Magnetotactic bacteria synthesize magnetic particles between 30 and 100 nm, big enough to have a permanent magnetic moment, but small enough to be a single domain. [images by R. James, University of Western Australia; see also R. Blakemore. "Magnetotactic Bacteria." Science 190, 377 (1975)].
High density magnetic recording: the rush to the nano
High density magnetic recording: the rush to the nano

Physical spacing and disk surface evolution

Server Products-3.5 Inches
Mobile Products-2.5
Lab Demos

Ed Grochowski
The recording mechanism

The writing-reading head is flying over the continuous magnetic media
Information storage in magnetic memory

TEM images of the magnetic layer in a MRAM. Each bit is made of a few hundreds of grains.

The bit size and shape is defined during writing by the head.


Single particle bit
Some basic questions …..
… simply looking at this picture

1) Why a grain has a magnetization?
2) Why the grain magnetization is pointing in one specific direction?
3) Why the magnetization direction change from grain to grain?
4) Why the grain magnetization does not fluctuate with time?
5) Are the grain magnetizations decoupled?
Exchange interaction: macrospin

The grain (particle) can be described as a single macrospin $S = \Sigma_i S_i$

- 1 bit = 100 grains
- 1 grain = 2 $10^4$ atoms
- Each atom has a spin

All atomic spins in the grain are ferromagnetically aligned:

Exchange energy: $J \sum_i S_i S_j$

Grain

The grain (particle) can be described as a single macrospin $S = \Sigma_i S_i$
The inter-grain exchange interaction is stopped by the oxide layer

The magnetic moment of SiO$_2$ is zero
Constraints on the magnetic grain:
1) Size below 8 nm (to reach the 1 Teradot/in²)
2) Uniform size distribution
3) Well defined boundary
4) Magnetically decoupled

The grain size distribution results in a rather wide switching field distribution.
Magnetism

In addition to the exchange energy other two fundamental parameters

1) magnetic moment $\mu$ or magnetization

- Why only a few elements (Fe, Co, and Ni) have a magnetic moment at atmosphere conditions?
- Is this true also at the nanoscale?
- What kind of element is preferable to built my new generation magnetic memory?

Note: the magnetic moment defines the intensity of the magnetic field generated by the system, via $H = - \text{grad} (\mu \cdot r / r^3)$ and the intensity of the force acting on the system when a magnetic field is applied, via $F = \text{grad} (\mu \cdot H)$
2) magnetic anisotropy energy $K$

a) Defines the space direction/s along which the magnetic moment prefer to align

This is why each grain has its own magnetization axis

Bulk systems: $K$ depends on the crystallographic structure

**Fe bcc**
- easy axis: (100)
- $K_1 = 4.8 \times 10^4$ J/m$^3$
  - = 2.4 $\mu$eV/atom

**Co hcp**
- easy axis: (0001)
- $K_1 = 4.1 \times 10^5$ J/m$^3$
  - = 45 $\mu$eV/atom

Complete isotropic
- $K = 0$
b) Defines the thermal stability of the magnetization orientation

Avg. time (relaxation time) taking to jump from one minimum to the other:

\[ \tau = \tau_0 \exp(\frac{K}{kT}) \quad \tau_0 \approx 10^{-10} \text{s} \]

Recording criterion

- \( \tau = 10 \text{ years} \quad K = 43 \text{ kT} \)
- \( \tau = 1 \text{ year} \quad K = 40 \text{ kT} \)
- \( \tau = 1 \text{ second} \quad K = 23 \text{ kT} \)
Atom in a magnetic field

$$\mathcal{H} = \sum_i \left( \frac{p_i^2}{2m} + V(\vec{r}_i) \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \mu_B B \frac{1}{\hbar} \sum_i (\ell_{z,i} + 2s_{z,i})$$

$$\Psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$$

- $R(r)$ -> principal quantum number $n = 1, 2, 3, \ldots$ (K, L, M,...)
- $\Theta(\theta)$ -> orbital quantum number $l = 0, 1, 2, \ldots, n-1$
- $\Phi(\phi)$ -> magnetic quantum number $m_l = -l, -(l-1), \ldots, 1, l$
- $\uparrow \downarrow$ -> spin quantum number $m_S = \pm 1/2$

Spin-orbit interaction:
Interaction of the spin of an electron with the magnetic field generated by its own orbital motion

$$\mathcal{H}_{\ell s} = \sum_i \zeta(\vec{r}_i) \ell_i \vec{s}_i$$

$$\zeta(\vec{r}) = \frac{e \hbar^2}{2m^2c^2} \frac{1}{r} \frac{\partial V(r)}{\partial r}$$

Orbital magnetism: $m_L = L \mu_B$
Spin Magnetism: $m_s = g_e S \mu_B = 2S \mu_B$
Atomic magnetic moment: $m_{\text{at}} = \mu_B(L + g_e S) = g J \mu_B$
Where $J = L + S$

$\mu_B$ -> Bohr magneton
$g = 3/2 + [S(S+1) - L(L+1)]/(2J(J+1))$ is the Landé g-factor
Magnetism of an isolated atom

Magnetism is given by:
1) The spin moments of the electrons
2) The orbital moments of the electrons
3) The filling of the atomic orbital

The orbitals in a shell are degenerate in energy; the occupation is defined by the Hund’s rules

Hund’s rules:
1) Total spin \( S = \sum_i s_i \) maximized
2) Total orbital momentum \( L = \sum_i l_i \) maximized
3) \( L \) and \( S \) couple parallel \( (J=|L+S|) \) if band more than half filled
\( L \) and \( S \) couple antiparallel \( (J=|L-S|) \) if band less than half filled

Ground state of a 3d\(^7\) ion (Co\(^{2+}\))

\[
\begin{array}{cccccc}
+2 & +1 & 0 & -1 & -2 \\
\uparrow \downarrow & \uparrow \downarrow & \uparrow & \uparrow & \uparrow \\
\end{array}
\]

\( L = 3, \ S = 3/2, \ J = 9/2 \)
\( m_L = L \ \mu_B = 3 \ \mu_B \),
\( m_S = g_e S \ \mu_B = 3 \ \mu_B \),
\( m_{at} = g J \ \mu_B = 6 \ \mu_B \)

Ground state of a 3d\(^5\) ion (Mn\(^{2+}\))

\[
\begin{array}{cccccc}
+2 & +1 & 0 & -1 & -2 \\
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
\end{array}
\]

\( L = 0, \ S = 5/2, \ J = 5/2 \)
\( m_L = L \ \mu_B = 0 \ \mu_B \),
\( m_S = g_e S \ \mu_B = 5 \ \mu_B \),
\( m_{at} = g J \ \mu_B = 5 \ \mu_B \)
Magnetic moment of mass-selected clusters in gas phase (N > 20 atoms)

Below about 200 atoms the magnetic moment strongly increases with respect to bulk values

From single atoms to aggregates of $d$ metals

1) Band formation

2) Crystal structure
A strong directional bond generates a reduction in the component of L perpendicular to the bonding direction.

Remember: L is connected to the precessional motion of the electrons around the nucleus. The bond formation locks the electron to the crystal structure -> precession stops -> L decreases.

Quenching of the orbital magnetic moment in bulk structure of d metals
Cristal structure

Quenching of the orbital magnetic moment in 3d metals: formal argument

Experiments show that 3d ions in solids have $L \approx 0$, $J \approx S$ and $g = 2$.

The crystal electric field produced by surrounding ions in a solid defines a particular set of (real) wave-functions for which the mean value of the orbital moment is zero (balance of +/- $m_L$).

\[
H = H_{\text{atom}} + H_{\text{Field}}
\]

\[
H_{\text{Field}} = -e\phi(r)
\]

For example for an octahedral crystal field we get
\[
\phi(r) = \sum_{i=1}^{6} eZ_i / r_i
\]

The crystal field gives a reduction of the orbital moment depending on its symmetry and strength.

\[
d_{x^2-y^2} = 1/2 (|+2\rangle + |-2\rangle)
\]

\[
d_{3z^2-r^2} = |0\rangle
\]

\[
d_{xy} = i/\sqrt{2} (|+2\rangle - |-2\rangle)
\]

\[
d_{yz} = i/\sqrt{2} (|+1\rangle + |-1\rangle)
\]

\[
d_{xz} = 1/\sqrt{2} (|-1\rangle - |+1\rangle)
\]
Electron bands can spontaneously split into up and down spins. This depends on the interaction of electrons via the Pauli exclusion principle.

**Stoner Exchange interaction \( \Delta \):**
Is the energy necessary to reverse the spin of one electron in the sea of all the other electrons -> spin up – spin down bands are shifted by \( \Delta = 1-2 \text{ eV} \)

Non magnetic state -> \( n(\text{up}) = n(\text{down}) \)
magnetic state -> splitting of electronic bands corresponding to opposite spin direction -> \( n(\text{up}) \neq n(\text{down}) \)
- s, p bands are extended (band width about 10 eV) -> contribute by about 5% to the spin moment

- d bands are narrow (band width about 3 eV) -> their splitting determines the magnetism

<table>
<thead>
<tr>
<th>Material</th>
<th>N holes</th>
<th>$m_{s \text{tot}}$</th>
<th>$m_{s \text{d}}$</th>
<th>$m_{s \text{sp}}$</th>
<th>$m_{\text{orb}}$</th>
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<tr>
<td>Fe</td>
<td>3.4</td>
<td>2.19</td>
<td>2.26</td>
<td>-0.07</td>
<td>0.09</td>
</tr>
<tr>
<td>Co</td>
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<td>1.57</td>
<td>1.64</td>
<td>-0.07</td>
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<tr>
<td>Ni</td>
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<td>0.62</td>
<td>0.64</td>
<td>-0.02</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Co on Pt(111)

Co monomer

Hybridization effect

Note: asymmetry in the Pt LDOS at $E_F$ when covered by Co-> induced magnetic moment

Size dependence

Cluster magnetism

Two atomic layer high Co islands on Cu(111)

Interface atoms

Surface atoms

The magnetic moment of the atoms in the islands depends on the local coordination

XMCD: X-rays Magnetic Circular Dichroism

Two step model:
1) spin-polarized photoelectrons are created by using circularly polarized x-rays
2) these polarized photoelectrons are used to analyze the spin-split final density of states, thus the valence band acts as a spin-sensitive detector.

Courtesy of P. Gambardella ETHZ
XMCD theory: basic idea

Photon-electron interaction: dipole approximation

\[ H_{\text{int}}(0,t) \approx r \cdot \varepsilon_q \left[ a_k \exp(-i\omega_k t) + c.c. \right] \]

The dipole operator \( P_{q=0}^{(1)} = r \cdot \varepsilon_q \) can be written in terms of Racah’s tensor operators (where \( Y_{l,m} \) are the spherical harmonics)

\[
P_{\pm 1}^{(1)} = \pm \frac{1}{\sqrt{2}} (x \pm iy) = rC_{\pm 1}^{(1)} = r\sqrt{\frac{4\pi}{3}} Y_{1,\pm 1}
\]

\[
P_0^{(1)} = z = rC_0^{(1)} = r\sqrt{\frac{4\pi}{3}} Y_{1,0}
\]

The photon absorption generates a transition from an initial core level to a final level close to the Fermi level (note that the spin is not affected)

\[ |i \rangle = R_i(r) |c, m_c; s = \frac{1}{2}, m_s \rangle \quad \rightarrow \quad |f \rangle = R_f(r) |l, m_l; s = \frac{1}{2}, m_s \rangle \]

\[
\langle l, m_c | C_{\pm 1}^{(1)} | l-1, m \rangle = \sqrt{\frac{(l \pm m)(l \pm m - 1)}{2(l-1)(2l+1)}}
\]

\[
\langle l, m_c | C_0^{(1)} | l-1, m \rangle = \sqrt{\frac{l^2 - m^2}{2(l-1)(2l+1)}}
\]

\[
\langle l, m | C_{\pm 1}^{(1)} | l+1, m \rangle = -\sqrt{\frac{(l \mp m + 2)(l \mp m + 1)}{2(l+3)(2l+1)}}
\]

\[
\langle l, m | C_0^{(1)} | l+1, m \rangle = \sqrt{\frac{(l+1)^2 - m^2}{(2l+3)(2l+1)}}
\]

**Table 1.3:** Electric dipole matrix elements \( \langle l, m_l | C_q^{(1)} | c, m_c \rangle \) in the one electron model. The matrix elements are non-vanishing when \( c = l - 1 \) (left column) or \( c = l + 1 \) (right column), and when \( m_c + q = m_l \). \( q \) denotes the state of polarization of the photons which mix the states \( |l, m_l \rangle \) and \( |c, m_c \rangle \).

Remember: things become easily complicate. For example, if spin-orbit interaction is not negligible the \( (L, m_L, S, m_S) \) is not the good basis and you have to use the \( (L, S, J, m_J) \) basis.
Right ($\Delta m = +1$) and Left ($\Delta m = -1$) circularly polarized photons create photoelectrons with opposite spins.

Since:

- $p_{3/2}$ (L+S coupling)
- $p_{1/2}$ (L-S coupling)

The spin polarization of the photoelectrons generated by circularly polarized light is opposite at the $L_3$ and $L_2$ edges.

Transition probability represented by the line thickness for right circularly polarized x-rays. For clarity the transitions to the 4s levels are neglected (account for less than 5%)
Sum Rules

Separate determination of orbital and spin moment (actually their projections along the light propagation direction)

\[ m_S = -3 \, n_h \, \mu_B \, (A_3 - 2A_2) + m_T \]
\[ m_L = -2 \, n_h \, \mu_B \, (A_3 + A_2) \]

Where \( A_3 \) (\( A_2 \)) is the XMCD measured at the \( L_3 \) (\( L_2 \)) edge, \( n_h \) is the number of unoccupied d state (number of holes) and \( m_T \) is the magnetic spin dipole moment (\( T = S - 3 \, r \cdot S \)).

These rules hold only for itinerant magnetism.

XMCD: the difference between the XAS spectrum acquired with R and L polarized light

Operatively:

1) Measure of the XAS spectra with light polarized R and L in a saturating external magnetic field
2) For fcc and bcc crystallographic structures a magic angle (~57°) for the photon incidence exists at which \( m_T = 0 \)
3) XMCD acquired at different angles gives \( m_S \), \( m_L \), and \( m_T \)

Fe/V/Fe(110) trilayer

Normalized XAS of L (dashed line) and R (solid line) circularly polarized light and the XMCD at the $L_{2,3}$ edges of V and Fe for a Fe/V4/Fe(110) trilayer.

a) V is non magnetic in bulk but it shows magnetic moment at the nanoscale

b) Antiferromagnetic coupling: XMCD signal for V and Fe have opposite signs

c) The magnetic moment in V atoms strongly reduces with increasing the V thickness

Sum rules can not be applied due to overlapping between $2p^{1/2}$ and $2p^{3/2}$ states

Magnetism of single atoms at surface

Electronic hybridization with the substrate (charge transfer)
Single atoms on alkali metals surfaces

Fe, Co atoms (<0.01 ML)

Cs, K, Na, or Li film

Cu(100)

$T = 10$ K, $B = 7$ Tesla

The spectra do not depend on the magnetic field direction $\rightarrow K = 0$

Atomic like behavior + 1 e⁻ transferred from surface to atom

Iron

Fe atom: \(d^6 \rightarrow d^7\)
- \(m_L = 2 \mu_B \rightarrow 3 \mu_B\)
- \(m_S = 4 \mu_B \rightarrow 3 \mu_B\)

Co atom: \(d^7 \rightarrow d^8\)
- \(m_L = 3 \mu_B \rightarrow 3 \mu_B\)
- \(m_S = 3 \mu_B \rightarrow 2 \mu_B\)

Note: in the simulation L – R is plotted in place of the R – L of the experimental data

XAS spectra for 3d\(^6\) \(\rightarrow\) 2p\(^5\) 3d\(^7\) transitions with (\(z = 1\)) and without (\(z = 0\)) spin-orbit interactions

2) The orbital moment strongly decreases by increasing the cluster size -> coordination effect

Isolated atoms

STM image 85 x 85 Å²

The spectrum depends on the magnetic field direction -> K ≠ 0 (anisotropic system)

1) Bulk stile spectrum:
   sum rules
   \[ m_L \sim \mu_B (A_3 + A_2) \]

\[ S = 2.1 \mu_B \text{/atom} \]

Size independent

P. Gambardella et al., Science
300, 1130 (2003)
2D metal-organic supramolecular network: Fe and TPA molecules on Cu(100)

terephthalic acid (TPA)

Fe : TPA ≈ 1:4


metal on metal

hybrid metal-organic complex

Courtesy of P. Gambardella ETHZ
Fe-Cu(100) de-hybridization

Fe ground state in Fe(TPA)₄ and O₂-Fe(TPA)₄ mainly 3d⁶

Fe-Cu metal interactions progressively weaken with increasing number of ligands

The magnetic moment depends on the ligands (see the amplitude of the XMCD signal)

P. Gambardella et al., Nature Mater. 8, 189 (2009)