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X. Shangda, G.M. Williams, and N.M. Edelstein

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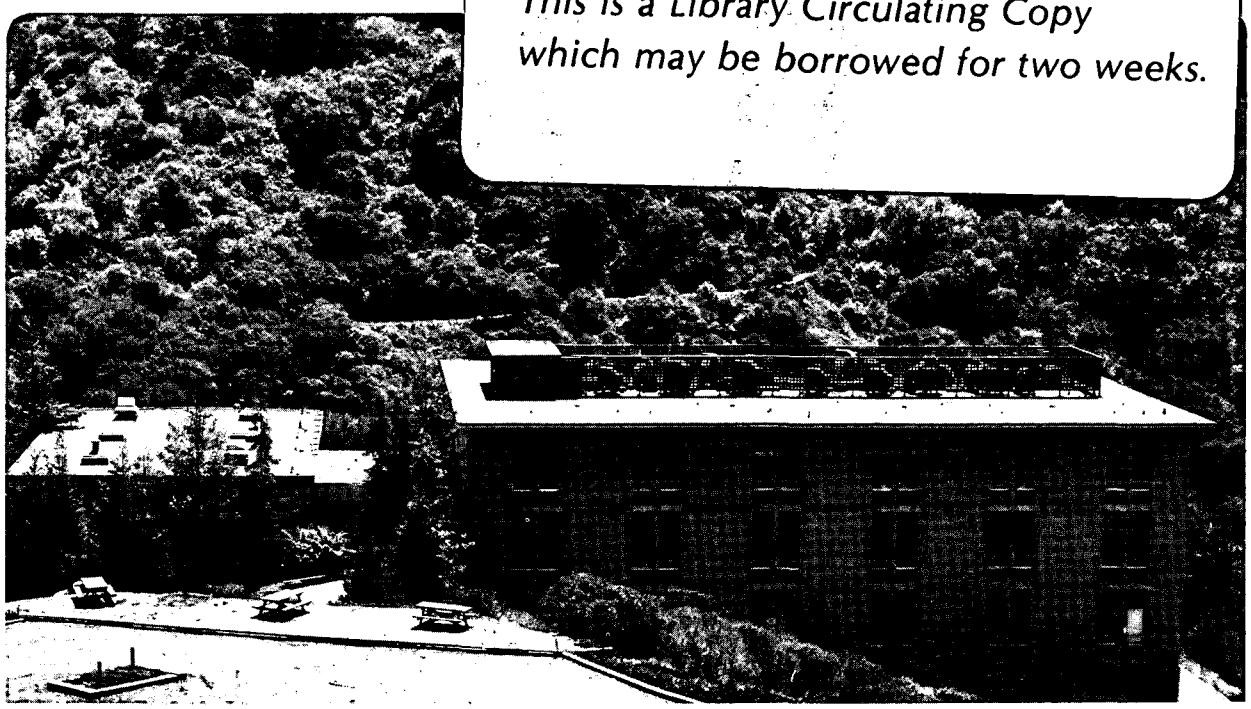

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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LBL-26122

Contributions of the Energy Level Structure of the $4f^{11}5d^1$ Intermediate Configuration to the Electronic Raman Scattering Intensities of $TmPO_4$

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Abstract

We present a direct calculation of electronic Raman scattering intensities of $TmPO_4$ by considering the detailed energy structure of the intermediate configuration $4f^{11}5d^1$. The calculated relative intensities for 24 electronic Raman transitions are improved (as compared to the experimental results) and the scattering intensities are about five times larger than the predictions of the Judd-Ofelt-Axe theory when the same value of the radial factor $|\langle 4f|r|5d\rangle|^2$ is used. The asymmetry of the $^3H_6\Gamma_1 \rightarrow {}^3H_6\Gamma_5$ transition intensities and the contributions of "quantum number mixing" of intermediate states caused by various stationary perturbations are discussed. In addition, we discuss the significance of this direct calculation to the Judd-Ofelt theory of one-photon processes in rare earth crystals.

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(I) Introduction

The availability of laser sources has resulted in detailed investigations of two-photon processes of rare-earth ions in crystals. For example, transitions which are not allowed by one-photon processes can be studied experimentally by two-photon processes.[1,2] The Judd-Ofelt-Axe (J-O-A) formulation[3,4] for the intensities of rare earth transitions has been applied to the results of these studies and appears to be somewhat inadequate. To explain the disagreement between experimental data and J-O-A calculation, higher-order terms of the stationary perturbations including spin-orbit coupling, crystal-field interaction, etc. are required.[1,5] Even with these corrections, J-O-A theory does not seem able to solve all the discrepancies. For instance, the calculated asymmetry of the electronic Raman scattering of the $^3H_6\Gamma_1 \rightarrow {}^3H_6\Gamma_5$ transition in a crystal of $TmPO_4$ disagrees markedly with the observed value.[2,6,7] It is worthwhile to do further calculations to find the reasons for the discrepancies.

In this paper, we have used the analyzed experimental data for $Er^{3+}(4f^{11})$ and $Ce^{3+}(5d^1)$ to estimate the energy level structure of the intermediate configuration $4f^{11}5d^1$ of $TmPO_4$.[8,9] By neglecting both the Coulomb interaction between the $4f^{11}$ core and the $5d^1$ electron, and the crystal-field splitting within the $4f^{11}$ term, we have carried out a direct calculation of the intensities of the electronic Raman scattering of $TmPO_4$. The calculation scheme and formulas are explained in Section II, Table 1, and Appendices A and B. The results are presented and discussed in Section III and Table 2.

(II) Calculation Scheme and Formulas

(1) Formulas for the Electronic Raman Scattering Amplitude

The scattering tensor, which represents the amplitude of the scattering of an incident photon of polarization σ and energy $\hbar\omega$ into a photon of polarization ρ and energy $\hbar\omega_s$ with the atomic system making a transition from the initial electronic state $|I\rangle$ to the final state $|F\rangle$, can be written [1]:

$$(\alpha_{\rho\sigma})_{FI} = -\sum_J \left[\frac{\langle F|D_\rho|J\rangle\langle J|D_\sigma|I\rangle}{\hbar\omega_J-\hbar\omega} + \frac{\langle F|D_\sigma|J\rangle\langle J|D_\rho|I\rangle}{\hbar\omega_J+\hbar\omega_s} \right]. \qquad (1)$$

Quite often this equation is quoted in the literature without the minus sign that precedes it. This can lead to serious error if interference with other amplitude channels are being considered or some correction terms are being added. It is easy to see that this minus sign comes from the second term of the following time-dependent perturbation formula for the radiative transition rate:

$$\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \left| \langle F|H_I|I\rangle - \frac{1}{\hbar}\sum_J \frac{\langle F|H_I|J\rangle\langle J|H_I|I\rangle}{\omega_J-\omega_I} + \cdots \right|^2 \qquad (2)$$

where H_I is the material-radiation interaction Hamiltonian.

We want to emphasize here the intermediate state $|J\rangle$ and its energy $E_J=\hbar\omega_J$. Based on time-dependent perturbation theory, state $|J\rangle$ should belong to the same stationary basis-function set as $|I\rangle$ and $|F\rangle$, and the

energy E_J should be the corresponding stationary energy. We may expand state $|J\rangle$ and keep the energy E_J.

We now look at the well-known "closure" suggested by B.R. Judd[3] and G.S. Ofelt and J.D. Axe, Jr.[4] from the above point of view. They assumed all the states in a given intermediate configuration, for example $4f^{N-1}5d^1$, are totally degenerate. We can consider the states $|J\rangle$ as the 0th order antisymmetric determinant function $\Psi_0 = |(4fm_s m_\ell)^{11}(5dm_s' m_\ell')^1\rangle$ which is an eigenfunction of the central field Hamiltonian H_0 in a stationary perturbation treatment while the Coulomb interaction H_1 between (N-1) electrons, the spin-orbit interaction H_2, and crystal-field interaction H_3 are perturbation Hamiltonians. Due to the complete degeneracy of E_J and in the limit of a given intermediate configuration, no matter what kind of eigenfunction, (i.e. the eigenfunctions of H_0 or $H_0 + H_i$ (i=1,2,3) or $H_0 + H_i + H_j$ (i≠j=1,2,3) or $H_0 + H_1 + H_2 + H_3$) we take as $|J\rangle$ the same results will be obtained by the summation over $|J\rangle$ in formula (1). The reason for this is the eigenfunctions $|J\rangle$ are linear combination of Ψ_0's and all the cross-terms will totally cancel. The errors introduced by "closure" are due to the use of average energy denominators for the summation of non-cross-terms in $|J\rangle\langle J|$, and the total cancellation of cross-terms.

(2) Direct Calculation Scheme

We present a direct and detailed calculation of the contributions in Equation (1) from the most important intermediate configuration $4f^{11}5d^1$ of the $TmPO_4$ crystal, by ignoring for simplicity both the

Coulomb interaction between $4f^{11}$ and $5d^1$ and the crystal-field splitting of $4f^{11}$. The energy levels and wavefunctions of $4f^{11}$ are obtained by diagonalizing the energy matrix of Er^{3+} in $LuPO_4$[8] assuming $B_0^2 = B_0^4 = B_0^6 = B_4^6 = 0$. Energy levels and wavefunctions for $5d^1$ are obtained from the analysis of experimental absorption data of Ce^{3+} in $LuPO_4$.[9] The Ce^{3+} wavefunctions and energy levels are shown in Table 1. The neglect of interactions between $4f^{11}$ and $5d^1$ makes the energy structure of the configuration $4f^{11}5d^1$ of $TmPO_4$ very simple. Every one of the 41 levels for $4f^{11}$ is split into 5 levels corresponding to the 5 Kramers doublets of $5d^1$. The crystal-field parameter B_4^4 of $5d^1$ is large so that the J_z mixing ($\Delta J_z = \pm 4$) is extensive as shown in Table 1. The energy difference between the lowest level of the $4f^{11}5d^1$ configuration and the ground state of the $TmPO_4$ crystal is estimated to be $63040 + 136\ cm^{-1} = 63176\ cm^{-1}$ where $63040\ cm^{-1}$ is the energy of the lowest 0-phonon $f \rightarrow d$ transition in the absorption data of Tm^{3+} in CaF_2[10] and $136\ cm^{-1}$ is the half-width of crystal-field split band of the lowest multiplet $[^4I]_{15/2}$ of Er^{3+} in $LuPO_4$.[8] The energies and wavefunctions of the initial and final states of electronic Raman scattering of the $TmPO_4$ crystal are obtained from Ref. 6. The details of the calculation are shown in Appendix A.

(3) Contributions of "cross-terms" of $|J\rangle\langle J|$ caused by stationary perturbations

To explain disagreements between the J-O-A predictions and the experimental data of two-photon processes in lanthanide(III) systems,

various authors have introduced higher-order correction terms for the intermediate configurations. For example, Judd and Pooler[5] have introduced higher-order terms involving spin-orbit mixing, Downer[1] included higher-order terms of the crystal-field and spin-orbit interactions, Sztucki and Strek, and Reid and Richardson[11-13] considered the so-called static and dynamic coupling between the lanthanide ion and ligand ions, etc. In our calculation we can separate out the contributions from the various kinds of cross-terms which are caused by the respective perturbation Hamiltonians and which lead to the corresponding "mixing" of state quantum numbers. The details of these calculations are shown in Appendix B.

(III). Results and Discussions

The calculated results are listed together with the J-O-A calculations and with the experimental data in Table 2. There are several points to note.

(1) Improvement in the calculation of the relative scattering intensities

For most of the transitions our calculations of the relative intensities are closer to the experimental values than the J-O-A theory (especially for transition Nos. 2, 4, 6, 14, 16, 24). Two transitions are predicted to be weak and were unobserved (No. 15 and No. 23), and for our calculations were a little worse. Transitions 7, 8, and 9 are predicted to be observable but were not. We have explained their absence by considering a "two optical phonon decay" model for the final states Γ_1 (248 cm^{-1}) and Γ_4 (254 cm^{-1}).[14]

(2) Values of the scattering amplitudes

It is surprising that our values of $(\alpha_{\rho\sigma})_{FI}$ are very different from the J-O-A's values. Generally speaking, most of our $(\alpha_{\rho\sigma})_{FI}$ values are just over twice the J-O-A values as shown in Table 2. Therefore our values of $|(\alpha_{\rho\sigma})_{FI}|^2$ will be about five times greater if the same value of the radial factor $|\langle 4f|r|5d\rangle|^2$ is used in both cases. The reason for this large difference is that the initial and final multiplets of Tm^{3+} are the lowest or next lowest multiplets of the ground configuration $4f^{12}$, that is $^3H_6$ and $[^3F]_4$ of the $TmPO_4$ crystal. These multiplets are related mainly to the lowest or the very low terms of the configuration

$4f^{11}5d^1$. Indeed the summation $\sum_{\alpha_1 S_1 L_1} |\langle f^{12}\,{}^3H(|f^{11}\alpha_1 S_1 L_1\rangle|^2 = 0.70$ when $(\alpha_1 S_1 L_1)$ only goes over the lowest five terms ^4I, ^4F, $^2H2$, ^2K, ^4G, while it equals 1.00 when $(\alpha_1 S_1 L_1)$ goes over all 17 terms of the $4f^{11}$ configuration. These low-lying terms play the main part as intermediate states of the scattering, and usually decide the signs of the scattering matrix elements.

We can compare the two kinds of calculation as follows. In our example $\bar{E}_{df} \approx 110 \times 10^3$ cm^{-1}, $\hbar\omega \approx 20 \times 10^3$ cm^{-1}; and the lowest crystal field level $E_{Jm} = E(^4I_{15/2};\ \Gamma_7^a) \approx 63 \times 10^3$ cm^{-1}. So

$$\frac{1}{E_{Jm}-\hbar\omega} + \frac{1}{E_{Jm}+\hbar\omega} \approx \frac{2E_{Jm}}{E_{Jm}^2-\hbar^2\omega^2} = 0.0353 \times 10^{-3} \text{ cm.}$$

For the J-O-A calculation

$$\frac{1}{E_J-\hbar\omega} + \frac{1}{E_J+\hbar\omega} \approx \frac{2\bar{E}_{df}}{\bar{E}_{df}^2-\hbar^2\omega^2} \approx \frac{2}{\bar{E}_{df}} = 0.0182 \times 10^{-3} \text{ cm.}$$

In the above example the ratio between our calculation and the J-O-A value is close to 2 if all the energy levels of the $4f^{11}d^1$ configuration are assumed to be at the energy of the lowest level E_{Jm}. Furthermore, contributions to the scattering matrix elements from higher-lying states are usually of the opposite sign, but their higher energy denominators make their contributions less important than in the assumed case in which $E_J = E_{Jm}$ for any J. Therefore we expect the ratios to be larger than 2 for most transitions. Thus, the lower states of the intermediate configuration are the most important which results

in values of the scattering amplitude in our direct calculation that are more than twice as large as the J-O-A values.

It is possible that our values of $(\alpha_{\rho\sigma})_{FI}$ can help explain the discrepancy mentioned by Judd[3] when he presented his theory 25 years ago. He pointed out that the empirical values of T_2, T_4, T_6 of Er^{3+} were 5-10 times larger than the calculated ones. If the numerical estimates of the configuration average energy $\Delta(n'\ell')$ in the expression $\Xi(\lambda,t)$ were changed to be about half as large as found for the Raman case, the calculated values of the radial parameters T_λ would be about four to five times larger and would be approximately equal to the empirical values. Since most studies have used the J-O-A formalism for the calculation of relative intensities or for the fitting of empirical parameters, the absolute values of the parameters have not been important.

(3) Contributions of various cross-terms to the scattering amplitude

Calculations described in Appendix B allow the various "cross-term contributions" to be separated out and are shown in columns (A), (B), (C), (D) of Table 2.

As can be seen from column (B), the cross-term contribution from $H_{S_1L_1}$ is very important for some transitions. For example, even for the strongest transition 3, the contribution is about 10%. We find a similar contribution for transitions 4, 9, 11, 14, etc. For transitions 17, 18, and 24, the contribution is around 20%. Thus our results are consistent with earlier work by Judd and Pooler.[5]

The cross-term contributions from h_{cd} of $5d^1$ [see column (C)], usually are less than from $H_{S_1L_1}$, but most are of the same order of magnitude. For transitions 5 and 12, they are much bigger than from $H_{S_1L_1}$. So they cannot be neglected, as others have noted.[1,11,12]

The contributions from cross-terms caused by $h_{s\ell}$ of $5d^1$ [see column (D)] are one order of magnitude smaller than those caused by h_{cd} and are not important.

(4) The asymmetry of transitions $^3H_6\Gamma_1 \rightarrow {}^3H_6\Gamma_5$

(a) In the J-O-A theory the scattering asymmetries are related to the ratio of two parameters F_1 and F_2. These parameters are given by

$$F_t^{(5d)} = (-1)^t \cdot 7 \cdot (2\times 2+1) \cdot \begin{pmatrix} 3 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 \cdot \langle 4f|r|5d\rangle^2 \cdot \sqrt{2t+1} \cdot \begin{Bmatrix} 1 & 3 & 2 \\ 3 & 1 & t \end{Bmatrix}$$

$$\cdot \left[\frac{1}{E_{df} - \hbar\omega} + \frac{(-1)^t}{E_{df} + \hbar\omega} \right] \qquad (3)$$

Using the value of E_{df} of 109,400 cm^{-1}, $\frac{F_1}{F_2} = .238$. Values for $\frac{F_1}{F_2}$ may also be determined by equating the expressions derived from the J-O-A theory for the scattering asymmetries with the values of the scattering asymmetries determined from the results of our direct calculation. For the pairs 1-2, 4-5, and 10-11 we find that $\frac{F_1}{F_2}$ is 0.127, 0.184, and 0.127 (average 0.146), respectively. Thus the "closure" overestimates the value of $\frac{F_1}{F_2}$.

(b) However, the corrections introduced by our calculation still do not adequately explain the asymmetry. Becker et al.[6] found that the observed asymmetries were best fit by a value of $\frac{F_1}{F_2} = -.03 \sim 0$.

Our direct calculation neglects the crystal-field interaction of $4f^{11}$ but this does not seem important here. We have also ignored the Coulomb interaction between the $4f^{11}$ and $5d^1$ configurations including the removal of Kramers degeneracies, but the inclusion of this interaction does not seem able to change the sign of the ratio $F_1^{(5d)}/F_2^{(5d)}$. The removal of the Kramers degeneracy cannot change α_D of transitions 2, 5, and 11 because the matrix elements of $(\alpha_{\rho\sigma})_{FI}$ are of the type $\langle F|D_0|J\rangle\langle J|D_{-1}|I\rangle$ where D_{-1} belongs to an irreducible basis of Γ_5-symmetry (D_{2d}), $|I\rangle$ is of Γ_1-symmetry, so $\langle J|$ must be of the Γ_5-symmetry which is doubly degenerate and similar to a Kramers degeneracy. Thus the intermediate states for these transitions would be doubly-degenerate after inclusion of the Coulomb interaction. Keeping these three α_D's unchanged, it is difficult to believe the ratio $F_1^{(5d)}/F_2^{(5d)}$ could change greatly.

J. Sztucki and W. Strek[11] suggested that the crystal field might have important contributions to the asymmetry problem. According to our results, the cross-terms caused by h_{cd} do not solve this discrepancy. On the contrary, α_D of transition 5 decreased markedly which is the reason why the ratio $F_1^{(5d)}/F_2^{(5d)} = 0.184$ for the second pair is bigger than 0.127 for the other two pairs.

Conclusion

A calculation of the Raman scattering cross-section for $Tm^{3+}:LuPO_4$ including the detailed structure in the intermediate configuration $4f^{11}5d^1$ has been given. It has been shown that the lowest-lying states of this intermediate configuration are the major contributors to the Raman cross-section. The contributions to the cross-sections from the intermediate state mixing caused by various terms in the stationary Hamiltonian have been evaluated.

Acknowledgement

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Table 1. Energy Levels and Eigenfunctions for the $5d^1$ Configuration in $Ce^{3+}:LuPO_4$

Energy (cm^{-1})		Eigenfunctions[z]		
50000	Γ_7^c	$0.376\|5/2,-3/2\rangle$	$-0.742\|5/2,5/2\rangle$	$+0.555\|3/2,-3/2\rangle$
	Γ_7^{ck}	$0.376\|5/2,3/2\rangle$	$-0.742\|5/2,5/2\rangle$	$-0.555\|3/2,3/2\rangle$
43734	Γ_6^b	$-0.299\|3/2,1/2\rangle$	$-0.954\|5/2,1/2\rangle$	
	Γ_6^{bk}	$-0.299\|3/2,-1/2\rangle$	$0.954\|5/2,-1/2\rangle$	
41360	Γ_7^b	$-0.888\|5/2,-3/2\rangle$	$-0.118\|5/2,5/2\rangle$	$+0.445\|3/2,-3/2\rangle$
	Γ_7^{bk}	$-0.888\|5/2,3/2\rangle$	$-0.118\|5/2,-5/2\rangle$	$-0.445\|3/2,3/2\rangle$
39641	Γ_6^a	$0.954\|3/2,-1/2\rangle$	$+0.300\|5/2,-1/2\rangle$	
	Γ_6^{ak}	$0.954\|3/2,1/2\rangle$	$-0.300\|5/2,1/2\rangle$	
30338	Γ_7^a	$0.264\|5/2,-3/2\rangle$	$+0.660\|5/2,5/2\rangle$	$+0.704\|3/2,-3/2\rangle$
	Γ_7^{ak}	$0.264\|5/2,3/2\rangle$	$+0.660\|5/2,-5/2\rangle$	$-0.704\|3/2,3/2\rangle$

[z] $5d^1$ configuration in D_{2d} symmetry; parameters used to obtain energies, eigenfunctions: $F^0 = 41015\ cm^{-1}$, $\zeta_{5d} = 1154\ cm^{-1}$, $B_0^2 = 3615\ cm^{-1}$, $B_0^4 = 3922\ cm^{-1}$, $B_4^4 = -24333\ cm^{-1}$. Basis set $|J,J_z\rangle$, Kramers degenerate state $|J,J_z\rangle^k = (-1)^{J-J_z}|J,-J_z\rangle$ Reference 9.

Table 2. Calculated Results and Comparisons for $TmPO_4$

Final State[a]	Energy (cm^{-1})	Polarization[a]	Direct Calculation Contributions to α_D[f] (A)[b]	(B)[c]	(C)[d]	(D)[e]	α_D[f]	Relative Intensities Direct[g]	Exp.[a]	J-O-A[a]	α_J[h]	α_D/α_J	Transition No.
$^3H_6$ Γ_5	30	XZ,YZ	-0.0122	-0.0096	0.0077	0.0008	-0.0133	0.2	3.7	13.2	-0.0459	0.29	1
		ZX,ZY	0.1805	0.0213	-0.0209	-0.0015	0.1794	34.8	1.2	86.4	0.1218	1.47	2
Γ_3	86	XY,YX	0.4308	0.0458	-0.0152	-0.0024	0.4590	228.0	228.0	228.0	0.2041	2.25	3
Γ_5	138	XZ,YZ	0.1772	0.0166	-0.0149	-0.0009	0.1780	34.3	21.6	51.6	0.0958	1.86	4
		ZX,ZY	0.1208	-0.0020	-0.0306	0.0012	0.0894	8.7	24.0	7.4	0.0390	2.29	5
Γ_2	183	XY,YX	0.0405	0.0178	-0.0108	-0.0014	0.0461	2.3	j	11.1	0.0433	1.07	6
Γ_1	248	XX,YY	0.0705	0.0450	-0.0059	0.0008	0.1104	13.2	1	10.2	0.0437	2.53	7
		ZZ	-0.2178	0.0112	-0.0143	0.0029	-0.2180	51.4	1	41.0	-0.0873	2.50	8
Γ_4	254	XX,YY	-0.1978	-0.0226	-0.0212	0.0016	-0.1976	42.3	1	47.6	-0.0934	2.12	9
Γ_5	280	XZ,YZ	0.1121	0.0049	0.0015	0.0004	0.1189	15.3	23.4	11.2	0.0446	2.67	10
		ZX,ZY	0.1259	0.0171	0.0014	-0.0015	0.1429	22.1	20.3	23.4	0.0640	2.23	11
Γ_3	303	XY,YX	0.0122	0.0052	0.0132	0.0000	0.0306	1.0	j	0.4	0.0068	4.50	12
Γ_4	321	XX,YY	-0.0760	-0.0141	-0.0053	0.0008	-0.0946	9.7	j	7.8	-0.0370	2.41	13

Table 2.(continued)

$^3F_4$	Γ_3 5602	XY,YX	-0.1370	-0.0260	0.0078	0.0006	-0.1546	25.9	19.7	30.3	-0.0726	2.13	14
	Γ_1 5676	XX,YY	-0.0857	-0.0191	-0.0053	-0.0007	-0.1108	13.3	j	10.9	-0.0438	2.53	15
		ZZ	0.1702	0.0247	-0.0152	-0.0009	0.1788	34.6	4.6	43.6	0.0877	2.04	16
	Γ_5 5688	XZ,YZ	-0.1695	-0.0331	0.0071	0.0011	-0.1944	40.9	5.0	48.0	-0.0911	2.13	17
		ZX,ZY	-0.1723	-0.0339	0.0010	0.0009	-0.2043	45.2	5.0	48.0	-0.0911	2.24	18
	Γ_2 5735	XY,YX	-0.0038	0.0020	-0.0013	-0.0010	-0.0041	0.0	j	0.0	0.0000	-	19
	Γ_4 5763	XX,YY	-0.0255	-0.0097	-0.0070	0.0024	-0.0398	1.7	j	2.0	-0.0179	2.22	20
	Γ_5 5842	XZ,YZ	0.0172	0.0100	-0.0002	-0.0014	0.0256	0.7	j	1.0	0.0138	1.86	21
		ZX,ZY	0.0269	0.0074	0.0040	0.0002	0.0385	1.6	j	1.0	0.0138	2.79	22
	Γ_1 5870	XX,YY	0.0827	0.0288	0.0132	-0.0020	0.1227	16.3	j	13.0	0.0475	2.58	23
		ZZ	-0.1629	-0.0383	0.0034	0.0047	-0.1931	40.4	10.5	51.8	-0.0951	2.03	24

[a]From References 2 and 6.

[b]This work including all the non-cross terms $|(4f\ m_s m_s)^{11}\ (5d\ m_\ell' m_s')^1\rangle\langle(4f\ m_s m_s)^{11}\ (5d\ m_\ell' m_s')^1|$ and the cross terms caused by Coulomb Hamiltonian H_{CL} of $4f^{11}$.

[c]This work from the cross terms caused by spin-orbit Hamiltonian H_{SL} of $4f^{11}$.

[d]This work from the cross terms caused by crystal-field Hamiltonian h_{cd} of $5d^1$.

[e]This work from the cross terms caused by spin-orbit Hamiltonian h_{sd} of $5d^1$.

[f]in units of $(10^{-5}\text{cm}\langle 4f|r|5d\rangle^2/hc)$. Sum of columns A-D.

[g]This calculation. The normalization of References 2 and 6 is used.

[h]in units of $(10^{-5}\text{cm}\langle 4f|r|5d\rangle^2/hc)$. Values obtained from the J-O-A approximation.

[i]Not observed. Disappearance explained by consideration of a two optical phonon decay, Ref. 14.

[j]Not observed.

Appendix A

The most convenient way to describe the intermediate states here is by use of the following uncoupled functions:

$$|J\rangle = |\mu;\ell\rangle = \left|\,|4f^{N-1}\ [\alpha_1 S_1 L_1]J_1 J_{z1}\rangle_\mu ; |5d^1\ {}^2D\ \Gamma_d\gamma_d\rangle_\ell\right\rangle^A \qquad \text{(A-1)}$$

where instead of using one index J we use the index pair $(\mu;\ell)$ to define a state in which 11 electrons occupy the μth state of $4f^{11}$ and one electron occupies the ℓth state of $5d^1$, and "A" means anti-symmetric with respect to electron exchange.

Then the fundamental matrix element in formula (1) is:

$$\langle F|D_\rho|J\rangle$$

$$= {}^A\langle 4f^N\ \alpha_f S_f L_f J_f \Gamma_f \gamma_f \left|\sum_i r_i C^{(1)}_{i\rho}\right| |4f^{N-1}[\alpha_1 S_1 L_1]J_1 J_{z1}\rangle_\mu ; |5d^1\ {}^2D\ \Gamma_d\gamma_d\rangle_\ell\rangle^A$$

$$= N\ {}^A\langle 4f^N\ \alpha_f S_f L_f J_f \Gamma_f \gamma_f \left| r_N\ C^{(1)}_{N\rho}\right| |4f^{N-1}[\alpha_1 S_1 L_1]J_1 J_{z1}\rangle_\mu ; |5d^1\ {}^2D\ \Gamma_d\gamma_d\rangle_\ell\rangle^A$$

$$= \frac{N}{\sqrt{N}}\ {}^A\langle 4f^N\ \alpha_f S_f L_f J_f \Gamma_f \gamma_f \left| r_N\ C^{(1)}_{N\rho}\right| |4f^{N-1}[\alpha_1 S_1 L_1]J_1 J_{z1}\rangle^A_\mu \cdot |5d^1\ {}^2D\ \Gamma_d\gamma_d\rangle^N_\ell\rangle \qquad \text{(A-2)}$$

The last step means the probability that the Nth electron occupies the ℓth state of $5d^1$ while the other (N-1) electrons occupy the μth state of $4f^{11}$ is $\left|\frac{1}{\sqrt{N}}\right|^2 = \frac{1}{N}$. Formula (A-2) combined with formula

(A-5) (see below) is similar to the formula (2-75) of B.G. Wybourne's book [15].

We expand the wavefunctions as:

$$|5d^1\ {}^{2D}\ \Gamma_d\gamma_d\rangle_\ell = \sum_p d_{\ell p}|j_{dp}j_{zdp}\rangle \qquad \text{(A-3)}$$

where the coefficients $d_{\ell p}$ are obtained from Ref. [5] (Table 1) and

$$|4f^{N-1}\ [\alpha_1 S_1 L_1]J_1 J_{z1}\rangle^A_\mu = \sum_\nu C_{\mu\nu}\ |4f^{N-1}\ \alpha_{1\nu}S_{1\nu}L_{1\nu}J_{1\mu}J_{z1\mu}\rangle^A$$

$$- \sum_{\nu, M_{S1}, M_1} C_{\mu\nu}\ \langle S_{1\nu}L_{1\nu}M_{S1}M_1|J_{1\mu}J_{z1\mu}\rangle\ |4f^{N-1}\ \alpha_{1\nu}S_{1\nu}L_{1\nu}M_{S1}M_1\rangle^A. \qquad \text{(A-4)}$$

The coefficients $C_{\mu\nu}$ are obtained from Ref [4] by setting all $B^k_q = 0$ as mentioned earlier. Now

$${}^A\langle 4f^N\ \alpha_f S_f L_f J_f J_{zf}| = \sum_{M_{Sf}, M_f} \langle J_f J_{zf}|S_f L_f M_{Sf} M_f\rangle \cdot {}^A\langle 4f^N \alpha_f S_f L_f M_{Sf} M_f|$$

$$- \sum_{\substack{M_{sf}M_f \\ \alpha_i S_i L_i \\ M_i m_f M_{Si} m_{sf}}} \langle J_f J_{zf}|S_f L_f M_{Sf} M_f\rangle \cdot \langle 4f^N\ \alpha_f S_f L_f(|\alpha_i S_i L_i\rangle \cdot \langle L_f M_f|L_i 3 M_i m_f\rangle$$

$$\cdot \langle S_f M_{Sf}|S_i \tfrac{1}{2} M_{Si} m_{sf}\rangle \cdot \langle \tfrac{1}{2}\ m_{sf}\ 3\ m_f|\cdot {}^A\langle 4f^{N-1}\alpha_i S_i L_i M_{Si} M_i| \qquad \text{(A-5)}$$

By substituting (A-3), (A-4), and (A-5) into (A-2) we have

$$\langle F|D_\rho|J\rangle = \langle F|D_\rho|\mu;\ell\rangle$$

$$= {}^{A}\langle 4f^{N}\alpha_f S_f L_f J_f J_{zf}\Big|\sum_i r_i C^{(1)}_{i\rho}\Big||4f^{N-1}[\alpha_1 S_1 L_1]J_1 J_{z1}\rangle_{\mu};\ |5d^1\ {}^2D\ \Gamma_d\gamma_d\rangle_{\ell}\rangle^{A}$$

$$= \sqrt{N}\ {}^{A}\langle 4f^{N}\alpha_f S_f L_f J_f J_{zf}\Big|r_N C^{(1)}_{N\rho}\Big[\sum_{(\nu p)} C_{\mu\nu}|4f^{N-1}\alpha_{1\nu}S_{1\nu}L_{1\nu}J_{1\mu}J_{z1\mu}\rangle^{A} \cdot d_{\ell p}|j_{dp}j_{zdp}\rangle^{N}\Big] \tag{A-6}$$

$$= \sqrt{N}\ {}^{A}\langle 4f^{N}\alpha_f S_f L_f J_f J_{zf}\Big|r_N C^{(1)}_{N\rho}\Big[\sum_{\substack{\nu p\\ M_{S1}M_1}} C_{\mu\nu}\langle S_{1\nu}L_{1\nu}M_{S1}M_1|J_{1\mu}J_{z1\mu}\rangle \cdot |4f^{N-1}\alpha_{1\nu}S_{1\nu}L_{1\nu}M_{S1}M_1\rangle^{A}\cdot d_{\ell p}|j_{dp}j_{zdp}\rangle^{N}\Big] \tag{A-7}$$

$$= \sqrt{N}\ {}^{A}\langle 4f^{N}\alpha_f S_f L_f J_f J_{zf}\Big|r_N C^{(1)}_{N\rho}\Big[\sum_{\substack{\nu p\\ M_{S1}M_1\\ m_{sd}m_d}} C_{\mu\nu}\langle S_{1\nu}L_{1\nu}M_{S1}M_1|J_{1\mu}J_{z1\mu}\rangle \cdot |4f^{N-1}\alpha_{1\nu}S_{1\nu}L_{1\nu}M_{S1}M_1\rangle^{A}\cdot d_{\ell p}\cdot\langle\tfrac{1}{2}\ 2m_{sd}m_d|j_{dp}j_{zdp}\rangle|\tfrac{1}{2}\ m_{sd}2m_d\rangle^{N}\Big] \tag{A-8}$$

$$= \sqrt{N}\sum_{\substack{\nu p\\ M_{Sf}M_f M_{S1}M_1\\ m_{sf}m_f m_{sd}m_d}} C_{\mu\nu}d_{\ell p}\langle J_f J_{zf}|S_f L_f M_{Sf}M_f\rangle\langle S_{1\nu}L_{1\nu}M_{S1}M_1|J_{1\mu}J_{z1\mu}\rangle \cdot\langle\tfrac{1}{2}\ 2\ m_{sd}m_d|j_{dp}j_{zdp}\rangle\ \langle 4f^N\ \alpha_f S_f L_f|\alpha_{1\nu}S_{1\nu}L_{1\nu}\rangle\ \langle L_f M_f|L_{1\nu}3\ M_1 m_f\rangle \cdot\langle S_f M_{Sf}|S_{1\nu}\ \tfrac{1}{2}\ M_{S1}m_{sd}\rangle\cdot\langle 3\ m_f|rC^{(1)}_{\rho}|2\ m_d\rangle \tag{A-9}$$

While the functions of $4f^{N-1}$ are written as eigenfunctions of the Er^{3+} free ion in Equation (A-6), they are expressed in (A-7) as a linear summation of $|4f^{N-1}\alpha_{1\nu}S_{1\nu}L_{1\nu}M_{S1}M_1\rangle^{A}$ which are eigenfunctions of a Hamiltonian containing

only the central field and the Coulomb interaction between the (N-1) f electrons. This formalism is convenient for separating out the spin-orbit cross-term contributions as will be shown. This is also true for the $5d^1$ functions in formula (A-8).

Similar formulas can be obtained for $\langle J|D_\sigma|I\rangle = \langle \mu;\ell|D_\sigma|I\rangle$ in the same way. By substituting formula (A-9) for the matrix elements $\langle F|D_\rho|J\rangle$ into the numerators, and the energies $E_{\mu\ell} - \hbar\omega_J$ into the denominators of Equation (1), the scattering amplitudes $(\alpha_{\rho\sigma})_{FI}$ can be calculated directly. Of course, only contributions from the intermediate configuration $4f^{N-1}5d^1$ are included.

Appendix B.

In the calculation of $(\alpha_{\rho\sigma})_{FI}$, instead of formula (A-9), we substitute formula (A-6) into (1), and have for $|J\rangle\langle J|$:

$$|J\rangle\langle J| = |\mu,\ell\rangle\langle\mu,\ell| = \sum_{\substack{\nu p \\ \lambda q}} C_{\mu\nu}|\alpha_{1\nu}S_{1\nu}L_{1\nu}J_{1\mu}J_{z1\mu}\rangle \cdot d_{\ell p}|j_{dp}j_{zdp}\rangle$$
$$\cdot C_{\mu\lambda}\langle\alpha_{1\lambda}S_{1\lambda}L_{1\lambda}J_{1\mu}J_{z1\mu}| \cdot d_{\ell q}\langle j_{dq}j_{zdq}| \qquad \text{(B-1)}$$

We can easily separate many kinds of "cross-term contributions" by completing different kinds of summations over $|J\rangle\langle J|$ in formula (1) as follows:

(a) using (A-8) and neglecting "cross terms", we have

$$\sum_{\substack{\nu p \\ M_{S1}M_1 \\ m_{sd}m_d}} C_{\mu\nu} \cdot \langle S_{1\nu}L_{1\nu}M_{S1}M_1|J_{1\mu}J_{z1\mu}\rangle \cdot |\alpha_{1\nu}S_{1\nu}L_{1\nu}M_{S1}M_1\rangle^A$$
$$\cdot d_{\ell p}\langle\tfrac{1}{2}\ 2m_{sd}m_d|j_{dp}j_{zdp}\rangle \cdot |\tfrac{1}{2}m_{sd}2m_d\rangle^N$$
$$\cdot C_{\mu\nu} \cdot \langle S_{1\nu}L_{1\nu}M_{S1}M_1|J_{1\mu}J_{z1\mu}\rangle \cdot {}^A\langle\alpha_{1\nu}S_{1\nu}L_{1\nu}M_{S1}M_1| \cdot d_{\ell p}\langle\tfrac{1}{2}\ 2m_{sd}m_d|j_{dp}j_{zdp}\rangle$$
$$\cdot {}^N\langle\tfrac{1}{2}m_{sd}\ 2m_d| \qquad \text{(B-2)}$$

This summation does not contain the "cross terms" caused by the spin-orbit coupling $H_{S_1L_1}$ of $4f^{11}$ and $h_{s\ell}$ of $5d^1$ and those caused by the crystal-field Hamiltonian h_{cd} of $5d^1$, but it does contain the "cross terms" caused by the Coulomb interaction between the 11 f electrons. Of course, the non-cross terms of 0th order functions

$$|(4fm_s m_\ell)^{11}(5dm_{sd}m_d)^1\rangle\langle(4fm_s m_\ell)^{11}(5dm_{sd}m_d)^1|$$

are a fundamental part of it.

(b) Using (A-7) and neglecting "cross terms", we have

$$\sum_{\substack{\nu p \\ M_{S1}M_1}} C_{\mu\nu}\cdot\langle S_{1\nu}L_{1\nu}M_{S1}M_1|J_{1\mu}J_{z1\mu}\rangle\cdot|\alpha_{1\nu}S_{1\nu}L_{1\nu}M_{S1}M_1\rangle^A\cdot d_{\ell p}|j_{dp}j_{zdp}\rangle^N$$

$$\cdot C_{\mu\nu}\cdot\langle S_{1\nu}L_{1\nu}M_{S1}M_1|J_{1\mu}J_{z1\mu}\rangle\cdot{}^A\langle\alpha_{1\nu}S_{1\nu}L_{1\nu}M_{S1}M_1|\cdot d_{\ell p}{}^N\langle j_{dp}j_{zdp}| \qquad \text{(B-3)}$$

The difference between (B-3) and (B-2) will give the cross-term contribution caused by $h_{s\ell}$ when the cross terms caused by $H_{S_1L_1}$ and h_{cd} are ignored. Because $h_{s\ell}$ is small it can be considered as a "cross-term contribution" to a good approximation.

(c) Using (A-6) and only neglecting the "cross term" caused by h_{cd}, we have

$$\sum_{\substack{\nu\lambda \\ p}} C_{\mu\nu}|\alpha_{1\nu}S_{1\nu}L_{1\nu}J_{1\mu}J_{z1\mu}\rangle^A\cdot d_{\ell p}|j_{dp}j_{zdp}\rangle^N\cdot C_{\mu\lambda}{}^A\langle\alpha_{1\lambda}S_{1\lambda}L_{1\lambda}J_{1\mu}J_{z1\mu}|\cdot d_{\ell p}{}^N\langle j_{dp}j_{zdp}| \qquad \text{(B-4)}$$

The difference between (B-4) and (B-3) is the "cross-term contribution" caused by $H_{S_1L_1}$ when the cross terms caused by h_{cd} are ignored.

(d) Using (A-6) and only doing the summation for "cross terms" caused by h_{cd} we have

$$\sum_{\substack{\nu\lambda \\ p\neq q}} C_{\mu\nu}|\alpha_{1\nu}S_{1\nu}L_{1\nu}J_{1\mu}J_{z1\mu}\rangle^{A}\cdot d_{\ell p}|j_d j_{zd}\rangle_p^N \cdot C_{\mu\lambda}{}^{A}\langle\alpha_{1\lambda}S_{1\lambda}L_{1\lambda}J_{1\mu}J_{z1\mu}|\cdot d_{\ell q}\,{}_q^N\langle j_d j_{zd}| \quad \text{(B-5)}$$

This summation corresponds to the "cross-term contribution" caused by h_{cd}.

The summations of (B-4) and (B-5) are the complete contributions of the $4f^{11}5d^1$ configuration to the scattering amplitude $(\alpha_{\rho\sigma})_{FI}$. It is easy to see that our scheme to separate "cross-term contributions" is direct and contains the contributions to all orders of stationary perturbation theory.

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