Lecture contents

• Magnetic properties
• Diamagnetism
• Band paramagnetism
• Atomic paramagnetism
Magnetic units

Magnetic induction (tesla): \( 1 \text{T} = 10^4 \text{gauss} \) (=1 Wb. m\(^{-2}\)). \( \mathbf{B} \)

\( \mathbf{B} \) can be called magnetic induction, magnetic induction field or magnetic flux density.

Magnetic field (ampere / metre): \( 1 \text{A.m}^{-1} = 4 \pi \times 10^{-3} \text{œrsted} \). \( \mathbf{H} \)

The magnetic field \( \mathbf{H} \) is often expressed in units of \( \mu_0 \mathbf{H} \), hence in tesla (T) or its submultiple, the gamma (\( \gamma \)) which is equal to \( 10^{-9} \text{T} \). A field of 1 A.m\(^{-1}\) corresponds to 1.2566 \( \mu \text{T} \).

Magnetisation (ampere / metre): \( 1 \text{A.m}^{-1} = 10^{-3} \text{emu . cm}^{-3} \). \( \mathbf{M} \)

Magnetic moment (ampere-square metre or joule per tesla): \( 1 \text{A.m}^2 = 1 \text{J.T}^{-1} = 10^3 \text{emu} \). \( \mu \)

Specific magnetic moment:

\( 1 \text{A.m}^2 . \text{kg}^{-1} = 1 \text{emu.g}^{-1} \). \( \text{M/\mu} \)

Note that, sometimes, magnetisation (\( \mathbf{M} \)), magnetic moment (\( \mathbf{m} \)) and specific magnetic moment (\( \mathbf{\sigma} \)) are expressed in tesla, Weber-meter and Weber-meter per kilogram, respectively: the reason is that we have adopted as definition of magnetisation (\( \text{dm/dV} \)):

\[ \mathbf{M} = \mathbf{B} / \mu_0 - \mathbf{H} \]

whereas some authors call “magnetisation” the quantity \( \mathbf{B}_i = \mathbf{J} = \mathbf{B} - \mu_0 \mathbf{H} \)

which is usually called “(magnetic) polarisation”.

\[ 1 \text{Wb} = T \cdot m^2 \]

\[ 1 \text{T} = \frac{V \cdot s}{m^2} \]

\[ 1H = \frac{Wb}{A} = \frac{T \cdot m^2}{A} \]

From Tremolet de Lacheisserie, 2005
Magnetic susceptibility

**SI:**
\[
\begin{align*}
\vec{B} &= \mu_0 \left( \vec{H} + \vec{M} \right) \\
\vec{B} &= \mu_0 \mu_R \vec{H} \\
\vec{M} &= \chi \vec{H} \\
\mu_R &= 1 + \chi
\end{align*}
\]

**CGS:**
\[
\begin{align*}
\vec{B} &= \vec{H} + 4\pi \vec{M} \\
\vec{B} &= \mu_R \vec{H} \\
\vec{M} &= \chi \vec{H} \\
\mu_R &= 1 + 4\pi \chi
\end{align*}
\]

susceptibility \( \chi \): 
\[
\chi = \frac{M}{H} \, \text{emu} \, \text{Oe}^{-1} \, \text{cm}^3.
\]

Note that, since \( M \) has units \( \text{A} \cdot \text{cm}^2/\text{cm}^3 \), and \( H \) has units \( \text{A}/\text{cm} \), \( \chi \) is actually dimensionless. Since \( M \) is the magnetic moment per unit volume, \( \chi \) also refers to unit volume and is sometimes called the *volume susceptibility* and given the symbol \( \chi_v \) to emphasize this fact. Other susceptibilities can be defined, as follows:

\[
\begin{align*}
\chi_m &= \chi_v / \rho = \text{mass susceptibility (emu/Oe g)}, \quad \text{where } \rho = \text{density}, \\
\chi_A &= \chi_m A = \text{atomic susceptibility (emu/Oe g atom)}, \quad \text{where } A = \text{atomic weight}, \\
\chi_M &= \chi_m M' = \text{molar susceptibility (emu/Oe mol)}, \quad \text{where } M' = \text{molecular weight}.
\end{align*}
\]

From Cullity, 2009
Magnetic properties of materials

- M – magnetization or magnetic dipole density
- Diamagnetic $\chi \sim -10^{-5}$
- Paramagnetic $\chi \sim +10^{-5}$
- Ferromagnetic – spontaneous magnetization, large $\chi$
- ...

<table>
<thead>
<tr>
<th>Material</th>
<th>$\chi_M$ (dim'less)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>$-1.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>Ag</td>
<td>$-2.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$-9.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Nb (4K)</td>
<td>-1</td>
</tr>
<tr>
<td>Na</td>
<td>$8.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>Al</td>
<td>$2.1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Pt</td>
<td>$2.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Gd</td>
<td>0.48</td>
</tr>
<tr>
<td>Fe (annealed)</td>
<td>20,000</td>
</tr>
<tr>
<td>NdFe$_{14}$B</td>
<td>$\sim 0$</td>
</tr>
</tbody>
</table>

From Cusack, 1963
Diamagnetism (classical)

- Arises from Lentz’s law: when magnetic flux changes in a circuit, a current is induced which opposes the change of flux.

- Orbiting electron creates magnetic dipole (circulating current)
  \[ I = \frac{\text{charge}}{\text{period}} = q \frac{\omega}{2\pi} \]
  \[ \mu = IA = \frac{1}{2} q\omega R^2 \]

- In magnetic field, Lorentz’s force is added to centrifugal force
  \[ m\omega^2 R = F - q\omega R \mu_0 H \]

- And corresponding change of rotational frequency
  \[ \omega^2 - \omega_0^2 = -\frac{q\omega\mu_0 H}{m} \]
  \[ \Delta \omega = -\frac{q\mu_0 H}{2m} \]

- If change in orbital motion is small (\( \omega \approx \omega_0 \))
  \[ \Delta E = \hbar \Delta \omega = -\frac{q\hbar \mu_0 H}{2m} = -\mu_B \mu_0 H \]

- The energy associated with this frequency is

  \[ \mu_B = \frac{q\hbar}{2m} = 9.274 \cdot 10^{-24} \text{ J/T} \equiv \text{A} \cdot \text{m}^2 \]

- The change in frequency can be associated with induced magnetic dipole moment:
  \[ \mu_m = -\frac{q^2 R^2}{4m} \mu_0 H \]
Diamagnetism (classical) contd.

• Small magnetic field-induced magnetic dipole moment:

\[ \mu_m = -\frac{q^2 R^2}{4m} \mu_0 H \]

• Now we can apply the result to spherical closed-shell atom
  • Averaging over 3D gives mean square radial distance
  • Sum over all Z electrons in the atom
  • Sum over all atoms in a unit volume, density \( N \), to obtain magnetization

\[ \left\langle R^2 \right\rangle = \frac{3}{2} R^2 \quad \left\langle x^2 \right\rangle = \left\langle y^2 \right\rangle = \left\langle z^2 \right\rangle = \frac{1}{3} \left\langle R^2 \right\rangle \]

\[ M = -\frac{q^2 ZN}{6m} \mu_0 H \left\langle R^2 \right\rangle \]

Larmor or Langevin diamagnetic susceptibility

• Finally susceptibility

\[ \chi = \frac{M}{H} = -\frac{q^2 ZN \mu_0}{6m} \left\langle R^2 \right\rangle \]

• All atoms and ions display diamagnetic response
• Almost independent of temperature

Molar susceptibilities of some atoms and ions (x10^{-6} cm^3/mole)

<table>
<thead>
<tr>
<th>Ion</th>
<th>( \chi_M )</th>
<th>Atom</th>
<th>( \chi_M )</th>
<th>Ion</th>
<th>( \chi_M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>-1.9</td>
<td>Li+</td>
<td>-0.7</td>
<td>F^-</td>
<td>-9.4</td>
</tr>
<tr>
<td>Ne</td>
<td>-7.2</td>
<td>Na+</td>
<td>-6.1</td>
<td>Cl^-</td>
<td>-24.2</td>
</tr>
<tr>
<td>A</td>
<td>-19.4</td>
<td>K+</td>
<td>-14.6</td>
<td>Br^-</td>
<td>-34.5</td>
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<tr>
<td>Kr</td>
<td>-28</td>
<td>Rb+</td>
<td>-22.0</td>
<td>I^-</td>
<td>-50.6</td>
</tr>
<tr>
<td>Xe</td>
<td>-43</td>
<td>Cs+</td>
<td>-35.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From Burns, 1990
Paramagnetism

• Contrary to diamagnetism, paramagnetism arises from non-zero magnetic moments:
  • Free electron (Pauli) spin paramagnetism
  • Langevin atomic paramagnetism
• An electron has an intrinsic magnetic dipole moment associated with its spin S, equal to Bohr magneton:

\[ \hat{\mu} = -g_s \frac{q}{2m} \hat{S} \]

\[ \mu_B = \frac{q\hbar}{2m} = 9.274 \times 10^{-24} \left\{ \frac{J}{T} \right\} \equiv \left\{ A \cdot m^2 \right\} \]

For \( B = 1 \text{T} \) (\( H = 8 \times 10^5 \text{ A/m} \))
\[ U = \mu_B B = 58 \mu\text{eV} \rightarrow 0.67 \text{K} \]

Field alignment is weak!

• We can expect that the magnetic dipoles will rotate towards low-energy state \( (U = \text{from} -\hat{\mu} \cdot \vec{B} \text{ to } +\hat{\mu} \cdot \vec{B}) \)

• The fraction of electrons with magnetic moments parallel to magnetic field exceeds the anti-parallel fraction by

\[ \approx \frac{\mu_B \mu_0 H}{k_B T} \]

• For \( n \) free electrons, the magnetization

\[ M \approx n \mu_B \frac{\mu_B \mu_0 H}{k_B T} \]
Paramagnetism of free spins

- Magnetization
  \[ M \approx n \mu_B \frac{\mu_B \mu_0 H}{k_B T} \]
  is \( \sim 100 \) times higher than observed in real materials

- In a band only a “thermal” fraction of electrons contributes to paramagnetism (compare to transport)
  \[ \approx \frac{k_B T}{E_F} \]

- Magnetization is
  \[ M \approx n \mu_B \frac{\mu_B \mu_0}{k_B T_F} H \]

- Similar to transport, more accurate averaging over the distribution function gives susceptibility
  \[ \chi = \frac{3 \mu_0}{2} \frac{n \mu_B^2}{k_B T_F} \]

- For example, for Na \[ \chi = -8.4 \cdot 10^{-6} \]

From Burns, 1990
Langevin atomic paramagnetism

- Similar to free spins, if an atom has a magnetic moment $\mu_{\text{eff}}$, it can align along the magnetic field.
- Magnetization of a material with atomic density $N$ is (averaging included)
  \[
  M = \frac{1}{3} N \mu_{\text{eff}} \frac{\mu_{\text{eff}} \mu_0 H}{k_B T}
  \]
- And susceptibility
  \[
  \chi = \frac{\mu_0 N \mu_{\text{eff}}^2}{3 k_B T}
  \]
  \[
  \chi = \frac{C}{T}
  \]
- Atom with orbital, spin and total angular momenta, $L, S,$ and $J = L + S$, will have magnetic moment
  \[
  \mu_{\text{eff}} = g_J \mu_B J
  \]
  With Lindé $g$-factor
  \[
  g_J = 1 + \frac{J^2 + S^2 - L^2}{2J^2}
  \]
- Complications
  - Quantum mechanical averaging of $m_J$
  - Ions
  - Quenching of orbital momentum in the crystal field (Stark splitting of $2L+1$ degeneracy)

Curie law for paramagnetics

With Curie constant

\[
C = \frac{N \mu_0 \mu_{\text{eff}}^2}{3k_B}
\]

Often “spin-only” moment is used with convention:

$g_J=2$, $L=0$, $J=S$

and maximum moment $\mu_H=2J\mu_B$

Need to be careful with scientific texts!
• Quantum mechanical averaging over (2J+1) projections

\[
M = N \sum_{-J}^{+J} g_J \mu_B m_J e^{\frac{g_J \mu_B m_J B}{k_B T}} \\
\approx Ng_J \mu_B JB_J(y) = N \mu_{eff} B_J(y)
\]

• With Brillouin function:

\[
B_J(y) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} y\right) - \frac{1}{2J} \coth\left(\frac{y}{2J}\right)
\]

with

\[
y = \frac{\mu_{eff} B}{k_B T} = \frac{g_J \mu_B JB}{k_B T}
\]

• If magnetic energy is small compared to thermal energy, \(y \ll 1\), Brillouin function gives

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

• This results in classic susceptibility

\[
\chi = \frac{\mu_0}{3} \frac{N \mu_{eff}^2}{k_B T}
\]

with quantum averaged

\[
\mu_{eff}^2 = (g_J \mu_B)^2 J(J+1)
\]
# Magnetic moments of ions

Ground states of ions predicted by Hund’s rules

<table>
<thead>
<tr>
<th>n</th>
<th>m_j</th>
<th>S</th>
<th>L =</th>
<th></th>
<th>J</th>
<th>g_J</th>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2S_0</td>
<td>0</td>
<td>La^{3+}</td>
</tr>
<tr>
<td>1</td>
<td>1/2</td>
<td>3</td>
<td>5/2</td>
<td>2F_5/2</td>
<td>6/7</td>
<td>Ce^{3+}</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>5</td>
<td>4</td>
<td>3H_4</td>
<td>4/5</td>
<td>Pr^{3+}</td>
</tr>
<tr>
<td>3</td>
<td>3/2</td>
<td>6</td>
<td>9/2</td>
<td>4I_9/2</td>
<td>8/11</td>
<td>Nd^{3+}</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>6</td>
<td>4</td>
<td>5L_6</td>
<td>3/5</td>
<td>Pm^{3+}</td>
</tr>
<tr>
<td>5</td>
<td>5/2</td>
<td>5</td>
<td>5/2</td>
<td>6H_{5/2}</td>
<td>2/7</td>
<td>Sm^{3+}</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>7F_0</td>
<td>-</td>
<td>Eu^{3+}</td>
</tr>
<tr>
<td>7</td>
<td>7/2</td>
<td>0</td>
<td>7/2</td>
<td>8S_{7/2}</td>
<td>2</td>
<td>Gd^{3+}</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>3</td>
<td>6</td>
<td>3F_6</td>
<td>3/2</td>
<td>Tb^{3+}</td>
</tr>
<tr>
<td>9</td>
<td>5/2</td>
<td>5</td>
<td>15/2</td>
<td>6H_{15/2}</td>
<td>4/3</td>
<td>Dy^{3+}</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>6</td>
<td>8</td>
<td>5L_6</td>
<td>5/4</td>
<td>Ho^{3+}</td>
</tr>
<tr>
<td>11</td>
<td>3/2</td>
<td>6</td>
<td>16/2</td>
<td>4I_{16/2}</td>
<td>6/5</td>
<td>Er^{3+}</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>5</td>
<td>6</td>
<td>3H_6</td>
<td>7/6</td>
<td>Tm^{3+}</td>
</tr>
<tr>
<td>13</td>
<td>1/2</td>
<td>3</td>
<td>7/2</td>
<td>2F_{7/2}</td>
<td>8/7</td>
<td>Yb^{3+}</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1S_0</td>
<td>0</td>
<td>Lu^{3+}</td>
</tr>
</tbody>
</table>

Values of magnetic moments of 4f and 3d ions in insulating compounds

<table>
<thead>
<tr>
<th>Ion</th>
<th>4f^n</th>
<th>State</th>
<th>( \mu_{eff}/\mu_B ) (Calc.)</th>
<th>( \mu_{eff}/\mu_B ) (Exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La^{3+}</td>
<td>4f^0</td>
<td>( ^1S_0 )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ce^{3+}</td>
<td>4f^1</td>
<td>( ^2F_{5/2} )</td>
<td>2.54</td>
<td>2.4</td>
</tr>
<tr>
<td>Pr^{3+}</td>
<td>4f^2</td>
<td>( ^3H_4 )</td>
<td>3.58</td>
<td>3.5</td>
</tr>
<tr>
<td>Nd^{3+}</td>
<td>4f^3</td>
<td>( ^4I_{9/2} )</td>
<td>3.62</td>
<td>3.5</td>
</tr>
<tr>
<td>Pm^{3+}</td>
<td>4f^4</td>
<td>( ^5I_4 )</td>
<td>2.68</td>
<td>-</td>
</tr>
<tr>
<td>Sm^{3+}</td>
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<td>( ^6H_{5/2} )</td>
<td>0.84</td>
<td>1.5</td>
</tr>
<tr>
<td>Eu^{3+}</td>
<td>4f^6</td>
<td>( ^7F_0 )</td>
<td>0</td>
<td>3.4</td>
</tr>
<tr>
<td>Gd^{3+}</td>
<td>4f^7</td>
<td>( ^8S_{7/2} )</td>
<td>7.94</td>
<td>8.0</td>
</tr>
<tr>
<td>Tb^{3+}</td>
<td>4f^8</td>
<td>( ^7F_6 )</td>
<td>9.72</td>
<td>9.5</td>
</tr>
<tr>
<td>Dy^{3+}</td>
<td>4f^9</td>
<td>( ^6H_{15/2} )</td>
<td>10.63</td>
<td>10.6</td>
</tr>
<tr>
<td>Ho^{3+}</td>
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<td>10.60</td>
<td>10.4</td>
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<tr>
<td>Er^{3+}</td>
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<td>9.59</td>
<td>9.5</td>
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<tr>
<td>Tm^{3+}</td>
<td>4f^12</td>
<td>( ^3H_6 )</td>
<td>7.57</td>
<td>7.3</td>
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<tr>
<td>Yb^{3+}</td>
<td>4f^13</td>
<td>( ^2F_{7/2} )</td>
<td>4.54</td>
<td>4.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ion</th>
<th>3d^n</th>
<th>State</th>
<th>( \mu_{eff}/\mu_B ) (Calc.-J)</th>
<th>( \mu_{eff}/\mu_B ) (Calc.-J=S)</th>
<th>( \mu_{eff}/\mu_B ) (Exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti^{3+}, V^{4+}</td>
<td>3d^1</td>
<td>( ^2D_{3/2} )</td>
<td>1.55</td>
<td>1.73</td>
<td>1.8</td>
</tr>
<tr>
<td>V^{3+}</td>
<td>3d^2</td>
<td>( ^3F_2 )</td>
<td>1.63</td>
<td>2.83</td>
<td>2.8</td>
</tr>
<tr>
<td>Cr^{3+}, V^{2+}</td>
<td>3d^3</td>
<td>( ^4F_{3/2} )</td>
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<td>3.8</td>
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<td>Mn^{3+}, Cr^{2+}</td>
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<td>( ^5D_0 )</td>
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<tr>
<td>Fe^{3+}, Mn^{2+}</td>
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<td>5.92</td>
<td>5.9</td>
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<tr>
<td>Fe^{2+}</td>
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<td>( ^5D_4 )</td>
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<td>5.4</td>
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<tr>
<td>Co^{2+}</td>
<td>3d^7</td>
<td>( ^4F_{9/2} )</td>
<td>6.63</td>
<td>3.87</td>
<td>4.8</td>
</tr>
<tr>
<td>Ni^{2+}</td>
<td>3d^8</td>
<td>( ^3F_4 )</td>
<td>5.59</td>
<td>2.83</td>
<td>3.2</td>
</tr>
<tr>
<td>Cu^{2+}</td>
<td>3d^9</td>
<td>( ^2D_{5/2} )</td>
<td>3.55</td>
<td>1.73</td>
<td>1.9</td>
</tr>
</tbody>
</table>

From Burns, 1990
In KCr(SO$_4$)$_2$·12 H$_2$O compound, the only magnetic atom is Cr$^{3+}$:

- 3 d-electrons:
  - $S=3/2$, $L=3$, $J=3/2$ →
    \[
g_J = 1 + \frac{J^2 + S^2 - L^2}{2J^2} = \frac{2}{5}
\]

- From experiment: $g_J=2$, $L=0$, $J=S=3/2$, moment is determined by spin, orbital component is quenched
  \[
  \mu_{\text{eff}}^2 = g_J \sqrt{J(J+1)} \mu_B = \sqrt{15} \mu_B = 3.87 \mu_B
  \]

- Maximum (asymptotic) value:
  \[
  \mu_H = 2J \mu_B = 3 \mu_B
  \]
  (compare to the classic value)

Magnetic moment of KCr(SO$_4$)$_2$·12 H$_2$O, at fields up to 50,000 Oe and at 4.2 K

From Cullity, 2009
Lecture recap

- **Diamagnetism (susceptibility is negative)**
  - All atoms
  - Classical, due to addition of magnetic moment to the electron orbital current

- **Band (Pauli) paramagnetism**
  - Due to alignment of spins of free electrons
  - Spins of the electrons at the Fermi surface can be affected

- **Atomic paramagnetism**
  - Due to alignment of existing magnetic moments of atomic electrons
  - Needs quantum assessment of magnetic moments of electrons (S, L, J) and statistics