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# Theoretical analysis and intensity calculation for the $f \rightarrow d$ absorption spectrum of $U^{3+}$ in the $LiYF_4$ crystal

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## Abstract

The  $5f^3 \rightarrow 5f^26d$  absorption spectrum of  $U^{3+}$  in  $LiYF_4$  has been well calculated using the model proposed by Reid for calculations of  $4f^N \leftrightarrow 4f^{N-1}5d$  spectra. The relevant formulae for the matrix element calculations which were omitted in this model are now described in detail, and the values of the direct and exchange coefficients associated with the  $f$ – $d$  Coulomb interactions within the  $f^2d$  configuration are derived and listed. The amount of reduction for the  $f$ – $d$  Coulomb interaction parameters from the free-ion values is found to be  $\sim 67\%$ , which is much larger than the value of 26% for the isoelectronic  $Nd^{3+}$  lanthanide ion in the same host.

## 1. Introduction

The  $f^N \rightarrow f^N$  spectra of lanthanide and actinide ions in crystals have been extensively investigated over the past 50 years. The experimental energy levels derived from the electronic spectra may be analysed with a parametrized crystal–field Hamiltonian  $H$  [1], and the spectroscopic coefficients existing in the  $H$  matrix elements between  $f^N$  states have been calculated and gathered into a handbook [2] which is very useful for the analysis of experimental results. Recently it has been demonstrated that the  $4f^N \leftrightarrow 4f^{N-1}5d$  spectra of lanthanide ions in crystals may be modelled using a straightforward extension of the standard calculations for the  $4f^N$  configuration to include the  $4f^{N-1}5d$  configuration. Extensive calculations have been carried out for trivalent lanthanide ions in crystals [3–5] which gave satisfactory agreement with experimental  $4f^N \leftrightarrow 4f^{N-1}5d$  spectra, but the relevant formulae for calculating spectroscopic coefficients for the  $f^{N-1}d$  configuration were not given by the authors.

Trivalent uranium in  $CaF_2$  and  $SrF_2$  has been studied for potential use as an IR laser [6, 7], but interpretation of the optical spectra is difficult because  $U^{3+}$  ions occupy two different crystal sites. Hubert *et al* have shown that  $LiYF_4:U^{3+}$  is also a good candidate for an IR laser [8], and the absorption spectra ( $5f^3 \rightarrow 5f^3$  and  $5f^3 \rightarrow 5f^26d$ ) of this system have been

measured [9, 10]. Moreover, the  $5f^3 \rightarrow 5f^3$  spectra have been analysed using the crystal-field model for the  $f^3$  configuration, where the electrostatic, spin-orbit and crystal-field parameters were derived [10]. Therefore, it is interesting to analyse the  $5f^3 \rightarrow 5f^25d$  absorption spectra of  $U^{3+}$  in  $LiYF_4$  using the extended model mentioned above.

In this paper, we demonstrate that the energy levels of  $U^{3+}$  in  $LiYF_4$ , and the intensities of the  $5f^3 \rightarrow 5f^26d$  transitions of  $U^{3+}$  in this host, can be modelled and calculated by Reid's extended program in the same manner as for the  $4f^N$  and  $4f^{N-1}5d$  configurations. The literature values for atomic and crystal-field parameters for the  $5f^3$  configuration have been used and the crystal-field parameters for the 6d electron were approximated by those for the 5d electron in the same host [3]. However, the five Coulomb (direct and exchange) f-d interaction parameters for the  $5f^26d$  configuration needed to be adjusted even more seriously from the values obtained with the standard atomic calculations [11]. At the same time, the relevant formulae for  $f^{N-1}d$  energy-level calculations and for  $f \rightarrow d$  electric dipole transition intensities are described in detail in this study, using the irreducible tensor operator formalism of [11]. The Coulomb f-d spectroscopic coefficients for the  $f^2d$  system are listed in tables for convenient reference. The calculated energies and intensities of zero-phonon lines are successfully used to model the experimental  $5f \rightarrow 6d$  absorption spectrum.

## 2. Theory

### 2.1. Matrix elements of Hamiltonians

The Hamiltonian for the  $f^{N-1}d$  configuration of an ion in a crystal environment can be written as

$$H = H_0 + H_C + H_{SO} + H_{CF} + \dots, \quad (1)$$

where

$$H_C = \sum_{i < j} \frac{1}{r_{ij}} = \sum_{i < j} \sum_k \frac{r_{<}^k}{r_{>}^{k+1}} (c_i^{(k)} \cdot c_j^{(k)}), \quad (2)$$

$$H_{SO} = \sum_i \xi_i(r_i) s_i \cdot l_i \quad (3)$$

and

$$H_{CF} = \sum_i \sum_{k,q} B_q^k c_q^{(k)}(i) \quad (4)$$

are the Coulomb interaction between the  $N$  electrons, the spin-orbit interaction and the crystal-field interaction respectively. The summation involving  $i$  or  $j$  is over all the electrons (i.e. the  $(N-1)$  f electrons and one d electron). The  $H_0$  in equation (1) is the sum of the kinetic energies and the potential energies of the  $N$  electrons in the field of the ion core, and the suspension points indicate other small interactions [1] which have to be considered in the energy level calculations in order to get a good agreement between experiment and calculation. The  $r_{<}$  and  $r_{>}$  are respectively the lesser and greater of the distances of the electrons  $i$  and  $j$  from the nucleus. The meanings of the other symbols in the above expressions are fully described in [1]. In the following subsections, the matrix elements of the Hamiltonians  $H_C$ ,  $H_{SO}$  and  $H_{CF}$  between the completely antisymmetric basis states  $|(f^{N-1}\alpha_1 S_1 L_1, s_d l_d) SLJM\rangle$  of the  $f^{N-1}d$  configuration are evaluated, and the explicit expressions for the angular parts of these matrix elements, i.e. the spectroscopic coefficients, are given.

2.1.1. *Matrix elements of the Coulomb interaction  $H_C$ .* With the above basis wavefunctions  $|(f^{N-1}\alpha_1 S_1 L_1, s_d l_d) SLJM\rangle$ , the matrix element of the Hamiltonian  $H_C$  is diagonal in the quantum numbers  $S$ ,  $L$ ,  $J$  and  $M$  and is independent of  $J$  and  $M$ . Accordingly, the matrix element can be written as

$$\begin{aligned} & \langle (f^{N-1}\alpha_1 S_1 L_1, s_d l_d) SLJM | H_C | (f^{N-1}\alpha'_1 S'_1 L'_1, s_d l_d) SLJM \rangle \\ &= \sum_{k_1} f_{k_1}(\text{ff}) F^{k_1}(\text{ff}) + \sum_{k_2} f_{k_2}(\text{fd}) F^{k_2}(\text{fd}) + \sum_j g_j(\text{fd}) G^j(\text{fd}), \end{aligned} \quad (5)$$

where  $f_{k_1}(\text{ff})$  ( $k_1 = 0, 2, 4, 6$ ) are the coefficients which represent the angular parts of the matrix elements of the f–f Coulomb interaction within the  $f^{N-1}$  core, and  $f_{k_2}(\text{fd})$  ( $k_2 = 0, 2, 4$ ) and  $g_j(\text{fd})$  ( $j = 1, 3, 5$ ) represent the angular parts of matrix elements of the f–d Coulomb direct and exchange interactions respectively. The  $F^{k_1}(\text{ff})$ ,  $F^{k_2}(\text{fd})$  and  $G^j(\text{fd})$  fitting parameters are the corresponding radial integrals, and may be written respectively as

$$F^{k_1}(\text{ff}) = e^2 \int_0^\infty \int_0^\infty \frac{r_1^{k_1}}{r_2^{k_1+1}} |R_f(r_1) R_f(r_2)|^2 r_1^2 r_2^2 dr_1 dr_2, \quad (6)$$

$$F^{k_2}(\text{fd}) = e^2 \int_0^\infty \int_0^\infty \frac{r_1^{k_2}}{r_2^{k_2+1}} |R_f(r_1) R_d(r_2)|^2 r_1^2 r_2^2 dr_1 dr_2, \quad (7)$$

and

$$G^j(\text{fd}) = e^2 \int_0^\infty \int_0^\infty \frac{r_1^j}{r_2^{j+1}} R_f^*(r_1) R_d^*(r_2) R_f(r_2) R_d(r_1) r_1^2 r_2^2 dr_1 dr_2. \quad (8)$$

The  $f_{k_1}(\text{ff})$  coefficients may be expressed as

$$\begin{aligned} f_{k_1}(\text{ff}) &= \frac{1}{2}(N-1)(N-2) \\ &\times {}_{\text{NA}} \langle (f^{N-1}\alpha_1 S_1 L_1, s_d l_d) SLJM | c_f^{(k_1)} \cdot c_f^{(k_1)} | (f^{N-1}\alpha'_1 S'_1 L'_1, s_d l_d) SLJM \rangle_{\text{NA}} \\ &= \delta_{S_1 L_1, S'_1 L'_1} \frac{1}{2}(N-1)(N-2) \\ &\times \langle f^{N-1}\alpha_1 S_1 L_1 M_{S_1} M_{L_1} | c_f^{(k_1)} \cdot c_f^{(k_1)} | f^{N-1}\alpha'_1 S_1 L_1 M_{S_1} M_{L_1} \rangle, \end{aligned} \quad (9)$$

which are the same as the Coulomb spectroscopic coefficients for the  $f^{N-1}$  configuration, and are independent of  $S$ ,  $L$ ,  $J$ ,  $M$  and  $M_{S_1}$ ,  $M_{L_1}$ . As is well known, their values can be obtained easily from [2], using the transformation relationships [2] between the Slater radial integrals  $F^k$  and Racah parameters  $E^k$ . The subscripts ‘NA’ in the above expression (and following sections) denote that the wavefunction is non-antisymmetric with respect to the exchange of the d electron with any one of the  $f^{N-1}$  electrons.

The direct coefficient  $f_k(\text{fd})$  for the f–d interaction can be expressed as [11]

$$\begin{aligned} f_{k_2}(\text{fd}) &= (N-1) {}_{\text{NA}} \langle (f^{N-1}\alpha_1 S_1 L_1, s_d l_d) SLJM | c_f^{(k_2)} \cdot c_d^{(k_2)} | (f^{N-1}\alpha'_1 S'_1 L'_1, s_d l_d) SLJM \rangle_{\text{NA}} \\ &= \langle l_f \| c^{(k_2)} \| l_f \rangle \langle l_d \| c^{(k_2)} \| l_d \rangle I_{\text{fd}}^{(k_2)}, \end{aligned} \quad (10)$$

and the exchange coefficient  $g_j(\text{fd})$  is

$$g_j(\text{fd}) = -\frac{1}{2} \langle l_f \| c^{(j)} \| l_d \rangle^2 \left[ \sum_{r=0}^4 (-1)^r (2r+1) \begin{Bmatrix} l_f & l_f & r \\ l_d & l_d & j \end{Bmatrix} [I_{\text{fd}}^{(r)} + 4I_{\text{fd}}^{(1r)}] \right]. \quad (11)$$

In the above two expressions

$$I_{\text{fd}}^{(k)} = \delta_{S'_1, S_1} (-1)^{L'_1 + L + l_d} \begin{Bmatrix} L_1 & l_d & L \\ l_d & L'_1 & k \end{Bmatrix} \langle f^{N-1}\alpha_1 S_1 L_1 \| U^{(k)} \| f^{N-1}\alpha'_1 S_1 L'_1 \rangle \quad (12)$$

and

$$I_{fd}^{(1r)} = (-1)^{s_d+l_d+S_1+L_1+S+L} \begin{Bmatrix} S_1 & s_d & S \\ s_d & S_1' & 1 \end{Bmatrix} \begin{Bmatrix} L_1 & l_d & L \\ l_d & L_1' & r \end{Bmatrix} \left(\frac{3}{2}\right)^{\frac{1}{2}} \\ \times \langle f^{N-1}\alpha_1 S_1 L_1 \| V^{(1r)} \| f^{N-1}\alpha_1' S_1' L_1' \rangle \quad (13)$$

where  $s_d = 1/2$ , and  $l_d = 2$ . The numerical values of 6- $j$  symbols in the above expressions (and 3- $j$ , 6- $j$  symbols in the following sections) can be calculated from the relations given in [12]. The values of the reduced matrix elements of the unit tensor operator  $U^{(k)}$  and double tensor operator  $V^{(11)}$  have been tabulated by Nielson and Koster [2], and those for  $V^{(1r)}$  with  $r > 1$  can be calculated by the formula (11.68) of [11] in terms of the coefficients of fractional parentage (cfps) in [2]. With the above formulae, the direct and exchange coefficients  $f_{k_2}(\text{fd})$  and  $g_j(\text{fd})$  for the case  $N = 3$  were calculated, and the results are displayed in tables 1 and 2 for convenient reference, in which the spectral term  $|(f^2\alpha_1 S_1 L_1, s_d l_d)SL)$  is abbreviated to  $|(L_1)L)$  and  $|(S_1 L_1)SL)$  respectively for conciseness. Since the matrix element,

$$\langle (f^{N-1}\alpha_1 S_1 L_1, s_d l_d)SLJM | H_C | (f^{N-1}\alpha_1' S_1' L_1', s_d l_d)SLJM \rangle \\ = \langle (f^{N-1}\alpha_1' S_1' L_1', s_d l_d)SLJM | H_C | (f^{N-1}\alpha_1 S_1 L_1, s_d l_d)SLJM \rangle \quad (14)$$

is independent of quantum numbers  $J$  and  $M$ , only the values of the direct and exchange coefficients on and above the diagonal are listed in tables 1 and 2. Then, there are 45 and 92 different non-zero matrix elements for the Coulomb direct and exchange interactions respectively for the  $f^2d$  configuration with 42 spectral terms.

**2.1.2. Matrix elements of the spin-orbit interaction  $H_{SO}$ .** With the basis states  $|(f^{N-1}\alpha_1 S_1 L_1, s_d l_d)SLJM)$ , the matrix element of  $H_{SO}$  is diagonal in quantum numbers  $J$  and  $M$ , and independent of  $M$ , and can be expressed as

$$\langle (f^{N-1}\alpha_1 S_1 L_1, s_d l_d)SLJM | H_{SO} | (f^{N-1}\alpha_1' S_1' L_1', s_d l_d)S' L' J M \rangle = \zeta_f A_{SO}(f) + \zeta_d A_{SO}(d), \quad (15)$$

where  $A_{SO}(f)$  and  $A_{SO}(d)$  are the angular parts of the matrix elements of the spin-orbit interactions for  $f$  electrons and  $d$  electron respectively and  $\zeta_f$  and  $\zeta_d$  are corresponding spin-orbit radial integral parameters.

The explicit expressions for the  $A_{SO}(f)$  may be obtained as follows:

$$A_{SO}(f) = (N-1) \cdot N_A \langle (f^{N-1}\alpha_1 S_1 L_1, s_d l_d)SLJM | s_f \cdot l_f | (f^{N-1}\alpha_1' S_1' L_1', s_d l_d)S' L' J M \rangle_{NA} \\ = (-1)^{S'+L+J} (N-1) \begin{Bmatrix} S & L & J \\ L' & S' & 1 \end{Bmatrix} \\ \times N_A \langle (f^{N-1}\alpha_1 S_1, s_d)S \| s_f \| (f^{N-1}\alpha_1' S_1', s_d)S' \rangle_{NA} \\ \times N_A \langle (f^{N-1}\alpha_1 L_1, l_d)L \| l_f \| (f^{N-1}\alpha_1' L_1', l_d)L' \rangle_{NA} \\ = (-1)^{S'+L+J} \langle l_f \| l_f \| l_f \rangle \begin{Bmatrix} S & L & J \\ L' & S' & 1 \end{Bmatrix} \\ \times N_A \langle (f^{N-1}\alpha_1 S_1 L_1, s_d l_d)SL \| V_f^{(11)} \| (f^{N-1}\alpha_1' S_1' L_1', s_d l_d)S' L' \rangle_{NA}, \quad (16)$$

and, in a similar way, the expression of  $A_{SO}(d)$  may be written as

$$A_{SO}(d) = N_A \langle (f^{N-1}\alpha_1 S_1 L_1, s_d l_d)SLJM | s_d \cdot l_d | (f^{N-1}\alpha_1' S_1' L_1', s_d l_d)S' L' J' M' \rangle_{NA} \\ = (-1)^{S'+L+J} \langle l_d \| l_d \| l_d \rangle \begin{Bmatrix} S & L & J \\ L' & S' & 1 \end{Bmatrix} \\ \times N_A \langle (f^{N-1}\alpha_1 S_1 L_1, s_d l_d)SL \| v_d^{(11)} \| (f^{N-1}\alpha_1' S_1' L_1', s_d l_d)S' L' \rangle_{NA}, \quad (17)$$

where  $\langle l_f \| l_f \| l_f \rangle = \sqrt{84}$  and  $\langle l_d \| l_d \| l_d \rangle = \sqrt{30}$ .

**Table 1.** The direct coefficients calculated between  $\langle (f^2\alpha_1 S_1 L_1, s_d l_d) SL \rangle$  and  $|(f^2\alpha'_1 S'_1 L'_1, s_d l_d) SL\rangle$  for the  $f^2d$  configuration. The  $f_{k_2}(\text{fd})$  ( $k_2 = 0, 2, 4$ ) are the direct coefficients defined by equation (10) in the text, and the  $f'_{k_2}(\text{fd})$  are the coefficients of parameters  $F_{k_2}(\text{fd})$ , whose relationships with  $F^{k_2}(\text{fd})$  are:  $F_0(\text{fd}) = F^0(\text{fd})$ ,  $F_2(\text{fd}) = F^2(\text{fd})/105$  and  $F_4(\text{fd}) = F^4(\text{fd})/693$ .

$(L_1) L$	$(L'_1) L'$	$f_0(\text{fd})$	$f_2(\text{fd})$	$f_4(\text{fd})$	$f'_0(\text{fd})$	$f'_2(\text{fd})$	$f'_4(\text{fd})$
(P) P	(P) P	2	-0.2	0	2	-21	0
(P) P	(F) P	0	0.066	-0.165	0	6.9282	-114.3154
(P) D	(P) D	2	0.2	0	2	21	0
(P) D	(F) D	0	0.1616	0.0673	0	16.9706	46.6691
(P) F	(P) F	2	-0.0571	0	2	-6	0
(P) F	(F) F	0	0.2116	-0.0147	0	22.2197	-10.184
(P) F	(H) F	0	0	0.1172	0	0	81.2404
(F) P	(F) P	2	-0.0762	-0.0317	2	-8	-22
(F) D	(F) D	2	-0.019	0.0476	2	-2	33
(F) F	(F) F	2	0.0349	-0.0317	2	3.6667	-22
(F) F	(H) F	0	0.0796	0.1176	0	8.3571	81.4818
(F) G	(F) G	2	0.0476	0.0106	2	5	7.3333
(F) G	(H) G	0	0.1263	-0.1037	0	13.2665	-71.8602
(F) H	(F) H	2	-0.0317	-0.0014	2	-3.3333	-1
(F) H	(H) H	0	0.1295	0.0368	0	13.5974	25.4951
(H) F	(H) F	2	0.1651	-0.0375	2	17.3333	-26
(H) G	(H) G	2	0	0.0875	2	0	60.6667
(H) H	(H) H	2	-0.1111	-0.0808	2	-11.6667	-56
(H) I	(H) I	2	-0.1048	0.0346	2	-11	24
(H) K	(H) K	2	0.0952	-0.0058	2	10	-4
(S) D	(S) D	2	0	0	2	0	0
(S) D	(D) D	0	0.2469	0	0	25.923	0
(S) D	(G) D	0	0	0.1519	0	0	105.2996
(D) S	(D) S	2	-0.2095	0.1905	2	-22	132.0001
(D) P	(D) P	2	-0.1048	-0.127	2	-11	-88
(D) D	(D) D	2	0.0449	0.0544	2	4.7143	37.7143
(D) D	(G) D	0	0.0884	0.0251	0	9.2846	17.4086
(D) F	(D) F	2	0.1197	-0.0136	2	12.5714	-9.4286
(D) F	(G) F	0	0.1563	-0.0178	0	16.413	-12.3098
(D) G	(D) G	2	-0.0599	0.0015	2	-6.2857	1.0476
(D) G	(G) G	0	0.1728	0.0054	0	18.1453	3.7115
(D) G	(I) G	0	0	0.0649	0	0	44.9691
(G) D	(G) D	2	0.0408	-0.0616	2	4.2857	-42.7143
(G) F	(G) F	2	0.0041	0.1233	2	0.4286	85.4286
(G) G	(G) G	2	-0.0241	-0.1009	2	-2.5325	-69.8961
(G) G	(I) G	0	0.0539	0.1379	0	5.6646	95.5908
(G) H	(G) H	2	-0.026	0.0392	2	-2.7273	27.1818
(G) H	(I) H	0	0.0809	-0.1379	0	8.497	-95.5908
(G) I	(G) I	2	0.0208	-0.006	2	2.1818	-4.1818
(G) I	(I) I	0	0.0794	0.0541	0	8.332	37.4938
(I) G	(I) G	2	0.303	0.0416	2	31.8182	28.8485
(I) H	(I) H	2	-0.0216	-0.107	2	-2.2727	-74.1818
(I) I	(I) I	2	-0.2208	0.107	2	-23.1818	74.1818
(I) K	(I) K	2	-0.1905	-0.0491	2	-20	-34
(I) L	(I) L	2	0.1905	0.0087	2	20	6

**Table 2.** The exchange coefficients calculated between  $\langle (f^2\alpha_1 S_1 L_1, s_d l_d) SL \rangle$  and  $|(f^2\alpha'_1 S'_1 L'_1, s_d l_d) SL\rangle$  for the  $f^2d$  configuration. The  $g_j(\text{fd})$  ( $j = 1, 3, 5$ ) are the exchange coefficients defined by equation (11) in the text, and the  $g'_j(\text{fd})$  are the coefficients of parameters  $G_j(\text{fd})$ , whose relationships with  $G^j(\text{fd})$  are:  $G_1(\text{fd}) = G^1(\text{fd})/35$ ,  $G_3(\text{fd}) = G^3(\text{fd})/315$  and  $G_5(\text{fd}) = 5G^5(\text{fd})/7693$ .

$(S_1 L_1) SL$	$(S'_1 L'_1) S' L'$	$g_1(\text{fd})$	$g_3(\text{fd})$	$g_5(\text{fd})$	$g'_1(\text{fd})$	$g'_3(\text{fd})$	$g'_5(\text{fd})$
$(^3P) ^2P$	$(^3P) ^2P$	-0.0857	0.0571	0.0325	-3	18	49.5
$(^3P) ^2P$	$(^3F) ^2P$	-0.1485	-0.0385	0.0125	-5.1962	-12.1243	19.0526
$(^3P) ^2P$	$(^1D) ^2P$	0.2571	-0.1238	0.0541	9	-39	82.5
$(^3P) ^4P$	$(^3P) ^4P$	0.1714	-0.1143	-0.0649	6	-36	-98.9999
$(^3P) ^4P$	$(^3F) ^4P$	0.2969	0.077	-0.025	10.3923	24.2487	-38.1051
$(^3P) ^2D$	$(^3P) ^2D$	0.2	0.0095	0.0758	7	3	115.5
$(^3P) ^2D$	$(^3F) ^2D$	0.0606	0.0269	0.0306	2.1213	8.4853	46.669
$(^3P) ^2D$	$(^1S) ^2D$	-0.2424	-0.0404	0.0918	-8.4853	-12.7279	140.0072
$(^3P) ^2D$	$(^1D) ^2D$	-0.2806	0	0.1063	-9.8198	0	162.0267
$(^3P) ^2D$	$(^1G) ^2D$	0.076	0.1182	0.014	2.6592	37.229	21.2737
$(^3P) ^4D$	$(^3P) ^4D$	-0.4	-0.019	-0.1515	-14	-6	-231
$(^3P) ^4D$	$(^3F) ^4D$	-0.1212	-0.0539	-0.0612	-4.2426	-16.9706	-93.3381
$(^3P) ^2F$	$(^3P) ^2F$	0.0776	0.0503	0.0247	2.7143	15.8571	37.7142
$(^3P) ^2F$	$(^3F) ^2F$	0.1852	-0.05	0.0234	6.4807	-15.7389	35.644
$(^3P) ^2F$	$(^3H) ^2F$	0.0829	0.0368	0.0019	2.9014	11.6058	2.9014
$(^3P) ^2F$	$(^1D) ^2F$	-0.2549	-0.03	0.0568	-8.9231	-9.448	86.6069
$(^3P) ^2F$	$(^1G) ^2F$	-0.2872	0.0319	0.0165	-10.0509	10.0509	25.1272
$(^3P) ^4F$	$(^3P) ^4F$	-0.1551	-0.1007	-0.0495	-5.4286	-31.7143	-75.4285
$(^3P) ^4F$	$(^3F) ^4F$	-0.3703	0.0999	-0.0468	-12.9615	31.4779	-71.2881
$(^3P) ^4F$	$(^3H) ^4F$	-0.1658	-0.0737	-0.0038	-5.8029	-23.2115	-5.8029
$(^3F) ^2P$	$(^3F) ^2P$	0.0286	-0.019	0.0649	1	-6	99
$(^3F) ^2P$	$(^1D) ^2P$	-0.0495	-0.1595	0.0625	-1.7321	-50.2295	95.2628
$(^3F) ^4P$	$(^3F) ^4P$	-0.0571	0.0381	-0.1299	-2	12	-198
$(^3F) ^2D$	$(^3F) ^2D$	-0.0429	0.0603	0.0794	-1.5	19	121
$(^3F) ^2D$	$(^1S) ^2D$	-0.2571	0.0762	0.0216	-9	24	33
$(^3F) ^2D$	$(^1D) ^2D$	0.1984	0	0.1002	6.9437	0	152.7603
$(^3F) ^2D$	$(^1G) ^2D$	-0.0537	-0.0836	0.0937	-1.8804	-26.3249	142.9065
$(^3F) ^4D$	$(^3F) ^4D$	0.0857	-0.1206	-0.1587	3	-38	-242
$(^3F) ^2F$	$(^3F) ^2F$	-0.0429	0.0418	0.0709	-1.5	13.1667	108.1667
$(^3F) ^2F$	$(^3H) ^2F$	0	0.0663	0.024	0	20.8928	36.5624
$(^3F) ^2F$	$(^1D) ^2F$	-0.2592	-0.0552	0.0886	-9.0711	-17.3864	135.1223
$(^3F) ^2F$	$(^1G) ^2F$	0.1551	-0.0172	0.1032	5.4281	-5.4281	157.4149
$(^3F) ^4F$	$(^3F) ^4F$	0.0857	-0.0836	-0.1419	3	-26.3333	-216.3333
$(^3F) ^4F$	$(^3H) ^4F$	0	-0.1327	-0.048	0	-41.7855	-73.1247
$(^3F) ^2G$	$(^3F) ^2G$	0.2238	0.0122	0.0373	7.8333	3.8333	56.8333
$(^3F) ^2G$	$(^3H) ^2G$	-0.0632	-0.0281	0.0214	-2.2111	-8.8443	32.6135
$(^3F) ^2G$	$(^1D) ^2G$	-0.3117	0	0.0354	-10.9109	0	54.0089
$(^3F) ^2G$	$(^1G) ^2G$	-0.1458	-0.0798	0.0661	-5.1025	-25.1346	100.7275
$(^3F) ^2G$	$(^1I) ^2G$	0.0841	0.0841	0.0087	2.9439	26.4953	13.2476
$(^3F) ^4G$	$(^3F) ^4G$	-0.4476	-0.0243	-0.0746	-15.6667	-7.6667	-113.6667
$(^3F) ^4G$	$(^3H) ^4G$	0.1263	0.0562	-0.0428	4.4222	17.6887	-65.227
$(^3F) ^2H$	$(^3F) ^2H$	0.1286	0.0624	0.0083	4.5	19.6667	12.6667
$(^3F) ^2H$	$(^3H) ^2H$	0.2185	-0.0378	0.0089	7.6485	-11.8977	13.5974
$(^3F) ^2H$	$(^1G) ^2H$	-0.3954	0.0315	0.0209	-13.8392	9.9224	31.8562
$(^3F) ^2H$	$(^1I) ^2H$	-0.1743	-0.0129	0.0053	-6.1014	-4.0676	8.1352
$(^3F) ^4H$	$(^3F) ^4H$	-0.2571	-0.1249	-0.0166	-9	-39.3333	-25.3333
$(^3F) ^4H$	$(^3H) ^4H$	-0.4371	0.0755	-0.0178	-15.2971	23.7954	-27.1948
$(^3H) ^2F$	$(^3H) ^2F$	-0.0061	-0.0239	0.1299	-0.2143	-7.5238	198.1191

**Table 2.** (Continued.)

(S <sub>1</sub> L <sub>1</sub> ) SL	(S' <sub>1</sub> L' <sub>1</sub> ) S'L'	g <sub>1</sub> (fd)	g <sub>3</sub> (fd)	g <sub>5</sub> (fd)	g' <sub>1</sub> (fd)	g' <sub>3</sub> (fd)	g' <sub>5</sub> (fd)
( <sup>3</sup> H) <sup>2</sup> F	( <sup>1</sup> D) <sup>2</sup> F	0.1015	0.1203	0.0132	3.5535	37.9043	20.1367
( <sup>3</sup> H) <sup>2</sup> F	( <sup>1</sup> G) <sup>2</sup> F	-0.0283	0.0031	0.109	-0.9897	0.9897	166.1531
( <sup>3</sup> H) <sup>4</sup> F	( <sup>3</sup> H) <sup>4</sup> F	0.0122	0.0478	-0.2599	0.4286	15.0476	-396.2381
( <sup>3</sup> H) <sup>2</sup> G	( <sup>3</sup> H) <sup>2</sup> G	0.0333	0.0466	0.088	1.1667	14.6667	134.1667
( <sup>3</sup> H) <sup>2</sup> G	( <sup>1</sup> D) <sup>2</sup> G	-0.2585	0	0.0107	-9.0468	0	16.2843
( <sup>3</sup> H) <sup>2</sup> G	( <sup>1</sup> G) <sup>2</sup> G	0.0586	-0.0861	0.0895	2.0513	-27.1226	136.4678
( <sup>3</sup> H) <sup>2</sup> G	( <sup>1</sup> I) <sup>2</sup> G	0.0127	0.0761	0.1022	0.4438	23.9659	155.7783
( <sup>3</sup> H) <sup>4</sup> G	( <sup>3</sup> H) <sup>4</sup> G	-0.0667	-0.0931	-0.176	-2.3333	-29.3333	-268.3333
( <sup>3</sup> H) <sup>2</sup> H	( <sup>3</sup> H) <sup>2</sup> H	-0.0857	0.0201	0.0432	-3	6.3333	65.8334
( <sup>3</sup> H) <sup>2</sup> H	( <sup>1</sup> G) <sup>2</sup> H	0.038	-0.0676	0.0437	1.3314	-21.303	66.5719
( <sup>3</sup> H) <sup>2</sup> H	( <sup>1</sup> I) <sup>2</sup> H	-0.0684	-0.157	0.0625	-2.3932	-49.4589	95.328
( <sup>3</sup> H) <sup>4</sup> H	( <sup>3</sup> H) <sup>4</sup> H	0.1714	-0.0402	-0.0864	6	-12.6667	-131.6667
( <sup>3</sup> H) <sup>2</sup> I	( <sup>3</sup> H) <sup>2</sup> I	0.0857	0.0698	0.0134	3	22	20.5
( <sup>3</sup> H) <sup>2</sup> I	( <sup>1</sup> G) <sup>2</sup> I	-0.4786	0.0532	0.011	-16.7522	16.7522	16.7522
( <sup>3</sup> H) <sup>2</sup> I	( <sup>1</sup> I) <sup>2</sup> I	0.2238	-0.0249	0.0231	7.8335	-7.8335	35.2507
( <sup>3</sup> H) <sup>4</sup> I	( <sup>3</sup> H) <sup>4</sup> I	-0.1714	-0.1397	-0.0269	-6	-44	-41
( <sup>3</sup> H) <sup>2</sup> K	( <sup>3</sup> H) <sup>2</sup> K	0.2857	0.0476	0.002	10	15	2.9999
( <sup>3</sup> H) <sup>2</sup> K	( <sup>1</sup> I) <sup>2</sup> K	-0.4949	0.055	0.0045	-17.3205	17.3205	6.9282
( <sup>3</sup> H) <sup>4</sup> K	( <sup>3</sup> H) <sup>4</sup> K	-0.5714	-0.0952	-0.0039	-20	-30	-6
( <sup>1</sup> S) <sup>2</sup> D	( <sup>1</sup> S) <sup>2</sup> D	-0.0857	-0.0381	-0.0433	-3	-12	-66
( <sup>1</sup> S) <sup>2</sup> D	( <sup>1</sup> D) <sup>2</sup> D	-0.1587	0.0323	-0.0334	-5.5549	10.184	-50.9201
( <sup>1</sup> S) <sup>2</sup> D	( <sup>1</sup> G) <sup>2</sup> D	-0.1074	-0.0478	-0.0025	-3.7607	-15.0428	-3.7607
( <sup>1</sup> D) <sup>2</sup> S	( <sup>1</sup> D) <sup>2</sup> S	-0.1714	-0.0603	-0.0361	-6	-19	-55
( <sup>1</sup> D) <sup>2</sup> P	( <sup>1</sup> D) <sup>2</sup> P	0.1429	0	-0.0541	5	0	-82.5
( <sup>1</sup> D) <sup>2</sup> D	( <sup>1</sup> D) <sup>2</sup> D	-0.0122	-0.0712	-0.0747	-0.4286	-22.4286	-113.9286
( <sup>1</sup> D) <sup>2</sup> D	( <sup>1</sup> G) <sup>2</sup> D	0.0497	-0.0332	-0.0228	1.7409	-10.4452	-34.8173
( <sup>1</sup> D) <sup>2</sup> F	( <sup>1</sup> D) <sup>2</sup> F	-0.2143	0	-0.0541	-7.5	0	-82.5
( <sup>1</sup> D) <sup>2</sup> F	( <sup>1</sup> G) <sup>2</sup> F	0	0	-0.0283	0	0	-43.0842
( <sup>1</sup> D) <sup>2</sup> G	( <sup>1</sup> D) <sup>2</sup> G	-0.0932	-0.0596	-0.0146	-3.2619	-18.7619	-22.2619
( <sup>1</sup> D) <sup>2</sup> G	( <sup>1</sup> G) <sup>2</sup> G	-0.2121	0.0497	-0.0153	-7.4231	15.6709	-23.3002
( <sup>1</sup> D) <sup>2</sup> G	( <sup>1</sup> I) <sup>2</sup> G	-0.0459	-0.0204	-0.0011	-1.606	-6.4242	-1.606
( <sup>1</sup> G) <sup>2</sup> D	( <sup>1</sup> G) <sup>2</sup> D	-0.002	0.0331	-0.0955	-0.0714	10.4286	-145.5714
( <sup>1</sup> G) <sup>2</sup> F	( <sup>1</sup> G) <sup>2</sup> F	-0.0143	-0.0778	-0.0889	-0.5	-24.5	-135.5
( <sup>1</sup> G) <sup>2</sup> G	( <sup>1</sup> G) <sup>2</sup> G	0.0941	-0.0173	-0.0588	3.2922	-5.4351	-89.7078
( <sup>1</sup> G) <sup>2</sup> G	( <sup>1</sup> I) <sup>2</sup> G	-0.026	-0.0678	-0.0185	-0.9104	-21.3436	-28.1715
( <sup>1</sup> G) <sup>2</sup> H	( <sup>1</sup> G) <sup>2</sup> H	-0.1935	-0.0384	-0.0239	-6.7727	-12.0909	-36.3636
( <sup>1</sup> G) <sup>2</sup> H	( <sup>1</sup> I) <sup>2</sup> H	0.091	0.0405	-0.0125	3.1864	12.7454	-19.1182
( <sup>1</sup> G) <sup>2</sup> I	( <sup>1</sup> G) <sup>2</sup> I	-0.1896	-0.0583	-0.0044	-6.6364	-18.3636	-6.6364
( <sup>1</sup> G) <sup>2</sup> I	( <sup>1</sup> I) <sup>2</sup> I	-0.1785	0.0198	-0.0041	-6.249	6.249	-6.249
( <sup>1</sup> I) <sup>2</sup> G	( <sup>1</sup> I) <sup>2</sup> G	-0.0009	-0.0105	-0.1699	-0.0303	-3.303	-259.0303
( <sup>1</sup> I) <sup>2</sup> H	( <sup>1</sup> I) <sup>2</sup> H	0.0078	0.0511	-0.0768	0.2727	16.0909	-117.1364
( <sup>1</sup> I) <sup>2</sup> I	( <sup>1</sup> I) <sup>2</sup> I	-0.039	-0.075	-0.0261	-1.3636	-23.6364	-39.8637
( <sup>1</sup> I) <sup>2</sup> K	( <sup>1</sup> I) <sup>2</sup> K	0.1429	-0.0952	-0.0059	5	-30	-9
( <sup>1</sup> I) <sup>2</sup> L	( <sup>1</sup> I) <sup>2</sup> L	-0.4286	-0.0317	-0.0007	-15	-10	-1

The reduced matrix elements of the double tensor operator in the above two equations can be further expanded as

$$\begin{aligned}
& {}_{\text{NA}} \langle (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) S L \| \mathbf{V}_f^{(11)} \| (f^{N-1} \alpha'_1 S'_1 L'_1, s_d l_d) S' L' \rangle_{\text{NA}} \\
& = (-1)^{S_1+s_d+S'+L_1+l_d+L'} [(2S+1)(2S'+1)(2L+1)(2L'+1)]^{1/2}
\end{aligned}$$



$$\times \begin{Bmatrix} S_1 & s_d & S \\ S' & 1 & S'_1 \end{Bmatrix} \begin{Bmatrix} L_1 & l_d & L \\ L' & 1 & L'_1 \end{Bmatrix} \langle f^{N-1} \alpha_1 S_1 L_1 \| \mathbf{V}_f^{(11)} \| f^{N-1} \alpha'_1 S'_1 L'_1 \rangle \quad (18)$$

and

$$\begin{aligned} & \text{NA} \langle (f^{N-1} S_1 L_1, s_d l_d) S L \| \mathbf{v}_d^{(11)} \| (f^{N-1} S'_1 L'_1, s_d l_d) S' L' \rangle_{\text{NA}} \\ &= \delta_{\alpha_1 S_1 L_1, \alpha'_1 S'_1 L'_1} (-1)^{S_1 + s_d + S + L_1 + l_d + L} [(2S + 1)(2S' + 1)(2L + 1)(2L' + 1)]^{1/2} \\ & \times \begin{Bmatrix} S_1 & s_d & S \\ 1 & S' & s_d \end{Bmatrix} \begin{Bmatrix} L_1 & l_d & L \\ 1 & L' & l_d \end{Bmatrix} \langle s_d l_d \| \mathbf{v}_d^{(11)} \| s_d l_d \rangle, \end{aligned} \quad (19)$$

where the values for the reduced matrix elements  $\langle f^{N-1} \alpha_1 S_1 L_1 \| \mathbf{V}_f^{(11)} \| f^{N-1} \alpha'_1 S'_1 L'_1 \rangle$  can be found in [2], and  $\langle s_d l_d \| \mathbf{v}_d^{(11)} \| s_d l_d \rangle = (\frac{3}{2})^{1/2}$ . Note that both the reduced matrix elements (18) and (19) of  $\mathbf{V}_f^{(11)}$  and  $\mathbf{v}_d^{(11)}$  are  $(S, L)$  dependent. In addition,

$$\begin{aligned} & \langle (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) S L J M | H_{\text{SO}} | (f^{N-1} \alpha'_1 S'_1 L'_1, s_d l_d) S' L' J M \rangle \\ &= \langle (f^{N-1} \alpha'_1 S'_1 L'_1, s_d l_d) S' L' J M | H_{\text{SO}} | (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) S L J M \rangle. \end{aligned} \quad (20)$$

**2.1.3. Matrix elements of the crystal–field interaction  $H_{\text{CF}}$ .** The matrix elements of the Hamiltonian  $H_{\text{CF}}$  are given by

$$\begin{aligned} & \langle (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) S L J M | H_{\text{CF}} | (f^{N-1} \alpha'_1 S'_1 L'_1, s_d l_d) S' L' J' M' \rangle \\ &= \sum_{k_1 q_1} B_{q_1}^{k_1}(f) \cdot d_{q_1}^{k_1}(f) + \sum_{k_2 q_2} B_{q_2}^{k_2}(d) \cdot d_{q_2}^{k_2}(d), \end{aligned} \quad (21)$$

where  $d_{q_1}^{k_1}(f)$  and  $d_{q_2}^{k_2}(d)$  are the angular parts of the matrix elements of the crystal–field interactions for  $f$  electrons and  $d$  electrons respectively. The crystal–field parameters  $B_{q_1}^{k_1}(f)$  and  $B_{q_2}^{k_2}(d)$  and are generally taken as fitting parameters. The two matrix elements of the spherical tensor operators may be further expanded as follows:

$$\begin{aligned} d_{q_1}^{k_1}(f) &= (N - 1) \cdot \text{NA} \langle (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) S L J M | c_{q_1}^{(k_1)}(f) | (f^{N-1} \alpha'_1 S'_1 L'_1, s_d l_d) S' L' J' M' \rangle_{\text{NA}} \\ &= \text{NA} \langle (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) S L J M | C_{q_1}^{(k_1)}(f) | (f^{N-1} \alpha'_1 S'_1 L'_1, s_d l_d) S' L' J' M' \rangle_{\text{NA}} \\ &= (-1)^{J-M} \begin{pmatrix} J & k_1 & J' \\ -M & q_1 & M' \end{pmatrix} \\ & \times \text{NA} \langle (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) S L J \| C^{(k_1)}(f) \| (f^{N-1} \alpha'_1 S'_1 L'_1, s_d l_d) S' L' J' \rangle_{\text{NA}} \\ &= \delta_{S, S'} (-1)^{J-M+S+L'+J+k_1} \\ & \times [(2J + 1)(2J' + 1)]^{1/2} \begin{pmatrix} J & k_1 & J' \\ -M & q_1 & M' \end{pmatrix} \begin{Bmatrix} S & L & J \\ k_1 & J' & L' \end{Bmatrix} \\ & \times \text{NA} \langle (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) S L \| C^{(k_1)}(f) \| (f^{N-1} \alpha'_1 S'_1 L'_1, s_d l_d) S L' \rangle_{\text{NA}} \end{aligned} \quad (22)$$

and, in a similar way,

$$\begin{aligned} d_{q_2}^{k_2}(d) &= \text{NA} \langle (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) S L J M | c_{q_2}^{(k_2)}(d) | (f^{N-1} \alpha'_1 S'_1 L'_1, s_d l_d) S' L' J' M' \rangle_{\text{NA}} \\ &= \delta_{S, S'} (-1)^{J-M+S+L'+J+k_2} \\ & \times [(2J + 1)(2J' + 1)]^{1/2} \begin{pmatrix} J & k_2 & J' \\ -M & q_2 & M' \end{pmatrix} \begin{Bmatrix} S & L & J \\ k_2 & J' & L' \end{Bmatrix} \\ & \times \text{NA} \langle (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) S L \| c^{(k_2)}(d) \| (f^{N-1} \alpha'_1 S'_1 L'_1, s_d l_d) S L' \rangle_{\text{NA}}. \end{aligned} \quad (23)$$

The two reduced matrix elements in the above two expressions can be expressed as:

$$\text{NA} \langle (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) S L \| C^{(k_1)}(f) \| (f^{N-1} \alpha'_1 S'_1 L'_1, s_d l_d) S L' \rangle_{\text{NA}}$$

$$\begin{aligned}
&= (-1)^{L_1+l_d+L'+k_1} [(2L+1)(2L'+1)]^{1/2} \begin{Bmatrix} L_1 & l_d & L \\ L' & k_1 & L'_1 \end{Bmatrix} \langle I_f \| c^{k_1}(f) \| I_f \rangle \\
&\quad \times \langle f^{N-1} \alpha_1 S_1 L_1 \| U^{(k_1)}(f) \| f^{N-1} \alpha'_1 S'_1 L'_1 \rangle
\end{aligned} \tag{24}$$

and

$$\begin{aligned}
&{}_{\text{NA}} \langle (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) SL \| c^{(k_2)}(d) \| (f^{N-1} \alpha'_1 S'_1 L'_1, s_d l_d) SL' \rangle_{\text{NA}} \\
&= \delta_{\alpha_1 S_1 L_1, \alpha'_1 S'_1 L'_1} (-1)^{L_1+l_d+L+k_2} [(2L+1)(2L'+1)]^{1/2} \\
&\quad \times \begin{Bmatrix} L_1 & l_d & L \\ k_2 & L' & l_d \end{Bmatrix} \langle I_d \| c^{(k_2)}(d) \| I_d \rangle
\end{aligned} \tag{25}$$

where the values of the reduced matrix elements of the unit tensor operator  $U^{(k_1)}(f)$  are listed in [2];  $\langle I_f \| c^{(k_1)}(f) \| I_f \rangle = -7 \cdot \begin{pmatrix} 3 & k_1 & 3 \\ 0 & 0 & 0 \end{pmatrix}$  and  $\langle I_d \| c^{(k_2)}(d) \| I_d \rangle = 5 \cdot \begin{pmatrix} 2 & k_2 & 2 \\ 0 & 0 & 0 \end{pmatrix}$ . By combining the expressions (22)–(25), the angular parts of the matrix elements of the crystal-field Hamiltonian  $H_C$ , can be calculated straightforwardly.

## 2.2. Matrix elements of $f^N \rightarrow f^{N-1}d$ transitions

The transition matrix element of the electric dipole operator  $D_q^{(1)}$  between the initial  $f^N$  state  $|f^N \Gamma' \gamma' \rangle$  and the final  $f^{N-1}d$  state  $|f^{N-1} d \Gamma \gamma \rangle$  can be expressed as

$$\begin{aligned}
&\langle f^N \Gamma' \gamma' | D_q^{(1)} | f^{N-1} d \Gamma \gamma \rangle \\
&= \sum_{\eta' S' L' J' M'} \sum_{S_1 L_1 SLJM} a_{\Gamma' \gamma'}(\eta' S' L' J' M') a_{\Gamma \gamma}(\alpha_1 S_1 L_1 SLJM) \\
&\quad \times \langle f^N \eta' S' L' J' M' | D_q^{(1)} | (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) SLJM \rangle.
\end{aligned} \tag{26}$$

The transition matrix element between the basis states of  $f^N$  and  $f^{N-1}d$  configurations can be written as

$$\begin{aligned}
&\langle f^N \eta' S' L' J' M' | D_q^{(1)} | (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) SLJM \rangle \\
&= \langle f^N \eta' S' L' J' M' | \sum_{i=1}^N r_i c_q^{(1)}(i) | (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) SLJM \rangle \\
&= \frac{N}{\sqrt{N}} \langle f^N \eta' S' L' J' M' | r_N c_q^{(1)}(N) | (f^{N-1} S_1 L_1, s_d l_d) SLJM \rangle_{\text{NA}},
\end{aligned} \tag{27}$$

where the electric dipole operator  $D_q^{(1)}$  is expressed in terms of the spherical tensor operator  $c_q^{(1)}(N)$  acting on the state of the  $N$ th electron, which is the d electron of the non-antisymmetric  $f^{N-1}d$  states. The factor  $1/\sqrt{N}$  in the last step relates to the probability  $1/N$  that the  $N$ th electron occupies the d state while the other  $(N-1)$  electrons occupy the  $f^{N-1}$  states. The matrix element can be further expanded as follows:

$$\begin{aligned}
&\langle f^N \eta' S' L' J' M' | r_N c_q^{(1)}(N) | (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) SLJM \rangle_{\text{NA}} \\
&= (-1)^{J'-M'} \begin{pmatrix} J' & 1 & J \\ -M' & q & M \end{pmatrix} \\
&\quad \times \langle f^N \eta' S' L' J' \| r_N c^{(1)}(N) \| (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) SLJ \rangle_{\text{NA}} \\
&= \delta_{S'S} (-1)^{2J'-M'+S+L+1} [(2J'+1)(2J+1)]^{1/2} \begin{pmatrix} J' & 1 & J \\ -M' & q & M \end{pmatrix} \begin{Bmatrix} S & L' & J' \\ 1 & J & L \end{Bmatrix} \\
&\quad \times \langle f^N \eta' S' L' \| r_N c^{(1)}(N) \| (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) SL \rangle_{\text{NA}} \\
&= \delta_{S'S} (-1)^{2J'-M'+S+L+1} [(2J'+1)(2J+1)]^{1/2}
\end{aligned}$$

$$\begin{aligned}
& \times \begin{pmatrix} J' & 1 & J \\ -M' & q & M \end{pmatrix} \begin{Bmatrix} S & L' & J' \\ 1 & J & L \end{Bmatrix} \sum_{\bar{\alpha}\bar{S}\bar{L}} \langle f^N \eta' SL' \{ | f^{N-1} \bar{\alpha} \bar{S} \bar{L} \rangle \\
& \times \text{NA} \langle (f^{N-1} \bar{\alpha} \bar{S} \bar{L}, s_f l_f) \eta' SL' \| r_N c^{(1)}(N) \| (f^{N-1} \alpha_1 S_1 L_1, s_d l_d) SL \rangle_{\text{NA}} \\
& = \delta_{S'S} (-1)^{2J'-M'+S+L+J+1} [(2J'+1)(2J+1)]^{1/2} \\
& \times \begin{pmatrix} J' & 1 & J \\ -M' & q & M \end{pmatrix} \begin{Bmatrix} S & L' & J' \\ 1 & J & L \end{Bmatrix} \\
& \times \langle f^N \eta' SL' \{ | f^{N-1} \alpha_1 S_1 L_1 \rangle \langle f | r | d \rangle (-1)^{L_1+l_d+L'+1} \\
& \times [(2L'+1)(2L+1)]^{1/2} \begin{Bmatrix} L_1 & l_f & L' \\ 1 & L & l_d \end{Bmatrix} \langle l_f \| c^{(1)} \| l_d \rangle \\
& = \delta_{S'S} (-1)^{2J'-M'+S+L+J+L_1+l_d+L'} [(2J'+1)(2J+1)(2L'+1)(2L+1)]^{1/2} \\
& \times \begin{pmatrix} J' & 1 & J \\ -M' & q & M \end{pmatrix} \begin{Bmatrix} S & L' & J' \\ 1 & J & L \end{Bmatrix} \\
& \times \begin{Bmatrix} L_1 & l_f & L' \\ 1 & L & l_d \end{Bmatrix} \langle f^N \eta' SL' \{ | f^{N-1} \alpha_1 S_1 L_1 \rangle \langle f | r | d \rangle \langle l_f \| c^{(1)} \| l_d \rangle, \quad (28)
\end{aligned}$$

where  $l_f = 3$ , and the subscript ‘NA’ in the third step means that the wavefunction is non-antisymmetric with respect to exchange between any one of the  $(N-1)$  electrons of  $f^{N-1}$  core and the  $N$ th  $f$  electron denoted by  $s_f l_f$ , and  $\langle l_f \| c^{(1)} \| l_d \rangle = \sqrt{3}$ . The values of cfps are available in [2]. By combining equations (26)–(28), the electric dipole matrix element between  $f^N$  states and  $f^{N-1}d$  states can be evaluated easily, while the radial integral  $\langle f | r | d \rangle$  can be kept as a fitting parameter, or omitted if only the relative transition intensities are of interest.

### 3. Results and discussion

#### 3.1. Calculation of energy levels

Our calculation of the energy levels of the  $5f^26d$  configuration of  $U^{3+}$  in  $LiYF_4$  has used the extended program of Reid, in which the electronic energy levels for the  $5f^26d$  configuration were calculated by simultaneous diagonalization of the various Hamiltonians in equation (1), and the relevant formulae have been given in detail in section 2, based on Cowan’s book [11].  $LiYF_4$  crystallizes in the tetragonal space group  $I4_1/a$ , with  $Z = 4$  [13]. In this host, the  $U^{3+}$  ions occupy the  $S_4$  site of  $Y^{3+}$ , although the slightly distorted dodecahedral coordination is well-approximated by  $D_{2d}$  [10], so that then the crystal field parameters required to fit the  $5f^3$  energy levels are all real.

The parameters for Coulomb interaction between the  $5f$  electrons, spin–orbit interaction and other small atomic interactions are needed for the calculations, as well as the crystal–field interaction parameters for the  $5f$  electrons. The values for these parameters have been determined from fits of the experimentally observed positions of the  $5f^3$  energy levels of  $U^{3+}$  in  $LiYF_4$  [10]. In addition, the energy-level calculations of  $5f^26d$  levels require crystal–field and spin–orbit parameters for the  $6d$  electron of  $U^{3+}$  in  $LiYF_4$ , which are not available in the literature. Finally, the Coulomb interactions between the  $5f$  electrons and the  $6d$  electron have to be included. These  $f$ – $d$  interaction parameters can be obtained from *ab initio* calculations using standard atomic computer programs [11]. In addition to the splitting into many energy levels due to interactions within the  $5f^26d$  configuration, the position of the energy levels is determined also by the difference  $\Delta_E(fd)$  between the average energies of the  $5f^26d$  and  $5f^3$  configurations, since the energy levels of the  $5f^3$  and  $5f^26d$  configurations are simultaneously calculated in the model. This energy difference comprises several sources, including kinetic

energy, Coulomb and (isotropic) crystal–field effects. The influence of  $\Delta_E(\text{fd})$  is to shift all the  $5f^26d$  energy levels by the same amount relative to the ground state, and  $\Delta_E(\text{fd})$  is adjusted to obtain the best agreement between calculation and experiment.

In our calculations on the  $5f^26d$  states of U<sup>3+</sup> in LiYF<sub>4</sub>, the atomic and crystal–field parameters of the  $5f^3$  ground configuration [10] were used. This is only an approximation since there is not enough information to test the effect of varying these parameters from the  $5f^3$  values. The crystal–field parameters of the 6d electron were approximated to be the same as those of the 5d electron of Ce<sup>3+</sup> in LiYF<sub>4</sub>. The use of this approximation may be justified by the fact that the crystal–field splitting of the 6d electron may be slightly smaller than the lower energy limit of the crystal–field splitting of the 5d electron [14] and, second, the good agreement of our calculation with experiment. The atomic parameters calculated from the standard atomic computer programs [11] were used for the f–d Coulomb interaction and the spin–orbit interaction of the 6d electron. Due to the delocalizations of the 5f and 6d electrons over the ligands in a crystalline host, the f–d Coulomb interaction parameters can be expected to be reduced from the free ion values in a similar manner to the reductions of f–d Coulomb interaction parameters of lanthanide ions (the nephelauxetic effect) [3, 4]. Thus, our calculations were performed with the  $F^k(\text{fd})$  and  $G^k(\text{fd})$  as adjustable parameters, and the best agreement was obtained between calculation and experiment when the f–d interaction parameters were reduced to ~33% of the calculated free ion values. The amount of reduction (~67%) is much larger than the value 26% used for the isoelectronic Nd<sup>3+</sup> lanthanide ion in the same host [3], at least partly because the 5f and 6d orbitals have larger extensions with respect to 4f and 5d orbitals. The energy parameters used in the calculation of the  $5f^26d$  energy levels are collected in table 3.

### 3.2. Simulation of the $5f^3 \rightarrow 5f^26d$ spectrum

The electronic ground state of the  $5f^3$  configuration of U<sup>3+</sup> in LiYF<sub>4</sub> transforms as the irrep  $\Gamma_6$  of the molecular point group  $D_{2d}$  [10]. The transitions from  $5f^3$  to  $5f^26d$  are all electric dipole allowed and the electric dipole matrix elements for the transitions can be calculated using the formulae displayed in section 2.2 in the case of  $N = 3$ . Because the 6d orbital is more extended than the 5f orbitals, there is a displacement of the equilibrium positions of the ligands in the excited states and most of the intensity is located in a broad vibronic band [15]. In the simulation of the unpolarized absorption spectrum of U<sup>3+</sup> in LiYF<sub>4</sub>, we made the approximation that the oscillator strengths of the vibronic bands are proportional to the electric dipole transition line strength  $S$  between the ground  $5f^3$  states  $|f^3\Gamma'\gamma'\rangle$  and the final  $5f^26d$  states  $|f^2d\Gamma\gamma\rangle$ , multiplied by the transition wavenumber  $\sigma$  of the zero-phonon line. The line strength  $S$  is the sum of its components as

$$S = \sum_q S_q \quad (q = 1, 0, -1) \quad (29)$$

where

$$S_q = \sum_{\gamma'\gamma} | \langle f^3\Gamma'\gamma' | D_q^1 | f^2d\Gamma\gamma \rangle |^2 \quad (30)$$

and the explicit expression for the matrix element has been given in section 2.2. There are many vibrational modes for LiYF<sub>4</sub> crystals [16] and the spectra contain superpositions of several vibronic progressions [15], giving rather featureless vibronic bands. Therefore, we assume that superposition of several side bands corresponding to progressions in different vibrational modes gives rise to a Gaussian shape of the vibronic band. The energy-level calculations are performed to generate the zero-phonon line positions. To reproduce the experimentally

**Table 3.** Energy parameters for the  $5f^26d$  configuration of  $U^{3+}$  in  $LiYF_4$ . Parameters for the splitting of the  $5f^2$  core (such as the parameters for Coulomb interaction, spin-orbit interaction and crystal-field splitting) are obtained from the literature [10]. The spin-orbit interaction parameter of the  $6d$  electron is calculated using Cowan's code [11], and the parameters for the crystal-field splitting of the  $6d$  state are derived from those of the  $5d$  states of  $Ce^{3+}$  in  $LiYF_4$  [3]. Refer to the text for further details.

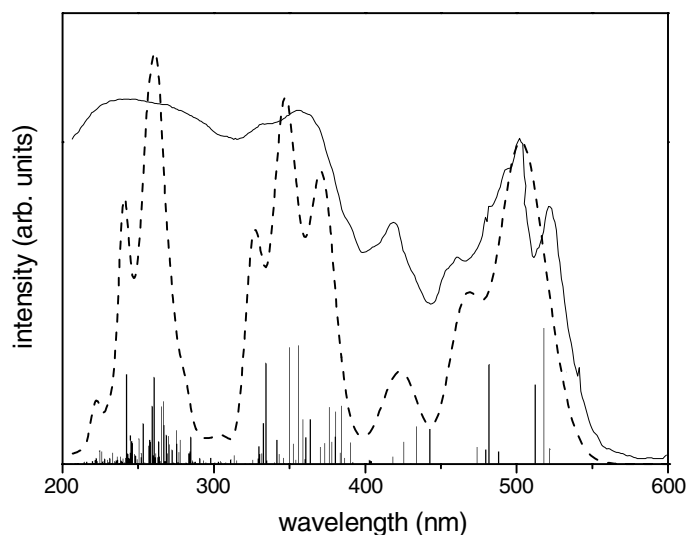
Parameters	( $cm^{-1}$ )
$F^2(ff)$	$35\ 055^{10}$
$F^4(ff)$	$29\ 334^{10}$
$F^6(ff)$	$19\ 186^{10}$
$\zeta_f$	$1642^{10}$
$\alpha(f)$	$23^{10}$
$\beta(f)$	$-852^{10}$
$\gamma(f)$	$1070^{10}$
$M^0(f)^a$	$0.7^{10}$
$P^2(f)^b$	$1216^{10}$
$B_0^2(f)$	$420^{10}$
$B_0^4(f)$	$-2458^{10}$
$B_4^4(f)$	$-2845^{10}$
$B_0^6(f)$	$93^{10}$
$B_4^6(f)$	$-3280^{10}$
$\zeta_d$	$2714^{11}$
$B_0^2(d)$	$4673^3$
$B_0^4(d)$	$-18\ 649^3$
$B_4^4(d)$	$-23\ 871^3$
$\Delta_E(fd)$	$24\ 383$
$F^2(fd)$	$11\ 516$
$F^4(fd)$	$6365$
$G^1(fd)$	$6757$
$G^3(fd)$	$5177$
$G^5(fd)$	$3939$

<sup>a</sup>  $M^2$  and  $M^4$  parameters were included with the ratios  $M^2/M^0 = 0.56$  and  $M^4/M^0 = 0.31$ .

<sup>b</sup>  $P^4$  and  $P^6$  parameters were included with the ratios  $P^4/P^2 = 0.5$  and  $P^6/P^2 = 0.1$ .

observed spectrum, Gaussian shaped bands are superimposed on the zero-phonon lines, with the maximum displacement from the zero-phonon line (by an increase) of  $400\ cm^{-1}$ , with width (full width at half-maximum (FWHM))  $1200\ cm^{-1}$ , and with the oscillator strength proportional to  $S\sigma$  calculated for the zero-phonon line. The above values of displacement and width are estimated from the excitation spectrum of  $Ce^{3+}$  in  $LiYF_4$  [17], of which the width of all the  $4f \rightarrow 5d$  bands is approximately  $1200\ cm^{-1}$ , and the peak of the first band is offset from the zero-phonon line by  $400\ cm^{-1}$ .

The simulated spectrum of  $U^{3+}$  in  $LiYF_4$  is shown as the dashed curve in figure 1, whereas the solid curve is the experimental spectrum from [9]. The calculated positions and relative oscillator strengths of zero-phonon lines are indicated by vertical lines. The agreement between the simulated spectrum and the experimentally observed spectrum is quite good. The splitting and intensity pattern of the low-energy region (400–600 nm) is explained well by the calculation. The lowest peak in the experimentally observed spectrum is not reproduced by the simulated spectrum, but when the width of the Gaussian shaped band is reduced to  $400\ cm^{-1}$ , this peak shows clearly. For the high-energy region (200–400 nm) an exact comparison cannot be made between calculation and experiment, since the fine structure is not present in the observed spectrum. This is attributed to peak overlap of the vibrational



**Figure 1.** Experimental (solid curve from [9]) and simulated  $5f^3 \rightarrow 5f^26d$  absorption spectrum of  $U^{3+}$  in  $LiYF_4$ . The vertical lines are the predicted positions of zero-phonon lines, with heights proportional to predicted intensities, and the dashed curve is a simulated spectrum of the vibronic bands.

progressions based upon numerous zero-phonon lines, so that broad unresolved bands result. However, the calculated results do appear to be consistent with experiment, with a minimum intensity at around 300 nm.

#### 4. Conclusions

Energy-level calculations for the  $5f^26d$  configuration of  $U^{3+}$  in  $LiYF_4$  have been performed using the extended model developed by Reid [17] for the calculation of the  $4f^{N-1}5d$  energy levels, and the  $5f^3 \rightarrow 5f^26d$  absorption spectrum has been simulated. For the  $f^{N-1}d$  configuration, the matrix elements of the Hamiltonians  $H_C$ ,  $H_{SO}$  and  $H_{CF}$  between  $f^{N-1}d$  basis states, and the  $f^N \rightarrow f^{N-1}d$  electric dipole transition matrix elements have been expressed in detail, using the irreducible tensor operator formalism described in [11]. The direct and exchange coefficients of f–d Coulomb interaction within the  $f^2d$  configuration have also been calculated and tabulated. The calculated absorption spectrum is consistent with the experimentally observed 10 K spectrum [9]. The energy parameters for the f–d Coulomb interactions within the  $5f^26d$  configuration of  $U^{3+}$  in  $LiYF_4$  are reduced to  $\sim 33\%$  of the free-ion values calculated by the standard atomic programs [11]. The amount of reduction ( $\sim 67\%$ ) is much larger than the value of 26% for the isoelectronic  $Nd^{3+}$  lanthanide ion in the same host [3].

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