COMPARISON BETWEEN STANDARD AND MODIFIED JUDD–OFELT THEORIES IN A Pr^{3+}-DOPED FLUORIDE GLASS

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A method which takes into account normalized oscillator strengths is detailed for the calculation of parameters in Judd–Ofelt theory (B.R. Judd, *Phys. Rev.* **127**, 750 (1962), G.S. Ofelt, *J. Chem. Phys.* **37**, 511 (1962)). In the case of a Pr^{3+}-doped fluorozirconate glass, the Judd–Ofelt parameters obtained in this way do not depend strongly on the transitions included in the fit. Particularly, it is no longer necessary to exclude the $^3H_4 \rightarrow {}^3P_2$ transition from the analysis. Three modified theories (F. Auzel, S. Hubert, P. Delamoye, *J. Lumin.* **26**, 251 (1982), A.A. Kornienko, A.A. Kaminskii, E.B. Dunina, *Phys. Status Solidi B* **157**, 267 (1990)) are also considered but do not improve the calculated intensities when the energy of the 5d level is set to its experimentally determined value. Finally, in connection with 1.3 μm amplification, the 1.3 μm reabsorption ($^1G_4 \rightarrow {}^1D_2$) oscillator strength is computed from the various models as well as the 1.3 μm emission branching ratio ($^1G_4 \rightarrow {}^3H_5 / {}^1G_4 \rightarrow {}^3H_6$). The best agreement with experiment is obtained with the standard Judd–Ofelt theory.

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1. Introduction

The Judd–Ofelt theory [1, 2] is widely used to calculate $4f$ transition intensities of rare earth ions in various hosts [3]. Its application requires the computation of three parameters Ω_2, Ω_4 and Ω_6 by a fit to a number of experimental data usually obtained by ground state absorption. These three parameters are then used to calculate the electric dipole oscillator strength between any states. Although this theory is successful for most rare earth doped materials, it is well known that its application to Pr^{3+} suffers from several problems [3]. Large deviations between calculations and experimental data are observed as well as negative Ω_2 parameters when the $^3H_4 \rightarrow {}^3P_2$ transition is included in the experimental data.

In this study, we first show that unnecessary assumptions are made during the fitting procedure and that they can be easily removed by normalizing the experimental oscillator strengths. This method avoids the exclusion of the $^3H_4 \to {}^3P_2$ transition and is then used to deal with the standard Judd–Ofelt theory as well as three modified ones. The results are applied to a Pr^{3+}-doped fluorozirconate glass which could be used as the starting material for 1.3 μm fiber amplifiers.

2. Theory

2.1. Normalized method

In the Judd–Ofelt theory, the electric dipole oscillator strength between states $|a\rangle$ and $|b\rangle$ is:

$$f_{ed} = \frac{8\pi^2 mc\sigma}{3h(2J+1)}\chi \sum_{\lambda=2,4,6} \Omega_\lambda |\langle a||U^\lambda||b\rangle|^2, \tag{1}$$

where m is the electron mass, c — the speed of light, h — Planck's constant and χ — the field correction factor ($\chi = (n^2+2)^2/9n$, where n is the refractive index). σ is the transition's wave number and $2J+1$ the degeneracy of $|a\rangle$. The doubly reduced matrix elements $\langle||U^\lambda||\rangle$ for Pr^{3+} ions can be found in Ref. [4]. The Judd–Ofelt parameters Ω_2, Ω_4 and Ω_6 are usually determined by a least square fit to a set of M experimental values. The standard least square method minimizes the so-called root mean square (RMS)

$$RMS = \sqrt{\frac{\sum_i (f_i^{exp} - f_i^{calc})^2}{M-3}}. \tag{2}$$

Equation (2) takes into account absolute differences between experimental and calculated values. A small discrepancy on a large experimental value increases the sum in Eq. (2) as much as a large error on a small oscillator strength. Therefore, the Ω_λ parameters deduced this way can depend strongly on the relative magnitude of the data included in the fit. However, the Judd–Ofelt theory is supposed to predict equally well large and small oscillator strengths and this should be considered in the fitting procedure. For this purpose, we propose to use a method which minimizes the *relative* deviation between experimental and calculated values. This is obtained by introducing the uncertainty associated with a given experimental intensity. The latter is measured by the standard deviation σ_i. The least square fit is now performed on the normalized quantities f_i^{exp}/σ_i.

$$RMS_{norm} = \sqrt{\frac{1}{M-3} \sum_i \left(\frac{f_i^{exp} - f_i^{calc}}{\sigma_i}\right)^2}. \tag{3}$$

In Sec. 3 all parameters have been computed using the normalized method.

2.2. Modified Judd–Ofelt theories

In the derivation of Eq. (1) it is assumed that the energy difference between the $4f^N$ states and the perturbing configurations is constant. It is possible to

include the energy dependent factors if the perturbing configuration is limited to $4f^{N-1}5d$ [5]

$$f_{ed} = \frac{8\pi^2 mc\sigma}{3h(2J+1)}\chi \sum_{\lambda=1,2,3,4,5,6} \left[\frac{1}{E(J)-E(4f5d)} + (-1)^\lambda \frac{1}{E(J')-E(4f5d)}\right]^2$$

$$\times \frac{[E(4f) - E(4f5d)]^2}{4} \Omega_\lambda |\langle a||U^\lambda||b\rangle|^2. \tag{4}$$

In the above equation $E(J')$ denotes the energy of the final state of the transition and $E(4f)$ is the mean energy of the 4f levels.

Another expression which takes into account the energy dependence can be found in Ref. [6]. The authors have however considered the non-orthogonality of the wave functions to get the following formula:

$$f_{ed} = \frac{8\pi^2 mc\sigma}{3h(2J+1)}\chi \sum_{\lambda=2,4,6} \Omega_\lambda |\langle a||U^\lambda||b\rangle|^2 \{1 + 2\alpha[E(J) + E(J') - 2E(4f)]\}. \tag{5}$$

The parameter α equals $(1/2)[E(4f5d) - E(4f)]$ but is considered in practice as an additional fitting parameter. Despite the different approaches between Refs. [5] and [6], it can be noted that Eq. (5) can be easily obtained as a first order development of Eq. (4) (even terms only) with respect to $[E(J) - E(4f)]/[E(4f) - E(4f5d)]$ and $[E(J') - E(4f)]/[E(4f) - E(4f5d)]$.

3. Application to Pr^{3+}-doped fluorozirconate glass

3.1. Experiments

The fluorozirconate glass used to determine the experimental oscillator strengths has the following molar composition : ZrF_4:60%, BaF_2:31%, YF_3:4%, PbF_2:2%, AlF_3:2% and LaF_3:1%. This sample is doped with 1% mol. of Pr^{3+}. The experimental oscillator strengths [7] are presented in Table I. A standard deviation σ_i of $0.025 f_i^{exp}$ is estimated for all experimental data. This roughly corresponds to an error of $\pm 2\sigma/f^{exp} = 5\%$ on the measured oscillator strengths.

3.2. Standard Judd–Ofelt theory

Table I gives the Judd–Ofelt parameters obtained by the least square fit using Eq. (1) and the normalized method. A detail of the calculated oscillator strengths is also included in Table I. It has been shown that the normalized method is much more independent of the number of equations taken into account than is the usual method. More precisely, the introduction of the $^3H_4 \rightarrow {}^3P_2$ transition does not dramatically increase the RMS_{norm} and the Ω_λ parameters (and of course the calculated oscillator strengths) are quite insensitive to this transition. Another important point is that no negative Ω_2 parameter is obtained with the normalized method.

The stable behavior of the normalized method is explained first by the proper scaling of the intensities but also because a large relative error is made on the $^3H_4 \rightarrow {}^1G_4$ and $^3H_4 \rightarrow {}^1D_2$ transitions (Table I); for this reason, adding the $^3H_4 \rightarrow {}^3P_2$ transition to the fitted data does not strongly influence the Ω_λ parameters.

TABLE I
Experimental and calculated oscillator strengths for standard and modified Judd–Ofelt theories using the normalized method. All transitions are from the ground state $^3H_4$. Ω are in units of 10^{-20} cm^2. Oscillator strengths are multiplied by 10^6.

Final level	f^{exp}	$f^{\mathrm{calc}}/f^{\mathrm{exp}}$		
		Equation (1) (even terms only)	Equation (4)	Equation (5)
$^3P_0$	2.16	1.03	1.02	1.02
$^1D_2$	1.85	0.55	0.68	0.68
$^1G_4$	0.291	0.52	0.55	0.56
$^3F_4$	2.89	1.25	1.27	1.27
$^3F_3$	5.48	1.11	1.07	1.07
$^3F_2$	3.12	1.02	1.03	1.03
Ω_2		3.3	5.7	6.2
Ω_4		3.8	3.4	3.7
Ω_6		6.1	7.9	8.4
α				1.0×10^{-5}
RMS_{norm}		16.5	14.3	14.0

TABLE II
Comparison between experimental and calculated oscillator strengths using the normalized method for selected models using parameters of Table I. Oscillator strengths are multiplied by 10^6. β is the branching ratio between $^1G_4 \rightarrow {}^3H_5$ and $^1G_4 \rightarrow {}^3H_4$ transitions.

	Judd–Ofelt Equation (1)	Judd–Ofelt with energy correction Equation (4) (even terms only)	Kornienko et al. [6] Equation (5) ($\alpha = 10^{-5}$)
$f^{\mathrm{calc}}\ {}^1G_4 \rightarrow {}^3H_5$	2.95	3.3	3.4
β^{calc}	6.0	6.7	6.9
$\beta^{\mathrm{exp}} = 8.6^a$			
$f^{\mathrm{calc}}\ {}^1G_4 \rightarrow {}^1D_2$	2.25	4.0	4.2
$f^{\mathrm{exp}} = 2^b$			

^{a}Ref. [9]. ^{b}Ref. [8].

We have calculated the oscillator strengths of the $^1G_4 \rightarrow {}^3H_5$ and $^1G_4 \rightarrow {}^1D_2$ transitions with the parameters deduced from our data set (Table II). The first transition can be stimulated at 1.3 μm and excited state absorption at the same

wavelength is possible through the second one. These transitions are therefore of considerable interest for 1.3 μm amplification in Pr^{3+}-doped fibers. The computed value (Table II) of the $^1G_4 \rightarrow {}^1D_2$ transition (2.25×10^{-6}) compares well with the experimental value of 2×10^{-6} [8]. The branching ratio β between $^1G_4 \rightarrow {}^3H_5$ and $^1G_4 \rightarrow {}^3H_4$ spontaneous emission rates is in reasonable agreement with the value measured in a fluoride fiber [9]: $\beta^{\mathrm{calc}} = 6.0$, $\beta^{\mathrm{exp}} = 8.6$.

3.3. Modified Judd–Ofelt theories

The modified Judd–Ofelt theory corresponding to Eq. (4) has been considered first with an energy correction to the even terms but without the odd ones [5]. The energy of the $4f5d$ configuration is set at 60000 cm^{-1} [10]. Although the new Judd–Ofelt parameters do not significantly modify the calculated values of the ground state absorptions included in the fit, they can lead to different intensities for a transition between excited states (like $^1G_4 \rightarrow {}^1D_2$, see Table II).

In opposition, the use of the complete Eq. (4) is much less justified: since the energy factors of the odd terms is very small, the least square fit with the six Ω_λ parameters gives unreliable results [11] (negative or very large parameters).

The last model, which has been previously used for Pr^{3+}-doped fluorozirconate glass in Ref. [12], is quite close to the first examined in Sec. 2.2. When α is set to an experimentally determined value and not let vary freely, the results obtained are very similar to those of the first modified model (Tables I, II).

Calculated oscillator strengths for the $^1G_4 \rightarrow {}^3H_5$ and $^1G_4 \rightarrow {}^1D_2$ transitions are included in Table II for the modified models, which seem to be the most consistent both with theory and experiment, i.e. the modified Judd–Ofelt theory with even terms only and the model of Ref. [6] with $\alpha = 1 \times 10^{-5}$. The values obtained this way for the $^1G_4 \rightarrow {}^3H_5$ transition are quite close to those of the standard model. Concerning the $^1G_4 \rightarrow {}^1D_2$ absorption, the best value with respect to experiment is still given by the standard model. The modified models do not predict a correct oscillator strength in this case.

4. Conclusion

We have shown that a normalized method is necessary to derive the Judd–Ofelt parameters in order to get a proper scaling of the measurements. Used together with the standard Judd–Ofelt theory for Pr^{3+}-doped fluorozirconate glass, it gives positive, stable parameters with a reduced number of equations. It also avoids the arbitrary exclusion of the $^3H_4 \rightarrow {}^3P_2$ transition from the fit and shows that other oscillator strengths are badly approximated. If reasonable values for the $4f5d$ transition are taken into account, modified theories do not improve the fit but the Judd–Ofelt parameters and the calculated intensities are modified. Concerning the $^1G_4 \rightarrow {}^1D_2$ transition, the best approximation is given by the standard model. This can be qualitatively explained by the closure procedure used in the latter model which takes into account all the perturbing configurations. The energy correction describes the $4f5d$ perturbation better but eliminates other configurations like $4fn'g$. However, to get a more precise idea of the model to be used, a larger set of experimental points should be studied, including emission data.

References

[1] B.R. Judd, *Phys. Rev.* **127**, 750 (1962).

[2] G.S. Ofelt, *J. Chem. Phys.* **37**, 511 (1962).

[3] R.D. Peacock, *Struct. Bonding* **22**, 83 (1975).

[4] M.J. Weber, *J. Chem. Phys.* **48**, 4774 (1968).

[5] F. Auzel, S. Hubert, P. Delamoye, *J. Lumin.* **26**, 251 (1982).

[6] A.A. Kornienko, A.A. Kaminskii, E.B. Dunina, *Phys. Status Solidi B* **157**, 267 (1990).

[7] F. Auzel, J. Chavignon, D. Meichenin, T. Merlet, M. Monerie, P. Sansonetti, T. Whitley, RACE-GAIN R 2018 EC contract, deliverable WP3.2N.9, *Report on the detailed spectroscopy of praseodymium*, June 1993, unpublished.

[8] R.S. Quimby, W.J. Miniscalco, *J. Appl. Phys.* **75**, 613 (1994).

[9] S.C. Fleming, T.J. Whitley, R. Wyatt, *Electron. Lett.* **29**, 590 (1993).

[10] G.H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals*, John Wiley &Sons, New York 1968, p. 52.

[11] P. Goldner, F. Auzel, *J. Appl. Phys.* (1996), in press.

[12] J.A. Medeiros Neto, D.W. Hewak, H. Tate, *J. Non-Cryst. Solids* **183**, 201 (1995).