Spectroscopic Investigations of Magnetic Anisotropy in Molecular Nanomagnets

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A.J. Orchard – Magnetochemistry, 2003
1. Introduction
2. Single Crystal Magnetometry
3. High-Frequency EPR Spectroscopy
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Magnetic anisotropy. The highly simplified, hand-waving explanation

- Magnetic anisotropy means that the magnetic properties (of the molecule) have an orientational dependence.
- This means that the response to an external magnetic field depends on the direction in the molecule along which the field is applied, e.g., $g$-value anisotropy, hard/easy axes of magnetization.
- Susceptibility becomes anisotropic. $\mathbf{M} = \chi \mathbf{H}$
  $$\chi = \begin{pmatrix} \chi_{xx} & 0 & 0 \\ 0 & \chi_{yy} & 0 \\ 0 & 0 & \chi_{zz} \end{pmatrix}$$
- This also means that the magnetic moment of the molecule prefers (lower potential energy) to lie along a certain direction, e.g., double well picture in transition metals.

\[
\Delta E = |D|S^2
\]
Ch. 1. Introduction
Section 1.1 Magnetic anisotropy

Magnetic anisotropy. The highly simplified, hand-waving explanation

- Electrons experience the following interactions:
  - attraction to the nucleus (Coulomb)
  - repulsion by other electrons
  - spin-orbit coupling
  - crystal field (Coulomb)
  - magnetic field (Zeeman)

<table>
<thead>
<tr>
<th>Effect</th>
<th>System</th>
<th>Energy equivalent wavenumber/cm⁻¹ (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron-electron interaction (H_{ee})</td>
<td>3d, 4d, 5d</td>
<td>3d &gt; 4d &gt; 5d (\approx 10^4) (^b)</td>
</tr>
<tr>
<td></td>
<td>4f, 5f</td>
<td>4f &gt; 5f (\approx 10^4) (^b)</td>
</tr>
<tr>
<td>Ligand-field potential  (H_{LF})</td>
<td>3d, 4d, 5d</td>
<td>3d &gt; 4d &lt; 5d (\approx 2 \times 10^3) (^b)</td>
</tr>
<tr>
<td></td>
<td>4f</td>
<td>(\approx 10^2)</td>
</tr>
<tr>
<td></td>
<td>5f</td>
<td>(\approx 10^3)</td>
</tr>
<tr>
<td>Spin-orbit coupling     (H_{SO})</td>
<td>3d, 4d, 5d</td>
<td>3d &lt; 4d &lt; 5d (\approx 10^3) (^b)</td>
</tr>
<tr>
<td></td>
<td>4f, 5f</td>
<td>4f &lt; 5f (\approx 10^3) (^b)</td>
</tr>
<tr>
<td>Exchange interaction (H_{ex})</td>
<td>nd</td>
<td>(\leq 10^2)</td>
</tr>
<tr>
<td></td>
<td>4f</td>
<td>(&lt; 1)</td>
</tr>
<tr>
<td></td>
<td>nd-4f</td>
<td>(&lt; 10)</td>
</tr>
<tr>
<td>Magnetic field          (H_{mag})</td>
<td>(\approx 0.5) (1 T)</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) | (a) strong field lanthanide system ; (b) weak field lanthanide system

- The main difference between 3d transition metals and f-elements is that the crystal field and exchange interactions are much weaker in the latter, while spin-orbit coupling can be much stronger.

Lueken99, Lueken08
A highly simplified, hand-waving explanation.

- Most free ions have an orbital angular momentum (except d⁵ high-spin).
- In most complexes, the orbital angular momentum appears to have disappeared. (quenching of the orbital moment).
- This is due to the crystal field splitting of the d-orbitals ("t_{2g} - e_g").
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Section 1.2 Magnetic anisotropy in Transition Metal Clusters

Quenching of the orbital moment.

- Orbital angular momentum is generally pictured as a circular motion of electrons around the nucleus.
- The (classical) orbital angular momentum is
  \[ \vec{l} = \vec{r} \times \vec{p} \]
- Translated into quantum mechanics, we can picture orbital angular momentum as being due to a circular motion of the electron through degenerate orbitals, that are related by a rotation.
- For example:
  - \( d_{xz} / d_{xy} \) (x axis)
  - \( d_{xy} / d_{x^2 - y^2} \) (z axis)
  - \( p_x / p_y \) (z axis).
Quenching of the orbital moment.

- In transition metal complexes, the degeneracy of the d-orbitals is lifted by the interaction with the ligands (crystal/ligand field splitting).

- As a result, the circular motion is no longer possible and the orbital angular momentum disappears.

- For $O_h$ and $T_d$ complexes, only in certain cases an orbital angular momentum is retained.

- Importantly, in lower symmetry, fewer orbitals are degenerate:

<table>
<thead>
<tr>
<th>Orbital contribution?</th>
<th>Ground state type</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>E</td>
</tr>
<tr>
<td>Yes</td>
<td>T</td>
</tr>
<tr>
<td>No</td>
<td>A</td>
</tr>
</tbody>
</table>
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Section 1.2 Magnetic anisotropy in Transition Metal Clusters

g-Value anisotropy.

- Spin orbit coupling reintroduces orbital angular momentum (2nd order perturbation).

- Quantitative formula:

\[ g_{\alpha\alpha} = g_e + 2\lambda \sum_m \frac{\langle m | \hat{L}_\alpha | 0 \rangle \langle 0 | \hat{L}_\alpha | m \rangle}{E_m - E_0} \]

\[ g = g_e E + 2\lambda \Lambda \]

- \( \alpha = x, y, \) or \( z; \) \( m \) is the excited d-orbital.

- For \( d_{xy} - d_{x^2-y^2} \) mixing induced by \( l_z \):

\[ g_{zz} = g_e + 2\lambda \frac{-2i \times 2i}{E_{xy} - E_{x^2-y^2}} = g_e - \frac{8\lambda}{E_{xy} - E_{x^2-y^2}} \]

- \( \lambda > 0 \) for \( d^1 \) \( \Rightarrow \) \( g_z = g_{||} < g_e \).

- Anisotropy must correspond to point group symmetry.
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Section 1.2 Magnetic anisotropy in Transition Metal Clusters

Types of anisotropy.

• In transition metals we have three kinds:

1. Zero-field splitting: We can express the $D$ tensor in terms of $\Lambda$.

\[
D_{\alpha\alpha} = \lambda^2 \sum_m \frac{\langle m|\hat{I}_\alpha|0 \rangle \langle 0|\hat{I}_\alpha|m \rangle}{E_m - E_0}; \quad D = \lambda^2 \Lambda
\]

2. $g$-anisotropy:

\[
g_{\alpha\alpha} = g_e + 2\lambda \sum_m \frac{\langle m|\hat{I}_\alpha|0 \rangle \langle 0|\hat{I}_\alpha|m \rangle}{E_m - E_0}; \quad g = g_e E + 2\lambda \Lambda
\]

• Relation between ZFS and $g$ value anisotropy (this relation does not always hold).

\[
D = \frac{\lambda}{2} \left[ g_z - \frac{g_x + g_y}{2} \right]
\]

\[
E = \frac{\lambda}{4} (g_x - g_y)
\]

3. Anisotropic, antisymmetric exchange interactions

Mabbs/Machin; Atherton; Abragam/Bleaney

\[
D = \begin{pmatrix}
D_{xx} & 0 & 0 \\
0 & D_{yy} & 0 \\
0 & 0 & D_{zz}
\end{pmatrix}
\]

\[
D = \frac{3}{2} D_{zz}, \quad E = \frac{1}{2} |D_{xx} - D_{yy}|
\]

\[
g = \begin{pmatrix}
g_{xx} & 0 & 0 \\
0 & g_{yy} & 0 \\
0 & 0 & g_{zz}
\end{pmatrix}
\]

Table 4.2 [E] Angular momentum operations on the real p and d orbitals

<table>
<thead>
<tr>
<th>$l_z$</th>
<th>$l_y$</th>
<th>$l_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>x\rangle$</td>
<td>0</td>
</tr>
<tr>
<td>$</td>
<td>y\rangle$</td>
<td>$i</td>
</tr>
<tr>
<td>$</td>
<td>z\rangle$</td>
<td>$-i</td>
</tr>
<tr>
<td>$</td>
<td>x^2-y^2\rangle$</td>
<td>$-i</td>
</tr>
<tr>
<td>$</td>
<td>xy\rangle$</td>
<td>$i</td>
</tr>
<tr>
<td>$</td>
<td>yz\rangle$</td>
<td>$-i</td>
</tr>
<tr>
<td>$</td>
<td>zx\rangle$</td>
<td>$-\sqrt{3}i</td>
</tr>
</tbody>
</table>
Zero-Field Splitting in Transition Metal Clusters.

- The cluster zero-field splitting is a linear combination of:
  - single-ion zero-field splittings,
  - dipolar spin-spin interaction (usually a minor contribution)

\[
D^{si}_S = \sum_i d_i D_i + \sum_{i<j} d_{ij} D_{ij}
\]

- In addition anisotropic and antisymmetric exchange interactions lead to energy splittings in zero field.

Factors of Importance

1. Magnitude and sign of projection coefficients \(d_i\).
2. Orientation of single ion zero-field splitting.
3. Magnitude and sign of single ion zero-field splitting.
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Section 1.2 Magnetic anisotropy in Transition Metal Clusters

Zero-Field Splitting in Transition Metal Clusters.

1. Magnitude and sign of projection coefficients $d_i$.
   
   - Projection coefficients $d_i < 1$.
   - For each pairwise coupling $D$ decreases.
   - In the end the energy barrier is only linearly dependent on the spin of the ground state:

   $$d_i = \frac{S_i(2S_i - 1)}{S(2S - 1)}$$

   $$\Delta E_{\text{max}} = \left( \sum_{i=1}^{N} \frac{2 - 1 / S_i}{2 - 1 / S} \right) |D^S| S^S_i$$

   For $S = n \times S_i$ Waldmann, IC, 2007; Sessoli, ICA, 2008: "Waldmann's dire prediction" (Hill, DT, 2009)
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Zero-Field Splitting in Transition Metal Clusters.

• Example: Mn_{19}: S = 83/2 but very small D. Why?

2. Orientation of single ion zero-field splitting.

$$D_{S}^{si} = \sum_{i} d_{i} D_{i}$$

Ako, Powell, ACIE, 2006

[Mn_6O_4Br_4(Me_2dbm)_6]
Aromí, JACS, 99
S = 12
D = 0.009 cm\(^{-1}\)

[Mn_6O_2(sao)_6(O_2CPh)_2(EtOH)_4]
Milios, JACS, 07
S = 12
D = -0.43 cm\(^{-1}\)
Energy scales in Transition Metals.

- Example Mn$^{3+}$, d$^4$ HS

\[ E = \frac{1}{2} J_s \pm \frac{1}{2} \alpha \cdot \mathbf{S} \cdot \mathbf{L} \]

- Electron repulsion
- Ligand Field $O_h$
- Ligand Field $D_{4h}$ elongated
- Spin-Orbit Coupling

ZFS
- $m_s = 0$
- $m_s = \pm 1$
- $m_s = \pm 2$
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Section 1.3 Magnetic anisotropy in f-Elements

Energy scale of interactions- Example Tb^{3+}

- Electron repulsion
- Spin-orbit coupling
- Crystal-field splitting

describe ground doublet as effective spin 1/2 with very anisotropic $g$
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Section 1.3 Magnetic anisotropy in f-Elements

Dieke Diagram

- Because f-electrons are little influenced by metal-ligand bonding, a general scheme of energy levels in lanthanides can be constructed (Dieke diagram).

- To a first approximation, the energy difference between multiplets that differ in $J$ only is due to spin-orbit coupling.

- The energy difference between groups of multiplets that differ in $L$ and or $S$ is due to electron repulsion.

- Originally obtained by analysis of the optical (absorption/luminescence) spectra of Ln$^{3+}$:LaCl$_3$ and Ln$^{3+}$:LaF$_3$.

- The thickness of the lines indicates the crystal field splitting.
Susceptibility of free ions

- The susceptibilities of lanthanide compounds at room temperature are often very close to the free ion values.
- Exceptions are Sm\(^{3+}\), Eu\(^{3+}\) (low lying excited J-multiplets).

Table 2: Lanthanide ions: term symbol (ground state), one-electron spin-orbit coupling parameter \(\zeta_{4f}\) [cm\(^{-1}\)], \(g_J\), \(g_J J\), \(J(J + 1)^{1/2}\) and \(\mu_{\text{eff}}^{\text{exp}}\) (295 K) [7]

<table>
<thead>
<tr>
<th>Ln(^{3+})</th>
<th>(4f^N)</th>
<th>(2S+1L_J)</th>
<th>(\zeta_{4f}) (^{(a)})</th>
<th>(g_J)</th>
<th>(g_J J)</th>
<th>(J(J + 1)^{1/2})</th>
<th>(\mu_{\text{eff}}^{\text{exp}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(^{3+})</td>
<td>4f(^{0})</td>
<td>1S(_0)</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce(^{3+})</td>
<td>4f(^{1})</td>
<td>2F(_{5/2})</td>
<td>625</td>
<td>6/7</td>
<td>15/7</td>
<td>2.535</td>
<td>2.3–2.5</td>
</tr>
<tr>
<td>Pr(^{3+})</td>
<td>4f(^{2})</td>
<td>3H(_4)</td>
<td>758</td>
<td>4/5</td>
<td>16/5</td>
<td>3.578</td>
<td>3.4–3.6</td>
</tr>
<tr>
<td>Nd(^{3+})</td>
<td>4f(^{3})</td>
<td>4I(_9/2)</td>
<td>884</td>
<td>8/11</td>
<td>36/11</td>
<td>3.618</td>
<td>3.4–3.5</td>
</tr>
<tr>
<td>Pm(^{3+})</td>
<td>4f(^{4})</td>
<td>5I(_4)</td>
<td>1000</td>
<td>3/5</td>
<td>12/5</td>
<td>2.683</td>
<td>2.9(^{(d)})</td>
</tr>
<tr>
<td>Sm(^{3+})</td>
<td>4f(^{5})</td>
<td>6H(_5/2)</td>
<td>1157</td>
<td>2/7</td>
<td>5/7</td>
<td>0.845</td>
<td>1.6</td>
</tr>
<tr>
<td>Eu(^{3+})</td>
<td>4f(^{6})</td>
<td>7F(_0)</td>
<td>1326</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.5</td>
</tr>
<tr>
<td>Gd(^{3+})</td>
<td>4f(^{7})</td>
<td>8S(_7/2)</td>
<td>1450</td>
<td>2</td>
<td>7</td>
<td>7.937</td>
<td>7.8–7.9</td>
</tr>
<tr>
<td>Tb(^{3+})</td>
<td>4f(^{8})</td>
<td>7F(_0)</td>
<td>1709</td>
<td>3/2</td>
<td>9</td>
<td>9.721</td>
<td>9.7–9.8</td>
</tr>
<tr>
<td>Dy(^{3+})</td>
<td>4f(^{9})</td>
<td>6H(_{15/2})</td>
<td>1932</td>
<td>4/3</td>
<td>10</td>
<td>10.646</td>
<td>10.2–10.6</td>
</tr>
<tr>
<td>Ho(^{3+})</td>
<td>4f(^{10})</td>
<td>5I(_8)</td>
<td>2141</td>
<td>5/4</td>
<td>10</td>
<td>10.607</td>
<td>10.3–10.5</td>
</tr>
<tr>
<td>Er(^{3+})</td>
<td>4f(^{11})</td>
<td>4I(_{15/2})</td>
<td>2369</td>
<td>6/5</td>
<td>9</td>
<td>9.581</td>
<td>9.4–9.5</td>
</tr>
<tr>
<td>Tm(^{3+})</td>
<td>4f(^{12})</td>
<td>3H(_6)</td>
<td>2628</td>
<td>7/6</td>
<td>7</td>
<td>7.561</td>
<td>7.5</td>
</tr>
<tr>
<td>Yb(^{3+})</td>
<td>4f(^{13})</td>
<td>2F(_{7/2})</td>
<td>2870</td>
<td>8/7</td>
<td>4</td>
<td>4.536</td>
<td>4.5</td>
</tr>
<tr>
<td>Lu(^{3+})</td>
<td>4f(^{14})</td>
<td>1S(_0)</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{(a)}\) The relation between \(\zeta_{4f}\) and \(\lambda_{LS}\) of the Russell-Saunders ground term is given by \(\lambda_{LS} = \pm (\zeta_{4f} / 2S)\), where (+) and (−) sign correspond to \(N ≤ 2l + 1\) and \(N ≥ 2l + 1\), respectively.

\(^{(b)}\) Definition: \(X_m = \mu_0 N_s \mu_B^2 \mu_{\text{eff}}^{\text{exp}} / (3 k_0 T)\).

\(^{(d)}\) diamagnetic

\(^{(d)}\) observed for Nd\(^{3+}\) compounds.
Ch. 1. Introduction
Section 1.3 Magnetic anisotropy in f-Elements

Crystal field splitting

• Going from a free ion to a compound, the symmetry around the f-element ion is lowered, leading to splitting of the states.

• Group theory can be exploited to predict the way in which the terms split (symmetry aspect).

• The magnitude of the splitting can be obtained from crystal field theory (purely Coulombic interaction of point dipoles) or ligand field theory (taking into account σ-bonding) (energy aspect).
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Crystal field splitting: Stevens operator equivalents

• We can write the electrostatic potential created by the ligands as an expansion in terms of spherical harmonics.

• The resulting operators act on each f-electron separately, hence for each state \( |J M_J\rangle \), the corresponding wavefunction must be determined. This is rather complicated.

• In order to reproduce the splittings, we can replace the coordinates in the spherical harmonics by angular momentum operator components, which have simple properties.

• \( x \rightarrow \hat{J}_x, \; y \rightarrow \hat{J}_y, \; z \rightarrow \hat{J}_z, \; r \rightarrow \sqrt{J(J+1)} \)

• To take into account the noncommutation between the angular momentum operators, we have to form symmetrized products, e.g.

\[
x y \rightarrow \frac{1}{2} \left( \hat{J}_x \hat{J}_y + \hat{J}_y \hat{J}_x \right)
\]

• We end up with a Hamiltonian of the form

\[
\hat{H}_{LF} = \sum_{q=-2}^{+2} B^q_2 \hat{O}^q_2 + \sum_{q=-4}^{+4} B^q_4 \hat{O}^q_4 + \sum_{q=-6}^{+6} B^q_6 \hat{O}^q_6
\]

• The parameters \( B^q_k \) are taken as free parameters

Lueken; Boča
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Section 1.3 Magnetic anisotropy in f-Elements

Crystal field splitting: Stevens operator equivalents

- A table of common Stevens operator equivalents and the related spherical harmonics

\[ Y_0^2 = \frac{\sqrt{5} \cdot 3z^2 - r^2}{16\pi \cdot r^2} \]
\[ \hat{O}_z^2 = \frac{\sqrt{15} \cdot (x \pm iy)^2}{32\pi \cdot r^2} \]
\[ \hat{O}_z^2 = \frac{\sqrt{9} \cdot 35z^4 - 30z^2r^2 + 3r^4}{256\pi \cdot r^4} \]
\[ \hat{O}_z^2 = \frac{\sqrt{315} \cdot (x \pm iy)^4}{512\pi \cdot r^4} \]

- The properties of the angular momentum operators.

\[ \hat{J}^2 | J \, m_j > = J(J + 1) | J \, m_j > \]
\[ \hat{J}_z | J \, m_j > = m_j | J \, m_j > \]
\[ \hat{J}_+ | J \, m_j > = \sqrt{J(J + 1) - m_j(m_j + 1)} | J \, m_j + 1 > \]
\[ \hat{J}_- | J \, m_j > = \sqrt{J(J + 1) - m_j(m_j - 1)} | J \, m_j - 1 > \]

Lueken; Abragam, Bleany.
Crystal field splitting: Symmetry

- Furthermore, the CF Hamiltonian must have the same symmetry as the complexed ion.
- Hence, with increasing symmetry, more terms must be zero by symmetry.
- For example in $D_{4d}$ symmetry, the crystal field Hamiltonian reads: $\hat{H}_{CF} = B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_6^0 \hat{O}_6^0$
- A Table of nonzero CF parameters in different symmetries, ± means parameters with both +q and −q are nonzero.

| $k$ | $|q|$ | $D_{2h}$ | $D_{3h}$ | $D_{4h}$ | $D_{5h}$ | $D_{2d}$ | $C_{2v}$ | $C_{3v}$ | $C_{4v}$ | $C_{5v}$ | $C_{2h}$ | $C_{3h}$ | $C_{4h}$ | $C_{5h}$ | $S_4$ | $C_1$ |
|-----|------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|-------|-------|
| 2   | 0    | +       | +       | +       | +       | +       | +       | +       | +       | +       | +       | +       | +       | ±     | ±     |
| 2   | 1    |         |         |         |         |         |         |         |         |         |         |         |         |         |       |       |
| 2   | 2    | +       |         |         |         |         |         |         |         | ±       | ±       | ±       | ±       |         | ±     | ±     |
| 4   | 0    | +       | +       | +       | +       | +       | +       | +       | +       | +       | +       | +       | +       |       | ±     |
| 4   | 1    |         |         |         |         |         |         |         |         | ±       | ±       | ±       | ±       |         | ±     | ±     |
| 4   | 2    | +       |         |         | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       |         | ±     | ±     |
| 4   | 3    | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       |         | ±     | ±     |
| 6   | 0    | +       | +       | +       | +       | +       | +       | +       | +       | +       | +       | +       | +       |       | ±     |
| 6   | 1    |         |         |         |         |         |         |         |         |         | ±       | ±       | ±       | ±       | ±       | ±     | ±     |
| 6   | 2    | +       |         |         | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±     | ±     |
| 6   | 3    | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±     | ±     |
| 6   | 4    | +       | +       | +       | +       | +       | +       | +       | +       | +       | +       | +       | +       | ±       | ±     | ±     |
| 6   | 5    |         |         |         |         |         |         |         |         |         | ±       | ±       | ±       | ±       | ±       | ±     | ±     |
| 6   | 6    | +       | +       |         |         |         |         | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±       | ±     | ±     |
Crystal field splitting: Kramers Theorem

- Whatever the symmetry, for an odd number of electrons, all microstates are doubly degenerate, in the absence of a magnetic field.
- This is known as Kramers' theorem, and ions with half integer angular momentum ground states are called Kramers ions.
- This degeneracy has major implications for spin dynamics, in that quantum tunnelling cannot be induced by the crystal field.
Ch. 1. Introduction
Section 1.3 Magnetic anisotropy in f-Elements

Crystal field splitting: Crystal quantum number

- A crystal field interaction term $B_k^q \hat{O}_k^q$ will mix $m_J$ states only if $m_J - m_J' = q$.
- We can define a new quantum number, the crystal quantum number $\mu$ to designate a group of states satisfying $m_J = \mu \pmod{q}$, i.e. $m_J = \mu + n q$ ($n$ = integer).

- For even numbers of electrons:
  \[ q = 2 : \quad \mu = 0^+, 0^-, 1^+, 1^-; \]
  \[ q = 3 : \quad \mu = 0^+, 0^-, \pm 1; \]
  \[ q = 4 : \quad \mu = 0^+, 0^-, \pm 1, 2^+, 2^-; \]
  \[ q = 5 : \quad \mu = 0^+, 0^-; \pm 1, \pm 2; \]
  \[ q = 6 : \quad \mu = 0^+, 0^-, \pm 1, \pm 2, 3^+, 3^-; \]

- For odd numbers of electrons:
  \[ q = 2 : \quad \mu = \pm \frac{1}{2}; \]
  \[ q = 3 : \quad \mu = \pm \frac{1}{2}, \pm \frac{3}{2}; \]
  \[ q = 4 : \quad \mu = \pm \frac{1}{2}, \pm \frac{3}{2}; \]
  \[ q = 5 : \quad \mu = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2}; \]
  \[ q = 6 : \quad \mu = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2}. \]

- For odd numbers of electrons, there is a one-to-one correspondence with the irreducible representations that the states belong to.
- For even numbers of electrons, the groups of states can contain states belonging to two different irreducible representations, which can be distinguished using $0^+, 0^-$ and $1^+, 1^-$. 
- $\pm \mu$ states are degenerate
Ch. 1. Introduction
Section 1.3 Magnetic anisotropy in f-Elements

Crystal field splitting: Crystal field ground states

- The shape of the electron distribution is different for the different CF states.
- Hence by choosing the ligands, one can influence the CF state energies.
- Hence different ground states can be obtained.
- The ground state and the energy splittings can be influenced by judicious choice of the ligands.
- Note that the $m_J$ states are the eigenstates only in $C_{oo'}$, $D_{oo'h}$ and $D_{4d}$ symmetries.

Ch. 1. Introduction
Section 1.3 Magnetic anisotropy in f-Elements

**Magnetic and spectroscopic measurements**

- The magnetic susceptibility is the thermal average of the contributions due to the occupied microstates.
- Luminescence spectroscopy allows direct determination of the splitting of the ground Russell-Saunders multiplet.
- Absorption/MCD spectroscopy allows determination of CF splittings of excited states: beyond Russell-Saunders coupling. (intermediate coupling: CF and SOC at same level)
- Far infrared/inelastic neutron scattering allows investigation of intramultiplet excitations.
1. Introduction
2. Single Crystal Magnetometry
3. High-Frequency EPR Spectroscopy
4. Inelastic Neutron Scattering
5. Electronic Absorption and Luminescence
Ch. 2. Single Crystal Magnetometry

Contents

2.1 Motivation

2.2 Magnetic susceptibility tensor

2.3 Determination

(0) Large enough crystal
(1) Faceindex
(2) Define the experimental space
(3) Transformation matrix
(4) Mount the crystal
(5) Three orthogonal rotations
(6) Fitting the tensor elements
(7) Symmetry and equivalent considerations
(8) Diagonalization
(9) Express in abc space
(10) ground state determination
Ch. 2. Single Crystal Magnetometry

Section 2.1 Motivation

- Determination of the molecular principal axes
- magneto-relations
- Possibility of ground state determination

\[ g_{//}^{\text{eff}} = 2 g_J \langle \pm J_z | \hat{J}_z | \pm J_z \rangle \]

Ch. 2. Single Crystal Magnetometry

Section 2.2 magnetic susceptibility tensor

- Molecular $\chi$ tensor relation:

\[
\chi_{ij}^m = (A_p^q)\chi_{ij}^m (A_p^q)^+ 
\]

- In the paramagnetic limit, crystal behavior is the sum of all the molecules’ one in the unit cell, so is $\chi$ tensor;

\[
\chi_{ij}^{\text{Cry}} = \sum_q \chi_{ij}^m = \sum_q (A_p^q)\chi_{ij}^m (A_p^q)^+ 
\]

- In the paramagnetic limit, the molecular $\chi$ tensor can be fully determined only when the molecule symmetry is not lower than the crystal symmetry:

(a) Only one symmetrically independent molecule in the unit cell;
(b1) The molecules are related by inversion center (P-1 space group) or
(b2) The molecule is at highest symmetry position;

Neumann’s Principle:

*the symmetry elements of any physical property of a crystal must include all the symmetry elements of the point group of the crystal*
Ch. 2. Single Crystal Magnetometry

Section 2.3 Determination

(0) large enough single crystal
- The background of the rotator provided by Quantum Design MPMS-XL SQUID is around $10^{-4}$ emu;
- The crystal should be larger than 0.5 mg;

(1) Face index
Ch. 2. Single Crystal Magnetometry
Section 2.3 Determination

(2) Define the experimental space
• b as X axis;
• (001) is XY plane;
• Z follows right hand rule;

(3) Transformation matrix
• Derive the abc unit vector into the same length!
• High school geometry game
• Complicated!

\[
\begin{pmatrix}
\vec{a} \\
\vec{b} \\
\vec{c}
\end{pmatrix} = \begin{bmatrix}
1.78 & 9.41 & 0 \\
11.93 & 0 & 0 \\
2.40 & 0.71 & 12.18
\end{bmatrix} \begin{pmatrix}
\vec{X} \\
\vec{Y} \\
\vec{Z}
\end{pmatrix}
\]
(4) **Mount the crystal**

- L shaped Cu-Be support: small background;
- Fixed with Apiezon N-grease;

This abc-XYZ relation is not the one defined before.
Ch. 2. Single Crystal Magnetometry
Section 2.3 Determination

(5) Three orthogonal rotations

![Diagram showing three orthogonal rotations](image)
Ch. 2. Single Crystal Magnetometry

Section 2.3 Determination

(6) Fitting the $\chi$ tensor elements

\[
M = H_0 \begin{pmatrix} \sin \theta \cos \varphi \\ \sin \theta \sin \varphi \\ \cos \theta \end{pmatrix}^T \begin{pmatrix} \chi_{xx} & \chi_{xy} & \chi_{xz} \\ \chi_{yx} & \chi_{yy} & \chi_{yz} \\ \chi_{zx} & \chi_{zy} & \chi_{zz} \end{pmatrix} \begin{pmatrix} \sin \theta \cos \varphi \\ \sin \theta \sin \varphi \\ \cos \theta \end{pmatrix}
\]

\[
\chi = \frac{M}{H_0} = \chi_{xx} \sin^2 \theta \cos^2 \varphi + \chi_{yy} \sin^2 \theta \sin^2 \varphi + \chi_{zz} \cos^2 \theta + 2\chi_{xy} \sin^2 \theta \cos \varphi \sin \varphi + 2\chi_{xz} \cos \theta \sin \theta \cos \varphi + 2\chi_{yz} \cos \theta \sin \theta \sin \varphi.
\]

\[
\chi_x(\delta) = \chi_{yy} \cos^2(\delta) + \chi_{zz} \sin^2(\delta) + 2\chi_{yz} \sin(\delta) \cos(\delta),
\]

\[
\chi_y(\delta) = \chi_{xx} \sin^2(\delta) + \chi_{zz} \cos^2(\delta) - 2\chi_{xz} \sin(\delta) \cos(\delta),
\]

\[
\chi_z(\delta) = \chi_{xx} \sin^2(\delta) + \chi_{yy} \cos^2(\delta) + 2\chi_{xy} \sin(\delta) \cos(\delta).
\]

Surface fitting with two variables

Curve fitting with one variables (three functions parallelly)
(7) Symmetry and equivalent considerations

- Neuman’s principle: \( \mathbf{b} \) of monoclinic system is always one of the principal axes
- equivalent positions

\[
\begin{bmatrix}
8.40 & 1.43 & -10.61 \\
1.43 & 1.22 & -1.96 \\
-10.61 & -1.96 & 15.7019
\end{bmatrix}
\]

\( \chi \) tensor in XYZ space
Ch. 2. Single Crystal Magnetometry
Section 2.3 Determination

(8) Diagonalization

Fitting results
\[
\begin{bmatrix}
8.40 & 1.43 & -10.61 \\
1.43 & 1.22 & -1.96 \\
-10.61 & -1.96 & 15.7019
\end{bmatrix}
\]

Diagonalization

\[
\begin{bmatrix}
23.54 \\
0.96 \\
0.82
\end{bmatrix}
\]
eigenvalues

Eigenvectors in abc
\[
\{-0.0164857,-0.0593218,0.0664437\}
\]
\[
\{-0.102119,0.00984252,-0.0168336\}
\]
\[
\{0.0249881,-0.0625164,-0.0452197\}
\]

\[
\begin{bmatrix}
\bar{a} \\
\bar{b} \\
\bar{c}
\end{bmatrix}
= \begin{bmatrix}
1.78 & 9.41 & 0 \\
11.93 & 0 & 0 \\
2.40 & 0.71 & 12.18
\end{bmatrix}
\begin{bmatrix}
\bar{X} \\
\bar{Y} \\
\bar{Z}
\end{bmatrix}
\]
eigenvectors in XYZ
Ch. 2. Single Crystal Magnetometry

Section 2.3 Determination

(9) expressed in abc space
(10) **Ground state determination**

- Curie Law: Population is not changed a lot in the temperature range
- The first excited state is high enough.

\[
\chi T = \frac{1}{8} g^2 S(S + 1)
\]

\[
g_{\parallel}^{\text{eff}} = 2 g_J \left\langle \pm J_z \left| \hat{J}_z \right| \pm J_z \right\rangle
\]
Ch. 1. Introduction

Magnetic Anisotropy

Field-independent:
Crystal-Field Splitting

Field-independent:
Zero-Field Splitting

Field-dependent:
g-value Anisotropy

Transition Metal Clusters

Molecular Nanomagnets

Spectroscopic techniques

high-frequency
electron paramagnetic resonance

inelastic neutron scattering

electronic absorption,
luminescence
1. Introduction
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Ch. 3. High-Frequency EPR
Section 3.1 Theoretical Background and Experimental Considerations

Basics of EPR

- The **Zeeman term** describes the interaction of the spin with a magnetic field.
- In the absence of other interactions the field is chosen along the z-axis.
- The electronic Zeeman term then has the form:
  \[ \hat{H}^{\text{Zeeman}} = g \mu_B B \hat{S}_z \]
- Accordingly, the energies of the spin states depend on \( m_S \):
  \[ E = g \mu_B B m_S \]
  \( \text{Note: remember } \hat{S}_z |S m_s l m_l> = m_s |S m_s l m_l> \).
- \( g = 2.00235... \) for a free electron.

\[
\begin{align*}
E &= +\frac{1}{2} g \mu_B B & \alpha \\
E &= -\frac{1}{2} g \mu_B B & \beta
\end{align*}
\]

For \( S = 1/2 \)

\[
\begin{align*}
E &= +\frac{5}{2} g \mu_B B \\
E &= +\frac{3}{2} g \mu_B B \\
E &= +\frac{1}{2} g \mu_B B \\
E &= -\frac{1}{2} g \mu_B B \\
E &= -\frac{3}{2} g \mu_B B \\
E &= -\frac{5}{2} g \mu_B B
\end{align*}
\]

For \( S = 5/2 \)
Ch. 3. High-Frequency EPR

Section 3.1 Theoretical Background and Experimental Considerations

Basics of EPR

• For $S = 1/2$, the energy difference between the two $m_S$ levels is: $\Delta E = g \mu_B B$

• If the energy of the electromagnetic radiation matches the energy difference, radiation can be absorbed. The spin interacts with the magnetic field of the electromagnetic radiation.

• This is called the **resonance condition**: $h\nu = g \mu_B B$

• For technical reasons, in EPR conventionally the frequency is kept constant, while the field is swept.

• The EPR selection rule is therefore $\Delta S = 0, \Delta m_S = \pm 1$ (perpendicular mode)
Basics of EPR – Selection rules.

• Which transitions can be observed?

• Typically microwave magnetic field \( \mathbf{b}_1 \perp \) external magnetic field \( \mathbf{B}_0 \).

• What about the Zeeman interaction of \( \mathbf{b}_1 \) with the spin?
  \[
  \hat{H}^{\text{Zeeman}} = g \mu_B \mathbf{b}_1 \hat{S}_{x,y}
  \]

• What is the action of \( \hat{S}_x \) and \( \hat{S}_y \) on the spin state \( |S \, m_s \, l \, m_l > \) ?

• It is useful to make combinations of \( \hat{S}_x \) and \( \hat{S}_y \), called shift operators:
  \[
  \hat{S}^+_i = \hat{S}_x + i \hat{S}_y \quad \hat{S}^-_i = \hat{S}_x - i \hat{S}_y
  \]

• The shift operators change the \( m_s \) quantum number by \( \pm 1 \):
  \[
  \hat{S}^+_i |S \, m_s > = \sqrt{S(S+1) - m_s (m_s + 1)} \quad |S \, m_s + 1 > \\
  \hat{S}^-_i |S \, m_s > = \sqrt{S(S+1) - m_s (m_s - 1)} \quad |S \, m_s - 1 >
  \]

• The EPR selection rule is therefore \( \Delta m_s = \pm 1 \)

• In addition \( \Delta S = 0 \).
Basics of EPR – High-frequency EPR

- Conventional EPR uses 9 GHz radiation frequency.
- High-frequency EPR with frequencies up to 1000 GHz possible.
- High-frequency means high field, which gives increased g-value resolution.
- This is usually not of interest in molecular magnetism.
Ch. 3. High-Frequency EPR
Section 3.1 Theoretical Background and Experimental Considerations

Zero-Field Splitting: Axial ZFS

- Spin Hamiltonian: \( \hat{H}_{ZFS} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) = D\hat{S}_z^2 + \frac{1}{2} E(\hat{S}_+^2 + \hat{S}_-^2) \)
- The \( D \) parameter lifts the degeneracy of the \( m_s \) levels.
- For \( D < 0 \), the \( m_s = \pm S \) levels are lowest in energy.
- For \( D > 0 \), the \( m_s = 0 \) or \( m_s = \pm \frac{1}{2} \) are lowest in energy.
- \( D \) can be \( 0-10^2 \) cm\(^{-1} \).

- For \( S = 1 \), energy gap between \( m_s = 0 \) or \( m_s = \pm 1 \) equals \( D \).

\[
\begin{align*}
S = 1 \\
m_S = +1 & \quad m_S = 0 & \quad m_S = \pm 1 \\
m_S = 0 & \quad m_S = \pm 1 & \quad m_S = 0 \\
m_S = -1 & \quad D < 0 & \quad D > 0
\end{align*}
\]
Ch. 3. High-Frequency EPR
Section 3.1 Theoretical Background and Experimental Considerations

Large Zero-Field Splitting.

- Only $\Delta M_S = \pm 1$ allowed.
- At X-band microwave quantum too small.
- At higher frequencies transitions can be observed.
- Large ZFS ions with integer spin are therefore traditionally called EPR silent.
Ch. 3. High-Frequency EPR
Section 3.1 Theoretical Background and Experimental Considerations

High-Field limit

\( S = 1, \ D = -1 \ \text{cm}^{-1} = -30 \ \text{GHz}, \ \nu = 150 \ \text{GHz}, \ T = 300 \ \text{K} \)

\[ \vartheta = 0: B_0 || z \quad \text{and} \quad \vartheta = 90: B_0 || z \]
Ch. 3. High-Frequency EPR

Section 3.1 Theoretical Background and Experimental Considerations

High-Field limit

$S = 1, D = -1 \text{ cm}^{-1} = -30 \text{ GHz}, \nu = 150 \text{ GHz}, T = 300 \text{ K}$

Absorption

First derivative

Forbidden transition
Ch. 3. High-Frequency EPR

Section 3.1 Theoretical Background and Experimental Considerations

High-Field limit

- \([\text{Ni}(5\text{-methylpyrazole})_6](\text{ClO}_4)_2\]
- \(S = 1, D = 0.72 \text{ cm}^{-1} = 21.6 \text{ GHz}, T = 100 \text{ K}\)

Ch. 3. High-Frequency EPR
Section 3.1 Theoretical Background and Experimental Considerations

High-Field limit

- HF EPR allows the determination of the sign of D

At low temperature, and $B_0 \parallel z$:

- For $D < 0$ the low field line remains.
- For $D > 0$, the high field line remains.

$B_0 \parallel z$, $S = 3$, $D < 0$

$S = 3$, $D > 0$
High-Frequency EPR

Section 3.1 Theoretical Background and Experimental Considerations

High-Field limit

- For $g m_B H >> D$ and uniaxial anisotropy there are 2S resonance lines.
- The resonance fields are given by:
  - $B_{//} = (g_e/g_\parallel)[B_0+(2M_S-1)D]$  
  - $B_{\perp} = (g_e/g_\perp)[B_0-(2M_S-1)D/2]$
- Spacing: $2D/g\mu_B$ for $B_{//}$  
  $D/g\mu_B$ for $B_{\perp}$
- Example: $D$ negative
Ch. 3. High-Frequency EPR

Section 3.2 Examples

Example \([\text{Fe}_4(L)_2(dpm)_6]\)

- \(L = 2\)-(bromomethyl)-2-(hydroxymethyl)-1,3-propanediol.
- Antiferromagnetic exchange coupling leads to \(S = 5\) ground state. \(M_S = -5, -4, \ldots, 4, 5\).
- Lines with large spacing at low fields, lines with small spacing at high field.
- That means that \(D < 0\).
- From fit (black): \(D = -0.432\) cm\(^{-1}\), \(B_4^0 = 2 \times 10^{-5}\) cm\(^{-1}\).
- \(B_4^0\) is a higher order ZFS term. \(H_{ZFS} = D \hat{S}_z^2 + B_4^0 \hat{O}_4^0\).

[Accorsi, JACS, 2006]
Ch. 3. High-Frequency EPR

Section 3.2 Examples

Example Ni(PPh₃)₂Cl₂

\[ S = 1, \quad D = +13.20 \text{ cm}^{-1} = 396 \text{ GHz}, \quad E = 1.85 \text{ cm}^{-1}, \quad g = 2.20 \text{ (isotropic)}, \quad T = 4.5 \text{ K} \]

\begin{align*}
2E &= 3.7 \text{ cm}^{-1} \\
D &= 13.2 \text{ cm}^{-1}
\end{align*}

Ch. 3. High-Frequency EPR

Section 3.2 Examples

**Example Ni(PPh₃)₂Cl₂**

\( S = 1, \ D = +13.20 \ \text{cm}^{-1} = 396 \ \text{GHz}, \ E = 1.85 \ \text{cm}^{-1}, \ g = 2.20 \) (isotropic), \( T = 4.5 \ \text{K} \)

Rhombic anisotropy: \( x \)- and \( y \)-axis different, \( \theta \) and \( \varphi \) both important.

\( \theta = 0, \ \varphi = 0: \ B_0 \parallel z \)

\( \theta = 90, \ \varphi = 90: \ B_0 \parallel y \)

\( \theta = 90, \ \varphi = 0: \ B_0 \parallel x \)

Ch. 3. High-Frequency EPR

Section 3.2 Examples

Example Ni(PPh₃)₂Cl₂

$S = 1, \ D = +13.20 \text{ cm}^{-1} = 396 \text{ GHz}, \ E = 1.85 \text{ cm}^{-1}, \ g = 2.20$ (isotropic), \(T = 4.5 \text{ K}\)

Rhombic anisotropy: x- and y-axis different, \(\theta\) and \(\varphi\) both important.

yz-plane  \hspace{1cm} xz-plane  \hspace{1cm} xy-plane

Ch. 3. High-Frequency EPR

Section 3.2 Examples

Example Ni(PPh₃)₂Cl₂

- $B$ not much larger than $D$: no high-field simplification.
- Fictitious 2000 GHz spectrum goes up to 80 T.
Ch. 3. High-Frequency EPR

Section 3.2 Examples

Example Ni(PPh₃)₂Cl₂

- $B$ not much larger than $D$: no high-field simplification.
- Fictitious 2000 GHz spectrum goes up to 80 T.
Ch. 3. High-Frequency EPR
Section 3.1 Theoretical Background and Experimental Considerations

Where can I do high-frequency (ν > 95 GHz) EPR on molecular nanomagnets?

• France: LNCMI Grenoble (Barra)
• Germany: IFW Dresden (Kataev)
• Germany: HLD Dresden (Zvyagin)
• Germany: Uni Stuttgart (Van Slageren)
• Italy: CNR Pisa (Pardi)
• USA: HMFL Tallahassee (Hill, Krzystek, Ozarowski).
• Japan: Kobe (Nojiri)
Ch. 3. High-Frequency EPR
Section 3.3 Frequency domain methods

Frequency Domain Magnetic Resonance

\[ S = \frac{1}{2} \]

**EPR:** External field required

\[ m_S = \frac{1}{2} \]

\[ m_S = -\frac{1}{2} \]

**FDMR:** No field required

Monochromatic sweepable sources vs interferometer (FTIR) based methods

Monochromatic sweepable sources

- synthesizer + multipliers or backward-wave oscillators (+ multipliers)
  - high resolution, easier below 10 cm\(^{-1}\).
  - limited range

Interferometer

- Mercury lamp or synchrotron
  - easy to obtain ultra broad band spectrum, easier at higher frequencies > 25 cm\(^{-1}\)
  - field/frequency not independent.

Ch. 3. High-Frequency EPR
Section 3.3 Frequency domain methods

Example 1. $\left[ \text{Mn}^{\text{III}} \right]_6 \text{O}_2 \left( \text{Me}_2 \text{Bz} \right)_2 \left( \text{Et-sao} \right)_6 \left( \text{EtOH} \right)_4 \right] (\Delta E = 84 \text{ K})$

- $S = 12$. $D = -0.43 \text{ cm}^{-1}$ from magnetisation. $\Delta E = 84 \text{ K}$ (record).
- Powder pellet sample. 6 sharp magnetic resonance lines
- Oscillating baseline due to interference within pellet
- Single scan takes ca. 30 seconds

![Graph showing EPR transmission at different temperatures](image)

Carretta, Van Slageren et al., PRL 2008, Pieper, Van Slageren et al. PRB 2010
Example 1. \([\text{Mn}^{III}_6\text{O}_2(\text{Me}_2\text{Bz})_2(\text{Et-sao})_6(\text{EtOH})_4]\) (\(\Delta E = 84\) K)

- Giant spin model (ground state only).
- \(\mathcal{H} = D\hat{S}_z^2 + B_4^0 \hat{O}_4^0\)
- \(D = -0.362\) cm\(^{-1}\)
- \(B_4^0 = -6.08 \times 10^{-6}\) cm\(^{-1}\)

Carretta, Van Slageren et al., PRL 2008, Pieper, Van Slageren et al. PRB 2010
Section 3.3 Frequency domain methods

Example 1. [Mn$^{III}_6$O$_2$(Me$_2$Bz)$_2$(Et-sao)$_6$(EtOH)$_4$] ($\Delta E = 84$ K)

- Comparison with HFEPR
- Single crystal.
- $D = -0.360(5)$ cm$^{-1}$
- $B_4^0 = -5.7(5) \times 10^{-6}$ cm$^{-1}$
- 7 Frequencies x 7 T sweep....

Datta, Dalton Trans. 2009
Example 2. \([\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]\)

- Read off D and E from single scan.

\[
\begin{align*}
D &= 13.2 \text{ cm}^{-1} \\
2E &= 3.7 \text{ cm}^{-1}
\end{align*}
\]
Ch. 3. High-Frequency EPR
Section 3.3 Frequency domain methods

Example 3. \((\text{NBu}_4)^+\text{[Ln(Pc)]}_2^-\)

- Bruker 113v FTIR, Ln = Ho.

Marx, Dörfel, Moro, Waters, Van Slageren, unpublished
1. Introduction
2. Single Crystal Magnetometry
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4. Inelastic Neutron Scattering
5. Electronic Absorption and Luminescence
Introduction

• Neutrons can have energies in the same range as the microwave/THz electromagnetic radiation used in EPR.

• However, the neutron wavelength is much shorter, and can be of the order of bond distances.

• Some data on the neutron:
  • Mass \( m = 1.674927351(74) \times 10^{-27} \text{ kg} \)
  • Magnetic moment \( \mu = -1.04187563(25) \times 10^{-3} \mu_B \).
  • Spin \( s = \frac{1}{2} \).
  • De Broglie wavelength: \( \lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} = \frac{9.044605}{\sqrt{E[\text{meV}]}} \text{[Å]} \)

• For an energy of \( E = 25 \text{ cm}^{-1} \approx 3 \text{ meV}, \lambda = 5 \text{ Å} \)
• Rather than the wavelength, we can deal with the wave vector \( \vec{k} = \frac{2\pi}{\lambda} \)
Introduction

• Because the wavelength is much shorter than for photons of the same energy, we have to consider momentum conservation in addition to energy conservation.

• Energy conservation: the energy change of the neutron is taken up by the sample: \( \Delta E = \hbar \omega = E_f - E_i \).

• Momentum conservation: \( \Delta k = \hbar Q = \hbar (k_i - k_f) \)

• Neutrons are detected at different angles.

• Time of arrival corresponds to kinetic energy

• Plot of \( S(Q, \omega) \).

• Selection rules \( \Delta S = 0, \pm 1; \Delta m_s = 0, \pm 1 \)
Introduction

• Determining the nature of the excitaton from the Q-dependence.
• Magnetic excitation:

\[ \Delta S = \pm 1: \quad I_{i\rightarrow f}(Q, \omega) \rightarrow 0 \]

\[ \Delta S = 0: \quad I_{i\rightarrow f}(Q, \omega) \rightarrow \text{max} \]

• Phonons:

\[ I(Q, \omega, T) \propto Q^2 \times \frac{1}{1 - e^{\hbar \omega/k_B T}} \]

• Generally confine to low Q to focus on magnetic transitions
Ch. 4. Inelastic Neutron Scattering

Section 4.1 Theoretical background and experimental considerations

Example: Mn6

- Compare INS with FDMR

\[ \lambda = 6.7 \, \text{Å} \]

\[ T = 1.5 \, \text{K} \]

\[ T = 12.0 \, \text{K} \]

\[ T = 17.0 \, \text{K} \]

Pieper, PRB, 2010
Ch. 4. Inelastic Neutron Scattering

Section 4.1 Theoretical background and experimental considerations

FDMR vs HFPEP vs INS

<table>
<thead>
<tr>
<th></th>
<th>HF Cavity EPR</th>
<th>HFPEP/FDMRS</th>
<th>INS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection rules</td>
<td>$\Delta M_S = \pm 1, \Delta S = 0$</td>
<td>$\Delta M_S = \pm 1, \Delta S = 0$</td>
<td>$\Delta M_S = 0, \pm 1, \Delta S = 0, \pm 1$</td>
</tr>
<tr>
<td>Sample quantity</td>
<td>Few mg</td>
<td>50 – 200 mg</td>
<td>1 g</td>
</tr>
<tr>
<td>Resolution</td>
<td>$10^{-2}$ cm$^{-1}$</td>
<td>$10^{-2}$ cm$^{-1}$</td>
<td>0.5 cm$^{-1}$</td>
</tr>
</tbody>
</table>

Intensity determined by Boltzmann populations

Temperature (K)
Example: Mn$_6$

- Take advantage of the $\Delta S = 0, \pm 1$ selection rule of INS
Ch. 4. Inelastic Neutron Scattering
Section 4.1 Theoretical background and experimental considerations

Example: Mn6

- The Q dependence reveals the nature of the spin excitation

\[ \Delta S = \pm 1: \quad I_{i \rightarrow f}(Q, \omega) \rightarrow 0 \]

\[ \Delta S = 0: \quad I_{i \rightarrow f}(Q, \omega) \rightarrow \text{max} \]
1. Introduction
2. Single Crystal Magnetometry
3. High-Frequency EPR Spectroscopy
4. Inelastic Neutron Scattering
5. Electronic Absorption and Luminescence
Ch. 5. Electronic Absorption and Luminescence

Section 5.1 Electronic Absorption

Lanthanides

- f-Orbitals are buried deep within the electron cloud
- ff-transitions are Laporte-forbidden ($u \leftrightarrow u$)
- Hence, the extinction coefficients are very small ($\varepsilon \sim 1 \text{ M}^{-1} \text{ cm}^{-1}$), cf. dd $10^2$, CT $10^4$.
- On the other hand, the absorption bands are very narrow, and split due to the CF splitting of the excited state.

Bünzli in Lanthanide Luminescence: Photophysical, Analytical and Biological Aspects, Springer Ser Fluoresc (2010), DOI 0.1007/4243_2010_3
Ch. 5. Electronic Absorption and Luminescence

Section 5.1 Electronic Absorption

Lanthanides

- Excitations can be electric dipole, magnetic dipole, or electric quadrupole.
- In actinides, extinction coefficients are larger.
- Judd-Ofelt theory describes the absorption intensity of ED transitions.

\[ D_{ED} = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \left| \langle \Psi \| U_j^\lambda \| \Psi' \rangle \right|^2, \]

- Parameters \( \Omega \) are phenomenological.

<table>
<thead>
<tr>
<th>Operator</th>
<th>Parity</th>
<th>( \Delta S )</th>
<th>( \Delta L )</th>
<th>( \Delta J^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ED</td>
<td>Opposite</td>
<td>0</td>
<td>( \leq 6 )</td>
<td>( \leq 6 (2,4,6 \text{ if } J \text{ or } J' = 0) )</td>
</tr>
<tr>
<td>MD</td>
<td>Same</td>
<td>0</td>
<td>0</td>
<td>0, ±1</td>
</tr>
<tr>
<td>EQ</td>
<td>Same</td>
<td>0</td>
<td>0, ±1, ±2</td>
<td>0, ±1, ±2</td>
</tr>
</tbody>
</table>

\( ^aJ = 0 \text{ to } J' = 0 \text{ transitions are always forbidden} \)
Ch. 5. Electronic Absorption and Luminescence
Section 5.2 Luminescence

Lanthanides

- Many lanthanides are strongly luminescent.
Ch. 5. Electronic Absorption and Luminescence

Section 5.2 Luminescence

Lanthanides

- The splitting of the luminescence band yields information on the crystal field splitting of the ground state.

Fig. 1. Luminescence spectra of NdOx, in the range 10000–11000 cm⁻¹: (a) π spectrum; (b) π spectrum. a, b, c, d resp. σ, π, σ, π light transitions initiating at 10F_{5/2} and 10F_{7/2}, respectively, and terminating at the states 1T_{1/2} (ground state), 3T_{1/2}, 1T_{1/2}, 2F_{5/2} and 2F_{7/2} of the ground multiplet l_{6}^{+}. k denotes polarization factor.

H.-D. Amberger, many publications; Görller-Wallrand, many publications; Boulon, ACIE, 2013
Ch. 5. Electronic Absorption and Luminescence

Section 5.3 Magnetic Circular Dichroism

**Magnetic Circular Dichroism**

- The intensity of an absorption band due to an electronic transition between two states is proportional to the square of the electric dipole matrix element:
  \[ I \propto \left| \langle X | \mathbf{\varepsilon} | G \rangle \right|^2 \]

- In MCD, the difference in absorption between left- (\(\sigma^-\)) and right- (\(\sigma^+\))-circularly polarised light is measured:
  \[ \varepsilon_{MCD} = \frac{1}{2} (\varepsilon_+ - \varepsilon_-) \]

- No MCD without field.

**Applied magnetic field** can:

- Lift magnetic degeneracies of the ground and excited states.
- Change the population of the levels via a new Boltzmann distribution.
- Mix the levels G and X with other electronic levels.
Magnetic Circular Dichroism

• This leads to three contributions to the MCD spectrum:
  • the A-term, due to Zeeman splitting of the ground and/or excited degenerate states,
  • the B-term, due to field-induced mixing of states,
  • the C-term, due to a change in the population of molecules over the Zeeman sublevels of a paramagnetic ground state.

\[
\frac{\Delta \varepsilon}{E} = \gamma \mu_B B \left[ -A_1 \frac{\partial f(E)}{\partial E} + \left( B_0 + \frac{C_0}{k_B T} \right) f(E) \right]
\]

• \( \Delta \varepsilon \) is MCD extinction coefficient.
• \( E = h \nu \).
• \( \gamma \) is bunch of constants including dielectric permittivity.
• \( \mu_B \) is Bohr magneton.
• \( f(E) \) is lineshape function.
Ch. 5. Electronic Absorption and Luminescence

Section 5.3 Magnetic Circular Dichroism

Magnetic Circular Dichroism. Example 1 [Cr_{8}F_{8}Piv_{16}]

- UV/Vis spectrum gives energies of excited states.
- Spin-allowed transitions stronger than spin-forbidden.
- Exchange coupling enhances intensity of spin-forbidden transitions.
- Resolution typically not enough to resolve all transitions.
Magnetic Circular Dichroism. Example 1 [Cr₈F₈Piv₁₆]

- MCD signal can be both positive and negative.
- This often leads to much better resolution.
- Spin forbidden transitions are often pronounced.

Piligkos, Van Slageren, Dalton Trans. 2010
Ch. 5. Electronic Absorption and Luminescence

Section 5.3 Magnetic Circular Dichroism

Magnetic Circular Dichroism. Example 1 \([\text{Cr}_8\text{F}_8\text{Piv}_{16}]\)

- MCD splitting of absorption bands is related to ZFS.
- \(\mathcal{H} = d \hat{S}_z^2 + e (\hat{S}_x^2 - \hat{S}_y^2)\).
- \(d = -0.364 \text{ cm}^{-1}; e = 0.119 \text{ cm}^{-1}\).
- cf. \(d = -0.334 \text{ cm}^{-1}\) (strong exchange)
- cf. \(d = -0.24 \text{ cm}^{-1}; e = 0.032 \text{ cm}^{-1}\) (microscopic, neglecting dipolar).
Ch. 5. Electronic Absorption and Luminescence

Section 5.3 Magnetic Circular Dichroism

**Magnetic Circular Dichroism. Example 1 [Cr$_8$F$_8$Piv$_{16}$]**

- MCD intensity is related to the magnetization of the sample.
- It gives information about the magnetic properties of the cluster.
- MCD intensity vs. B or vs. B/T shows more than just a step at the level crossing from $S = 0$ to $S = 1$.
- No MCD intensity is expected for the $S = 0$ state.

---

**Cr$_8$F$_8$Piv$_{16}$ MCD in poly(dimethylsiloxane) mull**

$\lambda = 415 \text{ nm}$

---

**Graphs and plots:**

- Plot of MCD intensity vs. $B/T$ for different temperatures.
- Plot of rotation vs. $\beta H/2kT$ for different temperatures and transitions $^4A_2 \rightarrow ^4T_1$.

---

Piligkos, Van Slageren, Dalton Trans. 2010
Ch. 5. Electronic Absorption and Luminescence

Section 5.3 Magnetic Circular Dichroism

**Magnetic Circular Dichroism. Example 1 [Cr₈F₈Piv₁₆]**

- MCD curves cannot be simulated by summing contributions due to different spin states.
- Mixing between spin states occurs.
- Rhombic term ($E$) necessary.
- Spin Hamiltonian:

$$\mathcal{H} = -2J \sum_{i>j} \hat{S}_i \cdot \hat{S}_j + \sum_i d_i \hat{S}_i^2 + \sum_i e_i \left( \hat{S}_i^2 - \hat{S}_i^2 \right) + \mu_B \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B}$$

- MCD intensity

$$\frac{\Delta \varepsilon}{E} = \frac{\gamma}{4\pi S} \int_0^\pi \int_0^{2\pi} \sum_i N_i \begin{pmatrix} l_x \langle \hat{S}_x \rangle_i M_{yz} + \\ l_y \langle \hat{S}_y \rangle_i M_{xz} + \\ l_z \langle \hat{S}_z \rangle_i M_{xy} \end{pmatrix} \sin \theta \text{d}\theta \text{d}\varphi$$

- $S = 3/2$
- $g = 1.98$
- $D = -0.58 \text{ cm}^{-1}$
- $E / D = 0.1$
- $J = -3.5 \text{ cm}^{-1}$
Ch. 5. Electronic Absorption and Luminescence

Section 5.1 Theoretical background and experimental considerations

**Magnetic Circular Dichroism. Example 2 [Ln(Pc)₂]⁻**

- Anions in EtOH:MeOH glass.
- Transitions based on ligand.
- MCD bands have derivative lineshapes: A-term intensity.
- Lowest-energy transition has opposite MCD sign for Tb³⁺ and Dy³⁺.

![UV/Vis and MCD plots](image)

Krivokapic, Waters, Van Slageren, unpublished
Ch. 5. Electronic Absorption and Luminescence
Section 5.3 Magnetic Circular Dichroism

Magnetic Circular Dichroism. Example 2 \([\text{Ln(Pc)}_2]^{0/-}\)

- Hysteresis is observed for all complexes in spite of ligand based nature of transitions.
- For \([\text{DyPc}_2]^0\) no hysteresis is observed in powder magnetisation measurements.

Krivokapic, Waters, Van Slageren, unpublished; Gonidec, JACS, 2010
Ch. 5. Electronic Absorption and Luminescence

Section 5.3 Magnetic Circular Dichroism

Magnetic Circular Dichroism. Example 3 \([\text{C(NH}_2\text{)}_3]_5\text{[Ln(CO}_3\text{)}_4\text{]}\ (1-\text{Ln})\) with \(\text{Ln} = \text{Dy, Er}\)

- Crystal field split ff transitions

Rechkemmer, Van Slageren, unpublished
Ch. 6. Some words on relaxation of the magnetization

Section 6.1 Spin-Lattice relaxation

The fundamental difference between magnetization dynamics in single-ion and polynuclear species

- In polynuclear TM clusters, Arrhenius behaviour over many orders of magnitude; sharp transition to tunnelling
- In f-elements generally curved Arrhenius plots. Different temperature regime.
- The reason is that in single-ion systems, there are many relaxation pathways with different field- and temperature dependences (direct process, tunnelling, Raman, Orbach, multistep direct process).
- Hence a straight line in the Arrhenius plot is not necessarily expected

\[ [\text{Mn}_3 \text{O(Me-salox)}_3(2,4'-\text{bpy})_3(\text{ClO}_4)], \text{ Yang, Tsai, IC, 2008} \]
\[ [\text{Dy(hfac)}_3(\text{PyNO})], \text{ Yi, CEJ, 2012} \]
The fundamental difference between magnetization dynamics in single-ion and polynuclear species

The first f-element "single-molecule magnets".

- Relaxation parameters
  \[ \Delta E/k_B \quad \tau_0 \quad \text{ref} \]
  - Dy/0 –

- Many substituted (terbium) double deckers known

- Strong correlation between \( \Delta E \) and \( \tau_0 \).
Chapter 6. Some words on relaxation of the magnetization

Section 6.1 Spin-Lattice relaxation

**Basic Spin-Lattice Relaxation Mechanisms in dilute systems**

- Assume dilute systems.
- A further mechanism is quantum tunnelling

![Diagram of energy conservation in both steps]

- Note that the figure was changed compared to literature. It seems to be more logical this way.

Bertini in Handbook of Electron Spin Resonance, Misra in Multifrequency Electron Paramagnetic Resonance, Orbach in Electron Paramagnetic Resonance, Geschwind (Ed.), 1972; Abragam and Bleaney
General formulas (not considering tunnelling)

- non-Kramers ions:

\[
T_1^{-1} = R_d \left( \frac{\hbar \omega}{2kT_0} \right)^3 \coth \left( \frac{\hbar \omega}{2kT_0} \right) + R_{or} \Delta^3 \left\{ \exp \left( \frac{\Delta}{kT_0} \right) - 1 \right\}^{-1} + R_T T_0^7
\]

- Kramers ions:

\[
T_1^{-1} = R_d \left( \frac{\hbar \omega}{2kT_0} \right)^5 \coth \left( \frac{\hbar \omega}{2kT_0} \right) + R_{or} \Delta^3 \left\{ \exp \left( \frac{\Delta}{kT_0} \right) - 1 \right\}^{-1} + R_T T_0^9 + R_{or}' \left( \frac{\hbar \omega}{k} \right) T_0^7
\]