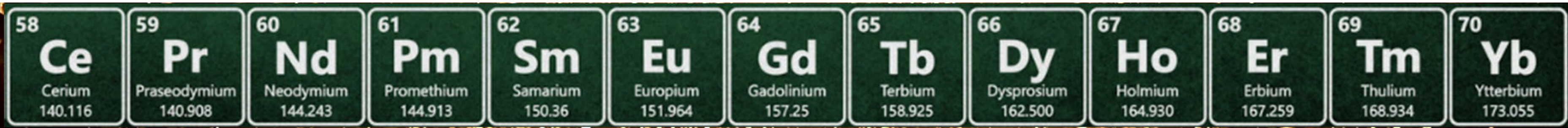

Luminescence Intensity Ratio of Lanthanides

modeling and simulation using Judd-Ofelt theory

Aleksandar Ćirić

University of Belgrade

OMAS Optical Materials and Spectroscopy Group

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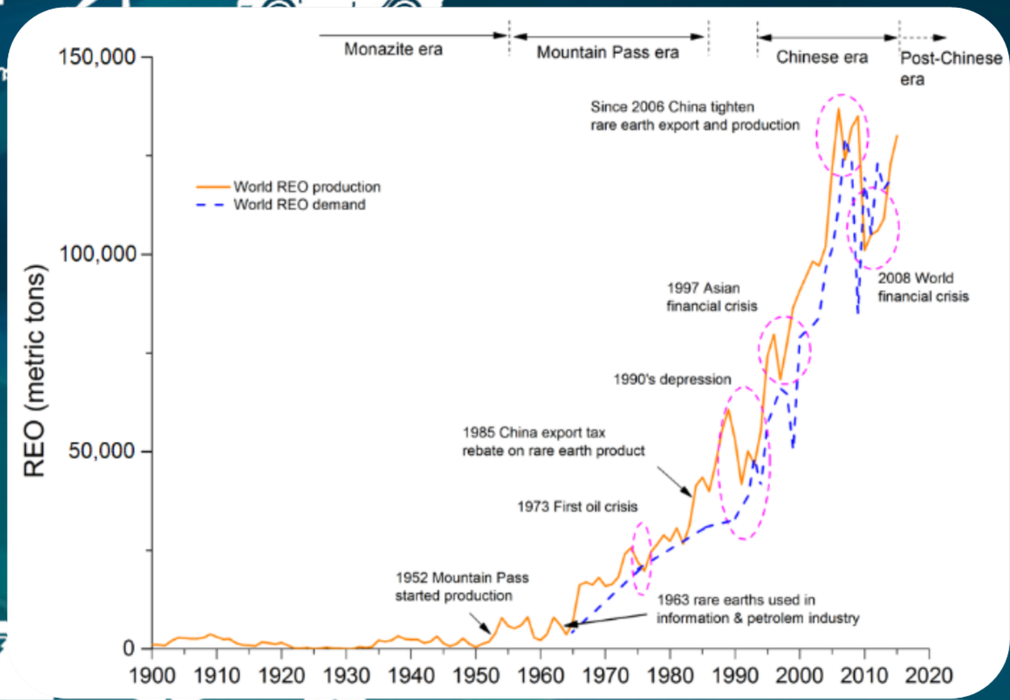
Global RE production and demand



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Rare-Earth elements

Group → / Period ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La *	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac **	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			**	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

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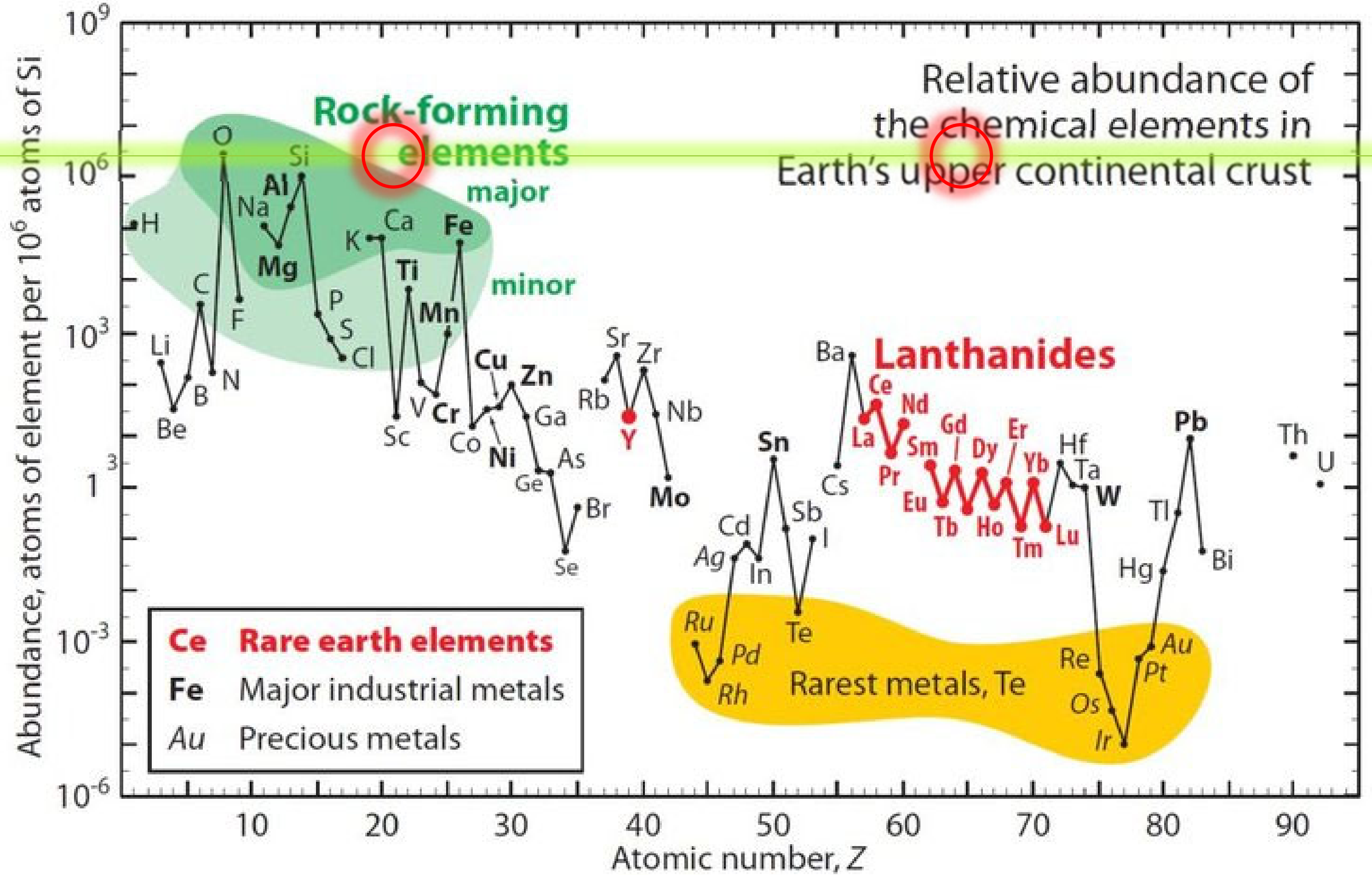
Abundance



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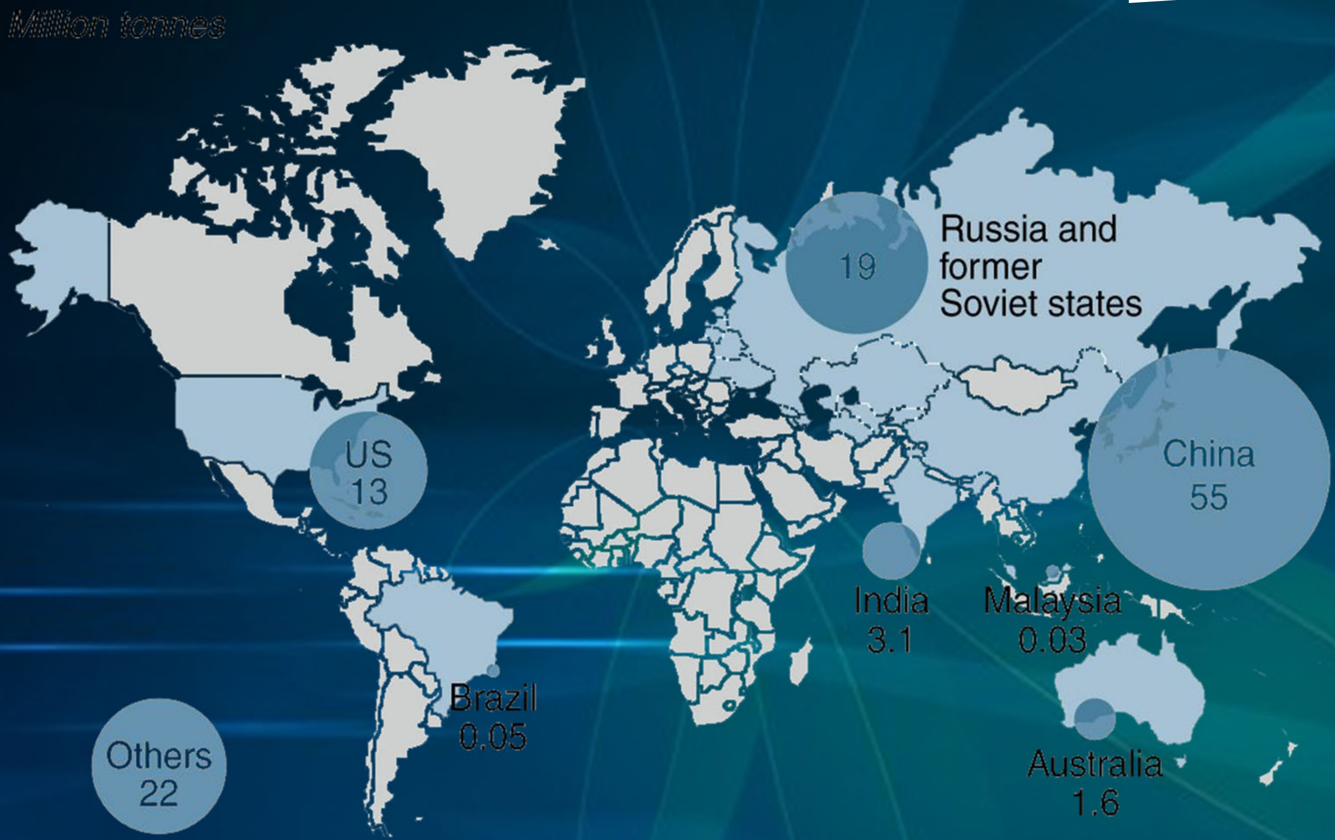
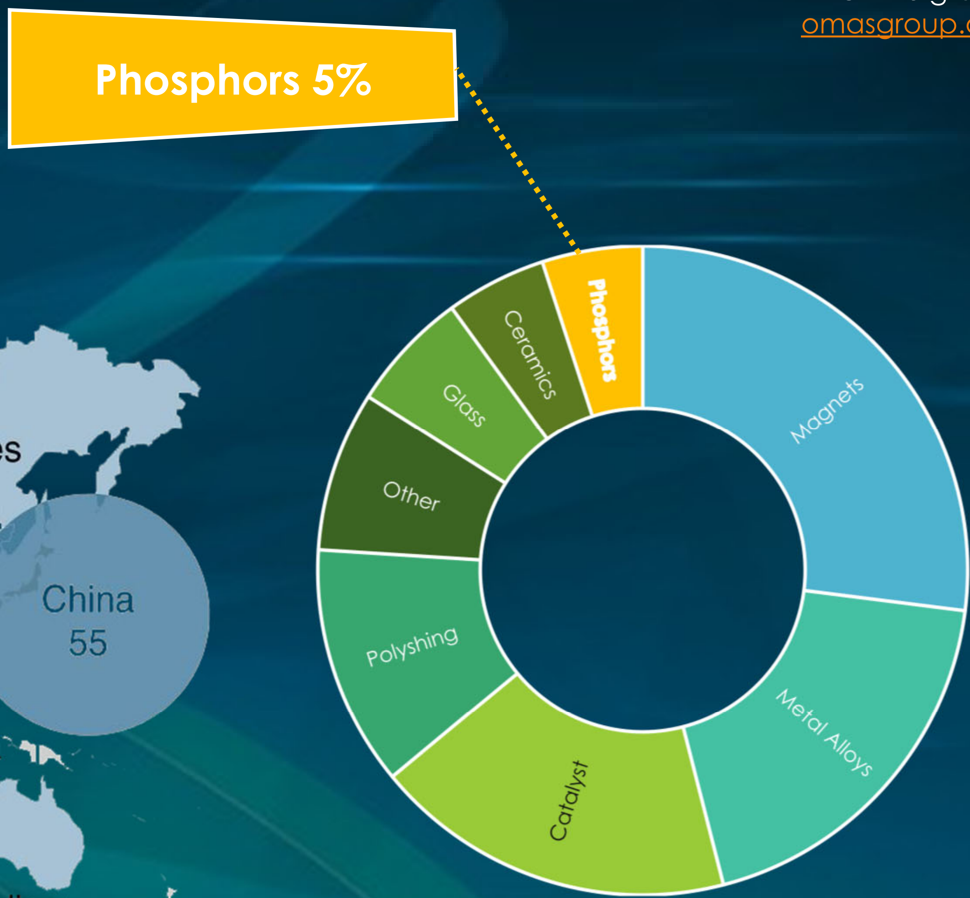
Abudance & Usage





Lanthanide Electronic Configurations

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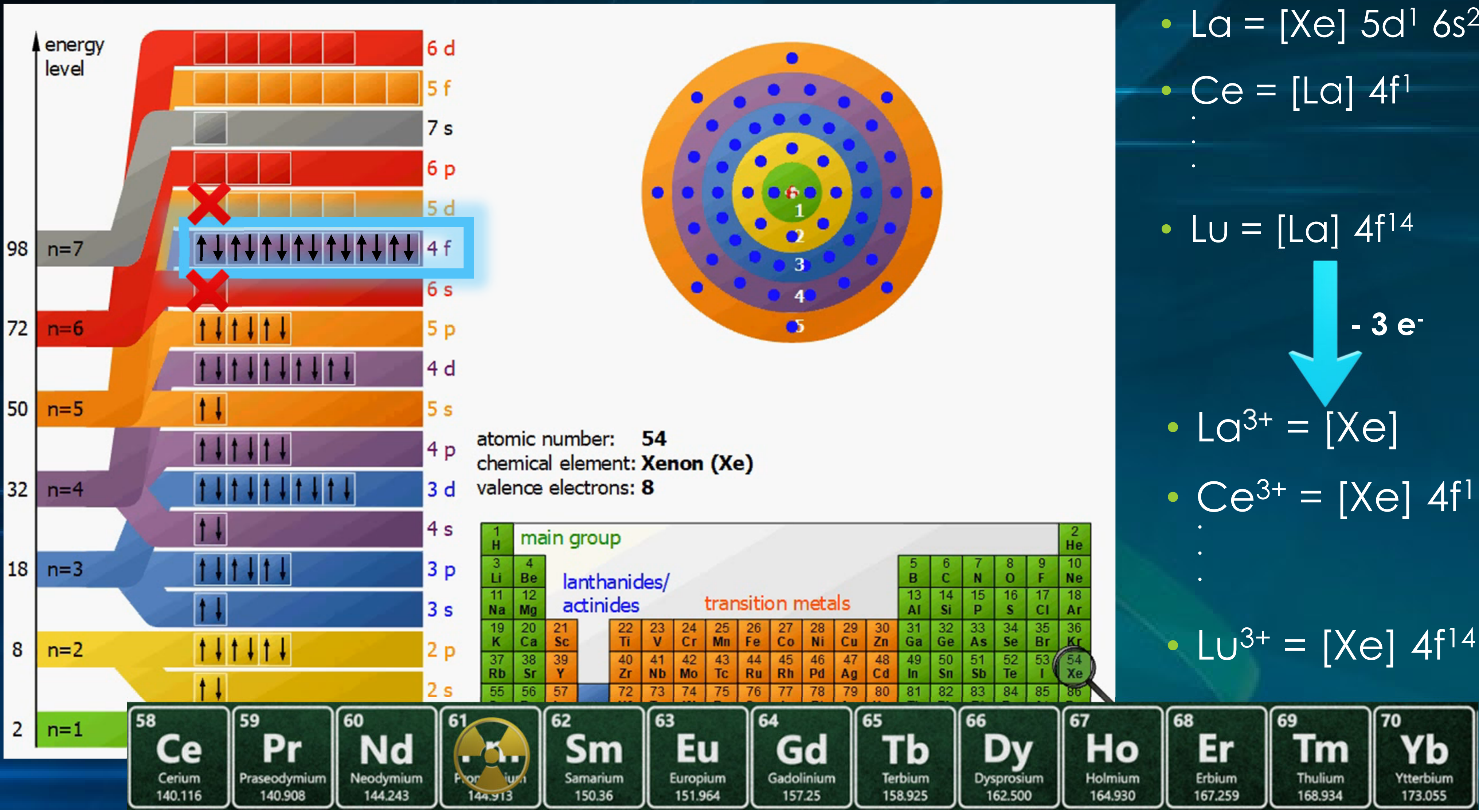


- La = [Xe] $5d^1$ $6s^2$
- Ce = [La] $4f^1$

  ⋮
- Lu = [La] $4f^{14}$

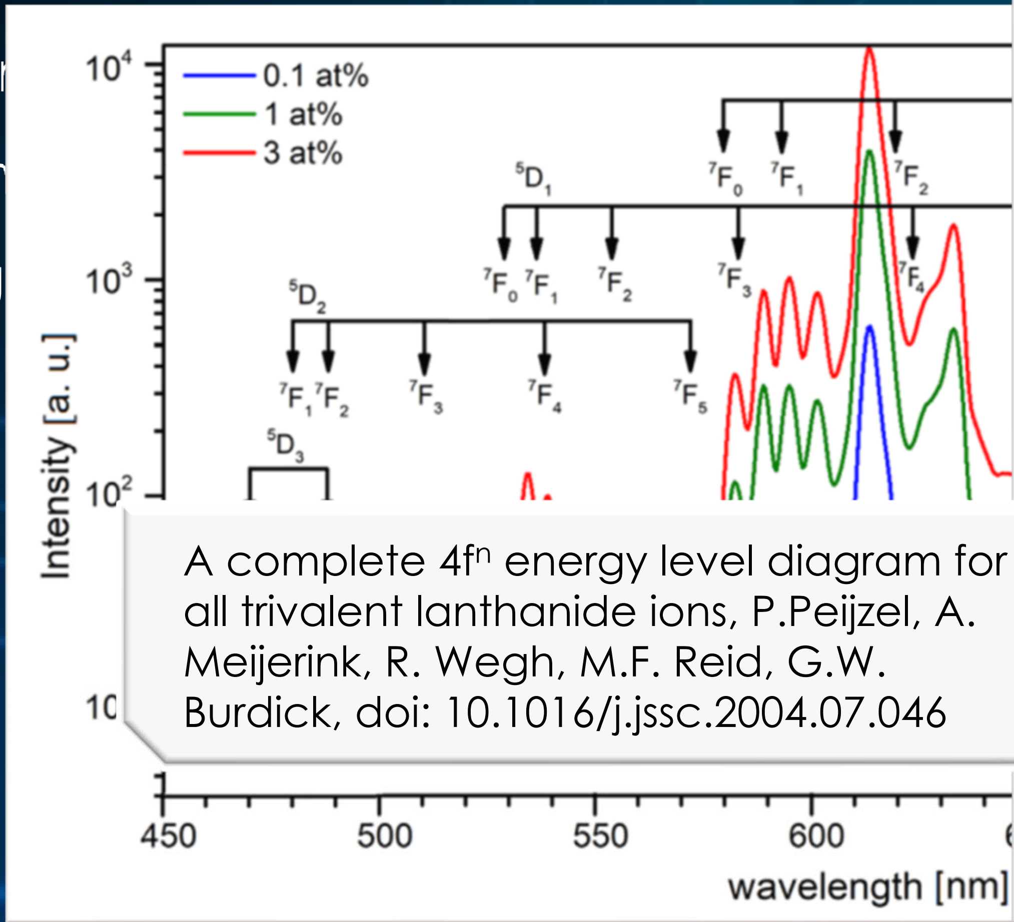
- 3 e^-

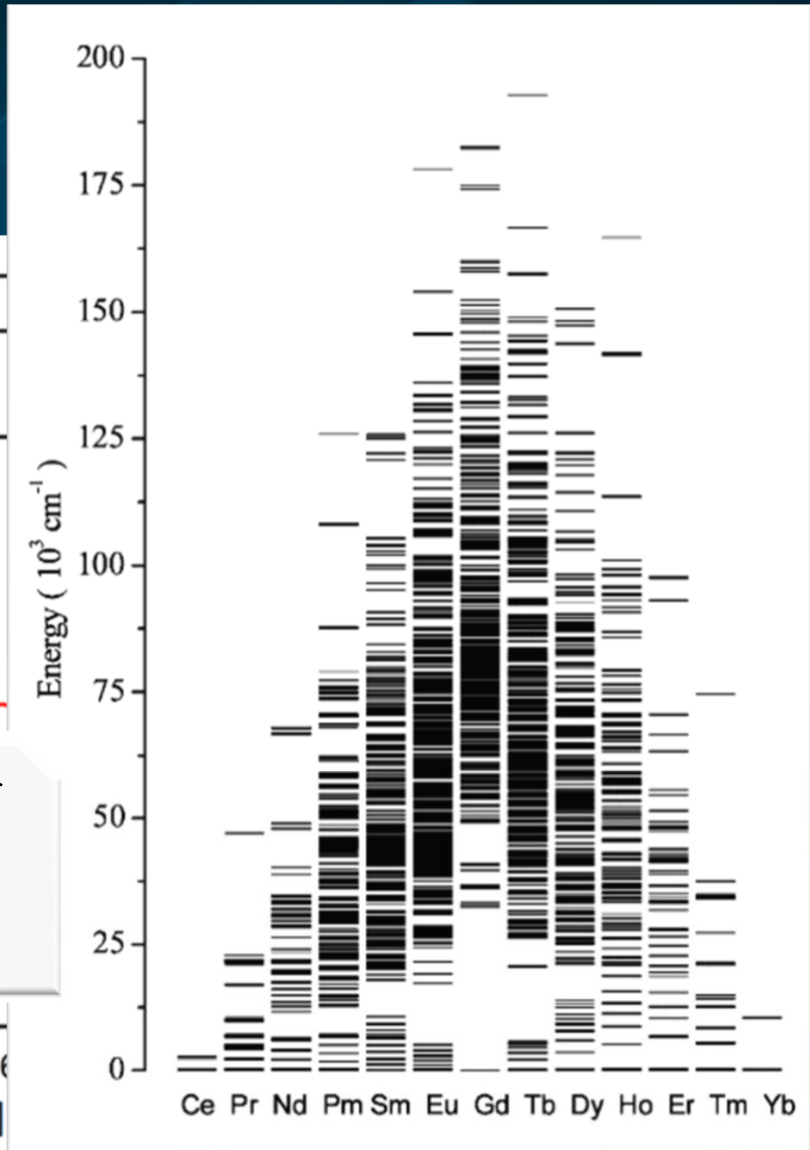
- La^{3+} = [Xe]
- Ce^{3+} = [Xe] $4f^1$

  ⋮
- Lu^{3+} = [Xe] $4f^{14}$

Trivalent Lanthanides

- Sharp emission & absorption lines
- Tra
- Lon
- Hig





A complete 4f^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

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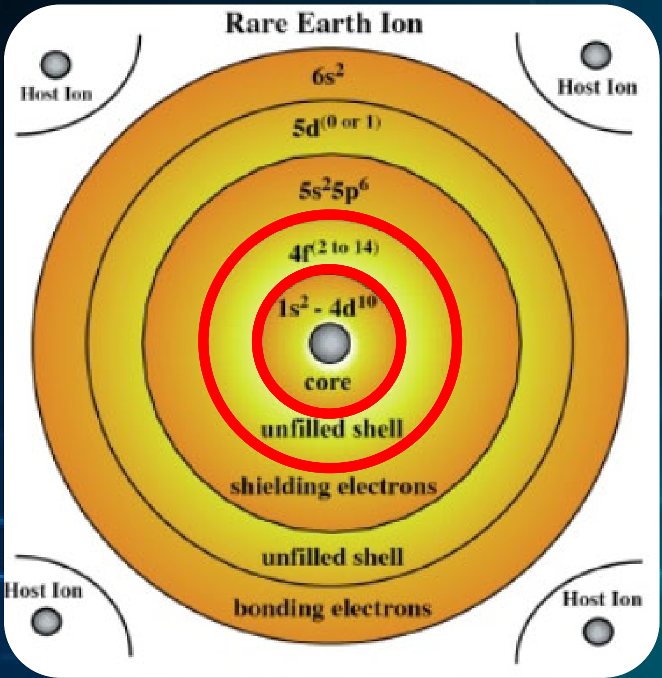
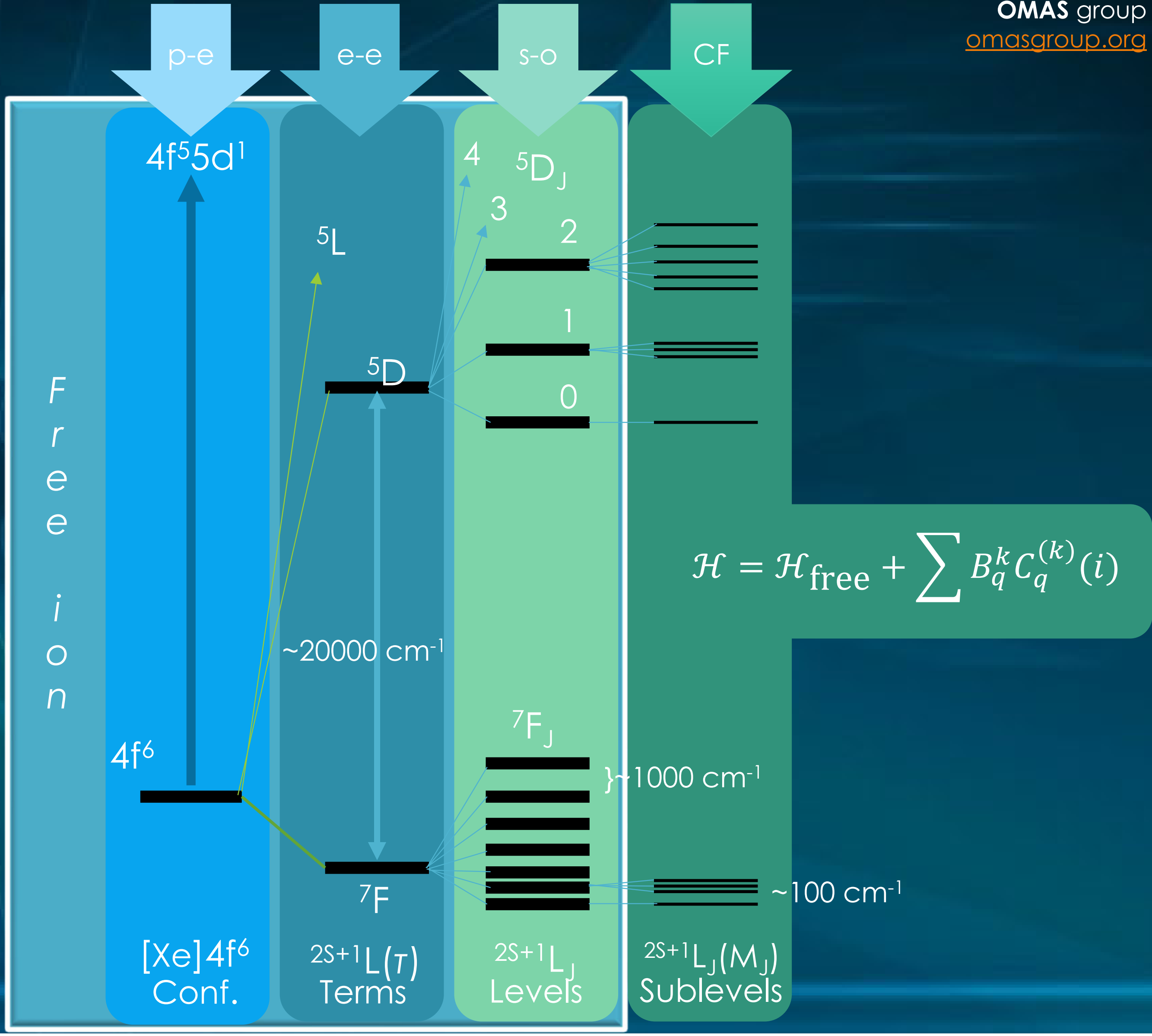
Ln^{3+} Energy Levels





Intensities

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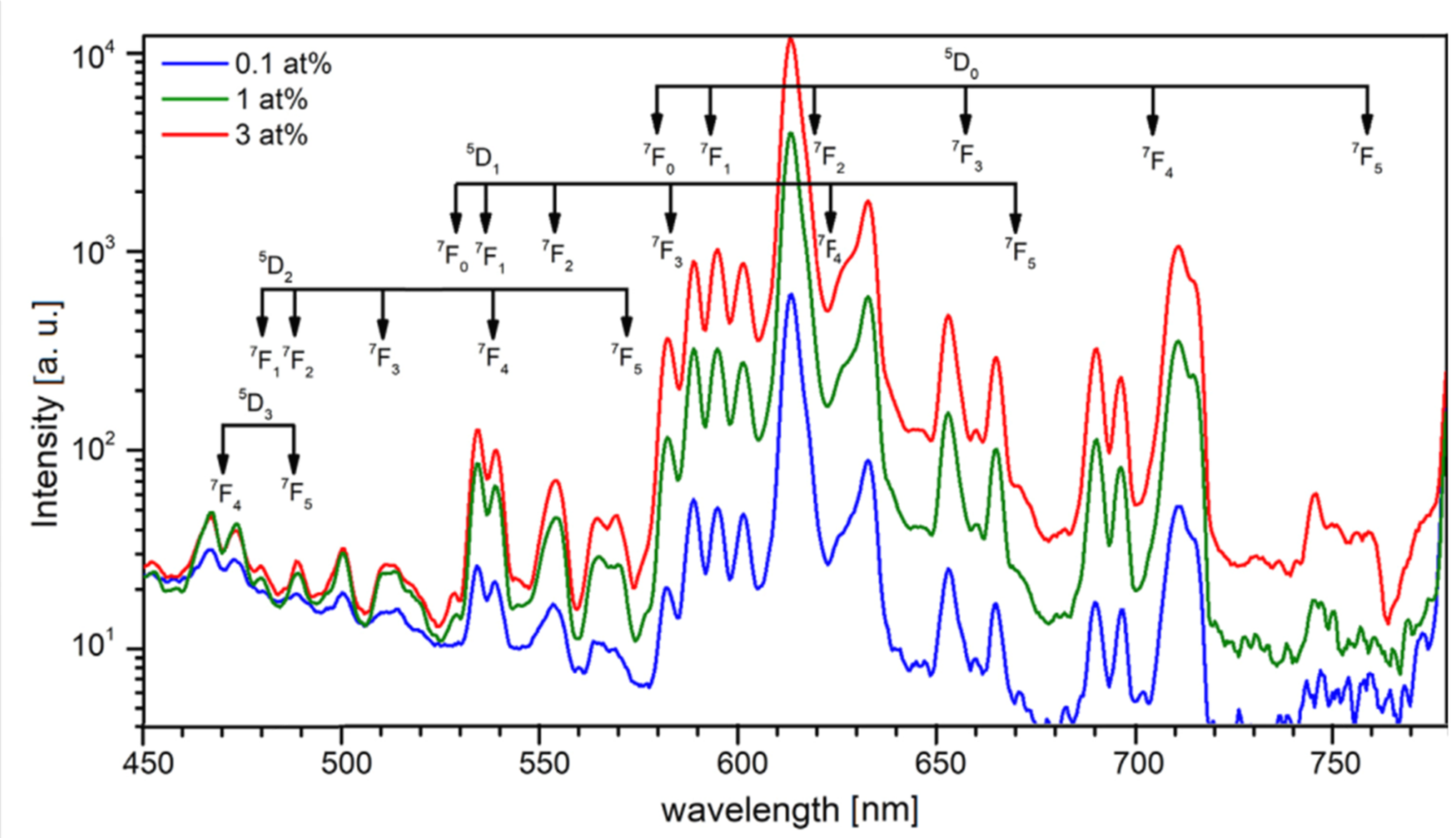

Judd-Ofelt theory – Prehistory

- 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).
- 1959. - Computers – tabulation of angular momentum coupling coefficients.
- 1962. – The solution to the "RE puzzle" simultaneously by Judd and Offelt.

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

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1962.-

PHYSICAL REVIEW VOLUME 127, NUMBER 3 AUGUST 1, 1962

Optical Absorption Intensities of Rare-Earth Ions

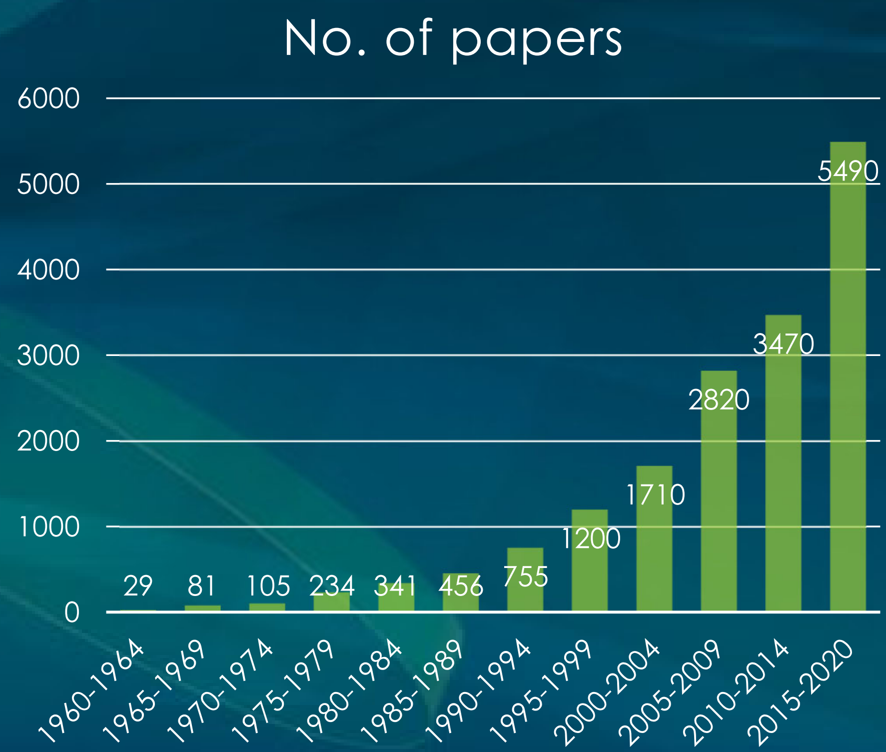
B. R. Judd
Lawrence Radiation Laboratory, University of California, Berkeley, California
(Received March 12, 1962)

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)

- *"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!



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Ω_λ Parametrization

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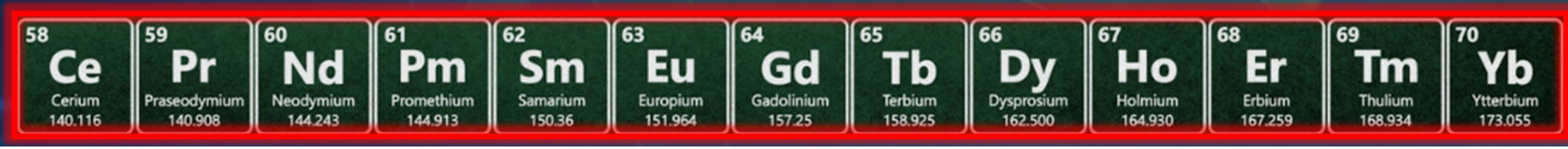
Ab initio Parametrization

- $\Omega_\lambda = (2\lambda + 1) \sum_p \sum_{t=1,3,5} \frac{|A_{tp}|^2}{2t+1} Y^2(t, \lambda)$
- A_{tp} – parameters of the static CF expansion

- Intensities of 4f-4f Transitions in Glass Materials, O.L. Malta, L.D. Carlos, doi: 10.1590/S0100-40422003000600018
- Judd-Ofelt theory: Principles and Practices, B.M. Walsh, doi: 10.1007/1-4020-4789-4_21
- Judd-Ofelt Theory - The Golden (and the Only One) Theoretical Tool of f-Electron Spectroscopy, L. Smentek, 10.1002/9781118688304.ch10
- Spectral Intensities of f-f transitions, C.G. Walrand, K. Binnemans, doi: 10.1016/S0168-1273(98)25006-9
- 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



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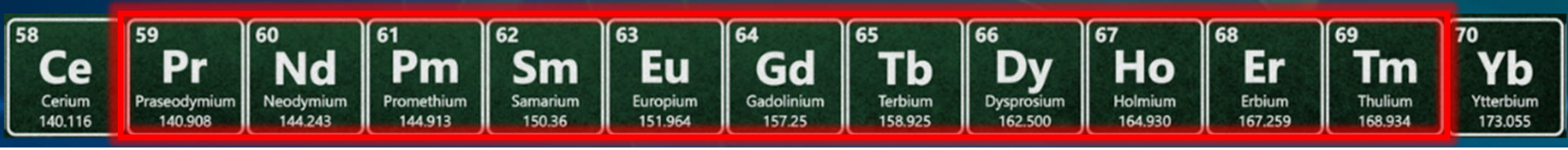
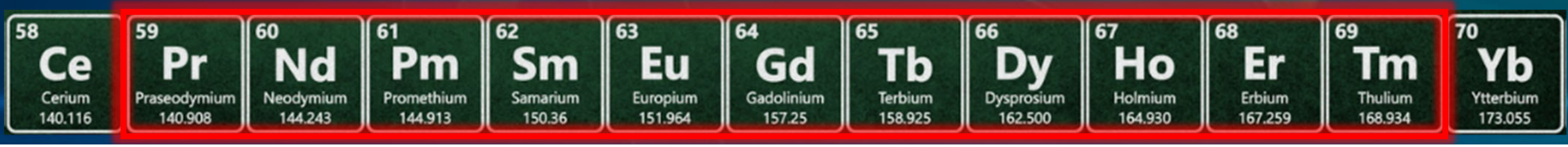
Parametrization from Absorption

- M. Helhen, M. Brik, K. Kramer, 50th anniversary of the Judd-Ofelt theory: An experimentalist's view of the formalism and its application, doi: 10.1016/j.jlumin.2012.10.035
- $f_{\text{exp}} = 4.319 \cdot 10^{-9} \frac{\text{mol}\cdot\text{cm}}{L} \int \varepsilon(\nu) d\nu$
- $f_{abs} = \frac{8\pi^2 m_e}{3h} \frac{\nu}{2J+1} \frac{\chi_{ED}^{abs}}{n} \sum_{\lambda=2,4,6} \Omega_\lambda |\langle l^N SLJ || U^\lambda || l^N S'L'J' \rangle|^2 + \frac{h\nu}{6 m_e c^2} \frac{n}{2J+1} |\langle l^N SLJ || L + gS || l^N S'L'J' \rangle|^2$
- 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



Parametrization from Excitation or DR

- Determination of Judd-Ofelt intensity parameters from the excitation spectra for rare-earth doped luminescent materials, W. Luo et al., doi: 10.1039/b921581f
- $S_{ex} = \frac{c}{\lambda\chi}\Gamma_{ex}, S_{th} = \sum_{\lambda=2,4,6}\Omega_\lambda \left|\langle l^N SLJ \| U^\lambda \| l^N S'L'J' \rangle\right|^2 \Rightarrow \Omega_2 : \Omega_4 : \Omega_6$
- For absolute values calibration is needed!
- $\tau_r^{-1} = \sum A_{J'}$
- Problem: Assumption that the non-radiative lifetime of the used level is 0!
- Xue et al. Validity of Judd-Ofelt spectroscopy based on diffuse reflectance spectrum and fluorescence lifetime of phosphor, doi: 10.1016/j.jlumin.2020.117304



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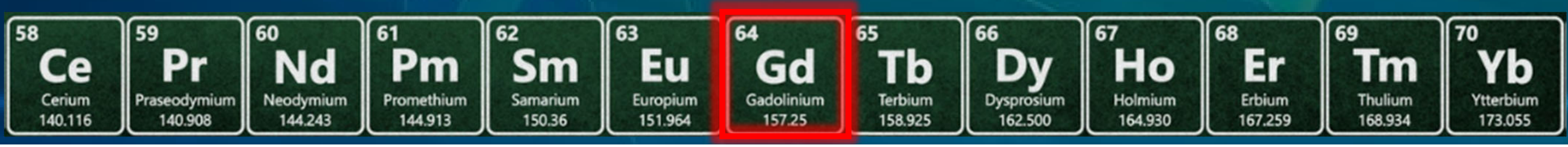
Parametrization from Emission: Gd^{3+}

- 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 $A_{J'}$

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

$$\tau_R = 1/\sum A_{SLJ\rightarrow S'L'J'}$$



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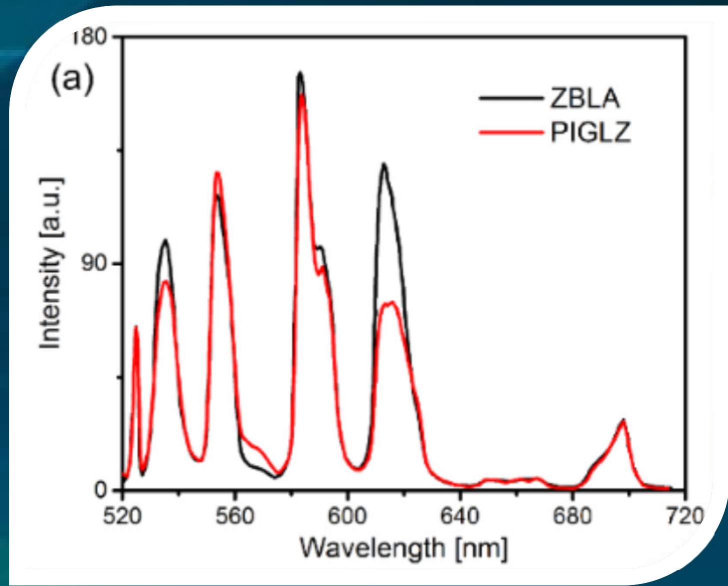
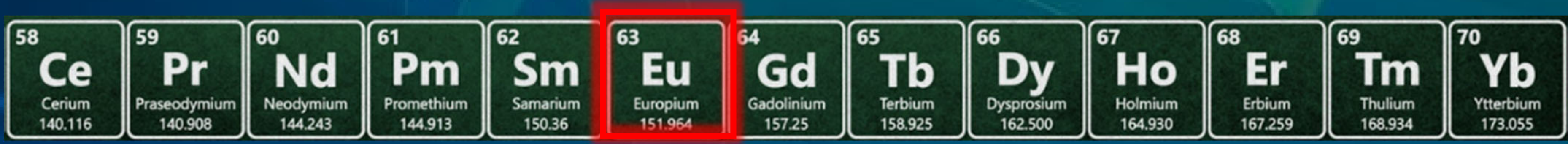
Parametrization from Emission: Eu^{3+} - Introduction

- Krupke, William F. "Optical absorption and fluorescence intensities in several rare-earth-doped Y_2O_3 and LaF_3 single crystals." *Physical Review* 145.1 (1966): 325.
  - 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+}

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

Baricenter

Local field correction

Dipole strength

$$\begin{cases} A_\lambda = \dfrac{64\pi^4\tilde{\nu}^3_\lambda}{3h}\chi_{ED}D^\lambda_{ED}, \lambda = 2,4,6 \\ A_{MD} = \dfrac{64\pi^4\tilde{\nu}^3_{MD}}{3h}\chi_{MD}D_{MD} \end{cases}$$

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

Population

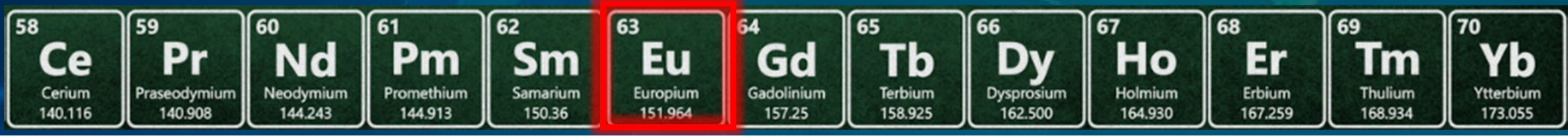
$$\frac{I_\lambda}{I_{MD}} = \frac{\tilde{\nu}_\lambda A_\lambda}{\tilde{\nu}_{MD}A_{MD}} = \left(\frac{\tilde{\nu}_\lambda}{\tilde{\nu}_{MD}}\right)^4 \frac{\chi_{ED}D^\lambda_{ED}}{\chi_{MD}D_{MD}}$$

+

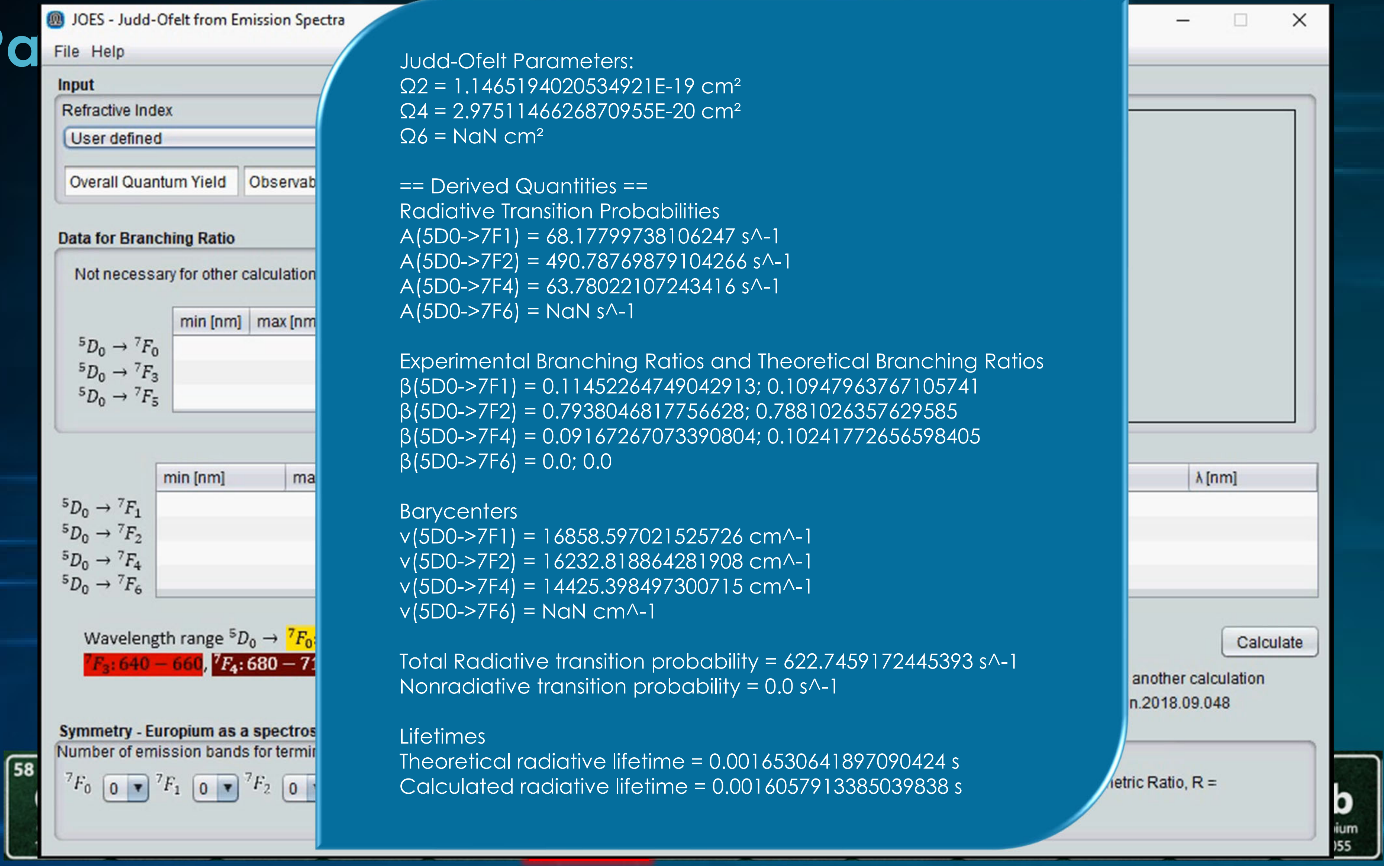
$$D^\lambda_{ED} = e^2\Omega_\lambda U^\lambda$$

RME

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



DOWNLOAD from: https://omasgroup.org/joes-software/ Assistance: aleksandar.ciric@ff.bg.ac.rs



Judd-Ofelt Parameters:
Ω2 = 1.1465194020534921E-19 cm²
Ω4 = 2.9751146626870955E-20 cm²
Ω6 = NaN cm²

== Derived Quantities ==
Radiative Transition Probabilities
A(5D0->7F1) = 68.17799738106247 s^-1
A(5D0->7F2) = 490.78769879104266 s^-1
A(5D0->7F4) = 63.78022107243416 s^-1
A(5D0->7F6) = NaN s^-1

Experimental Branching Ratios and Theoretical Branching Ratios
β(5D0->7F1) = 0.11452264749042913; 0.10947963767105741
β(5D0->7F2) = 0.7938046817756628; 0.7881026357629585
β(5D0->7F4) = 0.09167267073390804; 0.10241772656598405
β(5D0->7F6) = 0.0; 0.0

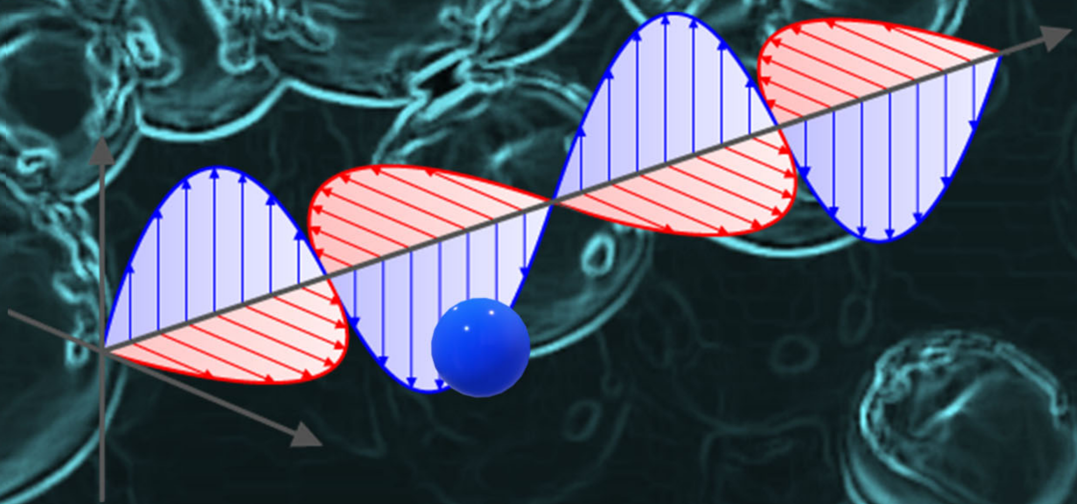
Barycenters
v(5D0->7F1) = 16858.597021525726 cm^-1
v(5D0->7F2) = 16232.818864281908 cm^-1
v(5D0->7F4) = 14425.398497300715 cm^-1
v(5D0->7F6) = NaN cm^-1

Total Radiative transition probability = 622.7459172445393 s^-1
Nonradiative transition probability = 0.0 s^-1

Lifetimes
Theoretical radiative lifetime = 0.0016530641897090424 s
Calculated radiative lifetime = 0.0016057913385039838 s

Nanomaterials

- Correction for nanocrystals << λ
- $n_{eff} = n(\lambda)_{np} x + (1 - x) n_{med}$
  - 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. $n_{air} \approx 1$)



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Luminescence thermometry

- Steady State
  - Luminescence Intensity Ratio (LIR)
  - Bandshift
  - Bandwidth
- Time Resolved
  - Lifetime & Risetime
  - Phase-shift

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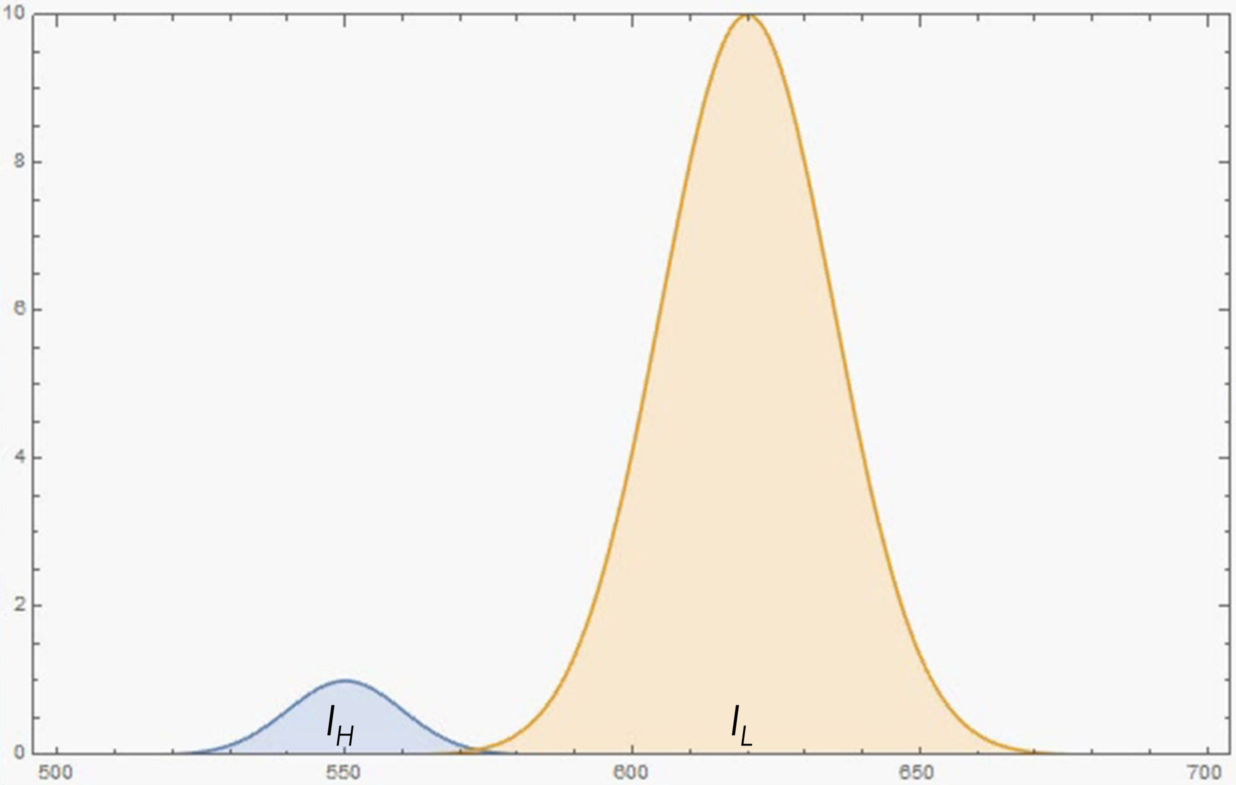
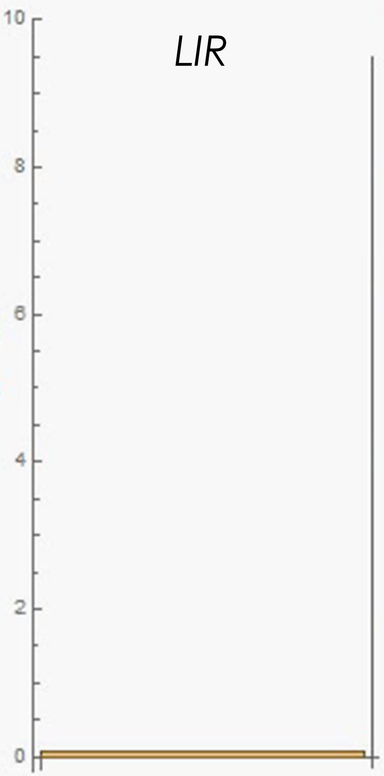
Luminescence Intensity Ratio (LIR)

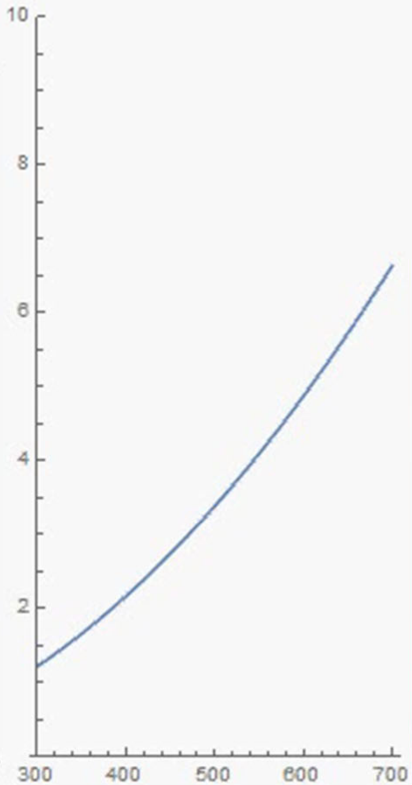
The most widely used method!

$$LIR = \frac{I_H}{I_L} = \left| \frac{N_H}{N_L} = \frac{g_H}{g_L} e^{-\Delta E/kT} \right| = Be^{-\Delta E/kT}$$



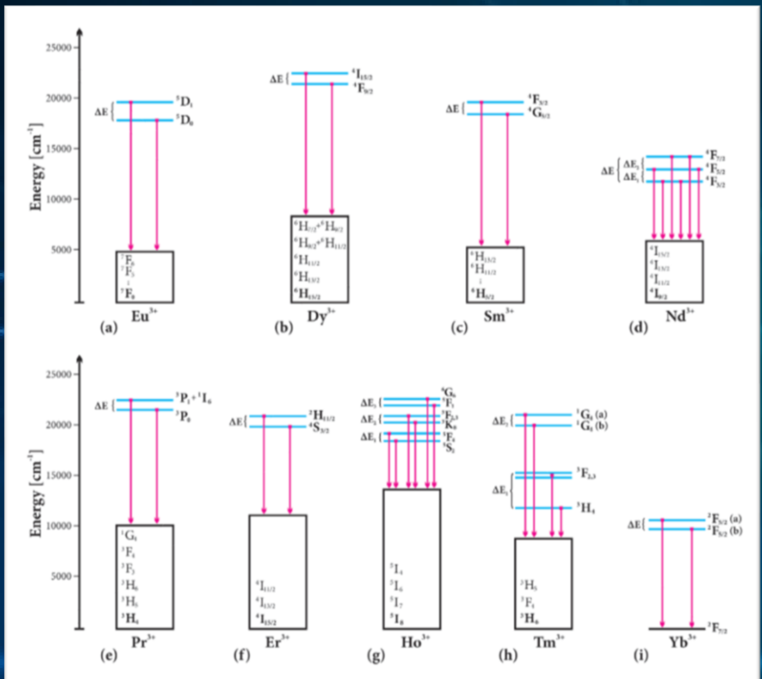
300K

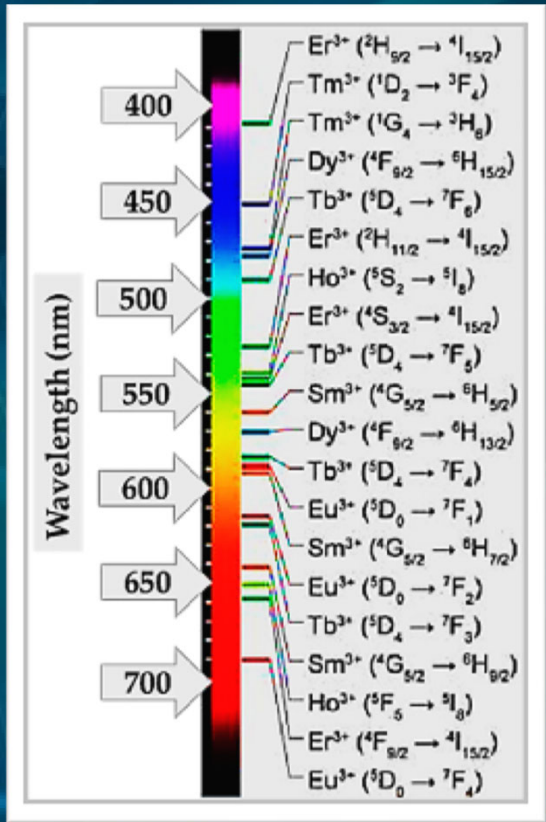


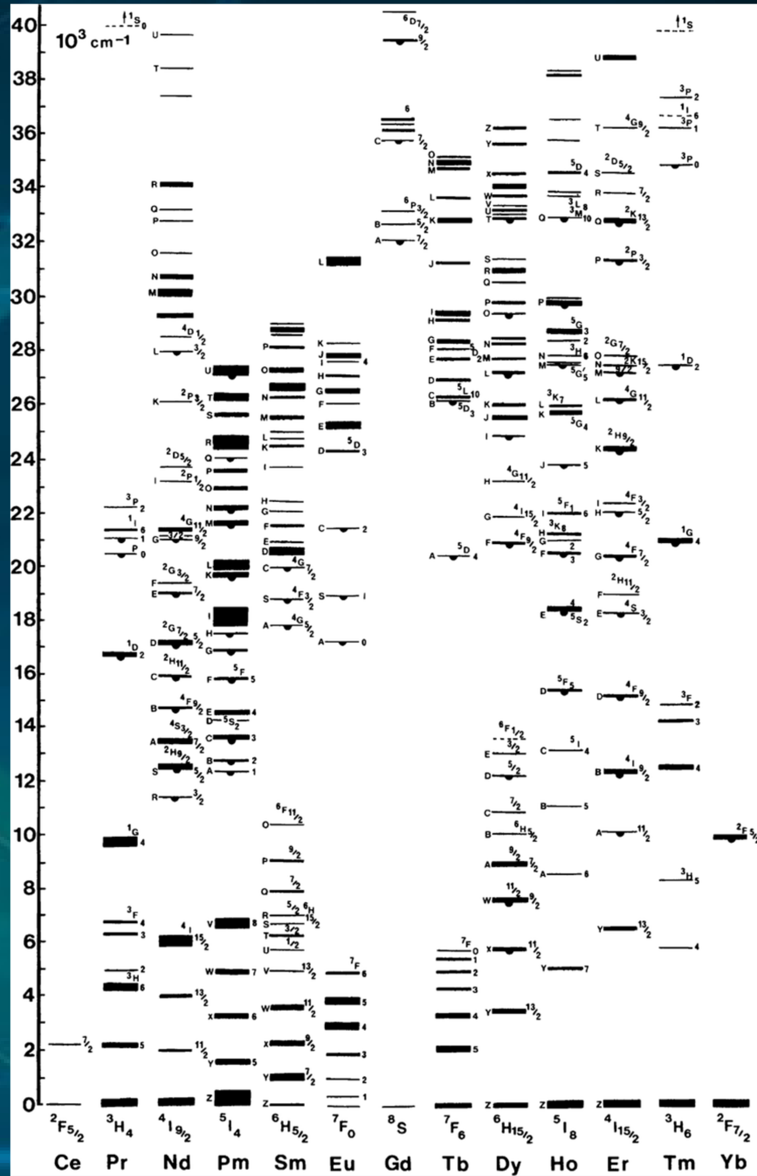


LIR & Ln

- 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_2S_3, Y.Yang et al., doi: 10.1111/jace.12822

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Judd-Ofelt and LIR

$$LIR = \frac{I_H}{I_L} = \left| I = h\tilde{\nu}NA,\ \frac{N_H}{N_L} = \frac{g_H}{g_L} e^{-\frac{\Delta E}{kT}} \right| = \frac{h\tilde{\nu}_H N_H A_H}{h\tilde{\nu}_L N_L A_L} = \underbrace{\frac{g_H h\tilde{\nu}_H A_H}{g_L h\tilde{\nu}_L A_L}}_{B} e^{-\frac{\Delta E}{kT}}$$

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

+

$$B = \frac{g_H h\tilde{\nu}_H A_H}{g_L h\tilde{\nu}_L A_L}$$

→

$$B = \left(\frac{\tilde{\nu}_H}{\tilde{\nu}_L}\right)^4 \frac{\chi^H_{ED} D^H_{ED} + \chi^H_{MD} D^H_{MD}}{\chi^L_{ED} D^L_{ED} + \chi^L_{MD} D^L_{MD}}$$

$$D^\lambda_{ED} = e^2 \sum_\lambda \Omega_\lambda U^\lambda$$

U^λ and D_{MD} are tabulated and host independent

58	59	60	61	62	63	64	65	66	67	68	69	70
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium
140.116	140.908	144.243	144.913	150.36	151.964	157.25	158.925	162.500	164.930	167.259	168.934	173.055

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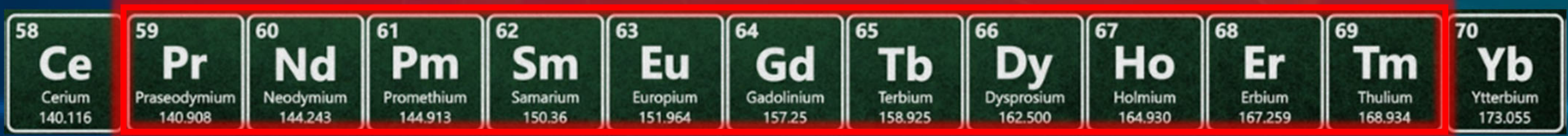
Figures of Merit via Ω_λ

$$S(T) = \frac{\Delta E}{kT^2} B \exp\left(-\frac{\Delta E}{kT}\right) = \frac{\Delta E}{kT^2}\left(\frac{\tilde{\nu}_H}{\tilde{\nu}_L}\right)^4 \frac{\chi_{ED}^H D_{ED}^H + \chi_{MD}^H D_{MD}^H}{\chi_{ED}^L D_{ED}^L + \chi_{MD}^L D_{MD}^L} \exp\left(-\frac{\Delta E}{kT}\right)$$

$$S_{max} = \frac{4k}{e^2 \Delta E}\left(\frac{\tilde{\nu}_H}{\tilde{\nu}_L}\right)^4 \frac{\chi_{ED}^H D_{ED}^H + \chi_{MD}^H D_{MD}^H}{\chi_{ED}^L D_{ED}^L + \chi_{MD}^L D_{MD}^L}$$

$$\Delta T = \frac{kT^2 \sigma(\chi_{ED}^L D_{ED}^L + \chi_{MD}^L D_{MD}^L)}{\Delta E(\chi_{ED}^H D_{ED}^H + \chi_{MD}^H D_{MD}^H) \exp(-\Delta E/kT)}$$

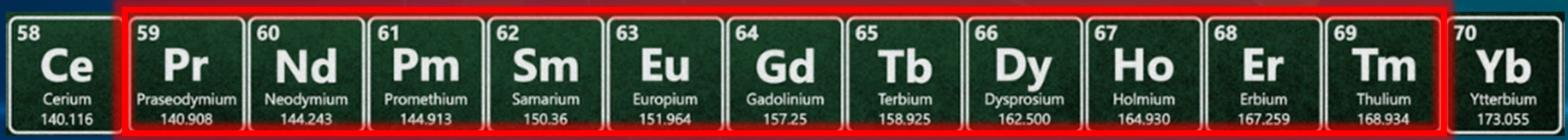
An Extension of the Judd-Ofelt theory to the field of lanthanide thermometry, A. Ćirić, S. Stojadinović, M.D. Dramićanin, doi: 10.1016/j.jlumin.2019.116749

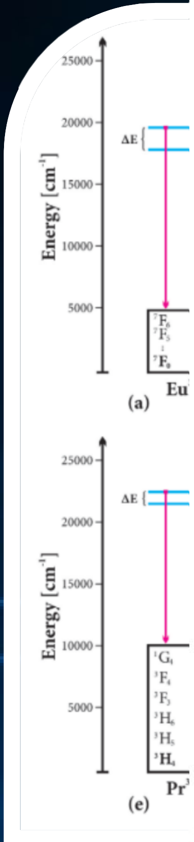


Significance

- Ω_λ is easier to obtain (single spectrum @ RT)
- Large number of Ω_λ in literature
  - Largest #: Spectral Intensities of f-f transitions, C.G. Walrand, K. Binnemans, doi: 10.1016/S0168-1273(98)25006-9

	JO-LIR	Experimental
Setup Price	**Low**	High
Speed	**High**	Low
Knowledge Level	**Mid**	High
Accuracy	Mid	**High**





Transition	High or Low	λ [nm]	U^2	U^4	U^6	$D_{MD} \cdot 10^{42}$ [esu^2 cm^2]	$\chi_{ED}D_{ED} + \chi_{MD}D_{MD}$ [esu^2 cm^2]
Pr^{3+} [57,58]							
$^3P_1 \rightarrow {}^3H_5$	H	525	0	0.2857	0.0892	0	$\eta(0.2857\Omega_4 + 0.0892\Omega_6)$
$^3P_0 \rightarrow {}^3H_5$	L	540	0	0	0	0	0
Nd^{3+} [46,47]							
$^4F_{7/2} \rightarrow {}^4I_{9/2}$	H	740	0.0011	0.0406	0.4272	≈0[c]	$\eta(0.0011\Omega_2 + 0.0406\Omega_4 + 0.4272\Omega_6)$
$^4F_{5/2} \rightarrow {}^4I_{9/2}$	H or L	815	0.0006	0.2337	0.3983	0	$\eta(0.0006\Omega_2 + 0.2337\Omega_4 + 0.3983\Omega_6)$
$^4F_{3/2} \rightarrow {}^4I_{9/2}$	L	900	0	0.2283	0.0554	0	$\eta(0.2283\Omega_4 + 0.0554\Omega_6)$
$^4F_{7/2} \rightarrow {}^4I_{11/2}$	L	1075	0.0009	0.2335	0.3076	0	$\eta(0.0009\Omega_2 + 0.2335\Omega_4 + 0.3076\Omega_6)$
Sm^{3+}							
$^4F_{3/2} \rightarrow {}^6H_{5/2}$	H	530	0.00003[a]	0.00008[a]	0	0.3[c]	$\eta(0.00003\Omega_2 + 0.00008\Omega_4) + n^3 \cdot 0.2 \cdot 10^{-42}$
$^4G_{5/2} \rightarrow {}^6H_{5/2}$	L	560	0.0004[a]	0.0001[a]	0	12.2[c]	$\eta(0.0004\Omega_2 + 0.0001\Omega_4) + n^3 \cdot 0.8 \cdot 10^{-42}$
$^4G_{5/2} \rightarrow {}^6H_{7/2}$	L	587	0	0.0078	0.0075	12.2[c]	$\eta(0.0078\Omega_4 + 0.0075\Omega_6) + n^3 \cdot 1.3 \cdot 10^{-42}$
$^4G_{5/2} \rightarrow {}^6H_{9/2}$	L	650	0.0096	0.0061	0.0019	0	$\eta(0.0096\Omega_2 + 0.0061\Omega_4 + 0.0019\Omega_6)$
$^4G_{5/2} \rightarrow {}^6H_{11/2}$	L	710	0	0.0045	0.0018	0	$\eta(0.0045\Omega_4 + 0.0018\Omega_6)$
Eu^{3+} [a]							
$^5D_1 \rightarrow {}^7F_1$	H	535	0.0026	0	0	≈0[c]	$\eta \cdot 0.0026\Omega_2$
$^5D_1 \rightarrow {}^7F_2$	H	555	0.0008	0	0	11.2	$\eta \cdot 0.0008\Omega_2 + n^3 \cdot 11.2 \cdot 10^{-42}$
$^5D_0 \rightarrow {}^7F_1$	L	585	0	0	0	9.6	$n^3 \cdot 9.6 \cdot 10^{-42}$
$^5D_0 \rightarrow {}^7F_2$	L	612	0.0032	0	0	0	$\eta \cdot 0.0032\Omega_2$
$^5D_0 \rightarrow {}^7F_4$	L	695	0	0.0023	0	0	$\eta \cdot 0.0023\Omega_4$
Dy^{3+}							
$^4I_{15/2} \rightarrow {}^6H_{15/2}$	H	455	0.0071	0.0003	0.0659	82.3[c]	$\eta(0.0071\Omega_2 + 0.0003\Omega_4 + 0.0659\Omega_6) + n^3 \cdot 90 \cdot 10^{-42}$
$^4F_{9/2} \rightarrow {}^6H_{15/2}$	L	490	0	0.0046	0.0292	0	$\eta(0.0046\Omega_4 + 0.0292\Omega_6)$
$^4F_{9/2} \rightarrow {}^6H_{13/2}$	L	570	0.0490	0.0164	0.0545	0	$\eta(0.0490\Omega_2 + 0.0164\Omega_4 + 0.0545\Omega_6)$
$^4F_{9/2} \rightarrow {}^6H_{11/2}$	L	660	0.0093	0.0018	0.0033	26.3[c]	$\eta(0.0093\Omega_2 + 0.0018\Omega_4 + 0.0033\Omega_6) + n^3 \cdot 27.5 \cdot 10^{-42}$
$^4F_{9/2} \rightarrow {}^6H_{9/2}$	L	735	0.0021	0.0024	0.0032	8.9[c]	$\eta(0.0021\Omega_2 + 0.0024\Omega_4 + 0.0032\Omega_6) + n^3 \cdot 8.9 \cdot 10^{-42}$
Ho^{3+} [b]							
$^5F_4 \rightarrow {}^7I_8$	H	530	0	0.2385	0.7090	0	$\eta(0.2385\Omega_4 + 0.7090\Omega_6)$
$^5S_2 \rightarrow {}^7I_8$	H or L	545	0	0	0.2145	0	$\eta \cdot 0.2145\Omega_6$
$^5F_4 \rightarrow {}^7I_7$	H or L	750	0	0.1965	0.0320	0	$\eta(0.1965\Omega_4 + 0.0320\Omega_6)$
$^5S_2 \rightarrow {}^7I_7$	L	710	0	0	0.4195	0	$\eta \cdot 0.4195\Omega_6$
Er^{3+} [a]							
$^2H_{11/2} \rightarrow {}^4I_{15/2}$	H	525	0.5977	0.3456	0.0790	0	$\eta(0.5977\Omega_2 + 0.3456\Omega_4 + 0.0790\Omega_6)$
$^4S_{3/2} \rightarrow {}^4I_{15/2}$	L	550	0	0	0.2119	0	$\eta \cdot 0.2119\Omega_6$
Tm^{3+}							
$^3F_2 \rightarrow {}^3H_6$	H	670	0	0	0.2550	0	$\eta \cdot 0.2550\Omega_6$
$^3F_3 \rightarrow {}^3H_6$	H	695	0	0.3164	0.8413	0	$\eta(0.3164\Omega_4 + 0.8413\Omega_6)$
$^3H_4 \rightarrow {}^3H_6$	L	800	0.2357	0.1081	0.5916	0	$\eta(0.2357\Omega_2 + 0.1081\Omega_4 + 0.5916\Omega_6)$

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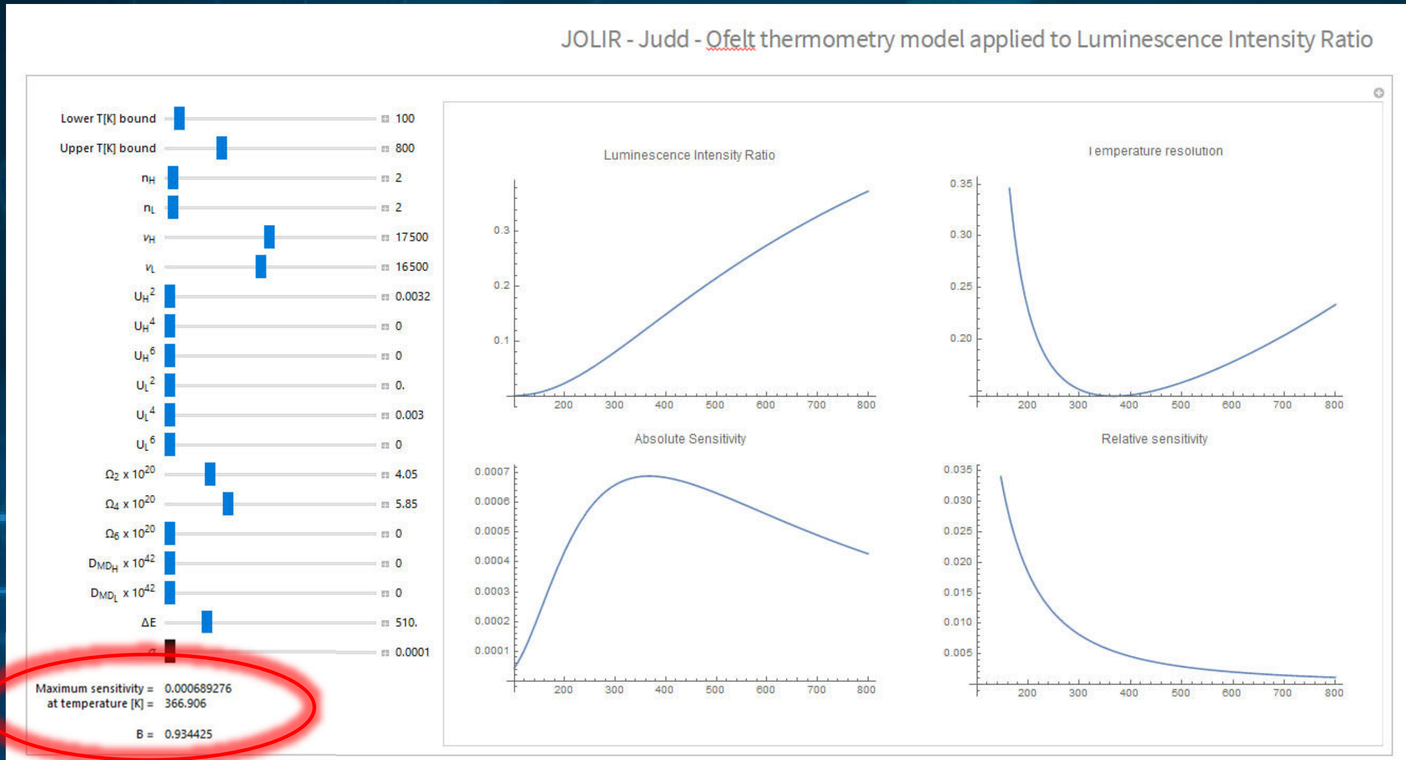
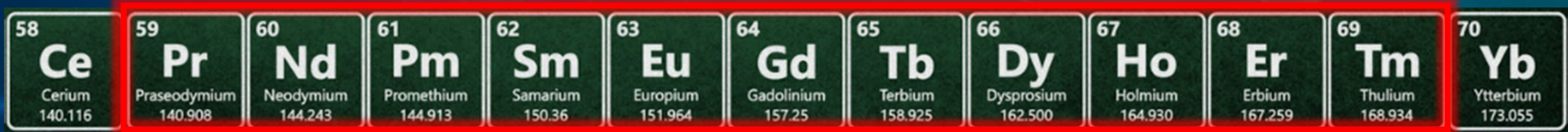
JOLIR applet

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

Magnetic dipole and electric quadrupole transitions in the trivalent lanthanide series: Calculated emission rates and oscillator strengths, doi: 10.1103/PhysRevB.86.125102





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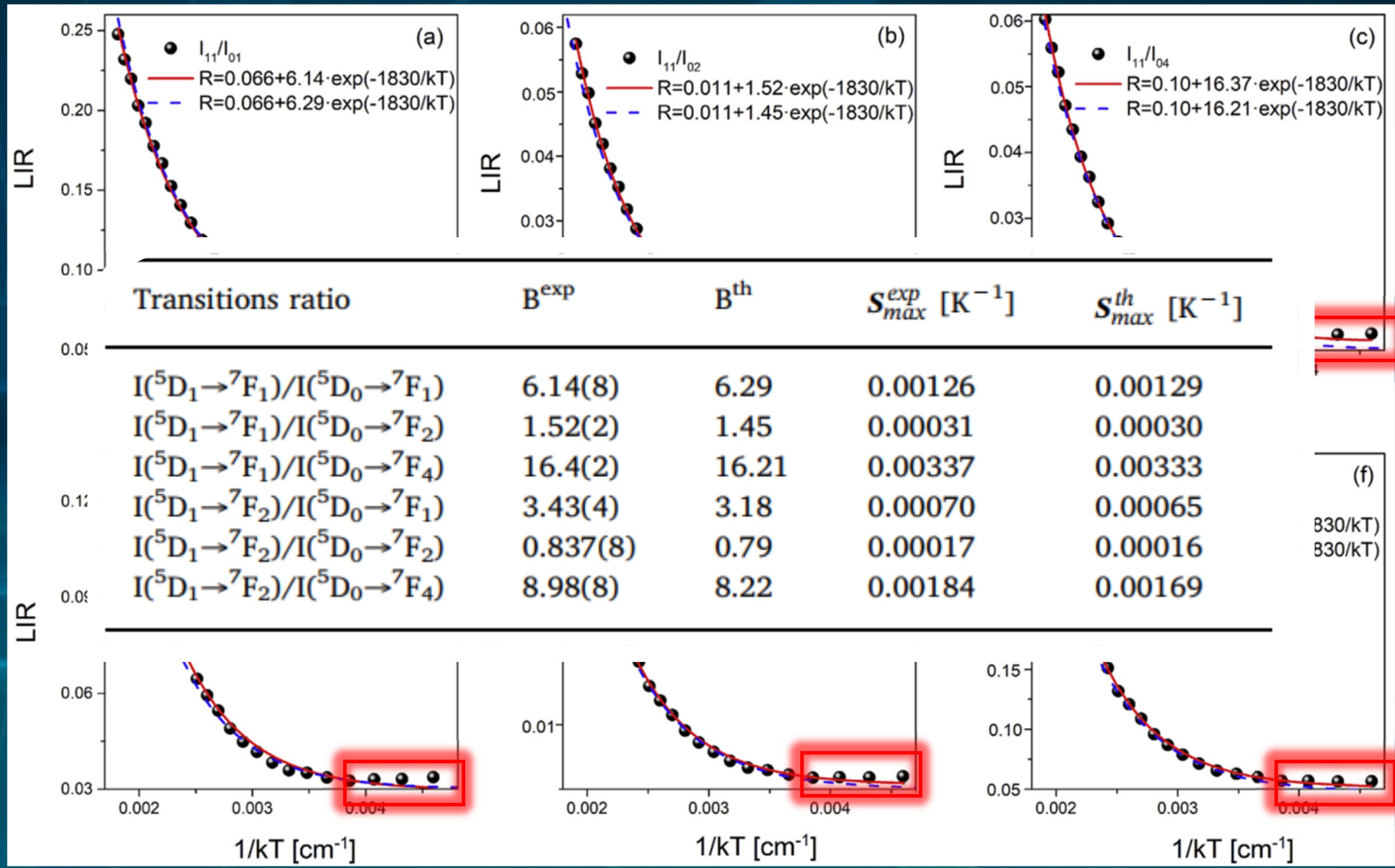
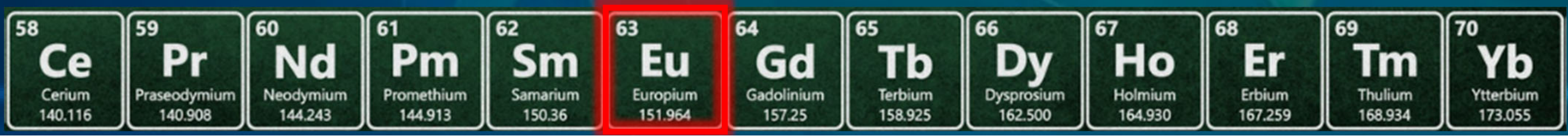
Testing on $Y_2O_3:Eu^{3+}$

- LIR of $^5D_1 \rightarrow {}^7F_{1,2}$ and $^5D_0 \rightarrow {}^7F_{1,2,4}$
- $LIR = C\,\dfrac{\alpha A_R + M\rho g_2 n^p}{\beta A_R + M\rho g_1 (1+n)^p}$
- R. Geitenbeek, H.W. de Wijn, A. Meijerink, doi: 10.1103/PhysRevApplied.10.064006



Transitions ratio	B^{exp}	B^{th}	S_{max}^{exp} [K^{-1}]	S_{max}^{th} [K^{-1}]
$I(^5D_1\rightarrow{}^7F_1)/I(^5D_0\rightarrow{}^7F_1)$	6.14(8)	6.29	0.00126	0.00129
$I(^5D_1\rightarrow{}^7F_1)/I(^5D_0\rightarrow{}^7F_2)$	1.52(2)	1.45	0.00031	0.00030
$I(^5D_1\rightarrow{}^7F_1)/I(^5D_0\rightarrow{}^7F_4)$	16.4(2)	16.21	0.00337	0.00333
$I(^5D_1\rightarrow{}^7F_2)/I(^5D_0\rightarrow{}^7F_1)$	3.43(4)	3.18	0.00070	0.00065
$I(^5D_1\rightarrow{}^7F_2)/I(^5D_0\rightarrow{}^7F_2)$	0.837(8)	0.79	0.00017	0.00016
$I(^5D_1\rightarrow{}^7F_2)/I(^5D_0\rightarrow{}^7F_4)$	8.98(8)	8.22	0.00184	0.00169



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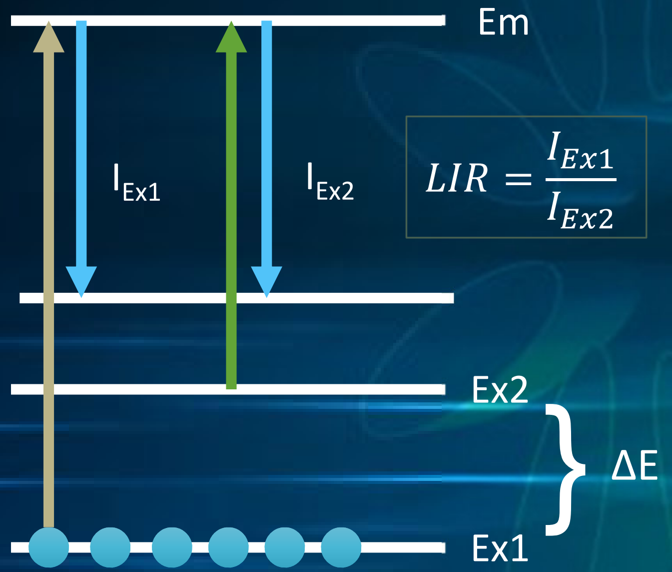
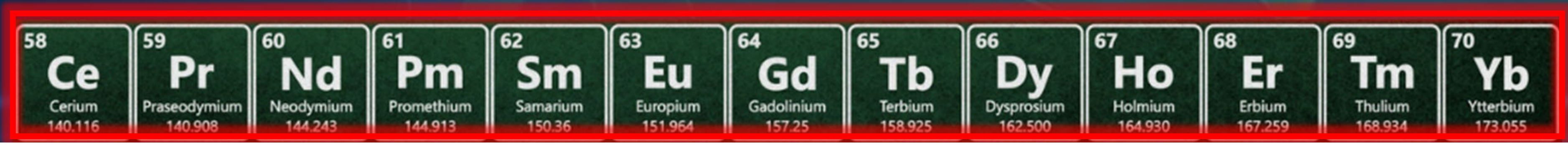
Dual-excited single band LIR



$$LIR = \frac{I_{Ex1}}{I_{Ex2}}$$

- 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 > 0K : 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 ΔE → larger S_r



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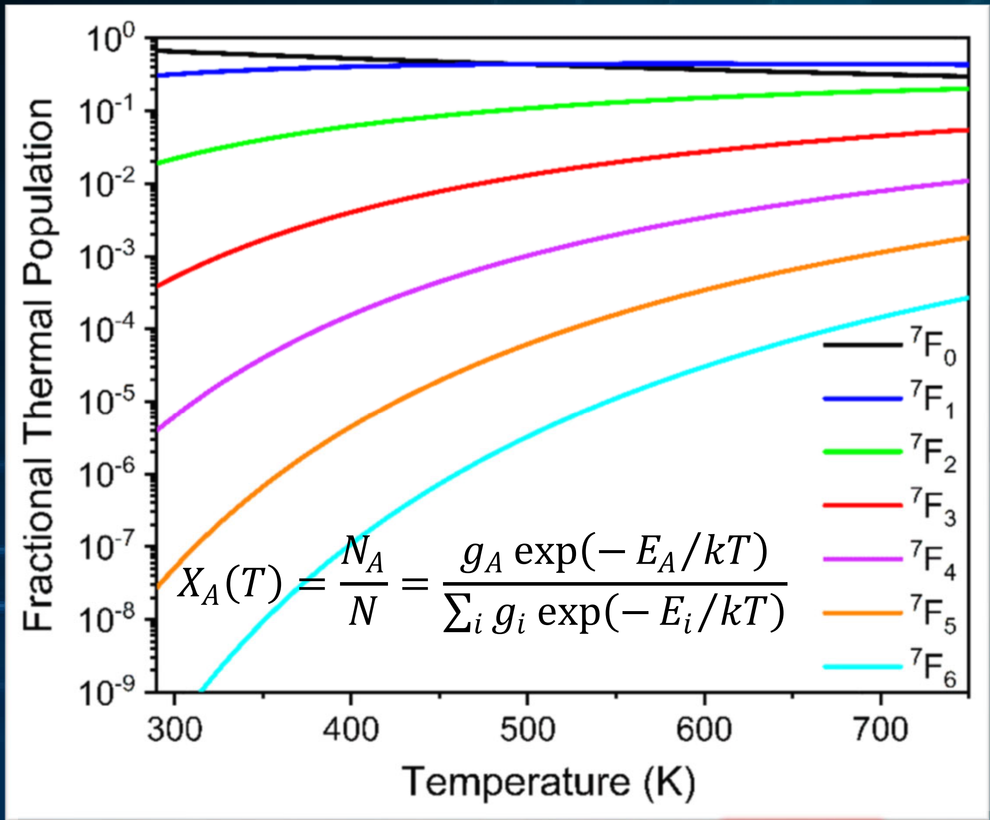
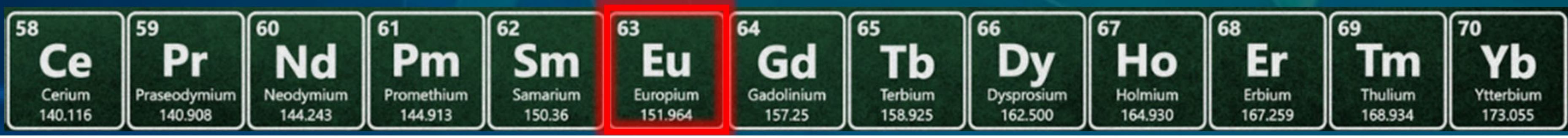
How? Optical centers redistribution



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



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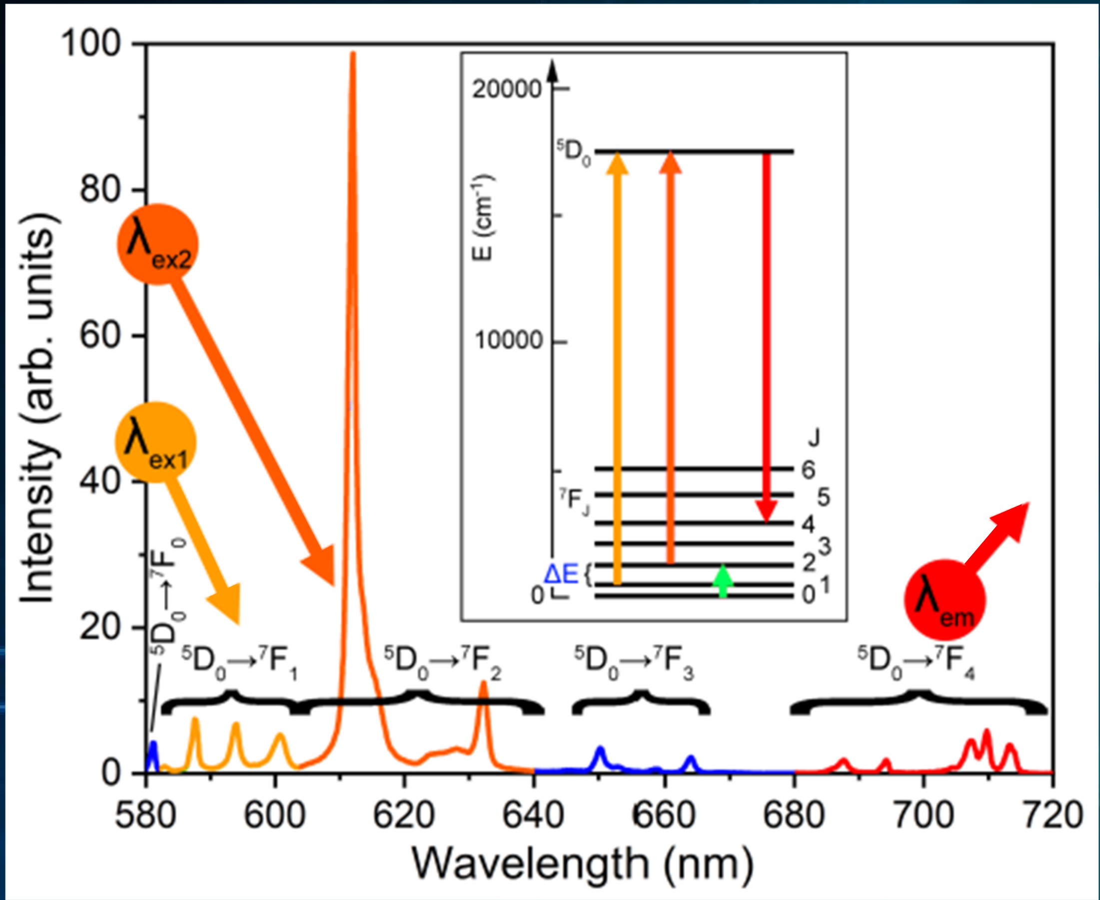
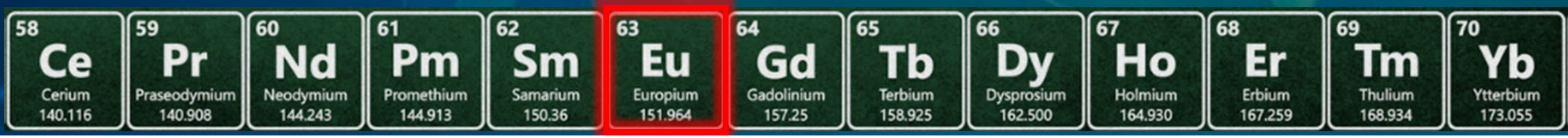
How? Excitations and emission



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



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Judd-Ofelt model

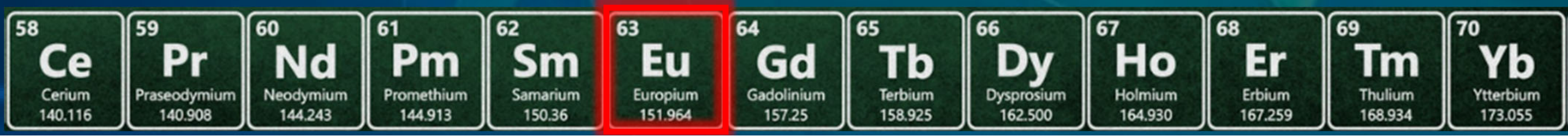
$$A_\lambda = \frac{64\pi^4 \tilde{v}_\lambda^3}{3h} \chi_{ED} D_{ED}^\lambda \qquad A_{MD} = \frac{64\pi^4 \tilde{v}_{MD}^3}{3h} \chi_{MD} D_{MD}$$

$$I_{SLJ \to S'L'J'} = h\tilde{v}_{SLJ \to S'L'J'} N_{SLJ} A_{SLJ \to S'L'J'}$$

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

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

- Prediction of the B parameter.
- $D_{ED}^\lambda = e^2 \Omega_\lambda U^\lambda$
- $D_{MD} = 9.6 \cdot 10^{-42}\ esu^2 cm^2$
- ΔE can be obtained from spectrum.



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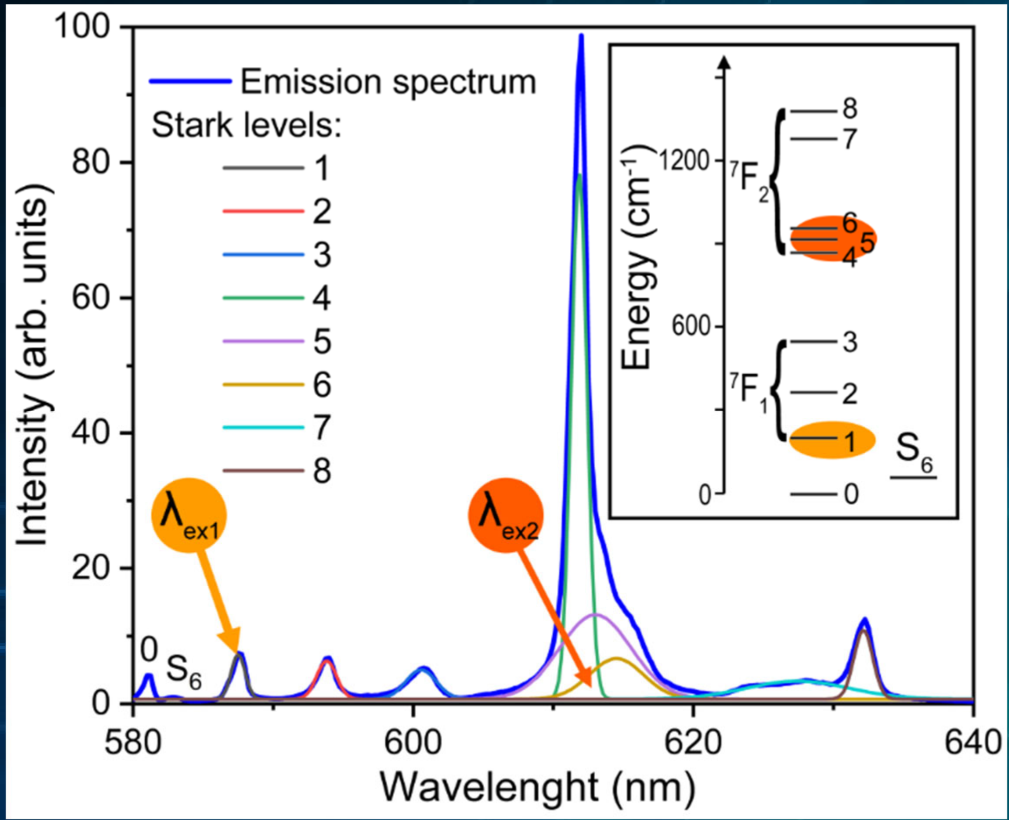
Corrections

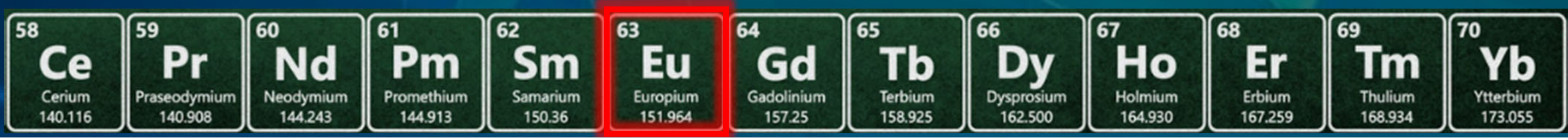


- Excitations are performed in some Stark sublevels.
- Correction factors are needed:

$$\varphi_1 = \frac{I_{1,1}}{\sum_{j=1}^{3} I_{1,j}}, \varphi_2 = \frac{\sum_{j=4}^{6} I_{2,j}}{\sum_{j=4}^{8} I_{2,j}}$$

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

Judd-Ofelt modelling of the dual-excited single band ratiometric luminescence thermometry, A. Ćirić, I. Zeković, M. Medić, Ž. Antić, M.D. Dramićanin, doi: 10.1016/j.jlumin.2020.117369



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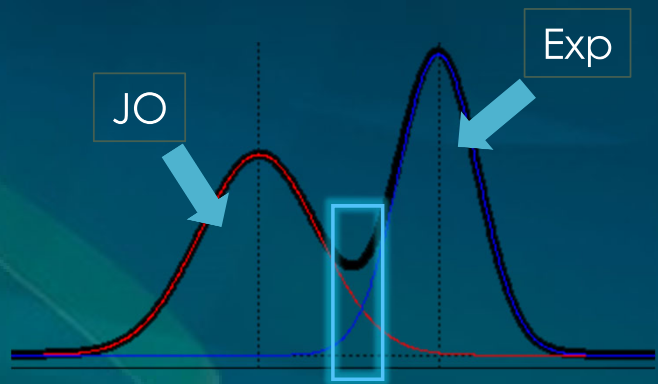
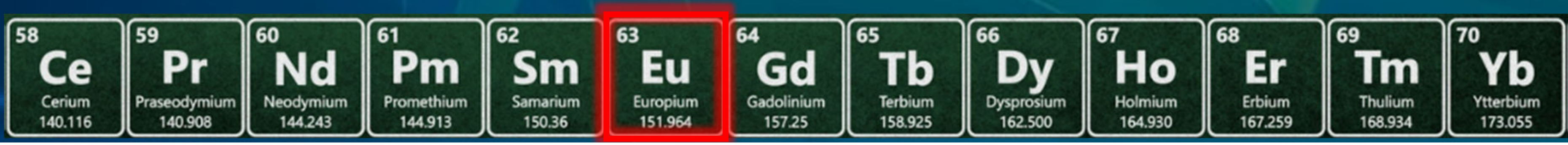
TEST ON $Lu_2O_3{:}Eu^{3+}$

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





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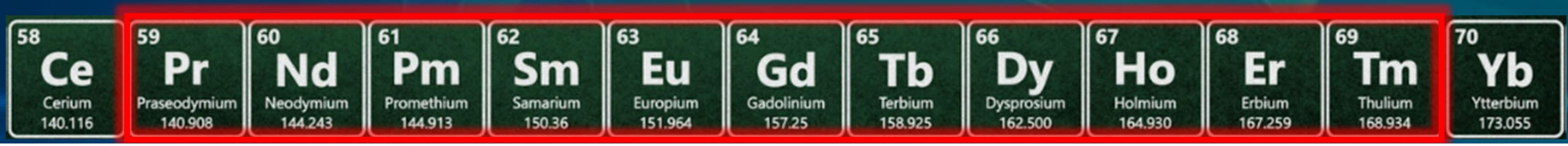
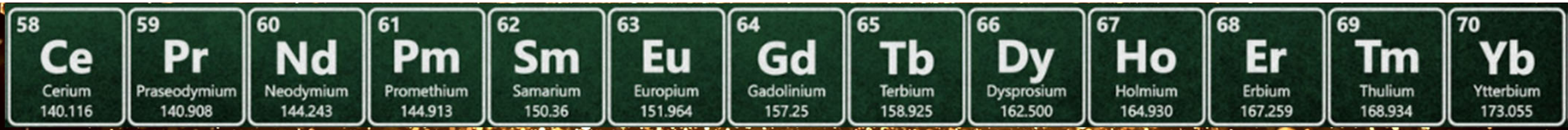
CONCLUSIONS

- 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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