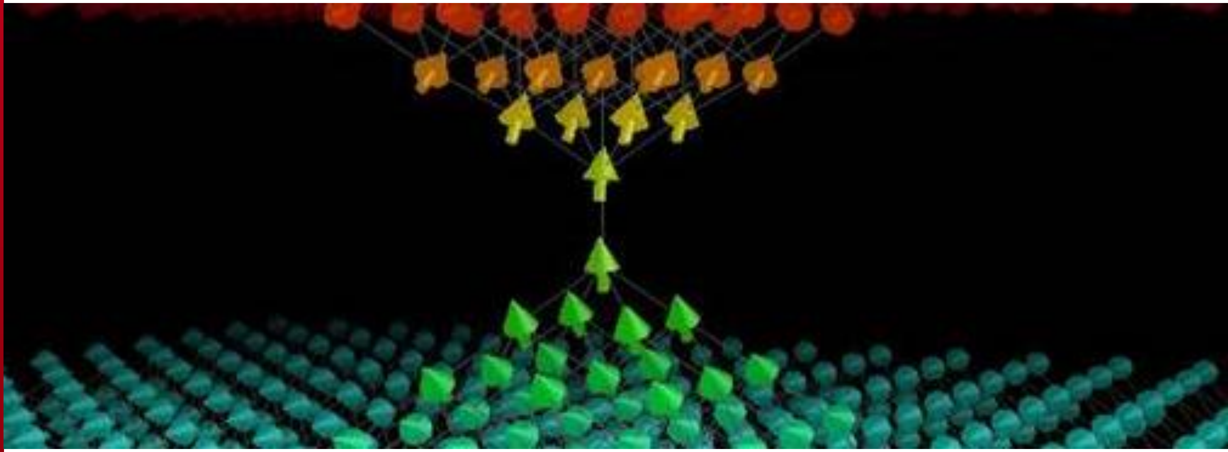
DE LA RECHERCHE À L'INDUSTRIE

MAGNETIC ANISOTROPY IN TIGHT-BINDING



Cyrille Barreteau

www.cea.fr

Magnetic Tight-Binding Workshop, London10-11 Sept. 2012

SOMMAIRE

TB Model

Determination of parameters

Applications

TB MODEL

TB$_0$: MEHL AND PAPACONSTANOPOULOS

Non magnetic Hamiltonian

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

$i, j :$ atoms

$\lambda, \mu :$ orbitals

$\lambda =$ s p_x p_y p_z d_{xy} d_{xz} d_{xz} $d_{x^2-y^2}$ $d_{3z^2-r^2}$

Hopping integrals

overlap integrals

On-site elements

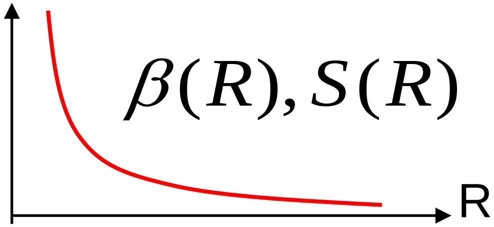
Two-center SK formulation

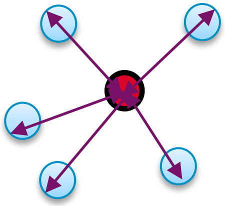
$$\beta_{i\lambda,j\mu} = \langle i\lambda|H|j\mu\rangle$$

$$S_{i\lambda,j\mu} = \langle i\lambda|j\mu\rangle$$

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

$$\varepsilon_{i\lambda} = f(\rho_i)$$





Analytical expressions

$$\beta(R), S(R) = (e + fR + \cdots)\exp(-gR)F_C(R)$$

$$\varepsilon_{i\lambda} = a + b\rho_i^{2/3} + c\rho_i^{4/3} + d\rho_i^2 \qquad \rho_i = \sum_{j\neq i} \exp(-\lambda R_{ij})F_C(R_{ij})$$

Approximately 70-80 parameters per element

Total energy: the MP trick

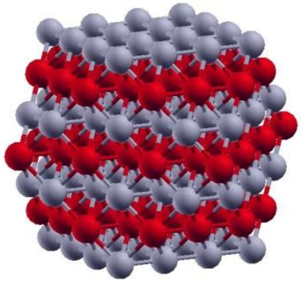
$$E_{tot} = \sum_{\alpha} f_\alpha \varepsilon_\alpha$$

The usual pair-potential « repulsive term » is hidden in the environment dependence of the on-site elements

PRB **54**, 4519 (1996)

PRB **58**, 9721 (1998)

TB$_{LCN}$: LOCAL CHARGE NEUTRALITY



Inhomogeneous systems

$$H_{LCN}^{i\lambda,i\lambda} = U_i(n_i - n_{i,0})$$

$$H_{LCN}^{i\lambda,j\mu} = \frac{1}{2}\left[U_i(n_i - n_{i,0}) + U_j(n_j - n_{j,0})\right]S_{i\lambda,j\mu}$$

Avoid charge transfers between unequivalent atoms

LCN = penalization on the local charge

$$E_{tot} = \sum_{\alpha occ}\sum_{i,j} c_i^\alpha c_j^\alpha H_{ij} + \tfrac{1}{2}\sum_i U_i(n_i - n_{i,0})^2$$

$$\text{Min } E_{\text{tot}} / \sum_i \left(c_i^\alpha\right)^2 = 1 \Rightarrow H = H_0 + H_{LCN}$$

Double counting

$$E_{tot} = \sum_\alpha f_\alpha \varepsilon_\alpha - \tfrac{1}{2}\sum_i U_i(n_i^2 - n_{i,0}^2)$$

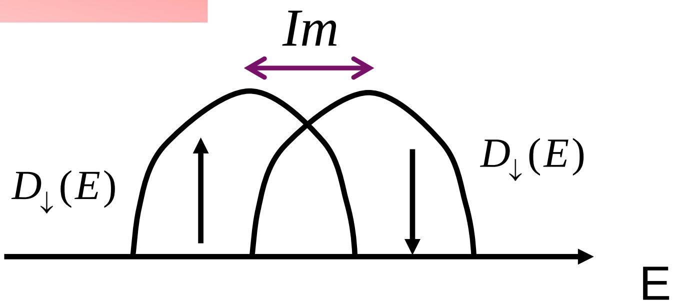
TB$_{MAG}$: STONER MODEL

Exchange splitting

$$\boxed{H_{mag} = -\tfrac{1}{2}\sum_{i,\lambda} I_{i,\lambda}\,\vec{m}_{i\lambda}.\vec{\sigma}}$$

$$\varepsilon_{i,\lambda,\sigma} \rightarrow \varepsilon_{i,\lambda,0} - \tfrac{1}{2} I_{i,\lambda} m_{i,\lambda} \underset{\pm 1}{\sigma}$$

$$I_s = I_p = \tfrac{1}{10} I_d$$



$$D_\sigma(E) = D_0(E + \tfrac{1}{2}\sigma IM)$$

Stoner criterion

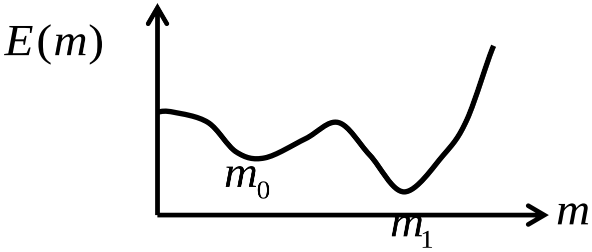
Onset of magnetism when: $\boxed{ID_0(E_F) \geq 1}$

Double counting

$$E_{tot} = \sum_{\alpha_{occ}} \varepsilon_\alpha + \tfrac{1}{4}\sum_{i,\lambda} I_i m_{i,\lambda}^2 = \int^{E_F} ED(E)dE + \tfrac{1}{4}\sum_{i,\lambda} I_i m_{i,\lambda}^2$$

Fixed spin moment calculation

$$E_{tot} = \int^{E_F^{\uparrow}} ED_{\downarrow}(E)dE + \int^{E_F^{\downarrow}} ED_{\downarrow}(E)dE + \tfrac{1}{4}\,\mathrm{Im}^2 \qquad D_{\sigma}(E) = D_0(E + \tfrac{1}{2}\sigma IM)$$



$$E_{tot}(M) = \int^{E_F^{+}} ED_0(E)dE + \int^{E_F^{-}} ED_0(E)dE - \tfrac{1}{4}\,\mathrm{Im}^2$$

$$M = \int^{E_F^{+}} ED_0(E)dE - \int^{E_F^{-}} ED_0(E)dE \qquad E_F^{+} = E_F^{\uparrow} + \tfrac{1}{2} Im$$

$$N = \int^{E_F^{+}} ED_0(E)dE + \int^{E_F^{-}} ED_0(E)dE \qquad E_F^{-} = E_F^{\uparrow} - \tfrac{1}{2} Im$$

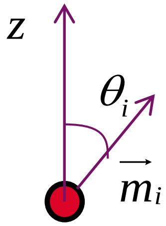
Penalization of local magnetization

$$E_{tot} = \sum_{\alpha occ} \sum_{i,j} c_i^{\alpha} c_j^{\alpha} H_{ij} + E_{\mathrm{pen}}$$

$$E_{\mathrm{pen}} = \sum_i \lambda_i (m_i - m_{i,0})^2$$

$$E_{\mathrm{pen}} = \sum_i \lambda_i (\cos\theta_i - \cos\theta_{i,0})^2$$

$$\bullet\bullet\bullet$$



$$\mathrm{Min}\ E_{\mathrm{tot}} \,/ \sum_i \left(c_i^{\alpha}\right)^2 = 1 \Rightarrow H = H_0 + H_{\mathrm{pen}}$$

BEYOND STONER MODEL= TB+U

$$\boxed{H = H_0 + H_{\text{int}}}$$

$$H_{\text{int}} = \frac{1}{2} \sum_{i\alpha_1\alpha_2\alpha_3\alpha_4} U_{i\alpha_1\alpha_2\alpha_3\alpha_4} c^{+}_{i\alpha_1\sigma} c^{+}_{i\alpha_2\sigma'} c_{i\alpha_4\sigma'} c_{i\alpha_3\sigma}$$

$\alpha_n = d(f)$orbitals

i : atomic site

Hartree Fock decoupling (mean field)

$$H^{HF}_{\text{int}} = \frac{1}{2} \sum_{\substack{i\alpha_1\alpha_2\alpha_3\alpha_4 \\ \sigma\sigma'}} \left(U_{i\alpha_4\alpha_2\alpha_3\alpha_1} \left\langle c^{+}_{i\alpha_4\sigma} c_{i\alpha_3\sigma} \right\rangle c^{+}_{i\alpha_2\sigma'} c_{i\alpha_1\sigma'} - U_{i\alpha_4\alpha_2\alpha_1\alpha_3} \left\langle c^{+}_{i\alpha_4\sigma} c_{i\alpha_3\sigma'} \right\rangle c^{+}_{i\alpha_2\sigma'} c_{i\alpha_1\sigma} \right)$$

$$U_{m_1m_2m_3m_4} = \int_{-\infty}^{+\infty} d^3r \int_{-\infty}^{+\infty} d^3r' \varphi^{*}_{im_1\sigma}(\vec{r}) \varphi^{*}_{im_2\sigma'}(\vec{r}\,') \frac{e^2}{\left|\vec{r} - \vec{r}\,'\right|} \varphi_{im_3\sigma}(\vec{r}) \varphi_{im_4\sigma'}(\vec{r}\,')$$

$$U_{\lambda_1\lambda_2\lambda_3\lambda_4} = \int_{-\infty}^{+\infty} d^3r \int_{-\infty}^{+\infty} d^3r' \varphi_{i\lambda_1\sigma}(\vec{r}) \varphi_{i\lambda_2\sigma'}(\vec{r}\,') \frac{e^2}{\left|\vec{r} - \vec{r}\,'\right|} \varphi_{i\lambda_3\sigma}(\vec{r}) \varphi_{i\lambda_4\sigma'}(\vec{r}\,')$$

$$\boxed{U_{\alpha_1\alpha_2\alpha_3\alpha_4} = \text{linear combination}(A, B, C)}$$

Racah parameters:

$$\boxed{(F_0, F_2, F_4)}$$

Slater intergrals

PRB **76**, 024412 (2007)

New set of parameters

$$(A,B,C) \Rightarrow (U,J,B)$$

real orbitals

$$U = \frac{1}{4}\sum_{\mu,\mu\neq\lambda} U_{\lambda\mu\lambda\mu} = A - B + C = F^0 - \frac{1}{49}(F^2 + F^4)$$

$$J = \frac{1}{4}\sum_{\mu,\mu\neq\lambda} U_{\lambda\mu\mu\lambda} = \tfrac{5}{2}B + C = \frac{5}{98}(F^2 + F^4)$$

spherical harmonics (Anisimov)

$$U_A = \frac{1}{25}\sum_{mm'} U_{mm'} = A + \frac{7}{5}C = F^0 \qquad U_A - J_A = \frac{1}{20}\sum_{\substack{mm' \\ m\neq m'}} (U_{mm'} - J_{mm'})$$

$$J_A = \frac{7}{2}B + \frac{7}{5}C = \frac{1}{14}(F^2 + F^4)$$

$$\begin{cases} U_A = U + \dfrac{2J}{5} \\ J_A = \dfrac{7}{5}J \end{cases} \Leftrightarrow \begin{cases} U = U_A - \dfrac{2J_A}{7} \\ J = \dfrac{5}{7}J_A \end{cases}$$

From HF to Stoner

$$n_{i,\lambda\sigma,\mu\sigma'} = \bar{n}_{i,\sigma}\delta_{\lambda\sigma,\mu\sigma'} \qquad \bar{n}_{i,\sigma} = \tfrac{1}{5}\sum_{\lambda} n_{i,\lambda,\sigma}$$

$$H_{\text{int}} \rightarrow H = \sum_{i\lambda\sigma} (U_{eff} n_{i\lambda\sigma} - \tfrac{1}{2} I_{dd} m_{i\lambda\sigma}) c^{\dagger}_{i\lambda\sigma} c_{i\lambda\sigma}$$

$$U_{eff} = (9U - 2J)/5 \qquad I_{dd} = (U + 6J)/5$$

I_{dd}	Controls the spin-moment
$U - J, B$	Controls the orbital-moment and anisotropy

What about TB+V

$$H_{\text{int}} = \frac{1}{2} \sum_{\substack{ij,\lambda\sigma,\mu\sigma' \\ i\neq j}} V_{ij} c^{+}_{i\lambda\sigma} c^{+}_{j\mu\sigma'} c_{j\mu\sigma'} c_{i\lambda\sigma}$$

$$V_{ij}^{\lambda\mu} = \left\langle \phi_{i\lambda}(\mathbf{r}) \phi_{j\mu}(\mathbf{r}') \middle| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \middle| \phi_{i\lambda}(\mathbf{r}) \phi_{j\mu}(\mathbf{r}') \right\rangle = V_{ij} = V_0 \frac{R_0}{R_{ij}}$$

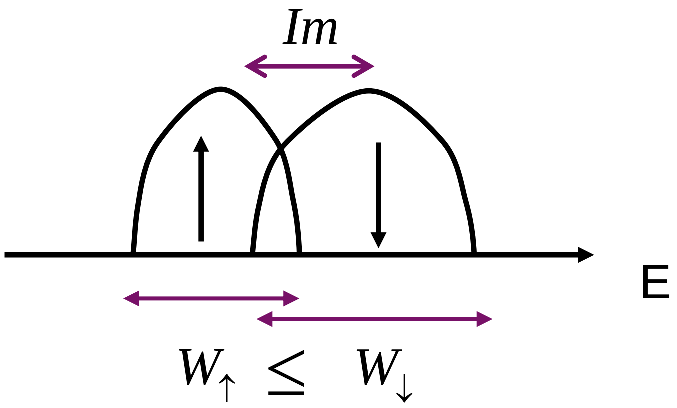
Hartree Fock decoupling (mean field)

On-site renormalization

$$\varepsilon_{i\lambda\sigma} = \varepsilon_{i\lambda\sigma} + \sum_{j} V_{ij} \left\langle n_j \right\rangle$$

Spin dependent hopping integrals

$$\beta^{\sigma}_{i\lambda,j\mu} = \beta_{i\lambda,j\mu} + V_{ij} \left\langle c^{\dagger}_{j\mu\sigma} c_{i\lambda\sigma} \right\rangle$$



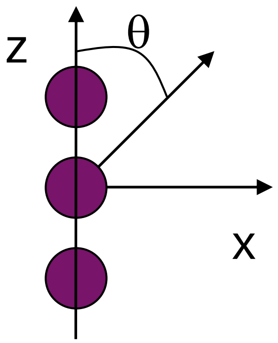
PRB **69**, 064432 (2004)

SPIN-ORBIT COUPLING

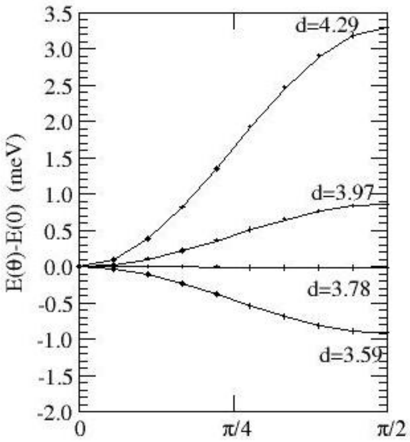
$$H_{\mathrm{SOC}} = \sum_i \xi_i(r)\vec{L}_i.\vec{S}_i$$

We keep d orbitals only

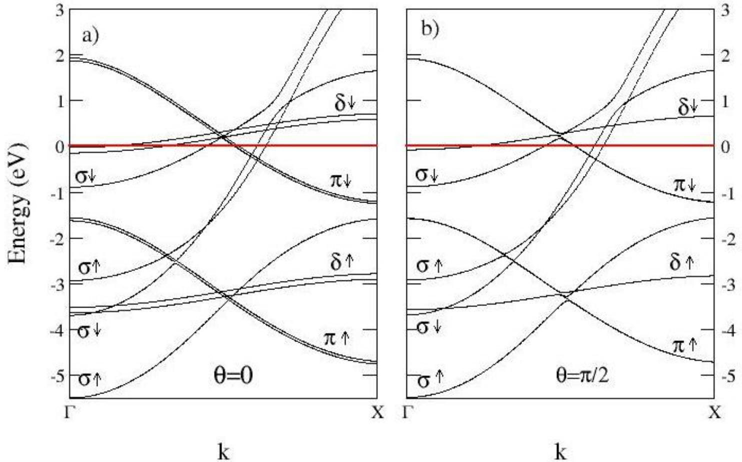
$$\xi_{i,d} = \int R^2_{i,d}(r) r^2 dr$$



Magnetic anisotropy



Band structure anisotropy



J. Phys.: Cond. Matter **18**, 6785 (2006)

Orbital moment

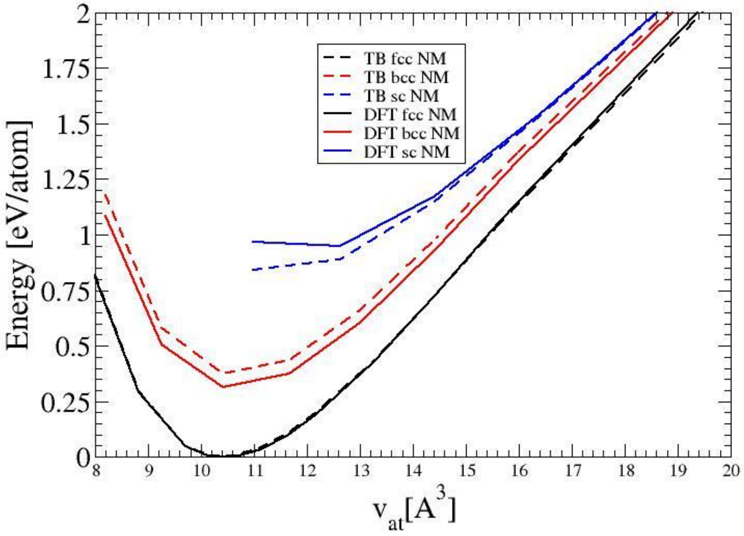
$M_L \sim 0.1\mu_B$ (bulk)
$M_L \sim 0.5 - 1\mu_B$ (wire)

TB PARAMETERS

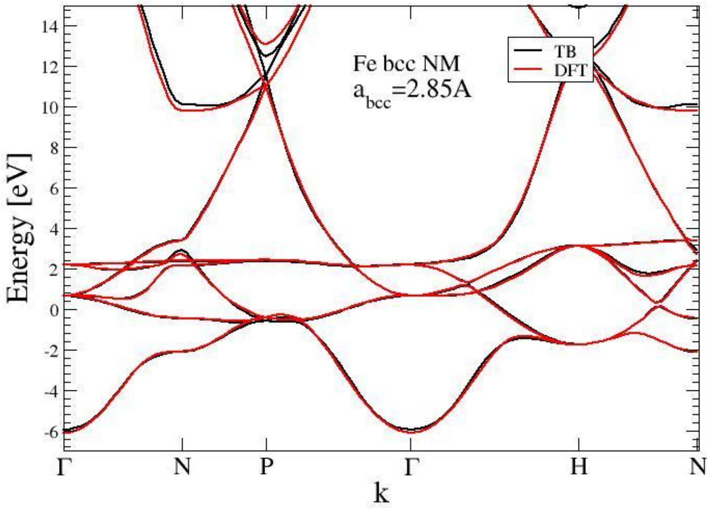
TB$_0$

Fit on ab-initio band structures and total energy of non-magnetic bulk systems

Total energy



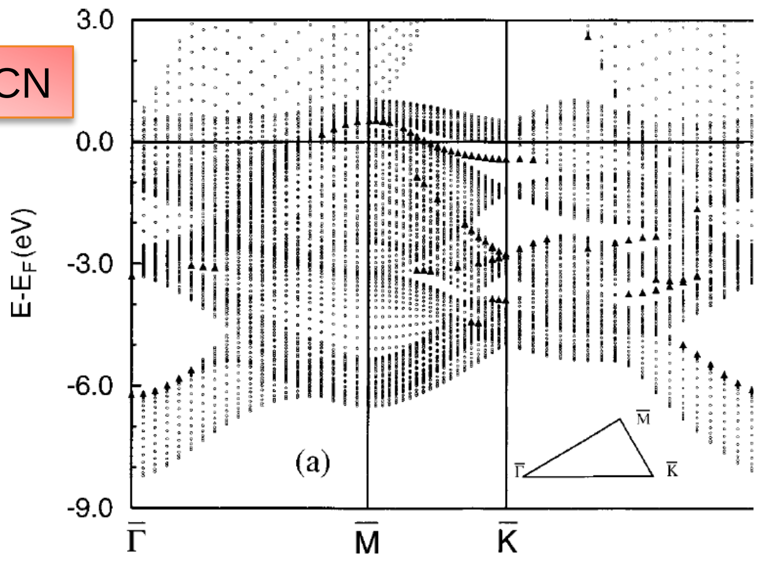
Band structure

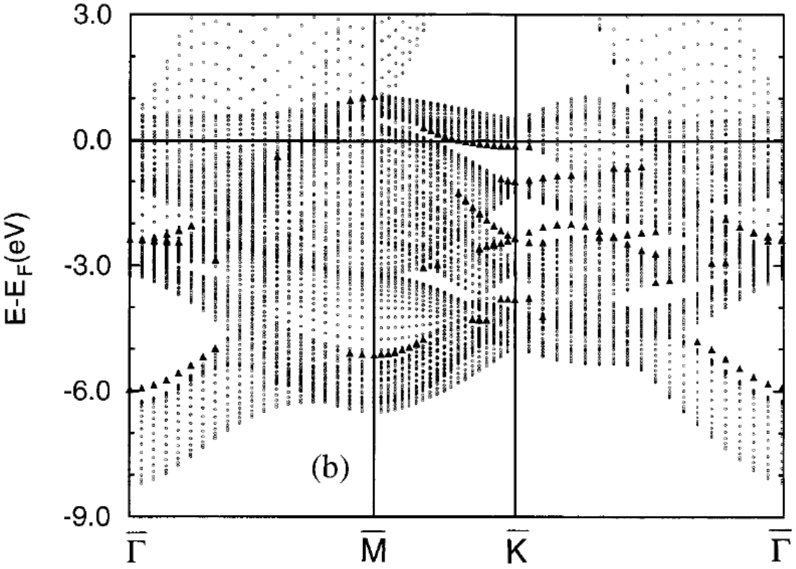


$\mathrm{TB}_{\mathrm{LCN}}$

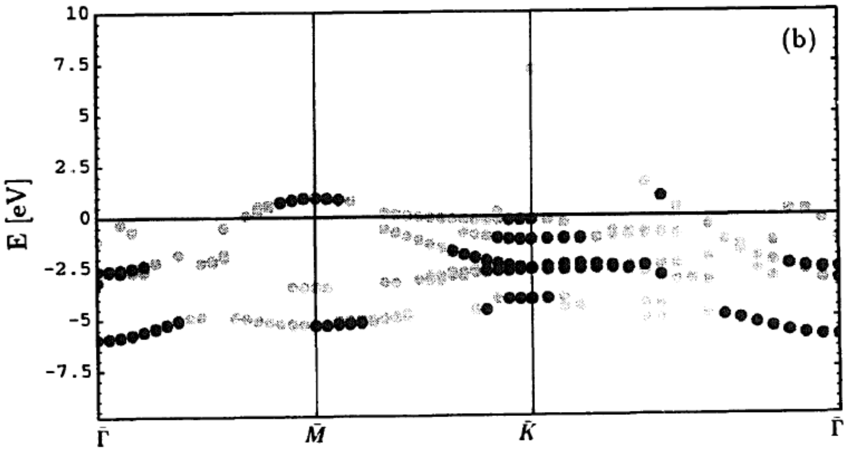
Influence of local charge neutrality on surface band structure

No LCN





With LCN



Rh(111) surface

Surf. Sci. **346**, 300 (1996)

PRB **58**, 9721 (1998)

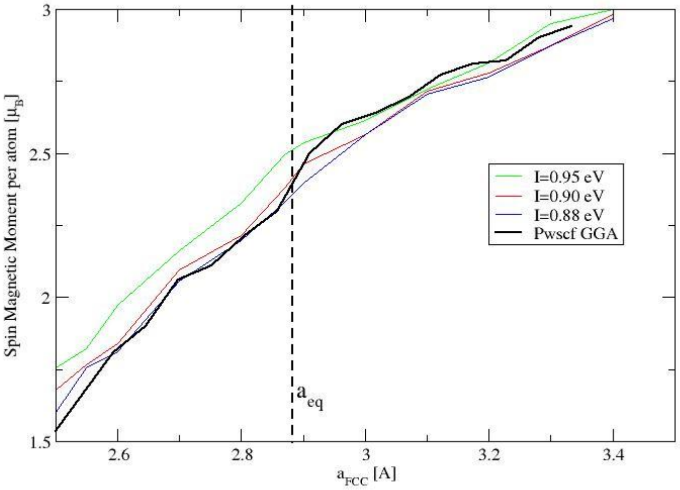
$\mathrm{TB}_{\mathrm{MAG}}$

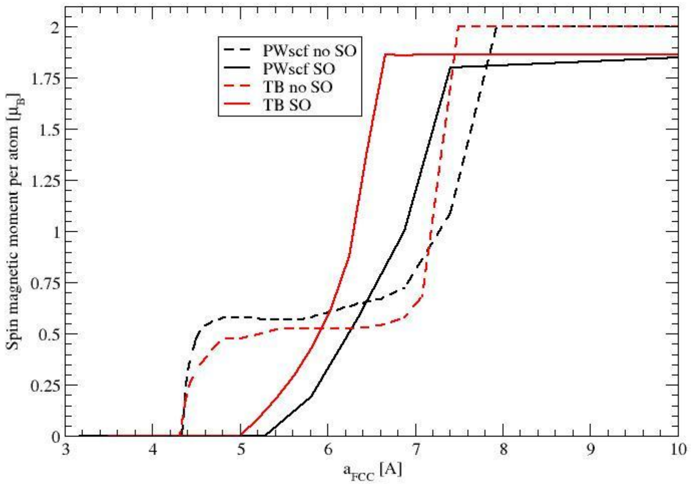
Determination of the Stoner parameter

On-set of magnetism with lattice parameter expansion

$I_{Fe} \in [0.88, 0.95] eV$

$I_{Pt} = 0.60 eV$





What about U,J,B parameters

$I = (U + 6J)/5$

U/J

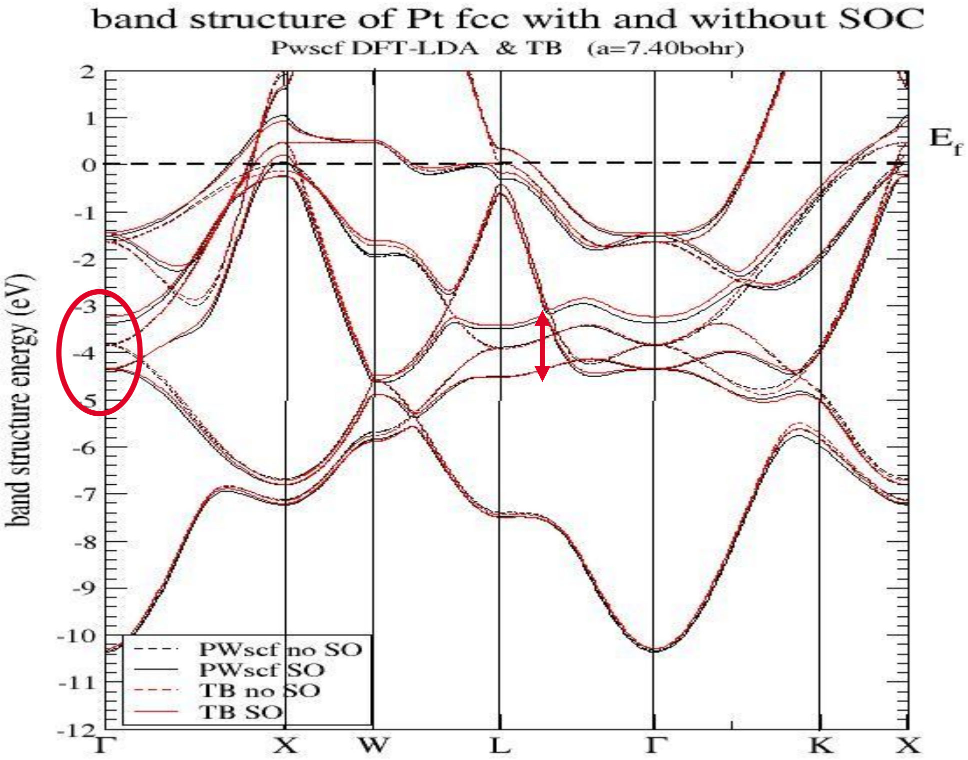
$B/J = 0.14 \Rightarrow B \approx 0.1 eV$

J. Phys.: Cond. Matter **accepted** (2012)

TB$_{SOC}$

Determination of the Spin-Orbit Coupling constant

Non-magnetic band structure



$$\xi_{Fe} = 0.06eV$$

$$\xi_{Pt} \in [0,45,0.55]eV$$

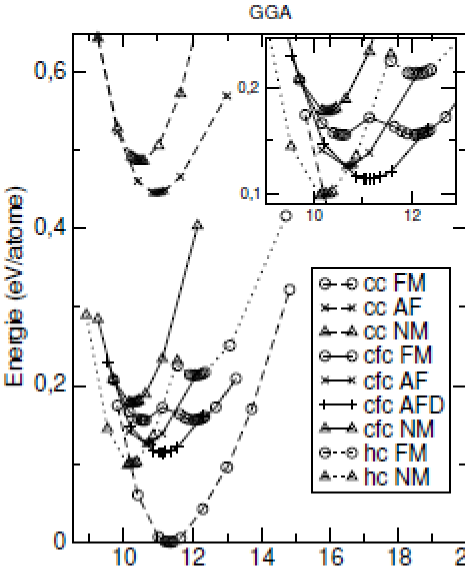
Absolutely not « structure » dependent
(same SOC parameter for fcc, bcc, or wire)

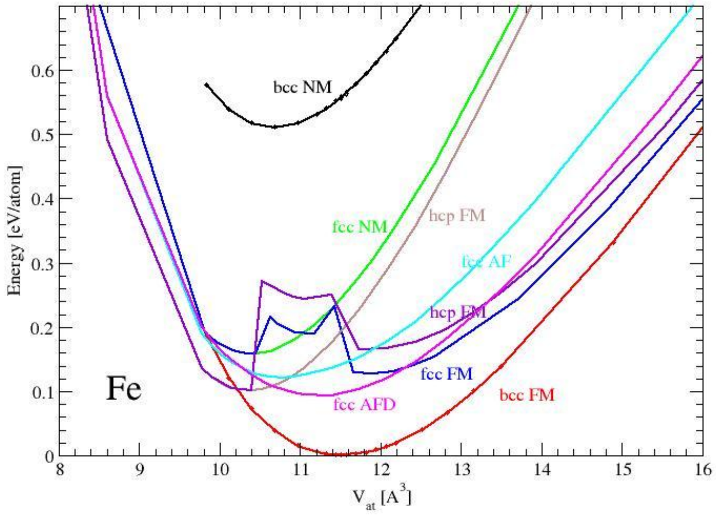
APPLICATIONS

IRON FROM BULK TO WIRE

BULK IRON

Phase stability





$I_{Fe} = 0.95eV$

❶Fe bcc stabilized by magnetism

For $I_{Fe} = 0.88eV$ hcp is the ground state.

❷Complex magnetic structure of Fe fcc

LS and HS, AF, spin spiral

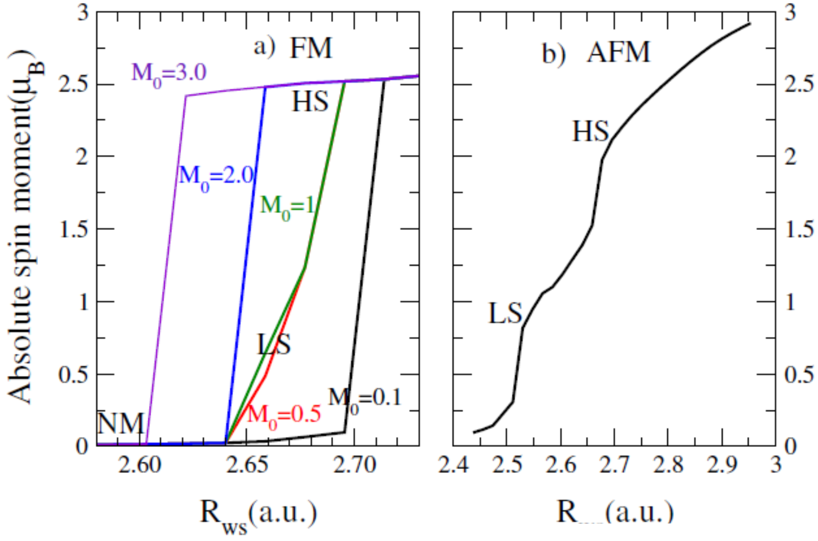
J. Phys.: Cond. Matter **18**, 6785 (2006)

J. Phys.: Cond. Matter **22**, 295502(2010)

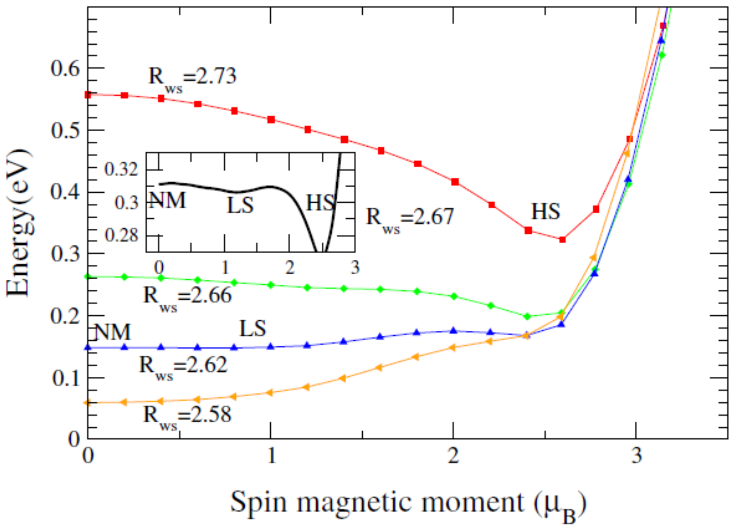
BULK IRON

Complex magnetic structure of Fe fcc

$M(d)$



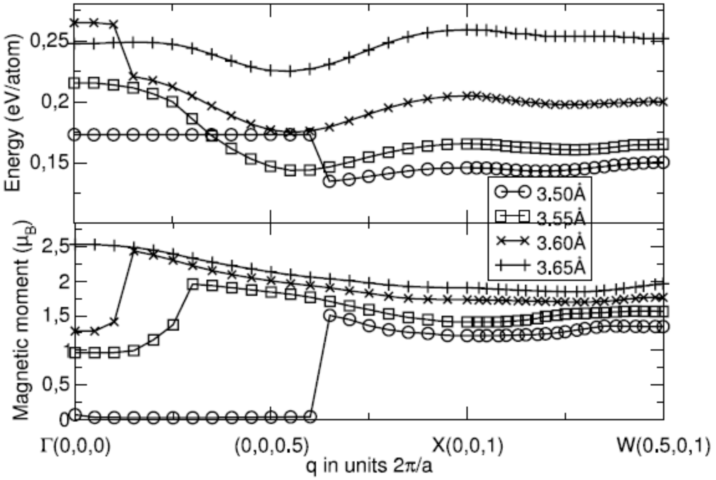
$E(M)$



Spin spiral

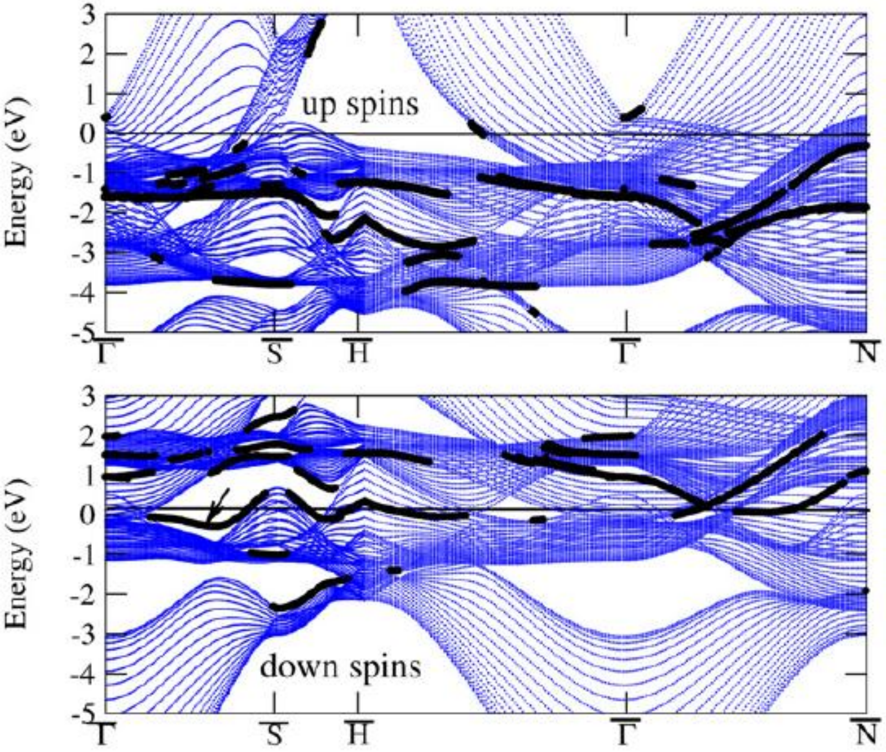
$E(q)$

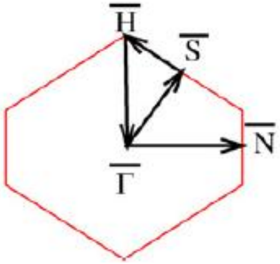
$M(q)$



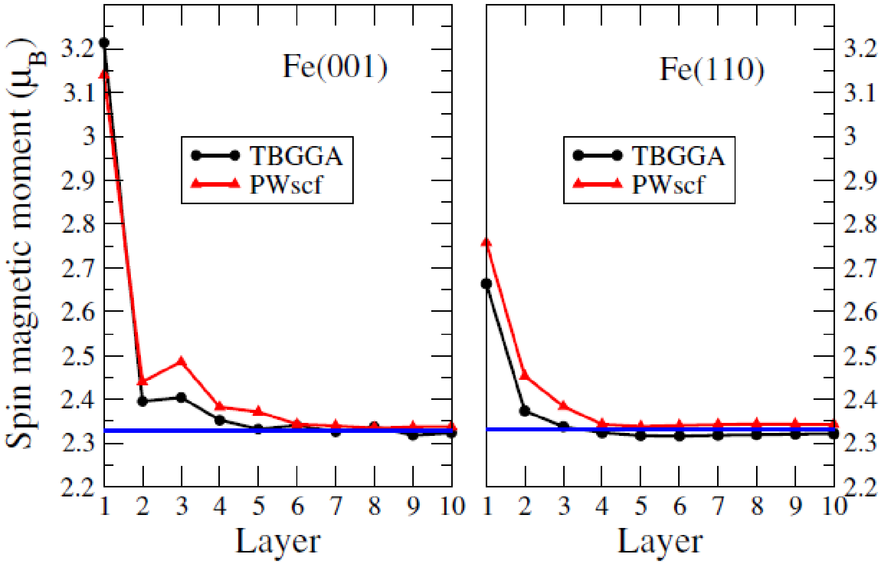
IRON SURFACE

(110) Band structure





$E(l)$



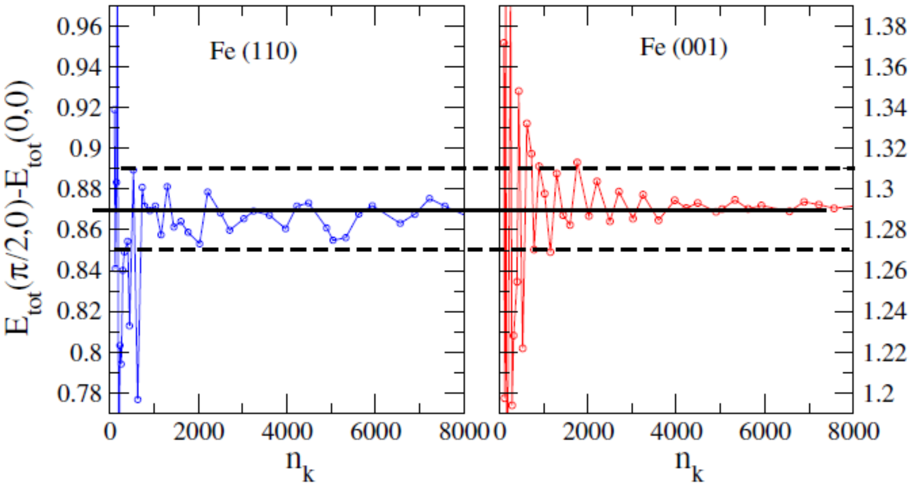
J. Phys.: Cond. Matter **18**, 6785 (2006)

IRON SURFACE

Magnetic anisotropy energy (MAE)

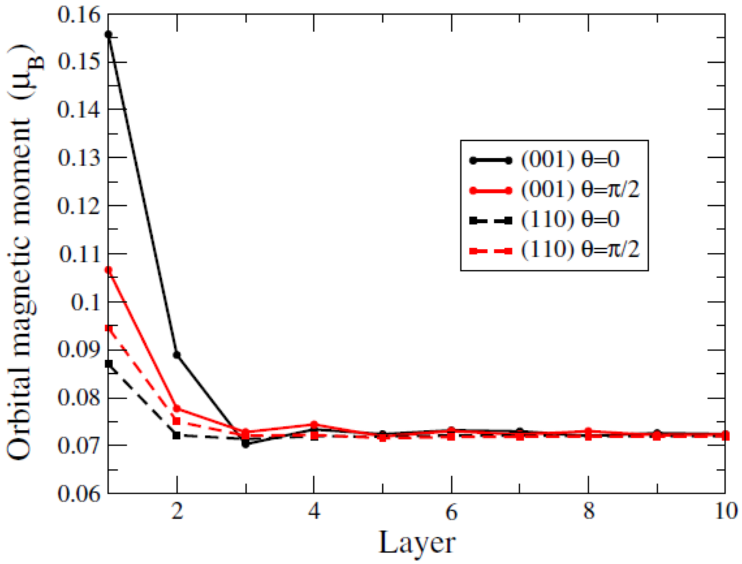
MAE Convergence / k points

monolayers



Easy axis: ⊥ surface

Orbital moment



❶ Enhancement of anisotropy

❷ De-quenching of orbital moment

Bruno's formula

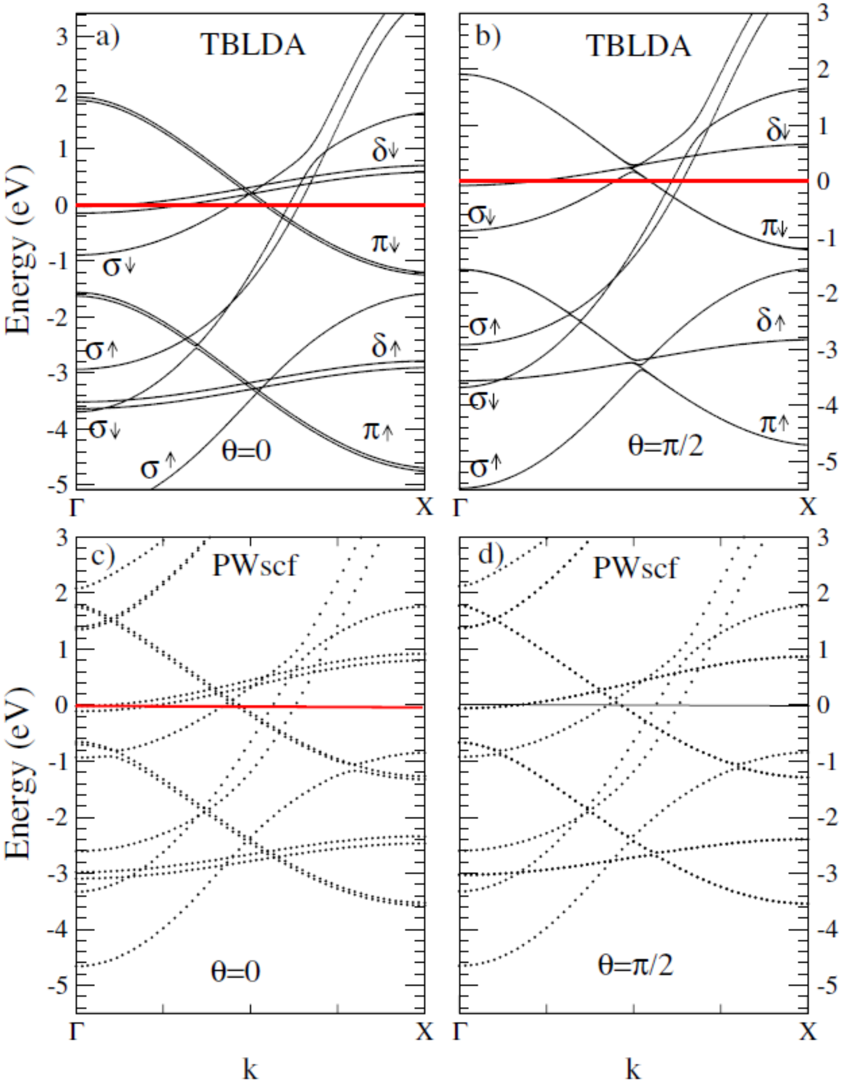
$$\Delta E(\theta,\varphi)=-\frac{\xi}{4}\Delta L(\theta,\varphi)$$

Works well for saturated systems

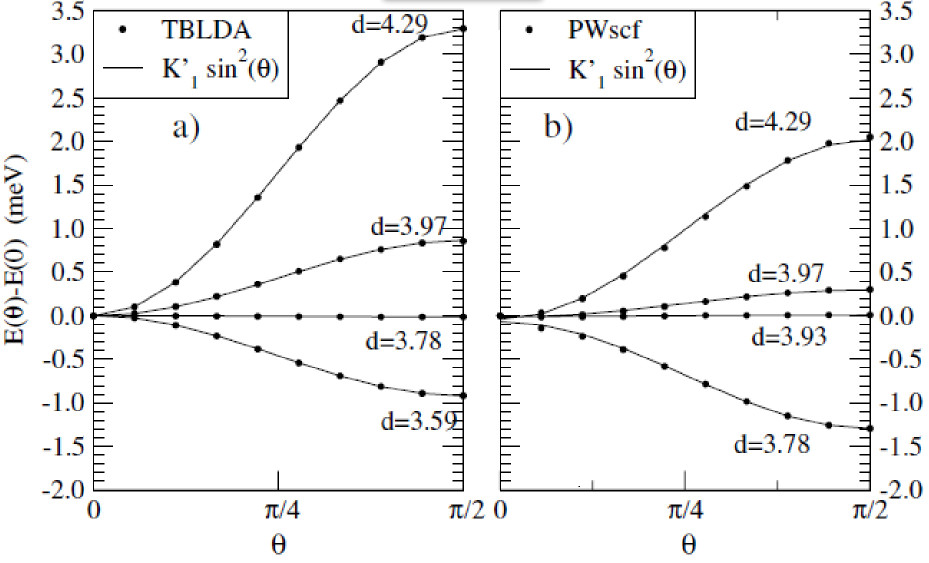
IRON WIRE

Magnetic anisotropy energy (MAE)

Band structure



MAE



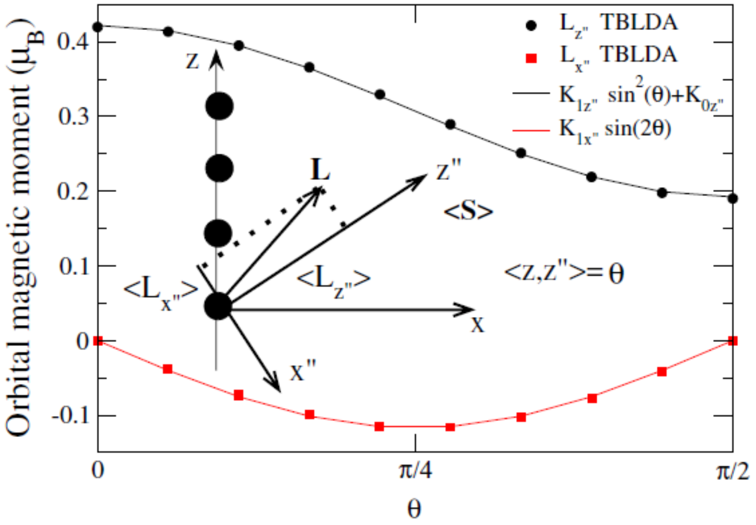
❶ Band structure anisotropy (origin of AMR)

❷ Easy axis reversal ⊥ → //

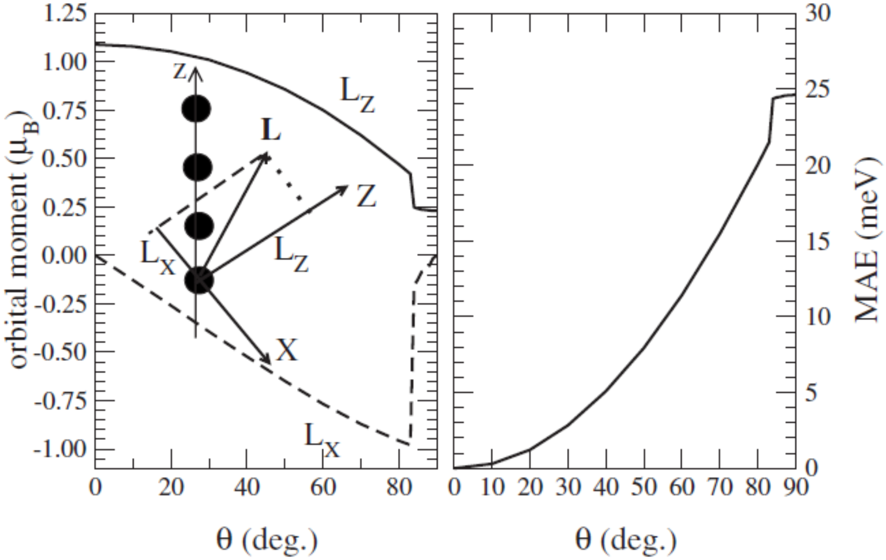
IRON WIRE

Beyond Stoner: Orbital Polarization

Stoner



TB+(U,J,**B**)

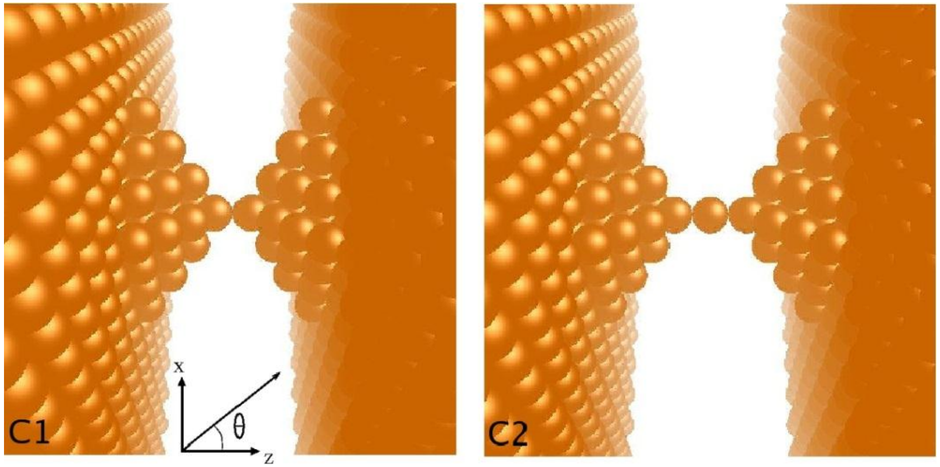


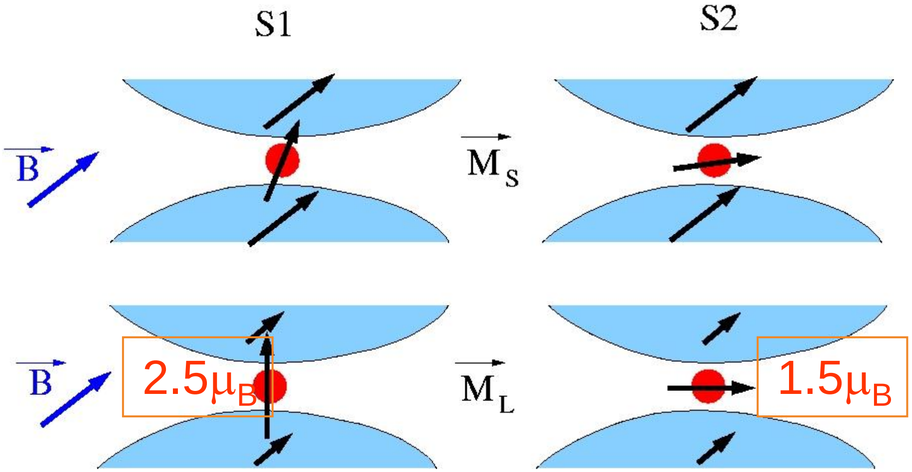
Is the Orbital Polarization ansatz verified?

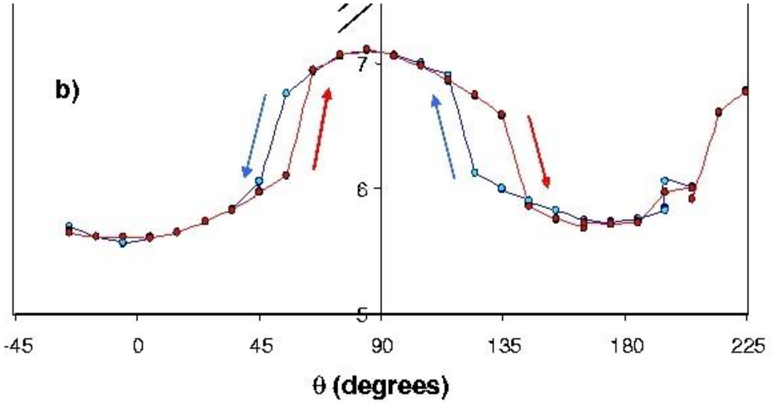
$$H_{\mathrm{TB}} + (U,J,B) \underset{?}{\approx} H_{\mathrm{TB}} - B\langle L_z \rangle L_z$$

PRB **76**, 024412 (2007)

IRON ATOMIC CONTACTGAMR







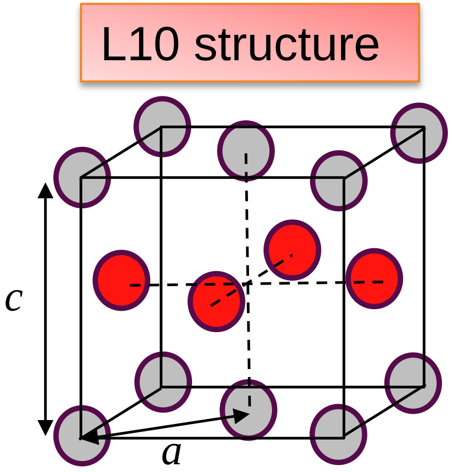
2 magnetic solutions

hysteresis

EPL **83**, 17010 (2008)

FePt L10: FROM BULK TO CLUSTERS

BULK FePt



$$a_{\exp} = \frac{3.86}{\sqrt{2}} = 2.73A$$

$$\frac{c_{\exp}}{a_{\exp}} = 1.36$$

$$c_{\exp} = 3.72A$$

$$V_{\exp} = 27.7A^{3}$$

Very high magnetic uniaxial anisotropy

MAE=1.4meV/fu (exp.)

TB model

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

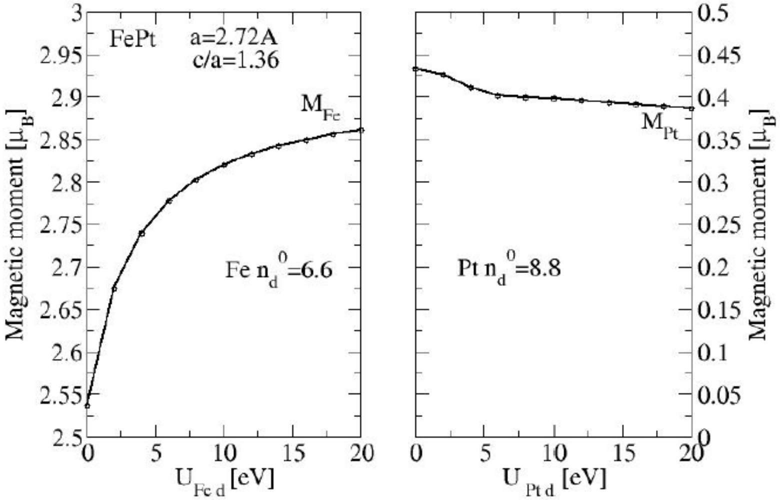
Charge neutrality

“d” orbital filling

$$U = U_d = 20eV$$

$n_{i,d}^0$ adjusted to reproduce electronic and magnetic properties of FePt L10

$$n_{Fe,d}^0 = 6.6 \quad n_{Pt,d}^0 = 8.8 \quad \Rightarrow \quad M_{Fe} \sim 3\mu_B \quad M_{Pt} \sim 0.35\mu_B$$



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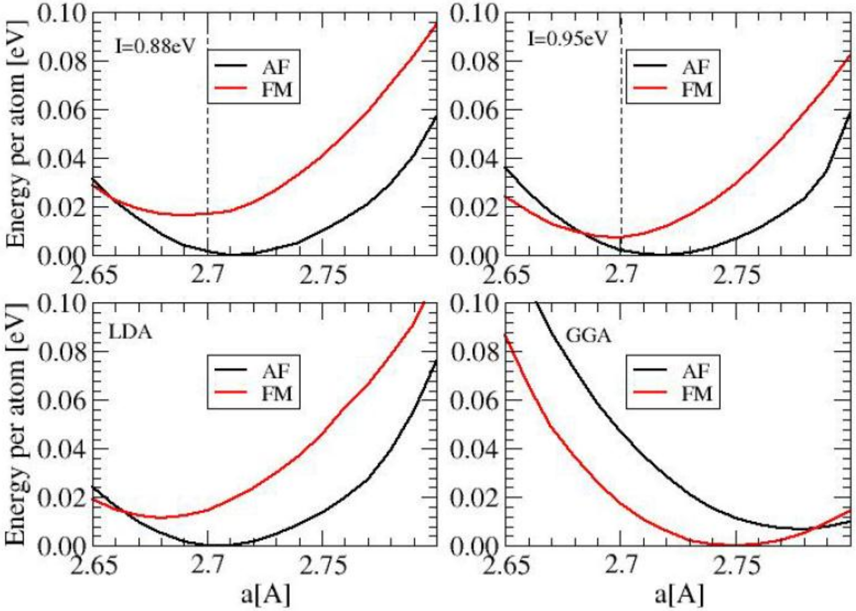
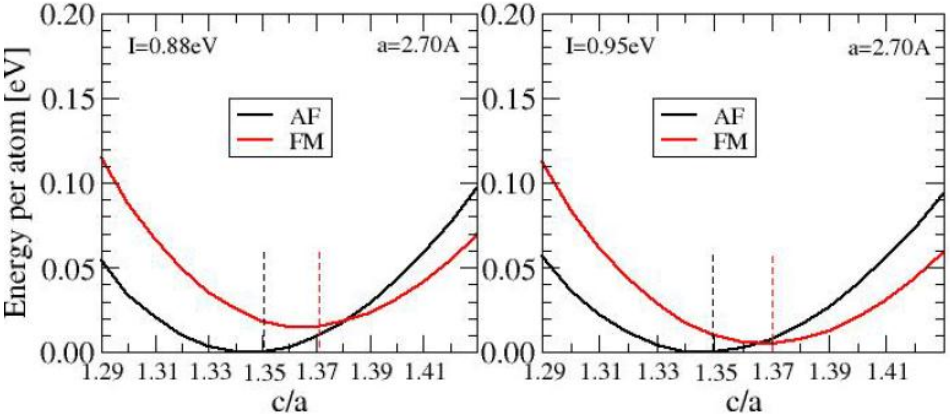
BULK FePt

Phase stability

Functional effect



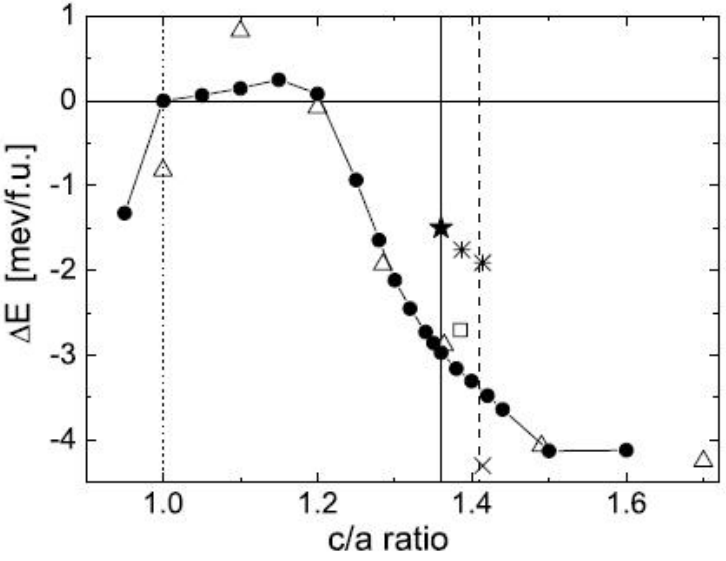
Structural effect



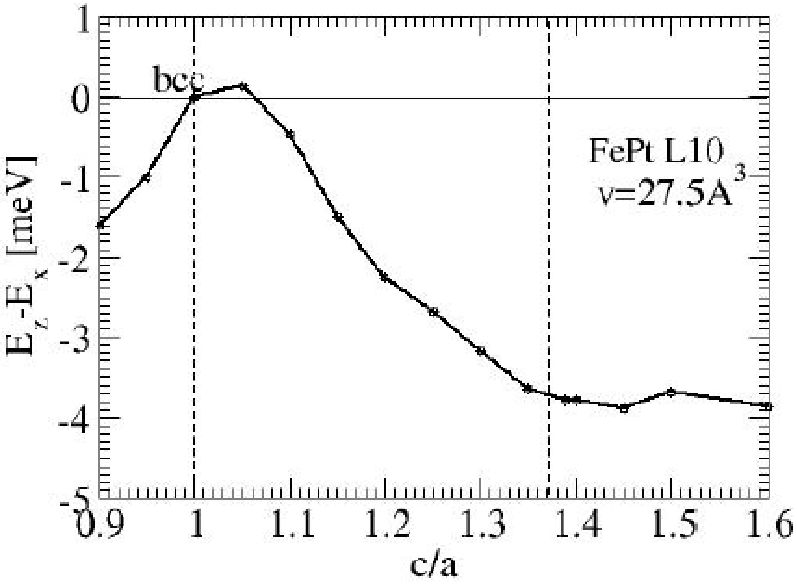
BULK FePt

MAE (c/a)

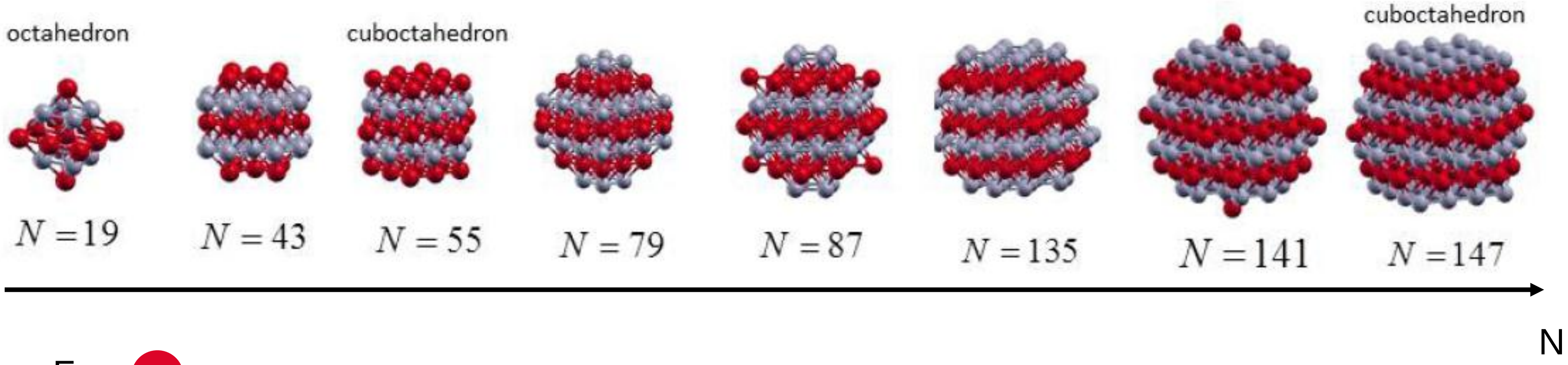
DFT



TB

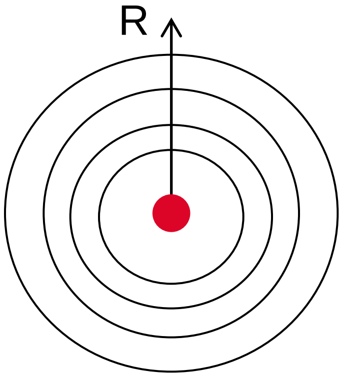


Clusters



Fe ●

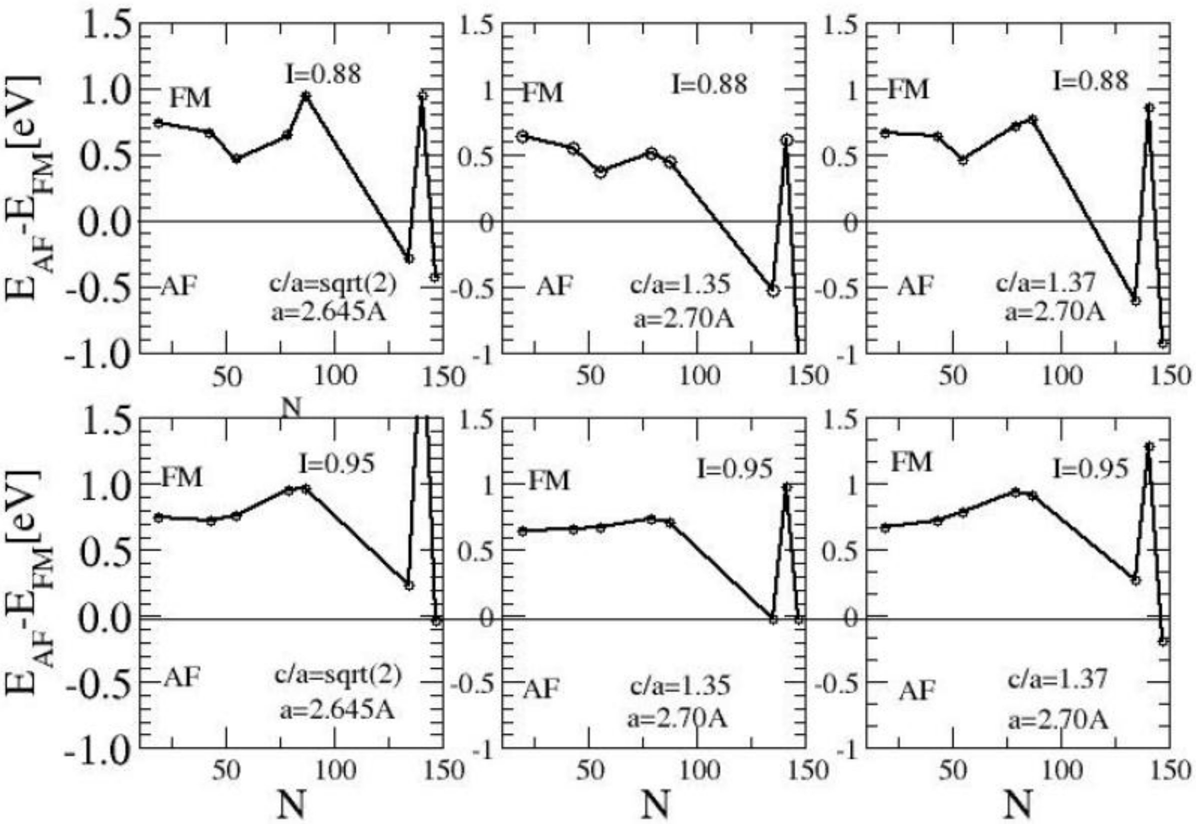
Pt ●



Concentric spheres

Clusters

FM vs AFM

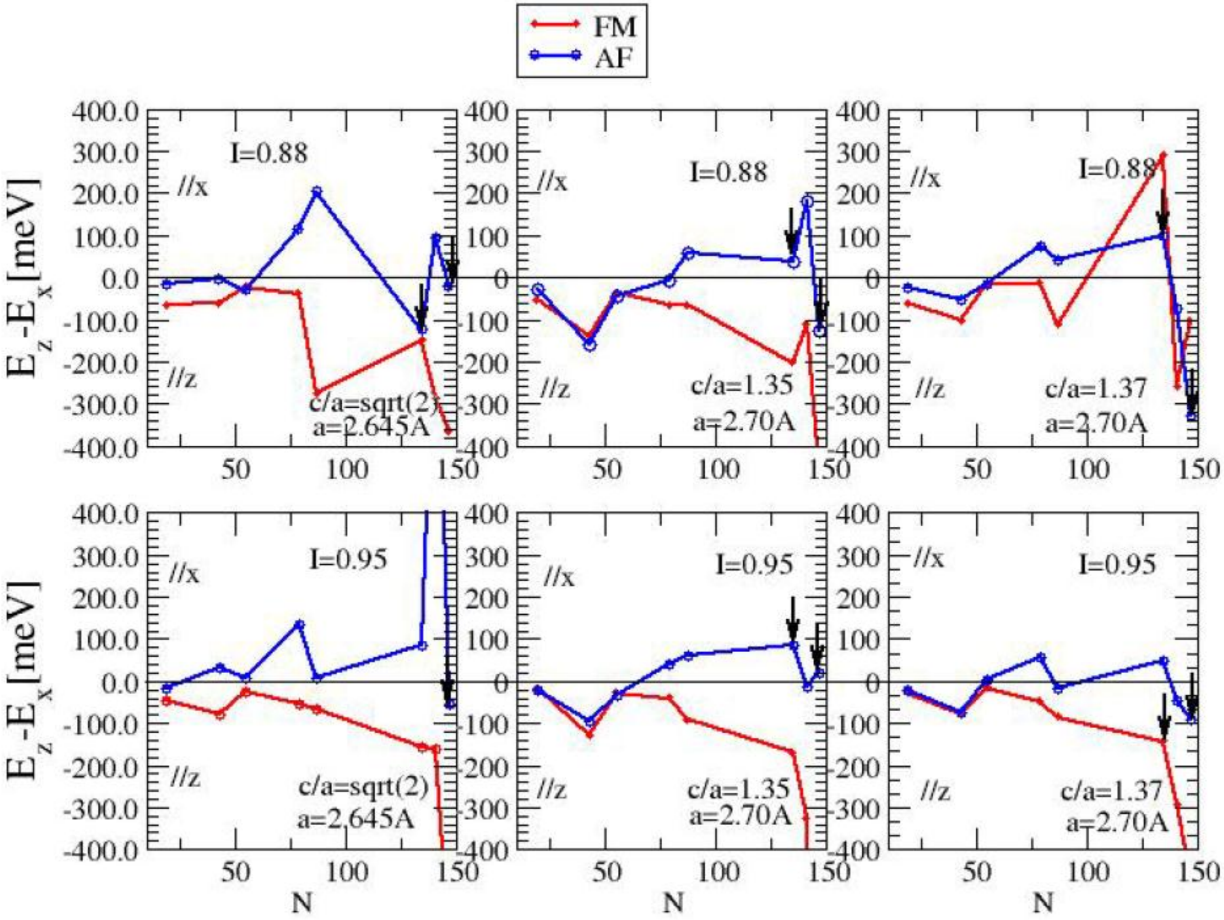


❶ Larger Stoner parameters favors FM

❷ Pt surfaces favors AFM (Fe favors FM)

Clusters

MAE



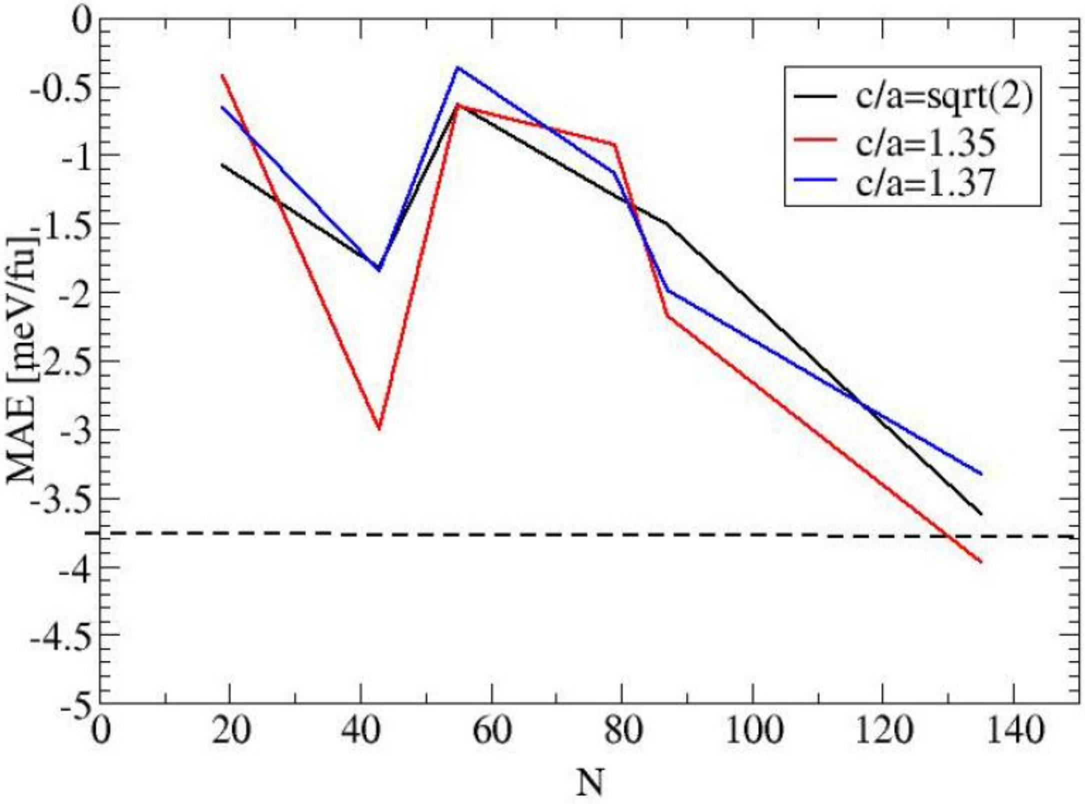
❶ FM favors uniaxial anisotropy

❷ AFM favors in-plane anisotropy

Clusters

MAE(N)

(per formula unit)



❶ MAE of clusters is below the bulk value

CONCLUSION

advantages

❶ TB is an efficient and versatile method

❷TB is useful to obtain trends by tuning parameters

❸ Magnetism is well described by simple Stoner models

❹ SOC is easily described in a TB scheme

❺ Local basis are well suited to electronic transport formalism

disadvantages

❶ Often (very) painful to determine parameters

❷ It should be handled with care: always check its transferability

❸ MAE is a subtle quantity …

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THANK YOU FOR YOUR ATTENTION

Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 69 08 29 51 | F. +33 (0)1 60 08 84 46

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