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Observation and interpretation of the Tm^{3+} free ion spectrum

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Abstract. The emission spectrum of thulium produced by a vacuum spark source was observed in the wavelength range from 700 to 2320 Å on the 10.7 m normal-incidence vacuum ultraviolet spectrograph at the Paris-Meudon observatory. In the unknown spectrum of Tm IV, more than 760 lines have been identified for the first time as transitions between 157 levels of $4f^{11}5d$, 33 levels of $4f^{11}6p$, 9 levels of $4f^{11}6s$ and 10 levels of the $4f^{12}$ ground configuration. A parametric interpretation of the levels has been carried out using the Cowan codes. Configuration interaction effects are discussed, in particular with the core-excited configurations $5p^54f^{13}$ and $5p^54f^{12}5d$. Radial Slater parameters derived from $4f^{12}$ levels are larger than those pertaining to trivalent Tm ions in compounds. A selection of 105 prominent lines is given.

PACS. 31.15.Md Perturbation theory – 32.70.Cs Oscillator strengths, lifetimes, transition moments – 42.55.Rz Doped-insulator lasers and other solid state lasers – 52.80.Yr Discharges for spectral sources (including inductively coupled plasma)

1 Introduction

Investigations of weakly ionized lanthanide spectra were undertaken recently in our groups for several purposes. Spectra of lanthanides produced by mild sparks comprise doubly charged ions which are of current interest for astrophysical plasma modelling. The applications of triply-ionized lanthanide elements in compounds are numerous in the fields of materials for lasers, quantum information, phosphors in lighting industry, but their spectroscopy is still poorly known. In the critical compilation of energy levels by Martin et al. [1], the free ion spectra IV of La, Ce, Pr, Yb and Lu are well described and 25 levels are reported for the spectrum of Tb IV. However the free ion spectra IV of Nd, Pm, Sm, Eu, Gd, Dy, Ho, Er and Tm were all missing. The reported levels of the $4f^N$ ground configuration were either theoretical values or centroids of Stark sublevels derived from absorption or fluorescence experiments on lanthanide ions in crystal hosts or aquo-ions. In the period of 1978–2005, only limited revisions and extensions were performed on emission spectra of Yb IV [2] and Pr IV [3], whereas hundreds of publications dealt with trivalent lanthanides in compounds. Consequently the latest theoretical developments in the far configuration interaction effects on $4f^N$ configurations [4] could not be applied to accurate energy levels of free ions for configurations with more than two electrons (or holes) in the $4f$ subshell.

With regard to complexity, the most accessible of the unknown fourth spectra (IV) in the gap Pr-Yb were obviously Nd IV and Tm IV, respectively close to the beginning and the end of the $4f$ subshell filling. For the first interpretation of Nd IV, we combined new data recorded on the 10.7 m normal incidence vacuum ultraviolet spectrograph at Meudon observatory with spectrograms recorded previously at the National Bureau of Standards (NBS) in 1980. Initial results of our current analysis of Nd IV comprise the theoretical interpretation of 37 levels of $4f^3$ derived from 550 classified lines $4f^3$–$4f^25d$ [5]. Close to the end of the lanthanide period, the spectrum of Tm IV has the same number (1728) of $4f^{12}$–$4f^{11}5d$ transitions allowed by electric dipole decay as for the $4f^3$–$4f^25d$ transitions of Nd IV, according to a semi-complementarity property demonstrated in reference [6]. However the situation is largely unbalanced between the excited configuration $4f^{11}5d$ for which 364 levels are expected, and the ground configuration $4f^{12}$ for which only 13 levels are predicted. In such a case, the intermediate coupling conditions allow many intercombination lines and the level intervals within the $4f^{12}$ configuration appear in many repeating wavenumber differences. Consequently the breakthrough in the Tm IV analysis in our investigations can be considered as highly reliable.

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2 Experiment

The light source in the present observations was a sliding spark [7,8]. The cathode was a rod of aluminum and the anode a rod of 99.9% pure thulium. The electric circuit included a capacitance of 4.82 μF charged to 7 kV and an inductance with three possible values of 11, 38 and 63 μH, which led to different peak current and allowed the discrimination of ionic charges according to different behaviors of their line intensities. Several exposures were performed in overlapping wavelength sections, due to the large dispersion of the grating (0.26 Å per mm). In the regions 700–1363 Å and 1250–2320 Å, spectral plates Kodak SWR and Ilford Q2 were used respectively. A few exposures were also tried at short wavelengths using the phosphor image plate technique [15].

The wavelength calibration used known wavelengths [9] of spectral lines of impurities present in the spark, namely C II, C III, O II, O III, O IV, Al II, Al III, Si II, Si III, some of them in the second order of the grating. Quadratic dispersion polynomials were fitted by means of a least squares program written by J.L. Tech (NBS) and they led to estimated wavelength errors better than 0.0025 Å in all the sections of the spectrum below 1300 Å. Due to a relative lack of standards at higher wavelengths, copper was added in the spark and a few lines of Cu IV provided us with standards of poor quality. Some of the Tm III lines classified by Sugar [10], were used as standards in the region 2000–2300 Å. The estimated wavelength error given by the Tech code was nowhere larger than 0.005 Å above 1300 Å. There is no description of thulium spark spectrum in the literature below 1977 Å. However we compared our wavelength list with the results by Li et al. [11,12], who used the Cowan codes [13] and the compiled Tm III levels of [1] to derive transition probabilities and Ritz wavelengths. We concluded that below 2000 Å only the strongest predicted line ($\lambda = 1649.055$ Å) is present on our spectrograms. The wavenumber consistency of the classifications supports our wavelength list and is discussed in the next section.

3 Determination of energy levels

The Cowan codes [13] were used to calculate Hartree-Fock radial parameters in the HFR option without correlation and to predict the overall spectral ranges of the strong transitions in the Tm III, IV and V spectra. In order to improve the predictions of Tm IV levels, a scaling factor $SF(P)$ was applied to the Hartree Fock value of the radial parameters P_{HFR}. The appropriate scaling factors were obtained by comparisons of radial parameters P_{fit} fitted from experimental levels with their Hartree-Fock values P_{HFR} in Tm III and in the neighbouring lanthanide elements Yb [2] and Lu [14,17,18]. The E_{av} energies of the studied configurations $4f^{11}5d$, $4f^{11}6s$ and $4f^{11}6p$ were chosen so as to place their lowest energy levels at values which fitted the level trends in ten known third spectra (III) and six known fourth spectra (IV). The comparison of observed wavelengths and intensities with theoretical wavelengths and weighted theoretical transition probabilities in emission led to identification of strong lines ending on the lowest levels $^3H_6$, $^3F_4$, $^3H_5$. The radial parameter values were fitted iteratively as the number of known levels increased and this improved the level predictions accordingly.

Starting from classifications in the region 800–1000 Å where $4f^{12}$–$4f^{11}5d$ transitions are strong, we moved to longer wavelengths, aiming to determine the lowest levels of $4f^{11}5d$. These levels have mostly quintet characters and weakly decay to the triplets and singlets of $4f^{12}$. Moreover, the very dense array $4f^{11}5d$–$4f^{11}6p$ dominates the spectrum above 1200 Å and masks the scarce $4f^{12}$–$4f^{11}5d$ transitions. The final steps in the classification of $5d$–$6p$ and $6s$–$6p$ transitions owe much to the high resolution of the Meudon spectrograph and to the good agreement between predicted and observed lines for both wavelengths and intensities.

In this first investigation of the Tm IV spectrum, for the even parity, 10 levels of $4f^{12}$ and 33 levels of $4f^{11}6p$ have been determined and are given in Table 1, whereas for the odd parity, 157 levels of $4f^{11}5d$ and 9 levels of $4f^{11}6s$ have been determined and are given in Table 2. Their determination derived from the classification of 767 observed spectral lines. The level energies and their uncertainties reported in Tables 1 and 2 were their best values calculated with the ELCALC code [21] which applies an iterative procedure to minimize the differences between wave numbers calculated from level energies and the observed ones. As input to the code, 680 lines were used, with uncertainties on their wave numbers smoothly decreasing from 0.50 to 0.13 cm^{-1} between 764 and 2230 Å. We have deposited the line list with wavelengths, intensity estimates and classifications on the MOLAT database of the Paris-Meudon Observatory [22]. All the wavelengths of classified lines are compared to the Ritz wavelengths derived from the best values collected in Tables 1 and 2. For 797 classifications, including 21 double classifications, one line triply classified and 9 blends, the average of the wavelength deviations is 0.0038 Å, which we consider as a good support of our analysis. Table 3 presents all the transitions to the ground level $4f^{12}$ $^3H_6$. All the $5d$–$6p$ and $6s$–$6p$ transitions involving the six levels of the $4f^{11}(^4I_{15/2})6p$ subconfiguration are given in Table 4. In both Tables 3 and 4, the reported intensities are visual estimates of plate blackening over a scale of 1–1000 without correction of plate sensitivity. In spite of their large uncertainties (about 30%) these intensity estimates were very useful for identification of lines. Since more significant intensity measurements are soon expected from phosphor image plates, the publication of all classified lines is left for the near future.

The inversion of the fine structure in the heavier lanthanides hinders our locating the levels with small J-values, which combine a weaker thermal population with relatively low transition probabilities. Only 9 levels with $J = 2$ have been found in $4f^{11}5d$ and the level search stopped at $J = 4$ in $4f^{11}6p$ and $4f^{11}6s$. Consequently our efforts to find the 3 missing levels of $4f^{12}$,

Table 1. Even parity energy levels of Tm IV with energy value (in cm^{-1}) and corresponding uncertainty between parenthesis, number of transitions involved N and calculated Landé factors g_{calc}. The deviations $\Delta E = E_{exp} - E_{calc}$ (in cm^{-1}) use calculated energies derived by means of the Cowan codes [13] with parameters given in Table 5. The leading components of the eigenfunctions are given in the LS coupling scheme. The dominant subconfiguration in $J - j$ coupling is reported in the first column if larger than 50%. The percentages of squared components in the three configurations $4f^{12}$, $4f^{11}6p$ and $5p^5 4f^{13}$ are given in the three last columns.

Conf.	J	E_{exp} (unc.)	N	g_{calc}	ΔE	1st comp.	%	$4f^{12}$ %	$4f^{11}6p$ %	$5p^5 4f^{13}$ %
$4f^{12}$	6	0.00 (.07)	58	1.166	−25	^{3}H	99	100	0.01	0
$4f^{12}$	4	5634.02 (.07)	63	1.138	−10	^{3}F	62	99.98	0.01	0.01
$4f^{12}$	5	8216.73 (.06)	67	1.033	22	^{3}H	100	99.99	0.01	0
$4f^{12}$	4	12547.23 (.07)	55	0.952	−16	^{3}H	59	99.99	0.01	0
$4f^{12}$	3	14410.41 (.08)	46	1.084	−42	^{3}F	100	99.98	0.01	0.01
$4f^{12}$	2	15089.60 (.11)	25	0.750	17	^{3}F	78	99.98	0.01	0.01
$4f^{12}$	4	21174.20 (.10)	39	0.960	−19	^{1}G	57	99.99	0.01	0.01
$4f^{12}$	2	28163.25 (.14)	14	1.132	−32	^{1}D	43	99.98	0.02	0
$4f^{12}$	6	35329.31 (.10)	21	1.001	−3	^{1}I	99	99.98	0.02	0
$4f^{12}$	2	38532.46 (.17)	8	1.286	58	^{3}P	60	99.98	0.02	0
$4f^{11}(^4I_{15/2})6p_{1/2}$	7	144991.40 (.13)	6	1.241	−15	(^{4}I)^{5}H	66	0	100	0
$4f^{11}(^4I_{15/2})6p_{1/2}$	8	145564.25 (.10)	8	1.163	16	(^{4}I)^{3}K	47	0	100	0
$4f^{11}(^4I_{13/2})6p_{1/2}$	6	152729.67 (.09)	11	1.155	−8	(^{4}I)^{5}H	63	0	100	0
$4f^{11}(^4I_{13/2})6p_{1/2}$	7	153028.54 (.07)	13	1.084	−1	(^{4}I)^{5}K	42	0	100	0
$4f^{11}(^4I_{15/2})6p_{3/2}$	9	153217.84 (.15)	5	1.219	−8	(^{4}I)^{5}K	97	0	100	0
$4f^{11}(^4I_{15/2})6p_{3/2}$	8	153952.89 (.12)	10	1.208	−7	(^{4}I)^{5}I	67	0	100	0
$4f^{11}(^4I_{15/2})6p_{3/2}$	7	154466.21 (.08)	13	1.171	−5	(^{4}I)^{3}I	69	0	100	0
$4f^{11}(^4I_{15/2})6p_{3/2}$	6	154491.66 (.11)	14	1.156	−7	(^{4}I)^{3}H	88	0	100	0
$4f^{11}(^4I_{11/2})6p_{1/2}$	5	157024.55 (.08)	14	1.027	0	(^{4}I)^{5}I	28	0	100	0
$4f^{11}(^4I_{11/2})6p_{1/2}$	6	157221.39 (.08)	16	0.969	16	(^{4}I)^{5}K	48	0	100	0
$4f^{11}(^4I_{9/2})6p_{1/2}$	4	159250.39 (.08)	14	1.000	56	(^{4}I)^{3}H	15	0	100	0
$4f^{11}(^4I_{9/2})6p_{1/2}$	5	159400.74 (.09)	14	0.919	73	(^{4}I)^{5}K	32	0	100	0
$4f^{11}(^4I_{13/2})6p_{3/2}$	8	161113.30 (.10)	9	1.148	−2	(^{4}I)^{5}K	74	0	100	0
$4f^{11}(^4I_{13/2})6p_{3/2}$	5	161402.13 (.09)	17	1.061	0	(^{4}I)^{3}H	47	0	100	0
$4f^{11}(^4I_{13/2})6p_{3/2}$	7	161679.40 (.09)	13	1.130	−10	(^{4}I)^{5}I	58	0	100	0
$4f^{11}(^4I_{13/2})6p_{3/2}$	6	161783.68 (.09)	17	1.092	−3	(^{4}I)^{3}I	45	0	100	0
$4f^{11}(^4F_{9/2})6p_{1/2}$	5	162661.03 (.08)	15	1.062	−10	(^{4}I)^{5}K	27	0	100	0
$4f^{11}(^4F_{9/2})6p_{1/2}$	4	162680.11 (.10)	9	1.103	−3	(^{4}F)^{5}D	24	0	100	0
$4f^{11}(^4I_{11/2})6p_{3/2}$	4	165251.03 (.10)	11	0.902	28	(^{4}I)^{5}H	57	0	100	0
$4f^{11}(^4I_{11/2})6p_{3/2}$	7	165411.44 (.12)	10	1.065	22	(^{4}I)^{5}K	39	0	100	0
$4f^{11}(^4I_{11/2})6p_{3/2}$	5	165710.96 (.08)	19	0.975	−12	(^{4}I)^{5}I	30	0	100	0
$4f^{11}(^4I_{11/2})6p_{3/2}$	6	165724.96 (.10)	14	1.047	−3	(^{4}I)^{5}I	29	0	100	0
$4f^{11}6p$	5	166583.10 (.11)	13	1.182	−80	(^{4}G)^{5}F	19	0	100	0
$4f^{11}6p$	6	167021.69 (.10)	13	1.092	−93	(^{2}H2)^{1}I	22	0	100	0
$4f^{11}6p$	6	167952.24 (.09)	12	1.041	55	(^{4}I)^{3}K	34	0	100	0
$4f^{11}6p$	5	168065.80 (.08)	17	1.028	2	(^{4}I)^{5}I	16	0	100	0
$4f^{11}6p$	4	168149.43 (.10)	12	0.949	51	(^{4}I)^{5}I	23	0	100	0
$4f^{11}6p$	4	168777.63 (.10)	10	1.131	36	(^{4}F)^{5}G	36	0	100	0
$4f^{11}6p$	5	170949.35 (.09)	15	1.086	−14	(^{4}F)^{5}F	32	0	100	0
$4f^{11}6p$	6	171069.80 (.14)	6	1.145	−16	(^{4}F)^{5}G	50	0	100	0
$4f^{11}6p$	4	171296.50 (.09)	12	1.095	−7	(^{4}F)^{5}D	26	0	100	0
$4f^{11}6p$	4	173151.59 (.11)	9	1.157	31	(^{4}F)^{5}F	16	0	100	0
$4f^{11}6p$	5	173348.49 (.11)	9	1.046	−41	(^{4}F)^{3}G	18	0	99.99	0.01

Table 2. Odd parity energy levels of Tm IV with energy value (in cm^{-1}) and corresponding uncertainty between parenthesis, number of transitions involved N and calculated Landé factors g_{calc}. The deviations $\Delta E = E_{exp} - E_{calc}$ (in cm^{-1}) use calculated energies derived by means of the Cowan codes [13] with parameters given in Table 6. The leading components of the eigenfunctions are given in the LS coupling scheme. Repeating doublets of $4f^{11}$ are labeled as in [26].

Conf.	J	E_{exp} (unc.)	N	g_{calc}	ΔE	1st comp.	%	$4f^{11}5d$ %	$4f^{11}6s$ %	$5p^5 4f^{12}5d$ %
$4f^{11}5d$	6	72011.02 (.20)	4	1.299	−62	$(^4I)^5K$	75	99.9	0	0.1
$4f^{11}5d$	7	72931.67 (.13)	6	1.258	−83	$(^4I)^5H$	76	99.9	0	0.1
$4f^{11}5d$	9	74506.41 (.18)	3	1.136	−24	$(^4I)^3L$	46	100	0	0
$4f^{11}5d$	8	75585.02 (.16)	6	1.176	28	$(^4I)^5I$	39	100	0	0
$4f^{11}5d$	5	78413.63 (.13)	7	1.209	−31	$(^4I)^5G$	64	99.9	0	0.1
$4f^{11}5d$	9	78677.88 (.23)	2	1.193	−38	$(^4I)^5K$	74	100	0	0
$4f^{11}5d$	6	79225.87 (.13)	9	1.203	−19	$(^4I)^5H$	51	99.9	0	0.1
$4f^{11}5d$	8	80122.71 (.27)	4	1.173	−4	$(^4I)^5I$	50	100	0	0
$4f^{11}5d$	7	80264.65 (.10)	10	1.144	15	$(^4I)^5I$	27	99.9	0	0.1
$4f^{11}5d$	8	82258.89 (.13)	6	1.061	−3	$(^4I)^5L$	47	100	0	0
$4f^{11}5d$	5	83293.13 (.13)	11	1.137	−25	$(^4I)^3G$	50	99.9	0	0.1
$4f^{11}5d$	7	83530.02 (.12)	11	1.056	12	$(^4I)^3I$	36	99.9	0	0.1
$4f^{11}5d$	4	83548.79 (.15)	5	1.070	−30	$(^4I)^5G$	46	99.9	0	0.1
$4f^{11}5d$	6	84485.81 (.12)	11	1.066	17	$(^4I)^3H$	31	99.9	0	0.1
$4f^{11}5d$	5	85541.93 (.12)	11	1.156	10	$(^4I)^3G$	30	99.9	0	0.1
$4f^{11}5d$	7	86145.56 (.13)	7	0.991	24	$(^4I)^5L$	47	100	0	0
$4f^{11}5d$	4	86577.02 (.12)	8	1.143	−2	$(^4I)^5G$	25	99.9	0	0.1
$4f^{11}5d$	6	86717.61 (.11)	10	1.054	−8	$(^4I)^3H$	32	99.9	0	0.1
$4f^{11}5d$	8	86796.75 (.32)	2	1.128	−17	$(^4I)^5K$	57	100	0	0
$4f^{11}5d$	5	87090.72 (.09)	15	1.023	33	$(^2H2)^3H$	16	99.9	0	0.1
$4f^{11}5d$	7	87872.31 (.17)	6	1.108	12	$(^4I)^5I$	46	100	0	0
$4f^{11}5d$	6	87952.02 (.12)	11	0.957	66	$(^4I)^5L$	25	100	0	0
$4f^{11}5d$	4	87990.56 (.10)	13	1.084	38	$(^4I)^5H$	29	99.9	0	0.1
$4f^{11}5d$	5	88121.99 (.09)	15	1.086	67	$(^4F)^5G$	11	99.9	0	0.1
$4f^{11}5d$	6	88226.85 (.11)	10	0.955	40	$(^4I)^5L$	22	100	0	0
$4f^{11}5d$	4	89918.98 (.12)	12	1.000	14	$(^4I)^3G$	26	99.9	0	0.1
$4f^{11}5d$	5	90160.38 (.12)	12	0.977	42	$(^4I)^5K$	42	100	0	0
$4f^{11}5d$	6	90842.21 (.13)	8	1.125	34	$(^4F)^5G$	35	100	0	0
$4f^{11}5d$	4	90973.89 (.11)	10	0.976	34	$(^4I)^5I$	16	99.9	0	0.1
$4f^{11}5d$	7	91061.55 (.17)	7	1.084	−29	$(^4I)^3K$	31	99.9	0	0.1
$4f^{11}5d$	5	92006.67 (.11)	11	0.983	24	$(^4I)^3I$	25	99.9	0	0.1
$4f^{11}5d$	6	92583.34 (.11)	9	1.047	−25	$(^4I)^3K$	22	99.9	0	0.1
$4f^{11}5d$	7	92971.03 (.17)	3	1.040	55	$(^4I)^3L$	36	99.9	0	0.1
$4f^{11}5d$	4	93826.93 (.14)	8	1.149	−12	$(^4F)^5G$	27	99.9	0	0.1
$4f^{11}5d$	6	94119.93 (.14)	7	1.120	6	$(^4F)^3H$	22	99.9	0	0.1
$4f^{11}5d$	3	94619.16 (.14)	5	1.269	−4	$(^4S)^5D$	40	99.9	0	0.1
$4f^{11}5d$	5	94854.50 (.12)	11	1.128	4	$(^4F)^5F$	22	99.9	0	0.1
$4f^{11}5d$	5	95379.52 (.14)	8	0.987	28	$(^4F)^5I$	21	99.9	0	0.1
$4f^{11}5d$	7	95637.50 (.20)	2	1.088	−16	$(^4F)^5H$	31	100	0	0
$4f^{11}5d$	6	95685.30 (.15)	7	0.998	−9	$(^4I)^3K$	33	100	0	0
$4f^{11}5d$	3	96078.53 (.15)	5	1.069	30	$(^4F)^5G$	21	99.9	0	0.1
$4f^{11}5d$	4	96463.05 (.13)	9	0.965	63	$(^4I)^5I$	21	99.9	0	0.1
$4f^{11}5d$	2	96518.62 (.22)	2	0.988	−242	$(^4F)^5G$	22	99.9	0	0.1
$4f^{11}5d$	6	96982.12 (.15)	8	1.142	−48	$(^4G)^5G$	25	99.9	0	0.1
$4f^{11}5d$	4	97319.40 (.16)	5	1.228	31	$(^4F)^5D$	29	99.9	0	0.1
$4f^{11}5d$	3	97437.93 (.17)	5	1.172	−19	$(^4F)^3D$	20	99.9	0	0.1
$4f^{11}5d$	5	97637.17 (.13)	10	1.091	−40	$(^4F)^3G$	21	99.9	0	0.1
$4f^{11}5d$	4	98135.23 (.20)	4	1.074	39	$(^4F)^5H$	23	99.9	0	0.1
$4f^{11}5d$	5	98321.42 (.17)	5	1.126	33	$(^4F)^5H$	22	99.9	0	0.1
$4f^{11}5d$	3	98787.43 (.21)	3	0.885	−6	$(^4F)^5H$	30	99.9	0	0.1
$4f^{11}6s$	8	98972.81 (.10)	5	1.245	3	$6s(^4I)^5I$	95	1.8	98.2	0
$4f^{11}5d$	4	99082.59 (.19)	4	1.042	16	$(^4F)^5H$	27	99.9	0	0.1
$4f^{11}5d$	4	99544.71 (.17)	6	1.252	−22	$(^4S)^5D$	23	99.9	0	0.1
$4f^{11}5d$	5	100027.46 (.24)	4	1.192	73	$(^4F)^5G$	44	99.9	0	0.1
$4f^{11}6s$	7	100145.05 (.10)	8	1.148	4	$6s(^4I)^3I$	69	2.1	97.9	0
$4f^{11}5d$	5	101925.68 (.16)	7	1.100	−30	$(^2H2)^3G$	20	99.9	0	0.1

Table 2. *Continued.*

Conf.	J	E_{exp} (unc.)	N	g_{calc}	ΔE	1st comp.	%	$4f^{11}5d$ %	$4f^{11}6s$ %	$5p^5 4f^{12}5d$ %
$4f^{11}5d$	6	102020.08 (.23)	4	1.069	−44	$(^2K)^3H$	21	99.7	0.3	0.1
$4f^{11}5d$	5	102098.60 (.16)	5	1.100	−23	$(^4G)^5G$	12	99.9	0	0.1
$4f^{11}5d$	2	102581.33 (.35)	3	1.005	19	$(^4F)^3F$	25	99.9	0	0.1
$4f^{11}5d$	4	102738.24 (.20)	5	1.129	−57	$(^4G)^5G$	19	99.9	0	0.1
$4f^{11}5d$	2	103397.05 (.27)	2	1.198	−93	$(^4F)^5P$	24	99.9	0	0.1
$4f^{11}5d$	4	103781.31 (.29)	3	1.088	60	$(^4F)^3F$	27	99.9	0	0.1
$4f^{11}5d$	6	103799.19 (.26)	2	1.098	−2	$(^4F)^3H$	14	99.9	0	0.1
$4f^{11}5d$	5	104570.90 (.26)	3	1.064	−38	$(^4F)^3H$	21	99.9	0	0.1
$4f^{11}5d$	5	105156.00 (.21)	4	1.079	20	$(^4F)^3G$	25	99.9	0	0.1
$4f^{11}5d$	6	105879.41 (.44)	1	1.143	29	$(^2H2)^3G$	22	99.9	0	0.1
$4f^{11}5d$	6	106101.98 (.44)	1	1.047	−15	$(^4G)^5I$	38	99.7	0.2	0.1
$4f^{11}5d$	2	106461.65 (.26)	2	0.880	−51	$(^4F)^3D$	19	99.9	0	0.1
$4f^{11}5d$	4	106684.87 (.18)	5	1.056	67	$(^4F)^3G$	13	99.8	0.1	0.1
$4f^{11}5d$	3	106770.52 (.26)	4	1.009	13	$(^4G)^5G$	14	99.8	0	0.2
$4f^{11}6s$	7	106895.45 (.08)	8	1.159	−111	$6s(^4I)^5I$	57	21.8	78.2	0
$4f^{11}5d$	4	107073.00 (.28)	5	1.085	55	$(^2G2)^3F$	13	99.9	0	0.1
$4f^{11}5d$	6	107294.13 (.10)	9	1.099	−124	$(^2K)^3H$	15	67.2	32.6	0.2
$4f^{11}6s$	6	107603.36 (.08)	9	1.072	48	$6s(^4I)^5I$	37	34.4	65.6	0.1
$4f^{11}5d$	7	107885.74 (.10)	7	1.118	19	$(^2K)^3I$	38	80.6	19.3	0.1
$4f^{11}5d$	4	108205.10 (.29)	3	0.942	−10	$(^2G2)^3H$	13	99.8	0.1	0.1
$4f^{11}5d$	5	108273.35 (.29)	3	1.035	76	$(^2K)^3H$	21	99.9	0	0.1
$4f^{11}5d$	3	108304.84 (.34)	2	1.129	171	$(^4F)^3D$	21	99.9	0	0.1
$4f^{11}5d$	6	109128.14 (.30)	2	1.077	19	$(^4G)^3H$	26	99.6	0.3	0.1
$4f^{11}5d$	3	109386.12 (.26)	3	1.124	−12	$(^4G)^5G$	25	99.9	0	0.1
$4f^{11}5d$	5	109463.34 (.28)	3	1.300	35	$(^4G)^5F$	46	99.8	0.1	0.1
$4f^{11}5d$	3	109693.61 (.28)	3	1.067	−69	$(^4G)^3F$	10	99.9	0	0.1
$4f^{11}5d$	4	109967.25 (.28)	3	1.093	−45	$(^4G)^3F$	31	99.8	0.1	0.1
$4f^{11}5d$	6	110092.40 (.24)	4	1.068	3	$(^2K)^1I$	23	97.7	2.2	0.1
$4f^{11}5d$	5	110723.68 (.14)	4	1.070	16	$(^2K)^3H$	21	98.5	1.4	0.1
$4f^{11}6s$	5	111236.63 (.11)	7	0.924	−32	$6s(^4I)^5I$	65	2.4	97.6	0
$4f^{11}5d$	6	111381.45 (.09)	6	1.026	−24	$(^2K)^3H$	16	94.9	5.0	0.1
$4f^{11}6s$	6	111598.24 (.09)	6	1.085	−30	$6s(^4I)^3I$	31	38.9	61.1	0
$4f^{11}5d$	5	111881.49 (.39)	2	1.077	−6	$(^4G)^3G$	28	99.5	0.4	0.1
$4f^{11}5d$	3	112218.37 (.31)	3	0.935	−56	$(^4G)^5H$	17	99.8	0	0.1
$4f^{11}5d$	7	112290.52 (.25)	2	1.007	−1	$(^2K)^3L$	26	99.7	0.2	0.1
$4f^{11}5d$	4	112408.89 (.33)	2	0.798	−190	$(^4G)^5I$	52	98.9	1.0	0.1
$4f^{11}5d$	5	112491.99 (.32)	2	1.094	65	$(^4G)^3G$	26	96.9	2.9	0.2
$4f^{11}5d$	3	113175.70 (.21)	4	1.199	−10	$(^4G)^3D$	26	99.9	0	0.1
$4f^{11}6s$	5	113441.16 (.09)	7	1.017	−57	$6s(^4I)^3I$	16	47.8	52.1	0
$4f^{11}6s$	4	113442.32 (.09)	4	0.807	38	$6s(^4I)^5I$	47	6.2	93.0	0
$4f^{11}5d$	3	113453.35 (.33)	2	1.026	28	$(^4G)^5F$	20	99.8	0.1	0.1
$4f^{11}5d$	5	113965.49 (.12)	8	1.022	37	$(^4G)^5I$	19	55.9	44.0	0.1
$4f^{11}5d$	5	114168.84 (.13)	6	0.952	41	$(^2K)^3I$	35	98.8	1.0	0.2
$4f^{11}5d$	3	114987.37 (.31)	2	0.907	16	$(^4G)^5H$	26	99.9	0	0.1
$4f^{11}5d$	2	115069.24 (.29)	2	0.896	5	$(^4G)^5G$	15	99.8	0	0.2
$4f^{11}5d$	5	115778.36 (.20)	5	0.968	48	$(^2K)^3I$	22	98.4	1.4	0.2
$4f^{11}5d$	3	115807.55 (.24)	4	0.990	−13	$(^4G)^5H$	18	99.8	0	0.2
$4f^{11}5d$	4	116283.34 (.39)	4	1.059	−25	$(^2D1)^3F$	22	98.4	1.5	0.2
$4f^{11}5d$	4	116373.53 (.39)	2	1.109	−22	$(^2D1)^3F$	33	99.7	0.2	0.1
$4f^{11}5d$	4	116738.25 (.23)	4	1.012	−4	$(^2K)^3H$	13	99.5	0.3	0.2
$4f^{11}5d$	5	116881.54 (.09)	5	1.056	−29	$6s(^4F)^5F$	19	52.1	47.8	0.1
$4f^{11}5d$	5	116946.33 (.19)	6	1.078	−23	$6s(^4F)^5F$	21	53.5	46.4	0.1
$4f^{11}6s$	4	117225.30 (.11)	3	1.051	−18	$6s(^4F)^3F$	40	3.6	96.4	0
$4f^{11}5d$	7	117531.05 (.28)	2	1.092	−29	$(^2L)^3I$	49	99.7	0	0.3
$4f^{11}5d$	6	117607.00 (.24)	3	0.933	42	$(^2K)^3K$	52	99.7	0.3	0.1
$4f^{11}5d$	2	117828.10 (.34)	2	0.936	85	$(^4G)^3F$	46	99.8	0.1	0.1
$4f^{11}5d$	5	118287.97 (.26)	4	1.103	179	$(^2D1)^3G$	10	98.4	1.5	0.1
$4f^{11}5d$	3	118493.86 (.22)	4	1.248	−51	$(^4G)^5F$	12	99.6	0.3	0.1
$4f^{11}5d$	5	119057.80 (.26)	4	0.983	−84	$(^4G)^3I$	26	99.4	0.5	0.1

Table 2. *Continued.*

Conf.	J	E_{exp} (unc.)	N	g_{calc}	ΔE	1st comp.	%	$4f^{11}5d$ %	$4f^{11}6s$ %	$5p^5 4f^{12}5d$ %
$4f^{11}5d$	7	119100.52 (.28)	2	1.010	−12	$(^2I)^3L$	23	99.9	0	0.1
$4f^{11}5d$	4	119103.32 (.34)	2	1.050	53	$(^2D1)^1G$	16	99.4	0.5	0.1
$4f^{11}5d$	3	119149.30 (.19)	4	1.324	80	$(^4D)^5P$	27	99.7	0.2	0.1
$4f^{11}5d$	4	119685.65 (.40)	2	1.039	−48	$(^4G)^3G$	22	99.5	0.3	0.1
$4f^{11}5d$	3	120140.74 (.25)	4	1.025	61	$(^4D)^5G$	18	99.8	0	0.2
$4f^{11}5d$	7	120223.30 (.28)	2	0.974	40	$(^2I)^3L$	29	99.9	0	0.1
$4f^{11}5d$	2	120227.62 (.32)	1	1.067	−38	$(^4G)^5F$	13	99.7	0.2	0.1
$4f^{11}5d$	4	120467.68 (.28)	4	1.075	24	$(^2H1)^1G$	11	99.7	0.1	0.2
$4f^{11}5d$	6	120621.37 (.35)	3	0.971	−14	$(^2I)^3K$	33	99.9	0	0.1
$4f^{11}5d$	4	120776.11 (.34)	3	0.935	16	$(^4G)^3H$	40	99.7	0.1	0.2
$4f^{11}5d$	5	120875.97 (.36)	2	1.161	−23	$(^2D1)^3G$	34	99.7	0.1	0.2
$4f^{11}5d$	3	121130.44 (.28)	4	1.023	−89	$(^2D1)^3G$	18	99.4	0.3	0.2
$4f^{11}5d$	2	121249.45 (.23)	3	1.308	53	$(^4D)^3P$	17	97.9	1.9	0.2
$4f^{11}5d$	5	122038.11 (.17)	3	0.969	−34	$(^2I)^3I$	33	88.2	0.1	0.1
$4f^{11}5d$	4	122049.47 (.26)	4	1.165	4	$(^4D)^5D$	25	98.5	1.3	0.2
$4f^{11}5d$	2	122366.42 (.45)	1	1.292	34	$(^4G)^3D$	17	99.5	0.2	0.2
$4f^{11}5d$	4	122424.99 (.16)	4	1.240	54	$6s(^4F)^5F$	18	74.5	25.4	0.1
$4f^{11}5d$	5	123086.74 (.54)	1	1.204	−59	$(^4D)^3G$	41	98.0	1.8	0.2
$4f^{11}5d$	6	123253.77 (.32)	4	0.991	57	$(^2L)^3I$	57	99.7	0.1	0.2
$4f^{11}5d$	4	123881.66 (.33)	2	1.133	−34	$(^2D1)^3F$	12	99.5	0.4	0.1
$4f^{11}5d$	6	124370.09 (.42)	2	1.085	−144	$(^2I)^3H$	44	99.5	0.3	0.2
$4f^{11}5d$	5	124636.37 (.25)	4	1.130	11	$(^2I)^3G$	44	99.3	0.3	0.4
$4f^{11}5d$	2	125233.64 (.35)	2	1.050	−14	$(^2D1)^3F$	8	92.9	7.0	0.2
$4f^{11}5d$	3	125262.34 (.44)	2	1.144	28	$(^4D)^3D$	27	98.4	1.5	0.1
$4f^{11}5d$	4	125809.14 (.17)	5	0.997	40	$(^2I)^3H$	31	98.6	1.2	0.3
$4f^{11}5d$	7	126043.76 (.32)	2	1.046	17	$(^2I)^1K$	17	99.7	0.2	0.1
$4f^{11}5d$	6	126144.12 (.30)	3	1.048	−52	$(^2H1)^3H$	25	99.8	0.1	0.1
$4f^{11}5d$	3	126325.66 (.39)	3	0.931	72	$(^2I)^3G$	35	99.3	0.5	0.2
$4f^{11}5d$	3	126715.67 (.23)	4	1.043	11	$(^2I)^3G$	16	99.7	0.1	0.2
$4f^{11}5d$	5	126990.55 (.39)	3	1.305	136	$(^4D)^5F$	57	97.9	1.9	0.1
$4f^{11}5d$	4	127029.42 (.30)	3	1.107	−109	$(^2P)^3F$	14	86.0	13.9	0.1
$4f^{11}5d$	3	127872.85 (.28)	4	1.046	−130	$(^2P)^1F$	20	99.3	0.4	0.3
$4f^{11}5d$	6	127939.33 (.37)	2	1.003	54	$(^2L)^1I$	26	99.7	0.2	0.1
$4f^{11}5d$	4	127949.51 (.16)	3	1.058	40	$6s(^4F)^3F$	11	55.6	44.3	0.1
$4f^{11}5d$	3	128381.62 (.34)	3	1.131	0	$(^4D)^3D$	16	99.3	0.4	0.2
$4f^{11}5d$	3	129265.87 (.29)	3	1.059	−123	$(^4D)^3G$	18	99.2	0.7	0.1
$4f^{11}5d$	4	129767.30 (.32)	4	0.925	−89	$(^2H1)^3H$	26	98.0	1.7	0.2
$4f^{11}5d$	6	130181.47 (.31)	2	0.970	−5	$(^2L)^3K$	23	99.7	0.2	0.1
$4f^{11}5d$	3	130732.72 (.32)	3	0.983	34	$(^2H1)^3F$	29	98.2	1.5	0.3
$4f^{11}5d$	5	130836.09 (.32)	4	0.944	63	$(^2L)^3I$	47	89.0	10.7	0.3
$4f^{11}5d$	4	131791.26 (.48)	2	1.078	−112	$6s(^4G)^3G$	16	70.1	29.7	0.2
$4f^{11}5d$	4	132211.24 (.25)	5	1.116	26	$(^2H1)^3F$	26	89.7	10.0	0.2
$4f^{11}5d$	5	133524.48 (.35)	3	1.002	−35	$(^2H1)^3H$	26	99.7	0.2	0.1
$4f^{11}5d$	3	134332.29 (.32)	3	0.856	29	$(^2H1)^3G$	46	98.5	1.3	0.2
$4f^{11}5d$	3	135286.39 (.31)	3	1.130	−81	$(^2F2)^3D$	16	99.3	0.6	0.1
$4f^{11}5d$	5	135577.89 (.33)	3	1.066	139	$(^2H1)^3G$	18	99.7	0.1	0.2
$4f^{11}5d$	4	136837.71 (.30)	4	1.037	21	$(^2H1)^1G$	18	99.5	0.3	0.2
$4f^{11}5d$	3	138100.22 (.30)	5	0.977	45	$(^2H1)^1F$	27	98.8	0.9	0.3
$4f^{11}5d$	4	138248.06 (.39)	3	1.120	−127	$(^2F2)^3G$	12	65.8	34.1	0.1
$4f^{11}5d$	6	139066.49 (.59)	2	0.996	78	$(^2H1)^1I$	41	99.5	0.1	0.4
$4f^{11}5d$	3	139734.18 (.56)	2	0.937	−211	$(^2D2)^3G$	19	92.0	7.8	0.3

Table 3. Observed transitions with the ground level of $4f^{12}\ ^3H_6$. The experimental wavelength (in Å) is followed by its deviation from the Ritz wavelength (in mÅ), the intensity of the line, the calculated $\log(gf)$ (g being the statistical weight 13 of the ground level and f the absorption oscillator strength of the transition). The *CI* columns include the interactions with $5p^54f^{13}$ and $5p^54f^{12}5d$ whereas the *no CI* values do not. The identifications of the upper levels are detailed in Table 2. A comment is given after the intensity for one doubly classified line (D) and for one line blended with a stronger transition (B).

λ_{vac} (Å)	$\Delta\lambda$ (mÅ)	Int	$\log(gf)$ *CI*	$\log(gf)$ *no CI*	E^u (cm^{-1})	λ_{vac} (Å)	$\Delta\lambda$ (mÅ)	Int	$\log(gf)$ *CI*	$\log(gf)$ *no CI*	E^u (cm^{-1})
1275.288	0	50	−2.528	−2.331	78413.63	929.338	−1	250	−0.908	−0.311	107603.36
1262.212	−2	300	−1.593	−1.416	79225.87	926.904	−2	250	−1.079	−0.872	107885.74
1245.880	1	400	−1.260	−1.076	80264.65	916.354	0	80	−1.394	−1.227	109128.14
1200.580	1	300	−1.601	−1.418	83293.13	913.550	2	80	−1.405	−1.257	109463.34
1197.175	1	400	−1.208	−1.042	83530.02	908.328	1	60	−1.528	−1.305	110092.40
1183.627	−3	400	−1.037	−0.859	84485.81	903.148	−1	250	−0.918	−0.738	110723.68
1169.015	−2	200	−1.644	−1.458	85542.07	898.984	0	100	−1.280	−1.285	111236.63
1160.827	2	250	−1.470	−1.300	86145.56	897.819	4	150	−1.136	−0.810	111381.45
1153.166	−3	400	−0.953	−0.800	86717.61	893.806	3	150	−1.308	−1.224	111881.49
1148.226	−2	3	−2.671	−2.470	87090.72	890.547	0	100	−1.240	−1.054	112290.52
1138.014	0	120	−1.837	−1.672	87872.31	888.951	−1	200	−0.595	−0.379	112491.99
1133.437	−4	100	−1.754	−1.598	88226.85	875.898	3	100 B	−2.923	−2.785	114168.84
1098.150	−8	80	−1.625	−1.414	91061.55	863.720	1	20	−1.954	−1.717	115778.36
1080.102	−6	200	−1.031	−0.875	92583.34	850.838	−1	400	−0.287	−0.083	117531.05
1062.470	−4	250	−1.048	−0.869	94119.93	850.291	2	30	−1.814	−1.647	117607.00
1054.249	3	120	−1.536	−1.337	94854.50	839.927	−1	20	−2.535	−2.335	119057.80
1048.446	2	80	−1.653	−1.479	95379.52	839.626	−1	300	−0.916	−0.718	119100.52
1045.098	5	3	−2.242	−2.057	95685.30	831.785	0	250	−1.143	−0.883	120223.30
1031.126	8	10	−2.155	−2.039	96982.12	829.041	0	40	−1.923	−1.728	120621.39
1024.207	7	8	−2.043	−1.899	97637.17	827.296	1	400 D	−0.726	−0.512	120875.97
999.724	−2	100	−1.650	−1.483	100027.46	812.435	0	300	−0.685	−0.483	123086.74
981.108	1	60	−1.702	−1.455	101925.68	811.339	4	30	−2.230	−1.989	123253.77
980.201	1	40	−1.807	−1.606	102020.08	804.050	−2	250	−1.323	−1.183	124370.09
979.447	2	60	−1.751	−1.649	102098.46	802.337	0	3	−1.827	−1.382	124636.37
963.402	3	250	−1.032	−0.835	103799.19	793.374	−1	25	−2.018	−1.963	126043.76
950.964	−4	150	−1.087	−0.910	105156.00	792.742	−2	30	−1.733	−1.579	126144.12
944.471	0	250	−0.882	−0.682	105879.41	787.460	0	150	−1.266	−1.011	126990.55
942.489	0	100	−1.385	−1.259	106101.98	781.617	−3	20	−2.000	−1.892	127939.33
935.493	0	100	−1.507	−1.398	106895.45	748.928	2	3	−1.996	−1.825	133524.48
932.017	−1	300	−0.546	−0.937	107294.13						

$^3P_0$ ($E_{calc} = 35791$ cm^{-1}), $^3P_1$ ($E_{calc} = 36718$ cm^{-1}) and $^1S_0$ ($E_{calc} = 75268$ cm^{-1}), remained fruitless.

The level energies from Tables 1 and 2 were used in the final least squares fit of the parametric studies of the configurations, and the root mean-square deviations were 38 cm^{-1} for the even parity levels and 54 cm^{-1} for the odd parity levels. Tables 5 and 6 report the fitted values of the radial parameters.

4 Configuration interaction effects

In energy level calculations, the terms of the electrostatic interactions connecting different configurations in the Hamiltonian may be described by effective operators applied to the studied configurations, or by a straight extension of the diagonalized matrices. The use of two-body second-order parameters (α, β and γ) which improve drastically the theoretical energies in $4f^N$ and of the Slater parameters F^k and G^k of 'forbidden' rank k is made possible in the Cowan codes [13]. It is seen in Tables 5 and 6 that all these parameters have been introduced in the present work, their initial values being average values of other spectra. Some parameters converged to well-defined values, others had large uncertainties with the present set of experimental data and were constrained. Finally the effective parameters $G^3(4f, 6p)$ in Table 5 and $F^3(4f, 5d)$ in Table 6 had an undefined sign and were removed.

Moreover the moderate size of $4f^{11}nl$ configurations also allows some extension of the basis set. Due to the detection of $5p^54f^3$ in Pr IV [3] and $5p^54f^4$ in Nd IV [5], we have studied in Tm IV how the $5p^54f^{13}$ and $5p^54f^{12}5d$ configurations modify the lowest level calculated energies and transition probabilities. In order to get a realistic description of open-core configurations, the scaling factors of Slater integrals $R^k(5p, nl)$ and spin-orbit integral ζ_{5p} have been derived from the $5p^5nl$ configurations of the unique appropriate fourth spectrum La IV [16]. In spite of a gap of 12 elements from La to Tm, we have applied

Table 4. Classified lines of Tm IV having $4f^{11}(^4I_{15/2})6p$ as upper subconfiguration. The experimental wavelengths in vacuum (λ in Å) are followed by the deviations from the Ritz wavelength (in mÅ), intensities (in arbitrary units), calculated transition probabilities gA, g being the statistical weight of the upper level). The *CI* columns include the interactions with $5p^54f^{13}$ and $5p^54f^{12}5d$ whereas the *no CI* values do not. The wavenumbers and the combining levels are in cm^{-1}. The level identifications are detailed in Tables 1 and 2. The comments D and B after the intensities have the same meaning as in Table 3.

λ_{vac} (Å)	$\Delta\lambda$ (mÅ)	Int	gA_{CI} (10^6 s^{-1})	$gA_{no\ CI}$ (10^6 s^{-1})	Wavenumber (cm^{-1})	Upper level E^o (cm^{-1})	J	Lower level E^e (cm^{-1})	J
1212.409	3	12	282	284	82480.41	154491.66	6	72011.02	6
1212.793	14	200 D	1269	1244	82454.27	154466.21	7	72011.02	6
1226.090	−1	3	194	194	81560.07	154491.66	6	72931.67	7
1226.478	4	40	397	392	81534.30	154466.21	7	72931.67	7
1234.245	0	250	3029	3045	81021.22	153952.89	8	72931.67	7
1258.711	2	60	549	568	79446.35	153952.89	8	74506.41	9
1267.731	2	100	644	670	78881.08	154466.21	7	75585.02	8
1270.461	−3	300	2475	2436	78711.60	153217.84	9	74506.41	9
1276.030	−3	200	1086	1072	78368.07	153952.89	8	75585.02	8
1288.111	−4	150	1128	1116	77633.06	153217.84	9	75585.02	8
1314.439	−1	150	1217	1206	76078.11	154491.66	6	78413.63	5
1328.460	−2	500	10570	10540	75275.15	153952.89	8	78677.88	9
1329.077	2	200	1524	1538	75240.20	154466.21	7	79225.87	6
1341.565	2	400	4484	4521	74539.83	153217.84	9	78677.88	9
1345.118	10	400	3114	3144	74342.93	154466.21	7	80122.71	8
1347.219	1	80	854	857	74227.00	154491.66	6	80264.65	7
1347.679	−2	200	3500	3524	74201.66	154466.21	7	80264.65	7
1354.448	−12	400 D	5964	6033	73830.84	153952.89	8	80122.71	8
1357.073	5	80	851	853	73688.00	153952.89	8	80264.65	7
1368.085	6	50	542	553	73094.88	153217.84	9	80122.71	8
1370.232	1	200	8091	8100	72980.35	144991.40	7	72011.02	6
1376.791	−1	150	2232	2222	72632.66	145564.25	8	72931.67	7
1384.904	3	150	3026	3009	72207.18	154466.21	7	82258.89	8
1387.735	−3	250	5515	5520	72059.87	144991.40	7	72931.67	7
1394.817	0	30	473	442	71693.99	153952.89	8	82258.89	8
1404.524	0	150	4373	4425	71198.51	154491.66	6	83293.13	5
1407.305	1	300	10570	10600	71057.80	145564.25	8	74506.41	9
1409.212	10	120	1673	1691	70961.65	154491.66	6	83530.02	7
1409.721	3	180	2183	2167	70936.03	154466.21	7	83530.02	7
1420.008	14	8 B	203	199	70422.16	153952.89	8	83530.02	7
1428.465	13	150	2382	2448	70005.21	154491.66	6	84485.81	6
1429.001	6	250	5603	5607	69978.95	145564.25	8	75585.02	8
1440.801	11	200	2915	2912	69405.83	144991.40	7	75585.02	8
1531.399	−3	40	243	247	65299.75	145564.25	8	80264.65	7
1544.960	4	30	328	328	64726.60	144991.40	7	80264.65	7
1615.952	−4	2	111	109	61883.03	154466.21	7	92583.34	6
1802.012	−4	100	2798	2757	55493.52	154466.21	7	98972.81	8
1818.839	−1	300	10270	10230	54980.12	153952.89	8	98972.81	8
1840.039	−2	200	9450	9356	54346.66	154491.66	6	100145.04	7
1840.910	7	250	10010	9995	54320.96	154466.21	7	100145.04	7
1843.486	−1	300	18200	18110	54245.05	153217.84	9	98972.81	8
1858.450	−15	150	5893	5860	53808.27	153952.89	8	100145.04	7
2145.639	−2	300	3811	3770	46591.49	145564.25	8	98972.81	8
2172.361	8	600	6913	6887	46018.43	144991.40	7	98972.81	6
2201.026	1	400	5835	5852	45419.17	145564.25	8	100145.04	7
2229.134	−8	400	1659	1647	44846.52	144991.40	7	100145.04	7

Table 5. Fitted parameters (in cm^{-1}) for $4f^{12}$ and $4f^{11}6p$ in Tm IV compared with HF integrals. The perturbing configuration $5p^54f^{13}$ is introduced in the basis set with all relevant parameters (scaled HFR) and E_{av} = 243611 cm^{-1} fixed. Constrained parameters are indicated by 'r' and fixed parameters by 'f' in the columns St. Dev.

Param.	Fitted $4f^{12}$	St. dev.	HF	Scaling factor	Tm:YAG Ref. [21]	Fitted $4f^{11}6p$	St. dev.	HF	Scaling factor
E_{av}	17990	14			17683	191175	30		
$F^2(ff)$	104272	164	132844	0.785	99737	109693	172	139572	0.786
$F^4(ff)$	72333	479	83323	0.868	69925	77400	513	87892	0.881
$F^6(ff)$	51233	525	59937	0.855	50519	55596	569	63324	0.878
α	21	1			10.3	17	r		
β	−834	74			−623	−621	r		
γ	1991	r			(1820)	1735	r		
ζ_f	2640	7	2689	0.982	2616	2796	6	2843	0.983
ζ_p						5568	14	4758	1.170
$F^1(fp)$						305	69		
$F^2(fp)$						8113	237	9357	0.867
$G^2(fp)$						2403	77	2399	1.002
$G^3(fp)$						0	f		
$G^4(fp)$						1976	185	2172	0.910
$R^2(ff, fp)$	−3599	f	−3599	(1.000)					
$R^4(ff, fp)$	−1910	f	−1910	(1.000)					

these scaling factors to the ab initio radial integrals of Tm IV. In the odd parity study, all the Slater and spin-orbit parameters of the unknown $5p^54f^{12}5d$ configuration were fixed, but its effect on $4f^{11}5d$ and $4f^{11}6s$ was fitted by means of one single parameter that is the common ratio P_{fit}/P_{HFR} for the nine relevant CI Slater integrals. It is seen in Table 6 that the CI integral $R^2(4f5p, 4f4f)$ converges to -7926 ± 1122 cm^{-1}, smaller than the ab initio value, with a well-defined scaling factor 0.542 ± 0.077. In the even parity, significant CI parameters for the $4f^{12}$–$5p^54f^{13}$ and $4f^{11}6p$–$5p^54f^{13}$ interactions could not be determined by a similar process because of negligible mixings in the known levels. Therefore they were scaled with the same factor (0.542) and fixed through the least-squares iterations.

The configuration sharings (sums of squared amplitudes belonging to the same configurations in the eigenfunctions) of odd levels are reported in the last three columns of Table 2. We note that very small contributions of $5p^54f^{12}5d$, which is predicted far in the energy range 236 000–403 000 cm^{-1}, are steadily constant in the wavefunctions of $4f^{11}5d$ known levels (72 011–139 733 cm^{-1}). On the other hand, the $4f^{11}5d$–$4f^{11}6s$ mixing appears more accidental and only affects a few pairs of close levels. Three obvious cases are the $J = 7$ levels at 106 895 and 107 885 cm^{-1}, the $J = 6$ levels at 107 294 and 107 603 cm^{-1} and the $J = 5$ levels at 113 441 and 113 964 cm^{-1}. The lowest four of these levels decay to the ground state and comparison of the observed intensities with the $\log(gf)$ values reported in Table 3 support the validity of the configuration mixings in these eigenfunctions. It should be stressed that Table 2 does not report a full list of the calculated odd parity levels but is limited to the experimentally found levels. For the mixed levels at 111 598 cm^{-1} ($J = 6$) and 122 424 cm^{-1} ($J = 4$), the perturbers have not yet been found.

Evidence of an important consequence of the configuration mixing is seen by comparing the parametric studies with and without $5p^54f^{13}$ and $5p^54f^{12}5d$ in their respective parities. In Table 4 it is seen that the probabilities for $6p$–$6s$ and $6p$–$5d$ decays are almost unaffected by the extension of the basis. The situation for the resonance transitions appears quite different in Table 3. The calculated transition probabilities of the $5p^64f^{12}$–$5p^54f^{12}5d$ array are about 100 times larger than for the $5p^64f^{12}$–$5p^64f^{11}5d$ transitions and this produces a quenching effect of the $4f$–$5d$ array by the short wavelength $5p$–$5d$ transitions. Such an effect had been first described in the $n = 4$ and $n = 3$ shells [19] and was later evaluated in isoelectronic sequences [20]. These previous examples dealt with the opening of the last completed subshell, similar to the opening of the $5p^6$ subshell in our case. In terms of absorption oscillator strengths reported in the Table 3, the $\log(gf)$ values are reduced by an average value of 0.18. The changes are more important for the two $J = 6$ levels mentioned above at 107 294 and 107 603 cm^{-1}, and the observed intensities are in better agreement with the theoretical values of the extended calculation. However, for such close levels, the eigenfunctions obtained at different steps of the theoretical analysis are very sensitive to small changes in parameter values.

5 Comparison with Tm^{3+} in crystals

The fitted parameters for $4f^{12}$ in the free ion Tm^{3+} are compared in Table 5 with those of the ion embedded in Y-Al garnets [23]. Other parameter sets are available in the literature (for example [24,25]), but they exclude the γ parameter whose effect is taken into account by other electrostatic parameters of $4f^{12}$. In the latter reference, the theoretical description of the Stark sublevels was also

Table 6. Fitted parameters (in cm^{-1}) for $4f^{11}5d$ and $4f^{11}6s$ in Tm IV compared with HF integrals. The perturbing configuration $5p^5 4f^{12}5d$ is introduced in the basis set with all parameters (scaled HFR) and $E_{av} = 291894$ cm^{-1} fixed. The nine configuration interaction parameters connecting $5p^5 4f^{12}5d$ with $4f^{11}5d$ and $4f^{11}6s$ are reduced to a single one. They are varied in a constant HF ratio and converge to a well-defined value of their scaling factor 0.542 ± 0.077. Constrained parameters are indicated by an 'r' in the columns St. Dev.

Param.	Fitted $4f^{11}5d$	St. dev.	HF	Scaling factor	Fitted $4f^{11}6s$	St. dev.	HF	Scaling factor
E_{av}	118207	54			139861	130		
$F^2(ff)$	109718	130	139053	0.789	110087	r	139518	(0.789)
$F^4(ff)$	77239	307	87539	0.882	77496	r	87855	(0.882)
$F^6(ff)$	56208	337	63063	0.891	56395	r	63297	(0.891)
α	15	1			15	r		
β	−488	32			−488	r		
γ	1480	96			1480	r		
ζ_f	2782	6	2836	0.981	2830	18	2842	0.996
ζ_d	1704	9	1837	0.928				
$F^1(fd)$	866	106						
$F^2(fd)$	24370	153	30228	0.806				
$F^3(fd)$	0	f						
$F^4(fd)$	16110	266	14288	1.132				
$G^1(fd)$	9275	202	12344	0.751				
$G^2(fd)$	2262	174						
$G^3(fl)$	10149	185	10424	0.974	2866	197	3288	0.872
$G^4(fd)$	2468	301						
$G^5(fd)$	6679	226	8043	0.830				

C.I. Slater Param.	Fitted	St. dev.	HF	Scaling
$R^2(fd, fs)$ $4f^{11}5d$-$4f^{11}6s$	1408	131	1357	1.038
$R^3(fd, sf)$ $4f^{11}5d$-$4f^{11}6s$	3199	r	3085	(1.038)
$R^2(fp, ff)$ $5p^6 4f^{11}5d$-$5p^5 4f^{12}5d$	−7926	1122	−14612	0.542
$R^4(fp, ff)$ $5p^6 4f^{11}5d$-$5p^5 4f^{12}5d$	−3469	r	−6396	(0.542)
$R^2(pp, fp)$ $5p^6 4f^{11}5d$-$5p^5 4f^{12}5d$	−21446	r	−39536	(0.542)
$R^2(pd, fd)$ $5p^6 4f^{11}5d$-$5p^5 4f^{12}5d$	−14234	r	−26241	(0.542)
$R^4(pd, fd)$ $5p^6 4f^{11}5d$-$5p^5 4f^{12}5d$	−8826	r	−16272	(0.542)
$R^1(pd, df)$ $5p^6 4f^{11}5d$-$5p^5 4f^{12}5d$	−13091	r	−24133	(0.542)
$R^3(pd, df)$ $5p^6 4f^{11}5d$-$5p^5 4f^{12}5d$	−9025	r	−16638	(0.542)
$R^3(ps, fd)$ $5p^6 4f^{11}6s$-$5p^5 4f^{12}5d$	3431	r	6326	(0.542)
$R^3(ps, df)$ $5p^6 4f^{11}6s$-$5p^5 4f^{12}5d$	−910	r	−1679	(0.542)

improved by a detailed calculation of the $5p^6 4f^{12}$–$5p^5 4f^{13}$ interaction. A well-defined reduction of Slater parameters F^k is noticed for the compound, whereas the spin-orbit ζ_{4f} parameter is barely affected.

6 Conclusion

The emission spectrum of thulium was observed in the range 700–2300 Å and the first classification of the most important transitions of Tm IV is reported. The lowest energy levels of the first four configurations $4f^{12}$, $4f^{11}5d$, $4f^{11}6s$ and $4f^{11}6p$ were found and their parametric interpretation was achieved. Further work on Tm IV is in progress and there is some hope of determining more levels with $J = 2$ and 1, as well as the lowest levels of $4f^{11}6d$ and $4f^{11}7s$ as was done in Yb IV and Lu IV. The observed intensities compare well with the calculated transition probabilities and deserve an improved determination from phosphor image plates. A significant reduction of the resonance transition probabilities $4f$–$5d$ is noticed when the interaction $5p^6 4f^{11}5d$–$5p^5 4f^{12}5d$ is treated explicitly. This reduction is comparable in size to the empirical core-polarization effects introduced in the close spectrum of Yb IV [2]. Systematic evaluations of similar interaction effects in other lanthanide spectra are in progress. The $5p^5 4f^N 5d$ configurations are close to the ionization limits in lanthanide IV spectra and the observation of $5p$–$5d$ transitions near 300 Å seems an interesting challenge.

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