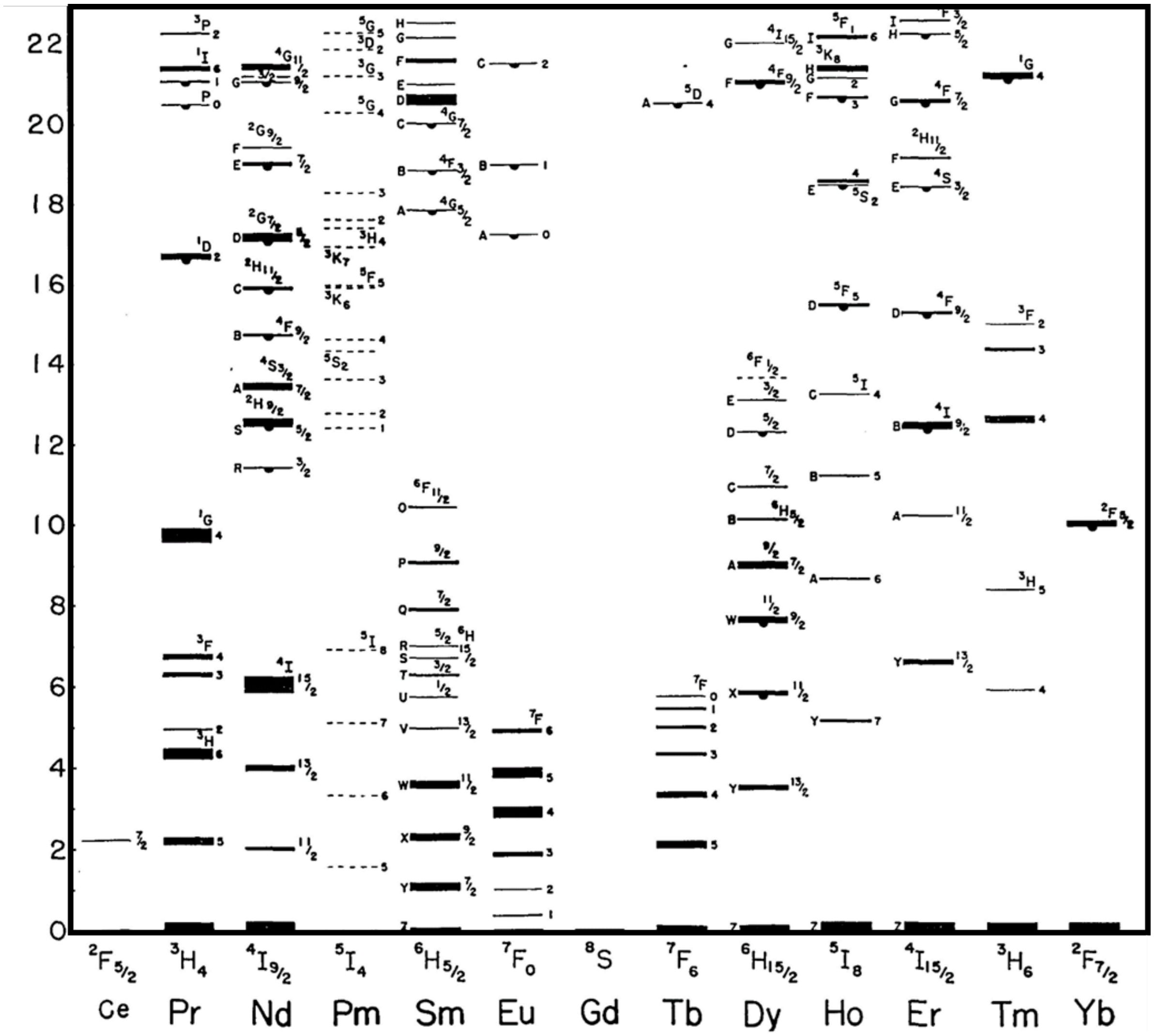
Judd-Ofelt theory (Brief Notes)

Judd–Ofelt theory is a model describing the intensity of electron transitions within the 4f shell of rare-earth ions (RE) in solids (solutions) due to process of absorption or emission of electromagnetic radiation. The theory was introduced independently by Brian R. Judd and George S. Ofelt in 1962 [Judd, Ofelt]. This theory provides convenient tool to calculate a probability of the radiation emission and absorption process using few parameters.

The different fillings of 4f shell of RE^{3+} ions by electrons result in formation of multiple energy states of RE^{3+} ions. The energy level diagram for all lanthanides was published in [Dieke] and known as the `Dieke diagram'. Part of the Dieke diagram in the energy range 0–23 000 cm^{-1} is shown below.



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Energy levels of trivalent Rare-Earth ions

In the case of RE^{3+} ions each energy manifolds are labeled by three indexes ${}^{2S+1}L_J$, where S and L are the spin and orbital angular momenta and $J = L + S$. In this notation, the orbital quantum numbers L = 0, 1, 2, 3, 4, 5, are expressed by the capital letters S, P, D, F, G, H, I. Thus, the symbol ${}^4F_{3/2}$ shows an energy level with an orbital quantum number L = 3, a spin of S =3/2, and a total angular momentum of J = 3/2.

The Judd-Ofelt theory states that intensity of any transmission of specific ion in specific crystalline host dependence on only combination of six parameters ($U^{(2)}$, $U^{(4)}$, $U^{(6)}$ and $\Omega_{(2)}$, $\Omega_{(4)}$, $\Omega_{(6)}$), where parameters $U^{(\lambda)}$ do not depend on crystal host and calculated and tabulated for all RE ion and all transition, while Ω_λ parameters are the same for all transitions of specific ion in specific crystalline host. Most important spectroscopic parameters of radiation transitions could be expressed using liner combination of these parameters called "line strength":

$$S_{ED}(J;J') = \sum_{\lambda=2,4,6} \Omega_\lambda U^{(\lambda)} = \Omega_2 U^2 + \Omega_4 U^4 + \Omega_6 U^6$$ (eq. 6, Walsh)

In this equation the S_{ED} is line strength for transition between energy levels J and J' due to electric-dipole interaction. The definition for the line strength could be differ by e^2 [Kaminskii].

Using Judd–Ofelt theory, the probability of the spontaneous emission ($A = 1/T_{rad}, where\ T_{rad}\ is\ radiative\ lietime$) from the upper-level J' to the terminal level J could be written as

$$A(J';J) = \frac{64\pi^4 e^2}{3h(2J'+1)\bar{\lambda}^3}\left[n\left(\frac{n^2+2}{3}\right)^2 S_{ED}\right]$$ (eq.33 Walsh; eq. 4.14 Kaminski; eq. 8.3.15 Powell)

Where J'-level is initial level, and λ is mean wavelength for J'→J. In SI units this expression could be written as

$$A(J';J) = \frac{1}{4\pi\epsilon_0}\frac{64\pi^4 e^2}{3h(2J'+1)\bar{\lambda}^3}\left[n\left(\frac{n^2+2}{3}\right)^2 S_{ED}\right]$$ (eq. 1.5 Imbusch)

The relation between cross-section and line strength is useful for comparison between experimental data and theoretical calculations and could be expressed as :

$$\int_{manifold} \sigma(\lambda)\, d\lambda = \frac{8\pi^3 e^2 \bar{\lambda}}{3ch(2J\ \ +1)} \left[\frac{1}{n}\left(\frac{n^2+2}{3}\right)^2 S_{ED}\right]$$

(eq. 28 Walsh, eq. 4.15 Kaminskii, eq. 8.3.23 Powell)

The equivalent equation in SI units is

$$\int_{manifold} \sigma(\nu)\, d\nu = \frac{1}{4\pi\epsilon_0} \frac{8\pi^3 e^2 \bar{\nu}}{3ch(2J\ \ +1)} \left[\frac{1}{n}\left(\frac{n^2+2}{3}\right)^2 S_{ED}\right]$$

(eq. 1.4 Imbush.)

The expression for oscillator strength is another frequently used parameter in calculation

$$f = \frac{8\pi^2 mc}{3h\bar{\lambda}(2J'+1)} n \left(\frac{n^2+2}{3}\right)^2 S_{ED}$$

(eq. 27 Walsh, eq. 8.3.11 Powell)

However, some authors use definitions of oscillator strength without local field factor.

Example

Let's consider laser transitions of Nd^{3+} ion in YAG crystal as an example. In the most practical applications, the metastable upper laser level is $^4F_{3/2}$ while low laser levels could be one of the four manifolds ($^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, $^4I_{15/2}$). The omega parameters for Nd^{3+} ions in YAG crystal were estimated to be : $\Omega_{(2)}=0.37\times10^{-20}$ cm^2, $\Omega_{(4)}=2.29\times10^{-20}$ cm^2 , $\Omega_{(6)}=5.97\times10^{-20}$ cm^2; and tabulated $U^{(\lambda)}$ from[Kaminski] are shown in the Table.

Transition	Effective frequency (wavelength)	$U^{(2)}$	$U^{(4)}$	$U^{(6)}$	S_{ED} $\times10^{-20}$ cm^2
$^4F_{3/2} \leftrightarrow\ ^4I_{9/2}$	11530 cm^{-1} (~0.870 μm)	0	0.230	0.056	0.86
$^4F_{3/2} \leftrightarrow\ ^4I_{11/2}$	9520 cm^{-1}(~1.05 μm)	0	0.142	0.407	2.75
$^4F_{3/2} \leftrightarrow\ ^4I_{13/2}$	7520 cm^{-1} (~1.33 μm)	0	0	0.212	1.27
$^4F_{3/2} \leftrightarrow\ ^4I_{15/2}$	5450 cm^{-1} (~1.83 μm)	0	0	0.028	0.17

As one can see from the Table, the estimated line strength is largest for at $^4F_{3/2} \leftrightarrow\ ^4I_{11/2}$. In deed, the Nd:YAG laser with oscillation wavelength at 1064 nm is one of the commonly used solid state laser. The laser oscillation at 1322nm in Nd:YAG gain element is also reported in the literature, however, the line strength at this transition is approximately twice smaller. Therefore, to design a Nd:YAG laser with oscillation at 1332 nm a special precautions should be taking to the account to avoid parasitic lasing at 1064 nm .

Appendix A. Magnetic Dipole Interaction

Generally, a magnetic dipole interaction is more than an order of magnitude weaker than electric dipole interaction. However, in some cases, the contributions to a transition from both interactions should be considered. The above equations could be modified as

$$\int_{manifold} \sigma(\lambda)\, d\lambda = \frac{8\pi^3 e^2 \bar{\lambda}}{3ch(2J\quad +1)}\left[\frac{1}{n}\left(\frac{n^2+2}{3}\right)^2 S_{ED} + nS_{MD}\right]$$ (eq. 8.3.23 Powell, eq. 1-3 Rademaker)

, where S_{MD} is line strength for transition between energy levels J and J’ due to magnetic-dipole interaction.

Using equation for relation between emission cross-section and radiative life-time as

$$\int \sigma_{em}(\lambda)\, d\lambda = \frac{\bar{\lambda}^4}{8\pi c n^2 T_{rad}} = \frac{\bar{\lambda}^4}{8\pi c n^2} A$$ (eq. 234 Görller-Walrand)

, where $g_{em}(\nu)$ is line form factor with integral $\int g_{em}(\nu) d\nu = 1$, then

$$A(J';J) = \frac{64\pi^4 e^2}{3h(2J'+1)\bar{\lambda}^3}\left[n\left(\frac{n^2+2}{3}\right)^2 S_{ED} + n^3 S_{MD}\right]$$ (eq. 8.3.22 Powell, page 3 Imbusch; eq.230 Görller-Walrand; eq.13 Carnall)

*) It should be noted that in the book [eq. 33 Walsh] the factor before S_{MD} is mistyped as n^2.

The selection rules for magnetic dipole transitions are $\Delta l = 0$, $\Delta S = 0$, $\Delta L = 0$, $\Delta J = 0, \pm 1, no\ 0 \leftrightarrow 0$, $\Delta M_J(\sigma) = 0$, $\Delta M_J(\pi) = \pm 1$ [Powell, Carnall W.T(1979)]. The selection rules on $\Delta J = 0, \mp 1$ restricts consideration to the three cases [eq. 24.12-14 Carnall W.T(1979)].:

(1) $J' = J$ $\qquad S_{MD} = g\hbar[J(J+1)(2J+1)]^{1/2}$,where $g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$

(2) $J' = J - 1$ $\qquad S_{MD} = \hbar\left[\frac{(S+L+J+1)(S+L+1-J)(J+S-L)(J+L-S)}{4J}\right]^{1/2}$

(3) $J' = J + 1$ $\qquad S_{MD} = \hbar\left[\frac{(S+L+J+2)(S+J+1-L)(L+J+1-S)(S+L-J)}{4J}\right]^{1/2}$

Appendix B. Where $U^{(2)}$ *and* $\Omega_{(2)}$ *Parameters were tabled ?*

The reduced matrix elements ($U^{(2)}$) were summarized in

- The Nielson, C.W., and J.E Koster, 1963, Spectroscopic Coefficients for the pn dn and fn configurations (MI.T. Press, Cambridge, MA).
- Carnall W.T., Crosswhite H., Crosswhite H.M. Energy Level Structure and Transition Probabilities in the Spectra of the Trivalent Lanthanides in LaF3 Argonne National Lab. (ANL, Argonne, IL (United States (1978)

Some reduced matrix elements and Ω parameters for laser active transmission are summarized in [Kaminskii]. The review of the Ω parameters are presented in [Görller-Walrand]

References

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Görller-Walrand *Christiane Görller-Walrand, Koen Binnemans "Chapter 167 Spectral intensities of f-f transitions " Handbook on the Physics and Chemistry of Rare Earths, Volume 25, 1998, Pages 101-264, DOI:10.1016/S0168-1273(98)25006-9Corpus ID: 94620258*