Surface magnetism

So far, magnetic effects of surfaces entirely neglected

Not only the surfaces of magnetic materials have magnetic surfaces, but structures in reduced dimensions can exhibit enhanced magnetism

Magnetic properties of structures at surfaces technologically tremendously relevant in the context of the minituarization of magnetic storage devices, but also for spintronics

We will focus on magnetic effects that are present in the absence of any external magnetic field, i.e., on ferromagnetic and antiferromagnetic surfaces, and not on diamagnetism and paramagnetism

Origin of magnetism

Free atoms: two origins for magnetism:

1. orbital angular momentum of electrons
2. intrinsic spin of electrons

Molecules, solids and surfaces:

exchange interaction contributes to magnetism even if the spin is not explicitly considered in the Hamiltonian

Exchange interaction in transition metals due to interaction between localized d-electrons
⇒ Exchange interaction can be explained within a local picture using the H_2 molecule as a example

Exchange interaction in the H_2 molecule

Hamiltonian for the H_2 molecule:

$$\begin{aligned} H &= \frac{\vec{p}_1}{2m_e} + \frac{\vec{p}_1}{2m_e} - \frac{e^2}{|\vec{r}_1 - \vec{R}_1|} - \frac{e^2}{|\vec{r}_1 - \vec{R}_2|} \\ &\quad - \frac{e^2}{|\vec{r}_2 - \vec{R}_1|} - \frac{e^2}{|\vec{r}_2 - \vec{R}_2|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + \frac{e^2}{|\vec{R}_1 - \vec{R}_2|} \ , \end{aligned} \tag{161}$$

Hamiltonian does not depend on spin

⇒ separation of spatial and spin part of total wave function

$$\Psi = \psi(\vec{r}_1, \vec{r}_2)\,|m_{s_1} m_{s_2}\rangle \ . \tag{162}$$

Spin part: linear combination of the four spin states:

$$|m_{s_1} m_{s_2}\rangle \ = \ |\uparrow\uparrow\rangle\,,\ |\uparrow\downarrow\rangle\,,\ |\downarrow\uparrow\rangle\,,\ |\downarrow\downarrow\rangle \ . \tag{163}$$

Singlet ↔ triplet states

$|\uparrow\uparrow\rangle\,,\ |\uparrow\downarrow\rangle\,,\ |\downarrow\uparrow\rangle\,,\ |\downarrow\downarrow\rangle$ common eigenvectors of the operators $\vec{S}_1^2$, $\vec{S}_2^2$, S_{1z}, and S_{2z}.

Alternatively, the spin states may also be expressed in the $\{s, m\}$ or triplet-singlet representation based on the eigenkets of the total spin operator $\vec{S}^2 = (\vec{S}_1 + \vec{S}_2)^2$ and its component S_z along the z-axis:

$$\begin{aligned} |s=1, m=1\rangle &= |\uparrow\uparrow\rangle \ , \\ |s=1, m=0\rangle &= \left(\frac{1}{\sqrt{2}}\right)(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \ , \\ |s=1, m=-1\rangle &= |\downarrow\downarrow\rangle \ , \\ |s=0, m=0\rangle &= \left(\frac{1}{\sqrt{2}}\right)(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \ , \end{aligned} \tag{164}$$

The three $|s=1, m=\pm 1, 0\rangle$ states are referred to as the spin **triplet**, while $|s=0, m=0\rangle$ is called the spin **singlet** state.

Quantum statistics

Electrons are fermions

⇒ Total electronic wavefunction must be anti-symmetric with respect to the exchange of two electrons

Singlet state antisymmetric ⇒ spatial part has to be symmetric
Triplet state symmetric ⇒ spatial part has to be antisymmetric

Approximate Heitler-London ansatz for electronic H_2 wave function:

$$\psi_{s,t}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\left(\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) \pm \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)\right) . \tag{165}$$

Difference between eigenenergies: singlet-triplet or exchange splitting

$$\begin{aligned} E_s - E_t &= \langle\, \psi_s(\vec{r}_1,\vec{r}_2)|H|\psi_s(\vec{r}_1,\vec{r}_2)\rangle \;-\; \langle\, \psi_t(\vec{r}_1,\vec{r}_2)|H|\psi_t(\vec{r}_1,\vec{r}_2)\rangle \\ &= 2\int d^3r_1 d^3r_2\, \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\left(\frac{e^2}{|\vec{r}_1-\vec{r}_2|} + \frac{e^2}{|\vec{R}_1-\vec{R}_2|}\right. \\ &\quad \left. -\frac{e^2}{|\vec{r}_1-\vec{R}_1|} - \frac{e^2}{|\vec{r}_2-\vec{R}_2|}\right)\phi_1(\vec{r}_2)\phi_2(\vec{r}_1) \; . \end{aligned} \tag{166}$$

Spin Hamiltonian

Consider only the singlet and triplet states and note that

$$\vec{S}^2 \;=\; (\vec{S}_1+\vec{S}_2)^2 \;=\; \vec{S}_1^2+\vec{S}_2^2+2\,\vec{S}_1\cdot\vec{S}_2 \;=\; \frac{3}{2}\mathbf{1} \;+\; 2\,\vec{S}_1\cdot\vec{S}_2 \;, \tag{167}$$

⇒ Eigenvalues of the **spin Hamiltonian**

$$H_{\text{spin}} \;=\; \frac{1}{4}(E_s \,+\, 3E_t) \,-\, (E_s \,-\, E_t)\,\vec{S}_1\cdot\vec{S}_2 \;\; : \tag{168}$$

E_s in the singlet state and E_t in each of the three triplet states

Now redefine energy zero so that the constant $(E_s+3E_t)/4$ vanishes:

$$H_{\text{spin}} \;=\; -J\,\vec{S}_1\cdot\vec{S}_2 \;, \tag{169}$$

with the exchange coupling parameter J

$$J \;=\; (E_s \,-\, E_t) \; . \tag{170}$$

Ferromagnetism and Antiferromagnetism

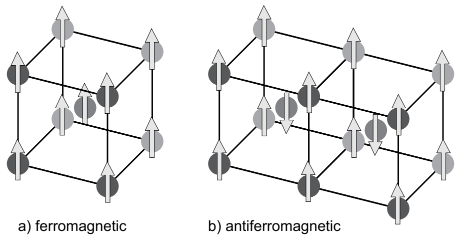
Heisenberg Hamiltonian of a solid

$$H_{\text{spin}} \;=\; -\frac{1}{2}\sum_{i\neq j} J_{ij}\,\vec{S}_i\cdot\vec{S}_j \; . \tag{171}$$

$J_{ij} = J_{ji} \geq 0$

⇒ spontaneous magnetization with macroscopic net magnetization: ferromagnetism

$$H \;=\; \frac{1}{2}\sum_{i\neq j\; n.n.} |J_{ij}|\,\vec{S}_i\cdot\vec{S}_j \;\Rightarrow \text{antiferromagnetic ordering} \tag{172}$$



a) ferromagnetic

b) antiferromagnetic

Stoner Criterion

Energy of a system of N atoms with total spin $S_z = \frac{1}{2}mN$

$$E(S_z) = \sum_\sigma\sum_i \varepsilon_{i\sigma} + \frac{1}{4}NI\left(n^2-m^2\right), \tag{173}$$

with I Stoner parameter related to the exchange interaction and

$$n = n_\uparrow + n_\downarrow \;, \qquad m = n_\uparrow - n_\downarrow . \tag{174}$$

It can be shown that the creation of the ferromagnetic phase is associated with the energy

$$\begin{aligned} \Delta E_{\text{fm}} &= E(S_z = \frac{1}{2}mN) - E(S_z = 0) \\ &= \frac{N}{4}\left(\frac{1}{g(\varepsilon_F)} - I\right)\; m^2 \; . \end{aligned} \tag{175}$$

This leads to the Stoner criterion that a ferromagnetic phase may form for

$$I\,g(\varepsilon_F) \;>\; 1 \; . \tag{176}$$

Spin-density formalism

Generalization of DFT for spin-dependent cases (Barth and Hedin 1972)

Hermitian 2×2 density matrix ρ:

$$\rho = \frac{1}{2}\left(n\mathbf{1} + \vec{\sigma}\cdot\vec{m}\right) = \frac{1}{2}\begin{pmatrix} n+m_z & m_x - im_y \\ m_x + im_y & n+m_z \end{pmatrix}, \tag{177}$$

$\mathbf{1}$: 2×2 unit matrix, $\vec{\sigma}$ vector of the Pauli matrices
n charge density, $\vec{m}$ are the magnetization density vector field

Two-component formalism: Kohn-Sham orbitals $\vec{\psi}_i = (\psi_{i,1}, \psi_{i,2})$

$$n(\vec{r}) = \sum_{i=1}^{N} \vec{\psi}_i^{\dagger}(\vec{r})\,\mathbf{1}\,\vec{\psi}_i(\vec{r}) \ , \qquad \vec{m}(\vec{r}) = \sum_{i=1}^{N} \vec{\psi}_i^{\dagger}(\vec{r})\,\vec{\sigma}\,\vec{\psi}_i(\vec{r}) \ . \tag{178}$$

$$\text{Density matrix}: \ \rho_{kl} \ = \ \sum_{i=1}^{N} \psi_{i,k}^{*}\psi_{i,l} \ , \quad k,l = 1,2 \ . \tag{179}$$

$$\text{Potential matrix}: \ \mathbf{V} \ = \ V\,\mathbf{1} \ + \ \mu_{\mathrm{B}}\,\vec{\sigma}\cdot\vec{B} \tag{180}$$

Local spin-density approximation (LSDA)

Exchange-correlation energy in the LSDA

$$E_{\mathrm{xc}}^{\mathrm{LSDA}}[\rho_{kl}] = \int d^3\vec{r}\ \left\{\rho^{+}(\vec{r}) + \rho^{-}(\vec{r})\right\}\ \varepsilon_{\mathrm{xc}}^{\mathrm{LDA}}(\rho^{+}(\vec{r}), \rho^{-}(\vec{r}))\ , \tag{181}$$

$\rho^{+}(\vec{r})$ and $\rho^{-}(\vec{r})$: eigenvalues of the density matrix $\rho_{kl}(\vec{r})$.

Exchange-correlation potential

$$v_{\mathrm{xc}}^{(\alpha)} = \frac{\partial}{\partial\rho^{(\alpha)}}\left\{\left(\rho^{+}(\vec{r}) + \rho^{-}(\vec{r})\right)\ \varepsilon_{\mathrm{xc}}^{\mathrm{LDA}}(\rho^{+}(\vec{r}), \rho^{-}(\vec{r}))\right\} \ . \tag{182}$$

Kohn-Sham equations:

$$\left\{-\frac{\hbar^2}{2m}\nabla^2\,\mathbf{1} \ + \ \mathbf{V}\right\}\ \vec{\psi}_k \ = \ \varepsilon_k\,\vec{\psi}_k \ . \tag{183}$$

Kinetic energy diagonal in the two-dimensional spin state + collinear B field
⇒ total Hamiltonian diagonal in spin space ⇒ spin-up and the spin-down problem decouple
so that they can be treated almost independently as two non-magnetic calculations.

Proper theoretical treatment of non-collinear spin structures much more involved

Two-dimensional Ferro- and Antiferromagnetism

3D transition metal bulk systems: spontaneous magnetism limited to $3d$ metals, in particular Fe, Co, Ni.

Outer d electrons less localized when moving from $3d$ to $4d$ and $5d$ metals
⇒ larger overlap, broader d band and smaller LDOS at ε_{F}

In addition, Stoner parameter I smaller ⇒ Stoner criterion (176) no longer satisfied for $4d$ and $5d$ metals.

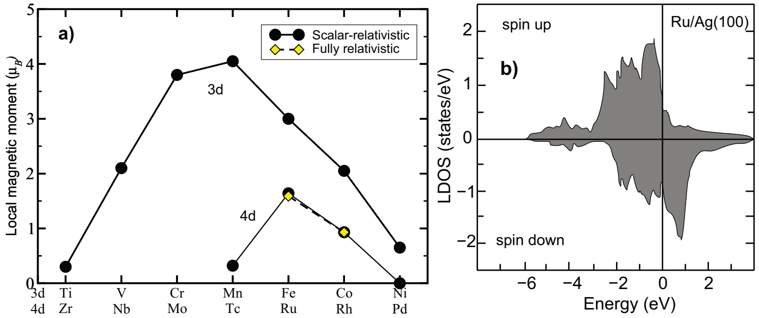
2D layer of transition metal atoms:
Coordination of the atoms lower and d band width smaller
In addition, there are band structure effects which can also stabilize magnetic phases.

Realization

Transition metal overlayers grown on noble metal substrates
(small interaction between the overlayer and the noble metal substrate)

Two-dimensional ferromagnetic structures

$3d$ and $4d$ monolayers on Ag(100)



Scalar-relativistic LSDA calculations, i.e. without spin-orbit coupling, and fully relativistic LSDA calculations.

Theoretical predications (S. Blügel, PRL **68**, 851 (1992)) not confirmed yet

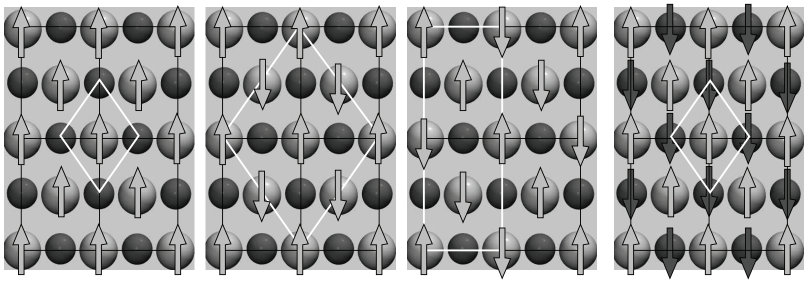
Two-dimensional ferro- and antiferromagnetic structures

Heisenberg Hamiltonian of a two-dimensional layer

$$H_{\rm spin} \;=\; -\frac{1}{2}\sum_{i\neq j} J_{ij}\,\vec{S}_i\cdot\vec{S}_j \;. \qquad (184)$$

$J_1 > 0$: ferromagnetic monolayers, $J_1 < 0$ $c(2\times 2)$ antiferromagnetic structure

Mn/W(110)



a) FM b) c(2x2) AF c) p(2x1) AF d) AF layer−by−layer

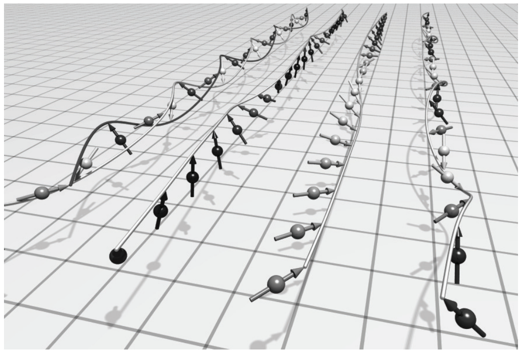
Energetic order (DFT): AF $c(2\times 2)$ → AF $p(2\times 1)$ → FM
due to longer range interactions

Spin spirals

Mn/W(110): spin-polarized STM → long-wave modulation with a period of 6 nm in addition to a magnetic corrugation associated with the row-wise AF $c(2\times 2)$ structure

Explanation: spin-orbit induced variation caused by the Dzyaloshinskii-Moriya interaction (DMI) ⇒ Spin spirals

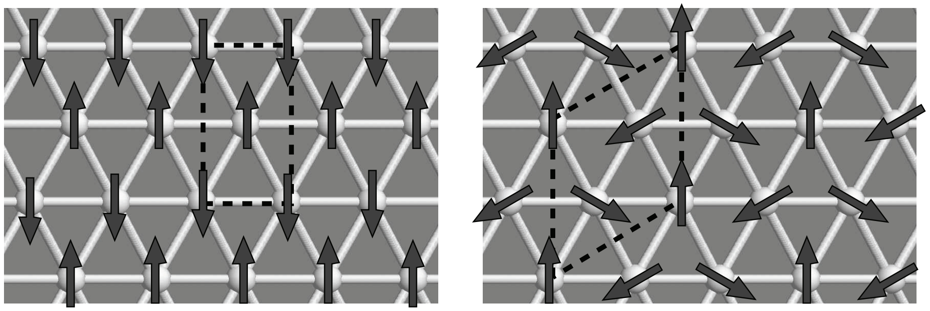
$$E_{\rm DM} = \sum_{ij}\mathbf{D}_{ij}\cdot(\mathbf{S}_i\times\mathbf{S}_j)\ , \qquad (185)$$



Frustrated spin structures

Antiferromagnetic system with triangular of hexagonal symmetry:
solution possible where all nearest neighbors are arranged antiferromagnetically

⇒ Frustrated spin systems



a) row−wise antiferromagnetic b) non−collinear 120° Néel structure

Heisenberg Hamiltonian (171) with nearest and next-nearest neighbor interactions J_1 and J_2:
J_1 and J_2 positive ⇒ ferromagnetic order, J_2 negative ⇒ non-collinear 120° Néel
J_1 also negative ⇒ row-wise antiferromagnetic state incommensurable spiral spin-density waves (SSDW)

Magnetic nanostructures at surfaces

Magnetic nanostructures at surface technologically interesting as storage devices

Magnetic anisotropy: dependence of magnetic properties on a preferred direction

⇒ existence of easy and hard directions in magnetic materials
⇒ interpretaion of the two possible magnetization directions along the easy axis in terms of the bits "0" and "1".

Several contributions to magnetic anisotropy:

Magnetocrystalline anisotropy: intrinsic property due to the interaction of the spin magnetic moments with the crystal lattice via spin-orbit coupling.

Shape anisotropy: due to long range magnetic dipolar interaction leading to a influence of the outer boundaries of an sample or a grain in a magnetic material

Magnetic anisotropy

Magnetic anisotropy: in general a complex function of the orientation of the magnetization with respect to the crystal axes

Low-dimensional systems with most relevant twofold symmetries:

$$H_{\mathrm{MA}} = \sum_i \mathbf{S}_i \cdot \mathbf{K} \cdot \mathbf{S}_i \; , \tag{186}$$

$\mathbf{K}$: tensor of single-site constants.

Perfect films and isolated wires:

$$E_{\mathrm{MA}}(\theta) = -K \, \cos^2\theta , \tag{187}$$

θ: angle between the magnetization and the film or wire normal

Shape anisotropy constant K_{shape} for infinitely extended perfectly flat films or perfectly cylindrical wires of infinite length:

$$K^{2D}_{\mathrm{shape}} = -2\pi \frac{2}{c^2} \frac{m^2}{V} \; , \quad K^{1D}_{\mathrm{shape}} = -\pi \frac{2}{c^2} \frac{m^2}{V} \; , \tag{188}$$

Magnetic nanowires

DFT calculations for free standing metal wires (Weinert and Freeman 1983)

Metal	Magnetic moment (μ_{B})	
	bulk	wire
Ni	0.6	1.07
Fe	2.2	3.36

Ni and Fe chains strong Stoner ferromagnets, i.e., their majority d bands are completely filled, in contrast to the bulk where Fe is a weak ferromagnet.

Magnetic anisotropy

Tight-binding Hamiltonian:

Free Co chains: $E_{\mathrm{MA}} \approx -10$ meV with the easy axis along the wire axis

Co wires on Pd(100): $E_{\mathrm{MA}} \approx 1$ meV with easy axis not parallel to the wire axis

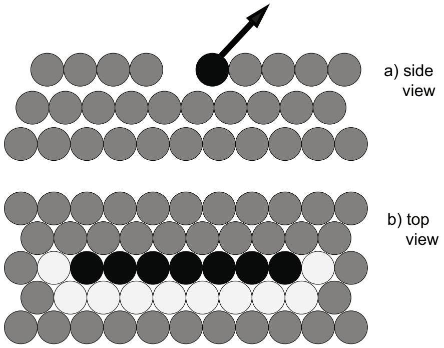
Linear chains of metal atoms can indeed be realized by deposition on a stepped surface:

Experiment: Co/Pt(997) $E_{\mathrm{MA}} \approx -2$ meV, Co bulk $E_{\mathrm{MA}} = -40\,\mu$eV
Easy axis at an angle of 43° with respect to the normal of the (111) facets of the (997) surface normal

DFT description of deposited metal nanowires

Green's function approach (Ebert *et al.*):

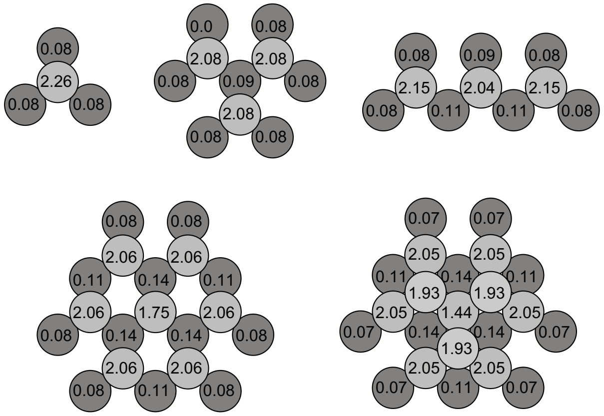
$$\begin{aligned} G(\vec{r},\vec{r}\,',E) &= G^0(\vec{r},\vec{r}\,',E) \\ &\quad + \int d^3r'' G^0(\vec{r},\vec{r}\,'',E)\Delta V(\vec{r}\,'')G(\vec{r},\vec{r}\,',E) \; . \end{aligned} \tag{189}$$



Experimental findings reproduced

Magnetic clusters on surfaces

Calculated local spin magnetic moments of Co$_n$ clusters on Pt(111) (Ebert *et al.*):



Enhanced spin magnetization of deposited Co clusters compared to the bulk value of $1.73\,\mu_{\mathrm{B}}$.