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Abstract. The complex multiplet structure of the partially filled 4f shell in the rare-earth metals is calculated using intermediate coupling. The eigenfunctions obtained are used for a calculation of photoemission intensities in the fractional parentage scheme including all final states. The result is in excellent agreement with recent x-ray photoemission spectra and demonstrates the importance of intermediate coupling in the rare earths.

1. Introduction

Recent high-quality x-ray photoemission experiments on rare-earth metals (Lang *et al* 1981) have been quite successful in proving the validity of the fractional parentage scheme for calculating the relative photoemission intensities of the different atomic 4f final state multiplets (Cox 1975, Cox *et al* 1981). Differences between theory and experiment, especially for the heavy rare earths, were explained as an indication of the breakdown of *LS* coupling (Russell–Saunders coupling) in which the calculation was carried out for most of the elements while intermediate coupling was used only in some restricted energy ranges.

   An improvement of the theory becomes desirable since surface-sensitive photoemission experiments in the VUV region show different binding energies for bulk and surface core levels in the rare-earth metals ('surface shift') (Kammerer *et al* 1982, Gerken 1982, Gerken *et al* 1982a, 1983). The spectra consist of a superposition of multiplet lines originating from bulk atoms and from the surface atoms which are rigidly shifted to higher binding energies by about 0.5–0.7 eV. Bulk and surface components can only be separated by use of an accurate theory for the photoemission intensities (Kammerer *et al* 1982, Gerken *et al* 1982a).

   Therefore a complete calculation in intermediate coupling was carried out. The result is tabulated and the multiplet lines, convoluted with the lineshapes of Donaich and Sunjic (1970), are presented as calculated spectra which compare well with experimental results on rare-earth metals.

   The calculation of the energy levels in intermediate coupling has been carried out already by Carnall *et al* (1968) and the energy positions of the multiplet lines have been tabulated up to about 5×10^4 cm^{-1} for all the rare-earth ions. This energy corresponds to the highest structure which could be identified in their absorption spectra of rare-earth ions in dilute acid solution.

   The energy level calculation was repeated, however, because in photoemission a 4f multiplet splitting of up to about 12 eV (about 10^5 cm^{-1}) appears in the spectra and the

eigenfunctions of the levels are required for the photoemission intensity calculation. A detailed treatment of the theory has been discussed by Wybourne (1965) and Sobelman (1979). Therefore only the general outline of the calculation needs to be included here.

According to the theory of Racah (1949) the different states of the f shell may be classified in LS coupling notation by the quantum numbers W, U, ν, S, L, J and M_J. The quantum numbers S, L, J and M_J represent, as usual, the total spin and orbital angular momentum, the resultant total angular momentum and its projection. The seniority number ν and the quantum numbers U and W are necessary to distinguish between states with the same S, L, J, M_J assignment which appear in the f shell. W and U consist respectively of three and two integer numbers:

$$W = (w_1 \, w_2 \, w_3) \qquad U = (u_1 \, u_2). \tag{1}$$

The energy level structure of the f^N configurations arises mainly from electrostatic and spin–orbit interaction between the f electrons. The electrostatic part of the total energy matrix can be written in the form (Racah 1949)

$$E_C = \sum_{k=0}^{3} e_k E^k. \tag{2}$$

The e_k represent the angular part while the E^k are linear combinations of the Slater radial integrals F_k. This representation was chosen by Racah since it has simple transformation properties with respect to the symmetry groups used to classify the states. The electrostatic interaction is diagonal in the quantum numbers S and L and independent of J and M_J, but it is not diagonal in the additional quantum numbers W, U and ν. Therefore the e_k are generally matrices which have been calculated and tabulated completely (Nielson and Koster 1964). The electrostatic electron–electron interaction is responsible for a breakdown of the degeneration of different LS terms in a f^N configuration.

The energy of the spin–orbit interaction E_{SO} is given by

$$E_{SO} = \xi_{4f} \sum_{i=1}^{N} (s_i \cdot l_i) = \xi_{4f} A_{SO} \tag{3}$$

where ξ_{4f} represents the radial integral and A_{SO} is the angular part of the spin–orbit interaction. s and l are the spin and orbital angular momentum of the electrons. The matrix elements of E_{SO} can be calculated by the formula (Wybourne 1965)

$$\left(l^N \tau SLJM_J \left| \xi_{nl} \sum_{i=1}^{N} (s_i \cdot l_i) \right| l^N \tau' S'L'JM_J \right)$$

$$= \xi_{nl}(-1)^{J+L+S'} \begin{Bmatrix} L & L' & 1 \\ S' & S & J \end{Bmatrix} [l(l+1)(2l+1)]^{1/2} (l^N \tau SL \| V^{11} \| l^N \tau' S'L') \tag{4}$$

where τ represents the additional quantum numbers W, U and ν. The reduced matrix elements V^{11} are given by

$$(l^N \tau SL \| V^{11} \| l^N \tau' S'L')$$

$$= N[s(s+1)(2s+1)(2S+1)(2L+1)(2S'+1)(2L'+1)]^{1/2}$$

$$\times \sum_{\tau''S''L''} G_{\tau''S''L''}^{\tau SL} G_{\tau''S''L''}^{\tau'S'L'} (-1)^{S''+L''+S+L+s+l} \begin{Bmatrix} S & S' & 1 \\ s & s & S'' \end{Bmatrix} \begin{Bmatrix} L & L' & 1 \\ l & l & L'' \end{Bmatrix} \tag{5}$$

where $G_{\tau''S''L''}^{\tau SL}$ are the fractional parentage coefficients (FPC) which give the construction of

a state $(l^N \tau SL)$ from the possible states $(l^{N-1} \tau'' S'' L'')$. They have been calculated by Nielson and Koster (1964) for p, d and f electrons using the methods given by Racah. The spin–orbit interaction is diagonal in the quantum number J, independent of M_J but not diagonal in the other quantum numbers. If the spin–orbit interaction parameter ζ_{nl} exceeds a certain value, the off-diagonal matrix elements cannot be neglected and the diagonalisation of the total energy matrix results in a mixing of different LS states with the same total angular momentum J (intermediate coupling).

In the theory given above the important influence of the configuration interaction has not been considered. This interaction can be treated in a second-order perturbation theory. For f^N configurations it may be written as (see e.g. Carnall *et al* (1968), Wybourne (1965) and references therein)

$$E_{CI} = \alpha L(L + 1) + \beta G(G_2) + \gamma G(R_7).$$ (6)

α, β and γ are linear combinations of radial integrals and $G(G_2)$ and $G(R_7)$ are eigenvalues of Casimir's operator of the groups G_2 and R_7, respectively, and may be calculated using the quantum numbers U and W (Racah 1949, Judd 1959):

$$G(G_2) = g(U) = g(u_1 u_2) = \tfrac{1}{12}(u_1^2 + u_1 u_2 + u_2^2 + 5u_1 + 4u_2)$$ (7)

$$G(R_7) = g(W) = g(w_1 w_2 w_3) = \tfrac{1}{10}[w_1(w_1 + 5) + w_2(w_2 + 3) + w_3(w_3 + 1)].$$ (8)

For the energy level calculation the total energy matrices including all the interactions described above were built up for all possible quantum numbers J using the radial energy parameters published by Carnall *et al*. They are given in table 1. The parameter E^0 in equation (2) was omitted since it only has the effect of shifting the centre of gravity of the entire f^N configuration without contributing to the structure of the configuration. The matrices were diagonalised for all states from the configuration $4f^2$ up to $4f^{13}$ except for $4f^7$ where only the three highest multiplicities (8, 6 and 4) were considered. This restriction is only because about 35% of more than 20 000 FPC that exist for the states from f^2 to f^7 belong to the states of f^7 with the lowest multiplicity 2. Since only small changes in the eigenfunctions are expected for the two highest multiplicities which appear in the photoemission spectrum of Tb ($4f^8 \rightarrow 4f^7$) when the multiplicity 2 is neglected, we did not undertake the laborious task of putting these FPC into the computer.

The resultant eigenfunctions and eigenvalues of the calculation fill about 100 pages which is rather too lengthy to be published here. The energy levels are characterised by the

Table 1. Radial energy parameters used to diagonalise the total energy matrices. Energies are given in cm^{-1}. The values are taken from Carnall *et al* (1968).

f^N	Element	E^1	E^2	E^3	ζ_{4f}	α	β	γ
f^2	Pr^{3+}	4548.2	21.937	466.73	740.75	21.255	−799.94	1342.9
f^3	Nd^{3+}	4739.3	23.999	485.96	884.58	0.5611	−117.15	1321.3
f^4	Pm^{3+}	4921.6	24.522	525.53	1000.8	10.991	−244.88	789.74
f^5	Sm^{3+}	5496.9	25.809	556.40	1157.3	22.250	−742.55	796.64
f^6	Eu^{3+}	5573.0	26.708	557.39	1326.0	25.336	−580.25	1155.7
f^7	Gd^{3+}	5761.0	28.02	582.0	1450.0	22.55	−103.7	997.0
f^8	Tb^{3+}	6021.5	29.03	608.54	1709.5	20.131	−370.7	1255.9
f^9	Dy^{3+}	6119.6	30.012	610.14	1932.0	37.062	−1139.1	2395.3
f^{10}	Ho^{3+}	6440.6	30.22	624.39	2141.3	23.635	−807.2	1278.4
f^{11}	Er^{3+}	6769.9	32.388	646.62	2380.7	18.347	−509.28	649.71
f^{12}	Tm^{3+}	7142.4	33.795	674.27	2628.7	14.677	−631.79	0

remaining good quantum numbers J and M_J. The eigenfunctions give the composition of these intermediate coupling states in the LS basis and may be written in the form

$$|4f^N J M_J\rangle = \sum_{\tau SL} C_{\tau SL}^J |4f^N \tau SL J M_J\rangle \tag{9}$$

with

$$\sum_{\tau SL} |C_{\tau SL}^J|^2 = 1. \tag{10}$$

The calculation of the photoemission intensities in the sudden approximation has been discussed in detail by Cox (1975) for the LS coupling case. In a recent paper (Cox *et al* 1981) this theory is extended to bremsstrahlung isochromat spectroscopy (BIS) which may be viewed as an inverse photoemission process. For BIS the intensity calculation is also derived for the more general intermediate coupling case. This can easily be transformed to the photoemission case. According to this theory the intensity for a transition from the initial state $|l^N J M_J\rangle$ to the final state $|l^{N-1} J' M_J'\rangle$ is proportional to

$$N(2J'+1) \sum_j \left[(2j+1) \left(\sum_{\substack{\tau SL \\ \tau'S'L'}} C_{\tau SL}^J C_{\tau'S'L'}^{J'} [(2S+1)(2L+1)]^{1/2} \begin{Bmatrix} s & l & j \\ S & L & J \\ S' & L' & J' \end{Bmatrix} G_{\tau'S'L'}^{\tau SL} \right)^2 \right] \tag{11}$$

where j is the total angular momentum of a single electron which is 5/2 and 7/2 for f electrons with $l = 3$. The sum of the intensities of a state l^N equals the number of electrons N. Formulae for the $9-j$ and $6-j$ symbols which appear in equations (4), (5) and (11) were taken from the appendix of a book by Messiah (1979).

The calculation is performed for all $4f^N \rightarrow 4f^{N-1}$ transitions except for the trivial cases $4f^2 \rightarrow 4f^1$(Pr) and $4f^{14} \rightarrow 4f^{13}$(Yb, Lu) where only the two final states $^2F_{5/2}$ and $^2F_{7/2}$ appear.

The lowest energy level for each $4f^N$ configuration represents its ground state and the relevant eigenfunctions were therefore used as the initial state in the intensity calculation. The results are given in table 2. The different final states are characterised by the main LS contribution of the eigenfunction.

In addition, the multiplet lines are convoluted with the lineshapes of Doniach and Sunjic (1970) to account for the many-body reaction on the sudden creation of a core hole in a metal, and with Gaussian profiles to account for the experimental resolution, and then plotted on a binding energy scale (figure 1). The parameters are listed in table 3. They are close to the values used by Lang *et al* (1981) to fit their experimental results. The spectra, except for Eu, are scaled in energy by a factor of 1.1 compared with the energy positions listed in table 2, in order to account for the different nuclear charge in photoemission final states and the absorption experiments of Carnall *et al* (1968). Finally a background of scattered electrons computed with a program which simulates the travel of the photoelectrons through the metal (Gerken 1982) is added to the curves.

As a result the calculated spectra agree well with the photoemission spectra published by Lang *et al*. A strong improvement of the intermediate coupling calculation compared with the LS coupling for the heavy rare-earth metals is obtained. Since the calculation presented here includes all possible final states of the different $4f^N$ configurations, several structures appear at relatively high binding energies. Although these structures have only low intensities they should also appear in experimental spectra and demonstrate the quality of the theory.

Some small differences in the relative intensities of multiplet lines found from theory and experiment may be explained by the following arguments.

It has been shown that the binding energy of the multiplets in the rare-earth metals is different for bulk and surface atoms (Kammerer *et al* 1982, Gerken *et al* 1982a). Although

Table 2. Energy positions and intensities of the multiplet lines for the transitions $f^N \rightarrow f^{N-1}$ with $N = 3$–13. Intensities lower than 0.01 are omitted. For the initial states the complete eigenfunctions and for the final state only the main contribution in the representation $(w_1 w_2 w_3)$, $(u_1 u_2)$, seniority, $2S + 1$, L are given.

Photoemission intensity in intermediate coupling transition from $4f^3$ to $4f^2$
Initial state eigenfunction: $J = 4.5$

0.9846	(111)(20) 3	4 I
0.0564	(210)(11) 3	2 H
−0.1635	(210)(21) 3	2 H

Final state intensities:

		J	E (eV)	Intensity
(110)(10) 2	3 F	2.0	0.6080	0.5856
(110)(10) 2	3 F	3.0	0.7805	0.0761
(110)(11) 2	3 H	4.0	0.0000	2.0280
(110)(11) 2	3 H	5.0	0.2576	0.2968

Photoemission intensity in intermediate coupling transition from $4f^6$ to $4f^5$
Initial state eigenfunction: $J = 0$

0.9666	(100)(10) 6	7 F
−0.1868	(111)(20) 4	5 D
0.1676	(210)(21) 6	5 D

Final state intensities:

		J	E (eV)	Intensity
(211)(30) 5	4 P	2.5	4.0663	0.0354
(110)(11) 5	6 P	2.5	3.4330	0.2679
(110)(11) 5	6 P	2.5	2.9791	0.4745
(211)(21) 5	4 F	2.5	2.7364	0.0165
(110)(10) 5	6 F	2.5	0.8813	1.5167
(110)(11) 5	6 H	2.5	0.0000	1.3743
(110)(11) 5	6 P	3.5	3.2910	0.0249
(110)(10) 5	6 F	3.5	0.9863	0.4233
(110)(11) 5	6 H	3.5	0.1285	1.8309

Photoemission intensity in intermediate coupling transition from $4f^4$ to $4f^3$
Initial state eigenfunction: $J = 4.0$

0.9850	(111)(20) 4	5 I
0.0777	(110)(11) 2	3 H
0.0835	(211)(21) 4	3 H
−0.1270	(211)(30) 4	3 H

Final state intensities:

		J	E (eV)	Intensity
(111)(10) 3	4 F	1.5	1.4130	0.3752
(111)(20) 3	4 G	2.5	2.1123	0.6864
(111)(10) 3	4 F	2.5	1.5428	0.1210
(111)(20) 3	4 G	3.5	2.3213	0.1580
(210)(20) 3	2 G	3.5	2.0622	0.0780
(111)(20) 3	4 G	4.5	2.3833	0.0123
(111)(20) 3	4 I	4.5	0.0000	2.0319
(111)(20) 3	4 I	5.5	0.2327	0.4885
(111)(20) 3	4 I	6.5	0.4804	0.0244

Photoemission intensity in intermediate coupling transition from $4f^5$ to $4f^4$
Initial state eigenfunction: $J = 2.5$

0.9788	(110)(11) 5	6 H
−0.1246	(111)(20) 3	4 G
0.0293	(211)(20) 5	4 G
0.0350	(211)(21) 5	4 G
−0.1523	(211)(30) 5	4 G

Final state intensities:

		J	E (eV)	Intensity
(111)(20) 4	5 D	0.0	3.7045	0.1581
(111)(20) 4	5 D	1.0	3.7654	0.2206
(111)(10) 4	5 F	1.0	1.5247	0.1765
(111)(20) 4	5 D	2.0	3.8641	0.0764
(111)(20) 4	5 G	2.0	2.2017	0.5020
(111)(10) 4	5 F	2.0	1.5760	0.2730
(211)(21) 4	3 G	3.0	2.6040	0.0856
(111)(20) 4	5 G	3.0	2.2510	0.4762
(111)(10) 4	5 F	3.0	1.6802	0.0829
(111)(20) 4	5 G	4.0	2.4897	0.1085
(211)(30) 4	3 H	4.0	2.1359	0.0226
(111)(20) 4	5 I	4.0	0.0000	1.9381
(111)(20) 4	5 I	5.0	0.1832	0.7728
(111)(20) 4	5 I	6.0	0.3827	0.0476

Photoemission intensity in intermediate coupling transition from $4f^7$ to $4f^6$

Initial state eigenfunction: $J = 3.5$

0.9869	(0)(0) 7	8 S
0.1600	(110)(11) 5	6 P
−0.0117	(200)(20) 7	6 D

Final state intensities:

			J	E (eV)	Intensity
(100)(10) 6	7 F		0.0	0.0000	0.1487
(100)(10) 6	7 F		1.0	0.0473	0.4453
(100)(10) 6	7 F		2.0	0.1301	0.7361
(100)(10) 6	7 F		3.0	0.2368	1.0165
(100)(10) 6	7 F		4.0	0.3591	1.2855
(100)(10) 6	7 F		5.0	0.4911	1.5458
(100)(10) 6	7 F		6.0	0.6287	1.8016

Photoemission intensity in intermediate coupling transition from $4f^9$ to $4f^8$

Initial state eigenfunction: $J = 7.5$

0.9707	(110)(11) 5	6 H
−0.1101	(111)(20) 3	4 I
−0.2109	(111)(30) 5	4 I
−0.0233	(211)(21) 5	4 K

Final state intensities:

			J	E (eV)	Intensity
(210)(21) 6	5 F		4.0	4.3759	0.0409
(210)(21) 6	5 D		4.0	2.5045	0.4154
(100)(10) 6	7 F		4.0	0.4045	0.1539
(111)(10) 4	5 F		5.0	8.0699	0.0105
(210)(20) 6	5 G		5.0	5.2199	0.0433
(210)(21) 6	5 F		5.0	4.3078	0.2685
(210)(21) 6	5 G		5.0	3.5028	0.0573
(100)(10) 6	7 F		5.0	0.2505	0.5778
(221)(31) 6	3 I		6.0	6.0375	0.0137
(221)(31) 6	3 H		6.0	5.8580	0.0109
(210)(20) 6	5 G		6.0	5.0630	0.4286
(210)(11) 6	5 H		6.0	4.0594	0.0241
(210)(21) 6	5 G		6.0	3.4414	0.3686
(100)(10) 6	7 F		6.0	0.0000	1.7419
(111)(20) 4	5 I		7.0	8.0008	0.0560
(221)(30) 6	3 I		7.0	7.7136	0.0128
(221)(31) 6	3 K		7.0	6.3025	0.0217
(210)(21) 6	5 H		7.0	5.8097	0.3456
(221)(31) 6	3 K		7.0	5.5909	0.0433
(210)(21) 6	5 K		7.0	5.1427	0.0106
(210)(20) 6	5 I		7.0	4.5570	0.0274
(210)(11) 6	5 H		7.0	3.9107	0.3837
(210)(21) 6	5 L		7.0	3.6192	0.0724
(221)(31) 6	3 L		8.0	7.9523	0.0249
(111)(20) 4	5 I		8.0	7.7813	0.3991
(210)(21) 6	5 K		8.0	5.0534	0.1230
(210)(20) 6	5 I		8.0	4.3670	0.4670
(210)(21) 6	5 L		8.0	3.6057	0.1049
(210)(21) 6	5 K		9.0	4.8361	0.8905
(210)(21) 6	5 L		9.0	3.5206	0.3457
(210)(21) 6	5 L		10.0	3.3584	1.3589

Photoemission intensity in intermediate coupling transition from $4f^8$ to $4f^7$

Initial state eigenfunction: $J = 6.0$

0.9786	(100)(10) 6	7 F
−0.1431	(111)(20) 4	5 G
0.0565	(210)(20) 6	5 G
0.1341	(210)(21) 6	5 G
0.0130	(210)(21) 6	5 H

Final state intensities:

			J	E (eV)	Intensity
(200)(20) 7	6 D		2.5	5.0783	0.0311
(110)(11) 5	6 P		2.5	4.0627	0.2804
(110)(10) 5	6 F		3.5	6.7767	0.0252
(200)(20) 7	6 G		3.5	6.1717	0.0574
(200)(20) 7	6 D		3.5	5.0511	0.1854
(110)(11) 5	6 P		3.5	4.0106	0.4287
(0)(0) 7	8 S		3.5	0.0000	1.1809
(110)(10) 5	6 F		4.5	6.7887	0.0497
(200)(20) 7	6 G		4.5	6.1569	0.3327
(200)(20) 7	6 D		4.5	4.9330	0.4494
(110)(11) 5	6 H		5.5	7.3015	0.0173
(211)(21) 5	4 H		5.5	7.1523	0.0160
(110)(10) 5	6 F		5.5	6.7117	0.0106
(200)(20) 7	6 G		5.5	6.1621	0.9388
(200)(20) 7	6 I		5.5	4.5280	0.0172
(110)(11) 5	6 H		6.5	7.4495	0.0838
(211)(21) 5	4 H		6.5	7.0398	0.1189
(200)(20) 7	6 G		6.5	6.3591	0.8465
(200)(20) 7	6 I		6.5	4.5512	0.0939
(220)(20) 7	4 I		7.5	8.2659	0.0186
(220)(21) 7	4 L		7.5	7.3060	0.0213
(110)(11) 5	6 H		7.5	7.2400	0.8748
(200)(20) 7	6 I		7.5	4.5523	0.4053
(200)(20) 7	6 I		8.5	4.5214	1.4569

Photoemission intensity in intermediate coupling transition from $4f^{10}$ to $4f^9$

Initial state eigenfunction: $J = 8.0$

0.9666	(111)(20) 4	5 I
0.1180	(211)(21) 4	3 K
−0.2224	(211)(30) 4	3 K
−0.0318	(211)(21) 4	3 L

Final state intensities:

			J	E (eV)	Intensity
(211)(21) 5	4 F		4.5	2.6050	0.3033
(110)(10) 5	6 F		4.5	1.1174	0.1997
(110)(11) 5	6 H		4.5	0.9424	0.0428
(211)(21) 5	4 G		5.5	6.1565	0.0272
(211)(20) 5	4 G		5.5	4.3673	0.0404
(211)(11) 5	4 H		5.5	4.2120	0.0138
(211)(30) 5	4 G		5.5	2.8184	0.4920
(110)(10) 5	6 F		5.5	0.9499	0.7590
(110)(11) 5	6 H		5.5	0.7101	0.2441
(111)(20) 3	4 I		6.5	9.4050	0.0120
(221)(31) 5	2 I		6.5	6.7236	0.0125
(211)(11) 5	4 H		6.5	6.2930	0.0266
(211)(30) 5	4 H		6.5	5.9177	0.0266

(211)(20) 5	4 I		6.5	5.3287	0.0216
(211)(21) 5	4 K		6.5	4.1767	0.0317
(211)(11) 5	4 H		6.5	4.1649	0.1279
(211)(30) 5	4 I		6.5	3.2680	0.1015
(110)(11) 5	6 H		6.5	0.4257	0.6307
(111)(20) 3	4 I		7.5	9.2255	0.1093
(211)(30) 5	4 K		7.5	6.8926	0.0215
(221)(30) 5	2 K		7.5	6.1742	0.0196
(211)(20) 5	4 I		7.5	5.1511	0.1131
(211)(21) 5	4 K		7.5	3.9883	0.0250
(211)(30) 5	4 I		7.5	3.0013	0.6888
(110)(11) 5	6 H		7.5	0.0000	2.1067
(221)(21) 5	2 L		8.5	6.9797	0.0262
(211)(30) 5	4 K		8.5	6.6976	0.0815
(211)(30) 5	4 M		8.5	3.8207	0.1345
(211)(21) 5	4 K		8.5	3.2594	0.8551
(211)(21) 5	4 L		9.5	3.9812	0.3025
(211)(30) 5	4 M		9.5	3.3653	0.9105
(211)(30) 5	4 M		10.5	3.2564	1.3334

Photoemission intensity in intermediate coupling transition from $4f^{11}$ to $4f^{10}$

Initial state eigenfunction: $J = 7.5$

0.9853	(111)(20) 3	4	I
−0.1702	(210)(21) 3	2	K
−0.0173	(210)(21) 3	2	L

Final state intensities:

			J	E (eV)	Intensity
(211)(21) 4	3	F	4.0	4.7644	0.1740
(111)(20) 4	5	G	4.0	4.3037	0.0189
(111)(20) 4	5	G	4.0	3.1919	0.2065
(111)(10) 4	5	F	4.0	2.2975	0.1500
(211)(30) 4	3	G	5.0	8.5036	0.0108
(211)(21) 4	3	H	5.0	7.4712	0.0119
(111)(20) 4	5	G	5.0	3.4185	0.0448
(111)(20) 4	5	G	5.0	2.9516	0.6014
(111)(10) 4	5	F	5.0	1.9141	0.5520
(111)(20) 4	5	I	5.0	1.3742	0.0716
(110)(11) 2	3	H	6.0	11.5694	0.0354
(211)(21) 4	3	K	6.0	7.2880	0.0215
(211)(21) 4	3	H	6.0	6.9850	0.0909
(211)(11) 4	3	H	6.0	6.5996	0.0142
(211)(20) 4	3	I	6.0	4.9281	0.0341
(211)(30) 4	3	H	6.0	3.4212	0.4247
(111)(20) 4	5	G	6.0	2.7293	0.9833
(111)(20) 4	5	I	6.0	1.0580	0.2943
(211)(30) 4	3	I	7.0	8.0653	0.0392
(211)(21) 4	3	K	7.0	7.2367	0.0168
(220)(21) 4	1	K	7.0	6.2424	0.0281
(211)(20) 4	3	I	7.0	4.7595	0.1252
(211)(21) 4	3	L	7.0	4.7040	0.0138
(211)(30) 4	3	K	7.0	3.2280	0.1504
(111)(20) 4	5	I	7.0	0.6243	0.7072
(211)(21) 4	3	K	8.0	6.8333	0.0645
(220)(22) 4	1	L	8.0	4.5174	0.0325
(211)(30) 4	3	K	8.0	2.6318	1.0015
(111)(20) 4	5	I	8.0	0.0000	2.4197
(211)(21) 4	3	L	9.0	3.5880	1.2397
(211)(30) 4	3	M	10.0	4.2380	1.3609

Photoemission intensity in intermediate coupling transition from $4f^{12}$ to $4f^{11}$

Initial state eigenfunction: $J = 6.0$

0.9956	(110)(11) 2	3	H
0.0932	(200)(20) 2	1	I

Final state intensities:

|			J	E (eV)	Intensity
(210)(21) 3	2	D	2.5	6.0651	0.0333
(111)(20) 3	4	D	2.5	4.7686	0.1267
(210)(20) 3	2	D	2.5	4.3010	0.1642
(111)(20) 3	4	G	2.5	4.1256	0.0190
(111)(10) 3	4	F	2.5	2.7230	0.1096
(100)(10) 1	2	F	3.5	12.0490	0.0401
(210)(21) 3	2	F	3.5	6.8249	0.2398
(111)(20) 3	4	D	3.5	4.8410	0.5824
(111)(20) 3	4	G	3.5	4.1555	0.0253
(111)(20) 3	4	G	3.5	3.3651	0.2662
(111)(10) 3	4	F	3.5	2.5079	0.1206
(210)(21) 3	2	G	4.5	8.4283	0.0108
(210)(11) 3	2	H	4.5	5.9047	0.0181
(111)(20) 3	4	G	4.5	3.3921	0.2978
(111)(10) 3	4	F	4.5	2.9689	0.3985
(111)(10) 3	4	F	4.5	1.8603	0.2858
(111)(20) 3	4	I	4.5	1.5002	0.3408
(210)(11) 3	2	H	5.5	6.3090	0.0264
(210)(20) 3	2	I	5.5	5.0704	0.0870
(111)(20) 3	4	G	5.5	3.2717	0.6506
(210)(21) 3	2	H	5.5	2.3740	0.9438
(111)(20) 3	4	I	5.5	1.2532	0.6229
(210)(20) 3	2	I	6.5	5.4061	0.1224
(210)(21) 3	2	K	6.5	4.0880	0.1439
(111)(20) 3	4	I	6.5	0.8057	0.9018
(210)(21) 3	2	K	7.5	3.4330	1.2899
(111)(20) 3	4	I	7.5	0.0000	2.6637
(210)(21) 3	2	L	8.5	5.1545	1.4524

Photoemission intensity in intermediate coupling transition from $4f^{13}$ to $4f^{12}$

Initial state eigenfunction: $J = 3.5$

1.0000	(100)(10) 1	2	F

Final state intensities:

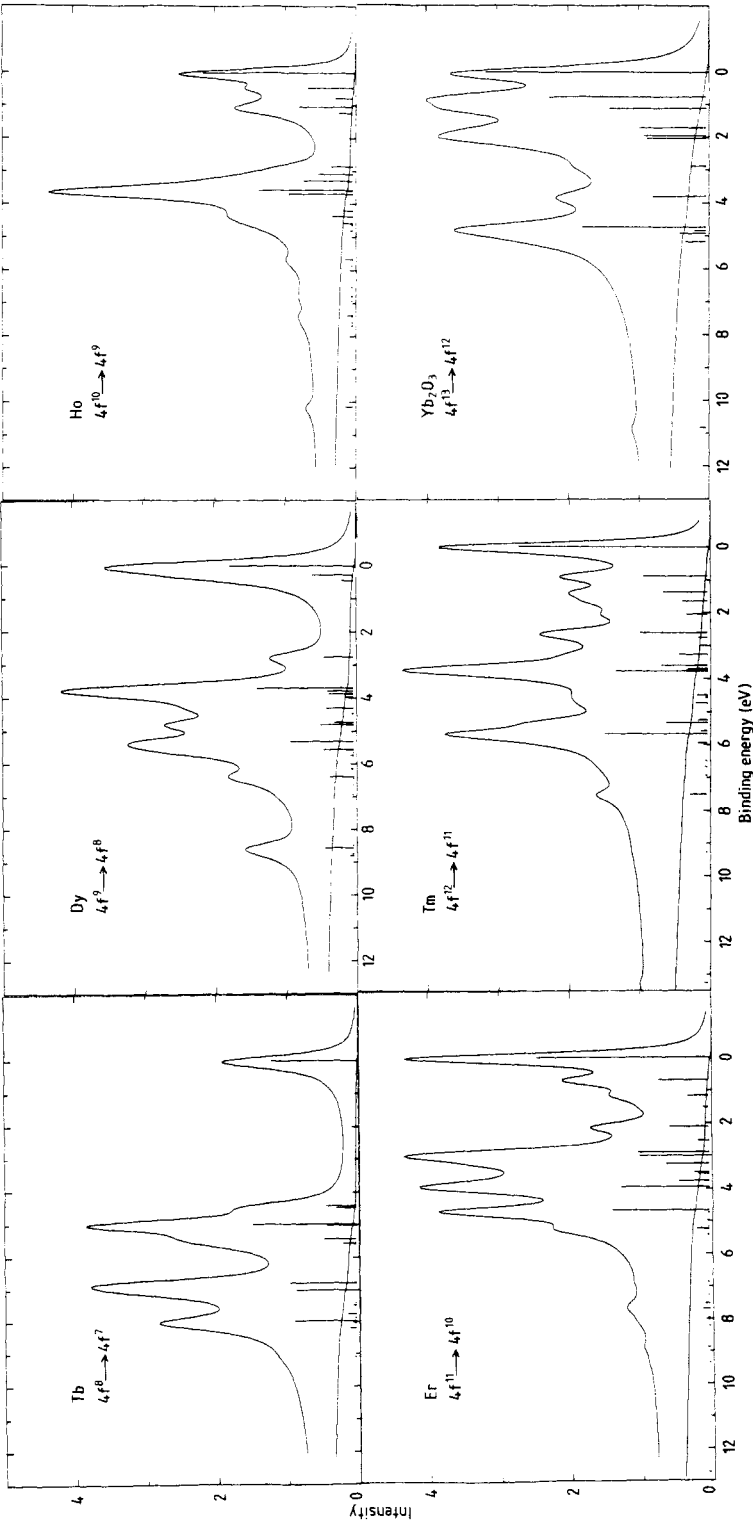|			J	E (eV)	Intensity
(0)(0) 0	1	S	0.0	9.8428	0.0900
(110)(11) 2	3	P	0.0	4.3932	0.1600
(110)(11) 2	3	P	1.0	4.4752	0.3750
(110)(11) 2	3	P	2.0	4.7101	0.2872
(200)(20) 2	1	D	2.0	3.4503	0.7502
(110)(10) 2	3	F	2.0	1.8491	0.8376
(110)(10) 2	3	F	3.0	1.7739	0.8750
(200)(20) 2	1	G	4.0	2.6250	0.2199
(110)(11) 2	3	H	4.0	1.5520	0.9373
(110)(10) 2	3	F	4.0	0.6955	2.2177
(110)(11) 2	3	H	5.0	1.0151	1.3750
(200)(20) 2	1	I	6.0	4.3002	1.7617
(110)(11) 2	3	H	6.0	0.0000	3.1133
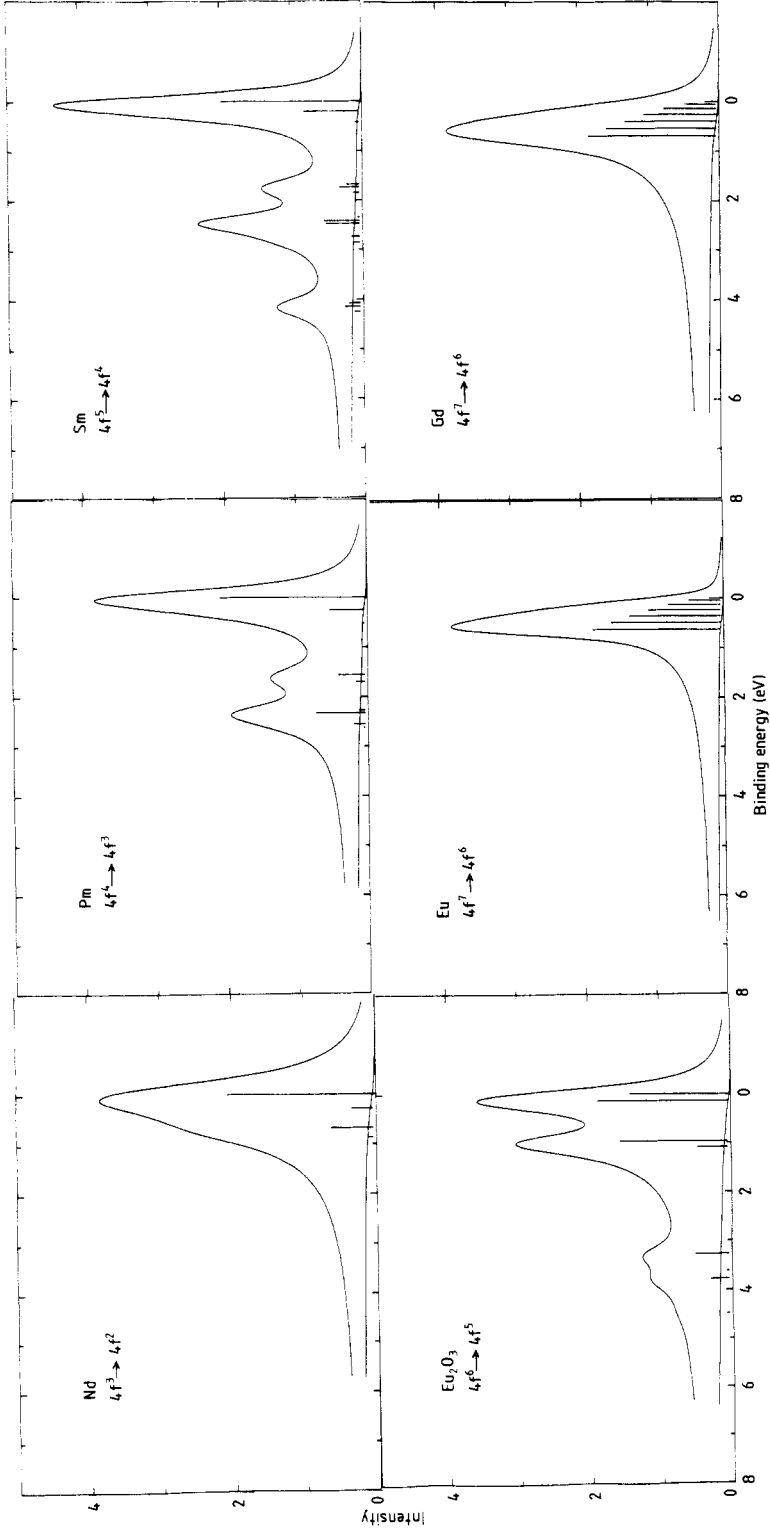
Figure 1. Theoretical spectra of the rare-earth metals on a binding energy scale relative to the lowest multiplet. The calculated multiplet lines from table 2 are convoluted with the lineshapes of Doniach and Sunjic (1970) using the parameters listed in table 3. A calculated background is added and the resultant curve folded with a Gaussian profile of 0.2 eV FWHM to account for experimental resolution.

Table 3. Parameters of the curves of Doniach and Sunjic (1970) from figure 1.

Element	Nd	Pm	Sm	Eu$_2$O$_3$	Eu	Gd
Transition	$f^3 \rightarrow f^2$	$f^4 \rightarrow f^3$	$f^5 \rightarrow f^4$	$f^6 \rightarrow f^5$	$f^7 \rightarrow f^6$	$f^7 \rightarrow f^6$
HWHM γ (eV)	0.37	0.2	0.16	0.2	0.06	0.18
Asymmetry α	0.12	0.12	0.11	0.2	0.18	0.19
Scaling factor	1.1	1.1	1.1	1.1	1.0	1.1
Element	Tb	Dy	Ho	Er	Tm	Yb$_2$O$_3$
Transition	$f^8 \rightarrow f^7$	$f^9 \rightarrow f^8$	$f^{10} \rightarrow f^9$	$f^{11} \rightarrow f^{10}$	$f^{12} \rightarrow f^{11}$	$f^{13} \rightarrow f^{12}$
HWHM γ (eV)	0.17	0.17	0.12	0.12	0.12	0.2
Asymmetry α	0.16	0.13	0.19	0.16	0.21	0.2
Scaling factor	1.1	1.1	1.1	1.1	1.1	1.1

the mean free path in XPS is already as large as 20 Å, it can be estimated (Barth 1982) that a fraction of 10–20% surface emission should be contained in angular integrated spectra. Depending on the structure of the spectrum and the value for the surface shift, this fact may influence the relative intensity of the multiplet structure or else change the fit parameters slightly (e.g. the asymmetry parameter).

Furthermore for Er and Tm the 3d → 4f excitation energy (Fischer and Baun 1967) is close to the photon energy in XPS chosen by Lang *et al* (1981). Recent photoemission experiments with synchrotron radiation in the energy range of the 4d → 4f excitation ('resonant photoemission' experiments) demonstrate that intershell interaction gives rise to drastic changes in the relative intensities of the 4f multiplet structures which cannot be described in the framework of the fractional parentage theory (Gerken *et al* 1982b). Similar effects cannot be excluded for the 3d → 4f excitations also.

The agreement between the theory presented here and experiment, however, is very satisfactory and stresses the importance of a full intermediate coupling calculation for the rare earths. The present theory may be adapted to other problems by use of the tabulated eigenvalues and intensities; for example, if photoemission spectra of other rare-earth systems (atoms, single crystals, compounds) are to be compared with the theory, the values of table 2 enable the reader to construct theoretical spectra with different sets of lineshape parameters. Additional high-resolution photoemission experiments with different photon energies (e.g. Mg Kα, Cu Kα or synchrotron radiation), carried out with the same excellent quality as the results of Lang *et al*, would help to exclude surface effects and intershell interaction and would test the validity of the theory.

Results from an equivalent calculation for the 5f states in the actinides will be presented in a further publication.

Acknowledgment

References

Barth J 1982 *Thesis* University of Hamburg
Carnall W T, Fields P R and Rajnak K 1968 *J. Chem. Phys.* **49** 4412–55

Cox P A 1975 *Structure and Bonding* **24** 59

Cox P A, Lang J K and Baer Y 1981 *J. Phys. F: Met. Phys.* **11** 113

Doniach S and Sunjic M 1970 *J. Phys. C: Solid State Phys.* **3** 285

Fischer D W and Baun W L 1967 *J. Appl. Phys.* **38** 4830

Gerken F 1982 *Thesis* University of Hamburg

Gerken F, Barth J, Johansson L I and Flodström A 1983 to be published

Gerken F, Barth J, Kammerer R, Johansson L I and Flodström A 1982a *Surf. Sci* **117** 468

Gerken F, Barth J and Kunz C 1982b *Int. Conf. on X-Ray and Atomic Inner-Shell Physics, Eugene, Oregon (USA)* (Am. Inst. Phys. Conf. Ser.) to be published

Judd B R 1959 *Proc. R. Soc.* A **250** 562

Kammerer R, Barth J, Gerken F, Johansson L I and Flodström A 1982 *Solid State Commun.* **41** 427

Lang J K, Baer Y and Cox P A 1981 *J. Phys. F: Met. Phys.* **11** 121

Messiah A 1979 *Quantum Mechanics II* (Berlin: de Gruyter)

Nielson C W and Koster G F 1964 *Spectroscopic Coefficients for p^n, d^n and f^n Configurations* (Cambridge, Mass: MIT)

Racah G 1949 *Phys. Rev.* **76** 1352

Sobelman I I 1979 *Atomic Spectra and Radiative Transitions* (Berlin: Springer)

Wybourne B G 1965 *Spectroscopic Properties of Rare Earth* (New York: Wiley)