Magnetic anisotropy in f-electron systems: A crystal-field perspective

Nicola Magnani

(nicola.magnani@kit.edu)
Outline

- Part 1: An introduction to crystal field in f-electron systems
- Part 2: Crystal-field anisotropy in lanthanide-based SMMs (selected examples)
- Part 3: Crystal-field anisotropy in actinide-based SMMs (selected examples)
Part 1

An introduction to crystal field in \textit{f}-electron systems
f-electron orbitals: the central field approximation

\[ \hat{H} = \sum_{i=1}^{N} \left( \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i>j=1}^{N} \frac{e^2}{r_{ij}} \]

\( \hat{H}_0 = \sum_{i=1}^{N} \left[ \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} + U(r_i) \right] \)  
(one-body)

\( \hat{H}_1 = \sum_{i>j=1}^{N} \left[ \frac{e^2}{r_{ij}} - U(r_j) \right] \)  
(two-body)

\[ \Psi_0 = \prod_{i=1}^{N} r_i^{-1} R_{n_i l_i} (r_i) Y_{l_m} (\theta_i, \phi_i) \]

\[ L = \sum_i l_i \text{ and } S = \sum_i s_i \text{ both commute with } \hat{H}_1 \]
Spherical harmonics $Y_l^m$

For $l = 0$:
$$Y_0^0 = \frac{1}{2\sqrt{\pi}}$$

For $l = 1$:
$$Y_1^0 = \frac{1}{2\sqrt{\pi}} \cos \theta$$
$$Y_1^{\pm1} = \mp \frac{1}{2\sqrt{\pi}} \sin \theta \exp(\pm i\varphi)$$

For $l = 2$:
$$Y_2^0 = \frac{1}{4\sqrt{\pi}} (3\cos^2 \theta - 1)$$
$$Y_2^{\pm1} = \mp \frac{1}{2\sqrt{2\pi}} \sin \theta \cos \theta \exp(\pm i\varphi)$$
$$Y_2^{\pm2} = \frac{1}{4\sqrt{2\pi}} \sin^2 \theta \exp(\pm 2i\varphi)$$

For $l = 3$, $l = 4$, $l = 5$, $l = 6$, the expressions become more complex with $m$ ranging from $m = 0$ to $m = \pm l$.

The diagrams illustrate the spatial distribution of these harmonics in spherical coordinates $r$, $\theta$, $\varphi$. The different $m$ values lead to variations in the symmetry and orientation of the patterns.
The spectra of rare-earth ions

\[ H_0 + H_1 \]

\[ \hat{H}_0 \]

\[ 4f^n \]

\[ \hat{H}_0 + \hat{H}_1 + \hat{H}_{SO} \]

\[ \mu_{eff} = g_J \sqrt{J(J+1)} \]

\[ l = 3 \quad 2 \quad 1 \quad 0 \quad -1 \quad -2 \quad -3 \]

\[ 4f^3: L = 6, S = 3/2 \]

\[ \hat{H}_{SO} = \sum_{i=1}^{N} \xi(r_i) l_i \cdot s_i \]

\[ J_{max} = L + S \quad J_{min} = |L - S| \]

\[ \begin{array}{c}
N < 7 \\
N > 7
\end{array} \quad \text{or} \quad \begin{array}{c}
J_{max} = L + S \\
J_{min} = |L - S|
\end{array} \]
The crystal field: a simple point-charge example

A magnetic ion placed at the origin of the Cartesian coordinate system, with two equal ligands (of effective charge Ze) placed at the same distance along the z axis.

\[ V = -\sum_k \frac{Z_k e^2}{|R_k - r|} = -\frac{Ze^2}{\sqrt{x^2 + y^2 + (z - R)^2}} - \frac{Ze^2}{\sqrt{x^2 + y^2 + (z + R)^2}} \]

\[ = -\frac{Ze^2}{R} \left( \frac{1}{\sqrt{1 - 2z / R + r^2 / R^2}} + \frac{1}{\sqrt{1 + 2z / R + r^2 / R^2}} \right) \]

\[ \frac{1}{\sqrt{1+a}} = \sum_{n=0}^{\infty} \frac{(2n)!}{(2^n n!)^2} (-a)^n = 1 - \frac{1}{2} a + \frac{3}{8} a^2 - \frac{5}{16} a^3 + \frac{35}{128} a^4 - \frac{63}{256} a^5 + \frac{231}{1024} a^6 + O(x^7) \]
The crystal field: a simple point-charge example

\[
\frac{1}{\sqrt{1 - 2z / R + r^2 / R^2}} = \left( \frac{1}{R} + \frac{z R}{2 R^3} + \frac{3z^2 - r^2}{2 R^4} + \frac{5z^3 - 3r^2 z}{2 R^5} + \frac{3r^4 - 30r^2 z^2 + 35z^4}{8 R^6} \right)
\]

\[+ \frac{63z^5 - 70r^2 z^3 + 15r^4 z}{8 R^6} + \frac{231z^6 - 315r^2 z^4 + 105r^4 z^2 - 5r^6}{16 R^7} \]

\[2\sqrt{\frac{\pi}{5}} \frac{r^2}{R^3} Y_2^0 \quad 2\sqrt{\frac{\pi}{13}} \frac{r^6}{R^7} Y_6^0 \quad 2\sqrt{\frac{\pi}{3}} \frac{r^4}{R^5} Y_4^0 \]

\[V_{\text{axial}} = -4\sqrt{\pi} Ze^2 \left( \frac{1}{5} \frac{r^2}{R^3} Y_2^0 + \frac{1}{13} \frac{r^4}{R^5} Y_4^0 + \frac{1}{3} \frac{r^6}{R^7} Y_6^0 + \ldots \right) \]
The crystal field: a simple point-charge example

\[ V_{\text{cubic}} = -Ze^2 \left\{ \frac{7\sqrt{\pi}}{3} \frac{r^4}{R^5} \left[ Y_4^0 + \sqrt{\frac{5}{14}} \left( Y_4^4 + Y_4^{-4} \right) \right] + \frac{3}{2} \frac{\sqrt{\pi} r^6}{13 \sqrt{13} R^7} \left[ Y_6^0 - \frac{7}{2} \left( Y_6^4 + Y_6^{-4} \right) \right] \right\} + \ldots \]
Constraints on non-zero matrix elements

Once $\hat{H}_{CF}$ has been rewritten as a function of spherical harmonics, each contribution to its matrix elements have the form

$$\int \psi_{nl'm'}^* Y_{l'm'} \psi_{n'l''m''} r^2 \, dr \sin \theta \, d\theta \, d\varphi =$$

$$\int R_{nl'm'}^* R_{n'l''m''} \, dr \times \int Y_{l'm'}^* Y_{l'm'} Y_{l''m''} \sin \theta \, d\theta \, d\varphi$$

Since

$$\int_0^{2\pi} e^{i(m-m'+m'')} \, d\varphi = 2\pi \delta_{m-m'+m''},$$

integrating on $\varphi$ requires the condition $m = m' - m''$ to be fulfilled for the result to be nonzero.

Similarly, integrating on $\theta$ results in two additional constraints:

$l + l' + l''$ must be even and $|l' - l''| \leq l \leq l' + l''$.

For $f$ electrons ($l' = l'' = 3$) this means that $l$ must be even and $\leq 6$. 

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Nicola Magnani – Magnetic anisotropy in f-electron system: A crystal-field perspective
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Constraints on non-zero matrix elements

\[ V_{\text{axial}} = A_2^0 \sum_i r_i^2 Y_2^0(i) + A_4^0 \sum_i r_i^4 Y_4^0(i) + A_6^0 \sum_i r_i^6 Y_6^0(i) + \times. \]

\[ V_{\text{cubic}} = A_4 \sum_i r_i^4 \left[ Y_4^0(i) + \sqrt{\frac{5}{14}} (Y_4^4(i) + Y_4^{-4}(i)) \right] \]

\[ + A_6 \sum_i r_i^6 \left[ Y_6^0(i) - \sqrt{\frac{7}{2}} (Y_6^4(i) + Y_6^{-4}(i)) \right] + \times. \]

(even less contributions for \( d \) electrons: \( l \leq 4 \))

Now all that’s left to do is to calculate these matrix elements!
Angular momentum space: operator equivalents

\[ \sum_i r_i \left[ Y_l^m + (-1)^m Y_l^{-m} \right] \rightarrow \langle r' \rangle \Theta_l \hat{O}_l^m \]

\[ \hat{H}_{CF} = \sum_{l,m} \tilde{A}_l^m \langle r' \rangle \Theta_l \hat{O}_l^m \]

Matrix Elements and Operator Equivalents Connected with the Magnetic Properties of Rare Earth Ions

By K. W. H. STEVENS
The Clarendon Laboratory, Oxford

Communicated by B. Bleaney; MS. received 16th August 1951

ABSTRACT. An account is given of the methods used to determine the matrix elements of crystal field potentials with particular reference to rare earth ions. Emphasis is laid on the importance of Wigner coefficients in such problems and the idea of using equivalent angular momentum operators is developed. For convenience in applying the results tables of matrix elements are included.

§ 1 INTRODUCTION

In the course of some recent work on rare earth ions in crystals it has been necessary to evaluate the matrix elements of certain potential functions in representations in which the states are eigen states of the total angular momentum. Somewhat similar problems arise in connection with the magnetic properties of iron group ions in crystals, with the difference that the usual representations are then those in which the states are eigen states of the total orbital angular momentum and it is not necessary to include spin variables. In the case of rare earth ions the perturbations due to the crystal fields are usually small compared with the spin–orbit couplings, whereas in the iron group the inequality is reversed. This difference means that the evaluation of the relevant rare earth matrix elements is generally more complicated than is the case for iron group ions. It is the purpose of the paper to give an account of a method for obtaining their values in terms of one-electron radial integrals.
Angular momentum space: operator equivalents

<table>
<thead>
<tr>
<th>$N$</th>
<th>Prototype RE ion</th>
<th>Ground multiplet</th>
<th>$\alpha_J$</th>
<th>$\beta_J$</th>
<th>$\gamma_J$</th>
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<tr>
<td>1</td>
<td>Ce$^{3+}$</td>
<td>$^2F_{5/2}$</td>
<td>$^2_5.7$</td>
<td>$^2_3.5.7$</td>
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<tr>
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<td>$^3H_4$</td>
<td>$^2_7_{2.13}$</td>
<td>$^2_3.5.11^2$</td>
<td>$^2_{3.5.7.11^2.13}$</td>
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<td>$^4I_{9/2}$</td>
<td>$^7_{3.11^2}$</td>
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<td>$^5I_{4}$</td>
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<td>$^2_{3.5.7.11}$</td>
<td>$^2_{3.7.11^2.13}$</td>
</tr>
</tbody>
</table>
Angular momentum space: operator equivalents

\[ \sum_i r_i^l [Y^m_l + (-1)^m Y^{-m}_l] \rightarrow \left< r' \right> \Theta_l \hat{O}^m_l \]

Basis set states: \( |LSM_L M_S \rangle \)

\((x, y, z) \rightarrow (\hat{L}_x, \hat{L}_y, \hat{L}_z)\)

e.g. \( r^2 Y_2^0 \propto 3z^2 - r^2 \rightarrow 3\hat{L}_z^2 - L(L + 1) \)

\( r^2 (Y_2^2 + Y_2^{-2}) \propto x^2 - y^2 \rightarrow \hat{L}_x^2 - \hat{L}_y^2 \)

Basis set states: \( |LSJM_J \rangle \)

\( J_{\text{max}} = L + S \)

\( J_{\text{min}} = |L - S| \)

\( \hat{L}_k \rightarrow \hat{J}_k \)

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Angular momentum space: operator equivalents

\[ \sum_i r_i \left[ Y_l^m + (-1)^m Y_l^{-m} \right] \rightarrow \langle r^l \rangle \Theta_l \hat{O}_l^m \]

\[ 2J + 1 \text{ states with } M_J = -J, \ldots, J; \]

\[ \hat{H}_{CF} = \sum_{l,m} \tilde{A}_l^m \langle r^l \rangle \Theta_l \hat{O}_l^m = \sum_{l,m} \tilde{B}_l^m \hat{O}_l^m \]

lifts their degeneracy (in some cases only partially).

The validity of the above Hamiltonian extends beyond the electrostatic model.
Angular momentum space: operator equivalents

Simple example: \(4f^1\) (Ce\(^{3+}\)), \(2F_{5/2}\), in a cubic CF

\[
\hat{H}_{\text{CF}} = \hat{B}_4 \left( \hat{O}^0_4 + 5 \hat{O}^4_4 \right) + \hat{B}_6 \left( \hat{O}^0_6 - 21 \hat{O}^4_6 \right)
\]

\[
\hat{O}^4_4 = \left( \hat{J}^4_+ + \hat{J}^4_- \right) / 2
\]

\[
\hat{J}^J_+ \, | M_J \rangle = \sqrt{J(J+1)-M_J(M_J+1)} \, | M_J+1 \rangle
\]

\[
| -5/2 \rangle = \sqrt{(5/2)(7/2) - (-5/2)(-3/2)} \hat{J}^3_+ | -3/2 \rangle = \sqrt{5} \hat{J}^3_+ | -3/2 \rangle = \frac{\sqrt{5} \times \sqrt{8} \hat{J}^2_+ | -1/2 \rangle}{\sqrt{5} \times \sqrt{8} \times \sqrt{9} \hat{J}^1_+ | 1/2 \rangle} = \frac{\sqrt{5} \times \sqrt{8} \times \sqrt{9} \times \sqrt{8} | 3/2 \rangle}{\sqrt{5} \times \sqrt{8} \times \sqrt{9} \times \sqrt{8} + 3/2 \rangle}
\]

\[
\Rightarrow \langle M_J | \hat{O}^4_4 | M_J+4 \rangle = 12\sqrt{5}
\]
Angular momentum space: operator equivalents

Simple example: $4f^1$ (Ce$^{3+}$), $^2F_{5/2}$, in a cubic CF

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<th>$M_J$</th>
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<th>-3/2</th>
<th>-5/2</th>
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<th>1/2</th>
<th>-1/2</th>
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<td>$60\sqrt{5}$</td>
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<td>-180</td>
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<td>0</td>
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<tr>
<td>-5/2</td>
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<td>3/2</td>
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<td>-180</td>
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<td>0</td>
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<td>0</td>
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<td>120</td>
</tr>
</tbody>
</table>

$\tilde{B}_4 \times$
Angular momentum space: operator equivalents

Simple example: \( 4f^1 \) (Ce\(^{3+}\)), \( ^2F_{5/2} \), in a cubic CF

\[
360 \tilde{B}_4 = \frac{\left(\sqrt{5}\left|\pm \frac{3}{2}\right\rangle - \left|\mp \frac{5}{2}\right\rangle\right)}{\sqrt{6}}
\]

\[
\left\{\left|\pm \frac{1}{2}\right\rangle \right. + \frac{\left(\sqrt{5}\left|\pm \frac{5}{2}\right\rangle + \left|\mp \frac{3}{2}\right\rangle\right)}{\sqrt{6}}\right\}
\]
Crystal-field splitting: cerium(III)

\[ \frac{E}{B_4^0} \]

<table>
<thead>
<tr>
<th>( J )</th>
<th>Irreducible representations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>( \Gamma_6^- )</td>
</tr>
<tr>
<td>3/2</td>
<td>( \Gamma_5^- )</td>
</tr>
<tr>
<td>5/2</td>
<td>( \Gamma_7^- + \Gamma_8^- )</td>
</tr>
<tr>
<td>7/2</td>
<td>( \Gamma_6^- + \Gamma_7^- + \Gamma_8^- )</td>
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<td>11/2</td>
<td>( \Gamma_6^- + \Gamma_7^- + 2\Gamma_8^- )</td>
</tr>
<tr>
<td>13/2</td>
<td>( \Gamma_6^- + 2\Gamma_7^- + 2\Gamma_8^- )</td>
</tr>
<tr>
<td>15/2</td>
<td>( \Gamma_6^- + 2\Gamma_7^- + 3\Gamma_8^- )</td>
</tr>
<tr>
<td>17/2</td>
<td>( 2\Gamma_6^- + \Gamma_7^- + 3\Gamma_8^- )</td>
</tr>
</tbody>
</table>

\( \Omega_b \)
Kramers’ theorem: all the crystal-field states of an ion with an odd number of electrons have even degeneracy.
Zero-field splitting in S-state ions

Ions with a L = 0 ground term should in principle have no spatial anisotropy. However, small mixing with higher-lying multiplets can give rise to zero-field splitting.

\[ \hat{H}_{ZFS} = \sum_{l,m} \tilde{B}_l^m \hat{O}_l^m(S) \]

Assuming only rank-2 contributions:

\[ \hat{H}_{ZFS} = \tilde{B}_2^0 \hat{O}_2^0(S) + \tilde{B}_2^2 \hat{O}_2^2(S) + \tilde{B}_2^{-2} \hat{O}_2^{-2}(S) + \tilde{B}_2^1 \hat{O}_2^1(S) + \tilde{B}_2^{-1} \hat{O}_2^{-1}(S) \]

\[ = \tilde{B}_2^0 \left[ 3S_z^2 - S(S+1) \right] + \tilde{B}_2^2 \left( S_x^2 - S_y^2 \right) \]

\[ \rightarrow DS_z^2 + E \left( S_x^2 - S_y^2 \right) + \text{cost}. \]
Full configuration diagonalization

\[ \hat{H}_{\text{FI}} = E_{av} + \sum_k F_k f_k + \zeta \hat{H}_{\text{SO}} + \alpha \hat{L}(\hat{L} + 1) + \beta \hat{G}(G_2) + \gamma \hat{G}(R_7) + \sum_i T_i t_i + \sum_j M_j m_j + \sum_k P_k p_k, \]

\[ \hat{H}_{\text{CF}} = \sum_k \sum_q B_k^q \hat{C}_k^q, \]
LS versus jj coupling

J mixing can be taken into account perturbatively:
N. M. et al., PRB 71, 054405 (2005)
End of part 1 - Bibliography


- SMMS: cluster.univpm.it/_build/html/productsdir/smms/magnetism.html
Part 2

Crystal-field anisotropy in rare-earth based SMMs: some examples
Origin of magnetic relaxation in rare-earth-based single-ion complexes

Direct process

Orbach process

Allowed if $J_z$ is not a good quantum number (like QTM)

Thermally activated (slow at low T)
Origin of uniaxial anisotropy in SMMs

‘sandwich’ structures naturally accommodate oblate 4f orbitals

Crystal-field splitting in $[\text{Pc}_2 R]$ complexes

$U_{\text{eff}} \sim 260$ cm$^{-1}$

$\Delta \sim 440$ cm$^{-1}$

Tb might be the best SMM, but Tm is much better for studying the crystal field of the series!

N. Ishikawa et al.,

JACS 125 (2003) 8694
Pc$_2$Tm: optical spectroscopy

\begin{figure}
\centering
\includegraphics[width=\textwidth]{spectroscopy_plot.png}
\caption{Absorbance spectra for Tm(I) at temperatures of 9 K and 40 K. The energy levels $^3H_6$ and $^3H_5$ are shown on the right.}
\end{figure}

N.M. et al, PRB 79 (2009) 104407
Pc$_2$Tm: neutron spectroscopy

N.M. et al, PRB 79 (2009) 104407
Specific heat can help fixing the degeneracy

Doublet: GS 1ES 2ES 3ES

\[ C_m = \left( k_B T^2 \right)^{-1} \frac{\partial^2 \ln \sum g_n \exp(-\beta E_n)}{\partial \beta^2} \]
$Pc_2Tm$: specific heat

N.M. et al, PRB 79 (2009) 104407
Crystal-field states assignment

- States nearest to the GS must have small $J_z$ to reproduce low-temperature susceptibility.

- States with $J_z = \pm 6$ are much lower in energy than expected.

- All excited levels detected below 2 meV must correspond to singly-degenerate states; presence of a significant $C_4$ contribution is evident.

N.M. et al, PRB 79 (2009) 104407
## Crystal-field states assignment

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Model A</th>
<th>Model B</th>
<th>Model C</th>
</tr>
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<tbody>
<tr>
<td>$A_2^0 \langle r^2 \rangle$</td>
<td>15.8</td>
<td>11.8</td>
<td>33.4</td>
</tr>
<tr>
<td>$A_4^0 \langle r^4 \rangle$</td>
<td>-16.0</td>
<td>-11.7</td>
<td>-35.0</td>
</tr>
<tr>
<td>$A_6^0 \langle r^6 \rangle$</td>
<td>4.84</td>
<td>3.29</td>
<td>11.7</td>
</tr>
<tr>
<td>$A_4^4 \langle r^4 \rangle$</td>
<td>±7.33</td>
<td>±1.36</td>
<td>±5.88</td>
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<tr>
<td>$A_6^4 \langle r^6 \rangle$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Pc\textsubscript{2}Tm: field-dependent specific heat

![Graph showing specific heat versus magnetic field for different temperatures (T = 3 K, 4 K, 5 K). The graph compares model A and model C.](image)

N.M. et al, PRB 79 (2009) 104407
$\chi T$: magnetic susceptibility

Model B

Model A

N.M. et al, PRB 79 (2009) 104407
The revised crystal-field model is perfectly compatible with the relaxation properties.

N.M. et al, PRB 79 (2009) 104407
End of part 2 (almost) – Conclusions

- The CF parameters for Tm-DD complex were unambiguously determined by a variety of experimental techniques.

- $D_{4d}$ terms are qualitatively in line with those previously determined (signs and orders of magnitude)

- NOT quantitatively: $A_{2}^{0}$ smaller by a factor 3!

- $C_{4}$-symmetry terms small (with respect to the axial potential) but not negligible (clear effect on the energy spectra)

- Lower-symmetry terms have a much smaller influence on the low-energy wavefunction, even if present ($|A_{2}^{2}\langle r^{2}\rangle| < 0.5 \text{ cm}^{-1}$)
Addendum: Exploiting magnetically active radicals


\[ H_{HD} = -2J(S_1 + S_2) \cdot S_r \]

<table>
<thead>
<tr>
<th>Ln</th>
<th>g</th>
<th>2J (cm(^{-1}))</th>
<th>g_J</th>
<th>U_{eff} (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er</td>
<td>1.18</td>
<td>21</td>
<td>1.20</td>
<td>36</td>
</tr>
<tr>
<td>Ho</td>
<td>1.25</td>
<td>83</td>
<td>1.25</td>
<td>73</td>
</tr>
<tr>
<td>Dy</td>
<td>1.28</td>
<td>102</td>
<td>1.33</td>
<td>123</td>
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<tr>
<td>Tb</td>
<td>1.45</td>
<td>108</td>
<td>1.50</td>
<td>227</td>
</tr>
<tr>
<td>Gd</td>
<td>2.00*</td>
<td>54</td>
<td>2.00</td>
<td>–</td>
</tr>
</tbody>
</table>

*Fixed.

How can the coupling be strengthened further?

\[ \Delta E_{S-T} \approx \frac{2t^2}{U} \]

- Increase $t$: for direct spin exchange, this means increasing the overlap.
- Actinides’ 5$f$ shell has a larger extension than rare earths’ 4$f$
- Decrease $U$, matching the reduction potential of the ligand and metal.
- Actinides have much richer chemistry than lanthanides (exp. more oxidation states)

How can the coupling be strengthened further?

Lanthanides with accessible tetravalent states should be coupled with oxidizing radicals.

Lanthanides with accessible divalent states should be coupled with reducing radicals.

Actinides have a much richer chemistry!
Part 3

Anisotropy in actinide-based SMMs: some examples
Why actinides?

![Diagram showing the atomic radius of actinides and their transition to metallic 5f and atomic 5f electrons.](image)

- **Metallic 5f electrons**
  - Ce, Pr, Nd, Pm, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu
- **Atomic 5f electrons**
  - δ-Pu
- **Actinide (5f)**
  - Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Lr
- **Transition metal (5d)**
  - Rare earth (4f)

![Graph showing the length change of pure plutonium.](image)

- **Pure plutonium**
  - δ, δ', ε, Liq.
- **Body-centered ortho. 8-atom cell**
- **Face-centered cubic 4-atom cell**
- **Body-centered monoclinic 34-atom cell**
- **Monoclinic 16-atom cell**

**Temperature (°C)**: 100, 200, 300, 400, 500, 600
Why actinides?

Switching to actinide-based SMMs could combine the best of both worlds (3d and 4f), since 5f electrons can lead to the simultaneous presence of strong ligand-field potential and magnetic superexchange coupling.
A paradigmatic case: \(\text{UTp}_3\)

\[U_{\text{eff}} \approx \Delta/100 \]

More complex relaxation processes than expected from the energy spectrum

\[\Delta = 267 \text{ cm}^{-1}\]

Direct processes are enhanced by the non-axial part of the ligand-field potential.

Possible solution: ACTINOCENES ($D_{8h}$)

(Karraker et al., JACS 1970, 92, 4841)

PROBLEM: tetravalent $\text{U} \rightarrow 5f^2$
"Butterfly" magnetic hysteresis in neptunocene ($5f^3$)

Exchange coupling and slow relaxation in the heterovalent Np trimetallic \([\text{Np}^{VI}\text{O}_2\text{Cl}_2][\text{Np}^{V}\text{O}_2\text{Cl}(\text{thf})_3]_2\)

\[ \Delta \approx 140 \text{ K} \]

\[ \tilde{\chi} = 10.8 \text{ K} \]

\[ \tilde{\chi}' = 0.56 \text{ K} \]

Exchange coupling in U(V) complexes

\( g_\parallel = 2.8 \)
\( g_\perp = 0.7 \)
\( J_{ex} = -33 \text{ cm}^{-1} \)

(Arnold et al., *Nat. Chem.* 2012, 4, 221)
$5f^1 - 4f^n$ complexes

(Arnold et al., *JACS* 2013, 135, 3841)
Both the ligand-field anisotropy and the superexchange interaction in actinide-based magnetic molecules are generally stronger than in their lanthanide counterparts. This could make light actinides a better choice to design SMMs, despite their lower magnetic moments...

...but unfortunately, some fundamental interactions which give rise to fast relaxation processes (non-axial ligand field, hyperfine coupling, orbital moment reduction) seem to be enhanced too.

Challenge: exploit the richer actinide chemistry (more oxidation states, larger coordination sphere…) to obtain a favorable balance.

Pu(V): strong exchange and large moment?
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