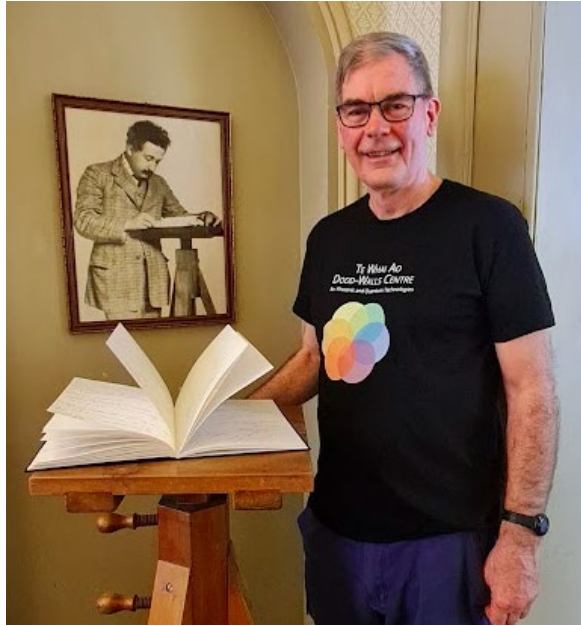# Making Sense of
Rare Earth Electronic Structure.
A Tutorial.

Chongqing, November 2024

Mike Reid
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Christchurch
New Zealand
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https://www2.phys.canterbury.ac.nz/~mfr24/

Fred Richardson

June 8,1939 – April 25, 2024

ANISOTROPIC LIGAND POLARIZABILITY CONTRIBUTIONS TO LANTHANIDE 4f → 4f INTENSITY PARAMETERS

Michael F. REID and Frederick S. RICHARDSON

Department of Chemistry, University of Virginia, Charlottesvolle, Virginia 22901, USA

The $A_{tp}\Xi(t,\lambda)$ parameterization scheme of the Judd–Ofelt 4f → 4f intensity model is shown to be inadequate for representing effects due to optically *anisotropic* ligand dipolar polarizations. "Extra" intensity parameters are needed when the lanthanide–ligand pairwise interactions are not cylindrically symmetric. Selection rules regarding these "extra" parameters are derived, and their possible significance to the hypersensitivity phenomenon is discussed.

Excited-State Chiral Discrimination Observed by Time-Resolved Circularly Polarized Luminescence Measurements

David H. Metcalf,*,† Seth W. Snyder,‡ Shuguang Wu,§
Gary L. Hilmes,§ James P. Riehl,§ J. N. Demas,† and
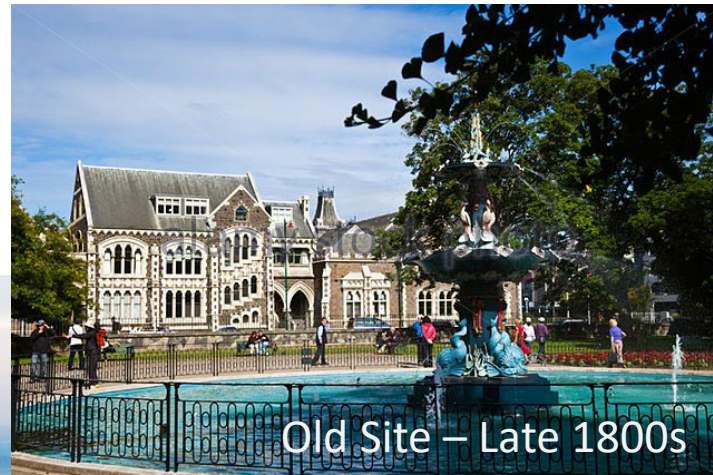F. S. Richardson*,†

ion: Public

Sergey Feofilov

François Auzel

Georges Boulon

Alexander Kaplyanskii.

Interactions with Duan (2004) and Ma (2007)

Christchurch, New Zealand

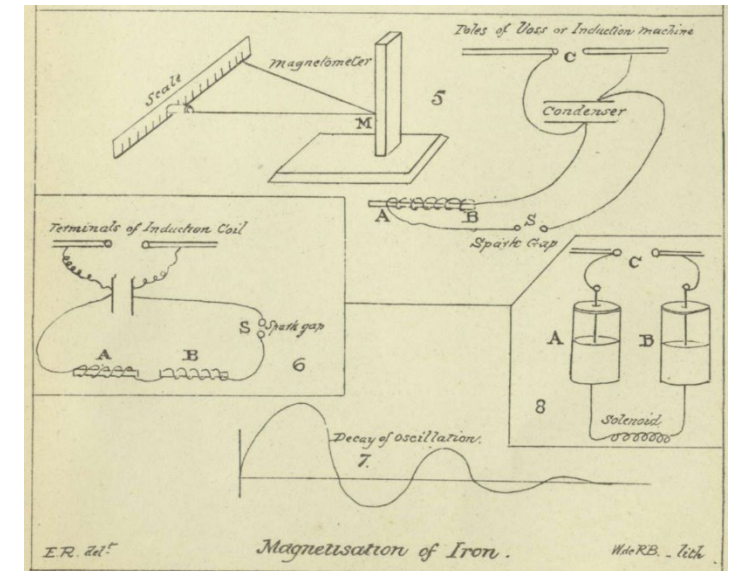Old Site – Late 1800s

1960s

Ernest Rutherford building, 2018

ÀRT. LIX.—*Magnetization of Iron by High-frequency Discharges.*

By E. RUTHERFORD, M.A.

[*Read before the Philosophical Institute of Canterbury, 7th November, 1894.*]
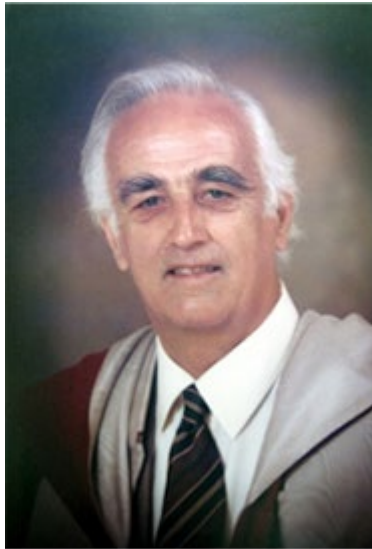
Mike Reid and Jon-Paul Wells: Our Motivation

- Develop fundamental knowledge relevant to practical applications of rare earths (lanthanides) in nano-particle imaging and quantum-information.

- Detailed understanding of spectroscopy, dynamics, electronic structure.

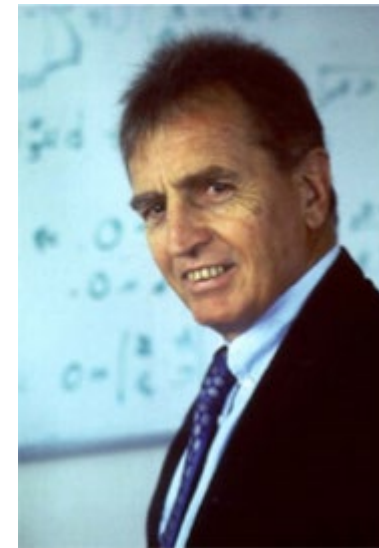- Jon Wells also leads a project on ring-laser gyroscope development.

UNIVERSITY OF CANTERBURY
Te Whare Wānanga o Waitaha
CHRISTCHURCH NEW ZEALAND

TE WHAI AO
DODD-WALLS CENTRE
for Photonic and Quantum Technologies

https://www.otago.ac.nz/dodd-walls/index.html

Jack Dodd

Dan Walls

Te Whai Ao
Dodd-Walls Centre
for Photonic and Quantum Technologies

Theory of Modulation of Light in a Double Resonance Experiment

J. N. Dodd and G. W. Series
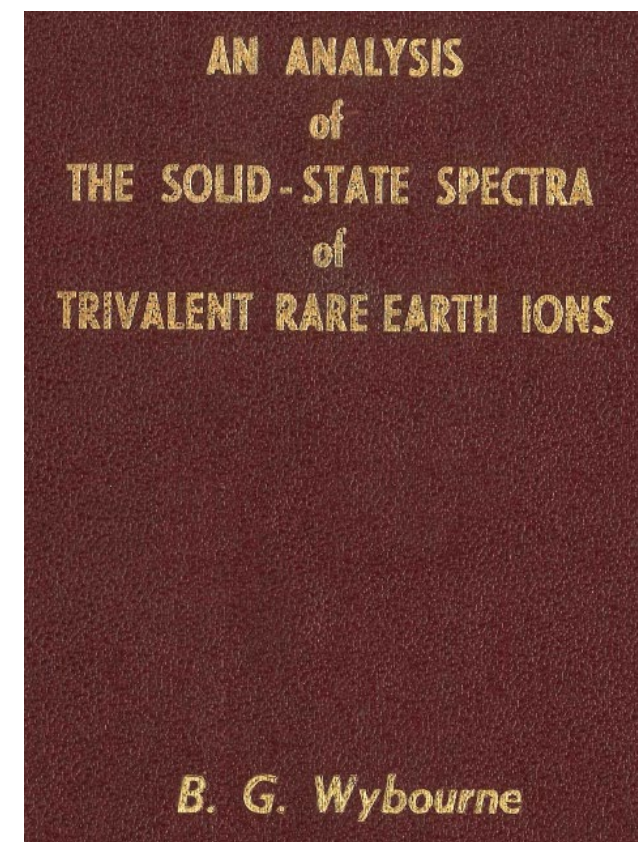Proceedings of the Royal Society of London.
Series A, Mathematical and Physical Sciences
Vol. 263, 353 (1961)

Generation of squeezed states via degenerate four-wave mixing

M. D. Reid and D. F. Walls
Phys. Rev. A 31, 1622 (1985)

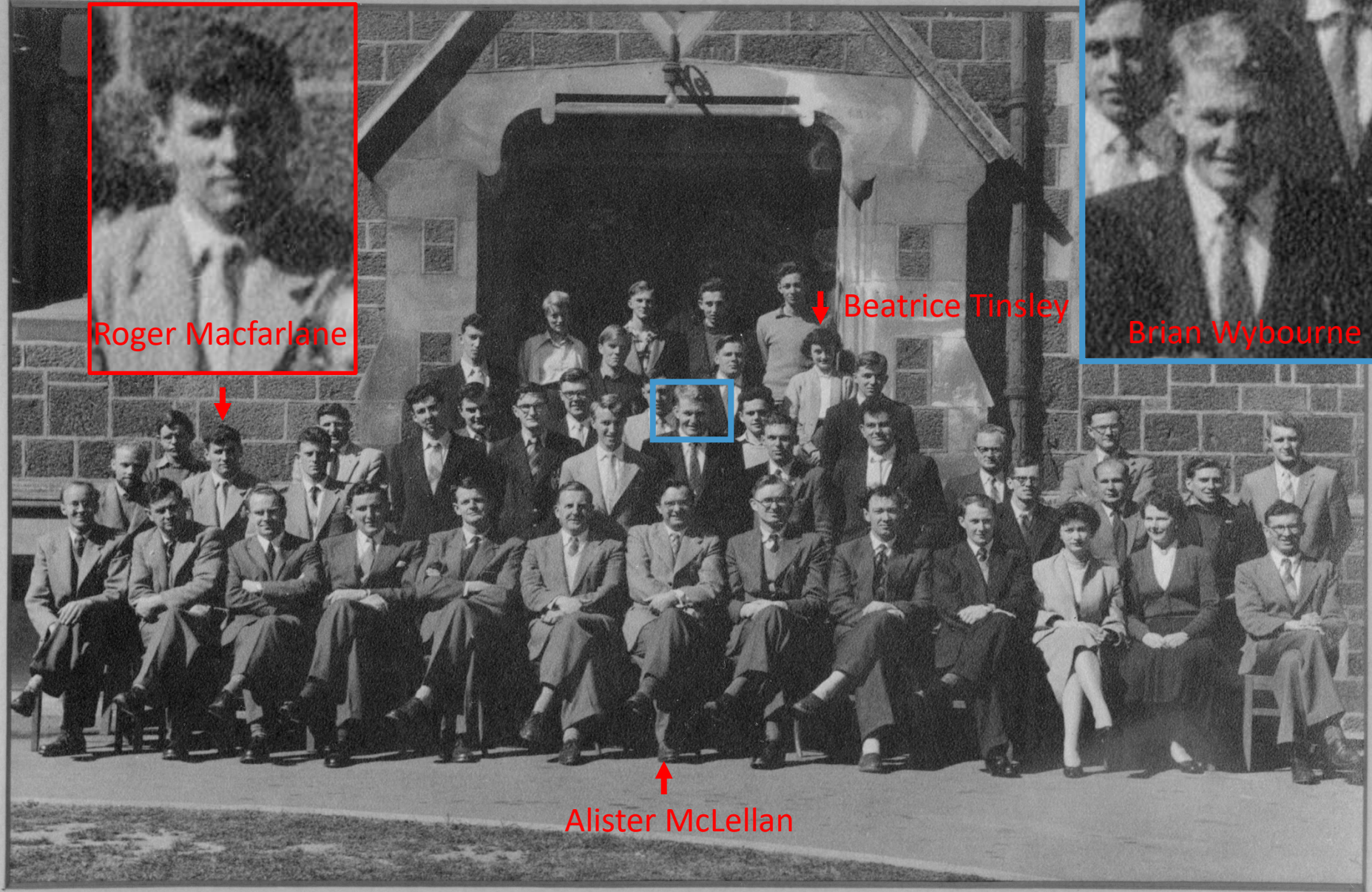Brian Judd (1930-2023) George Ofelt (1937-2014) Brian Wybourne (1935-2003)

Roger Macfarlane

Beatrice Tinsley

Brian Wybourne

Alister McLellan

Absent:
Glynn Jones
Rod Syme

Physics Department
University of Canterbury
1959

Optical and Magnetic Properties of some Transition Ion Complexes. PhD 1963

R.M. Macfarlane

Physics Department

University of Canterbury.

R.M.Macfarlane.

## SUB-KILOHERTZ OPTICAL LINEWIDTHS OF THE $^7F_0 \leftrightarrow {}^5D_0$ TRANSITION IN Y_2O_3:Eu^{3+}

R.M. MACFARLANE and R.M. SHELBY

IBM Research Laboratory, San Jose, CA 95193, USA

Homogeneous optical linewidths as small as 760 Hz (fwhm) have been observed in Y_2O_3:Eu^{3+} using delayed heterodyne photon echoes. Hyperfine and lifetime contributions to dephasing are estimated to contribute < 300 Hz to this width, and the remainder is attributed to quasi-resonant energy transfer.

Lanthanide (Rare Earth) 3+ ground state: $5s^2 \, 5p^6 \, 4f^N \, 5d^0$
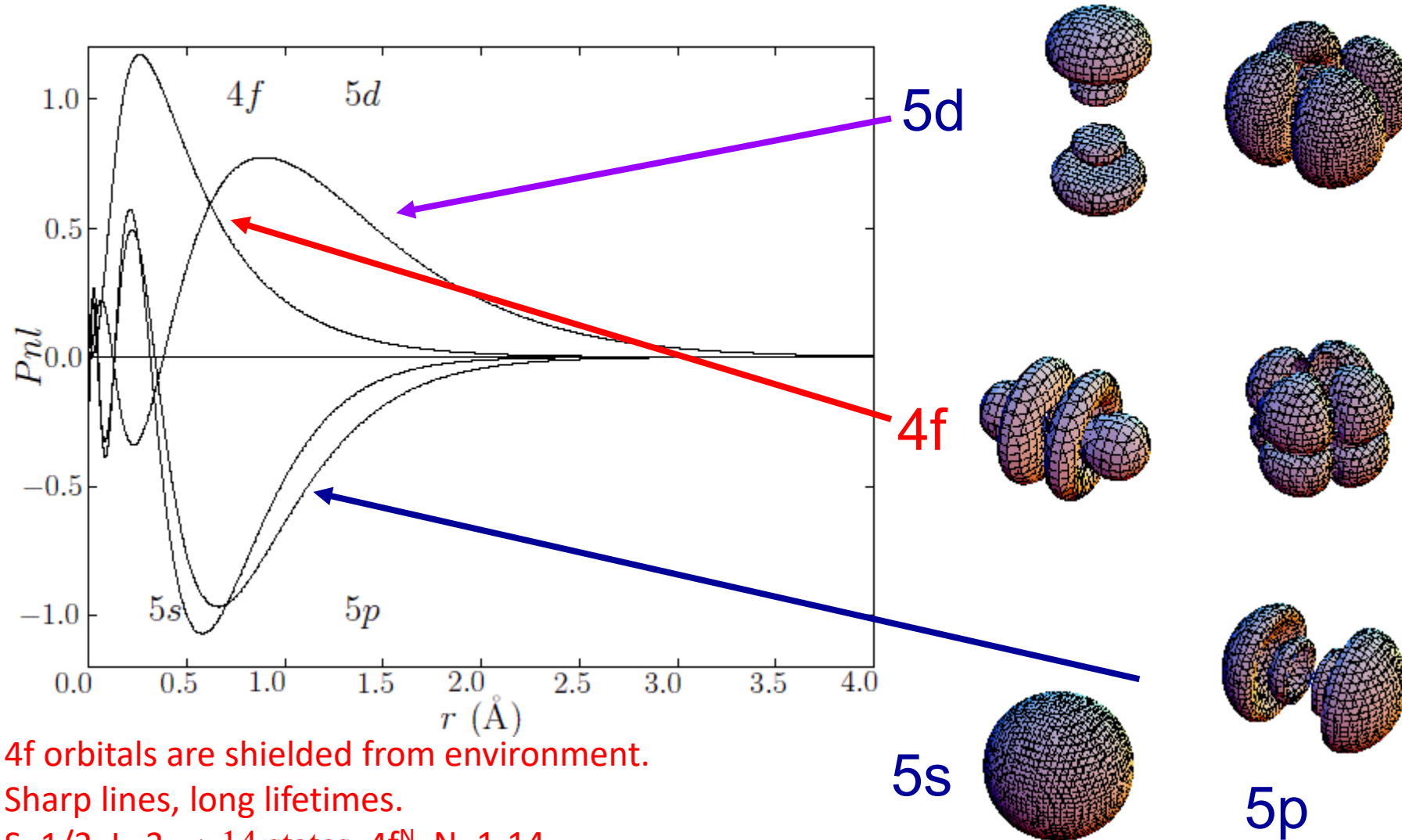
4f orbitals are shielded from environment.
Sharp lines, long lifetimes.
S=1/2, L=3 → 14 states, $4f^N$, N=1-14
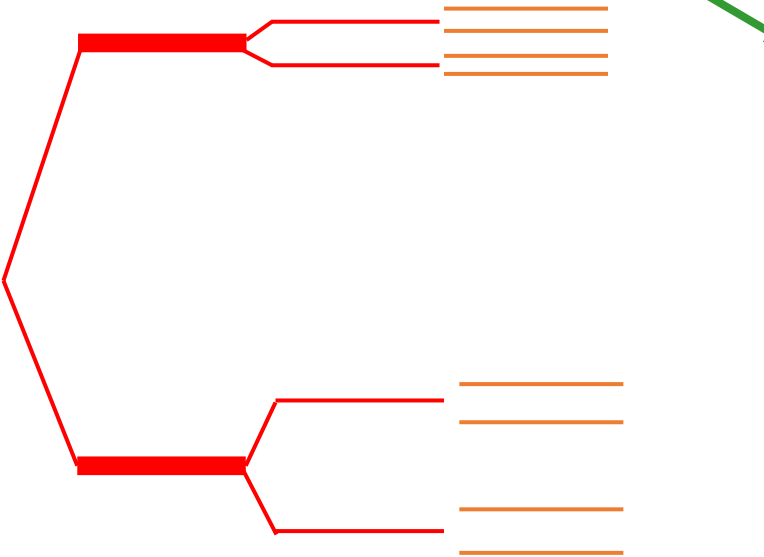Many transitions available for applications.

"Dieke Diagram" 1960s
Carnall, Goodman,
Rajnak, Rana, 1988

4f: S=1/2, L=3, → 14 states
$4f^N$: N=1-14

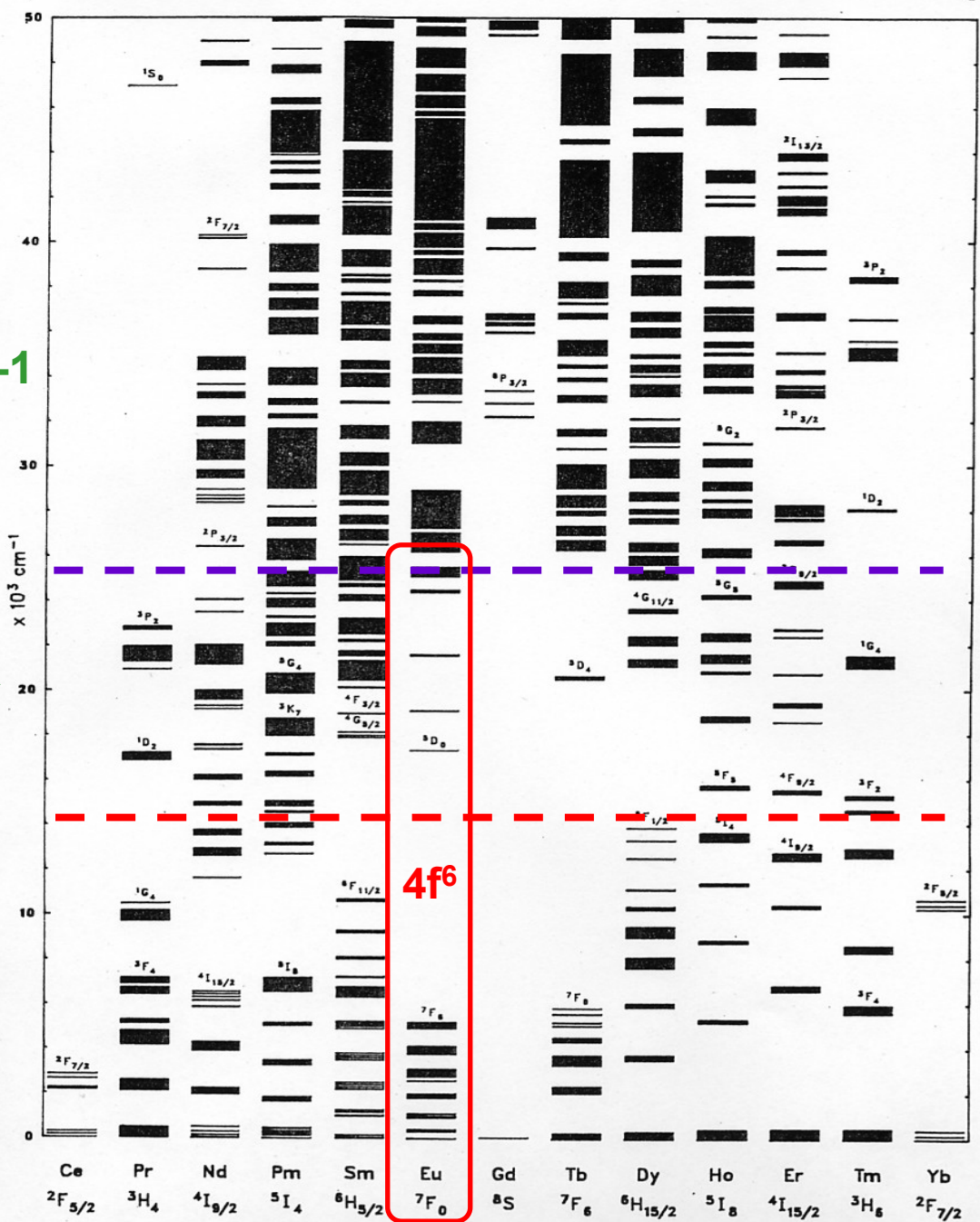Eu^{3+}, $4f^6$
3003 electronic states

20,000 cm^{-1}
500 nm
2.5 eV

$4f^6$

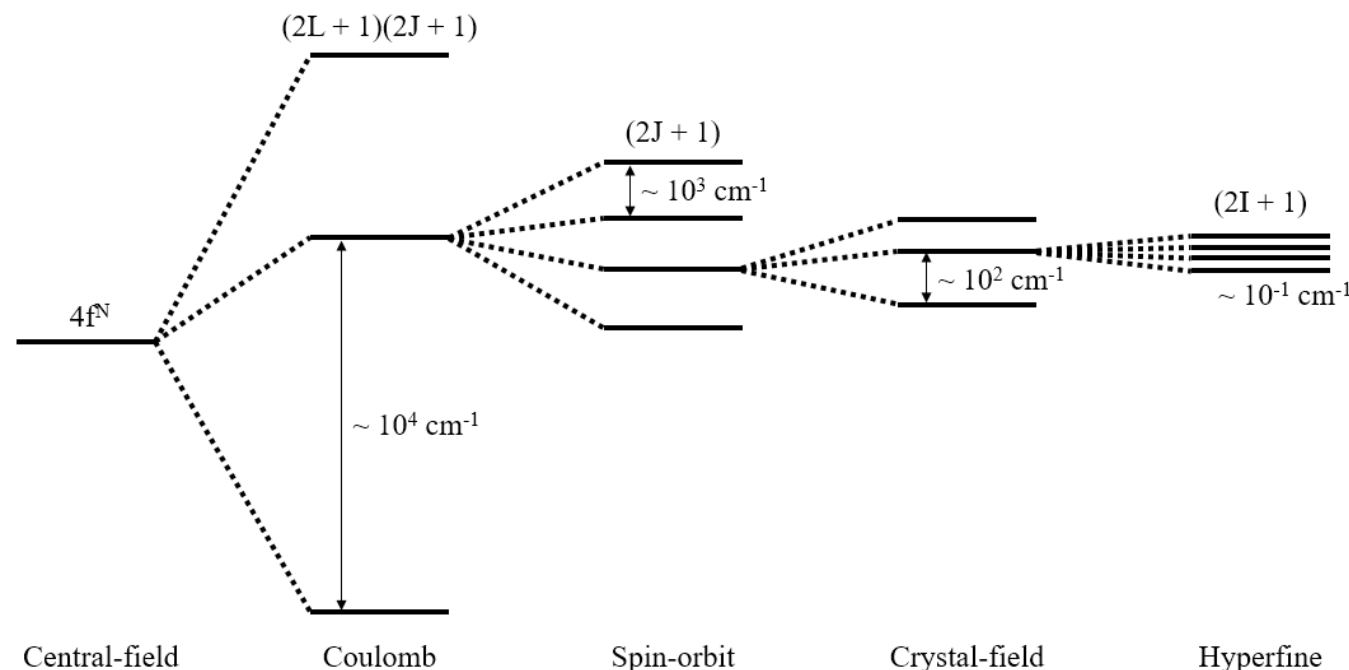Free ion   Crystal Field   Hyperfine/Magnetic

ENERGY LEVELS OF THE +3 LANTHANIDES IN LaF_3

Modelling the 4f^N structure of rare-earth doped crystals

$$H = H_{FI} + H_{CF} + H_Z + H_{HF}$$

Free Ion   Crystal Field   Zeeman   Hyperfine
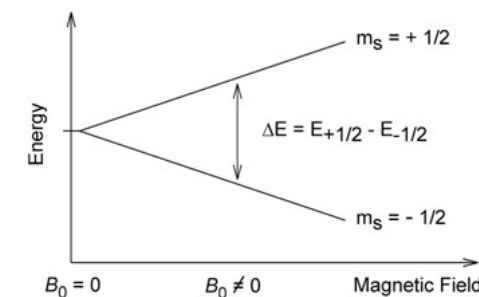
$$H_{CF} = \sum_{k,q} B_q^k C_q^{(k)}$$

C_1 symmetry → 27 crystal-field parameters

(2L + 1)(2J + 1)

(2J + 1)

$\sim 10^3$ cm^{-1}

(2I + 1)

(2I + 1)

$\sim 10^2$ cm^{-1}

$\sim 10^{-1}$ cm^{-1}

4f^N

$\sim 10^4$ cm^{-1}

Central-field   Coulomb   Spin-orbit   Crystal-field   Hyperfine

Zeeman

$$H_Z = \mu_B \, \boldsymbol{B} \cdot (\boldsymbol{L} + 2\boldsymbol{S})$$

Magnetic field can be experimentally varied.

$m_S = +1/2$

$\Delta E = E_{+1/2} - E_{-1/2}$

$m_S = -1/2$

Energy

$B_0 = 0$ $B_0 \neq 0$ Magnetic Field

Hyperfine

$$H_{HF} = A \, \boldsymbol{N} \cdot \boldsymbol{I} + Q \, H_Q$$

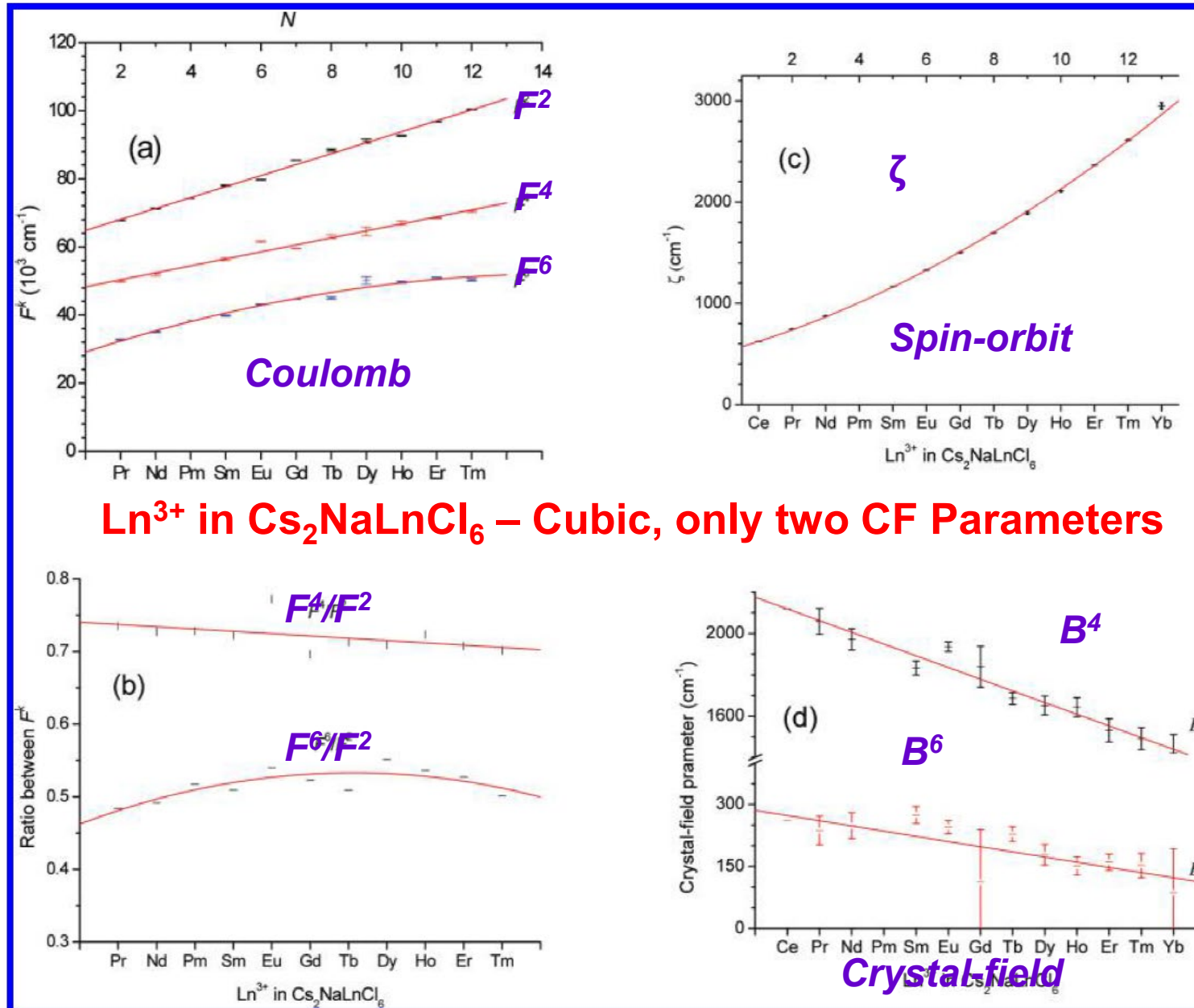*A and Q are parameters*

B_0

μ_N

N

B_N

μ_e
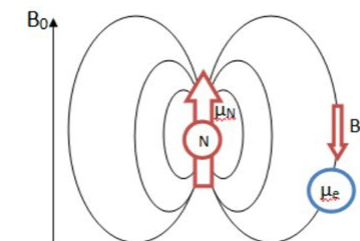
Eu^{3+} $^7F_0$ and $^5D_0$: electronic effects are small so Direct interaction of nucleus with magnetic field and lattice are important.

Understanding the energy levels: 4f^N
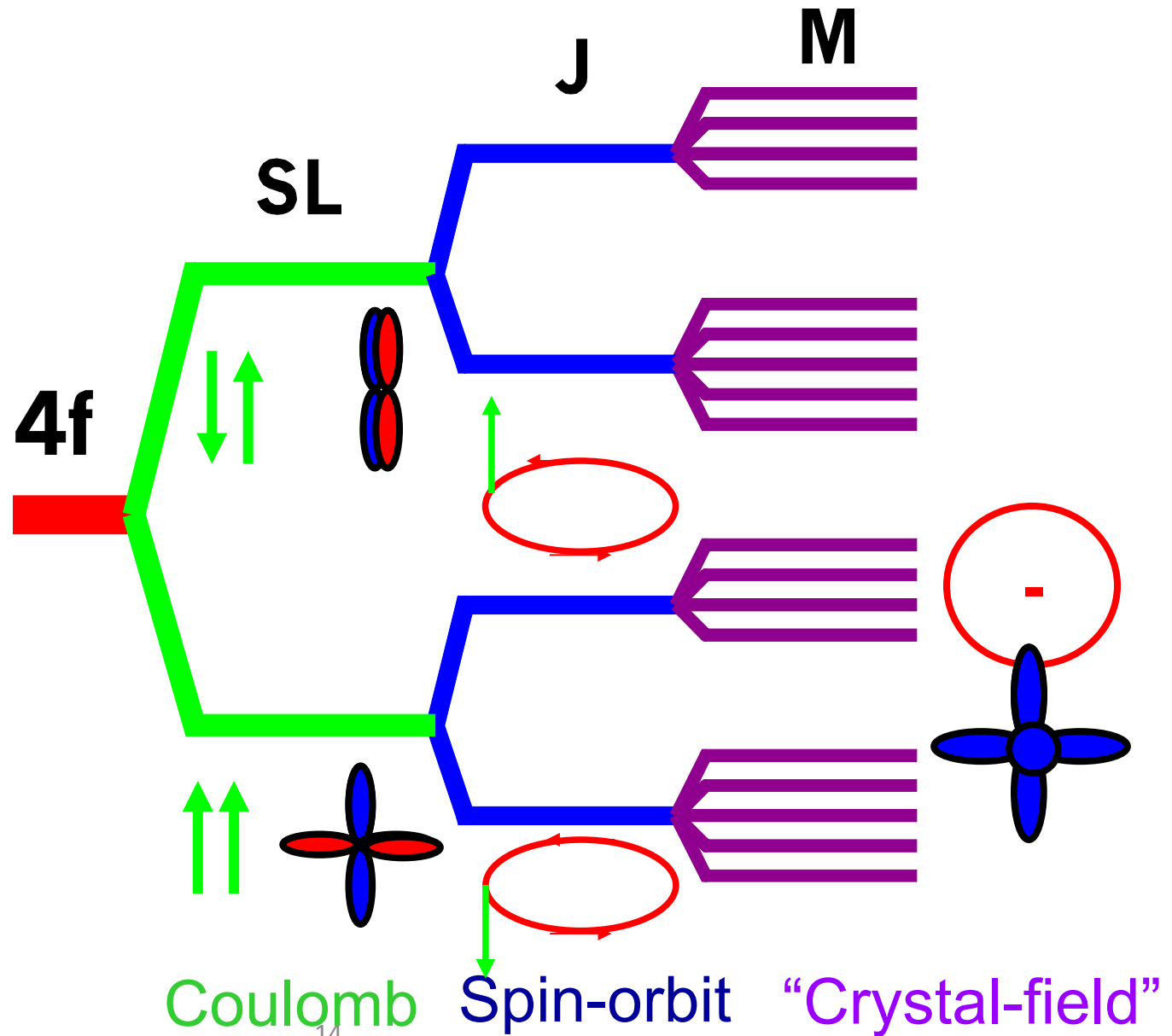
Coulomb   Spin-orbit   "Crystal-field"

Ln^{3+} in Cs$_2$NaLnCl$_6$ – Cubic, only two CF Parameters

Angular momentum states and tensor operators

$$[J_x, J_y] = iJ_z, \qquad \mathbf{J}^2 \equiv J_x^2 + J_y^2 + J_z^2$$

Rather than classifying
states by eigenvalues
and
operators by commutators,
it is helpful to classify *both*
in terms of
behaviour under rotations.

This is easier to relate to group representation theory.

$$
\begin{aligned}
J_z |jm\rangle &= m|jm\rangle, \\
\mathbf{J}^2 |jm\rangle &= j(j+1)|jm\rangle, \\
D(R)|jm\rangle &= \sum_{m'} D^{(j)}_{m'm}(R)|jm'\rangle
\end{aligned}
$$

$$[J_z, T_q^{(k)}] = qT_q^{(k)}$$

$$D(R)T_q^{(k)}D(R)^\dagger = \sum_{q'} D^{(k)}_{q'q}(R)T_{q'}^{(k)}$$

Wigner-Eckart theorem

$$\langle \alpha J M | T_q^{(k)} | \alpha' J' M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \langle \alpha J || T^{(k)} || \alpha' J' \rangle.$$

$$\langle \alpha J M | T_q^{(k)} | \alpha' J' M' \rangle = \langle J' M', kq | J M \rangle \frac{1}{\sqrt{2J+1}} \langle \alpha, J || T^{(k)} || \alpha', J' \rangle$$

Key idea: Matrix element = 3j symbol or Clebsch-Gordan coefficient x Reduced matrix element
"**geometry**" "**physics**"

Selection rules: $M' + q = M \text{ and } |J - J'| \leq k \leq J + J'.$

The easiest proof is to recall that operators transform as kets. We can therefore couple the operator and ket (up to a possible normalization):

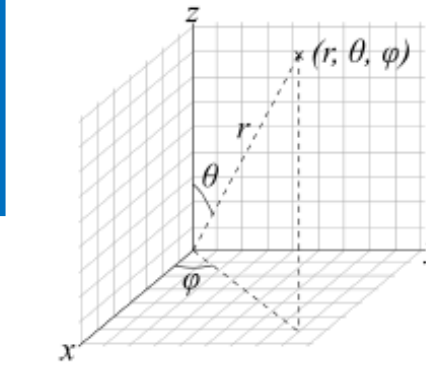$$|\alpha'', J'' M''\rangle \propto \sum_{q, M'} T_q^{(k)} |\alpha' J' M'\rangle \langle kq, J' M' | J'' M'' \rangle$$

We can use orthogonality to obtain an expression for $T_q^{(k)} |\alpha' J' M'\rangle$ and derive the result.

Spherical Tensors: Potentials

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} \sqrt{\frac{(l-m)!}{(l+m!)}} P_{lm}(\cos\theta) e^{im\phi}$$

$$C_q^{(k)}(\hat{\mathbf{r}}) = C_q^{(k)}(\theta, \phi) = \sqrt{\frac{4\pi}{2k+1}} Y_{kq}(\theta, \phi)$$

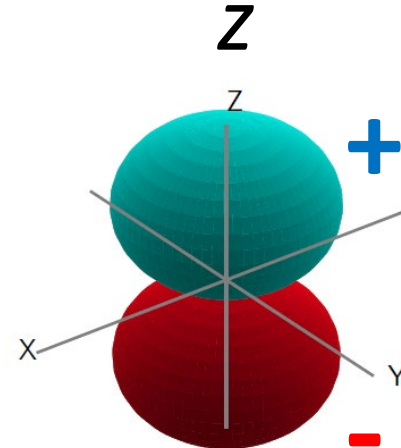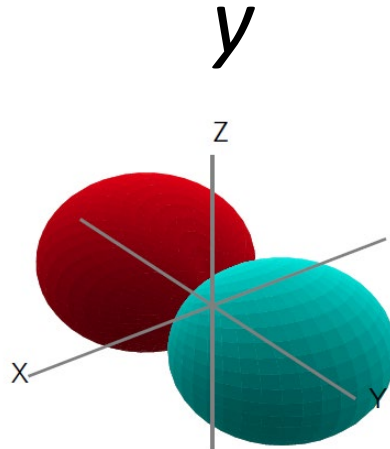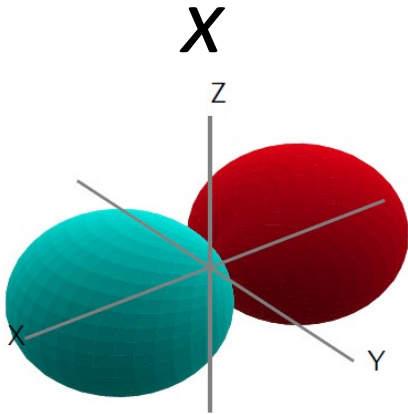| k	q	$C_q^{(k)}(x, y, z)$	$C_q^{(k)}(\theta, \phi)$
0	0	1	1
1	0	z/r	$\cos\theta$
1	± 1	$\mp\sqrt{\frac{1}{2}}(x \pm iy)/r$	$\mp\sqrt{\frac{1}{2}}\sin\theta\, e^{\pm i\phi}$
2	0	$\sqrt{\frac{1}{4}}(3z^2 - r^2)/r^2$	$\sqrt{\frac{1}{4}}(3\cos^2\theta - 1)$
2	± 1	$\mp\sqrt{\frac{3}{2}}z(x \pm iy)/r^2$	$\mp\sqrt{\frac{3}{2}}\cos\theta\sin\theta\, e^{\pm i\phi}$
2	± 2	$\sqrt{\frac{3}{8}}(x \pm iy)^2/r^2$	$\sqrt{\frac{3}{8}}\sin^2\theta\, e^{\pm 2i\phi}$

monopole

dipole

quadrupole...

Electric and Magnetic Dipoles

$$-e\mathbf{r} = -er\mathbf{C}^{(1)}$$

k	q	$C_q^{(k)}(x, y, z)$
0	0	1
1	0	z/r
1	± 1	$\mp\sqrt{\frac{1}{2}}(x \pm iy)/r$
2	0	$\sqrt{\frac{1}{4}(3z^2 - r^2)}/r^2$
2	± 1	$\mp\sqrt{\frac{3}{2}}z(x \pm iy)/r^2$
2	± 2	$\sqrt{\frac{3}{8}}(x \pm iy)^2/r^2$

$$x = r\frac{1}{\sqrt{2}}\left(-C_1^{(1)} + C_{-1}^{(1)}\right), \qquad y = r\frac{i}{\sqrt{2}}\left(C_1^{(1)} + C_{-1}^{(1)}\right), \qquad z = r\,C_0^{(1)}.$$

x
y
z
+
−

$$\mathbf{B} \cdot \mathbf{J} = \sum_{i=x,y,z} B_i J_i.$$

$$J_x = r\frac{1}{\sqrt{2}}\left(-J_1^{(1)} + J_{-1}^{(1)}\right), \qquad J_y = r\frac{i}{\sqrt{2}}\left(J_1^{(1)} + J_{-1}^{(1)}\right), \qquad J_z = r\,J_0^{(1)}.$$
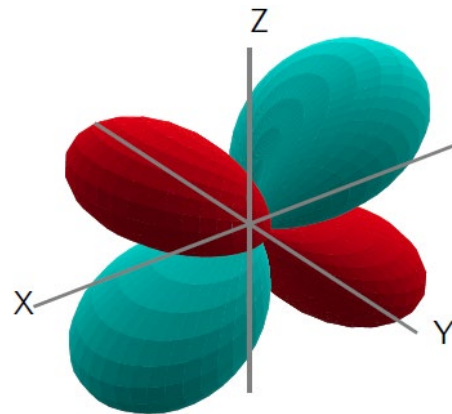
Crystal Field Potential – Quantum Mechanical!

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} \sqrt{\frac{(l-m)!}{(l+m!)}} P_{lm}(\cos\theta) e^{im\phi}$$

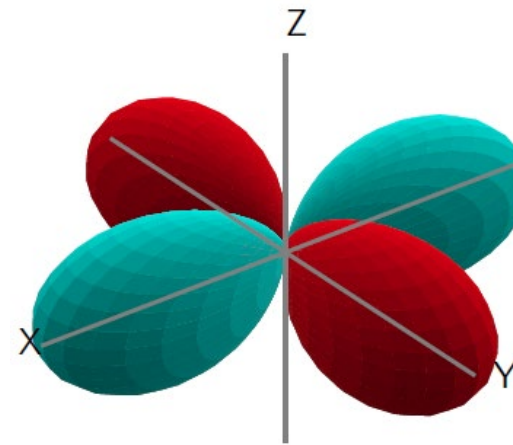$$C_q^{(k)}(\hat{\mathbf{r}}) = C_q^{(k)}(\theta, \phi) = \sqrt{\frac{4\pi}{2k+1}} Y_{kq}(\theta, \phi)$$

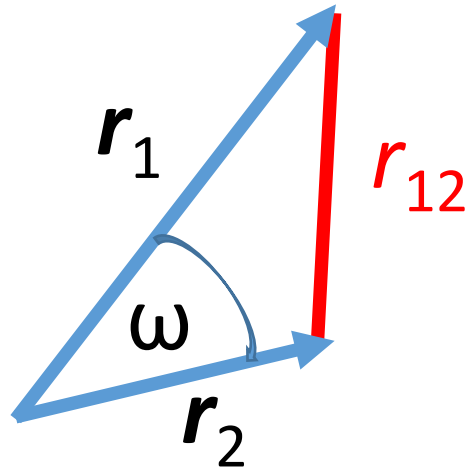| k	q	$C_q^{(k)}(x,y,z)$	$C_q^{(k)}(\theta, \phi)$
0	0	1	1
1	0	z/r	$\cos\theta$
1	± 1	$\mp\sqrt{\frac{1}{2}}(x \pm iy)/r$	$\mp\sqrt{\frac{1}{2}}\sin\theta\, e^{\pm i\phi}$
2	0	$\sqrt{\frac{1}{4}}(3z^2 - r^2)/r^2$	$\sqrt{\frac{1}{4}}(3\cos^2\theta - 1)$
2	± 1	$\mp\sqrt{\frac{3}{2}}z(x \pm iy)/r^2$	$\mp\sqrt{\frac{3}{2}}\cos\theta\sin\theta\, e^{\pm i\phi}$
2	± 2	$\sqrt{\frac{3}{8}}(x \pm iy)^2/r^2$	$\sqrt{\frac{3}{8}}\sin^2\theta\, e^{\pm 2i\phi}$

$$H_{CF} = \sum_{k,q} B_q^k C_q^{(k)}$$

Note: Potential is **real**. **Phases** of parameters determine **orientation**, e.g. $e^{iq\phi}$

$C^2_0(r)$ $C^2_1(r) - C^2_{-1}(r)$ $C^2_2(r) + C^2_{-2}(r)$

Coulomb interaction and crystal field: Addition theorem

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} P_k(\cos\omega)$$

cos ω: -1..1

$$= \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \mathbf{C}^{(k)}(\hat{\mathbf{r}}_1) \cdot \mathbf{C}^{(k)}(\hat{\mathbf{r}}_2)$$

$$= \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{+k} C_q^{(k)}(\hat{\mathbf{r}}_1) C_{-q}^{(k)}(\hat{\mathbf{r}}_2)(-1)^q.$$
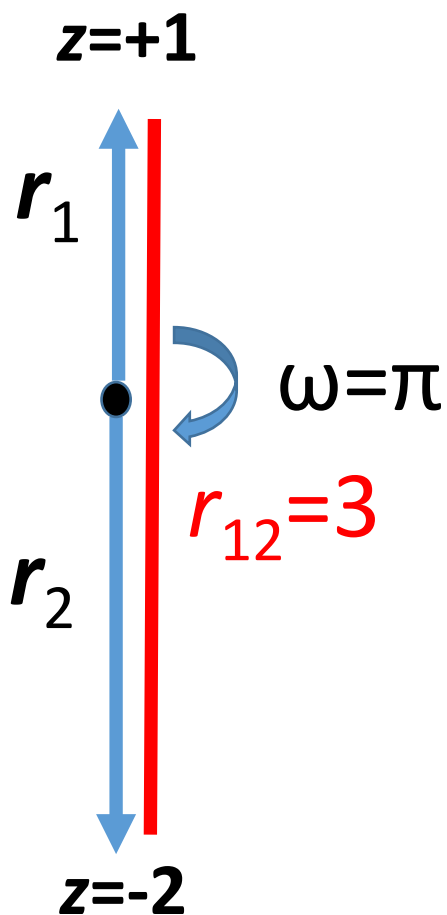
Key idea:
$1/r_{12}$ is a function
of r_1 and r_2

Legendre Polynomials
orthogonal: -1..1

k	P_k
0	1
1	x
2	$(3x^2 - 1)/2$

k	q	$C_q^{(k)}(x,y,z)$
0	0	1
1	0	z/r
1	± 1	$\mp\sqrt{\frac{1}{2}}(x \pm iy)/r$
2	0	$\sqrt{\frac{1}{4}}(3z^2 - r^2)/r^2$
2	± 1	$\mp\sqrt{\frac{3}{2}}z(x \pm iy)/r^2$
2	± 2	$\sqrt{\frac{3}{8}}(x \pm iy)^2/r^2$

Addition Theorem - Example

$$1/r_{12} = 1/3 \qquad \cos\omega = \cos\pi = -1$$

z=+1

r_1

$\omega=\pi$

$r_{12}=3$

r_2

z=-2

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} P_k(\cos\omega)$$

$$= \frac{1^0}{2^1} \times (1) + \frac{1^1}{2^2} \times (-1) + \frac{1^2}{2^3} \times \left(\frac{1}{2}\left(3 \times (-1)^2 - 1\right)\right) + \ldots$$
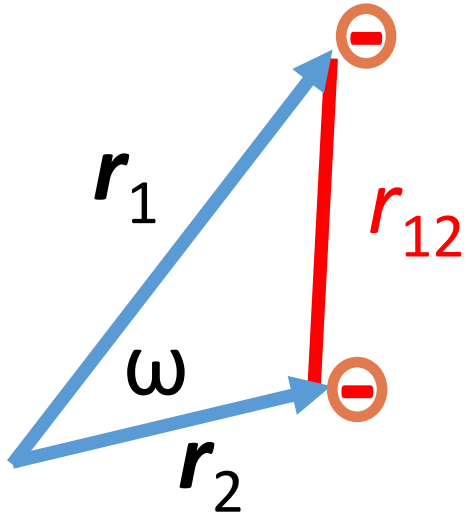
$$= \frac{1}{2} - \frac{1}{4} + \frac{1}{8} + \ldots$$

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{+k} C_q^{(k)}(\hat{\mathbf{r}}_1) C_{-q}^{(k)}(\hat{\mathbf{r}}_2)(-1)^q$$

$$= \frac{1^0}{2^1} \times 1 \times 1 + \frac{1^1}{2^2} \times (+1) \times (-1) + \frac{1^2}{2^3} \times \left(\left(\sqrt{\tfrac{1}{4}}(3-1)\right) \times \left(\sqrt{\tfrac{1}{4}}(3-1)\right)\right) + .$$

$$= \frac{1}{2} - \frac{1}{4} + \frac{1}{8} + \ldots$$

Legendre Polynomials
orthogonal: -1..1

k	P_k
0	1
1	x
2	$(3x^2 - 1)/2$

k	q	$C_q^{(k)}(x,y,z)$
0	0	1
1	0	z/r
1	± 1	$\mp\sqrt{\tfrac{1}{2}}(x \pm iy)/r$
2	0	$\sqrt{\tfrac{1}{4}(3z^2 - r^2)}/r^2$
2	± 1	$\mp\sqrt{\tfrac{3}{2}}z(x \pm iy)/r^2$
2	± 2	$\sqrt{\tfrac{3}{8}}(x \pm iy)^2/r^2$

Coulomb Interaction

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} P_k(\cos\omega)$$

$$= \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} \mathbf{C}^{(k)}(\hat{\mathbf{r}}_1) \cdot \mathbf{C}^{(k)}(\hat{\mathbf{r}}_2)$$

$$= \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} \sum_{q=-k}^{+k} C_q^{(k)}(\hat{\mathbf{r}}_1) C_{-q}^{(k)}(\hat{\mathbf{r}}_2)(-1)^q.$$

$$H_{\text{Coulomb}} = \frac{e^2}{4\pi\epsilon_0} \sum_{k}^{\text{even}} \sum_{i<j} \frac{r_{<}^k}{r_{>}^{k+1}} \left[\mathbf{C}^{(k)}(\hat{\mathbf{r}}_i) \cdot \mathbf{C}^{(k)}(\hat{\mathbf{r}}_j)\right]$$

$$= \sum_{k}^{\text{even}} F^k \left[\sum_{i<j} \mathbf{C}^{(k)}(\hat{\mathbf{r}}_i) \cdot \mathbf{C}^{(k)}(\hat{\mathbf{r}}_j)\right]$$

$$= \sum_{k}^{\text{even}} F^k f_k.$$

Two-centre addition theorem:
Ligand polarization(dynamic coupling) and energy transfer

f electron

Ligand electron

r_j

r_{jk}

r_{kL}

R_L

Key idea:
$1/r_{jk}$ **is a function of** r_j, r_{kL}, **and** R_L.

Ionic transitions hypersensitive to environment

B. R. Judd

Physics Department, The Johns Hopkins University, Baltimore, Maryland 21218

$$r_{jk}^{-1} = \sum_{l,t} r_j^l r_{kL}^t R_L^{-l-t-1} [(2l+2t)! / (2l)!(2t)!]^{1/2}$$
$$\times (-1)^t (C_j^{(l)} C_{kL}^{(t)})^{(l+t)} \cdot C_L^{(l+t)} .$$

Interaction between f electron and Ligand electron

Energy transfer

In this case there is an interaction between f electrons on two ions. Dipole-dipole is $l=t=1$, so we have $1/R^3$. Square gives $1/R^6$. Exchange interaction gives a different distance dependence.

Electrostatic Crystal Field

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} P_k(\cos\omega)$$

$$= \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \mathbf{C}^{(k)}(\hat{\mathbf{r}}_1) \cdot \mathbf{C}^{(k)}(\hat{\mathbf{r}}_2)$$

$$= \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{+k} C_q^{(k)}(\hat{\mathbf{r}}_1) C_{-q}^{(k)}(\hat{\mathbf{r}}_2)(-1)^q.$$
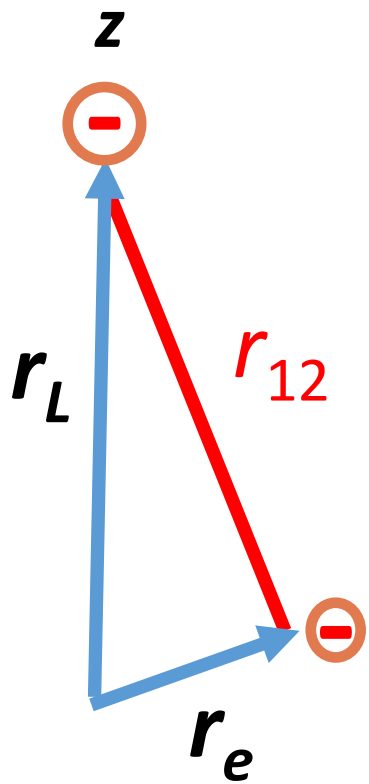
$$V = \frac{e^2}{4\pi\epsilon_0} \sum_{kq} \langle r^k \rangle C_q^{(k)}(\theta_e, \phi_e) \frac{1}{r_L^{k+1}} C_{-q}^{(k)}(\theta_L, \phi_L)(-1)^q$$

$$= \sum_{kq} \left[\frac{e^2}{4\pi\epsilon_0} \langle r^k \rangle \frac{1}{r_L^{k+1}} C_{-q}^{(k)}(\theta_L, \phi_L)(-1)^q \right] \left[C_q^{(k)}(\theta_e, \phi_e) \right]$$

$$= \sum_{kq} B_q^k C_q^{(k)}.$$

$$C_0^{(2)} = \sqrt{\frac{1}{4}}(3z^2 - r^2)/r^2 = 1,$$

$$r_L = 3\,\text{Å} = 3 \times 10^{-10}\,\text{m},$$

$$\langle r^2 \rangle = 0.2\,\text{Å} = 0.2 \times 10^{-20}\,\text{m}^2.$$

$\mathbf{C}^2{}_0(r)$

$$B_0^2 = \frac{e^2}{4\pi\epsilon_0} \times \frac{1}{r_L^3} C_0^{(2)}(0,0)(-1)^0 = \frac{(1.6 \times 10^{-19})^2}{4\pi \times 8.85 \times 10^{-12}} \times \frac{0.2 \times 10^{-20}}{(3 \times 10^{-10})^3} = 1.7 \times 10^{-20}\,\text{J}.$$

We can convert to eV by dividing by 1.6×10^{-19} C, and multiply by 8066 to convert to cm^{-1}. So B_0^2 is $0.11\,\text{eV}$, or $860\,\text{cm}^{-1}$.

"Crystal Field" $\sum_{k,q} B_q^k C_q^{(k)}$

[Diagrams use p orbitals for simplicity.]

Do the ``Ligand Field'' Parameters in Lanthanides Represent Weak Covalent Bonding?
C.K. Jorgensen, R. Pappalardo, H.H. Schmidtke J. Chem. Phys. 1963

z

x,y

z   x,y

L

Electrostatic   **Overlap**   **Covalency**
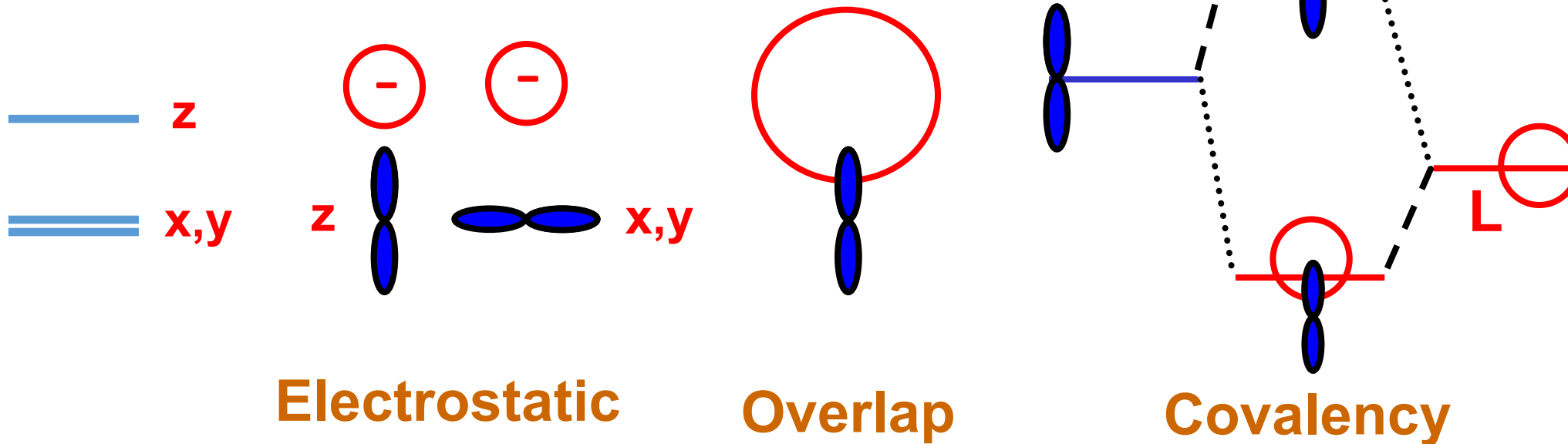
All increase energy of z orbital more than x,y

Orbital energies or Hamiltonian matrix ↔ crystal-field parameters

Do the ``Ligand Field'' Parameters in Lanthanides Represent Weak Covalent Bonding?

C.K. Jorgensen, R. Pappalardo, H.H. Schmidtke, J. Chem. Phys. 1963

Abstract: Instead of explaining the seven different f-orbital energies or five different d-orbital energies by parameters $A_{nm} \langle r_n \rangle$ of the electrostatic ligand field model, we propose to classify the energy levels according to the actual one-electron energies and to interpret these quantities by the weak effects of σ antibonding on the partly filled shell. Calculations of the relative angular dependence of such effects are made in a simple model and compared with experimental data for nine- and eight-coordinated lanthanide compounds The agreement is judged to be much more satisfactory than when the electrostatic model is applied, and the number of freely chosen parameters is much smaller.

L

Covalency
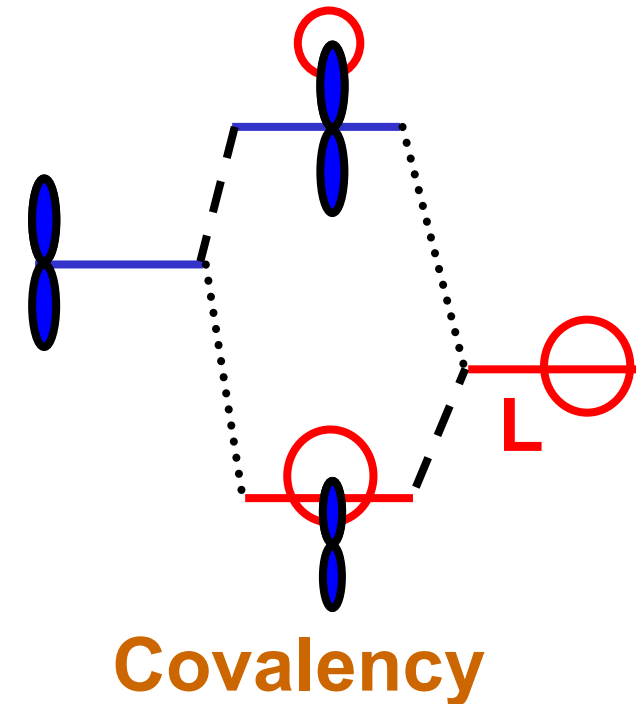
Rotations and the Superposition Model
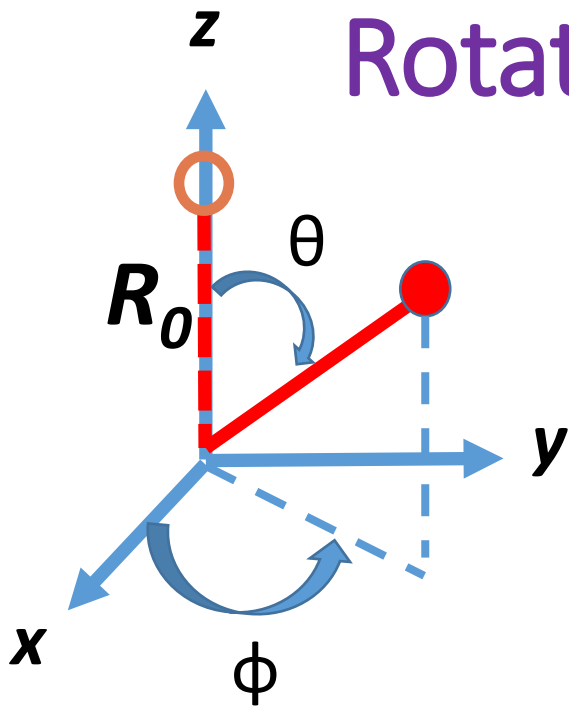
Electrostatic model:

$$B_q^k = \frac{e^2}{4\pi\epsilon_0}\langle r^k\rangle \sum_L \frac{1}{r_L^{k+1}} C_{-q}^{(k)}(\theta_L, \phi_L)(-1)^q$$

Rotation matrix is related to the spherical tensors:

$$D_{q'0}^{(j)}(\alpha = \phi, \beta = \theta, \gamma = 0) = (-1)^{q'} C_{-q'}^{(K)}(\theta, \phi).$$

Rotate from Z and change the distance to build up CF in terms of single ligand CF ("intrinsic parameters"):

$$B_q^k = \bar{B}_k(R_0) \sum_L C_{-q}^{(k)}(\theta_L, \phi_L)(-1)^q \left(\frac{R_0}{R_L}\right)^{t_k}$$

$$B_0^k(R_L) \equiv \bar{B}_k(R_L)$$

Key idea: Crystal-field parameters are a product of single-ligand interaction ("intrinsic parameters") and geometry (distances and angles).

Table A.1. The Wigner rotation matrices $D_{m',m}^1(\alpha, \beta, \gamma)$.

m'	m		
	1	0	-1
1	$\frac{1+\cos\beta}{2} e^{-i(\alpha+\gamma)}$	$-\frac{1}{\sqrt{2}}\sin\beta e^{-i\alpha}$	$\frac{1-\cos\beta}{2} e^{-i(\alpha-\gamma)}$
0	$\frac{1}{\sqrt{2}}\sin\beta e^{-i\gamma}$	$\cos\beta$	$-\frac{1}{\sqrt{2}}\sin\beta e^{i\gamma}$
-1	$\frac{1-\cos\beta}{2} e^{i(\alpha-\gamma)}$	$\frac{1}{\sqrt{2}}\sin\beta e^{i\alpha}$	$\frac{1+\cos\beta}{2} e^{i(\alpha+\gamma)}$
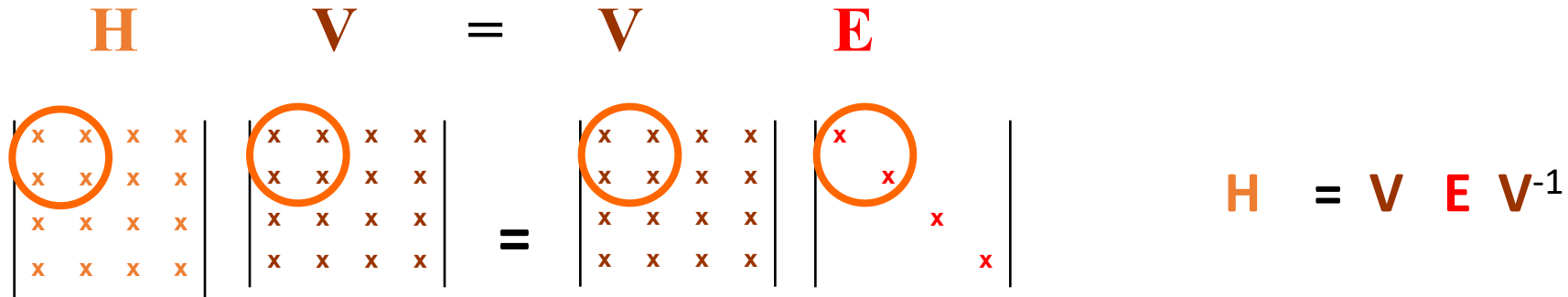
k	q	$C_q^{(k)}(x,y,z)$	$C_q^{(k)}(\theta,\phi)$
0	0	1	1
1	0	z/r	$\cos\theta$
1	± 1	$\mp\sqrt{\frac{1}{2}}(x\pm iy)/r$	$\mp\sqrt{\frac{1}{2}}\sin\theta\, e^{\pm i\phi}$

Relating ab-initio (first principles) calculations to crystal-field calculations

- Modern quantum-chemistry calculations for rare-earth materials:
    - DFT calculation using VASP.
    - 4f energies (without spin-orbit) using AIMP embedded cluster approach
    - [Seijo et al J. Chem. Phys. 114, 118 (2001).]
    - SA-CASSCF calculation using MOLCAS.

- Use calculations for Ce^{3+} to estimate parameters for the series.
    - For high symmetry we can just fit the energy levels of the ab-initio calculation.
    - Not possible in low symmetries such as D_2 (YAG), C_1 (YSO)
    - Need to relate the matrices.
    - Project the Hamiltonian into the model space.
      (Hurtubise and Freed, Adv. Chem. Phys. 83, 465, 1993).

Springer Series in Materials Science 322

Zoila Barandiarán
Jonas Joos
Luis Seijo

Luminescent Materials

A Quantum Chemical Approach for Computer-Aided Discovery and Design

Springer
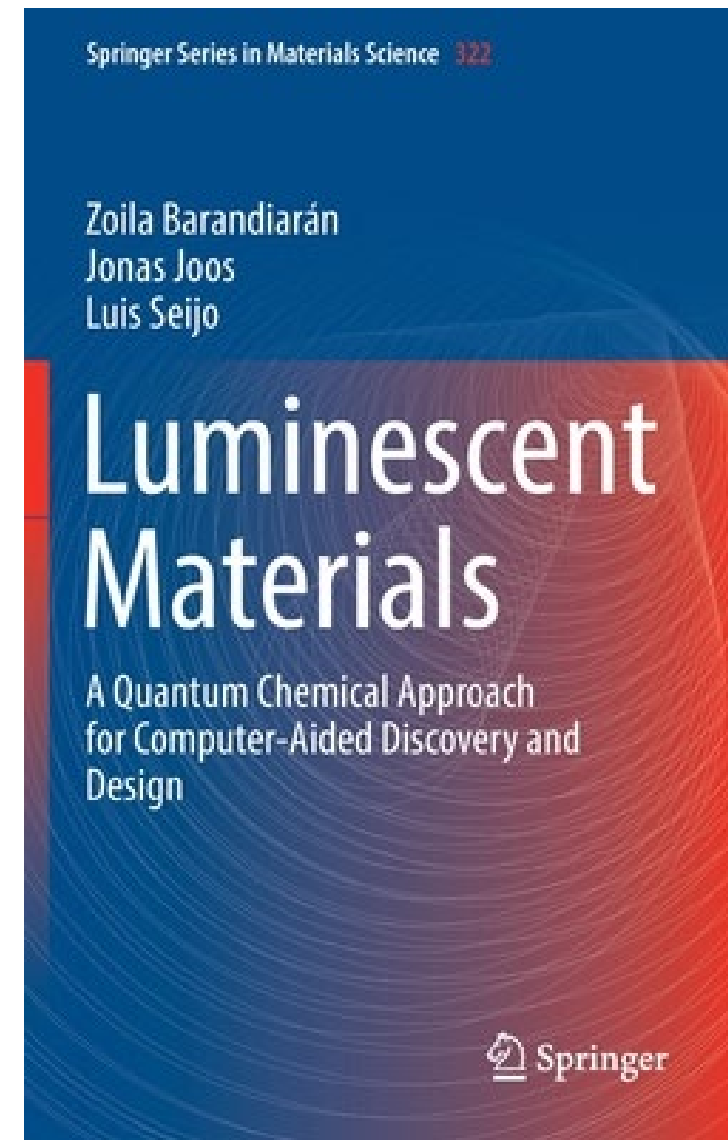
Relate H_{eff} to full H

$$\mathbf{H} \quad \mathbf{V} \quad = \quad \mathbf{V} \quad \mathbf{E}$$

$$H = V \, E \, V^{-1}$$

Use a subset of energies and eigenvectors from ab-initio calculation:

$$H_{eff}^{NH} = V_p \, E_p \, V_p^{-1} \quad \text{(non-Hermitian)} \quad [\text{'p' is the small, 'projected' matrix}]$$

$$V_k = (V_p \, V_p^+)^{-1/2} \, V_p \quad \text{(orthonormal)}$$

$$H_{eff} = V_k \, E_p \, V_k^{-1} \quad \text{(Hermitian)}$$

Can Solve: $\quad H_{eff} = \Sigma_\alpha \, P_\alpha T_\alpha \quad$ for parameters P_α

Reid MF., Duan CK. and Zhou HW. (2009) Crystal-field parameters from ab initio calculations. Journal of Alloys and Compounds 488: 591-594.

Alternative approach

The above approach can be hard to implement if there is more than one f electron as it is hard to work out the quantum numbers.

An alternative is use ab-initio calculations of expectation values of angular momentum operators (J_x J_y J_z etc) and use those to determine the quantum numbers.

Nicholas Chilton's group use this approach:

Gould et al., Science, 2022, 375, 198 (supplementary material)

Example: LiYF$_4$:Ce^{3+}

A Theoretical Study on the Structural and Energy Spectral Properties of Ce^{3+} Ions Doped in Various Fluoride Compounds

Jun Wen,[†] Lixin Ning,[‡] Chang-Kui Duan,[*,†] Yonghu Chen,[†] Yongfan Zhang,[§] and Min Yin[†]

DFT calculation using VASP.
4f energies (without spin-orbit) using AIMP embedded cluster approach
[Seijo et al J. Chem. Phys. 114, 118 (2001).]
SA-CASSCF calculation using MOLCAS.

(4f from Pr^{3+})

	LiYF$_4$		
	CF	CF + SO	exptl[b]
	0	0	0
	196	247	
	196	481	
4f^1	297	2214	
	504	2255	
	504	2409	
	1321	3016	
	32389	33378	33433
	40274	41142	41101
	48640	49404	48564
5d^1	48640	50144	50499
	52213	53520	52790
	44431	45518	45277

Parameter	Experiment	Theory
B_0^2(4f)	481	310
B_0^4(4f)	−1150	−1104
B_4^4(4f)	−1228	−1418
B_0^6(4f)	−89	−70
B_4^6(4f)	−1213	−1140 + 237i
B_0^2(5d)	4673	4312
B_0^4(5d)	−18649	−18862
B_4^4(5d)	−23871	−23871

Temperature dependent infrared absorption, crystal-field and intensity analysis of Ce^{3+} doped $LiYF_4$

Jon-Paul R. Wells[a,b,*], S. P. Horvath[a], Michael F. Reid[a,c]

Sebastian Horvath

Table 1: Experimental, fitted, and ab-initio [21] energy levels $(cm^{-1} \pm 0.1)$, ground state g-values for Ce^{3+} in $LiYF_4$.

State	Experiment	Fitted	Ab-initio
$Z_1 \gamma_{7,8}$	0.0	1.5	0
$Z_2 \gamma_{5,6}$	216	213.8	247
$Z_3 \gamma_{7,8}$	-	414.4	481
$Y_1 \gamma_{5,6}$	2216.1	2215.5	2214
$Y_2 \gamma_{7,8}$	2312.8	2312.1	2255
$Y_3 \gamma_{5,6}$	2428.8	2430.1	2409
$Y_4 \gamma_{7,8}$	3157.8	3158.6	3016
$g_{\parallel}$	2.765	2.751	
$g_{\perp}$	1.473	1.514	

Table 2: Fitted and ab-initio [21] spin-orbit and S_4 symmetry crystal-field parameters (cm^{-1}) for Ce^{3+} in $LiYF_4$.

Parameter	Fitted	Ab-initio
ζ	626	-
B_0^2	298	310
B_0^4	-1328	-1104
B_4^4	-1282	-1418
B_0^6	-192	-70
B_4^6	-1743	-1140
$B_4^{6'}$	693	237

Note use of magnetic splittings in crystal-field fit. We now expand on this idea.

CF calculations with magnetic splittings
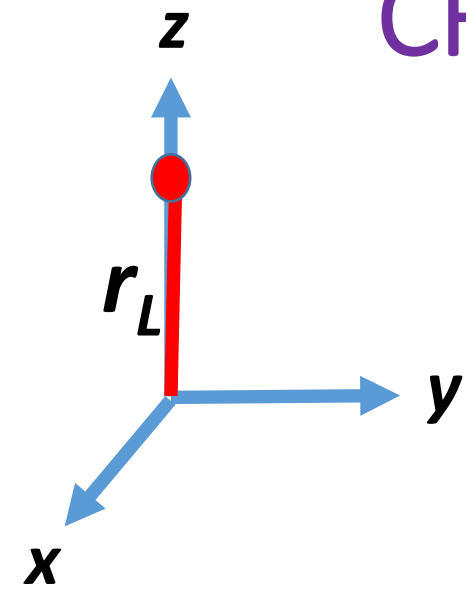
$$B_q^k = \bar{B}_k(R_0) \sum_L C_{-q}^{(k)}(\theta_L, \phi_L)(-1)^q \left(\frac{R_0}{R_L}\right)^{t_k}$$

Consider the $^4F_{3/2}$ multiplet of Nd^{3+}.
We only need B_q^2 in this case.

E.g. Single ligand on Z, B_0^2 = 500 cm^{-1}

But there are many sets of parameters that would give the same splitting.

We can use magnetic splittings to determine the orientation of the potential...

m=±3/2

75.6 cm^{-1}

m=±1/2

Potential

$C_0^2(r)$
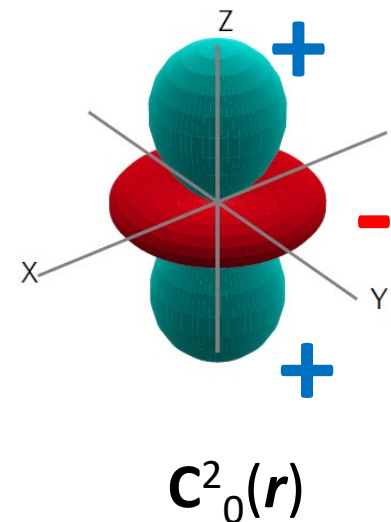
f orbitals:
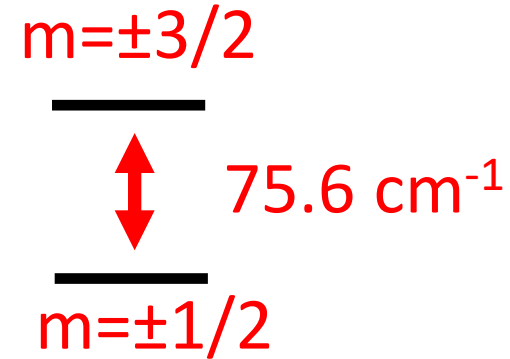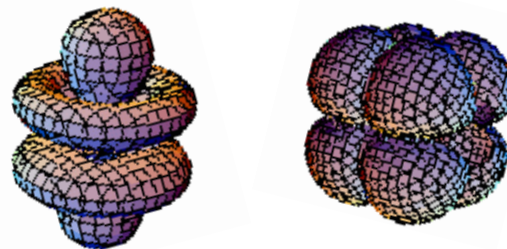
k	q	$C_q^{(k)}(x,y,z)$
0	0	1
1	0	z/r
1	±1	$\mp\sqrt{\frac{1}{2}}(x \pm iy)/r$
2	0	$\sqrt{\frac{1}{4}}(3z^2 - r^2)/r^2$
2	±1	$\mp\sqrt{\frac{3}{2}}z(x \pm iy)/r^2$
2	±2	$\sqrt{\frac{3}{8}}(x \pm iy)^2/r^2$

CF calculations with magnetic splittings

Single ligand on Z, $B^2_0 = 500$ cm^{-1}

Calculate magnetic splitting of upper state: B=4T
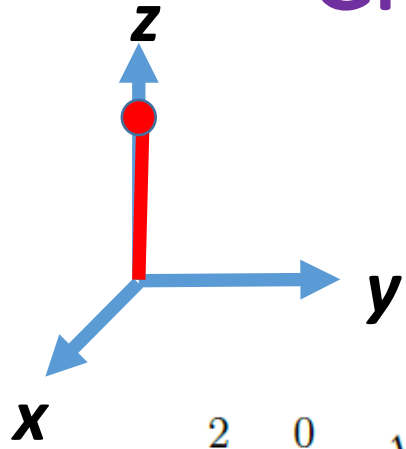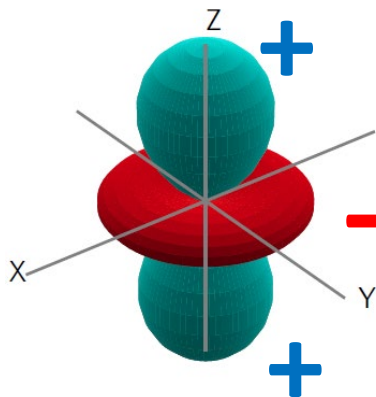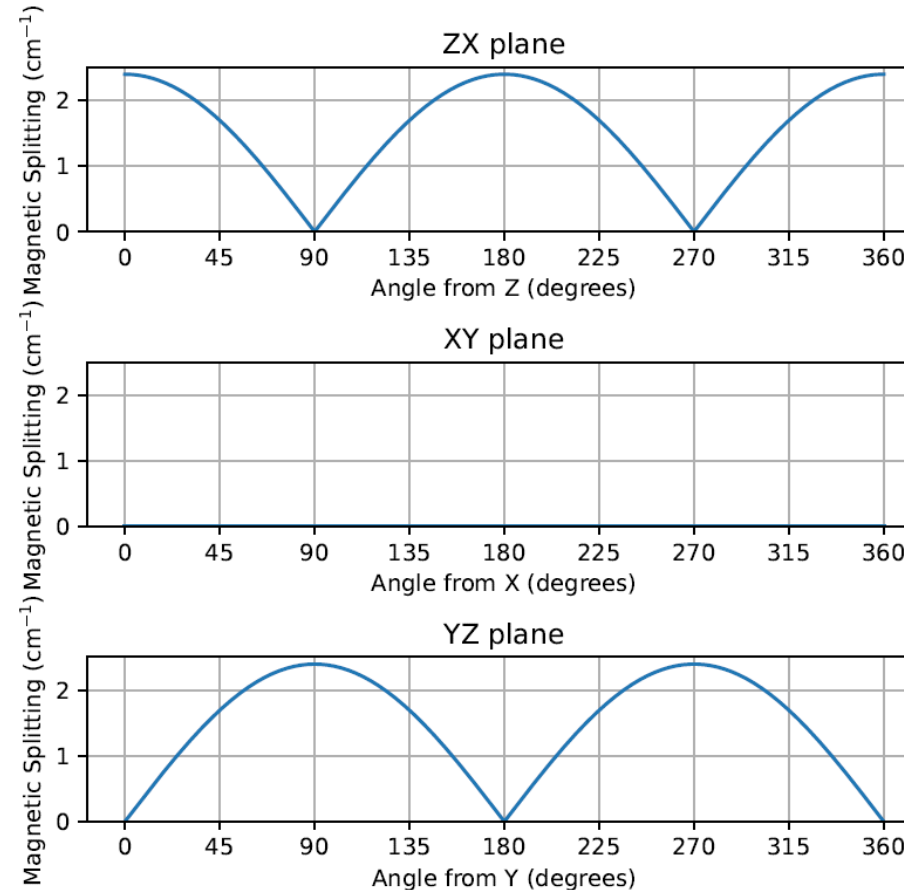
m=±3/2

75.6 cm^{-1}

m=±1/2

Magnetic Splitting

2	0	$\sqrt{\frac{1}{4}}(3z^2 - r^2)/r^2$
2	±1	$\mp\sqrt{\frac{3}{2}}z(x \pm iy)/r^2$
2	±2	$\sqrt{\frac{3}{8}}(x \pm iy)^2/r^2$

Potential

$C^2_0(r)$
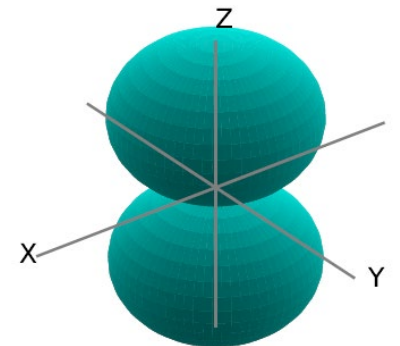
Change orientation!

Single ligand on X, B^2_0 = -250 cm^{-1} B^2_2 = +306 cm^{-1}
Calculate magnetic splitting of upper state: B=4T
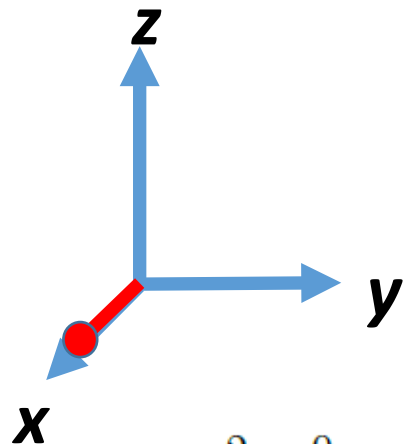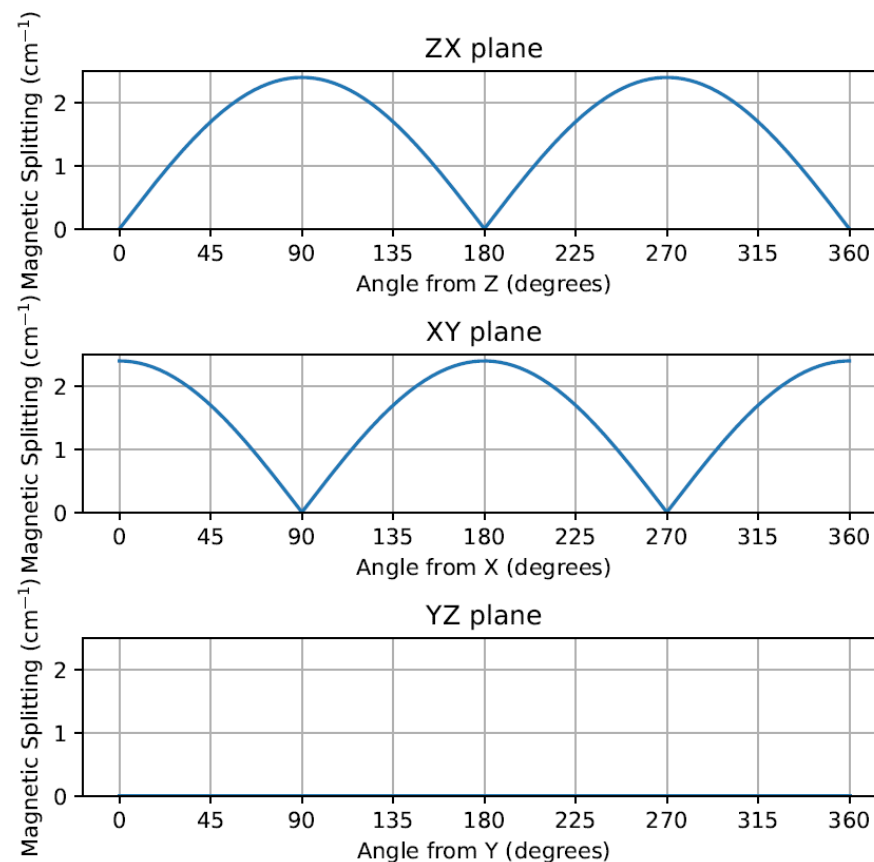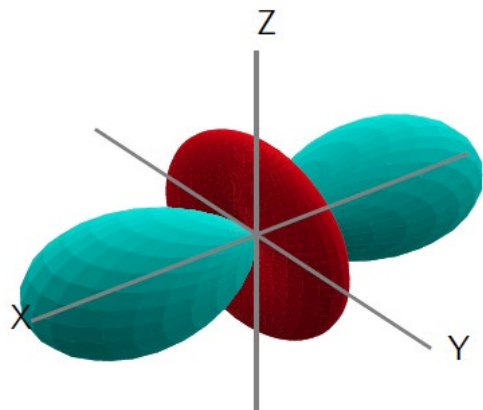
m=mixture

75.6 cm^{-1}

m=mixture

Magnetic Splitting

$$2 \quad 0 \quad \sqrt{\tfrac{1}{4}}(3z^2 - r^2)/r^2$$

$$2 \quad \pm1 \quad \mp\sqrt{\tfrac{3}{2}}z(x \pm iy)/r^2$$

$$2 \quad \pm2 \quad \sqrt{\tfrac{3}{8}}(x \pm iy)^2/r^2$$

Potential
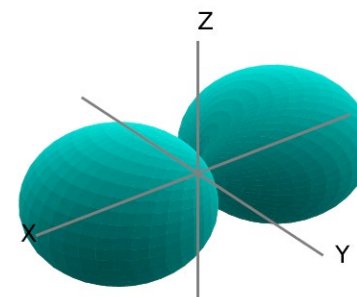
Transition Intensities

- Electric Dipole, Magnetic Dipole, …
- ED between $4f^N$ and $4f^{N-1}5d$ can be calculated directly
  - But require modelling of vibronic bands.
- ED within $4f^N$ are parity forbidden.
  - "Forced electric dipole" transitions.
  - Construct Effective electric dipole operator that accounts for mixing of configurations of opposite parity on ion or ligand.
  - First detailed treatment: Judd, Ofelt, 1962.

Effective Electric Dipole Operator

$$D_{\text{eff},q} = D_q^{(1)} + D_q^{(1)} \sum_{\beta \notin M} \frac{|\beta\rangle\langle\beta|V}{E_0 - E_\beta^{(0)}} + \sum_{\beta \notin M} \frac{V|\beta\rangle\langle\beta|}{E_0 - E_\beta^{(0)}} D_q^{(1)} + \dots$$

β

D   V

If all denominators are the same then the sum over $|\beta\rangle\langle\beta|$ is 1. Couple the operators:

$$T_\ell^{(\lambda)} = \sum_{q,t,p} D_q^{(1)} V_p^{(t)} \langle 1\,q, t\,p | \lambda\,\ell\rangle$$

Our parametrization. $\lambda = 2, 4, 6$, $t = \lambda \pm 1, \lambda$

$$D_{\text{eff},q} = \sum_{\lambda,t,p} A_{tp}^\lambda U_{p+q}^{(\lambda)} (-1)^q \langle \lambda(p+q), 1-q | tp\rangle$$

Dipole strength

$$S_{FI,q}^{\text{ED}} = \sum_i \sum_f e^2 \left| \langle F f | D_q^{(1)} | I i \rangle \right|^2$$

> **Key idea:**
>
> **Couple**
>   **electric dipole operator: _D_**
> **and**
>   **perturbing potential: _V_**
> _to obtain:_
>   **effective electric dipole operator: _D_eff**

Oscillator strength

$$f_{FI,q}^{\text{ED}} = \frac{2m\omega}{\hbar e^2} \frac{\chi_L}{n} \frac{1}{g_I} S_{FI,q}^{\text{ED}}$$

Einstein A coefficients $(1/\tau)$

$$A_{FI,q}^{\text{ED}} = \frac{1}{4\pi\epsilon_0} \frac{4\omega^3}{\hbar c^3} n \chi_L \frac{1}{g_I} S_{FI,q}^{\text{ED}}$$

Nd:YAG diode band absorption coefficient

Simulation

Burdick, et al.
Phys. Rev. B: 50: 16309 (1994)

ISOTROPIC
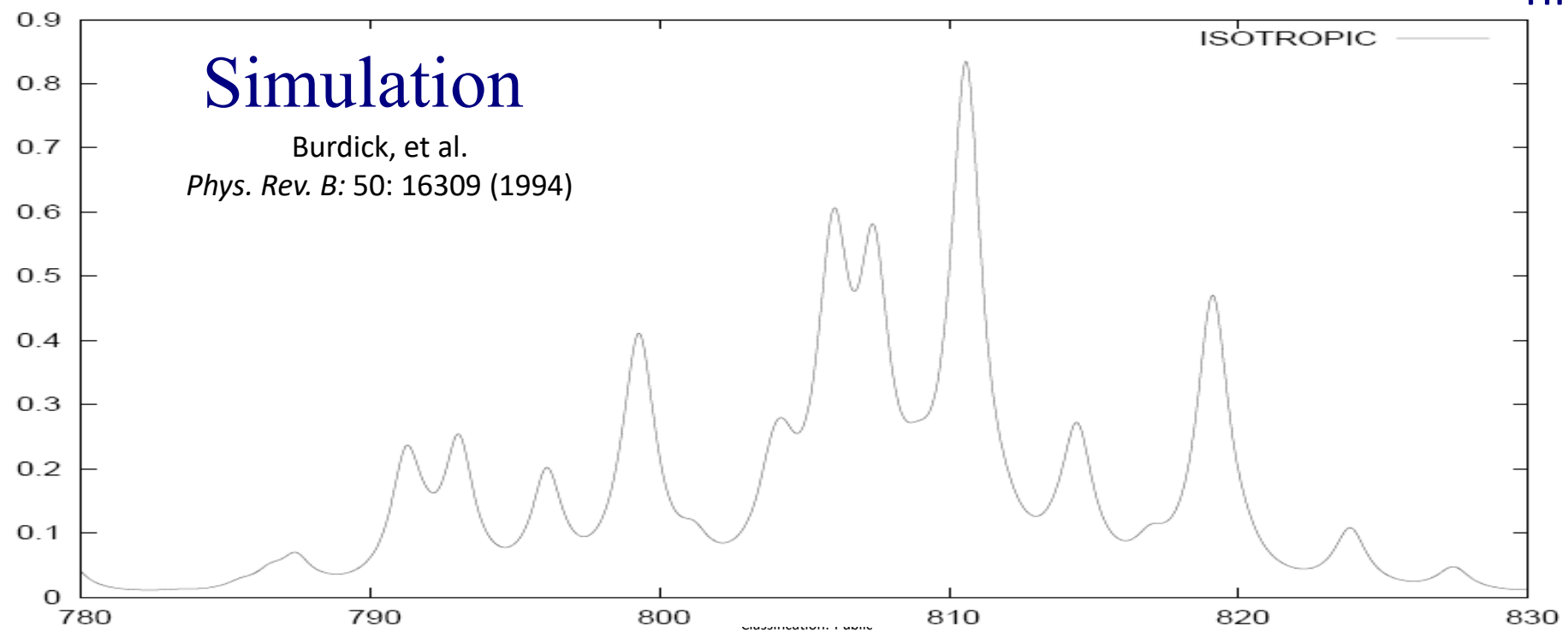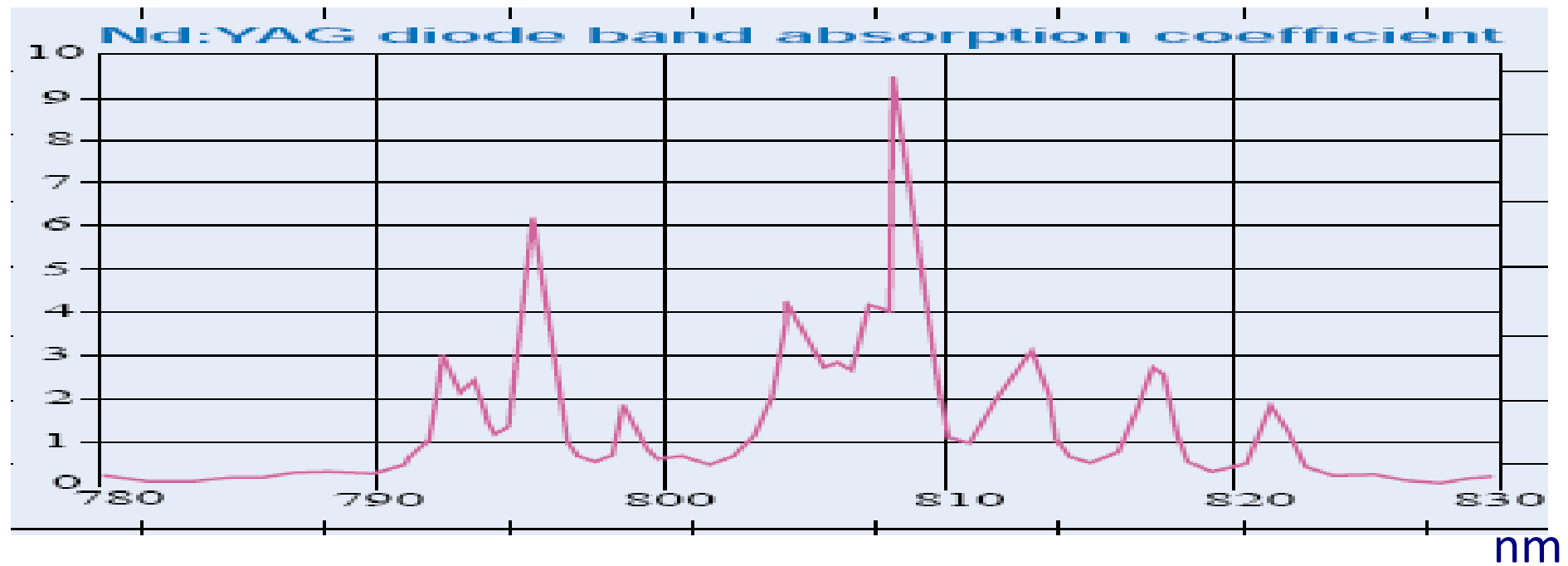
Multiplet-Multiplet transitions

- Judd 1962
  - For solutions and glasses at room temperature.
  - Sum over all states in a multiplet and all polarizations.
  - Reduces to three-parameter *linear* fit. ←**huge simplification!**
  - Ω_λ parameters with $\lambda=2,4,6$
  - 1000s of citations!
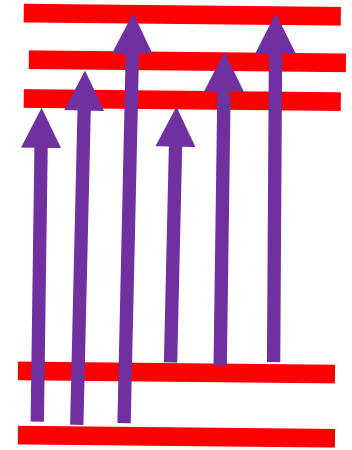
$$\bar{S}^{\text{ED}}_{\alpha_F J_F, \alpha_I J_I} = \frac{1}{3}e^2 \sum_\lambda \Omega_\lambda \langle \alpha_F J_F \| U^{(\lambda)} \| \alpha_I J_I \rangle^2$$

$$\Omega_\lambda = \sum_{t,p} \frac{1}{2\lambda+1} \left| A^\lambda_{tp} \right|^2$$
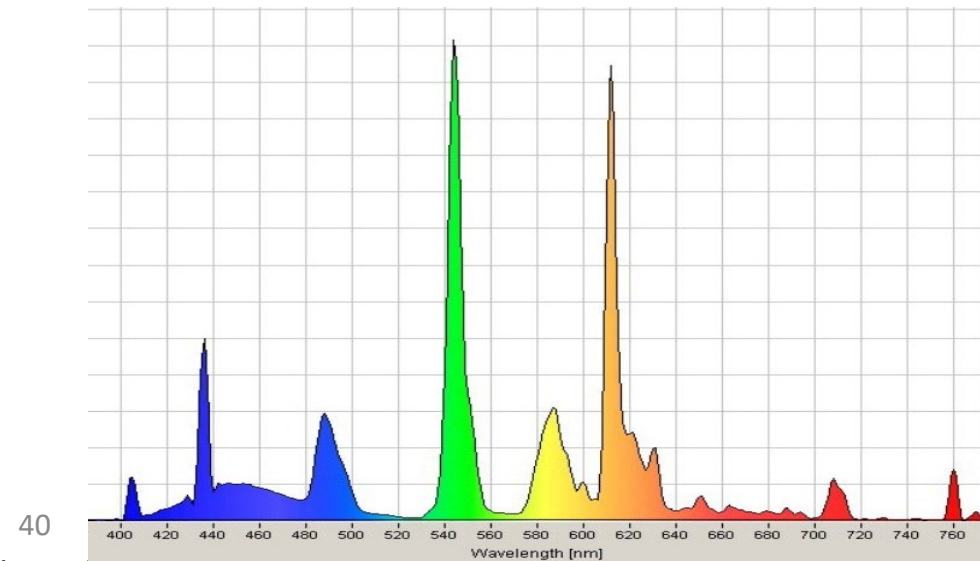
Reminiscencies of a quenched luminescence investigatory

George Blasse

University Utrecht, Debye Institute, P.O. Box 80 000, 3508 TA Utrecht, The Netherlands

Hypersensitivity: The emission of Eu^{3+} consists of an orange allowed magnetic-dipole transition ($^5D_0-^7F_1$), a red parity—forbidden electric-dipole (ED) transition ($^5D_0-^7F_2$), and further infrared ED transitions. For application, the emission should consist of as much $^5D_0-^7F_2$ emissions as possible. This requires Eu^{3+} to occupy a site without inversion symmetry. This, however, induces also the infrared emission. Fortunately, the rare-earth transitions with $\Delta J = 2$ are hypersensitive to the surroundings, i.e. a small deviation from inversion symmetry induces strong red emission whereas the infrared emission is still weak. By comparing many systems I found that a certain amount of covalency is a condition for this hypersensitivity. Later calculations by others confirmed this, but to me they are not transparent. It remains striking that the high quality of colour displays like in TV is due to this hypersensitivity effect.

George Blasse
1934-2020
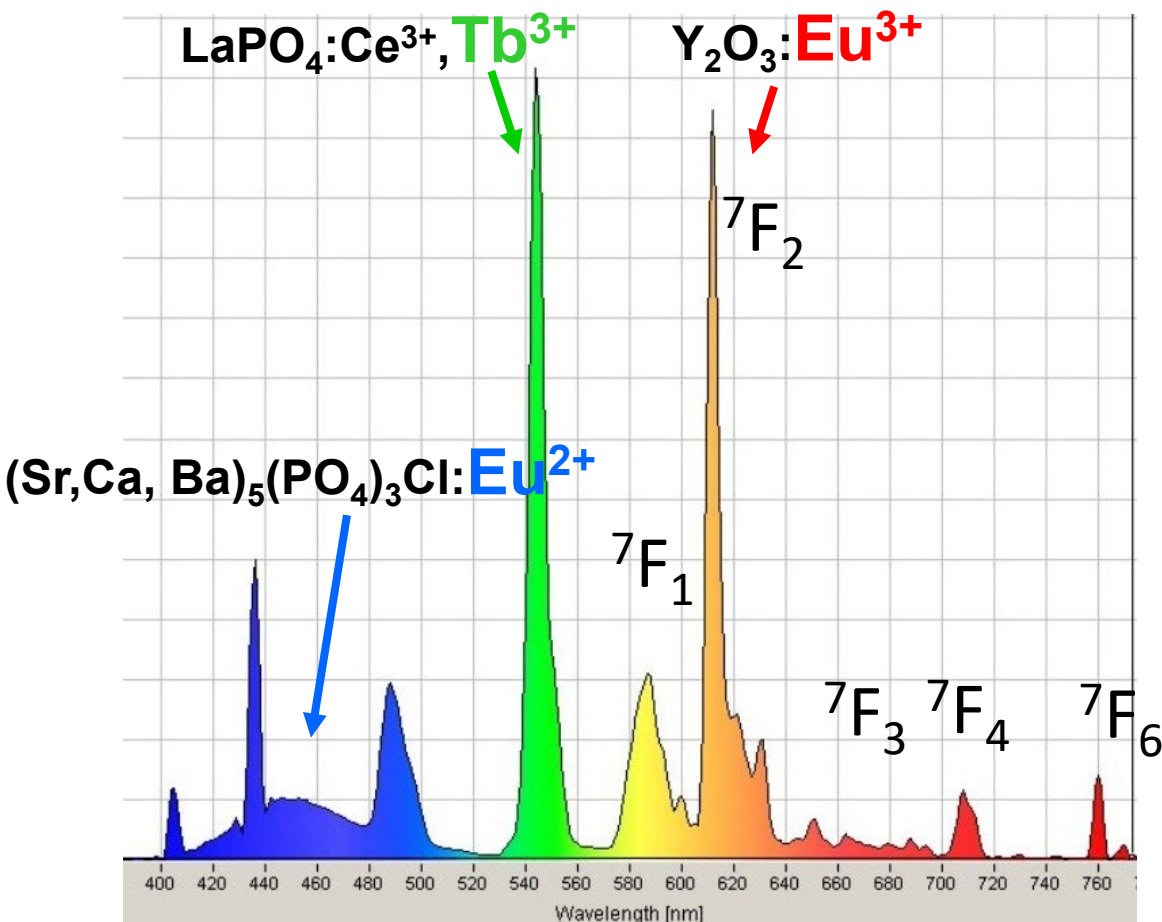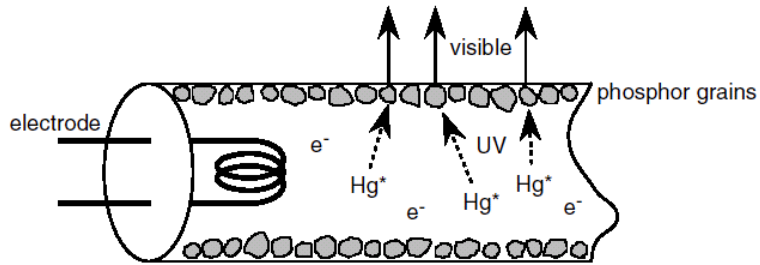
Quantum Information Applications?
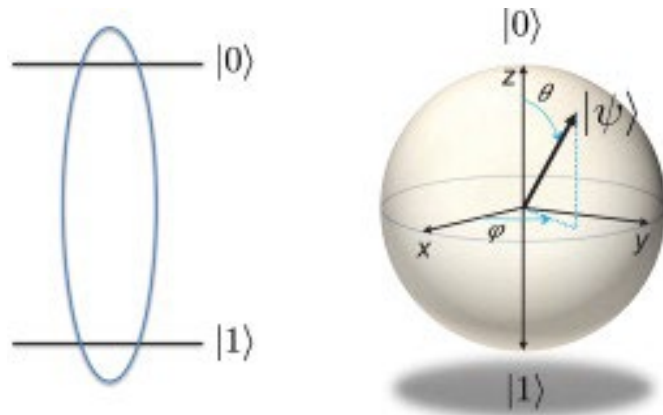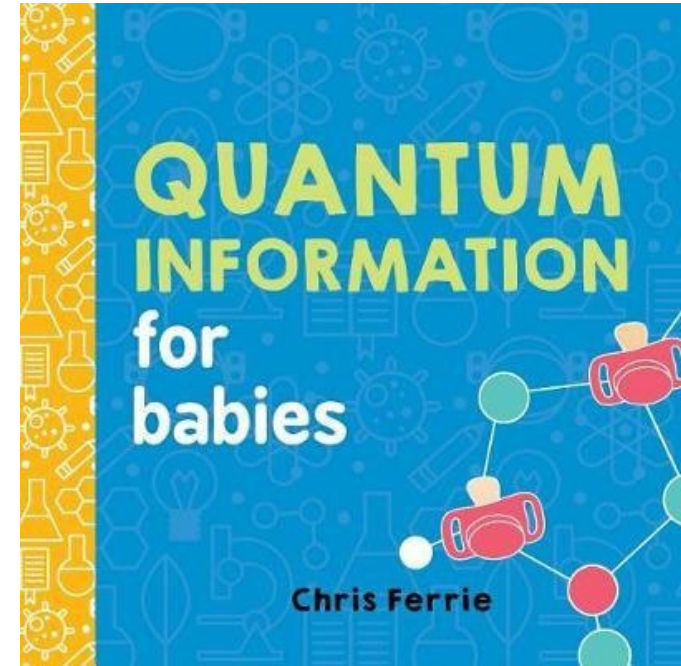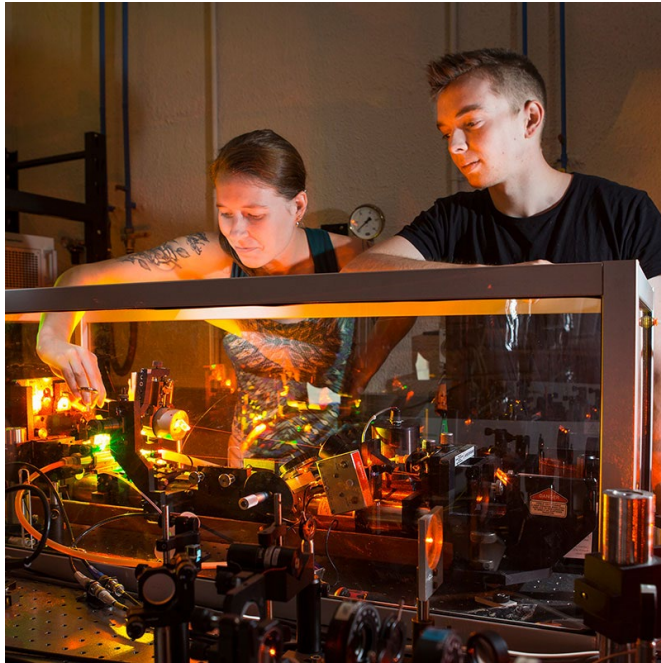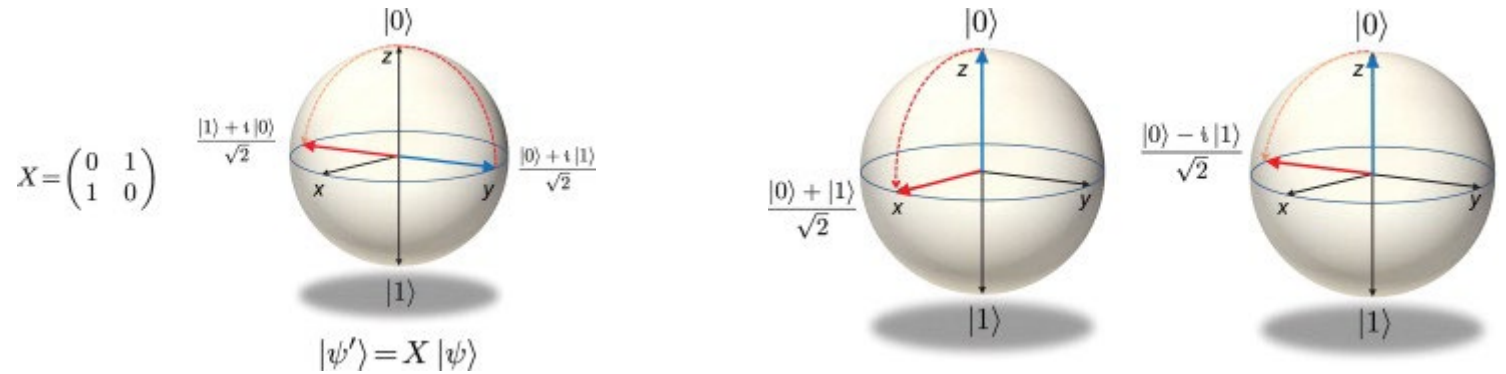
Spin Echoes*†

E. L. HAHN‡
Physics Department, University of Illinois, Urbana, Illinois
(Received May 22, 1950)
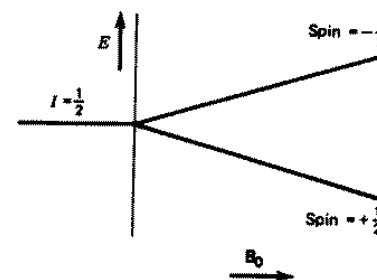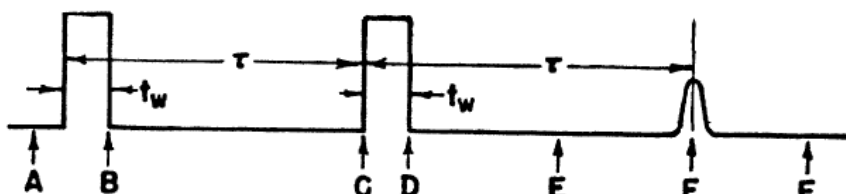
30MHz/0.7T
τ ≈ 100µs

Modern NMR
600MHz/14T
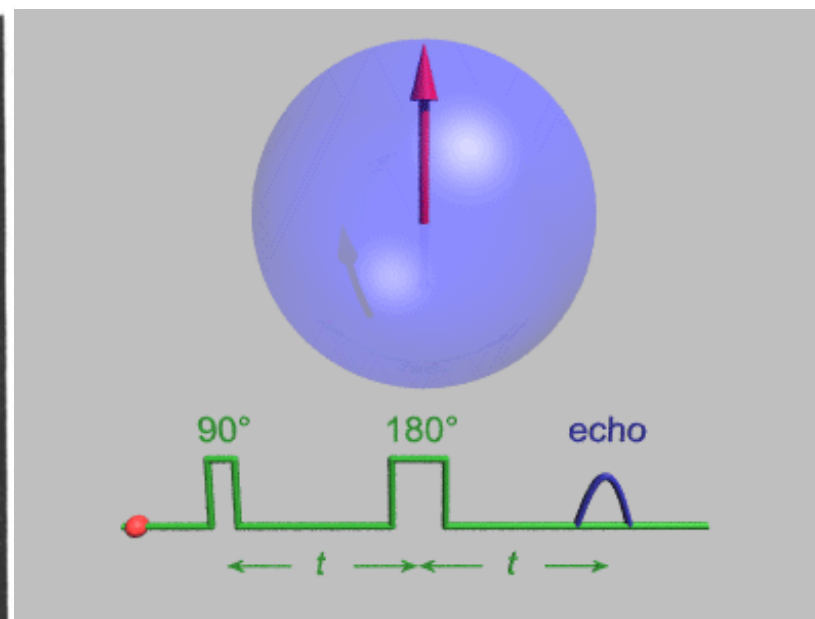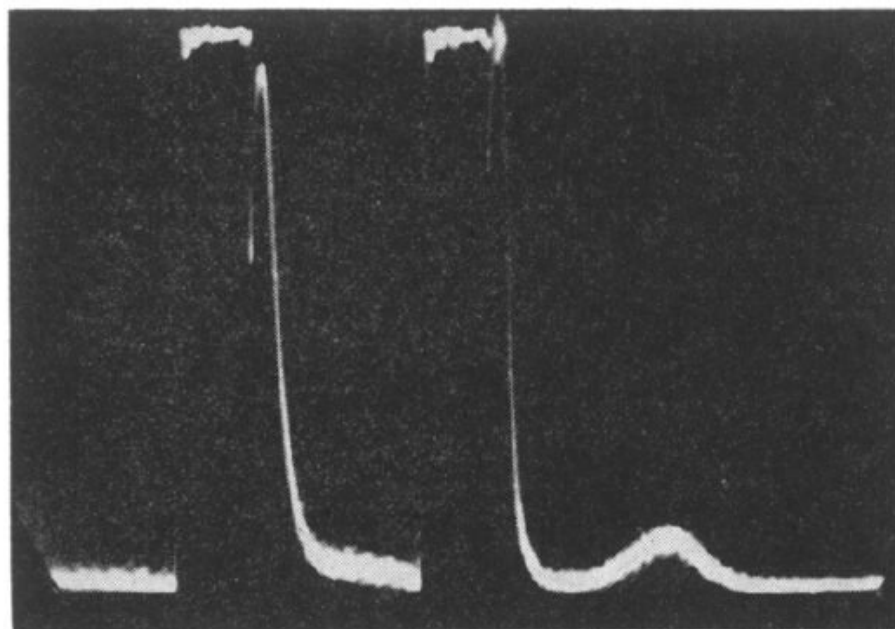
(N)MRI

FIG. 11. Free induction signals for protons in paraffin. The echo lasts for ~1.4×10⁻⁵ sec. The r-f pulses, about 25 µsec. wide, cause some blocking of the i.f. amplifier. The echo envelope decay time is also of the order of the single echo lifetime.

Spin Echo: Wikipedia

Six-Hour Coherence: $^{151}Eu^{3+}$
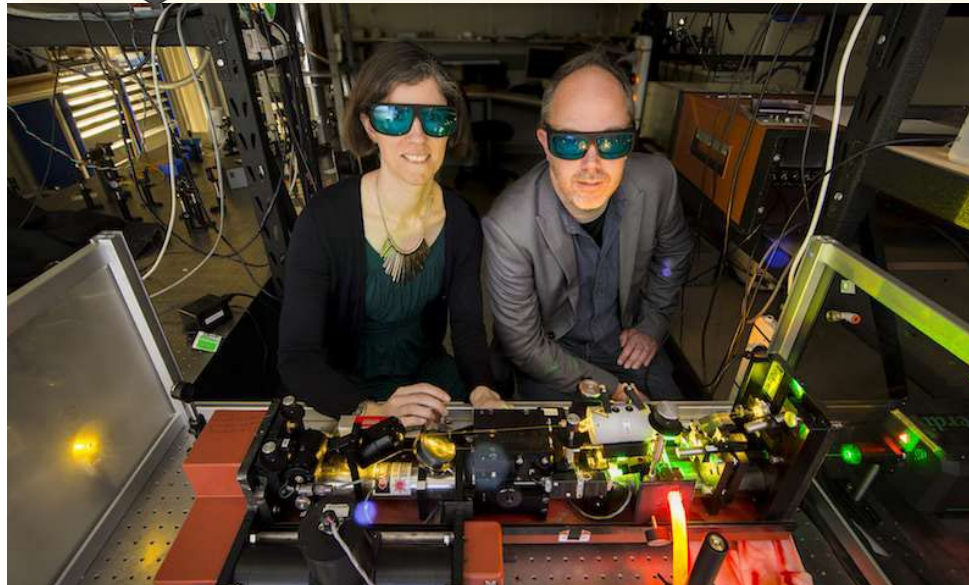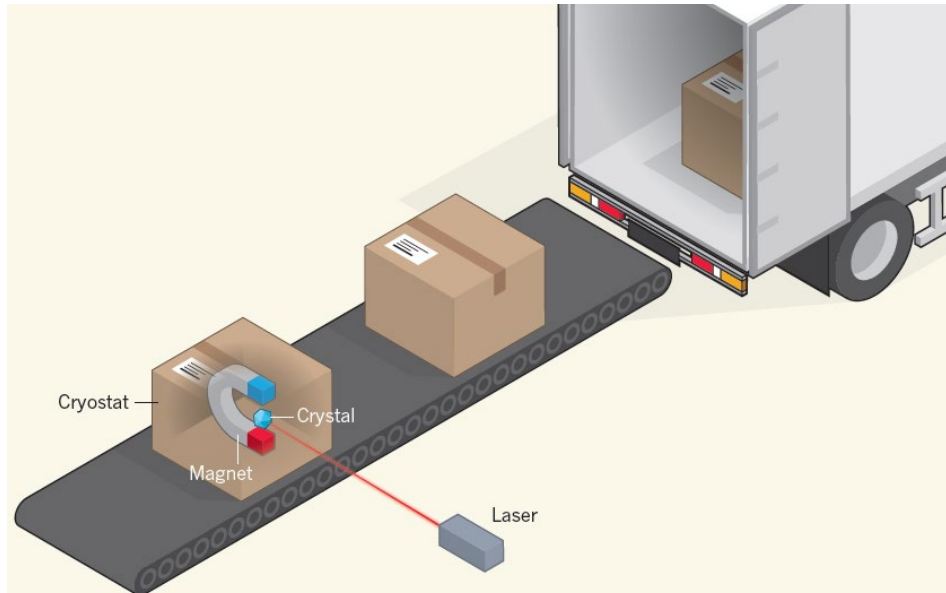
Rose Ahlefeldt, Matt Sellars, ANU, Australia.
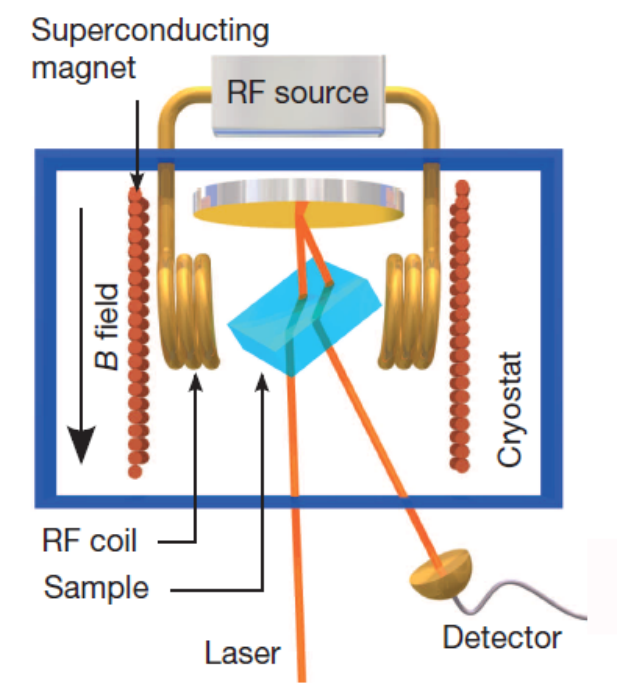
Manjin Zhong, SUSTech, Shenzhen

Optically addressable nuclear spins in a solid with a six-hour coherence time

Manjin Zhong[1], Morgan P. Hedges[1,2], Rose L. Ahlefeldt[1,3], John G. Bartholomew[1], Sarah E. Beavan[1,4], Sven M. Wittig[1,5], Jevon J. Longdell[6] & Matthew J. Sellars[1]

$$^{151}Eu^{3+} : Y_2SiO_5$$

ZEro First Order Zeeman

$T_2 \approx 20$ seconds

$T_2 \approx 370$ minutes

I=5/2

(Note that recent work has re-ordered the states relative to those shown on the left.)

Crystal-Field Calculations for Y_2SiO_5 (YSO)

In low symmetry the use of magnetic measurements to fix the orientation of the crystal-field potential is crucial.

Sebastian Horvath worked on this problem during his PhD and we have since extended this work to several rare-earth ions.

Y1 and Y2 sites are six and seven-coordinate respectively.
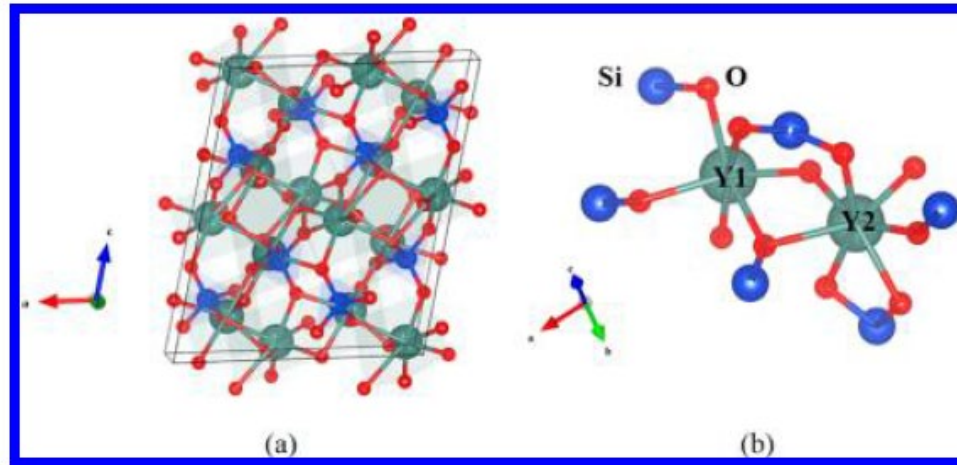
Figure 1. Schematic representations of local atomic structures around the two types of yttrium (Y1 and Y2) sites along with the unit cell of X2-YSO.

Crystal-Field Calculation for $^{167}Er^{3+}$:YSO Site 1

$$H = H_{FI} + H_{CF} + H_Z + H_{HF} + H_Q.$$

- Use literature and new data for electronic energy levels, magnetic, and hyperfine splitting.

- Directional magnetic data is crucial to fixing orientation of CF Hamiltonian for low-symmetry sites.

- Separately calculate:
  - Electronic energy levels
  - Magnetic splitting for various field orientations
  - Hyperfine splitting.

- Data (Effectively 95 data points)
  - 35 Electronic energies
  - 12 Ground-state hyperfine levels
  - 12 Zeeman rotation points
  - Raman heterodyne hyperfine data (15 MHz accuracy)

- 34 Parameters (similar to spin-Hamiltonian parameter number…)

Sebastian Horvath et al. Phys. Rev. Lett. **123**, 057401 (2019)

47

Classification: Public
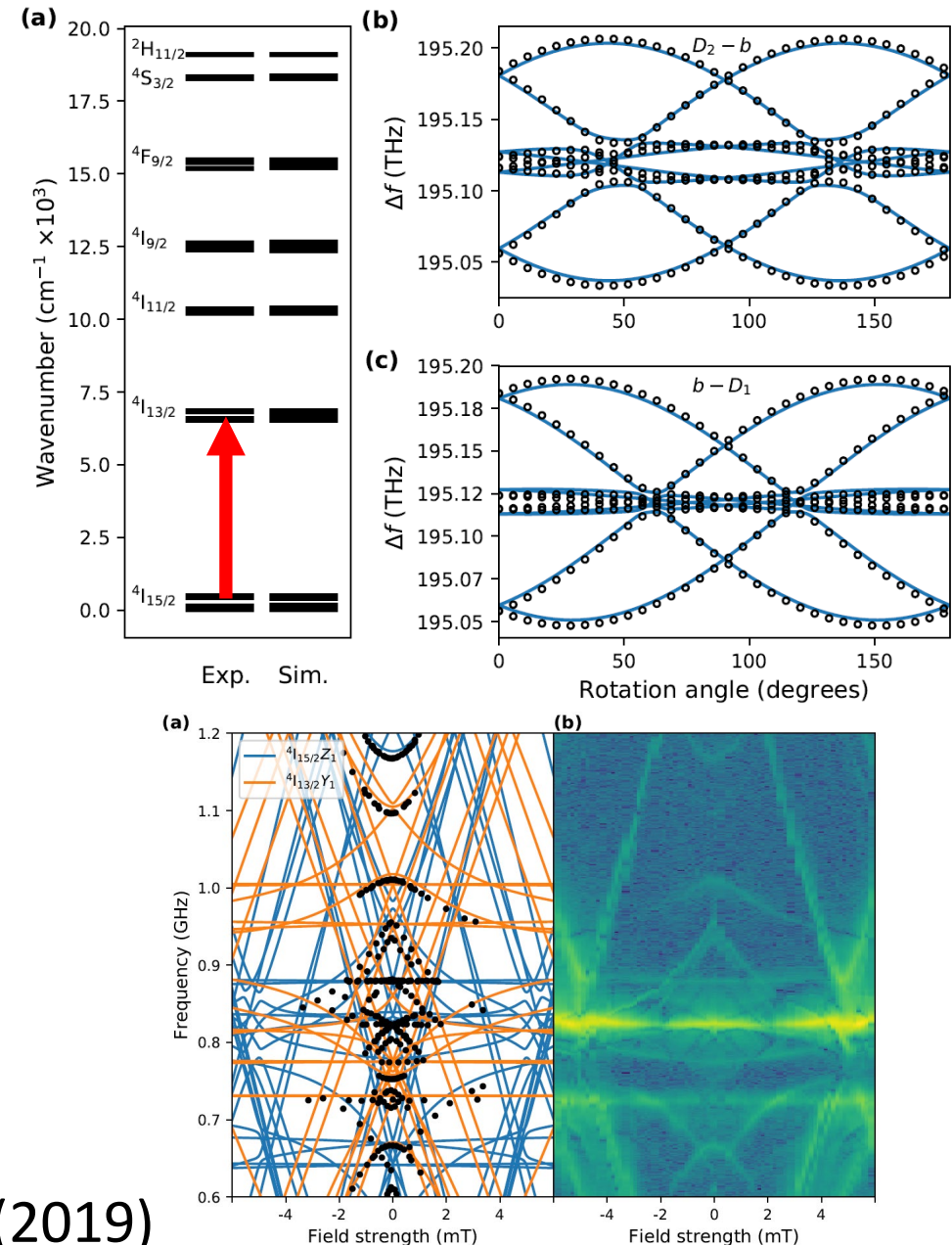
Extension to other ions:
Zeeman spectroscopy of $Sm^{3+}:Y_2SiO_5$

N.L. Jobbitt et al. J. Phys. Condensed Matter 34:325502 (2022)

Er³⁺:YSO N.L. Jobbitt et al. Phys. Rev. B 104, 155121 (2021)
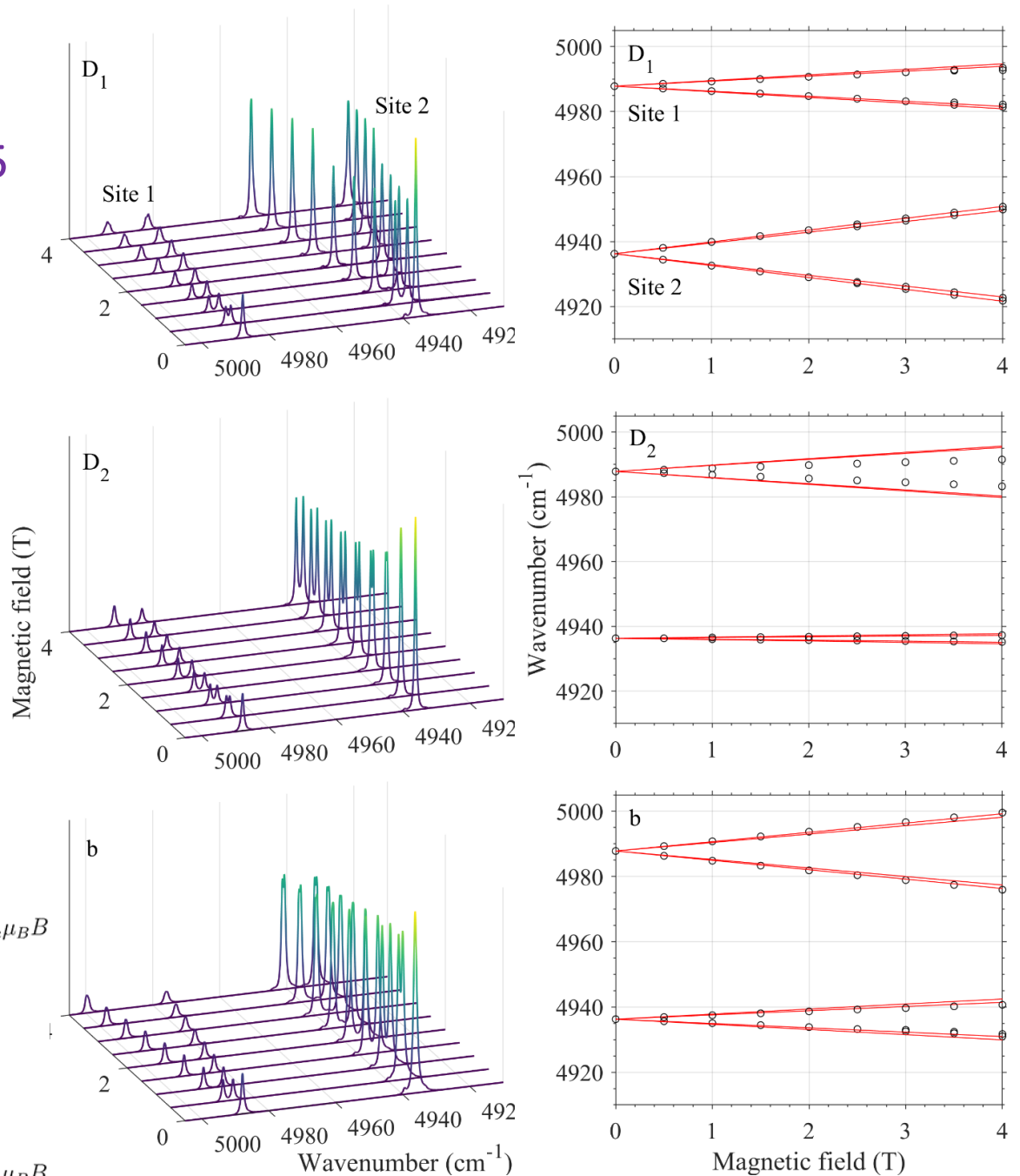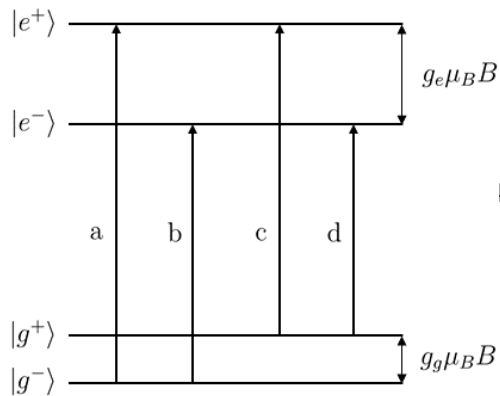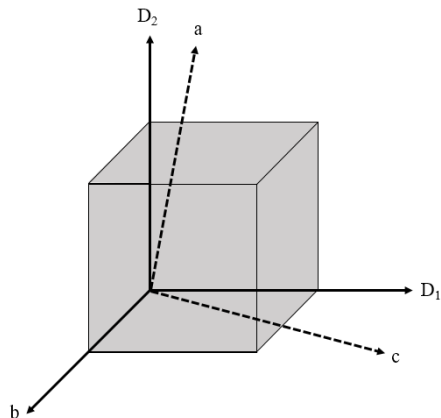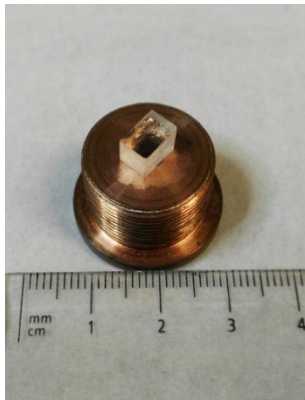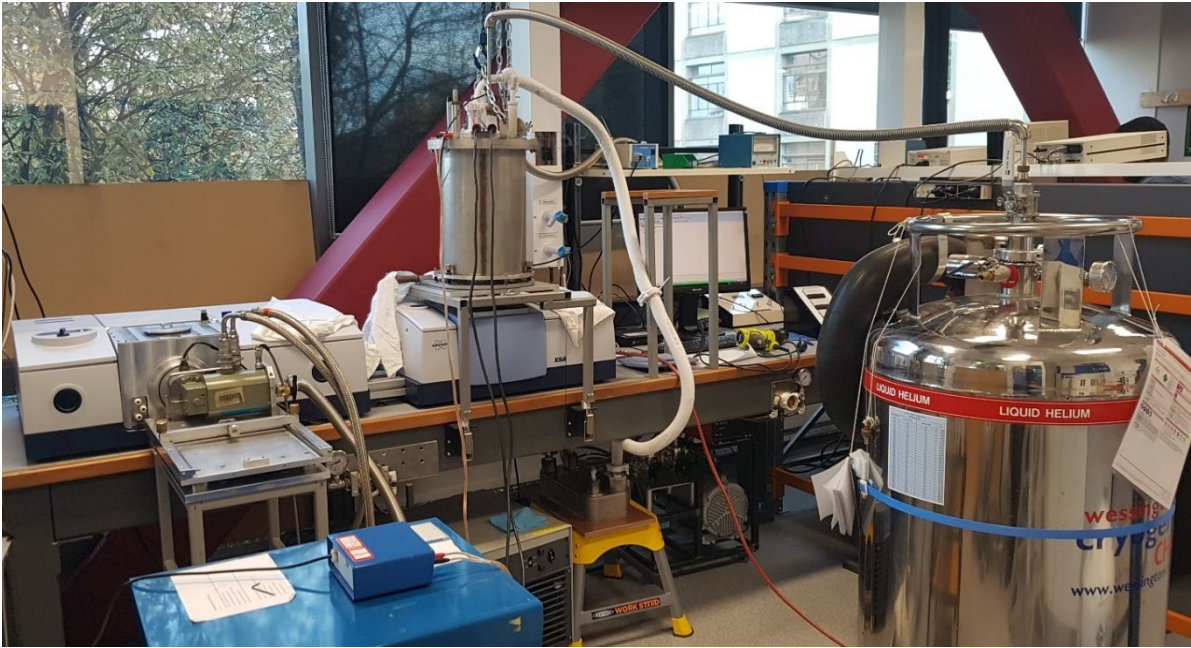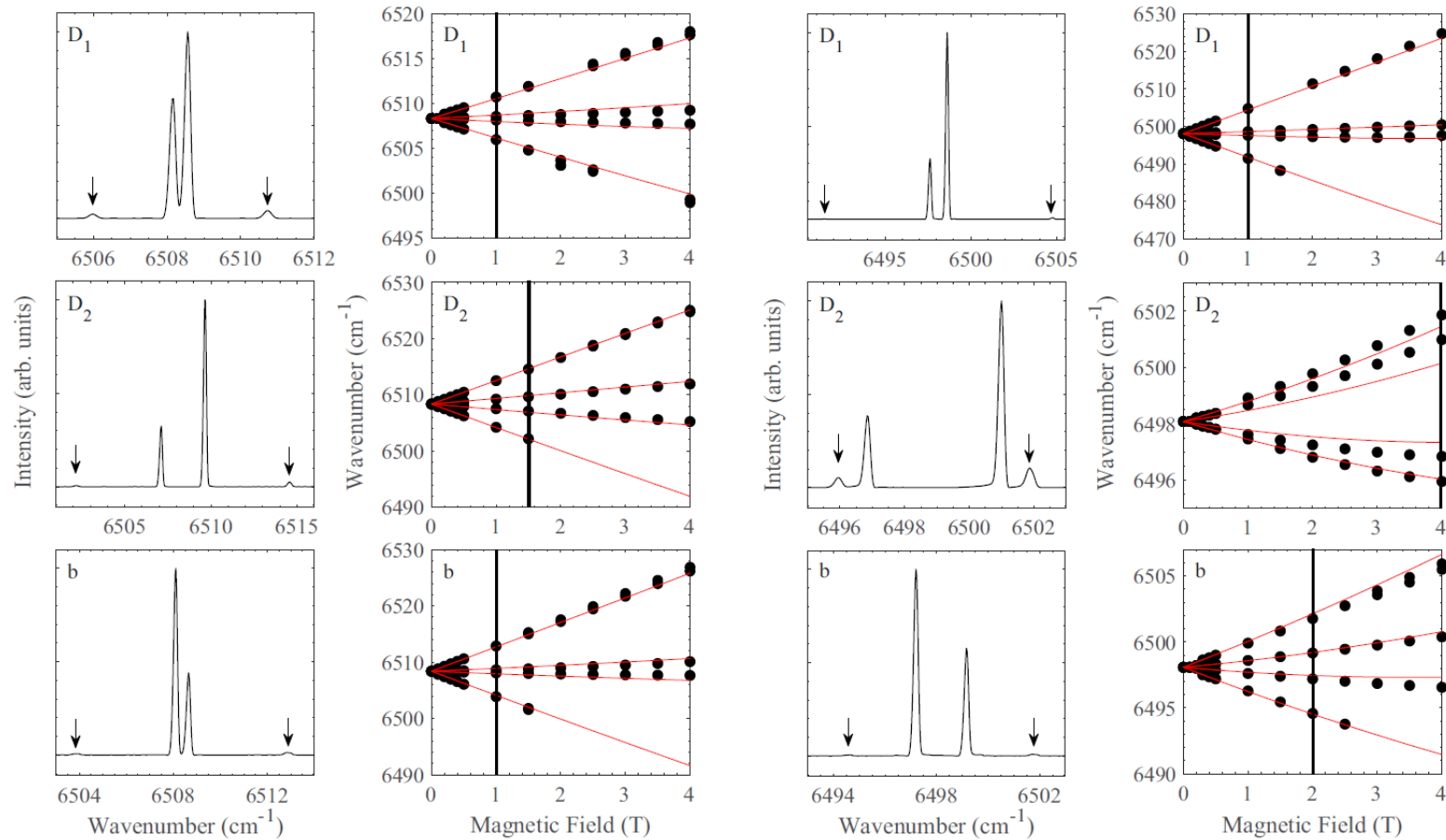
FIG. 2. Magnetic splittings of the site 1 $Z_1 \rightarrow Y_1$ transition for magnetic fields applied along the three crystallographic axes of Y_2SiO_5. The top, middle, and bottom panels shows $B \parallel D_1$, $B \parallel D_2$, and $B \parallel b$, respectively. The left panels show 4.2-K Zeeman absorption spectra at magnetic field strengths represented by the vertical lines in the right panels. The weak outer transitions are labeled with arrows to assist the reader. The right panels show the experimental splittings, represented by the circles, and the calculated splittings are represented by the red lines.

Site 1

FIG. 3. Magnetic splittings of the site 2 $Z_1 \rightarrow Y_1$ transition for magnetic fields applied along the three crystallographic axes of Y_2SiO_5. The top, middle and bottom panels shows $B \parallel D_1$, $B \parallel D_2$, and $B \parallel b$, respectively. The left panels show 4.2-K Zeeman absorption spectra at magnetic field strengths represented by the vertical lines in the right panels. The weak outer transitions are labeled with arrows to assist the reader. The right panels show the experimental splittings, represented by the circles, and the calculated splittings are represented by the red lines.

Site 2
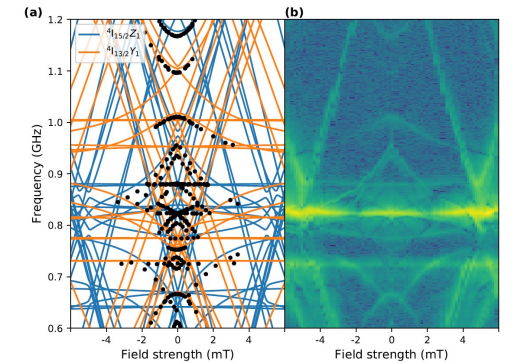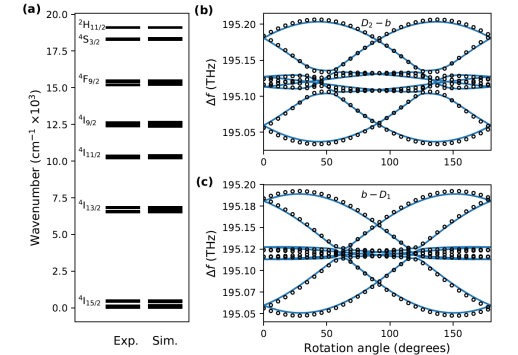
Site 1 ground state magnetic splitting

g value max: 14
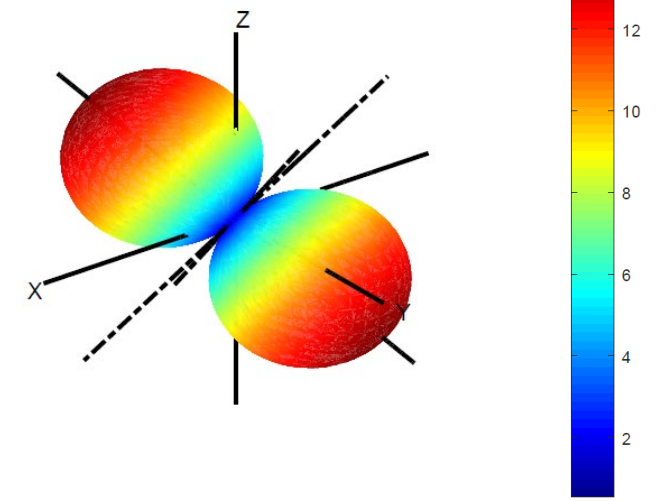
Er³⁺:YSO Nick Jobbitt et al. Phys. Rev. B 104, 155121 (2021)

TABLE III. Fitted values for the free-ion, crystal-field and hyperfine parameters and their related uncertainties of site 1 and site 2 in $Er^{3+}:Y_2SiO_5$. All values are in cm^{-1}. Parameters determined by Horvath *et al.* are also included for comparison [16,18].

Parameter	Site 1				Site 2		
	This study	Uncertainty	Ref. [16]	Ref. [18]	This study	Uncertainty	Ref. [18]
E_{avg}	35491.3	0.1	35503.5	–	35507.5	0.1	–
F^2	95805.7	1.0	96029.6	95346	96121.9	1.3	95721
F^4	67869.7	3.4	67670.6	68525	67722.4	4.5	68564
F^6	53148.2	2.5	53167.1	52804	53241.2	3.1	52999
ζ	2360.5	0.1	2362.9	2358	2362.3	0.1	2356
B_0^2	−479.6	6.1	−149.8	−563	389.0	3.7	354
B_1^2	471.4+143.8i	2.9 + 3.0i	420.6+396.0i	558+280i	−325.7 − 95.8i	2.7 + 3.0i	498.6807+274i
B_2^2	125.5−2.0i	2.8 + 2.3i	−228.5+27.6i	143−121i	−368.5+53.7i	1.8 + 2.0i	−75.8028+60i
B_0^4	−640.6	31.3	1131.2	−125	17.2	15.5	226
B_1^4	288.8+924.1i	7.2 + 25.3i	985.7+34.2i	225−831i	−378.7 − 519.5i	5.1 + 9.3i	−657.8381+593i
B_2^4	−273.9+320.9i	11.1 + 16.7i	296.8+145.0i	−48 − 945i	−72.0 − 146.0i	5.7 + 6.7i	335.7827+253i
B_3^4	−873.7 − 367.8i	20.7 + 9.7i	−402.3 − 381.7i	−615 − 688i	−890.8+570.4i	9.5 + 7.3i	−71.3262 − 46i
B_4^4	−600.8+1210.5i	23.7 + 9.2i	−282.3+1114.3i	744−102i	−198.7 − 567.9i	7.8 + 5.2i	−813.9654+64i
B_0^6	145.7	13.2	−263.2	−28	73.4	4.3	219
B_1^6	−105.9 − 329.0i	2.9 + 4.0i	111.9+222.9i	49+199i	−37.5+49.9i	3.4 + 5.7i	−127+197i
B_2^6	−119.9+164.1i	7.7 + 8.8i	124.7+195.9i	120−107i	135.5+60.6i	4.5 + 1.5i	−36 − 47i
B_3^6	1.1+133.3i	6.7 + 4.5i	−97.9+139.7i	195−55i	−166.7+131.8i	2.6 + 4.0i	17−108i
B_4^6	−84.6+36.9i	5.0 + 4.5i	−93.7 − 145.0i	−287 − 161i	227.2+47.6i	1.2 + 3.0i	−100+77i
B_5^6	75.5+6.9i	4.3 + 6.6i	13.9+109.5i	−117+162i	119.5+64.3i	3.7 + 3.2i	−263+103i
B_6^6	−48.5+118.0i	6.2 + 4.2i	3.0−108.6i	136+186i	37.6−41.3i	3.5 + 2.8i	12−26i
S^2	386.6	–	399.0	483.0	363.1	–	397.9
S^4	948.2	–	862.9	824.6	653.3	–	607.5
S^6	183.8	–	189.6	218.6	151.5	–	171.4
a_l	0.005306	0.000008	0.005466	0.0059	0.005389	0.000012	0.0069
a_Q	0.0554	0.0020	0.0716	0.0800	0.0240	0.0024	0.0808

Note that 34 parameters is the same as the number of spin Hamiltonian parameters for Z1 and Y1.

g, A, Q tensors: (6+6+5)*2

Er^{3+}:Y$_2$SiO$_5$ predictions: Polarization Measurements

Polarization measurements for 1550 μm transitions

Y. Petit et al. Opt. Mater. X, **8**, 100062 (2020)

Blue: E‖b → Magnetic dipole variation.

Red: M‖b → Electric dipole variation.
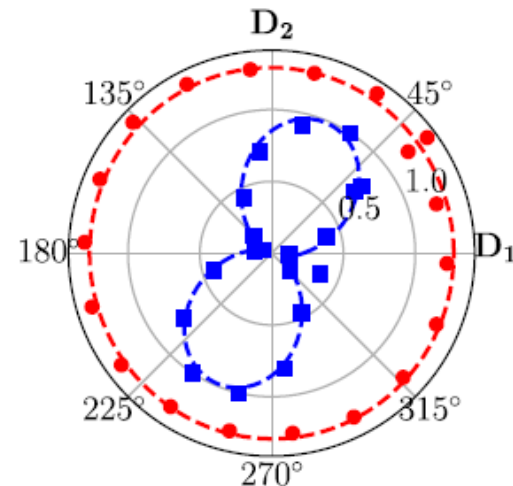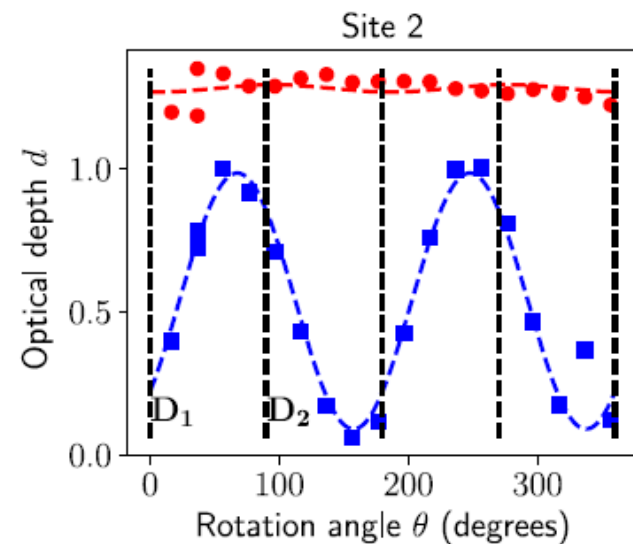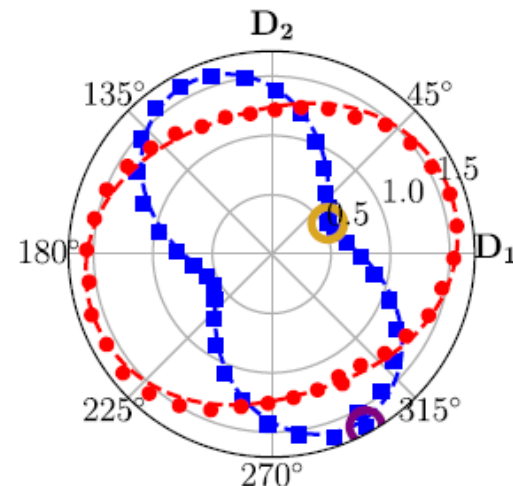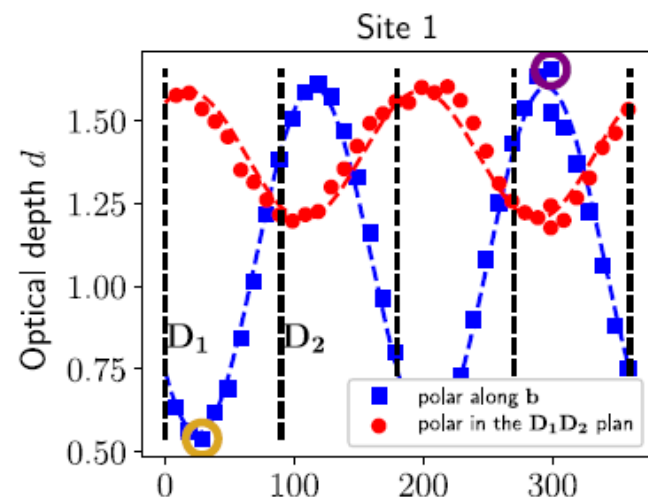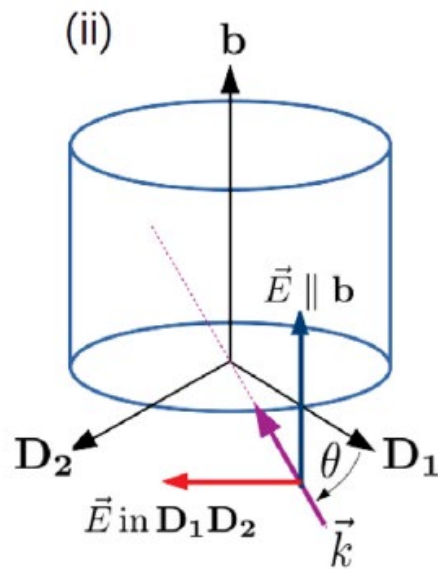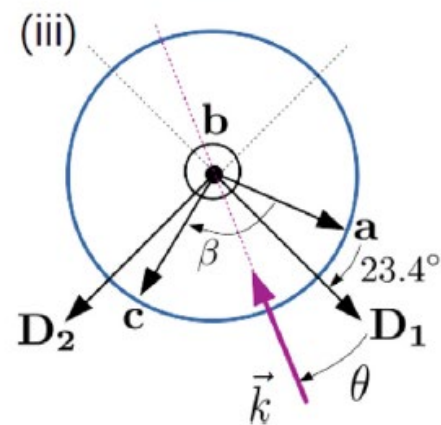
Er³⁺:Y₂SiO₅ Predictions: Polarization

- We cannot (yet) calculate electric-dipole moments in low symmetry, but can calculate magnetic dipole moments (same matrix elements as Zeeman).
- Our predictions for Site 1 have improved with more data.
- Site 2 is still out of phase...
    Calculation or measurement?
- Interesting that all fits reproduce Zeeman splitting, but not dipole moments **between** states.

Zeeman splitting

Zeeman splitting

Transition dipole

Site 1 – magnetic dipole

○ Petit et al.
This study
Horvath et al.
Hovarth thesis

PHASE CHANGES!

Site 2 – magnetic dipole

DATA IS INCORRECT

○ Petit et al.
This study
Horvath thesis
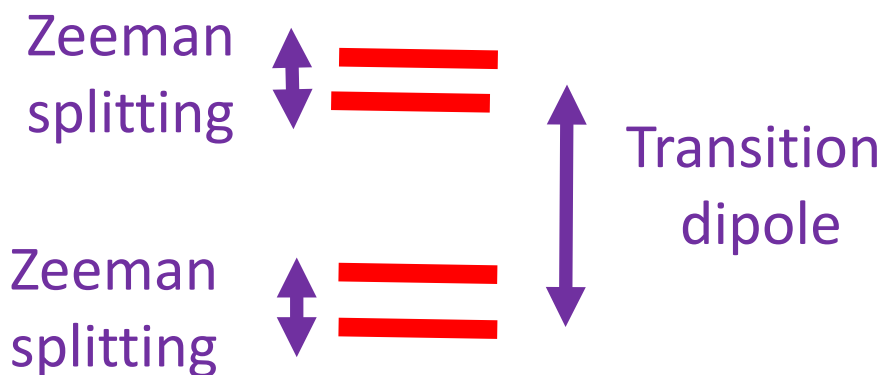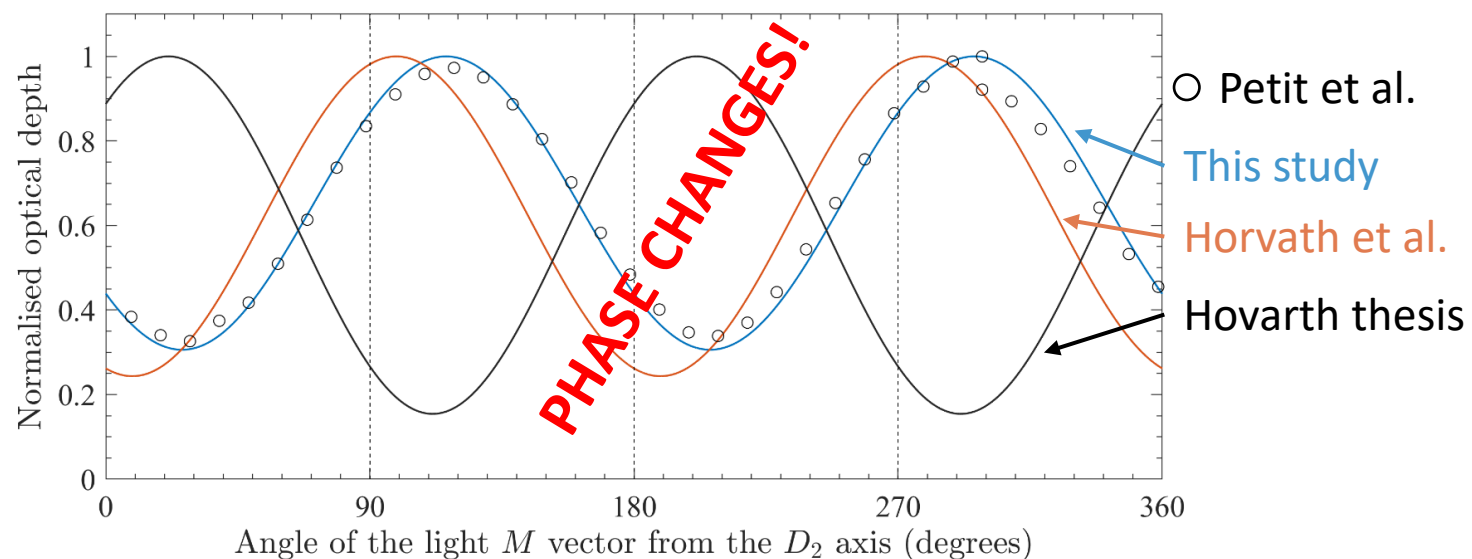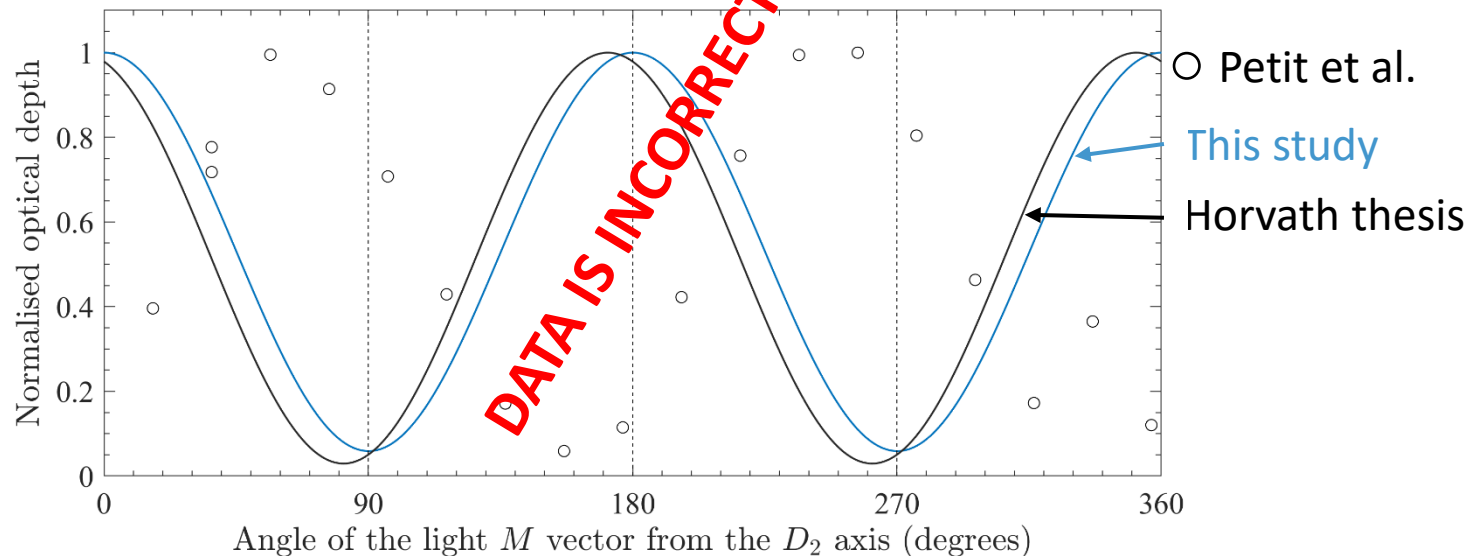
Er^{3+}:Y$_2$SiO$_5$ predictions: high-field hyperfine

Hyperfine structure of Site 2 1.5µm transition:
7T along D$_1$.
Miloš Rančić et al. Nat. Phys., **4**, 50-54 (2018)
Non-linear regime where spin-Hamiltonian approach
breaks down.
Unlike Site 1, our Site 2 fit does not include Y$_1$
hyperfine data – this is a *prediction*.

| Splittings | $^4I_{15/2}Z_1$ | | $^4I_{13/2}Y_1$ | |
ΔE	This study	Ref. [5]	This study	Ref. [5]
$\Delta(1,2)$	897	995	928	994
$\Delta(2,3)$	881	943	912	972
$\Delta(3,4)$	865	898	895	953
$\Delta(4,5)$	849	862	879	935
$\Delta(5,6)$	833	831	863	918
$\Delta(6,7)$	817	810	847	903
$\Delta(7,8)$	801	796	831	889

Other work by our group on Y_2SiO_5

$Ce^{3+}:Y_2SiO_5$
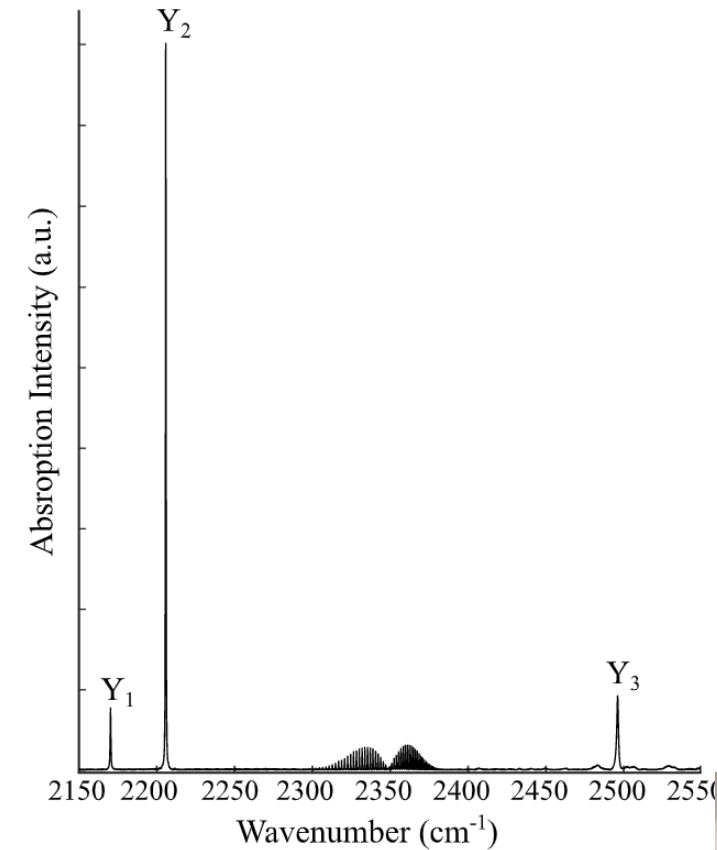
$Nd^{3+}:Y_2SiO_5$
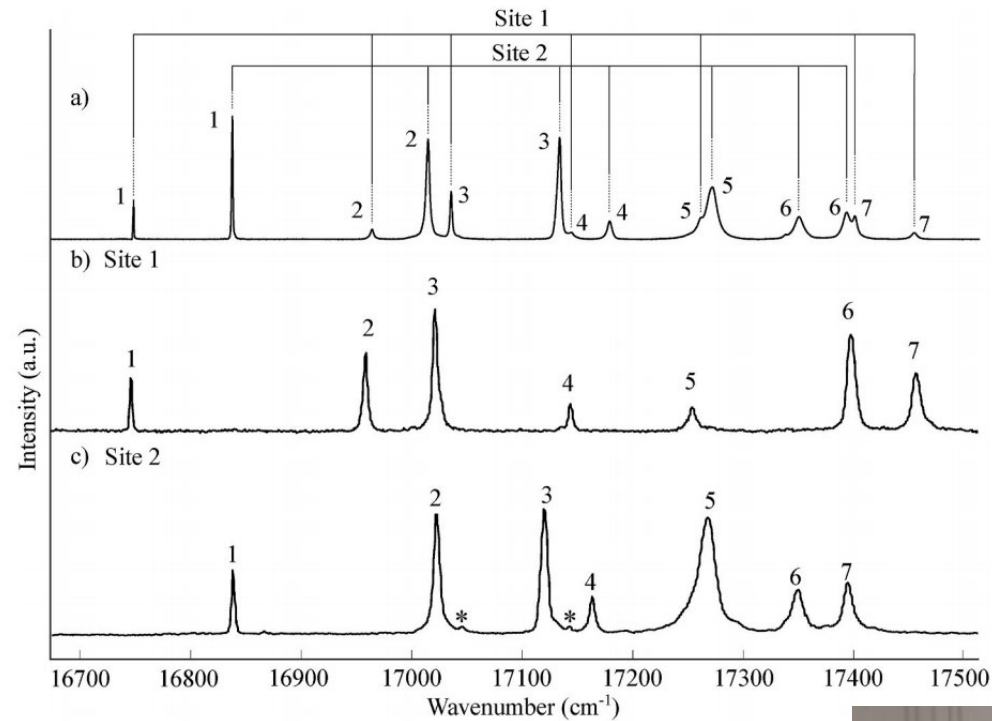
$Ho^{3+}:Y_2SiO_5$
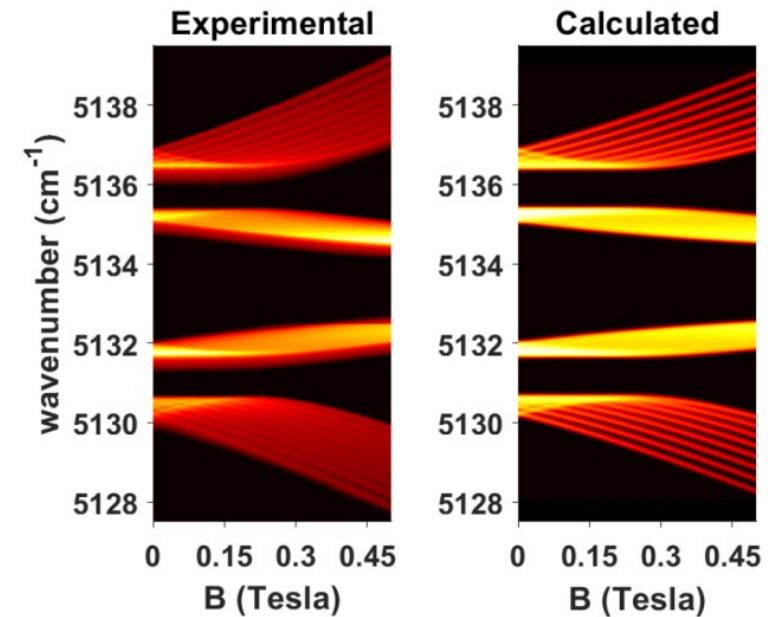
Yashar Alizadeh et al.
Opt. Mater., **117**, 111114 (2021)
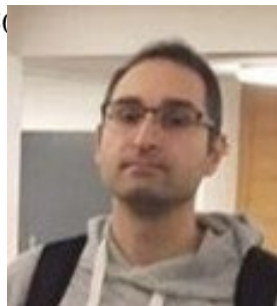
Yashar Alizadeh et al.
J. Lumin., **234**, 117959 (2021)

Sagar Mothkuri et al.
Phys. Rev. B, **103**, 104109 (2021)

Summary of spectroscopic work on Y_2SiO_5

We have shown that we can do crystal-field fits on low-symmetry systems.

But:

Proving that our fits are **unique** is still an open question.

Comparing fits with 27 parameters is difficult!

Perhaps ab-initio calculations are good enough to guide the fits?

Spectroscopic Distinctions between Two Types of Ce^{3+} Ions in X2-Y$_2$SiO$_5$: A Theoretical Investigation

Jun Wen,[*,†] Chang-Kui Duan,[‡] Lixin Ning,[*,§] Yucheng Huang,[§] Shengbao Zhan,[†] Jie Zhang,[†] and Min Yin[‡]

Chang-Kui Duan   Jiajia Cai   Jun Wen

Table 5. Calculated Principal Values of the g-Tensors for Ce^{3+} Ions in X2-YSO in Comparison with the Experimental Values for Ce^{3+} Ions in LSO

principal values	site 1 (CN = 6)		site 2 (CN = 7)	
	calcd	exptl[a]	calcd	exptl[a]
g_x	0.015	0	0.394	0.55
g_y	1.317	1.3	1.743	1.69
g_z	2.297	2.3	2.216	2.25
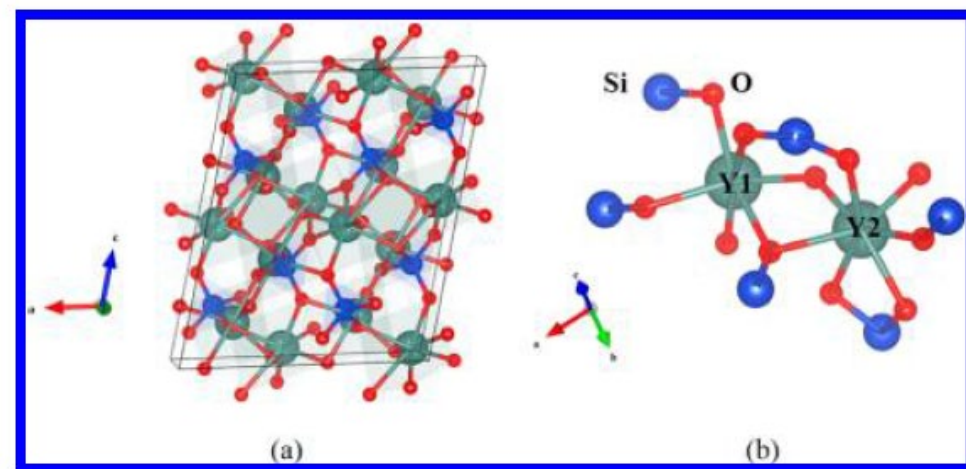
Figure 1. Schematic representations of local atomic structures around the two types of yttrium (Y1 and Y2) sites along with the unit cell of X2-YSO.

56

Ce³⁺ in X2-YSO

郝锐杰（Ruijie HAO），景伟国（Weiguo JING）*

Chang-Kui Duan

USTC, Hefei, China

K=2 Spherical Harmonics - Potential
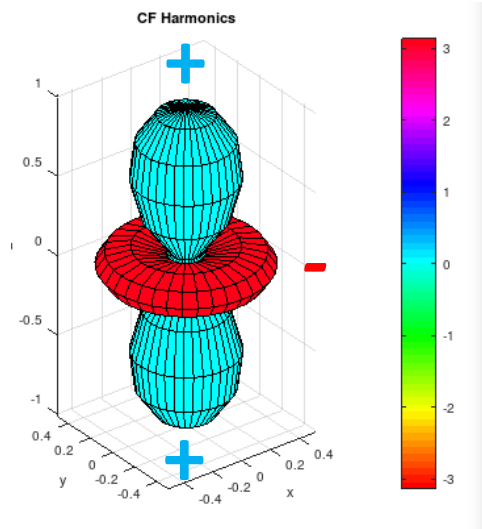
$C^2_0(\mathbf{r})$
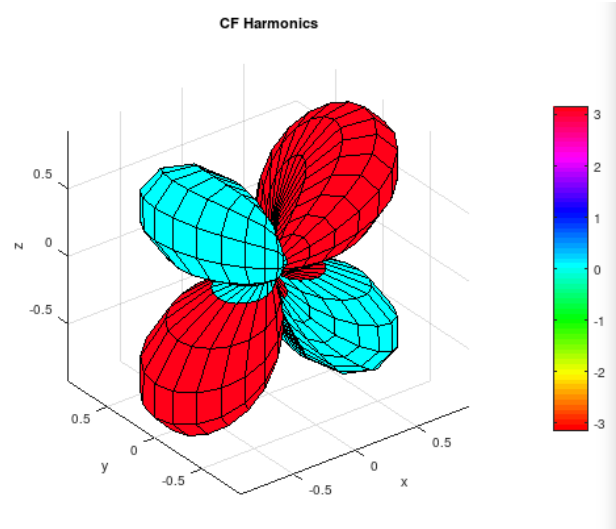
$C^2_1(\mathbf{r}) - C^2_{-1}(\mathbf{r})$
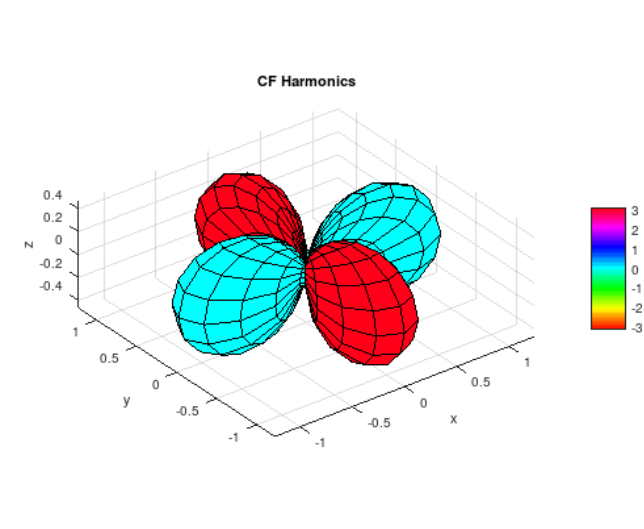
$C^2_2(\mathbf{r}) + C^2_{-2}(\mathbf{r})$

$C^2_0(\mathbf{r}) \sim 3z^2 - r^2 \sim 3\cos^2\theta - 1,$ etc.

Potential acts on 4f orbitals:
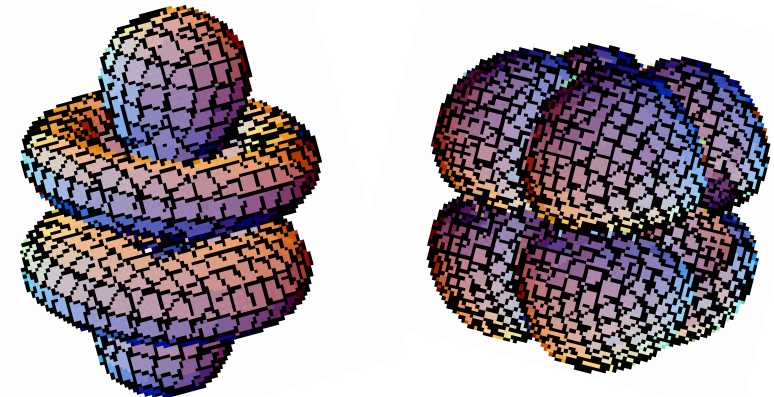
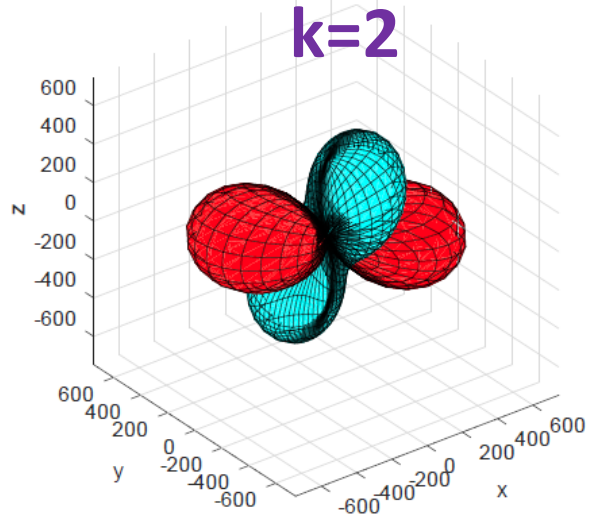# Fitted and ab-initio parameters for the k=2 part of the crystal-field potential (Er^{3+}:YSO, site 1).

$$H_{CF} = \sum_{k,q} B_q^k C_q^{(k)}$$

Parameter fit

Ab-initio calculation

$C^2_0(\mathbf{r})$

$C^2_1(\mathbf{r}) - C^2_{-1}(\mathbf{r})$
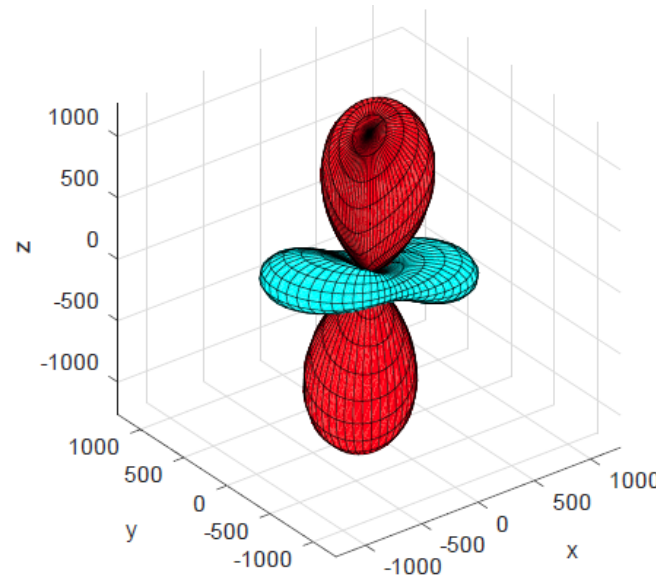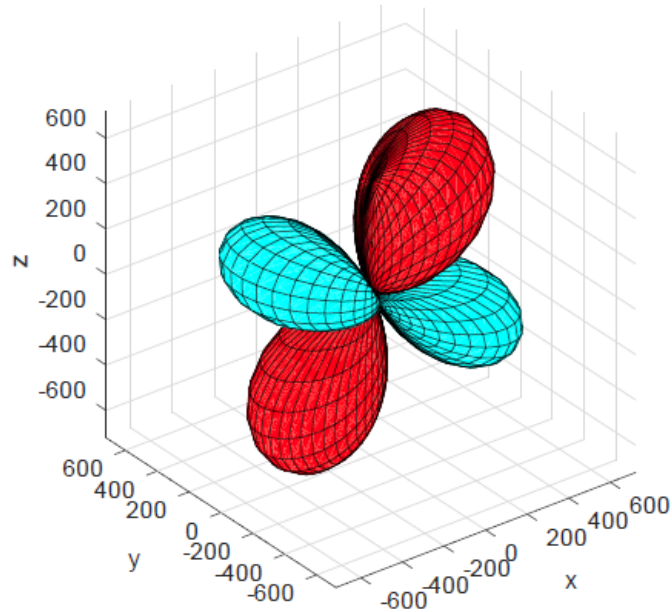
$C^2_2(\mathbf{r}) + C^2_{-2}(\mathbf{r})$

Parameter fit for Er^{3+}

B20 = -479.6
B21 = 471.4+143.8i
B22 = 125.5-2.0i

Ab-initio calculation for Ce^{3+}

B20 = -1162;
B21 = 362-198i;
B22 = 129+76i;
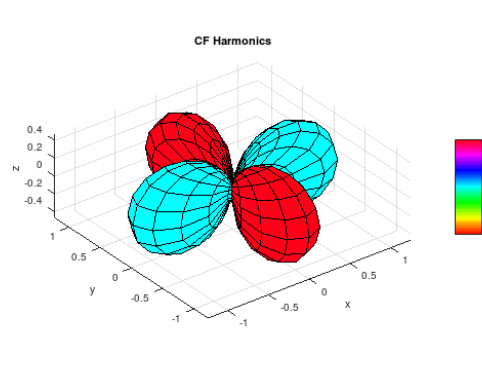
Fitted and ab-initio parameters for the k=2 part of the crystal-field potential (Er^{3+}:YSO, site 2).

Parameter fit

Ab-initio calculation

$$H_{CF} = \sum_{k,q} B_q^k C_q^{(k)}$$

Parameter fit for Er^{3+}

B20 =   389
B21 = -325.7-95.8i
B22 = -368.5+53.7i

Ab-initio calculation for Ce^{3+}

B20 =   925;
B21 = -30-219i
B22 = -496+46i

$C^2_0(\mathbf{r})$
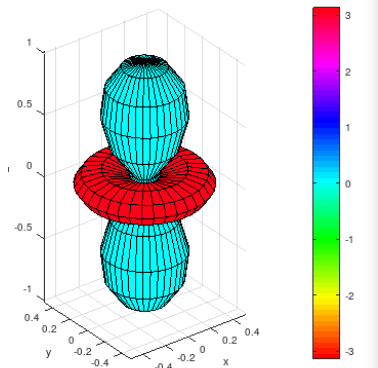
$C^2_1(\mathbf{r}) - C^2_{-1}(\mathbf{r})$
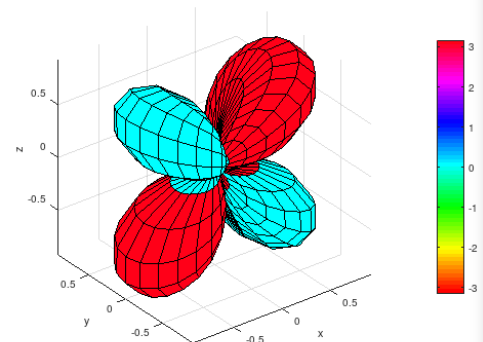
$C^2_2(\mathbf{r}) + C^2_{-2}(\mathbf{r})$
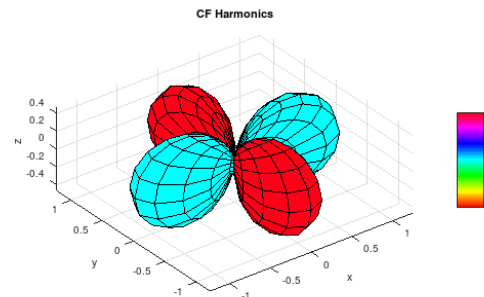
Fitted and ab-initio parameters for the k=2,4,6 parts of the crystal-field potential (Er^{3+}:YSO, site 1).

k=2　　　　　**k=4**　　　　　**k=6**
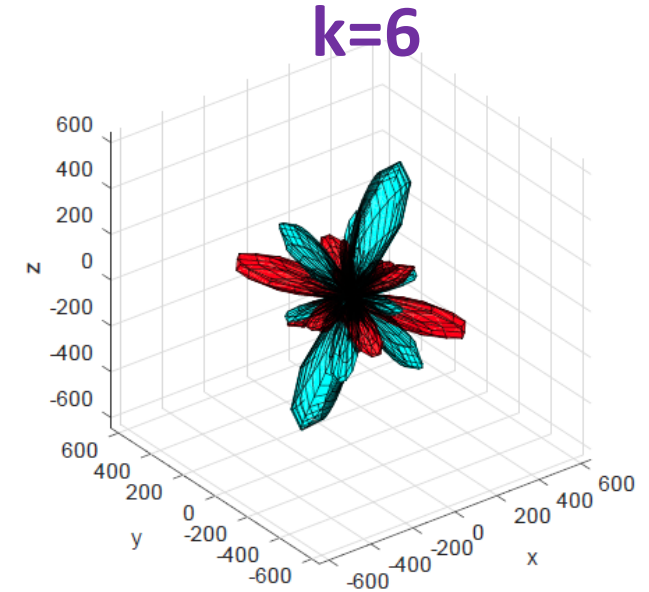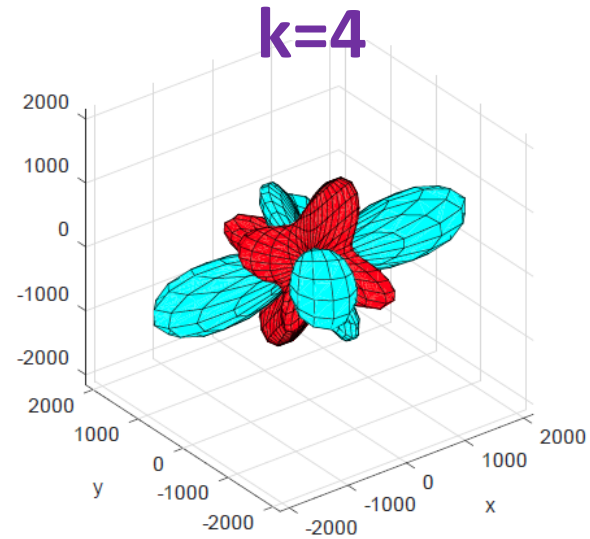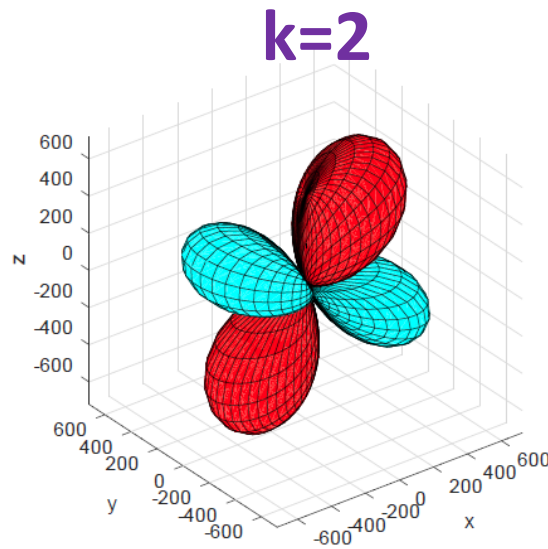
Parameter fit
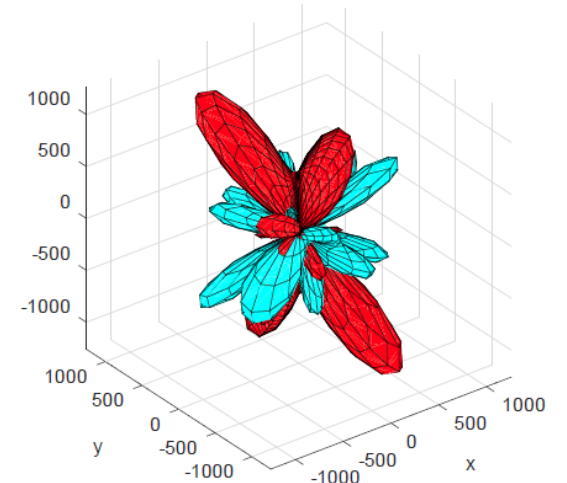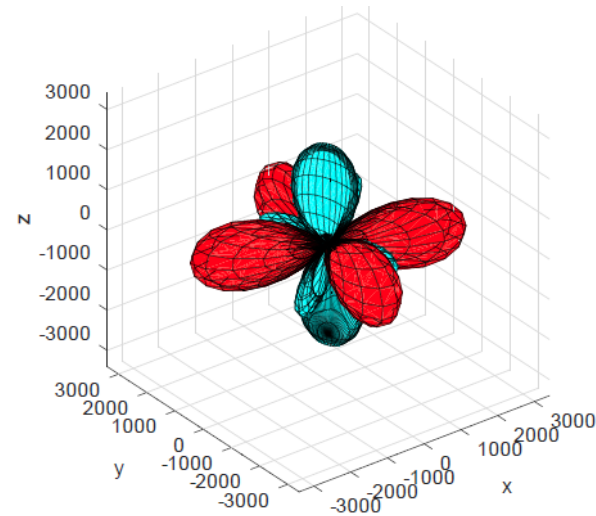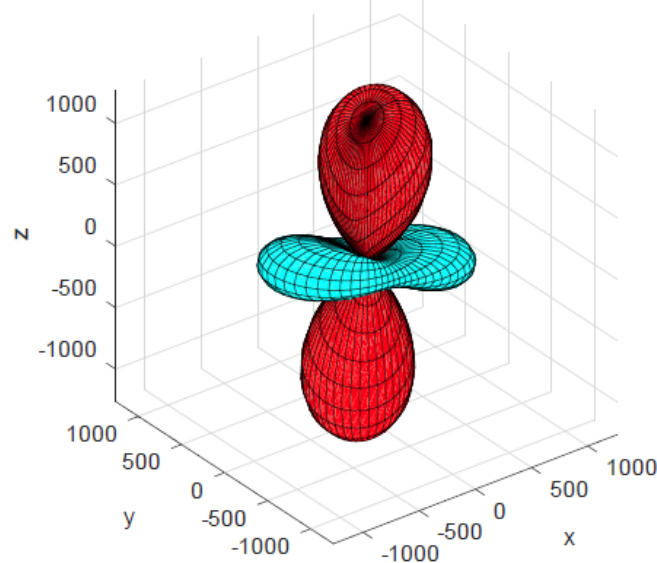
Ab-initio

Fitted and ab-initio parameters for the k=2,4,6 part of the crystal-field potential (Er^{3+}:YSO, site 2).

In Progress: Prediction of the hyperfine structure of $^{151}Eu^{3+}:Y_2SiO_5$

The $Sm^{3+}:Y_2SiO_5$ parameters are scaled and fitted to predict the
hyperfine structure of the $^7F_0$ ground state of $Eu^{3+}:Y_2SiO_5$ (Site 1)

Spin Hamiltonian: $\mathscr{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{Q} \cdot \mathbf{I} - \mu_n g_n \mathbf{B} \cdot \mathbf{I}$

Contributions from

1. Electronic effects due to mixing of $^7F_2$ with $^7F_0$ by crystal field.

2. Direct interaction of lattice and magnetic field with nucleus.

See: Smith et al, Complete crystal-field calculation of Zeeman hyperfine splittings in europium.
Phys. Rev. B 105: 125141
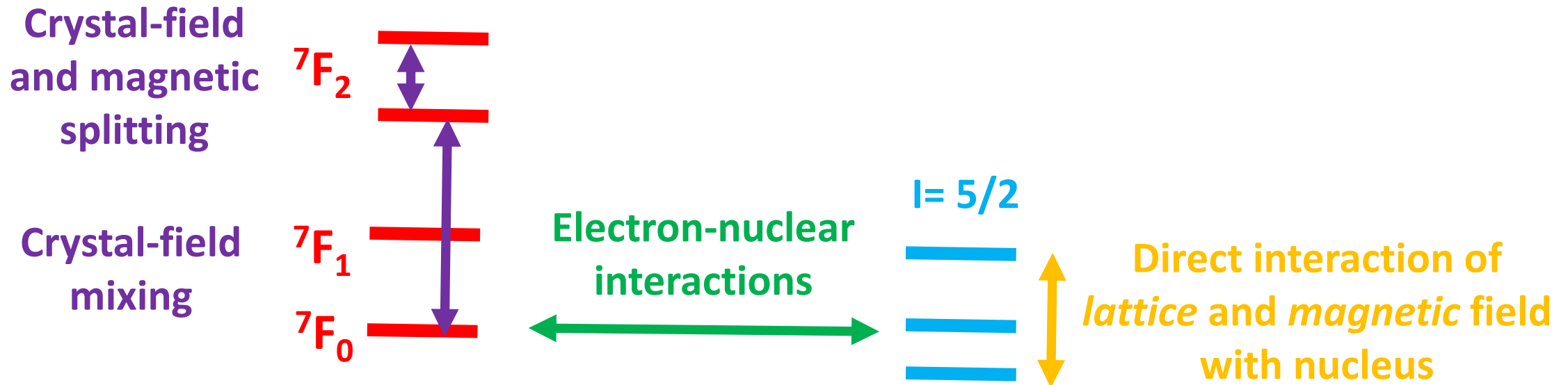
In Progress: Predictions of the hyperfine structure of $^{151}Eu^{3+}:Y_2SiO_5$

Nuclear spin: I=5/2
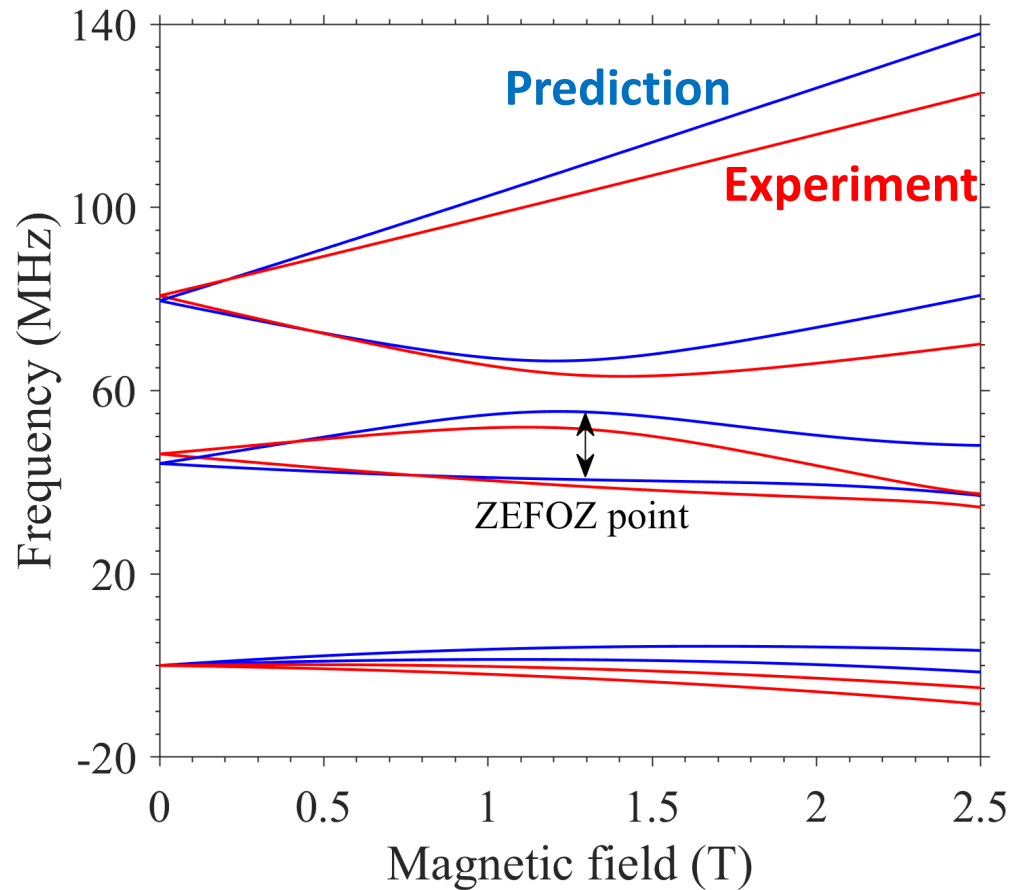
The $Sm^{3+}:Y_2SiO_5$ parameters were scaled to predict the hyperfine structure of the $^7F_0$ ground state of $Eu^{3+}:Y_2SiO_5$ (Site 1)

The experiment and prediction are for a magnetic field in the particular direction that gives the ZEFOZ point used in Zhong et al. Nature paper demonstrating six-hour coherence.

Contributions from:

1. Electronic effects due to mixing of $^7F_2$ with $^7F_0$ by crystal field.
2. Direct interaction of lattice and magnetic field with nucleus.
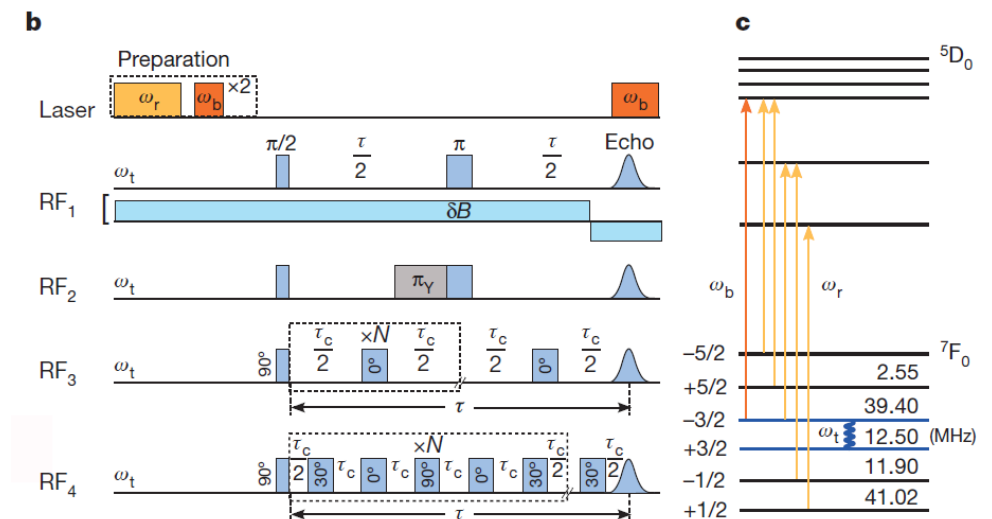
# Magnetic field effects in nanoparticles - Jamin Martin
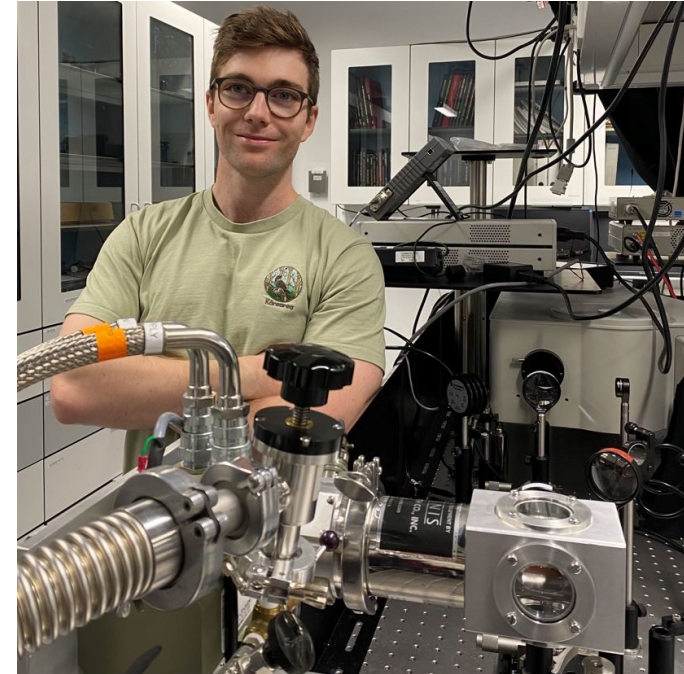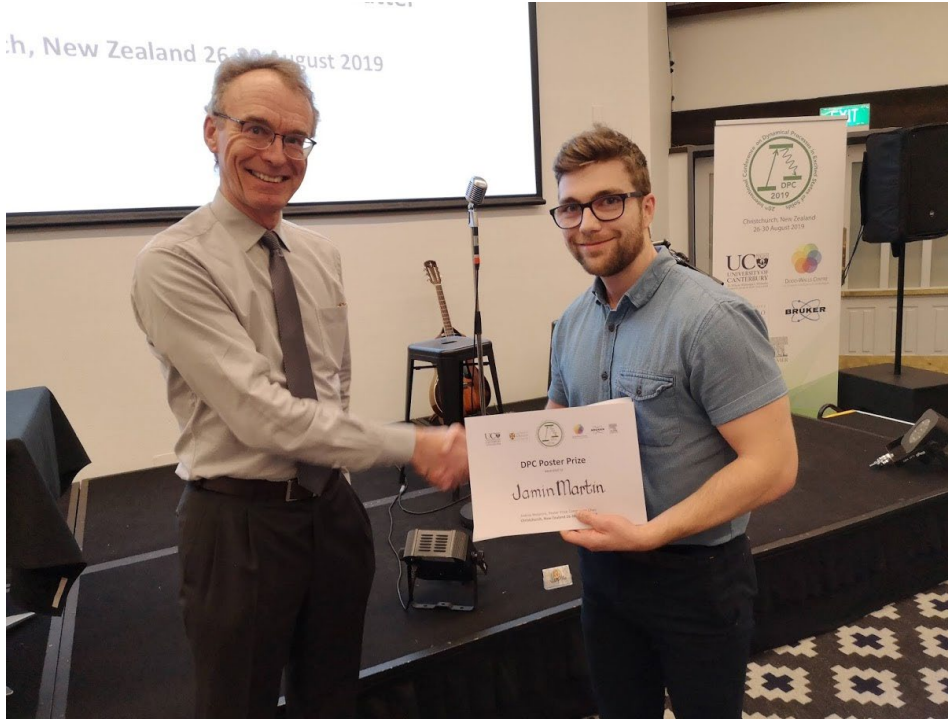
Review: Y. Luo, Z. Chen, S. Wen, Q. Han, L. Fu, L. Yan, D. Jin, J.-C. G. Bünzli, G. Bao, Magnetic regulation of the luminescence of hybrid lanthanide-doped nanoparticles, Coordination Chemistry Reviews 469 (2022) 214653

We use KY_3F_{10}, which has high symmetry (C_{4v}) and so calculations are possible of energy levels and intensities.

Magnetic Fields Yb/Er NaYF₄
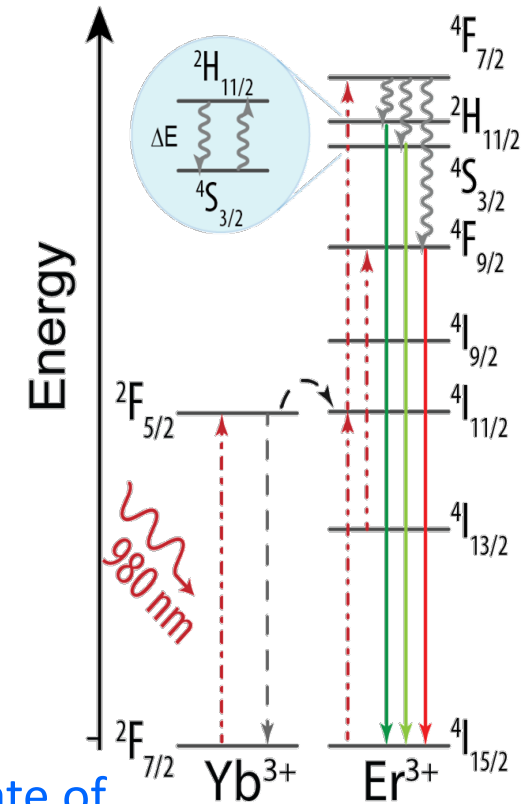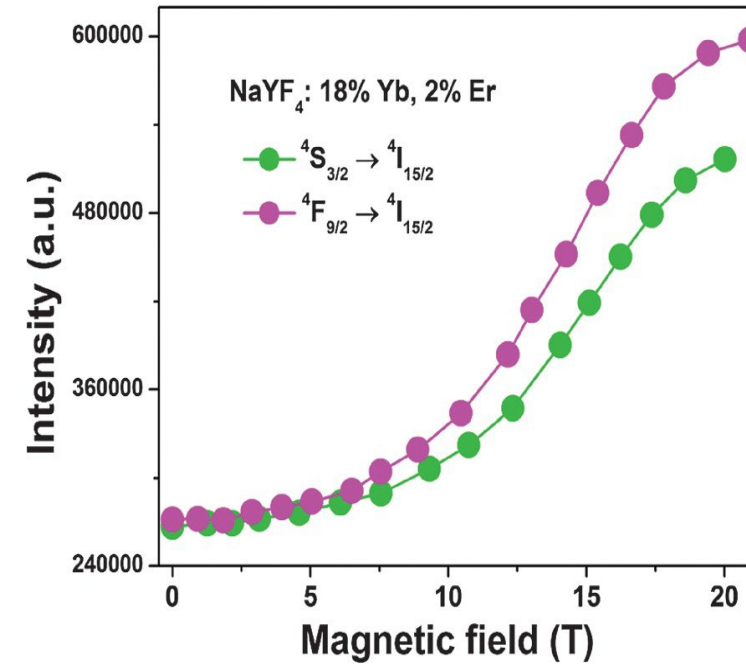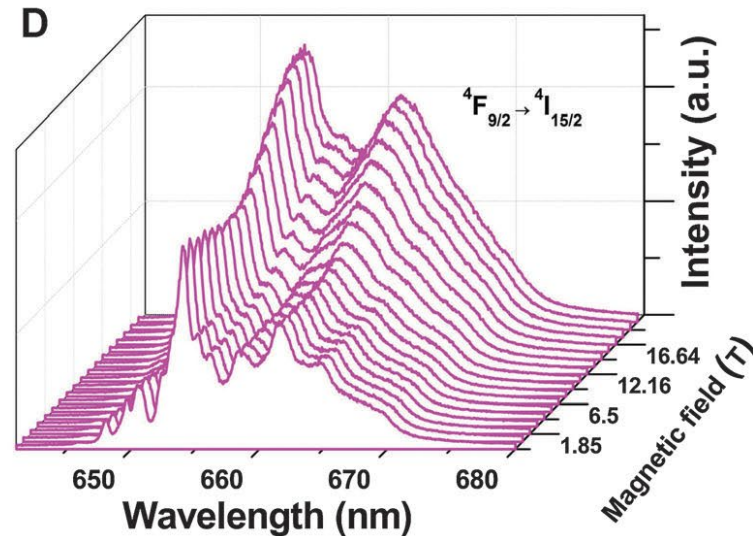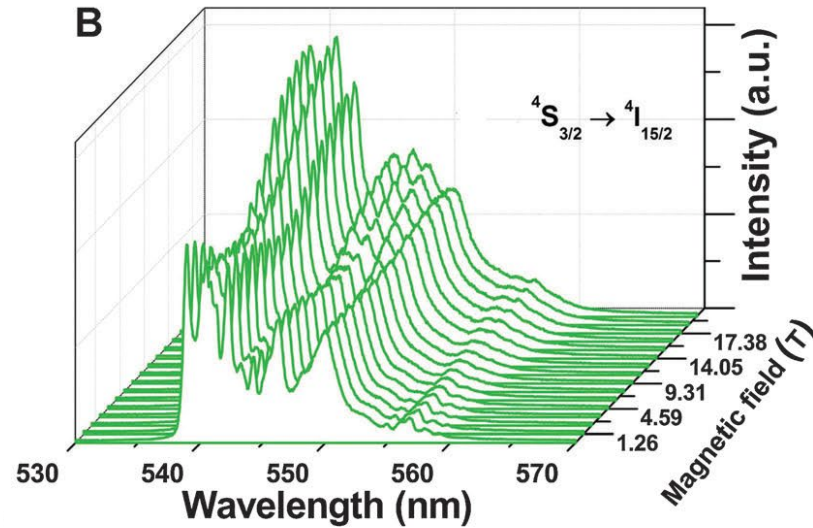
"... It is **highly possible** that the rate of excited state absorption of Er^{3+} is enhanced with magnetic field, because the energy level splitting **might** reduce the energy difference between the excitation light (975 nm) and the gap between the $^4I_{11/2}$ and $4F_{7/2}$ levels of Er^{3+}..."

Yb/Er NaYF₄: P. Chen et al, J. Mater. Chem. C, 2015, 3, 8794

Er³⁺/Nd³⁺/ :KY₃F₁₀

Jamin Martin
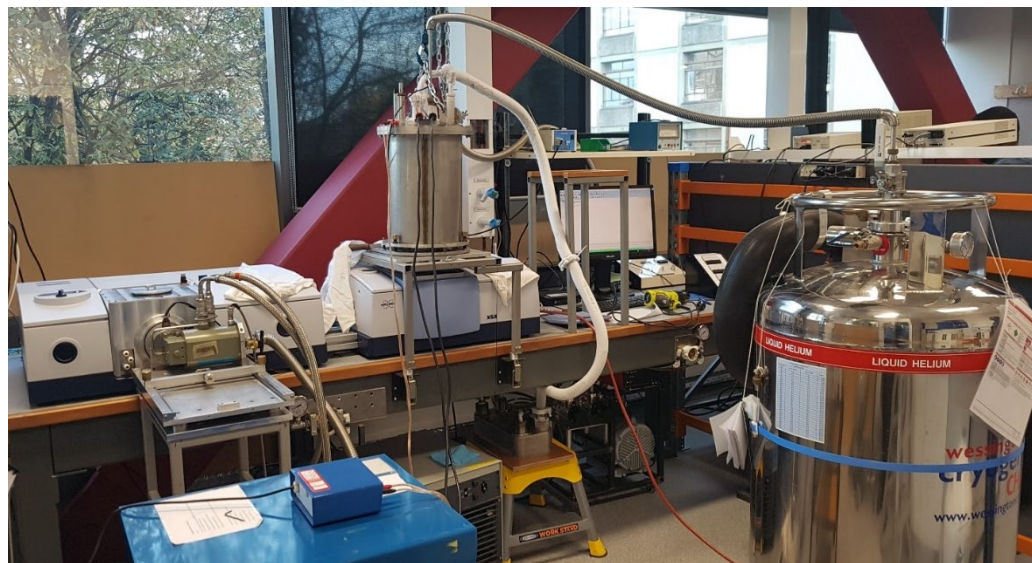
ENERGY LEVELS OF THE +3 LANTHANIDES IN LaF₃
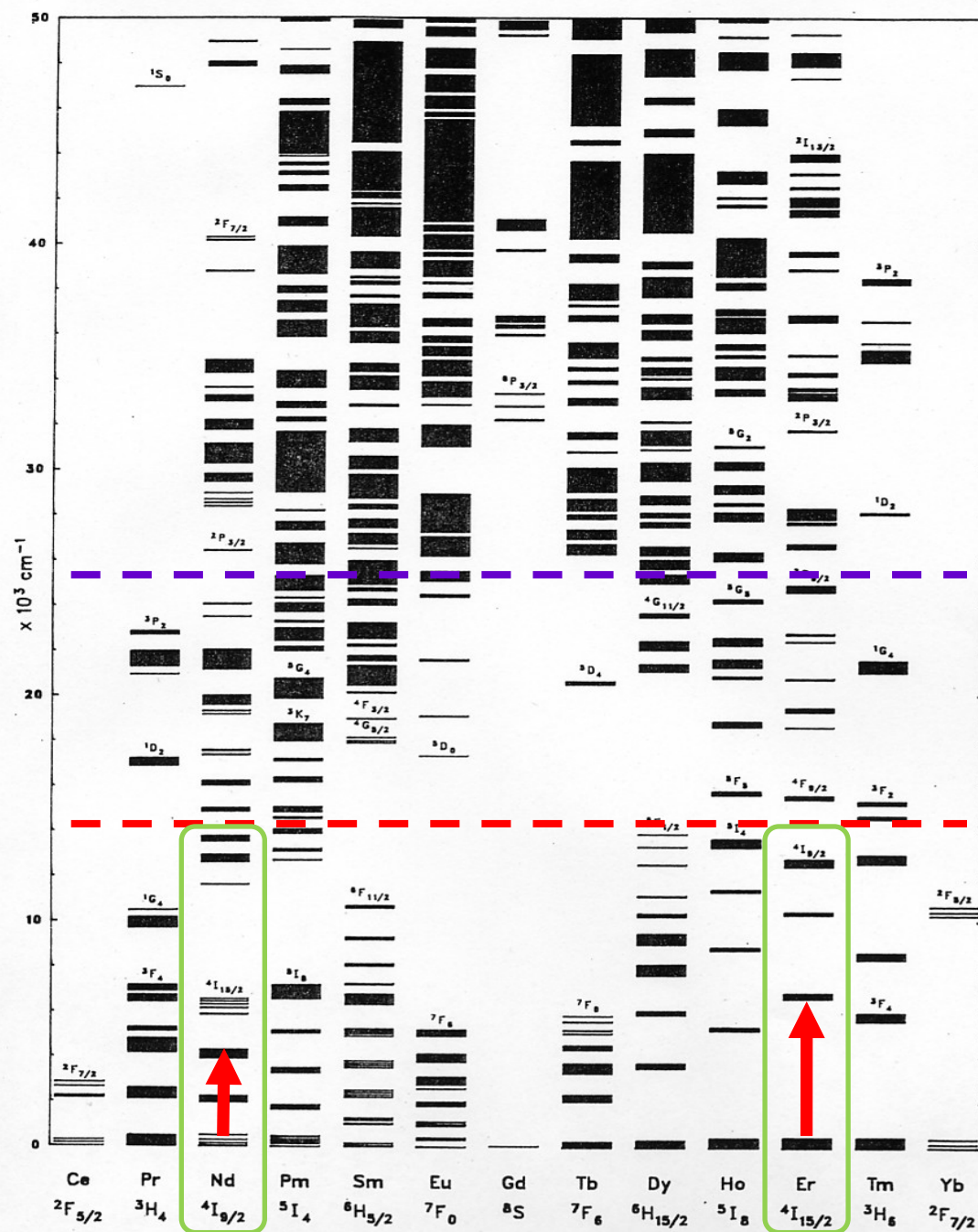
Er^{3+}:KY$_3$F$_{10}$ nanoparticles

B
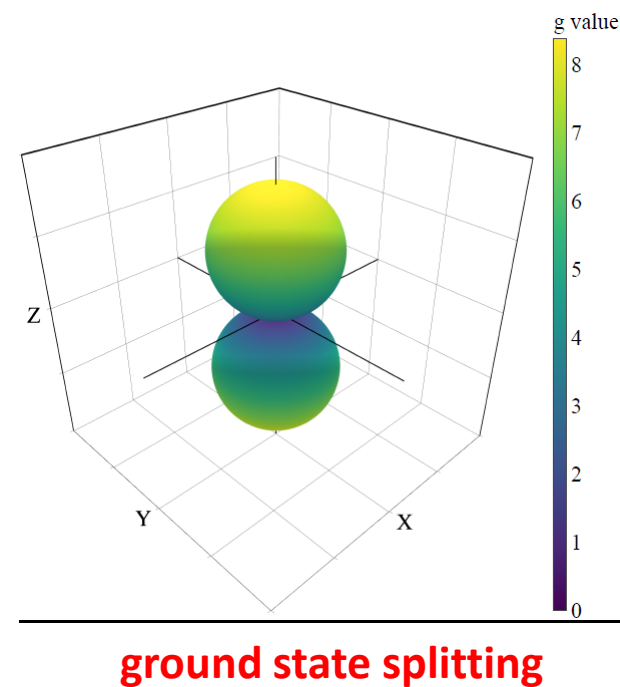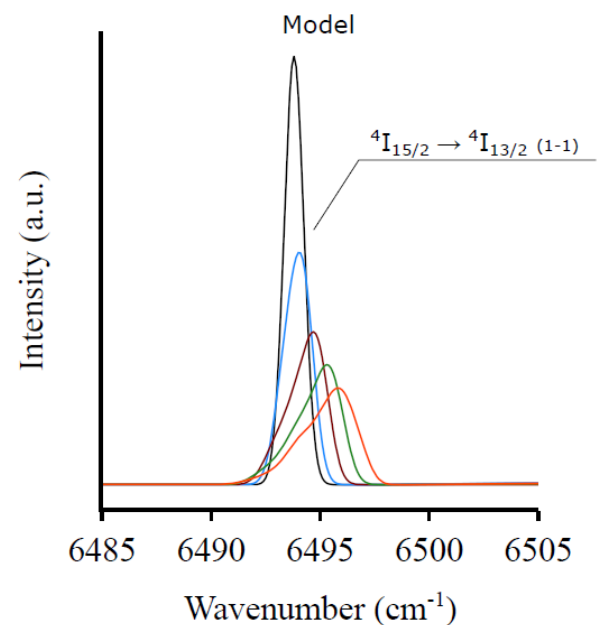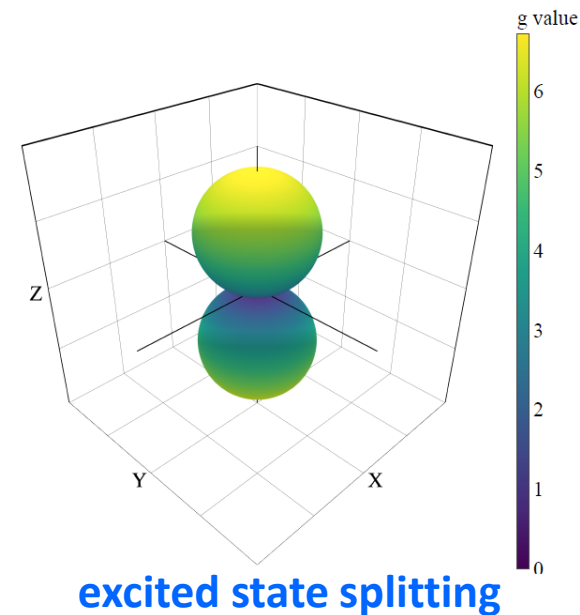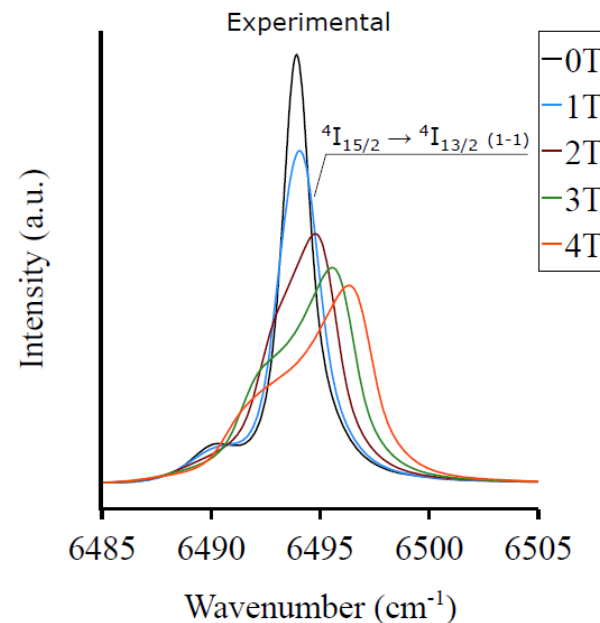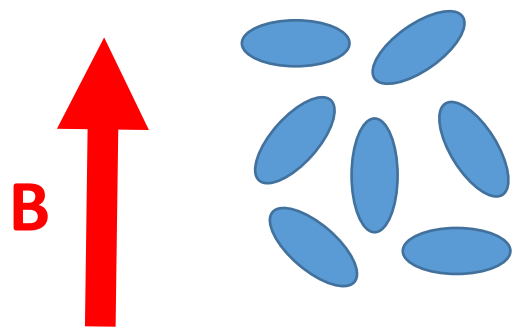
Not symmetrical: Transitions from lower ground state are more intense due to Boltzmann factors.

Experimental

$^4I_{15/2} \rightarrow {}^4I_{13/2}$ (1-1)

— 0T
— 1T
— 2T
— 3T
— 4T

Intensity (a.u.)

6485   6490   6495   6500   6505

Wavenumber (cm^{-1})

Model

$^4I_{15/2} \rightarrow {}^4I_{13/2}$ (1-1)

Intensity (a.u.)

6485   6490   6495   6500   6505

Wavenumber (cm^{-1})

g value

excited state splitting

g value

ground state splitting

$^4I_{9/2}$

$^4I_{15/2}$

Er

$^4I_{15/2}$

Er³⁺:KY₃F₁₀

Model

$^4I_{15/2} \rightarrow \,^4I_{13/2}$ (1-1)

6485 6490 6495 6500 6505

1   2   3   4

Random orientation probes populations at various angles of magnetic field.

1 2 3 4
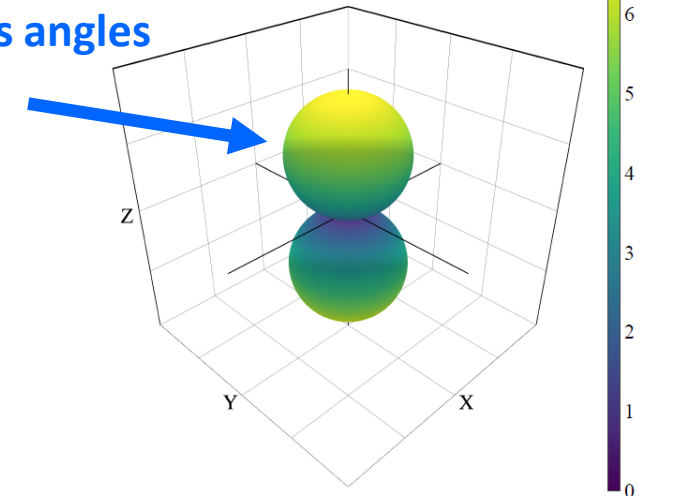
excited state splitting

ground state splitting

lower ground state – higher population
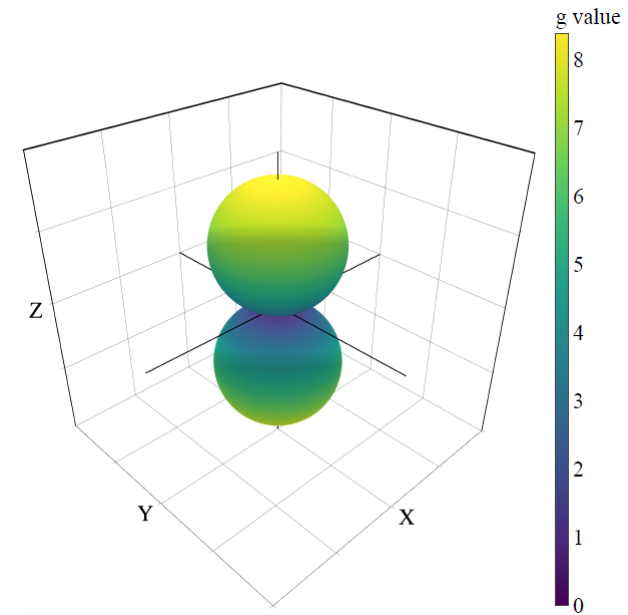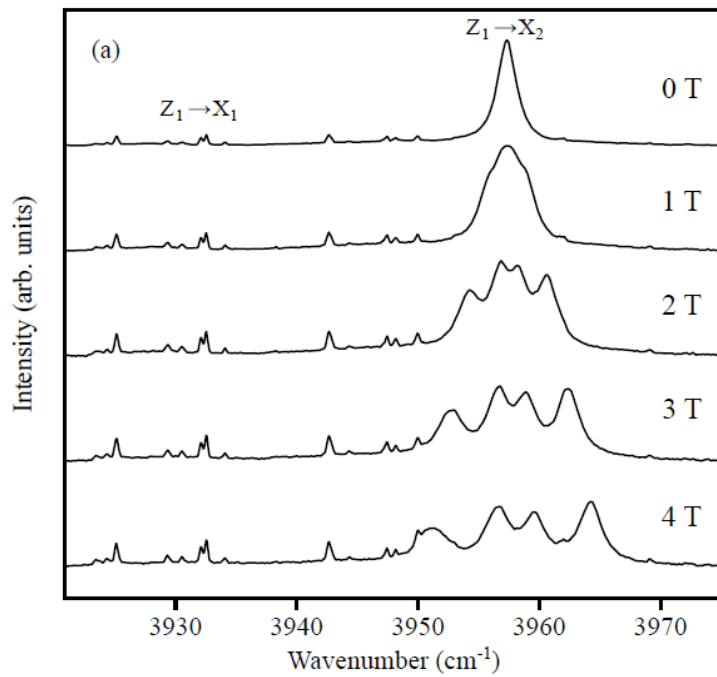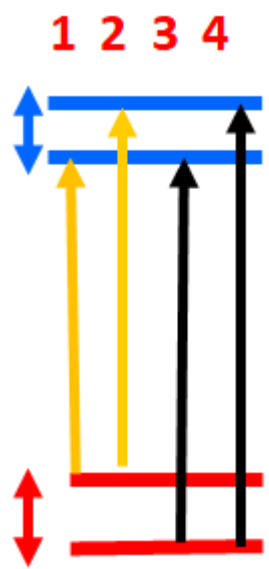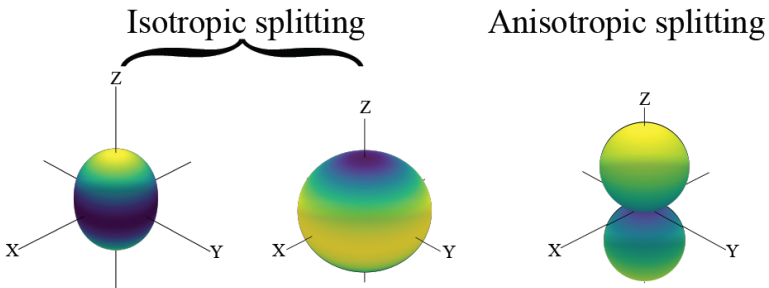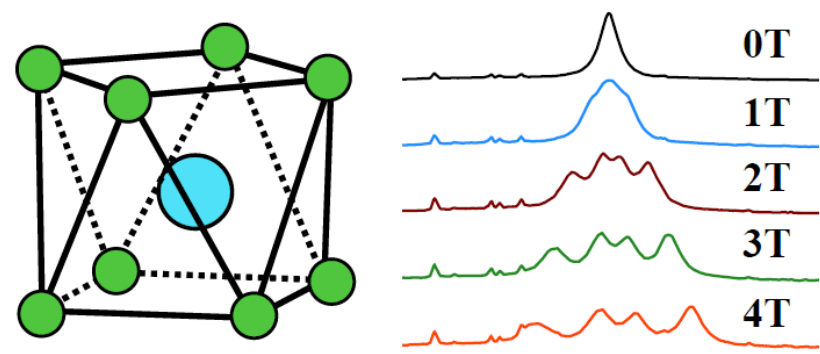
Peak splitting not at maximum possible splitting. This has to do with integral over solid angle of splitting function.

Classification: Public

Nd³⁺:KY₃F₁₀

Transition selected for isotropic splitting

Crystal-field and Zeeman interactions in lanthanide doped nanocrystals: KY$_3$F$_{10}$:Nd^{3+}

Jamin L. B. Martin, Jon-Paul R. Wells, Michael F. Reid
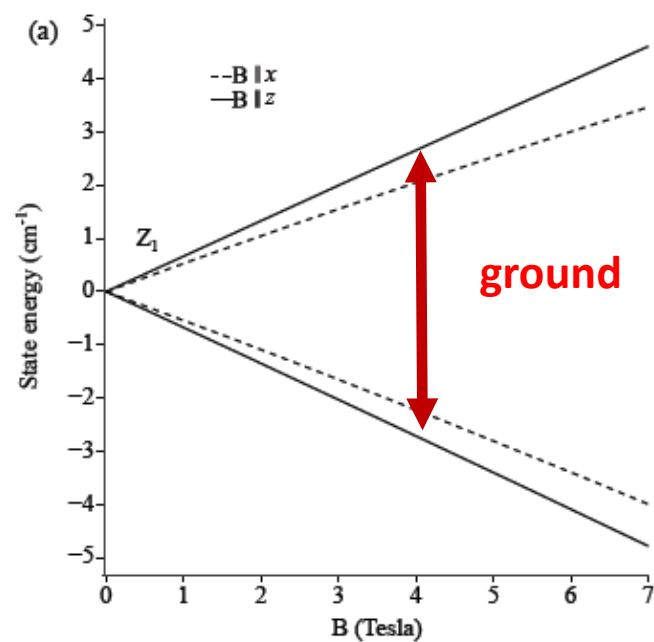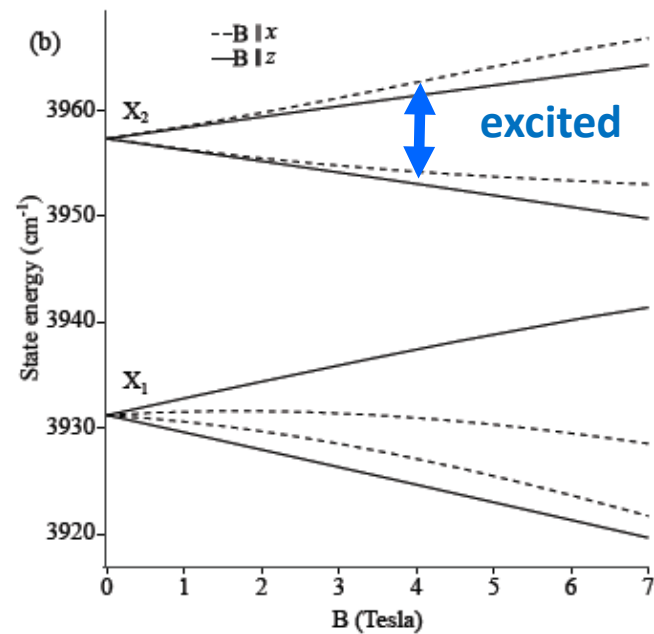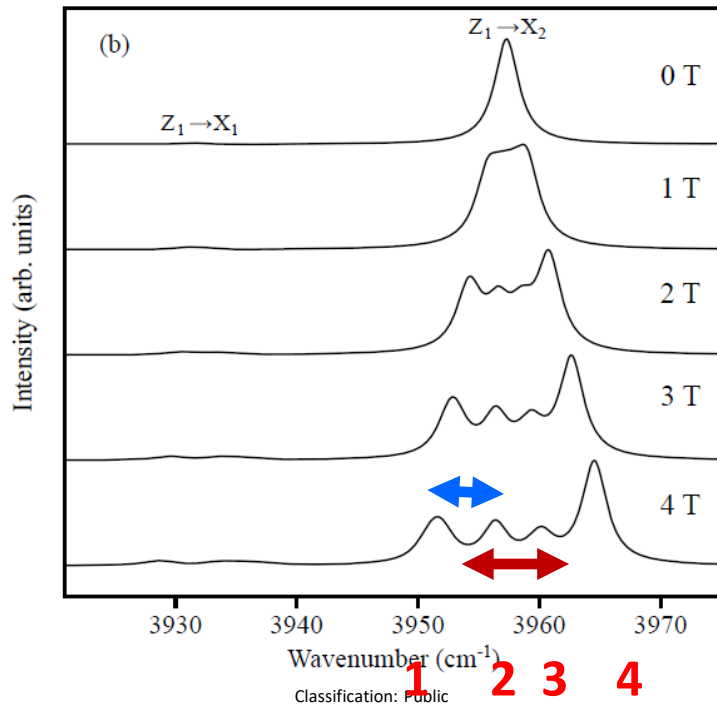
Fit including magnetic splittings gives a good reproduction in the splittings, including non-linear effects.
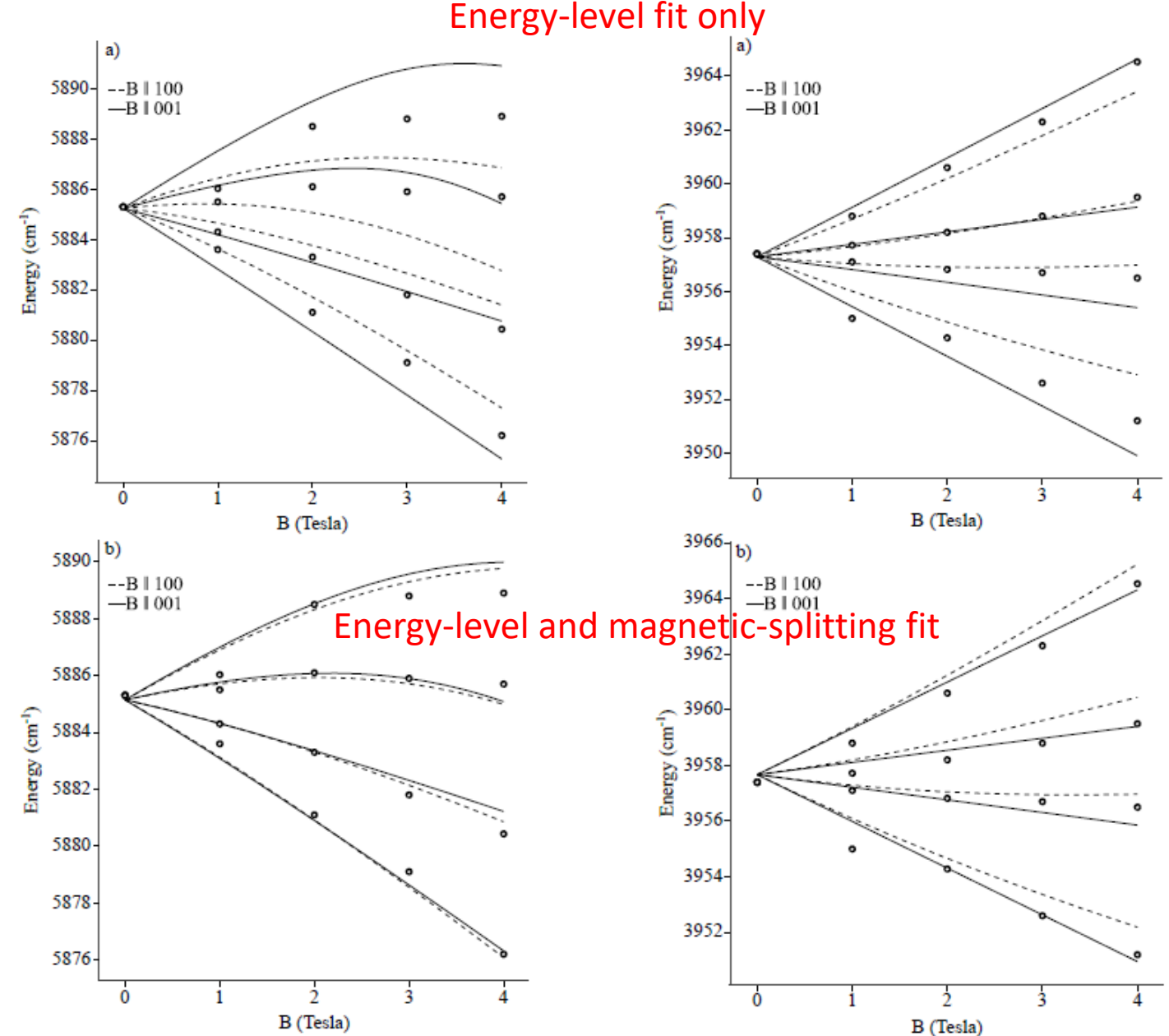
Jamin Martin et al.
Optical Materials X, 2022, 100181.

Energy-level fit only

Energy-level and magnetic-splitting fit

Figure 3: Calculated Zeeman splittings for the Z$_1$γ$_6$ ⟶ W$_1$γ$_7$ transition. Energies only fit (a) and energies + splittings fit (b)

Figure 4: Calculated Zeeman splittings for the Z$_1$γ$_6$ ⟶ X$_2$γ$_6$ transition. Energies only fit (a) and energies + splittings fit (b)

Conclusions

- Crystal-field modelling for several rare-earth ions: Ce^{3+}, Nd^{3+}, Sm^{3+}, Ho^{3+}, Er^{3+} in Y_2SiO_5 (YSO).

- Other groups include Yb^{3+}: Zhou et al. Inorganic Chemistry 59:13144 (2020).

- Due to the C_1 symmetry, directional magnetic data is required to determine unique sets of parameters. [May still not be unique!]

- Parameters can be scaled between ions.

- Prediction of polarization and high-field hyperfine structure for Er^{3+}:Y_2SiO_5.

- In progress:
  - Comparison with ab-initio calculations.
  - Micro and nanocrystals.
  - Prediction of magnetic-hyperfine structure for Eu^{3+}:Y_2SiO_5.
  - Work on other ions.

Tutorials on Electronic Structure

www2.phys.canterbury.ac.nz/~mfr24/

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