III. Line Spectra

Atomic Spectra of Rare Earth Elements

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THE so-called "rare earth" elements are notorious for the trouble they have caused both chemists and physicists. It required more than a century to complete their discovery, and even now most of them are not available in quantity nor in a state of spectroscopic purity. Satisfactory descriptions of the atomic emission spectra are still lacking for many of these elements, partly because pure samples of some have not been produced and partly because of the extreme complexity of the spectra in most cases. Furthermore, the Zeeman effect in spectra of the rare earth elements was either not observed or not resolved until a few years ago. Under these circumstances it is not surprising that the rare earths were the last group of elements to succumb to structural analyses of their characteristic atomic spectra.

During the past dozen years improved descriptions of certain rare earth spectra, assignments of lines to different stages of ionization or successive spectra, and especially the resolution of complex Zeeman patterns, made it possible to interpret the principal features of a considerable number of these puzzles. Rapid progress justified the hope that in a relatively short time all the mystery of rare earth spectra would be explained. Unfortunately the world suddenly became engaged in other activities, and non-essential spectroscopic research was discouraged or suspended. At this time it appears appropriate to review what has been accomplished so that the remaining problems in rare earth spectra will be clearly recognized when the opportunity comes to resume work on them. The following review is restricted to the attempts to find and interpret regularities in the atomic emission spectra of the rare earth elements, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium. The elements are considered in order of their atomic numbers and the principal results of efforts to detect law and order are summarized for successive spectra. References to published papers are collected at the end.

When fully developed the spectra of most rare earths are so complex that it is a hopeless and thankless task to classify all the lines, but in every case it should be possible to explain a majority of the stronger lines. The latter usually include all easily absorbed or self-reversed lines and most of the easily excited lines. They involve either the normal state or neighboring metastable states of the atoms or ions, and if the character of these states can be determined the electron configurations responsible for them can be inferred. The available Zeeman data of rare earth spectra indicate that the ground states and most low levels result from pure (or almost pure) *LS* coupling, while higher levels in general exhibit overlapping configurations and perturbations.

Obviously the first thing to seek in any spectrum is its lowest term. Its identification fixes the electron configuration of the normal state and this is perhaps the most interesting fact concerning any atom or ion. If series-forming terms can be identified a spectroscopic ionization potential may be derived and this is perhaps the second most interesting fact concerning any atom or ion. The ground states and ionization potentials now known for rare earth elements are collected in the following review.

CERIUM, Ce, 58

Ce I

The first published attempt to find regularities among cerium lines dates back to 1914 when Paulson[1] reported four pairs of lines separated by 78.5 and five pairs separated by 1131.4 wave numbers. Unfortunately these differences are not constant when tested with modern wave-lengths.

In 1933 Karlson[2] published an analysis of the arc spectrum of cerium in which 540 Ce I lines were classified as combinations of 105 levels. Critical examination of this analysis suggests that it is only one of many that are possible when unjustified wave number tolerances and disregard of physical features are countenanced. It probably has no physical significance.

Similarly, the interpretation by Frish[3] of five lines as a $^3P-{}^3P$ multiplet in which both ^3P terms have identical intervals must be regarded as pure numerology.

To this hour it remains doubtful if any true regularities have been detected among Ce I lines.

Ce II

In 1935 Haspas[4] claimed to have classified 430 Ce II lines. Assuming that the cerium atom was ionized by loss of its $4f$ electron he called the ground state ^2D and thought a close similarity existed between the Ce II and La I spectra. This analysis may also be rated as wholly fictitious.

A preliminary analysis of the first spark spectrum of cerium by Albertson and Harrison[5] classified 584 Ce II lines as combinations of 31 low and 51 high levels. Simultaneously, this spectrum was successfully attacked by Tsein[6] who published in 1939 a list of 925 classified lines including those classified by Albertson and Harrison. In 1940 the analysis by Albertson and Harrison[7] was reported to include 3407 Ce II lines, or 98 percent of the total Ce II intensity between 2500 and 9000A. Finally in 1941, Harrison, Albertson, and Hosford[8] gave resolved Zeeman effect data for 427 Ce II lines from which g and J values were derived for 280 levels. Combinations of 316 levels explain 3600 lines and the Ce II spectrum now leads all others in the total number of lines accounted for. This spectrum exhibits two separate groups of levels and the outstanding problem is to find the connection between them. The lower and larger group arises from electron configurations $4f^2\,6s$, $4f^2\,5d$, $4f^2\,6p$, and $4f^3$ while the higher group probably originates in $4f\,5d\,6s$, $4f\,5d^2$, $4f\,5d\,6p$, $4f\,6s\,6p$, etc. The average interval between these two groups is estimated to be about 5000 cm^{-1} so that it will be necessary to observe the spectrum beyond 20000A before the connections can be found. The lowest term in the Ce II spectrum is $4f^2\,(^3H)\,6s\;a^4H$.

Ce III

Regularities in the spectrum of doubly ionized cerium were published in 1933 by Kalia[9] but some of the levels have not been confirmed and the interpretation was shown to be wholly wrong when the Zeeman effect of Ce III lines was studied by DeBruin, Lier, and van de Vliet[10] in 1937. The most complete analysis of the third spectrum of cerium has been given by Russell, King, and Lang,[11] who recognized 33 triplet and singlet terms, and accounted for 294 lines. The electron configurations $4f\,5d$, $4f\,6p$, $5d^2$, $4f\,6s$, $4f\,6d$, and $5d\,6s$ have been almost completely identified, but no evidence for $4f^2$ has been found. The latter probably represents the normal state of Ce^{++} atoms but its term combinations with $4f\,5d$ may be infra-red, and with $4f\,6d$ extreme ultraviolet, both still unobserved.

TABLE I. Lowest terms of successive cerium spectra.

	Lowest term		
Spectrum	Symbol	Value	Electron configuration
Ce I	$^3H^\circ$(?)	?	$4f\,5d\,6s^2$(?)
Ce II	$a^4H_{3\frac{1}{2}}$	0.00	$4f^2\,6s$
	$a^4H_{4\frac{1}{2}}$	311.55	
	$a^4H_{5\frac{1}{2}}$	1659.70	
	$a^4H_{6\frac{1}{2}}$	3113.56	
Ce III	^3H (?)	?	$4f^2$ (?)
Ce IV	$^2F^\circ_{2\frac{1}{2}}$	0	$4f$
	$^2F^\circ_{3\frac{1}{2}}$	2253.0	

Ce IV

A number of attempts to detect regularities in the fourth spectrum of cerium are summarized by Lang[12] who observed the spectrum to 500A, and classified some 30 Ce IV lines as combinations of doublet terms associated with $6s$, $7s$, $8s$, $6p$, $5d$, $6d$, $7d$, $4f$, $5f$, $5g$, and $6g$ electrons. The normal state of Ce^{+++} is $4f\;^2F$.

The lowest terms of successive Ce spectra are summarized in Table I.

PRASEODYMIUM, Pr, 59

Pr I

The first regularities proposed for Pr lines are 2 triplets announced by Paulson;[13] they have no physical meaning.

Pr II

Recently, Rosen, Harrison, and Rand McNally[14] obtained resolved Zeeman patterns for 141 Pr II lines which permitted identification of 74 levels combining to give 312 observed lines.

TABLE II. Lowest terms in successive praseodymium spectra.

Spectrum	Lowest term		Electron configuration
	Symbol	Value	
Pr I	^4K (?)	?	$4f^2\,5d\,6s^2$ (?)
Pr II	$a^5I^\circ_4$	0.00	$4f^3\,6s$
	$a^5I^\circ_5$	441.94	
	$a^5I^\circ_6$	1649.01	
	$a^5I^\circ_7$	2998.31	
	$a^5I^\circ_8$	4437.09	

The expected and established lowest terms of Pr spectra are shown in Table II.

NEODYMIUM, Nd, 60

Nd I

Nothing is known concerning the structure of the first spectrum of neodymium. Two pairs of Nd lines proposed by Paulson[13] differ by $\frac{1}{3}$ wave number and are therefore not significant.

Nd II

Albertson, Harrison, and Rand McNally[15] have recently published a preliminary classification accounting for 367 Nd II lines as combinations of 30 lower and 57 higher levels. The Zeeman effect of many lines was resolved at 87,180 gausses, and j, g and L values were determined. The normal state of Nd^+ atoms is represented by $4f^4\,(^5I)\,6s\cdot a^6I$ as shown in Table III.

ILLINIUM, Il, 61

Illinium has not been concentrated in sufficient quantity to permit a study of its characteristic emission spectra.

SAMARIUM, Sm, 62

Sm I

A partial analysis of the first spectrum of samarium is due to Albertson[16] who has classified nearly 600 lines. The normal state was found to be $4f^6\,6s^2\cdot a^7F$, and an ionization potential of about 5.6 volts was derived from the spectral terms.

Sm II

Paulson,[1] in 1914, announced that 16 intense Sm lines (now recognized as Sm II) were connected by recurring wave number differences, but these are not constant when tested with modern wave-length data. Albertson[17] explained more than 1200 Sm II lines resulting from transitions between 41 low (even) levels and more than 200 high (odd) levels. He found that the normal state of Sm^+ atoms is described by a ^8F term given by $4f^6\,6s$ electrons. This analysis is supported by Zeeman effect observations. The lowest terms of successive samarium spectra are given in Table IV.

EUROPIUM, Eu, 63

Eu I

In 1912, Hicks[18] stated that europium has a spectrum of triplets with separations 2632 and 1004 wave numbers, but it is now obvious that his sharp and diffuse series are entirely artificial.

The first spectrum of europium has been almost completely interpreted by Russell and King[19] who classified 1156 lines as combinations of sextet, octet, and decet terms, and fixed the lowest level as $4f^7\,6s^2\cdot a^8S$. All the terms arising from the added electrons $6s\,7s$, $6s\,8s$, $6s\,5d$, $6s\,6d$, $6s\,6p$, $6s\,7p$, and $5d\,6p$ have been identified, and some from $6s\,7d$, $6s\,5f$, $6s\,6f$, $5d^2$, and $6p^2$. An ionization potential of 5.64 volts was derived from spectral series.

Eu II

In 1914, Paulson[1] stated that he found wave number differences of 265, 433, and 1669.7 to occur frequently among the stronger Eu lines. The first two are not real but the last one was confirmed by Albertson[20] who interpreted it as the interval $^9S^\circ_4 - {}^7S^\circ_3$ of Eu II, $^9S^\circ_4$ representing the ground state of Eu^+ atoms. This analysis was extended by Russell, Albertson, and Davis[21] to include 156 identified levels and 467 classified

TABLE III. Lowest terms in successive neodymium spectra.

Spectrum	Lowest term		Electron configuration
	Symbol	Value	
Nd I	^5L (?)	?	$4f^3\,5d\,6s^2$ (?)
Nd II	$a^6I_{3\frac{1}{2}}$	0.00	$4f^4\,6s$
	$a^6I_{4\frac{1}{2}}$	513.33	
	$a^6I_{5\frac{1}{2}}$	1470.09	
	$a^6I_{6\frac{1}{2}}$	2585.46	
	$a^6I_{7\frac{1}{2}}$	3801.91	
	$a^6I_{8\frac{1}{2}}$	5085.61	

lines. Series of three successive $^9S^\circ$ and $^7S^\circ$ terms give an ionization potential of 11.21 volts. Zeeman patterns for 459 lines observed with a field of 87,850 gausses support this analysis.

Eu III

Zeeman patterns of several Eu III lines indicate[21] that the normal state of Eu^{++} atoms is $f^7\ a^8S^\circ$. The lowest terms in successive europium spectra are given in Table V.

GADOLINIUM, Gd, 64

Gd I

Upon subtracting the wave numbers of 30 Gd lines, Paulson[13] reported that the differences 398 and 1206 each occurred twice. It now appears that these differences are not constant, and in most cases the lines belong to the second spectrum.

The first significant regularities among Gd I lines were announced in 1935 by Albertson[22] who showed that a great majority of the intense, easily excited lines sprang from five levels which he interpreted as a $^9D^\circ$ term from $4f^7\ 5d\ 6s^2$ electrons.

Recently Russell[33] extended the analysis of Gd I to include terms of multiplicity eleven, and derived a spectroscopic ionization potential of 6.16 volts.

Gd II

In 1915 Paulson[23] published a table of gadolinium lines containing 8 columns and 21 rows. Critical examination of this table indicates that the lines belong to Gd II, but when tested with modern wave-lengths the wave number differences deviate from average by more than a whole unit and are therefore physically meaningless.

TABLE IV. Lowest terms of successive samarium spectra.

Spectrum	Lowest term Symbol	Value	Electron configuration
Sm I	a^7F_0	0.00	$4f^6\ 6s^2$
	a^7F_1	292.58	
	a^7F_2	811.92	
	a^7F_3	1489.55	
	a^7F_4	2273.09	
	a^7F_5	3125.46	
	a^7F_6	4020.66	
Sm II	$a^8F_{\frac{1}{2}}$	0.00	$4f^6\ 6s$
	$a^8F_{1\frac{1}{2}}$	326.64	
	$a^8F_{2\frac{1}{2}}$	838.22	
	$a^8F_{3\frac{1}{2}}$	1489.16	
	$a^8F_{4\frac{1}{2}}$	2237.97	
	$a^8F_{5\frac{1}{2}}$	3052.65	
	$a^8F_{6\frac{1}{2}}$	3909.62	

Observations of the Zeeman effect at 81,500 gausses enabled Albertson, Bruynes, and Hanau[24] to classify all of the low and nearly all of the middle temperature class Gd II lines. The normal state of the Gd^+ ion was definitely established as a $^{10}D^\circ$ term, the lowest given by the $4f^7\ 5d\ 6s$ configuration. The lowest terms in successive gadolinium spectra are given in Table VI.

TABLE V. Lowest terms in successive europium spectra.

Spectrum	Lowest term Symbol	Value	Electron configuration
Eu I	$a^8S^\circ_{3\frac{1}{2}}$	0.00	$4f^7\ 6s^2$
Eu II	$a^9S^\circ_4$	0.00	$4f^7\ 6s$
Eu III	$a^8S^\circ_{3\frac{1}{2}}$	0.00	$4f^7$

TERBIUM, Tb, 65

The only regularities reported for Tb spectra are the recurring differences of 30, 180, and 514 wave numbers which Paulson[13] reported in 1914. Unfortunately the differences are not constant and the data are not entirely consistent. Terbium spectra are exceptionally rich in lines but none has great intensity. Structural analyses of these spectra will be impossible without improved wave numbers, separation of ionization stages, and resolved Zeeman effects.

DYSPROSIUM, Dy, 66

Two so-called constant differences, 137 and 828, between wave numbers of dysprosium lines were first mentioned by Paulson[1] in 1914. The first is certainly spurious but the second may be a real difference between related Dy II lines. The following six pairs, including three given by Paulson, are present in King's[25] brief list of Dy II lines (Table VII).

HOLMIUM, Ho, 67

The wave number differences 349 and 717 which Paulson[13] reported finding among the

TABLE VI. Lowest terms in successive gadolinium spectra.

Spectrum	Lowest term Symbol	Lowest term Value	Electron configuration
Gd I	$^9D^\circ_2$	0.00	$4f^7\,5d\,6s^2$
	$^9D^\circ_3$	215.12	
	$^9D^\circ_4$	532.99	
	$^9D^\circ_5$	999.14	
	$^9D^\circ_6$	1719.09	
Gd II	$^{10}D^\circ_{2\frac{1}{2}}$	0.00	$4f^7\,5d\,6s$
	$^{10}D^\circ_{3\frac{1}{2}}$	261.87	
	$^{10}D^\circ_{4\frac{1}{2}}$	633.28	
	$^{10}D^\circ_{5\frac{1}{2}}$	1158.95	
	$^{10}D^\circ_{6\frac{1}{2}}$	1935.31	

TABLE VII. Constant difference between Dy II lines.

4077.974 (600 III)	Δν	3944.688 (600 III)
24515.08	828.32	25343.40
4103.312 (500 IV)		3968.393 (1000 III)
24363.71	828.31	25192.02
4256.323 (15 IV)		4111.346 (150 IV)
23487.82	828.28	24316.10
4358.47 (12 IV)		4206.544 (25 IV)
22937.4	828.4	23765.81
4538.74 (5 V)		4374.24 (20 IV)
22026.4	828.3	22854.7
4602.02 (10 V)		4449.702 (60 IV)
21638.9	828.2	22467.1

TABLE VIII. Doublets in the Tm I spectrum.

$a^2F^\circ_{3\frac{1}{2}}=0.0$	Δν	$a^2F^\circ_{2\frac{1}{2}}=8771.25$
21161.45(40)	8771.29	12390.16(4)
22791.18(200)	.23	14019.95(5)
22929.73(300)	.29	14158.44(10)
25656.04(40)	.25	16884.79(4)
25717.22(200)	.25	16945.97(40)
26126.94(40)	.28	17355.66(50)
26439.52(15)	.27	17668.25(50)
28051.35(40)	.22	19280.13(10)
30302.45(8)	.22	21531.23(30)
31431.89(12)	.23	22660.66(4)
31510.24(20)	.21	22739.03(15)
32174.47(9)	.22	23403.25(30)
32446.30(40)	.23	23675.07(40)
32811.04(25)	.25	24039.79(6)
34085.25(15)	.27	25313.98(100)
34297.27(15)	.32	25525.95(200)

stronger lines of Ho are far from constant and consequently without physical meaning. Before true regularities can be found in Ho spectra it will be necessary to improve and extend the fundamental data.

ERBIUM, Er, 68

Three wave number differences, 440, 510, and 1070, which Paulson[13] regarded as constant when he found them among 20 Er lines, are now known to be false. Erbium spectra are extremely complex, and up to the present no separation of successive spectra has been effected and no Zeeman effects have been observed.

THULIUM, Tm, 69

Tm I

Paulson,[1] in 1914, examined wave number differences between 30 strong lines of Tm and reported 3 pairs of 71, 2 pairs of 245, and 2 triplets of 243 and 666 wave numbers. In the light of recent data some of these lines belong to different spectra and none of the differences is really constant.

The arc and spark spectra of Tm have recently been remeasured[26] at the National Bureau of Standards, and on the basis of their appearance in different light sources most of the lines have been positively assigned to successive spectra. Without Zeeman effect data for Tm I lines, the only way at present to find regularities in this spectrum is by searching for repeated wave number differences between the lines. Upon selecting 90 strong Tm I lines, taking their wave number differences to 9000 cm^{-1}, and examining the resulting 3500 differences for recurring ones (tolerance ±0.1 cm^{-1}) it was found that among 175 repeating differences 171 occurred only twice, 3 occurred 3 times, and one occurred 9 times. The last has the value 8771.25 cm^{-1} and is tentatively regarded as the separation of two levels constituting the ^2F term resulting from the normal electron configuration $4f^{13}\,6s^2$ of neutral Tm atoms.

Since no details of regularities in the Tm I spectrum have been published, a few of the recognized doublets are shown in Table VIII.

Tm II

In 1915 Paulson[27] published 17 pairs of Tm lines with wave number difference of 237 cm^{-1}. Twenty-five years later at the National Bureau of Standards this difference was confirmed and interpreted as the separation of the first two levels in the Tm II spectrum. By selecting 70 easily excited spark lines (strong in arc spectra) and subtracting their wave numbers from each other, two significant differences (187.79 and 236.94 cm^{-1}) were found to connect 50 of these lines.[28] However, the two groups of pairs remained unconnected until the wave number subtractions were extended beyond 9000 cm^{-1}. The Zeeman effect positively identifies these four levels as ($4f^{13}\,6s$) $^1F^\circ_3$, $^3F^\circ_2$, $^3F^\circ_3$, and $^3F_4^\circ$, the last being the ground state of Tm$^+$ ions. Since no details of these regularities have been published by the author, typical combinations of these levels are shown in Table IX.

The lowest states of successive Tm spectra are summarized in Table X.

YTTERBIUM, Yb, 70

Yb I

In a new description of the arc spectrum of ytterbium Meggers and Scribner[29] announced the discovery of singlet and triplet terms and indicated that the normal state of neutral Yb atoms was represented by ($4f^{14}\,6s^2$) $^1S_0$. The first ionization potential of Yb atoms is about 6.22 volts but further details concerning this spectrum are reserved for another publication.

Yb II

A new description of the spark spectrum of Yb by Meggers and Scribner[29] led to the discovery of two systems of regularities in the Yb II spectrum. The simpler system includes two lines of extraordinary intensity which recent observations of the Zeeman effect prove to be $^2S_{1/2}-{}^2P_{1/2,3/2}$ transitions. The normal state of Yb$^+$ ions is described by ($4f^{14}\,6s$) $^2S_{1/2}$, and the ionization potential is approximately 12.05 volts. The second system of levels arises from other electron configurations; further details about it will be given in another publication including Zeeman effect data. The lowest terms and normal configurations for successive spectra of ytterbium are summarized in Table XI.

LUTECIUM, Lu, 71

Lu I

The first regularities in the Lu I spectrum were reported in 1930 by Meggers and Scribner[30] when they examined the wave number differences between strong arc lines and found a majority of them to be separated by 1993.9 cm^{-1}. This difference was interpreted as ($4f^{14}\,5d\,6s^2$) ^2D, and $^2D_{1\frac{1}{2}}$ was regarded as the zero level.

Lu II

In 1914, Paulson[1] examined the wave number separations of 48 Lu lines and reported repeating differences of 639, 1764, 2217, 2631, and 5771 cm^{-1}. It appears that most of the lines examined are Lu II, but only the first two differences have been confirmed. These were found independently by Meggers and Scribner[30] and interpreted as intervals of a metastable ^3D term. The ground level of the Lu II spectrum was determined to be

TABLE IX. Singlets and triplets in the Tm II spectrum.

Level value	$^3F^\circ_4$	$^3F^\circ_3$	$^3F^\circ_2$	$^1F^\circ_3$
	0.00	236.94	8769.69	8957.48
21608.28	21608.28(80)	21371.34(40)	12838.6(1)	
22308.86	22308.85(200)	22071.92(80)	13539.0(1)	
23803.28	23803.31(100)	22566.32(300)		
25257.52	25257.52(200)	25020.57(80)		16300.0(3)
25696.20	25696.20(60)	25459.27(8)		
25980.04	25980.03(1000)	25743.12(200)	17210.35(2)	17022.54(10)
26574.69	26574.70(600)	26337.74(600)		
26578.80	26578.81(800)	26341.84(80)		17621.29(4)
27009.40	27009.41(250)	26772.46(300)		
27254.43	27254.42(120)	27017.50(300)		
27702.45	27702.44(200)	27465.53(10)	18932.75(3)	
28267.89	28267.89(80)	28030.94(100)		19310.41(4)
29183.41	29183.37(150)	28946.49(200)		
29424.99	29425.00(100)	29188.04(300)*		20467.6(1)
30377.17	30377.17(120)	30140.23(60)		21419.69(10)
30508.74	30508.71(50)	30271.83(150)		
30684.43	30684.41(150)	30447.49(50)	21914.75(20)	21726.96(20)
30840.74	30840.76(200)	30603.77(80)		21883.28(4)
31036.59	31036.57(15)	30799.66(30)	22266.9(30)	22079.2(3)
31135.68	31135.68(50)	30898.73(90)		
31745.49	31745.48(20)	31508.54(200)	22975.82(15)	
31900.03	31900.05(250)	31663.06(180)		22942.55(8)
32500.27		32263.34(100)	23730.56(4)	23542.80(15)
33049.22	33049.25(5)	32812.24(20)		
33096.78		32859.83(30)	24327.11(2)	24139.29(3)
33391.55	33391.53(30)	33154.61(100)		24434.09(8)
33398.70	33398.66(40)	33161.74(60)	24629.07(4)	24441.22(7)
33490.16	33490.14(20)	33253.21(20)		24532.72(1)
33565.09	33565.09(40)	33328.12(50)	24795.42(5)	
33665.98	33665.95(30)	33429.06(150)		
34307.54	34307.55(20)	34070.56(2)		25350.08(3)
34398.31		34161.39(5)	25628.60(90)	25440.82(100)
34404.27		34167.31(20)	25634.59(5)	25446.79(20)
34871.38	34871.40(5)	34634.44(40)		25913.88(25)
34913.89	34913.91(15)	34676.94(2)	26144.20(5)	25956.41(6)
35004.01			26234.31(50)	26046.53(200)
35185.01	35184.96(3)	34948.07(15)		26227.57(4)
35274.48		35037.52(6)	26504.81(3)	26316.99(80)
35380.14		35143.23(60)	26610.44(100)	26422.65(60)
35753.73	35753.76(15)	35516.80(7)	26984.01(50)	26796.24(40)
35833.65		35596.72(30)		26876.17(20)
35966.44	35966.44(40)	35729.49(10)		
36041.04	36041.02(15)	35804.14(30)	27271.35(60)	27083.56(4)
36132.06	36132.02(6)	35895.12(80)	27362.39(80)	27174.61(80)
36547.88	36547.86(10)	36310.95(20)		27590.41(6)
36869.00	36868.98(10)	36632.07(20)	28099.29(80)	27911.53(6)
37151.1		36914.1(8)	28381.41(25)	
37482.70		37245.7(15)	28713.00(30)	28525.22(6)
37841.23		37604.3(30)	29071.52(15)	28883.77(20)
37957.74	37957.8(2)	37720.8(30)	29188.04(300)*	29000.27(10)
38093.50	38093.50(80)	37856.53(50)		29136.04(100)
38361.29	38361.4(20)	38124.37(15)		39403.78(70)
38582.95		38346.1(50)	29813.28(10)	29625.44(100)
39000.75			30231.05(30)	30043.28(40)
39196.71		38959.8(5)	30427.02(60)	30239.23(20)
39554.08	39554.2(4)	39317.1(6)	30784.41(30)	30596.58(80)
39843.25	39843.3(50)	39606.3(10)		30885.77(150)
39893.85	39894.0(4)	39656.9(8)	31124.14(60)	30936.39(60)
40056.34			31286.66(40)	31098.84(20)
40232.30			31462.62(40)	31274.82(30)
40505.88			31736.17(10)	31548.41(20)
40545.26		40308.3(40)	31775.57(40)	31587.79(25)
42469.62	42469.7(2)	42232.7(5)	33699.95(4)	33512.11(15)
43366.02		43129.1(1)	34596.33(20)	34408.54(20)
44047.47			35277.78(15)	35089.99(10)
45034.34	45034.4(3)	44797.4(8)	36264.66(30)	36076.84(20)

* Classified twice.

Table X. Lowest terms of successive thulium spectra.

Spectrum	Lowest term Symbol	Value	Electron configuration
Tm I	$^2F^\circ_{3\frac{1}{2}}$	0.00	$4f^{13}\,6s^2$
	$^2F^\circ_{2\frac{1}{2}}$	8771.25	
Tm II	$^3F^\circ_4$	0.00	$4f^{13}\,6s$
	$^3F^\circ_3$	236.94	
	$^3F^\circ_2$	8769.69	
	$^1F^\circ_3$	8957.48	

Table XI. Lowest terms in successive ytterbium spectra.

Spectrum	Lowest term Symbol	Value	Electron configuration
Yb I	$^1S_0$	0.0	$4f^{14}\,6s^2$
Yb II	$^2S_{\frac{1}{2}}$	0.0	$4f^{14}\,6s$

$^1S_0$ from the configuration $4f^{14}\,6s^2$. This analysis has recently received support from unpublished Zeeman effect observations.

Lu III

Meggers and Scribner[30] classified 5 Lu III lines as combinations of 3 doublet levels, and concluded that the normal state of Lu^{++} ions is represented by $(4f^{14}\,6s)\ ^2S$. The lowest terms of successive lutecium spectra are given in Table XII.

SUMMARY

For purposes of comparison and discussion the known electron configurations and lowest terms of the first three spectra are collected in Table XIII.

The above survey of normal states and corresponding electron configurations determined from analyses of successive spectra of the rare earth elements is ample proof that these spectra are amenable to analysis and interpretation. Real progress has been limited to the past dozen years, but many interesting and important results have already been obtained. For example, the exceptions to the general rule that all rare earth elements are trivalent can now be understood. Thus the fact that Ce is sometimes quadrivalent, and Sm, Eu, and Yb are sometimes divalent can be expected from the character of their atomic emission spectra. The properties of these atoms depend on the relative strength of binding of electrons of type *f*, *d*, and *s*, and such information can be obtained from the structures of successive spectra. The strength of binding of *d*-type electrons appears to be most variable. It probably has three maxima in the group, first at the beginning (Ce), second at the middle (Gd), and third at the end (Lu). Twice, in this group, the *f*-type electrons take precedence over the *d*, but just where this begins in the first half and in the second half of the group cannot be stated until more spectra of neutral rare earth atoms have been analyzed. The tendency of the *f* group to fill or to half fill itself appears to be considerably stronger than that of the *d* group. It seems likely that the first ionization always occurs as the result of removing one of the two 6*s* electrons, except in the case of Lu where the 5*d* electron is removed.

The observed complexity of rare earth spectra ranges from moderate (Lu) to extreme (Ce), and such differences are now clearly seen as consequences of electron configurations. The number of optically active electrons ranges from 1 to 8, and each configuration may include 1 to 4 different types of electrons. Configurations containing a considerable number and variety of

Table XII. Lowest terms of successive lutecium spectra.

Spectrum	Lowest term Symbol	Value	Electron configuration
Lu I	$^2D_{1\frac{1}{2}}$	0.0	$4f^{14}\,5d\,6s^2$
	$^2D_{2\frac{1}{2}}$	1993.9	
Lu II	$^1S_0$	0.0	$4f^{14}\,6s^2$
Lu III	$^2S_{\frac{1}{2}}$	0.0	$4f^{14}\,6s$

Table XIII. Electron configurations and lowest terms of rare earth spectra.

				Experimental					
		Theoretical*		Neutral atoms		Singly ionized		Doubly ionized	
Atomic number	Element	Electrons	Term	Electrons	Term	Electrons	Term	Electrons	Term
58	Ce	fds^2	^3H	—	—	f^2s	^4H	—	—
59	Pr	f^2ds^2	^4K	—	—	f^3s	$^5I^\circ$	—	—
60	Nd	f^3ds^2	^5L	—	—	f^4s	^6I	—	—
61	Il	f^4ds^2	^6L	—	—	—	—	—	—
62	Sm	f^5ds^2	^7K	f^6s^2	^7F	f^6s	^8F	—	—
63	Eu	f^6ds^2	^8H	f^7s^2	$^8S^\circ$	f^7s	$^9S^\circ$	f^7	$^8S^\circ$
64	Gd	f^7ds^2	^9D	f^7ds^2	$^9D^\circ$	f^7ds	$^{10}D^\circ$	—	—
65	Tb	f^8ds^2	^8H	—	—	—	—	—	—
66	Dy	f^9ds^2	^7K	—	—	—	—	—	—
67	Ho	$f^{10}ds^2$	^6L	—	—	—	—	—	—
68	Er	$f^{11}ds^2$	^5L	—	—	—	—	—	—
69	Tm	$f^{12}ds^2$	^4K	$f^{13}s^2$	$^2F^\circ$	$f^{13}s$	$^3F^\circ$	—	—
70	Yb	$f^{13}ds^2$	^3H	$f^{14}s^2$	^1S	$f^{14}s$	^2S	—	—
71	Lu	$f^{14}ds^2$	^2D	$f^{14}ds^2$	^2D	$f^{14}s^2$	^1S	$f^{14}s$	^2S

* F. Hund, *Linienspektren und periodisches System der Elemente* (Julius Springer, Berlin, 1927), p. 176.

electrons yield an amazing number of discrete atomic energy states or levels. Thus, f gives 2 levels, fs 4, f^2s 24, f^7s^2 98, f^2ps 134, f^2ds 214, f^6dp 334, etc. An increase in the number of similar electrons is accompanied by an increase in the number of multiplicity systems and by larger L and J values. Rare earth spectra have already disclosed the entire range of multiplicities, 1 to 11, that can be observed in atomic spectra.[33]

Up to the present time the spectroscopic ground states and configurations are known for only 6 of the 14 rare earths. Similar information is at hand for singly-ionized atoms in 9 cases and for doubly-ionized atoms in only 2 cases. First ionization potentials have been determined for only 4 of these elements and second ionization potentials for 2. Thus, it is seen that the rare earths still present the outstanding spectroscopic problem. Further progress involves the preparation of improved descriptions of the remaining unanalyzed spectra, and especially the separation of successive spectra and the observation of resolved Zeeman patterns. It appears that all the rare earth elements are relatively easy to ionize, and the practical consequence of this is that conventional arcs and sparks always show a mixture of successive spectra and a general weakness of the first spectra. King[31] has demonstrated that excitation in the electric furnace at various temperatures yields much information not obtainable from a direct comparison of arc and spark spectrograms.

The Zeeman effect technique developed by Harrison and Bitter[32] deserves major credit for the positive interpretation of low energy states in rare earth spectra but on account of the low ionization potentials of these elements most of the magnetic data obtained thus far are for second spectra. A method must be found to observe the spectral lines of neutral rare earth atoms (perhaps the absorption spectra) in strong magnetic fields.

In a considerable number of cases the low levels from even and those from odd configurations will lie so near each other that transitions will give rise to infra-red lines far beyond the present photographic limit. These cases should inspire someone to develop a satisfactory technique for observing complex spectra in the far infra-red.

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