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Parametrization of 5f-5f Transition Probabilities Between Stark Levels of U^{3+} in $LiYF_4$

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Abstract. — In order to simulate intensities of the 5f-5f transitions of U^{3+} in $LiYF_4$, we applied the Judd-Ofelt theory. Because of the large crystal-field splitting of the J -multiplets in the actinides, a set of phenomenological intensity parameters $B_{\lambda k q}$ is introduced to describe the transition probabilities between the crystal-field sublevels of U^{3+} . The intensities of the absorption transitions between the crystal field levels calculated and a set of six phenomenological intensity parameters give a rather good simulation of the experimental intensities, and the applicability of the Judd-Ofelt theory is discussed for the 5f \rightarrow 5f transitions of the actinides. From these values, the oscillator strengths between the excited states involved in the laser transition ${}^4I_{11/2} \rightarrow {}^4I_{9/2}$ are calculated and the corresponding radiative lifetime is compared to the experimental one. Moreover, a comparison between the actinide ion U^{3+} ($5f^3$) and the lanthanide ions Nd^{3+} ($4f^3$) and Er^{3+} ($4f^{11}$) in $LiYF_4$ is made.

1. Introduction

Up to now, most of the published intensity data [1–6] deal with a simulation of the f-f transition intensity between J -multiplets for the rare-earth ions doped in a host material. The electronic transition intensities are interpreted in terms of magnetic dipole and induced electric dipole mechanism [7]. The magnetic dipole transitions (MD) are allowed between states of the same parity, i.e., within the same configuration and their intensities are calculated directly from the eigenvectors of the initial and final states, obtained from the crystal-field analysis. On the contrary, the electric dipole transitions are forbidden by the Laporte selection rules and are explained by the mixing of the opposite parity states with the f-state, due to the crystal-field interaction. The Judd-Ofelt theory [8, 9] is used to simulate the probabilities of the induced electric dipole transitions (ED) between J -multiplets. In this way, three phenomenological parameters Ω_λ ($\lambda = 2, 4, 6$) are necessary to describe the intensity of the transitions involved in this electric dipole mechanism. This theory usually gives a good simulation of the experimental intensities for the lanthanides. However, in the case of Pr^{3+} ($4f^2$), Peacock [10] has shown that negative values have been found sometimes for the Ω_λ parameters. This is rather not

consistent with Judd's theory, which requires positive values. The set of the Ω_λ parameters is inconsistent with the experimental intensities. This discrepancy is ascribed to the proximity of the 5d configuration which makes the approximations made in the Judd-Ofelt theory no longer valid.

On the other hand, few published studies [11, 12] deal with the intensity of the 5f-5f transitions. Carnall *et al.* [7] show that the oscillator strengths of $\text{An}^{3+}(\text{aquo})$ bands tend to be greater by a factor of 10-100 than those observed for the lanthanides and systematic treatment of the band intensities for An^{3+} spectra could be successfully carried out with only Ω_4 and Ω_6 . Auzel *et al.* [11] calculated the absolute oscillator strengths of $5f^2$ transitions of U^{4+} in ThBr_4 and in an aqueous solution between J -multiplets. They were found to be two orders of magnitude larger than those for $4f \rightarrow 4f$ transitions. However, as in the case of $4f^2$ configuration lanthanide, a similar discrepancy occurs for some of the transitions studied and a negative value is found for Ω_6 . In order to take into account the proximity of the 6d configuration, the authors introduce the odd λ matrix elements in the calculations and variable energy denominator with respect to a degenerate 6d configuration. However this correction did not improve the fit.

For trivalent actinides, the crystal-field strength is about twice larger for the 5f ions than for the 4f ones [13, 14] and the crystal-field effect cannot be neglected. Then, we must consider the transitions between Stark levels. Recently, phenomenological intensity parameters $B_{\lambda k q}$ have been used to simulate the electric dipole intensities of the 4f-4f transitions between Stark levels [15, 17]. The results obtained, for some lanthanides doped in a host material [18-21], give a reasonable simulation of the experimental transition intensities. But, as far as we know, no calculation for the transitions between the 5f Stark levels has carried out.

The subject of this study consists of simulating intensities of the 5f-5f transitions between crystal field components for U^{3+} ($5f^3$) in LiYF_4 . Recently, U^{3+} -doped LiYF_4 has been studied for its laser action at $2.83 \mu\text{m}$ [22, 23] and a crystal-field analysis permits the energy level structure of U^{3+} in LiYF_4 to be obtained [14]. The experimental intensities are determined from the α -polarized and unpolarized absorption spectra at low temperature. Using the Judd-Ofelt theory, the intensities of induced electric dipole absorption transitions have been calculated. A set of six phenomenological $B_{\lambda k q}$ parameters, giving a good simulation of the experimental data, has been determined. The validity of the Judd-Ofelt theory for $5f^3$ configuration is discussed.

Moreover, we compare the intensities of U^{3+} ($5f^3$) with those of some lanthanide ions such as Nd^{3+} ($4f^3$) and Er^{3+} ($4f^{11}$), in the same host crystal, which also present laser emission in the IR region.

2. Experimental

2.1. EXPERIMENTAL SET UP. — The LiYF_4 single crystals doped with U^{3+} were grown by the Czochralski method, as described elsewhere [22, 23]. The U^{3+} concentration was determined by HF-induced plasma emission spectrometry.

Unpolarized absorption spectra of LiYF_4 doped with 350 ppm of U^{3+} were recorded at 10 K on a Cary 17 double beam spectrophotometer from 800 to 2400 nm, using a cryogenic cryostat.

The lifetime of the emitting $^4I_{11/2}$ Stark level was measured with a multichannel analyzer (Wave form digitizer CAMAC M2256) coupled with LECROY 3500 computer.

2.2. OSCILLATOR STRENGTHS MEASUREMENTS. — The optical absorption spectrum has been described in reference [14] where the experimental energy levels are given.

The experimental oscillator strengths f_e , are determined from the integration of the low temperature absorption lines, following this relation:

$$f_e = \frac{m c_0^2}{N e^2 \pi \chi} \int \alpha(\nu) d\nu$$

Where m and e are the mass and the charge of the electron, χ is the local field correction depending on the refractive index, c_0 is the vacuum velocity of the light, N is the number of active ions per cm^3 , α the absorption coefficient and ν the wavenumber. Since the population of the first excited state of $^4I_{9/2}$ multiplet, already determined at 257 cm^{-1} [14], is negligible at 10 K, the absorption occurs mainly from the ground state.

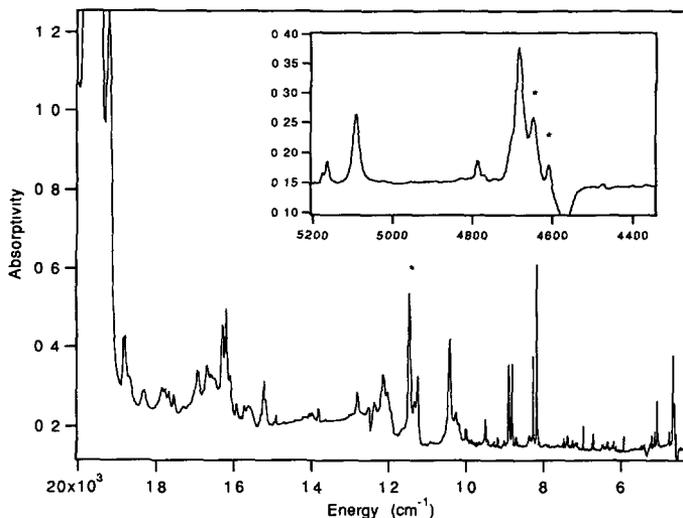


Fig. 1 — Unpolarized absorption spectrum at 10 K between $20\,000$ and 4350 cm^{-1} (*): lines not taken into account in the calculation)

To overcome the difficulties of measuring absolute intensities, only the lines in the IR region between 850 (11760 cm^{-1}) and 2200 nm (4540 cm^{-1}), which are the most isolated in comparison with the lines in the visible, are taken into account. Nevertheless, for some lines observed in the IR, the determination of the peak area is rather approximate because of the large overlap with other lines (see Fig 1).

3. Theoretical

The theoretical oscillator strength f_t , for a transition between an initial $\langle i |$ and final $| f \rangle$ crystal-field level can be obtained by the relation:

$$f_t = \frac{8\pi^2 m c_0 \sigma}{3 h e^2 g} \left(\frac{(n^2 + 2)^2}{9n} |\langle i | P_{ED} | f \rangle|^2 + \frac{h^2 n}{16\pi^2 m^2 c^2} |\langle i | P_{MD} | f \rangle|^2 \right)$$

where g represents the degeneracy of the sublevels ($g = 2$ for f^3 configuration, following Kramer's theorem) and σ is the energy of the transition.

$\langle i|P_{ED}|f \rangle$ represents the ED operator matrix element between the initial and final state.

$\langle i|P_{MD}|f \rangle$ is the MD operator matrix element between initial and final state, which is calculated following this relation.

$$\langle i|P_{MD}|f \rangle = \sum_{\substack{\alpha SLJM \\ \alpha' S' L' J' M'}} a_{\alpha, S, L, J, M} a_{\alpha', S', L', J', M'} \\ \times (-1)^{J-M} \begin{pmatrix} J & 1 & J' \\ -M & \rho & M' \end{pmatrix} \langle 5f^n, \alpha, S, L, J, |L + 2S| 5f^n, \alpha', S', L', J' \rangle$$

In D_{2d} symmetry, the crossing term is neglected and the relation is simplified as follows [24]:

$$f_f = \frac{8\pi^2 m c_0 \sigma}{3 h e^2 g} \left(\frac{(n^2 + 2)^2}{9n} |\langle i|P_{ED}|f \rangle|^2 + \frac{h^2 n}{16\pi^2 m^2 c^2} |\langle i|P_{MD}|f \rangle|^2 \right)$$

The oscillator strength between crystal field components corresponding to the electric dipole transition is given by equation (1):

$$\langle i|P_{ED}|f \rangle = -e \sum_{\substack{\alpha SLJM \\ \alpha' S' L' J' M'}} a_{\alpha SLJM} a_{\alpha' S' L' J' M'} \\ \sum_{\lambda, k, q} (-1)^{\rho+q+\lambda+L'+S-M+2J} [J, J']^{1/2} [\lambda] \begin{pmatrix} 1\lambda & k \\ \rho - (q + \rho) & q \end{pmatrix} \begin{pmatrix} J & \lambda & J' \\ M & q + \rho & M' \end{pmatrix} \left\{ \begin{matrix} J & J' & \lambda \\ L' & L & S \end{matrix} \right\} \\ A_q^k \Xi(k, \lambda) \langle 5f^n \alpha SL || U^\lambda || 5f^n \alpha' S' L' \rangle$$

where A_q^k is the crystal field parameters, $\langle 5f^n \alpha SL || U^\lambda || 5f^n \alpha' S' L' \rangle$ is the reduced matrix element and

$$\Xi(k, \lambda) = 2 \sum_{n', \ell'} [\ell, \ell'] (-1)^{\ell+\ell'} \begin{Bmatrix} 1 & \lambda & k \\ \ell & \ell' & \ell \end{Bmatrix} \begin{pmatrix} \ell & 1 & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \frac{\langle n\ell|r|n'\ell' \rangle \langle n\ell|r^k|n'\ell' \rangle}{\Delta E}$$

Here, r and r^k are the radial integrals and ΔE is an average energy $\Delta E = E_{5f} - E_\Psi$. E_{5f} is the energy of the considered state and E_Ψ , the energy of the opposite parity configuration state.

The terms A_q^k and Ξ are difficult to evaluate. A_q^k depends on the position of the atoms in the crystal. In the case of doped crystal, the accurate position of the atoms surrounding the U^{3+} impurities is difficult to calculate, and the radial integral part cannot be easily estimated in the crystal. Then, the product ($A_q^k \cdot \Xi$) is usually considered as a phenomenological intensity parameter, which is written as $B_{\lambda k q}$.

In a previous paper [14], the complete $5f^3$ configuration of U^{3+} in $LiYF_4$ has been diagonalized by using the free ion and the crystal-field Hamiltonians. This crystal-field analysis gives a rather good correlation between the calculated and the experimental energy levels. Then the composition of the eigenfunctions associated with each crystal field component was used in these intensity calculations. On the other hand, as in the crystal-field parametrization, all the calculations have been performed in D_{2d} and in S_4 symmetry, corresponding to the real U^{3+} site. The calculation in S_4 shows that we can neglect the effect of the imaginary part,

assuming that D_{2d} is a good approximation for the S_4 symmetry. Therefore, six non-zero $B_{\lambda k q}$ are necessary: B_{232} , B_{652} , B_{432} , B_{672} , B_{452} and B_{676} .

At last, to save space, relation (1) can be reduced to its lowest term [18]:

$$|\langle i|P_{ED}|f\rangle|^2 = \left[\sum_{\lambda k q} a_{\lambda k q} B_{\lambda k q} \right]^2$$

Here, $B_{\lambda k q}$ are the intensity parameters and $a_{\lambda k q}$ contains the reduced matrix element, 3- j and 6- j symbols.

4. Results and Discussion

The values of the intensity parameters $B_{\lambda k q}$ are obtained by fitting the calculated oscillator strengths to the experimental ones determined from both unpolarized and α -polarized absorption spectra at low temperatures.

The initial values of $B_{\lambda k q}$ introduced in the calculation were about twice those obtained for Nd^{3+} in $LiYF_4$ [19], according to the larger radial extension of the 5f orbital compared to the 4f one. On the other hand, the ratio B_{672}/B_{676} depending mainly on the lattice parameters can be considered as constant whatever the ion considered. Then the value used for this ratio was close to that obtained for Nd^{3+} in $LiYF_4$.

After several iterations, convergence of the intensity parameters is obtained by minimizing the function

$$F = \sum \left(\frac{\sqrt{f_e} - \sqrt{f_t}}{\sqrt{f_e} + \sqrt{f_t}} \right)^2$$

using 19 experimental data from the unpolarized and α -polarized spectra. The set of the $B_{\lambda k q}$ parameters is given in Table I with a quadratic error of 0.3. These intensity parameters are then used to calculate the oscillator strengths for transitions originating from the ${}^4I_{9/2}$ crystal field ground level. All the results are summarized in Table II. This set of intensity parameters gives a rather good simulation except for three values corresponding to the transitions at 4607, 4645 and 11454 cm^{-1} , for which a large discrepancy occurs between experimental and calculated oscillator strengths. They were not taken into account in the calculation (see Tab. II). However, the deviation between the calculated and the experimental intensities has

Table I. — *Intensity parameters for $LiYF_4:U^{3+}$.*

B_{232}	3.33×10^{-9} cm
B_{432}	4.50×10^{-9} cm
B_{452}	0.27×10^{-9} cm
B_{652}	-3.94×10^{-9} cm
B_{672}	1.91×10^{-9} cm
B_{676}	-0.29×10^{-9} cm

$$\Delta = 0.3$$

Table II. — Experimental and calculated oscillator strengths for transitions originating from the $^4I_{9/2}$ crystal field ground level of U^{3+} in $LiYF_4$.

Transitions $^4I_{9/2} \rightarrow$	λ (μm)	energy transition (cm^{-1})	Isotropic (10^{-5})		α Polarized (10^{-5})	
			f_{exp}	$f_t = f_{\text{ED}} + f_{\text{MD}}$	f_{exp}	$f_t = f_{\text{ED}} + f_{\text{MD}}$
$^4I_{11/2}$	2.23	4473	0.090	0.080	0.088	0.120
$^4I_{11/2}$	2.17	4607	0.070*	4.187	0.039	0.030
$^4I_{11/2}$	2.15	4645	0.363	0.608	0.178*	0.912
$^4I_{11/2}$	1.96	5085	3.556	6.467	0.230	0.169
$^4I_{13/2}$	1.22	8160	1.013	0.642	0.622	0.429
$^4I_{13/2}$	1.13	8816	0.635	1.019	0.377	0.354
$^4I_{13/2}$	1.12	8896	1.469	0.654	1.133	0.981
$^4F_{5/2} + ^4G_{5/2}$	0.96	10409	1.106	0.935	0.538	0.481
$^4G_{5/2} + ^4F_{5/2}$	0.95	10450	1.892	1.116	0.649	1.674
$^4I_{15/2} + ^4G_{5/2}$	0.88	11283	0.679	1.288	0.504	1.932
$^4G_{5/2} + ^4F_{7/2}$	0.87	11454	2.276	5.356	0.908*	6.726

* Transitions not taken into account in the calculations.

to be carefully examined because different multiplets can slightly overlap and then introduce inaccuracy in the surface integration, all the more so since the $B_{\lambda k q}$ determination involves a non-linear fitting.

As pointed out in the introduction of this paper, the validity of the Judd-Ofelt theory for 5f transitions between Stark level should be discussed with regard to the proximity of the f-d transitions. As a matter of fact, it is well-known that, in the actinide, the energy of the ground electronic state in the $5f^{n-1}6d$ configuration is considerably lower than that of the corresponding $4f^{n-1}5d$. Particularly in the case of the $5f^3$ configuration the lowest energy $5f^26d$ occurs around 20000 cm^{-1} . The proximity of the 6d band to the 5f ones can cause a breakdown of the validity of the approximations of the Judd-Ofelt theory for the electric dipole transition between Stark levels. This theory shows that the matrix element of the transitions

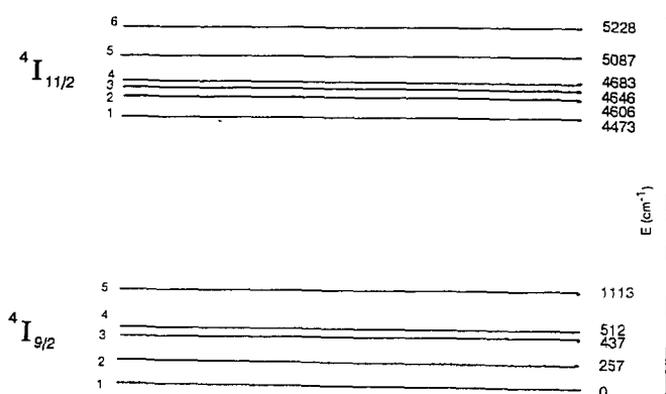


Fig. 2. — Stark levels for ${}^4I_{9/2}$ and ${}^4I_{11/2}$ multiplets.

Table III. — Oscillator strengths and spontaneous emission probability between ${}^4I_{11/2}$ and ${}^4I_{9/2}$.

Transition ${}^4I_{11/2} \rightarrow {}^4I_{9/2}$	Energy (cm^{-1})	Wavelength (μm)	ft ($\times 10^{-5}$)	A_i (s^{-1})
	3361	2.97	0.074	16.0
from 4474 cm^{-1}	3962	2.52	2.031	597.9
Stark level	4037	2.47	2.917	900.4
	4216	2.37	0.899	287.6
	4474	2.23	0.080	30.1

can be written as:

$$\langle i | PED | f \rangle = - \sum_{\substack{\alpha SLJM \\ \alpha' S' L' J' M'}} a_{\alpha SLJM} a_{\alpha' S' L' J' M'} \times \left\{ \frac{\langle 5f^n \alpha SLJM | P_p^{(1)} | \psi \rangle \langle \psi | H_C^{odd} | 5f^n \alpha' S' L' J' M' \rangle}{E_{5f^n \alpha SLJM} - E_\psi} + \frac{\langle 5f^n \alpha SLJM | H_C^{odd} | \psi \rangle \langle \psi | P_p^{(1)} | 5f^n \alpha' S' L' J' M' \rangle}{E_{5f^n \alpha' S' L' J' M'} - E_\psi} \right\}$$

where $\sum_{\alpha SLJM} |5f^n \alpha SLJM \rangle$ and $\sum_{\alpha' S' L' J' M'} |5f^n \alpha' S' L' J' M' \rangle$ are the eigenfunctions of the ground and excited state crystal field level. The terms $E_{5f^n \alpha SLJM}$ and $E_{5f^n \alpha' S' L' J' M'}$ are the corresponding energy. $|\psi \rangle$ is the eigenfunction and E_ψ the energy of the opposite parity $5f^{n-1}6d$ configuration. The crystal field is considered, here, as a first order perturbation necessary to mix another opposite parity into the $5f^n$ configuration. This equation can not be used in this form, then one way to simplify this expression is to use the approximation made by Judd. The configuration having opposite parity is usually considered as degenerate and the transitions $5f^n \rightarrow 5f^{n-1}6d$ are much higher than the $5f \rightarrow 5f$ ones. Consequently, the terms $(E_{5f^n \alpha SLJM} - E_\psi)$ and $(E_{5f^n \alpha' S' L' J' M'} - E_\psi)$ can be replaced by an average energy

denominator ΔE .

These assumptions lead to obtain relation (1), used in this study. But these approximations may no longer be valid in the case of $\text{LiYF}_4:\text{U}^{3+}$, where the 5f-6d transitions occurs from 20000 cm^{-1} . Then they are near the top of the 5f levels, and cannot be neglected compared to the f-f transition energies. Moreover, they extend from 20000 cm^{-1} to 33000 cm^{-1} and the term E_ψ cannot be considered as constant.

Nevertheless, despite the 6d configuration proximity, the simulation of the electric dipole intensities, using this theoretical approach is rather good. This result corroborates the calculations made by Auzel *et al.* [11] on $\text{U}^{4+}:\text{ThBr}_4$, who showed that the 5f-6d proximity corrections do not modify the oscillator strength calculations. Krupke [3] has pointed out that the use of excited $4f^{n-1}g$ configurations describes the observed intensities better than the excited $4f^{n-1}5d$. Since the g-state is close to the ionization limit, the assumptions made in the Judd-Ofelt theory remain valid. Therefore, this study shows that the excited $5f^26d$ configuration seems to contribute weakly in the parity mixing with f^3 configuration.

One way to check the validity of the intensity parameters is the comparison between theoretical intensity and other experimental data not used in the calculation. For example, the radiative lifetime τ_0 can be calculated from the following expression:

$$\tau_0 = \frac{1}{\sum_i A_i}, \text{ where } A_i = \frac{g_2}{g_1} \frac{8\pi^2 e^2 \chi f_i}{m c_0 \lambda_0^2}$$

Then, the experimental lifetime of an emitting level measured at 10 K can be compared with the calculated radiative lifetime.

From the $B_{\lambda k q}$ parameters, we calculate the oscillator strengths between the lowest emitting Stark level (at 4474 cm^{-1}) of $^4\text{I}_{11/2}$ and all the $^4\text{I}_{9/2}$ Stark levels (see Fig. 2). Then the corresponding spontaneous emission probabilities A_i are deduced in Table III.

The radiative lifetime obtained is $\tau_0 = 540\ \mu\text{s}$. This value is of the same order of magnitude as the experimental lifetime of the lowest Stark level of the $^4\text{I}_{11/2}$ multiplet measured at 10 K ($\tau = 400\ \mu\text{s}$). The good agreement between the theoretical approach and the observed values

Table IV. — Values of $B_{\lambda k q}$ parameters for U^{3+} and some lanthanides in LiYF_4 .

$B_{\lambda k q}$ (* 10^9 cm)	U^{3+}	Nd^{3+} [19]	Er^{3+} [21]
B_{232}	3.33	0.15	-0.12
B_{432}	4.50	-0.03	-0.14
B_{452}	0.27	-0.05	-0.05
B_{652}	-3.94	-0.19	-0.02
B_{672}	1.91	0.32	0.01
B_{676}	-0.29	-0.07	0.03
r.m.s	0.3		0.33

Table V. — Oscillator strengths in the IR region, for U^{3+} and Er^{3+} in $LiYF_4$.

Wavelength (μm)	f ($\cdot 10^{-5}$) U^{3+}	Wavelength (μm)	f ($\cdot 10^{-6}$) Er^{3+}
$4I_{11/2} \rightarrow 4I_{9/2}$		$4I_{11/2} \rightarrow 4I_{13/2}$	
2.15 (3 \rightarrow 1)	0.608	2.66 *	0.16
2.23 (1 \rightarrow 1)	0.080	2.67	0.46
2.27 (3 \rightarrow 1)	0.002	2.71 *	0.13
2.36 (3 \rightarrow 3)	0.093	2.75	0.16
2.37 (1 \rightarrow 2)	0.899	2.77	0.18
2.43 (3 \rightarrow 4)	1.447	2.79	0.31
2.46 (1 \rightarrow 3)	2.917	2.81 *	0.04
2.54 (1 \rightarrow 4)	2.031	2.82	0.13
2.83* (3 \rightarrow 5)	0.008	2.86	0.36
2.97 (1 \rightarrow 5)	0.074	2.87	0.10

* lasing transition

indicates that the $B_{\lambda k q}$ parameters are reliable. The small discrepancy between experimental and calculated values is probably due to a weak non radiative contribution to the total decay.

Up to now, the intensity parameters $B_{\lambda k q}$ and the oscillator strengths have been determined only for lanthanide ions such as Nd^{3+} , Er^{3+} and Eu^{3+} in $LiYF_4$. Then, it is interesting to compare these values with those obtained in our study. The results are given in Tables IV and V.

Compared to the isoelectronic lanthanide ion Nd^{3+} , the $B_{\lambda k q}$ parameters for U^{3+} are larger by about one order of magnitude. However compared to other rare earth ions such as Er^{3+} [21] used for IR laser in the same range as U^{3+} , the intensity parameters and the oscillator strengths are larger by about two orders of magnitude. This trend is mainly due to the increase of $\Xi(k, \lambda)$ because of the larger spatial extension of the 5f orbitals compared to the 4f ones. In this way, the results obtained are consistent with the expected ones.

5. Conclusion

To the best of our knowledge, it is the first time that calculations of intensity transitions between Stark levels for a 5f ion, have been carried out with the use of $B_{\lambda k q}$. These parameters allow a good correlation between calculated and observed transition probabilities. This shows that the Judd-Ofelt theory is able to simulate the 5f intensity transitions between Stark levels. The proximity of the 5f6d configuration does not seem to introduce any errors in the applicability of the Judd-Ofelt theory.

The radiative lifetime of the lowest emitting Stark level of the $4I_{11/2}$ multiplet calculated from these intensity parameters is consistent with the experimental data, showing the reliability of the theoretical model. On the other hand, the comparison between lanthanide and actinide ions indicates, as expected, that the oscillator strengths of U^{3+} are 50 to 100 times larger than the isoelectronic rare-earth ones.

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