Journal of Luminescence 94–95 (2001) 119–122

JOURNAL OF LUMINESCENCE

www.elsevier.com/locate/jlumin

The mixing of the $4f^2$ $^1S_0$ state with the 4f5d states in Pr^{3+} doped $SrAl_{12}O_{19}$

Shihua Huang[a,b], Xiao-jun Wang[a,c], R.S. Meltzer[a,*], A.M. Srivastava[d], A.A. Setlur[d], W.M. Yen[a]

[a] *Department of Physics and Astronomy, University of Georgia, Athens, GA 30602, USA*
[b] *Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics, and Physics, Changchun 130021, China*
[c] *Department of Physics, Georgia Southern University, Statesboro, GA 30460, USA*
[d] *6E Corporate Research and Development, 1 Research Cycle, Niskayuna, NY 12309, USA*

Abstract

The $^1S_0$ state of Pr^{3+} in $SrAl_{12}O_{19}$ lies near to the 4f5d band. The admixing of the opposite parity 5d components by the crystal field without a symmetry center can be significant, thus affecting the properties of the $^1S_0$ state. In a crystal with D_{3h} symmetry, the major 4f5d components which can be mixed into $^1S_0$ are $2^{-1/2}(|fd\Gamma_1\,^1F_3\,3\rangle\text{-}|fd\Gamma_1\,^1F_3\text{-}3\rangle)$ and $2^{-1/2}(|fd\Gamma_1\,^1H_5\,3\rangle\text{-}|fd\Gamma_1\,^1H_5\text{-}3\rangle)$. A calculation of the 4f5d wavefunctions indicates that the states which may be mixed into $^1S_0$ lie mainly at the middle and upper parts of the 4f5d configuration. The mixed $4f^2$ $^1S_0$ wavefunction is then calculated and its spectral properties are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: $SrAl_{12}O_{19}$; $^1S_0$ state; Praseodymium; State mixing

I. Introduction

In $SrAl_{12}O_{19}$, the Pr ions occupy high coordination sites and hence experience a weaker crystal field environment such that the $4f^2$ $^1S_0$ state lies below the lowest 4f5d state, making it is possible to observe the photon cascade emission [1]. Transitions within the 4f configuration are of a static forced electric dipole nature, and the amount of the opposite parity wavefunctions mixed into the 4f state is affected critically by their separation in energy. Therefore, one would expect the $^1S_0$ state, which is energetically quite close to the 4f5d configuration, to show some unique properties different from that of other low-lying $4f^2$ states.

The questions of concern in this paper about the spectroscopic properties of the $^1S_0$ state include: (1) which components of the 4f5d wavefunctions can be mixed into the $4f^{2\,1}S_0$ state and (2) can the properties of the $^1S_0$ state be accounted for by this mixing.

In Sections 2, we describe the calculation of the wavefunctions of the states in 4f5d configuration and, in Section 3, we present the results of the mixing of $^1S_0$ with the 4f5d states based on these wavefunctions.

*Corresponding author. Tel.: +1-706-52-5515; fax: +1-706-542-2492.
E-mail address: rmeltzer@hal.physast.uga.edu (R.S. Meltzer).

PII: S0022-2313(01)00386-6

2. Energy levels of the 4f5d configuration of Pr^{3+} ions in $SrAl_{12}O_{19}$

The Hamiltonian of rare earth ions in solids can be written as

$$H = H_{\text{fi}} + H_{\text{CF}} + \cdots, \tag{1}$$

where H_{fi} is the free ion Hamiltonian and H_{CF} the crystal field interaction taken as a perturbation.

In the calculation of the free ion wavefunctions of the 4f5d states, we apply the anti-symmetrized combinations of Russell–Saunders states as the basis states and take the Racah parameters (F's and G's) and spin–orbit coupling parameters ($\zeta_{4\text{f}}$, $\zeta_{5\text{d}}$) from Ref. [2].

The crystal field Hamiltonian can be written as

$$H_{\text{CF}} = \sum_{k,\,q,\,i} B_{kq} C_q^{(k)}(i), \tag{2}$$

where $C_{kq}(i)$ is the irreducible tensor operate on the ith electron and the index i runs through all the valence electrons. The crystal field parameters B_{kq}'s are generally taken as fitting parameters. With the anti-symmetrized wavefunctions, the matrix element of H_{CF} for a pair of 4f5d spectral terms is

$$\begin{aligned}
&\langle SLJM|H_{\text{CF}}|S'L'J'M'\rangle = \delta_{SS'}(-1)^{S+L'-M+l_1+l_2} \\
&\sqrt{(2J+1)(2J'+1)(2L+1)(2L'+1)} \\
&\quad\times \sum_{k,\,q} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \left[\begin{pmatrix} l_1 & k & l_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L & k & L' \\ l_1 & l_2 & l_1 \end{Bmatrix} \right. \\
&\quad\times (-1)^{l_1}(2l_1+1)B_{kq}(l_1) + \begin{pmatrix} l_2 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L & k & L' \\ l_2 & l_1 & l_2 \end{Bmatrix} \\
&\quad\left. \times (-1)^{l_2}(2l_2+1)B_{kq}(l_2) \right].
\end{aligned} \tag{3}$$

Here () and {} are Wigner $3j$ and $6j$ symbols, respectively. The crystal field matrix elements between odd and even L will be zero. The energy levels can be obtained by diagonalizing the Hamiltonian of Eq. (1).

Pr^{3+} occupies the Sr^{2+} site in $SrAl_{12}O_{19}$ and its local symmetry is $D_{3\text{h}}$ [3]. For the fd configuration in $D_{3\text{h}}$ symmetry, the nonzero crystal field parameters are B_{20}, B_{40}, B_{60}, and B_{66} for the f electron and B_{20} and B_{40} for the d electron. The crystal field Hamiltonian can be written as

$$\begin{aligned}
H_{\text{CF}} = &\sum_{k=2,4,6} B_{k0}(f) C_0^{(k)}(f) + B_{66}(f) \\
&\times \left[C_6^{(6)}(f) + C_{-6}^{(6)}(f) \right] + \sum_{k=2,4} B_{k0}(d) C_0^{(k)}(d).
\end{aligned} \tag{4}$$

According to the properties of the $3j$ and $6j$ symbols, the Hamiltonian can be divided into six sub matrixes and diagonalized separately. The nonzero matrix elements are those between the wavefunctions with (1) $M = 0$ and $M' = 0$ or ± 6; (2) $M = 1$ and $M' = 1$ or -5; (2′) $M = -1$ and $M' = -1$ or 5; (3) $M = 2$, $M' = 2$ or -4; (3′) $M = -2$, $M' = -2$ or 4; and (4) $M = \pm 3$, $M' = \pm 3$. Thus the dimensions of the six sub matrixes are 22, 23, 23, 24, 24, and 24. The matrices (2′) and (2), as well as (3) and (3′), are the same, corresponding to 2-fold degenerate states. In the calculation, the crystal field parameters of the f electron are taken from Ref. [3]. The crystal field parameters of the d electron, $B_{20}(d) = 500\,\text{cm}^{-1}$ and $B_{40}(d) = 15810\,\text{cm}^{-1}$, are chosen as the parameters that best fit the vacuum UV part of the absorption spectrum.

The density of the state is defined as $D(E) = \sum_i g_i \varphi_i(E - E_i) / \sum_i g_i$, where E_i is the eigenvalue of the ith eigenstate, g_i is its degeneracy, φ_i is the normalized lineshape of this state. The dotted line in Fig. 1 shows $D(E)$ of all the 4f5d states that is calculated by assuming a Gaussian profile with a spectral width (half width at $1/e$ maximum) of $1500\,\text{cm}^{-1}$ for all the 4f5d states. The other two curves in the figure will be discussed in the next section.

3. The mixing of the $4f^2$ $^1S_0$ state with the 4f5d states

The odd terms of the crystal field mix wavefunctions with opposite parities. For $D_{3\text{h}}$ symmetry, the nonzero odd crystal field terms are

$$\begin{aligned}
H_{\text{CF}}(\text{odd}) = &A_{33}\langle 4f|r^3|5d\rangle \sum_i \left(C_3^{(3)}(i) + C_{-3}^{(3)}(i) \right) \\
&+ A_{53}\langle 4f|r^5|5d\rangle \sum_i \left(C_3^{(5)}(i) + C_{-3}^{(5)}(i) \right) + \cdots.
\end{aligned} \tag{5}$$

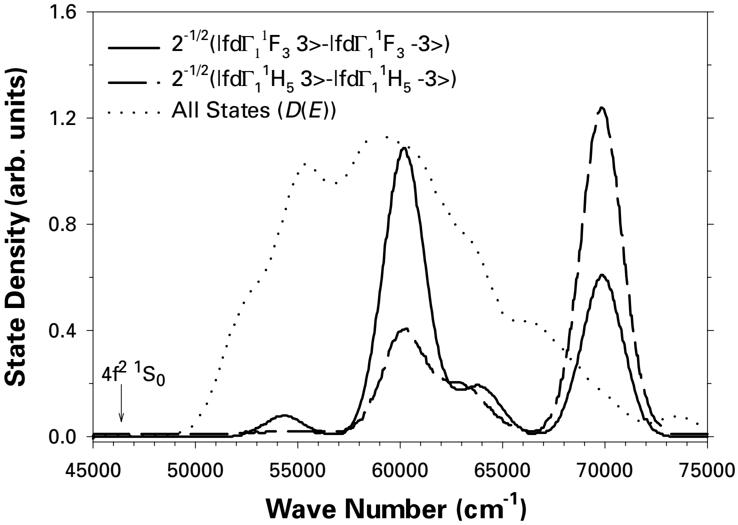

Fig. 1. The densities of the 4f5d states, $2^{-1/2}(|\mathrm{fd}\Gamma_1\,{}^1\mathrm{F}_3\ \text{-}3\rangle\text{-}|\mathrm{fd}\Gamma_1\,{}^1\mathrm{F}_3\text{-}3\rangle)$ (solid line) and $2^{-1/2}(|\mathrm{fd}\Gamma_1\,{}^1\mathrm{H}_5\ 3\rangle\text{-}|\mathrm{fd}\Gamma_1\,{}^1\mathrm{H}_5\text{-}3\rangle)$ (dashed line), which can be mixed into the $4\mathrm{f}^2\ {}^1\mathrm{S}_0$ state. For comparison, the total density of states ($D(E)$, dotted line) is also plotted.

With the wavefunctions obtained based on the procedures described in Section 2, we may consider the type of 4f5d wavefunctions that can be mixed into the $4\mathrm{f}^2\ {}^1\mathrm{S}_0$ state.

Since ${}^1\mathrm{S}_0$ is a singlet and belongs to the identity representation, Γ_1, of the crystal symmetry group, the 4f5d state that can be mixed into ${}^1\mathrm{S}_0$ by the crystal field must also be a singlet with Γ_1 symmetry. The Γ_1 singlet states in the 4f5d configuration contain anti-symmetric spin and symmetric orbital components. The orbital component can be written as $1/\sqrt{2}\times(l_1l_2SLJM\rangle+|l_2l_1SLJM\rangle)$. The matrix element that determines this admixing is

$$\begin{aligned}&\frac{1}{\sqrt{2}}\Big[\langle \mathrm{fd}SLJM|C_q^k(1)+C_q^k(2)|f\!f0000\rangle\\&\quad+\langle \mathrm{df}SLJM|C_q^k(1)+C_q^k(2)|f\!f0000\rangle\Big]\\&\quad=\frac{(-1)^{-M}}{\sqrt{2}}\big[(-1)^L-1\big]\delta_{S0}\sqrt{35(2J+1)(2L+1)}\\&\quad\times\begin{pmatrix}J&k&0\\-M&q&0\end{pmatrix}\begin{Bmatrix}J&k&J\\0&0&L\end{Bmatrix}\begin{Bmatrix}L&k&0\\3&3&2\end{Bmatrix}\begin{pmatrix}2&k&3\\0&0&0\end{pmatrix}.\end{aligned}\tag{6}$$

It is nonzero if $S=0$, $L=J=k=\text{odd}$, $k\leqslant5$, and $M=q$. Thus, only $2^{-1/2}(|\mathrm{fd}\Gamma_1\,{}^1\mathrm{F}_3\ 3\rangle\text{-}|\mathrm{fd}\Gamma_1\,{}^1\mathrm{F}_3\text{-}3\rangle)$ and $2^{-1/2}(|\mathrm{fd}\Gamma_1\,{}^1\mathrm{H}_5\ 3\rangle\text{-}|\mathrm{fd}\Gamma_1\,{}^1\mathrm{H}_5\text{-}3\rangle)$ can be mixed into ${}^1\mathrm{S}_0$. The calculated densities of these two wavefunctions are shown in Fig. 1. Nonzero density appears at $3000\,\mathrm{cm}^{-1}$ above the bottom of the 4f5d configuration, while the maxima of the state densities are $10{,}000\,\mathrm{cm}^{-1}$ or higher above the bottom.

Taking $4\mathrm{f}^2\ {}^1\mathrm{S}_0$ and $4\mathrm{f}5\mathrm{d}\Gamma_1$ states as zero-order wavefunctions and obtaining the odd-rank crystal field parameters A_{kq} from Ref. [3] and $\langle 4\mathrm{f}|r^k|5\mathrm{d}\rangle$ from Ref. [4], we diagonalized the Hamiltonian and obtained the mixed wavefunctions. The admixture of 4f5d into $4\mathrm{f}^2\ {}^1\mathrm{S}_0$, $|4\mathrm{f}^2\,{}^1\mathrm{S}_0\rangle'$, can be written as

$$\begin{aligned}|4\mathrm{f}^2\,{}^1\mathrm{S}_0\rangle'&=0.9986|4\mathrm{f}^2\,{}^1\mathrm{S}_0\,0\rangle\\&\quad-0.0342\big(|4\mathrm{f}5\mathrm{d}^1\mathrm{F}_3\,3\rangle-|4\mathrm{f}5\mathrm{d}^1\mathrm{F}_3-3\rangle\big)\\&\quad+0.0143\big(|4\mathrm{f}5\mathrm{d}^1\mathrm{H}_5\,3\rangle-|4\mathrm{f}5\mathrm{d}^1\mathrm{H}_5-3\rangle\big).\end{aligned}\tag{7}$$

The state contains about a 0.003 admixture of 4f5d wavefunctions. Its lifetime is expected to be 300 times longer than the parity allowed transition and should be of the order of magnitude of μs, which is longer than the measured value of 650 ns. Closer agreement may occur if the mixing of the 4f5d states with the final states in the emission transition and the mixing of ${}^1\mathrm{S}_0$ with the configurations higher than 5d are taken into account.

Table 1
Relative intensities of the $^1S_0$ emission lines

Final state ($^{2S+1}L_J$)	Transition dipole matrix element		Total relative emission intensity	
	π	σ	Calculated[a]	Measured[b]
$^1D_2$	0	0.15306	0.081	0.067
$^3F_2$	0	0.00370	0.005	—
$^3P_2$	0	0.01346	0.004	—
$^3F_4$	0.02414	0.33736	0.460	0.549
$^1G_4$	0.06677	0.93323	1.000	1.000
$^3H_4$	0.00219	0.03061	0.068	0.125
$^3H_6$	0.00015	0.00081	0.001	—
$^1I_6$	0.05202	0.27321	0.103	0.344

[a] Sum of column 2 and 3 multiplied by ω^3.
[b] Calculated from the data in Ref. [1] and private communication with A.M. Srivastava.

Spin–orbit coupling interaction mixes the wavefunctions with the same J, thus the $|4f^2\ ^1S_0\rangle$ state is actually a Russell–Saunders admixture of $^1S_0$ and $^3P_0$. In D_{3h} field, the $^3P_0$ component can mix with $|4f5d\ ^3F_{3,4}\ \Gamma_1\rangle$ and $|4f5d\ ^3H_{4,5,6}\ \Gamma_1\rangle$. In $LaF_3:Pr^{3+}$, the admixture $= 0.9962|^1S_0\rangle + 0.0876|^3P_0\rangle$ [5], suggesting the coefficient of the $^3P_0$ state in our system also to be very small. In our system, additional 4f5d components being mixed into $^1S_0$ is estimated using the data in LaF_3 to be a value (coefficient) of 6×10^{-5}, yielding a 2% deviation from the result without accounting for $^3P_0$ component. We therefore neglect $^3P_0$ component in our calculation.

The emission spectrum from the admixed $^1S_0$ to the $4f^2$ state can be predicted from the calculated wavefunctions. Since the 4f5d spectral terms mixed into $^1S_0$ are $2^{-1/2}(|fd\Gamma_1\ ^1F_3\ 3\rangle$-$|fd\Gamma_1\ ^1F_3$-$3\rangle)$ and $2^{-1/2}(|fd\Gamma_1\ ^1H_5\ 3\rangle$-$|fd\Gamma_1\ ^1H_5$-$3\rangle)$, the spin-allowed transitions are to $^1D_2$, $^1G_4$, and $^1I_6$. However, spin–orbit coupling mixes $4f^2$ states with the same J, yielding possible transitions to $^3P_2$, $^3F_2$, $^3F_4$, $^3H_4$, and $^3H_6$. The calculated intensities of the $^1S_0$ emission lines relative to that of the $^1S_0$–$^1G_4$ emission are given in Table 1. For comparison, the measured values are listed in the last column. The transitions ending on $^1I_6$, $^1G_4$, $^3F_4$, and $^1D_2$ are relatively strong. The high intensity of $^1S_0\rightarrow{}^3F_4$ is due to the fact that the $^3F_4$ state contains about 1/4 of the $^1G_4$ character through spin–orbit coupling [5]. Weak lines related to the transitions to $^3H_4$ and $^3P_2$ may be observed, which qualitatively agree with the measured emission spectrum.

There is a significant discrepancy in the intensity of the $^1S_0\rightarrow{}^1I_6$ transition that is theoretically expected to be much weaker than that of $^1S_0\rightarrow{}^1G_4$, while experimentally it is only slightly weaker. Since the $^1S_0\rightarrow{}^1I_6$ emission is dominated by vibronic transitions, the discrepancy may be attributed to the existence of dynamic coupling between the $4f^2$ and 4f5d states that is not considered in our calculations.

In summary, the crystal field of $SrAl_{12}O_{19}$ mixes the $^4f_2\ ^1S_0$ state of Pr^{3+} ions with 4f5d $^1F_3$ and $^1H_5$. The spectroscopic properties of the $^1S_0$ state can be explained, at least qualitatively, by this admixing.

Acknowledgements

This work was supported by the U.S. Department of Energy (Grant No. DE-FC26-99 FT40632). S.H. Huang would like to thank the State Key Project of Basic Research of China (G1998061314) for partial support. X.J. Wang is grateful for the support of Faculty Research Grant from Georgia Southern University.

References

[1] A.M. Srivastava, W.W. Beers, J. Lumin. 71 (1997) 285.
[2] M. Laroche, J.-L. Doualan, S. Girard, J. Margerie, R. Moncorge, J. Opt. Soc. Am. B 17 (2000) 1291.
[3] B. Zandi, L.D. Merkle, J.B. Gruber, D.E. Wortman, C.A. Morrison, J. Appl. Phys. 81 (1997) 1047.
[4] B. Judd, Phys. Rev. 127 (1962) 750.
[5] R.C. Pappalardo, J. Lumin. 14 (1976) 159.