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LETTER TO THE EDITOR

Energy levels of $4f^3$ in the Nd^{3+} free ion from emission spectra

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Abstract
The emission spectrum of neodymium produced by vacuum spark sources was observed in the vacuum ultraviolet on two normal-incidence spectrographs. In an initial result, more than 550 lines have been identified as transitions from 85 $4f^25d$ levels to 37 levels of the $4f^3$ ground configuration in the free ion Nd^{3+}. The levels $4f^3\,{}^4F_{3/2}$ and ${}^4I_{11/2}$, responsible for the well-known 1064 nm laser line, have respective positions of 11 698.57 ±0.1 cm^{-1} and 1897.07 ±0.1 cm^{-1} above the ground level ${}^4I_{9/2}$. The newly found levels of $4f^3$ constitute the first *isolated* $4f^N$ configuration ($N > 2$) and therefore enable checks of effective parameters that represent far configuration interaction. Slater parameters $F^k(4f, 4f)$ derived from Nd^{3+}:$LaCl_3$ are 3% to 5% smaller than in the free ion.

The spectroscopic properties of triply ionized lanthanides (fourth spectra) are mainly known from absorption experiments on ions embedded in crystal lattices, in compounds or in solutions. The last spectrum of a triply ionized rare earth to be interpreted was that of Tb IV, carried out some 30 years ago [1]. Only limited revisions and extensions appeared recently [2, 3].

In the case of neodymium, a tentative analysis of Nd IV [4] was not considered as reliable enough to be included in the critical compilation by Martin *et al* [5]. There are several reasons for studying the Nd^{3+} emission spectrum, a famous ion because of the laser transition at 1064 nm occurring between Stark sublevels of $4f^3\,{}^4F_{3/2}$ and ${}^4I_{11/2}$ in crystals. An exhaustive bibliography of observations and theoretical studies on Nd^{3+} in compounds exceeds the limits of this publication but, so far, the effect of ligand fields on atomic radial parameters could not be derived from experimental data. Furthermore, theoretical

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studies of $4f^N$ configurations in the Racah–Slater approach [6] lead to large sets of effective configuration interaction (CI) parameters if corrections beyond the first-order perturbation theory are taken into account [7]. Until now, the large number of levels needed for the determination of these parameters by least-squares fits are available only from praseodymium spark spectra. However, the upper terms of Pr III $4f^3$ are too close to $4f5d^2$ and $4f^26p$ perturbers to consider the ground configuration as *isolated*. On the other hand, the number of known levels of the well-isolated $4f^2$ configuration of Pr IV (12) is too small for a parametric evaluation of third-order perturbation effects. Comparatively, the next lanthanide element Nd offers in this respect a more favourable case study. As for astrophysical applications, neodymium is an overabundant element in a number of chemically peculiar stars and the presence of Nd^{3+} in hot stellar outer layers remains to be ascertained. Finally, trivalent lanthanides are crucially important for new phosphor developments in the lighting industry [8].

In the present work, the neodymium spectrum emitted by a sliding spark [9, 10] was photographed on the 10.7 m normal incidence vacuum ultraviolet spectrograph at National Bureau of Standards (NBS) some years ago with the aim of extending to Nd V the sequence of two-electron spectra La II, Ce III and Pr IV. The source operating conditions were varied to produce peak currents of 50, 200, 500 and 1200 A in order to select lines of Nd III to Nd V. Recently, new observations were undertaken at the Paris-Meudon Observatory. The light source and the vacuum spectrograph used were similar to those used in the earlier experiments, except for the 3600 l mm^{-1} grating which leads to a dispersion plate factor of 0.26 Å mm^{-1} instead of 0.78 Å mm^{-1} on the NBS plates. Wavelength measurements were made on a semi-automatic photoelectric comparator. Wavelength standards for polynomial interpolation were taken from impurity lines of ionized low-Z elements (C,N,O,Al,Si) present in the Nd tracks or from the reference spectrum of a Cu/Ge hollow cathode lamp. The probable errors for wavelengths of single sharp lines are ± 0.003 Å ; i.e., wavenumber uncertainties are ± 0.2 cm^{-1} in the bulk of Nd IV resonance transitions. In the vacuum ultraviolet region, none of the spark lines of Nd had been reported in the literature.

The method and codes of Cowan [11] were used to predict the spectral ranges of the strong transitions in the three spectra Nd III, IV and V. Furthermore, comparisons with the well-known III, IV and V spectra of the close element Pr [5, 12, 13] were helpful. The experimental selection of Nd IV emission lines was derived from the following facts. One array of lines (1000–1080 Å) in the 50 A track disappears at peak currents above 200 A. Its attribution to the decay of $4f^35f$ to $4f^35d$ in Nd III leaves no doubt. A few strong lines in the 750–950 Å region of the track at 1200 A vanish at peak currents smaller than 500 A and they pertain obviously to the 4f–5d and 5d–6p transitions in Nd V. One particular class of lines is present at all peak currents, some of them barely stronger in the 500 A than in the 50 A tracks. These lines have been selected for searching for the $4f^3$–$4f^25d$ array of Nd IV in the present work.

Systematic calculations of the low configurations $4f^N$ and $4f^{N-1}nl$ in various lanthanide ions prepared the way to precise estimates of the Slater and spin–orbit parameters for the application of the Racah–Slater method by means of the Cowan codes [11]. Therefore, there was little doubt as to the strong transitions ending on the ground term ^4I, which allowed the breakthrough in our analysis. Figure 1 shows the predicted odd parity levels of Nd IV. In order to reject accidental coincidences in the search for repeating wavenumber intervals, the observed intensities were compared systematically with calculated transition probabilities.

At present, more than 550 lines have been identified as transitions from 85 (out of 107 possible) levels of $4f^25d$ to 37 (out of 41 possible) levels of $4f^3$. None of these levels

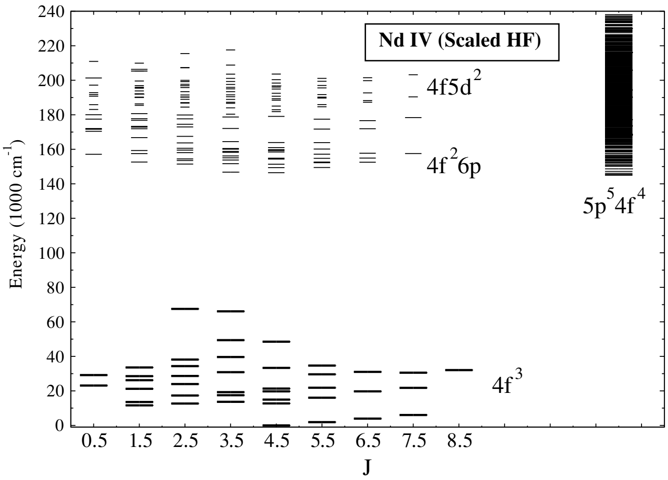

Figure 1. Energy levels of Nd^{3+} odd parity predicted from scaled Hartree–Fock parameters. The lowest four configurations are drawn, $5p^64f5d^2$ with short bars. Above 200 000 cm^{-1}, $5p^64f^25f$ is also present. For clarity reason, all J-values of $5p^54f^4$ are listed in a single column.

were determined in [4]. A selection of classified lines shows in table 1 the good qualitative agreement between observed intensities and the calculated transition probabilities. A glimpse of $4f^25d$ is given in the last three columns of table 1. The purity of the states in the LS coupling is low for many of the levels, including the first one at 70 819.18 cm^{-1}. The averaged values of the derived $4f^3$ level energies (accurate to 0.1 cm^{-1} or better) are given in table 2. The customary unit cm^{-1} for level energies used here is related to the unit for energy (joule) by 1 cm^{-1} = 1.986 445 61(34) × 10^{-23} J [14]. A comparison between experimental energies and their theoretical values is also given in table 2. The theoretical energies which lead to the reported deviations ΔE^a to ΔE^d have been obtained in four different parametric fits, by means of the codes of [15] and without $(2J + 1)$ weighting of the energies. The four approximations start from the following: (a) the 5-parameter set of the first-order perturbation theory (Racah's electrostatic parameters E^i [6] and the spin–orbit parameter ζ_f), then the effective parameters of the second order of perturbation are added by order of decreasing importance; (b) the three two-body parameters of the $\alpha L(L + 1) + \beta G(R7) + \gamma G(G2)$ correction derived from [16]; (c) the six three-body T parameters of Judd [17]; (d) the 13 magnetic parameters a^i [18] which replace Marvin integrals M^k and parameters P^k used in many applications. It is seen on the bottom line of table 2 that each step reduces the average deviations of the energies by a factor of more than 4. For comparison with earlier works, we have still used the classical sets of non-orthogonal operators. Although the determination of a complete set of orthogonal T parameters [19] has to be delayed until the discovery of the four upper levels of $4f^3$, we may anticipate from table 2 that only minor improvements should be expected from T parameters related with third-order perturbations. Our experimental data suggest that the completion of $4f^3$ is achievable, but the upper part of the $4f^3$–$4f^25d$ array is overlapped by other transition arrays.

Least-squares fits using the experimental levels of $4f^3$ from the present work and from absorption in $LaCl_3$ [20] lead to the parameter sets reported in table 3. It is remarked that in the latter case, 39 levels of table III from [20] lead to an average deviation of 4.4 cm^{-1} and that two levels with much larger deviations, respectively E = 32 203 (E_{calc} = 33 203 cm^{-1}) and E = 12 447 (E_{calc} = 12 478 cm^{-1}), are not used in the present least-squares fit as they might be

Table 1. Classified lines $4f^3$–$4f^25d$ in Nd IV for three selected $4f^3$ levels. Lower and upper levels (E^l and E^u) are in cm^{-1}. The intensities (visual estimates of plate blackening) are followed by calculated weighted transition probabilities in emission (in $10^6 s^{-1}$). For the levels of $4f^25d$ the percentage (squared amplitude) for the largest component in the LS coupling is given in the last column.

E^l	λ (Å)	Int	gA	E^u	First LS comp	%
$^4I_{9/2}$	1412.085	300	1039[a]	70 819.18	$(^3H)^4I_{9/2}$	46
0.00	1363.025	150	590	73 366.12	$(^3H)^4I_{9/2}$	50
	1359.492	40	77	73 556.89	$(^3H)^2H_{11/2}$	37
	1344.731	300	1781	74 364.11	$(^3H)^4H_{7/2}$	83
	1321.578	50	151	75 667.00	$(^3H)^4G_{7/2}$	60
	1308.698	30	112	76 411.88	$(^3H)^4H_{9/2}$	86
	1285.188	3	23	77 809.48	$(^3H)^4G_{9/2}$	61
	1284.805	200	1764	77 832.84	$(^3F)^4H_{7/2}$	92
	1254.792	10	79	79 694.70	$(^3F)^4H_{9/2}$	92
$^4I_{11/2}$	1399.208	50	149	73 366.12	$(^3H)^4I_{9/2}$	50
1897.07	1395.481	300	1010	73 556.89	$(^3H)^2H_{11/2}$	37
	1375.993	180	872	74 571.86	$(^3H)^4I_{11/2}$	54
	1342.012	300	2153	76 411.88	$(^3H)^4H_{9/2}$	86
	1340.948	30	167	76 471.06	$(^3H)^4I_{13/2}$	98
	1317.408	50	168	77 809.48	$(^3H)^4G_{9/2}$	61
	1315.525	20	72	77 912.50	$(^3H)^2I_{11/2}$	42
	1301.987	30	108	78 702.72	$(^3H)^4H_{11/2}$	83
	1285.385	180	1994	79 694.70	$(^3F)^4H_{9/2}$	92
	1261.706	10	56	81 155.38	$(^1G)^2H_{9/2}$	26
	1253.236	10	113	81 691.02	$(^3F)^4H_{11/2}$	69
$^4F_{3/2}$	1615.045	150	245	73 616.30	$(^3H)^4G_{5/2}$	47
11 698.57	1485.316	70	154	79 024.20	$(^3F)^2P_{1/2}$	56
	1478.404	150	511	79 339.05	$(^3H)^4F_{3/2}$	71
	1461.348	30	66	80 128.43	$(^3H)^4F_{5/2}$	32
	1434.216	20	9	81 422.93	$(^3F)^4P_{5/2}$	33
	1432.583	20	60	81 502.51	$(^3F)^4P_{1/2}$	77
	1423.442	60	225	81 950.86	$(^3F)^4D_{3/2}$	37
	1385.051	10	41	83 898.02	$(^3F)^4F_{5/2}$	36
	1378.014	100	224	84 266.95	$(^3F)^4D_{1/2}$	60
	1369.859	20	47	84 698.78	$(^3F)^4F_{3/2}$	34
	1368.414	12	68	84 775.98	$(^3F)^2P_{3/2}$	41

[a] g is the statistical weight $(2J_u+1)$ of the upper level and A the Einstein coefficient calculated by means of [9] with seven odd ($4f^3$, $4f^2(6p, 5f, 6f)$, $4f(5d + 6s)^2$) and two even configurations $4f^2(5d, 6s)$.

misprinted values. By converting E^i into F^k parameters, it is easily seen that the ligand-field effect on 4f orbitals reduces the Slater parameters $F^2(4f, 4f)$, $F^4(4f, 4f)$ and $F^6(4f, 4f)$ to 95.1%, 95.5% and 96.4%, respectively, of their values in the free ion. Table 3 also shows that the parameters a^1 to a^4 connected to spin–spin interaction are not yet well defined by the present set of levels.

In conclusion, the first energy level analysis of the free ion spectrum of Nd^{3+} has led to the determination of 37 levels of the ground configuration $4f^3$. Only the highest terms ^2G and ^2F are still unknown. The energy gap between the levels $^4F_{3/2}$ and $^4I_{11/2}$ corresponds to an air wavelength of 1019.97(2) nm, i.e., slightly shorter than the 1064 nm laser transition between Stark sublevels in crystals. The derived free ion energy parameters will allow fruitful

Table 2. Energy levels of $4f^3$ in Nd IV. The experimental levels E_{exp} are followed by deviations $\Delta E^n = E_{exp} - E^n_{th}$ using theoretical energies E^n_{th} derived from four approximations (see the text). The theoretical energies of missing levels are taken from case (c). For the ^{2}D,^{2} F,^{2} G and ^{2}H terms which occur twice in $4f^3$, the percentage given is the combined total term purity for that level in the LS coupling.

Term	J	E_{exp} (cm^{-1})	ΔE^a	ΔE^b	ΔE^c	ΔE^d	%
^{4}I	9/2	0.00	−148	11	2.0	7.2	97
^{4}I	11/2	1897.07	−95	25	11.1	3.8	99
^{4}I	13/2	3907.30	−58	24	5.8	−1.6	99
^{4}I	15/2	5988.50	−36	8	−12.1	−9.7	99
^{4}F	3/2	11 698.57	−100	−44	13.9	2.5	94
^{4}F	5/2	12 748.00	−74	−47	7.8	−1.5	98
^{4}F	7/2	13 719.82	−93	−79	−16.0	−0.3	93
^{4}F	9/2	14 994.84	−119	−85	−13.8	−0.4	77
^{2}H	9/2	12 800.33	−363	−160	−33.8	−1.2	65
^{2}H	11/2	16 161.49	−287	−109	10.0	4.1	94
^{4}S	3/2	13 792.52	135	98	−4.9	−0.2	95
^{2}G	7/2	17 655.08	−180	−61	4.8	−1.8	62
^{2}G	9/2	21 493.19	−122	−67	27.1	−1.1	59
^{4}G	5/2	17 707.34	8	133	23.8	−4.7	99
^{4}G	7/2	19 540.79	−55	34	34.0	3.5	66
^{4}G	9/2	19 969.79	−36	30	−10.8	−0.1	69
^{4}G	11/2	22 047.26	29	41	−47.5	4.7	93
^{2}K	13/2	20 005.18	409	18	−7.7	−3.3	99
^{2}K	15/2	22 043.53	463	27	−1.2	−0.3	95
^{2}D	3/2	21 700.96	−170	51	−6.4	1.1	51
^{2}D	5/2	24 333.18	−159	−21	0.3	0.6	98
^{2}P	1/2	23 788.93	32	230	5.1	0.6	94
^{2}P	3/2	26 761.25	−69	95	16.7	−3.1	52
^{4}D	3/2	29 010.52	−147	−39	−23.7	3.2	82
^{4}D	5/2	29 190.94	−174	−15	13.6	−2.3	80
^{4}D	1/2	29 540.43	−147	−85	−60.0	−2.5	94
^{4}D	7/2	31 355.08	−24	32	68.5	6.2	99
^{2}I	11/2	30 179.66	746	77	10.7	−2.6	84
^{2}I	13/2	31 582.60	837	116	−5.2	2.3	99
^{2}L	15/2	31 035.45	951	43	4.1	−4.6	96
^{2}L	17/2	32 563.14	991	44	2.4	5.4	100
^{2}H	9/2	33 741.10	305	−225	1.0	−5.3	87
^{2}H	11/2	35 136.42	401	−161	−10.0	7.0	83
^{2}D	3/2	34 275.31	−152	63	−4.9	2.0	84
^{2}D	5/2	35 214.00	−398	−4	−2.0	−1.7	83
^{2}F	5/2	39 568.32	−1050	35	−13.1	0.7	79
^{2}F	7/2	41 012.60	−1039	−37	10.4	−0.4	98
^{2}G	9/2	49 140					99
^{2}G	7/2	50 037					99
^{2}F	7/2	68 582					99
^{2}F	5/2	69 815					100
$\|\Delta E\|_{ave}$			286	67	14.8	2.8	

comparisons with those pertaining to Nd^{3+} in compounds, and this might help to improve eigenfunctions in the calculations of transition rates for Nd-lasers.

Table 3. Fitted parameters (in cm^{-1}) for $4f^3$ in the Nd IV emission spectrum (this work) compared with those derived from the levels of Nd^{3+}:$LaCl_3$ [20]. In the latter case, all magnetic effective parameters are fixed to the Nd IV values.

Parameter	This work	Standard error	Nd^{3+}:$LaCl_3$	Parameter	This work	Standard error
E^1	5009.0	6	4786.2	a^0	0.38	2.5
E^2	24.455	0.03	23.275	a^1	0.26	2.9
E^3	507.94	0.67	481.85	a^2	−0.07	0.13
α	22.83	0.16	22.17	a^3	41	71
β	1249	25	1580	a^4	−32	55
γ	−590	9	−656	a^5	4.9	1.8
T^2	270	20	381	a^6	−98	19
T^3	44.6	2.1	40.3	a^7	2.3	1.8
T^4	52.6	4.6	60.8	a^8	−186	34
T^6	−305	5.4	−289	a^9	−15.4	2.5
T^7	356	12	356	a^{10}	47.3	19
T^8	321	14	360	a^{11}	259	87
ζ_f	894	3	880	a^c	4.0	3.5

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References

[1] Spector N and Sugar J 1976 *J. Opt. Soc. Am.* B **66** 436
[2] Wyart J-F *et al* 2001 *Phys. Scr.* **63** 113
[3] Wyart J-F, Blaise J and Worden E F 2005 *J. Solid State Chem.* **178** 589
[4] Irwin D J G 1968 *Thesis* Johns Hopkins University, Baltimore
[5] Martin W C, Zalubas R and Hagan L 1978 *Atomic Energy Levels, The Rare-Earth Elements* NSRDS-NBS 60
[6] Racah G 1949 *Phys. Rev.* **76** 1352
[7] Judd B R 1985 *Rep. Prog. Phys.* **48** 907
[8] Sommerer T J 1998 *Atomic and Molecular Data and their Applications (AIP Conf. Proc.* vol 434*)* ed P J Mohr and W L Wiese (New York: AIP) p 295
[9] Bockasten K 1955 *Ark. Fys.* **9** 457
[10] Sugar J 1963 *J. Opt. Soc. Am.* **53** 831
[11] Cowan R D 1981 *The Theory of Atomic Structure and Spectra* (Berkeley, CA: University of California Press)
[12] Sugar J 1969 *J. Res. Natl Bur. Stand.* A **73** 333
[13] Sugar J 1974 *J. Res. Natl Bur. Stand.* A **78** 555
[14] Mohr P J and Taylor B N 2003 *The Codata Recommended Values of the Fundamental Physical Constants* National Institute of Standards and Technology, Gaithersburg, MD 20899 (physics.nist.gov/constants)
[15] Bordarier Y, Bachelier Y and Sinzelle J 1980 *Chain of Codes AGENAC, ASSAC, DIAGAC, GRAMAC for Racah–Slater Studies of Configurations,* Orsay
[16] Rajnak K and Wybourne B G 1963 *Phys. Rev.* **132** 280
[17] Judd B R 1966 *Phys. Rev.* **141** 4
[18] Judd B R, Crosswhite H M and Crosswhite H 1968 *Phys. Rev.* **169** 130
[19] Judd B R and Suskin M 1984 *J. Opt. Soc. Am.* B **1** 261
[20] Crosswhite H, Crosswhite H M, Kaseta F W and Sarup R J 1976 *J. Chem. Phys.* **64** 1981