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Crystal-field analysis of the energy levels and spectroscopic characteristics of Nd^{3+} in YVO_4

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Abstract. Based on the method previously proposed by the authors, the crystal-field analysis and investigation of the polarization and relative intensities of transitions between the sublevels ${}^4\text{F}_{3/2}$ to ${}^4\text{I}_{13/2}$, ${}^4\text{I}_{11/2}$ and ${}^4\text{I}_{9/2}$ in $\text{Nd}^{3+}:\text{YVO}_4$ crystals have been performed, in which the Nd^{3+} ions occupy positions with point symmetry D_{2d} . The predicted polarization characteristics of all the emission lines under discussion are in complete agreement with those observed in experiments by other authors, and the emission lines with highest or comparatively high calculated intensities correspond to the laser emission lines that have been realized. In these calculations, the effect of seventh-order odd crystal field on the emission intensities was first omitted and then estimated by the method suggested by Judd in 1962. It turned out that this effect should be taken into account explicitly and cannot be completely made up only by multiplying a factor suggested by Judd. However, the simple method introduced can be seen as useful in the study of new laser crystals.

1. Introduction

As a solid-state laser material, triply ionized neodymium-doped yttrium orthovanadate ($\text{Nd}^{3+}:\text{YVO}_4$) has many good performances superior to those of standard $\text{Nd}^{3+}:\text{YAG}$ (Nd^{3+} -doped yttrium–aluminium–garnet) [1–6]. It is said that $\text{Nd}^{3+}:\text{YVO}_4$ is suitable to be used as an efficient solar pumped laser material [7]. Nowadays, this crystal has become an ideal material for laser diode (LD) pumped solid-state lasers. It has tetragonal symmetry (space group D_{4h}^{19}) with the Y^{3+} site symmetry D_{2d} [8, 9], which is responsible for the polarized transitions of Nd^{3+} and the plane-polarized laser output useful in many applications.

The spectroscopic properties and crystal-field (CF) energy levels for $\text{Nd}^{3+}:\text{YVO}_4$ have been studied by many authors [10–16]. It is very interesting to note that this crystal has an especially large emission cross section many times that of $\text{Nd}^{3+}:\text{YAG}$. Nevertheless, except for a qualitative discussion presented by Yaney *et al* in 1976 [11], no further investigation has been presented in the literature. To correlate these special spectroscopic properties with the microstructure of the crystal, it is important to make a quantitative theoretical study on the phenomenon mentioned.

In previous work [17, 18], the ratios of CF parameters for the same rank of k , i.e. C_{μ}^k/C_0^k , calculated by a simple point-charge model were used as constraints in the CF parameter calculations and the Stark sublevel fitting.

This method as well as conventional crystal-field theory will be used in this paper to analyse the same problems for $\text{Nd}^{3+}:\text{YVO}_4$. The relative transition intensities between Stark sublevels in the same pair of J manifolds together with polarization states of these

transitions will be calculated. A comparison with the experimental polarized absorption and fluorescence spectra obtained by Yaney *et al* [11] and Karayianis *et al* [12] will be made.

2. Crystal-field analysis

Consider the group chain $O_3 \supset O_h \supset T_d \supset D_{2d}$; the detailed CF Hamiltonian can be expressed in Butler's notation

$$H_{cf} = C_{22}^2 b_{22}^2 + C_{0-0}^3 b_{0-0}^3 C_{00}^4 b_{00}^4 + C_{22}^4 b_{22}^4 + C_{2-2}^5 b_{2-2}^5 + C_{00}^6 b_{00}^6 + C_{22}^6 b_{22}^6 + C_{0-0}^7 b_{0-0}^7 + C_{2-2}^7 b_{2-2}^7. \quad (1)$$

Here $b_{\mu\nu}^k$ are the basis functions of the group chain $O_3 \supset O_h \supset T_d \supset D_{2d}$ and are identical to $|k\mu\nu 0\rangle$ in [19]; and $C_{\mu\nu}^k$ are the expansion coefficients of H_{cf} by these bases. Because all the basis functions belong to the 0 representation of D_{2d} in the calculations concerned, the index 0 for D_{2d} group has been omitted in equation (1). The k -even CF components result in the experimentally observed Stark splitting of rare-earth spectra, while the k -odd CF components, via configuration admixing, bring about the electric dipole transition within the $4f^n$ configuration according to the Judd-Ofelt (JO) theory.

The ratios of the CF parameters with the same rank k

$$r_0 = C_{22}^4 / C_{00}^4 \quad r_1 = C_{22}^6 / C_{00}^6 \quad (2)$$

are calculated by the simple point-charge model. Taking into account the structure distortion when the Nd^{3+} ions occupy some of the Y^{3+} sites, r_i ($i = 0, 1$) are calculated from the structure constants of YVO_4 [8] and $NdVO_4$ [9] respectively. Only eight O^{2-} ions nearest to the Nd^{3+} or Y^{3+} are considered in the calculation, as shown in figure 1 of [9]. The results are listed in table 1.

Table 1. The parameters r_i ($i = 0, 1$) in YVO_4 and $NdVO_4$ crystals.

Crystal	r_0	r_1
YVO_4	-1.8854	-1.8337
$NdVO_4$	-1.9561	-2.1742
Cal. $Nd^{3+}:YVO_4$	-2.0738	-1.6869

On the basis of the group-subgroup chain $O_3 \supset O_h \supset T_d \supset D_{2d}$, some of the wavefunctions of the $4f^3$ configuration in Nd^{3+} at the D_{2d} symmetry position are expressed as linear combinations of the bases $|^{2S+1}L_J \mu \nu \xi\rangle$ in Butler's group-chain scheme, and are listed in appendix 1, where μ , ν and ξ are the irreducible representations of O_h , T_d and D_{2d} respectively.

The matrix elements of the CF Hamiltonian in the group-chain scheme can be calculated by means of the Wigner-Eckart theorem and the factorization lemma of the $3jm$ factors. The Stark energy sublevels of ${}^4F_{3/2}$, ${}^4I_{13/2}$, ${}^4I_{11/2}$ and ${}^4I_{9/2}$ were assigned by the fluorescence and absorption spectra at 77 K [10]. As usually adopted in this field, the intermediate coupling has been taken into account by using reduced matrix elements $\langle f^n SLJ || U_k || f^n SL'J' \rangle$ in the intermediate-coupling approximation [20]. By using the ratios listed in table 1 as constraints in the fitting, only one minimum was obtained, irrespective of the initial values adopted.

Further work on the fitting is to adjust the ratios to minimize the RMS deviation of the energy levels. In table 1, comparisons of the initial and final ratios are given, and the corresponding k -even CF parameters $C_{\mu\nu}^k$ (cm^{-1}) are

$$C_{22}^2 = 18 \quad C_{00}^4 = -799 \quad C_{22}^4 = 1657 \quad C_{00}^6 = 626 \quad C_{22}^6 = -1056.$$

The experimental and calculated energy levels are compared in table 2. It can be expected that taking into account the two-electron CF interaction, the agreement between experimental energy levels and the calculated eigenvalues can be improved considerably.

Table 2. Comparison of the observed and calculated Stark splitting from the centre of gravity of ${}^4F_{3/2}$, ${}^4I_{13/2}$, ${}^4I_{11/2}$ and ${}^4I_{9/2}$ manifolds of Nd^{3+} in YVO_4 at 77 K.

Multiplet	Observed splitting (cm^{-1})	Calculated splitting (cm^{-1})	Δ (cm^{-1})
${}^4F_{3/2}$	9	1.4	-7.6
	-9	-1.4	7.6
${}^4I_{13/2}$	130.1	122.5	-7.6
	118.1	120.9	2.8
	48.1	36.5	-11.6
	2.1	16.2	14.1
	-59.9	-53.5	6.4
	-108.9	-109.5	-0.6
${}^4I_{11/2}$	-129.9	-133.0	-3.1
	115.5	108.5	-7.0
	87.5	78.6	-8.9
	-4.5	1.6	6.1
	-19.5	-15.9	3.6
	-78.5	-64.4	14.1
${}^4I_{9/2}$	-100.5	-108.4	-7.9
	245	244.2	-0.8
	38	24.0	-14.0
	-15	-5.3	9.7
	-80	-55.0	25.0
	-188	-207.9	-19.9
RMS			12.4

Compared with the conventional CF Hamiltonian expressed in [12], the relationship between the CF parameters of the two different schemes will be

$$\begin{aligned}
 B_{20} &= -(2/3)^{1/2} C_{22}^2 \\
 B_{40} &= 2(2/35)^{1/2} [(1/2)(7/3)^{1/2} C_{00}^4 + (1/2)(5/3)^{1/2} C_{22}^4] \\
 B_{44} &= 2(2/35)^{1/2} [(1/2)(5/6)^{1/2} C_{00}^4 - (1/2)(7/6)^{1/2} C_{22}^4] \\
 B_{60} &= 4(1/231)^{1/2} [(-1/2)(1/2)^{1/2} C_{00}^6 + (1/2)(7/2)^{1/2} C_{22}^6] \\
 B_{64} &= 4(1/231)^{1/2} [(1/4)(7)^{1/2} C_{00}^6 + (1/4) C_{22}^6].
 \end{aligned} \tag{3}$$

The CF parameters B_{kq} can be obtained from equation (3) and they are listed in table 3. From this table, we can see that the CF parameters calculated under the ratio constraint condition are quite different from those published before [12]. This difference will be discussed in section 4. The eigenfunctions of the Stark sublevels of ${}^4F_{3/2}$, ${}^4I_{13/2}$, ${}^4I_{11/2}$ and ${}^4I_{9/2}$ manifolds can be calculated and expressed as linear combinations of group-chain basis functions $|\mu\nu\xi\rangle$ simply as those listed in appendix 2. The wavefunctions are normalized and listed in order of decreasing energy. In the case of D_{2d} point group, Butler's notations 1/2 and 3/2 correspond to Γ_6 and Γ_7 of Bethe's notation respectively. Both of them are two-dimensional representations, so that all of the wavefunctions are doubly degenerate, in agreement with Kramers theorem.

Table 3. CF parameters B_{kq} for $Nd^{3+}:\text{YVO}_4$ crystal.

B_{20}	B_{40}	B_{44}	B_{60}	B_{64}	Ref.
-135.7	625.9	1023.9	-1169.5	-251.4	[12]
-14.7	219.6	-602.2	-318.2	39.5	This work

As Γ_6 and Γ_7 correspond to the CF quantum numbers 1/2 and 3/2, it is shown that all of the theoretical results of the irreducible representations for the states concerned are in agreement with those deduced from absorption and fluorescence spectra by Karayianis *et al* [12] and Yaney *et al* [11]. It should be noted that there was a mistake in the corresponding relation between irreducible representations Γ_6 and Γ_7 and CF quantum numbers 1/2 and 3/2 in [12].

3. Study of the polarization and relative emission intensities

Based on the wavefunctions obtained from CF analysis, we tried to calculate the relative intensities quantitatively for the emissions ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$, ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$, and the results will be presented in the following.

JO theory [15, 16] demonstrates that the k -odd CF parameters, via configuration admixing, allow the occurrence of electric dipole transitions within the $4f^n$ configurations. For Nd^{3+} ions in the YVO_4 crystal, as shown in equation (1), the k -odd CF components $C_{0-0}^{3-}b_{0-0}^{3-}$, $C_{2-2}^{5-}b_{2-2}^{5-}$, $C_{0-0}^{7-}b_{0-0}^{7-}$ and $C_{2-2}^{7-}b_{2-2}^{7-}$ make the electric dipole transitions possible. However, as pointed out by Judd [15], the energy gap between $4f^3$ and $4f^25d$ is the smallest of all the energy denominators in the expressions for the electric dipole transition rates [21]. Also, because the degree of overlap between a $4f$ eigenfunction and other orbitals of $n'l$ for $n' \geq 6$ is smaller than those between $4f$ and $5d$, this will result in considerably reduced radial integrals in the related matrix elements. Therefore we can concentrate only on the excited configuration of $4f^25d$, at least in the first-order approximation, and neglect the effects of all others and consider only the actions of components $C_{0-0}^{3-}b_{0-0}^{3-}$ and $C_{2-2}^{5-}b_{2-2}^{5-}$. In view of the consistency of the notations, in the following expressions we will still use Butler's scheme. In the case of D_{2d} point group, based on the group chain of $O_3 \supset O_h \supset T_d \supset D_{2d}$, the electric dipole moment operations are given by

$$P_{\xi\beta} = -e \sum_i (b_{1-\bar{i}\xi\beta}^{1-})_i \quad (4)$$

where ξ and β are irreducible representations of D_{2d} and its projection respectively; and $|\xi\beta\rangle = |22\rangle$ and $|1 \pm 1\rangle$ correspond to π and σ polarization absorption or emission respectively.

If the nI^N configuration is admixed with the $nI^{N-1}I'$ configuration, the electric dipole transition is allowed. To find the probabilities, we rewrote equation (3) of [18] in Butler's scheme. For states $\langle I^H SLJ a_1 a_2 a_3 \alpha |$ and $| I^N SL' J' d_1 d_2 d_3 \gamma \rangle$, where a, d and a_i, d_i ($i = 1, 2, 3$) correspond to the irreducible representations of group chain $O_3 \supset O_h \supset T_d \supset D_{2d}$, and α and γ are projections of a_3 and d_3 respectively, the transition matrix element can be written as

$$\begin{aligned} & \langle I^H SLJ a_1 a_2 a_3 \alpha | P_{\xi\beta} | I^H SL' J' d_1 d_2 d_3 \gamma \rangle \\ &= -\frac{2e}{E_{av}} \sum_{k,c_1,c_2} C_{c_1 c_2}^k \sum_{\lambda,s,s_1,s_2,s_3} (-1)^{k-\lambda-1} (2\lambda+1) \begin{pmatrix} \lambda \\ e_1 \end{pmatrix} \begin{pmatrix} e_1 \\ e_2 \end{pmatrix} \begin{pmatrix} e_2 \\ e_3 \end{pmatrix} \begin{pmatrix} e_3 \\ \mu \end{pmatrix} \\ & \times \begin{pmatrix} 1^- & k & \lambda^* \\ 1^- & c_1 & e_1^* \end{pmatrix}_{s_1} \begin{pmatrix} 1^- & c_1 & e_1^* \\ \bar{1} & c_2 & e_2^* \end{pmatrix}_{s_2} \begin{pmatrix} \bar{1} & c_2 & e_2^* \\ b_3 & 0 & e_3^* \end{pmatrix}_{s_3} \begin{pmatrix} b_3 & 0 & e_3^* \\ \beta & 0 & \mu^* \end{pmatrix}_{s_3} \\ & \times (-1)^{\lambda+I'+I} (2I+1)(2I'+1) \begin{Bmatrix} 1 & k & \lambda \\ I & I & I' \end{Bmatrix} \langle I \| C^{(1)} \| I' \rangle \langle I' \| C^{(k)} \| I \rangle \\ & \times \begin{pmatrix} a \\ a_1 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \begin{pmatrix} a_2 \\ a_3 \end{pmatrix} \begin{pmatrix} a_3 \\ \alpha \end{pmatrix} \sum_{r,r_1,r_2,r_3} \begin{pmatrix} a^* & \lambda & d \\ a_1^* & e_1 & d_1 \end{pmatrix}_{r_1} \begin{pmatrix} a_1^* & e_1 & d_1 \\ a_2^* & e_2 & d_2 \end{pmatrix}_{r_2} \\ & \times \begin{pmatrix} a_2^* & e_2 & d_2 \\ a_3^* & e_3 & d_3 \end{pmatrix}_{r_3} \begin{pmatrix} a_3^* & e_3 & d_3 \\ \alpha^* & \mu & \gamma \end{pmatrix}_{r_3} \langle I^N SLJ \| U^{(\lambda)} \| I^N SL' J' \rangle. \quad (5) \end{aligned}$$

Here C_{c_1,c_2}^k are the k -odd CF parameters; E_{av} is the energy separation between the initial (or final) states and the intermediate states belonging to the configuration with different parity; λ, e_1, e_2 and e_3 are the coupling irreducible representations between the electric dipole moments and the k -odd CF Hamiltonians corresponding to the group chain $O_3 \supset O_h \supset T_d \supset D_{2d}$; μ is the projection of e_3 ; and all the other symbols represent the same physical quantities as in [17]. All of the $3jm$ and $2jm$ factors can be found from [19] and [22]. The states of the Stark sublevel have been expressed as

$$\sum_{a_1,a_2,a_3} A_{a_1 a_2 a_3} |^{2S+1} L_J a_1 a_2 a_3 \rangle$$

and so the transition matrix element between two of these states $\langle A |$ and

$$| B \rangle = \sum_{b_1,b_2,b_3} B_{b_1 b_2 b_3} |^{2S+1} L'_J b_1 b_2 b_3 \rangle$$

can be written as

$$\langle A | P_{\xi\beta} | B \rangle = \sum_{\substack{a_1,a_2,a_3 \\ b_1,b_2,b_3}} A_{a_1 a_2 a_3} B_{b_1 b_2 b_3} \langle ^{2S+1} L_J a_1 a_2 a_3 | P_{\xi\beta} | ^{2S+1} L'_J b_1 b_2 b_3 \rangle. \quad (6)$$

In the cases discussed, the energy separations between the initial and final states inside the $4f^3$ configuration are much smaller than those between configurations $4f^3$ and $4f^2 5d$. Therefore, in the calculation, E_{av} is referred to as the average energy separation of these two configurations.

First, the k -odd CF parameters must be evaluated. The non-zero $6j$ symbols in which λ is a component require that $\lambda \leq 2l$ and so $\lambda = 2, 4, 6$ for the configuration f^N . Considering the intermediate-coupling approximation, the irreducible matrix elements appearing in equation (5) can be written as [23]

$$\begin{aligned} \langle 4f^3 \ ^4F_{3/2} \| U^{(4)} \| 4f^3 \ ^4I_{9/2} \rangle &= 0.4779 \\ \langle 4f^3 \ ^4F_{3/2} \| U^{(6)} \| 4f^3 \ ^4I_{9/2} \rangle &= 0.2316 \\ \langle 4f^3 \ ^4F_{3/2} \| U^{(4)} \| 4f^3 \ ^4I_{11/2} \rangle &= 0.3769 \\ \langle 4f^3 \ ^4F_{3/2} \| U^{(6)} \| 4f^3 \ ^4I_{11/2} \rangle &= 0.6416 \\ \langle 4f^3 \ ^4F_{3/2} \| U^{(6)} \| 4f^3 \ ^4I_{13/2} \rangle &= 0.4601. \end{aligned}$$

To calculate the intensities for the transitions from the sublevels of the $^4F_{3/2}$ manifold to those of the $^3I_{13/2}$, $^4I_{11/2}$ and $^4I_{9/2}$ manifolds, the ratio of the particle distribution in the upper Stark sublevel to that in the lower sublevel of $^4F_{3/2}$ should be considered. If ΔE is the energy separation of the two $^4F_{3/2}$ sublevels, then this factor is, by the Boltzmann distribution, $\exp(-\Delta E/kT)$, where k is Boltzmann's constant. Hence, the intensities for the emissions between sublevels $^4F_{3/2}$ and $^4I_{13/2}$, between $^4F_{3/2}$ and $^4I_{11/2}$ and between $^4F_{3/2}$ and $^4I_{9/2}$ were evaluated. To this end, the following equation for the transition intensities of spontaneous radiation was used:

$$A(\alpha J, \alpha' J') = [64\pi^4 f^3 e^2 / 3h(2J + 1)][n(n^2 + 2)^2 / 9] S_{JJ'}. \quad (7)$$

In this equation,

$$S_{JJ'} = (1/e^2) \sum_{i,f} \langle \psi_{Ji} | P_{\xi\beta} | \psi_{J'f} \rangle$$

where f is the wavenumber corresponding to the transition, n is the effective refractive index at this wavelength, and ψ_{Ji} and $\psi_{J'f}$ are the states of the sublevels in the initial and final terms respectively. As pointed out in [7], since we have refractive indices that are operative separately for light of π and σ polarization, we have to calculate an effective-index factor for $n(n^2 + 2)^2 / 9$. That is,

$$N = (N_\pi + 2N_\sigma) / 3 \quad (8)$$

where

$$N_{\sigma,\pi} = n_{\sigma,\pi} (n_{\sigma,\pi}^2 + 2)^2 / 9.$$

Therefore equation (7) is rewritten as

$$A(\alpha J, \alpha' J') = [64\pi^4 f^3 e^2 / 3h(2J + 1)] N S_{JJ'}. \quad (9)$$

If the fluorescence ratio β is expressed as

$$\beta(\alpha J, \alpha' J') = A(\alpha J, \alpha' J') / \sum_{\alpha', J'} A(\alpha J, \alpha' J') \quad (10)$$

Table 4. Spectroscopic experimental results for the Nd³⁺:YVO₄ crystal.

Transition	f (cm ⁻¹)	n_{π}	n_{σ}	N	β
⁴ F _{3/2} → ⁴ I _{13/2}	7.41 × 10 ³	2.15811	1.95139	8.41846	0.110
⁴ F _{3/2} → ⁴ I _{11/2}	9.39 × 10 ³	2.16741	1.95797	8.53678	0.467
⁴ F _{3/2} → ⁴ I _{9/2}	11.3 × 10 ³	2.17866	1.96592	8.68166	0.420

Table 5. Calculated relative values of the transition intensity for ⁴F_{3/2} → ⁴I_{13/2} sublevels in the Nd³⁺:YVO₄ crystal at 77 K.

Transition	f (cm ⁻¹)	$A_{ij} = A'_{ij}$	
		σ	π
⁴ F _{3/2} → ⁴ I _{13/2}			
b → a	7474	0.00977	0
a → a ^a	7456	0.12618	0.00001
b → b	7453	0.03451	0.04856
a → b	7435	0.11545	0
b → c	7404	0.04724	0.03300
a → c	7386	0.10493	0
b → d	7342	0.00004	0.00184
a → d	7324	0.00140	0
b → e	7296	0.00015	0
a → e	7278	0.16970	0.07063
b → f	7226	0.09205	0.03753
a → f	7208	0.00040	0
b → g	7214	0.03259	0
a → g	7196	0.00037	0.07364

^a The transition which has been realized as a laser emission.

then using the experimental data in [7], which are listed in table 4 of this paper, the following relationships can be established:

$$C_{0-0}^{3-} = 2.2136A^{1/2} \quad C_{2-2}^{5-} = 2.2748A^{1/2}$$

where A is a factor proportional to the total transition intensities $\sum_{\alpha, J'} A(\alpha J, \alpha' J')$. From equation (6), the relative intensities and polarizations of radiative transitions between sublevels of ⁴F_{3/2} and those of ⁴I_{13/2}, ⁴F_{3/2} and ⁴I_{11/2} as well as ⁴F_{3/2} and ⁴I_{9/2} can be estimated, and the results are listed in tables 5–7.

Considering the effects of the type 4f^{N-1}n'g configurations, by the means proposed by Judd [15], the modified transition matrix elements can be obtained from the original one by multiplying by a factor of

$$M(k, \lambda) = 1 + \frac{(k+7)!(6-k)!}{(\lambda+7)!(6-\lambda)!} \frac{\langle 4f|r^{k+1}|4f \rangle}{\langle 4f|r^k|5d \rangle} \frac{\Delta(5d)}{\Delta(n'g)} \quad (11)$$

For Nd³⁺ ions, we can find the following data from [15]: $\langle 4f|r^4|4f \rangle = 4.96$, $\langle 4f|r^6|4f \rangle = 36.4$, $\langle 4f|r|5d \rangle = 0.869$, $\langle 4f|r^3|5d \rangle = 5.17$, $\langle 4f|r^5|5d \rangle = 47.1$, and $\Delta(5d) = 58\,000$ cm⁻¹, $\Delta(n'g) = 167\,000$ cm⁻¹; so that $M(k, \lambda)$ was estimated as $M(3, 4) = 1.105$, $M(5, 4) = 2.853$ and $M(5, 6) = 1.024$. Repeating the calculations, we finally obtained

$$C_{0-0}^{3-'} = 1.9833A^{1/2} \quad C_{2-2}^{5-'} = 2.1466A^{1/2}$$

Table 6. Calculated relative values of the transition intensity for ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ sublevels in the $\text{Nd}^{3+}:\text{YVO}_4$ crystal at 77 K.

Transition ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$	f (cm^{-1})	A_{ij}		A'_{ij}	
		σ	π	σ	π
b \rightarrow a	9418	0.09435	0	0.08480	0
a \rightarrow a	9400	0.00566	0.00037	0.00339	0.00017
b \rightarrow b	9396	0.03747	0.19119	0.02197	0.22914
a \rightarrow b	9378	0.16805	0	0.17840	0
b \rightarrow c	9337	0.07245	0	0.05921	0
a \rightarrow c	9319	0.01985	0.01884	0.01681	0.01052
b \rightarrow d	9322	0.00157	0.02363	0.00092	0.02747
a \rightarrow d	9304	0.00859	0	0.01005	0
b \rightarrow e	9230	0.18640	0	0.18155	0
a \rightarrow e	9212	0.01372	0.02071	0.01499	0.03220
b \rightarrow f	9202	0.01110	0.10463	0.00651	0.11000
a \rightarrow f	9184	0.02144	0	0.01190	0

Table 7. Calculated relative values of the transition intensity for ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ sublevels in the $\text{Nd}^{3+}:\text{YVO}_4$ crystal at 77 K.

Transition ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$	f (cm^{-1})	A_{ij}		A'_{ij}	
		σ	π	σ	π
b \rightarrow a	9418	0.05454	0	0.02982	0
a \rightarrow a	9400	0.03543	0.01403	0.01140	0.04253
b \rightarrow b	9396	0.06913	0	0.04114	0
a \rightarrow b	9378	0.00930	0.04070	0.00103	0.07604
b \rightarrow c	9337	0.18428	0.20694	0.15487	0.24386
a \rightarrow c	9319	0.01006	0	0.00071	0
b \rightarrow d	9322	0.00314	0	0.00166	0
a \rightarrow d	9304	0.10535	0.00213	0.09641	0.01968
b \rightarrow e	9230	0.18257	0.08077	0.16090	0.11887
a \rightarrow e	9212	0.00163	0	0.00108	0

All of the results are also listed in tables 5–7 and denoted as A'_{ij} . The modifications do not change the calculated relative intensities of the ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ emissions, because these emission intensities only depend on the odd CF parameters with $k = 5$. In these tables, the π and σ transitions correspond to the emission of light polarized parallel and perpendicular to the C axis respectively. The calculated results are relative emission intensities. Divided by $\sum_{i,j} A_{ij}$, the A_{ij} are normalized and can be compared with experimental results.

Comparing the theoretically deduced polarization results with those obtained by experiments in [11,12], we find that they are in excellent agreement. With respect to intensity, from tables 5 and 8 we can see that the transitions that have been realized as laser emissions [10] correspond to those with highest or/and higher calculated emission intensities. However, the calculated results obtained cannot completely agree with those of the experimental data in [11]. To discuss this problem further, we would like to compare them with the experimental spectroscopic data of the emissions between sublevels of ${}^4F_{3/2}$ and those of ${}^4I_{11/2}$ listed in table IV in [11] quantitatively. Based on equation (2.23) of [10], we have the following relation

$$A_{ij} \propto \sigma_e \Delta \nu f^2 \quad (12)$$

where σ_c is the peak cross section and $\Delta\nu$ is the linewidth of luminescence. Then the relative emission intensities were calculated and normalized by the method mentioned. The theoretical and experimental results are listed in table 8. The RMS deviation of the experimental and theoretical intensities is defined as

$$\text{RMS} = \left(\sum_{i,j} (A_{\text{exp}} - A_{ij})^2 / (\text{number of emissions}) \right)^{1/2}. \quad (13)$$

From the calculated RMS, we can find that the modification proposed by Judd cannot totally make up the contribution by the seventh-order odd crystal field, although it can make the differences between calculated and experimental values a little smaller. This result confirms the conclusion that the effect of $A_{\pm 6}^7$ CF component on the induced electric dipole moments is significantly greater than those of the $A_{\pm 2}^k$ ($k = 3, 5, 7$) components, which is deduced in [11] from experimental data.

Table 8. Comparison of the experimental and calculated transition intensity for ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ of Nd³⁺:YVO₄.^a

Transition	σ			π		
	Exp.	$A_{JJ'}$	$A'_{JJ'}$	Exp.	$A_{JJ'}$	$A'_{JJ'}$
b \rightarrow a ^{σ}	0.09762	0.09435	0.08480		0	0
a \rightarrow a ^{π}	0.07872	0.00566	0.00339		0.00037	0.00017
b \rightarrow b ^{σ}	0.05670	0.03747	0.02197	0.3690 ^b	0.19119	0.22914
a \rightarrow b ^{σ}	0.12847	0.16805	0.17840		0	0
b \rightarrow c	0.03601	0.07245	0.05921		0	0
a \rightarrow c	weak	0.01985	0.01681	0.05101	0.01884	0.01052
b \rightarrow d	n/o	0.00157	0.00092	n/o	0.02363	0.02747
a \rightarrow d	n/o	0.00859	0.01005	n/o	0	0
b \rightarrow e	0.08375	0.18640	0.18155	n/o	0	0
a \rightarrow e	weak	0.01372	0.01499	0.04679	0.02071	0.03220
b \rightarrow f	0.05193	0.01110	0.00651	weak	0.10463	0.11000
a \rightarrow f	weak	0.02144	0.01190	n/o	0	0
RMS		0.04276	0.04323		0.09455	0.08272

^a Experimental data taken from table IV of [11]. n/o means not observed.

^b These lines are too obscured by the a \rightarrow a line for measurement.

^{σ} The transitions which have been realized as laser emissions with σ polarization.

^{π} The transitions which have been realized as laser emission with π polarization.

4. Conclusion

The CF energy level fitting has been performed for Nd³⁺:YVO₄ by constraining the energy level fitting by one set of CF parameter ratios calculated by the simple point-charge model. The CF parameters with real physical meaning and the wavefunctions of Stark sublevels belonging to the manifolds ${}^4F_{3/2}$, ${}^4I_{13/2}$, ${}^4I_{11/2}$ and ${}^4I_{9/2}$ have been obtained.

The polarization characteristics of the radiative transitions and the possible laser emissions for rare-earth-doped crystals can be predicted theoretically. These calculations prove the correctness of the method proposed and give a simple and reliable judgement about the physical reality of the CF parameters, which has not been considered in conventional crystal-field energy level fitting.

Although the calculations carried out are comparatively simple and only the admixing between configurations $4f^25d$ and $4f^3$ was taken into consideration, the emission lines with highest or comparatively high calculated intensities exactly corresponded to laser emission lines that have been realized in experiments. However, for the reason that the model introduced is relatively simple, it has not included the effect of k -odd crystal field with $k = 7$, which is important to the transition intensities for Nd^{3+} in YVO_4 . On the other hand, because the local structure data used in the calculation might not be sufficiently precise, and the intensity measurement in spectroscopy may not always be so accurate, the calculation results were not in complete agreement with all of the experimental intensities. In these calculations, the data needed are the point symmetry of rare-earth ions, the crystallographic location of the nearest anions and the Stark level splitting obtained from spectroscopy. It might be argued that the exact positions of the nearest anions and even the point symmetry of the doped ions are difficult to determine in certain situations, because the doped rare-earth ions appear as one kind of impurity in a crystal and conventional x-ray diffraction cannot be used to determine the local structure around impurities. Nevertheless, in most of the circumstances concerned, the radius of the dopant is almost the same as that of the ions replaced by them, and so the distortion introduced by the doping can be ignored in the first-order approximation. However, in the fitting procedure introduced, the ratios of the CF parameters initially assumed a set of values but were adjusted to reach the minimum according to the energy levels obtained from spectroscopic data. This procedure implies that the local structure data used in the calculation are a set of values somewhat more consistent with the real situation. Recently, advanced techniques for determining local structure in crystals, for example extended x-ray absorption fine structure (EXAFS) [24], have been developed, and one can expect that, by using more precise local structure data, the agreement between calculated and experimental results can be further improved. Certainly, one way to improve the agreement is to take account of all the effects of k -odd CF with $k = 3, 5, 7$ by the same method, such as that proposed in this paper.

In conclusion we would like to say that the simple method introduced turns out to be useful in the investigation of new laser crystals.

Acknowledgments

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Appendix 1. Wavefunctions for spectroscopic terms concerned

$$|^4F_{3/2}\rangle \rightarrow |^4F_{3/2} \frac{3^-}{2} \frac{3}{2} \frac{1}{2}\rangle + |^4F_{3/2} \frac{3^-}{2} \frac{3}{2} \frac{3}{2}\rangle$$

$$|^4I_{13/2}\rangle \rightarrow |^4I_{13/2} \frac{1^-}{2} \frac{1}{2} \frac{3}{2}\rangle + |^4I_{13/2} \frac{3^-}{20} \frac{3}{2} \frac{1}{2}\rangle + |^4I_{13/2} \frac{3^-}{20} \frac{3}{2} \frac{3}{2}\rangle + |^4I_{13/2} \frac{3^-}{21} \frac{3}{2} \frac{1}{2}\rangle + |^4I_{13/2} \frac{3^-}{21} \frac{3}{2} \frac{3}{2}\rangle \\ + |^4I_{13/2} \frac{1^-}{20} \frac{1}{2} \frac{1}{2}\rangle + |^4I_{13/2} \frac{1^-}{21} \frac{1}{2} \frac{1}{2}\rangle$$

$$|^4I_{11/2}\rangle \rightarrow |^4I_{11/2} \frac{1^-}{2} \frac{1}{2} \frac{3}{2}\rangle + |^4I_{11/2} \frac{3^-}{20} \frac{3}{2} \frac{1}{2}\rangle + |^4I_{11/2} \frac{3^-}{20} \frac{3}{2} \frac{3}{2}\rangle + |^4I_{11/2} \frac{3^-}{21} \frac{3}{2} \frac{1}{2}\rangle \\ + |^4I_{13/2} \frac{3^-}{21} \frac{3}{2} \frac{3}{2}\rangle + |^4I_{13/2} \frac{1^-}{2} \frac{1}{2} \frac{1}{2}\rangle$$

$$|^4I_{9/2}\rangle \rightarrow |^4I_{9/2} \frac{1^-}{2} \frac{1}{2} \frac{3}{2}\rangle + |^4I_{9/2} \frac{3^-}{20} \frac{3}{2} \frac{1}{2}\rangle + |^4I_{9/2} \frac{3^-}{20} \frac{3}{2} \frac{3}{2}\rangle + |^4I_{9/2} \frac{3^-}{21} \frac{3}{2} \frac{1}{2}\rangle + |^4I_{9/2} \frac{3^-}{21} \frac{3}{2} \frac{3}{2}\rangle.$$

Appendix 2. Wavefunctions for the crystal-field energy levels

$${}^4F_{3/2}(b) \quad \left| \frac{3^-}{2} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_7)$$

$${}^4F_{3/2}(a) \quad \left| \frac{3^-}{2} \frac{3}{2} \frac{1}{2} \right\rangle. \quad (\Gamma_6)$$

$${}^4I_{13/2}(g) \quad 0.4352 \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \right\rangle + 0.9003 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \right\rangle + 0.0057 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_7)$$

$${}^4I_{13/2}(f) \quad -0.7517 \left| \frac{1^-}{2_0} \frac{1}{2} \frac{1}{2} \right\rangle - 0.0123 \left| \frac{1^-}{2_1} \frac{1}{2} \frac{1}{2} \right\rangle + 0.3821 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \right\rangle + 0.5373 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \right\rangle \quad (\Gamma_6)$$

$${}^4I_{13/2}(e) \quad 0.5269 \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \right\rangle - 0.2598 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \right\rangle + 0.8093 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_7)$$

$${}^4I_{13/2}(d) \quad 0.6103 \left| \frac{1^-}{2_0} \frac{1}{2} \frac{1}{2} \right\rangle + 0.2666 \left| \frac{1^-}{2_1} \frac{1}{2} \frac{1}{2} \right\rangle + 0.6145 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \right\rangle + 0.4229 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \right\rangle \quad (\Gamma_6)$$

$${}^4I_{13/2}(c) \quad 0.1918 \left| \frac{1^-}{2_0} \frac{1}{2} \frac{1}{2} \right\rangle - 0.9607 \left| \frac{1^-}{2_1} \frac{1}{2} \frac{1}{2} \right\rangle + 0.1114 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \right\rangle + 0.1671 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \right\rangle \quad (\Gamma_6)$$

$${}^4I_{13/2}(b) \quad 0.1602 \left| \frac{1^-}{2_0} \frac{1}{2} \frac{1}{2} \right\rangle + 0.0765 \left| \frac{1^-}{2_1} \frac{1}{2} \frac{1}{2} \right\rangle - 0.6812 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \right\rangle + 0.7103 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \right\rangle \quad (\Gamma_6)$$

$${}^4I_{13/2}(a) \quad 0.7301 \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \right\rangle + 0.3492 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \right\rangle + 0.5874 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \right\rangle. \quad (\Gamma_7)$$

$${}^4I_{11/2}(f) \quad 0.7218 \left| \frac{1^-}{2} \frac{1}{2} \frac{1}{2} \right\rangle - 0.4815 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \right\rangle + 0.4972 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \right\rangle \quad (\Gamma_6)$$

$${}^4I_{11/2}(e) \quad 0.6240 \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \right\rangle - 0.3896 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \right\rangle + 0.6774 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_7)$$

$${}^4I_{11/2}(d) \quad 0.5540 \left| \frac{1^-}{2} \frac{1}{2} \frac{1}{2} \right\rangle - 0.0286 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \right\rangle - 0.8320 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \right\rangle \quad (\Gamma_6)$$

$${}^4I_{11/2}(c) \quad 0.1209 \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \right\rangle - 0.8084 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \right\rangle - 0.5762 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_7)$$

$${}^4I_{11/2}(b) \quad 0.4148 \left| \frac{1^-}{2} \frac{1}{2} \frac{1}{2} \right\rangle + 0.8760 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \right\rangle + 0.2461 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \right\rangle \quad (\Gamma_6)$$

$${}^4I_{11/2}(a) \quad 0.7721 \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \right\rangle + 0.4414 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \right\rangle + 0.4573 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \right\rangle. \quad (\Gamma_7)$$

$${}^4I_{9/2}(e) \quad 0.0364 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \right\rangle + 0.9993 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \right\rangle \quad (\Gamma_6)$$

$${}^4I_{9/2}(d) \quad 0.7658 \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \right\rangle - 0.2118 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \right\rangle - 0.6071 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_7)$$

$${}^4I_{9/2}(c) \quad 0.9993 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \right\rangle - 0.0364 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \right\rangle \quad (\Gamma_6)$$

$${}^4I_{9/2}(b) \quad -0.5163 \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \right\rangle - 0.7655 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \right\rangle - 0.3841 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_7)$$

$${}^4I_{9/2}(a) \quad 0.3834 \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \right\rangle + 0.6076 \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \right\rangle + 0.6956 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \right\rangle. \quad (\Gamma_7)$$

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