The atomic, electronic, and magnetic structure of disordered metal surfaces - interpretation of the STM

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The research i am going to present on this occasion
has been accomplished
during my doctoral studies (2003-2008)
as a material for my PhD thesis

under the supervision of

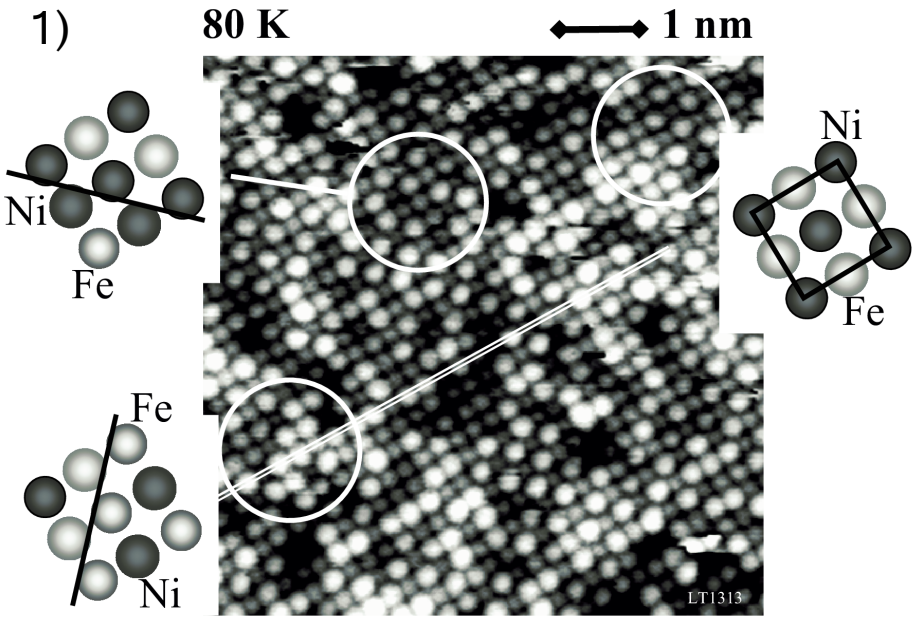
dr. František Máca

and in close collaboration with

dr. Josef Kudrnovský

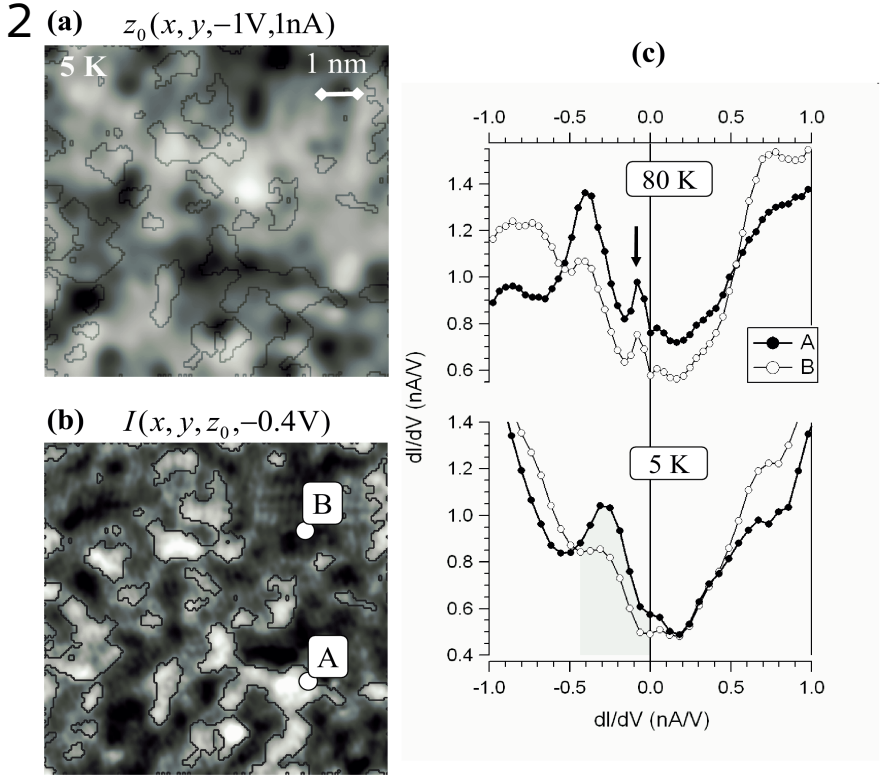
to both of whom I am largely indebted
along with all others not named here
who supported me during the time of my studies.

Experimental results for the $Fe_{64}Ni_{36}$ (100) surface



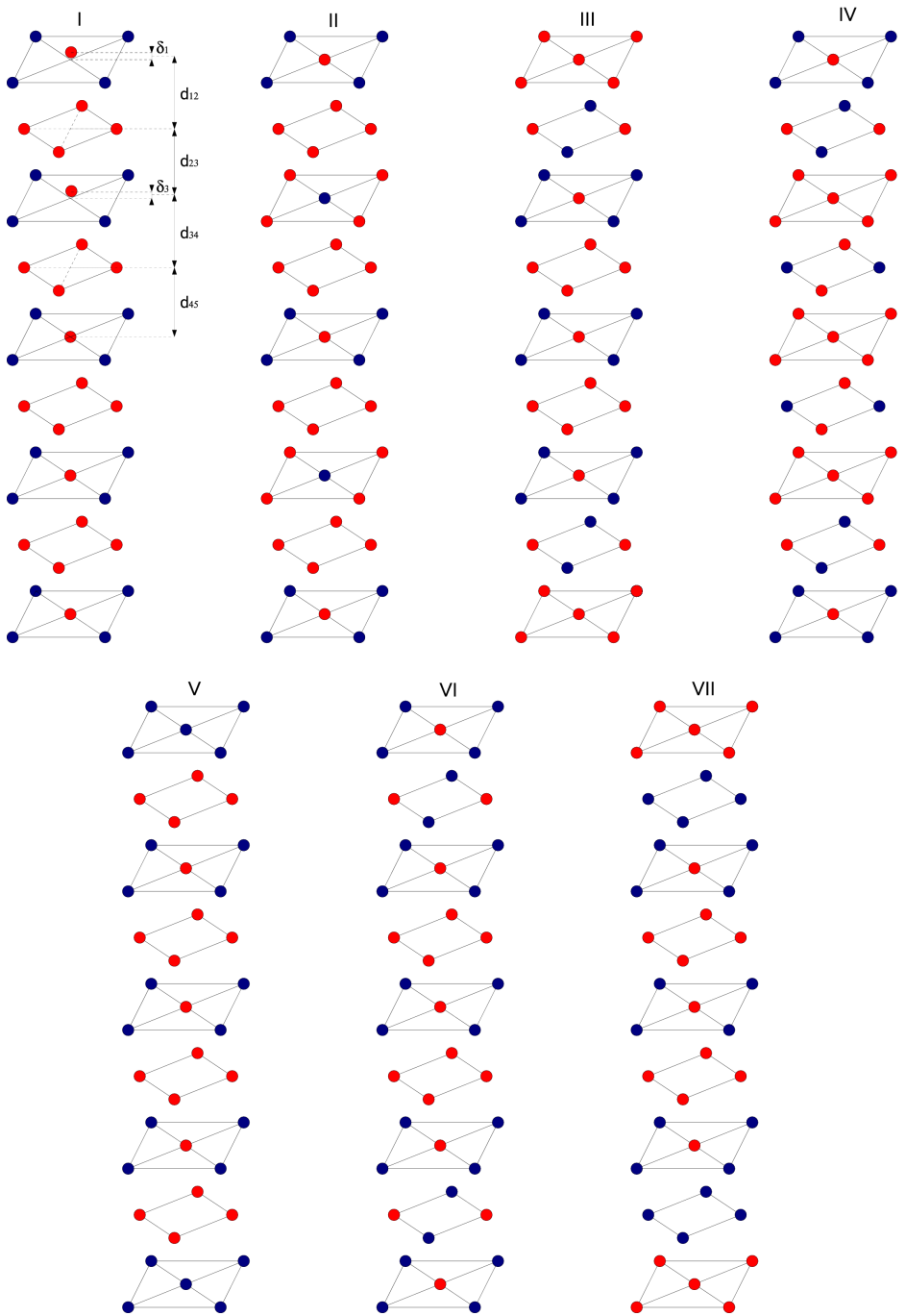
constant current STM image with atomic resolution, I = 8 nA, U = -2 mV

1) chemical resolution achieved (Fe brighter, i.e. "higher", Ni darker, i.e. "lower")
2) patches of the FeNi–*c*(2x2) structure prevail on the surface
3) peak of tunnelling conductance in STS at $U \approx$ -0.3 V



(a) constant current STM image (U = -1V),
(b) current map at -0.4 V (voltage corresponding to the STS peak)
(c) typical STS curves (differential conductance vs voltage) averaged over selected areas on the surface

Models of the FeNi (001) atomic surface structure



FP-LAPW calculations (WIEN2k):

- *atomic structure relaxation*
- *total energy calculation*
- *d_0 = a/2 = 1.8 Å*

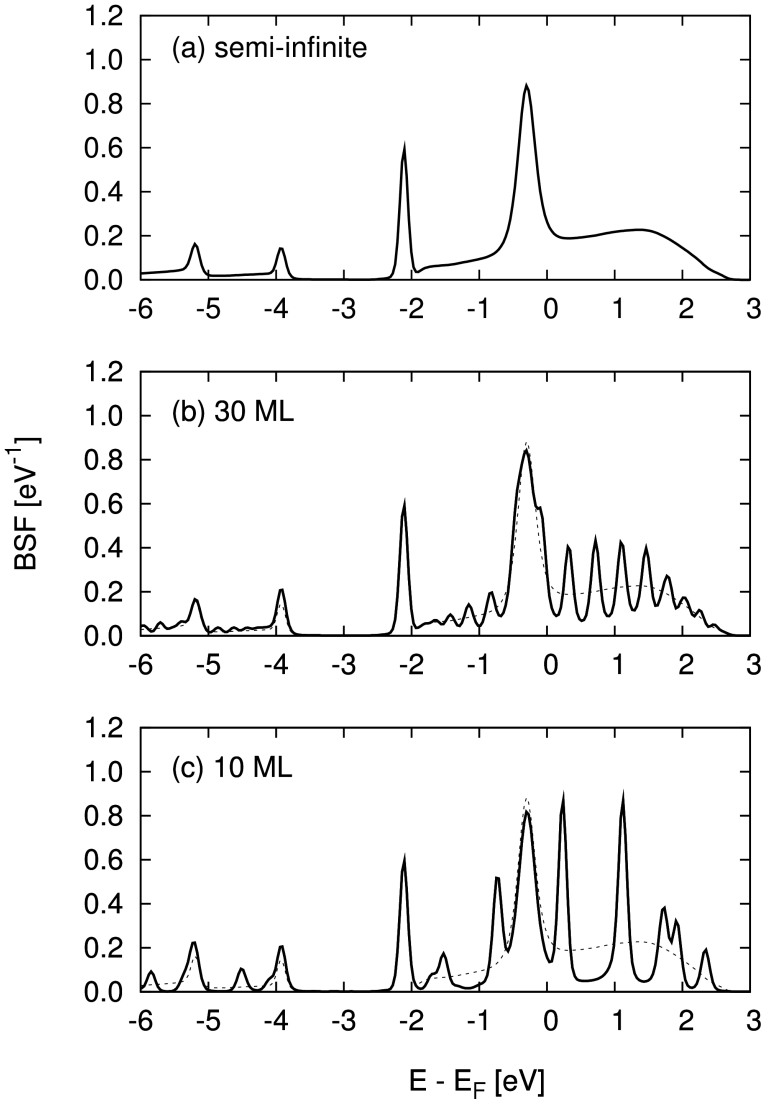
model #	I	II	III	IV
δ_1 / d_0	**+3.3%**	**+7.5%**	-4.1%	**+2.8%**
$(d_{12}-d_0) / d_0$	-1.0%	0.0%	+1.4%	-4.5%
δ_2 / d_0	0	0	+0.3%	+0.9%
$(d_{23}-d_0) / d_0$	1.4%	+2.6%	-2.3%	+2.6%
δ_3 / d_0	-1.0%	-0.1%	-0.4%	+1.5%
$(d_{34}-d_0) / d_0$	+1.2%	+1.9%	+2.3%	+1.5%
$E - E_I$ [meV]	0	*+13*	+39	–

model #	V	VI	VII
δ_1 / d_0	0.0%	**+2.6%**	+2.2%
$(d_{12}-d_0) / d_0$	-6.0%	-3.9%	-2.1%
δ_2 / d_0	0	+0.5%	0
$(d_{23}-d_0) / d_0$	+2.8%	-1.4%	-2.6%
δ_3 / d_0	-0.9%	+0.2%	+0.3%
$(d_{34}-d_0) / d_0$	+1.5%	+2.5%	+2.7%
$E - E_{VI}$ [meV]	+27	*0*	+127

- *Fe atoms in the top surface layer always stick out, Ni atoms sit lower*
- *Deeper atomic layers are also influence the surface buckling.*
- *The c(2x2)–FeNi surface structure is especially favored in terms of total energy*

The necessity of proper boundary conditions

The projected Bloch spectral function for $k_{||} = 0$ 1.8 Å above the Fe / $Fe_{64}Ni_{36}$ (100) surface depending on the slab thickness

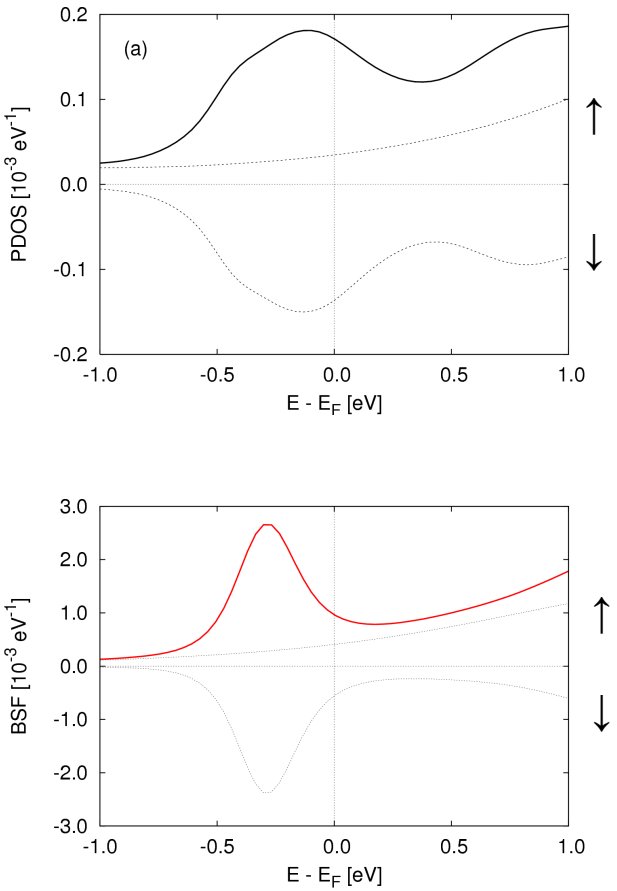


Method for the calculations that aim to interpret the STS:

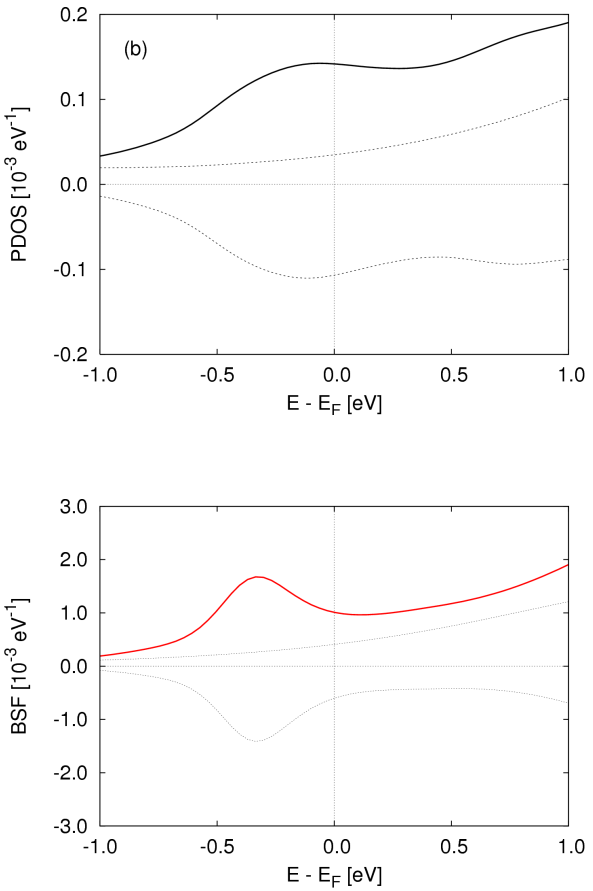
- TB-LMTO in ASA (tight-binding linear muffin-tin orbital method in atomic sphere approximation)
- Surface Green's function formalism (employed to account for the boundary conditions)
- CPA (coherent potential approximation) to treat the chemical disorder in the alloy

Projected densities of states (PDOS) and Bloch spectral functions for $k_{||} = 0$ (BSF) at a site situated 5.4 Å above the surface (spin-resolved components and total)

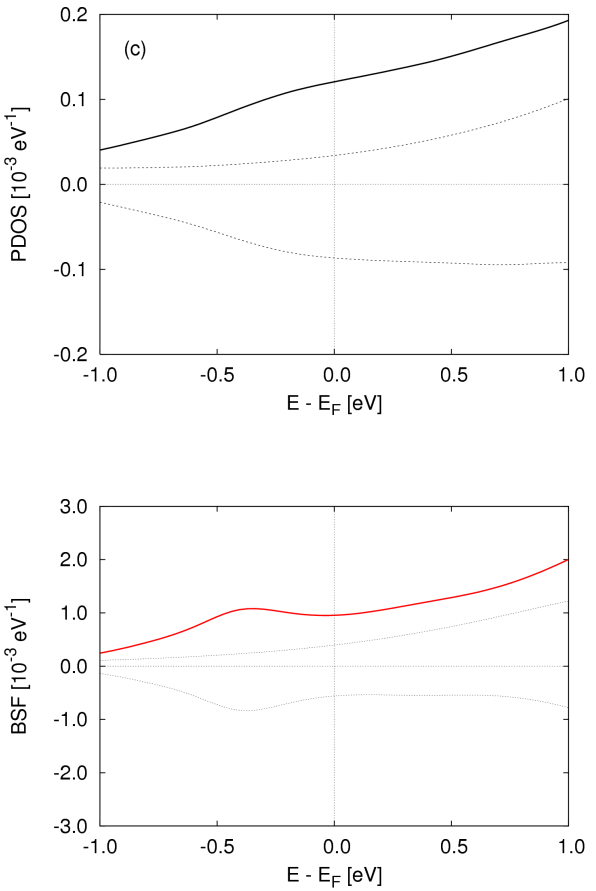
(a) Fe / $Fe_{0.64}Ni_{0.36}$



(b) $Fe_{0.875}Ni_{0.125}$ / $Fe_{0.64}Ni_{0.36}$



(c) $Fe_{0.75}Ni_{0.25}$ / $Fe_{0.64}Ni_{0.36}$



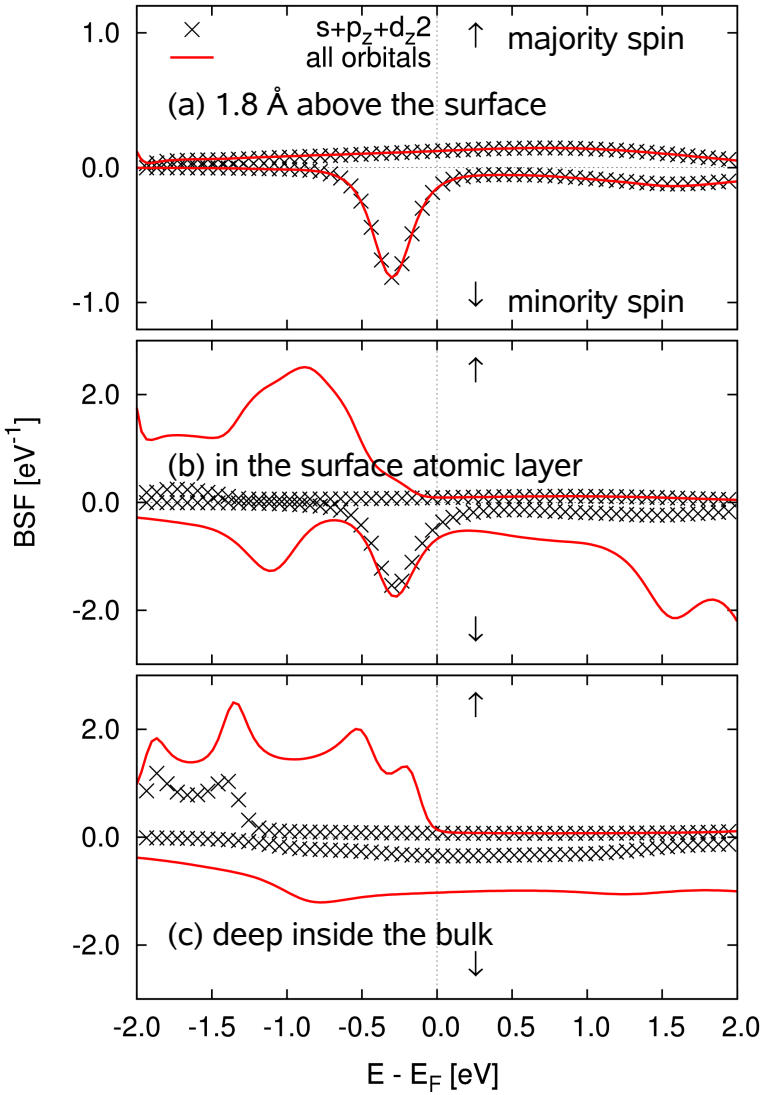
Spin components
- *positive half-plane: majority spin (↑)*
- *negative half-plane: minority spin (↓)*
- *full line: total (all spin)*

There is a peak of the LDOS for the minority-spin electrons ≈ 0.3 eV below E_F originating mainly from the central part of the Brillouin zone, which appears in the vacuum above Fe-rich surfaces

Bloch spectral functions for $k_{||} = 0$ (BSF) and projected densities of state (PDOS)

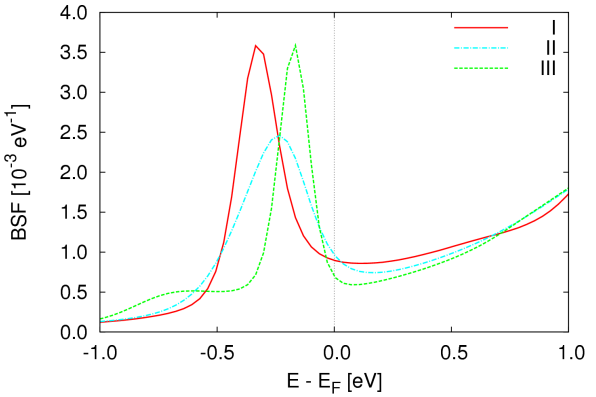
$Fe / Fe_{0.64}Ni_{0.36}$

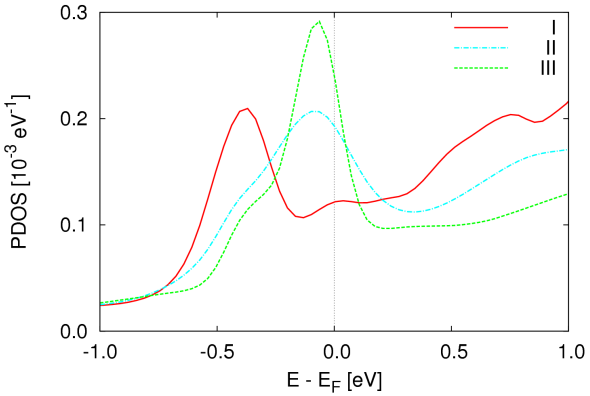
Spin-resolved and orbital-projected BSF above the surface, on it, and beneath



BSF for $k_{||} = 0$ and PDOS 5.4 Å above the surface depending on the sub-surface composition

I. $Fe / Fe / Fe_{0.64}Ni_{0.36}$
II. $Fe / Fe_{0.5}Ni_{0.5} / Fe_{0.64}Ni_{0.36}$
III. $Fe / Ni / Fe_{0.64}Ni_{0.36}$



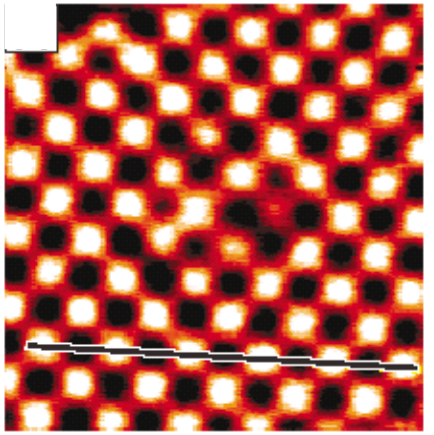


- The surface resonance of the minority-spin electrons is centered at $k_{||} = 0$ and predominantly of a d_z2-orbital character.
- Its existence depends mainly on the composition of the top surface atomic layer but its position on the energy scale also depends on the sub-surface layers.

Magnetic overlayers of *3d* transition metals on the W(100) substrate

Motivation:

- Fe / W(100) was shown to form a *c*(2x2) anti-ferromagnetic monolayer by an SP-STM (Kubetzka *et al.* 2005).
- *Ab-initio* calculations predict ferromagnetic monolayers of V, Cr, and Mn and *c*(2x2) anti-ferromagnetic monolayers of Fe and Co on the W(100). surface (Ferriani *et al.*, 2005).
- This is in contrast to the magnetic order of these metals in monoatomic layers on, e.g., Ag(100), Pd(100), W(110).
- Transition from ferromagnetic to anti-ferromagnetic configuration has been studied for Fe/Ta_xW_{1-x} (Ferriani *et al.*, 2007).



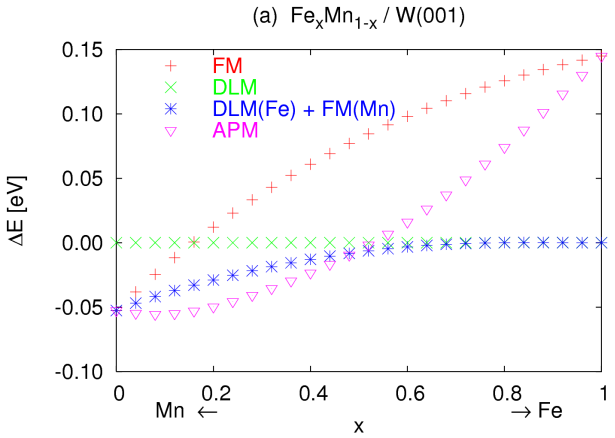
Spin-polarized STM image of the c(2x2) anti-ferromagnetic Fe/W(100) surface (Kubetzka et al. 2005)

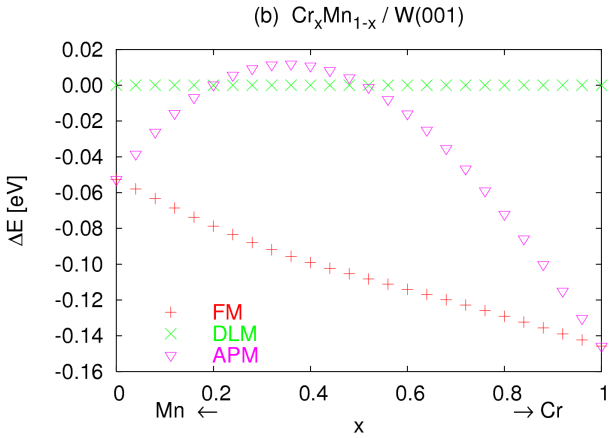
Questions:

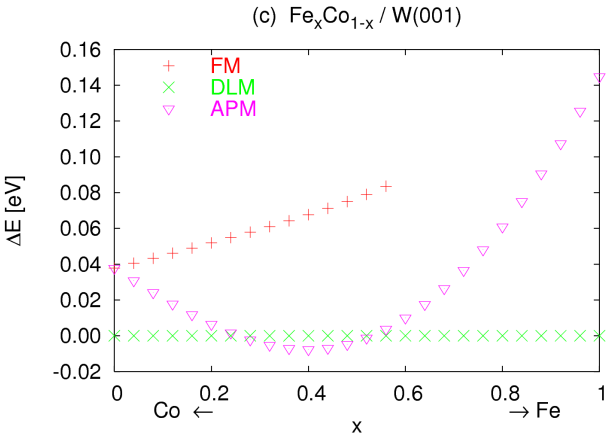
- What would be the effect of disorder in the monolayers?
- Effect of mixing elements with different tendencies to ferromagnetic/anti-ferromagnetic order?
- Magnetism in ultra-thin (sub-monolayer) films and the effect of disorder therein?

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

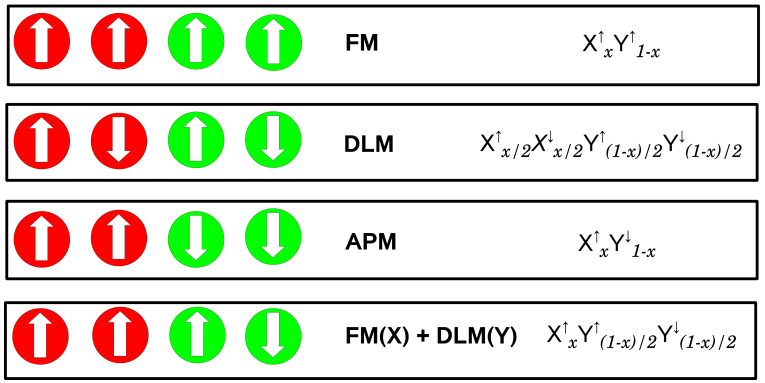
Total energies of selected magnetic configurations for the binary surface alloys on W(100)







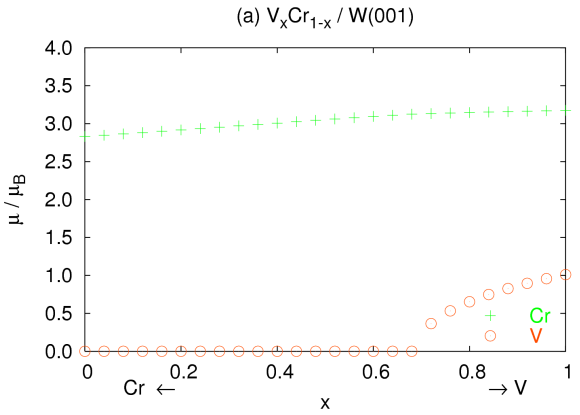
Selected magnetic configurations

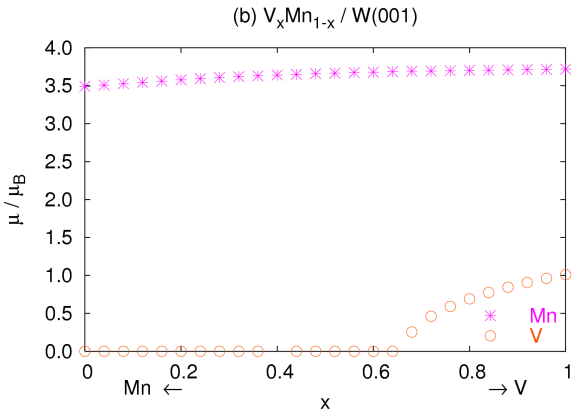


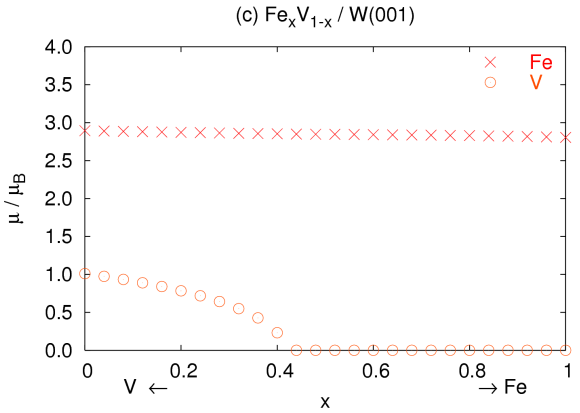
Tendencies of alignment between magnetic moments of the 3d elements on the W(100) substrate

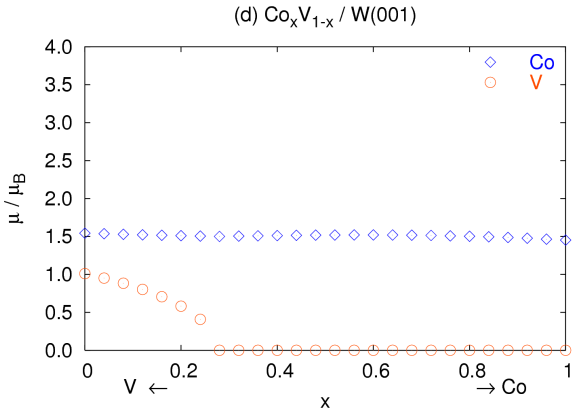
- parallel alignment for V, Cr, and Mn (including mixed pairs like (CrMn)
- anti-parallel alignment for Fe and Co (including FeCo)
- anti-parallel alignment also for FeMn, FeCr, CoMn, CoCr, and CoV
- weak tendency to parallel alignment also for FeV

Magnetic moments of atoms in the binary surface alloys









- *magnitudes of atomic magnetic moments of **Cr**, **Mn**, **Fe**, and **Co** **change** only **little** with magnetic configuration and chemical composition of the alloy (well localized moments)*
- *magnetic moments of **V** (vanadium) are very **sensitive** to both magnetic configuration and alloy composition (more itinerant character)*

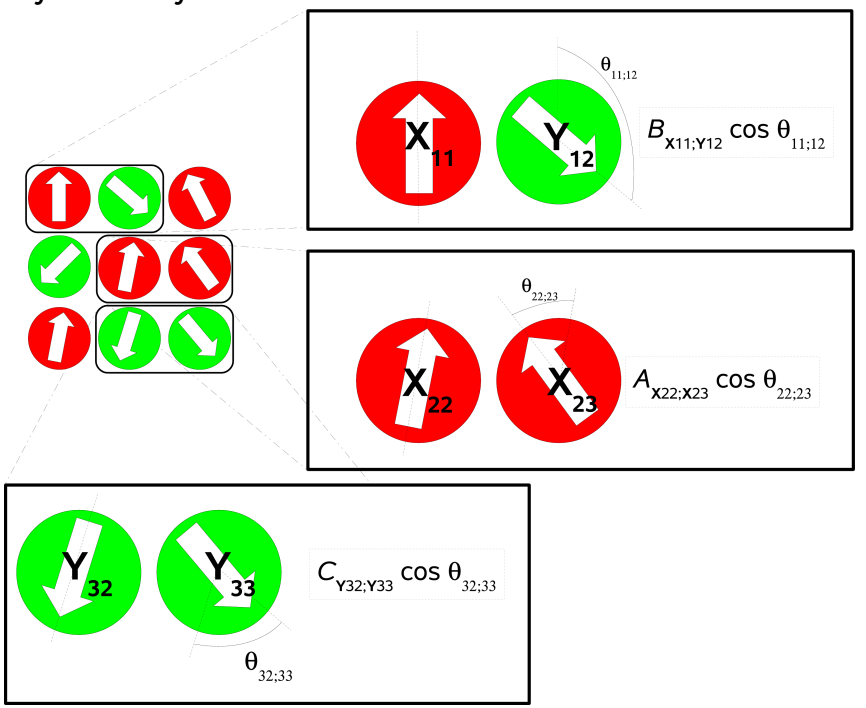
Theoretical models for the magnetic interactions

$$E_{mag} = E_0 + \sum_{Xi,Xj} A_{ij} \cos\theta_{ij} + \sum_{Xi,Yj} B_{ij} \cos\theta_{ij} + \sum_{Yi,Yj} C_{ij} \cos\theta_{ij}$$

We further restricted the models to
- **collinear** ($\theta_{ij} = \pm 1$) and
- completely **disordered** (no correlation among sites),

so they can be described as a four-component alloy with the **general formula**

$$\mathbf{X}^{\uparrow}_{x\uparrow}\ \mathbf{X}^{\downarrow}_{x\downarrow}\ \mathbf{Y}^{\uparrow}_{y\uparrow}\ \mathbf{Y}^{\downarrow}_{y\downarrow}$$

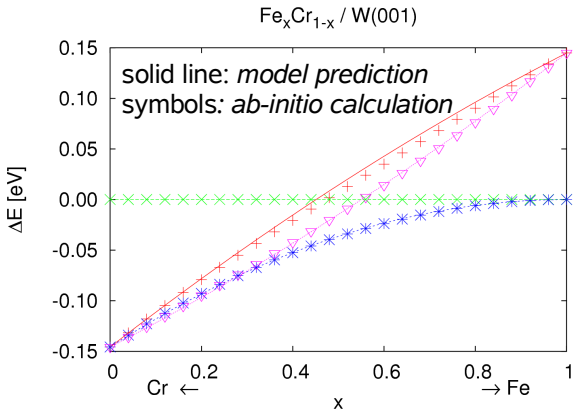


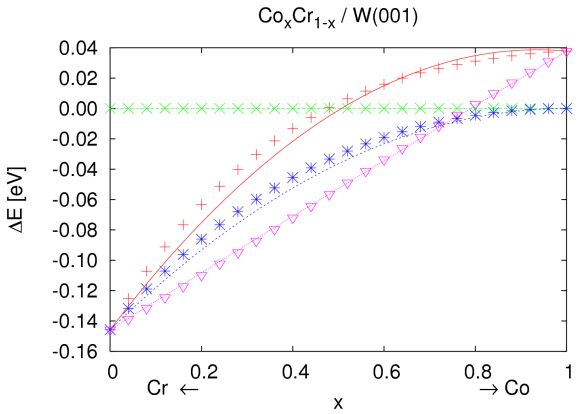
Condition for thickness of 1 ML: $x^{\uparrow} + x^{\downarrow} + y^{\uparrow} + y^{\downarrow} = 1$

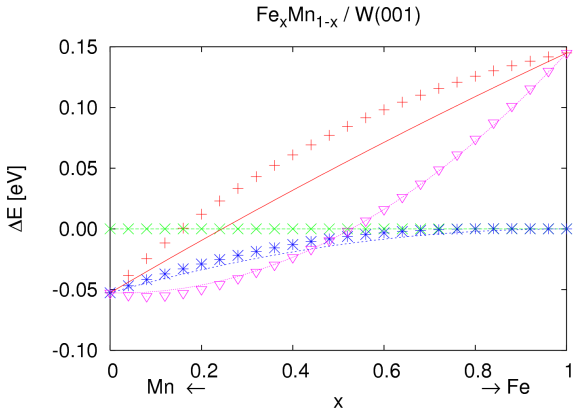
$$\bar{E} = \bar{E}_{DLM} + \tfrac{1}{2} J_{XX} (x^{\uparrow} - x^{\downarrow})^2 + J_{XY} (x^{\uparrow} - x^{\downarrow})(y^{\uparrow} - y^{\downarrow}) + \tfrac{1}{2} J_{YY} (y^{\uparrow} - y^{\downarrow})^2$$

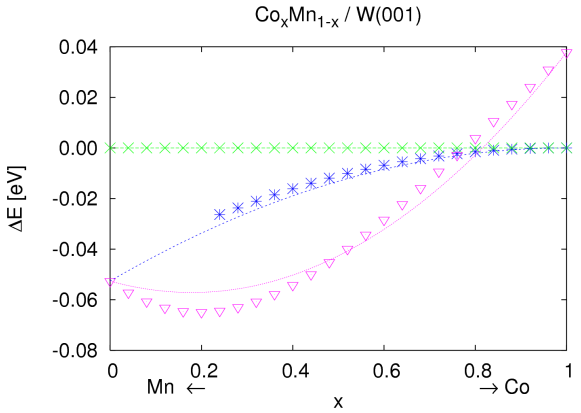
$$J_{XX} = \sum_{i \neq j} A_{ij} / N \qquad J_{XY} = \sum_{i \neq j} B_{ij} / N \qquad J_{YY} = \sum_{i \neq j} C_{ij} / N$$

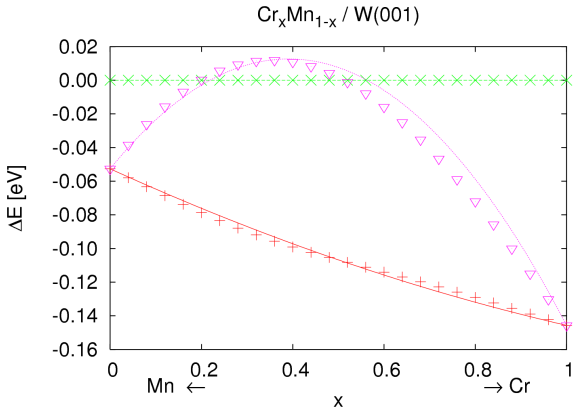
Estimate of the model parameters and test of the model against *ab-initio* calculations

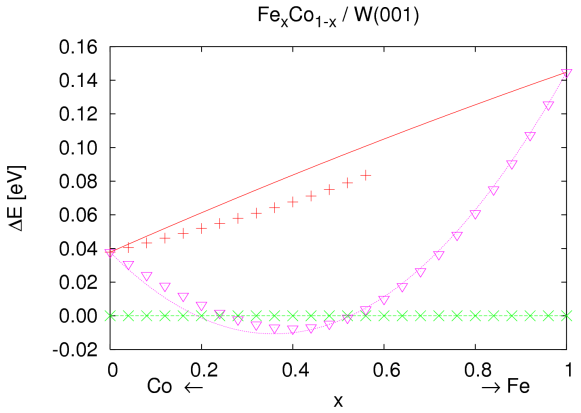










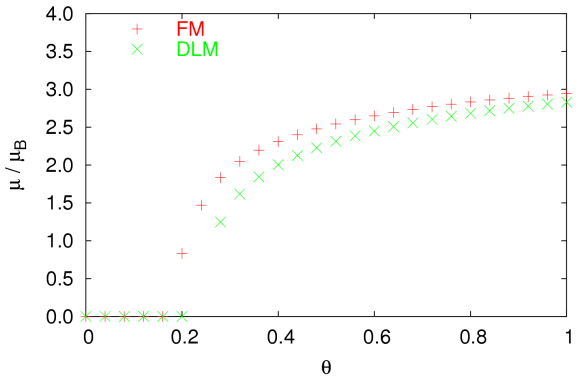


$J_{\text{Cr-Cr}}$	= –0.292 eV
$J_{\text{Mn-Mn}}$	= –0.105 eV
$J_{\text{Fe-Fe}}$	= +0.290 eV
$J_{\text{Co-Co}}$	= +0.076 eV
$J_{\text{Cr-Mn}}$	= –0.229 eV
$J_{\text{Fe-Cr}}$	= +0.058 eV
$J_{\text{Fe-Mn}}$	= +0.115 eV
$J_{\text{Co-Cr}}$	= +0.103 eV
$J_{\text{Co-Mn}}$	= +0.156 eV
$J_{\text{Fe-Co}}$	= +0.195 eV

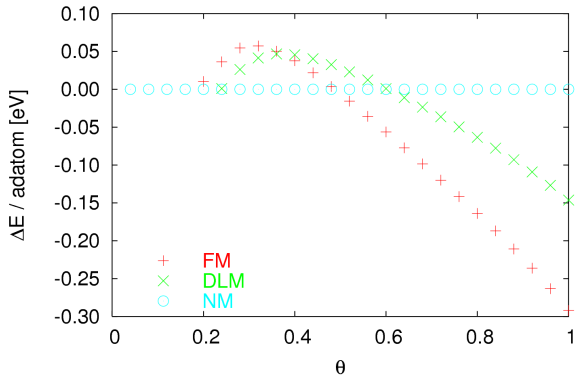
Estimates of the configuration with the lowest total energy (among those of the $X^{\uparrow}_{x\uparrow}$ $X^{\downarrow}_{x\downarrow}$ $Y^{\uparrow}_{y\uparrow}$ $Y^{\downarrow}_{y\downarrow}$ type) also well agree with *ab-initio* results

Magnetic moments (μ) at submonolayer coverage (θ): Cr / W(100)

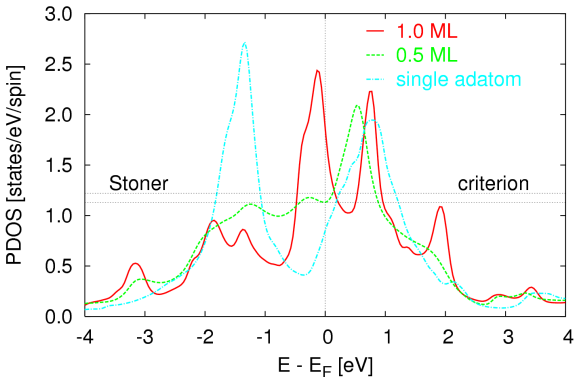
magnetic moments in magnetic states



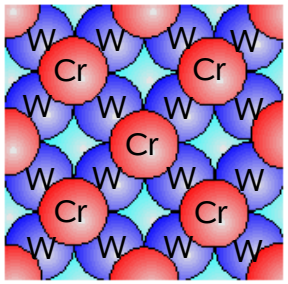
total energies of various magnetic configurations

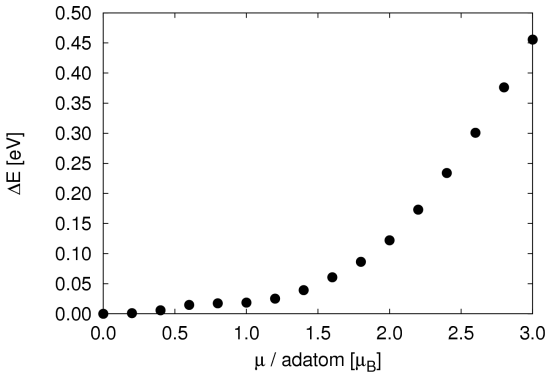


Stoner criterion for Cr / W(100):
$I \cdot DOS(E_F) > 1$

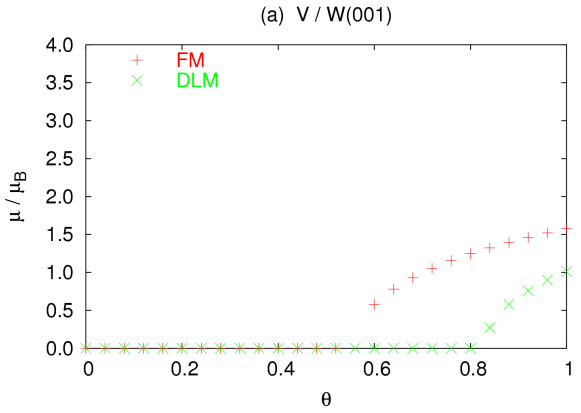


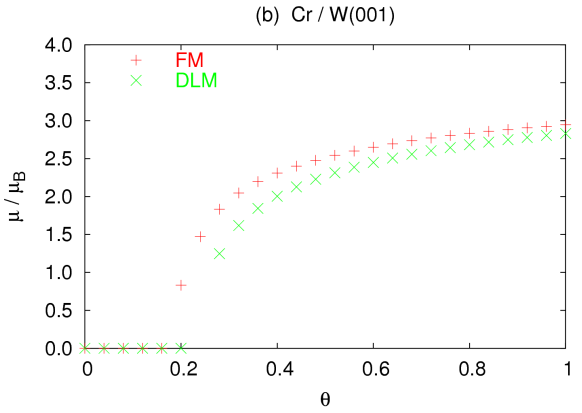
Fixed-spin FP-LAPW calculations for the *c(2x2)*–Cr / W(100) structure:
verification of the non-magnetic ground state

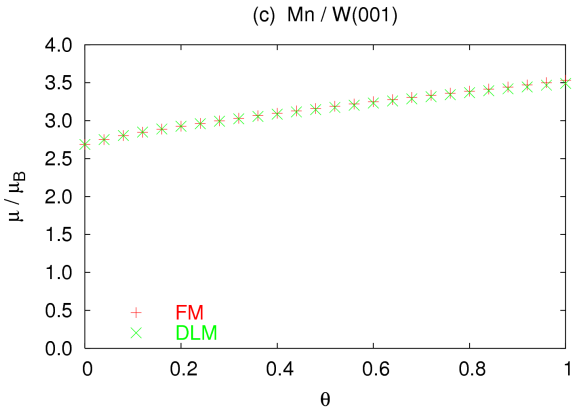


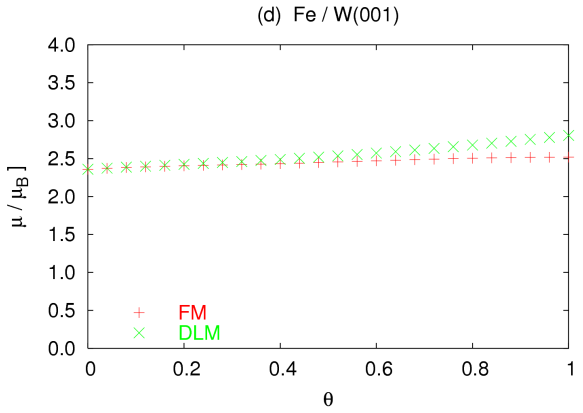


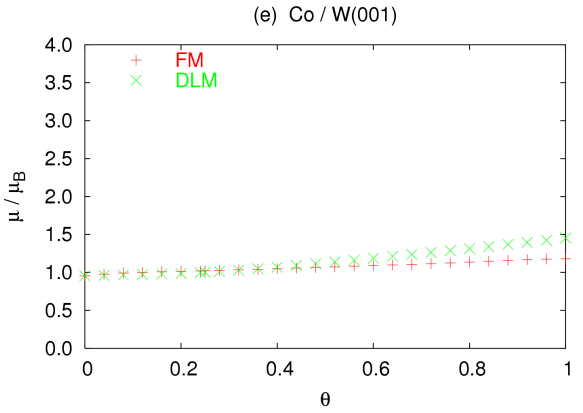
Magnetic moments (μ) at submonolayer coverage (θ): overview for all elements











Surface magneto-crystalline anisotropy

Preferential orientation of the magnetic axis has been studied for monolayers of V, Cr, and Mn on W(100) (and for the Fe / W(100) monolayer previously by Kubetzka *et al.*).

- Spin-orbit coupling and dipole-dipole interaction has to be included.
- Surface Brillouin zone sampled by a mesh of 60x60 *k*-points.
- Plane waves up to E_{kin} = 17 Ry in the basis set.

composition of the surface layer	**MAE per surface atom** (MAE = $E_{\parallel} - E_{\perp}$)
V / W(100)	–2.0 meV ∥
Cr / W(100)	+2.6 meV ⊥
Mn/ W(100)	+5.1 meV ⊥
Fe / W(100)	+2.4 meV ⊥

- Dipole-dipole interaction is almost negligible.
- *Shick et al.*: The large anisotropy of Mn/W(100) is caused by
  1. large SO-coupling at W atoms.
  2. strong exchange coupling between the Mn overlayer and the top W layer.
  3. large magnetic moment of Mn atoms.

Conclusion

The utility of the *ab-initio* calculations as an aid to the analysis of surface structures by the STM has been demonstrated for:

1) Invar

- The observed apparent corrugation in the STM images (chemically sensitive contrast between atoms as well as variations on a large scale) has been related to real surface buckling (actual shift of the atomic positions, Fe up and Ni down).
- The peak in the STS spectra was explained for Fe-enriched areas on the surface by a surface resonance at energy ≈ 0.3 eV below the Fermi level, arising near the center of the Brillouin zone, and derived predominantly from the d_z2 orbitals.

2) Magnetic overlayers of *3d* metals on W(100)

- Magnetic moments of Cr, Mn, Fe, and Co are almost constant. Surface alloys of these elements may be described along the lines of the Heisenberg or Ising model.
- Magnetic moment of V is very sensitive to its environment.
- Surface magnetocrystalline anisotropy: in-plane alignment for V, normal-to-plane for Cr, Mn, and Fe. Especially large anisotropy found for Mn/W(100).
- The interplay of competing alignment tendencies (different signs of J_{XY} and of the magnetic anisotropy) may lead to complex non-collinear magnetic structures.