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Third-order contributions to the $^7F_0 \rightarrow {}^5D_2$ two-photon transition of Eu^{3+} in a cubic lattice

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Abstract

The relative intensities in two polarization directions of the incident radiation, and the line strengths of the $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g} transitions of Eu^{3+} in the cubic crystal host Cs_2NaYF_6 have been calculated using the third-order Judd–Pooler (JP) formalism. The calculated relative intensities are in semiquantitative agreement with experiment, and in good agreement with the results of the direct calculation. The ratio of the line strengths of the $\Gamma_{1g} \rightarrow \Gamma_{3g}$ transition from the JP and direct calculations is similar for the cases when the initial and final states are assumed to be pure to that when the multiplets with spin–orbit admixtures are included in the initial and final states. The ratio assumes the correct order of magnitude when the intermediate-state barycentre energy is lowered from the formal Judd–Ofelt–Axe value to a physically intuitive one.

1. Introduction

The theory of two-photon transitions was formulated by Axe [1] using the conventional Judd–Ofelt (JO) closure approximation [2, 3] in second-order perturbation theory, by coupling the two electric dipole operators into an effective operator acting between same-parity initial and final states. Further developments were initiated by Judd and Pooler (JP) [4] who used second-quantization techniques and constructed the transition operator for a two-photon process connecting states of different spin multiplicity. Later, Downer [5, 6] extended JP theory to higher-order analysis by including the crystal field interaction acting on the intermediate 5d electronic states to explain the two-photon transitions forbidden by SLJ selection rules.

Recently, we have theoretically investigated the transition line strengths and relative intensities of the $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g} and $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$, a Γ_{5g} two-photon transitions of Eu^{3+} in the cubic Cs_2NaYF_6 host [7]. In the direct evaluation of transition line strengths of these four transitions, we found that, for $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g}, the calculated

relative intensities of the two transitions were in reasonable agreement with experiment, and the neglect of J-mixing in the initial state had only a small effect upon the calculation. For the $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}, \Gamma_{5g}$ transitions, satisfactory agreement of calculation with experiment was obtained by using $4f^5$ crystal field states instead of the $4f^5$ free-ion states in constructing the intermediate states.

Our intention in making the present study was to show that TPA intensity calculations for lanthanide ions doped into cubic hosts are at least semiquantitative in accuracy. It is also of interest to undertake a calculation of transition intensities using the JO closure approximation in order to compare both the calculated relative and absolute intensities with those of direct calculations. It is noted that the results calculated using the closure approach have usually only been used for the investigation of *relative* and not *absolute* intensities. In the present study, a calculation has been performed for the $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}, \Gamma_{3g}$ two-photon transitions of Eu^{3+} in the Cs_2NaYF_6 host crystal, using the JP third-order formalism with the JO closure approximation. Since for these two transitions results of experiment [8] and direct calculation [7] are both available, the JP-calculated relative transition intensities are compared with those from experiment and direct calculation. In particular, by comparison of absolute intensities for transitions between the closure and direct calculations, the influence of the barycentre energy of the intermediate configuration upon the absolute transition intensities can be considered in some detail.

2. Judd–Pooler formalism

For the two-photon transitions under investigation, the matrix element M_{JP} connecting the initial state $|\Gamma_i\gamma_i\rangle$ to the final state $|\Gamma_f\gamma_f\rangle$ can be expressed using the JP third-order formalism [4]:

$$M_{JP} = \sum_{m,n} \frac{\langle\Gamma_i\gamma_i|\varepsilon\cdot D|m\rangle\langle m|H_{SO}|n\rangle\langle n|\varepsilon\cdot D|\Gamma_f\gamma_f\rangle}{\Delta E_m\,\Delta E_n}, \tag{1}$$

where H_{SO} is the spin–orbit operator, and the summation is over all the intermediate states $|m\rangle$ and $|n\rangle$.

The TPA transition line strength can be expressed as

$$S_{\Gamma_i\rightarrow\Gamma_f} = \sum_{\gamma_i,\gamma_f} |M_{\Gamma_i\gamma_i\rightarrow\Gamma_f\gamma_f}|^2. \tag{2}$$

To simplify the calculation, JP applied the JO closure approximation twice and coupled the two electric dipole operators and spin–orbit operator into a single effective operator H_{eff}. The matrix element of equation (1) then becomes

$$(\Delta E_{\rm fd}^{-1})^2\langle\Gamma_i\gamma_i|H_{eff}|\Gamma_f\gamma_f\rangle, \tag{3}$$

where $\Delta E_{\rm fd}$ is the energy separation between the barycentres of the intermediate and ground configurations, but is usually taken as the gap from the lowest state of the ground configuration to the excited configuration barycentre.

Ceulemans and Vandenberghe [9] made some minor changes to the expression for the effective operator derived by JP. The master expression for the spin–orbit part of the third-order mechanism consists of three terms, written as [9]

$$-(2l+1)(2l'+1)\langle nl|r|n'l'\rangle^2 \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \Delta E_{ll'}^{-2}$$
$$\times \left[-\xi_l(l(l+1)(2l+1))^{1/2}\sum_t \begin{Bmatrix} 1 & l & l' \\ l & 1 & t \end{Bmatrix} (\varepsilon\varepsilon)^{(0t)}\cdot(a^+a)^{(0t)t}(a^+a)^{(11)0}\right.$$

$$+ \xi_l(2)^{-1/2}(l(l+1)(2l+1))^{1/2} \sum_{t,k} \begin{Bmatrix} 1 & l & l' \\ l & 1 & t \end{Bmatrix} \begin{Bmatrix} t & l & l \\ l & 1 & k \end{Bmatrix}$$
$$\times (-1)^{k+1}(2k+1)^{1/2}(\varepsilon\varepsilon)^{(0t)} \cdot (a^+a)^{(1k)t}$$
$$+ \xi_{l'}(2)^{-1/2}(l'(l'+1)(2l'+1))^{1/2} \sum_{t,k} \begin{Bmatrix} 1 & l & l' \\ 1 & l & l' \\ t & k & 1 \end{Bmatrix}$$
$$\times (-1)^{k+1}(2k+1)^{1/2}(\varepsilon\varepsilon)^{(0t)} \cdot (a^+a)^{(1k)t} \Bigg], \tag{4}$$

where l and l' refer to the 4f and 5d shells, respectively. The second-quantization operators a^+ and a create and annihilate the $4l+2$ states of an l-electron ($l = 3$). The transition dipoles reach intermediate states of $l^{N-1}l'$ configurations at an energy distance $\Delta E_{ll'}$ ($l' = 2$). The electric vector of the radiation field is written as the tensor quantity $\varepsilon^{(01)}$.

Clearly, the first term of equation (4) consists of a simple product of the spin–orbit coupling operator $(a^+a)^{(11)0}$ acting on the states of the l-shell and the operator $(a^+a)^{(0t)t}$. In the remaining two terms the spin–orbit coupling operator and the two-photon operator are merged into an effective operator of the form $(a^+a)^{(1k)t}$. The two labels in the bracket $(1k)$ identify the rank of the spin and orbit operator, respectively. In this way a two-photon process can link states that differ by three units of angular momentum, provided that the transition is accompanied by a $\Delta S = 1$ spin change. The final term takes into account the effect of spin–orbit coupling in the l'-shell. The numerical values of 3-j, 6-j symbols up to a certain rank are available in [10]. All other 3-j, 6-j, and 9-j symbols can be calculated from relations given in [11].

In general, the scalar product of two tensors is defined as [12]

$$T^{(t)} \cdot U^{(t)} = \sum_m (-1)^m T^{(t)}_m U^{(t)}_{-m}. \tag{5}$$

All tensors in equation (4) are expressed as scalar products of an electronic part and a so-called physical part [13]. This physical part involves the coupling of the two ε-tensors. In what follows, we will calculate these two parts separately and combine them to yield the total transition matrix element.

2.1. Electronic part

As described above, the change of electronic state is caused by the one-electron operators $(a^+a)^{(0t)t}(a^+a)^{(11)0}$ and $(a^+a)^{(1k)t}$ in equation (4). The matrix elements of these operators constitute the electronic part of the total transition matrix element. Before considering these matrix elements in some detail, the actual nature of the ground and final states must be examined. Quantitative calculations of Eu^{3+} free-ion energy levels using Reid's f-shell empirical programs and the input parameters reported by Thorne [8] indicate that $^7F_0$ and $^5D_2$ are fairly pure Russell–Saunders multiplets. The ground level consists of 93% of $^7F_0$ and some 7% of $^5D_0$. The excited level comprises $^5D_2$ (92%), with small admixtures mainly of $^7F_2$ (3%) and $^5F_2$ (1%). Possible contributions from these additional multiplet terms will be commented on later. Here we will restrict the treatment to the unperturbed $^7F_0$ and $^5D_2$ multiplets. In the f^6 configuration there are three ^5D states, which are denoted by $^5D_1$, $^5D_2$ and $^5D_3$. Judd [12] has shown that the lowest in energy of these states can be expressed as linear combinations of these three ^5D basis states:

$$|5D\rangle = -0.607|^5D_1\rangle - 0.196|^5D_2\rangle + 0.77|^5D_3\rangle. \tag{6}$$

In the present section the TP transition rate will be calculated for all three ^5D basis states, and these results will be combined to yield the transition matrix element of the lowest ^5D state.

The $(^7F_0)\Gamma_{1g}$ and $(^5D_2)\Gamma_{5g}$, Γ_{3g} wavefunctions under consideration are easily projected out of the $J = 0$ and 2 manifolds using the cubic subduction relations. Following Griffith [14], one has

$$\begin{aligned}
&\langle {}^7\mathrm{F}_0, \Gamma_{1g}| = \langle 0, 0| \\
&|{}^5\mathrm{D}_2, \Gamma_{3g}\theta\rangle = |2, 0\rangle \\
&|{}^5\mathrm{D}_2, \Gamma_{3g}\varepsilon\rangle = \frac{1}{\sqrt{2}}|2, 2\rangle + \frac{1}{\sqrt{2}}|2, -2\rangle \\
&|{}^5\mathrm{D}_2, \Gamma_{5g}1\rangle = |2, 1\rangle \\
&|{}^5\mathrm{D}_2, \Gamma_{5g}0\rangle = \frac{1}{\sqrt{2}}|2, 2\rangle - \frac{1}{\sqrt{2}}|2, -2\rangle \\
&|{}^5\mathrm{D}_2, \Gamma_{5g}-1\rangle = |2, -1\rangle.
\end{aligned} \tag{7}$$

These expressions allow one to relate the $\Gamma_{1g} \rightarrow \Gamma_{3g}$ and $\Gamma_{1g} \rightarrow \Gamma_{5g}$ transition matrix elements $M_{\Gamma_i\gamma_i\rightarrow\Gamma_f\gamma_f}$ in equation (2) to the following standard $M_J \rightarrow M_{J'}$ transition elements in equation (8). The general form of the one-electron operator matrix element is given by Judd [12, 15]:

$$\begin{aligned}
\langle l^N \eta S L J M_J|(a^+a)^{(\kappa k)t}_{-m}|l^N\eta' S' L' J' M'_J\rangle &= -(-1)^{J-M_J} \\
&\times \begin{pmatrix} J & t & J' \\ -M_J & -m & M'_J \end{pmatrix} \langle l^N \eta S L J||W^{(\kappa k)t}||l^N\eta' S' L' J'\rangle \\
&= -(-1)^{J-M_J} \begin{pmatrix} J & t & J' \\ -M_J & -m & M'_J \end{pmatrix} \\
&\times \begin{Bmatrix} S & S' & \kappa \\ L & L' & k \\ J & J' & t \end{Bmatrix} ([J][J'][t])^{1/2} \langle l^N \eta S L||W^{(\kappa k)}||l^N\eta' S' L'\rangle,
\end{aligned} \tag{8}$$

where $(a^+a)^{(\kappa k)t}$ represents the second-quantized form of $-W^{(\kappa k)t}$, which is a sum of single-particle operators. As usual, the degeneracy numbers such as $2J + 1$ are written as $[J]$. η and η' stand for any other quantum numbers that are needed when the set $SLJM_J$ fails to define the states uniquely.

The $W^{(\kappa k)}$ doubly reduced matrix element can be calculated as [12]

$$\begin{aligned}
\langle l^N \eta S L||W^{(\kappa k)}||l^N\eta' S' L'\rangle &= N\{[S][\kappa][S'][L][k][L']\}^{1/2} \sum_{\bar\eta \bar S \bar L} \langle \eta S L\{|\bar\eta \bar S \bar L\rangle\langle \bar\eta \bar S \bar L|\}\eta' S' L'\rangle \\
&\times (-1)^{\bar S+s+S+\kappa+\bar L+l+L+k} \begin{Bmatrix} S & \kappa & S' \\ s & \bar S & s \end{Bmatrix} \begin{Bmatrix} L & k & L' \\ l & \bar L & l \end{Bmatrix},
\end{aligned} \tag{9}$$

where $\bar\eta \bar S \bar L$ is defined as the parent state of the initial and final states, and $\langle \eta S L\{|\bar\eta \bar S \bar L\rangle$ and $\langle \bar\eta \bar S \bar L|\}\eta' S' L'\rangle$ are the fractional parentage coefficients which are available in [16]. For those $W^{(\kappa k)}$ with $\kappa = 0$, the reduced matrix elements can calculated in a alternative way:

$$\langle l^N \eta S L||W^{(0k)}||l^N\eta' S' L'\rangle = \delta_{SS'}[s]^{-1/2}\{[S][k]\}^{1/2}\langle l^N \eta S L||U^k||l^N\eta' S L'\rangle, \tag{10}$$

where the reduced matrix elements of unit tensors U^k for $k = 2, 4, 6$ can be found in [16]. In table 1, the values of the reduced matrix elements, which are calculated from equations (9), (10) and used in the calculations, are listed.

In working out these expressions, several selection rules become apparent. The orbital rank k in equation (4) forms a triangle with F and D and thus must be constrained between 1 and 5. The only allowed value of total rank t is 2 since it forms a triangle with $J = 0$ and $J' = 2$. Thus, in the second and third terms of equation (4), only $k = 1, 2, 3$ are allowed with the spin rank $\kappa = 1$. Actually $k = 2$ is not allowed in the third term. This is because the 9-j symbol in (4) will vanish unless the sum of all its nine parameters is even.

Table 1. The doubly reduced matrix element $\langle f^6\,{}^7F||W^{(\kappa k)}|f^6\eta' S'L'\rangle$ for various $|f^6\eta' S'L'\rangle$ and (κ, k) used in the calculations.

	(κ, k)			
$\eta' S'L'$	(0, 2)	(1, 1)	(1, 2)	(1, 3)
^7F	−4.182	0.0	0.0	0.0
$^5D_1$	0.0	−5.476	−0.007	−3.943
$^5D_2$	0.0	1.465	4.136	−3.682
$^5D_3$	0.0	2.802	−5.948	−3.125

Finally, to evaluate matrix elements of the electronic operator $(a^+a)^{(0t)t}(a^+a)^{(11)0}(t = 2)$, which appears in the first part of the master expression, the following relation is used:

$$\langle\psi|(a^+a)^{(0t)t}(a^+a)^{(11)0}|\psi'\rangle = \sum_{\psi''}\langle\psi|(a^+a)^{(0t)t}|\psi''\rangle\langle\psi''|(a^+a)^{(11)0}|\psi'\rangle. \quad (11)$$

In this equation the only possible intermediate state ψ'' between $\psi = {}^7F_0$ and $\psi' = {}^5D_2$ is the $^7F_2$ state.

2.2. Physical part

The physical part involves only the tensor $(\varepsilon\varepsilon)^{(0t)}$. For two photons of the same source, a vector addition of two electric dipoles yields a totally symmetric ($t = 0$) and a quadrupolar term ($t = 2$). In the case of $^7F_0 \rightarrow {}^5D_2$ TPA transition, only $t = 2$ is allowed, as described in the above section. Then, the tensor $(\varepsilon\varepsilon)^{(02)}_{0,m}$ is defined as follows:

$$(\varepsilon\varepsilon)^{(02)}_{0,m} = \sum_{m_1,m_2}\langle 1m_1 1m_2|112m\rangle\varepsilon^{(01)}_{0,m_1}\varepsilon^{(01)}_{0,m_2}. \quad (12)$$

For the transitions under investigation, m_1 and m_2 are only allowed to be ±1, since the spectra were obtained in the polarizations of $\theta = 0°$ and $45°$ (where θ is the angle between the [100] crystal axis and the unit electric vector of the excitation beam propagating along the [001] crystal axis) [8]. Thus, the allowed values of m are 0 and ±2, and the following relations are used in the calculation:

$$\begin{aligned}(\varepsilon\varepsilon)^{(02)}_{0,0} &= \frac{1}{\sqrt{6}}(2\varepsilon^{(01)}_{0,0}\varepsilon^{(01)}_{0,0} + \varepsilon^{(01)}_{0,1}\varepsilon^{(01)}_{0,-1} + \varepsilon^{(01)}_{0,-1}\varepsilon^{(01)}_{0,1})\\ (\varepsilon\varepsilon)^{(02)}_{0,2} &= \varepsilon^{(01)}_{0,1}\varepsilon^{(01)}_{0,1}\\ (\varepsilon\varepsilon)^{(02)}_{0,-2} &= \varepsilon^{(01)}_{0,-1}\varepsilon^{(01)}_{0,-1}.\end{aligned} \quad (13)$$

Furthermore, from equations (5), (7), and (8), we can see that the final states $|{}^5D_2, T_2 \pm 1\rangle$ give no contributions to the $^7F_0(\Gamma_{1g}) \rightarrow {}^5D_2(\Gamma_{5g})$ transition matrix element, since $m = 0, \pm2$ required that $M_{J'} = 0, \pm2$ from $M_J = 0$.

3. Results and discussion

It is obvious from equation (7) that the matrix elements of $({}^7F_0)\Gamma_{1g} \rightarrow ({}^5D_2)\Gamma_{5g}, \Gamma_{3g}$ transitions can be easily calculated from combinations of the matrix elements of $\langle {}^7F_0, 0| \rightarrow |{}^5D_2, M_{J'} = 0, \pm2\rangle$ transitions. In addition, there is only one rank of the polarization factors $(\varepsilon\varepsilon)^{(0t)}_{0,m}$ ($t = 2$) in equation (4). In table 2, the matrix elements of $\langle {}^7F_0, 0| \rightarrow |{}^5D_2, M_{J'} = 0, \pm2\rangle$ transitions for various polarizations $\varepsilon^{(01)}_{0,m_1}\varepsilon^{(01)}_{0,m_2}$ ($m_1, m_2 = \pm1$) are given. From this

Table 2. Matrix elements of $\langle {}^7F_0, 0| \rightarrow |{}^5D_2, M_{J'} = 0, \pm 2\rangle$ transitions for various polarizations $\varepsilon^{(01)}_{0,m_1}\varepsilon^{(01)}_{0,m_2}$ $(m_1, m_2 = \pm 1)$ expressed in terms of χ ($\chi = -10^{-2} \times (43.40\xi_{4f} - 7.32\xi_{5d})\langle f|r|d\rangle^2\, \Delta E_{fd}^{-2}$, where ξ_{4f}, ξ_{5d}, and ΔE_{fd} are all in units of cm $^{-1}$).

	(m_1, m_2)			
$\|{}^5D_2, M_{J'}\rangle$	(1, 1)	(1, −1)	(−1, 1)	(−1, −1)
$\|{}^5D_2, 0\rangle$	0.0	$\frac{1}{\sqrt{6}}\chi$	$\frac{1}{\sqrt{6}}\chi$	0.0
$\|{}^5D_2, 2\rangle$	χ	0.0	0.0	0.0
$\|{}^5D_2, -2\rangle$	0.0	0.0	0.0	χ

Table 3. Calculated and observed intensities for the $({}^7F_0)\Gamma_{1g} \rightarrow ({}^5D_2)\Gamma_{5g}$, Γ_{3g} TPA transitions of Eu^{3+} doped in the Cs_2NaYF_6 host lattice.

	Final state	Transition No[a]	Energy (cm^{-1})[a]	Calculated transition line strength[b]		Calculated transition line strength[c]		Relative intensities calc.[b], calc.[c] (obs.[a])	
				$\theta = 0°$	$\theta = 45°$	$\theta = 0°$	$\theta = 45°$	$\theta = 0°$	$\theta = 45°$
A[d]	Γ_{5g}	24	21 389	0.0	3.0	0.0	182.5	0.00, 0.00 (0.12)	3.0, 3.17 (9.9)
	Γ_{3g}	25	21 568	4.0	1.0	227.5	57.5	1.00, 1.00 (1.00)	1.00, 1.00 (1.00)
B[e]	Γ_{5g}	24	21 389	0.0	3.0	0.0	870.0	0.00, 0.00 (0.12)	3.0, 3.08 (9.9)
	Γ_{3g}	25	21 568	4.0	1.0	1130.0	282.5	1.00, 1.00 (1.00)	1.00, 1.00 (1.00)

[a] Reference [8].
[b] From this work. The transition line strengths are in units of $7.94 \times 10^{49}\langle f|r|d\rangle^4\, \Delta E_{fd}^{-4}$ $m^4\, J^{-2}$ in row A and $4.22 \times 10^{44} \times (11.72 \times 10^{-3}\, \Delta E_{fd}^{-1} - 4.34 \times 10^2\, \Delta E_{fd}^{-2})^2\langle f|r|d\rangle^4$ $m^4\, J^{-2}$ in row B.
[c] From the direct calculations [7], where the transition line strengths are in units of $2.53 \times 10^{29}\langle f|r|d\rangle^4$ $m^4\, J^{-2}$.
[d] The pure Russell–Saunders multiplets were used for the initial and final states in the calculations.
[e] The multiplets with spin–orbit admixtures were used for the initial and final states in the calculations.

table, we can calculate the transition line strengths, the polarization dependence, and the relative intensities of the $({}^7F_0)\Gamma_{1g} \rightarrow ({}^5D_2)\Gamma_{5g}$, Γ_{3g} transitions. The results are listed in row A of table 3, in which the results from the direct calculations [7] and experimental observations [8] are also included.

As shown in row A of table 3, the ratio between the TPA intensities of $\Gamma_{1g} \rightarrow \Gamma_{5g}$ and $\Gamma_{1g} \rightarrow \Gamma_{3g}$ at $\theta = 45°$ is calculated to be 3.0, which is almost the same as that from direct calculations and in qualitative agreement with the experimental result. The calculated intensity ratios between $\theta = 0°$ and 45° for these two transitions are equal to 0.0 and 4.0 respectively, which are almost the same as those derived from direct calculation.

It is interesting to compare the transition line strengths calculated from JP formalism with those from direct calculations. In the following, we choose the $\Gamma_{1g} \rightarrow \Gamma_{3g}$ transition at $\theta = 45°$ for investigation. From JP formalisms, the matrix element of this transition at $\theta = 45°$ is given as

$$M_{JP} = \frac{1}{\sqrt{6}} \times 10^{-2}(43.40\xi_{4f} - 7.32\xi_{5d})\langle f|r|d\rangle^2\, \Delta E_{fd}^{-2} \tag{14}$$

with $\langle f|r|d\rangle$ in m; and ξ_{4f}, ξ_{5d}, and ΔE_{fd} all in cm^{-1}. When employing $\xi_{4f} = 1167.69\,cm^{-1}$ [17] and $\xi_{5d} = 996.00\,cm^{-1}$ [18], we can express the transition line strength M_{JP}^2 (in units of $m^4\, J^{-2}$) as

$$M_{JP}^2 = 7.94 \times 10^{49}\langle f|r|d\rangle^4\, \Delta E_{fd}^{-4}, \tag{15}$$

as listed in row A of table 3. The line strength of this transition from the direct calculation can be derived from table 3, written as (in units of $m^4\ J^{-2}$)

$$M_D^2 = 57.5 \times 2.53 \times 10^{29} \langle f|r|d\rangle^4 \cong 1.45 \times 10^{31} \langle f|r|d\rangle^4. \tag{16}$$

The ratio R is thus

$$R = \left(\frac{M_{JP}}{M_D}\right)^2 = \frac{5.48 \times 10^{18}}{\Delta E_{fd}^4}. \tag{17}$$

The ratio is inversely proportional to the fourth power of the energy difference between the intermediate and ground configurations. The barycentre of the $4f^5 5d$ configuration of Eu^{3+} has been estimated by Dieke and Crosswhite [19] to be approximately 125 000 cm^{-1}. Upon substitution of this value into the above equation, the ratio R is found to be 0.022. This serious discrepancy between the results from two methods prompts us to the following discussion.

First, as we have indicated in section 2.1, the energy level calculations reveal that $^7F_0$ and $^5D_2$ show small deviations from being pure Russell–Saunders multiplets, so we have also performed the calculations with these admixtures taken into account. This gives rise to complications, since several more second-order and third-order contributions have to be calculated: namely $^7F_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^5D_2$, and $^5D_0 \rightarrow {}^5F_2$ in second order, and $^5D_0 \rightarrow {}^7F_2$ in third order. The formalism in [9] has been used to calculate the second-order contributions, and for third-order contribution, the method described in the above section has been used. The calculated results are listed in row B of table 3, from which we can see that the relative intensities of the two transitions and their polarization dependences are in agreement with those from direct calculations and experiment. We still choose the $\Gamma_{1g} \rightarrow \Gamma_{3g}$ transition, with $\theta = 45°$ as an example for investigation; its JP transition matrix element is

$$M_{JP} = \frac{1}{\sqrt{6}}[-11.72 \times 10^{-3}\ \Delta E_{fd}^{-1} + (43.40\xi_{4f} - 7.32\xi_{5d})\ \Delta E_{fd}^{-2}]\langle f|r|d\rangle^2. \tag{18}$$

The units of the symbols in this equation are the same as those in equation [14]. When $\xi_{4f} = 1167.69\ cm^{-1}$, $\xi_{5d} = 996\ cm^{-1}$ and $\Delta E_{fd} = 125\,000\ cm^{-1}$ are used, the transition line strength M_{JP}^2 is (in units of $m^4\ J^{-2}$)

$$M_{JP}^2 = 1.84 \times 10^{30} \langle f|r|d\rangle^4. \tag{19}$$

In this case, the transition line strength from the direct calculation [7] is (in units of $m^4\ J^{-2}$)

$$M_D^2 = 282.5 \times 2.53 \times 10^{29} \langle f|r|d\rangle^4 \cong 7.15 \times 10^{31} \langle f|r|d\rangle^4. \tag{20}$$

which is larger, by a factor of 5, than that calculated from pure Russell–Saunders multiplets for the initial and final states. However, the ratio R, as defined in equation (17), is calculated to be 0.026, which is almost identical to that from the calculations using the pure Russell–Saunders multiplets for the initial and final states. Therefore, the disagreement about the ratio R remains unresolved even when the spin–orbit admixtures of the initial and final states are taken into consideration.

Second, in the use of the closure approximation, the zeroth-order basis of the intermediate states is implicit, and all of the intermediate states are assumed to be degenerate. Xia [20] considered the energy structures of $4f^{N-1}(\bar{\eta}\bar{S}\bar{L})$ in the intermediate configuration $4f^{N-1}5d$, and derived a revised Judd–Ofelt–Axe (JOA) formula, in which a correction factor was introduced to multiply the matrix elements of the unit tensor operators. In this correction factor, the energy differences between the weight-averaged level of the $4f^{N-1}(\bar{\eta}\bar{S}\bar{L})5d$ configuration and that of the whole $4f^{N-1}5d$ configuration were taken into account. The fractional parentage coefficients relating $4f^{N-1}(\bar{\eta}\bar{S}\bar{L})$ to the initial and final states of the transitions are also considered. Using the revised JOA formula, Xia was able to explain the large differences between the Raman

scattering intensities of $TmPO_4$ crystal from direct and JOA calculations [21]. The lowest multiplets of the ground configuration $4f^{11}$ were found to be related mainly to the lowest or very low terms of the intermediate $4f^{11}5d$ configuration, which made the most important contributions to the Raman scattering intensities of $^3H \rightarrow {}^3H$ and $^3H \rightarrow {}^3F$ transitions (of the $4f^{12}$ configuration).

In the present work, the initial and final states of the TPA transitions arise from the lowest or next-lowest terms of the ground configuration $4f^6$, i.e. ^7F and ^5D of Eu^{3+}. These two terms are related mainly to the lowest terms of the configuration $4f^55d$, which can be seen from the fractional parentage coefficients, in that their common parents in the $4f^5$ configuration are ^6H, ^6F, and ^6P. Among these three terms, ^6H and ^6F are more important than ^6P, as shown by the values of the fractional parentage coefficients relating them to ^7F and ^5D. A quantitative calculation of the energy levels of the $4f^5$ configuration using the free-ion parameters of Sm^{3+} [17] indicated that the weight-averaged energy of these three terms is about 5000 cm^{-1} above that of the lowest intermediate $4f^55d$ state.

From this discussion, it seems to us that the approach using the closure approximation will provide reasonable results when the barycentre energy of the intermediate states is appropriately lowered from that used in conventional JOA formalism. If we lower this barycentre energy to 70 000 cm^{-1}, according to our energy analysis in which the energy of the lowest intermediate state is about 65 000 cm^{-1} [7], then the ratio R of equation (17) will be equal to 0.23. In the above analysis, the barycentre energy ΔE_{fd} of $4f^55d^1$ has been used as the denominator of the third-order formula as in equation (1). This denominator is actually $(\Delta E_{fd} - \hbar\omega)$, where $\hbar\omega$ stands for the incident photon energy, which is about 10 000 cm^{-1} for the $^7F_0 \rightarrow {}^5D_2$ TPA transitions. Hence, we lowered the energy in equation (17) to 60 000 cm^{-1}, and then found that the ratio R was 0.42. The transition line strength magnitude calculated using the JP formalism is slightly smaller than that obtained by direct calculation. This small difference may be, at least in part, due to the fact that in the direct calculations both the spin–orbit interactions of $4f^55d$ and the crystal field interaction of 5d electrons are taken into account, whilst in the JP formalism used in this work, only the former of the above two interactions was considered.

4. Conclusions

Reid *et al* [22] have asserted that the direct, many-body perturbative and JP methods of calculation are equivalent in the calculation of two-photon transition line strengths. The present study has taken the $^7F_0 \rightarrow {}^5D_2$ transition of Eu^{3+} in the cubic host Cs_2NaYF_6 as a case study. Although the JP-calculated transition relative intensities are in agreement with those from the direct calculation, a modification of the formal JOA effective barycentre is required in order to obtain agreement of the transition line strengths. The agreement of theory with experiment for the relative intensities of transitions is reasonable.

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