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The Spectra of the Rare Gases and their Zeeman Effects

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The Zeeman effect of the rare gases is discussed from the standpoint of the coupling scheme of Shortley and Fried. The matrices for this type of interaction are calculated and also the g factors from the transformations to LS coupling for the p^5f configurations. These enable us to determine the Paschen-Back patterns to be expected. The calculated patterns are compared with observed structures and the agreement is very satisfactory in most cases.

WE have become so accustomed to hearing the phrase "transition from LS to jj coupling" that whenever we think of the variation in coupling in a series of levels, we automatically think of the change taking place from the LS condition toward a jj coupling limit. The spectra of the rare gases afford examples which show that this simple picture is inadequate. The work of Shortley and Fried[1] has shown that in the spectra of Cu II and A, a very striking example of a special type of intermediate coupling exists. This may be shown by calculations which neglect all parameters in the energy matrix excepting F_2 and ζ_p. This is equivalent to assigning a J value to the core (p^5) and using only one electrostatic parameter in addition. The result is to break up the spectrum into two widely separated groups ($^2P_{3/2}$ and $^2P_{1/2}$ of the p^5 core) each of these in turn being broken up into a group of closely-packed levels. These closely-packed levels in turn exhibit the peculiarity of being levels with multiple J values. Shortley and Fried[1] applied their results only to the spectrum of argon among the rare gases, but since then a considerable amount of data on the Zeeman effect has been published which helps to substantiate this picture.

Some years ago,[2] the author had occasion to investigate the genealogy of the p^5p configurations of the rare gases as it could be determined from the g factors. Satisfactory curves could be drawn for the values known up to that time showing the transition from LS coupling toward jj coupling, but the slopes of some of the curves seemed to be too abrupt at the jj end. Since that time, a large amount of data on the p^5d and some data on the p^5f configurations have been given.[3] It was primarily the data on the p^5f configuration which led to the considerations discussed in this paper.

Table I gives the matrices for the transformation from LS to jj coupling of the p^5f configuration, together with the g values to be derived from it by performing the operation

$$g(\alpha J)=\sum_{\gamma SL} g(SLJ)(\gamma SLJ|\alpha J)^2. \qquad (1)$$

Thus, to find the g value corresponding to a particular row JJ', square the numbers appearing in that row and multiply each of the numbers thus obtained by the $g(SLJ)$ occurring below the LS designation at the head of the column in which the number lies. Add all the terms thus obtained and this will be the g value for jj coupling. This same method applied to the transformation matrix between any other type of coupling and LS coupling will yield the g value for that type of coupling.

It is, of course, not necessary to perform these laborious calculations for the sole purpose of determining the g factors in any limiting case of coupling. Closed formulas for the calculation of g factors have been given for a number of these.[4] But for the calculations of intensities and energy levels in intermediate fields, the complete matrix must be known.[5]

[1] G. H. Shortley and B. Fried, Phys. Rev. **54**, 749 (1938).
[2] J. B. Green, Phys. Rev. **52**, 736 (1937).

[3] Summary bibliographies may be found as follows: (a) Neon: J. B. Green and J. A. Peoples, Phys. Rev. **54**, 602 (1938). (b) Argon: J. B. Green and B. Fried, Phys. Rev. **54**, 876 (1938). (c) Krypton: Green, Bowman, and Hurlburt, Phys. Rev. **58**, 1094 (1940). (d) Xenon: Green, Hurlburt, and Bowman, Phys. Rev. **59**, 72 (1941).
[4] See, e.g., Pauling and Goudsmit, *The Structure of Line Spectra* (McGraw-Hill, New York, 1930).
[5] G. Racah, Phys. Rev. **61**, 537 (1942) has used the vector coupling method to calculate g formulas for this

TABLE I. Matrices for transformation from LS to jj coupling for p^5f.

	$^3G_5$	$g(jj)$	
$a\ \frac{3}{2}\ \frac{7}{2}$	1	1.200	$J=5$
$g(LS)$	1.200		

	$^3G_4$	$^3F_4$	$^1G_4$		$g(jj)$	
$a\ \frac{3}{2}\ \frac{7}{2}$	2	$2(15)^{\frac{1}{2}}$	$2\sqrt{5}$		1.181	
$b\ \frac{3}{2}\ \frac{5}{2}$	$3\sqrt{5}$	$\sqrt{3}$	-6	$\cdot\frac{1}{2\sqrt{21}}$	1.034	$J=4$
$c\ \frac{1}{2}\ \frac{7}{2}$	$(35)^{\frac{1}{2}}$	$-(21)^{\frac{1}{2}}$	$2\sqrt{7}$		1.083	
$g(LS)$	1.050	1.250	1.000			

	$^3G_3$	$^3F_3$	$^3D_3$	$^1F_3$		$g(jj)$	
$a\ \frac{3}{2}\ \frac{7}{2}$	-6	$6\sqrt{7}$	$-12\sqrt{5}$	$6(21)^{\frac{1}{2}}$		1.142	
$b\ \frac{3}{2}\ \frac{5}{2}$	$9\sqrt{5}$	$5(35)^{\frac{1}{2}}$	-8	$-2(105)^{\frac{1}{2}}$	$\cdot\frac{1}{42}$	0.997	$J=3$
$c\ \frac{1}{2}\ \frac{7}{2}$	$-3\sqrt{3}$	$5(21)^{\frac{1}{2}}$	$8(15)^{\frac{1}{2}}$	$6\sqrt{7}$		1.202	
$d\ \frac{1}{2}\ \frac{5}{2}$	36	$-4\sqrt{7}$	$2\sqrt{5}$	$4(21)^{\frac{1}{2}}$		0.825	
$g(LS)$	.750	1.083	1.333	1.000			

	$^3F_2$	$^3D_2$	$^1D_2$		$g(jj)$	
$a\ \frac{3}{2}\ \frac{7}{2}$	$-\sqrt{3}$	$2\sqrt{6}$	6		1.047	
$b\ \frac{3}{2}\ \frac{5}{2}$	$4\sqrt{2}$	5	$-\sqrt{6}$	$\cdot\frac{1}{3\sqrt{7}}$	0.897	$J=2$
$d\ \frac{1}{2}\ \frac{5}{2}$	$2\sqrt{7}$	$-(14)^{\frac{1}{2}}$	$(21)^{\frac{1}{2}}$		0.889	
$g(LS)$	0.667	1.167	1.000			

	$^3D_1$	$g(jj)$	
$b\ \frac{3}{2}\ \frac{5}{2}$	1	0.500	$J=1$
$g(LS)$	0.500		

TABLE II. Matrices of electrostatic energy F_2 in jj coupling for p^5f.

$-F_0+$

	5a	
5a	$-5F_2$	$J=5$

	4a	4b	4c	
4a	$\frac{65}{7}F_2$	$\frac{\sqrt{5}\cdot 10}{7}F_2$	$-\frac{10(35)^{\frac{1}{2}}}{7}F_2$	
4b		$-\frac{30}{7}F_2$	$-\frac{5\sqrt{7}}{7}F_2$	$J=4$
4c			0	

	3a	3b	3c	3d	
3a	$\frac{25}{7}F_2$	$-\frac{6\sqrt{5}}{7}F_2$	$\frac{50\sqrt{3}}{7}F_2$	$\frac{30}{7}F_2$	
3b		$\frac{66}{7}F_2$	$\frac{9(15)^{\frac{1}{2}}}{7}F_2$	$-\frac{24\sqrt{5}}{7}F_2$	$J=3$
3c			0	0	
3d				0	

	2a	2b	2d	
2a	$-\frac{75}{7}F_2$	$-\frac{12\sqrt{6}}{7}F_2$	$-\frac{6(21)^{\frac{1}{2}}}{7}F_2$	
2b		$\frac{12}{7}F_2$	$\frac{24(14)^{\frac{1}{2}}}{7}F_2$	$J=2$
2d			0	

	1b	
1b	$-12F_2$	$J=1$

TABLE III. Transformation matrices from jj to intermediate coupling.

	4a	4b	
4a′	$(20)^{\frac{1}{2}}$	1	$\cdot\frac{1}{(21)^{\frac{1}{2}}}$
4b′	-1	$(20)^{\frac{1}{2}}$	

	3a	3b	
3a′	2	$-3\sqrt{5}$	$\cdot\frac{1}{7}$
3b′	$3\sqrt{5}$	2	

	3c	3d	
3c′	$4\sqrt{3}$	1	$\cdot\frac{1}{7}$
3d′	-1	$4\sqrt{3}$	

	2a	2b	
2a′	$\sqrt{3}$	$-4\sqrt{2}$	$\cdot\frac{1}{35}$
2b′	$4\sqrt{2}$	$\sqrt{3}$	

Table II gives the matrices of the electrostatic parameter F_2, the only one to be considered in

type of coupling, but they give the same result as the $\{[(l_1s_1)l_2]s_2\}$ formulas that are given in Pauling and Goudsmit (reference 4), or Candler, *Atomic Spectra* (Cambridge Univ. Press, 1937, p. 143–145).

this example, and if the determinants of these matrices are solved, they yield the following results, after adding the electromagnetic parameter ζ_p to the higher set (c and d), and subtracting $\frac{1}{2}\zeta_p$ from the lower set (a and b).

$$\begin{aligned} &\text{Upper set } 4c,\ 3c,\ 3d,\ 2d = -F_0+\zeta_p.\\ &\text{Lower set } 5a,\ 4b' = -F_0-\tfrac{1}{2}\zeta_p-5F_2, \qquad (1)\\ &\qquad 4a',\ 3a' = -F_0-\tfrac{1}{2}\zeta_p+10F_2,\\ &\qquad 3b',\ 2a' = -F_0-\tfrac{1}{2}\zeta_p+3F_2,\\ &\qquad 2b',\ 1b = -F_0-\tfrac{1}{2}\zeta_p-12F_2. \end{aligned}$$

These solutions, inserted in Table II, give the transformation matrices for jj coupling to this particular variety of intermediate coupling and are given in Table III. When we apply these transformations to the matrices of Table I we arrive at Table IV, which gives the transformation from LS to this intermediate type of coupling. Listed with Table IV are the g values for this special coupling scheme. A striking difference is shown between the g values for the intermediate case and those for jj coupling, even though they seem to be quite close together at first glance. Perhaps even more striking is the difference of phase between several homologous elements of the two sets of matrices.

A study of the p^5f configurations of the rare gases from the standpoint of Eqs. (1) shows some interesting points.[6]

Neon

Strangely enough the spectrum of neon shows the least conformity with the above results. The levels labeled W (except $4W$) are separated from the others of the lower ($^2P_{3/2}$) set by about 100 cm^{-1}. Except for $4W$, all the members of the upper set are piled together, as indicated by (1). The author is of the opinion that interaction with the p^5p configurations is not sufficiently large to account for such large perturbations, and suggests that some revision of these assignments is necessary.

Argon

As indicated by Shortley and Fried[1] the p^5f configurations of argon represent an almost perfect example of the application of Eqs. (1). Each of the levels of the lower ($^2P_{3/2}$) set can be assigned a double J value, and the spacings of the four observed levels are in almost perfect accord with the theory. The upper ($^2P_{1/2}$) set should consist of four levels lumped into one, but evidence of splitting into two levels is noticed.

Krypton

In krypton, we see for the first time the splitting of the levels of the lower ($^2P_{3/2}$) set into pairs. This appears as a separation of the lowest level ($J=1$, 2) into two separate levels (X, Z); and of the third ($J=2$, 3) into two separate (but

[6] W. F. Meggers and C. J. Humphreys, Bur. Stand. J. Research **10**, 427 (1933) (RP 540). C. J. Humphreys and W. F. Meggers, Bur. Stand. J. Research **10**, 139 (1933) (RP 521). C. J. Humphreys, J. Research Nat. Bur. Stand. **20**, 17 (1938) (RP 1061).

TABLE IV. Matrices for transformation from LS to intermediate coupling.

$J=5$

	$^3G_5$	$g(jj)$
$5a'$	1	1.200
$g(LS)$	1.200	

$J=4$ (matrix multiplied by $\frac{1}{6}$)

	$^3G_4$	$^3F_4$	$^1G_4$	g(Int.)
$4a'$	$\sqrt{5}$	$3\sqrt{3}$	2	1.195
$4b'$	4	0	$-2\sqrt{5}$	1.022
$4c'$	$(15)^{\frac{1}{2}}$	-3	$2\sqrt{3}$	1.083
$g(LS)$	1.050	1.250	1.000	

$J=3$ (matrix multiplied by $\frac{1}{42}$)

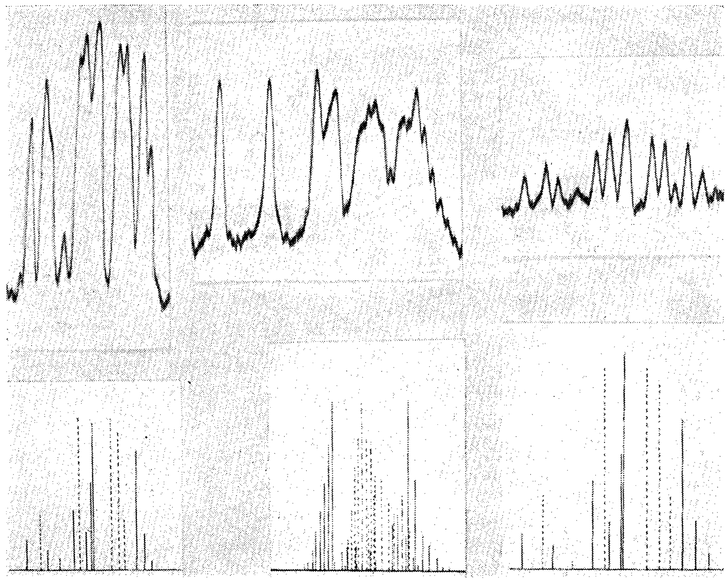
	$^3G_3$	$^3F_3$	$^3D_3$	$^1F_3$	g(Int.)
$3a'$	-21	$-9\sqrt{7}$	0	$6\sqrt{21}$	0.964
$3b'$	0	$4(35)^{\frac{1}{2}}$	-28	$2(105)^{\frac{1}{2}}$	1.175
$3c'$	0	$8\sqrt{7}$	$14\sqrt{5}$	$4(21)^{\frac{1}{2}}$	1.206
$3d'$	$21\sqrt{3}$	$-3(21)^{\frac{1}{2}}$	0	$6\sqrt{7}$	0.821
$g(LS)$	.750	1.083	1.333	1.000	

$J=2$ (matrix multiplied by $\frac{1}{3\sqrt{5}}$)

	$^3F_2$	$^3D_2$	$^1D_2$	g(Int.)
$2a'$	-5	$-2\sqrt{2}$	$2\sqrt{3}$	0.844
$2b'$	0	$3\sqrt{3}$	$3\sqrt{2}$	1.100
$2d'$	$2\sqrt{5}$	$-(10)^{\frac{1}{2}}$	$(15)^{\frac{1}{2}}$	0.889
$g(LS)$	.667	1.167	1.000	

$J=1$

	$^3D_1$	g(Int.)
$1b'$	1	0.500
$g(LS)$	.500	



(a) (b) (c)

FIG. 1. (a) λλ 6178–9, Xe $1s_2-5Y$, $5X$. (b) λλ 7584, Xe $3d_4'-5T$, $5Z$. (The lines to the right of the figure are Kr.) (c) λλ 7472–4, Xe $3d_5-5Y$, $5X$. Above are shown microphotograms of original plates; below are shown calculated patterns. Full lines are perpendicular polarizations; dotted lines parallel polarizations; dot and dash, mixed polarizations.

very close) levels (Y, T). $5X$ and $5Z$ are perturbed by the upper terms of p^53p and are therefore more widely separated than we should expect. No levels of the upper ($^2P_{1/2}$) set are known for krypton.

Xenon

This is probably the best known spectrum as far as the p^5f configurations are concerned. The members of the lower set are all separated with the exception of the highest (W), but lines involving these levels show Paschen-Back effect, indicating that the W levels are complex. All of the levels of the upper ($^2P_{1/2}$) set lie in the negative energy region and none has been found.

Lines involving the p^5f configurations in neon and argon did not appear on the plates. A few of these lines appeared on the krypton plates, and many of them on the xenon plates.

Examples of the Paschen-Back effect of xenon chosen for this paper were the $p^55f(2b', 1b)$ and the $p^55f(5a, 4b')$ known as $5Y$, $5X$ and $5T$, $5Z$, respectively. These particular levels were chosen because each pair contains one pure level ($5X={}^3D_1$ and $5T={}^3F_5$). The results are shown in the accompanying figure. The method of making these calculations has been outlined in a

TABLE V. g values for p^5p of rare gases.

$J=1$	p_{10}	Ne	1.984	1.929			Limits
		A	1.985	1.90			JJ 1.500
		Kr	1.898	1.834	1.795	1.795	Int. 1.778
		Xe	1.852	1.728*	1.801		
$J=1$	p_7	Ne	0.669	0.974			
		A	0.838	1.01			JJ 1.333
		Kr	1.004	1.034	1.041	1.014	Int. 1.056
		Xe	1.022	0.903*	1.036		
$J=1$	p_5	Ne	0.999	0.685			
	p_4	A	0.819	0.61			JJ 0.667
	p_4	Kr	0.647	0.648			Int. 0.611
	p_4	Xe	0.790*				
$J=1$	p_2	Ne	1.340	1.397			
	p_2	A	1.380	1.45			JJ 1.500
	p_3	Kr	1.452	1.401			Int. 1.556
	p_3	Xe	1.552*				
$J=2$	p_4	Ne	1.301	1.184			
	p_3	A	1.260	1.18			JJ 1.067
	p_2	Kr	1.181	1.158			Int. 1.067
	p_3	Xe	1.195				
$J=2$	p_6	Ne	1.229	1.360			
	p_6	A	1.305	1.42			JJ 1.333
	p_6	Kr	1.388	1.403	1.403	1.411	Int. 1.433
	p_6	Xe	1.379	1.347	1.395	1.386	
$J=2$	p_8	Ne	1.137	1.112			
	p_8	A	1.112	1.09			JJ 1.167
	p_8	Kr	1.099	1.107			Int. 1.067
	p_9	Xe	1.106	1.123	1.103		

* These levels from different configurations are close enough to perturb each other.

TABLE VI. g values for p^5d configurations of the rare gases.

								Limits
$J=1$	s_1'	Ne	0.752	0.797				JJ 0.833
		A	0.877	0.768				Int. 0.833
$J=1$	d_2	Ne	0.860	0.812	0.791			
		A	0.768	0.813	(1.186)?			JJ 1.110
		Kr	0.935	0.823	0.797			Int. 0.833
		Xe	0.919	0.914	0.899			
$J=1$	d_5	Ne	1.397	1.391	1.383			
		A	1.467	1.400	1.283			JJ 1.333
		Kr	1.098	1.348	1.355	1.294	1.208	Int. 1.067
		Xe	1.395		1.273	1.180	1.217	1.308
$J=2$	d_1''	Ne	0.948	0.990				
		A	0.908	0.941	1.107			JJ 1.121
		Kr		1.006	0.965	0.954	1.005	Int. 0.978
		Xe			1.073	0.987	0.980	
$J=2$	d_3	Ne	1.356	1.322	1.298			
		A	1.437	1.387	1.206			JJ 1.067
		Kr		1.295	1.318	1.315		Int. 1.300
		Xe	1.376	1.196?	1.303	1.298		
$J=2$	s_1''	Ne	1.242	1.230	1.251			
		A	0.987	1.265	1.264			JJ 1.289
		Kr	0.899					Int. 1.300
$J=2$	s_1''''	Ne	0.781	0.783				
		A	1.057	0.802	0.777			JJ 0.767
		Kr	1.169					Int. 0.756
		Xe	1.274*					
$J=3$	d_4	Ne	1.034	1.040	1.093			
		A		1.077	1.076	1.052		JJ 1.068
		Kr		1.050	1.073	1.094	1.037	Int. 1.036
		Xe		1.026	1.076	1.078	1.081	1.082
$J=3$	d_1'	Ne	1.249	1.248				
		A			1.199	1.245		JJ 1.237
		Kr		1.243	1.254	1.231	1.227	Int. 1.270
		Xe		1.263	1.246	1.225		
$J=3$	s_1'''	Ne	1.125	1.116				
		A		1.133	1.127	1.098		JJ 1.111
		Kr		1.140				Int. 1.111
		Xe	1.126					

* Should probably be labelled s_1''.

TABLE VII. g values for p^5f configurations of the rare gases.

						JJ	Int.
$J=1$	X	Kr	0.50	0.61*		0.500	0.500
$J=1$	X	Xe	0.504	0.50	0.50	0.500	0.500
$J=2$	V	Xe	0.86	0.87	0.87	1.047	0.844
$J=2$	Y	Xe	1.11	1.10	1.09	0.897	1.100
$J=3$	U	Xe	1.18	1.17		0.997	1.175
$J=4$	W_4	Xe	1.19			1.181	1.195
$J=4$	Z	Xe	1.02			1.034	1.022

* Perturbed by $4p^56p$.

previous paper.[7] Excellent agreement is seen to exist between calculation and experiment. In the case of $5Y$, $5X$ the theoretical g values are 1.10 and 0.50. The values calculated from the pattern are 1.11 and 0.50. The difference between the observed and theoretical g value of the $5Y$ level can be accounted for by the fact that the $5Y$ and $5X$ levels are separated by 3.6 cm^{-1} instead of falling on top of each other. (See Fig. 1.)

[7] J. B. Green, Phys. Rev. 59, 69 (1941).

With respect to the V, U ($3b'$, $2a'$) interaction, a serious discrepancy must be noted. Although the g values fit the theoretical calculations extremely well, the magnetic levels should not perturb each other very much because the interaction to be expected in this case almost cancels out. Yet the observed patterns are materially perturbed, and enough so to be somewhat greater than experimental error. Either the theory described here is too simple to be used in this particular case, or some perturbations from outside configurations are at work.

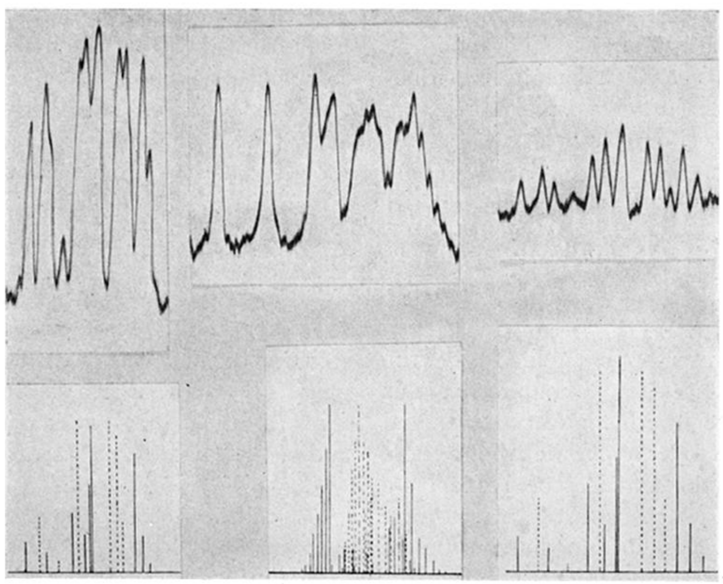
Table V gives a summary of the available data on the g factors of the rare gases for p^5p.

The tendency toward the limit for intermediate coupling is particularly evident for p_{10}.

Table VI gives a summary of the data for p^5d configurations.

Table VII gives the summary of experimental data for p^5f configurations.

It is in this configuration that the evidence in favor of the particular type of coupling assumed in this paper is most striking.



(a) (b) (c)

FIG. 1. (a) λλ 6178–9, Xe $1s_2-5Y$, $5X$. (b) λλ 7584, Xe $3d_4'-5T$, $5Z$. (The lines to the right of the figure are Kr.) (c) λλ 7472–4, Xe $3d_5-5Y$, $5X$. Above are shown microphotograms of original plates; below are shown calculated patterns. Full lines are perpendicular polarizations; dotted lines parallel polarizations; dot and dash, mixed polarizations.