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Fourth-order contributions to the $^8S_{7/2} \rightarrow {}^6I_{17/2}$ two-photon transition of Gd^{3+} in a cubic lattice

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Abstract

Model calculations are performed to illustrate the recently proposed general tensor expressions for the intensity of orbit- and spin-forbidden two-photon transitions in lanthanide compounds. Attention is focused on the $^8S_{7/2} \rightarrow {}^6I_{17/2}$ transition of the Gd^{3+}-ion in a cubic lattice. A transition operator of the required symmetry is obtained by a fourth-order combination of the two dipole operators with spin-orbit coupling and crystal field interactions. The calculation makes use of a symbolic algorithm to evaluate 9j and 12j symbols.

1. Introduction

Several theoretical papers have been devoted to higher-order corrections to the second-order theory of two-photon transitions in lanthanide compounds [1–4]. A critical examination of the use of perturbation theory in such intensity calculations has also been presented [5,6]. In a recent contribution we have offered general expressions for the fourth-order mechanism involving a combination of spin-orbit coupling (s.o.c.) and crystal field interactions [7]. This work generalized partial results obtained previously by Downer and Bivas for the specific case of the $^8S \rightarrow {}^6I$ transition in the Gd^{3+} ion [8]. The transition operator corresponding to the fourth-order mechanism is given in eqn. (1).

$$
\begin{aligned}
&(-1)^{l'}(2l+1)(2l'+1)^2\langle nl|r|n'l'\rangle^2\begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \\
&\times E_{ll'}^{-3}\sum_k(-1)^k\begin{pmatrix} l' & k & l' \\ 0 & 0 & 0 \end{pmatrix} \\
&\times\Bigg[2\xi_l(l(l+1)(2l+1))^{1/2}\sum_{n,m}(-1)^n(2m+1)^{1/2} \\
&\times\begin{Bmatrix} 1 & l' & l \\ 1 & l' & l \\ m & k & n \end{Bmatrix} \\
&\times((\epsilon\epsilon)^{(0m)}\mathbf{B}^{(0k)})^{(0n)}\cdot(\mathbf{a}^+\mathbf{a})^{(0n)}(\mathbf{a}^+\mathbf{a})^{(11)0} \\
&+\xi_l 2^{1/2}(l(l+1)(2l+1))^{1/2}\sum_{n,m,\lambda}(-1)^{n+\lambda} \\
&\times[(2\lambda+1)(2m+1)]^{1/2}\begin{Bmatrix} 1 & l' & l \\ 1 & l' & l \\ m & k & n \end{Bmatrix}\begin{Bmatrix} 1 & \lambda & n \\ l & l & l \end{Bmatrix} \\
&\times((\epsilon\epsilon)^{(0m)}\mathbf{B}^{(0k)})^{(0n)}\cdot(\mathbf{a}^+\mathbf{a})^{(1\lambda)n} \\
&+\xi_{l'}2^{1/2}(l'(l'+1)(2l'+1))^{1/2}\sum_{n,m}\sum_{\lambda\text{even}} \\
&\times(-1)^{n+1}[(2\lambda+1)(2m+1)]^{1/2}\begin{Bmatrix} 1 & 1 & m & n \\ l & l & \lambda & l' \\ l' & l' & k & 1 \end{Bmatrix} \\
&\times((\epsilon\epsilon)^{(0m)}\mathbf{B}^{(0k)})^{(0n)}\cdot(\mathbf{a}^+\mathbf{a})^{(1\lambda)n}\Bigg] \qquad (1)
\end{aligned}
$$

The second-quantization operators $\mathbf{a}^+$ and $\mathbf{a}$ create and annihilate the $4l+2$ states of an l-electron ($l=3$). The transition dipoles reach intermediate states of the $l^{N-1}l'$ configuration at an energy distance $E^{ll'}$ ($l'=2$ or 4). The electric vector of the radiation field is written as the tensor quantity $\epsilon^{(01)}$ while the crystal field experienced by the l' electrons is denoted by the $\mathbf{B}^{(0k)}$ tensor. The results in eqn.(1) are derived for two photons of the same source. This implies that the antisymmetric $m=1$ combination of the two photons vanishes. However, the expression can easily be generalized to describe a two-beam two-photon experiment. The required extension has been outlined for the case of a third-order mechanism by Sztucki and Stręk [9].

The present paper provides an example of the explicit calculation of the transition operator. Our purpose is twofold: (i) to illustrate the use of the expression in spectroscopic applications; (ii) to obtain an independent check of the results in eqn. (1). The transition we have picked is between the highest M_J components of the

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$^8S_{7/2}$ and $^6I_{17/2}$ terms of the Gd^{3+} ion in a cubic lattice. This transition has the advantage that it can be calculated by hand at the determinant level, thereby offering a particularly transparent example of the selective sequence of shell openings and closings underlying the two-photon process.

2. Preliminaries

The scalar product of two tensors is defined as

$$\mathbf{T}^{(n)}\cdot\mathbf{U}^{(n)}=\sum_t(-1)^t T_t^{(n)}U_{-t}^{(n)} \tag{2}$$

The components of the one-electron operator $(\mathbf{a}^+\mathbf{a})_t^{(1\lambda)n}$ can be obtained in explicit form by the following decoupling relation:

$$\begin{aligned}&(\mathbf{a}^+\mathbf{a})_t^{(\kappa k)n}\\&=\sum_{\pi q}\sum_{\xi\eta}(-1)^{k-\kappa+l+s+m_{l_\eta}+m_{s_\eta}}\\&\times\{(2\kappa+1)(2k+1)(2n+1)\}^{1/2}\begin{pmatrix}\kappa & k & n\\ \pi & q & -t\end{pmatrix}\\&\times\begin{pmatrix}s & s & \kappa\\ m_{s_\xi} & -m_{s_\eta} & -\pi\end{pmatrix}\begin{pmatrix}l & l & k\\ m_{l_\xi} & -m_{l_\eta} & -q\end{pmatrix}a_\xi^+a_\eta\end{aligned} \tag{3}$$

where a_ξ^+ creates an electron with labels $(s, m_{s\xi}, l, m_{l\xi})$ and a_η annihilates an electron with labels $(s, m_{s\eta}, l, m_{l\eta})$.

In the following, we substitute **a** by **f**. The orbit rank λ is equal to 6 to realize the $I\leftarrow S$ transition ($\Delta L=6$) while the total rank n can be 5, 6 or 7 ($\Delta J=5$). The ΔM_J change in going from $\langle{}^8S_{7/2},7/2|$ to $|{}^6I_{17/2},17/2\rangle$ amounts to 5, which implies that t must be equal to -5. All possible $t=-5$ components of $(\mathbf{f}^+\mathbf{f})^{(1\lambda)n}$ are listed in Table 1.

The so-called physical part of the expression in eqn. (1) involves the coupling of the ϵ and **B** tensors. It is defined as follows:

$$\begin{aligned}&((\epsilon\epsilon)^{(0m)}\mathbf{B}^{(0k)})_{0,t}^{(0n)}\\&=\sum_{x,y}(-1)^{k-m+t}(2n+1)^{1/2}(\epsilon\epsilon)_{0,x}^{(0m)}B_{0,y}^{(0k)}\begin{pmatrix}m & k & n\\ x & y & -t\end{pmatrix}\end{aligned} \tag{4}$$

For a cubic crystal in a d-shell the $\mathbf{B}^{(04)}$ tensor has only three non-zero components [10]

$$\mathscr{H}_{CF}=B_{0,0}^{(04)}C_{0,0}^{(04)}+B_{0,4}^{(04)}C_{0,4}^{(04)}+B_{0,-4}^{(04)}C_{0,-4}^{(04)} \tag{5}$$

where

$$\begin{aligned}&B_{0,0}^{(04)}=21Dq\\&B_{0,4}^{(04)}=B_{0,-4}^{(04)}=\sqrt{5/14}B_{0,0}^{(04)}\end{aligned} \tag{6}$$

As a result, the sum in eqn. (4) will be simplified considerably. The $t=+5$ components required for a $\Delta M_J=5$ transition adopt the following form:

$$((\epsilon\epsilon)^{(02)}\mathbf{B}^{(04)})_{0,5}^{(06)}=\frac{1}{\sqrt{3}}(\epsilon\epsilon)_{0,1}^{(02)}B_{0,4}^{(04)} \tag{7}$$

$$((\epsilon\epsilon)^{(02)}\mathbf{B}^{(04)})_{0,5}^{(05)}=-\frac{\sqrt{2}}{\sqrt{3}}(\epsilon\epsilon)_{0,1}^{(02)}B_{0,4}^{(04)} \tag{8}$$

$$((\epsilon\epsilon)^{(01)}\mathbf{B}^{(04)})_{0,5}^{(05)}=(\epsilon\epsilon)_{0,1}^{(01)}B_{0,4}^{(04)} \tag{9}$$

In addition to these operator parts, the general expression also involves several *nj*-symbols ($n=6$, 9, 12). Only the 6j-symbols up to a certain rank are available from tables [11]. All other symbols were evaluated by means of a symbolic algorithm based on a factorization routine [12]. Some relevant results are specified below.

$$\begin{Bmatrix}1&2&3\\1&2&3\\1&4&5\end{Bmatrix}=\frac{1}{3^2\times7}\qquad\begin{Bmatrix}1&2&3\\1&2&3\\2&4&5\end{Bmatrix}=0$$

$$\begin{Bmatrix}1&2&3\\1&2&3\\2&4&6\end{Bmatrix}=\frac{1}{3\times7\sqrt{5}}$$

$$\begin{Bmatrix}1&1&2&5\\3&3&6&2\\2&2&4&1\end{Bmatrix}=\frac{-1}{3^2\times5\times7\sqrt{2\times11}}$$

$$\begin{Bmatrix}1&1&1&5\\3&3&6&2\\2&2&4&1\end{Bmatrix}=0$$

$$\begin{Bmatrix}1&1&2&6\\3&3&6&2\\2&2&4&1\end{Bmatrix}=\frac{1}{3^2\times5\sqrt{7\times13}} \tag{10}$$

3. The ground and excited state

The $M_J=+7/2$ component of the ground state reads as follows:

$$\begin{aligned}&\langle{}^8S_{7/2},\,7/2|\\&=\{3^+\ \ 2^+\ \ 1^+\ \ 0^+\ \ -1^+\ \ -2^+\ \ -3^+\}^*\end{aligned} \tag{11}$$

where the asterisk denotes the complex conjugate. The $M_J=+17/2$ component of $^6I_{17/2}$ also involves a single determinant, namely $\{3^+\ 3^-\ 2^+\ 1^+\ 0^+\ -1^+\ -2^+\}$. It must be realized that the phase of this component cannot be chosen arbitrarily but is fixed within the

TABLE 1. Components of the one-electron operator with $\Delta M_J = 5$

	$f^+_{-2}f_{3+}$	$f^+_{-3}f_{2+}$	$f^+_{-2}f_{3-}$	$f^+_{-3}f_{2-}$	$f^+_{-1}f_{3+}$	$f^+_{-3}f_{1+}$	$f^+_{-2}f_{2+}$	$f^+_{-3}f_{3-}$
$(f^+f)^{(16)7}_{-5}$	$-\frac{\sqrt{2\times3}}{\sqrt{7\times13}}$	$\frac{\sqrt{2\times3}}{\sqrt{7\times13}}$	$\frac{\sqrt{2\times3}}{\sqrt{7\times13}}$	$-\frac{\sqrt{2\times3}}{\sqrt{7\times13}}$	$-\frac{\sqrt{3\times5}}{\sqrt{7\times13}}$	$-\frac{\sqrt{3\times5}}{\sqrt{7\times13}}$	$\frac{6}{\sqrt{7\times13}}$	$\frac{1}{\sqrt{7\times13}}$
$(f^+f)^{(16)6}_{-5}$	$-\frac{5}{2\sqrt{2\times3\times7}}$	$\frac{5}{2\sqrt{2\times3\times7}}$	$\frac{5}{2\sqrt{2\times3\times7}}$	$-\frac{5}{2\sqrt{2\times3\times7}}$	$\frac{\sqrt{5}}{2\sqrt{3\times7}}$	$\frac{\sqrt{5}}{2\sqrt{3\times7}}$	$\frac{-1}{\sqrt{7}}$	$\frac{1}{\sqrt{7}}$
$(f^+f)^{(16)5}_{-5}$	$\frac{\sqrt{11}}{2\sqrt{2\times3\times13}}$	$\frac{-\sqrt{11}}{2\sqrt{2\times3\times13}}$	$\frac{-\sqrt{11}}{2\sqrt{2\times3\times13}}$	$\frac{\sqrt{11}}{2\sqrt{2\times3\times13}}$	$\frac{-\sqrt{5}}{2\sqrt{3\times11\times13}}$	$\frac{-\sqrt{5}}{2\sqrt{3\times11\times13}}$	$\frac{1}{\sqrt{11\times13}}$	$\frac{\sqrt{11}}{\sqrt{13}}$
$(f^+f)^{(06)6}_{-5}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	0	0	0	0
$(f^+f)^{(15)6}_{-5}$	$\frac{-1}{2\sqrt{2\times3}}$	$\frac{1}{2\sqrt{2\times3}}$	$\frac{-1}{2\sqrt{2\times3}}$	$\frac{1}{2\sqrt{2\times3}}$	$\frac{-\sqrt{5}}{2\sqrt{3}}$	$\frac{\sqrt{5}}{2\sqrt{3}}$	0	0
$(f^+f)^{(15)5}_{-5}$	$\frac{-\sqrt{5}}{2\sqrt{2\times3}}$	$\frac{-\sqrt{5}}{2\sqrt{2\times3}}$	$\frac{\sqrt{5}}{2\sqrt{2\times3}}$	$\frac{\sqrt{5}}{2\sqrt{2\times3}}$	$\frac{1}{2\sqrt{3}}$	$\frac{-1}{2\sqrt{3}}$	0	0
$(f^+f)^{(05)5}_{-5}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0
$(f^2f)^{(14)5}_{-5}$	0	0	0	0	$\frac{-\sqrt{3}}{\sqrt{11}}$	$\frac{-\sqrt{3}}{\sqrt{11}}$	$-\frac{\sqrt{5}}{\sqrt{11}}$	0

Wigner–Racah construction of the f^N states on which all the tensor formulae are based [1]. To determine this phase, we work out a standard matrix element connecting the two components. The general form of these matrix elements is given by Judd [13]:

$$\langle SLJM_J|(\mathbf{f}^+\mathbf{f})^{(\kappa k)n}_t|S'L'J'M'_J\rangle$$

$$= -(-1)^{J-M_J}\begin{pmatrix} J & n & J' \\ -M_J & -t & M'_J\end{pmatrix}\langle SLJ\|\mathbf{W}^{(\kappa k)n}\|S'L'J'\rangle$$

$$= -(-1)^{J-M_J}\begin{pmatrix} J & n & J' \\ -M_J & -t & M'_J\end{pmatrix}\begin{Bmatrix} S & S' & \kappa \\ L & L' & k \\ J & J' & n\end{Bmatrix}$$

$$\times([J][J'][n])^{1/2}\langle SL\|W^{(\kappa k)}\|S'L'\rangle \qquad (12)$$

where $(\mathbf{f}^+\mathbf{f})^{(\kappa k)n}$ represents the second quantized form of $-\mathbf{W}^{(\kappa k)n}$, which is a sum of single-particle operators [14]. As usual, degeneracy numbers such as $2J+1$ are contracted to $[J]$. The $\mathbf{W}^{(\kappa k)}$ doubly reduced matrix element can be calculated using the fractional parentage coefficients tabulated by Nielson and Koster [15]:

$$\langle l^N SL\|\mathbf{W}^{(\kappa k)}\|l^N S'L'\rangle = N\{[S][\kappa][S'][L][k][L']\}^{1/2}$$
$$\times\Sigma_\theta(\theta\{|\bar\theta)(\theta'\{|\bar\theta)(-1)^{\bar S+s+S+\kappa+l+\bar L+L+k}$$
$$\times\begin{Bmatrix} S & \kappa & S' \\ s & \bar S & s\end{Bmatrix}\begin{Bmatrix} L & k & L' \\ l & \bar L & l\end{Bmatrix} \qquad (13)$$

Some relevant reduced matrix elements between $^8S_{7/2}$ and $^6I_{J'}$ are listed in Table 2 [8].

TABLE 2. Reduced matrix elements[a]

J'	$\langle {}^8S_{7/2}\|W^{(16)5}\|{}^6I_{J'}\rangle$	$\langle {}^8S_{7/2}\|W^{(16)6}\|{}^6I_{J'}\rangle$
7/2	$\frac{-2}{\sqrt{3\times13}}$	$\frac{-2}{\sqrt{3}}$
9/2	$\frac{2\sqrt{5}}{\sqrt{3\times13}}$	$\frac{10\sqrt{5}}{7\sqrt{3}}$
11/2	$\frac{-12}{\sqrt{7\times13}}$	$\frac{-12\sqrt{2}}{7}$
13/2	$\frac{5\sqrt{2}}{\sqrt{13}}$	$\frac{\sqrt{2\times5\times17}}{\sqrt{3\times7}}$
15/2	$\frac{-10\sqrt{2\times11}}{\sqrt{3\times7\times13}}$	$\frac{-2\sqrt{2\times5\times11}}{7}$
17/2	$\frac{3\sqrt{2\times11}}{\sqrt{13}}$	$\frac{3\sqrt{2\times19}}{7}$

[a]Downer and Bivas [8] have listed results for $7/2 \leqslant J' \leqslant 15/2$. Their $W^{(16)5}$ values for $J' = 11/2$, 15/2 appear to be incorrect.

From these results, a suitable allowed matrix element can now be calculated:

$$\langle {}^8S_{7/2},\ 7/2|(\mathbf{f}^+\mathbf{f})^{(16)6}_{-5}|{}^6I_{17/2},\ 17/2\rangle = -\frac{1}{\sqrt{7}} \qquad (14)$$

We recall that the explicit form of the $(\mathbf{f}^+\mathbf{f})^{(16)6}_{-5}$ operator

is listed in Table 1. Of all its constituent parts, only the $f^{+}_{-3+}f_{3-}$ combination will be active. It is indeed the only combination which produces the correct change of spin orbitals as required by the transition between the $\langle {}^8S_{7/2}, 7/2|$ and $|{}^6I_{17/2}, 17/2\rangle$ determinants. The expansion coefficient of $f^{+}_{-3+}f_{3-}$ in $(\mathbf{f}^{+}\mathbf{f})^{(16)6}_{-5}$ being $1/\sqrt{7}$ (see Table 1), eqn. (14) can be rewritten as

$$\langle {}^8S_{7/2}, 7/2|f^{+}_{-3+}f_{3-} = -\langle {}^6I_{17/2}, 17/2| \tag{15}$$

Substitution of the determinant form of the ground state component then finally yields

$$|{}^6I_{17/2}, 17/2\rangle = \{3^{+} \quad 3^{-} \quad 2^{+} \quad 1^{+} \quad 0^{+} \quad -1^{+} \quad -2^{+} \quad \} \tag{16}$$

The relative phase of this component is now fixed in accord with the tensorial method.

4. Evaluation of the fourth-order expression

In the master expression of eqn. (1), a series of recouplings has given rise to the first term in which the spin-orbit coupling operator $(\mathbf{a}^{+}\mathbf{a})^{(11)0}$ appears on the far right of the operator part, directly confronting the $|{}^6I_{17/2},17/2\rangle$ ket. Clearly this term cannot contribute to the intensity since s.o.c. is unable to raise the spin of the ${}^6I$ term. To simplify the treatment, we will neglect contributions from g electrons and limit our attention to intermediate f^6d configurations. As a result of the various selection rules governing the changes of S, L and J, eqn. (1) then reduces to

$$(-1)^2 7\times 5^2 \langle 4f|r|5d\rangle^2 \begin{pmatrix} 3 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 E_{fd}^{-3} \begin{pmatrix} 2 & 4 & 2 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \Bigg[\xi_f (-1)^{5+6} 2\times 3\sqrt{2\times 7\times 13} \times \begin{Bmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \\ 1 & 4 & 5 \end{Bmatrix} \begin{Bmatrix} 1 & 6 & 5 \\ 3 & 3 & 3 \end{Bmatrix} \times ((\epsilon\epsilon)^{(01)}\mathbf{B}^{(04)})^{(05)} \cdot (\mathbf{f}^{+}\mathbf{f})^{(16)5}$$

$$+ \xi_f (-1)^{6+6} 2\sqrt{2\times 3\times 5\times 7\times 13} \times \begin{Bmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \\ 2 & 4 & 6 \end{Bmatrix} \begin{Bmatrix} 1 & 6 & 6 \\ 3 & 3 & 3 \end{Bmatrix} \times ((\epsilon\epsilon)^{(02)}\mathbf{B}^{(04)})^{(06)} \cdot (\mathbf{f}^{+}\mathbf{f})^{(16)6}$$

$$+ \xi_d (-1)^{5+1} 2\times 5\sqrt{3\times 13} \begin{Bmatrix} 1 & 1 & 2 & 5 \\ 3 & 3 & 6 & 2 \\ 2 & 2 & 4 & 1 \end{Bmatrix} \times ((\epsilon\epsilon)^{(02)}\mathbf{B}^{(04)})^{(05)} \cdot (\mathbf{f}^{+}\mathbf{f})^{(16)5}$$

$$+ \xi_d (-1)^{6+1} 2\times 5\sqrt{3\times 13} \begin{Bmatrix} 1 & 1 & 2 & 6 \\ 3 & 3 & 6 & 2 \\ 2 & 2 & 4 & 1 \end{Bmatrix} \times ((\epsilon\epsilon)^{(02)}\mathbf{B}^{(04)})^{(06)} \cdot (\mathbf{f}^{+}\mathbf{f})^{(16)6} \Bigg] \tag{17}$$

where terms with vanishing 9j and 12j symbols (cf. eqn. (10)) have been omitted. When working out the operator tensors only the active $f^{+}_{-3+}f_{3-}$ parts have to be retained. After a number of substitutions involving the results from Table 1, eqns. (7)–(10), the transition operator then reduces to

$$\frac{\sqrt{2\times 5}}{7\sqrt{7}} \langle 4f|r|5d\rangle^2 E_{fd}^{-3} \xi_f [(\epsilon\epsilon)^{(01)}_{0,1} + (\epsilon\epsilon)^{(02)}_{0,1}] B^{(04)}_{0,4} f^{+}_{-3+}f_{3-} \tag{18}$$

Surprisingly, the terms in ξ_d have cancelled. An excitation channel involving s.o.c. in the intermediate d-shell is thus effectively forbidden. This selection rule is clarified in the next section. Now the electric radiation fields may be decoupled in the usual way:

$$(\epsilon\epsilon)^{(01)}_{0,1} = \frac{1}{\sqrt{2}} [(\epsilon^{(01)}_{0,1}\epsilon^{(01)}_{0,0}) - (\epsilon^{(01)}_{0,0}\epsilon^{(01)}_{0,1})] \tag{19}$$

$$(\epsilon\epsilon)^{(02)}_{0,1} = \frac{1}{\sqrt{2}} [(\epsilon^{(01)}_{0,1}\epsilon^{(01)}_{0,0}) + (\epsilon^{(01)}_{0,0}\epsilon^{(01)}_{0,1})] \tag{20}$$

In a single source experiment, the tensor of rank 1 in eqn. (19) vanishes. The 'physical' part of the operator thus reduces to

$$[(\epsilon\epsilon)^{(01)}_{0,1} + (\epsilon\epsilon)^{(02)}_{0,1}] B^{(04)}_{0,4} = \sqrt{2}\epsilon^{(01)}_{0,1}\epsilon^{(01)}_{0,0} B^{(04)}_{0,4} \tag{21}$$

Bracketing the $f^{+}_{-3+}f_{3-}$ operator yields -1 in accordance with eqn. (15). The entire transition moment integral then finally becomes

$$-\frac{2\sqrt{5}}{7\sqrt{7}} \langle 4f|r|5d\rangle^2 E_{fd}^{-3} \xi_f \epsilon^{(01)}_{0,1}\epsilon^{(01)}_{0,0} B^{(04)}_{0,4} \tag{22}$$

A spin-orbit coupling and crystal field assisted two-photon process between the highest M_J components of ${}^8S_{7/2}$ and ${}^6I_{17/2}$ of Gd^{3+} in elpasolite lattices is thus allowed. It is seen to require an incident beam with an electric component along the z direction ($\epsilon^{(01)}_{0,0}$) and in the x, y plane ($\epsilon^{(01)}_{0,1}$).

5. Fourth-order mechanism step by step

In the following flow chart, we view the two-photon process at the determinant level, starting from the excited state. The sequence of steps involves, in con-

secutive order, the dipole operator, spin-orbit coupling, crystal field interaction, and again the dipole operator. The labels between brackets refer to d electrons. For each step the relevant operator is fully specified.

$$
\begin{aligned}
|^6I_{17/2},\ 17/2\rangle &= \{3^+\ \ 3^-\ \ 2^+\ \ 1^+\ \ 0^+\ \ -1^+\ \ -2^+\} \\
&\downarrow \frac{1}{\sqrt{7}}\,\epsilon^{(0,1)}_{0,0}\langle 4f|r|5d\rangle d^+_{2+}f_{2+} \\
&= \{3^+\ \ 3^-\ \ [2^+]\ \ 1^+\ \ 0^+\ \ -1^+\ \ -2^+\} \\
&\downarrow \frac{\sqrt{3}}{\sqrt{2}}\,\xi_f f^+_{2+}f_{3-} \\
&= \{3^+\ \ 2^+\ \ [2^+]\ \ 1^+\ \ 0^+\ \ -1^+\ \ -2^+\} \\
&\downarrow -\frac{\sqrt{2\times 5}}{3\sqrt{7}}\,\mathbf{B}^4_4 d^+_{2+}d_{2+} \\
&= \{3^+\ \ 2^+\ \ [-2^+]\ \ 1^+\ \ 0^+\ \ -1^+\ \ -2^+\} \\
&\downarrow \frac{-\sqrt{3}}{\sqrt{7}}\,\epsilon^{(0,1)}_{0,+1}\langle 4f|r|5d\rangle f^+_{-3+}d_{-2+} \\
&= \{3^+\ \ 2^+\ \ 1^+\ \ 0^+\ \ -1^+\ \ -2^+\ \ -3^+\} \\
&\downarrow \\
&= |^8S_{7/2},\ 7/2\rangle
\end{aligned}
$$

The total transition operator is obtained by taking the product of all individual operators, multiplied by an additional factor $-E_{fd}^{-3}$ from the perturbational formalism. This result must be taken twice since the interchange of the second and third step provides an alternative excitation channel with exactly the same transition moment. The resulting operator string is $f^+_{-3+}d_{-2+}d^+_{-2+}d_{2+}f^+_{2+}f_{3-}d^+_{2+}f_{2+}$ which reduces to $-f^+_{-3+}f_{3-}$. This is precisely the one-electron change during the transition (cf. eqn. (15)). The total transition moment then equals the coefficient preceding this operator, namely,

$$
-\frac{2\sqrt{5}}{7\sqrt{7}}\,\langle 4f|r|5d\rangle^2 E_{fd}^{-3}\,\xi_f\epsilon^{(01)}_{0,1}\epsilon^{(01)}_{0,0}B^{(04)}_{0,4} \qquad (23)
$$

which coincides with the result of the preceding section and thus provides an independent check of the formalism. The flow chart clarifies the selective aspects of the transition. It shows why s.o.c. cannot precede the photon process. Indeed the 3^- orbital cannot be changed into a 2^+ orbital before the 2^+ slot has been opened by the radiation field. Furthermore it also illustrates why s.o.c. in the d-shell cannot contribute; indeed, to realize the total $\Delta M_J = 5$ jump, we must take benefit of the maximal change of m_l quantum number allowed by the crystal field operator. Spin-orbit coupling in the d-shell would counteract this change thus rendering the total jump impossible. Finally, one can also easily verify why other photon polarizations would not yield the desired result.

6. Conclusions

In this paper we have calculated the transition moment integral between the highest M_J components of the $^8S_{7/2} \rightarrow {}^6I_{17/2}$ two-photon absorption line of Gd^{3+} in cubic lattices. Two different methods of calculation were found to yield the same results. This provides a gratifying test for the recently proposed [7] fourth-order expressions for spin- and orbit-forbidden two-photon transitions in lanthanide compounds. As the paper illustrates, these expressions can be calculated without a detailed knowledge of the determinant form of the ground and excited state wave functions. The way is thus open to more extensive applications to two-photon absorption spectra of Gd^{3+} in cubic lattices, such as elpasolite [16].

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