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HYPERFINE STRUCTURE IN SINGLY IONIZED PRASEODYMIUM

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Wave-lengths and frequency separations of the fine-structure components of 173 spectral lines in singly ionized praseodymium are given. It appears, as may be seen from a reproduction of some of the fine-structure, Fig. 1, that each group of six fine-structure lines has the same general appearance but varies in total intensity and width. In some lines given below the intensities and frequency separations within each group decrease toward the red, while all of the rest show similar degradation toward the violet.

Theoretical interpretation. These fine structures may be accounted for by assigning an angular momentum, $i=(5/2)\ (h/2\pi)$ to the nucleus of the praseodymium atom. This angular momentum space quantized with the total angular momentum of the outside electrons, J, yields for each energy level six components (provided $J\geqq 5/2$), the actual separations between which are given by the strength of coupling between i and J. Since a $6p$ electron in the atom of praseodymium is part of the time very close to the nucleus and part of the time outside of all of the other electrons, the strength of coupling for an electron configuration involving a single $6s$ electron should be very much greater than that for a $6s$ electron and still greater than that for a $5d$ or a $4f$ electron. According to the Bohr-Stoner scheme of the building up of the elements one should expect, and the fine-structure intervals confirm this, that practically all of the energy levels in Pr II have very large J values.

SPECTRA arising from neutral and ionized praseodymium atoms offer one of the most interesting studies of hyperfine structure. In a preliminary report[1] on the hyperfine structure in Pr II it was indicated that a large number of lines were made up of six components. At present the fine-structures of nearly two hundred lines have been measured, of which about one hundred have been completely resolved into six components. Every fine structure group that has been resolved not only shows six components, but also reveals within each group a decrease in intensity and interval, either toward longer or toward shorter wave-lengths.

The original spectrograms were taken in the fourth order of the 75 ft. grating spectrograph on Mt. Wilson. Although in the fourth order this grat-

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[1] Gibbs, White and Ruedy, Proc. Nat. Acad. Sci. **15**, 642 (1929).

ing reveals two sets of faint ghosts, an enormous resolving power and dispersion is obtainable as can be seen from the lines in Fig. 1. One set of ghosts, about 1.8A.U. on each side of the strong lines, cause no difficulty whatever. The other set of ghosts unsymmetrically placed, within 0.2A.U. of the strong lines, which might at first be mistaken for very faint fine structure components, undoubtedly reduce the resolution of the fine structures. These latter ghosts are too faint to show in the reproductions, Fig. 1.

According to King's[2] temperature classification of the lines in praseodymium nearly all the wide groups of fine structure belong to the ionized spectrum. The measurements of 173 of these groups are given in Tables I and II. The relative intensities given in column 1 represent the sum total intensity of the fine structure components. The intensities can be given in this way since in every case the fine structure intensities gradually decrease in the same direction as the intervals, either toward the violet, Table I, or toward the red, Table II. In columns 2 and 3, the wave-lengths and frequencies of the strongest component in each fine structure group is given. Wave-length intervals between fine structure components measured on high dispersion plates enable the $\Delta\nu$'s in column 4 to be given in hundredths of a cm^{-1}. In cases where only the first three or four lines are resolved, the end of the group has been measured and the intervening lines interpolated. The interpolated intervals are given in italics. In column 5, the total width of each line is given in cm^{-1}. Tabulation of these total separations shows that a classification into definite groups can be made. This classification, it is hoped, will enable the author to get a start on the term scheme of Pr II.

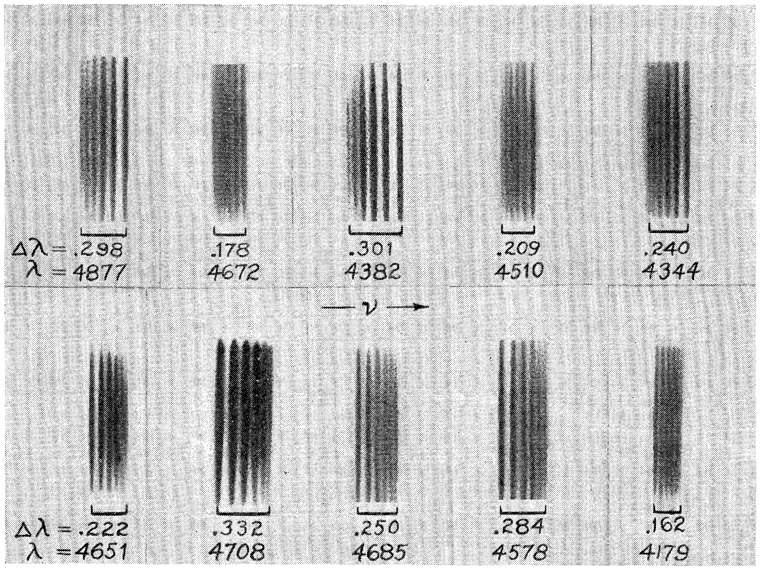

Fig. 1. Praseodymium fine structure

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[2] King, Astrophys. J. **68**, 1 (1928).

TABLE I. *Singly ionized praseodymium. Fine-structure intervals and intensities degraded toward the violet.*

Int.	λ(air)	Frequency† Numbers	$\Delta\nu$'s cm^{-1} in hundredths					Total $\Delta\nu$	Int.	λ(air)	Frequency Numbers	$\Delta\nu$'s cm^{-1} in hundredths					Total $\Delta\nu$
8	3938.36	25384.12	21	18	*15*	*12*	*09*	0.75	10	4293.66	23283.62	24	18	*15*	*12*	*09*	0.78
10	40.25	371.94	33	29	25	22	18	1.27	10	94.80	277.44	26	24	21	17	12	1.00
10	46.99	328.62	27	23	18	14	12	.94	50	4334.07	066.54	29	25	21	19	17	1.11
50	47.71	324.00	33	28	25	22	19	1.27	8	34.72	063.07	29	25	21	16	11	1.02
60	49.51	312.46	32	27	23	18	15	1.15	8	59.20	22933.56	30	25	20	17	14	1.06
60	53.58	286.40	31	27	23	20	17	1.18	10	74.42	853.77	29	21	*17*	*13*	*11*	.91
8	59.52	248.47	29	25	21	17	14	1.06	6	80.38	822.68	22	20	*17*	*13*	*10*	.82
125	64.90	214.21	31	25	20	16	12	1.04	10	99.40	724.01	23	20	*16*	*12*	*08*	.79
75	65.33	211.48	28	26	22	16	10	1.02	8	4400.09	720.45	24	21	*18*	*15*	*13*	.91
40	66.66	203.02	30	25	20	16	13	1.04	8	05.17	694.25	19	15	*12*	*10*	*08*	.64
50	72.24	167.61	33	29	24	19	13	1.18	40	05.90	690.49	25	23	20	18	16	1.02
3	74.39	154.00	30	25	20	15	10	1.00	10	12.23	657.94	28	24	21	19	16	1.08
20	82.54	102.53	35	32	27	21	16	1.31	15	19.10	622.71	27	17	*13*	*11*	*09*	.77
50	89.76	057.10	33	22	24	18	13	1.17	20	21.32	611.36	30	28	24	21	19	1.22
100	94.88	024.99	33	29	25	21	16	1.24	50	29.33	570.46	26	22	*18*	*14*	*10*	.90
20	97.12	010.96	30	26	22	18	12	1.08	15	32.36	555.03	30	28	21	15	11	1.05
20	4000.26	24991.33	32	28	24	21	18	1.23	75	49.90	466.13	24	21	18	16	*12*	.91
15	29.00	808.14	27	24	20	16	10	.97	15	54.43	443.29	25	22	19	16	12	.94
25	31.85	795.52	36	29	24	19	14	1.22	15	58.40	423.30	25	24	22	20	16	1.07
40	33.92	782.80	27	25	20	17	13	1.02	20	77.35	328.40	29	26	22	19	16	1.12
20	38.32	755.80	43	37	20	07	02	1.09	10	87.88	276.01	27	22	20	14	10	.93
15	39.44	748.94	30	25	20	16	12	1.03	6	93.14	249.92	28	26	23	16	12	1.05
10	51.21	677.04	27	22	*17*	*13*	*10*	.89	10	94.32	244.09	39	35	29	23	20	1.46
15	79.87	503.69	25	22	19	16	13	.95	100	96.56	233.01	30	25	22	18	12	1.07
25	81.09	496.37	30	27	24	21	16	1.18	20	4517.71	128.92	35	31	25	20	18	1.29
25	81.95	491.21	28	25	21	17	13	1.04	10	31.19	063.09	33	28	24	21	16	1.22
75	4100.79	378.69	27	24	21	18	15	1.05	5	50.85	21967.78	30	24	21	18	15	1.08
100	18.55	273.57	28	25	21	18	15	1.07	5	70.21	874.72	27	23	21	17	13	1.01
40	41.30	140.22	30	26	23	21	20	1.20	15	78.29	836.12	33	30	27	23	20	1.33
75	43.20	129.15	26	23	19	15	11	.94	8	4606.56	702.11	26	24	21	19	17	1.07
50	64.24	007.24	30	26	22	18	14	1.10	50	28.93	597.23	36	30	25	20	18	1.29
20	71.90	23963.16	29	26	22	19	16	1.12	20	43.67	528.68	33	30	25	20	17	1.25
25	72.33	960.70	31	27	24	21	15	1.18	40	51.64	491.79	27	23	21	18	13	1.02
10	78.71	924.12	29	25	21	18	16	1.09	10	85.07	338.44	32	26	23	20	13	1.14
75	79.46	919.82	27	23	19	15	11	.95	10	4707.65	236.10	25	22	20	16	12	.95
75	89.55	862.21	29	25	21	19	17	1.11	40	08.25	233.39	40	36	31	25	20	1.52
10	91.69	850.03	32	28	24	20	16	1.20	15	34.30	116.56	22	20	18	16	14	.90
7	4201.26	795.70	26	23	*17*	*12*	*07*	.85	20	45.03	068.80	25	21	19	17	13	.95
50	06.79	764.42	27	25	23	21	17	1.13	5	54.68	026.04	30	25	20	18	15	1.08
8	08.55	754.49	29	26	20	16	12	1.07?	5	56.18	019.41	40	35	29	23	18	1.45
75	23.01	673.16	25	21	*18*	*15*	*13*	.92	15	58.04	011.20	32	28	24	20	16	1.20
15	36.27	599.05	29	26	23	20	13	1.11	5	61.15	20997.48	35	28	21	18	16	1.18
15	40.09	577.79	18	16	*14*	*12*	*09*	.69	10	65.35	978.97	29	25	22	20	18	1.14
30	40.91	573.23	27	25	23	21	19	1.15	6	67.00	971.71	21	18	15	12	*09*	.75
30	47.74	535.33	31	26	22	17	12	1.08	5	78.40	921.67	34	31	26	21	17	1.29
10	51.59	514.01	35	30	26	21	16	1.28	15	83.43	899.67	19	17	*15*	*13*	*10*	.74
15	63.84	446.46	30	26	23	20	17	1.16	10	4832.19	688.79	31	27	22	19	14	1.13
40	72.36	399.70	28	26	24	21	15	1.14	10	37.14	667.61	27	24	21	18	15	1.05
15	80.21	356.79	35	30	25	20	15	1.25	10	48.68	618.42	31	27	23	19	14	1.14
30	82.55	344.03	26	24	22	19	16	1.07									

† The frequencies given in column 3 are only for the strong component of each group. The other frequencies may be obtained by adding successively the $\Delta\nu$'s in column 4.

THEORETICAL INTERPRETATION

Although an energy level analysis and the multiplet structure for Pr II has not yet been worked out, an attempt is here made, not only to give the origin of the fine structure, but also to explain why practically all of the lines reveal six components. Praseodymium occupies the position of fifth element in the sixth row of the periodic table, Cs, Ba, La, Ce, Pr, Nd, etc. According to the Bohr-Stoner scheme for the building up of the elements starting with cerium (the first of the fourteen rare-earth elements) *4f* electrons are added.

55	56	57	58	59	60	
Cs	Ba	La	Ce	Pr	Nd	
$6s$	$6s^2$	$6s^25d$	$6s^25d4f$	$6s^25d4f^2$	$6s^25d4f^3$	*etc.*

The normal state of Cs I is known to be a $^2S_{1/2}$ term arising from a *6s* electron. The normal state of Ba I, a $^1S_0$ term, arises from two *6s* electrons. The normal state of La I, a $^2D(6s^25d)$ term, has been verified by Meggers.[3] The normal state of the ionized atom, also given by Meggers,[4] is not given by *6s5d* as would be expected but by $5d^2$ which shows a very strong tendency for the binding of *d* electrons over *s* electrons. This tendency for the binding of *d* electrons in lanthanum might change our present ideas as to the number of *5d* electrons in the rare-earth elements. Analysis of the rare-earths from cerium on is as yet unknown.

TABLE II. *Singly ionized praseodymium. Fine-structure intervals and intensities degraded toward the red.*

Int.	λ(air)	Frequency†† Numbers	Δν's cm⁻¹ in hundredths					Total Δν	Int.	λ(air)	Frequency Numbers	Δν's cm⁻¹ in hundredths					Tota Δν
5	3928.61	25447.12	25	22	17	*12*	*08*	0.84	10	4403.46	22703.06	24	22	22	18	14	1.00
5	28.86	445.50	25	20	17	*14*	*10*	.86	100	08.70	676.08	24	21	17	*14*	*10*	.86
10	43.66	350.00	25	21	17	*14*	*10*	.87	15	19.53	620.51	31	27	22	19	17	1.16
20	64.19	218.72	19	18	*15*	*12*	*08*	.72	40	29.02	572.05	20	17	*14*	*11*	*08*	.70
6	67.06	200.48	27	24	18	*13*	*07*	.89	10	38.05	526.12	22	19	*16*	*13*	*11*	.81
20	71.06	175.10	23	19	*16*	*12*	*09*	.79	15	46.88	481.40	23	20	*16*	*12*	*07*	.78
75	81.97	106.12	24	21	*17*	*12*	*08*	.82	20	50.08	465.22	26	23	21	19	13	1.02
20	95.74	019.60	26	22	*18*	*14*	*11*	.91	5	61.20	409.22	16	*14*	*12*	*10*	*07*	.59
40	4008.62	24939.21	26	21	*17*	*14*	*10*	.88	15	65.87	385.79	27	*23*	21	*14*	*07*	.92
20	34.26	780.71	19	16	*13*	*11*	*10*	.69	75	68.55	372.37	26	22	20	*17*	*11*	.96
40	54.79	655.25	18	16	*14*	*12*	*10*	.70	10	72.81	351.06	26	20	13	*07*	*04*	.70
40	56.47	644.04	25	22	19	*15*	*12*	.93	5	79.50	317.68	27	20	16	*13*	*11*	.87
70	62.74	607.01	26	22	19	*16*	*12*	.95	5	85.43	288.17	23	20	17	*13*	*07*	.80
8	4169.37	23977.70	20	18	*16*	*14*	*12*	.80	10	88.10	274.91	20	14	*10*	*06*	*03*	.53
7	75.23	944.05	25	21	*17*	*13*	*10*	.86	8	92.31	254.04	23	21	18	*14*	*09*	.85
8	75.55	942.22	18	16	*13*	*11*	*08*	.66	60	96.24	234.59	21	19	*16*	*13*	*09*	.78?
75	4225.24	660.65	25	20	*16*	*13*	*11*	.85	50	4510.03	166.60	27	23	21	17	15	1.03
10	41.16	571.84	33	27	21	*15*	*09*	1.05	6	29.81	069.81	27	24	20	14	*09*	.94
10	43.44	559.17	22	19	17	*15*	*12*	.85	30	33.99	054.33	27	23	21	19	16	1.06
10	54.33	498.87	24	20	17	15	*13*	.89	30	35.80	040.67	18	16	*13*	*10*	*07*	.64
8	93.06	286.88	25	19	17	*15*	*13*	.89	10	70.44	21873.62	19	14	*11*	*09*	*07*	.60
6	95.04	276.14	20	17	*14*	*11*	*08*	.70	15	4646.03	517.74	17	13	*11*	*09*	*06*	.56
40	97.69	261.79	21	18	*15*	*12*	*09*	.75	10	64.60	432.08	17	16	*14*	*11*	*08*	.66
15	4323.47	123.09	24	21	18	*16*	*14*	.93	6	68.15	415.79	23	21	18	*15*	*12*	.89
8	23.81	121.27	25	18	16	*14*	*11*	.84	20	72.01	398.09	21	19	17	14	*10*	.81
8	33.04	072.02	24	23	19	15	11	.92	5	79.00	366.13	22	20	16	14	*10*	.82
12	38.61	042.40	26	19	*16*	*13*	*12*	.86	8	4728.53	142.32	24	22	17	13	*09*	.85
20	44.17	012.91	35	30	25	20	16	1.26	20	46.82	060.86	26	22	20	18	15	1.01
15	47.40	22995.81	23	22	18	*14*	*10*	.87	10	62.63	20990.95	21	17	14	*12*	*10*	.74
25	51.77	963.04	19	17	*14*	*11*	*08*	.69	5	66.24	975.05	23	21	17	15	*13*	.89
5	55.09	955.21	20	18	*15*	*11*	*08*	.72	4	4808.44	802.60	36	34	32	28	20	1.50
15	59.70	930.93	25	21	18	*16*	*14*	.94	20	22.87	128.76	22	18	15	*13*	*11*	.79
75	68.20	886.31	28	24	20	16	*12*	1.00	5	26.57	712.87	29	24	20	18	*16*	1.07
20	71.46	869.25	35	28	24	20	15	1.22	10	58.86	575.23	25	21	16	13	09	.84
10	82.61	811.07	44	37	31	25	20	1.57	20	77.71	495.71	31	28	26	21	18	1.24
5	83.97	803.99	29	26	24	22	17	1.18	5	79.00	490.30	27	25	21	18	*15*	1.06
20	95.97	741.74	27	24	20	18	15	1.04									

†† The frequencies given in column 3 are only for the strong component of each group. The other frequencies may be obtained by subtracting successively the Δν's in column 4.

A large number of the fine structure lines in Pr II can be accounted for by attributing them to the electron transition *6p* to *6s* in the presence of three other valence electrons, at least one of which is a *4f* electron. These electron configurations should be $6p5d4f^2$ and $6s5d4f^2$, or by analogy with La II should be $6p5d^24f$ and $6s5d^24f$. In either case the most prominent terms arising from any of these configurations have the necessary large inner quantum numbers. Theoretically $6s5d4f^2$ gives the following 214 terms.

$6s5d4f^2$

$^1(D)$	$^1(PDF)$	$^1(SPDFG)$	$^1(PDFGH)$	$^1(DFGHI)$	$^1(FGHIK)$	$^1(GHIKL)$
$^3(D)$	$^3(PDF)$	$^3(SPDFG)$	$^3(PDFGH)$	$^3(DFGHI)$	$^3(FGHIK)$	$^3(GHIKL)$
	$^3(PDF)$		$^3(PDFGH)$		$^3(FGHIK)$	
	$^5(PDF)$		$^5(PDFGH)$		$^5(FGHIK)$	

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[3] Meggers, Jour. Wash. Acad. Sci. **17,** 25 (1927).

[4] Meggers, J.O.S.A. **14,** 191 (1927).

Of all of these terms, according to Hund's rule,[5] the ^5K terms should lie deepest. Out of the 626 energy levels arising from $6p5d4f^2$ the multiplet term having the largest S and L values is a $^5L^0$ term. Of the hundreds of lines resulting from the electron transition $6p5d4f^2$ to $6s5d4f^2$ mostly those lines involving large S and L values can be expected to be observed.

THE LANDÉ INTERVAL RULE

Looking at each fine structure group in Fig. 1 one cannot help but think of each as the "diagonal lines" of a sextet multiplet which result from transitions between two sets of sextet terms where the Landé interval rule is in operation. In Fig. 2a a graphical representation of the Landé interval rule is shown for the $^5K_{5,6,7,8,9}$ terms mentioned above. The spin of the four valence electrons, $(\sum s = S)$ $S=2$, is space quantized with the four electrons, $(\sum l = L)$ $L=7$, giving the five whole integer values of $J=5,6,7,8$, and 9.

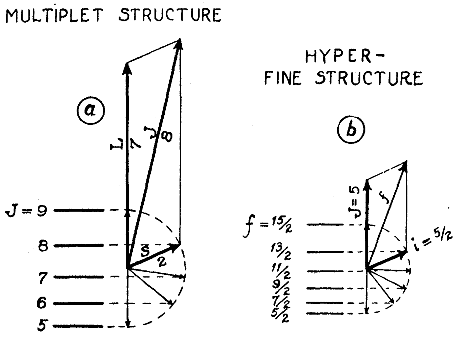

Fig. 2. The Landé interval rule.

The relative spacings between these energy levels, according to Landé, should be proportional to the cosine of the angle between S and L, a graphical representation being obtained by projecting the ends of the S vector onto the L vector when J is an integer. If now an angular momentum, $i=(5/2)$ $(h/2\pi)$ is assigned to the nucleus (kern) of praseodymium and this be allowed space quantization with the total angular momentum of the outer part of the atom, J, in such a way as to give resultant values, f, different from each other by $1h/2\pi$, then there will always result, for $J \geqq 5/2$, six values of f. This also is shown graphically in Fig. 2b for $J=5$. The resultant six fine structure levels, it is seen from the figure, should follow the Landé interval rule.[6]

The actual separation between fine structure levels depends upon the strength of coupling between the nucleus, i, and the valence electrons resultant, J. In caesium Jackson[7] has shown that the total separation of the $^2S_{1/2}(6s)$ fine structure components is about thirty times as large as the

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[5] The normal state in all line spectra, neutral or ionized, is given by the multiplet term involving the largest S and L values (in the order named), a violation of which has never been observed.

[6] The interval ratios should be proportional to the resultant quantum numbers with the smallest number omitted.

[7] Jackson, Proc. Roy. Soc. **A121**, 432 (1928).

$^2P(6p)$ fine structure components. Here in the simple case where one valence electron alone is responsible for the term, one can say that the relatively large $^2S_{1/2}$ separation is due to the extreme penetration of the *6s* electron. Because of this penetration the coupling is very strong. For the *6p* electron the penetration is less and hence the coupling is much weaker. Meggers and Burns[8] have pointed out that in most cases where hyperfine structure appears the energy levels arise from electron configurations involving one unbalanced *s* electron. For example, in La I[8] the normal state $^2D(6s^25d)$ shows no fine structure, while $^4F(6s5d^2)$ shows fine structure. In La II[8] the normal state $^3F(5d^2)$ shows no fine structure, while ^1D and $^3D(6s5d)$ show fine structure.

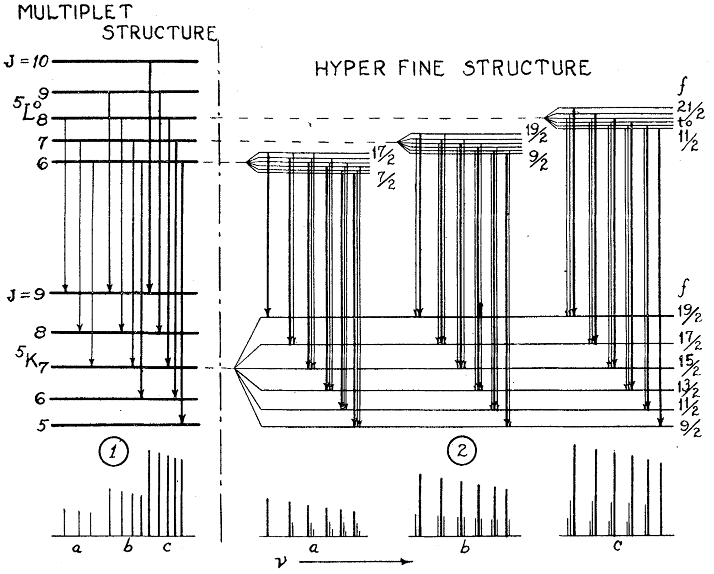

Fig. 3. Comparison of multiplet structure with fine structure.

Tentatively we can assign a low set of levels in Pr II to an electron configuration involving one *6s* electron namely: $6s5d4f^2$, and a higher set of levels involving a *6p* electron namely: $6p5d4f^2$. The 6*s* electron, for the low set of levels, being part of the time near the nucleus and part of the time outside of the atom, greatly strengthens the coupling between *i* and *J*. The *6p* electron does not penetrate so far into the atom and hence the coupling is weaker between *i* and *J*. By analogy with Cs the set of fine structure levels in Pr II involving a *6s* electron should be at least ten times as large as those involving a *6p* electron.

MULTIPLET STRUCTURE AND FINE STRUCTURE

The above reasoning leads to a comparison of multiplet structure with fine structure, Fig. 3. In Fig. 3_1 is an energy level diagram for a $^5K-^5L$

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[8] Meggers and Burns, J.O S.A. **14**, 449 (1927).

multiplet. The selection principle and intensity rule shows that such a multiplet should have five strong lines, Fig. 3_{1c}, four weaker lines, Fig. 3_{1b}, and three very weak lines, Fig. 3_{1a}. Assigning to the nucleus an angular momentum $i=(5/2)\ (h/2\pi)$ breaks each energy level of Fig. 3_1 into six fine structure levels as shown in Fig. 3_2 for $^5K_7$, $^5L_6{}^0$ $^5L_7{}^0$, and $^5L_8{}^0$. Applying again the selection principle and intensity rule for fine structure combinations, it is seen that each of the five lines Fig. 3_{1c}, enlarged some 50,000 times, should appear as Fig. 3_{2c}. Likewise each line of Fig. 3_{1b} and Fig. 3_{1a} should appear as Fig. 3_{2b} and Fig. 3_{2a} respectively.

If the above explanation of fine structure in Pr II is correct, then it is clear why the six components appear as they do in Fig. 1. Since the one set of levels is very narrow the frequency separations of the observed lines should be approximately those of the wide levels. For example the f values for $^5K_7$ are 19/2, 17/2, 15/2, 13/2, 11/2 and 9/2. By dropping the smallest numbers, as usual, the interval ratios 19:17:15:13:11 are obtained. An examination of the $\Delta\nu$'s (Table I) shows that a number of lines have very closely these interval ratios. Nearly all of the $\Delta\nu$'s given in Tables I and II show that they all come from levels having large f values and hence large J values.

Relative energy levels like those in Fig. 3 explain the origin of only those fine structure lines which are degraded toward the violet. The lines degraded toward the red may be explained by assuming a low set of levels in Pr II to have very narrow fine structure separations. By analogy with La II as indicated above, these even terms, including the normal state, should be given by $5d^24f^2$. Above this would be an odd set of terms, with wide fine structures, arising from $6s5d^24f$ and a still higher set of even terms with narrow fine structures arising from $6p5d^24f$. The high terms combine strongly with the middle terms giving fine structures degraded toward the violet. The middle terms in turn can combine with the low terms giving fine structures degraded toward the red. It is hoped that an analysis of the multiplet structure of Pr II will confirm these tentative assignments of electron configurations.

When hyperfine structure of spectral lines is to be attributed to the nucleus, then the spectra from the neutral atom, the singly ionized atom, the doubly ionized atom, etc, should all reveal the same angular momentum for the nucleus, (the same i value). This has not yet been verified for any element where fine structure has been studied. The fine structure lines arising from low terms in Pr I (using King's[2] temperature classification) are so close together that even with the enormous dispersion of 1.5A.U. per cm and a resolving power of 200,000 they appear in most cases sharp. In going to higher and higher temperatures, that is to other lines which come from higher and higher energy levels, the fine structures, although not resolved, become wider and wider until in Pr II the lines coming from all levels show definite fine structure and, wherever resolved, six components. The widest group in Pr II comes from the very highest temperature. The fine structure of Pr III, and of some of the widest lines in Pr I are now under investigation.

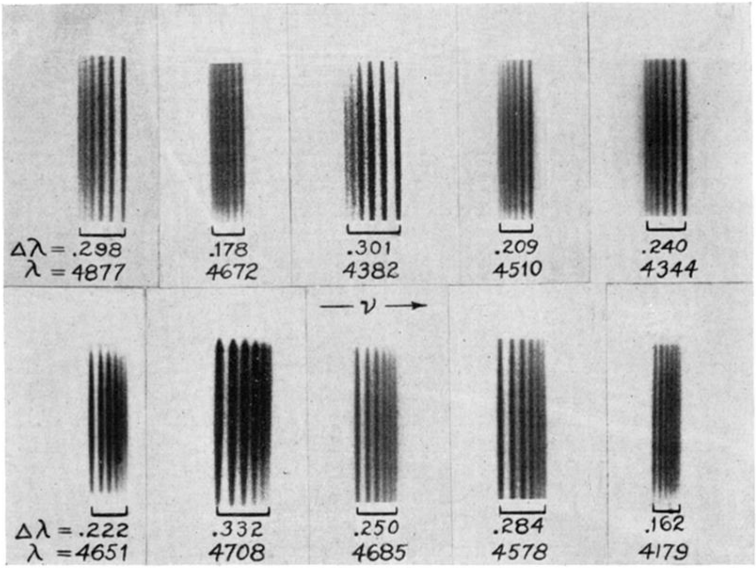

Fig. 1. Praseodymium fine structure