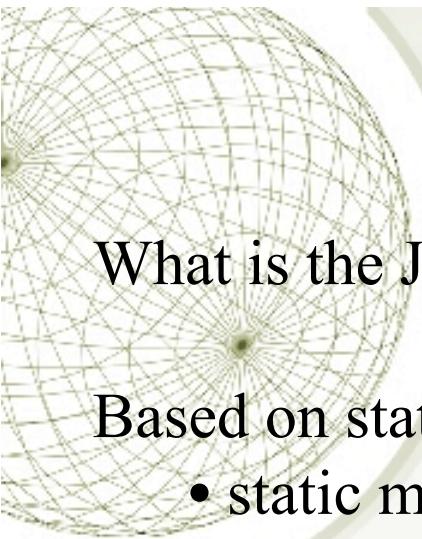


Judd-Ofelt Theory: Principles and Practices

Brian M. Walsh
NASA Langley Research Center



Part I: Principles

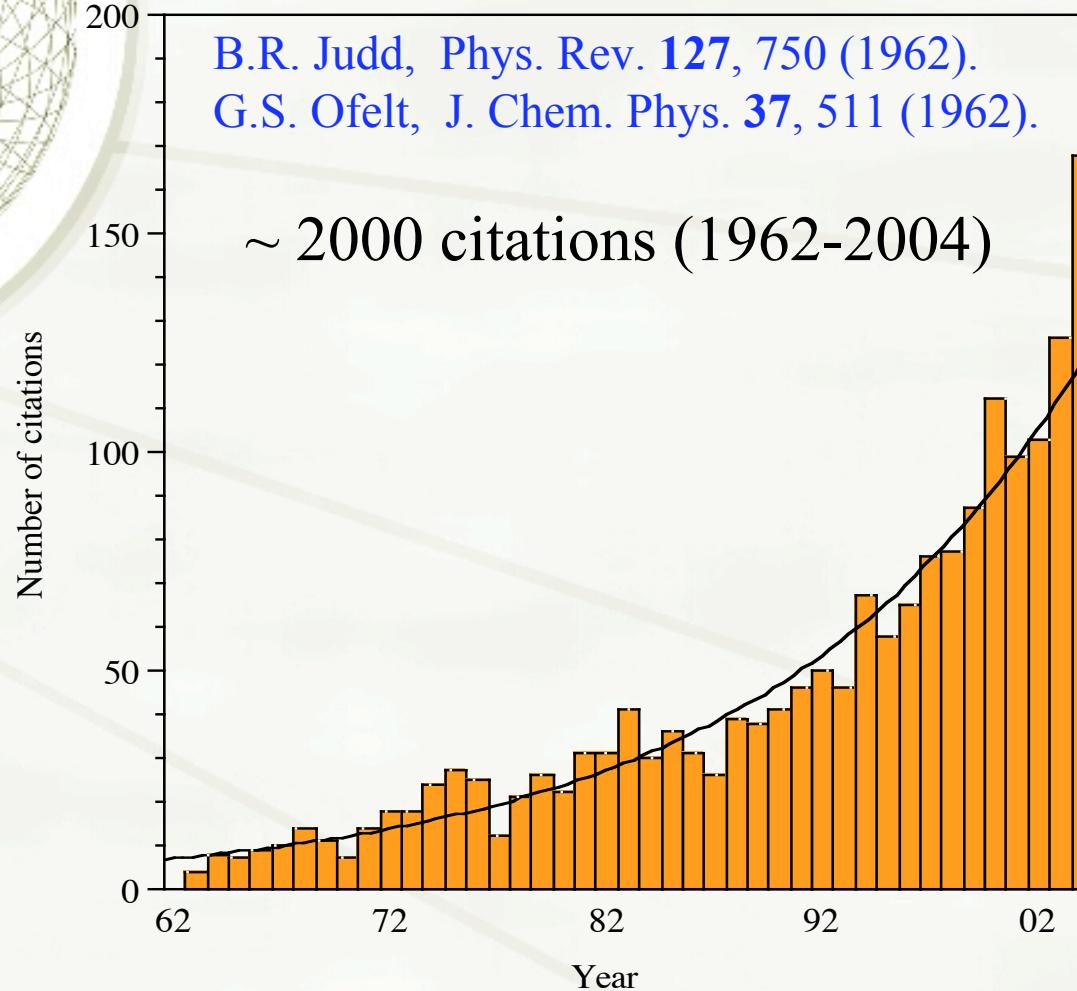
What is the Judd-Ofelt Theory?

Based on static, free-ion and single configuration approximations:

- static model - *Central ion is affected by the surrounding host ions via a 'static' electric field.*
- free ion model - *Host environment treated as a perturbation on the free ion Hamiltonian.*
- single configuration model - *Interaction of electrons between configurations are neglected.*

The Judd-Ofelt theory describes the intensities of 4f electrons in solids and solutions. *The remarkable success of this theory provides a sobering testament to simple approximations.*

Distribution of Citations by Year



Referenced in 169 Journal Titles

Top 20 Titles

	# of citations
PHYSICAL REVIEW B	127
JOURNAL OF NON-CRYSTALLINE SOLIDS	108
JOURNAL OF APPLIED PHYSICS	90
JOURNAL OF CHEMICAL PHYSICS	83
JOURNAL OF ALLOYS AND COMPOUNDS	81
JOURNAL OF LUMINESCENCE	77
JOURNAL OF PHYSICS-CONDENSED MATTER	58
MOLECULAR PHYSICS	57
CHEMICAL PHYSICS LETTERS	48
OPTICAL MATERIALS	43
JOURNAL OF THE OPTICAL SOCIETY OF AMERICA B	38
JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS	35
PHYSICA STATUS SOLIDI A-APPLIED RESEARCH	33
OPTIKA I SPEKTROSKOPIYA	30
IEEE JOURNAL OF QUANTUM ELECTRONICS	27
PHYSICS AND CHEMISTRY OF GLASSES	27
OPTICS COMMUNICATIONS	26
SPECTROCHIMICA ACTA PART A	26
INORGANIC CHEMISTRY	24
JOURNAL OF THE AMERICAN CERAMIC SOCIETY	19





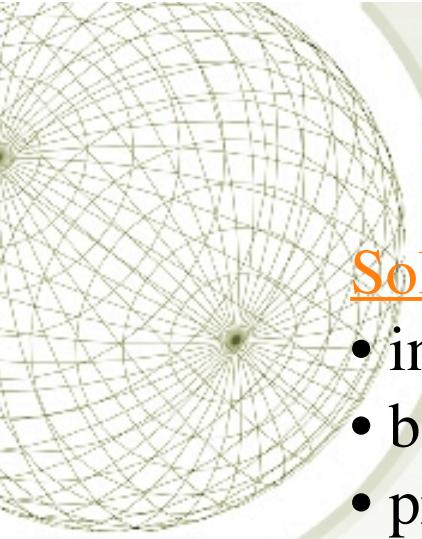
Prelude

“Lanthanum has only one oxidation state, the +3 state. With few exceptions, this tells the whole boring story about the other 14 lanthanides.”

G.C. Pimentel & R.D. Sprately,
"Understanding Chemistry",
Holden-Day, 1971, p. 862

<http://www.chem.ox.ac.uk/icl/heyes/LanthAct/I1.html>
(some amusing mnemonics for the Lanthanides and Actinides)

So much for ‘*Understanding Chemistry*’...
Let’s do some physics!



Ions in Solids

Solids

- insulators (not semiconductors)
- bandgaps are $> 5\text{ev}$ (VUV photon)
- produce a crystal field

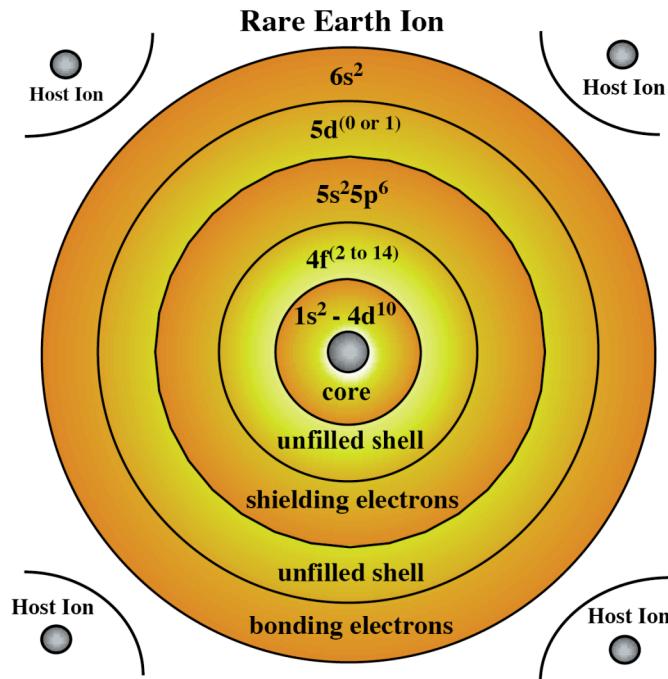
Ions

- replace host ions substitutionally
- transition metal and lanthanide series
- unfilled electronic shells
- Stark splitting from crystal field
- optical transitions occur within bandgap

Examples

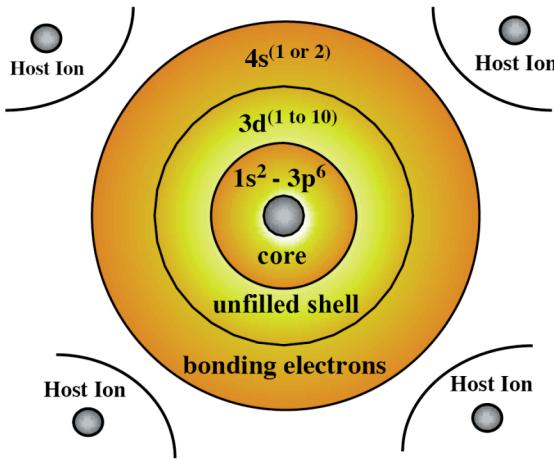
- Nd:Y₃Al₅O₁₂ - Er:fiber - Cr:Al₂O₃ (Ruby)

Atomic Structure of Laser Ions



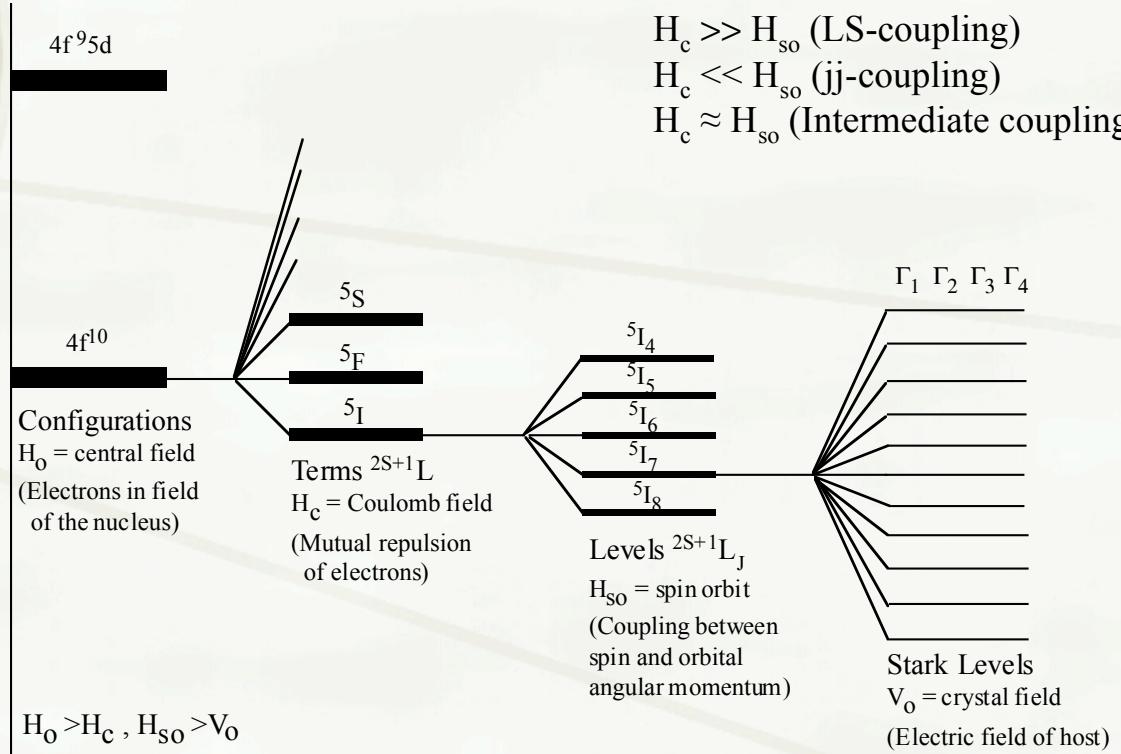
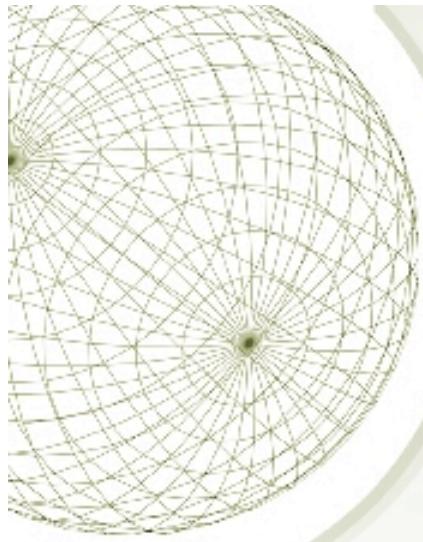
- La, Ce, Pr, Nd, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb
- 4f shell weakly affected by surrounding host ions.
- Free ion $2S+1L$ states split into $2S+1L_J$ multiplets.
- Narrow spectral lines, large cross sections.

Transition Metal Ion



- Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn
- 3d shell strongly affected by surrounding host ions
- Free ion $2S+1\Gamma$ states are split into $2S+1\Gamma(X)$ multiplets
- Broad spectral lines, small cross sections

Atomic Interactions



Hund's Rules*: F. Hund, Z. Phys. **33**, 345 (1925)

- 1.) Lowest state has maximum $2S+1$
- 2.) Of these, that with largest L will be lowest
- 3.) Shells $< 1/2$ full (smallest J is lowest), Shells $> 1/2$ full (largest J is lowest)

*These rules apply only to the ground state, not to excited states.

Transitions and Selection Rules

- Not all transitions between atomic states that are energetically feasible are "*allowed*".
- Forbidden transitions are "*forbidden**" to first order, which means they may occur in practice, but with low probabilities.
- Selection rules for transitions depend on type of transition
 - Electric dipole (E1)
 - Electric quadrupole (E2)
 - Magnetic dipole (M1)
- Wavefunctions must have correct parity (Laporte's rule)
- Symmetry plays a role in selection rules
 - Vibronics, crystal field, other perturbing effects.

* *This nomenclature is historically embedded, although not entirely accurate.*



Multipole Selection Rules

$$\vec{P} = -e \sum_i \vec{r}_i$$

$$\vec{M} = -\frac{e\hbar}{2mc} \sum_i \vec{I}_i + 2\vec{s}_i$$

$$\vec{Q} = -\frac{1}{2} \sum_i (\vec{k} \cdot \vec{r}_i) \times \vec{r}_i$$

Electric dipole operator (E1)
(odd operator)

Magnetic dipole operator (M1)
(even operator)

Quadrupole operator (E2)
(even operator)

	S	L	J (No $0 \leftrightarrow 0$)	Parity
Electric Dipole	$\Delta S = 0$	$\Delta L = 0, \pm 1$	$\Delta J = 0, \pm 1$	opposite
Magnetic dipole	$\Delta S = 0$	$\Delta L = 0$	$\Delta J = 0, \pm 1$	same
Electric quadrupole	$\Delta S = 0$	$\Delta L = 0, \pm 1, \pm 2$	$\Delta J = 0, \pm 1, \pm 2$	opposite

A Brief History of Parity



Otto Laporte (1902-1971) empirically discovered the law of parity conservation in physics. He divided states of the iron spectrum into two classes, even and odd, and found that no radiative transitions occurred between like states: [O.Laporte, Z. Physik 23 135 \(1924\)](#).

Eugene Paul Wigner (1902-1995) explicitly formulated the law of parity conservation and showed that Laporte's rule is a consequence of the invariance of systems under spatial reflection. [E. P. Wigner, "Gruppentheorie und Ihre Anwendung auf die Quantenmechanik der Atomspektren"](#). Braunschweig:F. Vieweg und Sohn, 1931. English translation by J. J. Griffin. New York: Academic Press, 1959.

Wavefunctions are classified as even (+1 parity) or odd (-1 parity). By convention, the parity of a photon is given by the radiation field involved: ED (-1), MD (+1). For mathematical reasons, the parity of any system is the product of parities of the individual components. If the initial and final wavefunction have same parity (± 1):

ED: $\pm 1 = (-1)(\pm 1)$ Parity is **NOT** conserved. Transition is *forbidden!*

MD: $\pm 1 = (+1)(\pm 1)$ Parity **IS** conserved. Transition is *allowed!*

Laporte Rule: States with even parity can be connected by ED transitions only with states of odd parity, and odd states only with even ones.

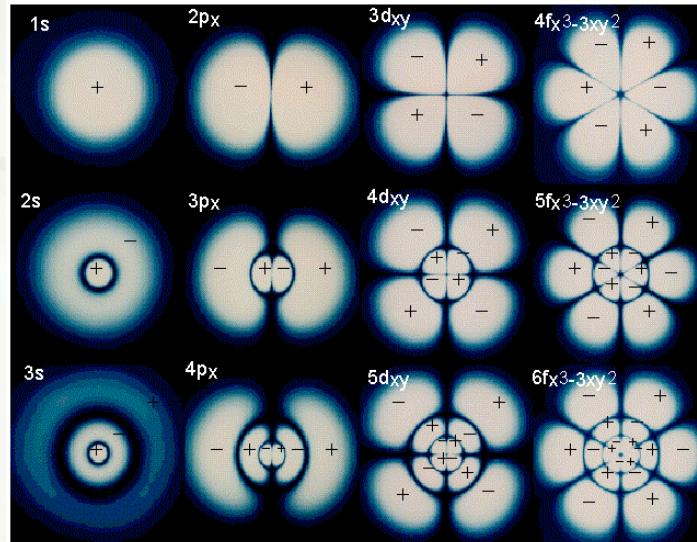
Parity Selection Rules

ED allowed
MD forbidden
EQ forbidden

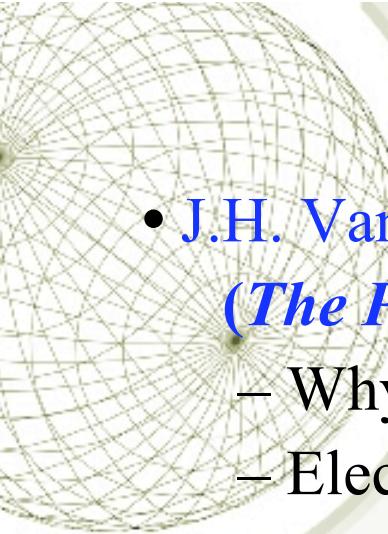
s → p
p → d
d → f
f → g
s → f
p → g

ED forbidden
MD allowed
EQ allowed

s → s
d → d
p → p
f → f
g → g



Orbital Angular momentum	ℓ	s	p	d	f	g
\mathcal{P} - odd # electrons	0	0	1	2	3	4
\mathcal{P} - even # electrons	$\mathcal{P} = (-1)^{\sum \ell_i}$	even	odd	even	odd	even
		odd	even	odd	even	odd

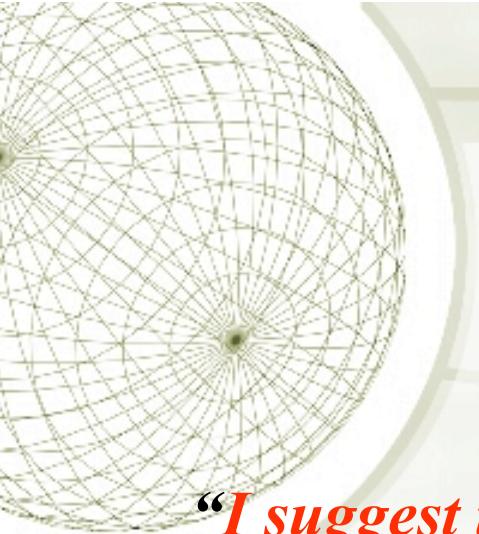


Historical Perspective I

- J.H. Van Vleck - J. Phys. Chem. 41, 67-80 (1937)
(The Puzzle of Rare-Earth Spectra in Solids)
 - Why are spectral lines in rare earths observable?
 - Electric dipole(E1), magnetic dipole(M1), quadrupole(E2)?
 - Concludes a combination is possible.
 - Suggests that crystal field makes mixed parity states (E1).
- L.J.F. Broer, et al., - Physica XI, 231- 250 (1945)
(On the Intensities and the multipole character in the spectra of the rare earth ions)
 - Considers all mechanisms.
 - Concludes quadrupole radiation is too weak.
 - Considers magnetic dipole , but as a special case only.
 - ED transitions dominate as suggested by Van Vleck!

Historical Perspective II

- G. Racah - Phys. Rev. 76, 1352 (1949)
(Theory of Complex Spectra IV)
 - Applies group theory to problems of complex spectra
 - Creates the tools required to make detailed spectroscopic calculations involving states of the 4f shell.
 - Revolutionizes the entire subject of rare earth spectroscopy.
- Subsequent developments
 - Racah's methods applied to crystal field theory.
 - Ideas of Racah applied to transition metal ions (**Griffiths**).
 - Practical calculations assisted by computer generated tables of angular momentum coupling coefficients.
- By 1962 the stage was set for the next major development:
The *Judd-Ofelt theory* of the intensities of RE transitions.



The Stage is Set

“I suggest that the coincidence of discovery was indicative that the time was right for the solution of the problem.”

Brian G. Wybourne

“The fascination of rare earths - then, now and in the future”

Journal of Alloys and Compounds 380, 96-100 (2004)

Judd and Ofelt Publish (1962)

PHYSICAL REVIEW

VOLUME 127, NUMBER 3

AUGUST 1, 1962

Optical Absorption Intensities of Rare-Earth Ions

B. R. JUDD

Lawrence Radiation Laboratory, University of California, Berkeley, California

(Received March 12, 1962)

Electric dipole transitions within the $4f$ shell of a rare-earth ion are permitted if the surroundings of the ion are such that its nucleus is not situated at a center of inversion. An expression is found for the oscillator strength of a transition between two states of the ground configuration $4f^N$, on the assumption that the levels of each excited configuration of the type $4f^N n'd$ or $4f^N n'g$ extend over an energy range small as compared to the energy of the configuration above the ground configuration. On summing over all transitions between the components of the ground level ψ_J and those of an excited level ψ'_J , both of $4f^N$, the oscillator strength P corresponding to the transition $\psi_J \rightarrow \psi'_J$, of frequency ν is found to be given by

$$P = \sum T_{\lambda} \nu (\psi_J \| U^{(\lambda)} \| \psi'_J)^2,$$

where $U^{(\lambda)}$ is a tensor operator of rank λ , and the sum runs over the three values 2, 4, and 6 of λ . Transitions that also involve changes in the vibrational modes of the complex comprising a rare-earth ion and its surroundings, provide a contribution to P of precisely similar form. It is shown that sets of parameters T_{λ} can be chosen to give a good fit with the experimental data on aqueous solutions of NdCl_3 and ErCl_3 . A calculation on the basis of a model, in which the first hydration layer of the rare-earth ion does not possess a center of symmetry, leads to parameters T_{λ} that are smaller than those observed for Nd^{3+} and Er^{3+} by factors of 2 and 8, respectively. Reasons for the discrepancies are discussed.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 37, NUMBER 3

AUGUST 1, 1962

Intensities of Crystal Spectra of Rare-Earth Ions*

G. S. OFELT

The Johns Hopkins University, Baltimore, Maryland

(Received February 26, 1962)

Magnetic and electric dipole transitions between levels of the $4f^z$ configuration perturbed by a static crystalline field are treated. The expression obtained for the pure-electronic electric-dipole transition probability involves matrix elements of an even-order unit tensor between the two $4f^z$ states involved in the transition. The contributions to the transition probability from interactions, via the crystalline field, with the nd^24f^{z-1} , $4f^{z-1}nd$, $4f^{z-1}ng$ configurations are shown to add linearly, in such a manner as to multiply each odd k crystal-field parameter A_{kz} by a constant. If "J mixing" in the $4f^z$ configuration is neglected ΔJ between the upper and lower $4f^z$ levels is restricted to six units or less. If "L mixing" is neglected then ΔL is also restricted to six units or less. Application is made to the fluorescence spectra of PrCl_3 and EuCl_3 . Many of the missing and weak transitions are explained.

National Aeronautics and
Space Administration

International School of Atomic and Molecular Spectroscopy
Erice, Italy (June 2005)



States of an Ion in the Crystal

The Crystal field, V , is considered as a first order perturbation that ‘*admixes*’ in higher energy opposite parity configurations:

$$\left. \begin{aligned} \langle \psi_a | &= \langle \varphi_a | + \sum_{\beta} \frac{\langle \varphi_a | V | \varphi_{\beta} \rangle}{E_a - E_{\beta}} \langle \varphi_{\beta} | \\ |\psi_b \rangle &= |\varphi_b \rangle + \sum_{\beta} \frac{\langle \varphi_{\beta} | V | \varphi_b \rangle}{E_b - E_{\beta}} |\varphi_{\beta} \rangle \end{aligned} \right\} \quad \text{Mixed Parity States}$$

$$\langle \psi_a | \vec{P} | \psi_b \rangle = \sum_{\beta} \left\{ \frac{\langle \varphi_a | V | \varphi_{\beta} \rangle \langle \varphi_{\beta} | \vec{P} | \varphi_b \rangle}{E_a - E_{\beta}} + \frac{\langle \varphi_a | \vec{P} | \varphi_{\beta} \rangle \langle \varphi_{\beta} | V | \varphi_b \rangle}{E_b - E_{\beta}} \right\}$$

φ_a and φ_b have the same parity ($4f^N$ states)

φ_{β} has opposite parity ($4f^{N-1}5d$ states)

V is the crystal field (treated as a perturbation)

\vec{P} is the electric dipole operator

Tensor Forms of Operators

Racah defined *irreducible tensors*, $C^{(k)}$, which transform as *spherical harmonics*, having the components:

$$C_q^{(k)} = \left(\frac{4\pi}{2k+1} \right)^{1/2} Y_{kq}$$

The position vector \mathbf{r} is a tensor of rank 1, defined as $\mathbf{r} = \mathbf{r} C^{(1)}$

	Dipole Operator	Crystal Field
Standard Form	$\vec{P} = -e \sum_i \vec{r}_i$	$V = \sum_i \sum_{kq} A_{kq} r_i^k Y_{kq}(\vartheta_i, \varphi_i)$
Tensor Form	$D_q^{(1)} = -e \sum_i r_i [C_q^{(1)}]_i$	$D_p^{(t)} = \sum_{tp} A_{tp} \sum_i r_i^t [C_p^{(t)}]_i$

Note: t is odd since only odd order terms contribute to parity mixing.

Even order terms are responsible for energy level splitting.

J-O Theory Assumptions 1&2

- 1.) The states of ϕ_β are completely degenerate in J.

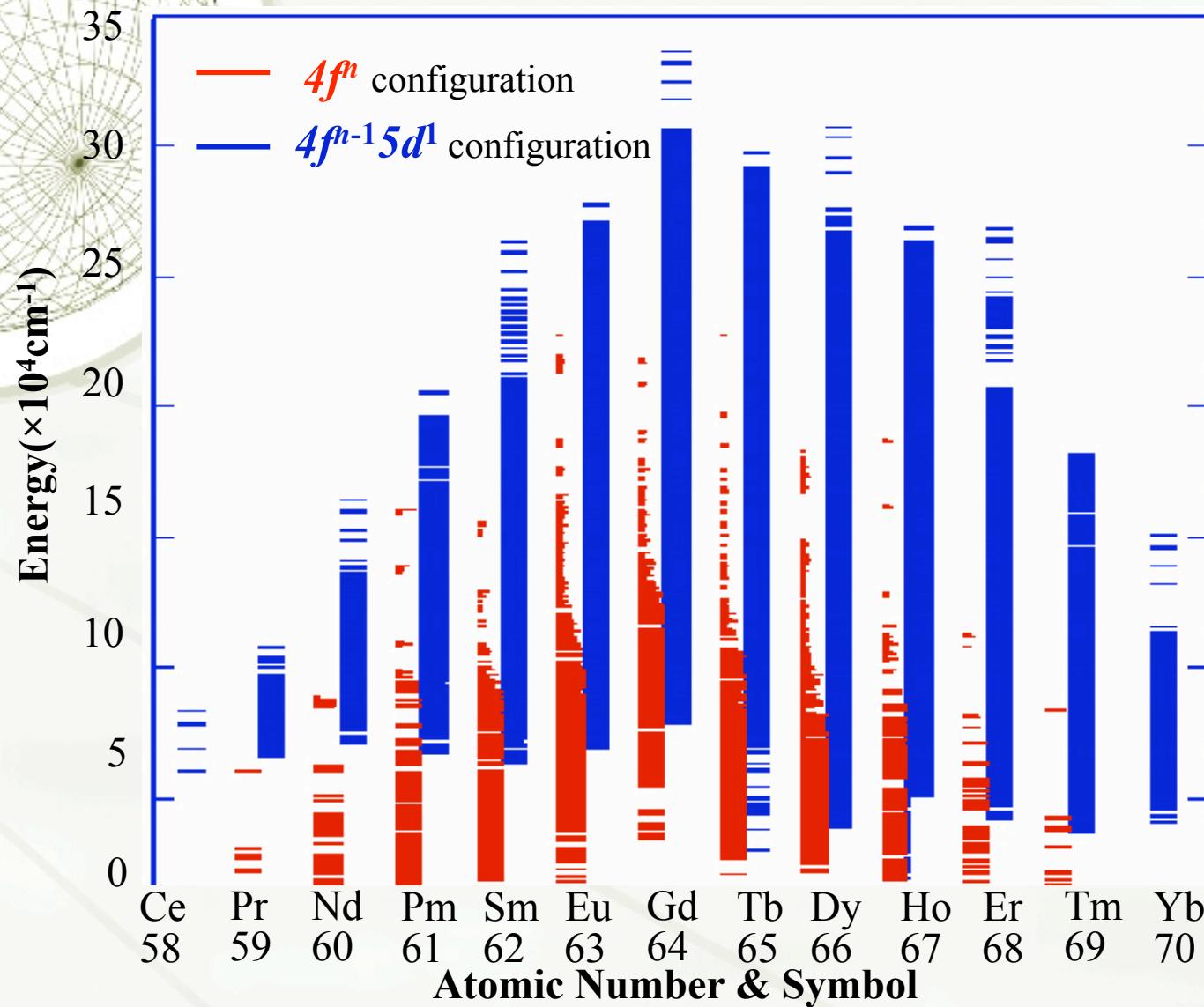
Assume an average energy for the excited configuration above the $4f^N$, that is, the $4f^{N-1}5d$.

- 2.) The energy denominators are equal ($E_a - E_\beta = E_b - E_\beta$)

Assume that the difference of average energies, $\Delta E(4f-5d)$, is the same as the difference between the average energy of the $4f^{N-1}5d$ and the energy of the initial and final states of the $4f^N$

These assumptions are only moderately met, but offer a great simplification. Otherwise, the many fold sum of perturbation expansions is not suitable for numerical applications.

$4f^N$ and $4f^{N-1}5d^1$ configurations



Lanthanides in YLF:
K. Ogasawara *et al.*,
J. Solid State Chem.
vol. 178, 412 (2005)

Advantages of the Assumptions

- I.) Energy denominators can be removed from the summations
- II.) *Closure* can be used (the excited configuration forms a complete *orthonormal* set of basis functions)

$$\sum_{\beta} |\varphi_{\beta}\rangle \langle \varphi_{\beta}| = 1$$

- III.) Angular parts of the electric dipole operator and crystal field

$$C_q^{(1)} = \langle \ell \| C^{(1)} \| \ell' \rangle U_q^{(1)} \quad \text{and} \quad C_p^{(t)} = \langle \ell \| C^{(t)} \| \ell' \rangle U_p^{(t)}$$

can be combined into an effective tensor operator

$$U_q^{(1)} U_p^{(t)} = \sum_{\lambda Q} (-1)^{1+t+\lambda+Q} (2\lambda+1) \begin{Bmatrix} t & 1 & \lambda \\ \ell & \ell & \ell' \end{Bmatrix} \begin{Bmatrix} t & 1 & \lambda \\ p & q & Q \end{Bmatrix} U_Q^{(\lambda)}$$

The 3j symbol () is related to the coupling probability for two angular momenta.
The 6j symbol { } is related to the coupling probability for three angular momenta.
The Wigner 3-j and 6-j symbols are related to Clebsch-Gordon coupling coefficients.

Reduced Matrix Elements

Nevertheless, combining the tensors for the electric dipole and crystal field terms in a combined tensor operator, $U_Q^{(\lambda)}$, can be simplified further by the *Wigner-Eckart Theorem*:

Geometry (transformations)	Physics (Dynamics)
$\langle f^N \psi JM U_Q^{(\lambda)} f^N \psi' J'M' \rangle = (-1)^{J-M} \begin{pmatrix} J & \lambda & J' \\ -M & Q & M' \end{pmatrix} \langle f^N \psi J \ U^{(\lambda)} \ f^N \psi' J' \rangle$	

The matrix elements on the right side have been tabulated:

“*Spectroscopic Coefficients of the p^N, d^N, and f^N Configurations*,”
C.W. Nielson and G.F. Koster, M.I.T Press, Cambridge, MA (1963).

The 3-j and 6-j symbols have also been tabulated:

“*The 3-j and 6-j symbols*,” M. Rotenberg, R. Bivens, N. Metropolis,
J.K. Wooten Jr., Technology Press, M.I.T, Cambridge, MA (1959).

“Full Judd-Ofelt Theory”

$$\langle \psi_a | \vec{P} | \psi_b \rangle = -e \sum_{tp} \sum_{\lambda Q} (-1)^{J-M-Q} (2\lambda+1) A_{tp} Y(t, \lambda) \begin{Bmatrix} 1 & \lambda & t \\ q & Q & p \end{Bmatrix} \begin{Bmatrix} J & \lambda & J' \\ -M & Q & M' \end{Bmatrix} \langle \varphi_a | U^{(\lambda)} | \varphi_b \rangle$$

Where, $Y(t, \lambda) = 2 \sum_{n\ell} \frac{\langle n\ell | r | n'\ell' \rangle \langle n'\ell' | r^t | n\ell \rangle}{E_a - E_{\beta}} \langle \ell | C^{(1)} | \ell' \rangle \langle \ell' | C^{(t)} | \ell \rangle \begin{Bmatrix} 1 & t & \lambda \\ \ell & \ell' & \ell \end{Bmatrix}$

This is the “**Full Solution**” of the Judd-Ofelt Theory. This form can be used to find electric dipole matrix elements between mixed parity states for individual Stark level to Stark level transitions.

Application of “Full Judd-Ofelt Theory”:

R.P. Leavitt and C.A. Morrison, “Crystal-field Analysis of triply Ionized lanthanum trifluoride. II. Intensity Calculations.” Journal Of Chemical Physics, **73**, 749-757 (1980).

J-O Theory Assumptions 3&4

Oscillator strength (f-number) for electric dipole transition:

$$f = \frac{8\pi^2 mc}{3\hbar\lambda(2J+1)e^2} n \left(\frac{n^2 + 2}{3n} \right)^2 \sum |\langle \alpha JM | \vec{P} | \alpha' J'M' \rangle|^2$$

L.J.F. Broer, et al., - Physica XI, 231- 250 (1945)

3.) Sum over Stark split J-levels

(Assumes all Stark levels equally populated)

$$\sum_{MM'} \begin{pmatrix} J & \lambda & J' \\ -M & Q & M' \end{pmatrix} \begin{pmatrix} J & \lambda' & J' \\ -M & Q' & M' \end{pmatrix} = \frac{1}{2\lambda+1} \delta_{\lambda\lambda'} \delta_{QQ'}$$

$$M = -J, -(J-1), \dots, 0, \dots, (J-1), J$$

4.) Sum over dipole orientations

(Assumes optically isotropic situation)

$$\sum_Q \begin{pmatrix} 1 & \lambda & t \\ q & Q & p \end{pmatrix} \begin{pmatrix} 1 & \lambda & t' \\ q & Q & p' \end{pmatrix} = \frac{1}{2t+1} \delta_{tt'} \delta_{pp'}$$

$$\begin{cases} Q = 0 (\pi\text{-polarized}, E \perp c) \\ Q = \pm 1 (\sigma\text{-polarized}, E \parallel c) \end{cases}$$

“Approximate Judd-Ofelt Theory”

$$f = \frac{8\pi^2 mc}{3h\bar{\lambda}(2J+1)} n \left(\frac{n^2 + 2}{3n} \right)^2 \sum_{\lambda=2,4,6} \sum_p \sum_{t=1,3,5} (2\lambda+1) \frac{|A_{tp}|^2}{(2t+1)} Y^2(t, \lambda) |\langle \varphi_a | U^{(\lambda)} | \varphi_b \rangle|^2$$

Defining Ω_λ as: $\Omega_\lambda = (2\lambda+1) \sum_p \sum_{t=1,3,5} \frac{|A_{tp}|^2}{(2t+1)} Y^2(t, \lambda)$ Judd-Ofelt parameters

$$f = \frac{8\pi^2 mc}{3h\bar{\lambda}(2J+1)} n \left(\frac{n^2 + 2}{3n} \right)^2 \sum_{\lambda=2,4,6} \Omega_\lambda |\langle \varphi_a | U^{(\lambda)} | \varphi_b \rangle|^2 \quad \text{Oscillator strength}$$

$S_{ED} = \sum_{\lambda=2,4,6} \Omega_\lambda |\langle \varphi_a | U^{(\lambda)} | \varphi_b \rangle|^2$ is called the Linestrength.

This is the “**Approximate Solution**” of the Judd-Ofelt theory. It can be used to find electric dipole matrix elements between mixed parity states for manifold to manifold transitions.

Judd-Ofelt Parameters

In principle, the Judd-Ofelt parameters can be calculated “*ab-initio*” if the crystal structure is known, and hence, A_{tp} :

$$\Omega_\lambda = (2\lambda + 1) \sum_p \sum_{t=1,3,5} \frac{|A_{tp}|^2}{(2t+1)} Y^2(t, \lambda)$$

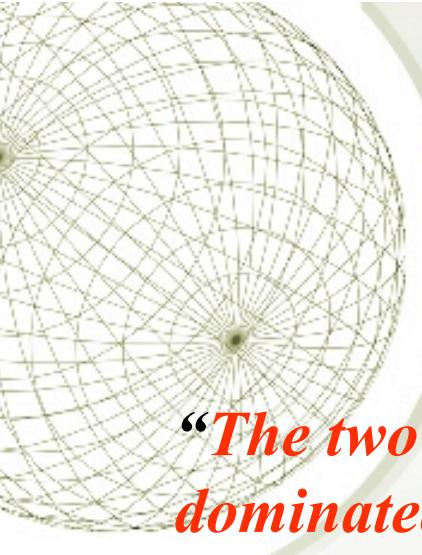
$$Y(t, \lambda) = 2 \sum_{nl} \frac{\langle n\ell | r | n'\ell' \rangle \langle n'\ell' | r^t | n\ell \rangle}{E_a - E_\beta} \langle \ell \| C^{(1)} \| \ell' \rangle \langle \ell' \| C^{(t)} \| \ell \rangle \begin{Bmatrix} 1 & t & \lambda \\ \ell & \ell' & \ell \end{Bmatrix}$$

$$\langle \ell \| C^{(1)} \| \ell' \rangle = (-1)^\ell \begin{pmatrix} \ell & 1 & \ell' \\ 0 & 0 & 0 \end{pmatrix} (2\ell + 1)^{1/2} (2\ell' + 1)^{1/2}$$

$$\langle \ell \| C^{(t)} \| \ell' \rangle = (-1)^{\ell'} \begin{pmatrix} \ell' & t & \ell \\ 0 & 0 & 0 \end{pmatrix} (2\ell' + 1)^{1/2} (2\ell + 1)^{1/2}$$

3-j and 6-j symbols can be calculated for $\ell = 3$ (4f) and $\ell' = 2$ (5d)

Radial integrals *between* configurations and crystal field components, A_{tp} , are difficult to calculate. Instead, *Judd-Ofelt parameters* are usually treated as *phenomenological* parameters, determined by fitting experimental *linestrength* data.



Intermission

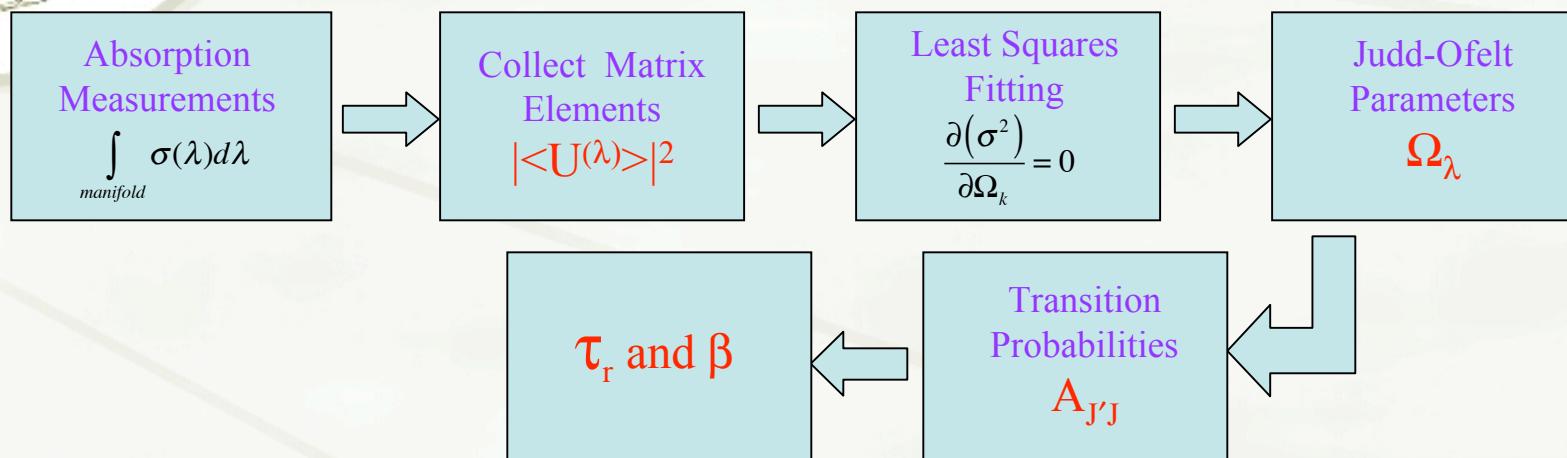
“The two papers of 1962 represent a paradigm that has dominated all further work on the intensities of rare earth transitions in solutions and solids up to the present time.”

Brian G. Wybourne

*“The fascination of rare earths - then, now and in the future”
Journal of Alloys and Compounds 380, 96-100 (2004).*

Part II: Practices

The Judd-Ofelt theory, in practice, is used to determine a set of phenomenological parameters, Ω_λ ($\lambda=2,4,6$), by fitting the experimental **absorption** or emission measurements, in a **least squares** difference sum, with the Judd-Ofelt expression.



The Judd-Ofelt parameters can then be used to calculate the transition probabilities, $A_{J'J}$, of all excited states. From these, the radiative lifetimes, τ_r , and branching ratios, β , are found.

Selection Rules Revisited

$$\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ \ell_1 & \ell_2 & \ell_3 \end{matrix} \right\} = 0$$

Unless:

$$j_i \geq 0$$

$$\ell_i \geq 0$$

$$|j_1 - j_2| \leq j_3 \leq j_1 + j_2$$

$$|\ell_2 - \ell_3| \leq j_1 \leq \ell_2 + \ell_3$$

$$|\ell_1 - \ell_3| \leq j_2 \leq \ell_1 + \ell_3$$

$$|\ell_1 - \ell_2| \leq j_3$$

$$\left\{ \begin{matrix} 1 & t & \lambda \\ \ell & \ell' & \ell \end{matrix} \right\}$$

$$\lambda = 2, 4, 6$$

$$t = 1, 3, 5, 7$$

$$\lambda \leq 1 + t$$

$$|\ell' - \ell| \leq 1$$

Only d or g
orbitals can
mix parity

$$\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{matrix} \right\} = 0$$

Unless:

$$j_i \geq 0$$

$$m_i \leq j_i$$

$$m_1 + m_2 + m_3 = 0$$

$$j_i, m_i \text{ (1, 1/2 integer)}$$

$$|j_1 - j_2| \leq j_3 \leq j_1 + j_2$$

$$\left(\begin{matrix} J & \lambda & J' \\ -M & Q & M' \end{matrix} \right)$$

$$|J' - J| \leq \lambda$$

$$\Delta J \leq 6$$

$$\Delta L \leq 6$$

$$\Delta S = 0$$

$$J = 0 : J' \rightarrow \text{even}$$

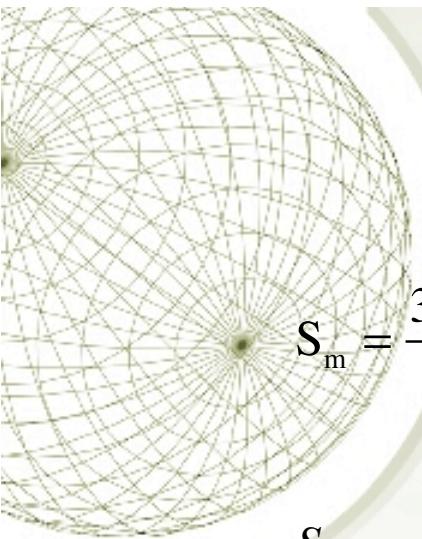
$$J' = 0 : J \rightarrow \text{even}$$

New Selection Rules From Judd-Ofelt Theory



	S	L	J (No $0 \leftrightarrow 0$)	Parity
Electric Dipole	$\Delta S = 0$	$\Delta L \leq 6$	$\Delta J \leq 6$ $\Delta J = 2, 4, 6$ (J or $J' = 0$)	opposite
Magnetic dipole	$\Delta S = 0$	$\Delta L = 0$	$\Delta J = 0, \pm 1$	same
Electric quadrupole	$\Delta S = 0$	$\Delta L = 0, \pm 1, \pm 2$	$\Delta J = 0, \pm 1, \pm 2$	opposite

Judd-Ofelt Analysis I



$$S_m = \frac{3ch(2J+1)}{8\pi^3 e^2 \bar{\lambda}} n \left(\frac{3}{n^2 + 2} \right)^2 \int_{\text{manifold}} \sigma(\lambda) d\lambda \xrightarrow{\text{Matrix Forms}} S_j^m \quad \begin{array}{c} \text{---} \\ \text{---} \end{array}$$

Components of
1 x N matrix

$$S_{ED} = \sum_{\lambda=2,4,6} \Omega_\lambda \left| \langle \varphi_a | U^{(\lambda)} | \varphi_b \rangle \right|^2 \xrightarrow{} S_j^t = \sum_{i=1}^3 M_{ij} \Omega_i \quad \begin{array}{c} \text{---} \\ \text{---} \end{array}$$

N = number of transitions

M_{ij} - components of $N \times 3$ matrix for square matrix elements of $U^{(2)}, U^{(4)}, U^{(6)}$

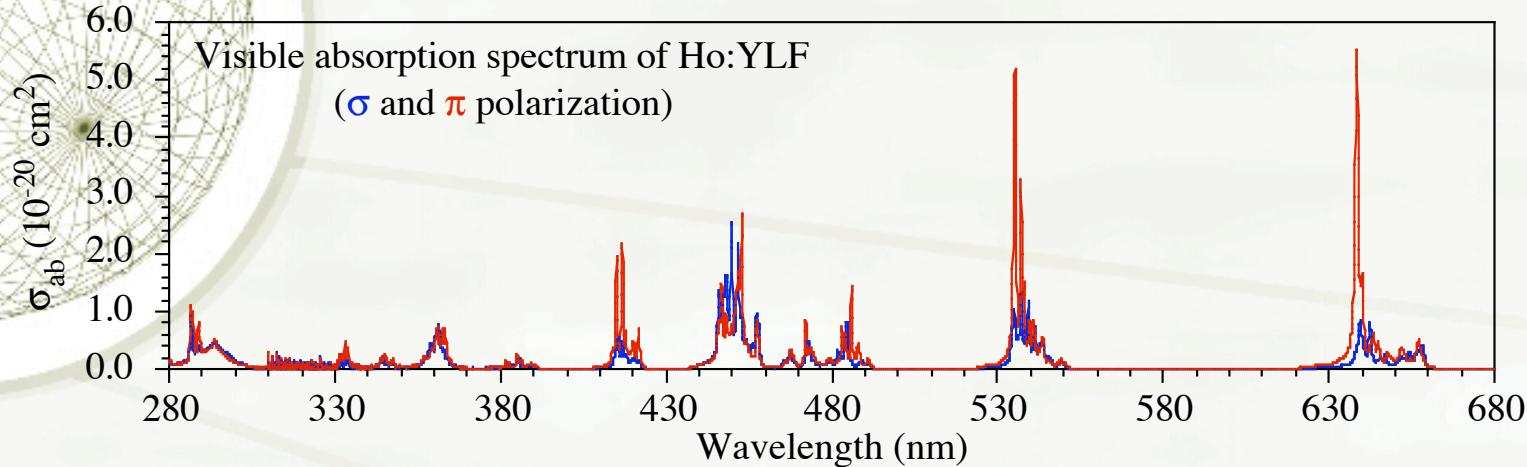
Ω_i - components of 1×3 matrix for Judd-Ofelt parameters $\Omega_2, \Omega_4, \Omega_6$

$$\sigma^2 = \sum_{j=1}^N \left(S_j^m - \sum_{i=1}^3 M_{ij} \Omega_i \right)^2 \quad \boxed{\text{LEAST SQUARES DIFFERENCE}}$$

$$\frac{\partial(\sigma^2)}{\partial \Omega_k} = -2 \sum_{j=1}^N M_{jk} \left(S_j^m - \sum_{i=1}^3 M_{ij} \Omega_i \right) = 0 \quad \boxed{\text{MINIMIZED}} \quad \rightarrow \Omega^{(0)} = (M^\dagger M)^{-1} M^\dagger S_m$$

Judd-Ofelt Parameters
1 x 3 Matrix

Judd-Ofelt Fit (Ho:YLF)



2776 J. Appl. Phys., Vol. 83, No. 5, 1 March 1998

Walsh, Barnes, and Di Bartolo

TABLE IV. Measured and calculated values for the line strength in Ho^{3+} YLF.

Transition (from 5I_8)	$ \langle U^{(2)} \rangle ^2$	$ \langle U^{(4)} \rangle ^2$	$ \langle U^{(6)} \rangle ^2$	$\bar{\lambda}$ (nm)	Line strength ^a Measured	Calculated
${}^3K_6 + {}^3F_4$	0.0026	0.1263	0.0073	334	0.2639	0.3097
${}^3L_9 + {}^5G_3$	0.0185	0.0052	0.1169	345	0.2920	0.3533
${}^3D_2 + {}^3H_6 + {}^5G_5$	0.2155	0.1969	0.1679	360	1.2803	1.0023
${}^3K_7 + {}^5G_4$	0.0058	0.0361	0.0697	385	0.2819	0.2243
5G_5	0.0000	0.5338	0.0002	418	1.1086	1.2396
${}^5F_1 + {}^5G_6$	1.5201	0.8410	0.1411	448	3.7492	3.7839
3K_8	0.0208	0.0334	0.1535	467	0.2282	0.3952
3F_2	0.0000	0.0000	0.2041	473	0.3488	0.3941
3F_3	0.0000	0.0000	0.3464	486	0.7587	0.6689
${}^5F_4 + {}^5S_2$	0.0000	0.2392	0.9339	540	2.5359	2.3587
5F_5	0.0000	0.4250	0.5687	645	2.1426	2.0848
5I_5	0.0000	0.0100	0.0936	886	0.1741	0.2039
5I_6	0.0084	0.0386	0.6921	1175	1.1067	1.4347

^aLine strength values are in units 10^{-20} cm^2 .

Judd-Ofelt Analysis II

With the Judd-Ofelt parameters, the ED transition probability for any excited state transition ($J' \rightarrow J$) can be calculated

$$A_{J'J} = \frac{64\pi^4 e^2}{3h(2J'+1)\bar{\lambda}^3} \left[n \left(\frac{n^2 + 2}{3} \right)^2 S_{ED} + n^2 S_{MD} \right]$$

Transition probability
(Einstein A coefficient)

$$\frac{1}{\tau_r} = \sum_J A_{J'J}$$

Radiative lifetime
(natural decay time)

$$\beta_{J'J} = \frac{A_{J'J}}{\sum_J A_{J'J}}$$

Branching ratio
(fraction of total photon flux)

MD transitions are normally *orders of magnitude* smaller than ED transitions. Since ED transitions for ions in solids occur as a result of a *perturbation*, some MD transitions will make significant contributions.

Magnetic Dipole Contributions

Magnetic dipole contributions can be easily calculated using an appropriate set of *intermediate coupled wavefunctions* for transitions obeying the selection rules ($\Delta S = 0, \Delta L = 0, \Delta J = 0, \pm 1$).

$$S_{MD} = \left(\frac{\hbar}{2mc} \right)^2 \left| \langle f^n [SL]J | \vec{L} + 2\vec{S} | f^n [S'L']J' \rangle \right|^2 \quad \text{MD Linestrength}$$

$$\langle f^n [SL]J | \vec{L} + 2\vec{S} | f^n [S'L']J' \rangle = \left\{ \left[(S+L+1)^2 - (J+1)^2 \left[\frac{(J+1)^2 - (L-S)^2}{4(J+1)} \right] \right] \right\}^{1/2} \quad \begin{array}{l} \text{LS-coupled} \\ \text{matrix elements} \\ \text{G.H. Shortley} \\ \text{Phys. Rev. 57, 225 (1940)} \end{array}$$

$$|f^n [SL]J\rangle = \sum_{SL} C(S,L) |f^n SLJ\rangle \quad \begin{array}{l} \text{Intermediate coupled wavefunctions} \\ \text{(linear combination of LS states)} \end{array}$$

$$\langle f^n [SL]J | \vec{L} + 2\vec{S} | f^n [S'L']J' \rangle = \sum_{SL, S'L'} C(S,L) C(S,L') \langle f^n SLJ | \vec{L} + 2\vec{S} | f^n S'L'J' \rangle$$

Intermediate coupled matrix elements



Judd-Ofelt Results (Ho:YLF)

J. Appl. Phys., Vol. 83, No. 5, 1 March 1998

Walsh, Barnes, and Di Bartolo 2777

TABLE VI. Calculated line strengths, branching ratios, and transition probabilities in Ho³⁺ YLF.

Transition	$ \langle U^{(2)} \rangle ^2$	$ \langle U^{(4)} \rangle ^2$	$ \langle U^{(6)} \rangle ^2$	$\bar{\lambda}(\text{nm})$	S_{ED}^{a}	$A_{\text{MD}}(\text{sec}^{-1})$	$A_{\text{ED}}(\text{sec}^{-1})$	β	$\tau_r(\mu\text{s})$
$^5F_4 \rightarrow ^5S_2$	0.0000	0.0159	0.0033	67656	0.0433		0.00	0.0000	
$^5F_4 \rightarrow ^5F_5$	0.1944	0.0923	0.0080	3173	0.4291	2.83	2.82	0.0017	
$^5F_4 \rightarrow ^5I_4$	0.0001	0.0234	0.2587	1887	0.5540		17.67	0.0052	
$^5F_4 \rightarrow ^5I_5$	0.0018	0.1314	0.4655	1327	1.2058		111.33	0.0330	
$^5F_4 \rightarrow ^5I_6$	0.0012	0.2580	0.1697	986	0.9279		207.79	0.0615	
$^5F_4 \rightarrow ^5I_7$	0.0000	0.1988	0.0324	738	0.5241		284.43	0.0843	
$^5F_4 \rightarrow ^5I_8$	0.0000	0.2402	0.7079	536	1.9246		2748.90	0.8143	295
$^5S_2 \rightarrow ^5F_5$	0.0000	0.0110	0.0036	3330	0.0325		0.33	0.0001	
$^5S_2 \rightarrow ^5I_4$	0.0013	0.0279	0.2795	1942	0.6058		31.92	0.0156	
$^5S_2 \rightarrow ^5I_5$	0.0000	0.0043	0.1062	1354	0.2151		33.67	0.0164	
$^5S_2 \rightarrow ^5I_6$	0.0000	0.0206	0.1541	1000	0.3454		133.16	0.0651	
$^5S_2 \rightarrow ^5I_7$	0.0000	0.0000	0.4096	746	0.7910		747.45	0.3652	
$^5S_2 \rightarrow ^5I_8$	0.0000	0.0000	0.2270	540	0.4383		1100.01	0.5375	489
$^5F_5 \rightarrow ^5I_4$	0.0001	0.0059	0.0040	4658	0.0154		0.03	0.000	
$^5F_5 \rightarrow ^5I_5$	0.0068	0.0271	0.1649	2282	0.2523		5.70	0.0032	
$^5F_5 \rightarrow ^5I_6$	0.0102	0.1213	0.4995	1430	0.8180		74.62	0.0415	
$^5F_5 \rightarrow ^5I_7$	0.0177	0.3298	0.4340	961	1.0800		324.00	0.1801	
$^5F_5 \rightarrow ^5I_8$	0.0000	0.4277	0.5686	645	1.3900		1394.42	0.7752	556
$^5I_4 \rightarrow ^5I_5$	0.0312	0.1237	0.9099	4472	2.0762	1.94	4.69	0.0787	
$^5I_4 \rightarrow ^5I_6$	0.0022	0.0281	0.6640	2064	1.3497		32.11	0.3813	
$^5I_4 \rightarrow ^5I_7$	0.0000	0.0033	0.1568	1211	0.3104		37.75	0.4482	
$^5I_4 \rightarrow ^5I_8$	0.0000	0.0000	0.0077	749	0.0149		7.72	0.0916	11 875
$^5I_5 \rightarrow ^5I_6$	0.0438	0.1705	0.5729	3831	1.5470	4.07	4.44	0.0674	
$^5I_5 \rightarrow ^5I_7$	0.0027	0.0226	0.8887	1662	1.7714		67.93	0.5381	
$^5I_5 \rightarrow ^5I_8$	0.0000	0.0099	0.0936	899	0.2037		49.79	0.3944	7922
$^5I_6 \rightarrow ^5I_7$	0.0319	0.1336	0.9308	2934	2.1403	8.11	12.78	0.1348	
$^5I_6 \rightarrow ^5I_8$	0.0083	0.0383	0.6918	1175	1.4333		134.03	0.8651	6455
$^5I_7 \rightarrow ^5I_8$	0.0249	0.1344	1.5217	1960	3.2760	15.91	55.92	1.000	13 921

^aLine strength values are in units 10^{-20} cm^2 .



Testing the J-O theory

Branching ratios can be measured directly from emission spectra. Use reciprocity of emission and absorption to indirectly “*measure*” the radiative lifetimes.

$$\sigma_{em}(\lambda) = \sigma_{ab}(\lambda) \frac{Z_\ell}{Z_u} \exp\left[\left(E_{ZL} - \frac{hc}{\lambda}\right)/kT\right]$$

D.E. McCumber
Phys. Rev. **136**, A954 (1964).

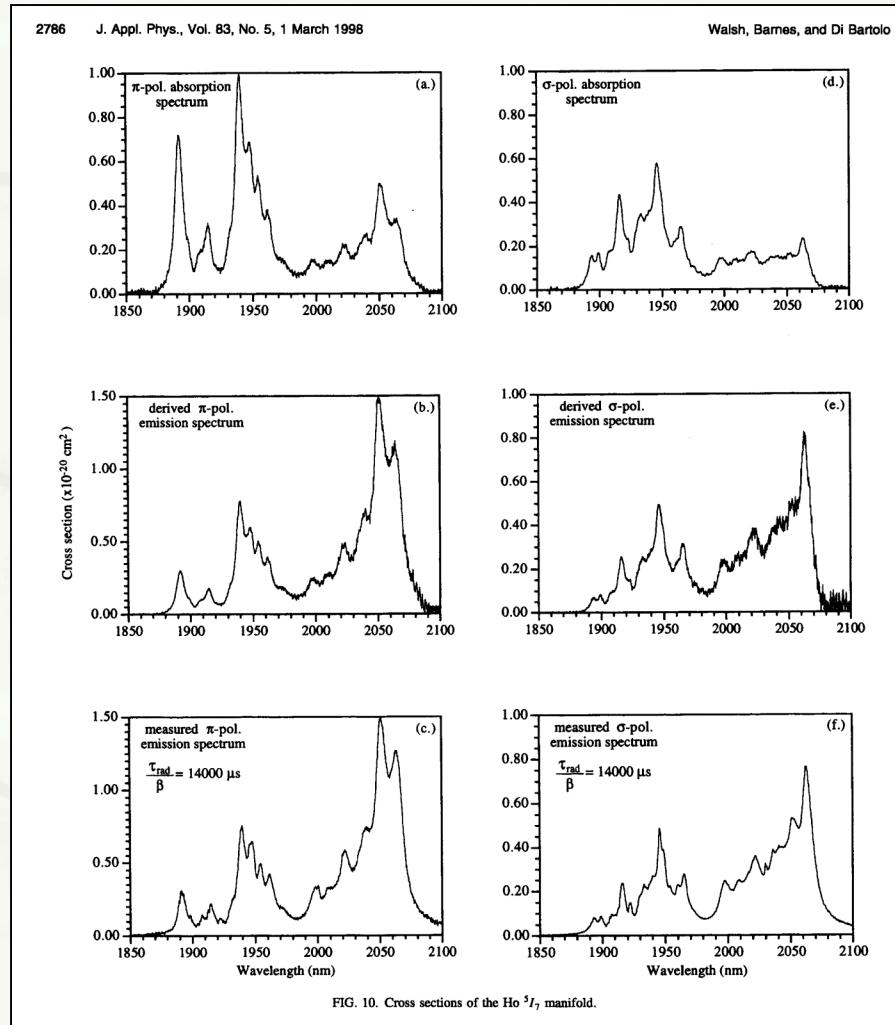
By comparing the measured emission cross section

$$\sigma(\lambda) = \frac{\lambda^5}{8\pi cn^2(\tau_r/\beta)} \frac{3I_\alpha(\lambda)}{\int [2I_\sigma(\lambda) + I_\pi(\lambda)]\lambda d\lambda}$$

P. Moulton
J. Opt. Soc Am. B **3**, 131 (1986).

with the emission cross section derived from absorption, the quantity (τ_r/β) can be determined and the radiative lifetime extracted for comparison with the Judd-Ofelt theory

Reciprocity of Ho:YLF (${}^5\text{I}_7 \leftrightarrow {}^5\text{I}_8$)



National Aeronautics and
Space Administration

International School of Atomic and Molecular Spectroscopy
Erice, Italy (June 2005)



Accuracy of J-O theory (Ho&Tm)

Results are somewhat better in Ho³⁺ than Tm³⁺. Overall, the accuracy of the Judd-Ofelt theory is quite good, despite the approximations used.

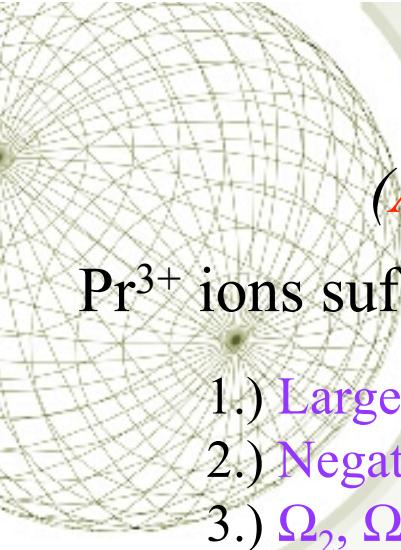
TABLE VIII. Measured and calculated radiative lifetimes in Tm:YLF and Ho:YLF.

Ion	Transition	β	$\tau_{\text{measured}} (\mu\text{s})$	$\tau_{\text{Judd-Ofelt}} (\mu\text{s})$	Percent difference
Tm	$^1G_4 \rightarrow ^3H_6$	0.5100	1158	837	26.8
Tm	$^3F_3 \rightarrow ^3H_6$	0.8730	715–873	650	10.0–25.5
Tm	$^3H_4 \rightarrow ^3H_6$	0.9032	2258	1521	32.6
Tm	$^3F_4 \rightarrow ^3H_6$	1.0000	15 000	9329	37.8
Ho	$^5S_2 \rightarrow ^5I_8$	0.6916	258–530	295–542	2.2–12.5
Ho	$^5F_5 \rightarrow ^5I_8$	0.8458	677	556	17.8
Ho	$^5I_5 \rightarrow ^5I_8$	0.3822	5790	7922	26.9
Ho	$^5I_6 \rightarrow ^5I_8$	0.8651	6592	6455	2.0
Ho	$^5I_7 \rightarrow ^5I_8$	1.0000	14 000	13 921	0.5

TABLE I. Measured and calculated branching ratios in Tm:YLF and Ho:YLF.

Ion	Transition	Wavelength range (nm)	β_{measured}	$\beta_{\text{Judd-Ofelt}}$	Percent difference
Tm	$^1G_4 \rightarrow ^3H_5$	753–803	0.4145	0.3681	11.2
Tm	$^1G_4 \rightarrow ^3F_4$	626–666	0.0771	0.0956	19.3
Tm	$^1G_4 \rightarrow ^3H_6$	463–486	0.5100	0.4257	16.5
Tm	$^3H_4 \rightarrow ^3H_5$	2170–2460	0.0271	0.0385	29.6
Tm	$^3H_4 \rightarrow ^3F_4$	1371–1508	0.0697	0.0953	26.8
Tm	$^3H_4 \rightarrow ^3H_6$	775–821	0.9032	0.8662	4.1
Ho	$^5S_2 \rightarrow ^5I_6$	1014–1032	0.0543	0.0633	14.2
Ho	$^5S_2 \rightarrow ^5I_7$	747–758	0.2540	0.2247	11.5
Ho	$^5S_2 \rightarrow ^5I_8$	539–550	0.6916	0.6759	2.3
Ho	$^5F_5 \rightarrow ^5I_7$	952–981	0.1541	0.1801	14.4
Ho	$^5F_5 \rightarrow ^5I_8$	638–659	0.8458	0.7752	8.3
Ho	$^5I_5 \rightarrow ^5I_7$	1618–1681	0.6174	0.5381	12.8
Ho	$^5I_5 \rightarrow ^5I_8$	882–915	0.3822	0.3944	3.1





Special Case I: Pr³⁺ ion

(*A failure of the standard Judd-Ofelt theory?*)

Pr³⁺ ions suffer from several problems in applying Judd-Ofelt theory

- 1.) Large deviations between calculations and experiment observations.
- 2.) Negative Ω_2 sometimes obtained, in opposition with definition.
- 3.) Ω_2 , Ω_4 , Ω_6 highly dependent on transitions used in fit.

These inconsistencies are usually explained by the small energy gap ($\sim 50,000 \text{ cm}^{-1}$) between the $4f^N$ and $4f^{N-1}5d$ configurations in Pr³⁺

Solutions:

1.) Modify the standard theory: $\Omega'_\lambda = \Omega_\lambda \left[1 + \left(\Delta E_{ij} - 2\bar{E}_{4f} \right) / \left(E_{5d}^0 - \bar{E}_{4f} \right) \right]$

E.E. Dunina, et al., Sov. Phys. Solid State **32**, 920 (1990).

2.) Remove ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ from the fit, or augment fit with fluorescence β 's

R.S. Quimby, et al., J. Appl. Phys. **75**, 613 (1994).

3.) Use normalized least squares fitting procedure: $\sigma^2 = \sum_{j=1}^N \left[\left(S_j^m - \sum_i M_{ij} \Omega_i \right) / \sigma_i \right]^2$

P. Goldner, et al., J. Appl. Phys. **79**, 7972 (1996).



Special Case II: Eu³⁺ ions

(*Beyond the standard Judd-Ofelt theory*)

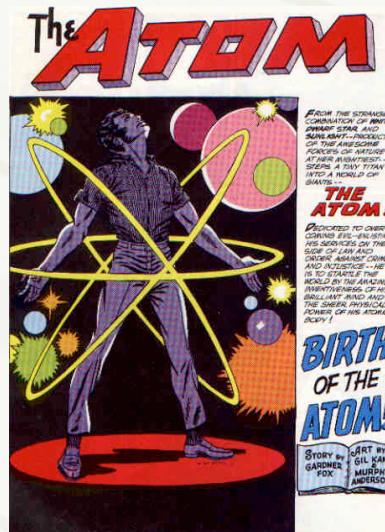
- The ED transitions $^7F_0 \leftrightarrow ^5D_{Jodd}$, $^7F_{Jodd} \leftrightarrow ^5D_0$ and $^7F_0 \leftrightarrow ^5D_0$ in Eu³⁺ are “*forbidden*” in standard JO-theory. They violate the selection rules:
 - $\Delta S = 0$
 - If $J = 0$ then J' is even
 - If $J' = 0$ then J is even
 - $0 \leftrightarrow 0$
- These transitions are primarily MD, but all three do occur as ED with low intensity in the spectra of some materials.
- This implies that the standard Judd-Ofelt theory is incomplete. These ‘*forbidden*’ transitions provide an ideal testing ground for extensions to the standard theory.
- What mechanism or mechanisms could be responsible? *Are they meaningful!*



Europium's Peculiar Properties

The Atom, Issue 2
August 1962
(DC Comics)

Coincident with the publications of Judd and Ofelt, who were both also interested in Europium's peculiar properties.



(Adventures of The Atom)





Extensions I

1) J-mixing:

The wavefunctions of the $J \neq 0$ state are mixed into the $J = 0$ state by *even* parity terms of the crystal field. Explains the radiative transition $^7F_3 \leftrightarrow ^5D_0$ in Eu^{3+} . J.E. Lowther, J. Phys. C: Solid State Phys. 7, 4393 (1974).

2) Electron correlation:

Electrostatic interaction between electrons is taken into account. Goes **beyond** the *single configuration approximation* and electron correlation within the 4f shell is incorporated by *configuration interactions*. Contributes to “*allowing*” the “*forbidden*” $0 \leftrightarrow 0$ transitions such as $^7F_0 \leftrightarrow ^5D_0$ in Eu^{3+} . K. Jankowski, J. Phys B: At. Mol. Phys. 14, 3345 (1981).

3) Dynamic coupling:

The mutual interaction of the lanthanide ion and the crystal environment are taken into account. Goes **beyond** the *static coupling model*. Explains *hypersensitive* transitions (transitions highly sensitive to changes in environment). M.F. Reid et al., J. Chem Phys. 79, 5735 (1983).



Extensions II

4) Wybourne-Downer mechanism:

Involves spin-orbit interaction among states of the excited configurations, leading to an admixing of spin states into the $4f^N$ configuration. This accounts for the observed spin “*forbidden*” transitions $\Delta S = 1$

B.G. Wybourne, J. Chem. Phys. **48**, 2596 (1968).

M.C. Downer et al., J. Chem. Phys **89**, 1787 (1988).

5) Relativistic contributions:

Relativistic treatment of $f \rightarrow f$ transitions in crystal fields. Reformulation of crystal field and operators in relativistic terms. Importance unknown.

L. Smentek, B.G. Wybourne, J. Phys. B: At. Mol. Opt. Phys. **33**, 3647 (2000).

L. Smentek, B.G. Wybourne, J. Phys. B: At. Mol. Opt. Phys. **34**, 625 (2001).

Review Articles

Early development:

R.D. Peacock, Structure and Bonding, vol. **22**, 83-122 (1975).

Later developments

L. Smentek, Physics Reports, vol. 297, 155-237 (1998).

Summary

Physical Mechanisms: (Not a complete list)

- Crystal field influence based on static model. *Second order* in the perturbation.
(This is the standard Judd-Ofelt theory).
- Crystal field influence based on static and dynamic model. *Second order*.
- Electron correlation based on static and dynamic model. *Third order*.
- Spin-orbit interaction. Intermediate coupling and *Third order* effects.
- Relativistic effects.

Remaining Problems:

- Estimating the relative importance of each mechanism is considerable.
(Many competing mechanisms producing various effects. Entangled situation)
- Ab-initio calculations still not entirely successful.
 - Theory of $f-f$ transitions not yet complete.
 - Calculation of Radial integrals and knowledge of odd crystal field parameters.
 - Vibronics (Vibrational lattice-ion coupling)
- Multitude of mechanisms and new parameters abandons simplicity.
 - Simple linear parametric fitting to observed spectra is lost.
 - Physically meaningful descriptions can be obscured.



What's next?

“It has been in a very real sense the first step in the journey to an understanding of the rare earths and their much heavier cousins, the actinides, but like many journeys into the unknown, the end is not in sight.”

Brian G. Wybourne

*“The fascination of rare earths - then, now and in the future”
Journal of Alloys and Compounds 380, 96-100 (2004).*

Judd and Ofelt Finally Meet

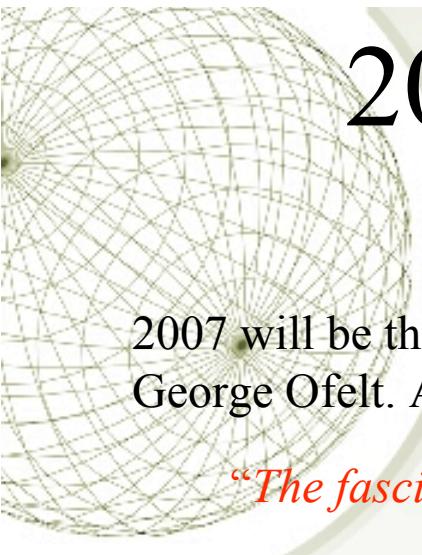
40 years after publications



B.R. Judd G.S. Ofelt B.G. Wybourne

Ladek Zdroj, Poland - June 22, 2003

***“4th International Workshop on Spectroscopy.
Structure and Synthesis of Rare Earth Systems.”***



2007 School of Atomic and Molecular Spectroscopy

2007 will be the 45th anniversary of the simultaneous publications of Brian Judd and George Ofelt. A special session is certainly worth considering in the next course.

“The fascination of the Rare Earths - 45th Anniversary of Judd-Ofelt theory”

Possible invited lecturers:

Brian R. Judd - The Johns Hopkins University, Baltimore, MD 21218, USA

E-mail: juddbr@eta.pha.edu

George S. Ofelt - 824 Saint Clement Road, Virginia Beach, VA 23455, USA

E-mail: gsofelt@pilot.infi.net

Lydia Smentek - Vanderbilt University, Box 1547, Station B. Nashville, TN 37235, USA

E-mail: sementek1@aol.com

G.W. Burdick - Andrews University, Berrien Springs, MI 49104, USA

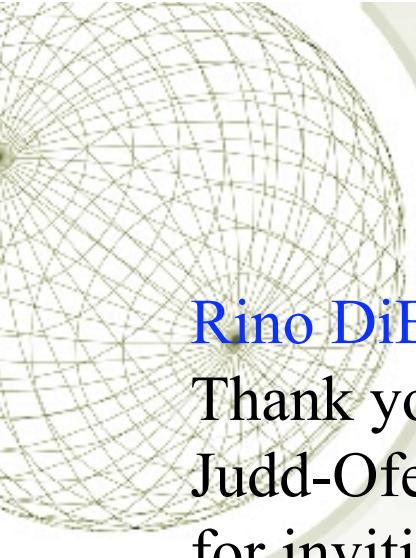
E-mail: gburdick@andrews.edu

Francois Auzel - UMR7574, CNRS, 92195 Meudon Cedex, France

E-mail: francois.auzel@wanadoo.fr

Sverker Edvardsson, Mid Sweden University, S-851 70, Sundsvall, Sweden

E-mail: Sverker.Edvardsson@mh.se



Acknowledgements

Rino DiBartolo-

Thank you for your years of wisdom and my first lecture on Judd-Ofelt theory in your office in ‘*old*’ Higgins Hall. Also for inviting me to Erice these last 10 years.

Norm Barnes-

Thank you for helping me see the *laser* side of life. The discussions we have had over the years remain with me.

Dedication

Brian G. Wybourne (1935-2003)

Professor Brian G Wybourne

Commemorative Meeting: Symmetry, Spectroscopy and Schur

Institute of Physics, Nicolaus Copernicus University, Torun, Poland

June 12-14, 2005.



A commemorative meeting in honor of Professor Brian G. Wybourne will be held in Torun, Poland from 12-th to 14-th June 2005. The aim is to celebrate Brian's academic life and his contributions to many aspects of physics and mathematics. This meeting will bring together friends, students, collaborators of Brian as well as people interested in the results and consequences of his research.

National Aeronautics and
Space Administration

International School of Atomic and Molecular Spectroscopy
Erice, Italy (June 2005)





National Aeronautics and
Space Administration

Erice, Italy (June 2005)





National Aeronautics and
Space Administration

International School of Atomic and Molecular Spectroscopy
Erice, Italy (June 2005)

