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Selection rules for $4f^2 \rightarrow 4f^2$ electric dipole transitions by considering mixing with 4f5d components of Pr^{3+} in $SrAl_{12}O_{19}$

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Abstract

A set of selection rules is deduced for the $4f^2$ transitional levels that mix with explicit 4f5d components. Based on these selection rules the dipole-allowed transitions between the $4f^2$ crystal field levels are determined in Pr^{3+} doped $SrAl_{12}O_{19}$. Meanwhile, the main 4f5d components mixed into $4f^2$ transitional levels are identified by determining the nonzero matrix elements of both the odd-rank crystal-field and the electric dipole operator. The selection rules have been applied to analyze the transitions from $^1S_0$ and $^3P_0$ to lower crystal field levels.

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1. Introduction

The transitions within $4f^n$ configuration of rare earth ions in solids are predominately of electric dipole nature and are made possible by the mixing of the $4f^n$ states with the $4f^{n-1}5d$ states. The first quantitative description of $4f^n \rightarrow 4f^n$ electric dipole transitions of rare earth ions was given by Judd [1] and Ofelt [2], respectively. The Judd–Ofelt theory has played an important role in the understanding of rare earth spectra. However, because of the characterization of the $4f^{n-1}5d$ configuration in various hosts is generally not well-known, the theory assumed that all the energies of the $4f^{n-1}5d$ states are a single average value in the calculation of the line intensities. The unknown energy-level structure of the $4f^{n-1}5d$ configuration inhibits any

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detailed analysis on the $4f^n \rightarrow 4f^n$ electric dipole transitions.

In $SrAl_{12}O_{19}$: Pr^{3+}, to clarify the transitions between two states of the $4f^2$ configuration, the properties of the 4f5d configuration are determined using a $|SLJM\rangle$ basis set [3]. The effects of the 4f5d configuration on the $4f^2 \rightarrow 4f^2$ electric dipole transitions are determined by the odd-rank crystal-field matrix elements and the electric dipole operator matrix elements. The two matrix elements are expressed by standard tensorial method and a set of selection rules is deduced. Based on these selection rules the dipole-allowed transitions between the $4f^2$ individual crystal field levels are determined and the main 4f5d components that can mix into $4f^2$ transitional levels are identified.

2. Description of theory

In order to understand the crystal field induced electric dipole transitions within the $4f^2$ configuration, the knowledge of the 4f5d configuration is required. The structure of 4f5d configuration should be clarified using LS coupling basis as the scheme of $4f^2$ configuration and the 4f5d components responsible for the mixture should be determined. Recently, many investigations on 4f5d calculation have been carried out to extend the standard model for $4f^2$ energy levels. In these studies, the crystal field and spin–orbit interactions are taken into account for the 5d electron as well as the *Coulomb* interaction between the 4f and 5d electrons [4,5]. However, not all of the 4f5d components can mix with the optional $4f^2$ states [6,7]. To describe the transitions between the $4f^2$ individual crystal field levels, those 4f5d components responsible for the mixing should be determined.

The nonzero matrix elements of the electric dipole operator between the parity mixed $4f^2$ initial state φ and $4f^2$ final state φ' are

$$\langle\varphi|D_p^1|\varphi'\rangle = e\sum_{\varphi'',k,q}\left[\frac{\langle\varphi|H_{\mathrm{CF}}(\mathrm{odd})|\varphi_{\mathrm{i}}''\rangle\langle\varphi_{\mathrm{i}}''|D_p^1|\varphi'\rangle}{E(\varphi)-E(\varphi_{\mathrm{i}}'')} + \frac{\langle\varphi|D_p^1|\varphi_{\mathrm{f}}''\rangle\langle\varphi_{\mathrm{f}}''|H_{\mathrm{CF}}(\mathrm{odd})|\varphi'\rangle}{E(\varphi')-E(\varphi_{\mathrm{f}}'')}\right], \quad (1)$$

with the odd-rank crystal-field interaction, $H_{\mathrm{CF}}(\mathrm{odd})$, and the electric dipole operators, D_p^1, defined by

$$H_{\mathrm{CF}}(\mathrm{odd}) = \sum_{k,q,j} B_{kq}(\mathrm{fd})C_q^k(j), \quad (2)$$

and

$$D_p^1 = e\sum_j r_j C_p^1(j). \quad (3)$$

In Eq. (1), $E(\varphi)$ and $E(\varphi')$ denote the energies of the initial and the final states of $4f^2$ respectively; $E(\varphi_{\mathrm{i}}'')$ and $E(\varphi_{\mathrm{f}}'')$ stand for the energies of the 4f5d states that are responsible for mixing with the initial and the final states, respectively. In Eqs. (2) and (3), $C_q^k(j)$ is an irreducible tensor operator of rank k; the values of k and q of the nonzero odd-rank crystal field parameters $B_{kq}(\mathrm{fd})$'s depend on the site symmetry; p the standard polarization of incident light (0 for π and ±1 for σ); e the elementary charge and r_j the radius of the jth electron.

From Eqs. (1)–(3), the effects of the 4f5d configuration on $4f^2 \rightarrow 4f^2$ electric dipole transitions are determined by both the odd-rank crystal field matrix element and the electric dipole operator matrix element. The two matrix elements can be expressed in terms of a standard tensorial method and the main 4f5d components that mix into $4f^2$ transitional levels can be determined by the nonzero conditions of the two matrix elements. In the present work, $|f^2SLJM\rangle$ and $|f^2S'L'J'M'\rangle$ denote the $4f^2$ initial and final states, respectively. In order to discuss the mixing of $4f^2$ states with 4f5d states, the structure of the 4f5d band is clarified using a scheme of *LS* coupling. The basis set of the 4f5d states which is responsible for the state mixing is $|\mathrm{fd}S''L''J''M''\rangle$. Crystal field interaction is usually carried out using a single-particle crystal field theory. The matrix elements of the irreducible tensor operator, which are related to the odd-rank crystal field interaction, in *LS* coupling basis are

$$\left\langle \mathrm{f}^2SLJM\left|\sum_j C_q^k(j)\right|\mathrm{fd}S''L''J''M''\right\rangle = [2,3,L,L'',J,J'']^{1/2}\delta_{SS''}(-1)^{S+M+L+L''}$$

$$\times \sum_{k,q} \begin{pmatrix} 3 & k & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J & k & J'' \\ -M & q & M'' \end{pmatrix} \times \begin{Bmatrix} L & k & L'' \\ 2 & 3 & 3 \end{Bmatrix} \begin{Bmatrix} J & k & J'' \\ L'' & S & L \end{Bmatrix}, \qquad (4)$$

where () and {} are 3j and 6j symbols, respectively, and $[l_1, l_2, \ldots]$ denotes $(2l_1+1)(2l_2+1)\ldots$. In contrast to the situation for crystal field interaction, the electric dipole operator is a two-particle interaction operator, which is calculated using antisymmetric wave functions. The corresponding matrix elements in LS coupling basis are

$$\frac{1}{\sqrt{2}}\left[\langle \mathrm{fd}S''L''J''M''|\sum_j C_p^1(j)|\mathrm{f}^2 S'L'J'M'\rangle + (-1)^{S''+L''+1}\langle \mathrm{df}S''L''J''M''|\sum_j C_p^1(j)|\mathrm{f}^2 S'L'J'M'\rangle\right]$$
$$= \frac{(-1)^{M''+L'}}{\sqrt{2}}[2,3,L',L'',J',J'']^{1/2} \times \delta_{S'S''}[(-1)^{S''+L''}-1]\begin{pmatrix} 2 & 1 & 3 \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times \begin{pmatrix} J'' & 1 & J' \\ -M'' & p & M' \end{pmatrix} \begin{Bmatrix} L'' & 1 & L' \\ 3 & 3 & 2 \end{Bmatrix} \times \begin{Bmatrix} J'' & 1 & J' \\ L' & S'' & L'' \end{Bmatrix}. \qquad (5)$$

From the nonzero conditions of the two matrix elements in Eqs. (4) and (5), a set of selection rules for the transitions between individual crystal field levels of Pr^{3+} are deduced as follows:

$$S = S' = S'', \quad S'' + L'' \text{ is odd},$$
$$M'' = M - q, \quad M' = M'' - p,$$
$$|L-k| \leqslant L'' \leqslant L+k, \quad |J-k| \leqslant J'' \leqslant J+k,$$
$$|L''-1| \leqslant L' \leqslant L''+1, \quad |J''-1| \leqslant J' \leqslant J''+1.$$

The $4\mathrm{f}^2$ intraconfigurational electric dipole transitions can be restricted and the main 4f5d components responsible for the mixing determined using these selection rules. The selection rules can be applied to Pr^{3+} in any host with known crystal structure.

3. Results and conclusion

Based on the selection rules, the main Stark levels of the final $4\mathrm{f}^2$ multiplets and the main 4f5d components mixed into the $4\mathrm{f}^2$ initial and final states are determined and presented in Table 1. The $^3\mathrm{P}_0$ emissions are observed as well as the

Table 1
The main Stark levels of the final $4\mathrm{f}^2$ multiplets and the main 4f5d components mixed into the $4\mathrm{f}^2$ initial and final states of Pr^{3+} in $\mathrm{SrAl_{12}O_{19}}$

$4\mathrm{f}^2$ configuration		4f5d configuration	
Initial state SLJ	Final states $S'L'J'(M')$	Mixed into initial state $S''L''J''(M'')$	Mixed into final states $S''L''J''(M'')$
$^1\mathrm{S}_0$	$^1\mathrm{I}_6$ $(\pm 2, \pm 4, -3, +3)$ $^1\mathrm{D}_2$ (± 2) $^1\mathrm{G}_4$ $(\pm 2, -3, \pm 4, +3)$ $^3\mathrm{F}_4$ $(\pm 2, -3, \pm 4, +3)$	$^1\mathrm{F}_3$ $(-3, +3)$ $^1\mathrm{H}_5$ $(-3, +3)$	$^1\mathrm{P}_1$ $(0, \pm 1)$
$^3\mathrm{P}_0$	$^3\mathrm{F}_4$ $(\pm 2, -3, \pm 4, +3)$ $^3\mathrm{F}_3$ $(+3, \pm 2, -3)$ $^3\mathrm{F}_2$ (± 2) $^3\mathrm{H}_6$ $(\pm 4, +3, \pm 2, -3)$ $^3\mathrm{H}_5$ $(\pm 4, -3, +3, \pm 2)$ $^3\mathrm{H}_4$ $(-3, +3, \pm 2, \pm 4)$	$^3\mathrm{D}_3$ $(-3, +3)$ $^3\mathrm{G}_3$ $(-3, +3)$ $^3\mathrm{G}_5$ $(-3, +3)$	$^3\mathrm{D}_1$ $(0, \pm 1)$

The entries in parentheses are the values of quantum number M.

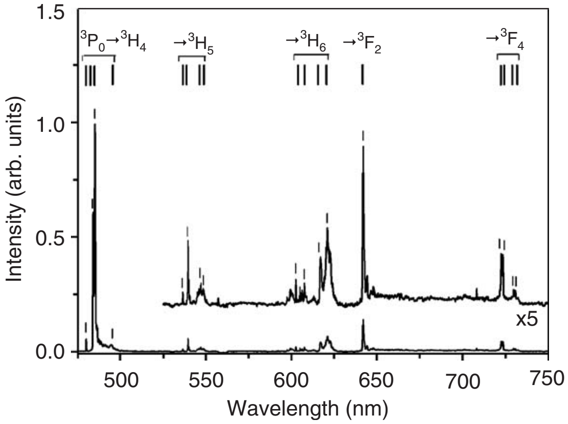

Fig. 1. Emission spectrum of $SrAl_{12}O_{19}$:0.005 Pr (single crystal) at 10 K with the excitation at 466 nm.

$^1S_0$ emissions, since the $^1S_0$ state lies below the lowest 4f5d states in $SrAl_{12}O_{19}$: Pr^{3+} system. The state mixing determines the optical properties of the $^1S_0$ [6,7] and $^3P_0$ states and the associated transitions.

In Fig. 1, lots of sharp lines are observed, which come from Stark sublevels of the final $4f^2$ multiplets. Optical emissions are measured with a resolution of 0.1 nm and are excited by optical parametric oscillator (OPO). It is clearly demonstrated by the data that the predictions from the proposed model have a good agreement with the measurements. Several unassigned minor peaks in Fig. 1 can be attributed to the effect of the strong *J*-mixing within the 4f5d configuration on the $4f^2 \rightarrow 4f^2$ electric dipole transitions. The effect will usually lead to a breakdown of the selection rules.

In summary, the selection rules have been applied to transitions originating from $^1S_0$ and $^3P_0$ states of Pr^{3+} in $SrAl_{12}O_{19}$. The effects of different 4f5d components on $4f^2$ intraconfigurational transitions can be separated. The selection rules can not only be applied to analyze the intraconfigurational transitions and opposite parity state mixing in present system but also be extended to Pr^{3+} in any hosts of known crystal structure. Meanwhile, the selection rules can possibly be useful for future calculations of the line intensities of $4f^2$ intra-configurational transitions.

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