Luminescence Intensity Ratio of Lanthanides

modeling and simulation using Judd-Ofelt theory

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Global RE production and demand
Rare-Earth elements

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Abundance

Relative abundance of the chemical elements in Earth's upper continental crust.

Rock-forming elements
- Major
- Minor

Rare earth elements
- Ce

Major industrial metals
- Fe

Precious metals
- Au

Rarest metals, Te

Atomic number, Z
Abundance & Usage

Phosphors 5%

Million tonnes

Russia and former Soviet states

19

China

55

India

3.1

Malaysia

0.83

Australia

1.6

Brazil

0.05

US

13

Others

22

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Lanthanide Electronic Configurations

- **La** = \([\text{Xe}] \, 5d^1 \, 6s^2\)
- **Ce** = \([\text{La}] \, 4f^1\)
- **Lu** = \([\text{La}] \, 4f^{14}\)
- **La\(^{3+}\)** = \([\text{Xe}]\)
- **Ce\(^{3+}\)** = \([\text{Xe}] \, 4f^1\)
- **Lu\(^{3+}\)** = \([\text{Xe}] \, 4f^{14}\)
Trivalent Lanthanides

- Sharp emission & absorption lines
- Transition energies independent on host
- Long lifetimes of emitting levels
- High intrinsic quantum yields

A complete 4f\textsuperscript{n} energy level diagram for all trivalent lanthanide ions, P. Peijzel, A. Meijerink, R. Wegh, M.F. Reid, G.W. Burdick, doi: 10.1016/j.jssc.2004.07.046
**Ln^3+ Energy Levels**

- **Terms:** 7F, 5L, 5D
- **Sublevels:** 2S+1L(J)
- **Conf.:** [Xe]4f^6
- **Free ion energy levels:** ~20000 cm^-1, ~1000 cm^-1, ~100 cm^-1
- **Hamiltonian:** \( H = H_{\text{free}} + \sum B_q^k C_q^{(k)}(i) \)

**Diagonalization:**
- **Fermi-contact (CF):**
- **Kersting-Young (KY):**
Intensities
Judd-Ofelt theory – Prehistory

• RE discovery: 18th – 20th century

• 1937. – Van Vleck “The Puzzle of RE spectra in solids”

• 1940s - Racah algebra – powerful set of tools that made possible many complex spectroscopic calculations (e.g. free ion energy levels).


• 1962. – The solution to the “RE puzzle” simultaneously by Judd and Offelt.
"The two papers of 1962 represent the paradigm that has dominated all future work...up to the present time" – B. Wybourne

- Popularity rise
- Very complex QM theory
- Ability to predict oscillator strengths, branching ratios, lifetimes, quantum efficiencies by using only 3 parameters!
$\Omega \lambda$ Parametrization

Ab Initio
Absorption
Diffuse-Reflectance, Excitation
Emission

$\Omega$

Derived quantities

Application
Ab initio Parametrization

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

• $A_{tp}$ – parameters of the static CF expansion

• Judd-Ofelt Theory - The Golden (and the Only One) Theoretical Tool of f-Electron Spectroscopy, L. Smentek, 10.1002/9781118688304.ch10
• Ab-initio calculations of Judd-Ofelt intensity parameters for transitions between crystal-field levels, J.Wen et al., doi: 10.1016/j.jlumin.2013.10.055
Parametrization from Absorption


\[ f_{\text{exp}} = 4.319 \cdot 10^{-9} \frac{\text{mol} \cdot \text{cm}^2}{L} \int \varepsilon(\nu) \, d\nu \]

\[ f_{\text{abs}} = \frac{8\pi^2 m_e}{3h} \frac{\nu}{2J+1} \frac{x_{ED}^{\text{abs}}}{n} \sum_{\lambda=2,4,6} \Omega_{\lambda} \left| \langle t^N S L J \parallel U^\lambda \parallel t^N S' L' J' \rangle \right|^2 + \frac{\hbar \nu}{6m_e c^2} \frac{1}{2J+1} \left| \langle t^N S L J \parallel L + gS \parallel t^N S' L' J' \rangle \right|^2 \]

- RELIC software

- Problems: “This method has two drawbacks: the density of ions in the sample must be accurately measured, and absorption can only be performed on single crystals and glasses but not on crystalline powders”, Blasse, doi: 10.1063/1.457106
Determination of Judd-Ofelt intensity parameters from the excitation spectra for rare-earth doped luminescent materials, W. Luo et al., doi: 10.1039/b921581f

\[ S_{ex} = \frac{c}{\lambda \chi} \Gamma_{ex}, \quad S_{th} = \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle l^N S L J | U^\lambda | l^N S^\prime L^\prime J^\prime \rangle|^2 \Rightarrow \Omega_2: \Omega_4: \Omega_6 \]

For absolute values calibration is needed!

\[ \tau^{-1}_R = \sum A_j' \]

Problem: Assumption that the non-radiative lifetime of the used level is 0!

Parametrization from Emission: Gd\(^{3+}\)

- The spectroscopy of Gd\(^{3+}\) in yttriumoxychloride: Judd-Ofelt parameters from emission data, J. Sytsma, G.F. Imusch, G. Blasse, doi: 10.1063/1.457106

- Similar to excitation, but by using \(A_J\):

\[
A_{SLJ \rightarrow S'L'J'} = \frac{64\pi^4 \tilde{\nu}_{SLJ \rightarrow S'L'J'}^3}{3h(2J + 1)} \left( \chi_{ED} D_{ED} + \chi_{MD} D_{MD} \right)
\]

\[
\tau_R = 1/ \sum A_{SLJ \rightarrow S'L'J'}
\]
Parametrization from Emission: Eu$^{3+}$

  - MD – host independent – can be used for calibration.
  - $^{5D_0} \rightarrow ^{7F_1}$
- Judd-Ofelt parametrization from emission spectra: The case study of the Eu$^{3+}$ $^{5D_1}$ emitting level, A. Ćirić, S. Stojadinović, M.G. Brik, M.D. Dramićanin, doi: 10.1016/j.chemphys.2019.110513
  - New: $^{5D_1} \rightarrow ^{7F_0}$
Parametrization from Emission: Eu$^{3+}$

$$A_{SLJ \rightarrow S'L'J'} = \frac{64\pi^4 \tilde{v}_{SLJ \rightarrow S'L'J'}^3}{3h(2J + 1)} (\chi_{ED}D_{ED} + \chi_{MD}D_{MD})$$

- **Baricenter**
- **Local field correction**
- **Dipole strength**
- **Population**

$$I_{SLJ \rightarrow S'L'J'} = \int i_{SLJ \rightarrow S'L'J'}(\tilde{v}) d\tilde{v} = h\tilde{v}_{SLJ \rightarrow S'L'J'}N_{SLJ}A_{SLJ \rightarrow S'L'J'}$$

$$\frac{I_\lambda}{I_{MD}} = \frac{\tilde{v}_\lambda A_\lambda}{\tilde{v}_{MD}A_{MD}} = \left(\frac{\tilde{v}_\lambda}{\tilde{v}_{MD}}\right)^4 \frac{\chi_{ED}D_{ED}^\lambda}{\chi_{MD}D_{MD}}$$

$$D_{ED}^\lambda = e^2 \Omega_\lambda U_\lambda$$

$$\Omega_\lambda = \frac{D_{MD}}{e^2 U_\lambda} \left(\frac{\tilde{v}_{MD}}{\tilde{v}_\lambda}\right)^4 \frac{9n_{MD}^3}{n_\lambda(n_\lambda^2 + 2)^2} \frac{I_\lambda}{I_{MD}}$$

- **RME**
Judd-Ofelt Parameters:
\( \Omega_2 = 1.146519402034921E-19 \text{ cm}^2 \)
\( \Omega_4 = 2.9751146626870955E-20 \text{ cm}^2 \)
\( \Omega_6 = \text{NaN cm}^2 \)

== Derived Quantities ==
Radiative Transition Probabilities
\( A(5D_0\rightarrow7F_1) = 68.17799738106247 \text{ s}^{-1} \)
\( A(5D_0\rightarrow7F_2) = 490.78769879104266 \text{ s}^{-1} \)
\( A(5D_0\rightarrow7F_4) = 63.78022107243416 \text{ s}^{-1} \)
\( A(5D_0\rightarrow7F_6) = \text{NaN s}^{-1} \)

Experimental Branching Ratios and Theoretical Branching Ratios
\( \beta(5D_0\rightarrow7F_1) = 0.11452264749042913; 0.10947963767105741 \)
\( \beta(5D_0\rightarrow7F_2) = 0.7938046817755628; 0.7881026357629585 \)
\( \beta(5D_0\rightarrow7F_4) = 0.09167267073390804; 0.10241772656598405 \)
\( \beta(5D_0\rightarrow7F_6) = 0.0; 0.0 \)

Barycenters
\( \nu(5D_0\rightarrow7F_1) = 16858.597021525726 \text{ cm}^{-1} \)
\( \nu(5D_0\rightarrow7F_2) = 16232.81884281908 \text{ cm}^{-1} \)
\( \nu(5D_0\rightarrow7F_4) = 14425.398497300715 \text{ cm}^{-1} \)
\( \nu(5D_0\rightarrow7F_6) = \text{NaN cm}^{-1} \)

Total Radiative transition probability = \(622.7459172445393 \text{ s}^{-1} \)
Nonradiative transition probability = 0.0 \(\text{s}^{-1} \)

Lifetimes
Theoretical radiative lifetime = 0.0016530641897090424 \(\text{s} \)
Calculated radiative lifetime = 0.0016057913385039838 \(\text{s} \)
Nanomaterials

- Correction for nanocrystals $\ll \lambda$

- $n_{eff} = n(\lambda)_{np}x + (1 - x)n_{med}$
  - $x$ – filling factor – fraction of space occupied by the nanoparticles
  - $n(\lambda)_{np}$ - refractive index of nanoparticles as they would be in bulk
  - $n_{med}$ - refractive index of surrounding media (e.g. $n_{air} \approx 1$)
Luminescence thermometry

Steady State
- Luminescence Intensity Ratio (LIR)
- Bandshift
- Bandwidth

Time Resolved
- Lifetime & Risetime
- Phase-shift
Luminescence Intensity Ratio (LIR)

The most widely used method!

\[
LIR = \frac{I_H}{I_L} = \left| \frac{N_H}{N_L} = \frac{g_H}{g_L} e^{-\Delta E/kT} \right| = B e^{-\Delta E/kT}
\]
LIR & Ln

• Abundance of sharp emissions to chose from, from UV to IR!

• Many of them are intense!

• Many well thermalized levels!
Judd-Ofelt and LIR: Acknowledgments

- Can JO be applied to LIR thermometry?

- Upconverting Nanoparticles Working As Primary Thermometers in Different Media, S. Balabhadra, M.L. Debasu, C. Brites, R. Ferreira, L.D. Carlos, doi:10.1021/acs.jpcc.7b04827

- A Novel Multifunctional Upconversion Phosphor: Yb$^{3+}$/Er$^{3+}$ Codoped La$_2$S$_3$, Y. Yang et al., doi: 10.1111/jace.12822
Judd-Ofelt and LIR

\[ \text{LIR} = \frac{I_H}{I_L} = \left| I = \hbar \tilde{\nu} N_A, \quad \frac{N_H}{N_L} = \frac{g_H}{g_L} e^{-\frac{\Delta E}{kT}} \right| = \frac{\hbar \tilde{\nu}_H N_H A_H}{\hbar \tilde{\nu}_L N_L A_L} = \frac{g_H \hbar \tilde{\nu}_H A_H}{g_L \hbar \tilde{\nu}_L A_L} e^{-\frac{\Delta E}{kT}} \]

\[ A_{SLJ \rightarrow S'L'J'} = \frac{64\pi^4 \tilde{\nu}_{SLJ \rightarrow S'L'J'}^3}{3h(2J + 1)} (\chi_{ED} D_{ED} + \chi_{MD} D_{MD}) \]

\[ B = \frac{g_H \hbar \tilde{\nu}_H A_H}{g_L \hbar \tilde{\nu}_L A_L} \quad \rightarrow \quad B = \left( \frac{\tilde{\nu}_H}{\tilde{\nu}_L} \right)^4 \frac{\chi_{ED}^H D_{ED}^H}{\chi_{ED}^L D_{ED}^L} + \frac{\chi_{MD}^H D_{MD}^H}{\chi_{MD}^L D_{MD}^L} \]

\[ D_{ED}^\lambda = e^2 \sum_{\lambda} \Omega_\lambda U^\lambda \]

\( \tilde{\nu} \) and \( D_{MD} \) are tabulated and host independent.

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Figures of Merit via $\Omega_{\lambda}$

$$S(T) = \frac{\Delta E}{kT^2} B \exp \left( -\frac{\Delta E}{kT} \right) = \frac{\Delta E}{kT^2} \left( \frac{\bar{\nu}_H}{\bar{\nu}_L} \right)^4 \frac{\chi^H_{ED}D^H_{ED} + \chi^H_{MD}D^H_{MD}}{\chi^L_{ED}D^L_{ED} + \chi^L_{MD}D^L_{MD}} \exp \left( -\frac{\Delta E}{kT} \right)$$

$$S_{\text{max}} = \frac{4k}{e^2\Delta E} \left( \frac{\bar{\nu}_H}{\bar{\nu}_L} \right)^4 \frac{\chi^H_{ED}D^H_{ED} + \chi^H_{MD}D^H_{MD}}{\chi^L_{ED}D^L_{ED} + \chi^L_{MD}D^L_{MD}}$$

$$\Delta T = \frac{kT^2 \sigma(\chi^L_{ED}D^L_{ED} + \chi^L_{MD}D^L_{MD})}{\Delta E(\chi^H_{ED}D^H_{ED} + \chi^H_{MD}D^H_{MD}) \exp(-\Delta E/kT)}$$

An Extension of the Judd-Ofelt theory to the field of lanthanide thermometry, A. Ćirić, S. Stojadinović, M.D. Dramićanin, doi: 10.1016/j.jlumin.2019.116749
Significance

• $\Omega$ is easier to obtain (single spectrum @ RT)
• Large number of $\Omega$ in literature

<table>
<thead>
<tr>
<th></th>
<th>JO-LIR</th>
<th>Experimental</th>
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<td>Setup Price</td>
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<tr>
<td>Speed</td>
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<td>Low</td>
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<tr>
<td>Knowledge Level</td>
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<tr>
<td>Accuracy</td>
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<td>High</td>
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<tr>
<td>Transition</td>
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<td>Pr^{3+} [57,58]</td>
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<tr>
<td>3P_1→4H_5</td>
<td>H</td>
<td>525</td>
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<tr>
<td>3P_2→4H_5</td>
<td>L</td>
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<td>Nd^{3+} [46,47]</td>
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<tr>
<td>4F_{7/2}→1I_{8/2}</td>
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<td>4F_{5/2}→1I_{8/2}</td>
<td>H or L</td>
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<td>4F_{3/2}→1I_{8/2}</td>
<td>L</td>
<td>900</td>
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<td>4F_{7/2}→1I_{11/2}</td>
<td>L</td>
<td>1075</td>
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<tr>
<td>Sm^{3+} [48]</td>
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<td>H</td>
<td>530</td>
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<tr>
<td>4G_{5/2}→4H_5</td>
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<td>560</td>
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<td>4F_{5/2}→4H_5</td>
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<td>587</td>
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<tr>
<td>4F_{5/2}→4H_4</td>
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<td>Eu^{3+} a</td>
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<td>D_{5/2}→F_{4}</td>
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<tr>
<td>D_{3/2}→F_{2}</td>
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<td>Ho^{3+} b</td>
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<td>5P_{3/2}→4I_{6}</td>
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<td>530</td>
</tr>
<tr>
<td>5S_{2/2}→4I_{6}</td>
<td>H or L</td>
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<td>5S_{1/2}→4I_{6}</td>
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<td>Er^{3+} a</td>
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<td>4H_{11/2}→4I_{15/2}</td>
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<tr>
<td>4S_{2/2}→4I_{15/2}</td>
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<td>Tm^{3+} a</td>
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<td>4F_{3/2}→4H_{4}</td>
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<td>4F_{3/2}→4H_{4}</td>
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<td>695</td>
</tr>
<tr>
<td>4H_{4}→4H_{6}</td>
<td>L</td>
<td>800</td>
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</tbody>
</table>
Magnetic dipole and electric quadrupole transitions in the trivalent lanthanide series: Calculated emission rates and oscillator strengths, doi: 10.1103/PhysRevB.86.125102
Testing on $Y_2O_3$:Eu$^{3+}$

- LIR of $^5D_1 \rightarrow ^7F_{1,2}$ and $^5D_0 \rightarrow ^7F_{1,2,4}$
- \[ LIR = C \frac{\alpha A_R + M \rho g_2 n^p}{\beta A_R + M \rho g_1 (1+n)^p} \]
Dual-excited single band LIR

- A. Souza, ..., R. Ferreira, L.D. Carlos, O.L. Malta, High-sensitive Eu$^{3+}$ ratiometric thermometers based on excited state absorption with predictable calibration, doi: 10.1039/C6NR00158K
- At 0 K all optical centers are at ground.
- $T > 0 K$: thermal population.
- Excitation from Ex1 and Ex2.
- Single emission is monitored.
- LIR of two emissions by excitations from Ex1 and Ex2.
- Dual-excited – much larger $\Delta E \rightarrow$ larger $S_r$
How? Optical centers redistribution

- $\text{Eu}^{3+}$ ion example.
- $^7\text{F}_j$ are thermally excited.
- Number of optical centers follows Boltzmann distribution.
- Excitation can be executed on higher levels of the ground multiplet.

\[
X_A(T) = \frac{N_A}{N} = \frac{g_A \exp(-E_A/kT)}{\sum_i g_i \exp(-E_i/kT)}
\]
How? Excitations and emission

- Excitations from $^7F_1$ and $^7F_2$
- Monitor emission to $^7F_4$
Judd-Ofelt model

\[ A_\lambda = \frac{64\pi^4 \tilde{v}_\lambda^3}{3\hbar} \chi_{ED} D_{ED}^\lambda \]

\[ A_{MD} = \frac{64\pi^4 \tilde{v}_{MD}^3}{3\hbar} \chi_{MD} D_{MD} \]

\[ I_{SLJ\rightarrow S'L'J'} = \hbar \tilde{\gamma}_{SLJ\rightarrow S'L'J'} N_{SLJ} A_{SLJ\rightarrow S'L'J'} \]

\[ LIR = \frac{I_1}{I_2} = B \exp \left( \frac{\Delta E}{kT} \right) \]

\[ B_{JO} = \left( \frac{\nu_1}{\nu_2} \right)^4 \frac{n_1^3 \cdot 9.6 \cdot 10^{-42} \text{ esu}^2 \text{ cm}^2}{e^2 \Omega_2 U^2 \cdot n_2(n_2^2 + 2)^2 / 9} \]

- Prediction of the B parameter.
- \( D_{ED}^\lambda = e^2 \Omega_\lambda U^\lambda \)
- \( D_{MD} = 9.6 \cdot 10^{-42} \text{ esu}^2 \text{ cm}^2 \)
- \( \Delta E \) can be obtained from spectrum.
Corrections

- Excitations are performed in some Stark sublevels.

- Correction factors are needed:
  \[ \varphi_1 = \frac{I_{1,1}}{\sum_{j=1}^{3} I_{1,j}}, \quad \varphi_2 = \frac{\sum_{j=4}^{6} I_{2,j}}{\sum_{j=4}^{8} I_{2,j}} \]

- \( LIR_{J0} = \frac{\varphi_1}{\varphi_2} B_{J0} \exp \left( \frac{\Delta E_{sp}}{kT} \right) \)

TEST ON Lu₂O₃:Eu³⁺

- \( B = 0.04773 \)
- \( \varphi_1 = 0.304, \varphi_2 = 0.873 \)
- **JOES**: \( \Omega_2 = 9.605 \cdot 10^{-20} \text{cm}^2, \Omega_4 = 2.928 \cdot 10^{-20} \text{cm}^2 \)
  
  \[ \text{https://omasgroup.org/joes\textendash software/} \]
- \( B_{JO} = 0.137 \)
- \( B_{JO} \frac{\varphi_1}{\varphi_2} = 0.04770 \)
- **99.9%** match between \( B \) and \( B_{JO} \frac{\varphi_1}{\varphi_2} \)
CONCLUSIONS

• Temperature invariant B parameter for LIR can be predicted
  • Prediction of Sensitivities!

• Needed: 1 RT spectrum or Ω from literature!

• Test showed high matching between experimental and theoretical B parameters.

• Applicability: tool for initial selection of phosphors!

• Applies to other Lanthanides.
Thank You!

Software:
https://omasgroup.org/jolir-interactive-software/
https://omasgroup.org/joes-software/

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