

## The Spectrum of Gadolinium II

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(Received December 18, 1952)

A comparison was made between theory and experimental data for the spectrum of Gd II. All barycenters of the terms fit very well to the theoretical formulas, but the calculation of the Landé  $g$  factors shows deviations from  $LS$  behavior.

### INTRODUCTION

OWING to the rarity of these elements on the one hand and the great number of electrons on the other, the spectra of the rare earths are only little known, and the theoretically possible terms are so numerous that a thorough classification of the spectrum has not been achieved in any case.<sup>1</sup>

However, in the Eu I isoelectronic series the lower part of the spectrum is essentially (apart from the high multiplicities) a two-electron spectrum, owing to the existence of a parent term,  $4f^7\ ^8S^\circ$  to which most of the lower levels belong. A partial analysis of the spectra based on this parent was accordingly made.<sup>2,3</sup> To make possible the analysis of the more complicated spectra belonging to the neighboring elements, a more theoretical guidance seems necessary, and the starting point should be the theoretical investigation of the comparatively simpler Eu I series spectra, and the evaluation of the Slater's parameters from them to serve as starting values for the calculations in the more complicated cases.

The known spectra belonging to the above-mentioned series are those of Eu I<sup>2</sup> and Gd II.<sup>3</sup> The ionization in the latter leads one to expect interconfigurations interaction in a lesser degree and a simpler structure of the spectrum. Accordingly we began working on this spectrum.

### CALCULATION OF THE ENERGY LEVELS

An inspection of the experimental data<sup>3</sup> shows that the Landé interval rule is almost exactly obeyed, and the  $LS$  approximation should be sufficient for our purposes; but the fact that Russell was unable to assign the configurations of the even  $P$  terms shows that interaction between configurations should be of importance.

#### I. The Electrostatic Energy

In our approximation the energy is the sum of four terms,

$$W(f^7l_1l_2) = W(f^7) + W(f^7l_1) + W(f^7l_2) + W(l_1l_2). \quad (1)$$

The first term  $W(f^7)$  is common to all the terms we shall consider, as they are all based on the same parent  $4f^7\ ^8S^\circ$ , so it is unnecessary to calculate it explicitly for their comparison.

The interaction of an  $fl$  pair is of the form

$$W(fl) = a(L) - \frac{1}{2}[1 + 4(\mathbf{s}_f \cdot \mathbf{s}_l)]b(L), \quad (2)$$

where  $a(L)$  and  $b(L)$  are linear combinations of Slater's  $F$ 's and  $G$ 's, respectively. The coefficients in these combinations are scalar products of tensors,<sup>4</sup> whose rank is determined by the well-known triangular conditions. Summing now over all the seven  $f$  electrons, the triangular conditions give the following: that because all our terms come from an  $S$  parent, the contributions of all tensors of rank different from zero vanish, and the contribution of an  $fl$  pair to the interaction between  $f^7\ ^8S^\circ$  and  $l$  reduces to

$$W(fl) = F_0(fl) - \frac{1}{2}[1 + 4(\mathbf{s}_f \cdot \mathbf{s}_l)]b, \quad (2')$$

where  $b$  is that part of the exchange interaction which is given by the term with  $r=0$  in Racah's equation (60) II.<sup>4</sup>

In the same way the interaction between the two outer electrons is

$$W(l_1l_2) = F_0(l_1l_2) + A(L) - \frac{1}{2}[1 + 4(\mathbf{s}_1 \cdot \mathbf{s}_2)]B(L), \quad (2'')$$

where  $A$  and  $B$  depend upon  $L$  and are given by Condon and Shortley.<sup>5</sup> Summing all this, one finally obtains

$$\begin{aligned} W(f^7l_1l_2) = & W(f^7) + 7(F_0(fl_1) + F_0(fl_2)) + F_0(l_1l_2) \\ & + A - (7/2)(b_1 + b_2) - B/2 - 2b_1(\mathbf{S}_1 \cdot \mathbf{s}_1) \\ & - 2b_2(\mathbf{S}_1 \cdot \mathbf{s}_2) - 2B(\mathbf{s}_1 \cdot \mathbf{s}_2), \quad (3) \end{aligned}$$

where  $\mathbf{S}_1$  is the spin of the parent term  $4f^7\ ^8S^\circ$ .

Calculating explicitly the matrices of these operators, which are of order two in the octuplets and reduce to simple elements in the decuplets and the sextuplets,<sup>6</sup> one obtains finally:

For decuplets,

$$W(^{10}L) = W_0 + A(L) - 7(b_1 + b_2) - B(L), \quad (3a)$$

for sextuplets,

$$W(^6L) = W_0 + A(L) + b_1 + b_2 - B(L), \quad (3b)$$

<sup>4</sup> G. Racah, Phys. Rev. **62**, 438 (1942).

<sup>1</sup> W. F. Meggers, J. Opt. Soc. Am. **41**, 143 (1951).  
<sup>2</sup> H. N. Russell and A. S. King, Astrophys. J. **90**, 155 (1939);  
 Russell, Albertson, and Davis, Phys. Rev. **60**, 641 (1941).

<sup>3</sup> H. N. Russell, J. Opt. Soc. Am. **40**, 550 (1950).

<sup>5</sup> E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935), Sec. 5. G. Racah, Physica **16**, 651 (1950), Eqs. (7)-(10).

<sup>6</sup> See reference 5, Condon and Shortley, Chap. III.

and for octuplets,

$$W(^8L) = \frac{0}{1} \left\| \begin{array}{cc} W_0 + A(L) - (7/2)(b_1 + b_2) + B(L) & (3/2)(7)^{\frac{1}{2}}(b_1 - b_2) \\ (3/2)(7)^{\frac{1}{2}}(b_1 - b_2) & W_0 + A(L) - (5/2)(b_1 + b_2) - B(L) \end{array} \right\| \quad (3c)$$

with  $W_0 = W(f^7) + 7F_0(fl_1) + 7F_0(fl_2) + F_0(l_1l_2)$ ; in the last matrix the rows and columns are labeled by the values of the resultant spin  $\mathbf{s}_1 + \mathbf{s}_2$  of the two outer electrons.

For two equivalent electrons the formulas are obtained from those above by putting  $F_0(fl_1) = F_0(fl_2)$ ,  $b_1 = b_2$ ,  $B(L) = 0$ .

The matrix elements of configurations-interaction for the cases needed in our problem are already explicitly calculated.<sup>7</sup> Table I gives the values of the  $b$ 's for the different  $l$  electrons.

## II. The Spin-Orbit Interaction

Its form is

$$\sum_i \zeta(n^i l^i) (\mathbf{l}_i \cdot \mathbf{s}_i), \quad (4)$$

where  $\zeta(n^i l^i)$  is the one-electron spin-orbit parameter, and the summation extends over all the electrons. But in the terms based on an  $^8S$  parent, the sum over the  $f$  electrons vanishes, and there remains an expression

$$\zeta_1(\mathbf{l}_1 \cdot \mathbf{s}_1) + \zeta_2(\mathbf{l}_2 \cdot \mathbf{s}_2). \quad (4')$$

As we are interested, in the  $LS$  approximation, only in averages of this expression, we may take in the scalar product only the components of  $\mathbf{l}$  parallel to  $\mathbf{L}$ , and likewise for  $\mathbf{s}$ . Since

$$\mathbf{l}_{||} = \frac{(\mathbf{L} \cdot \mathbf{l}) \mathbf{L}}{L(L+1)}, \quad \mathbf{s}_{||} = \frac{(\mathbf{S} \cdot \mathbf{s}) \mathbf{S}}{S(S+1)}, \quad (5)$$

one obtains finally for the spin-orbit interaction the expression

$$\zeta(\gamma SL) (\mathbf{S} \cdot \mathbf{L}), \quad (6)$$

with

$$\zeta(\gamma SL) = \zeta_1 \frac{(\mathbf{L} \cdot \mathbf{l}_1)(\mathbf{S} \cdot \mathbf{s}_1)}{L(L+1)S(S+1)} + \zeta_2 \frac{(\mathbf{L} \cdot \mathbf{l}_2)(\mathbf{S} \cdot \mathbf{s}_2)}{L(L+1)S(S+1)}, \quad (7)$$

and the matrices of the last operators can be calculated by the usual vector-coupling formulas.<sup>8</sup>

## COMPARISON WITH EXPERIMENT

### I. The Electrostatic Energy

Formulas (3a, b, c) show that from the four multiplets having the same  $L$  and belonging to the same

TABLE I. The "scalar" part of the exchange interaction for  $fl$ .

$l$	$b$
$s$	$G_3(fs)$
$p$	$15G_2(fp) + 12G_4(fp)$
$d$	$3G_1(fd) + 12G_3(fd) + 66G_5(fd)$

<sup>7</sup> See reference 5, G. Racah.

configuration, one can obtain, if configuration-interaction does not exist, the  $W_0 + A(L)$ ,  $b_1$ ,  $b_2$ ,  $B(L)$ . If the values obtained for the same parameter from different groups of multiplets are in bad agreement, or if one obtains unacceptable values (for instance, a negative value for an essentially positive parameter), configurations-interaction must be considered. Considerations of this kind brought us to assume interaction between the  $P$  terms of  $f^7 sp$  and  $f^7 dp$ , and between the  $^8D$  terms of  $f^7 sd$  and  $f^7 d^2$ .

TABLE II. The terms of Gd II.

Config	Term	Obs	Calc	Diff
6s5d	$a^{10}D^o$	991	1 018	- 27
6s5d	$a^8D^o$	3 883	3 925	- 42
5d <sup>2</sup>	$a^{10}P^o$	5 403	5 125	278
6s5d	$b^8D^o$	8 959	8 924	35
6s5d	$a^8D^o$	10 429	10 397	32
5d <sup>2</sup>	$a^{10}P^o$	11 112	11 108	4
5d <sup>2</sup>	$a^8F^o$	13 261	13 544	-283
5d <sup>2</sup>	$c^8D^o$	17 884	17 882	2
5d <sup>2</sup>	$a^8G^o$	18 472	18 482	- 10
6s6p	$z^{10}P$	27 067	26 906	161
5d6p	$z^{10}F$	28 435	28 342	93
6s6p	$z^8P$	29 014	29 625	-611
5d6p	$z^{10}D$	29 904	29 866	38
5d6p	$z^8D^*$	30 103	30 256	-153
6s6p	$y^8P^*$	32 252	32 208	44
6s6p	$z^6P$	32 471	32 097	374
5d6p	$z^8F$	32 816	33 009	-193
5d6p	$y^{10}P$	33 727	33 864	-137
5d6p	$y^8D$	36 670	36 654	16
5d6p	$z^6F$	38 456	38 245	211
5d6p	$x^8P$	39 167	38 950	217
5d6p	$z^6D$	39 803	39 769	34
5d6p	$y^8F^*$	40 978	40 903	75
5d6p	$y^6P$	42 743	42 891	-148
5d6p	$w^8P^*$	49 270	49 290	- 20
Mean deviation				$\pm 191$
Mean error				$\pm 338$

The comparison between theory and experiment is given in Table II, and is as good as could be desired in the approximation on which we are working, although it must be remembered that the number of "free" parameters is not much smaller than the number of terms (17 against 25). The most probable values of the parameters, as obtained by least-squares calculations, are given in Table III.

The percentages contribution of the different configurations to the eigenfunctions of the terms were calculated too, and are given in Tables IVa, b, and d. It is seen, that in all the terms, except the  $y, w^8P$ , one configuration contributes much more than the other, so that a configuration assignment to the terms can be made. Only in these two  $^8P$  terms the configuration loses its meaning.

In the case of the octuplets, for reasons of convenience, we calculated the matrices in the scheme of eigenstates of  $s_1+s_2$ , and in Table II we designated by a star (\*) the states where the spins of the two outer electrons are antiparallel, although this characterization has only a partial meaning, like the designation of the configuration, and the question arises: Which is the *most proper* designation? On the other hand, the conventional designation of the states is by their limit, i.e., by the parent term of Gd III to which they belong. To see which designation is more appropriate physically in the present cases, we also calculated the eigenfunctions corresponding to a given value of the spin of the parent terms and observed which functions were closer to the eigenfunctions of the energy.

TABLE III. Most probable values of Slater's parameters.

Parameter	Most probable value
$W_0(6s6p)$	37 752
$B(6s6p)$	5 243
$b(6s)$	237
$b(6p)$	302
$W_0(5d6p)$	39 892
$F_2(5d6p)$	389
$G_1(5d6p)$	600
$G_3(5d6p)$	21
$R^1(5d6p, 6s6p)$	12 101
$R^2(5d6p, 6s6p)$	9 325
$b(5d)$	935
$W_0(6s5d)$	11 038
$B(6s5d)$	1 813
$R^2(5d^2, 6s5d)$	12 746
$W_0(5d^2)$	22 828
$F_2(5d^2)$	543
$F_4(5d^2)$	29

The results are also given in Tables IVa, c, d, where the contributions of the different states to the real eigenfunctions are given in the two schemes. One sees that sometimes one designation is better, sometimes the other, without any clear superiority, and we retained, therefore, the designation of the scheme in which we calculated.

## II. The Spin-Orbit Energy

Here it was necessary to equate the diagonal elements of the  $\zeta(\gamma SL)$  of (6) in the scheme of eigenfunctions of the electrostatic-energy to the experimental values obtained for them, and to obtain the best values for  $\zeta_d$  and  $\zeta_p$  by least squares from the twenty-five linear

TABLE IV. Composition of the various terms of Gd II.

Term	(a) ${}^8D^o$ terms			$f^1s({}^8S)d$	$f^1s({}^7S)d$	$f^1d^2$
	$f^1({}^8S) + sd({}^8D)$	$f^1({}^8S) + sd({}^1D)$	$f^1({}^8S) + d^2({}^1D)$			
$a {}^8D$	55	40	5	0	95	5
$b {}^8D$	44	40	16	83	1	16
$c {}^8D$	1	20	79	16	5	79
Term	(b) ${}^{10}P$ and ${}^8P$ terms		$f^1sp$	$f^1dp$		
$z {}^{10}P$			72			28
$y {}^{10}P$			28			72
$z {}^8P$			90			10
$y {}^8P$			10			90
Term	(c) ${}^8D$ and ${}^8F$ terms		$f^1d({}^8D)p$	$f^1d({}^1D)p$		
$z {}^8D$	20	80	93			7
$y {}^8D$	80	20	7			93
$z {}^8F$	89	11	77			23
$y {}^8F$	11	89	23			77
Term	(d) ${}^8P$ terms					
	$f^1({}^8S) + sp({}^8P)$	$f^1({}^8S) + sp({}^1P)$	$f^1({}^8S) + dp({}^8P)$	$f^1({}^8S) + dp({}^1P)$		
$z {}^8P$	71	4	18			7
$y {}^8P$	15	39	1			45
$x {}^8P$	13	8	79			0
$w {}^8P$	0	49	3			48
Term	$f^1s({}^8S)p$	$f^1s({}^7S)p$	$f^1d({}^8D)p$	$f^1d({}^1D)p$		
$z {}^8P$	16	59	23			2
$y {}^8P$	53	1	31			15
$x {}^8P$	0	21	29			50
$w {}^8P$	30	19	18			33

equations so obtained for them. The deviations after fitting the parameters were much greater than the values of the  $\zeta(\gamma SL)$  themselves.

In fact, this can be seen without detailed calculations, from the experimental fact that the distance between the extreme levels of the decuplets is in almost all cases about twice or more as large as that of the sextuplets, while both the classical vector-model, and the rigorous quantum-mechanical treatment, show that it should be about equal.

In conclusion, it is seen that the calculation of the splittings of the multiplets in an  $LS$  approximation has no meaning, and in order to calculate them one needs to consider also the nondiagonal elements of the spin-orbit interaction.

I thank Professor Racah for his continual help throughout the work.