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Multiplet Structure Calculations for Rare Earth Ions

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ABSTRACT

We obtain the multiplet energies for several rare earth (RE) ions by *ab initio* molecular orbital calculations including the spin-orbit interaction working on $4f$ electrons of RE. Because of a limitation of the ability of computations, the lower lying multiplet energies for Ce^{3+}, Nd^{3+}, Eu^{3+}, Gd^{3+} and Er^{3+} ions were calculated in this report. For the excitations of $4f$ electrons, the spin multiplicity in the multiplet terms for $4f^n$ electrons does not hold (not always $\Delta S=0$) both in initial and final states by mixing different S states upon spin-orbit interaction. We estimated the possibility of the transitions for the multiplet terms for RE ions with use of the obtained electronic spin states of the $4f$ electrons.

1. Introduction

As fluorescent materials, a series of RE ions (REs) has been investigated upon the luminescence spectra and applied to a light source. The sharp luminescence spectra are observed due to the intra-transitions of $4f$ electrons in the $4f$ orbitals because the $4f$ orbitals are shielded by the outer $5s$, $5p$, $5d$ and $6s$ orbitals. The spectra keep sharp even in an applied electric potential field. RE ion doped fluorescent materials are utilized in the fluorescent lamps for the suitable feature of presenting the natural colour luminescence and of the stability of the luminescence spectra of RE ion for the highly applied voltage and at high temperature.

Multiplet energy structures for REs are constructed by Coulomb and the spin-orbit interactions working on the $4f$ electrons. The electronic configurations of $4f^n$ electrons of REs (n=1 ~ 13) show the complex energy levels in the region of energy in far-infrared and up to near-ultraviolet. Thus, it is important to take into account the interactions for obtaining the multiplet energy levels of REs.

The natural colour spectra in fluorescent lamps can be realized by the luminescence of REs because the luminescence of activated REs can be colourcoded by the three colours with the sharp spectra of blue, green and red at ~ 22700 ,18500 and 16400cm^{-1}, respectively. Actually Eu^{3+} is used for red fluorescent activator and Tb^{3+} is used for green natural colour. For blue spectra, the inter excitation of Eu^{2+} occures, $4f^6 5d^1 \rightarrow 4f^7$. The red ($Eu^{3+}$) and the green ($Tb^{3+}$) visible rays correspond to the transition from ^5D to ^7F. These are the cases that the total spin angular momentum changes by unity $\Delta S=1$ on the transiton, where ΔS indicates the difference of the spin multiplicities between the ground and the excited states.

Er^{3+} and Nd^{3+} are the most intensively investigated materials in RE doped semiconductor physics. The strong luminescence has been observed for the lower lying multiplet terms in an infrared region. However, the strong luminescence corresponds to the transition of $\Delta S=0$ as is generally understand as the selection rule. Thus a question is why visible rays for REs use the forbidden selection rule. An answer for that question is that the mixing of different S states in the multiplet terms due to spin-orbit interaction of $4f$ electron is essential for possible $\Delta S=0$ dipole transition, which will be partly shown here.

In the present paper, we report the multiplet energies for some of trivalent lanthanide ions, Ce^{3+}, Nd^{3+}, Eu^{3+}, Gd^{3+} and Er^{3+} by *ab initio* calculations and consider the relationship between the electronic structure and the luminescence. For this purpose we use spin-orbit version of the program package COLMBS at Institute of Molecular Science, Okazaki, Japan. Gaussian basis set and *ab initio* method for the multiplets have been successfully used in RE atoms and its cluster[1-3]. Very recently this package is possible for not only even number of electrons but also odd number of electrons, which is modified by Satoshi Yabushita. The effective core parameter is estimated by a spin-density local functional atomic calculation for REs [3].

Spin multiplicities are related to the possibility of luminescence because the selection rule is established for an atom in the Russell-Saunders approximation, i.e. $\Delta S=0$ in electric-dipole and magnetic-dipole transitions. In the case of strong spin-orbit coupling, spin multiplicities in the multiplet terms may be not always effective as a character for selection rule.

In the present case, different spin multiplicities are mixed to each other in a multiplet energy level. By counting the large components of mixed spin multiplicities, we estimate the possibility of transition.

2. Method

In *ab initio* calculation, the total energy and molecular orbital energy for REs are obtained in self-consistent field Hartree-Fock (SCF-HF) calculation. The Hamiltonian to be solved is ;

$$H = H_0 + H_1$$
$$= \sum_i \left\{ -\frac{\hbar^2}{2m}\nabla_i{}^2 - \frac{Z_{RE}e^2}{|R_{RE} - r_i|} + \frac{\alpha^2}{2}\frac{Z_{eff, RE}}{|R_{RE} - r_i|^3}l_i \cdot s_i \right\}$$
$$+ \sum_{<i,j>} \frac{e^2}{|r_i - r_j|} \tag{1}$$

where α is the fine structure constant. Z_{RE} and R_{RE} denote the nuclear charge and the position of the RE, respectively. $Z_{eff, RE}$ denotes effective nuclear charge for a trivalent rare earth ion. The one-body spin-orbit (SO) interaction is introduced in the third term of the one-electron Hamiltonian, H_0. The last term, H_1, represents electron-electron interactions. In the SCF-HF calculation, the third term of eq. (1) is not included, which is considered in spin-orbit configuration interaction (SOCI) calculation which is followed by SCF-HF.

A. SCF Hartree-Fock Procedure

In this section, we briefly describe the formulation of Hartree-Fock-Roothaan equation. Molecular orbitals (MO's) are obtained by solving the restricted Roothaan Hartree-Fock equations in which the spin-functions of up- and down- spins are not distinguished in many electrons wavefunctions. A MO Ψ_i consists of a linear combination of atomic orbitals (AO's) φ of various quantum numbers on the various atoms.

$$\Psi_i = \sum_{k=1}^{M} C_{ki}\varphi_k. \tag{2}$$

The overlap integral between two AO's is written by

$$S_{nk} = \int \varphi_n{}^*(1)\varphi_k(1)dr_1. \tag{3}$$

The total wavefunction for many electrons is represented by the determinantal function in terms of the MO's. A Hatree-Fock-Roothaan equation for i-th MO is,

$$f(1)\sum_{k=1}^{M} C_{ki}\varphi_k(1) = \epsilon_i \sum_{k=1}^{M} C_{ki}\varphi_k(1), \tag{4}$$

where the Fock operator for a electron 1, $f(1)$, is written by

$$f(1) = h(1) + \sum_{k'=1}^{M} \int dr_2\varphi_{k'}{}^*(2)r_{12}^{-1}(1 - P_{12})\varphi_{k'}(2), \tag{5}$$

and here $h(1)$ is a one-electron Hamiltonian and P_{12} is a operator which permutes the positions of the two electrons each other $(1 \leftrightarrow 2)$. The matrix elements of the secular equations for Hartree-Fock-Roothaan equations can be derived from the differential equation of eq. (4) by multiplying n-th atomic orbital φ_n and by integrate over the coordinate, then,

$$\sum_{k=1}^{M} C_{ki} \int dr_1\varphi_n{}^*(1)f(1)\varphi_k(1) = \epsilon_i \sum_{k=1}^{M} C_{ki} \int dr_1\varphi_n{}^*(1)\varphi_k(1). \tag{6}$$

The matrix component of Fock operator is written by

$$F_{\mu\nu} = \int dr_1\varphi_\mu{}^*(1)f(1)\varphi_\nu(1). \tag{7}$$

The consecutive Hartree-Fock-Roothaan equations for M MO's can be written by the matrix formula, as follows,

$$\sum_{k=1}^{M} F_{nk}C_{ki} = \epsilon_i \sum_{k=1}^{M} S_{nk}C_{ki} \quad (i = 1, \cdots, M), \tag{8}$$

where S, ε_i and C_i are the overlap matrix, eigenvalue and coefficient vector of the i-th MO, respectively. The degree M is the total number of MO's and F is Fock matrix which is the sum of the one-electron (F_1) and two-electron (F_2) operators,

$$F = F_1 + F_2. \tag{9}$$

The matrix elements of the Fock operators are given by

$$F_{nk} = 2[n|k] + 2\sum_{j=1}^{N}\sum_{p,q=1}^{M} C_{pj}^*C_{qj}^*\{[nk|pq] - [nq|pk]\}, \tag{10}$$

in which,

$$[n|k] = \int dr_1\varphi_n^*(1)[-\frac{1}{2}\nabla_1{}^2 - \sum_a \frac{Z_a}{r_{1a}}]\varphi_k(1) \tag{11}$$

$$[nk|pq] = \int dr_1 dr_2\varphi_n^*(1)\varphi_k(1)\frac{1}{r_{12}}\varphi_p^*(2)\varphi_q(2). \tag{12}$$

B. Multiplet Terms

In excited states, all of the intra-excitations in $4f$ orbitals and SO interaction are taken into account in the configuration interaction (CI) calculation and the multiplet energies for excitation of $4f$ electrons are obtained. The total angular momentum $J=L+S$ is a good quantum number by the selection rule under SO interactions, here L is the total orbital angular momentum and S is the total spin angular momentum and the multiplet terms are denoted by $^{2S+1}L_J$. In the CI method, different spin multiplicities from $2S+1$ in $^{2S+1}L_J$ can exist in a multiplet. The ratio of the multiplet with the different S is determined due to the strength of SO coupling with another multiplet terms with

the same J. For example, the ground state for Er^{3+}, $^4I_{\frac{15}{2}}$, is expressed as,

$$\Phi_{gr} = C_1\phi(^4I_{\frac{15}{2}}) + C_2\phi(^2K_{\frac{15}{2}}) + C_3\phi(^2L_{\frac{15}{2}}), \qquad (13)$$

where the ground state with $J=\frac{15}{2}$ in the left side consists of a linear combination of the ground (first term) and the excited (following ones) terms with the same J. On the right hand side, the multiplet eigenfunctions ϕ $(^{2S+1}L_J)$ are described by linear combinations of Slater's determinants in which the MO's obtained in eq. (8) are matrix elements. $4f$ electrons are allocated in the MO's as to obtain the resultant angular momentum. Multiplet energies and the coefficients in eq. (13) are determined by variation in which the total energy of Hamiltonian, eq. (1), are minimized with the SO wavefunction Φ in eq. (13).

The component of the first term may dominantly exist in the ground state by Hund's law and the second and the third excited states with the spin multiplicities of the value 2 can be mixed to the ground state. We calculated the percentages of the component with spin multiplicities of the value 4 as C_1^2 in order to estimate the largest spin component in the multiplet $^4I_{\frac{15}{2}}$. The dimensions of matrix to be solved for excited states always exceed ~ 5000 in the present case and it is difficult to obtain the higher multiplet energies lying in visible or ultraviolet region. However if we use the obtained spin multiplicities for multiplet terms, we can discuss the mixing of the spin multiplicities and the quoted oscillator strength[4,5].

3. Calculated Results

The calculated multiplet energies are listed in Table I. Corresponding experimental data[6] and the other calculation[7] are listed, too, in Table I. The results are in good agreement with the experiments and the former calculations. It should be mentioned that the effect of expansion of $4f$ wavefunctions toward outwards is important for obtaining the reasonable value of the multiplet terms. This effect of expansions for $4f$ wavefunctions can be thought to be a relativistic effect which is pointed out in some papers [3,8]. We took a special care in selecting Gaussian basis sets for including this effect. The remaining discrepancy may arise from the surrounding crystal field effect of aquo ions.

Spin multiplicities $2S+1$ obtained in the CI calculation for Nd^{3+}, Gd^{3+} and Er^{3+} are specified in Table II as well as oscillator strength printed in references [4,5]. In Table II, the percentages of the major "$2S+1$" components which mainly exists in the multiplet term are specified. It can be seen that different spin multiplicities from the major "$2S+1$" also exist in the $^{2S+1}L_J$ multiplet. For Gd^{3+}, the spin multiplicity for the ground state is dominantly (97%) $2S+1 = 8$ and another components are much small (3 %). On the other hand, for the first excited state it is mainly $2S+1 = 6$. Here, the same spin multiplicity as that in the ground state of

$2S+1 = 8$ is included only 2 % in the first excited state. On the other hand, for Er^{3+}, the spin multiplicity ($2S+1 = 4$) largely exists both in the ground and first excited states and also can be said for Nd^{3+}. From the Table II, it can be seen that the oscillator strengths are related to the obtained spin multiplicities. The listed oscillator strengths were evaluated in the Russell-Saunders approximation (weak limit of SO interaction), in which the multiplet eigenvectors for $^{2S+1}L_J$ are represented by a linear combination of the basis states for both L and S. Under the approximation, the selection rules for $4f^n$ intra-transitions are $\Delta J \leq 1$, $\Delta L = 0$, $\Delta S = 0$. Thus, the oscillator strengths for Nd^{3+} and Er^{3+}, in which $\Delta S = 0$, should be much larger than that for Gd^{3+}, in which $\Delta S = 1$, due to the above selection rule. On the other hand, in our calculations, the Russell-Saunders approximation is not adopted and only the restrictions of $\Delta J \leq 1$ is working. Nevertheless, it seems that the term of ΔS and the oscillator strength correlate in the Table. This shows that selection rule for spin multiplicity is still effective for REs even under the large SO interaction.

The large energy gap of between the ground and the first excited states for Gd^{3+} comes from the electronic configuration of the half filling in the $4f$ orbitals. For the configuration, the maximum spin multiplicity ($2S+1=8$) over trivalent lanthanide ions are established and the large excitation energy is needed for the spin conversion. The second excited state $^4I_{\frac{13}{2}}$ for Nd^{3+} consists of the spin multiplicity of $2S+1=4$ nearly perfectly though the first excited state $^4I_{\frac{13}{2}}$ for Er^{3+} involves about 12 % of the different spin multiplicity from the value 4. This is because of SO interaction with the multiplet term with the same total angular momentum $J = \frac{13}{2}$ as that of $^2K_{\frac{13}{2}}$ which exists in near ultraviolet region. This J-J coupling is not effective to the $^4I_{\frac{13}{2}}$ of Nd^{3+} since the effective state with the same J does not exist in the near upper states.

4. Conclusion

The multiplet energy levels for RE ions luminescence spectra of which are observed are calculated with use of *ab initio* molecular orbital calculations. For the lower lying multiplet terms in infrared and ultraviolet range, it is discussed that the multiplet terms with spin multiplicities which satisfy selection rule show strong oscillator strength for the multiplet terms. In order to compare the relative intensity, we should calculate the dipole matrix element between two multiplets for given CI wavefunctions, which we will be reported in the future.

Acknowledgments

TABLE I Multiplet Terms of RE^{3+} (in cm^{-1}).

RE^{3+}Ions.	$^{2S+1}L_J$	Multiplet Energy(cm^{-1})		
		Present Results	Calculation [7]	Experiment [6]
Ce^{3+}	$^2F_{\frac{7}{2}}$	2679.2	-	2300 [a]
	$^2F_{\frac{5}{2}}$	0.0	-	0 [a]
Nd^{3+}	$^4I_{\frac{13}{2}}$	4576.1	4659.	4050 [b]
	$^4I_{\frac{11}{2}}$	2208.0	2243.	2028 [b]
	$^4I_{\frac{9}{2}}$	0.0	0.	146 [b]
Eu^{3+}	$^7F_5$	4652.9	4692.	3909.0 [c]
	$^7F_4$	3401.9	3421.	2877.2 [c]
	$^7F_3$	2238.7	2246.	1882.0 [c]
	$^7F_2$	1229.1	1225.	1044.8 [c]
	$^7F_1$	488.4	441.	380.16 [c]
	$^7F_0$	0.0	0.	0.0 [c]
Gd^{3+}	$^6P_{\frac{5}{2}}$	42996.0	42352.	32780. [d]
	$^6P_{\frac{7}{2}}$	42315.6	41694.	32200. [d]
	$^8S_{\frac{7}{2}}$	0.0	0.	0.0 [d]
Er^{3+}	$^4I_{\frac{13}{2}}$	7126.5	7383.	6485.9 [e]
	$^4I_{\frac{15}{2}}$	0.0	0.	0. [e]

Experimental observations are summarized in a figure of ref. (6). Listed numerical data of experiments are referred to the following papers, respectively. [a] Reference (6), [b][e] Reference (9), [c] Reference (10) and [d] Reference (11).

TABLE II.Spin Multiplicities and Oscillator Strengths.

RE^{3+} Ions.	$^{2S+1}L_J$	2S + 1	ratio (%)	ΔS	Osc. Str. (× 10^6)
Nd^{3+}	$^4I_{\frac{13}{2}}$	4	99	0	0.71 [a]
	$^4I_{\frac{11}{2}}$	4	87	0	-
	$^4I_{\frac{9}{2}}$	4	84	-	-
Gd^{3+}	$^6P_{\frac{5}{2}}$	6	83*[ ]	1	0.041 [b]
	$^6P_{\frac{7}{2}}$	6	83*[ ]	1	0.073 [b]
	$^8S_{\frac{7}{2}}$	8	97	-	-
Er^{3+}	$^4I_{\frac{13}{2}}$	4	88	0	1.76 [a]
	$^4I_{\frac{15}{2}}$	4	84	-	-

*) The component with 2S+1=8 is 2 % at most. [a] Reference (4). [b] Reference (5). ΔS shows the difference of spin multiplicities between the ground and excited states and ratio is that of the component with 2S+1 in the multiplet. It is noted that different spin multiplicities from "2S+1" can be mixed by SO interaction.

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