Magnetism (FM, AFM, FSM)

Karlheinz Schwarz
Institute of Materials Chemistry
TU Wien
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)
  
  \[
  \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \quad M > 0
  \]

- **Antiferromagnetic (AFM)** (e.g. Cr)
  
  \[
  \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \quad M = 0
  \]

- **Ferrimagnetic cases**
  
  the moments at different atoms are antiparallel but of different magnitude
  
  \[
  \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \quad M > 0
  \]

- **Non-collinear magnetism (NCM)**
  
  the magnetic moments are not ligned up parallel.
Itinerant electron magnetism

Experimental facts:

<table>
<thead>
<tr>
<th></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</td>
<td>221.7</td>
<td>2.22</td>
<td>1044</td>
<td>7.875</td>
</tr>
<tr>
<td>Co</td>
<td>166.1</td>
<td>1.75</td>
<td>1388</td>
<td>8.793</td>
</tr>
<tr>
<td>Co</td>
<td>163.1</td>
<td>1.72</td>
<td>1360</td>
<td>8.804</td>
</tr>
<tr>
<td>Ni</td>
<td>58.6</td>
<td>0.62</td>
<td>627</td>
<td>8.912</td>
</tr>
</tbody>
</table>

Curie temperature
Stoner theory of itinerant electron magnetism

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

In a 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

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

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

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

- **I** is the Stoner parameter, which is \( \sim \) independent of structure.

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

P.James, O.Eriksson, B.Johansson, I.A.Abrikosov,
Phys.Rev.B 58, ... (1998)
bcc Fe

- Non magnetic case

ferromagnetic case

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
- non-spin polarized

Co:
- strong ferromagnet
Magnetism and crystal structure

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

- e.g. Fe-Co alloys
- Wigner delay times
Spin projected DOS of Fe-Co alloys

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

Itinerant or localized?

- Magnetization density difference between:
  - *Majority spin*
  - *Minority spin*

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

Bonding by Wigner delay time

\[ V(r) = \begin{cases} V(r) & r \leq b, \\ 0 & r > b. \end{cases} \tag{1} \]

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

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

single scatterer (Friedel)

\( V(r) = 0 \) solution:

\[ S_l(r) = A_l \left[ j_l(kr) \cos \eta_l(\varepsilon) - n_l(kr) \sin \eta_l(\varepsilon) \right], \tag{3} \]

\( R_l \) joined in value and slope defines phase shift:

\[ \tan \eta_l(\varepsilon) = \frac{R_l(\varepsilon, b) j_l'(kb) - j_l(kb) R'_l(\varepsilon, b)}{R_l(\varepsilon, b) n_l'(kb) - n_l(kb) R'_l(\varepsilon, b)}, \tag{4} \]

Friedel sum

Wigner delay time

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

\[ n(\varepsilon) = \frac{dN(\varepsilon)}{d\varepsilon} = \frac{1}{\pi} \sum_{l=0}^{\infty} (2l + 1) t_l^P(\varepsilon). \tag{6} \]
Phase shifts, Wigner delay times of Fe, Co, Ni

Wigner delay time

Phase shifts

resonance states
Covalent magnetism in FeCo

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
Magnetism and crystal structure

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

\[
\begin{align*}
\text{Cr}_1 &= \text{Cr}_2 \\
\text{Cr}_2 &= \text{Cr}_1
\end{align*}
\]
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
SES Sodium electro sodalite

- 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$^-$

Energy (relative stability)

![ SES PES diagram ]
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

- Fe$_{65}$Ni$_{35}$ alloy has vanishing thermal expansion around room temperature
Early explanations of INVAR

R.J. Weiss

fcc Fe

low spin
m = 0.5 \( \mu_B \), AF
a = 3.57 Å

high spin
m = 2.8 \( \mu_B \), FM
a = 3.64 Å

\( \gamma_1 \) AF

kT

high moment
large volume \( \gamma_2 \) FM

50% Fe

75% Fe

100% Fe

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

![Fe-Ni alloy diagram](image)
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

\[ H = V^{-1} \int d^3r \left( E(M + \mathbf{m}(r)), V + v(r) \right) \]
\[ + \frac{C}{2} \sum_{ij} \left( \nabla_j \mathbf{m}_i \right)^2 + \frac{D}{2} \left( \nabla v(r) \right)^2 \]
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
  
  \[ \begin{align*}
  E_F^\uparrow &= E_F^\downarrow \\
  Z_v &= N^\uparrow + N^\downarrow
  \end{align*} \]
  
  output

  \[ M = N^\uparrow - N^\downarrow \]

- Constrained (FSM) method
  
  \[ \begin{align*}
  E_F^\uparrow &\neq E_F^\downarrow \\
  Z_v &= N^\uparrow + N^\downarrow
  \end{align*} \]
  
  input

  output

Simple case:
- bcc Fe
  
  one SCF

  poor convergence

- Fe\textsubscript{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


K. Schwarz, P. Mohn

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)

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

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

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
The Nobel Prize in Physics 2007

This year’s Nobel Prize in Physics is awarded to Albert Fert and Peter Grünberg for their discovery of Giant Magnetoresistance. Applications of this phenomenon have revolutionized techniques for retrieving data from hard disks.

Scientific Background on the Nobel Prize in Physics 2007

The Discovery of Giant Magnetoresistance

compiled by the Class for Physics of the Royal Swedish Academy of Sciences

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 magneto-electronic 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 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)

- metallic

- spin-up

- spin-down

- gap

- 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)

Diagram showing the energy levels for spin-up and spin-down states, with a clear gap separating the metallic regions for each spin orientation.
CrO$_2$ spin-down (TiO$_2$) spin-up (RuO$_2$)
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*
- *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)

U [Xe] 4f\(^{14}\) core 5d\(^{10}\) 6s\(^2\) 6p\(^6\) semi-core 5f\(^3\) 6d\(^1\) 7s\(^2\) valence

<table>
<thead>
<tr>
<th>n</th>
<th>(\ell)</th>
<th>(\ell^{-})</th>
<th>(\ell^{+})</th>
<th>(E_j) (Ryd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7s</td>
<td></td>
<td>-0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6d</td>
<td>-0.29</td>
<td>-0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5f</td>
<td>-0.17</td>
<td>-0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6p</td>
<td>-1.46</td>
<td>-2.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6s</td>
<td></td>
<td>-3.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5d</td>
<td>-7.48</td>
<td>-6.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5p</td>
<td>-18.05</td>
<td>-14.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5s</td>
<td></td>
<td>-22.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4f</td>
<td>-27.58</td>
<td>-26.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1s</td>
<td></td>
<td>-8513.38</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(E_j\) (Ryd) refers to the energy level of each electron configuration. The graph shows the radial distribution of the electrons, with core-like and delocalized states indicated. The ordinate labels for the graph are not fully visible in the image.
non-collinear magnetism in UO$_2$

collinear 1k-

non-collinear 2k-

or 3k-structure
UO₂ 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:

- lapw0
- lapw1
- lapw2
- lcore
- mixer

non-magnetic case

\[ m = n_\uparrow - n_\downarrow = 0 \]

runsp_lapw script:

- lapw0
- lapw1 - up
- lapw1 - dn
- lapw2 - up
- lapw2 - dn
- lcore - up
- lcore - dn
- mixer

magnetic case

\[ m = n_\uparrow - n_\downarrow \neq 0 \]
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-dn
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