Theoretical analysis of the two-photon absorption spectrum of Tb^{3+} in $Cs_2NaTbCl_6$

2003 J. Phys.: Condens. Matter 15 2681

(http://iopscience.iop.org/0953-8984/15/17/320)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) 2681–2691 PII: S0953-8984(03)54453-8

Theoretical analysis of the two-photon absorption spectrum of Tb^{3+} in $Cs_2NaTbCl_6$

Dianyuan Wang[1], Lixin Ning[1], Shangda Xia[1,2] and Peter A Tanner[2]

[1] Structure Research Laboratory, Academica Sinica, Department of Physics, University of Science and Technology of China, Heifei, Anhui 230026, People's Republic of China

[2] Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR, People's Republic of China

Received 8 October 2002, in final form 12 March 2003
Published 22 April 2003
Online at stacks.iop.org/JPhysCM/15/2681

Abstract

Eighteen selected two-photon absorption (TPA) transition line strengths with polarization angles $\theta = 0°$ and $45°$, spanning several orders of magnitude, have been calculated for the Tb^{3+} ion in the cubic host $Cs_2NaTbCl_6$. The results are in reasonable agreement with experimental results in the literature. The calculation utilized the crystal field (CF) wavefunctions for the initial and final states of the $4f^8$ configuration, and utilized free ion or CF wavefunctions (with the corresponding energies) for $4f^7$ core states of the whole intermediate $4f^75d$ configuration comprising 34 320 states. The intensities of certain transitions were found to be very sensitive to the inclusion of the CF interaction within the $4f^7$ core. In contrast to previous fourth- or third-order calculations of the TPA transition line strength of the strong transition $(^7F_6)A_{1g} \rightarrow (^5D_4)A_{1g}$ using pure Russell–Saunders (RS) wavefunctions for the $|^7F_6\rangle$ initial and $\langle ^5D_4|$ final states, our second-order direct calculation shows that the admixed RS wavefunctions $|[^7F_6]\rangle$ and $\langle [^5D_4]|$ must be used to account for its high intensity. The effects of CF interactions within the $4f^7$ core, i.e. J-mixing and CF energy level splitting, upon the $(^7F_6)A_{1g} \rightarrow (^5D_4)E_g$ TPA transition line strength have been separated, and the latter effect is shown to be more important for the transition investigated.

1. Introduction

The theory for intraconfigurational $4f^N$–$4f^N$ two-photon absorption (TPA) transitions of rare earth (RE) ions was developed by Axe [1], using the conventional Judd–Ofelt closure approximation in the second-order perturbation [2, 3], by coupling the two electric dipole operators into an effective operator acting between same parity initial and final states. However, the results from recent TPA experimental studies on RE ions in various host crystals have proved that the standard second-order theory of Axe is inadequate to explain many of the rather strong transitions observed, the intensities of which are calculated to be zero when the Judd–Ofelt

approximation is employed in the theory of Axe. Therefore, Judd and Pooler (JP) [4] and Downer (JPD) [5–7] extended Axe's TPA treatment to include higher orders of perturbations (up to fourth order) by introducing the spin–orbit (SO) and crystal field (CF) interactions within the intermediate $4f^{N-1}5d$ configuration, and successfully explained the TPA transitions forbidden by SLJ selection rules under the Judd–Ofelt approximation.

The CF interaction within the $4f^{N-1}$ core of the $4f^{N-1}5d$ configuration is usually considered to be unimportant. Downer *et al* [5–7] did not consider this interaction in their TPA transition theory. However, recently, in the analysis of $(^7F_0)A_{1g} \rightarrow (^5L_6)A_{1g}$, aT_{2g} TPA transition of Cs_2NaYF_6:Eu^{3+}, we reported [8] for the first time that the CF interaction within the $4f^5$ core is really important since its inclusion makes the line strength of the $(^7F_0)A_{1g} \rightarrow (^5L_6)A_{1g}$ transition increase remarkably. In this paper we continue to make a detailed investigation on the effects of the CF interaction within the $4f^N$ core on the TPA transition elements of $4f^N$ ions.

In our investigations, we have chosen to calculate the line strengths of 18 TPA transitions, with two different polarizations for each, of Tb^{3+} in $Cs_2NaTbCl_6$. These transitions are separated into four groups: (A) $^7F_6 \rightarrow {}^5D_4$ (20 400–20 580 cm^{-1}), (B) $^7F_6 \rightarrow {}^5D_3$, $^5G_6$ (26 200–26 500 cm^{-1}), (C) $^7F_6 \rightarrow {}^5L_{10}$ (26 600–27 400 cm^{-1}) and (D) $^7F_6 \rightarrow {}^5D_0$, $^5H_7$ (31 200–31 500 cm^{-1}). This has been done because the 10 K one-colour two-photon excitation (TPE) spectra of these four groups of transitions have recently been measured [9] and the assignments are secure, while the relative transition intensities of all these TPA transitions, 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), have been semi-quantitatively determined by integration of the corresponding TPE spectra. Additionally, the direction averaged absolute transition intensities of the transitions are tabulated in [10], so that the comparison between the calculated and the observed line strengths is straightforward.

To evaluate the line strengths of these TPA transitions, the second-order direct calculation, which was put forward by Xia *et al* [11], is conducted in this work. Reid *et al* [12–14] have demonstrated that the direct and the JP type perturbation calculations are equivalent to some degree in calculating the TPA transition line strengths, provided that the appropriate eigenstates and eigenvalues were employed. As mentioned in [8] and will be explained below, this direct calculation implicitly includes the third-order and even the fourth-order calculation described in JP and JPD TPA transition theory, and the effects of various interactions within intermediate $4f^{N-1}5d$ configuration on the TPA transition intensities can be easily evaluated thereby. Notably, in our calculation, the approximative wavefunctions and energies of all the intermediate states within the whole $4f^7 5d$ intermediate configuration, as well as the CF wavefunctions for initial and final states within the ground $4f^8$ configuration, are used, which brings about some interesting observations, as will be apparent.

2. Theory

The transition element for the second-order process being studied—a TPA transition between the ground CF state $|\Gamma_i\gamma_i\rangle$ and the final CF state $|\Gamma_f\gamma_f\rangle$—can be written [1]:

$$M_{\Gamma_i\gamma_i\rightarrow\Gamma_f\gamma_f} = -\sum_n \left[\frac{\langle\Gamma_f\gamma_f|\varepsilon_2\cdot \mathrm{D}|n\rangle\langle n|\varepsilon_1\cdot \mathrm{D}|\Gamma_i\gamma_i\rangle}{\hbar\omega_n - \hbar\omega_1} + \frac{\langle\Gamma_f\gamma_f|\varepsilon_1\cdot \mathrm{D}|n\rangle\langle n|\varepsilon_2\cdot \mathrm{D}|\Gamma_i\gamma_i\rangle}{\hbar\omega_n - \hbar\omega_2} \right]. \quad (1)$$

In this expression, $\varepsilon \cdot \mathrm{D}$ is the scalar product of the polarization vector ε of the photon and the electric dipole operator D of the RE ion. $\hbar\omega_1$ and $\hbar\omega_2$ are the photon energies.

In our direct calculation, the intermediate states $|n\rangle$ refer to all the 34 320 states within the whole $4f^{N-1}5d$ configuration since this configuration, being lowest in energy, is probably the most important opposite parity configuration, and $\hbar\omega_n$ are the corresponding energies of these intermediate states $|n\rangle$ above the ground state energy of $4f^N$ configuration. Note that, by taking $|n\rangle$ and $\hbar\omega_n$ as eigenfunctions and eigenvalues of different approximate Hamiltonians H of the $4f^{N-1}5d$ configuration, H_1 and H_2 for example, the effects of the various interactions in this configuration, $H' = H_2 - H_1$ for example, on the TPA transition intensities can be evaluated. For example, we assume that the two intermediate states $|A\rangle$ and $|B\rangle$, degenerate with energy E_0 under H_1, change to be '*mixed*' $\frac{1}{\sqrt{2}}(|A\rangle + |B\rangle)$ and $\frac{1}{\sqrt{2}}(|A\rangle - |B\rangle)$ with 'split' energies E_{A+B} and E_{A-B} respectively under H_2 when the perturbation Hamiltonian $H' = H_2 - H_1$ of the $4f^{N-1}5d$ configuration is added. Then, the effects of this perturbation H' on TPA transition intensities can be estimated by the difference between the sums over the above two kinds of intermediate states in equation (1), as shown by

$$\left(\frac{1/2(|A\rangle + |B\rangle)(\langle A| + \langle B|)}{E_{A+B} - \hbar\omega} + \frac{1/2(|A\rangle - |B\rangle)(\langle A| - \langle B|)}{E_{A-B} - \hbar\omega}\right) - \left(\frac{|A\rangle\langle A|}{E_0 - \hbar\omega} + \frac{|B\rangle\langle B|}{E_0 - \hbar\omega}\right), \quad (2)$$

which is nonzero, now, contracting to the usual '*sum rule*' over a group of states. This is because the cross-terms involving $|A\rangle\langle B|$ and $|B\rangle\langle A|$ in the first sum over '*mixed*' intermediate wavefunctions in equation (2) cannot be cancelled because the energies in the denominators are '*split*'. Moreover, it is worth noting that the perturbation effect can greatly change the selection rules of the TPA transition.

In the present work, the wavefunctions of various states of Tb^{3+} used in the calculation are analogous to those in [8] for the case of Eu^{3+}. Therefore, we will only describe the wavefunctions briefly in what follows. Firstly, for the initial $|\Gamma_i\gamma_i\rangle$ and final states $|\Gamma_f\gamma_f\rangle$ of $Tb^{3+}(4f^8)$, the '*exact*' CF wavefunctions with the corresponding energies are reproduced using the f-shell empirical programs developed by Reid and the fitted parameters reported by Morrison *et al* [9]. Secondly, the intermediate states $|n\rangle$ of the $4f^75d$ configuration are obtained by a direct product of the $4f^7(Gd^{3+})$ core states and the single 5d-electron (Ce^{3+}) CF states. The Coulomb electrostatic interaction between the $4f^7$ core and the 5d electron is neglected for simplicity, as in [8, 11], and this is the most drastic approximation in this work [15]. For $4f^7$ core states, two kinds of wavefunctions, i.e. free ion and CF wavefunctions, are used in the calculation, which we call models A and B, respectively, from now on. These wavefunctions and the corresponding energies are also obtained using the f-shell empirical programs mentioned above and the input parameters in $Cs_2NaGdCl_6$ reported in [16]. For the $5d^1$ electron states, only CF wavefunctions (with energies 0 cm^{-1} for the $aU'(a\Gamma_8)$ level, 1239 cm^{-1} for $E''(\Gamma_7)$, and 18 929 cm^{-1} for $bU'(b\Gamma_8)$) are used for both models A and B, which are identical to those in [8]. In addition, an estimated value of 34 000 cm^{-1} for the energy difference between the lowest level of the $4f^75d$ configuration and the ground CF level of the $4f^8(Tb^{3+})$ configuration is employed in our direct calculation [17].

Using the above described wavefunctions for the initial and final states of the ground $4f^8$ configuration and for the $4f^75d$ intermediate states in model A, the fundamental matrix element in the second-order TPA formula can be expressed as

$$\begin{aligned}\langle\Gamma_f\gamma_f|D^1_q|n\rangle &= \sqrt{8}_A\langle 4f^8[\alpha_f S_f L_f J_f]\Gamma_f\gamma_f|r_N C^1_q(N)||4f^7[\bar{\alpha}\bar{S}\bar{L}]\bar{J}\bar{J}_z\rangle_A;\ |5d(\Gamma_l\Gamma_s\Gamma_d\gamma_d)\rangle_N\rangle \\ &= \sqrt{8}\sum_{\substack{v\alpha SLJJ_z \\ M_S M_L \bar{M}_S \bar{M}_L \\ \gamma_l\gamma_s m_{sd} m_{ld} m_{lf}}} C_v a_{\Gamma_f\gamma_f}(\alpha SLJJ_z)\langle JJ_z|SM_S LM_L\rangle\langle\bar{S}_v\bar{M}_S\bar{L}_v\bar{M}_L|\bar{J}\bar{J}_z\rangle \\ &\quad\times\langle\Gamma_l\gamma_l\Gamma_s\gamma_s|\Gamma_d\gamma_d\rangle\langle 2m_{ld}|\Gamma_l\gamma_l\rangle\langle\tfrac{1}{2}m_{sd}|\Gamma_s\gamma_s\rangle\langle 4f^8\alpha SL|4f^7\bar{\alpha}_v\bar{S}_v\bar{L}_v\rangle \\ &\quad\times\langle SM_S|\bar{S}_v\bar{M}_S\tfrac{1}{2}m_{sd}\rangle\langle LM_L|\bar{L}_v\bar{M}_L 3m_{lf}\rangle\langle 3m_{lf}|r_N C^1_q(N)|2m_{ld}\rangle. \end{aligned} \quad (3)$$

In the above expression, $C_v = C^{[\bar{\alpha}\bar{S}\bar{L}]}_{\bar{\alpha}_v\bar{S}_v\bar{L}_v}$ and $a_{\Gamma_f\gamma_f}(\alpha SLJJ_z) = a^{[\alpha_f S_f L_f J_f]\Gamma_f\gamma_f}_{(\alpha SLJJ_z)}$. The explanations of the various notations can be found in [8]. The expression for $\langle n|\mathrm{D}^1_q|\Gamma_i\gamma_i\rangle$ in equation (1) can also be obtained in the same way.

When another kind of wavefunction for $4f^7 5d$ intermediate states (i.e. the CF wavefunctions for $4f^7$ core states corresponding to the model B) is used, both $\langle\Gamma_f\gamma_f|\mathrm{D}^1_q|n\rangle$ and $\langle n|\mathrm{D}^1_q|\Gamma_i\gamma_i\rangle$ can be obtained by replacing $|4f^7[\bar{\alpha}\bar{S}\bar{L}]\bar{J}\bar{J}z\rangle$ by $|4f^7[\bar{\alpha}\bar{S}\bar{L}\bar{J}]\bar{\Gamma}\bar{\gamma}\rangle$.

It should be noted that the coefficients of fractional parentage $\langle 4f^8\alpha SL|4f^7\bar{\alpha}_v\bar{S}_v\bar{L}_v\rangle$ are obtained from $\langle 4f^7\bar{\alpha}_v\bar{S}_v\bar{L}_v|4f^6\alpha SL\rangle$, that is [18],

$$\langle 4f^8\alpha SL|4f^7\bar{\alpha}_v\bar{S}_v\bar{L}_v\rangle = \xi(-1)^{L+\bar{L}_v+S+\bar{S}_v-7/2}\sqrt{\frac{7(2\bar{L}_v+1)(2\bar{S}_v+1)}{8(2L+1)(2S+1)}}\langle 4f^7\bar{\alpha}_v\bar{S}_v\bar{L}_v|4f^6\alpha SL\rangle \tag{4}$$

where $\xi = (-1)^{\tilde{v}-1/2}$ and $\tilde{v}$ is seniority number, and the values of $\langle 4f^7\bar{\alpha}_v\bar{S}_v\bar{L}_v|4f^6\alpha SL\rangle$ are listed in [18].

By replacing the terms in equation (1) with the above mentioned expressions, and the energies in the denominators by the fitted ones for the corresponding states, the TPA transition matrix moment $M_{\Gamma_i\gamma_i\to\Gamma_f\gamma_f}$ can then be calculated directly, and so can the transition line strength [19], which is expressed as

$$S_{\Gamma_i\to\Gamma_f} = \sum_{\gamma_i,\gamma_f}|M_{\Gamma_i\gamma_i\to\Gamma_f\gamma_f}|^2. \tag{5}$$

The polarization dependence of one-colour TPA transitions in cubic crystals has previously been described [9, 10]. When $\theta = 0°$, $A_{1g} \to T_{2g}$ transitions are forbidden, while the intensity of $A_{1g} \to E_g$ transitions is at a maximum; when $\theta = 45°$, the $A_{1g} \to T_{2g}$ intensity is a maximum, whilst the intensity of $A_{1g} \to E_g$ transitions decreases by a factor of four. The intensity of $A_{1g} \to A_{1g}$ transitions is independent of θ.

3. Results and discussion

The electronic ground state of Tb^{3+} in $Cs_2NaTbCl_6$ transforms as the irreducible representation A_{1g} of the O_h point group, from which the allowed one-colour TPA transitions are to those final CF states transforming as A_{1g}, E_g and T_{2g} representations [9]. In the present work, we calculated the line strengths of four groups of TPA transitions (18 in total) of Tb^{3+} in $Cs_2NaTbCl_6$ with two polarizations as mentioned in section 1, and the calculated results are displayed in table 1. As shown in the table, the calculations are performed under the two models A and B, that is, the free ion and CF wavefunctions with the corresponding energies for $4f^7$ core states are used respectively. At the same time, the CF wavefunctions with the corresponding energies for $5d^1$ electron states are always used. For comparison with the calculated line strengths, the experimental intensities (polarized and polarization orientation averaged) of all these transitions are also listed. In the following subsections, a detailed analysis and discussion of these calculated results is presented.

3.1. Analysis of TPA transition line strengths

3.1.1. $(^7F_6)A_{1g} \to (^5D_4)A_{1g}, E_g, T_{2g}$ *transitions (20 400–20 580 cm*$^{-1}$*).* As can be seen in row A of table 1, under model A, the calculated intensity ratios between the $\theta = 0°$ and 45° polarizations for $A_{1g} \to A_{1g}, E_g, T_{2g}$ transitions are equal to 1.0, 4.0 and 0.0 respectively, which are in consistent with the ratios derived from simple group theory [9], whereas the

Table 1. Calculated and experimental intensities for TPA transitions of Tb^{3+} in $Cs_2NaTbCl_6$.

				Calculated absolute (relative) transition line strength[b]				Observed intensities for incident radiation propagating along [100]		
				Model A (using free ion wavefunctions with the corresponding energies for $4f^7$ core states)[e]		Model B (using CF wavefunctions with the corresponding energies for $4f^7$ core states)[e]		Relative (polarized)[c]		Absolute ($\times 10^5$) (Polarization orientation averaged)[d]
Group	Level no[a]	Final state	Energy (cm^{-1})[a]	$\theta = 0°$	$\theta = 45°$	$\theta = 0°$	$\theta = 45°$	$\theta = 0°$	$\theta = 45°$	
A	22	$^5D_4A_{1g}$	20 470	60(11.0)[f]	60.0(11.0)[f]	77.0 (11.0)[f]	77.0 (11.0)[f]	11.0	11.0	11.0
	24	$^5D_4E_g$	20 500	2.9(0.53)	0.73(0.13)	77.0(11.0)	20.0(2.9)	1.9	1.1	2.1
	25	$^5D_4T_{2g}$	20 553	0(0.0)	26(4.8)	0(0.0)	8.0(1.1)	0.3	1.0	1.5
B	27	$^5D_3T_{2g}$	26 261	0(0.0)	5.3(0.97)	0(0.0)	7.3(1.0)	n.a.	n.a.	1.2
	29	$^5G_6A_{1g}$	26 372	2179(399)	2179(399)	416(59)	416(59)	n.a.	n.a.	1.1
	30	$^5G_6aT_{2g}$	26 378	0(0.0)	235(43.1)	0(0.0)	260(37)	n.a.	11.5	n.a.
	32	$^5G_6E_g$	26 412	33(6.1)	8.6(1.6)	36(5.1)	9.0(1.3)	19	17.9	24.0
	33	$^5G_6bT_{2g}$	26 467	0(0.0)	81(15)	0(0.0)	96(14)	2.1	6.3	8.4
C	35	$^5L_{10}aE_g$	26 678	1.4(0.26)	0.40(0.07)	1.2(0.17)	0.32(0.05)	n.o.	n.o.	n.o.
	36	$^5L_{10}aT_{2g}$	26 694	0(0.0)	1.20(0.22)	0(0.0)	3.0(0.43)	2.9	5.2	6.2
	38	$^5L_{10}bT_{2g}$	26 925	0(0.0)	3.0(0.54)	0(0.0)	1.4(0.21)	n.a.	(1.69)	0.8
	40	$^5L_{10}A_{1g}$	27 086	37(6.73)	37(6.7)	10.2(1.5)	10.2(1.5)	n.a.	n.a.	5.3
	42	$^5L_{10}bE_g$	27 271	0.08(0.02)	0.02(0.0)	0.79(0.11)	0.20(0.03)	0.08	0.024	0.08
	43	$^5L_{10}cT_{2g}$	27 318	0(0.0)	0.33(0.06)	0(0.0)	0.80(0.11)	0.18	0.39	0.39

Table 1. (Continued.)

Group	Level no[a]	Final state	Energy (cm^{-1})[a]	Calculated absolute (relative) transition line strength[b]: Model A (using free ion wavefunctions with the corresponding energies for $4f^7$ core states)[e] $\theta = 0°$	Model A $\theta = 45°$	Model B (using CF wavefunctions with the corresponding energies for $4f^7$ core states)[e] $\theta = 0°$	Model B $\theta = 45°$	Observed intensities for incident radiation propagating along [100]: Relative (polarized)[c] $\theta = 0°$	Relative (polarized)[c] $\theta = 45°$	Absolute ($\times 10^5$) (Polarization orientation averaged)[d]
D	88	$^5H_7E_g$	31 247	0.43(0.08)	0.11(0.02)	9.0(1.29)	2.2(0.31)	2.0	0.84	n.a.
	89	$^5D_0A_{1g}$	31 256	0.20(0.04)	0.20(0.04)	3.1(0.44)	3.1(0.44)	0.04	0.04	0.01
	90	$^5H_7aT_{2g}$	31 272	0(0.0)	0.06(0.01)	0(0.0)	1.5(0.21)	0.12	0.26	0.38
	92	$^5H_7bT_{2g}$	31 448	0(0.0)	0.02(0.0)	0(0.0)	0.60(0.09)	0.004	0.008	n.a.

[a] Terminal level number, from [9].

[b] In units of $(10^{-14}\ cm^2\langle 4f|r|5d\rangle^4/h^2c^2)$. θ is the angle that the radiation electric vector makes with [001].

[c] The ratios between the values within each group for groups A, B, C, D are obtained by integration of the hard copy spectra in [10]; the values within each group are normalized such that the polarization orientation average of them for transitions 22, 33, 42 and 90 are equal to the corresponding values in the last column. The values in the two columns are semi-quantitative because of polarization leakage due to crystal imperfection and/or crystal alignment. For example, the value for transition 36 with $\theta = 0°$ is far away from zero (the correct value based on group theory) and the ratio between the values for $\theta = 0°$ and 45° for transition 24 or 32 is far from the correct value 4.

[d] Intensities tabulated in [10]. n.a. indicates not analysed; n.o. not observed.

[e] The CF wavefunctions (with the corresponding energies) for $5d^1$ electron states are always employed in the direct product states.

[f] The values in parentheses are normalized values, in which the value 11.0 for transition 22 in both polarizations is equal to the observed absolute value.

calculated relative TPA intensity of these three transitions for $\theta = 45°$ disagree seriously with the experimental results, as shown in row A, column 6 of table 1. However, under model B, where the CF wavefunctions for the $4f^7$ core states are employed, the agreement of calculated relative intensities with experimental ones is greatly improved, which can been seen in row A, column 8 of table 1. From a comparison of calculated *absolute* transition line strengths between these two models, we can easily find that, for the $A_{1g} \rightarrow E_g, T_{2g}$ transitions, the absolute values change remarkably, while for the $A_{1g} \rightarrow A_{1g}$ transition the value is almost invariant, which makes the theoretical relative intensities agree well with the experimental ones. This indicates that for $(^7F_6)A_{1g} \rightarrow (^5D_4)E_g, T_{2g}$ transitions, the effects caused by the CF interaction within the $4f^7$ core states cannot be neglected.

The line strength for the $(^7F_6)A_{1g} \rightarrow (^5D_4)A_{1g}$ transition, which is zero under the second-order Axe theory [1], is calculated to be the largest of the $(^7F_6)A_{1g} \rightarrow (^5D_4)A_{1g}, E_g, T_{2g}$ transitions, in agreement with experiment [9]. This result has also been studied by other authors, who employed a JPD fourth-order calculation [20] or third-order *incomplete* direct calculation [21], with the use of pure Russell–Saunders (RS) $^7F_6$ and $^5D_4$ multiplet wavefunctions for the initial and final states. Quantitative fitting of Tb^{3+} free ion energy levels in this work (section 3.1.1) indicates that both $^7F_6$ and $^5D_4$ states are not extremely pure RS multiplets. The ground $^7F_6(A_{1g})$ state consists of 94.9% of $^7F_6$, with $^5G_6$ (4.3%) and $^7F_4$ (0.6%), caused by SO and CF interactions, respectively, within the $4f^8$ ground configuration. The excited $^5D_4(A_{1g})$ state comprises 91.1% $^5D_4$ with small admixtures, mainly of $^7F_4$ (2.8%), $^3F_4$ (4.0%) and $^5F_4$ (1.44%), which were all caused by SO interaction within the $4f^8$ configuration. Thus, besides the main $^7F_6 \rightarrow {}^5D_4$ channel, these admixtures will lead to extra transition channels: $^7F_6 \rightarrow {}^7F_4, {}^3F_4, {}^5F_4, {}^5G_6 \rightarrow {}^5D_4, {}^7F_4, {}^3F_4, {}^5F_4$ and $^7F_4 \rightarrow {}^5D_4, {}^7F_4, {}^3F_4, {}^5F_4$, which can give rise to their respective contributions (multiplied by their corresponding weighted coefficients in the initial and final wavefunctions) to the $(^7F_6)A_{1g} \rightarrow (^5D_4)A_{1g}$ transition element. The calculated contributions for the model A are listed column 2 of table 2, in which we can see that the dominant channels are $^7F_4 \rightarrow {}^7F_4$, $^7F_6 \rightarrow {}^7F_4$ and $^7F_4 \rightarrow {}^5D_4$, not the pure $^7F_6 \rightarrow {}^5D_4$. For the channel $^7F_4 \rightarrow {}^7F_4$ with $\Delta S = \Delta L = \Delta J = 0$, it is the $A_{1g} = [\vec{D}\vec{D}]^{(0)}$ component from the direct product $\vec{D}\vec{D}$ of two electric dipole operators $\vec{D}$, which is a zero-order operator in orbital space (as well as in spin space), combined with the diagonal terms of the summation $\Lambda = \sum_n [|n\rangle\langle n|/(\hbar\omega_n - \hbar\omega)]$ which is an A_{1g}-type N-electron operator, that makes the most important contribution to the $(^7F_6)A_{1g} \rightarrow (^5D_4)A_{1g}$ transition. For the channel $^7F_6 \rightarrow {}^7F_4$ with $\Delta J = 2$, the important contributions may come from the above $A_{1g} = [\vec{D}\vec{D}]^{(0)}$ component and J-mixing cross-terms (which makes $\Delta J = 2$) of the summation Λ, since the second-order $[\vec{D}\vec{D}]^{(2)}$ has only E_g and T_{2g} components which cannot contribute to this $A_{1g} \rightarrow A_{1g}$ TPA transition. Regarding the $^7F_4 \rightarrow {}^5D_4$ channel, it is easy to see that the most important contributions are from the $[\vec{D}\vec{D}]^{(0)}$ and SO mixing cross-terms of the summation Λ, since $\Delta S = \Delta L = 1$ and $\Delta J = 0$ for this transition. Thus our analysis indicates that the $[\vec{D}\vec{D}]^{(0)}$ combined with the summation Λ makes the fundamental contribution to all these three transition channels. The above case is also true for the model B, as shown in column 3 of table 2. Therefore, it can be concluded that the dominant contribution to the line strength of the $(^7F_6)A_{1g} \rightarrow (^5D_4)A_{1g}$ transition arises mainly from the deviations from pure RS multiplets of both the initial and final states. The previous calculations [20, 21], which neglected these three most important transition channels, are thus inadequate to account for its high absolute line strength.

3.1.2. $^7F_6 \rightarrow {}^5D_3, {}^5G_6$ transitions (26 200–26 500 cm^{-1}). This group comprises levels 27–33 of table 1 in Morrison *et al* [9]. In the $^7F_6 \rightarrow {}^5D_3$ group, the only allowed transition is

Table 2. The contributions of sub-channels to the $(^7F_6)A_{1g} \rightarrow (^5D_4)A_{1g}$ TPA transition element.

Sub-channels of $(^7F_6)A_{1g} \rightarrow {}^5(D_4)A_{1g}$ TPA transition	Values of the calculated TPA transition element[a]	
	Model A (using free ion wavefunctions (with the corresponding energies) for $4f^7$ core states)[b]	Model B (using CF wavefunctions (with the corresponding energies) for $4f^7$ core states)[b]
$^7F_6 \rightarrow {}^5D_4$	−53.28	−76.92
$\rightarrow {}^7F_4$	−189.72	−196.98
$\rightarrow {}^3F_4$	0.90	4.76
$\rightarrow {}^5F_4$	−7.24	−17.16
$^5G_6 \rightarrow {}^5D_4$	20.80	41.42
$\rightarrow {}^7F_4$	5.24	10.80
$\rightarrow {}^3F_4$	−0.74	−1.76
$\rightarrow {}^5F_4$	3.66	1.74
$^7F_4 \rightarrow {}^5D_4$	−66.20	−134.50
$\rightarrow {}^7F_4$	−479.38	−494.80
$\rightarrow {}^3F_4$	−1.94	3.66
$\rightarrow {}^5F_4$	−8.94	−16.34
Sum	−777	−876

[a] In units of 10^{-9} cm $\langle 4f|r|5d\rangle^2/hc$.
[b] The CF wavefunctions with the corresponding energies for $5d^1$ electron states are used throughout in the direct product states.

to the $(^5D_3)T_{2g}$ terminal CF level. As shown in row B, column 6 of table 1, the theoretical $(^7F_6)A_{1g} \rightarrow (^5D_3)T_{2g}$ transition line strength is about 10% of that of $(^7F_6)A_{1g} \rightarrow (^5D_4)A_{1g}$, which is in good agreement with the experiment (in row B, the last column of table 1). The line strength of the $(^7F_6)A_{1g} \rightarrow (^5D_3)T_{2g}$ transition is almost invariant when the model B is used instead of the model A.

The next group of bands at higher energy in the TPE spectrum of $Cs_2NaTbCl_6$ comprises transitions to $^5G_6$. The TPA transitions to the $(^5G_6)A_{1g}$ and $(^5G_6)aT_{2g}$ excited states overlap [9], so that the experimental polarized intensities are not included in table 1 and the experimental absolute intensity (polarization orientation averaged) may be not reliable. Our calculated relative intensity for $(^7F_6)A_{1g} \rightarrow (^5G_6)A_{1g}$ transition is too large compared to the observed absolute intensity mentioned above, under model A, as can be seen from a comparison between the value in column 6 and the value in the last column of table 1. Then, when the model B is employed instead, the situation is still bad, though the calculated line strength is reduced remarkably. For the other three transitions $(^7F_6)A_{1g} \rightarrow (^5G_6)aT_{2g}, E_g, bT_{2g}$, the theoretical line strengths only change slightly when changing the model from A to B. By comparison with the intensity of $(^7F_6)A_{1g} \rightarrow (^5D_4)A_{1g}$, it is also found that the calculated line strengths of the $(^7F_6)A_{1g} \rightarrow (^5G_6)aT_{2g}$ and $(^5G_6)bT_{2g}$ transitions can be considered to be reasonable, whilst that of the $(^7F_6)A_{1g} \rightarrow (^5G_6)E_g$ transition with $\theta = 45°$ is smaller by one order of magnitude.

3.1.3. $^7F_6 \rightarrow {}^5L_{10}$ *transitions (26 600–27 400 cm*$^{-1}$*).* Group C corresponds to transitions terminating upon the $^5L_{10}$ multiplet, with six transitions from $(^7F_6)A_{1g}$ being clearly identified in the 7 K TPE spectra of [9]. The calculation is successful in predicting that $(^7F_6)A_{1g} \rightarrow (^5L_{10})aE_g$, bE_g are the weakest transitions of this group and have correct absolute intensities, and that $(^7F_6)A_{1g} \rightarrow (^5L_{10})A_{1g}, aT_{2g}$ ($\theta = 45°$, under model B) are the strongest. The calculated intensity of the $(^7F_6)A_{1g} \rightarrow (^5L_{10})bT_{2g}$ transition is also reasonable. The

Table 3. Contributions to the transition element caused by CF J-mixing and CF energy level splitting effects within the $4f^7$ core for the $(^7F_6)A_{1g} \rightarrow (^5D_4)E_g$ TPA transition[c] with polarization $\theta = 45°$.

Energy region distributed by $4f^7$ core states (cm^{-1})	Contribution of the CF J-admixing effect[a]	Contribution of CF energy level splitting effect[a]
39 434–40 925	64.48	1.78
53 545–54 630	42.53	30.08
55 381–58 392	7.24	302.20
59 390–61 074	0.03	−85.50
Sum[b]	114	249

[a] In units of 10^{-9} $cm\langle 4f|r|5d\rangle^2/hc$.
[b] Sum of contributions from the intermediate states distributed in the above energy region.
[c] The calculated values of the $(^7F_6)A_{1g} \rightarrow (^5D_4)E_g$ TPA transition element at $\theta = 45°$ are 82×10^{-9} and 458×10^{-9} $(cm\langle 4f|r|5d\rangle^2/hc)$, when the CF interaction within the $4f^7$ core is neglected (model A) and considered (model B), respectively. As a result, the increment of the transition element, $(458–82) \times 10^{-9} = 376 \times 10^{-9}$, is comparable to 458×10^{-9} and is just approximately equal to the sum of 114×10^{-9} and $249 \times 10^{-9}(cm\langle 4f|r|5d\rangle^2/hc)$ (as shown by the last row of the table).

most sensitive transition line strengths in the change from the model A to the model B are $(^7F_6)A_{1g} \rightarrow (^5L_{10})A_{1g}$, bE_g (table 1).

3.1.4. $^7F_6 \rightarrow {}^5D_0, {}^5H_7$ transitions (31 200–31 500 cm^{-1}). The final group of transitions that we have analysed corresponds to the $^7F_6 \rightarrow (^5H_7)E_g, aT_{2g}, bT_{2g}$ transitions, with $^7F_6 \rightarrow (^5D_0)A_{1g}$ also being in this region. The relative intensities within the $^5H_7$ group are well-reproduced, with the transition to the E_g CF level being most intense, and that to bT_{2g} the weakest. As shown in table 1, when going from the model A to B, the calculated absolute line strengths of these four transitions all increase considerably. However, the relative intensities within these four transitions only change slightly. By comparison with the observed absolute intensities, it is found that the theoretical calculated line strengths for all transitions in the $^7F_6 \rightarrow {}^5H_7$ group are all good, except the one for the transition to $^5H_7bT_{2g}$ with $\theta = 45°$, while the calculated line strength of $(^7F_6)A_{1g} \rightarrow (^5D_0)A_{1g}$ is too large.

3.2. Effects of CF interaction within the $4f^7$ core upon the TPA transition line strength of Tb^{3+}

For a $4f^{N-1}$ core in a crystal host, the CF interaction is sometimes important, with CF J-mixing and CF energy level splitting being two kinds of effects. These two effects will modify the energy levels and wavefunctions of the free ion core and thus influence the calculation of the TPA transition elements of the $4f^N$ RE ion. The calculated results listed in table 1 also confirm this point. To quantitatively evaluate and analyse these two effects of the CF interaction within $4f^7$ core states on the calculation, the $(^7F_6)A_{1g} \rightarrow (^5D_4)E_g$ transition with polarization $\theta = 45°$ is taken as an example, and the effects on its transition element are shown by the values listed in table 3.

3.2.1. J-mixing effect within the $4f^7$ core. J-mixing occurs when the states belonging to different free ion levels (characterized by different quantum numbers $[\alpha SL]J$) are mixed under the CF interaction. This is usually a very important effect when the energy gaps between these free ion levels are small. For the intermediate $4f^7$ configuration, the J-mixing effect is quite serious in some energy regions, as can be seen from the calculated wavefunctions for this

configuration using Reid's f-shell program and the input parameters of [16]. In the following, we calculated the contribution from these J-mixing effects among the $4f^7$ core states to the transition element for the $(^7F_6)A_{1g} \rightarrow (^5D_4)E_g$ transition of the Tb^{3+} ion at $\theta = 45°$, using the expression (1), by replacing the sum over intermediate states with the sum over cross-terms involving $|n(\bar{\alpha}\bar{S}\bar{L}\bar{J})\langle n(\bar{\alpha}'\bar{S}'\bar{L}'\bar{J}')|$, in which $\bar{\alpha}\bar{S}\bar{L}\bar{J}$ and $\bar{\alpha}'\bar{S}'\bar{L}'\bar{J}'$ are different quantum numbers of the $4f^7$ core states. The calculated results are listed in column 2 of table 3, from which we can see that the contribution of J-admixings in two particular energy regions in the $4f^7$ configuration are quite large. One region (39 434–40 925 cm^{-1}) concerns the J-mixing among $^6D_{9/2}$, $^6D_{1/2}$, $^6D_{7/2}$, $^6D_{3/2}$ and $^6D_{5/2}$, and the other region (53 545–54 630 cm^{-1}) concerns the J-mixing among $^6F_{3/2}$, $^6F_{11/2}$, $^6F_{5/2}$, $^6F_{9/2}$ and $^6F_{7/2}$. In addition, from the last row of table 3, we can see that the total contribution is about 25% of the total transition element of the transition (see footnote c of table 3), which indicates that J-mixing in the intermediate $4f^{N-1}$ states is sometimes one of the important factors influencing the line strengths of TPA transitions.

3.2.2. CF energy level splitting effect within the $4f^7$ core. If a $4f^7$ core is treated as a free ion, $(2J + 1)$ sub-states denoted by $|4f^7[\alpha SL]JJ_Z\rangle_A$ are degenerate in energy. This degeneracy will be partly removed when the CF interaction within the $4f^7$ core is taken into account, that is, when the resulting CF states $|4f^7[\alpha SLJ]\Gamma\gamma\rangle_A$ with different energy replace the corresponding free ion ones in equation (1), the calculated result will be changed due to the contribution caused by the CF interaction within the $4f^7$ core.

Thus, the CF splitting contribution can be obtained by subtracting the contribution caused by the J-mixing effect (see section 3.2.1) from that caused by the $4f^7$ CF interaction obtained above. The results are listed in column 3 of table 3, from which we can see that the contributions caused by CF splittings of energy levels from the following three regions are the largest: $^6F_{3/2,11/2,5/2,9/2,7/2}$ free ion states (53 545–54 630 cm^{-1}), $^4H_{7/2,11/2}$, $^4N_{17/2,19/2,23/2,21/2}$, $^4L_{17/2,13/2,15/2}$, $^6H_{13/2,5/2,15/2,7/2,11/2,9/2}$, $^4D_{3/2,1/2}$ and $^6G_{9/2}$ (55 381–58 392 cm^{-1}), and $^6H_{13/2}$, $^4L_{19/2}$, $^4K_{11/2}$ and $^4F_{9/2,7/2}$ (59 390–61 074 cm^{-1}). We also can see that, for the $(^7F_6)A_{1g} \rightarrow (^5D_4)E_g$ ($\theta = 45°$) TPA transition of Tb^{3+} in $Cs_2NaTbCl_6$, the contribution to the transition element caused by the CF splitting effect is larger than that caused by the J-mixing effect, and is more than half of the total transition element of the investigated transition.

4. Conclusions

This work has presented detailed calculations of 36 TPA line strengths of Tb^{3+} in the cubic host $Cs_2NaTbCl_6$. The agreement between theory and experiment can be generally considered to be reasonable. Since the CF wavefunctions for the initial and final states in the $4f^8$ ground configuration and the approximative wavefunctions with the corresponding energies for the whole $4f^75d$ intermediate configuration have been used, we believe that the fact that the calculated (absolute) line strengths of a few transitions are not in agreement with experiment (e.g. the calculated intensity for the $(^7F_6)A_{1g} \rightarrow (^5G_6)A_{1g}$ transition is too large), results from the approximation (mentioned in section 2) that the Coulomb electrostatic interaction between the $4f^7$ core and 5d electron in the $4f^75d$ intermediate configuration is neglected in our direct calculation. In addition, the role of intermediate states from configurations other than $4f^75d$ is at present unexplored.

Discussions of the main channels of the transition $(^7F_6)A_{1g} \rightarrow (^5D_4)A_{1g}$, and of the effects upon the TPA transition line strength resulting from the choice of free ion or CF states for $4f^7$ core, and of two kinds of effects caused by the CF interaction within $4f^7$ core have been given. The main findings about these are summarized in the abstract.

Acknowledgments

This work was supported by the Hong Kong UGC Research Grant CityU 1067/99P (to PAT), the National Natural Science Foundation of China Research Grants 10074061 and 10274079, and the PhD Training Base Fund of China Grant 20010358016 (to SX). We are indebted to Professor M F Reid for the use of the f-shell suite of programs, and also for the loan of [10] which provides the experimental data utilized in this work.

References

[1] Axe J D 1964 *Phys. Rev.* **136** 42
[2] Judd B R 1962 *Phys. Rev.* **127** 750
[3] Ofelt G S 1962 *J. Chem. Phys.* **37** 511
[4] Judd B R and Pooler D R 1982 *J. Phys. C: Solid State Phys.* **15** 591
[5] Downer M C, Bivas A and Bloembergen N 1982 *Opt. Commun.* **41** 335
[6] Downer M C and Bivas A 1983 *Phys. Rev.* B **28** 3677
[7] Downer M C, Cordero-Montalvo C D and Crosswhite H 1983 *Phys. Rev.* B **28** 4931
[8] Ning L, Wang D, Xia S, Thorne J R G and Tanner P A 2002 *J. Phys.: Condens. Matter* **14** 3833
[9] Morrison I D, Berry A J and Denning R G 1999 *Mol. Phys.* **96** 43
[10] Morrison I D 1992 *PhD Thesis* University College, Oxford
[11] Xia S, Williams G M and Edelstein N M 1989 *Chem. Phys.* **138** 255
[12] Burdick G W, Kooy H J and Reid M F 1993 *J. Phys.: Condens. Matter* **5** L323
[13] Burdick G W and Reid M F 1993 *Phys. Rev. Lett.* **70** 2491
[14] Reid M F, Burdick G W and Kooy H J 1994 *J. Alloys Compounds* **207/208** 78
[15] Duan C K, Reid M F and Burdick G W 2002 *Phys. Rev.* B **66** 155108
[16] Tanner P A, Kumar V V R K, Jayasankar C K and Reid M F 1994 *J. Alloys Compounds* **215** 349
[17] Dieke G H and Crosswhite H M 1963 *Appl. Opt.* **2** 675
[18] Nielson C W and Koster J F 1963 *Spectroscopic Coefficients for p^n, d^n and f^n Configurations* (Cambridge, MA: MIT Press)
[19] Tsukerblat B S 1994 *Group Theory in Chemistry and Spectroscopy* (New York: Academic)
[20] Ceulemans A and Vandenberghe G M 1996 *Phys. Rev.* B **53** 8310
[21] Chua M and Tanner P A 1996 *Phys. Rev.* **54** R11014