

Third-order contributions to the  ${}^8S_{7/2} \rightarrow {}^6P_{7/2}, {}^6P_{5/2}$  two-photon transitions of  $\text{Eu}^{2+}$  in  $\text{KMgF}_3$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 2773

(<http://iopscience.iop.org/0953-8984/16/16/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 14:26

Please note that [terms and conditions apply](#).

## Third-order contributions to the ${}^8S_{7/2} \rightarrow {}^6P_{7/2}, {}^6P_{5/2}$ two-photon transitions of $\text{Eu}^{2+}$ in $\text{KMgF}_3$

Ying Jiang<sup>1</sup>, Lixin Ning<sup>1</sup>, Shangda Xia<sup>1,2</sup>, Min Yin<sup>1</sup> and Peter A Tanner<sup>2</sup>

<sup>1</sup> Structure Research Laboratory, Academia Sinica, Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

<sup>2</sup> Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR, People's Republic of China

Received 20 January 2004

Published 8 April 2004

Online at [stacks.iop.org/JPhysCM/16/2773](http://stacks.iop.org/JPhysCM/16/2773)

DOI: 10.1088/0953-8984/16/16/002

### Abstract

The line strengths in four polarization directions of the incident radiation of the  $({}^8S_{7/2}) \rightarrow ({}^6P_{5/2})\Gamma_7, \Gamma_8$  and  $({}^8S_{7/2}) \rightarrow ({}^6P_{7/2})\Gamma_6, \Gamma_7, \Gamma_8$  two photon absorption (TPA) transitions of  $\text{Eu}^{2+}$  in the perovskite  $\text{KMgF}_3$  host have been calculated using the third-order Judd–Pooler (JP) formalism. In general, the calculated relative intensities are in good agreement with experiment, except for the ratios between the linear and circular polarizations in the  ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$  transitions. In particular, the scalar operator term in the third-order spin–orbital correction formula successfully explains nine  ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$  transitions with different linear polarizations.

### 1. Introduction

The divalent europium ion  $\text{Eu}^{2+}$  has the ground electronic configuration  $4f^7$  and the first excited one  $4f^65d$ . The interconfigurational electronic transition  $4f^7 \rightarrow 4f^65d$  (labelled  $4f \rightarrow 5d$  hereafter) is parity allowed, while the intraconfigurational transition  $4f^7 \rightarrow 4f^7$  (denoted  $4f \rightarrow 4f$  hereafter) is parity-forbidden, i.e. the electric dipole transition is not allowed. Therefore, the optical absorption bands due to the latter transition are much weaker than the absorption bands due to the former transition. Additionally, the high energy weak  $4f \rightarrow 4f$  absorption bands are close in energy to the intense parity-allowed  $4f \rightarrow 5d$  transition bands [1, 2]. For that reason it is difficult to assign the high-lying excited states of the  $4f^7$  configuration using one-photon spectroscopy. Two-photon excitation spectroscopy, however, is a useful tool for the investigation of those high-lying levels of the  $4f^7$  configuration, which are located close to the levels of the  $4f^65d$  configuration, because the  $4f \rightarrow 4f$  two-photon transition is parity allowed. In addition, two-photon spectroscopy has different polarization properties compared with one-photon spectroscopy and is therefore a useful, complementary technique.

The development of two-photon spectroscopy of lanthanide compounds has been characterized by an intensive interplay between theory and experiment, with successive refinements becoming necessary. The theory of two-photon transitions was formulated by Axe [3] using the conventional Judd–Ofelt (JO) closure approximation [4, 5] in second-order 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) [6], who added a matrix element of spin–orbit interaction  $H_{so}$  acting on the intermediate  $4f^{N-1}5d$  states  $|SM_s, LM_l\rangle$  (in the numerator) and a corresponding averaged energy difference (in the denominator) in constructing the two-photon transition amplitude in which the initial and the terminal states have different spin multiplicity, i.e. so-called third-order  $H_{so}$  correction terms were added. Following this approach, Downer [7, 8] considered the crystal–field interaction  $H_{cf}$  instead of the spin–orbit interaction  $H_{so}$  acting on the intermediate  $5d$  electronic states (i.e. so-called third-order  $H_{cf}$  correction terms), and the fourth-order correction terms (considering the crystal–field interaction  $H_{cf}$  and spin–orbit interactions  $H_{so}$  acting on the intermediate  $5d$  electronic states simultaneously) to explain the two-photon transitions forbidden by  $SLJ$  selection rules for the  $\text{Eu}^{2+}$  ion in  $\text{CaF}_2$  and  $\text{SrF}_2$ .

$\text{Eu}^{2+}(4f^7)$  is an attractive system for two-photon investigations because there is a wide transparent window between the  $^8S_{7/2}$  ground state and the first excited state,  $^6P_{7/2}$  at  $\sim 30\,000\text{ cm}^{-1}$ . There are several other reasons for our interest in this system, as follows. First, the analysis is facilitated by the presence of an orbitally nondegenerate ground state, which is not split by the crystal field. The configuration  $4f^7$  has more than 3000 states, and the most important intermediate configuration  $4f^65d$  has more than 30 000 states, so the situation is intricate. Actually, the investigations of two-photon transitions of  $\text{Eu}^{2+}$  in  $\text{CaF}_2$  and  $\text{SrF}_2$  [8] have really shown a puzzle, which could not be explained by standard second-order theory alone. Namely this comprises anomalous line-strength ratios and polarization anisotropy of most of the experimental data. Notably, the energy levels of the excited  $4f^65d$  configuration of  $\text{Eu}^{2+}$  are low-lying, so the denominator  $\Delta E$ , which is the average energy separation between the barycentres of the intermediate and ground configurations, used in the JP theory, might present a problem in the calculation. Finally, the line strengths of two-photon transitions are rather sensitive to the environment of the lanthanide ion. Francini *et al* [9] have investigated the intraconfigurational  $4f^7\ ^8S_{7/2} \rightarrow ^6P_{7/2}$  and  $^8S_{7/2} \rightarrow ^6P_{5/2}$  transitions of  $\text{Eu}^{2+}$  in  $\text{KMgF}_3$  by means of two-photon excitation spectroscopy. As is well-known, the crystal–field effect for  $\text{Eu}^{2+}$  in  $\text{KMgF}_3$  is relatively small in comparison with the hosts  $\text{CaF}_2$  and  $\text{SrF}_2$ . Later, Francini *et al* [10] analysed the intensity and polarization dependencies of  $^8S_{7/2} \rightarrow ^6P_{7/2,5/2}$  transitions in terms of second-order theory in which the spin admixture was included in both of the initial and terminal states. Whereas the relative intensities between the transition  $(^8S_{7/2}) \rightarrow (^6P_{5/2})\Gamma_7$  and the transition  $(^8S_{7/2}) \rightarrow (^6P_{5/2})\Gamma_8$  using various polarizations were satisfactorily interpreted, the second-order theory completely failed in predicting the intensity distributions among the three  $(^8S_{7/2}) \rightarrow (^6P_{7/2})\Gamma_6, \Gamma_7, \Gamma_8$  transitions for various linear polarization directions, as well as the their intensity ratios for circular and linear polarizations.

In this paper our intentions are to renew the two-photon absorption (TPA) intensity calculation for  $\text{Eu}^{2+}$  ions doped into the cubic host  $\text{KMgF}_3$ . By including the third-order Judd–Pooler spin–orbit formalism [6], we have investigated the transition line strengths and relative intensities of the  $(^8S_{7/2}) \rightarrow (^6P_{5/2})\Gamma_7, \Gamma_8$  and  $(^8S_{7/2}) \rightarrow (^6P_{7/2})\Gamma_6, \Gamma_7, \Gamma_8$  TPA transitions under various polarizations, including circular polarization. The calculated relative intensities have then been compared with those observed in experiment and calculated in the previous studies [9, 10].

## 2. Judd–Pooler formalism

For the two-photon transitions under investigation, one term of the matrix element  $M_{\text{JP}}$  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 [6],

$$M_{\text{JP}} = \sum_{m,n} \frac{\langle \Gamma_i\gamma_i | \varepsilon \cdot D | m \rangle \langle m | H_{\text{so}} | n \rangle \langle n | \varepsilon \cdot D | \Gamma_f\gamma_f \rangle}{\Delta E_m \Delta E_n} \quad (1)$$

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

According to electron paramagnetic resonance data [11] and previous calculations [12], the crystal–field components of the  ${}^8S_{7/2}$  multiplet of the  $4f^7$  configuration can be regarded as degenerate. In the present cases, the TPA line strengths of transitions from  ${}^8S_{7/2}$  to states  $|\Gamma_f\gamma_f\rangle$ , can be expressed as

$$S(\alpha_i J_i, \alpha_f J_f \Gamma_f) = \sum_{\Gamma_i} \sum_{\gamma_i \gamma_f} |M(\alpha_i J_i \Gamma_i \gamma_i \rightarrow \alpha_f J_f \Gamma_f \gamma_f)|^2 \quad (2)$$

where  $i$  and  $f$  represent the initial and final states, respectively,  $\alpha = \eta SL$  ( $\eta$  stands for any other quantum numbers that are needed when the set  $SLJM_J$  fails to uniquely define the states of the free ion  $\text{Eu}^{2+}$ ), and  $|\Gamma_i\gamma_i\rangle$  is the state transforming according to row  $\gamma_i$  of the irreducible representation  $\Gamma_i$  of the cubic point group. The sum over  $\Gamma_i$  extends over all the irreducible representations of the ground state  ${}^8S_{7/2}$ . To simplify the calculation, Judd and Pooler applied the JO closure approximation twice and coupled the two electric dipole operators and spin–orbit operator into a single effective operator  $H_{\text{eff}}$ . The matrix element of equation (1) then becomes:

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

where  $\Delta E_{\text{fd}}$  comes from  $\Delta E_m$  and  $\Delta E_n$  in equation (1), and is approximated to be 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 [13] 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 above consists of three parts, written as [13]

$$\begin{aligned} \Delta E_{\text{fd}}^{-2} H_{\text{eff}} = & -(2l+1)(2l'+1) \langle nl|r|n'l'\rangle^2 \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \Delta E_{ll'}^{-2} \\ & \times \left[ -\xi_l (l(l+1)(2l+1))^{1/2} \sum_t \begin{Bmatrix} 1 & l & l' \\ l & 1 & t \end{Bmatrix} (\varepsilon\varepsilon)^{(0t)} \cdot (a^+a)^{(0t)t} (a^+a)^{(11)0} \right. \\ & + \xi_l (2)^{-1/2} (l(l+1)(2l+1))^{1/2} \sum_{t,k} \begin{Bmatrix} 1 & l & l' \\ l & 1 & t \end{Bmatrix} \begin{Bmatrix} t & l & l \\ l & 1 & k \end{Bmatrix} \\ & \times (-1)^{k+1} (2k+1)^{1/2} (\varepsilon\varepsilon)^{(0t)} \cdot (a^+a)^{(1k)t} + \xi_{l'} (2)^{-1/2} (l'(l'+1)(2l'+1))^{1/2} \\ & \left. \times \sum_{t,k} \begin{Bmatrix} 1 & l & l' \\ 1 & l & l' \\ t & k & 1 \end{Bmatrix} \times (-1)^{k+1} (2k+1)^{1/2} (\varepsilon\varepsilon)^{(0t)} \cdot (a^+a)^{(1k)t} \right] \quad (4) \end{aligned}$$

where  $l$  and  $l'$  refer to the  $4f$  and  $5d$  orbitals, respectively. The symbols  $a^+$  and  $a$ , the second-quantization operators, create and annihilate the  $4l+2$  states of an  $l$ -electron ( $l=3$ ), respectively.  $\Delta E_{ll'}$  ( $l'=2$ ) is exactly the  $\Delta E_{\text{fd}}$  above. The electric vector of the radiation field

is written as the tensor  $\varepsilon^{(01)}$ . The two labels in the brackets (01) identify the rank of the tensor in spin and orbit space, respectively.  $(\varepsilon\varepsilon)^{(0t)}$  is a coupling tensor of two vectors  $\varepsilon^{(01)}$ , where  $t = 0, 1, 2$ . For two photons of the same source, a coupling of two electric dipoles yields a totally symmetric ( $t = 0$ ) and a quadrupolar term ( $t = 2$ ) while the dipolar term ( $t = 1$ ) is nonexistent.  $\xi_l$  and  $\xi_{l'}$  are spin-orbit parameters for the  $l$  and  $l'$  electron, respectively.

Clearly, the electronic operator in the first term of equation (4) consists of a simple product of spin-orbit coupling operator  $(a^+a)^{(11)0}$  and the operator  $(a^+a)^{(0t)t}$  acting on the states of the  $l$ -shell. In the remaining two terms, the spin-orbit coupling operator and the two-photon electric dipole operator are merged into an effective operator of the form  $(a^+a)^{(1k)t}$ . 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 [14]. All other 3- $j$ , 6- $j$  and 9- $j$  symbols can be calculated from relations given in [15].

In general, the scalar product of two tensors is defined as [16]:

$$T^{(t)} \cdot U^{(t)} = \sum_m (-1)^m T_m^{(t)} U_{-m}^{(t)}. \quad (5)$$

All terms in equation (4) are expressed as scalar products of an electronic part and a physical part [17]. This physical part involves the coupling of the two  $\varepsilon$ -tensors. In the following, 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  $\text{Eu}^{2+}$  free-ion energy levels using Reid's f-shell empirical programs and the input parameters reported by Downer [8] indicate that:

$$\begin{aligned} |[^8\text{S}_{7/2}] \rangle &= 0.99|^8\text{S}_{7/2}\rangle + 0.16|^6\text{P}_{7/2}\rangle \\ |[^6\text{P}_{7/2}] \rangle &= -0.89|^6\text{P}_{7/2}\rangle + 0.39|^6\text{D}_{7/2}\rangle + 0.17|^8\text{S}_{7/2}\rangle \\ |[^6\text{P}_{5/2}] \rangle &= -0.91|^6\text{P}_{5/2}\rangle + 0.38|^6\text{D}_{5/2}\rangle \end{aligned} \quad (6)$$

where the terms with coefficient less than 0.1 are ignored, since their contributions to the wavefunction are less than 1%. At first, we will first approximately (in scheme A) calculate the transitions between initial and final states being normalized pure Russell-Saunders multiplets, i.e. pure multiplets  $^8\text{S}_{7/2}$ ,  $^6\text{P}_{7/2}$  and  $^6\text{P}_{5/2}$ . In this approximation, only the third-order transition element  $M_{\text{JP}}$  in (1) is nonzero, since the second-order mechanism is spin-forbidden for TPA  $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$  and  $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{5/2}$ . Then, the contributions from spin-orbit admixture of multiplets in the equation (6) will be commented upon in scheme B.

The  $(^8\text{S}_{7/2})\Gamma_6$ ,  $\Gamma_7$ ,  $\Gamma_8$ ,  $(^6\text{P}_{7/2})\Gamma_6$ ,  $\Gamma_7$ ,  $\Gamma_8$ , and  $(^6\text{P}_{5/2})\Gamma_7$ ,  $\Gamma_8$  wavefunctions under consideration are easily projected out of the  $J = 7/2, 5/2$  manifolds using the cubic subduction relations. Following Griffith [18], one has

$$\begin{aligned} |^8\text{S}_{7/2}(^6\text{P}_{7/2}), \Gamma_6\alpha' \rangle &= \frac{\sqrt{5}}{\sqrt{12}} \left| \frac{7}{2}, -\frac{7}{2} \right\rangle + \frac{\sqrt{7}}{\sqrt{12}} \left| \frac{7}{2}, \frac{1}{2} \right\rangle \\ |^8\text{S}_{7/2}(^6\text{P}_{7/2}), \Gamma_6\beta' \rangle &= -\frac{\sqrt{5}}{\sqrt{12}} \left| \frac{7}{2}, \frac{7}{2} \right\rangle - \frac{\sqrt{7}}{\sqrt{12}} \left| \frac{7}{2}, -\frac{1}{2} \right\rangle \\ |^8\text{S}_{7/2}(^6\text{P}_{7/2}), \Gamma_7\alpha'' \rangle &= \frac{\sqrt{3}}{2} \left| \frac{7}{2}, \frac{5}{2} \right\rangle - \frac{1}{2} \left| \frac{7}{2}, -\frac{3}{2} \right\rangle \end{aligned}$$

$$\begin{aligned}
|{}^8S_{7/2}({}^6P_{7/2}), \Gamma_7\beta''\rangle &= -\frac{\sqrt{3}}{2} \left| \frac{7}{2}, -\frac{5}{2} \right\rangle + \frac{1}{2} \left| \frac{7}{2}, \frac{3}{2} \right\rangle \\
|{}^8S_{7/2}({}^6P_{7/2}), \Gamma_8\kappa\rangle &= \frac{1}{2} \left| \frac{7}{2}, -\frac{5}{2} \right\rangle + \frac{\sqrt{3}}{2} \left| \frac{7}{2}, \frac{3}{2} \right\rangle \\
|{}^8S_{7/2}({}^6P_{7/2}), \Gamma_8\lambda\rangle &= \frac{\sqrt{7}}{\sqrt{12}} \left| \frac{7}{2}, -\frac{7}{2} \right\rangle - \frac{\sqrt{5}}{\sqrt{12}} \left| \frac{7}{2}, \frac{1}{2} \right\rangle \\
|{}^8S_{7/2}({}^6P_{7/2}), \Gamma_8\mu\rangle &= \frac{\sqrt{7}}{\sqrt{12}} \left| \frac{7}{2}, \frac{7}{2} \right\rangle - \frac{\sqrt{5}}{\sqrt{12}} \left| \frac{7}{2}, -\frac{1}{2} \right\rangle \\
|{}^8S_{7/2}({}^6P_{7/2}), \Gamma_8\nu\rangle &= \frac{1}{2} \left| \frac{7}{2}, \frac{5}{2} \right\rangle + \frac{\sqrt{3}}{2} \left| \frac{7}{2}, -\frac{3}{2} \right\rangle \\
|{}^6P_{5/2}, \Gamma_7\alpha''\rangle &= \frac{1}{\sqrt{6}} \left| \frac{5}{2}, \frac{5}{2} \right\rangle - \frac{\sqrt{5}}{\sqrt{6}} \left| \frac{5}{2}, -\frac{3}{2} \right\rangle \\
|{}^6P_{5/2}, \Gamma_7\beta''\rangle &= \frac{1}{\sqrt{6}} \left| \frac{5}{2}, -\frac{5}{2} \right\rangle - \frac{\sqrt{5}}{\sqrt{6}} \left| \frac{5}{2}, \frac{3}{2} \right\rangle \\
|{}^6P_{5/2}, \Gamma_8\kappa\rangle &= -\frac{1}{\sqrt{6}} \left| \frac{5}{2}, \frac{3}{2} \right\rangle - \frac{\sqrt{5}}{\sqrt{6}} \left| \frac{5}{2}, -\frac{5}{2} \right\rangle \\
|{}^6P_{5/2}, \Gamma_8\lambda\rangle &= \left| \frac{5}{2}, \frac{1}{2} \right\rangle \\
|{}^6P_{5/2}, \Gamma_8\mu\rangle &= -\left| \frac{5}{2}, -\frac{1}{2} \right\rangle \\
|{}^6P_{5/2}, \Gamma_8\nu\rangle &= \frac{\sqrt{5}}{\sqrt{6}} \left| \frac{5}{2}, \frac{5}{2} \right\rangle + \frac{1}{\sqrt{6}} \left| \frac{5}{2}, -\frac{3}{2} \right\rangle.
\end{aligned} \tag{7}$$

These expressions, in addition to equations (3)–(5), allow one to relate the  $({}^8S_{7/2})\Gamma_6, \Gamma_7, \Gamma_8 \rightarrow ({}^6P_{7/2})\Gamma_6, \Gamma_7, \Gamma_8$  and  $({}^8S_{7/2})\Gamma_6, \Gamma_7, \Gamma_8 \rightarrow ({}^6P_{5/2})\Gamma_7, \Gamma_8$  transition matrix elements  $M(\alpha_i J_i \Gamma_i \gamma_i \rightarrow \alpha_f J_f \Gamma_f \gamma_f)$  in equation (2) to the standard  $M_J \rightarrow M_{J'}$  transition elements in the following equations (8) and (11). Firstly, equation (8) is the general form of the matrix element of the one-electron operator  $(a^+a)^{(\kappa k)t}$  given by Judd [16, 19]:

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

where  $(a^+a)^{(\kappa k)t}$  represents the second-quantized form of tensor operator  $-W^{(\kappa k)t}$ , which is a sum of single particle operators. As usual, the degeneracy numbers such as  $2J+1$  are written as  $[J]$ .

Secondly, the reduced matrix element of the double tensor  $W^{(\kappa k)}$  can be calculated as [16]:

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

**Table 1.** The doubly reduced matrix elements  $\langle f^7 \ ^8S || W^{(\kappa k)} || f^7 \eta' S' L' \rangle$  and  $(\kappa, k)$  used in the calculations.

$\eta' S' L'$	$(\kappa, k)$		
	(0, 0)	(1, 1)	(1, 2)
$^6P$	0	$2\sqrt{6}$	0
$^6D$	0	0	$2\sqrt{6}$
$^8S$	$2\sqrt{7}$	0	0

where  $\overline{\eta S \bar{L}}$  is defined as the parentage states of the initial and final states, and  $\langle \eta SL || \overline{\eta S \bar{L}} \rangle$  and  $\langle \overline{\eta S \bar{L}} || \eta' S' L' \rangle$  are the fractional parent coefficients which are available in [20]. For those  $W^{(\kappa k)}$  with  $\kappa = 0$ , the reduced matrix elements can be calculated in an alternative way:

$$\langle I^N \eta SL || W^{(0k)} || I^N \eta' S' L' \rangle = \delta_{S S'} [s]^{-1/2} \{ [S][k] \}^{1/2} \langle I^N \eta SL || U^{(k)} || I^N \eta' S' L' \rangle. \quad (10)$$

In table 1, the values of the reduced matrix elements, which are calculated from equations (9), (10) and used in the calculations of this paper, are listed.

Finally, to evaluate matrix elements of the electronic operator  $(a^+ a)^{(0r)t} (a^+ a)^{(11)0}$ , which appears in the first term of the master expression (4), the following relation is used:

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

where, with the initial state  $\psi = ^8S_{7/2}$ , the corresponding  $\psi''$  is nonexistent when  $\psi'$  is  $^6P_{5/2}$  (or  $^6D_{5/2}$ ,  $^6D_{7/2}$ ), while  $\psi''$  is  $^8S_{7/2}$  when  $\psi'$  is  $^6P_{7/2}$ , in which only  $t = 0$  is allowed.

From the above formulae (8)–(10), several selection rules in the second and the third terms of (4), become apparent. For the transition  $^8S \rightarrow ^6P$ , only the terms with  $k = 1$  are permitted, and for the transition  $^8S \rightarrow ^6D$ , only the terms with  $k = 2$  are permitted, while  $\kappa = 1$  links  $S = 7/2$  and  $5/2$ . In addition, while both  $t = 0, 2$  are allowed for  $^8S_{7/2} \rightarrow ^6P_{7/2}$ , only  $t = 2$  is allowed for the transitions  $^8S_{7/2} \rightarrow ^6P_{5/2}$ ,  $^8S_{7/2} \rightarrow ^6D_{5/2}$  and  $^8S_{7/2} \rightarrow ^6D_{7/2}$ , which can be derived from the property of 3- $j$  and 9- $j$  symbols in equation (8).

## 2.2. Physical part

The coupling tensor  $(\varepsilon \varepsilon)^{(0r)}$  in (4) is the physical part. The tensor  $(\varepsilon \varepsilon)_{0,m}^{(0r)}$  is defined as follows:

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

For the transitions under investigation,  $m_1$  and  $m_2$  are only allowed to be  $\pm 1$  (and not 0), since the experimental spectra were obtained with the excitation beam propagating along the [001] crystal axis [9, 10]. Thus, the allowed values of  $m$  are 0 and  $\pm 2$ , and the following relations are used in the calculation:

$$\begin{aligned} (\varepsilon \varepsilon)_{0,0}^{(00)} &= -\frac{1}{\sqrt{3}} (\varepsilon_{0,0}^{(01)} \varepsilon_{0,0}^{(01)} - \varepsilon_{0,1}^{(01)} \varepsilon_{0,-1}^{(01)} - \varepsilon_{0,-1}^{(01)} \varepsilon_{0,1}^{(01)}) \\ (\varepsilon \varepsilon)_{0,0}^{(02)} &= \frac{1}{\sqrt{6}} (2\varepsilon_{0,0}^{(01)} \varepsilon_{0,0}^{(01)} + \varepsilon_{0,1}^{(01)} \varepsilon_{0,-1}^{(01)} + \varepsilon_{0,-1}^{(01)} \varepsilon_{0,1}^{(01)}) \\ (\varepsilon \varepsilon)_{0,2}^{(02)} &= \varepsilon_{0,1}^{(01)} \varepsilon_{0,1}^{(01)} \\ (\varepsilon \varepsilon)_{0,-2}^{(02)} &= \varepsilon_{0,-1}^{(01)} \varepsilon_{0,-1}^{(01)}. \end{aligned} \quad (13)$$

In our work, the TPA transition line strengths are obtained in circular polarizations, where  $m_1 = m_2 = 1$  or  $-1$ , so that only the last two formulae of (13) with  $t = 2$ ,  $m = 2$  or  $-2$  are

involved, and in the linear polarizations of  $\theta = 0^\circ, 45^\circ$  and  $90^\circ$ , where  $\theta$  is the angle between the [100] crystal axis and the unit electric vector of the excitation beam propagating along the [001] crystal axis. Therefore, in addition to  $\varepsilon_{0,0}^{(01)} = 0$ , the following relationships between the electric dipole vectors and the angle  $\theta$  are used:

$$\begin{aligned}\varepsilon_{0,1}^{(01)} &= -\frac{\varepsilon}{\sqrt{2}}[\cos\theta + i\sin\theta] \\ \varepsilon_{0,-1}^{(01)} &= \frac{\varepsilon}{\sqrt{2}}[\cos\theta - i\sin\theta].\end{aligned}\quad (14)$$

With the above expressions and equation (4), the TPA transition line strengths using linear and circular polarizations can be calculated, and the results are displayed in tables 2 and 3.

### 3. Results and discussion

#### 3.1. ${}^8S_{7/2} \rightarrow ({}^6P_{5/2})\Gamma_7, \Gamma_8$ transitions

The calculated absolute transition line strengths of the  ${}^8S_{7/2} \rightarrow ({}^6P_{5/2})\Gamma_7, \Gamma_8$  TPA transitions are listed in table 2. These results are separated into two groups A and B, corresponding to two types of different wavefunctions (i.e. schemes A and B mentioned in section 2.1) used for the initial and final states, and for each group the experimental relative intensities are also listed for comparison. As indicated in equation (6), the energy level calculations reveal that  ${}^8S_{7/2}$  and  ${}^6P_{5/2}$  show some deviations from pure Russell–Saunders multiplets, so in scheme B we have performed the calculation 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  ${}^6P_{7/2} \rightarrow {}^6P_{5/2}$  and  ${}^6P_{7/2} \rightarrow {}^6D_{5/2}$  in second order and  ${}^8S_{7/2} \rightarrow {}^6D_{5/2}$  in third order. We have only calculated second-order contributions for the spin-allowed  ${}^6P_{7/2} \rightarrow {}^6P_{5/2}$  and  ${}^6P_{7/2} \rightarrow {}^6D_{5/2}$  processes, since in these cases the second-order contributions are much greater than the third-order contributions. The formula (3.4) in [13]:

$$M'_{\text{JP}} = (6\sqrt{70})\langle 4f|r|5d \rangle^2 E_{\text{fd}}^{-1}(\varepsilon\varepsilon)^{(02)} \cdot \langle i|U^{(2)}|f \rangle \quad (15)$$

has been used to calculate the second-order contributions, and for the third-order contributions the method described in the above section has been used.

The pure second-order calculated results in group B produce reasonable relative intensities compared with the experimental data, as can be seen from table 2. It is also shown that in the third-order approximation, the calculated absolute line strengths in group B are a little larger in comparison with group A, and are also larger in comparison with the second-order approximate ones of group B when  $\xi_f/\Delta E_{\text{fd}} = 0.03$  [8] and  $\xi_d/\xi_f = 0.60$  [22] are used. However, relative intensities between the two different transitions are surprisingly similar. As shown in table 2, the calculated ratio between the TPA intensities of  ${}^8S_{7/2} \rightarrow \Gamma_8$  and  ${}^8S_{7/2} \rightarrow \Gamma_7$  for any polarization (there are four kinds of polarization in all) in the third-order approximative calculation in scheme B is in good agreement with the experimental results, and is basically consistent with [10] except for  $\theta = 45^\circ$ . This means that the third-order correction is not very important for the relative intensities of the  ${}^8S_{7/2} \rightarrow {}^6P_{5/2}$  transition. Besides, when the line strength of circular and linear polarization for the  ${}^6P_{5/2}$  manifold is compared, our calculated ratio is around 1.5 (in scheme A or B), which agrees with the corresponding result in [10], and is not very different from the experimental value of 2.1. In addition, for the  ${}^8S_{7/2} \rightarrow \Gamma_8$  transition we can obtain the order of  $S(\theta = 0^\circ) < S(\theta = 45^\circ) < S(\text{circ.})$ , which is in agreement with experimental observations [10]. For the  ${}^8S_{7/2} \rightarrow \Gamma_7$  transition, the order of  $S(\theta = 45^\circ) \cong S(\theta = 0^\circ) < S(\text{circ.})$  is obtained, which is also in agreement with the experimental observations.

**Table 2.** Calculated and observed intensities for the  ${}^8S_{7/2} \rightarrow {}^6P_{5/2}(\Gamma_7, \Gamma_8)$  TPA transitions of  $\text{KMgF}_3:\text{Eu}^{2+}$ .

Final state	Energy ( $\text{cm}^{-1}$ ) <sup>a</sup>	Calculated transition line strength <sup>c</sup>				Relative intensities Calculated <sup>c,e</sup> Calculated <sup>c,f</sup> (Calculated <sup>b</sup> , Observed <sup>a,b</sup> )				
		$\theta = 0^\circ$	$\theta = 45^\circ$	$\theta = 90^\circ$	Circular	$\theta = 0^\circ$	$\theta = 45^\circ$	$\theta = 90^\circ$	Circular	
A <sup>d</sup>	$({}^6P_{5/2})\Gamma_8$	28 267.0	1.711	1.936	1.711	2.792	1.52 (1.29, 1.37)	2.15 (2.60, 2.10)	1.52 (—, 1.56)	1.91 (1.91, 1.80)
	$({}^6P_{5/2})\Gamma_7$	28 270.5	1.126	0.901	1.126	1.464	1.00 (1.00, 1.00)	1.00 (1.00, 1.00)	1.00 (—, 1.00)	1.00 (1.00, 1.00)
B	$({}^6P_{5/2})\Gamma_8$	e	<i>1.287</i>	<i>1.456</i>	<i>1.287</i>	<i>2.099</i>	<i>1.52</i>	<i>2.15</i>	<i>1.52</i>	<i>1.91</i>
		f	1.901	2.151	1.901	3.102	1.52 (1.29, 1.37)	2.15 (2.60, 2.10)	1.52 (—, 1.56)	1.91 (1.91, 1.80)
	$({}^6P_{5/2})\Gamma_7$	e	<i>0.847</i>	<i>0.677</i>	<i>0.847</i>	<i>1.101</i>	<i>1.00</i>	<i>1.00</i>	<i>1.00</i>	<i>1.00</i>
		f	1.251	1.001	1.251	1.626	1.00 (1.00, 1.00)	1.00 (1.00, 1.00)	1.00 (—, 1.00)	1.00 (1.00, 1.00)

<sup>a</sup> From [9].<sup>b</sup> From [10].<sup>c</sup> From this work.<sup>d</sup> In row A, the pure Russell–Saunders multiplets were used for the initial and final states and the transition line strengths are in units of  $2.54 \times 10^{45} \times [5.13 \times 10^{-2}\xi_f - 2.28 \times 10^{-2}\xi_d]^2 \Delta E_{fd}^{-4} \langle f|r|d \rangle^4 \text{ m}^4 \text{ J}^{-2}$ .<sup>e</sup> For the figures in italics in row B, the multiplets with spin–orbit admixtures were used as the initial and final states in the pure second-order calculations and the transition line strengths are in units of  $2.027 \times 10^{39} \Delta E_{fd}^{-2} \langle f|r|d \rangle^4 \text{ m}^4 \text{ J}^{-2}$ .<sup>f</sup> For the nonitalicized figures in row B, the multiplets with spin–orbit admixtures were used as the initial and final states in the third-order approximate calculations and the transition line strengths are in units of  $2.54 \times 10^{45} \times [6 \times 10^{-4} \Delta E_{fd} + (4.71 \times 10^{-2}\xi_f - 1.85 \times 10^{-2}\xi_d)]^2 \Delta E_{fd}^{-4} \langle f|r|d \rangle^4 \text{ m}^4 \text{ J}^{-2}$ .

**Table 3.** Calculated and observed intensities for the  $^8S_{7/2} \rightarrow ^6P_{7/2}(\Gamma_6, \Gamma_7, \Gamma_8)$  TPA transitions of  $\text{KMgF}_3:\text{Eu}^{2+}$ .

	Final state	Energy ( $\text{cm}^{-1}$ ) <sup>a</sup>	Calculated transition line strength <sup>c</sup>				Relative intensities				
			$\theta = 0^\circ$	$\theta = 45^\circ$	$\theta = 90^\circ$	Circular	Calculated <sup>d,e</sup>		Calculated <sup>c,f</sup> (Observed <sup>a,b</sup> ) <sup>g</sup>		
							$\theta = 0^\circ$	$\theta = 45^\circ$	$\theta = 90^\circ$	Circular	
A <sup>d</sup>	$(^6P_{7/2})\Gamma_6$	27 840.3	23.646	23.662	23.646	0.0184	1.00 (0.78)	1.00 (0.78)	1.00 (0.78)	1.296 (0.78)	
	$(^6P_{7/2})\Gamma_8$	27 845.8	47.624	47.343	47.624	0.0340	2.01 (1.85)	2.00 (1.85)	2.01 (1.85)	2.394 (1.85)	
	$(^6P_{7/2})\Gamma_7$	27 847.3	23.629	23.664	23.629	0.0142	1.00 (1.00)	1.00 (1.00)	1.00 (1.00)	1.000 (1.00)	
B	$(^6P_{7/2})\Gamma_6$	27 840.3	e	<i>0.0298</i>	<i>0.0149</i>	<i>0.0298</i>	<i>0.0273</i>	2.33	<i>0.69</i>	2.33	<i>1.258</i>
			f	17.730	17.694	17.730	0.0937	1.01 (0.78)	1.00 (0.78)	1.01 (0.78)	1.191 (0.78)
	$(^6P_{7/2})\Gamma_8$	27 845.8	e	<i>0.0260</i>	<i>0.0349</i>	<i>0.0260</i>	<i>0.0497</i>	2.03	<i>1.61</i>	2.03	<i>2.290</i>
			f	35.633	35.404	35.633	0.1778	2.02 (1.85)	2.00 (1.85)	2.02 (1.85)	2.259 (1.85)
	$(^6P_{7/2})\Gamma_7$	27 847.3	e	<i>0.0128</i>	<i>0.0217</i>	<i>0.0128</i>	<i>0.0217</i>	1.00	<i>1.00</i>	1.00	<i>1.000</i>
			f	17.635	17.712	17.635	0.0787	1.00 (1.00)	1.00 (1.00)	1.00 (1.00)	1.000 (1.00)

<sup>a</sup> From [9]. <sup>b</sup> From [10].<sup>c</sup> From this work. The transition line strengths are in the same unit of  $2.54 \times 10^{45} \xi_f^2 \Delta E_{fd}^{-4} (f|r|d)^4 \text{ m}^4 \text{ J}^{-2}$  for rows A and B.  $\xi_d/\xi_f = 0.60$  [22]. For row B, the value of  $\xi_f/\Delta E_{fd}$  was set to 0.03 [8].<sup>d</sup> The pure Russell–Saunders multiplets were used for the initial and final states in the calculations.<sup>e</sup> The multiplets with spin–orbit admixtures were used as the initial and final states in the pure second-order calculation for the italicized figures.<sup>f</sup> The multiplets with spin–orbit admixtures were used as the initial and final states in the third-order approximate calculations for the nonitalicized figures.<sup>g</sup> For the transition  $^8S_{7/2} \rightarrow ^6P_{7/2}(\Gamma_6, \Gamma_7, \Gamma_8)$ , the ratio of the three components is kept constant (0.78:1.85:1.00) [9] when the polarization changes from linear to circular [10].

**Table 4.** The values of matrix elements of three terms in (4) for the  ${}^8S_{7/2} \rightarrow ({}^6P_{7/2})\Gamma_6$  transition ( $\theta = 0^\circ$ ).

	The first term <sup>a</sup>	The second term <sup>a</sup>	The third term <sup>b</sup>
$\langle {}^8S_{7/2}\Gamma_{6\alpha'}   \rightarrow   {}^6P_{7/2}\Gamma_{6\alpha'} \rangle$	$-\sqrt{14}$	$\sqrt{2}/\sqrt{7}$	$-2\sqrt{2}/(3\sqrt{7})$
$\langle {}^8S_{7/2}\Gamma_{8\lambda}   \rightarrow   {}^6P_{7/2}\Gamma_{6\alpha'} \rangle$	0	$-3/(14\sqrt{10})$	$\sqrt{2}/(21\sqrt{5})$
$\langle {}^8S_{7/2}\Gamma_{8\nu}   \rightarrow   {}^6P_{7/2}\Gamma_{6\alpha'} \rangle$	0	$3\sqrt{3}/(14\sqrt{10})$	$-\sqrt{2}/(7\sqrt{15})$
$\langle {}^8S_{7/2}\Gamma_{6\beta'}   \rightarrow   {}^6P_{7/2}\Gamma_{6\beta'} \rangle$	$-\sqrt{14}$	$\sqrt{2}/\sqrt{7}$	$-2\sqrt{2}/(3\sqrt{7})$
$\langle {}^8S_{7/2}\Gamma_{8\kappa}   \rightarrow   {}^6P_{7/2}\Gamma_{6\beta'} \rangle$	0	$-3\sqrt{3}/(14\sqrt{10})$	$\sqrt{2}/(7\sqrt{15})$
$\langle {}^8S_{7/2}\Gamma_{8\mu}   \rightarrow   {}^6P_{7/2}\Gamma_{6\beta'} \rangle$	0	$3/(14\sqrt{10})$	$-\sqrt{2}/(21\sqrt{5})$

<sup>a</sup> In units of  $5.04 \times 10^{22} \times \langle f|r|d \rangle^2 \Delta E_{ff}^{-2} \xi_f m^2 J^{-1}$ .

<sup>b</sup> In units of  $5.04 \times 10^{22} \times \langle f|r|d \rangle^2 \Delta E_{fd}^{-2} \xi_d m^2 J^{-1}$ .

### 3.2. ${}^8S_{7/2} \rightarrow ({}^6P_{7/2})\Gamma_6, \Gamma_7, \Gamma_8$ transitions

The calculated intensities for the three transitions  ${}^8S_{7/2} \rightarrow ({}^6P_{7/2})\Gamma_6, \Gamma_7, \Gamma_8$ , are shown in table 3. As an example, the values of three terms in the matrix elements of the third-order equation (4) are listed in table 4 for the  ${}^8S_{7/2} \rightarrow ({}^6P_{7/2})\Gamma_6$  transition (when  $\theta = 0$ ). From this, we can see that the contribution of the first term of (4) is most dominant and the contributions from the first and third terms are opposite to the second term. As mentioned following equation (11), for  ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$  only when  $t = 0$ , the first term of (4) has a nonzero contribution (therefore it does not contribute to the circular polarization). If we are to retain only this term in scheme A, we would then predict that for linear polarization the TPA intensity to any Stark components  $\Gamma_i \gamma_i$  of  ${}^6P_{7/2}$  should be equal, since the matrix element  $\langle \psi | (a^+ a)^{(00)0} | \psi'' \rangle$  on the right-hand side of (11), which is proportional to:

$$(-1)^{J-M_J} \begin{pmatrix} J & 0 & J \\ -M_J & 0 & M_J'' \end{pmatrix} = (2J+1)^{-1/2} \delta_{M_J'', M_J} \quad (16)$$

is independent of  $M_J$  (as is the element  $\langle \psi'' | (a^+ a)^{(11)0} | \psi' \rangle$ ). Therefore the relative intensity between different final levels should be proportional to their degeneracy ratio ( $\Gamma_6:\Gamma_7:\Gamma_8 = 1:1:2$ ). Furthermore, none of the Stark component intensities will depend upon the direction of polarization, because  $\varepsilon_{0,1}^{(01)} \cdot \varepsilon_{0,-1}^{(01)}$  is independent of  $\theta$  (see equation (14)). So, as shown in row A of table 3, we obtain the ratios of the transition intensities between these three components  $\Gamma_6, \Gamma_7, \Gamma_8$ , which are basically independent of the polarization angle  $\theta$  and almost proportional to the degeneracy of the final state. These findings are consistent with the experimental observations. From table 3, the calculated results of scheme B still keep the above trends although the calculated absolute intensities are smaller. Then our calculation solves the contradiction left in [10], which declared a complete failure to explain the above observation for linear polarization, as can be seen in detail when we compare the pure second-order calculated results in scheme B with the observed ones from table 3. The key effect of the first term of equation (4) in solving this contradiction is evident.

Our calculated relative intensities for circular polarization are basically consistent with the calculated and experimental values in [10]. However, regarding the comparison with linear polarization we fail to explain the value of  $S(\text{linear})/S(\text{circular})$  which is about 8 from experiment while our calculated value is 1400 in scheme A. In fact, the same discrepancies are found in the work [21] for  $\text{Eu}^{2+}$  in both the  $\text{CaF}_2$  and  $\text{SrF}_2$  host lattices.

However, in our scheme B calculation, the calculated value of  $S(\text{linear})/S(\text{circular})$  is reduced to about 200 when  $\xi_f/\Delta E_{fd} = 0.03$  and  $\xi_d/\xi_f = 0.60$  are included, which is much improved compared with the value 1400. This is because in scheme B, several second order

${}^6P_{7/2} \rightarrow {}^6D_{7/2}$ ,  ${}^6P_{7/2} \rightarrow {}^6P_{7/2}$  and  ${}^8S_{7/2} \rightarrow {}^8S_{7/2}$  and third order  ${}^8S_{7/2} \rightarrow {}^6D_{7/2}$  and  ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$  contributions are included. The calculated results are listed in row B of table 3. Primarily because the contributions from  ${}^6P_{7/2} \rightarrow {}^6D_{7/2}$  and  ${}^8S_{7/2} \rightarrow {}^6D_{7/2}$  of linear polarization are opposite to those from the first (and third) terms in (4) in scheme A, and the coefficients of initial and final states are no longer '1', the absolute transition line strengths in scheme B are less than those in scheme A. However, for the circular polarization the results are opposite, since the second-order  ${}^6P_{7/2} \rightarrow {}^6D_{7/2}$  and the third-order  ${}^8S_{7/2} \rightarrow {}^6D_{7/2}$  transitions themselves make dominant contributions in scheme B for the circular polarization. In the following, we choose the ( $|\text{P}_{7/2}^8\rangle \rightarrow |\text{P}_{7/2}^6\rangle$ ) transition as an example. In scheme B, the matrix element of this transition at circular polarization is given as:

$$M'_{\text{JP}} = \left( 0.0941 + 0.0017 \frac{\Delta E_{\text{fd}}}{\xi_{\text{f}}} - 0.0264 \frac{\xi_{\text{d}}}{\xi_{\text{f}}} \right) \xi_{\text{f}} \langle f|r|d \rangle^2 \Delta E_{\text{fd}}^{-2}, \quad (17)$$

whereas for the pure Russell–Saunders multiplets used in scheme A, the corresponding matrix element is given as

$$M_{\text{JP}} = (-0.0678\xi_{\text{f}} + 0.03\xi_{\text{d}}) \langle f|r|d \rangle^2 \Delta E_{\text{fd}}^{-2}. \quad (18)$$

It is obvious that the transition line strength  $M'_{\text{JP}}{}^2$  is larger than  $M_{\text{JP}}{}^2$ , when  $\xi_{\text{f}}/\Delta E_{\text{fd}} = 0.03$  [8] and  $\xi_{\text{d}}/\xi_{\text{f}} = 0.60$  [22] are used. From (18) we can also see that the transition line strength  $M_{\text{JP}}{}^2$  (in units of  $2.54 \times 10^{45} \text{ m}^4 \text{ J}^{-2}$ ) will increase along with the increase of  $\Delta E_{\text{fd}}/\xi_{\text{f}}$ , which comes mainly from the second-order contribution of  ${}^6P_{7/2} \rightarrow {}^6D_{7/2}$ , and this is not included in scheme A.

It is noticed that the observed intensities could be fit by reducing  $\xi_{\text{f}}/\Delta E_{\text{fd}}$  artificially to about 0.005, but such a low value cannot be justified physically. At the same time,  $M'_{\text{JP}}{}^2$  (or  $M_{\text{JP}}{}^2$ ) will increase when the value of  $\xi_{\text{d}}/\xi_{\text{f}}$  is reduced but the effect is not distinct.

The most promising possibility for the discrepancy is that the closure approximation, which has been fundamental to the derivation of all operators so far, is no longer valid for this divalent ion, since the energy levels of the excited  $4f^65d$  configuration of  $\text{Eu}^{2+}$  are low-lying [23–25]. In addition, the influence of intermediate configurations other than  $4f^65d$  is also an unconsidered factor.

Finally, it is pointed out that the system under investigation does have the experimental disadvantages that as well as cubic sites, the  $\text{Eu}^{2+}$  ion also substitutes at trigonal sites (as in  $\text{Cs}_2\text{NaLaCl}_6$  [26]). Although these sites are in the minority, spectral features are present due to them in both the one- and two-photon spectra. Notably, the emission was monitored at 359 nm in the two-photon excitation spectra [9, 10] and energy transfer between the cubic and trigonal sites could lead to a change in TP transition intensity ratios.

#### 4. Conclusions

Reid *et al* [27] have asserted that the many-body perturbative and JP method of calculation are equivalent in the calculation of two-photon transition line strengths. The present work has taken the  ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ ,  ${}^6P_{5/2}$  transitions of  $\text{Eu}^{2+}$  in the host  $\text{KMgF}_3$  as a case to study. Using the third-order spin-orbital interaction correction, we can satisfactorily interpret these two transitions, especially the intensities of linear polarization TPA transition  ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ , to successfully solve the discrepancy presented in [10]. However, the discrepancy between the calculated ratio of  $S(\text{linear})/S(\text{circular})$  with experimental observations still remains unless an increase of the  $\Delta E_{\text{fd}}/\xi_{\text{f}}$  and  $\xi_{\text{f}}/\xi_{\text{d}}$  parameters is made.

## Acknowledgments

This work is supported by the National Natural Science Foundation of China Research Grant 10274079, and the Doctoral Project Foundation of the National Education Committee of China No 20020358003. We are indebted to Professor Mike Reid for the use of the f-shell programs.

## References

- [1] Rubio O J 1991 *J. Phys. Chem. Solids* **52** 101
- [2] Tsuboi T and Scacco A 1998 *J. Phys.: Condens. Matter* **10** 7259
- [3] Axe J D 1964 *Phys. Rev.* **136** 42
- [4] Judd B R 1962 *Phys. Rev.* **127** 750
- [5] Ofelt G S 1962 *J. Chem. Phys.* **37** 511
- [6] Judd B R and Pooler D R 1982 *J. Phys. C: Solid State Phys.* **15** 591
- [7] Downer M C and Bivas A 1983 *Phys. Rev. B* **28** 3677
- [8] Downer M C, Cordero-Montalvo C D and Crosswhite H 1983 *Phys. Rev. B* **28** 4931
- [9] Francini R, Grassano U M, Tomini M, Boiko S, Tarasov G G and Scacco A 1997 *Phys. Rev. B* **55** 7579
- [10] Francini R, Grassano U M, Boiko S, Tarasov G G and Scacco A 1999 *J. Chem. Phys.* **10** 457
- [11] Newman D J 1976 *Solid State Commun.* **18** 667
- [12] Bouazzoui M, Jacquier B, Linarès C, Stręk W and Cone R L 1991 *J. Lumin.* **48/49** 318
- [13] Ceulemans A and Vandenberghe G M 1993 *J. Chem. Phys.* **98** 9372
- [14] Rotenberg M, Bivins R, Metropolis N and Wooten J K 1959 *The 3-j and 6-j Symbols* (Reading, MA: Technology)
- [15] Tsukerblat B S 1994 *Group Theory in Chemistry and Spectroscopy* (New York: Academic)
- [16] Judd B R 1963 *Operator Techniques in Atomic Spectroscopy* (New York: McGraw-Hill)
- [17] Ceulemans A and Vandenberghe G M 1996 *Phys. Rev. B* **53** 8310
- [18] Griffith J S 1980 *The Theory of Transition Metal Ions* (Cambridge: Cambridge University Press)
- [19] Judd B R 1967 *Second Quantization and Atomic Spectroscopy* (Baltimore, MD: Johns Hopkins University Press)
- [20] Nielson C W and Koster J F 1963 *Spectroscopic Coefficients for  $p^n$ ,  $d^n$  and  $f^n$  Configurations* (Cambridge, MA: MIT Press)
- [21] Downer M C 1983 *PhD Thesis* Harvard University, Cambridge, MA
- [22] Duan C K, Reid M F and Burdick G W 2002 *Phys. Rev. B* **66** 155108
- [23] Altshuler N S, Livanova L D and Stolov A L 1974 *Opt. Spectrosc.* **36** 72
- [24] Ellens A, Meijerink A and Blasse G 1994 *J. Lumin.* **60/61** 70
- [25] Ellens A, Meijerink A and Blasse G 1994 *J. Lumin.* **59** 293
- [26] Boldú J L, Gleason R J, Quintanar C and Muñoz P 1996 *J. Phys. Chem. Solids* **57** 267
- [27] Reid M F, Burdick G W and Kooy H J 1994 *J. Alloys Compounds* **207/208** 78