Lecture contents

• Ferromagnetism
  – Molecular field theory
  – Exchange interaction
Ferromagnetism – Molecular field theory

- Spontaneous magnetization occurs in some (Ferromagnetic) materials composed of atoms with unfilled shells
- For some reason magnetic moments are aligned even at relatively high temperature

**Hypothesis:** magnetic order is due to strong local magnetic field (Weiss effective field) at the site of each dipole

\[ B_{loc} = B_a + \mu_0 \gamma M \]

with a constant \( \gamma \)

- Consider a collection of \( N \) identical atoms per unit volume, with total angular momentum \( J \), and use QM treatment of atomic paramagnetism

\[ M = M_{sat} B_J \left( y \right) \quad M_{sat} = N \mu_{eff} \]

with \( y = \frac{\mu_{eff} B_{loc}}{k_B T} \equiv \frac{\mu_{eff} \left( B_a + \mu_0 \gamma M \right)}{k_B T} = \frac{g_J \mu_B J \left( B_a + \mu_0 \gamma M \right)}{k_B T} \)

<table>
<thead>
<tr>
<th>Mat.</th>
<th>( T_c (^\circ \text{K}) )</th>
<th>( M_s )</th>
<th>Mat.</th>
<th>( T_c (^\circ \text{K}) )</th>
<th>( M_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1043</td>
<td>1752</td>
<td>CrBr3</td>
<td>37</td>
<td>270</td>
</tr>
<tr>
<td>Co</td>
<td>1388</td>
<td>1446</td>
<td>Au2MnAl</td>
<td>200</td>
<td>323</td>
</tr>
<tr>
<td>Ni</td>
<td>627</td>
<td>510</td>
<td>Cu2MnAl</td>
<td>630</td>
<td>726</td>
</tr>
<tr>
<td>Gd</td>
<td>293</td>
<td>1980</td>
<td>Cu2MnIn</td>
<td>500</td>
<td>613</td>
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<tr>
<td>Dy</td>
<td>85</td>
<td>3000</td>
<td>MnAs</td>
<td>318</td>
<td>870</td>
</tr>
<tr>
<td>EuO</td>
<td>77</td>
<td>1910</td>
<td>MnBi</td>
<td>670</td>
<td>675</td>
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<tr>
<td>EuS</td>
<td>16.5</td>
<td>1184</td>
<td>GdCl3</td>
<td>2.2</td>
<td>550</td>
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</table>

Values of Curie temperatures and spontaneous magnetism (at 0 K in Gauss) for a few ferromagnetic materials

<table>
<thead>
<tr>
<th>Mat.</th>
<th>( T_N (^\circ \text{K}) )</th>
<th>Mat.</th>
<th>( T_N (^\circ \text{K}) )</th>
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<tbody>
<tr>
<td>MnO</td>
<td>122</td>
<td>KCoF3</td>
<td>125</td>
</tr>
<tr>
<td>FeO</td>
<td>198</td>
<td>MnF2</td>
<td>67.34</td>
</tr>
<tr>
<td>CoO</td>
<td>291</td>
<td>FeF2</td>
<td>78.4</td>
</tr>
<tr>
<td>NiO</td>
<td>600</td>
<td>CoF2</td>
<td>37.7</td>
</tr>
<tr>
<td>RbMnF3</td>
<td>54.5</td>
<td>MnCl2</td>
<td>2</td>
</tr>
<tr>
<td>KFeF3</td>
<td>115</td>
<td>VS</td>
<td>1040</td>
</tr>
<tr>
<td>KMnF3</td>
<td>88.3</td>
<td>Cr</td>
<td>311</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Mat.</th>
<th>( T_c (^\circ \text{K}) )</th>
<th>( M_s )</th>
<th>Mat.</th>
<th>( T_c (^\circ \text{K}) )</th>
<th>( M_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe3O4</td>
<td>858</td>
<td>510</td>
<td>CuFe2O4</td>
<td>728</td>
<td>160</td>
</tr>
<tr>
<td>CoFe2O4</td>
<td>793</td>
<td>475</td>
<td>MnFe2O4</td>
<td>573</td>
<td>560</td>
</tr>
<tr>
<td>NiFe2O4</td>
<td>858</td>
<td>300</td>
<td>Y3Fe5O12</td>
<td>560</td>
<td>195</td>
</tr>
</tbody>
</table>

From Burns, 1990
Ferromagnetism – Molecular field theory

• Now let’s find the spontaneous magnetization \((B_a = 0)\)

\[
M = M_{sat} B_J (y)
\]

with \(y = \frac{\mu_{eff} \mu_0 \gamma M}{k_B T}\)

Solving equation against \(y\) :

\[
y \frac{k_B T}{\mu_{eff} \mu_0 \gamma M_{sat}} = B_J (y)
\]

• Depending on temperature spontaneous magnetization can be either \(M=0\) or finite

• At low \(y\)

\[
B_J (y \ll 1) \approx y \frac{J + 1}{3J}
\]

We can find critical Curie temperature:

\[
\frac{k_B T_C}{\mu_{eff} \mu_0 \gamma M_{sat}} = \frac{J + 1}{3J}
\]

\[
T_C = \frac{N \mu_0 \gamma}{3k_B} \left( g_J \mu_B \right)^2 J (J + 1)
\]

From Burns, 1990
Ferromagnetism – Molecular field theory

• At temperatures $T > T_c$, there is no spontaneous magnetization, and we can find temperature dependence of magnetization ($B_a > 0$)

$$M = M_{sat} B_J(y)$$

with

$$y = \frac{g_J \mu_B J(B_a + \mu_0 \gamma M)}{k_B T}$$

$$M = M_{sat} \frac{J + 1}{3J} = \frac{N \mu_{eff}^2}{3k_B T}(B_a + \mu_0 \gamma M)$$

• Solving for $M$:

$$M = \frac{C}{\mu_0 (T - C \gamma)} B_a$$

with Curie constant

$$C = \frac{N \mu_0 \mu_{eff}^2}{3k_B} = \frac{T_C}{\gamma}$$

• Then susceptibility of ferromagnet in paramagnetic region

$$\chi = \frac{C}{T - T_C}$$

• Some estimation for iron:

$$g_J = 2; \ J = 1; \ N = 8.5 \cdot 10^{28} m^{-3} \Rightarrow C = 1.77 K$$

$$T_C = 1043 K; \ \Rightarrow \ \gamma = 588$$

$$M \approx 1700 \text{ Gauss}; \ \Rightarrow \ B \sim 10^6 \text{ Gauss}=100 \ T$$

Huge!
Ferromagnetism – Heisenberg exchange interaction

• What is the reason for so high local magnetic field? – Exchange interaction

• Consider two electrons on two atoms. We need to find the energy difference = exchange integral $J_{ex}$:

  \[ H_{ex} = -J_{ex} \left( s_1 \cdot s_2 \right) \]

  \[ (s_1 \cdot s_2) = -\frac{3}{4} \quad \text{Singlet} \]

  \[ (s_1 \cdot s_2) = +\frac{1}{4} \quad \text{Triplet} \]

• Their wavefunction is antisymmetric due to Pauli exclusion principle

• Usually the interaction between the space and spin parts is small, and the variables can be separated:

• Antiparallel spins give antisymmetric spin wavefunction, etc.

• We can construct wavefunctions for singlet and triplet states with correct symmetry:

\[ \Psi \left( r_1, s_1, r_2, s_2 \right) = -\Psi \left( r_2, s_2, r_1, s_1 \right) \]

\[ \Psi \left( r_1, s_1, r_2, s_2 \right) = \varphi \left( r_1, r_2 \right) g \left( s_1, s_2 \right) \]

<table>
<thead>
<tr>
<th>Wavefunction</th>
<th>Singlet</th>
<th>Triplet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>Antisym.</td>
<td>Antisym.</td>
</tr>
<tr>
<td>Spin part</td>
<td>Antisym.</td>
<td>Symmetric</td>
</tr>
<tr>
<td>Space part</td>
<td>Symmetric</td>
<td>Antisym.</td>
</tr>
</tbody>
</table>

\[ \varphi_s \left( x_1, x_2 \right) = \phi_a \left( r_1 \right) \phi_b \left( r_2 \right) + \phi_a \left( r_2 \right) \phi_b \left( r_1 \right) = \Psi_1 + \Psi_2 \]

\[ \varphi_T \left( x_1, x_2 \right) = \phi_a \left( r_1 \right) \phi_b \left( r_2 \right) - \phi_a \left( r_2 \right) \phi_b \left( r_1 \right) = \Psi_1 - \Psi_2 \]
Ferromagnetism – Heisenberg exchange interaction contd

• The energy shift of singlet and triplet states can be calculated from perturbation theory:

\[
E_S = \langle \phi_s | V | \phi_s \rangle = \langle \Psi_1 | V | \Psi_1 \rangle + \langle \Psi_2 | V | \Psi_2 \rangle + \langle \Psi_1 | V | \Psi_2 \rangle + \langle \Psi_2 | V | \Psi_1 \rangle
\]

\[
E_T = \langle \phi_t | V | \phi_t \rangle = \langle \Psi_1 | V | \Psi_1 \rangle + \langle \Psi_2 | V | \Psi_2 \rangle - \langle \Psi_1 | V | \Psi_2 \rangle - \langle \Psi_2 | V | \Psi_1 \rangle
\]

\[
V(r_1, r_2) = \frac{e^2}{\varepsilon_0} \left[ \frac{1}{r_{ab}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{r_{12}} \right]
\]

• At small a-b distance \( J_{\text{exc}} < 0 \) and singlet state is favorable

• At large a-b distance \( J_{\text{exc}} > 0 \) and triplet state is favorable

• BTW if the electrons are on the same atom, the ion interaction change is zero, \( J_{\text{exc}} > 0 \) and antiparallel spins are favorable = Hund’s rule
Ferromagnetism – Heisenberg exchange interaction contd.

- Exchange interaction can be ferromagnetic or antiferromagnetic depending on interatomic distance.
- Exchange interaction is electrostatic (strong) in nature.
- To correlate it with molecular field theory, we can write:

\[ H_{ex} = - \sum_{i,j} J_{ex} (s_i \cdot s_j) \equiv \sum_i g_J \mu_B s_i B_{loc} \]

\[ zJ_{ex} s = g_J \mu_B B_{loc} \]

Number of nearest neighbors

- For Fe:

\[ J_{ex} = \frac{g_J \mu_B \mu_0 \gamma M}{zs} = \left( g_J \mu_B \right)^2 \frac{\mu_0 \gamma n}{z} \approx 11 \text{meV} \]

- Electrostatic interaction easily accounts for this value.
Role of band structure

Density of states in 3d and 4s bands

Dependence of the saturation magnetization on the number $n$ of $(3d + 4s)$ electrons per atom

$$\mu_H = (10.6 - n) \mu_B$$

$n =$ number of $(3d + 4s)$ electrons per atom

- For Ni ($n=10$) moment is $0.6\mu_B$

From Cullity, 2008
Ferromagnetic materials

- Energy is minimized by ordering spins into “domains”
  - Net moment, $M$, would cause external field, increase energy
  - Magnetic domains cancel so that $M = 0$
  - Natural ferromagnetism does not produce net magnetic field
- To magnetize a ferromagnet, impose $H$
  - Domain walls move to align $M$ and $H$
  - Defects impede domain wall motion
  - Magnetization ($M_r$) retained when $H$ removed
- Magnetic properties
  - $M_s = \text{saturation magnetization}$ (All spins aligned with field)
  - $M_r = \text{remanent magnetization}$ (Useful moment of permanent magnet)
  - $H_c = \text{coercive force}$ (Field required to “erase” moment)
  - Area inside curve = magnetic hysteresis (Governs energy lost in magnetic cycle)
High temperature:
- Spins disordered $\Rightarrow$ paramagnetism

Low Temperature ($T < T_c$)
- Spins align = ferromagnetism
  - Elements: Fe, Ni, Co, Gd, Dy
  - Alloys and compounds: AI Ni Co, Fe Cr Co, Sm Co $\delta$, Fe$_{14}$Nd$_{2}$B
- Like spins alternate = antiferromagnetism (RbMnF$_3$)
- Unlike spins alternate = ferrimagnetism
  - Compounds: Fe$_3$O$_4$ (lodestone, magnetite), CrO$_3$, SrFe$_2$O$_3$, other ferrites and garnets
Other types of exchange interaction

- Superexchange (transition metal oxides)
  - Can be ferromagnetic or antiferromagnetic depending upon the energy of delocalization of the p-electrons on $M_1$ and $M_2$
  - Ordering temperature up to 900 K in ferrites ($\text{NiFe}_2\text{O}_4$ - 863 K)
  - Sign mostly negative, though ferromagnetics are known: EuO ($T_c=69$K) or CrBr$_3$ ($T_c=37$K)

- RKKY interaction (Ruderman-Kittel-Kasuya-Yosida) - Indirect exchange over relatively large distances trough spin of conduction electrons (4f metals)
  - Interaction oscillates with $(k_F R)$, Fermi wavevector determines the wavelength of oscillations
  - The interaction is of the same order for all rare earths, but ordering temperatures vary due to magnetic moment: 19K for Nd, 289 K for Gd)
Magnetic materials

- Magnetic induction field is the same in a

From Goldberg, 2006
# Physical constants

<table>
<thead>
<tr>
<th>Name and symbol</th>
<th>Numerical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed of light in vacuum, $c$</td>
<td>$2.9979 \times 10^8 \text{ m} \cdot \text{s}^{-1}$</td>
</tr>
<tr>
<td>Permeability of vacuum, $\mu_0$</td>
<td>$4\pi \times 10^{-7} \text{ H} \cdot \text{m}^{-1}$</td>
</tr>
<tr>
<td>Permittivity of vacuum, $\varepsilon_0 = 1/c^2\mu_0$</td>
<td>$8.8542 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$</td>
</tr>
<tr>
<td>Planck’s constant, $h$</td>
<td>$6.6261 \times 10^{-34} \text{ J} \cdot \text{s}$</td>
</tr>
<tr>
<td>$\hbar = h/2\pi$</td>
<td>$1.0546 \times 10^{-34} \text{ J} \cdot \text{s}$</td>
</tr>
<tr>
<td>Acceleration of gravity, $g$</td>
<td>$9.8066 \text{ m} \cdot \text{s}^{-2}$</td>
</tr>
<tr>
<td>Electron rest mass, $m$</td>
<td>$9.1094 \times 10^{-31} \text{ kg}$</td>
</tr>
<tr>
<td>Electron charge (absolute value), $e$</td>
<td>$1.6022 \times 10^{-19} \text{ C}$</td>
</tr>
<tr>
<td>Bohr magneton, $\mu_B = e\hbar/2m$</td>
<td>$9.2742 \times 10^{-24} \text{ A} \cdot \text{m}^{2}$</td>
</tr>
<tr>
<td>Flux quantum, $h/2e$</td>
<td>$2.0678 \times 10^{-15} \text{ Wb}$</td>
</tr>
<tr>
<td>Avogadro’s number $N$</td>
<td>$6.0221 \times 10^{23} \text{ mol}^{-1}$</td>
</tr>
<tr>
<td>Boltzmann’s constant, $k_B$</td>
<td>$1.3807 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$</td>
</tr>
</tbody>
</table>

- **Length (metre)**: 1 m = $10^2$ cm = 39.37" (inch) = $10^{10}$ angström (Å).
- **Force (newton)**: 1 N = $10^5$ dyn = 0.102 kgf.
- **Energy (joule)**: 1 J = $10^7$ erg = $0.7243 \times 10^{23}$ K = $0.6241 \times 10^{19}$ eV.
- **Energy density**: 1 J.m$^{-3}$ = 10 erg.cm$^{-3}$.
- **Power (watt)**: 1 W = $10^7$ erg.s$^{-1}$ = $1.359 \times 10^{-3}$ CV = $1.340 \times 10^{-3}$ hp.
- **Pressure (pascal)**: 1 Pa = 10 baryes = $10^{-5}$ bar = $1.02 \times 10^{-5}$ kgf.cm$^{-2}$
  = $7.49 \times 10^{-3}$ torrs = $1.45 \times 10^{-4}$ psi.

From Tremolet de Lacheisserie, 2005