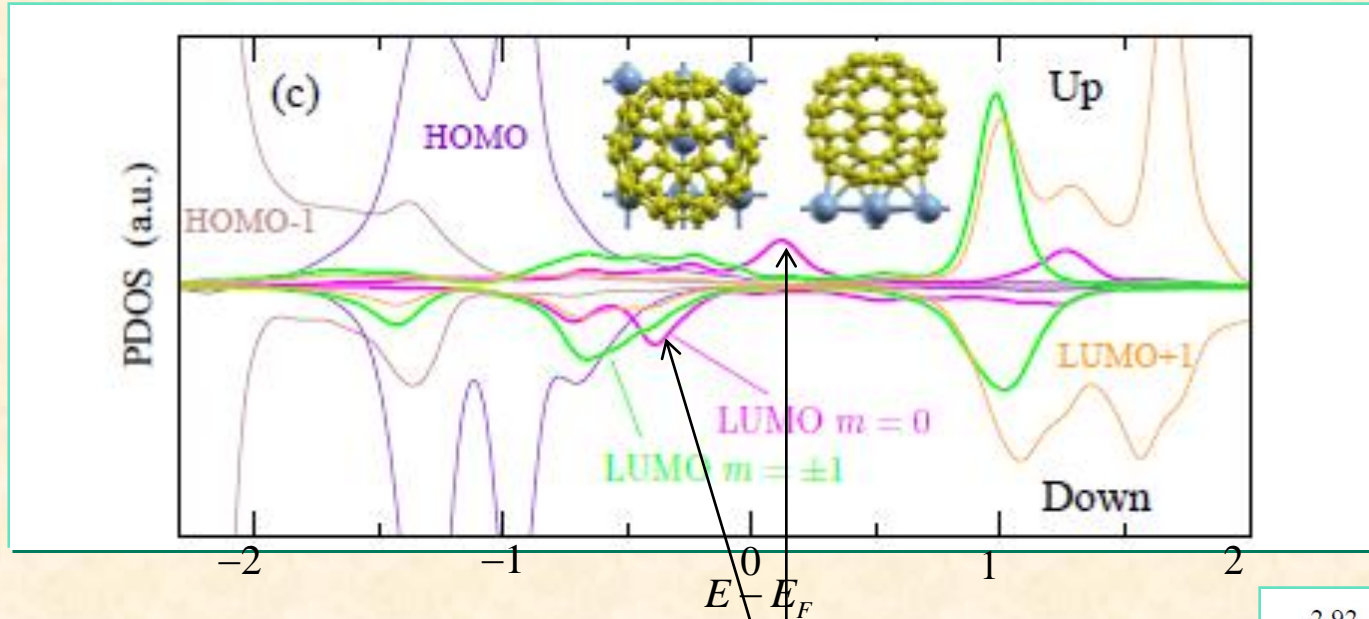
C60 sphérique

C60 « aplati »

Levée de dégénérescence due à distorsion
provoquée par l'interaction avec le substrat

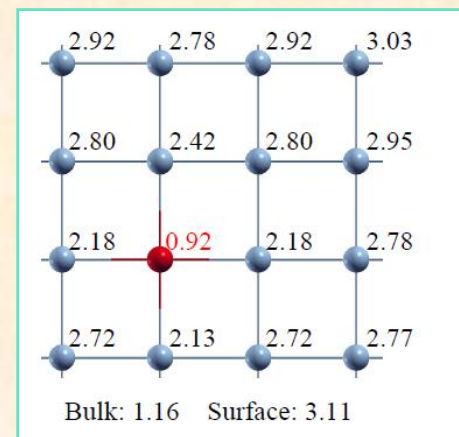
C60/Cr(001)

Densité d'état projetée sur les orbitales moléculaires



Splitting de la LUMO ($m=0$)

Polarisation inverse à la surface
Couplage AF +
Atténuation du magnétisme du Cr



C60/Cr(001)

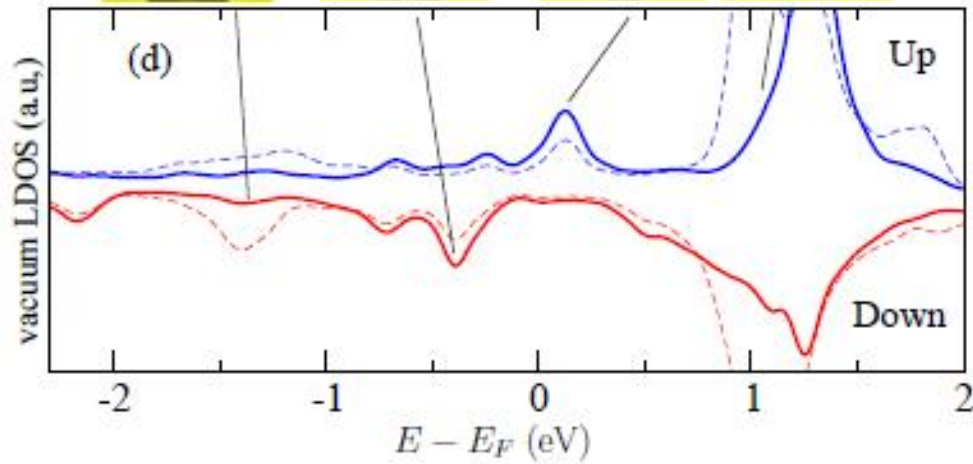
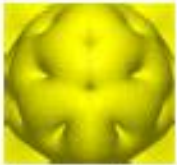
Densité d'état dans le vide

HOMO

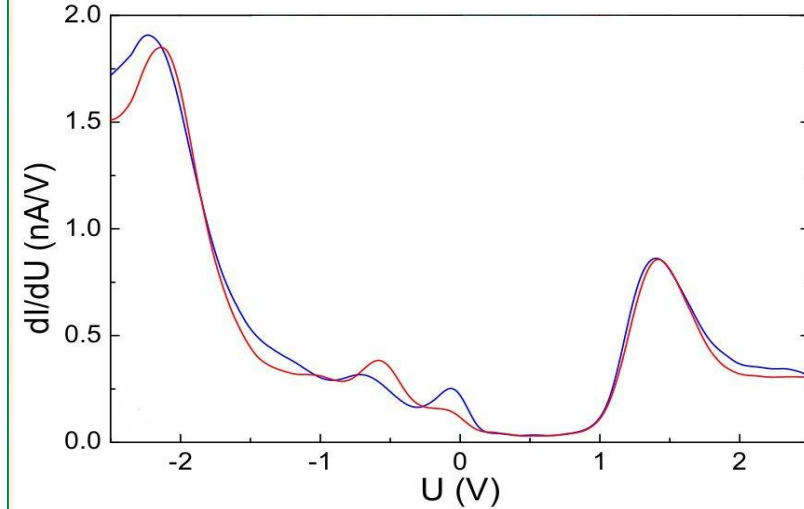
LUMO
 $m=0 \downarrow$

LUMO
 $m=0 \uparrow$

LUMO+1



SP-STS (exp)

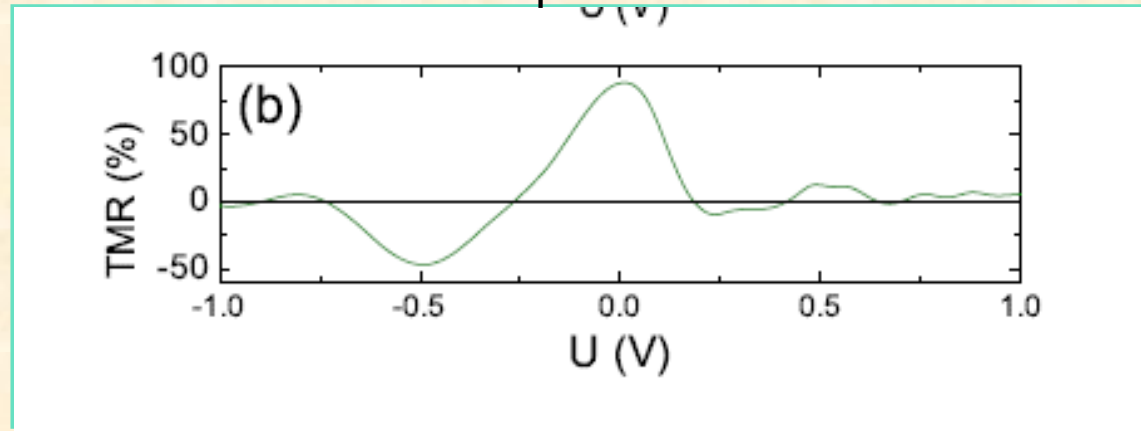


C60/Cr(001)

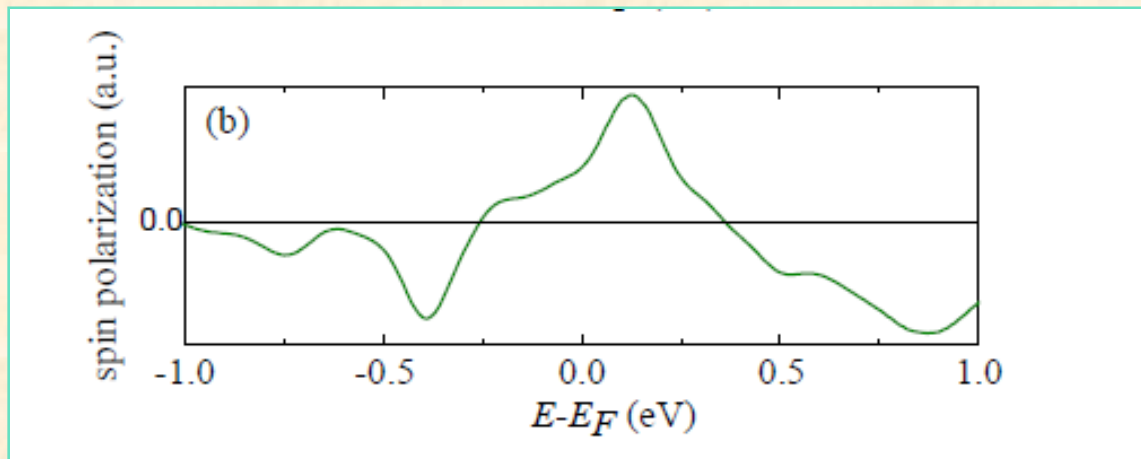
TMR

$$TMR = \frac{\left. \frac{dI}{dU} \right|_{up} - \left. \frac{dI}{dU} \right|_{down}}{\left. \frac{dI}{dU} \right|_{down}}$$

expérience

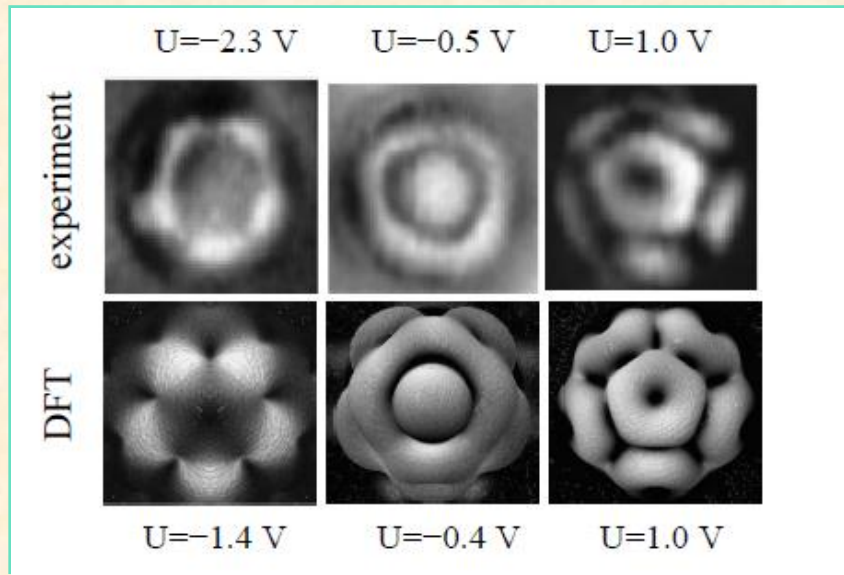


théorie



C60/Cr(001)

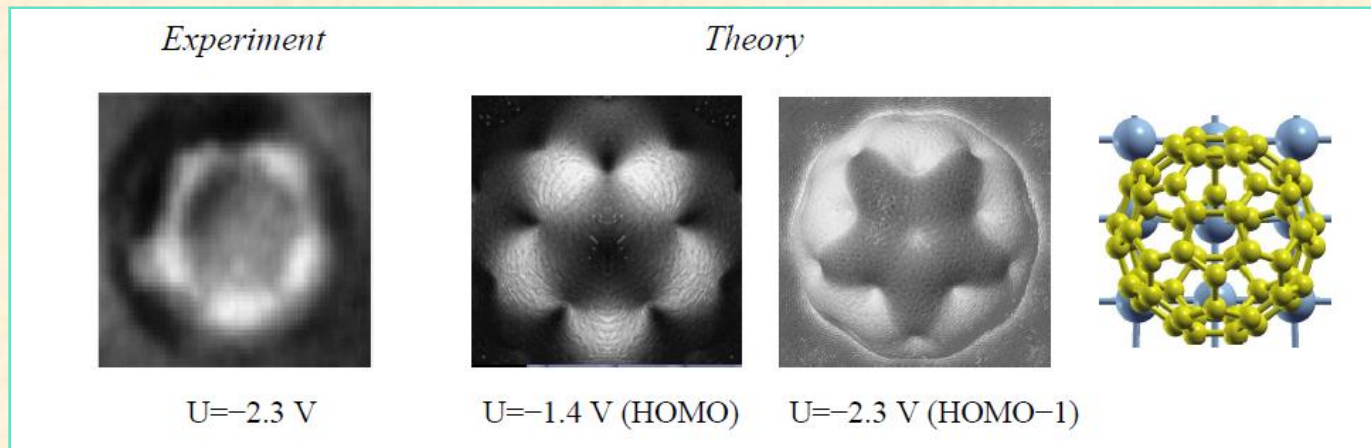
Imagerie SP-STS



Topographie $I(z(x, y), U) = cte$
 +
 spectroscopie $G = \frac{dI}{dU}(U)$

$$I_t(U) \sim \int_{E_F}^{E_F+eU} D_S(E, R_T(x, y, z)) dE$$

$$G \sim D_S(E_F + eU, R_T(x, y, z))$$



MERCI POUR VOTRE ATTENTION