Structure of the Configurations of High Azimuthal Quantum Number in Cu II and the Rare Gases

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The energy levels of configurations such as d^9f, d^9g of Cu II and p^5d, p^5f of the rare gases are split into two widely separated groups by the spin-orbit interaction of the almost closed shell. These groups have the two levels of the parent doublet as limits. The splitting within these groups is due to the small electrostatic interaction between the core and the outer electron and the spin-orbit interaction of the outer electron. It is found that if one neglects all of these except the leading term in the electrostatic interaction, the theory predicts that all levels should be double, two levels of different J value having the same energy. It further predicts definitely, without unknown constants, all details of the relative arrangement of these energy levels in the two groups. In the rare-gas configurations and Cu II d^9f, the levels tend to occur in these pairs and follow this arrangement approximately but the interactions which are neglected in this picture are not entirely negligible. Knowledge of the simple limiting structure should nevertheless be of value in such cases. Cu II $3d^95g$ however fits the simple picture in all details; the levels are observed to occur in pairs with precisely the energies predicted. Thus the 20 levels of this complex configuration are represented by simpler formulas and with better agreement (0.20 cm^{-1} average discrepancy) than in any other case which has been treated theoretically.

WE were led to undertake these theoretical considerations because of the peculiar structure of Cu II $3d^95g$ in which Shenstone[1] found that the 20 levels occur in 10 pairs which he was unable to resolve. We are able to explain this pairing in detail by assuming that all interactions involving the $5g$ electron are negligible except the largest term in the electrostatic interaction with the $3d^9$ core. In this approximation the theoretical formulas assume a very simple form. The intervals between double levels having the same parent j value are all predicted in terms of one parameter so that the values of 8-interval ratios are all definitely determined. The structure of this configuration is then more definitely predicted by theory than that of any other complex configuration, and the agreement with Shenstone's data is excellent. We find that a similar approximation will help to explain the observed structure of configurations like d^9f of Cu II and p^5d and p^5f of the rare gases. The simple formulas which are obtained should be of aid in the analysis of other such configurations.

I. d^9g

The observed levels of this configuration occur in two widely separated groups, the upper of which has $d^9\,{}^2D_{3/2}$ as parent, the lower, $d^9\,{}^2D_{5/2}$. If interaction between these groups is neglected, the jj-coupling electrostatic-energy matrices of the previous paper will split up as shown by the broken lines. When we add the diagonal spin-orbit interaction, we obtain the following formulas for the energy levels.[2]

Upper group

$$6c = -F_0+\tfrac{3}{2}\zeta_d-\tfrac{196}{5}F_2+396G_6+2\zeta_g$$

$$\left.\begin{matrix}5c'\\5d'\end{matrix}\right\} = -F_0+\tfrac{3}{2}\zeta_d+\tfrac{147}{10}F_2-\tfrac{1}{4}\zeta_g\pm\tfrac{1}{2}\left[\left(\tfrac{151}{15}F_2+\tfrac{9}{2}\zeta_g\right)^2+8\left(\tfrac{196}{15}F_2\right)^2\right]^{\frac{1}{2}}$$

$$\left.\begin{matrix}4c'\\4d'\end{matrix}\right\} = -F_0+\tfrac{3}{2}\zeta_d+\tfrac{497}{10}F_2+616G_4-\tfrac{1}{4}\zeta_g\pm\tfrac{1}{2}\left[\left(\tfrac{511}{15}F_2+\tfrac{2464}{9}G_4-\tfrac{9}{2}\zeta_g\right)^2+308\left(\tfrac{14}{15}F_2-\tfrac{616}{9}G_4\right)^2\right]^{\frac{1}{2}}$$

$$\left.\begin{matrix}3c'\\3d'\end{matrix}\right\} = -F_0+\tfrac{3}{2}\zeta_d-\tfrac{231}{10}F_2-\tfrac{1}{4}\zeta_g\pm\tfrac{1}{2}\left[\left(\tfrac{1463}{15}F_2-\tfrac{9}{2}\zeta_g\right)^2+20\left(\tfrac{154}{15}F_2\right)^2\right]^{\frac{1}{2}}$$

$$2d = -F_0+\tfrac{3}{2}\zeta_d-77F_2+\tfrac{504}{5}G_2-\tfrac{5}{2}\zeta_g$$

[1] Shenstone, Trans. Roy. Soc. **A235**, 195 (1936). All the Cu II data are taken from this comprehensive analysis.
[2] This treatment is similar to that previously given for the rare gases: Shortley, Phys. Rev. **44**, 666 (1933); Condon and Shortley, *Theory of Atomic Spectra*, pp. 306–315.

Lower group

$$7a = -F_0 - \zeta_d - 56F_2 - 14F_4 + 2\zeta_g$$

$$\left.\begin{matrix}6a'\\6b'\end{matrix}\right\} = -F_0 - \zeta_d - \tfrac{7}{5}F_2 + {}^{63}\!/_{2}F_4 + 297G_6 - \tfrac{1}{4}\zeta_g \pm \tfrac{1}{2}[({}^{1498}\!/_{15}F_2 + {}^{749}\!/_{9}F_4 - 286G_6 + {}^{9}\!/_{2}\zeta_g)^2 + 140({}^{56}\!/_{15}F_2 + {}^{28}\!/_{9}F_4 - 44G_6)^2]^{\frac{1}{2}}$$

$$\left.\begin{matrix}5a'\\5b'\end{matrix}\right\} = -F_0 - \zeta_d + {}^{299}\!/_{5}F_2 - {}^{63}\!/_{2}F_4 - \tfrac{1}{4}\zeta_g \pm \tfrac{1}{2}[({}^{1663}\!/_{15}F_2 - {}^{1660}\!/_{9}F_4 + {}^{9}\!/_{2}\zeta_g)^2 + 728({}^{4}\!/_{15}F_2 - {}^{40}\!/_{9}F_4)^2]^{\frac{1}{2}}$$

$$\left.\begin{matrix}4a'\\4b'\end{matrix}\right\} = -F_0 - \zeta_d + {}^{224}\!/_{5}F_2 - {}^{91}\!/_{2}F_4 + 924G_4 - \tfrac{1}{4}\zeta_g \pm \tfrac{1}{2}[({}^{504}\!/_{15}F_2 - {}^{1365}\!/_{9}F_4 - 616G_4 - {}^{9}\!/_{2}\zeta_g)^2 + 8({}^{144}\!/_{15}F_2 - {}^{390}\!/_{9}F_4 + 616G_4)^2]^{\frac{1}{2}}$$

$$\left.\begin{matrix}3a'\\3b'\end{matrix}\right\} = -F_0 - \zeta_d - {}^{52}\!/_{5}F_2 + {}^{195}\!/_{2}F_4 - \tfrac{1}{4}\zeta_g \pm \tfrac{1}{2}[(-{}^{752}\!/_{15}F_2 + {}^{611}\!/_{9}F_4 + {}^{9}\!/_{2}\zeta_g)^2 + 440({}^{32}\!/_{15}F_2 - {}^{26}\!/_{9}F_4)^2]^{\frac{1}{2}}$$

$$\left.\begin{matrix}2a'\\2b'\end{matrix}\right\} = -F_0 - \zeta_d - 77F_2 + {}^{378}\!/_{5}G_2 - \tfrac{1}{4}\zeta_g \pm \tfrac{1}{2}[({}^{770}\!/_{15}F_2 + {}^{2002}\!/_{9}F_4 - {}^{644}\!/_{5}G_2 - {}^{9}\!/_{2}\zeta_g)^2 + 8({}^{220}\!/_{15}F_2 + {}^{572}\!/_{9}F_4 + 28G_2)^2]^{\frac{1}{2}}$$

$$1b = -F_0 - \zeta_d - 110F_2 - 143F_4 - {}^{5}\!/_{2}\zeta_g.$$

Here F_0 is a constant which fixes the position of the configuration as a whole. ζ_d represents the spin-orbit integral for the d electrons: the configuration is split into two groups of levels with $^2D_{3/2}$ and $^2D_{5/2}$ as limits according to whether this integral occurs with coefficient $+{}^{3}\!/_{2}$ or -1; ${}^{5}\!/_{2}\zeta_d$ is the doublet splitting of the d^9 ion. Structure is given to the two groups by the smaller electrostatic integrals F_2, F_4, G_2, G_4, G_6, and the g-electron spin-orbit integral ζ_g. In the level designations, the number gives the J value, the letters a' and b' denote the higher and lower of two lower-group levels of the same J value, the letters c' and d' the higher and lower of two upper-group levels of the same J value.

In the case of Cu II $3d^95g$, the only d^9g which has been analyzed, if we follow the procedure previously used in the rare gases[2] and determine the eight integrals from the twelve linear equations expressing the energy of $7a$, the means of $6a'$ and $6b'$, of $5a'$ and $5b'$, etc., and then calculate the splitting of the levels of the same J by evaluating the radicals with these parameters, we get remarkably good agreement with observation. The parameter values obtained in this way are: $\zeta_d=828.59$, $F_2=0.3154$, $F_4=0.0027$, $G_2=0.0015$, $G_4=0.00004$, $G_6=0.0001$, $\zeta_g=0.028$ cm^{-1}. The contributions of F_4, G_2, G_4, G_6, ζ_g here are of the order of magnitude of the disagreement with experiment and of the expected error due to neglect of interaction between parents. The change in calculated values caused by setting these five integrals equal to zero is not significant. Furthermore, the levels are observed to occur in unresolved pairs, and neglect of these small parameters is just what gives this doubling.

If in the above formulas we retain only the parameters F_0, to represent the absolute position of the configuration in the energy scheme, ζ_d, to give the parent-doublet splitting, and the one integral F_2 to give structure to the groups, we find the levels to occur in pairs with energies given by the following simple formulas:

	Cu II $3d^95g$		
Upper group	Obs.	Calc.	Error
$6c,\ 5d' = -F_0 + {}^{3}\!/_{2}\zeta_d - {}^{1965}\!/_{5}F_2$	2094.43	2094.34	−0.09
$5c',\ 4c' = -F_0 + {}^{3}\!/_{2}\zeta_d + {}^{3435}\!/_{5}F_2$	2127.96	2128.31	0.35
$4d',\ 3c' = -F_0 + {}^{3}\!/_{2}\zeta_d + {}^{1545}\!/_{5}F_2$	2116.43	2116.40	−0.03
$3d',\ 2d = -F_0 + {}^{3}\!/_{2}\zeta_d - 77F_2$	2082.65	2082.42	−0.23
Lower group			
$7a,\ 6b' = -F_0 - \zeta_d - 56F_2$	17.67	17.57	−0.10
$6a',\ 5a' = -F_0 - \zeta_d + {}^{265}\!/_{5}F_2$	52.08	51.98	−0.10
$5b',\ 4a' = -F_0 - \zeta_d + {}^{335}\!/_{5}F_2$	55.99	56.14	0.15
$4b',\ 3a' = -F_0 - \zeta_d + {}^{1165}\!/_{5}F_2$	42.77	42.53	−0.24
$3b',\ 2a' = -F_0 - \zeta_d - 44F_2$	21.61	21.35	−0.26
$2b',\ 1b = -F_0 - \zeta_d - 110F_2$	0.	0.55	0.55

($F_0=-863.806$; $F_2=0.31515$; $\zeta_d=828.590$ cm^{-1})

When the observed Cu II levels are fitted to these formulas by least squares, the above parameters and computed levels are obtained. The levels are plotted in Fig. 1. These extremely simple formulas are seen to represent remarkably well the positions of the twenty levels of this configuration. The configuration is one of the most complex which has been completely analyzed, yet the formulas which represent its structure are simpler and the agreement better than in any other case which has been treated theoretically.

The two levels of a pair are, of course, not rigorously coincident, but Shenstone estimates his resolution as such that the separation of the two apparently coincident levels of different J

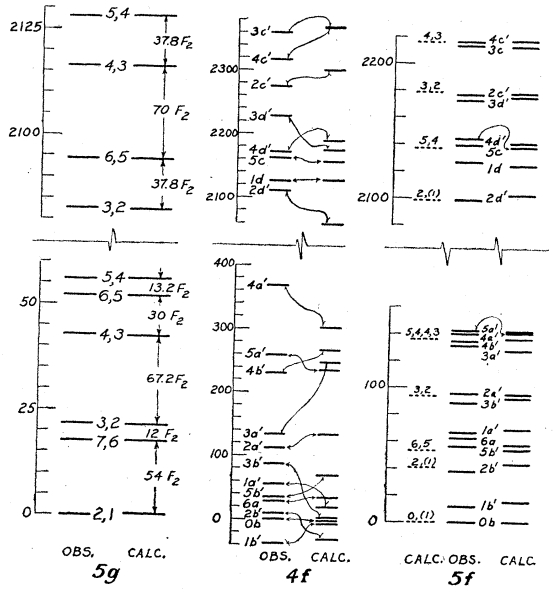

FIG. 1. Configurations $3d^95g$, $3d^94f$, and $3d^95f$ of Cu II. The broken lines in the $5f$ configuration show the arrangement of the levels when all parameters except F_2 are neglected; in this case the levels coincide in pairs and the relative positions are completely predicted, as in the $5g$ case above.

value must be considerably less than $\frac{1}{2}$ cm^{-1} in all cases.

To the approximation in which the above simple formulas hold, the eigenfunctions of the states are independent of the parameter values. The eigenfunctions of the actual (primed) levels are given in terms of the jj-coupling eigen-

TABLE I. *Eigenfunctions of d^9g levels.*

	$6a'\,6b'$		$5a'\,5b'$		$5c'\,5d'$		$4a'\,4b'$	
$6a$	$4\sqrt{7}\ -\sqrt{5}$	$\frac{1}{\sqrt{117}}$	$5a$ $4\ \sqrt{182}$	$\frac{1}{3\sqrt{22}}$	$5c$ $4\sqrt{2}\ -1$	$\frac{1}{\sqrt{33}}$	$4a$ $1\ 2\sqrt{2}$	$\frac{1}{3}$
$6b$	$\sqrt{5}\ 4\sqrt{7}$		$5b$ $-\sqrt{182}\ 4$		$5d$ $1\ 4\sqrt{2}$		$4b$ $-2\sqrt{2}\ 1$	
	$4c'\,4d'$		$3a'\,3b'$		$3c'\,3d'$		$2a'\,2b'$	
$4c$	$2\ \sqrt{77}$	$\frac{1}{9}$	$3a$ $4\ \sqrt{110}$	$\frac{1}{\sqrt{126}}$	$3c$ $1\ 2\sqrt{5}$	$\frac{1}{\sqrt{21}}$	$2a$ $1\ 2\sqrt{2}$	$\frac{1}{3}$
$4d$	$-\sqrt{77}\ 2$		$3b$ $-\sqrt{110}\ 4$		$3d$ $-2\sqrt{5}\ 1$		$2b$ $-2\sqrt{2}\ 1$	

functions by the transformation matrices of Table I. These matrices enable us to determine by means of second-order perturbation theory the amount of the electrostatic interaction between the levels of the upper and lower group, which has been neglected so far. The results here are remarkable in that this second-order interaction does not tend to split the pairs, so long as F_2 is the only significant term. $7a$, $6b'$ and $2b'$, $1b$ are not shifted at all. $6c$ interacts only with $6a'$, $5d'$ only with $5a'$, and the amount of interaction is exactly the same in these two cases. Similarly the pair $5c'$, $4c'$ interacts as a unit with $5b'$, $4a'$; the pair $4d'$, $3c'$ with $4b'$, $3a'$; and the pair $3d'$, $2d$ with $3b'$, $2a'$. In our particular case the maximum shift caused by this second-order interaction is 0.10 cm^{-1}, which is not significant.

II. d^9f

The formulas for the energy levels of d^9f, interaction between parents being neglected, are

Upper levels

$$5c = -F_0+\tfrac{3}{2}\zeta_d-\ 7F_2+\ 168G_5+\tfrac{3}{2}\zeta_f$$

$$\left.\begin{matrix}4c'\\4d'\end{matrix}\right\} = -F_0+\tfrac{3}{2}\zeta_d+\ \tfrac{7}{2}F_2\ -\tfrac{1}{4}\zeta_f\pm[(1\tfrac{9}{2}F_2+\tfrac{7}{4}\zeta_f)^2+20F_2^2]^{\frac{1}{2}}$$

$$\left.\begin{matrix}3c'\\3d'\end{matrix}\right\} = -F_0+\tfrac{3}{2}\zeta_d+9\tfrac{1}{10}F_2+\ 24G_3-\tfrac{1}{4}\zeta_f\pm[(4\tfrac{1}{10}F_2+4\tfrac{8}{7}G_3-\tfrac{7}{4}\zeta_f)^2+180(\tfrac{1}{5}F_2-1\tfrac{2}{7}G_3)^2]^{\frac{1}{2}}$$

$$\left.\begin{matrix}2c'\\2d'\end{matrix}\right\} = -F_0+\tfrac{3}{2}\zeta_d-6\tfrac{3}{10}F_2\ -\tfrac{1}{4}\zeta_f\pm[(8\tfrac{7}{10}F_2-\tfrac{7}{4}\zeta_f)^2+86\tfrac{4}{25}F_2^2]^{\frac{1}{2}}$$

$$1d = -F_0+\tfrac{3}{2}\zeta_d-\ 8\tfrac{4}{5}F_2+\ 28G_1-\ 2\zeta_f$$

Lower levels

$$6a = -F_0-\ \zeta_d-\ 10F_2-\ 3F_4\ +\tfrac{3}{2}\zeta_f$$

$$\left.\begin{matrix}5a'\\5b'\end{matrix}\right\} = -F_0-\ \zeta_d+\ F_2+\ 8F_4+\ 126G_5-\tfrac{1}{4}\zeta_f\pm[(6\tfrac{7}{7}F_2+6\tfrac{7}{7}F_4-54G_5+\tfrac{7}{4}\zeta_f)^2+1440(\tfrac{1}{7}F_2+\tfrac{1}{7}F_4-3G_5)^2]^{\frac{1}{2}}$$

$$\left.\begin{matrix}4a'\\4b'\end{matrix}\right\} = -F_0-\ \zeta_d+\ 12F_2-2\tfrac{5}{2}F_4\ -\tfrac{1}{4}\zeta_f\pm[(4\tfrac{7}{2}F_4-\tfrac{7}{4}\zeta_f)^2+440F_4^2]^{\frac{1}{2}}$$

$$\left.\begin{matrix}3a'\\3b'\end{matrix}\right\} = -F_0-\ \zeta_d+\ 3\tfrac{2}{5}F_2-1\tfrac{1}{2}F_4+\ 36G_3-\tfrac{1}{4}\zeta_f\pm[(12\tfrac{4}{35}F_2-34\tfrac{1}{14}F_4-10\tfrac{8}{7}G_3-\tfrac{7}{4}\zeta_f)^2$$
$$+36\tfrac{0}{49}(\tfrac{8}{5}F_2-11F_4+12G_3)^2]^{\frac{1}{2}}$$

$$\left.\begin{matrix}2a'\\2b'\end{matrix}\right\} = -F_0-\ \zeta_d-\ 3\tfrac{1}{5}F_2+\ 33F_4\ -\tfrac{1}{4}\zeta_f\pm[(1\tfrac{9}{5}F_2-\tfrac{7}{4}\zeta_f)^2+86\tfrac{4}{25}F_2^2]^{\frac{1}{2}}$$

$$\left.\begin{matrix}1a'\\1b'\end{matrix}\right\} = -F_0-\ \zeta_d-\ 9\tfrac{3}{5}F_2-3\tfrac{3}{2}F_4+\ 21G_1-\tfrac{1}{4}\zeta_f\pm[(9\tfrac{9}{35}F_2+36\tfrac{3}{14}F_4-19G_1-\tfrac{7}{4}\zeta_f)^2+80(1\tfrac{8}{35}F_2+3\tfrac{3}{7}F_4+G_1)^2]^{\frac{1}{2}}$$

$$0b = -F_0-\ \zeta_d-\ 24F_2-\ 66F_4\ -\ 2\zeta_f.$$

TABLE II. $3d^9nf$ *parameter values.*

	$4f$	$5f$
F_0	-984.7 cm^{-1}	-921.9 cm^{-1}
F_2	10.1	3.81
F_4	-1.09	-0.013
G_1	1.27	0.949
G_3	-2.65	-0.214
G_5	0.011	0.0046
ζ_d	837.4	828.4
ζ_f	-10.4	1.508

If the eight parameters are determined from the twelve linear equations which give the means of levels of the same J value and same parent, and then used to calculate the values of the radicals, one obtains for Cu II $3d^94f$ and $3d^95f$ the parameter values of Table II and the calculated energies which are plotted in Fig. 1. It will be noted that the predicted $5f$ levels are quite good but that the $4f$ levels are badly off. The poor agreement in the case of $4f$ is due to a large interaction of $3d^94f$ and the completely overlapping configuration $3d^84s4p$ which is neglected in the present theory, but which manifests itself experimentally[1] by strong forbidden combinations of the type d^8sp-d^9g, $d^9f-d^8s^2$, d^9f-d^9s. The value of ζ_d for $3d^95f$ agrees with the value 828.6 previously found in d^9g and with the value 828 obtained from the Cu III doublet splitting. The maximum interaction which occurs between the upper and the lower group of $5f$ is found to be of the order of 0.54 cm^{-1}, which is not significant.

In this configuration also, if one neglects all integrals except F_0, ζ_d, and F_2, one obtains simple formulas which give the levels in pairs:

Upper levels

$$\begin{aligned} 5c,\ 4d' &= -F_0+\tfrac{3}{2}\zeta_d- \tfrac{7}{7}F_2 \\ 4c',\ 3c' &= -F_0+\tfrac{3}{2}\zeta_d+ \tfrac{14}{7}F_2 \\ 3d',\ 2c' &= -F_0+\tfrac{3}{2}\zeta_d+2\tfrac{1}{7}F_2 \\ 2d',\ 1d &= -F_0+\tfrac{3}{2}\zeta_d-8\tfrac{4}{7}F_2 \end{aligned}$$

Lower levels

$$\begin{aligned} 6a,\ 5b' &= -F_0- \zeta_d- 10F_2 \\ 5a,\ 4a',\ 4b',\ 3a' &= -F_0- \zeta_d+ 12F_2 \\ 3b',\ 2a' &= -F_0- \zeta_d+ \tfrac{4}{5}F_2 \\ 2b',\ 1a' &= -F_0- \zeta_d-6\tfrac{6}{5}F_2 \\ 1b',\ 0b &= -F_0- \zeta_d- 24F_2. \end{aligned}$$

This tendency toward occurring in pairs is noted in the observed $5f$ of Fig. 1. The largest splitting of the pairs occurs in the case of levels with $J=1$, which is to be expected since G_1, the largest of the neglected parameters, is not particularly small compared to F_2; but G_1 occurs only in the formulas for $J=1$. However these simple formulas give a useful qualitative picture of the location of the levels, as may be seen from the broken lines of Fig. 1, which show the arrangement of energy levels which they give with $F_2=3.79$ cm^{-1}. Levels of $J=1$ were not considered in determining this F_2 value.

III. p^5d

In the configurations p^5p, p^5d, p^5f of the rare gases one obtains a similar doubling of all energy levels if one neglects all the small interaction terms except F_2. The occurrence of this doubling is especially striking in the Ne $2p^5nd$ configurations of high n value. The reduced p^5d formulas[3] are

Upper levels

$$3c,\ 2c,\ 2d,\ 1d = -F_0+ \zeta_p$$

Lower levels

$$\begin{aligned} 4a,\ 3b' &= -F_0-\tfrac{1}{2}\zeta_p-2F_2 \\ 3a',\ 2a' &= -F_0-\tfrac{1}{2}\zeta_p+5F_2 \\ 2b',\ 1a' &= -F_0-\tfrac{1}{2}\zeta_p \\ 1b',\ 0b &= -F_0-\tfrac{1}{2}\zeta_p-7F_2. \end{aligned}$$

In the neon case the largest G coefficient, G_1, is of size comparable to F_2; this coefficient occurs only in states of $J=1$, hence the observed levels[4] are arranged very closely as in the above formulas except for those of $J=1$. The near coincidence of $3c$, $2c$, $2d$; of $4a$, $3b'$; and of $3a'$, $2a'$ is conspicuous from $4d$ to $10d$, and the arrangement of all levels of $J\neq1$ follows closely the above formulas. By determining F_2 from these levels by the above formulas and then including G_1, we may place the three $J=1$ levels satisfactorily. This method should prove of use in locating the missing levels of the argon p^5d configurations, only one of which is complete.

IV. p^5f

The formulas which are obtained for p^5f when ζ_f, G_2, G_4 are neglected are:

Upper levels

$$4c,\ 3c,\ 3d,\ 2d = -F_0+ \zeta_p$$

Lower levels

$$\begin{aligned} 5a,\ 4b' &= -F_0-\tfrac{1}{2}\zeta_p- 5F_2 \\ 4a',\ 3a' &= -F_0-\tfrac{1}{2}\zeta_p+10F_2 \\ 3b',\ 2a' &= -F_0-\tfrac{1}{2}\zeta_p+ 3F_2 \\ 2b',\ 1b &= -F_0-\tfrac{1}{2}\zeta_p-12F_2. \end{aligned}$$

The only observations of p^5f are on argon, where there are sketchy data for a number of

[3] The complete formulas are in reference 2.
[4] See the plots given in reference 2.

these configurations. At most five of the twelve levels are observed, and not even the J values of these are certain.[5] It may be that the above formulas can be of use in interpreting these observations. Perhaps the five observed levels, four lower and one upper, are at the positions of the five collapsed levels given by these formulas. On the other hand, the $J=2$ levels may be displaced from these positions because of a non-negligible G_2 value. One would not expect G_4 and ζ_f to be large enough to give significant departures for the levels of other J values. If we attempt to fit the four lower observed levels by means of the above formulas we obtain the results of Fig. 2. The level W which is observed to have the J value 4 or 3 may well be a double 4 and 3 level. The level Y is observed to be 1 or 2. No $J=1$ is expected in this vicinity so this is probably $J=2$, with a $J=3$ nearby. The level U is observed as 4 or 3. It is probably 4 with a $J=5$ nearby. The level X is definitely observed as $J=1$. A level of $J=2$ should be near. The single observed *upper* level is listed as $J=1$ or 2. It cannot be $J=1$ since there is no level in the upper group with $J=1$. This upper level is observed only for $4f$, $5f$, and $6f$. Fig. 2 indicates fairly large perturbations of these two configurations which are expected since the lower group of $5f$ is overlapped by $6p$ and the upper group of $5f$ is close to the lower of $6f$. Nevertheless, the ζ_p values obtained from the position of the upper $J=2$ level according to the above formulas—955.0 cm^{-1} for both $5f$ and $6f$—agree well with the value 954 from the A II ^2P splitting. For $2p^54f$ only X, Y, and the upper $J=2$ are observed. The ζ_p value calculated from the above formulas for these is 955.24 cm^{-1}, which checks in this case also the interpretation which we have given.

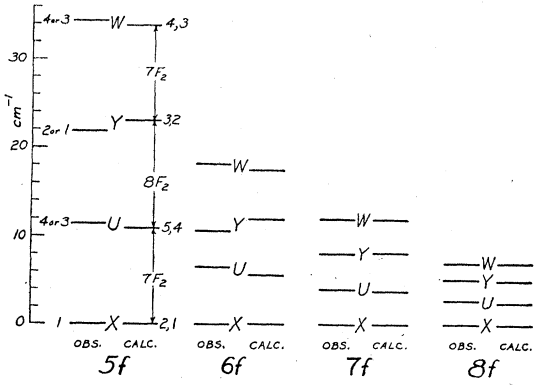

FIG. 2. Argon I $3p^5(^2P_{3/2})nf$.

[5] See Bacher and Goudsmit, *Atomic Energy States*, p. 28.

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The Contact Difference of Potential Between Barium and Magnesium

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With the purpose of subjecting the electronic method of contact potential measurement to a thorough test for consistency with independent photoelectric work function determinations, the Volta potential Ba-Mg has been measured for some 30 pairs of surfaces and the results compared with recent careful photoelectric studies of these metals. Each surface was prepared by fractionally distilling the metal in a gettered vacuum and revaporizing a middle fraction to form a thick film on glass at room temperature. Each film was measured a few seconds after deposition and tubes of two different designs used to minimize the possibility of errors originating in tube geometry. The majority of the observed Volta potentials fell within the range of values predicted by the photoelectric data, 1.08–1.16 v, and no values below this range were found. The magnesium films were largely responsible for variations in the Volta potential and a few gave potential settings sufficiently low (work functions sufficiently high) to raise the observed Volta potentials to a maximum of 1.26 v. Since all probable contaminations should lower the work function the maximum value is regarded as the most reliable. Assuming a work function of 2.52 ev for Ba this gives 3.78 ev for the work function of Mg. Observations on the optical reflection of the magnesium surfaces suggest, however, that a work function of 3.65 ± 0.05 ev may be characteristic of mirror-like surfaces of the metal; 3.78 ev of macrocrystalline (matte) surfaces.

IN recent photoelectric determinations of the work functions of barium by Jamison and Cashman[1] and of magnesium by Cashman and

[1] Jamison and Cashman, Phys. Rev. **50**, 624 (1936).