Crystal Electric Field in the magnetically frustrated pyrochlore compounds $R_2Ti_2O_7$

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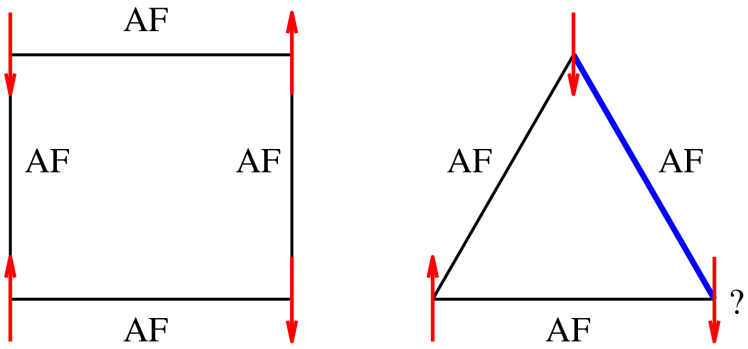
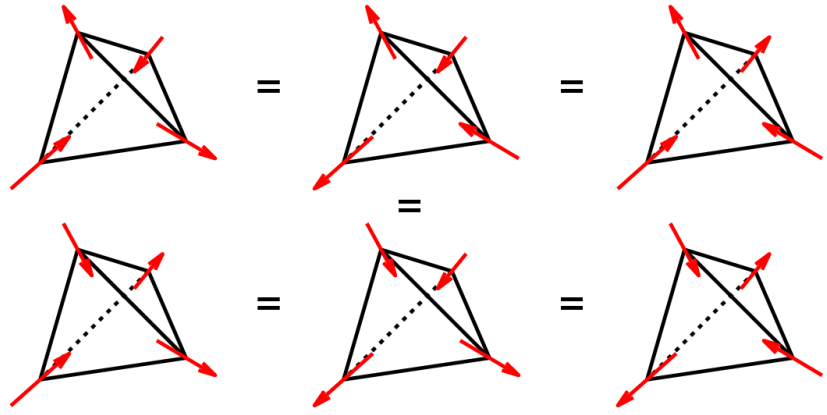
Outline

What is the geometrical frustration?

Geometrical frustration appears when all magnetic interactions cannot be simultaneously satisfied:



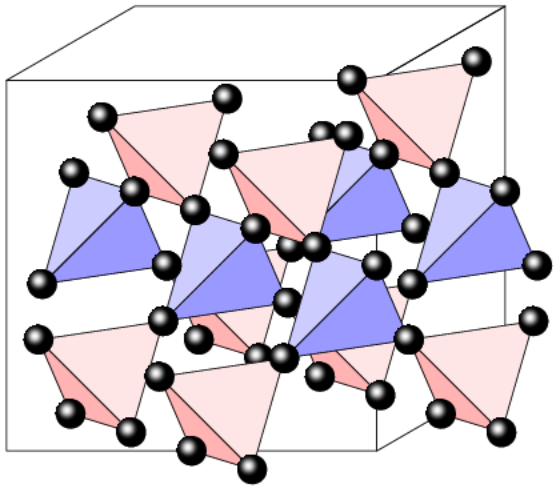
2D: Unfrustrated square lattice and frustrated triangular lattice



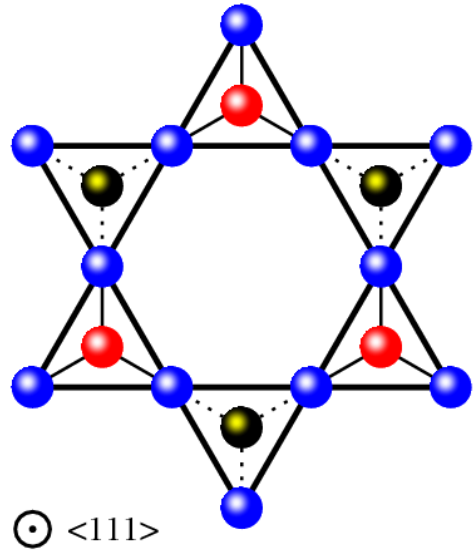
3D: spins located on the corner of a tetrahedra

The pyrochlore compounds $R_2Ti_2O_7$ (1)

- Insulating compounds
- Magnetism due to localized $4f$ electrons



Pyrochlore lattice: fcc lattice



A view along [111] shows the kagome and triangular planes.

The pyrochlore compounds $R_2Ti_2O_7$ (2)

- Large variety of magnetic ground states
- Competition of magnetic interactions: single ion anisotropy, exchange, and dipolar interactions
- Some examples of spins liquids:
  - The classical spin ice: $Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$

    Harris *et al.* Phys. Rev. Lett. **79**, 2554 (1998)

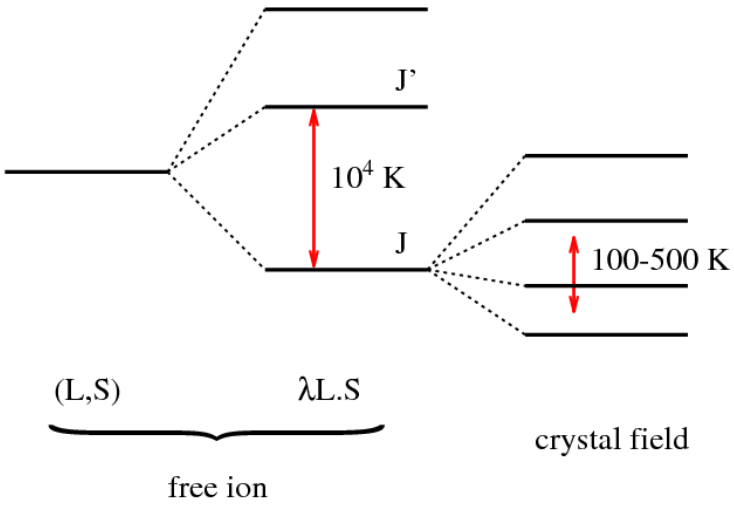
    Ramirez *et al.* Nature **399**, 333 (1999)
  - The quantum spin ice: $Yb_2Ti_2O_7$

    Hodges *et al.* Phys. Rev. Lett. **88**, 077204 (2002)

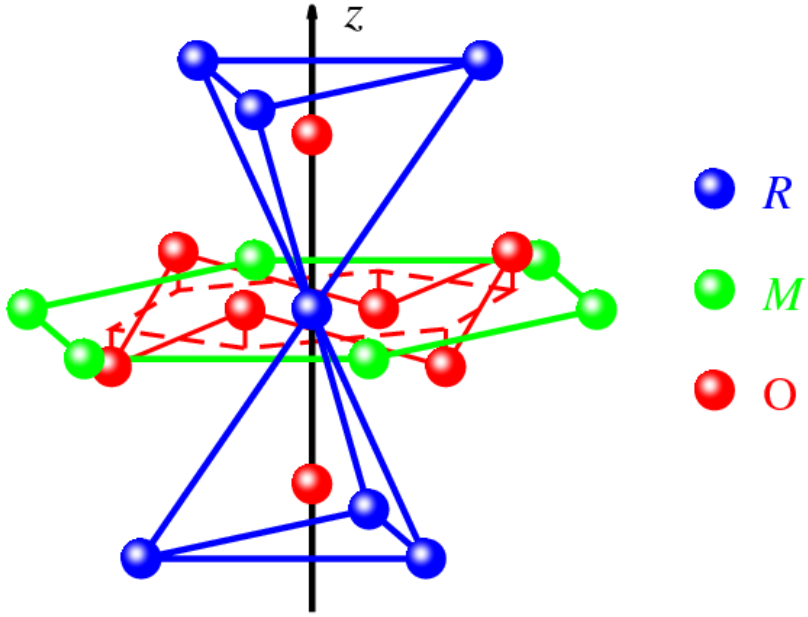
$\rightarrow$ **Need to determine the crystal electric field**

Crystal Electric Field (CEF)

Introduction (1)



Ground state term



Local environment at the rare earth site

- Strong spin-orbit coupling $\rightarrow$ Russel-Saunders splitting larger than $k_{\mathrm{B}}T$
- Crystal field acts as a perturbation of the ground state J multiplet

Rare earth	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}
First excited term (meV)	249	408	644	803	1026	1271

J.Jensen and A.R.Mackintosh *Rare Earth Magnetism; Structures and Excitations* Oxford:Clarendon (1991)

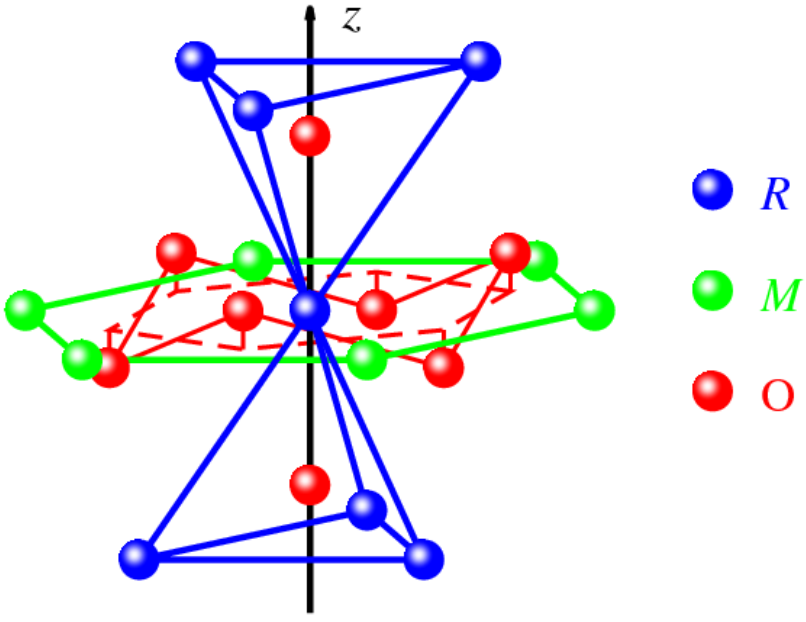
Introduction (2)

Kramers theorem

Rare earth	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}
Number of 4f e^-	8	9	10	11	12	13
J	6	15/2	8	15/2	6	7/2
g_J	3/2	4/3	5/4	6/5	7/6	8/7
Kramers ion	no	yes	no	yes	no	yes

- Time reversal symmetry operator $\hat{\Theta}$:
  - $\hat{\Theta}^2 = \hat{1}$ if J integer,
  - $\hat{\Theta}^2 = -\hat{1}$ if J half-integer.
- With no applied magnetic field, energy levels of an ion with an odd number of $4f$ electrons, i.e. with J half-integer, remains at least doubly degenerated (Kramers ion).

CEF Hamiltonian from point symmetry (1)



- Space group $Fd\bar{3}m$
- Point group at the rare earth site D_{3d}
- Local axis: a three-fold symmetry axis
- No structural distorsion at low temperature

- The CEF Hamiltonian is expressed as:

$$\mathcal{H}_{CEF} = \sum_{n,m \leq n} B_n^m O_n^m$$

- The CEF Hamiltonian is invariant under the symmetry operators associated with the point group.
- $4f$ electrons $\rightarrow n \leq 6$

CEF Hamiltonian from point symmetry (2)

- Using the three-fold symmetry z axis and looking at the mth power of $J_\pm$:

$$\left[J_\pm^m, R_z\left(\frac{2\pi}{3}\right)\right] = J_\pm^m \exp\left(-\frac{2i\pi}{3}J_z\right) - \exp\left(-\frac{2i\pi}{3}J_z\right) J_\pm^m$$

Invariance by symmetry gives us:

$$0 = \exp\left(-\frac{2i\pi m_J}{3}\right) - \exp\left(-\frac{2i\pi(m_J \pm m)}{3}\right)$$

- Only O_n^m with $m = 3p$ are allowed. For the pyrochlore compounds, the Hamiltonian is written as follows:

$$\mathcal{H}_{CEF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + B_6^0 O_6^0 + B_6^3 O_6^3 + B_6^6 O_6^6$$

CEF Hamiltonian from point symmetry (3)

List of the useful Stevens operators:

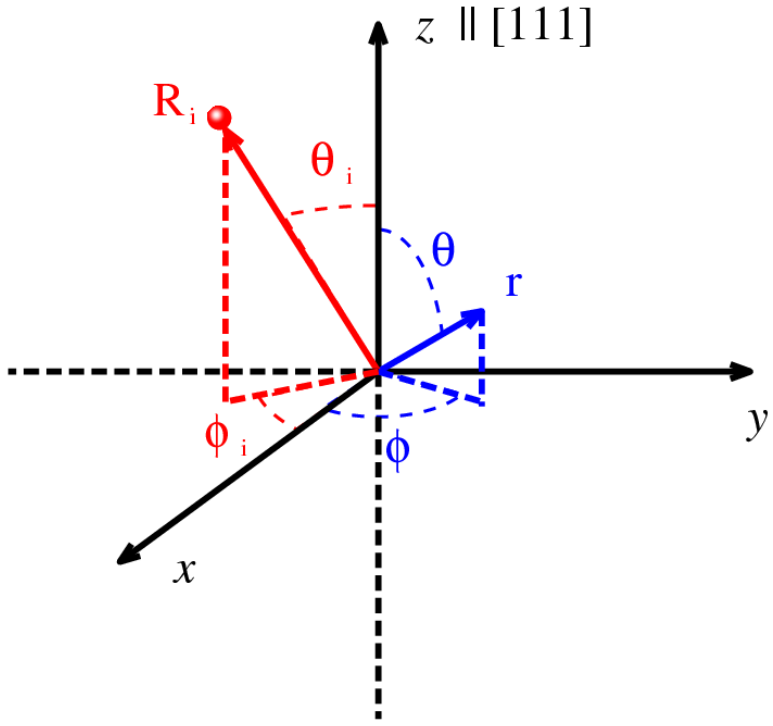
$$
\begin{aligned}
O_2^0 &= 3J_z^2 - J(J+1) \\
O_4^0 &= 35J_z^4 - 30J(J+1)J_z^2 + 25J_z^2 - 6J(J+1) + 3J^2(J+1)^2 \\
O_6^0 &= 231J_z^6 - 315J(J+1)J_z^4 + 735J_z^4 + 105J^2(J+1)^2 J_z^2 \\
&\quad -525J(J+1)J_z^2 + 294J_z^2 - 5J^3(J+1)^3 + 40J^2(J+1)^2 \\
&\quad -60J(J+1) \\
O_6^3 &= \frac{1}{4}\Big\{ \left[11J_z^3 - 3J(J+1)J_z - 59J_z\right](J_+^3 + J_-^3) \\
&\quad +(J_+^3 + J_-^3)\left[11J_z^3 - 3J(J+1)J_z - 59J_z\right] \Big\} \\
O_4^3 &= \frac{1}{4}\left[J_z(J_+^3 + J_-^3) + (J_+^3 + J_-^3)J_z\right] \\
O_6^6 &= \frac{1}{2}(J_+^6 + J_-^6)
\end{aligned}
$$

Note: For a given operator acting on a ket $|J, m_J\rangle$, only $|J, m_J\rangle, |J, m_J \pm 3\rangle, |J, m_J \pm 6\rangle$ will appear

Point charge model (1)

- Crystal electric field due to electric potential created by k surrounding ions, taken as point charges:

$$\mathcal{H}_{CEF} = -\frac{e}{4\pi\epsilon_0} V(r,\theta,\phi) = -\frac{e}{4\pi\epsilon_0} \sum_{i=1}^{k} \frac{q_i}{|\mathbf{r} - \mathbf{R_i}|}$$



Point charge model (2)

- The coulombic potential is developped using Legendre polynomials P_n as:

$$\frac{1}{|\mathbf{r} - \mathbf{R_i}|} = \sum_{n=0}^{\infty} \frac{r^n}{R_i^{n+1}} P_n(\cos \omega_i) \quad \text{with} \quad R_i \gg r$$

  where ω_i is the angle between $\mathbf{r}$ and $\mathbf{R_i}$

- Therefore the electric potential V at a point (r, θ, ϕ) for k surrounding charges located at (R_i, θ_i, ϕ_i) is:

$$\begin{aligned} V(r, \theta, \phi) &= \sum_{i=1}^{k} q_i \sum_{n} \frac{r^n}{R_i^{n+1}} \frac{4\pi}{(2n+1)} \\ &\quad \times \sum_{\ell=-n}^{n} (-1)^{\ell} Y_n^{-\ell}(\theta_i, \phi_i) Y_n^{\ell}(\theta, \phi) \end{aligned}$$

Point charge model (3)

- Within the $(2J+1)$-fold degenerate ground state multiplet $|J, m_J\rangle$, spherical harmonics can be replaced by combinations of the components of **J** (**Wigner-Eckart theorem**), resulting in the **Stevens operators** O_n^m.
- For instance:

$$\sum_i (3z_i^2 - r_i^2) \rightarrow \theta_2 \langle r^2 \rangle [3J_z^2 - J(J+1)] = \theta_2 \langle r^2 \rangle O_2^0$$

Point charge model (4)

- The CEF Hamiltonian is then expressed as:

$$\mathcal{H}_{CEF} = \sum_{n,m} B_n^m O_n^m = \sum_{n,m} A_n^m \langle r^n \rangle \theta_n O_n^m$$

- A_n^m are related to the crystallographic structure. For instance,

$$A_2^0 = -\frac{e}{4\pi\epsilon_0} \left(\frac{1}{4}\right)^2 \left(\frac{5}{\pi}\right)^{\frac{1}{2}} \sum_{i=1}^{k} q_i \frac{3Z_i^2 - R_i^2}{R_i^5}$$

  A_n^m **proportionnal to** $\frac{1}{a^{n+1}} \rightarrow$ one infers a scaling law based on lattice parameter a

- $\langle r^n \rangle$ is the expectation value of the nth power distance between a nucleus and the $4f$ electrons
- θ_n are Stevens parameters, strongly rare earth dependent

Determination of CEF parameters

Previous results from literature (1)

CEF parameters presented here:

- Analysis of inelastic neutron data on $Ho_2Ti_2O_7$

  Rosenkranz *et al.* J. Appl. Phys. **87**, 5914 (2000)

- Calculations using the exchange charge model on $Ho_2Ti_2O_7$

  Malkin it et al. Phys. Rev. B **70**, 075112 (2004)

- Analysis of inelastic neutron data on $Tb_2Ti_2O_7$

  Mirebeau *et al.* Phys. Rev. B **76**, 184436 (2007)

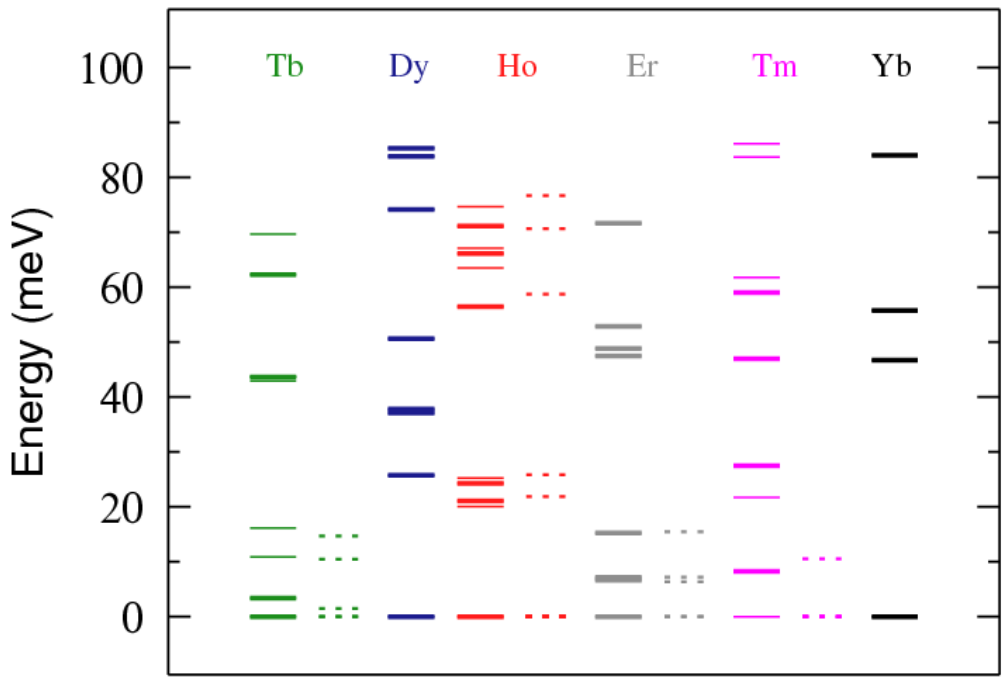
Experimental data come from inelastic neutron scattering:

- $Tm_2Ti_2O_7$ (TAS): Zinkin *et al.* J.Phys.: Condens. Matter **8**, 193-7 (1996)
- $Ho_2Ti_2O_7$ (TOF): Rosenkranz *et al.* J. Appl. Phys. **87**, 5914 (2000)
- $Er_2Ti_2O_7$ (TAS): Champion *et al.* Phys. Rev. B **68**, 020401(R) (2003)
- $Tb_2Ti_2O_7$ (TAS): Mirebeau *et al.* Phys. Rev. B **76**, 184436 (2007)

(TAS: triple axis spectrometer; TOF: time-of-flight spectrometer)

Previous results from literature (2)

$A_n^m(meV/a_0^n)$	A_2^0	A_4^0	A_4^3	A_6^0	A_6^3	A_6^6
	45	27	201	0.96	-16.4	17.6

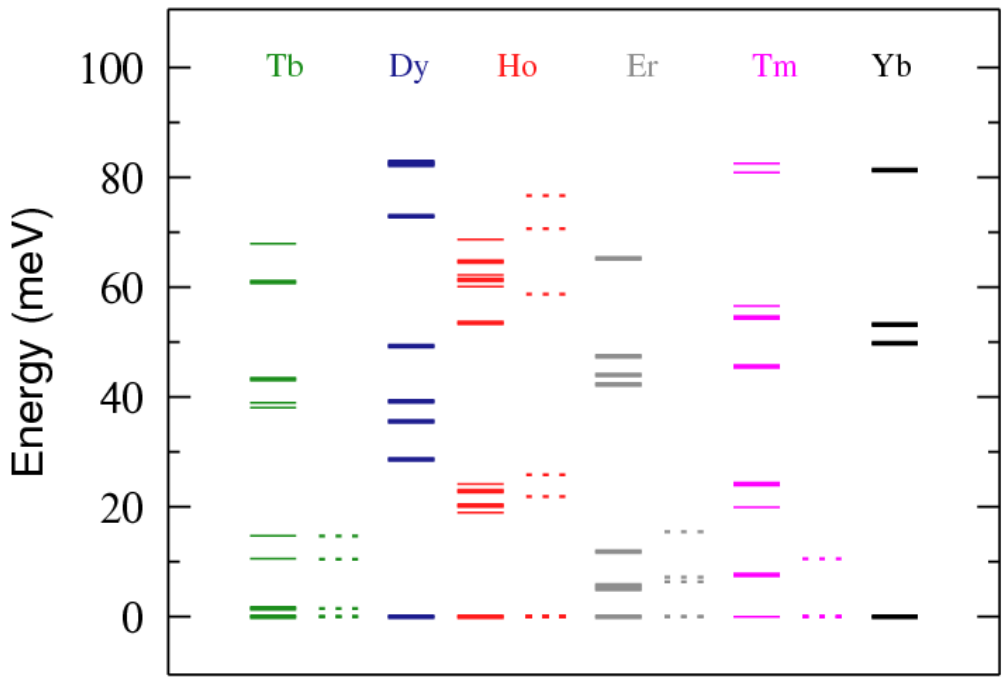


Computed CEF energy scheme with Malkin *et al.* parameters ($Ho_2Ti_2O_7$) vs experimental data

Malkin *et al.* Phys. Rev. B **70**, 075112 (2004)

Previous results from literature (3)

$A_n^m(meV/a_0^n)$	A_2^0	A_4^0	A_4^3	A_6^0	A_6^3	A_6^6
	37	22	184	0.88	-11.2	13.6

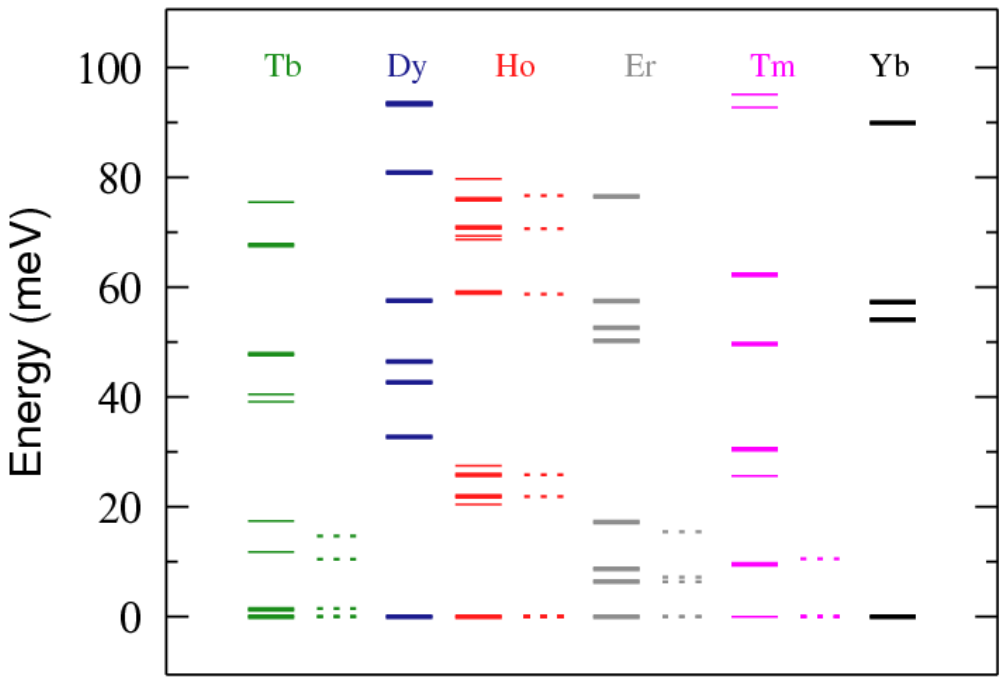


Computed CEF energy scheme with Mirebeau *et al.* parameters ($Tb_2Ti_2O_7$) vs experimental data

Mirebeau *et al.* Phys. Rev. B **76**, 184436 (2007)

Previous results from literature (4)

$A_n^m(meV/a_0^n)$	A_2^0	A_4^0	A_4^3	A_6^0	A_6^3	A_6^6
	44.8(5)	24.1(2)	173.5(1.7)	0.96(9)	-14.26(9)	17.1(3)



Computed CEF energy scheme with Rosenkranz *et al.* parameters ($Ho_2Ti_2O_7$) vs experimental data

Rosenkranz *et al.* J. Appl. Phys. **87**, 5914 (2000)

This work (1)

- Description of all the series assuming a simple scaling law:

$$A_n^m(R) = \frac{a^{n+1}(R')}{a^{n+1}(R)} A_n^m(R')$$

- Global fit of all published neutron measurements
- The neutron partial differential cross-section is:

$$\frac{d^2\sigma}{d\Omega dE'} \propto \frac{k'}{k} S(\mathbf{Q}, \omega)$$

with the scattering function:

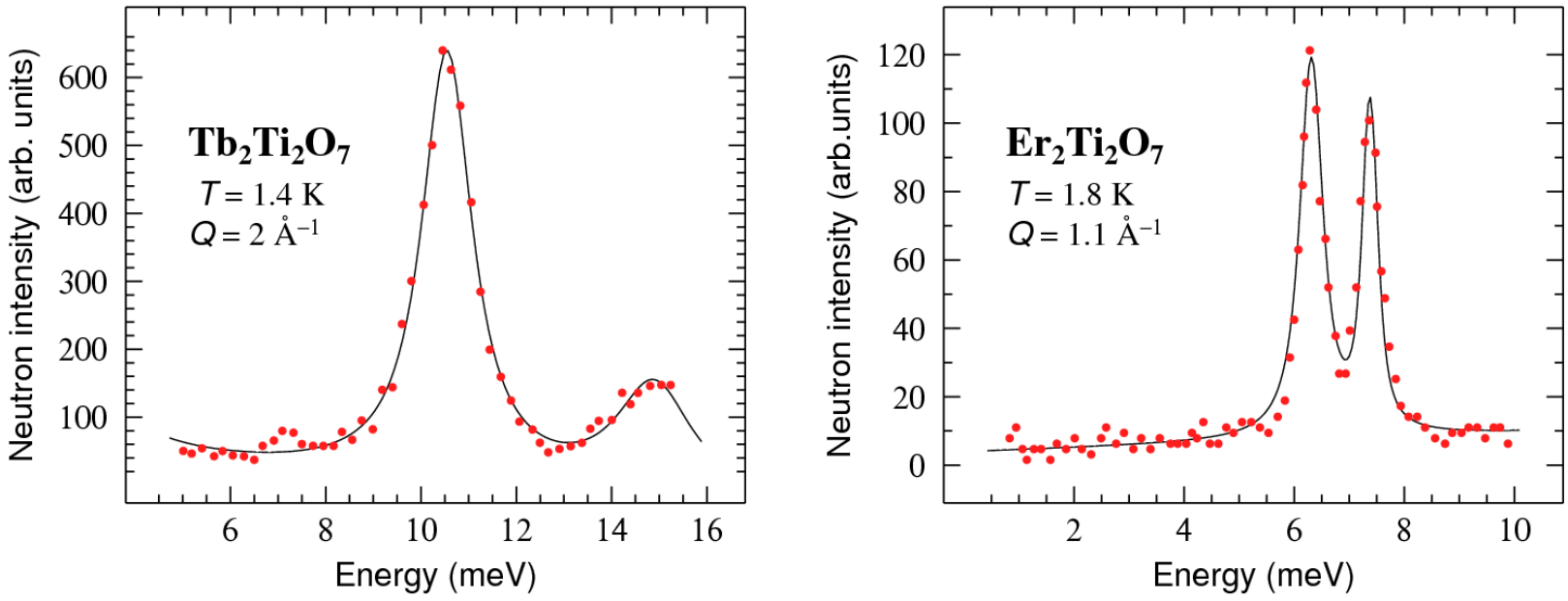
$$\begin{aligned} S(Q,\omega) &= I_0 \sum_{i,i'} \frac{\left(\sum_{\alpha=x,y,z} |\langle i|J_\alpha|i'\rangle|^2\right) \exp[-E_i/(k_B T)}{\sum_j \exp[-E_j/(k_B T)} \\ &\quad \times F(E_i - E_{i'} + \hbar\omega) \end{aligned}$$

This work (2)

Published data:

- $Tb_2Ti_2O_7$: Mirebeau *et al.*, PRB **76**, 184436 (2007)
- $Er_2Ti_2O_7$: Champion *et al.*, PRB **68**, 020401 (2003)

Our analysis:

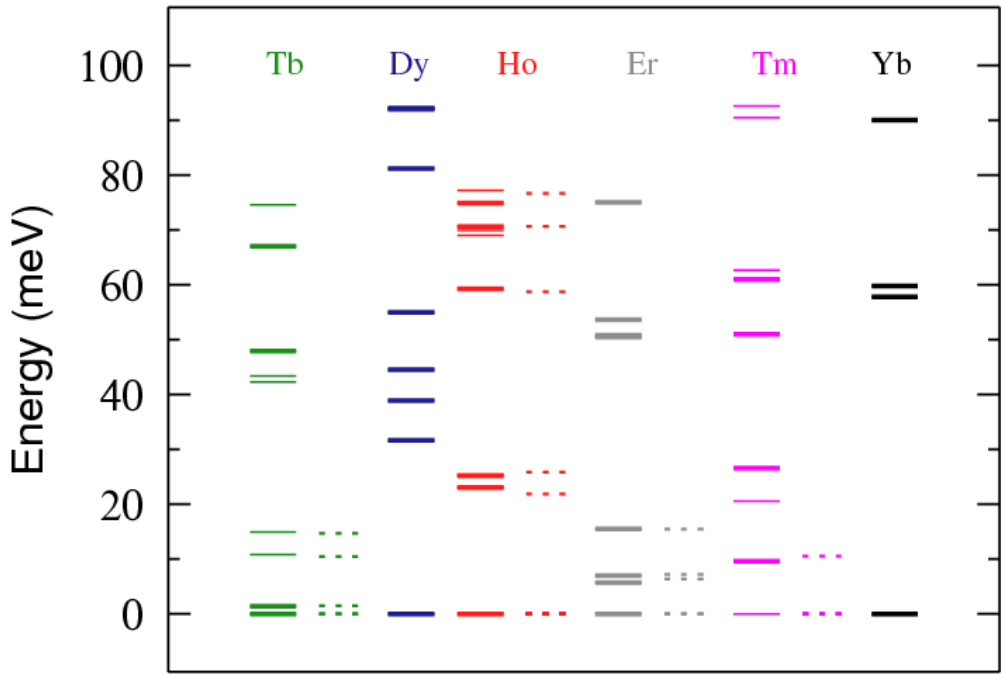


Simultaneous analysis of inelastic neutron scattering data on $Tb_2Ti_2O_7$ and $Er_2Ti_2O_7$

A.Bertin *et al.*, J. Phys.: Condens. Matter **24** 256003 (2012)

This work (3)

$A_n^m(meV/a_0^n)$	A_2^0	A_4^0	A_4^3	A_6^0	A_6^3	A_6^6
Results	40.5(1.0)	24(1)	213(13)	1.03(3)	-17(1)	14(1)
Explored region	$[0, 85]$	$[-34, 50]$	$[-300, 455]$	$[-3, 3]$	$[0, 34]$	$[-25, 30]$



Computed CEF energy scheme with our parameters vs experimental data

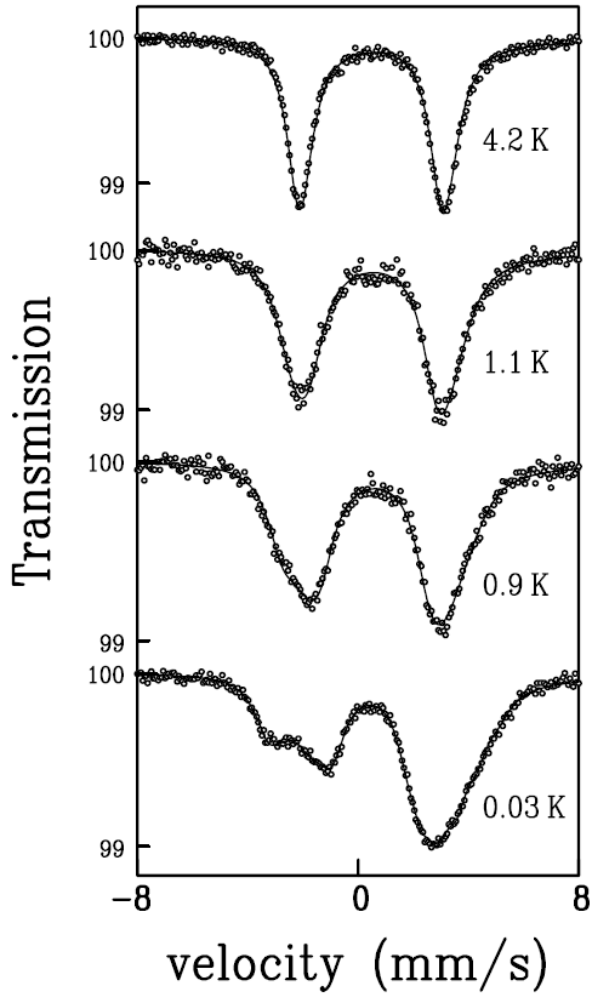
A.Bertin *et al.*, J. Phys.: Condens. Matter **24** 256003 (2012)

This work (4)

Comparison with Mössbauer data

- ^{155}Gd Mössbauer spectroscopy $\rightarrow$ nuclear quadrupolar splitting

  Armon *et al.* Phys. Lett. B **43** 380 (1973)
- Estimation of A_2^0 on $Gd_2Ti_2O_7$
- $A_2^0 = 95\ meV/a_0^2 \rightarrow 2.4$ larger than our result



Bonville *et al.* J.Phys.:Cond. Matter **15** 7777-87 (2003)

This work (5)

- Ground state wavefunctions have been calculated. For instance, in the case of $Tb_2Ti_2O_7$:

$$|\phi_0^{\pm}\rangle = 0.266|\pm 5\rangle \mp 0.133|\pm 2\rangle - 0.129|\mp 1\rangle \mp 0.946|\mp 4\rangle$$

- When the ground state is a doublet, we consider a $1/2$ effective spin and determine the spectroscopic g factors:

$$\begin{aligned} g_Z &= 2g_J|\langle\phi^{\pm}|J_z|\phi^{\pm}\rangle| \\ g_\perp &= g_J|\langle\phi^{+}|J_+|\phi^{-}\rangle| = g_J|\langle\phi^{-}|J_-|\phi^{+}\rangle| \end{aligned}$$

Rare earth	Tb	Dy	Ho	Er	Yb
$g_\parallel$	9.6(7)	19.6(2)	19.60(5)	1.8(5)	2.04(3)
$g_\perp$	0	0	0	7.7(1)	4.09(2)
Anisotropy	Ising	Ising	Ising	XY	XY

Conclusions and prospects

Conclusions and prospects

Point charge model $\rightarrow$ **scaling** law $\rightarrow$ **global analysis** of neutron data $\rightarrow$ **unique** and consistent CEF parameters

A.Bertin *et al.*, J. Phys.: Condens. Matter **24** 256003 (2012)

- Influence of the excited multiplets?
- Could the methodology be applied to the series $R_2Sn_2O_7$?

Thank you for your attention.

- Quadrupolar Hamiltonian:

$$\mathcal{H}_Q = \frac{eQ_{gs}V_{zz}}{4I(2I-1)}[3I_z^2 - I(I+1) + \frac{\eta}{2}(I_x^2 - I_y^2)]$$

- Nuclear quadrupolar splitting:

$$\Delta = \frac{eQ_{gs}V_{zz}}{2} \quad \text{with} \quad V_{zz} = V_{zz}^{latt} + V_{zz}^{4f}$$