

Direct calculation of the two-photon line strength of a Γ_{1g} - Γ_{1g} transition in octahedral symmetry

Michael Chua and Peter A. Tanner

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong

(Received 7 June 1996; revised manuscript received 16 July 1996)

Using a direct calculation, the line intensity of the two-photon (7F_6) Γ_{1g} - Γ_{1g} (5D_4) transition of Tb^{3+} in the elpasolite lattice has been accounted for under third-order perturbation theory. Employing the appropriate $4f^75d$ intermediate levels, χ and μ , the transition moment has been written in terms of electric-dipole allowed transitions between the $4f^8$ and $4f^75d$ configurations, and of the spin-orbit coupling between the intermediate states. The calculated line strength is sensitive to the locations of the intermediate-state energy levels. [S0163-1829(96)50540-0]

I. INTRODUCTION

Kaiser and Garrett¹ first observed the phenomenon of two-photon absorption in $Eu^{2+}:\text{CaF}_2$. Subsequently, the theory for two-photon intraconfigurational transitions was developed by Axe,² using the conventional Judd-Ofelt closure approximation^{3,4} in second-order perturbation, by coupling the two electric dipole operators into an effective operator acting between same parity initial and final states. A complete evaluation of second-order effects was given by Kibler and Gacon⁵ and by Reid and Ng.⁶ Third-order processes in intraconfigurational two-photon spectroscopy, including spin-orbit interaction in intermediate states^{7,8} were introduced to understand experimental results for Gd^{3+} . The extension to fourth order was carried out by Downer⁹ and Ceulemans.¹⁰ The group-theoretical solution rules and polarization dependence of two-photon transitions were derived by Bader and Gold¹¹ and generalized by Andrews¹² and Kibler and Daoud,¹³ and are substantially different from those for one-photon transitions. This provides a source of complementary information for the investigation of the energy levels and excited states of transition-metal and rare-earth ions. The use of linear or circularly polarized radiation with oriented cubic crystals has enabled detailed assignments to be made for s -electron [Tl^+ (Refs. 14 and 15), d -electron (Mn^{4+} ,¹⁶ Cu^+ ,¹⁷ and Ni^{2+} (Refs. 18–20)] and f -electron [Sm^{2+} ,^{21,22} Eu^{3+} ,²² and Eu^{2+} (Ref. 23)] systems. A more suitable cubic lattice for the investigation of tripositive cations is the elpasolite type,²⁴ and experimental two-photon studies have been performed for $Cs_2NaGdCl_6$.^{25–27} In this system all of the crystal field (CF) levels of the ${}^8S_{7/2}$ electronic ground state of the Gd^{3+} ion are nearly degenerate so that the selection rules for transitions to CF levels of excited multiplet terms are not restrictive. However, f^n systems in elpasolite lattices with even n may present more restrictive selection rules and more distinguishing polarization dependences for transitions between CF levels. In this study we focus upon the two-photon absorption strength of the 7F_6 to 5D_4 transition of the Tb^{3+} ion in the octahedral elpasolite lattice, which has been measured by Denning.²⁸ In particular, the observed intensity of the (7F_6) Γ_{1g} → Γ_{1g} (5D_4) transition was observed about 14 times greater than (7F_6) Γ_{1g} → Γ_{3g} (5D_4).²⁸ The intensity of the former transition is, however, calculated to be zero when

the Judd-Ofelt approximation is employed in third-order Judd-Pooler-Downer formalism.^{7,9} Ceulemans has attributed the intensity to a fourth-order mechanism,¹⁰ by contrast to the latter weaker transition which was attributed to a third-order mechanism. The current interest in direct calculations^{29,30} prompted us to perform a direct calculation of the intensities of transitions between the relevant CF levels of Tb^{3+} in order to resolve these problems. In what follows it is shown that the Γ_{1g} → Γ_{1g} transition can be explained by direct calculation using third-order perturbation theory, and that the calculated values are comparable with the experimental results.

II. GROUP-THEORETICAL BACKGROUND

The two-photon absorption between $4f^n$ states of the same parity can be described by using second-order perturbation theory.³¹ The initial state couples with the final state by two electric dipole operators via the opposite parity intermediate levels. The intermediate levels belong to configurations such as $4f^{n-1}d$, $4f^{n+1}d^{-1}$, and $4f^{n-1}g$,³² and for simplicity in this study we confine this to appropriate $4f^{n-1}5d$ states. Higher-order processes are necessary when the second-order contribution is $\Delta S \neq 0$, ΔL or $\Delta J > 2$, and/or the transition is forbidden by symmetry selection rules between CF states. In the third-order case, the transition matrix element between initial state $\Gamma_i\gamma_i$ and final state $\Gamma_f\gamma_f$ (where γ_i is a component of the representation Γ_i) can be written as^{7,9}

$$M_{\Gamma_i\gamma_i \rightarrow \Gamma_f\gamma_f} = \sum_{\mu,\chi} \left[\frac{\langle \Gamma_f\gamma_f | \epsilon_1 \cdot D | \mu \rangle \langle \mu | V | \chi \rangle \langle \chi | \epsilon_2 \cdot D | \Gamma_i\gamma_i \rangle}{(E_\chi - E_{\Gamma_i} - \hbar\omega_2)(E_{\Gamma_f} - E_\mu)} + \frac{\langle \Gamma_f\gamma_f | \epsilon_2 \cdot D | \mu \rangle \langle \mu | V | \chi \rangle \langle \chi | \epsilon_1 \cdot D | \Gamma_i\gamma_i \rangle}{(E_\chi - E_{\Gamma_i\gamma_i} - \hbar\omega_1)(E_{\Gamma_f} - E_\mu)} \right] \quad (1)$$

The summation is over all the intermediate states $|\chi\rangle$ and $|\mu\rangle$. V can be the spin-orbit or crystal-field operator, and the operator acts between intermediate (d -electron) states. $\hbar\omega_1$

and $\hbar\omega_2$ are the photon energies. $\varepsilon \cdot D$ is the scalar product of the polarization vector ε of the photon and of the electron dipolar operator D where

$$\begin{aligned} D_q^1 &= \sum_i r_i C_q^1, \\ C_x &= \frac{1}{\sqrt{2}}(C_{-1}^1 - C_1^1), \\ C_y &= \frac{i}{\sqrt{2}}(C_{-1}^1 + C_1^1), \\ C_z &= C_0^1. \end{aligned} \quad (2)$$

The two-photon transition line strength can be expressed as³¹

$$S_{\Gamma_i \rightarrow \Gamma_f} = \sum_{\gamma_i, \gamma_f} |M_{\Gamma_i \gamma_i \rightarrow \Gamma_f \gamma_f}|^2. \quad (3)$$

In \mathbf{O}_h point group symmetry the representation of the electric dipole operator is Γ_{4u} .³¹ Under second-order perturbation, for a Γ_{1g} initial CF state the allowed two-photon transitions are to terminal CF states contained in the direct product $\Gamma_{4u} \otimes \Gamma_{4u}$, i.e., to Γ_{1g} , Γ_{3g} , Γ_{4g} , and Γ_{5g} provided that the LSJ selection rules are complied with. A $\Gamma_{1g} - \Gamma_{2g}$ transition is therefore symmetry forbidden, and it can be shown a $\Gamma_{1g} - \Gamma_{4g}$ transition is forbidden when using two photons from a single beam.³³ Under the Judd-Ofelt approximation the two dipole operators are coupled into a second rank tensor operator which transforms as $\Gamma_{3g} + \Gamma_{5g}$ (\mathbf{O}_h). Therefore, only the transitions to terminal CF states with $\Gamma_{3g} + \Gamma_{5g}$ representations are allowed in second order. We will comment elsewhere concerning the use of the Judd-Ofelt approximation in this calculation, and the fourth-order formalism of Ceulemans.¹⁰

III. TWO-PHOTON ABSORPTION SPECTRUM OF $\text{Cs}_2\text{NaTbCl}_6$

This section presents the direct calculation of the intensity of the two-photon transition from the ground state of the $4f^8$ configuration of Tb^{3+} in $\text{Cs}_2\text{NaTbCl}_6$ (7F_6) Γ_1 , to the excited CF levels (5D_4) Γ_1 and (5D_4) Γ_3 . The polarization directions are not specified in the published²⁸ one-color two-photon absorption spectrum of $\text{Cs}_2\text{NaTbCl}_6$. Elpasolite crystals prepared by us are polycrystalline on a microscopic scale. In the following calculation we consider one-color linearly polarized radiation parallel to the [001] crystal axis. The initial and final states $|i\rangle$ and $|f\rangle$ described in the subgroup \mathbf{O} , can be written as³⁴

$$\begin{aligned} & |4f^8(2S^{+1}L_J\Gamma_J\gamma_J)\rangle \\ &= \sum_{\substack{M_J, M_S, M_L, \\ M_{S'}, M_{L'}, m_{f_s}, m_{f_l}}} \langle JM_J | \Gamma_J \gamma_J \rangle \langle SM_S LM_L | JM_J \rangle \\ & \times \langle S' M_{S'} \frac{1}{2} m_{f_s} | SM_S \rangle \langle L' M_{L'} 3 m_{f_l} | LM_L \rangle \\ & \times \langle J' M_{J'} | S' M_{S'} L' M_{L'} \rangle \\ & \times |4f^7(2S^{+1}L_{J'}J'M_{J'})\rangle |4f^1 \frac{1}{2} m_{f_s} 3 m_{f_l}\rangle. \end{aligned} \quad (4)$$

The values of the Clebsch-Gordan coefficients and the basis transformation coefficients are available in Refs. 35–37. Experimental data for the $4f^7 5d$ intermediate states are inadequate and we limit our calculation to the lowest/dominant intermediate levels. The lowest state results from the coupling of the core $4f^7({}^8S_{7/2})\Gamma_6, \Gamma_7$, and Γ_8 levels with the $5d$ states.^{38,39} The CF splitting of the core ${}^8S_{7/2}$ term multiplet is negligibly small.⁴⁰ The crystal-field splitting of the $5d^1$ state is greater than that due to the spin-orbit coupling, so that the d orbital first splits into Γ_5 and Γ_3 states.⁴¹ The energy of the Γ_5 state is lower than that of Γ_3 by more than $20\,000\text{ cm}^{-1}$.⁴¹ The orbital Γ_3 state will further couple with spin Γ_6 to give the Γ_8 spin-orbit-coupled state. Γ_5 will split into Γ_7 and Γ_8 via the spin-orbit coupling. The separation between Γ_7 and Γ_8 is about 1200 cm^{-1} .⁴¹

The transition between the initial state 7F_6 and the final state 5D_4 is spin forbidden, so that the third-order mechanism involving spin-orbit coupling ($V = H_{SO}$) has to be considered. The spin-orbit operator can be written as

$$H_{SO} = \zeta_f \sum_{n=1}^7 l_n \cdot s_n + \zeta_d l_d \cdot s_d. \quad (5)$$

The matrix element of spin-orbit coupling acting on the d electron is equal to zero in this case. The f -electron spin-orbit operator couples the core state 8S with 6P . The corresponding matrix element,

$$\left\langle 4f^7({}^8S) \left| \zeta_f \sum_{n=1}^7 l_n \cdot s_n \right| 4f^7({}^6P) \right\rangle,$$

is equal to $\zeta_f \sqrt{14}$, where $\zeta_f = 1696\text{ cm}^{-1}$.⁴² We neglect the electrostatic interaction between the $4f^7$ core and the $5d$ electron, and this approximation is not likely to lead to a serious error.³⁴ The wave function of the intermediate state can then be written as³⁴

$$|4f^7(2S^1 + 1L_{J'}\Gamma_{J'}\gamma_{J'})5d(\Gamma_s\Gamma_l\Gamma_d\gamma_d)\rangle, \quad (6)$$

where the irreducible representations describing the $5d$ electron refer to spin, orbit, and spin-orbit coupled states, respectively. The core $4f^7$ and the $5d$ representation of the intermediate states are transformed into JM and $sm_s lm_l$ bases, respectively,

$$\begin{aligned} & |4f^7(2S^{+1}L_{J'}\Gamma_{J'}\gamma_{J'})5d(\Gamma_s\Gamma_l\Gamma_d\gamma_d)\rangle \\ &= \sum_{M_{J'}, \gamma_s, \gamma_l, m_{ds}, m_{dl}} \langle J' M_{J'} | \Gamma_{J'} \gamma_{J'} \rangle \langle \Gamma_s \gamma_s \Gamma_l \gamma_l | \Gamma_d \gamma_d \rangle \\ & \times \langle \frac{1}{2} m_{ds} | \Gamma_s \gamma_s \rangle \langle 2 m_{dl} | \Gamma_l \gamma_l \rangle \\ & \times |4f^7(2S^{+1}L_{J'}J'M_{J'})\rangle |5d \frac{1}{2} m_{ds} 2 m_{dl}\rangle. \end{aligned} \quad (7)$$

The nonvanishing matrix elements of $4f^8({}^7F_6)\Gamma_1 \rightarrow 4f^7({}^8S_{7/2}\Gamma_{7/2}\gamma_{7/2})5d(\Gamma_d\gamma_d)$, and

$$4f^7({}^6P_{7/2}\Gamma_{7/2}\gamma_{7/2})5d(\Gamma_d\gamma_d) \rightarrow 4f^8({}^5D_4\Gamma_1)$$

and $4f^8({}^5D_4\Gamma_3\gamma)$ transitions can then be calculated by employing the Wigner-Eckart theorem,

$$\langle 3m_{fl}|rC_q^1|2m_{dl}\rangle = \langle 3||C^1||2\rangle \langle 3m_{fl}|1q2m_{dl}\rangle \langle f|r|d\rangle / \sqrt{7} \quad (8)$$

and

$$\langle 2m_{dl}|rC_q^1|3m_{fl}\rangle = \langle 2||C^1||3\rangle \langle 2m_{dl}|1q3m_{fl}\rangle \langle d|r|f\rangle / \sqrt{5}. \quad (9)$$

The results for the calculated matrix elements will be presented in detail elsewhere, and are the same when using Griffith's³⁵ or Watanabe's³⁶ and Koster's³⁷ tables. We take the energy of the intermediate levels $4f^7(^8S_{7/2}\Gamma_6, \Gamma_7, \text{ and } \Gamma_8) 5d\Gamma_5(\Gamma_8 \text{ and } \Gamma_7)$ (labeled $E1$ hereafter) and $4f^7(^8S_{7/2}\Gamma_6, \Gamma_7, \text{ and } \Gamma_8) 5d\Gamma_3(\Gamma_8)$ ($E2$) to be $37\,000\text{ cm}^{-1}$ and $57\,000\text{ cm}^{-1}$, respectively.³⁹ The energy levels due to the electrostatic interactions between the crystal-field levels of the core $4f^7(^6P_{7/2})$ and the $5d$ electron are expected to be much higher than those of the $4f$ shell and we approximate these energy levels to be degenerate. Upon substitution of the calculated matrix elements and the relevant energies into Eq. (1), the calculated two-photon transition strength is identical in the xx , yy , and zz polarization direction for the $\Gamma_{1g} \rightarrow \Gamma_{1g}$ or the $\Gamma_{1g} \rightarrow \Gamma_{3g}$ transition. The ratio (labeled R) between the two-photon transition strengths of $\Gamma_{1g} \rightarrow \Gamma_{1g}$ and $\Gamma_{1g} \rightarrow \Gamma_{3g}$ is estimated to be 5.6 which is in good agreement with the experimental result, considering the approximations in intermediate state energies, and the neglect of J mixing in our calculations. The calculated polarization dependences of the $(^7F_5)\Gamma_{1g} \rightarrow \Gamma_{1g}, \Gamma_{3g}, \Gamma_{5g}(^5D_4)$ transitions are in agreement with the predictions from simple group theory.³³ In particular, the intensity of the $(^7F_6)\Gamma_{1g} \rightarrow \Gamma_{5g}(^5D_4)$ transition is zero for one-color excitation by two photons of the same polarization. Figure 1 shows the sensitivity of the ratio R to the energies $E1$ and $E2$, keeping $E2$ constant. The energy of the intermediate $4f^{n-1}5d\Gamma_{4u}$ CF state plays a crucial role in the prediction of the correct ratio R .

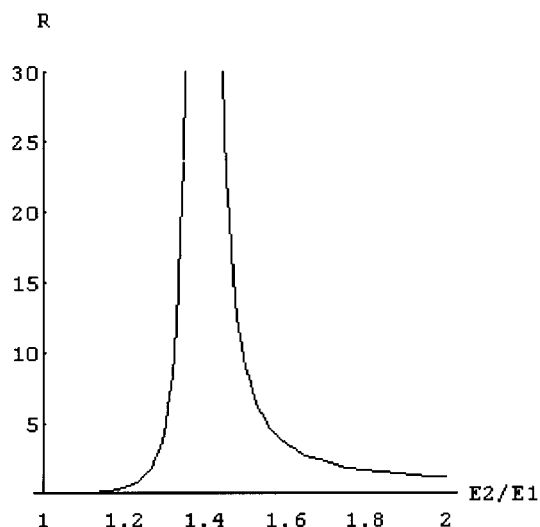


FIG. 1. Plot of the ratio (R) between the two-photon transition strengths of $\Gamma_{1g} \rightarrow \Gamma_{1g}$ and $\Gamma_{1g} \rightarrow \Gamma_{3g}$ against the ratio of the energies of the intermediate levels $4f^7(^8S_{7/2}\Gamma_6, \Gamma_7 \text{ and } \Gamma_8)5d\Gamma_5(\Gamma_8 \text{ and } \Gamma_7)$ ($E1$) and $4f^7(^8S_{7/2}\Gamma_6, \Gamma_7 \text{ and } \Gamma_8)5d\Gamma_3(\Gamma_8)$ ($E2$).

IV. CONCLUSIONS

In this study, we have demonstrated that the two-photon transition $(^7F_6)\Gamma_{1g} \rightarrow \Gamma_{1g}(^5D_4)$ of Tb^{3+} in the elpasolite lattice is allowed under third-order perturbation and that a direct calculation can reproduce the relative line strength in agreement with experiment. The sensitivity of our calculated result to the locations of the $5d$ -electron energy levels demonstrates that the approximation of an effective barycenter may not be justified.

P.A.T thanks the HK UGC for partial support of this work under RG9040098.

¹W. Kaiser and C. G. B. Garrett, Phys. Rev. Lett. **7**, 229 (1961).

²J. D. Axe, Jr., Phys. Rev. **42**, 136 (1964).

³B. R. Judd, Phys. Rev. **127**, 181 (1962).

⁴G. S. Ofelt, J. Chem. Phys. **62**, 511 (1962).

⁵M. Kibler and J.-C. Gacon, Croatica Chemica Acta **62**, 783 (1989).

⁶M. F. Reid and B. Ng, Mol. Phys. **67**, 407 (1989).

⁷B. R. Judd and D. R. Pooler, J. Phys. C **15**, 591 (1982).

⁸G. W. Burdick and M. F. Reid, Phys. Rev. Lett. **70**, 2491 (1993).

⁹M. C. Downer in *Laser Spectroscopy of Solids II*, edited by W. M. Yen (Springer, Berlin, 1989), p. 29.

¹⁰A. Ceulemans and G. M. Vandenberghe, J. Chem. Phys. **98**, 9372 (1993); **102**, 7762 (1995).

¹¹T. R. Bader and A. Gold, Phys. Rev. **171**, 997 (1968).

¹²D. L. Andrews, Spectrochim. Acta A **46**, 871 (1990).

¹³M. Kibler and M. Daoud, Lett. Math. Phys. **28**, 269 (1993).

¹⁴D. Frolich, B. Staginnus, and S. Thurm, Phys. Status Solidi **40**, 287 (1970).

¹⁵E. Doni, R. Giralanda, and G. P. Parravicini, Phys. Status Solidi **65**, 203 (1974).

¹⁶R.-L. Chien, J. M. Berg, D. S. McClure, P. Rabinowitz, and B. N. Perry, J. Chem. Phys. **84**, 4168 (1986).

¹⁷D. S. McClure and S. C. Weaver, J. Phys. Chem. Solids **52**, 81 (1991).

¹⁸C. Campochiaro, D. S. McClure, P. Rabinowitz, and S. Dougal, Phys. Rev. B **43**, 14 (1991).

¹⁹J. Sztucki, J. Lumin. **53**, 562 (1992).

²⁰J. Sztucki, M. Daoud, and M. Kibler, Phys. Rev. B **45**, 2023 (1992).

²¹J. Gacon, G. W. Burdick, B. Moine, and H. Bill, Phys. Rev. B **47**, 11 712 (1993).

²²J. C. Gacon, M. Bouazaoui, B. Jacquier, M. Kibler, L. A. Boatner, and M. M. Abraham, Eur. J. Solid State Inorg. Chem. **28**, 113 (1991).

²³C. Dujardin, B. Moine, and C. Pedrini, J. Lumin. **54**, 259 (1993).

²⁴L. R. Morss, M. Siegal, L. Stenger, and N. Edelstein, Inorg. Chem. **9**, 1771 (1970).

²⁵M. Bouazaoui, B. Jacquier, C. Linares, W. Streck, and R. L. Cone, J. Lumin. **48/49**, 318 (1991).

²⁶M. Bouazaoui, B. Jacquier, C. Linares, and W. Streck, J. Phys. C **3**, 921 (1991).

- ²⁷L. Kundu, A. K. Banerjee, and M. Chowdhury, *Chem. Phys. Lett.* **181**, 569 (1991).
- ²⁸R. G. Denning, *Eur. J. Solid State Inorg. Chem.* **28**, 33 (1991).
- ²⁹G. W. Burdick, H. J. Kooy, and M. F. Reid, *J. Phys., Condens. Matter.* **5**, L323 (1993).
- ³⁰M. F. Reid, G. W. Burdick, and H. J. Kooy, *J. Alloys Compd.* **207/208**, 78 (1994).
- ³¹B. S. Tsukerblat, *Group Theory in Chemistry and Spectroscopy* (Academic Press, New York, 1994).
- ³²P. C. Becker, N. Edelstein, B. R. Judd, R. C. Leavitt, and G. M. S. Lister, *J. Phys. C* **18**, L1063 (1985).
- ³³U. M. Grassano, *Optical Properties of Excited States in Solids*, edited by B. Di Bartolo (Plenum, New York, 1992), p. 643.
- ³⁴T. Hoshina, *J. Phys. Soc. Jpn.* **48**, 1261 (1980).
- ³⁵J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, 1980).
- ³⁶H. Watanabe, *Operator Methods in Ligand Field Theory* (Prentice-Hall, Englewood Cliffs, New Jersey, 1966).
- ³⁷G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, Massachusetts, 1963).
- ³⁸N. Spector and J. Sugar, *J. Opt. Soc. Am.* **66**, 436 (1976).
- ³⁹W. T. Carnall, J. V. Beitz, and H. Crosswhite, *J. Chem. Phys.* **80**, 2301 (1984).
- ⁴⁰C. A. Morrison, R. P. Leavitt, and D. E. Wortman, *J. Chem. Phys.* **73**, 2580 (1980).
- ⁴¹R. W. Schwartz and P. N. Schatz, *Phys. Rev. B* **8**, 3229 (1973).
- ⁴²P. A. Tanner, V. V. R. K. Kumar, C. K. Jayasankar, and M. F. Reid, *J. Alloys Compd.* **215**, 349 (1994).