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Direct calculation of transition intensities in LiYF$_4$: Nd^{3+}

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We will extend Duan's simple model to analyze the mixing of the $4f^{N-1}5d$-configuration with the $4f^N$-states. We consider the explicit static coupling and traditional dynamic coupling, and fit the parameters according to the absorption spectrum in LiYF$_4$: Nd^{3+}. The parameters obtained are $T_{32} = -28i \cdot 10^{-7}$, $T_{52} = -1151i \cdot 10^{-7}$, $A^2_{32} = 192i \cdot 10^{-12}$ cm, $A^4_{52} = i \cdot 10^{-12}$ cm, $A^6_{72} = 54i \cdot 10^{-12}$ cm and $A^6_{76} = -680i \cdot 10^{-12}$ cm. Compared to the experimental measurements, the present model yields better results than whose obtained from the Judd–Ofelt theory.

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1. Introduction

The Judd–Ofelt theory [1,2] has been widely used to calculate the optical transition properties of the $4f^N$-configuration in rare earth doped hosts. However, discrepancies are observed when the theory is applied to the high energy $4f^N$-excited states. Some work on considering the explicit effects of the $4f5d$-configuration on the $4f^2 \leftrightarrow 4f^2$ transitions of Pr^{2+} has been done [3]. For more than two electrons of trivalent lanthanide ions, it is difficult to distinguish between the $4f^{N-1}5d$-energy eigenstates. It is nearly impossible to give a detailed explanation of the $f-d$-transition spectrum. We look for a concise method to deal with the energy states, and at the same time, we search a simpler and more intuitionistic $4f^{N-1}5d$-configuration basic function form. Recently Duan et al. [4,5] developed a simple model to interpret the $4f^N \leftrightarrow 4f^{N-1}5d$-transitions by considering only the main interactions in the $4f^{N-1}5d$-configuration.

In this paper, we continue to use this to deal with the opposite parity $4f^{N-1}5d$-configuration which is related to the $f-f$-transitions. We use explicit $f-d$-mixing wave functions for the direct calculation of the $f-f$-transition intensities in the Nd^{3+}-doped LiYF$_4$. The site symmetry of the Y^{3+} sites in LiYF$_4$ is S_4, which is often approximated in calculations by the D_{2d} symmetry since the deviation between them is small. We introduce a set of intensity parameters, including explicit static coupling parts T_{32}, T_{52} and traditional dynamic coupling parameters A^2_{32}, A^4_{52}, A^6_{72} and A^6_{76} to be fitted together to the experimental data. Finally, we compare the results with the values obtained using the traditional Judd–Ofelt theory to the experimental measurements.

2. Calculation methods

The nonzero matrix elements of the electric dipole operator between the initial $|\varphi_i\rangle$ and final states $|\varphi_f\rangle$ belonging to $4f^3$ are

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

where the corresponding Hamiltonian can be written as

$$H_{CF}(\text{odd}) = \sum_{k,q,j} A^k_q r^k c^k_q(j), \quad k = \text{odd number}, \qquad (2)$$

the electric dipole operator D^1_p, which dominates the relevant transition, is then expressed as

$$D^1_p = \sum_j r c^1_p(j), \qquad (3)$$

where c^k_q is the irreducible tensor operator of rank k end the values of q are determined by site symmetry. In our calculation, we used the established $4f^N$-atomic and crystal field parameters [6] to treat the $4f^N$-energy levels. The calculation of the $4f^{N-1}5d$-states has been discussed in detail in Ref. [7] and the eigenvalues of the $4f^{N-1}5d$-eigenstates are given

$$\begin{aligned} E\big(\big|\big[(4f^{N-1}\bar{\eta}\bar{S}\bar{L}, s_d)S\bar{L}\big]J;\Gamma_d\big\rangle\big) &= E_0\big(4f^{N-1}\bar{\eta}\bar{S}\bar{L};\Gamma_d\big) \\ &- J_{\text{ex}}\big[S(S+1) - \bar{S}(\bar{S}+1) - s_d(s_d+1)\big]/2 \\ &+ \lambda_{\bar{\eta}\bar{S}\bar{L}S}\big[J(J+1) - S(S+1) - \bar{L}(\bar{L}+1)\big]/2, \qquad (4) \end{aligned}$$

where Γ_d is the irreducible representation of the site symmetry group.

The matrix element $\langle\varphi_i|D_p^1|\varphi_i''\rangle$ for the one-photon transition between the initial $4f^N$-states, $|4f^N\varphi_i\rangle$, and all the $4f^{N-1}5d$-states, $|4f^{N-1}5d\varphi_i''\rangle$, can be expressed as

$$\Big\langle 4f^N\eta SLJM_J|\sum_i c_p^i(j)|\big[(4f^{N-1}\overline{\eta}\overline{S}\overline{L},s_d)S''\overline{L}\big]J''M_j'';\Gamma_d\gamma_d\Big\rangle$$

$$=\sqrt{N}\sum_{m_d}C_{m_d}^{\Gamma_d r_d}\sum_{M_SM_LM_{Lf}m_f}\langle JM_J|SM_SLM_L\rangle\langle SM_S\overline{L}\overline{M}_L|J''M_J''\rangle$$

$$\times\langle LM_L|\overline{L}\overline{M}_L fm_f\rangle\langle\varphi\{|\overline{\varphi}\rangle\langle fm_f|c_p^1|dm_d\rangle, \qquad (5)$$

where the values of $\overline{L}$ and the fractional parentage coefficients $\langle\varphi\{|\overline{\varphi}\rangle$ are listed in Ref. [8]. The values of m_d are integers from -2 to 2 for the calculation.

The matrix elements $\langle\varphi_i''|H_{CF}|\varphi_f\rangle$ of irreducible tensor operator between the final $4f^N$-state and the $rf^{N-1}5d$-states, which relate to the odd-rank crystal-field interaction, can be written as

$$\sqrt{N}\big\langle\big[(4f^{N-1}\overline{\eta}\overline{S}\overline{L},s_d)S''\overline{L}\big]J''M_J'';\Gamma_d\gamma_d|\sum_j c_q^k(j)|$$

$$\times[4f^N\eta'S'L'J'M_J']\big\rangle=\sqrt{N}\delta_{S'S''}[J',J'',L']^{1/2}\langle\overline{\varphi}|\}\varphi'\rangle$$

$$\times\begin{Bmatrix}L' & \overline{L} & 3\\ J'' & J' & S\end{Bmatrix}\sum_{m_d'}C_{m_d'}^{\Gamma_d r_d}\sum_{m_f'}(-1)^{S-\overline{L}-3+M_J''m_f'}$$

$$\times\begin{pmatrix}3 & J'' & J'\\ m_f' & M_J'' & -M_J'\end{pmatrix}\langle dm_d'|c_q^k|fm_f'\rangle, \qquad (6)$$

where the one-electron tansor matrix elements $\langle fm_f|c_p^1|dm_d\rangle$ and $\langle dm_d'|c_q^k|fm_f'\rangle$ in Eq. (5) and Eq.(6) will then be expressed by the expression

$$\langle jm|c_q^k|j'm'\rangle$$

$$=(-1)^{2j-m}[j,j']^{1/2}\begin{pmatrix}j & k & j'\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}j & k & j'\\ -m & q & m'\end{pmatrix}. \qquad (7)$$

According to the $f-f$-electric dipole transition mechanism, the $4f^{N-1}5d$-state mixing with the initial $4f^N$-state are also the component which transfer to the final $4f^N$-configurations. The relevant matrix elements $\langle\varphi_f|D_p^1|\varphi_f''\rangle$ and $\langle\varphi_f''|H_{CF}|\varphi_i$ can be expressed by analogy with Eqs. (5) and (6).

The summation in Eq. (1) rens over all the $4f^{N-1}5d$-configuration components. The sum over Γ_d makes the terms vanish when $m_d\neq m_d'$ in Eqs. (5) and (6), leaving only the terms of $m_d=m_d'$ in the calculation.

We define the parametric expression of the $4f^N$-interconfiguration electric dipole transition matrix element in static coupling (SC) as

$$\langle 4f^N\varphi|D_p^1|4f^N\varphi'\rangle_{SC}=\sum_{k,q}T_{kq}b_q^{(k)}, \qquad (8)$$

where the $b_q^{(k)}$ contains the mathematic factors, representing the states related to the initial or final state mixing, and the energy denominator. $b_q^{(k)}$ is expressed by the standard tensor operator method

$$b_q^{(k)}=\sum_\kappa(-1)^p\delta_{SS''}\delta_{S'S''}N[\Gamma_d][J''][J,L,J',L']^{1/2}$$

$$\times\langle\varphi\{|\overline{\varphi}\rangle\langle\overline{\varphi}|\}\varphi'\rangle\begin{Bmatrix}L & \overline{L} & 3\\ J'' & J & S\end{Bmatrix}\begin{Bmatrix}L' & \overline{L} & 3\\ J'' & J' & S\end{Bmatrix}$$

$$\times\begin{pmatrix}3 & 1 & 2\\ -m_d-p & p & m_d\end{pmatrix}\begin{pmatrix}2 & k & 3\\ -m_d & q & m_d-q\end{pmatrix}$$

$$\times\Bigg[\begin{pmatrix}3 & J'' & J\\ m_d+p & M_J-m_d-p & -M_J\end{pmatrix}$$

$$\times\begin{pmatrix}3 & J'' & J'\\ m_d-q & M_J-m_d-p & -M_J+p+q\end{pmatrix}\Big/(E_f-E'')$$

$$+\begin{pmatrix}3 & J'' & J'\\ m_d+p & M_J-m_d+p & -M_J-p-q\end{pmatrix}$$

$$\times\begin{pmatrix}3 & J'' & J\\ m_d-q & M_J-m_d+p & -M_J\end{pmatrix}\Big/(E_i-E'')\Bigg], \qquad (9)$$

where κ denotes the summation that runs over all values of $\overline{L}, J''$ and m_d. The nonzero conditions of the 3-j, 6-j symbols and the fractional parentage coefficients set the selection rules for the $4f^N\leftrightarrow 4f^N$-dipole transitions and for the $4f^N$–$4f^{N-1}5d$-mixing of Nd^{3+} in $LiYF_4$.

We define the non-dimension phenomenology intensity parameter T_{kq} as

$$T_{kq}=-\sqrt{105}A_{kq}\langle r\rangle\langle r^k\rangle\begin{pmatrix}2 & k & 3\\ 0 & 0 & 0\end{pmatrix}, \qquad (10)$$

where A_{kq} is the odd-rank crystal-field parameter and can be obtained from lattice sum calculations, $\langle r\rangle$ and $\langle r^k\rangle$ denote the redial integrals between $f-d$-configurations.

The electric dipole transition matrix element in dynamic-coupling is expressed as

$$\langle 4f^2\varphi|D_p^1|4f^2\varphi'\rangle_{DC}=\sum_{\lambda,q}A_{(\lambda+1)q}^\lambda$$

$$\times(-1)^p\langle\lambda(p+q),1-p|(\lambda+1)q\rangle\langle 4f^2\varphi|U_{p+q}^\lambda|4f^2\varphi'\rangle, \qquad (11)$$

where $A_{(\lambda+1)q}^\lambda$ are the dymanic-coupling parameters. The values λ are 2, 4 and 6. In the D_{2d} site symmetry, the values q are 2 in T_{kq} and 2, 6 in $A_{(\lambda+1)q}^\lambda$. The intensity parameters T_{kq} and $A_{(\lambda+1)q}^\lambda$ are fitted to the experimental data [9] using the Nelder–Mead simplex search method. The fitting values can be used to calculated the $4f^3\leftrightarrow 4f^3$-transition intensities in the $LiYF_4:Nd^{3+}$ systems.

3. Results and Discussion

We apply the calculation methods to the $4f^3\leftrightarrow 4f^3$-transitions in the Nd^{3+}-doped $LiYF_4$. First, we determine the mixed $4f^25d$-components. For the ground state $4I_{9/2}$

Experimental and calculated strengths of transitions from the $^4I_{9/2}$ level in $LiYF_4:Nd^{3+}$

Final stated $\vert f^N[SL]J\rangle$	Energy difference, cm^{-1}	Oscillator strength, 10^{-20} cm^2		
		This work	$J-O$ [9]	Measured [9]
$^4F_{3/2}$	11 515	0.098	0.168	0.083
$^4F_{5/2}$, $^2H_{9/2}(2)$	12 519	0.426	0.234	0.500
$^4F_{7/2}$, $^4S_{3/2}$	13 470	1.648	1.568	1.708
$^4F_{9/2}$	14 725	3.013	3.002	2.991
$^2H_{11/2}(2)$	15 932	0.073	0.061	0.042
$^4G_{5/2}$, $^2G_{7/2}(1)$	17 233	0.201	0.234	0.248
$^4G_{7/2}$, $^4G_{9/2}$, $^2K_{13/2}$	19 298	3.306	3.374	3.228
$^4G_{11/2}$, $^2G_{9/2}(1)$, $^2D_{3/2}(1)$, $^2K_{15/2}$	21 377	3.167	3.481	3.650
$^4P_{1/2}$, $^2D_{5/2}(1)$	23 354	0.956	1.168	0.901
σ_{rms}		0.184	0.318	

absorption, according to the nonzero conditions of the fractional parentage coefficients, both initial and final mixing states of the $4f^25d$-configuration come from the terms $[(^3F)\,^4F_J\Gamma_d]$ and $[(^3H)\,^4H_J\Gamma_d]$ in the D_{2d} site symmetry. Based on the properties for the 3-j symbols in Eq. (8), the values of J can be determined. For exapmle, in the transition of $^4I_{9/2} \rightarrow {}^4F_{3/2}$, the following relations can be derived: $(3, J, 3/2)$ and $(3, J, 9/2)$, thus the $4f^25d$-states involved in the transition are $[(^3F)\,^4F_{3/2,5/2,7/2,9/2}\Gamma_d]$ and $[(^3H)\,^4H_{7/2,9/2}\Gamma_d]$.

In the D_{2d} symmetry, the static coupling parameters T_{32}, T_{52} and the dynamic-coupling parameters A^2_{32}, A^4_{52}, A^6_{72}, and A^6_{76} are fitted by the absolute absorption intensities of the transitions from the $^4I_{9/2}$ ground level to the upper J multiplets [9]. The fitted values $T_{32} = -28i \cdot 10^{-7}$, $T_{52} = -1151i \cdot 10^{-7}$, $A^2_{32} = 192i \cdot 10^{-12}$ cm, $A^4_{52} = i \cdot 10^{-12}$ cm, $A^6_{72} = 54i \cdot 10^{-12}$ cm, and $A^6_{76} = -680i \cdot 10^{-12}$ cm can be used to calculate the transition intensities originating from $^4I_{9/2}$, as listed in the Table. The values obtained using the traditional Judd–Ofelt method are also presented, together with the experimental measurements. The calculated results using the current method have been substantially improved in comparison with the traditional Judd–Ofelt theory, as indicated by the room mean square deviation, σ_{rms}, shown in the last row. Next step is to extend the method to treat the transitions from the higher Nd^{3+} energy levels in the system.

4. Conclusions

A simple model is introduced to deal with the opposite parity $4f^{N-1}5d$-configuration related to the $f-f$-transitions. New selection rules are applied to determine the $4f^25d$-components, which are able to mix with the $4f^3$-transtions states. Both static coupling and dynamic-coupling are taken into account and a set of parameters are obtained using the Nelder–Mead simplex search method. Compared to the values calculation by the traditional Judd–Ofelt theory, better results have been achieved using the new method.

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