Magnetism (FM, AFM, FSM)

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Localized vs. itinerant systems

- In **localized** systems (e.g. some rare earth) the magnetism is mainly governed by the atom (Hund’s rule).

- In **itinerant** (delocalized) systems (many transition metals) magnetism comes from partial occupation of states, which differ between spin-up and spin-down.

- **Boarderline** cases (some f-electron systems) details of the structure (e.g. lattice spacing) determine whether or not some electrons are localized or itinerant.
Ferro-, antiferro-, or ferri-magnetic

- **Ferromagnetic (FM)** (e.g. bcc Fe)  
  \[ M > 0 \]
  ![Diagram of ferromagnetic moments]

- **Antiferromagnetic (AFM)** (e.g. Cr)  
  \[ M = 0 \]
  ![Diagram of antiferromagnetic moments]

- **Ferrimagnetic cases**  
  The moments at different atoms are antiparallel but of different magnitude  
  \[ M > 0 \]
  ![Diagram of ferrimagnetic moments]

- **Non-collinear magnetism (NCM)**  
  The magnetic moments are not lined up parallel.  
  ![Diagram of non-collinear magnetism]
Itinerant electron magnetism

Experimental facts:

<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma$ [emu/g]</th>
<th>$\sigma$ [$\mu_B$]</th>
<th>$T_c$ [K]</th>
<th>$\rho$ at 298K [g/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (bcc)</td>
<td>221.7</td>
<td>2.22</td>
<td>1044</td>
<td>7.875</td>
</tr>
<tr>
<td>Co (fcc)</td>
<td>166.1</td>
<td>1.75</td>
<td>1388</td>
<td>8.793</td>
</tr>
<tr>
<td>Co (hcp)</td>
<td>163.1</td>
<td>1.72</td>
<td>1360</td>
<td>8.804</td>
</tr>
<tr>
<td>Ni (fcc)</td>
<td>58.6</td>
<td>0.62</td>
<td>627</td>
<td>8.912</td>
</tr>
</tbody>
</table>
1. The carriers of magnetism are the unsaturated spins in the d-band.

2. Effects of exchange are treated with a molecular field term.

3. One must conform to Fermi statistics.

Stoner, 1936
Stoner model for itinerant electrons

In a

- non magnetic (NM) case
  \[ N_\uparrow = N_\downarrow \] (spin-up and spin-down)

- ferromagnetic (FM) case
  \[ N_\uparrow > N_\downarrow \] (majority and minority spin)
  the moments at all sites are parallel (collinear)

- the (spin) magnetic moment \( \mathbf{m} \)
  \[ m = N_\uparrow - N_\downarrow \]
  its orientation with respect to the crystal axes is only defined by spin orbit coupling.

- there can also be an orbital moment
  it is often suppressed in 3d transition metals

\[
\chi = \frac{\chi_p}{1 - 2 \mu_B^2 I_s N(\varepsilon_F)} = \chi_p S
\]

Exchange splitting

![Exchange splitting diagram](image)

Stoner criterion

\[ 2 \mu_B^2 I_s N(\varepsilon_F) > 1 \]
The existence of ferromagnetism (FM) is governed by the Stoner criterion:

\[ I \cdot N(E_F) > 1 \]

- \( N(E_F) \): DOS at \( E_F \) (of NM case)
- \( I \): Stoner parameter
- \( I \) is independent of structure

Ferromagnetism appears when the gain in exchange energy is larger than the loss in kinetic energy.

bcc Fe

- Non magnetic case

![Graph showing spin-up and spin-down states in non-magnetic and ferromagnetic cases.]

**Exchange splitting**

$E_F$ at high DOS
DFT ground state of iron

- LSDA
  - NM
  - fcc
  - *in contrast to* experiment

- GGA
  - FM
  - bcc
  - *Correct lattice constant*

- Experiment
  - FM
  - bcc
Iron and its alloys

Fe: weak ferromagnet (almost)

Co: strong ferromagnet
V. Heine: „metals are systems with unsaturated covalent bonds“
Covalent magnetism Fe-Co alloys

- e.g. Fe-Co alloys
- Wigner delay times
The alloy is represented by ordered structures:
- $\text{Fe}_3\text{Co}$ and $\text{FeCo}_3$ (Heusler)
- FeCo Zintl or CsCl
- Fe, Co bcc
Iron and its alloys

Itinerant or localized?
Magnetization density in FeCo

- Magnetization density difference between
  - Majority spin
  - Minority spin

\[ m(r) = \rho^\uparrow(r) - \rho^\downarrow(r) \]

- Localized around
  - Fe and Co
  - Slightly negative between the atoms
- Itinerant electrons

K. Schwarz, P. Mohn, P. Blaha, J. Kübler, 
*Electronic and magnetic structure of bcc Fe-Co alloys from band theory*, 
Bonding by Wigner delay time

Inside such a sphere of radius $b$ the radial Schrödinger equation (in Rydberg atomic units)

$$
\left[ -\frac{d^2}{dr^2} - \frac{2}{r} \frac{d}{dr} + \frac{l(l + 1)}{r^2} + V(r) - \varepsilon \right] R_1(\varepsilon, r) = 0,
$$

(2)

**Single scatterer (Friedel)**

$V(r) = 0$ solution:

$$
S_1(r) = A_1 \left[ j_l(kr) \cos \eta_l(\varepsilon) - n_l(kr) \sin \eta_l(\varepsilon) \right],
$$

(3)

$R_1$ joined in value and slope defines phase shift:

$$
\tan \eta_l(\varepsilon) = \frac{R_1(\varepsilon, b) j_l'(kb) - j_l(kb) R_1'(\varepsilon, b)}{R_1(\varepsilon, b) n_l'(kb) - n_l(kb) R_1'(\varepsilon, b)},
$$

(4)

**Friedel sum**

$$
N(\varepsilon) = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l + 1) \eta_l(\varepsilon),
$$

$$
n(\varepsilon) = \frac{dN(\varepsilon)}{d\varepsilon} = \frac{1}{\pi} \sum_{l=0}^{\infty} (2l + 1) t_l(\varepsilon).
$$

(6)
Phase shifts, Wigner delay times of Fe, Co, Ni

Wigner delay time

Phase shifts

resonance states
Covalent magnetism in FeCo

Wigner delay time

- For spin up
  - Fe and Co equivalent
  - partial DOS similar
  - typical bcc DOS

- For spin down
  - Fe higher than Co

No charge transfer between Fe and Co
Covalent magnetism, FeCo:
Antiferromagnetic (AFM) Cr

- Cr has AFM bcc structure

- There is a symmetry, it is enough to do the spin-up calculation. Spin-down can be copied.
Zeolite, sodalite

- Al-silicate
- Corner shared
  - $SiO_4$ tetrahedra
  - $AlO_4$ tetrahedra
- $\beta$ cage
- $Al / Si$ ratio 1
- Alternating
- Ordered (cubic)
- 3 $e^-$ per cage
Si-Al zeolite (sodalite)

- Formed by corner-shared SiO$_4$ and AlO$_4$ tetrahedra
- Charge compensated by doping with 4 Na$^+$
- One e$^-$ (color center)
- Antiferromagnetic (AFM) order of e$^-$
AFM order between color centers (e⁻)

Spin density $\rho^\uparrow - \rho^\downarrow$

INVAR alloys (invariant)

- e.g. Fe-Ni

- Such systems essentially show no thermal expansion around room temperature
INVAR (invariant) of Fe-Ni alloys

- The thermal expansion of the Eifel tower
- Measured with a rigid Fe-Ni INVAR wire
- The length of the tower correlates with the temperature
- Fe$_{65}$Ni$_{35}$ alloy has vanishing thermal expansion around room temperature

Ch.E.Guillaume (1897)
What is magnetostriction?

Magnetostriction $\omega_{s0}$ is the difference in volume between the volume in the magnetic ground state and the volume in a hypothetical non-magnetic state.

Above the Curie temperature the magnetic contribution $\omega_m$ vanishes.
Fe-Ni Invar alloys

„classical“ Fe-Ni Invar

- Fe₆₅Ni₃₅ alloy has vanishing thermal expansion around room temperature
Early explanations of INVAR

R.J. Weiss

A.R. Williams, V.L. Moruzzi, G.D. Gelatt Jr., J. Kübler, K. Schwarz,
Aspects of transition metal magnetism,
Energy surfaces of Fe-Ni alloys

- This fcc structure
  - from non magnetic Fe (fcc)
  - to ferromagnetic Ni

- as the composition changes

At the INVAR composition
- There is a flat energy surface
  - as function of volume and moment
Finite temperature

- Energy surface at T=0 (DFT)
  - as a function of volume and moment
  - using fixed spin moment (FSM) calculations

- Finite temperature
  - Spin and volume fluctuations
  - Ginzburg-Landau model

\[ H = V^{-1} \int d^3r \left( E(M + \bar{m}(r)), V + \bar{v}(r) \right) \]
\[ + \frac{C}{2} \sum_{ij} (\nabla j m_i)^2 + \frac{D}{2} (\nabla v(r))^2 \]
FSM calculations

- fixed spin moment (FSM)
  e.g. Fe-Ni alloy

- allows to explore energy surface $E(V,M)$
  as function of
  - volume $V$
  - magnetic moment $M$
There are systems (e.g. like fcc Fe or fcc Co), for which the magnetization shows a hysteresis, when a magnetic field is applied (at a volume $V$).

The volume of the unit cell defines the Wigner-Seitz radius $r_{WS}$

$$V = \frac{4 \pi r_{WS}^3}{3}$$

The hysteresis causes numerical difficulties, since there are several solutions (in the present case 3 for a certain field $H$).

In order to solve this problem the FSM method was invented.
Fixed spin moment (FSM) method

- Conventional scheme
  \[ E^\uparrow_F = E^\downarrow_F \]
  \[ Z_v = N^\uparrow + N^\downarrow \]
  \[ M = N^\uparrow - N^\downarrow \]

- Constrained (FSM) method
  \[ E^\uparrow_F \neq E^\downarrow_F \]
  \[ Z_v = N^\uparrow + N^\downarrow \]
  \[ M = N^\uparrow - N^\downarrow \]

Simple case:
- bcc Fe
  - one SCF
  - poor convergence

Difficult case:
- Fe\(_3\)Ni
  - many calculations
  - good convergence
Physical situation:
- One applies a field $H$ and obtains $M$
- but this functions can be multivalued

Computational trick (unphysical):
- One interchanges the dependent and independent variable
- this function is single valued (unique)
- i.e. one chooses $M$ and calculates $H$ afterwards
FSM key references


Unusual magnetic systems

- GMR (Giant Magneto Resistance)
- half-metallic systems
  e.g. CrO$_2$
- important for spintronics
Once upon a time, in the early 1980’s …

“What happens if I bring two ferromagnets close—I mean really close—together?”

Peter Grünberg
Giant magnetoresistance (GMR)

Electrical resistance: $R_P$, $<(>)$, $R_{AP}$

The electrical resistance depends on the relative magnetic alignment of the ferromagnetic layers.

\[
GMR = \frac{R_{AP} - R_P}{R_P}
\]

19\% for trilayers @RT
80\% for multilayers @ RT

GMR is much larger than the anisotropic magnetoresistance (AMR)
1988: ... simultaneously, but independent ... 

“Does the electrical resistance depend on the magnetization alignment?”

Albert Fert

Peter Grünberg
4. Half-metals

Since magnetoresistance deals with electrical conductivity it is obvious that it is the behaviour of the electrons at the Fermi surface (defined by the Fermi energy) which is of primary interest. The more spin-polarized the density of states (DOS) at the Fermi energy, i.e., the more $N_\uparrow (E_F)$ deviates from $N_\downarrow (E_F)$, the more pronounced one expects the efficiency of the magnetoelectronic effects to be. In this respect a very interesting class of materials consists of what are called half-metals, a concept introduced by de Groot and co-workers \(23\). Such a property was then predicted theoretically for \(\text{CrO}_2\) by Schwarz in 1986 \(24\). The name half-metal originates from the particular feature that the spin down band is metallic while the spin up band is an insulator.

CrO$_2$ half-metallic ferromagnet

- CrO$_2$ (rutile structure)

Important for spintronics
The DOS features of \( \text{CrO}_2 \) are qualitatively like

- \( \text{TiO}_2 \) (for spin-down)
- \( \text{RuO}_2 \) (for spin-up)


All three compounds crystallize in the rutile structure.
Half-metallic ferromagnet

- CrO$_2$ (rutile structure)

spin-up

metallic

gap

spin-down
CrO₂ spin-down (TiO₂) spin-up (RuO₂)
Magnetic structure of uranium dioxide $\text{UO}_2$

- R. Laskowski
- G. K. H. Madsen
- P. Blaha
- K. Schwarz

- topics
  - non-collinear magnetism
  - spin-orbit coupling
  - $\text{LDA+U (correlation of U-5f electrons)}$
  - Structure relaxations
  - electric field gradient (EFG)

R. Laskowski, G. K. H. Madsen, P. Blaha, K. Schwarz:  
*Magnetic structure and electric-field gradients of uranium dioxide: An ab initio study*  
Atomic configuration of uranium (Z=92)

\[ \text{U} \quad [\text{Xe}] \quad 4f^{14} \quad 5d^{10} \quad 6s^2 \quad 6p^6 \quad 5f^3 \quad 6d^1 \quad 7s^2 \]

<table>
<thead>
<tr>
<th>( n, \ell )</th>
<th>( \ell-s )</th>
<th>( \ell+s )</th>
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<tbody>
<tr>
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<tr>
<td>1s</td>
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</tbody>
</table>

\( E_j \) (Ryd)

\[ \text{[Rn]} \]

- \( 6p_{1/2} \)
- \( 6p_{3/2} \)
- \( 7s_{1/2} \)
- \( 5f_{5/2} \)
- \( 6s_{1/2} \)
- \( 6d_{3/2} \)

\( \text{core-like} \)
\( \text{delocalized} \)
non-collinear magnetism in UO$_2$

collinear 1k-  non-collinear 2k-  or 3k-structure
UO$_2$ 2k structure, LDA+SO+U

- Magnetisation direction perpendicular at the two U sites (arrows)
- Magnetisation density (color)
Magnetism with WIEN2k

- Wien2k can only handle collinear or non-magnetic cases

**run_lapw script:**

**DOS**

- x lapw0
- x lapw1
- x lapw2
- x lcore
- x mixer

**non-magnetic case**

\[ m = n^\uparrow - n^\downarrow = 0 \]

**magnetic case**

\[ m = n^\uparrow - n^\downarrow \neq 0 \]

**run_lapw script:**

**DOS**

- x lapw0
- x lapw1 - up
- x lapw1 - dn
- x lapw2 - up
- x lapw2 - dn
- x lcore - up
- x lcore - dn
- x mixer
Spin polarized calculations

- `runsp_lapw` script (unconstrained magnetic calc.)
  - runs `lapw1/2` for both spins independently
  - `case.scf` contains extra information:
    - `grep :MMT case.scf` (for total moment)
    - `grep :MMI case.scf` (for atomic moments)
    - `grep :HFF case.scf` (for hyperfine fields)
Run spin-polarized, FSM or AFM calculations

- `runsp_lapw` script (unconstrained magnetic calc.)
  - runs `lapw1/2` for both spins independently
  - `case.scf` contains extra information:
    - `grep :MMT case.scf` (for total moment)
    - `grep :MMI case.scf` (for atomic moments)
    - `grep :HFF case.scf` (for hyperfine fields)
- `runfsm_lapw -m value` (constrained moment calc.)
  - for difficult to converge magnetic cases or simply to constrain a moment (→ 2 Fermi-energies → external magnetic field)
- `runafm_lapw` (anti-ferromagnetic calculation)
  - calculates only spin-up, uses symmetry to generate spin-down
Various magnetism cases

- `runsp_lapw` script (unconstrained magnetic calc.)
- `runfsm_lapw -m value` (constrained moment calc.)
- `runafm_lapw` (anti-ferromagnetic calculation)

- spin-orbit coupling can be included in second variational step
- never mix polarized and non-polarized calculations in one case directory !!!
Thank you for your attention