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2009 J. Phys.: Condens. Matter 21 095503

(http://iopscience.iop.org/0953-8984/21/9/095503)

J. Phys.: Condens. Matter **21** (2009) 095503 (7pp) doi:10.1088/0953-8984/21/9/095503

Direct calculation of $4f^3$–$4f^3$ transition intensities in Nd^{3+}-doped YPO_4 system involving explicit effects of $4f^25d$ configuration

Jinsu Zhang[1,2], **Feng Liu**[3], **Xia Zhang**[1], **Xiao-jun Wang**[1,4] **and Jiahua Zhang**[1,5]

[1] Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China
[2] Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China
[3] Department of Physics and Astronomy, University of Georgia, Athens, GA 30602, USA
[4] Department of Physics, Georgia Southern University, Statesboro, GA 30460, USA

E-mail: zhangjh@ciomp.ac.cn

Received 22 October 2008, in final form 9 January 2009
Published 4 February 2009
Online at stacks.iop.org/JPhysCM/21/095503

Abstract
The effects of the $4f^25d$ configuration on the intraconfigurational $4f^3 \leftrightarrow 4f^3$ electric dipole transitions of Nd^{3+} doped YPO_4 are taken into account by a 'direct' calculation. A simple model is applied to analyze the opposite-parity $4f^25d$ configuration admixing into $4f^3$ transitional states. The matrix elements of the odd-rank crystal-field interaction and the interconfigurational electric dipole transition are directly expressed using a standard tensor operator method. A set of selection rules for f–d mixing and f–f electric dipole transitions is built up. The admixture effect is considered including both explicit $4f^25d$ configuration and other opposite-parity states such as the $4f^2n'g$ configuration which is treated by a closure procedure. Using this calculation method in combination with the experimental data from the absorption spectrum, a set of intensity parameters is obtained. The transition intensities originating from the high-lying $^2G_{9/2}(2)$ level to the lower energy levels are then calculated, demonstrating a good agreement with the experimental results. The new calculation method is suitable for the electric dipole transitions within the $4f^N$ configurations of trivalent lanthanide ions with more than two f-electrons.

1. Introduction

In the past few decades the traditional Judd–Ofelt theory [1, 2] has been widely used to analyze the optical transition properties within the $4f^N$ configuration of rare-earth ions by considering admixture of the opposite-parity configuration into the $4f^N$ configuration. It has succeeded in treating $4f^N \leftrightarrow 4f^N$ (f–f) electric dipole transitions between the low-lying states of rare-earth ions [3, 4]. However, due to the closure procedure in the Judd–Ofelt theory, discrepancies are observed when the theory is applied to the high-lying energy levels of $4f^N$ excited states [5]. Several modifications of the traditional Judd–Ofelt theory have been made because of lack of knowledge about the opposite-parity configurations [6–9], which are generally considered as $4f^{N-1}5d$ and $4f^{N-1}n'g$. The $4f^{N-1}5d$ configuration is regarded as the dominant configuration mixing with the f–f electric dipole transitional states. The position of the lowest $4f^{N-1}5d$ state of rare-earth ions in hundreds of materials has been summarized by Dorenbos [10–12]. A theoretical model to calculate the energy of $4f^{N-1}5d$ states has also been established by Reid [13]. Research on the characteristics of $4f^{N-1}5d$

[5] Author to whom any correspondence should be addressed.

configuration made it possible to understand the explicit effects of $4f^{N-1}5d$ configuration on $4f^N \leftrightarrow 4f^N$ transitions, performed in Pr^{3+} with only two f-electrons [14]. For trivalent rare-earth ions with more the two f-electrons it is difficult to distinguish the $4f^{N-1}5d$ eigenstates. Consequently, a concise method for the calculation of $4f^N \leftrightarrow 4f^N$ electric dipole transitions is required to deal with the $4f^{N-1}5d$ opposite-parity configurations. Meanwhile, a simple and intuitive basic functional form of the $4f^{N-1}5d$ configuration is also needed. Recently Duan *et al* [15] and Duan and Reid [16] developed a simple model for trivalent lanthanide ions with more than two f-electrons, based on the idea of Yanase [17–19]. A clear description of the $4f^{N-1}5d \to 4f^N$ emission spectrum can be obtained by considering the main interactions in the $4f^{N-1}5d$ configuration [20–22].

In this paper a simple model is adopted to deal with the opposite-parity states which can mix with the f–f transitional states. Explicit f–d mixing wavefunctions are included to treat the f–f transition intensities in Nd^{3+} doped YPO_4 ($YPO_4{:}Nd^{3+}$) using direct tensor operator calculation, and the dimensionless intensity parameters T_{kq} are introduced in the electric dipole transition intensity calculation. The opposite-parity configuration of $4f^2n'g$ is treated by a closure procedure. The expression for the matrix element of an induced electric dipole transition between J-multiplets is given by Judd [1]. Furthermore, the intensity parameters have been developed to treat the transitions between the crystal-field levels, and a parameterization scheme based on the $A_{kq}\,\Xi(k,\lambda)$ parameter set has been introduced by Axe [23]. A more general parameter set was proposed by Reid and Richardson A^{λ}_{tp} [24], showing more information about the crystalline symmetry and the lanthanide–ligand interaction. The intensity parameters $\tilde{A}^{\lambda}_{kq}$ are introduced here to treat the f–g mixing. The rare-earth ions are believed to substitute in the Y^{3+} site with the point group symmetry of D_{2d} [25]. A set of intensity parameters are introduced, including the explicit $4f^25d$ configuration admixing terms $T_{kq}(T_{32}, T_{52})$, and other opposite-parity configuration admixing effects $\tilde{A}^{\lambda}_{kq}(\tilde{A}^2_{32}, \tilde{A}^4_{32}, \tilde{A}^4_{52}, \tilde{A}^6_{52}, \tilde{A}^6_{72}$ and $\tilde{A}^6_{76})$. The experimental data collected from absorption spectra are taken from [26]. The values of the parameters T_{kq} and $\tilde{A}^{\lambda}_{kq}$ are obtained by minimizing the least-squares deviation [27]. In addition, the UV emissions originating from ${}^2G_{9/2}(2)$ in $YPO_4{:}Nd^{3+}$ was detected and corrected by the method of Wegh *et al* [28] to obtain the data for the transition intensities. Finally, the calculated results are compared with the values obtained by both traditional Judd–Ofelt theory and experimental measurements.

2. Calculation

2.1. $4f^{N-1}5d$ contribution to f–f electric dipole transitions

The odd crystal field mixes both the initial φ_i and final φ_f transitional states of the $4f^N$ configuration with parity-opposite $4f^{N-1}5d$ states φ''_i and φ''_f, respectively. The nonzero matrix element of the electric dipole operator between the initial and final states within the $4f^N$ configuration is

$$\langle 4f^N\varphi_i|\hat{D}^{(1)}_p|4f^N\varphi_f\rangle = \sum_{\varphi''}\left[\frac{\langle\varphi_i|\hat{D}^{(1)}_p|\varphi''_i\rangle\langle\varphi''_i|H_{CF}|\varphi_f\rangle}{E(\varphi_f)-E(\varphi''_f)} + \frac{\langle\varphi_f|\hat{D}^{(1)}_p|\varphi''_f\rangle\langle\varphi''_f|H_{CF}|\varphi_i\rangle}{E(\varphi_i)-E(\varphi''_i)}\right], \quad (1)$$

where $E(\varphi_i)$ and $E(\varphi_f)$ are the energies of the initial and the final states of $4f^N$, respectively; $E(\varphi''_i)$ and $E(\varphi''_f)$ stand for the energies of the $4f^{N-1}5d$ states that are able to mix with the initial and the final $4f^N$ states, respectively.

H_{CF} is the odd-rank crystal-field interaction Hamiltonian and can be written as

$$H_{CF}(\text{odd}) = \sum_{k,q,j} A_{kq}\cdot\hat{r}^k_j\hat{C}^k_q(j), \qquad k = \text{odd number}, \quad (2)$$

where A_{kq} is the odd-rank crystal-field coefficient; $\hat{r}^k_j$ is the position vector of electron j; and $\hat{C}^k_q(j)$ is the irreducible tensor operator of rank k containing the angular coordinates of electron j. The values of k and q are determined by site symmetry.

The electric dipole operator $\hat{D}^1_p$, which dominates the relevant transition, is expressed as

$$\hat{D}^{(1)}_p = \sum_j \hat{r}_j\hat{C}^{(1)}_p(j). \quad (3)$$

The values of p depend on the standard polarization of incident light: 0 for π and ±1 for σ.

The direct calculation of the electric dipole transitions within the $4f^N$ configuration is based on equation (1). The opposite-parity components are treated as a degenerate energy level by the Judd–Ofelt theory because their energy positions are generally not well known. However, not all the opposite-parity components can mix with the $4f^N$ transitional states. The opposite-parity states which are responsible for the admixture will be determined by the nonzero condition of the matrix elements in equation (1) and their position can be confirmed by the energy-level calculation. The appearance of the vacuum ultraviolet beamline makes experimental evidence available. The corresponding $4f^{N-1}5d$ configuration calculation model was established by Reid [14]. A simple model for calculating the $4f^{N-1}5d$ configuration was proposed later by Duan [15].

In our calculations, established $4f^N$ atomic and crystal-field parameters [25] are used to treat the $4f^N$ energy levels [29]. The $4f^{N-1}5d$ energy levels are calculated using Duan's simple model and have been discussed in detail in [30] and [31]. The main interactions are considered, including Coulomb interaction within the 4f electrons, crystal-field interaction within the 5d electrons, Coulomb interaction between the 4f and 5d electrons, and spin–orbit interactions within the 4f electrons. The $4f^{N-1}5d$ eigenfunction is then obtained as $E(|[(4f^{N-1}\eta_f S_f L_f, s_d)SL_f]J;\Gamma_d\rangle)$ and the relevant eigenvalues are expressed as

$$\begin{aligned} &E(|[(4f^{N-1}\eta_f S_f L_f, s_d)SL_f]J;\Gamma_d\rangle) \\ &\quad = E_0(4f^{N-1}\eta_f S_f L_f;\Gamma_d) \\ &\qquad - J_{ex}[S(S+1) - S_f(S_f+1) - s_d(s_d+1)]/2 \\ &\qquad + \lambda_{\eta_f S_f L_f S}[J(J+1) - S(S+1) - L_f(L_f+1)]/2. \end{aligned} \quad (4)$$

The notation $|\varphi''\rangle$ in equation (1) is replaced by $E(|[(4\mathrm{f}^{N-1}\eta_\mathrm{f} S_\mathrm{f}L_\mathrm{f}, s_\mathrm{d})SL_\mathrm{f}]J;\Gamma_\mathrm{d}\rangle)$ and $|\varphi_i\rangle$ and $|\varphi_f\rangle$ by the zero-order wavefunctions $|\mathrm{f}^N SLJM\rangle$ and $|\mathrm{f}^N S'L'J'M'\rangle$, respectively. A 'direct' tensor operator calculation will be performed to give a detailed expression for the f–f transitions. The interconfigurational electric dipole transitions between the initial $4\mathrm{f}^N$ states $|4\mathrm{f}^N\varphi_i\rangle$ and the states $|4\mathrm{f}^{N-1}5\mathrm{d}\varphi_i''\rangle$ which mix with the final $4\mathrm{f}^N$ states are due to a two-body interaction, and the corresponding operator matrix element can be expressed as

$$\begin{aligned}
&\langle 4\mathrm{f}^N\eta SLJM_J|\sum_j \hat{C}_p^{(1)}(j)\\
&\quad\times|[(4\mathrm{f}^{N-1}\overline{\eta}\overline{SL}, s_\mathrm{d})S''\overline{L}]J''M_J''; \Gamma_\mathrm{d}\gamma_\mathrm{d}\rangle\\
&\quad=\sqrt{N}\sum_{m_\mathrm{d}} C_{m_\mathrm{d}}^{\Gamma_\mathrm{d}r_\mathrm{d}} \sum_{M_S M_L M_{Lf} m_f}\langle JM_J|SM_SLM_L\rangle\\
&\quad\times\langle SM_S\overline{LM_L}|J''M_J''\rangle\langle LM_L|\overline{LM_L}\mathrm{f}m_\mathrm{f}\rangle\\
&\quad\times\langle\varphi\{|\overline{\varphi}\rangle\langle \mathrm{f}m_\mathrm{f}|\hat{C}_p^{(1)}|\mathrm{d}m_\mathrm{d}\rangle,
\end{aligned}\tag{5}$$

where the three C–G (Clebsch–Gordan) coefficients can be replaced by the 3-j and 6-j symbols

$$\begin{aligned}
&\sum_{M_S M_L M_{L\mathrm{f}}}\langle JM_J|SM_SLM_L\rangle\langle SM_S\overline{LM_L}|J''M_J''\rangle\\
&\quad\times\langle LM_L|\overline{LM_L}\mathrm{f}m_\mathrm{f}\rangle\\
&\quad=(-1)^{S-\overline{L}-3+M_J''-m_\mathrm{f}}[J, J'', L]^{1/2}\\
&\quad\times\begin{Bmatrix} L & \overline{L} & 3\\ J'' & J & S\end{Bmatrix}\begin{pmatrix} 3 & J'' & J\\ m_\mathrm{f} & M_J'' & -M_J\end{pmatrix},
\end{aligned}\tag{6}$$

where $(\cdots)$ and $\{\cdots\}$ are 3-j and 6-j symbols, respectively, and $[l_1, l_2, \cdots]$ denotes $(2l_1+1)(2l_2+1)\ldots$. The matrix elements of the irreducible tensor operator between the states $4\mathrm{f}^N$ and $4\mathrm{f}^{N-1}5\mathrm{d}$, which relate to the odd-rank crystal-field interaction, can be treated in the same way as

$$\begin{aligned}
&\langle[(4\mathrm{f}^{N-1}\overline{\eta}\overline{SL}, s_\mathrm{d})S''\overline{L}]J''M_J''; \Gamma_\mathrm{d}\gamma_\mathrm{d}|\\
&\quad\times\sum_j \hat{C}_q^{(k)}(j)|4\mathrm{f}^N\eta'S'L'J'M_J'\rangle\\
&\quad=\sqrt{N}\delta_{S'S''}[J', J'', L']^{1/2}\langle\overline{\varphi}|\varphi'\rangle\\
&\quad\times\begin{Bmatrix} L' & \overline{L} & 3\\ J'' & J' & S\end{Bmatrix}\sum_{m_\mathrm{d}'} C_{m_\mathrm{d}'}^{\Gamma_\mathrm{d}r_\mathrm{d}}\sum_{m_\mathrm{f}'}(-1)^{S-\overline{L}-3+M_J''-m_\mathrm{f}'}\\
&\quad\times\begin{pmatrix} 3 & J'' & J'\\ m_\mathrm{f}' & M_J'' & -M_J'\end{pmatrix}\langle \mathrm{d}m_\mathrm{d}'|\hat{C}_q^{(k)}|\mathrm{f}m_\mathrm{f}'\rangle.
\end{aligned}\tag{7}$$

The first part of equation (1) becomes

$$\begin{aligned}
&\langle\varphi_i|\hat{D}_p^{(1)}|\varphi_i''\rangle\langle\varphi_i''|H_{\mathrm{CF}}|\varphi_f\rangle\\
&\quad=\langle 4\mathrm{f}^N\eta SLJM_J|\sum_j \hat{C}_p^{(1)}(j)\\
&\quad\times|[(4\mathrm{f}^{N-1}\overline{\eta}\overline{SL}, s_\mathrm{d})S''\overline{L}]J''M_J''; \Gamma_\mathrm{d}\gamma_\mathrm{d}\rangle\\
&\quad\times\langle[(4\mathrm{f}^{N-1}\overline{\eta}\overline{SL}, s_\mathrm{d})S''\overline{L}]J''M_J''; \Gamma_\mathrm{d}\gamma_\mathrm{d}|\\
&\quad\times\sum_j \hat{C}_q^{(k)}(j)|4\mathrm{f}^N\eta'S'L'J'M_J'\rangle A_{kq}\cdot\langle\hat{r}^k\rangle\cdot\langle\hat{r}\rangle\\
&\quad=\sum_\kappa(-1)^{-m_\mathrm{f}-m_\mathrm{f}'}\delta_{SS''}\delta_{S'S''}N\\
&\quad\times\sum_{m_\mathrm{d}} C_{m_\mathrm{d}}^{\Gamma_\mathrm{d}r_\mathrm{d}}\sum_{m_\mathrm{d}'} C_{m_\mathrm{d}'}^{\Gamma_\mathrm{d}r_\mathrm{d}}[J''][J, L, J', L']^{1/2}\langle\varphi\{|\overline{\varphi}\rangle\langle\overline{\varphi}|\}\varphi'\rangle\\
&\quad\times\begin{Bmatrix} L & \overline{L} & 3\\ J'' & J & S\end{Bmatrix}\begin{Bmatrix} L' & \overline{L} & 3\\ J'' & J' & S\end{Bmatrix}\begin{pmatrix} 3 & J'' & J\\ m_\mathrm{f} & M_J'' & -M_J\end{pmatrix}\\
&\quad\times\begin{pmatrix} 3 & J'' & J'\\ m_\mathrm{f}' & M_J'' & -M_J'\end{pmatrix}\\
&\quad\times\langle \mathrm{f}m_\mathrm{f}|\hat{C}_p^{(1)}|\mathrm{d}m_\mathrm{d}\rangle\langle \mathrm{d}m_\mathrm{d}'|\hat{C}_q^{(k)}|\mathrm{f}m_\mathrm{f}'\rangle A_{kq}\cdot\langle\hat{r}^k\rangle\cdot\langle\hat{r}\rangle.
\end{aligned}\tag{8}$$

Equation (8) describes the transitions between the initial $4\mathrm{f}^N$ states and the $4\mathrm{f}^{N-1}5\mathrm{d}$ states that are able to mix with the final $4\mathrm{f}^N$ states. According to the f–f electric dipole transition mechanism, the $4\mathrm{f}^{N-1}5\mathrm{d}$ states, which can mix with the initial $4\mathrm{f}^N$ states, are also the components that will transfer to the final $4\mathrm{f}^N$ states, and an analogous calculation should be done for the second part of equation (1).

The single-particle tensor matrix elements $\langle \mathrm{f}m_\mathrm{f}|\hat{C}_p^{(1)}|\mathrm{d}m_\mathrm{d}\rangle$ and $\langle \mathrm{d}m_\mathrm{d}'|\hat{C}_q^{(k)}|\mathrm{f}m_\mathrm{f}'\rangle$ in equations (5) and (6) will then be calculated using the following equation

$$\begin{aligned}
&\langle lm|\hat{C}_q^{(k)}|l'm'\rangle\\
&\quad=(-1)^m[l, l']^{1/2}\begin{pmatrix} l & k & l'\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & k & l'\\ -m & q & m'\end{pmatrix}.
\end{aligned}\tag{9}$$

A parametric expression of explicit effects of the $4\mathrm{f}^{N-1}5\mathrm{d}$ configuration on the $4\mathrm{f}^N$ intraconfigurational electric dipole transition matrix element is given as

$$\langle 4\mathrm{f}^N\varphi|\hat{D}_p^{(1)}|4\mathrm{f}^N\varphi'\rangle_{5\mathrm{d}}=\sum_{k,q}T_{kq}b_q^{(k)},\tag{10}$$

where the $b_q^{(k)}$ is the mathematical factor which contains information on the f–d mixing states and the energy denominator, and $b_q^{(k)}$ is expressed by standard tensor operator method

$$\begin{aligned}
b_q^{(k)}&=\sum_\kappa(-1)^p\delta_{SS''}\delta_{S'S''}N[\Gamma_\mathrm{d}][J'']\\
&\quad\times[J, L, J', L']^{1/2}\langle\varphi\{|\overline{\varphi}\rangle\langle\overline{\varphi}|\}\varphi'\rangle\\
&\quad\times\begin{Bmatrix} L & \overline{L} & 3\\ J'' & J & S\end{Bmatrix}\begin{Bmatrix} L' & \overline{L} & 3\\ J'' & J' & S\end{Bmatrix}\begin{pmatrix} 3 & 1 & 2\\ -m_\mathrm{d}-p & p & m_\mathrm{d}\end{pmatrix}\\
&\quad\times\begin{pmatrix} 2 & k & 3\\ -m_\mathrm{d} & q & m_\mathrm{d}-q\end{pmatrix}\\
&\quad\times\Bigg[\begin{pmatrix} 3 & J'' & J\\ m_\mathrm{d}+p & M_J-m_\mathrm{d}-p & -M_J\end{pmatrix}\\
&\quad\times\begin{pmatrix} 3 & J'' & J'\\ m_\mathrm{d}-q & M_J-m_\mathrm{d}-p & -M_J+p+q\end{pmatrix}\Big/(E_f-E'')\\
&\quad+\begin{pmatrix} 3 & J'' & J'\\ m_\mathrm{d}+p & M_J-m_\mathrm{d}+q & -M_J-p-q\end{pmatrix}\\
&\quad\times\begin{pmatrix} 3 & J'' & J\\ m_\mathrm{d}-q & M_J-m_\mathrm{d}+q & -M_J\end{pmatrix}\Big/(E_i-E'')\Bigg],
\end{aligned}\tag{11}$$

where κ denotes the summation that runs over all values of $\overline{L}$, J'' and m_d. $[\Gamma_\mathrm{d}]$ is the dimension of the irreducible representation of the site symmetry group. The values of $\overline{L}$ and the fractional parentage coefficients (FPC) are listed in [32], and the values of $m_\mathrm{d}'=m_\mathrm{d}$ are integers from -2 to 2. The nonzero conditions of the 3-j, 6-j symbol and FPC set the selection rules for the $4\mathrm{f}^N\leftrightarrow 4\mathrm{f}^N$ electric dipole transitions and for the $4\mathrm{f}^N$–$4\mathrm{f}^{N-1}5\mathrm{d}$ admixture.

The dimensionless intensity parameter T_{kq} is

$$T_{kq} = -\sqrt{105} A_{kq} \langle \hat{r} \rangle \langle \hat{r}^k \rangle \begin{pmatrix} 2 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} \tag{12}$$

where $\langle \hat{r} \rangle$ and $\langle \hat{r}^k \rangle$ denote the radial integral between the f–d configurations and can be calculated using the Hartree–Fock method [33, 34]. The odd-rank crystal-field parameter A_{kq} is obtained from a lattice sum calculation. In this paper they will be treated together as the intensity parameters T_{kq} and their values obtained by minimizing the least-squares deviation [27] between the calculated and experimental data.

2.2. *Other opposite-parity contributions to the f–f electric dipole transitions*

The opposite-parity configurations of the type $4f^{N-1}n'g$ remain to be considered. The closure procedure over all n' seems valid due to their comparative proximity to the ionizing limit. An expression about the matrix element of an induced electric dipole transition between two crystal-field levels is introduced to deal with the admixing contribution of the opposite-parity states which lie far above the $4f^N$ configuration

$$\begin{aligned} \langle i|\hat{D}_p^{(1)}|f\rangle_{ng} &= \sum_{k,q,\lambda} \tilde{A}_{kq}^{\lambda} [k]^{1/2} (-1)^{p+q+J-M} \\ &\times \begin{pmatrix} 1 & \lambda & k \\ p & -p-q & q \end{pmatrix} \begin{pmatrix} J & \lambda & J' \\ -M & p+q & M' \end{pmatrix} \\ &\times \langle \varphi J \parallel U^{(\lambda)} \parallel \varphi' J' \rangle. \end{aligned} \tag{13}$$

where $\tilde{A}_{kq}^{\lambda} = -A_{kq}\Xi(k,\lambda)(2\lambda+1)/\sqrt{2k+1}$ and $\Xi(k,\lambda) = -126 \begin{Bmatrix} 1 & \lambda & k \\ 3 & 4 & 3 \end{Bmatrix} \begin{pmatrix} 3 & 1 & 4 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 4 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} \frac{\langle \hat{r} \rangle \langle \hat{r}^k \rangle}{\Delta(ng)}$, $\Xi(k,\lambda)$ is obtained from the traditional Judd–Ofelt theory between crystal-field energy-level transition, and only the $4f^{N-1}n'g$ configuration is considered here. The $\tilde{A}_{kq}^{\lambda}$ parameters are in the expression to distinguish the traditional A_{tp}^{λ}, which includes the contribution of all opposite-parity states. The correlative intensity parameters $\tilde{A}_{kq}^{\lambda}$ will be derived together with T_{kq} by minimizing the error between the experimental and calculated data through the least-squares deviation. Finally, transition intensities between any two $4f^N$ levels will be obtained.

2.3. *Calculation of intensities*

A set of general formulas is given in this section to make the physical quantities clear. The electric dipole (ED) and magnetic dipole (MD) strength between the crystal-field levels are

$$S_p^{\mathrm{ED}} = e^2 \sum_{i,f} |\langle i|\hat{D}_p^{(1)}|f\rangle|^2, \tag{14}$$

$$S_p^{\mathrm{MD}} = \left(\frac{-eh}{4\pi m_e c}\right)^2 \sum_{i,f} \left|\langle i|(\hat{L}+2\hat{S})_p^{(1)}|f\rangle\right|^2, \tag{15}$$

where e is the elementary charge; m_e is the electron mass; h is Planck's constant; c is the speed of light. $\langle i|\hat{D}_p^{(1)}|f\rangle$ is given by equations (10) and (13) in the present paper. The dipole strength between J-multiplies $S_p^{\mathrm{ED/MD}}(\varphi J, \varphi' J')$ is summed over all the dipole strengths between the crystal-field levels.

The electric dipole strengths between the J-multipliers in Judd–Ofelt theory is expressed as

$$S_p^{\mathrm{ED}}(\varphi J, \varphi' J') = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda |\langle \mathrm{f}^N \varphi J \| U^{(\lambda)} \| \mathrm{f}^N \varphi' J' \rangle|. \tag{16}$$

The oscillator strength $f_p^{\mathrm{ED/MD}}(\varphi J, \varphi' J')$ is related to the dipole strength $S_p^{\mathrm{ED/MD}}(\varphi J, \varphi' J')$ by

$$\begin{aligned} &f_p^{\mathrm{ED/MD}}(\varphi J, \varphi' J') \\ &= \frac{8\pi^2 m_e \nu}{3h(2J+1)e^2} \cdot \chi^{\mathrm{ED/MD}} \cdot S_p^{\mathrm{ED/MD}}(\varphi J, \varphi' J'), \end{aligned} \tag{17}$$

where ν is the frequency at the absorption maximum and $\chi^{\mathrm{ED}} = \frac{(n^2+2)^2}{9n}$ or $\chi^{\mathrm{MD}} = n$ is the Lorentz local field correction factor for absorption. The total oscillator strength is the summation of the electric dipole and magnetic dipole oscillator strengths,

$$f(\varphi J, \varphi' J') = f_p^{\mathrm{ED}}(\varphi J, \varphi' J') + f_p^{\mathrm{MD}}(\varphi J, \varphi' J'). \tag{18}$$

In this paper, the oscillator strength is used to deal with the absorption spectrum. The intensity parameters are fitted according to the calculated results and the experimental data, which are taken from [26]. φJ and $\varphi' J'$ in $f(\varphi J, \varphi' J')$ denote $^4I_{9/2}$ and other high-lying states in $YPO_4:Nd^{3+}$, respectively.

The transition probability $A_p^{\mathrm{ED/MD}}(\varphi J, \varphi' J')$ is related to the dipole strength $S_p^{\mathrm{ED/MD}}(\varphi J, \varphi' J')$ by

$$\begin{aligned} &A_p^{\mathrm{ED/MD}}(\varphi J, \varphi' J') \\ &= \frac{1}{4\pi\varepsilon_0} \frac{64\pi^4 \nu^3}{3hc^3(2J+1)} \chi^{\mathrm{ED/MD}} S_p^{\mathrm{ED/MD}}(\varphi J, \varphi' J'), \end{aligned} \tag{19}$$

where $\chi^{\mathrm{ED}} = \frac{n(n^2+2)^2}{9}$ and $\chi^{\mathrm{MD}} = n^3$ for emission.

The total transition probability is the summation of the electric dipole and magnetic dipole transition probabilities,

$$A(\varphi J, \varphi' J') = A_p^{\mathrm{ED}}(\varphi J, \varphi' J') + A_p^{\mathrm{MD}}(\varphi J, \varphi' J'). \tag{20}$$

In this paper relative transition intensities are introduced to treat the emission spectrum originating from $^2G_{9/2}(2)$, which is from [28]. φJ and $\varphi' J'$ in $A(\varphi J, \varphi' J')$ denote $^2G_{9/2}(2)$ and other low-lying states in $YPO_4:Nd^{3+}$, respectively. The relative transition intensities are calculated by normalizing the transition probability from $^2G_{9/2}(2)$ to $^2H_{9/2}(1)$ and the corresponding expression is

$$\alpha(\varphi J, \varphi' J') = \frac{A(^2\mathrm{G}_{9/2}(2), \varphi' J')}{A(^2\mathrm{G}_{9/2}(2), {}^2\mathrm{H}_{9/2}(1))}. \tag{21}$$

The root-mean-square deviation

$$\sigma_{\mathrm{rms}} = \sum_{i=1}^{n} \sqrt{\frac{(S_{\mathrm{calc}(i)} - S_{\mathrm{meas}(i)})^2}{n}} \tag{22}$$

where $S_{\mathrm{calc}(i)}$ and $S_{\mathrm{meas}(i)}$ are the calculated results and experimental measurements of the initial state to the final state i.

Table 1. Calculated $4f^25d$ energy levels of $YPO_4:Nd^{3+}$ (cm^{-1}).

	$^4H_{7/2}$	$^4H_{9/2}$	$^4H_{11/2}$	$^4H_{13/2}$	$^4F_{3/2}$	$^4F_{5/2}$	$^4F_{7/2}$	$^4F_{9/2}$	
Γ_{d1}	53 248	54 571	56 188	58 099	58 948	59 683	60 712	62 035	
Γ_{d2}	63 513	64 836	66 453	68 364	69 213	69 948	70 977	72 300	
Γ_{d3}	63 513	64 836	66 453	68 364	69 213	69 948	70 977	72 300	
Γ_{d4}	65 625	66 948	68 565	70 476	71 325	72 060	73 089	74 412	
Γ_{d5}	71 135	72 458	74 075	75 986	76 835	77 570	78 599	79 922	
	$^4P_{1/2}$	$^4P_{3/2}$	$^4P_{5/2}$	$^2G_{7/2}$	$^2G_{9/2}$	$^2D_{3/2}$	$^2D_{5/2}$	$^2I_{11/2}$	$^2I_{13/2}$
Γ_{d1}	74 777	75 218	75 953	62 783	64 106	71 863	72 598	74 914	76 825
Γ_{d2}	85 042	85 483	86 218	73 048	74 371	82 128	82 863	85 179	87 090
Γ_{d3}	85 042	85 483	86 218	73 048	74 371	82 128	82 863	85 179	87 090
Γ_{d4}	87 154	87 595	88 330	75 160	76 483	84 240	84 975	87 291	89 202
Γ_{d5}	92 664	93 105	93 840	80 670	81 993	89 750	90 485	92 801	94 712

3. Results and discussion

Calculation for the $4f^3 \leftrightarrow 4f^3$ transitions in $YPO_4:Nd^{3+}$ is performed with the following steps. Firstly, the $4f^25d$ admixing states with the $4f^3$ transitional states are determined. The energy levels of the $4f^3$ states are calculated using the f-shell programs and the levels of $4f^25d$ states using equation (4) as listed in table 1. The parameters used for the energy-level calculation are obtained from [25]. For ground state $^4I_{9/2}$ absorption, according to the nonzero conditions of the FPC, both initial and final mixing states of the $4f^25d$ configuration come from the terms $[(^3F)\ ^4F_J\Gamma_{di}]$ and $[(^3H)\ ^4H_J\Gamma_{di}]$ and Γ_{di} is from Γ_{d1} to Γ_{d5} in the site symmetry of D_{2d}. Based on the triangular conditions of 3-j symbols $\begin{pmatrix} 3 & J'' & J \\ m_d+p & M_J-m_d-p & -M_J \end{pmatrix}$ and $\begin{pmatrix} 3 & J'' & J' \\ m_d-q & M_J-m_d-p & -M_J+p+q \end{pmatrix}$ in equation (11), the values of J'' can be determined. For example, in the transition of $^4I_{9/2} \rightarrow {}^4F_{3/2}$, the following triangular relations, $(3, J'', 3/2)$ and $(3, J'', 9/2)$, can be gained; thus the $4f^25d$ states which are able to mix with the initial $^4I_{9/2}$ and final $^4F_{3/2}$ state are $[(^3F)\ ^4F_{3/2,5/2,7/2,9/2}\Gamma_{di}]$ and $[(^3H)\ ^4H_{7/2,9/2}\Gamma_{di}]$. Similar analysis will be done for any $4f^3$ transitional states.

Secondly, the intensity parameters are fitted according to experimental absorption data from [26], which are listed in the fifth column of table 2. In general, the experimental measurements contain both induced electric dipole and magnetic dipole transitions and the corresponding dipole strengths are calculated using equations (14) and (15). Because the absorption spectra of neodymium oscillator strengths in [26] were obtained at room temperature, the occupations of Stark levels within the $^4I_{9/2}$ ground state satisfy the Boltzmann distribution [35]. The total dipole strengths for the transitions between J multiplets are obtained through summing over all the dipole strengths between crystal-field Stark levels. The intensity parameters should be fitted by minimizing the least-squares deviation between the experimental data and the calculated oscillator strengths in equation (18). In D_{2d} symmetry, the electric dipole intensity parameters T_{32}, T_{52}, $\tilde{A}^2_{32}$, $\tilde{A}^4_{32}$, $\tilde{A}^4_{52}$, $\tilde{A}^6_{52}$, $\tilde{A}^6_{72}$ and $\tilde{A}^6_{76}$ are fitted by the absorption oscillator strengths of transitions from the $^4I_{9/2}$ ground level to the upper states. The fitted values are $T_{32} = 1.4 \times 10^{-7}$, $T_{52} = -905.88 \times 10^{-7}$, $\tilde{A}^2_{32} = -1.299 \times 10^{-12}$ cm, $\tilde{A}^4_{32} = 3.877 \times 10^{-12}$ cm, $\tilde{A}^4_{52} = 0.906 \times 10^{-12}$ cm, $\tilde{A}^6_{52} = 2.075 \times 10^{-12}$ cm, $\tilde{A}^6_{72} = 7.815 \times 10^{-12}$ cm, and $\tilde{A}^6_{76} = -6.533 \times 10^{-12}$ cm in our calculation and $\Omega_2 = 0.4 \times 10^{-20}$ cm^2, $\Omega_4 = 4.8 \times 10^{-20}$ cm^2, $\Omega_6 = 9.6 \times 10^{-20}$ cm^2 in Judd–Ofelt theory treatments. These intensity parameters are reused in calculating the oscillator strengths originating from $^4I_{9/2}$. The results calculated by our method and Judd–Ofelt theory and experimental measurements are listed in table 2. The small σ_{rms} proves that the fitting intensity parameters are reasonable. Furthermore, this calculation method is used to treat the emission spectrum from the high-lying $^2G_{9/2}(2)$ level.

Table 2. Experimental and calculated transition strengths from $^4I_{9/2}$ in $YPO_4:Nd^{3+}$.

Final states $\vert f^N[SL]J\rangle$	Energy difference (cm^{-1})	The oscillator strengths $f(\varphi J, \varphi' J')$ (10^{-6} cm^2) This work	Judd–Ofelt[a]	Measured[a]
$^4F_{3/2}$	11 515	3.16	3.38	2.46
$^4F_{5/2}$, $^2H_{9/2}(2)$	12 519	13.72	13.51	14.37
$^4F_{7/2}$, $^4S_{3/2}$	13 470	14.46	15.55	14.86
$^4F_{9/2}$	14 725	1.04	1.15	1.14
$^2H_{11/2}(2)$	15 932	0.36	0.32	0.29
$^4G_{5/2}$, $^2G_{7/2}(1)$	17 233	11.83	11.80	11.77
$^4G_{7/2}$, $^4G_{9/2}$, $^2K_{13/2}$	19 298	8.08	7.87	8.30
$^4G_{11/2}$, $^2G_{9/2}(1)$, $^2D_{3/2}(1)$, $^2K_{15/2}$	21 377	2.25	2.14	2.34
$^2P_{1/2}$, $^2D_{5/2}(1)$	23 354	0.70	0.83	0.79
σ_{rms}		0.3376	0.3385	

[a] Reference [26].

Finally, the fitted values of the intensity parameters are used to calculate the transition intensities originating from the $^2G_{9/2}(2)$ level. The emission spectrum of Nd^{3+}-doped YPO_4 in the range from 200 to 700 nm has been reported by Wegh *et al* [28]. The absorption from the $^4I_{9/2}$ ground state to the high-lying $^2G_{9/2}(2)$ level is very weak, so it is difficult to detect the emission from $^2G_{9/2}(2)$ by directly exciting the level. Both the f–d emission and the $^2G_{9/2}(2)$ emission are observed upon f–d excitation in the system. There are four primary emission bands from the lowest $4f^25d$ state to the $4f^3$ transitional states, assigned to ^4I_j, ^4F_j, ^4G_j, and ^4D_j, respectively [25]. There is a large spectral overlap between the f–d emissions and the $^2G_{9/2}(2)$ emissions. The calculated results of the $^2G_{9/2}(2)$ emission intensities in this work compared with Judd–Ofelt theory treatments and experimental data are listed in table 3.

Table 3. Experimental and calculated relative intensities for transitions of YPO_4:Nd^{3+} from $^2G_{9/2}(2)$ to the lower states.

Final states $\|f^N[SL]J\rangle$	Energy difference (cm^{-1})	Relative transition intensities $\alpha(\varphi J, \varphi' J')$		
		This work	Judd–Ofelt[a]	Measured[a]
$^4F_{3/2}$	36 306	0.0898	0.0355	—
$^4F_{5/2}$, $^2H_{9/2}(2)$	35 266	1.6475	0.7037	13.8101
$^4F_{7/2}$, $^4S_{3/2}$	34 290	0.2237	0.0382	5.6449
$^4F_{9/2}$	32 983	0.4831	0.2136	0.9646
$^2H_{11/2}(2)$	31 651	3.4492	1.4460	8.3335
$^4G_{5/2}$, $^2G_{7/2}(1)$	30 258	0.6864	0.1358	6.4245
$^4G_{7/2}$, $^4G_{9/2}$, $^2K_{13/2}$	28 193	1.9407	0.5351	13.5086
$^4G_{11/2}$, $^2G_{9/2}(1)$, $^2D_{3/2}(1)$, $^2K_{15/2}$	26 114	8.2576	3.2136	42.4612
$^2P_{1/2}$, $^2D_{5/2}(1)$	23 354	2.3797	0.9730	13.0515
$^2P_{3/2}$	21 704	1.1695	0.5746	1.3386
$^4D_{3/2}$, $^4D_{1/2}$, $^4D_{5/2}$	19 672	1.3237	0.4897	1.9660
$^2I_{11/2}$	18 525	0.9864	0.6290	1.3625
$^2L_{15/2}$, $^4D_{7/2}$, $^2I_{13/2}$	17 583	3.5576	1.5850	5.1219
$^2L_{17/2}$	16 118	5.0661	2.9649	3.0706
$^2H_{9/2}(1)$	14 823	1.0000	1.0000	1.0000
σ_{rms}		0.5589	0.7472	

[a] Reference [28].

The experimental data are cited from the $^2G_{9/2}(2)$ emission spectrum [28], and the transition intensities are relative values in equation (21). For comparison with the results of the theoretical calculation, the intensity from $^2G_{9/2}(2)$ to $^2H_{9/2}(1)$ is evaluated as unity because there is no overlapping at that emission wavelength. Since the transition largely overlaps with the emissions from the $4f^25d$ state to the ^4G_j and ^4D_j levels, the experimental intensities originating from $^2G_{9/2}(2)$ in the spectral range 275–400 nm are much greater. The remaining experimental intensities in the spectral range 400–700 nm reveal better coherence with our calculated results than with Judd–Ofelt theory. The better agreement of relative intensities allows us to predict the transitions in the spectral range from 275 to 400 nm, thus the transitional component at a certain wavelength can be distinguished.

According to σ_{rms} in equation (22), much better agreement between the experimental data and our calculations is observed for the intensities originating from high-lying $4f^3$ energy levels, as shown in table 3. It is noted that the calculated intensities in this work are only for the J–J transitional states. Intensity calculations for the transitions between the crystal-field states are under way.

4. Conclusions

In summary, a new calculation method has been introduced for the electric dipole transitions within the $4f^N$ configurations of trivalent lanthanide ions with more than two f-electrons. The simple model is used to deal with the opposite-parity $4f^{N-1}5d$ configuration. A series of tensor matrix elements are calculated with the aim of giving an expression for f–f intensity. Satisfying results have been obtained in the YPO_4:Nd^{3+} system. A set of new selection rules are applied to determine the $4f^25d$ components, which are able to mix with $4f^3$ transitional states in D_{2d} symmetry. Both effects including explicit $4f^25d$ and traditional $4f^2n'g$ using the closure procedure treatment on the f–f electric dipole transitions are taken into account and a set of parameters are obtained by the least-squares fitting method. The fitted parameters can be used to calculate any intraconfigurational f–f transitions. Compared with the traditional Judd–Ofelt theory, the current method with the fitted parameters gives better agreement with experimental observation. It shows an effective method for calculating neodymium oscillator strengths and further work will be done for other rare-earth ions.

Acknowledgments

This work is financially supported by the MOST of China (2006CB601104 and 2006AA03A138) and the National Natural Science Foundation of China (10834006 and 10774141).

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