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Calculating line intensities of $^1S_0$ emission through mixing with 4f5d components in Pr^{3+}-doped $SrAl_{12}O_{19}$

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Abstract

The line intensities of emission from $4f^2$ $^1S_0$ are calculated in Pr^{3+}-doped $SrAl_{12}O_{19}$ by considering the mixing of $^1S_0$ state with the corresponding 4f5d components. The products of odd-rank crystal-field parameters B_{kq}(fd)'s and interconfigurational radial integral r are treated as new parameters and obtained from a best-fit of the calculated and measured relative intensities of transitions from the $^1S_0$ level to the lower J multiplets. The fitted values are $B_{33}(\text{fd})r = 1.207 \times 10^{-5}$ and $B_{53}(\text{fd})r = 1.522 \times 10^{-5}$, which are then used to calculate the line intensities of transitions from the $^1S_0$ to the lower crystal-field levels.

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Keywords: $SrAl_{12}O_{19}$; Pr^{3+}; 4f5d configuration; Line intensities; Crystal-field levels

1. Introduction

Historically, the Judd–Ofelt theory [1,2] has played an important role in understanding the optical transition properties of low-lying states of $4f^n$ configuration in rare earth doped with various hosts. However, discrepancies are observed when the theory is applied to the high-lying $4f^n$ excited states, such as the $^1S_0$ state of Pr^{3+} [3]. In the Judd–Ofelt approximation the $4f^{n-1}5d$ band of opposite parity is considered to be degenerate, and the closure procedure is applied in the calculation. The assumption may underestimate the degree of mixing of $4f^{n-1}5d$ states into the high-lying $4f^n$ states. The above discrepancies suggest the possible inadequacy of the present Judd–Ofelt theory for treating such states. Though several modifications of the standard Judd–Ofelt theory have been presented [3,4], unfortunately the characterization of $4f^{n-1}5d$ configuration in solids is generally not well known, inhibiting any detailed calculation to verify the breakdown of the closure approximation.

In $SrAl_{12}O_{19}$: Pr^{3+}, the $^1S_0$ state lies below the 4f5d band, and $^1S_0$ emission is observed. The mixing of $^1S_0$ state with the 4f5d states has been studied by Huang et al. [5,6], and the results are the starting point of this work. In current work, the mixing of the $4f^2$ transitional states with the 4f5d states is taken into account. Then, a theoretical calculation for the line intensities between the crystal-field energy levels was performed in which the products of odd-rank crystal-field parameters B_{kq}(fd)'s and interconfigurational radial integral r are treated as new parameters and obtained from a fit procedure. At last, the fitted values can be used to calculate the transition strength between any two crystal-field levels within $4f^2$ configuration of interest.

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2. Description of calculation

Recently, many investigations on $4f^{n-1}5d$ calculation have been done, which extend the standard model used for $4f^n$ energy levels by including crystal-field and spin–orbit interactions for the 5d electron and the *Coulomb* interaction between the 4f and 5d electrons [7,8]. These works make the detailed calculation on the $4f^n$ line intensities possible.

The $4f^2$ and 4f5d configurations can be coupled by the odd-rank crystal-field interaction of Pr^{3+} in crystals. The corresponding Hamiltonian can be written as

$$H_{CF}(\text{odd}) = \sum_{k,q,j} B_{kq}(\text{fd}) C_q^k(j), \tag{1}$$

where $C_q^{\,k}(j)$ is an irreducible tensor operator of rank k depending on the coordinates of the jth electron and the j sum runs over all electrons of the rare-earth ion; the values of k and q for which the odd-rank crystal-field parameters B_{kq}(fd)'s are nonzero depend on the site symmetry. Transitions within the $4f^2$ configuration are dominated by the electric dipole operator $\boldsymbol{D}$; the expression of its projection is given by

$$D_p^1 = e \sum_j r_j C_p^1(j), \tag{2}$$

where p is 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.

In the present model, $\left|f^2\,0\,0\,0\,0\right\rangle$ and $\left|f^2\,S'\,L'\,J'\,M'\right\rangle$ denote the $^1S_0$ state and final states, respectively. In order to discuss the mixing of $4f^2$ states with 4f5d states, the structure of the 4f5d band of Pr^{3+} is explained using a scheme of LS coupling [9]. The basis set of the 4f5d states which responsible for the mixing is $\left|\text{fd}\,S''\,L''\,J''\,M''\right\rangle$.

Only the mixing of the $^1S_0$ state with the 4f5d states is considered in the calculation because the $^1S_0$ state is close to the 4f5d configuration and has a large energy gap to the other $4f^2$ states. The nonzero matrix elements of the electric dipole operator between the parity mixed $^1S_0$ state and the final state are

$$\begin{aligned}\left\langle f^2\,0\,0\,0\,0\right|D_p^1\left|f^2\,S'\,L'\,J'\,M'\right\rangle &= e\sum_{\kappa}\Big[\left\langle f^2\,0\,0\,0\,0\right|C_q^k(j)\left|\text{fd}\,S''\,L''\,J''\,M''\right\rangle \\ &\quad\times\left\langle \text{fd}\,S''\,L''\,J''\,M''\right|C_p^1(j)\left|f^2\,S'\,L'\,J'\,M'\right\rangle \\ &\quad\times\frac{B_{kq}(\text{fd})r}{E(f^2 0\,0\,0\,0)-E(\text{fd}\,S''\,L''\,J''\,M'')}\Big],\end{aligned} \tag{3}$$

where the symbol κ denote the sum over L'', J'', M'', k, q, and j; r is the interconfigurational radial integral $\langle 4f|r|5d\rangle$.

To calculate Eq. (3), the energy denominators can be derived through calculating the energy levels of $4f^2$ and 4f5d configurations, meanwhile the values of B_{kq}(fd)'s and r should be determined.

3. Results and conclusion

In order to assign the transitions between two states of the $4f^2$ configuration, the exact structure of 4f5d configuration of Pr^{3+} in $SrAl_{12}O_{19}$ must be known. The 4f5d energy levels are calculated using a parameterized Hamiltonian that can be written as

$$H = H_{\text{fi}} + H_{\text{CF}} + \ldots, \tag{4}$$

where H_{fi} is the free-ion Hamiltonian and H_{CF} the crystal-field Hamiltonian [6]. In this calculation, the free-ion parameters for $4f^2$ and 4f5d are taken from Ref. [8]. The only crystal-field parameters in the $4f^2$ configuration, for D_{3h} point symmetry, are B_{20}(4f), B_{40}(4f), B_{60}(4f) and B_{66}(4f), and their values can be obtained from Ref. [10]. In the 4f5d configuration the B_{kq}(4f)'s are chosen equal to those of the $4f^2$ configuration. The crystal-field parameters for a *5d* electron, $B_{20}(5d) = 398\,\text{cm}^{-1}$ and $B_{40}(5d) = 13\,962\,\text{cm}^{-1}$, are chosen as the parameters that best fit the excitation spectrum of Ce^{3+} in $SrAl_{12}O_{19}$. The energies and eigenfunctions of 4f5d configuration have been calculated in a scheme of LS coupling according to the presented method, the predicted 4f5d band occurs between 48 592 and 72 252 cm^{-1}. From spin and symmetry considerations, the main opposite parity component mixed into $4f^2\,{}^1S_0$ are from the 4f5d $^1F_3$ and $^1H_5$ spectral terms [5].

From Eq. (3), to calculate the line intensity of selected electric dipole transition, the odd-rank crystal-field parameters B_{kq}(fd)'s and the radial integral r for the ion host system should be known. In D_{3h} symmetry, the fitted variants, $B_{33}(\text{fd})r$ and $B_{53}(\text{fd})r$, are adjusted to minimize the root mean square (rms) deviation of the calculated and measured relative emission intensities between the $^1S_0$ and the lower J multiplets. The total transition intensities between J-multiplets can be obtained by summing over all the line intensities between crystal-field levels within the multiplets of interest. The experimental data of $^1S_0$ are cited from Ref. [6]. The rms deviation is deduced to 0.032 and the fitted values are:

$$B_{33}(\text{fd})r = 1.207\times10^{-5},\ B_{53}(\text{fd})r = 1.522\times10^{-5}.$$

The associated transitions of the $^1S_0$ state are determined by state mixing. The main Stark levels of the final $4f^2$ multiplets are determined by the nonzero conditions of the odd-rank crystal-field and the electric dipole operator matrix elements using standard tensorial method and are presented in Table 1. The calculated intensities are in qualitative agreement with the measurements.

The fitting parameters may also apply for other radiative levels, such as $^3P_0$. In this case, different from the situation for $^1S_0$ emission, the mixing of both the $4f^2$ initial and final states with the 4f5d states should be taken into account.

In summary, the proposed fitting method is applied to calculate the line intensities of the electric dipole transitions from the $^1S_0$ level to the lower crystal-field levels. It is believed that the results from our method can be improved if the contributions of higher-order configurations and the

Table 1
Calculated relative intensities of the main $^1S_0$ emission lines of Pr^{3+} in $SrAl_{12}O_{19}$. The strongest line of these transitions is normalized to be 1

Final states	Irrep	$\lambda_{cal.}$ (nm)	Relative intensity
$^1I_6$	$E'(1)$	404.58	0.081
	$E'(2)$	397.88	0.376
	A_1'	397.35	0.121
	A_2''	397.33	0.121
$^1D_2$	E'	337.69	0.193
$^1G_4$	$E'(1)$	276.93	0.574
	A_1''	276.16	0.229
	$E'(2)$	273.15	1.000
	A_2''	272.68	0.229
$^3F_4$	A_1''	254.05	0.082
	$E'(1)$	253.94	0.204
	A_2''	253.31	0.082
	$E'(2)$	252.69	0.356

dynamic coupling mechanism [11–13] are taken into account.

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