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Assignment of $4f \rightarrow 5d$ excitation spectra of Nd^{3+} in crystals using the simple model

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Abstract

The measured low-temperature $(4f)^3 \rightarrow (4f)^2 5d$ excitation spectra of Nd^{3+} doped in crystals YPO_4, CaF_4 and $LiYF_4$ [van Pieterson et al., Phys. Rev. B **65** (2002) 045113] are assigned and analyzed using the simple model proposed by Duan et al. [Phys. Rev. B **66** (2002) 155108] and Ning et al. [J. Alloy. Compd. 366 (2004) 34]. The agreement between theoretical and observed energies and intensities are acceptable, and at the same time the spectra are assigned in more detail.
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1. Introduction

Recently, due to the need for new ultraviolet (uv) and vacuum-ultraviolet (vuv) phosphors, scintilator materials, and lasers, etc., and with the accessibility of uv and vuv regions by synchrotron radiation, there have been increased interest and efforts in the study of the high-energy $(4f)^n \leftrightarrow (4f)^{n-1}5d$, i.e., $4f \leftrightarrow 5d$, absorption and emission of rare-earth ions [1–6]. Optical spectra due to 4*f*–5*d* transitions are quite different from those due to 4*f*–4*f* transitions: it is well known that 4*f*–4*f* transitions consist of many zero-phonon lines since 4*f* orbitals are very localized and interact only weakly with the lattice, but 5*d* orbitals are much more extended and interact more strongly with the lattice than 4*f* orbitals and hence $4f \leftrightarrow 5d$ transitions consist of both zero-phonon lines and broad vibronic bands which vary dramatically with the host lattice, and are difficult to analyze.

There has been a theoretical scheme to calculate the $4f \leftrightarrow 5d$ transition [5,6]. However, it needs values of as many as 30 parameters for energy calculation. Furthermore, since the energy eigenstates are expanded with the basis $|(4f)^{N-1}\eta_f S_f L_f, 5ds_d d, SLJM\rangle$, the mixing of quantum numbers $\eta_f S_f L_f$ and SLJ (in addition to M) are, in general, quite strong, making it very difficult to interpret the $4f^{N-1}5d$ energy eigenstates and the $4f \leftrightarrow 5d$ transition peaks.

In the past 2 years, Duan and co-workers [7,8] developed a simple model to give a concise label of energy eigenstates of $4f^{N-1}5d$ and a clear interpretation of $4f \leftrightarrow 5d$ transitions by including only the main interactions in the $4f^{N-1}5d$ configuration. The model uses 2–3 parameters to estimate the energies of pure electronic transitions between these eigenstates (hereafter referred to as zero-phonon lines), and gives selection rules for $4f \rightarrow 5d$ transitions and relative line strengths between some transitions based on some quantum numbers of the initial and final states. The model was successfully applied to excitation spectra of Eu^{2+} and Sm^{3+}. In 2004, Ning et al. [9] extended the

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above model by giving an explicit expression for the $4f$–$5d$ transition line strength, so that the relative line strengths can be evaluated for $4f \leftrightarrow 5d$ transitions with the initial or/and final states differ by any quantum numbers. The extended model was successfully applied to give a semi-quantitative explanation of $5d \rightarrow 4f$ emission spectrum of Nd^{3+}:YPO_4.

In this paper, we use the extended version of the simple model [9] to understand the structure of the $(4f)^3 \rightarrow (4f)^2 5d$ low-temperature excitation spectra [5] of Nd^{3+} doped in CaF_2, LiYF_4 and YPO_4 crystals recorded by monitoring the $(4f)^2 5d^1 \rightarrow (4f)^3\,{}^4I_J$ emission. We focus on the assignment of bands of $4f$–$5d$ transitions based on the position of main zero phonon lines and the total line strengths of these transitions, which is temperature independent under the Condon approximation. For the sake of simplicity and ease of application of the method to exploring related materials, we do not focus on the shape and fine structure of each band.

2. Assignment of the $4f \rightarrow 5d$ excitation spectra

2.1. The eigenvalues of states $|[(4f^{N-1}\eta_f S_f L_f, s_d)SL_f]J;\Gamma_d\rangle$

For Nd^{3+}, $N=3$, and the low-energy terms of $(4f)^2$ are $\eta_f S_f L_f = {}^3H$ and ${}^3F$. So the spin allowed $4f \rightarrow 5d$ excitations from the ground multiplet $(4f)^3\,{}^4I_{9/2}$ can reach ${}^4H_J\Gamma_d$ ($J = 7/2,\ 9/2,\ 11/2,\ 13/2$) and ${}^4F_J\Gamma_d$ ($J = 3/2,\ 5/2,\ 7/2,\ 9/2$) multiplets.

As is presented in Eq. (7) of Ref. [9], the energy of $(4f)^2 5d$ multiplets are:

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

where the second term on the right-hand side gives the splitting between high-spin $S_h = S_f + 1/2$ and low-spin $S_l = S_f - 1/2$ terms, which is irrelevant to the observed splitting here, and the third term gives the spin–orbital splitting caused by $H_{\mathrm{so}}(f)$, i.e., make the energies J-dependent for ${}^4H_J\Gamma_d$ and ${}^4F_J\Gamma_d$.

As shown in Ref. [9], we have $\lambda_{\eta_f S_f L_f, S} = [2 - (2S+1)/(2S_f+1)]\lambda_{\eta_f S_f L_f}$, where $\lambda_{\eta_f S_f L_f} = \xi_{4f}/2S_f$. So $\lambda_{{}^3H,3/2} = (2-4/3)(\xi_{4f}/2) = \xi_{4f}/3 = \lambda_{{}^3F,2/3}$. Table II of Ref. [5] lists the values for ξ_{4f} for Nd^{3+} ions, i.e., $878\,\mathrm{cm}^{-1}$ in YPO_4, and $885.3\,\mathrm{cm}^{-1}$ in CaF_2 and LiYF_4. Here we use a single value $\xi_{4f} = 882\,\mathrm{cm}^{-1}$ for all the three hosts to simplify the analysis. We get the values of the third term of (1) for ${}^4H_J\Gamma_d$ as follows: $-2646\,\mathrm{cm}^{-1}$, $-1323\,\mathrm{cm}^{-1}$, $+294\,\mathrm{cm}^{-1}$, $+2205\,\mathrm{cm}^{-1}$ for $J = 7/2,\ 9/2,\ 11/2,\ 13/2$, respectively, i.e., the energies of $J = 9/2,\ 11/2.\ 13/2$ are separated from that of $J = 7/2$ by $1323\,\mathrm{cm}^{-1}$, $2940\,\mathrm{cm}^{-1}$ and $4851\,\mathrm{cm}^{-1}$, respectively. In the same way, we calculated the energies and splittings for ${}^4F_J\Gamma_d$ multiplets.

2.2. Relative line strengths of the $4f \rightarrow 5d$ transitions

To calculate the line strength of $4f \rightarrow 5d$ electric dipole transitions, we use the following formula originally given in Ref. [9]:

$$\begin{aligned} I(4f^N\eta' S' L' J' &\leftrightarrow [(4f^{N-1}\eta_f S_f L_f, s_d)SL_f]J;\Gamma_d) \\ &= \delta_{SS'}\frac{N[\Gamma_d]}{35}[(2J'+1)(2J+1)(2L'+1)]\cdot|\langle f|r|d\rangle|^2 \\ &\quad \times \begin{Bmatrix} L' & L_f & 3 \\ J & J' & S \end{Bmatrix}^2 \cdot |\langle 4f^N\eta' S' L'\{|4f^{N-1}\eta_f S_f L_f\rangle|^2. \end{aligned} \tag{2}$$

For the transitions studied here, the values of N, S', L', J', $\langle f|r|d\rangle$ are all fixed, and $[\Gamma_d] = [\Gamma_{d1}]$, the degeneracy of the lowest $5d$ crystal-field single electron level, is also fixed. Therefore, we may write the relative line strength as

$$\begin{aligned} I' &= (2J+1)\cdot\begin{Bmatrix} L' & L_f & 3 \\ J & J' & S \end{Bmatrix}^2 \\ &\quad \times|\langle 4f^N\eta' S' L'\{|4f^{N-1}\eta_f S_f L_f\rangle|^2. \end{aligned} \tag{3}$$

For the transitions to ${}^4H_J\Gamma_d$, we have $\eta_f S_f L_f = {}^3H$, and since $|\langle 4f^3\,{}^4I\{|4f^2\,{}^3H\rangle|^2 = 7/9$, we obtain $I' = 0.04200$, 0.01615, 0.00164, 0.00004 for $J = 7/2,\ 9/2,\ 11/2,\ 13/2$, respectively; for transitions to ${}^4F_J\Gamma_d$, $\eta_f S_f L_f = {}^3F$, since $|\langle 4f^3\,{}^4I\{|4f^2\,{}^3F\rangle|^2 = 2/9$, we have $I' = 0.01270$, 0.00390, 0.00048, 0.00002, for $J = 3/2,\ 5/2,\ 7/2$, and $9/2$, respectively.

2.3. Assignment of the excitation spectrum of Nd^{3+}:YPO_4

The energies of zero-phonon lines and relative line strengths obtained above using the simple model are given together with the reported excitation spectrum [5] of Nd^{3+} doped in YPO_4 in Fig. 1. The measured separation between A_1 and A_2 is $3200\,\mathrm{cm}^{-1}$, which is comparable with the calculated separation $2940\,\mathrm{cm}^{-1}$ between ${}^4H_{7/2}\Gamma_{d1}$ and ${}^4H_{11/2}\Gamma_{d1}$. This establishes the assignment of A_1 to ${}^4H_{7/2}\Gamma_{d1}$ and A_2 to ${}^4H_{11/2}\Gamma_{d1}$. Then ${}^4H_{9/2}\Gamma_{d1}$ can be assigned to a strong peak between A_1 and A_2, say, A' at 182.9 nm. Additionally, by referring to the calculated relative line strength I', we assign the observed strong peak A_3 to ${}^4F_{3/2}\Gamma_{d1}$, whose third term in Eq. (1) is $-1674\,\mathrm{cm}^{-1}$, $882\,\mathrm{cm}^{-1}$ larger than that for ${}^4H_{7/2}\Gamma_{d1}$. Since the second term of Eq. (1) is the same for ${}^4F_{3/2}\Gamma_{d1}$ and ${}^4H_{7/2}\Gamma_{d1}$, the energy difference,

$\Delta E_0 = E_0(4f^2\,{}^3F;\ \Gamma_{d1}) - E_0(4f^2\,{}^3H;\ \Gamma_{d1})$, is approximately $5700–882\,\text{cm}^{-1} = 4818\,\text{cm}^{-1}$ by using $E(A_3) - E(A_1) = 5700\,\text{cm}^{-1}$. By referring to the Dieke diagram, we have $E(4f^2\,{}^3F_2) - E(4f^2\,{}^3H_4) = 4880\,\text{cm}^{-1}$ for ion Pr^{3+} doped in LaCl_3, which is close to $4818\,\text{cm}^{-1}$. Therefore, it is reasonable to assign the peak A_3 to ${}^4F_{3/2}\Gamma_{d1}$. Finally, the energy of ${}^4F_{5/2}\Gamma_{d1}$ is expected to be $(\xi_{4f}/6)[(-7)-(-12)] = 735\,\text{cm}^{-1}$ higher than the energy of A_3, which probably corresponds to peak A'_3 at 166.9 nm. As mentioned in Ref. [5], the bands B and C are transitions to ${}^4H_J\Gamma_{d2}$ and ${}^4H_J\Gamma_{d3}$, etc., which lose fine structure due to ionization to the conduction band of the host. The assignments and calculated results are summarized in Table 1.

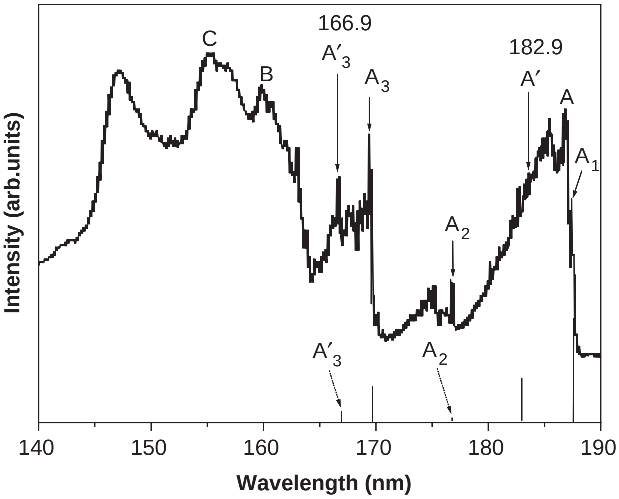

Fig. 1. Zero-phonon lines (shown with vertical lines) and relative line strengths (in proportional to their height) calculated with the simple model and measured excitation spectrum [5] of Nd^{3+} doped in YPO_4.

2.4. *The excitation spectra of* Nd^{3+} *doped in* LiYF_4 *and* CaF_2

The zero-phonon lines and relative line strengths for $\text{LiYF}_4:\text{Nd}^{3+}$ are calculated with the simple model and plotted in Fig. 2 together with the experimental spectrum given in Ref. [5]. The experimental spectrum for $\text{LiYF}_4:\text{Nd}^{3+}$ has the same properties as the spectrum for $\text{YPO}_4:\text{Nd}^{3+}$. However, the peaks corresponding to transitions ${}^4H_{9/2}\Gamma_{d1}$, and ${}^4H_{11/2}\Gamma_{d1}$ were not marked or assigned originally, which we assign as A'_1 at 173.2 nm and A''_1 at 168.2 nm, respectively, while the peak marked to be A_2 corresponds to ${}^4F_{3/2}\Gamma_{d1}$, which is $6000\,\text{cm}^{-1}$ (compared to $5700\,\text{cm}^{-1}$ in YPO_4) higher than ${}^4H_{7/2}\Gamma_{d1}$.

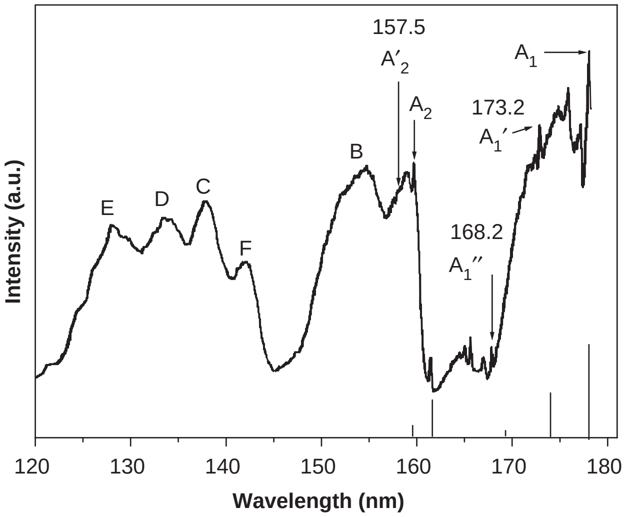

Fig. 2. Calculated zero-phonon lines (shown with vertical lines) and relative line strengths (in proportional to their height) calculated with the simple model and measured excitation spectrum [5] of Nd^{3+} doped in LiYF_4.

Table 1
Assignments of the 4*f*–5*d* excitation spectrum of YPO_4 doped with 1% Nd^{3+} recorded at 6 K by monitoring the $4f^25d^1 \rightarrow {}^4I_J$ emission at 197 nm

Final state	Energy of Z.P.L.			Relative line strength	
	Calc.		Obs.	Calc.	Obs.
	(cm^{-1})	(nm)	(nm)	(arb. unit)	
${}^4H_{7/2}\Gamma_{d1}$	53 248	187.8	187.8(A_1)	4200	Strongest
${}^4H_{9/2}\Gamma_{d1}$	54 571	183.3	182.9[A']	1615	Strong
${}^4H_{11/2}\Gamma_{d1}$	56 188	178.0	177.2(A_2)	164	Very weak
${}^4H_{13/2}\Gamma_{d1}$	58 099	172.1	Not obs.	4	Not obs.
${}^4F_{3/2}\Gamma_{d1}$	58 948	169.6	169.7(A_3)	1270	Strong
${}^4F_{5/2}\Gamma_{d1}$	59 683	167.6	167.9[A'_3]	390	Medium
${}^4F_{7/2}\Gamma_{d1}$	60 712	164.7		48	
${}^4F_{9/2}\Gamma_{d1}$	62 035	161.2	Buried	2	Buried

Notes: Parameter values used are $E_0[4f^2\,{}^3H_2;\Gamma_{d1}] = 57800\,\text{cm}^{-1}$, $J_{\text{ex}} = 3812\,\text{cm}^{-1}$, $E_0[4f^2\,{}^3F_2;\Gamma_{d1}] = 62618\,\text{cm}^{-1}$, and $\lambda_{{}^3H3/2} = \lambda_{{}^3F3/2} = \xi_{4f}/3 = 294\,\text{cm}^{-1}$; Z.P.L. means zero-phonon line; Calc. means calculated result, and Obs. means observed result. [A'] and [A'_3] are labelled and assigned by this work.

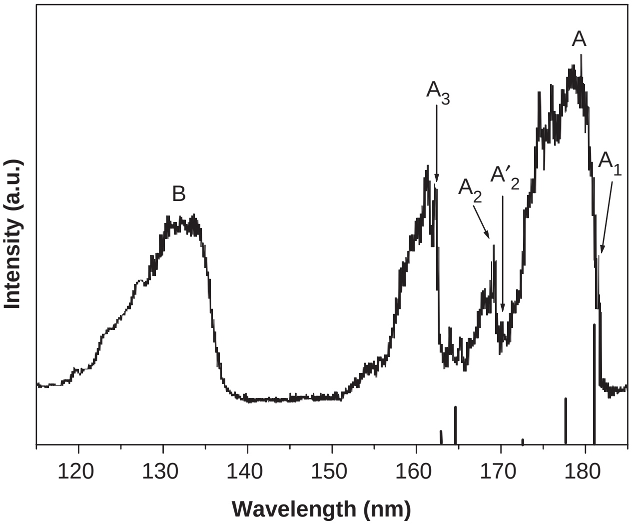

Fig. 3. Calculated zero-phonon lines (shown with vertical lines) and relative line strengths (in proportional to their height) calculated with the simple model and measured excitation spectrum [5] of Nd^{3+} doped in CaF_2.

Thus the shoulder A_2' at 157.5 nm can be the transition to $^4F_{5/2}\Gamma_{d1}$. Noticeably, the unexplained peak F can now be assigned to $^4F_{3/2}\Gamma_{d2}$, since the peak B was considered to be of $4f \to 5d$ transition to the second $5d$ crystal-field level, i.e., $^4H_{7/2}\Gamma_{d2}$ according to the simple model and the distance F-B is $6000\,\mathrm{cm}^{-1}$.

The calculated zero-phonon lines and relative line strengths for CaF_2:Nd^{3+} are plotted in Fig. 3 together with the experimental spectrum given in Ref. [5]. The experimental spectrum has also the same property as that for YPO_4:Nd^{3+}, except that there is roughly only two bands corresponding to two crystal-field levels of $5d$ electron of Nd^{3+} at cubic lattice site. Besides, the distance $A_2 - A_1$ is $4100\,\mathrm{cm}^{-1}$, instead of $3200\,\mathrm{cm}^{-1}$ in YPO_4, which is likely due to stronger spin–orbital effects of the f-electrons. Also, the value $4100\,\mathrm{cm}^{-1}$ is probably overestimated, since if the zero-phonon line A_2' on the right side of the peak A_2 were used to calculate the distance $A_2 - A_1$, the value is reduced to be about $3600\,\mathrm{cm}^{-1}$. The distance $A_3 - A_1$ is $6500\,\mathrm{cm}^{-1}$ instead of $5700\,\mathrm{cm}^{-1}$ in YPO_4, which is likely due to stronger $4f$–$4f$ interaction, i.e., bigger ΔE_0 in CaF_2 than in YPO_4. In the theoretical calculation of Ref. [5], Variations of the strength of these interactions with hosts were ignored.

Taking the values of $G^i(fd)$ with $i = 1, 3, 5$ from the Table II of Ref. [5], and using the Eq. (3) of Ref. [9], we obtain $J_{\mathrm{ex}} = 3815\,\mathrm{cm}^{-1}$ for the three hosts. By referring to the observed energies of zero-phonon line A_1 in them, we have the following values of E_0:

$$E_0[4f^2\,{}^3H_2; \Gamma_{d1}] = 57800,\ 59603,\ \text{and}\ 60732\,\mathrm{cm}^{-1};$$

$$E_0[4f^2\,{}^3F_2; \Gamma_{d1}] = 62618,\ 65221, \text{and}\ 65850\,\mathrm{cm}^{-1}$$

for the hosts YPO_4, CaF_2, and $LiYF_4$, respectively.

3. Conclusion

The simple model was originally proposed under the expection that it should work at least for $4f - 5d$ transitions of doped rare-earth ions with near half-filled $4f$ shell. It was originally applied to Sm^{3+} and Eu^{2+} ions [8] and recently to Eu^{3+} and Tb^{3+} [10], where the $4f$ shell is nearly half-filled. Here we have applied it to the Nd^{3+}, with only two $4f$ electrons for the excited configuration. The zero-phonon lines and relative line strengths of $4f - 5d$ excitation transition of Nd^{3+} doped in YPO_4, $LiYF_4$ and CaF_2 have been calculated using the simple model [9] and compared to available experimental data. It can be seen that the simple model works well for the $4f - 5d$ excitation spectra of Nd^{3+} doped in all the three hosts and is very useful in assigning and understanding the peaks in those spectra. This result, together with previous results [8,10], shows that the model can be applied to excited configurations with any rare-earth ions with $N - 1$ from 2 to 7 where experimental results are available. For rare-earth ions with $N - 1$ from 8 to 13, our recent unpublished results show that the model need revision to take into account the effect of weaker exchange interaction than $4f$ spin–orbit interaction, and will be presented elsewhere.

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