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THE SPECTRA OF CADMIUM

by

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ABSTRACT

In order to facilitate a later determination (which, incidentally, will involve the study of hyperfine structure) of various nuclear properties of Cadmium, a preliminary survey, both experimental and theoretical, has been undertaken of the gross spectral structure of that element.

A light source, consisting of an electrodeless discharge in which the excitation of the various spectra could be varied in some degree, was constructed and conditioned. The illumination from this source was then photographed with the aid of a Hilger EI Quartz Spectrograph; exposures were taken of the regions $6800\text{\AA} - 3300\text{\AA}$, $3300\text{\AA} - 2500\text{\AA}$, and $2500\text{\AA} - 2000\text{\AA}$. The positions of the spectral lines appearing on the plates were measured with the aid of a Hilger comparator, and the wavelengths were then calculated by means of the Standard Hartmann dispersion formula. About 150 Cadmium lines which had already been listed by previous workers were identified; 21 other lines - apparently new ones, since to the writer's knowledge they have not as yet been mentioned in the literature - also were found. These latter lines were concentrated in the region $6000\text{\AA} - 3900\text{\AA}$.

Theory reveals that the hyperfine structure of Cadmium II should be of greater value in the above-mentioned determination than that of the arc spectrum. Therefore a study of an

isoelectronic sequence involving Cadmium II was carried out with an eye to increasing the knowledge of this first spark spectrum's term structure. The validity of the various optical doublet laws has been tested for such an exemplary isoelectronic sequence.

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THE SPECTRA OF CADMIUM

I INTRODUCTION

Utilization of results obtained from researches in spectroscopy has been instrumental in the formulation of the atomic theory of matter, and indeed has contributed much to our knowledge of the atom itself. Through the study of the so-called spectral fine-structure, science has learned a multitude of facts about the outer part of the atom, i.e. about the arrangements and motions of the planetary electrons. This information has in turn been invaluable for an understanding of the periodic table.

Such a contribution however, great as it is, has by no means exhausted the usefulness of spectroscopic work. Given more modern equipment, possessing such advantages as very great resolving power and dispersion, the spectroscopist has in many cases been able to resolve the fine-structure into even more delicate hyperfine patterns. This new discovery has lead to an increase in the knowledge (which is still far from complete) of the main constituent of the atom, the nucleus; because, to account for the various rules pertaining to the formation of hyperfine structure, and for the exceptions to these rules, theoreticians have been lead to postulate such nuclear properties as a mechanical moment, a magnetic moment, and even an electric quadrupole effect. Since the advantages of the relatively easily excited hyperfine spectra usually far outweigh such disadvantages as pattern

complexity and smallness of component separation, spectral analysis has accounted for the major part of the information presently available about such nuclear properties.

A firm basis for the study of those hyperfine states best suited for the determination of nuclear characteristics demands a sound knowledge of the spectral gross structure of the element concerned. It is to satisfy such a need that the following study, both experimental and theoretical, of the pertinent element (Cadmium) has been undertaken.

II. SUMMARY OF PREVIOUS WORK

A. THE SPECTRA OF CADMIUM.

The first exhaustive classification of wave-lengths in the arc spectrum of Cadmium was made by Paschen ¹. His results have since been supplemented by those of Fowler ² and Ruark ³.

The most important analyses of the visible and near-ultra^{-violet} regions of the first spark spectrum have been made by von Salis⁴, Takahashi⁵, and Lang⁶. The extreme ultra-violet lines have been studied by the brothers Bloch⁷.

Earlier work on the spectrum of Cadmium III consisted mainly of the classification of several multiplets by Gibbs and White⁸, and, independently, by McLennan, McLay and Crawford⁹.

1 Paschen, F., Ann.d.Phys., 30, 746 : 1909.
Paschen, F., Ann.d.Phys., 35 860 : 1911.

2 Fowler, A., Report on Series in Line Spectra, Fleetway Press, 1922.

3 Ruark, A.E., Jour.Opt.Soc.Am., 11, 199: 1925.

4 von Salis, G., Ann.d.Phys., 76, 145: 1925.

5 Takahashi, Y., Ann.d.Phys., 3, 42: 1929.

6 Lang, R.J., Proc.Nat.Acad.Sci., 15, 414: 1929.

7 Bloch, L.and E., Ann.de Phys., 5, 325: 1936.

8 Gibbs, R.C., and H.E.White, Phys.Rev., 31, 776: 1928.

9 McLennan, J.C., A.B.McLay, and M.F.Crawford, Trans. Roy.Soc.Can., 22, 45:1928.

Recent research on the extreme-ultra violet has been conducted by Mazumder¹⁰.

Wave-lengths in the Cadmium IV spectrum have been given by Esclangan¹¹ and by the later work of Green¹².

Theoretical calculations, resulting in formulae for doublet and triplet separations, screening constants, quantum defects, and the like, have been made largely by Fues¹³, Landé¹⁴, Turner¹⁵, Sigiura¹⁶, Unsöld¹⁷ and Badami¹⁸.

B. The Hyperfine Structure of Cadmium.

The very considerable work done on the hyperfine structure of Cadmium is highlighted by the early paper of Schüller

-
- 10 Mazumder, K.C., Ind.Jour.Phys., 17, 229: 1943.
 - 11 Esclangan, F., Jour.de Phys.et radium, 7, 52: 1926.
 - 12 Green, M., Phys. Rev., 60, 117: 1941.
 - 13 Fues, E., Ann.d.Phys., 63, 1: 1920.
 - 14 Landé, A., Zeits. f.Phys., 25, 46: 1924.
 - 15 Turner, L.A., Phil. Mag., 48, 384: 1924.
 - 16 Sigiura, Y., Jap.Jour.Phys., 3, 155: 1924.
 - 17 Unsöld, A., Zeits. f.Phys., 36, 92: 1926.
 - 18 Badami, E., Proc.Phys.Soc., 43, 538: 1931.

and Brück¹⁹. These investigators found, by a study of the triplet arising from the transition $2\ ^3S_1 \rightarrow 2\ ^3P_{0,1,2}$, that the two odd isotopes - 111 and 113 - possess a nuclear "spin" I of $1/2$, while the four even isotopes - 110, 112, 114, 116 - have $I = 0$.

Isotope displacement in Cadmium II has been studied by Schüler and Westmeyer²⁰. Jones²¹ has shown that 12 out of 13 lines of Cadmium II he examined possessed no structure; the thirteenth, however, revealed the ground term, 2S , as double, which fact yielded an average value of -63 nuclear magnetons for the magnetic moment μ_I of the odd isotopes of Cadmium.

The hyperfine structure has also been studied by Albright²², while abnormal intensities in the structure have been examined by Schüler and Keyston²³.

Apparently there has not as yet been discovered, in the hyperfine structure of Cadmium, that type of deviation from the interval rule which would lead one to postulate the existence of a nuclear electric quadrupole moment.

19 Schüler, H., and H.Brück, Zeits.f.Phys.56,291: 1929.

20 Schüler, H., and H.Westmeyer, Zeits.f.Phys., 82, 685:1933.

21 Jones, E.G., Proc.Phys.Soc., 45, 625: 1933.

22 Albright, C.L., Phys. Rev., 36, 847: 1930.

23 Schüler, H., and J.E.Keyston, Zeits.f.Phys., 71, 413: 1931.

Attention is here drawn to a very complete bibliography, that of R.C.Gibbs²⁴, which thoroughly covers the earlier work (of the period 1920-31) in the fields summarized in the above sections.

²⁴ Gibbs, R.C., Rev.Mod.Phys., 4, 278: 1932.

III THEORY

A. Fine-Structure of Spectral Lines.

In their classifications of simple spectra, early workers relied almost wholly upon the discovery of series of lines. Such series were found to have the same general appearance as the series of hydrogen; the lines both became less intense on, and converged to limits on, the short wavelength side of the spectrum. Any series of hydrogen can be found by means of the formula

$$\tilde{\nu} = \frac{T_{\infty}}{n^2} - \frac{R}{n^2} \quad (1)$$

where T_{∞} is the wave-number of the particular series limit.

It was shown soon afterwards that this formula might be generalized for series of other "hydrogen-like" atoms by the expression

$$\tilde{\nu} = \frac{T_{\infty}}{M^2} - \frac{R}{(M + a)^2} \quad (2)$$

where a is a constant characteristic of the relevant series and M runs through a sequence of integral values. In both the above formulae, R represents the so-called Rydberg constant. These results, empirical in nature, showed conclusively that spectral lines must be produced by radiative transitions between stationary states of an atom.

The first successful attempts to explain the existence of the above series were made by Bohr²⁵ and Sommerfeld²⁶, who applied the earlier quantum theory to the hydrogen and hydrogen-like atoms. The work involved the hypothesis, which was found to be correct to a first approximation, that the total-energy levels of an atom can be completely described by the valence electron's orbital angular momentum. In the later stages of the work, this momentum was "quantized" to possess only integral multiples of \hbar , i.e., $k\hbar$, with k integral. (Subsequent theoretical developments have made it desirable to replace k by ℓ , where $\ell = k - 1$). Possible transitions between the energy levels were found to be given by the selection rule $\Delta k = \pm 1$.

The above mentioned theory does not, however, account for the well-known fact that many of the lines resulting from such transitions are found in reality to consist of two or more components. To account generally for this so-called "fine-structure", Goudsmit and Uhlenbeck²⁷ suggested that each electron in the atom be supposed to spin, and thus to possess a spin angular momentum, given in magnitude by $\frac{1}{2} \hbar$. Now, since a

25 Bohr, N., Phil.Mag., 26, 1, 476, 857: 1913.

26 Sommerfeld, A., Ann. d.Phys., 51, 1: 1916.

27 Uhlenbeck, G.E., and S.A.Goudsmit, Naturwissenschaften, 13, 953: 1925.

spinning electric charge gives rise to a magnetic field, and since an orbital motion of a charge is equivalent to a current with a resulting magnetic field, the spin and orbital angular momenta will combine because of the interaction of these two fields.

Consider first the general case of an atom containing several valence electrons. (The spin moment \vec{s} of each electron can be combined vectorially to form a resultant spin moment \vec{S} . A similar combination of the orbital angular momenta, each denoted by \vec{l} , gives \vec{L} . The resultant angular momentum as a whole is then in turn given vectorially by $\vec{L} + \vec{S}$ and is represented by \vec{J} . (The type of electronic interaction permitting such combinations is termed L - S, or Russell-Saunders, coupling).²⁸ To bring the results of such a vectorial treatment into accord with those of the more recent, i.e. quantum-mechanical, calculations, the magnitudes of the vectors \vec{J} , \vec{L} and \vec{S} are given by $\sqrt{J(J+1)} \hbar$, $\sqrt{L(L+1)} \hbar$, and $\sqrt{S(S+1)} \hbar$ respectively. The values that L can assume are integral, and those of S are integral, half-integral or zero. The values of J, which are integral or half-integral, are determined by the quantum-mechanical condition

²⁸ Russell, H.N., and F.A.Saunders, *Astrophys. Jour.*, 61, 38: 1925.

$$|(L + S)| \geq J \geq |(L - S)| \quad (3)$$

where the intermediate quantities - between the terminal ones shown - differ by unity. (Thus there exists $2L + 1$ possible values for J if $L < S$, and $2S + 1$ possible ones if $L > S$.) Each J , being the result of a different orientation of the quantum vectors \vec{L} and \vec{S} , corresponds to a different energy state of the atom in question. When the concept of electron spin is considered, therefore, it is found that transitions between levels characterized by different J (and L) give rise to the ordinary fine-structure multiplets. The two selections rules which determine such transitions are given by: $\Delta L = \pm 1$ or 0 , and $\Delta J = \pm 1$ or 0 , with the additional restrictions that the transitions $L = 0 \rightarrow L = 0$ and $J = 0 \rightarrow J = 0$ be forbidden. It is to be noted that, for the case of a single valence electron, the nomenclature J , L and S becomes j , l and s respectively. For each value of l , j can possess but two values; $l + \frac{1}{2}$ and $l - \frac{1}{2}$, corresponding respectively to the electron spin parallel or anti-parallel to the orbital angular momentum. Here then is the explanation of the doublet levels of the alkali-type atoms.

Not only the relative wave-lengths, but also the relative intensities of the fine-structure components may be deduced from the L and S (or l and s) values of the levels concerned. A very useful qualitative rule, established on the basis of the older quantum theory, was given by

Sommerfeld and Heisenberg²⁹: The strongest lines are due to the transitions where $\Delta J = \Delta L$; weaker lines - satellites of the first order - arise when $\Delta J = \Delta L \pm 1$; and the weakest lines - satellites of the second order - occur when

$\Delta J = \Delta L \pm 2$. Quantum-mechanical verification and elaboration of such rules have been given by Dirac³⁰.

A few of the more important quantitative results will next be given. First to be dealt with will be the doublet separations in alkali-like atoms. The interaction energy, i.e. the energy change of a fine structure level characterized by the quantum numbers n and l - due to the "magnetic" property of the electron has been calculated by Pauli³¹, Gordon³², Dirac³³, Darwin³⁴ and others. The results of the calculations give the term shift corresponding to this energy as

$$\Delta T = \frac{-R\alpha^2}{n^3} \frac{Z^4}{l(l+1)(l+\frac{1}{2})} \left(\frac{j^2 - l^2 - s^2}{2} \right) \text{ cm}^{-1} \quad (4)$$

29 Sommerfeld, A., and W. Heisenberg, Zeits. f. Phys. 11, 131: 1922.

30 Dirac, P.A.M., Proc. Roy. Soc., A 111, 281: 1926.

31 Pauli, W., Zeits. f. Phys., 43, 601: 1927.

32 Gordon, W., Zeits. f. Phys. 48, 11: 1929.

33 Dirac, P.A.M., Proc. Roy. Soc., A 117, 610: 1927.

34 Darwin, C.G., Proc. Roy. Soc., A 116, 227: 1927.

where the quantum vectors \vec{j} , \vec{l} , and \vec{s} have, of course, the magnitudes $\sqrt{j(j+1)} \hbar$, $\sqrt{l(l+1)} \hbar$, and $\sqrt{s(s+1)} \hbar$ respectively. α is the "Sommerfeld fine-structure constant," given by

$$\frac{2\pi e^2}{ch} \approx \frac{1}{137.3} \quad (5)$$

(4) is often written as

$$\Delta T = \frac{-a}{2} (\vec{j}^2 - \vec{l}^2 - \vec{s}^2)_{cm^{-1}} \quad (6)$$

where:

a(the fine-structure interaction constant) =

$$\frac{R_{\infty}^2 Z^4}{n^3 l(l+1) (l + \frac{1}{2})} \text{ cm}^{-1} \quad (7)$$

It is to be noted that for s electrons, having $l = 0$ and thus $j = \frac{1}{2}$, $\Delta T = 0$; therefore all s states should be single, a fact which has been amply confirmed by experiment.

For any doublet $j = l + \frac{1}{2}$ for the upper level and $j = l - \frac{1}{2}$ for the lower level. By substitution of these values in (4) one sees after some mathematical manipulation that the numerical value of the doublet separations for alkali-like atoms is given by:

$$\Delta V = \frac{R_{\infty}^2 Z^4}{n^3 l(l+1)} \text{ cm}^{-1} = \frac{5.82 Z^4}{n^3 l(l+1)} \text{ cm}^{-1} \quad (8)$$

Equation (8) may be modified to read

$$\Delta V = \frac{R\alpha^2 (Z - s)^4}{n^3 \ell(\ell + 1)} \text{ cm}^{-1} \quad (9)$$

where s is a "screening constant" which indicates the shielding of the nucleus by the one or more closed electron sub-shells.

Equations (8) and (9) hold good for the case of the non-penetrating orbits of the valence electron, i.e. those orbits for which the observed energies are almost equal to those of the corresponding hydrogen-like orbits.

In the event of penetrating orbits, which by definition have term values differing appreciably from those of the corresponding hydrogen-like orbits, still another modification of (8) must be employed. Landé³⁵, upon the basis of the older quantum theory, and before the introduction of the concept of electron spin, showed that in this case the doublet separation is given by

$$\Delta V = \frac{R\alpha^2 Z_o^2 Z_i^2}{n^3 \ell(\ell + 1)} \text{ cm}^{-1} \quad (10)$$

The electronic orbit was considered as being divided into two parts, an inner one, in which the electron was subject to the attraction of the charge Z_i , and an outer where the attracting charge was Z_o . Z_o will here be equal to unity for a

35 Landé, A., Zeits. f. Phys., 25, 46: 1924.

neutral atom, 2 for a singly ionized atom, and so forth. With the introduction of appropriate screening constants s_i and s_o , (10) becomes:

$$\Delta V = \frac{R\alpha^2 (Z - s_o)^2 (Z - s_i)^2}{n^*{}^3 \ell(\ell + 1)} \text{ cm}^{-1} \quad (11)$$

Here $n^* = n - u$ (with u the so-called "quantum defect") is the "effective quantum number" defined by $\frac{T}{R} = \frac{Z_o^2}{n^*{}^2}$, a

modification of the hydrogen-like term value formula. Equations (9), (10) and (11) are of value in the treatment of isoelectronic sequences, and will be mentioned further under that heading of theory.

Next will be given a few quantitative results for the triplets occurring in the spectra of atoms with two valence electrons. The following conclusions, which are discussed very fully by Pauling and Goudsmit ³⁶, are based upon the validity of L - S coupling. If but one of the electrons is in an s orbit, the interaction energy due to electron spin produces a term shift given by

$$\Delta T = -a_{1(non-s)} \left\{ \frac{J^2 - L^2 - S^2}{2} \right\} \text{ cm}^{-1} \quad (12)$$

where:

$$a_{1(non-s)} = \frac{+R\alpha^2 (Z - s_1)^4}{n_1^3 \ell_1 (\ell_1 + 1) (\ell_1 + \frac{1}{2})^2} \text{ cm}^{-1} \quad (13)$$

³⁶ Pauling, L., and S.A.Goudsmit, The Structure of Line Spectra, McGraw-Hill, 1930.

The above (with \bar{S}_1 a screening constant) holds for non-penetrating orbits; for a penetrating S orbit (13) becomes, of course,

$$a_1 = \frac{R\alpha^2 Z_0^2 Z_c^2}{n_1^{*3} \ell(\ell+1)(\ell+\frac{1}{2})^2} \text{ cm.}^{-1} \quad (14)$$

For neither electron an s - electron, the term displacement is expressed by

$$\Delta T = -(a_1 + a_2) \left(\frac{J^2 - L^2 - S^2}{2} \right) \text{ cm.}^{-1} \quad (15)$$

in which a_1 , equalling

$$\frac{R\alpha^2 (Z - \bar{S}_1)^4 \cdot s_1(s_1+1) + S(S+1) - s_2(s_2+1) \cdot \ell_1(\ell_1+1) + L(L+1) - \ell_2(\ell_2+1)}{n_1^3 \ell_1(\ell_1+1)(\ell_1+\frac{1}{2}) \cdot 2S(S+1) \cdot 2L(L+1)} \text{ cm.}^{-1} \quad (16)$$

and a_2 , given by (16) with subscripts 1 and 2 interchanged, are the interaction constants of the two electrons.

The total triplet separation for the case of one s-electron is

$$\Delta\nu = \frac{R\alpha^2 (Z - \bar{S}_1)^4}{n_1^3 \ell_1(\ell_1+1)} \text{ cm.}^{-1} \quad (17)$$

and is found by substitution of the maximum and minimum values (of J), $\ell_1 + 1$ and $\ell_1 - 1$ respectively, in (12). It is to be noted that (17) is identical in form with (9), the equation for the alkali doublet separation. For two like electrons, the total triplet width is, from (15), given by

$$\Delta\nu = \frac{R\alpha^2 (Z - \bar{S}_1)^4 (L + \frac{1}{2})}{n_1^3 \ell_1(\ell_1+1)(\ell_1+\frac{1}{2})} \text{ cm.}^{-1} \quad (18)$$

One of the simplest methods of determining whether the electron coupling is of the $L = S$, or Russell-Saunders, type is to test for the presence of the so-called interval rule, discovered by Landé.³⁷ This rule states that for any triplet, or for any multiplet of a higher order, the separation of two adjacent terms, associated with quantum numbers J and $J - 1$ respectively, is proportional to J , i.e. to the larger J value. For the energy of any multiplet term may be expressed by

$$T_G + \frac{A}{2} \left\{ J(J+1) - L(L+1) - S(S+1) \right\}$$

Where T_G is the hypothetical value of the doublet centroid.

The separation of two multiplet components characterized by values J and $J - 1$ is therefore

$$\frac{A}{2} \left\{ J(J+1) - (J-1)J \right\} = AJ \quad (19)$$

which is just Landé's empirical result.

In the following table are compared observed and theoretical interval ratios for various triplets of the Cadmium I spectrum:

Configuration	$3P_2 - 3P_1^o$	$3P_1^o - 3P_0^o$	$3D_3 - 3D_2$	$3D_2 - 3D_1$	Observed Interval Ratio	$\frac{J+1}{J}$
5s5p	1171.1	541.9	-	-	2.16	2
5s5d	-	-	18.2	11.7	1.55	1.5
5s6d	-	-	8.2	5.8	1.41	1.5

37 Landé, A., Zeits. f. Phys., 15, 189: 1923.

It should be mentioned in conclusion that L-S coupling, upon whose validity the results of the foregoing treatment of fine-structure are based, holds strictly only in the case of the lighter elements, i.e. those with small nuclear charge. Here the electrostatic interaction between the different extra-nuclear electrons is much greater than the various spin-orbit interactions. However, in the heavier elements, the latter interactions tend to predominate; such a tendency gives rise to the so-called "j-j coupling", in which the \vec{j} 's of each individual electron are strongly coupled together to form the resultant \vec{J} . Most spectral lines and energy levels can be classified by means of either coupling scheme, or by some intermediate modification of these schemes.

B. Hyperfine Structure of Spectral Lines.

Instruments of high resolving power, such as Michelson interferometers, revealed in many spectral lines a complex structure with component intervals ranging from about 0.1 to about 1.0 cm^{-1} in magnitude. The smallness of the intervals itself suggested that the so-called "hyperfine-structure" could hardly be attributed to the electron spin which helps to explain completely ordinary fine-structure. Thus it seemed necessary either to postulate some further fundamental property of the electron besides its mass, charge and spin, or, more acceptably, to ascribe the phenomenon to the nucleus.

Two means have been proposed by which the nucleus could be responsible for the hyperfine effect. The first concerns the existence of isotopes and gives rise to the so-called "isotope effect". The second, and more important, postulates the existence of a nuclear magnetic moment. The latter theory only will be considered here.

The hypothesis was first put forward by Pauli³⁸. It assigned to the nucleus an angular momentum \vec{I} equal to (in the form agreeing with quantum-mechanical results) $\sqrt{I(I+1)} \hbar$. With this angular momentum was to be associated a magnetic moment; it was presumed that, when the field of the nuclear magnetic dipole acted upon the valence electron $-(S)$, a splitting of the fine-structure electronic term occurred. \vec{I} , and the resultant electronic angular momentum given, as before, by \vec{J} , were assumed to combine forming a resultant atomic moment $\vec{F} = \sqrt{F(F+1)} \hbar$. Experience with similar linking of \vec{L} and \vec{S} suggested that possibly the selection rules $\Delta F = \pm 1$ or 0 (with $F = 0 \rightarrow 0$ forbidden) might hold in this case. Similarly one would expect $2I+1$ hyperfine levels for $I < J$ and $2J+1$ levels for $J < I$. Analogous to the case of ordinary fine-structure, however, the validity of such rules and of the Landé interval rule in hyperfine structure would demand that the interaction energy between the nuclear magnetic dipole and the valence electrons be proportional to the cosine of the angle

³⁸ Pauli, W., *Naturwissenschaften*, 12, 741: 1924.

between the quantum vectors \vec{I} and \vec{J} . It has been shown by Fermi³⁹, Breit⁴⁰, Goudsmit⁴¹, and others that - in the case of a single valence electron - the term shift corresponding to the interaction energy is indeed given by:

$$\begin{aligned} \Delta T &= a (\vec{I} \cdot \vec{J}) \text{ cm}^{-1} \\ &= \frac{a}{2} \left(F^2 - J^2 - I^2 \right) \text{ cm}^{-1} \\ &= \frac{a}{2} \left\{ F(F+1) - j(j+1) - I(I+1) \right\} \text{ cm}^{-1} \end{aligned} \quad (20)$$

where:

$$a(\text{the interaction constant}) = \frac{Rd^2 Z^3 g(I)}{n^3 (l + \frac{1}{2}) j(j+1) 1838} \text{ cm}^{-1} \quad (21)$$

for a non-penetrating orbit, and

$$a = \frac{Rd^2 Z_1 Z_o^2 g(I)}{n^{*3} (l + \frac{1}{2}) j(j+1) 1838} \text{ cm}^{-1} \quad (22)$$

for a penetrating orbit.

The so-called "nuclear g-factor" ($g(I)$) is the ratio of the nuclear magnetic and mechanical moments, and is defined by the equation:

$$\mu_I = g(I) \frac{e}{2M} \sqrt{I(I+1)} \hbar \quad (23)$$

where M is the proton mass.

39 Fermi, E., Zeits. f. Phys., 60, 320: 1930.

40 Breit, G., Phys.Rev., 37, 51: 1931.

41 Goudsmit, S.A., Phys. Rev., 37, 663: 1931.

By substitution in (22) of the Landé alkali-doublet formula - given previously by (10), - one obtains the relation:

$$a = \frac{g(I) \Delta V (\ell + 1) \ell}{1838 Z_1 (\ell + \frac{1}{2}) j (j+1)} \text{ cm}^{-1} \quad (24)$$

Breit⁴² and Racah⁴³ have pointed out that a relativistic correction must be made in the theory, especially for the case of the heavier elements. The correction can be given by multiplying (19) by $\frac{K}{\lambda}$ where:

$$K = \frac{4j(j+\frac{1}{2})(j+1)}{(4p^2 - 1)p}, \quad p^2 = (j + \frac{1}{2})^2 - (\alpha Z_1)^2 \quad (25)$$

$$\text{and } \lambda = \left[\frac{2\ell(\ell+1)}{(\alpha Z_1)^2} \right] \left[\left\{ (\ell+1)^2 - (\alpha Z_1)^2 \right\}^{\frac{1}{2}} - 1 - \left\{ \ell^2 - (\alpha Z_1)^2 \right\}^{\frac{1}{2}} \right] \quad (26)$$

For the special case of an s valence electron, where equation (24) theoretically should not hold, a satisfactory modification has been given by Goudsmit, namely that

$$a = \frac{g(I)}{1838} \frac{8R\alpha^2 Z_1 Z_0^2 K}{3n^*3} \quad (27)$$

In the event that the atom considered has two or more valence electrons direct application of the above expressions

42 Breit, G., Phys. Rev., 42, 636: 1931.

43 Racah, G. Zeits. f. Phys., 71, 431: 1931.

is impossible. Bethe⁴⁴ points out that frequently in this case the interaction is due to the presence of a single penetrating s electron in the group of valence electrons; here the separation for a given state can be obtained simply in terms of the interaction constant of the s electron. For 2 s-electrons the interval factor can be given by one-half the sum of the individual electronic factors. The very much more complicated cases concerning other configurations have been treated in great detail by Crawford, Breit, Wills and others ^{46, 45, 47}.

The chief reason advanced for the detailed study of the hyperfine structure of an element is that such study is, as previously mentioned, often instrumental in the determination of three very important nuclear properties. The presence of two of these is revealed by the holding of the interval rule, that of the remaining one by departures from this rule. The two cases will be discussed briefly.

(a) Validity of the interval rule.

Already at our disposal is the fact that there exists $2I+1$ levels for $I < J$, and $2J+1$ levels for $I > J$, I being the resultant nuclear angular momentum or "spin". If the number of hyperfine components of any hyperfine state is less than $2J+1$,

⁴⁴ Bethe, H., Rev.Mod.Phys., 8, 206-226: 1936.

⁴⁵ Crawford, M.F., Phys.Rev., 47, 768: 1935.

⁴⁶ Breit, G., and L.A.Wills, Phys.Rev. 44 470: 1933.

⁴⁷ Crawford, M.F., and L.A.Wills, Phys.Rev. 48 69: 1935.

one can immediately determine the fundamental nuclear property I. Here the so-called "flag patterns", in which the separations decrease uniformly across the pattern, are exceedingly helpful. In spectra of the one-electron type, there are often no states of sufficiently large J which have an appreciable hyperfine structure. By appealing to the interval rule one can here determine the F values of the hyperfine states. Thus, if J is known, the spin I can readily be found. The interval rule cannot, unfortunately, be applied to a state having $J = \frac{1}{2}$.

The second of the nuclear properties which may be determined by utilization of the interval rule is the magnetic moment μ_I . For the case of one valence electron, combination of (23) with (24) and (27) gives the following formulae for the magnetic moment:

$$\mu_I = \frac{a \ln^3 Z_1 (l + \frac{1}{2}) j (j+1) \lambda 1838}{\Delta V l (l + 1) K} \quad (28)$$

$$\text{and } \mu_I = \frac{3a \ln^3 1838}{8R \alpha^2 Z_1 Z_o^2 K} \quad (29)$$

Thus, by experimental determination of the interval factor a, the magnetic moment can often be readily found by (28) or (29). In the event that the atom possesses two or more valence electrons, the work of Crawford et al (loc.cit.) can be used to find relations which give the hyperfine structure size in terms of the interaction constants of the various electrons involved.

Then the magnetic moment can be found by again resorting to (28) or (29).

(b) Departures from the interval rule.

In general hyperfine multiplets obey the interval rule far better than do fine-structure multiplets; this very regularity makes the few exceptions the more striking. One explanation of these exceptions concerns the appearance, in hyperfine structure, of the perturbation effect. Such perturbation could occur if two hyperfine levels satisfied certain quantum conditions, the most important being that the values of F be identical. However, whereas two fine-structure components may perturb one another when as much as 2000 cm^{-1} apart, the levels of the finer structure must lie but a few units apart. Therefore it is much less probable that an unknown level could lie in a position to produce the observed distortion.

Recently deviations from the interval rule have been found for which the perturbation effect is an inadequate explanation. Instead of the displacements of the levels from the multiplet centroid being proportional simply to the cosine of the angle between \vec{I} and \vec{J} , a second term, proportional to the square of this cosine, appears. The form such deviations take suggests that the new disturbing force is electrostatic in origin and is due to a lack of spherical symmetry in the nuclear electric field. A so-called "electric quadrupole moment" is

then said to be brought about by the spherical asymmetry of the nuclear protonic charge.

Casimir⁴⁸ has shown that for a single valence electron the energy change of a hyperfine state F (associated with the atomic state $j = \ell - \frac{1}{2}$) due to the presence of a quadrupole moment Q can be given by:

$$\Delta W_F = -e^2 \left(\frac{3 \cos^2 \theta - 1}{r^3} \right) Q \frac{1}{Ij(2I-1)(2j-1)} \left[\frac{3C(C+1) - \frac{1}{2}Ij(I+1)(j+1)}{8} \right] \quad (30)$$

where $C = F(F+1) - I(I+1) - j(j+1)$. The quantity $\left(\frac{3 \cos^2 \theta - 1}{r^3} \right)$, an average over the extra-nuclear electronic charge density, is to be calculated for each relevant electron configuration.

It is seen from (30) that, for $j = \frac{1}{2}$, ΔW_F becomes equal to zero. Thus a quadrupole effect will be absent in the case of single s or $p_{\frac{1}{2}}$ electrons. Also it can be shown that other states will produce effects which are roughly proportional to the ordinary fine-structure doublet separation; therefore relatively large effects can be expected for the low $p_{\frac{3}{2}}$ and d electrons in the heavier elements. The extension of the theory to the case of two or more valence electrons is too complicated to be given here. Careful perusal of the original article is recommended.

⁴⁸ Casimir, H.B.G., Physica, 2, 710: 1935.

By choosing a hyperfine state, therefore, in which any deviation from the interval rule is definitely not due to perturbation effects, one can utilize such deviation to calculate the quadrupole moment Q of the nucleus. The result can often be used with good effect in determining the nuclear charge distribution; for Q having a positive, negative or zero value indicates respectively a prolate, oblate, or spherical charge distribution in the direction of nuclear "spin".

C. Isoelectronic Sequences.

The term "isoelectronic sequence" refers to a sequence of atoms possessing an identical number of extra-nuclear electrons but, of course, different nuclear charges. Because of this fact, the energy levels of each atom in such a sequence, and also the spectral lines resulting from transitions between these levels, show surprising similarities from element to element. Millikan and Bowen⁴⁹ and others have shown that the regular - and irregular - doublet laws of X-ray spectra could be applied to the optical doublets produced by alkali-like atoms. The application of these laws to alkali doublets will be discussed here in some detail.

⁴⁹ Millikan, R.A., and I.S. Bowen, Phys. Rev. 24, 209: 1924.

(a) The Irregular or Screening-Doublet Law.

This law was discovered in 1920 by Hertz⁵⁰ who had observed parallel lines in an X-ray level scheme. The law, which applies to those levels having the same n , S and J values, but values of L differing by unity, can be given - in its extension to isoelectronic sequences - thus: The difference between the square roots of the term values of the levels having the same principal quantum number n is independent of the atomic number Z .

The formulation of this rule can be simply given in the following manner. From the term-value equation of Hertz

$$T = \frac{R (Z - \sigma)^2}{n^2} \quad (31)$$

(where σ is the screening constant accounting for the difference between the term values of any atoms and those of hydrogen-like atoms given by $T = \frac{R Z^2}{n^2}$) one obtains

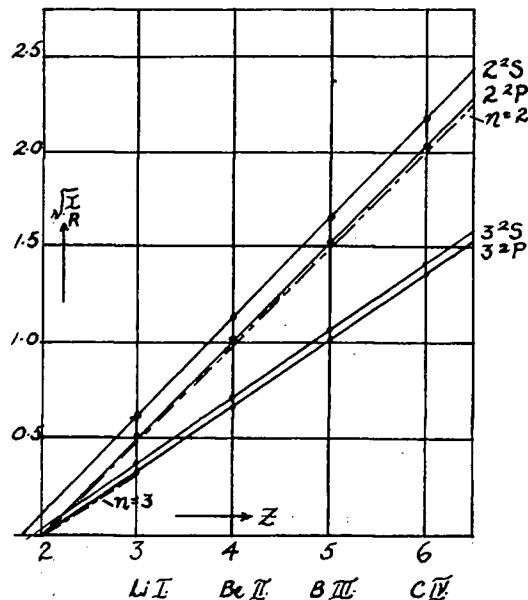
$$\sqrt{\frac{T}{R}} = \sqrt{\frac{E}{hcR}} = \frac{1}{n} (Z - \sigma)$$

With σ_1 and σ_2 the screening constants for the two levels of a doublet, the term difference between the levels can be given by

$$\Delta \sqrt{\frac{T}{R}} = \frac{\sigma_1 - \sigma_2}{n} = \frac{\Delta \sigma}{n} = \text{a constant} \quad (32)$$

50 Hertz, G., Zeits. f. Phys. 3, 19: 1920.

The following so-called "Moseley Diagram" depicts the validity of the irregular-doublet law for a typical 3-electron system.



The doublet fine-structure separations are so small in this system that they are omitted in the figure. (The dotted lines represent the ideal "hydrogen-like" condition that the two K electrons lie close enough to the nucleus to reduce the nuclear charge by two). It is to be observed that the plotted lines have their slopes closely equal to $\frac{1}{n}$, and that levels with the same n are closely parallel, in good agreement with the demands of the theory. The heavier the element, i.e. the greater the nuclear charge, the more pronounced become the deviations of the line slopes from the value $\frac{1}{n}$.

A second, and often more useful, form of the

irregular doublet law is given by the following statement:
The frequency differences between two levels having the same value of n are linear functions of the atomic number Z . This condition arises from the fact that, while selection rules do not allow both levels of a screening doublet to combine with a third level, the two are permitted to combine together. Such transitions have not as yet been observed in X-ray spectra, probably because of the low intensity of the resulting lines; however, they have been observed in optical spectra. The derivation of this second form of the irregular-doublet law can be given as follows. In an isoelectronic sequence, a pair of "Moseley lines" may be written as

$$\sqrt{\frac{E_1}{chR}} = \frac{1}{n_1} (Z - \sigma_1) \quad \text{and} \quad \sqrt{\frac{E_2}{chR}} = \frac{1}{n_2} (Z - \sigma_2)$$

If the lines are parallel, $n_1 = n_2 = n$. Thus the frequency of the resulting line will be given by:

$$\begin{aligned} \Delta\nu &= \frac{2R}{n^2} \left\{ (\sigma_1 - \sigma_2) Z + \frac{(\sigma_1^2 - \sigma_2^2)}{2} \right\} \\ &= C_1 Z + C_2 \end{aligned} \quad (33)$$

This form of the irregular-doublet law is therefore invaluable for predicting frequencies and wave-lengths of unidentified lines in multiply ionized atoms.

(b) The Regular-Doublet Law.

The term "spin-relativity" doublet or "regular" doublet refers to a pair of energy levels having the same n , S and L values, but values of J differing by unity. The regular doublet law can be stated in the following form: The doublet separation $\Delta\nu$, in wave numbers, is approximately proportional to the fourth power of the effective quantum number $Z - s$, where s is a screening constant expressing, as before, the shielding effect of the closed electron sub-shells. Sommerfeld, using the concept of the relativistic change of electron mass with velocity, was able to determine the mathematical form of the law. The formula, written in modern quantum notation, is given to a first approximation by

$$\Delta\nu = \frac{R\alpha^2(Z-s)^4}{n^3 \ell(\ell+1)} \text{ cm}^{-1} \quad (34)$$

It was applied originally to the theory of hydrogen fine-structure and of X-rays; still later it was applied by Millikan and Bowen to optical doublets. It is to be noted that this formula is identical with the one, given by (9), in whose derivation the more recent concept of electron spin was utilized.

The application of the formula to optical doublets in isoelectronic sequences showed that the screening constant s decreases slightly but regularly as Z increases; and, while s is quite regular within a single isoelectronic group, it varies from sequence to sequence in a totally irregular manner. The formula, of course, will hold only for the case of non-penetrating orbits

of the valence electron.

The above theory is quite adequate for elements in the short periods. For the long periods, however, another formula has been found to give more satisfactory results. It may be mentioned here that Sommerfeld developed his doublet formula on the assumption that the optically active electron moves in a uniform field equal to that of a point charge $(Z - s)e$. A refinement of the theory which gives better results in the case of the so-called penetrating orbits advocates use of the Landé doublet formula previously given by equations (10) and (11) as

$$\Delta V = \frac{R\alpha^2 Z_i^2 Z_o^2}{n^{*3} l(l+1)} \text{ cm}^{-1} = \frac{R\alpha^2 (Z - S_i)^2 (Z - S_o)^2}{n^{*3} l(l+1)} \text{ cm}^{-1}$$

where n^* , the effective quantum number, will differ by a relatively large amount from n .

The values of $S_i = Z - Z_i$ should, for P terms, theoretically lie between 2 and 10 to account for screening of the nucleus by the K shell of planetary electrons and perhaps by part of the L shell as well. By similar reasoning, D terms should give values of S_i greater than 10. In most cases the Landé formula confirms these assumptions by giving results of the proper order (Table II c.(1)). The formula is also useful in that it verifies two seemingly unrelated empirical rules of spectroscopy, namely that:

(1) In a sequence of isoelectronic spectra, the doublet interval will be approximately proportional to Z_0^2 , since Z_1 and n^* vary but little throughout the sequence. (Table II c.(1)).

(II) Inside a single term sequence, the doublet interval decreases roughly in the ratio $\frac{1}{n^{*2}}$. (Table II c.(2)).

IV EXPERIMENTAL

A. The Electrodeless Discharge.

The electrodeless discharge has been used - as a method of exciting the arc and spark spectra of various elements - with great success by several investigators⁵¹. The main advantages of this type of light source are twofold:

(1) The excitation can be controlled in some degree by the strength and frequency of the source current, and

(2) The pressure broadening of the spectral lines can be reduced to a minimum, thus ensuring more accurate determination of the wave-lengths of these lines.

In this means of excitation, the gaseous discharge is, as the name suggests, maintained in a closed tube without electrodes. The tube is placed within a coil carrying a high-frequency current, which may be generated by a vacuum-tube oscillator or, as in the present investigations, by the circuit to be described presently. The current in the coil sets up an oscillating high-frequency electric field within the tube; this field produces sufficient electron velocity to excite the atoms or molecules of the vapor within the vessel. The electron velocities depend upon the field strength, the length of time of application of the

⁵¹ e.g. Barss, W., Thesis, The Spectra of Iodine, The University of British Columbia, April, 1939.

field, and the distance an electron can travel before colliding with a molecule. These factors can be controlled by adjusting both the strength and frequency of the current and the gas pressure. Lower pressures will in general give rise to greater excitations because of the larger amount of energy obtained by the electron in the resulting greater mean free path. Thus any gas, or any metal which may be vaporized by temperatures to which the tube can be subjected, can be studied in the above manner.

The discharge tube used in the present investigations was constructed of translucent quartz combustion tubing; it measured about 35 centimetres in length and 2.5 centimetres in diameter. The type of tubing used was required because of the relatively high temperatures needed for the vaporization of Cadmium (whose boiling point is 767°C). Clear, flat quartz windows were fused to the ends of the vessel, and a side tube was provided near one end. The work was done by Mr. A. W. Pye of the Physics Department workshop of this university.

The excitation coil - denoted by A in Plate I - consisted of about twelve turns of #12 bare copper wire; it was separated from the discharge tube itself by a thin sheath of mica. The experimental arrangement permitted the coil to be easily detached - at B and B¹ - from the remainder of the circuit.

The transformer T possessed a secondary winding giving a voltage output of approximately 100KV with a power

rating of about 6KVA. A heavy-duty control rheostat R of 3-12 ohms was placed in series with the transformer primary, itself connected across a 110-volt A.C. supply. The excitation currents used could thus vary in range from about 10 to a maximum of over 30 amperes.

The capacitance C of the circuit consisted of 4 large Leyden jars constructed by shellacking tin foil to Pyrex containers. These jars are connected, in parallel, as shown. The spark gap S consisted of two iron cones and utilized a screw arrangement permitting the size of the gap to be varied at will. The leads in the circuit were kept as short as possible to prevent any undesirable capacitance effects.

B. The Spectrograph.

Spectrograms of the radiation were made on a Hilger EI Quartz Lithow-type spectrograph having a focal length of 165 centimetres for the sodium D-line. Because of its quartz optics, this instrument could be used in both the visible and ultra-violet regions of the spectrum. The dispersion ranged from about 1.5 \AA/mm. at 2000 \AA. to about 50 \AA/mm. at 6800 \AA.

Before the focussing proper of the spectrograph could be undertaken, it was necessary to locate the light source upon the optic axis of the collimating lens. A simple method for so doing is given by Sawyer⁵². The illumination used in this and

52 Sawyer, R.A., Experimental Spectroscopy, Prentice-Hall, 1944.
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the following adjustments, an ordinary iron arc, was selected because it provided a good number of intense lines well distributed throughout the spectrum.

In the present model of the spectrograph there were three variables to be considered in the focussing, namely:

- (1) The prism rotation
- (2) The prism translation, and
- (3) The plate-holder rotation.

These settings could not be fixed for any one spectral region because of the effect on them of temperature and pressure variations.

After the desired region had been established on the prism rotation drum, the approximate setting of the prism translation and of the plate-holder rotation could be made visually. The final accurate setting of the prism translation was made photographically - by the taking of a series of equally-spaced exposures in the region of best focus. The necessary amount of plate-holder rotation to give the correct plate tilt could then be interpolated in turn from these exposures. The taking of another plate - this time utilizing the discharge itself - to discover the best exposure times generally completed the adjustment of the spectrograph. This slit was visually adjusted to optimum width, and left unchanged for all regions.

C. Operation of the Source.

The tube was positioned, as depicted in Plates II and III, by plywood stands which held the tube coaxial with the spectrograph slit. The metallic Cadmium to be vaporized was introduced into the discharge vessel by means of small fragments. These fragments were concentrated at the centre of the tube, which was then connected to a Megavac pump producing a pressure of only 10^{-4} mm. of mercury. It was found that sufficient excitation could not be achieved by the applied electric field alone. A source of heat, in the form of an ordinary Bunsen burner, was therefore utilized. The burner was also equipped with a "fish-tail" cap - as clearly shown in plate III - to help localize the heat upon the portion of the tube in which the Cadmium was concentrated. Even more effective use of the heat was obtained by enclosing the discharge tube in a "box" - open at the bottom - made of Transite board. This arrangement, shown in Plate II, reduced the loss of flame heat by radiation and other means. Wiring the burner to the remainder of the circuit prevented any sparking which might occur because of the proximity of coil and burner. It was found necessary to evacuate the tube quite thoroughly before the electric field and the heat were applied; otherwise a deposit of Cadmium Oxide would produce a stain, upon the quartz end windows, which was almost impossible of removal.

The vapor pressure in the tube was controlled quite adequately by means of a variable pinch-clamp attached to the pump's rubber intake tube. To start the discharge, it was found necessary to "clamp off" the tube from the pump so that the cadmium vapor pressure could be built up. Upon examination of the ensuing radiation with a hand spectroscope, one could adjust the pressure and the current strength to give the maximum excitation and intensity. During the plate exposures, the tube's end windows were often "fogged" by a film of Cadmium; this condition seriously reduced the intensity of the radiation from the tube. The windows, however, could be cleared quite adequately by the application, for a few seconds, of a Bunsen flame.

D. Exposure and Measurement of Plates.

When the above work was completed, three spectral regions of the excitation were photographed - namely 6800\AA - 3300\AA , 3300\AA - 2500\AA and 2500\AA - 2000\AA . The plates used in the first two regions were of the Eastmann II-F type; in the last-mentioned region Ilford QI plates were found to give excellent results. The thinness of the emulsion used in the latter type, however, necessitated very careful handling in order to avoid scratching.

An exposure time of between $3\frac{1}{2}$ and 5 minutes, depending upon the fluctuations in the intensity of the discharge, was

found to be sufficient for all regions photographed. The exposures were taken at full slit length, and in the centre of each was superposed a comparison spectrum. This latter was obtained by decreasing the slit length and then shining axially through the discharge tube the light of either an iron arc (for the regions $6800\text{\AA} - 3300\text{\AA}$ and $3300\text{\AA} - 2500\text{\AA}$) or of a copper arc (for the region $2500\text{\AA} - 2000\text{\AA}$). An exposure time of about 25 seconds was found to suffice for the iron arc, while for the copper a period of about 3 minutes was needed. In Plate IV is shown a sample spectrogram (of the region $6800\text{\AA} - 3300\text{\AA}$).

The positions of the lines on the best plate for each region were measured by means of a Hilger comparator reading to .001 mm. The wave-lengths of all "prospective" Cadmium lines were calculated by means of the standard Hartmann formula:

$$\lambda = \lambda_0 + \frac{c}{d + d_0}$$

The comparison spectra were used merely for tentative identification of lines and not as "Hartmann standards"; this restriction was due to the fact that a difference in exposure times^{of} cadmium and of comparison spectra produced, because of temperature effects, a slight relative shift between lines of the two spectra. To facilitate the identi-

fication of Cadmium "Hartmann standards", a dispersion curve for the Hilger spectrograph was drawn up (Plate V).

V. RESULTS

A. Results of Wave-length Measurements.

The wave-lengths of approximately 330 lines appearing on the plates covering the three regions were measured by the means previously described. In Table I, the following resulting information on the Cadmium spectra is given:

- (1) The state of ionization, where known, giving rise to the relevant line.
- (2) The intensity of each line, obtained by visual means; the intensity scale ranges from 0 for exceptionally weak lines to 10 for very strong ones.
- (3) The wave-lengths (in air) in A.U.; these are of two kinds:
 - (a) Those - about 150 in number - whose values were found to agree with values given by previous investigators.
 - (b) A few - about 21 - whose values agreed neither with any Cadmium wave-lengths (known at this writing) nor with the wave-lengths of any possible impurity lines.
- (4) Remarks, listing as "new" the type of line mentioned in 3(b).

The work done corroborates the fact of the relative paucity of lines in the Cadmium spectrum. The so-called "new" lines were concentrated in the range 6000\AA - 3900\AA ; and very few

Cadmium III lines; and but one Cadmium IV line, were excited. The impurity lines and bands were, throughout the whole spectrum, produced mainly by the chief constituents of air, i.e. oxygen, nitrogen, and the inert gases.

B. Investigations of Isoelectronic Sequences.

It is readily seen from theory that the hyperfine intervals occurring in the spark spectra of an element will be larger than those associated with the arc spectrum; this fact has been generally confirmed by experiment. Thus a study of the hyperfine structure of, in this case, Cd II, should facilitate a far more accurate determination of the nuclear mechanical and magnetic moments of Cadmium. A study of the isoelectronic sequence Ag I, Cd II, Ind. III, Sn IV and Sb V was therefore undertaken in the belief that it would prove valuable in the necessary preliminary study of the grosser spectral structure of Cd II. Also the validity of the various aspects of the regular - and irregular - doublet laws could be tested in the case of such an exemplifying sequence. Tables IIA, IIB, ^{π} _A and IIC(1) represent term tables for the above "silver-like" isoelectronic group. Plates VI, VII and VIII graphically illustrate the form of the doublet laws. Plates IX and X illustrate two forms of the energy level diagram; the latter form is especially useful in evaluating terms and limits of spectral series. (To add to the general information concerning

the various Cadmium spectra, an energy level diagram of CdI has also been prepared - from the results of Table IIE).

The above work has availed itself of the published material of Pauling and Goudsmit⁵³.

⁵³ Pauling, L., and S.A.Goudsmit, The Structure of Line Spectra, McGraw-Hill, 1930.

TABLE I

ORIGIN	INT.	λ_{air}	REMARKS	ORIGIN	INT.	λ_{air}	REMARKS
Cd I	3	6778.10		Cd II	0	4102.00	
Cd II	6	6759.26		Cd II	6	4094.50	
Cd II	10	6725.83		Cd	3	4091.22	new
Cd II	4	6464.98		Cd	3	4049.15	new
Cd I	10	6438.4696		Cd	0	4043.20	new
Cd II	6	6359.93		Cd II	7	4029.08	
Cd II	4	6354.72		Cd	1	4017.98	new
Cd I	4	6325.19		Cd	1	4006.68	
Cd I	5	6111.52					
Cd I	5	6099.18		Cd	3	3993.80	new
Cd	1	6003.03	new	Cd	4	3977.47	new
Cd	0	5938.34	new	Cd II	7	3957.40	
Cd II	6	5843.175		Cd	2	3950.45	new
Cd	2	5796.51	new	Cd	3	3935.09	new
Cd	1	5780.47	new	Cd II	3	3827.41	
Cd	1	5664.90	new	Cd	4	3776.32	
Cd	2	5393.92	new	Cd II	4	3768.10	
Cd II	10	5381.82		Cd I	2	3649.597	
Cd II	7	5337.492		Cd III	1	3626.70	
Cd	1	5311.57	new	Cd I	7	3614.45	
Cd I	9	5085.824		Cd I	9	3612.875	
Cd I	10	4799.918		Cd I	10	3610.51	
Cd I	10	4678.156		Cd	3	3576.51	
Cd I	0	4614.17		Cd II	8	3535.687	
Cd II	1	4605.81		Cd III	0	3529.80	
Cd	1	4511.34		Cd II	1	3524.072	
Cd	10	4414.63		Cd	2	3518.99	new
Cd II	4	4412.31		Cd I	3	3500.00	
Cd I	2	4302.82		Cd II	9	3495.34	
Cd II	2	4285.07		Cd III	1	3486.00	
Cd	1	4278.03	new	Cd II	1	3483.04	
Cd	4	4245.869		Cd I	10	3467.656	
Cd	3	4243.39		Cd I	10	3466.201	
Cd	1	4148.51	new	Cd II	8	3464.37	
Cd II	4	4141.58		Cd II	0	3422.964	
Cd	4	4140.50		Cd II	0	3420.16	
Cd II	8	4134.78		Cd II	2	3417.396	
Cd II	1	4130.57		Cd II	7	3402.16	
Cd	4	4126.20	new	Cd II	0	3388.85	
Cd	0	4123.72	new	Cd II	4	3385.40	

TABLE I

ORIGIN	INT.	λ_{air}	REMARKS	ORIGIN	INT.	λ_{air}	REMARKS
Cd	1	3385.346	new	Cd II	1	2914.69	
Cd	4	3370.91		Cd I	10	2880.77	
Cd	3	3359.82		Cd I	6	2868.26	
Cd II	2	3343.15		Cd I	1	2862.31	
Cd III	1	3333.20		Cd I	9	2836.907	
Cd III	2	3283.82		Cd II	10	2834.19	
Cd II	0	3279.17		Cd II	5	2823.19	
Cd I	9	3261.057		Cd III	2	2780.28	
Cd I	10	3252.525		Cd I	5	2775.047	
Cd II	4	3250.301		Cd II	1	2767.49	
Cd II	10	3250.17		Cd I	10	2763.89	
Cd III	5	3217.80		Cd II	9	2748.58	
Cd II	2	3185.55		Cd I	3	2733.86	
Cd II	0	3174.489		Cd I	3	2712.57	
Cd	0	3173.613		Cd II	1	2707.14	
Cd	2	3160.814		Cd I	10	2677.64	
Cd I	9	3133.167		Cd I	8	2660.40	
Cd	2	3129.206		Cd I	7	2639.50	
Cd III	2	3124.4		Cd I	1	2632.244	
Cd III	2	3121.80		Cd I	2	2629.05	
Cd	2	3118.915		Cd I	5	2602.18	
Cd	3	3095.45		Cd I	0	2592.14	
Cd II	1	3092.393		Cd I	7	2580.30	
Cd II	0	3089.856		Cd II	10	2573.09	
Cd	3	3084.866		Cd II	8	2552.18	
Cd I	8	3080.827		Cd I	2	2544.71	
Cd II	1	3068.790		Cd II	2	2509.25	
Cd	3	3064.955		Cd II	5	2495.73	
Cd II	1	3059.22		Cd II	2	2470.61	
Cd III	0	3053.10		Cd II	8	2469.84	
Cd III	1	3048.82		Cd II	3	2419.40	
Cd II	0	3008.02		Cd II	1	2377.63	
Cd III	0	2987.20		Cd III	5	2350.30	
Cd I	10	2981.89		Cd	6	2329.282	
Cd I	10	2981.34		Cd II	5	2321.15	
Cd III	0	2971.20		Cd II	4	2312.84	
Cd I	1	2961.47		Cd II	1	2295.32	
Cd III	1	2948.16					
Cd II	2	2929.285					
Cd IV	2	2919.13					

TABLE I

ORIGIN	INT.	λ_{air}	REMARKS
Cd I	9	2288.018	
Cd II	0	2272.38	
Cd	2	2267.47	
Cd II	9	2265.017	
Cd	5	2239.86	
Cd	0	2236.32	
Cd II	4	2210.37	
Cd	2	2195.35	
Cd	6	2194.63	
Cd II	8	2188.55	
Cd II	1	2176.88	
Cd II	5	2155.70	
Cd II	9	2144.382	
Cd II	3	2129.12	
Cd	3	2112.17	
Cd II	7	2096.63	
Cd II	1	2036.79	

TABLE IIA

FIRST FORM OF IRREGULAR-DOUBLET LAW: $\Delta\sqrt{\frac{T}{R}}$ Independent of Z , $\Delta n = 0$.

(1)					(2)			(3)		
Config. $4d^{10} 5s - 2s_{\frac{1}{2}}$					$4d^{10} 5p - 2p_{\frac{1}{2}}$			$4d^{10} 5p - 2p_{\frac{3}{2}}$		
Atom	Z	$T(\text{cm}^{-1})$	\sqrt{T}	$\sqrt{\frac{T}{R}}$	$T(\text{cm}^{-1})$	\sqrt{T}	$\sqrt{\frac{T}{R}}$	$T(\text{cm}^{-1})$	\sqrt{T}	$\sqrt{\frac{T}{R}}$
Ag I	47	61104.4	247	.746	31552.1	177.5	.536	30631.5	175	.528
Cd II	48	136376.6	379	1.115	92241.3	304	.920	89758.1	299	.90
Ind. III	49	226133	476	1.435	168948	411	1.240	164606	406	1.23
Sn IV	50	328671	573	1.73	259112	509	1.535	252594	503	1.52
Sb V	51	449300	670	2.02	367734	606	1.83	358746	598	1.81

(4)					(5)			(6)		
Config. $4d^{10} 6s - 2s_{\frac{1}{2}}$					$4d^{10} 6p - 2p_{\frac{1}{2}}$			$4d^{10} 6p - 2p_{\frac{3}{2}}$		
Atom	Z	$T(\text{cm}^{-1})$	\sqrt{T}	$\sqrt{\frac{T}{R}}$	$T(\text{cm}^{-1})$	\sqrt{T}	$\sqrt{\frac{T}{R}}$	$T(\text{cm}^{-1})$	\sqrt{T}	$\sqrt{\frac{T}{R}}$
Ag I	47	18548.5	136	.411	12808.2	113	.342	12604.3	112.3	.339
Cd II	48	53386.4	231	.697	41665.8	204	.618	40992.5	202	.611
Ind III	49	99255	315	.952	81545	286	.864	80208	283	.856
Sn IV	50	154540	393	1.189	130826	362	1.09	128649	359	1.08
Sb V	51	224713	473	1.435	-	-	-	-	-	-

TABLE IIA

(Continued)

FIRST FORM OF IRREGULAR-DOUBLET LAW: $\Delta \sqrt{\frac{T}{R}}$ independent of Z , $\Delta n = 0$.

(7)					(8)			(9)		
Config.	$4d^{10}$	$5d$	$-$	$2D \ 3/2$	$4d^{10}$	$5d$	$-$	$2D \ 5/2$	$4d^{10}$	$7s - 2s_{\frac{1}{2}}$
Atom	Z	$T(\text{cm}^{-1})$	\sqrt{T}	$\sqrt{T/R}$	$T(\text{cm}^{-1})$	\sqrt{T}	$\sqrt{T/R}$	$T(\text{cm}^{-1})$	\sqrt{T}	$\sqrt{T/R}$
Ag I	47	12360	111.2	.318	12339.9	111.1	.318	9217.3	95	.290
Cd II	48	46685.3	215.8	.653	46531.0	215.7	.651	29077.1	170.5	.516
IndIII	49	97675	312.5	.945	97385	312.1	.944	56706	238	.719
Sn IV	50	163374	404.2	1.22	163267	404.1	1.22	91063	302	.913
Sb V	51	247393	497.4	1.50	246564	496.6	1.50	-	-	-

TABLE IIA (Continued)

FIRST FORM OF IRREGULAR-DOUBLET LAW: $\sqrt{T/R}$ independent of $Z, \Delta n = 0$.

(10)					(11)		
Config.	$4d^{10} 6d - 2D_{3/2}$				$4d^{10} 6d - 2D_{5/2}$		
Atom	Z	$T(\text{cm}^{-1})$	\sqrt{T}	$\sqrt{T/R}$	$T(\text{cm}^{-1})$	\sqrt{T}	$\sqrt{T/R}$
Ag I	47	6899.8	83	.250	6890.5	83	.251
Cd II	48	26202.1	161.8	.488	26128.6	161.7	.487
Ind III	49	55602	235.8	.711	55420	235.4	.710
Sn IV	50	93885	306.4	.923	93553	305.8	.925
Sb V	51	-	-	-	-	-	-

(12)					(13)		
Config.	$4d^{10} 4f - 2F^{\circ}_{5/2}$				$4d^{10} 4f - 2F^{\circ}_{7/2}$		
Atom	Z	$T(\text{cm}^{-1})$	\sqrt{T}	$\sqrt{T/R}$	$T(\text{cm}^{-1})$	\sqrt{T}	$\sqrt{T/R}$
Ag I	47	6990.4	83.6	.252	6990.4	83.6	.252
Cd II	48	27955.1	167.2	.504	27942.3	167.2	.504
Ind III	49	64154	253	.765	64154	253	.765
Sn IV	50	211243	460	1.39	211231	460	1.39
Sb V	51	-	-	-	-	-	-

TABLE IIB

ALTERNATIVE FORM OF IRREGULAR-DOUBLET LAW

(V a linear function of Z)

TRANSITION	V(CM. ⁻¹)				
	Ag I	Cd II	Ind III	Sn IV	Sb V
A $4d^{10}5s\ 2S_{\frac{1}{2}} - 4d^{10}5p\ 2P_{\frac{1}{2}}$	29552.3	44135.3	57185.0	69559.0	81566.0
B $4d^{10}6s\ 2S_{\frac{1}{2}} - 4d^{10}6p\ 2P_{\frac{3}{2}}$	5943.7	12393.9	19047.0	25891.0	-
C $4d^{10}5p\ 2P_{\frac{3}{2}} - 4d^{10}5d\ 2D_{\frac{3}{2}}$	18291.6	43227.1	67221.0	89327.0	112182.0
D $4d^{10}6s\ 2S_{\frac{1}{2}} - 4d^{10}6d\ 2D_{\frac{3}{2}}$	11648.7	27184.3	43653.0	60655.0	-

TABLE IIC (1)

REGULAR-DOUBLET LAW: Application of Landé Doublet Formula to Second Long Period

Configuration		$4d^{10}6p$	$\Delta V = {}^2P_{\frac{1}{2}}^o - {}^2P_{\frac{3}{2}}^o$						$4d^{10}6d$	$\Delta V = {}^2D_{3/2} - {}^2D_{5/2}$					
Atom	Z	$\Delta V(\text{cm}^{-1})$ observed	n^*	$u =$ $n - n^*$	Z_o	$S_o =$ $Z - Z_o$	Z_i	$s_i =$ $Z - Z_i$	$\Delta V(\text{cm}^{-1})$ observed	n^*	$u =$ $n - n^*$	Z_o	$S_o =$ $Z - Z_o$	Z_i	$s_i =$ $Z - Z_i$
AgI	47	203.4	2.927	3.073	1	46	41.87	5.13	9.3	3.988	2.012	1	46	24.66	22.34
CdII	48	673.3	3.246	2.754	2	46	44.38	3.62	73.5	4.093	1.907	2	46	36.04	11.96
IndIII	49	1337	3.480	2.520	3	46	46.38	2.62	182	4.214	1.786	3	46	39.50	9.5
SnIV	50	2177	3.663	2.337	4	46	47.94	2.06	332	4.324	1.676	4	46	41.59	8.41
SbV	51	-	-	-	5	46	-	-	-	-	-	5	46	-	-

Configuration		$4d^{10}5p$	$\Delta V = {}^2P_{\frac{1}{2}}^o - {}^2P_{\frac{3}{2}}^o$					
Atom	Z	$\Delta V(\text{cm}^{-1})$ (observed)	n^*	$u =$ $n - n^*$	Z_o	$S_o =$ $Z - Z_o$	Z_i	$s_i =$ $Z - Z_i$
AgI	47	920.6	1.865	3.135	1	46	45.31	1.69
CdII	48	2483.2	2.181	2.819	2	46	47.00	1.00
IndIII	49	4342	2.418	2.582	3	46	48.43	.57
SnIV	50	6518	2.602	2.398	4	46	49.71	.29
SbV	51	8988	2.731	2.269	5	46	50.16	.84

TABLE IIC (2)

CADMIUM II

Config.	$\Delta V \text{ cm}^{-1}$ ($\Delta {}^2P_{\frac{3}{2}}^o$)	n^*3 2	Config.	$\Delta V(\text{cm}^{-1})$ ($\Delta {}^2D_{3,5}$)	n^*3 2 2
5p	2483.2	10.37	5d	154.3	28.82
6p	673.3	34.20	6d	73.5	68.57
7p	115.4	78.24	7d	39.8	132.9
8p	54.4	147.5	8d	23.5	228
9p	31.6	246.9	9d	14.9	359.7
			10d	9.9	534.2

TABLE IID

TERM TABLE FOR AG-LIKE ISOELECTRONIC SEQUENCE

AG I (Z = 47)					CD II (Z = 48)					
Config	Symbol	J	Term Value (cm^{-1}) ($= \frac{1}{\lambda}$) ₀	n^*	Config	Symbol	J	Term Value (cm^{-1})	n^*	$\frac{T}{Z^2}$ ₀
4d ¹⁰ 5s 5p	2S 2Po	1	61104.4	1.340	4d ¹⁰ 5s 5p	2S 2Po	1	136376.6	1.794	34094
		2	31552.1	1.865			2	92241.3	2.181	23060
		3	30631.5	1.893			3	89758.1	2.211	22440
6s 6p	2S 2Po	1	18548.5	2.432	4d ⁹ 5s ²	2D	3/2	67117.8	2.551	16779
		2	12808.2	2.927			5/2	61483.0	2.672	15371
5d	2D	3/2	12604.8	2.951	4d ¹⁰ 6s 5d	2S 2D	1	53386.4	2.867	13347
		5/2	12360.0	2.980			3/2	46685.8	3.066	11671
7s	2S	1	12339.9	2.982	6p	2Po	5/2	46531.0	3.071	11633
4f	2Fo	5/2,	9217.3	3.450			1	41665.8	3.246	10416
		7/2	6900.4	3.988			3/2	40992.5	3.272	10248
6d	2D	3/2	6899.8	3.988	7s	2S	1	29077.1	3.885	7269
		5/2	6890.5	3.991	4f	2F	5/2	27955.1	3.962	6989
8s	2S	1	5523.3	4.457			7/2	27942.3	3.963	6986
7d	2D	3/2	4404.1	4.992	6d	2D	3/2	26202.1	4.093	6551
		5/2	4398.6	4.995			5/2	26128.6	4.099	6532
5f	2Fo	5/2,	4394.8	4.997	7p	2Po	1	24001.7	4.277	6000
		7/2					3/2	23886.3	4.287	5972
9s	2S	1	3680.5	5.460	8s	2S	1	18335.5	4.893	4584
8d	2D	3/2	3054.6	5.994	5f	2Fo	5/2	17828.7	4.962	4457
		5/2	3050.9	5.998						

TABLE IID

Continued....

AG I ($Z=47$)					CD II ($Z=48$)					
Config	Symbol	J	Term Value (cm^{-1}) ($=T/Z_o^2$)	n *	Config	Symbol	J	Term Value (cm^{-1})	n *	$\frac{T}{Z_o^2}$
10s	2S	$\frac{1}{2}$	2626.7	6.464			7/2			
9d	2D	3/2	2241.7	6.997	5g	2G	7/2, 9/2	17624.0	4.991	4406
		5/2	2239.9	6.999	7d	2D	3/2	16854.0	5.103	4214
11s	2S	$\frac{1}{2}$	1968.0	7.467			5/2	16814.2	5.109	4204
10d	2D	3/2	1714.9	7.999	8p	2Po	$\frac{1}{2}$	15722.4	5.284	3931
		5/2	1713.8	8.002			3/2	15668.0	5.293	3917
12s	2S	$\frac{1}{2}$	1524.8	8.4845	9s	2S	$\frac{1}{2}$	12624.3	5.896	3157
11d	2D	3/2	1353.9	9.003	6f	2Fo	5/2	12386.8	5.953	3097
		5/2	1353.4	9.005			7/2	12403.0	5.949	3101
12d	2D	3/2	1100.5	9.986	6g	2G	7/2, 9/2	12223.2	5.993	3056
					8d	2D	3/2	11762.4	6.109	2941
							5/2	11738.9	6.115	2935
					9p	2Po	$\frac{1}{2}$	11151.4	6.274	2788
							3/2	11119.8	6.283	2780
					10s	2S	$\frac{1}{2}$	9223.2	6.899	2306
					7f	2Fo	5/2	9092.5	6.948	2273
							7/2	9126.5	6.935	2282

TABLE IID (Continued)

CD II ($Z = 48$) Continued						SN IV ($Z = 50$)					
Config	Symbol	J	Term Value (CM^{-1})	n^*	$\frac{T}{Z_o^2}$	Config	Symbol	J	Term Value (CM^{-1})	n^*	$\frac{T}{Z_o^2}$
$4d^{10}7g$	$2G$	$7/2,$ $9/2$	8977.9	6.992	2244	$4d^{10}5s$	$2S$	$\frac{1}{2}$	328671	2.311	20542
9d	$2D$	$3/2$	8678.8	7.112	2169	5p	$2P^o$	$\frac{1}{2}$	259112	2.603	16194
		$5/2$	8663.9	7.118	2166			$3/2$	252594	2.6365	15787
11s	$2S$	$\frac{1}{2}$	7033.8	7.900	1758	4f	$2F^o$	$5/2$	211243	2.883	13203
8f	$2F^o$	$5/2$	6957.5	7.943	1739			$7/2$	211231	2.883	13202
		$7/2$				5d	$2D$	$3/2$	163374	3.278	10211
8g	$2G$	$7/2,$ $9/2$	6872.1	7.992	1718			$5/2$	163267	3.280	10204
10d	$2D$	$3/2$	6667.6	8.114	1667	6s	$2S$	$\frac{1}{2}$	154540	3.370	9659
		$5/2$	6657.7	8.120	1664	6p	$2P^o$	$\frac{1}{2}$	130826	3.663	8177
12s	$2S$	$\frac{1}{2}$	5540.6	8.901	1385			$3/2$	128649	3.694	8041
11d	$2D$	$3/2$	5275.8	9.122	1319	5f	$2F^o$	$5/2$	115411	3.900	7213
		$5/2$	5283.3	9.115	1321			$7/2$	115246	3.903	7203
						6d	$2D$	$3/2$	93885	4.324	5868
								$5/2$	93553	4.332	5847
						7s	$2S$	$\frac{1}{2}$	91063	4.391	5691
						6f	$2F^o$	$5/2,$ $7/2$	74993	4.839	4687
						6g	$2G$	$7/2,$ $9/2$	70400	4.994	4400

TABLE IID (Continued)

[illegible]

TABLE II E

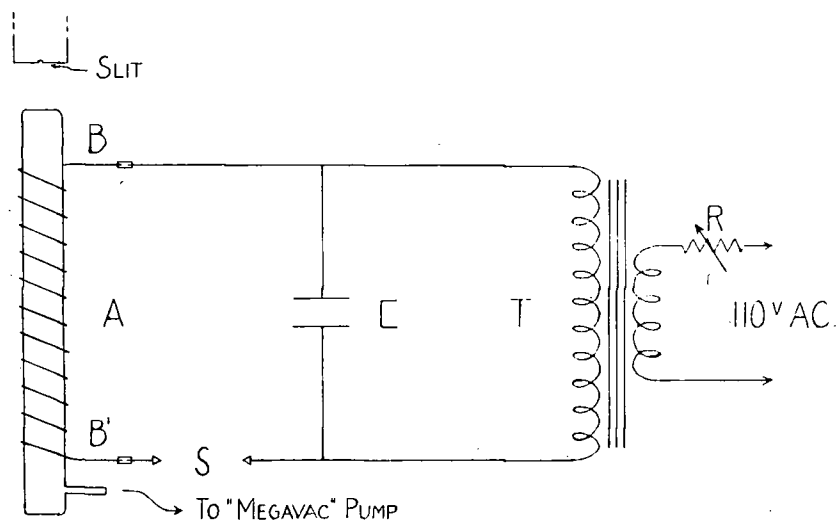
TERM TABLE FOR CADMIUM I - GIVING EFFECTIVE QUANTUM NOS. n^*

Config	Symbol	J	Term Value (CM ⁻¹) $= \frac{T}{Z_o^2}$	n^*	Config	Symbol	J	Term Value (CM ⁻¹) $= \frac{T}{Z_o^2}$	n^*
5s ²	1s	0	72538.8	1.230	5s8d	1d	2	3246.3	5.814
5s5p	3po	0	42424.5	1.608	9p	3po	0	3224.3	5.834
		1	41882.6	1.619			1	3217.4	5.840
		2	40711.5	1.642			2	3198.6	5.857
5p	1po	1	28846.6	1.950	8d	3D	1	3139.2	5.912
6s	3s	1	21054.7	2.283			2	3138.5	5.913
6s	1s	0	19229.3	2.389			3	3134.5	5.917
6p	3po	0	14147.9	2.785	9p	1po	1	3103.1	5.947
		1	14077.2	2.792	10s	3s	1	2732.9	6.337
		2	13903.1	2.809	10s	1s	0	2665.7	6.416
5d	1D	2	13319.2	2.870	9d	1D	2	2362.9	6.815
5d	3D	1	13052.4	2.900	10p	3po	0	2331.5	6.861
		2	13040.7	2.901			1	2331.5	6.861
		3	13022.5	2.903			2	2331.5	6.861
6p	1po	1	12633.2	2.947	9d	3D	2	2294.5	6.916
7s	3s	1	9975.6	3.317	10p	1po	1	2276.2	6.943
7s	1s	0	9452.1	3.407	11s	3s	1	2037.6	7.339
7p	3po	0	7542.9	3.814	11s	1s	0	1995.6	7.416
		1	7517.5	3.821	10d	1D	2	1796.9	7.815
		2	7446.0	3.839	10d	3D	2	1751.3	7.916
6d	1D	2	7404.9	3.850	11p	1po	1	1738.8	7.944
6d	3D	1	7185.3	3.908	12s	3s	1	1576.8	8.342
		2	7179.5	3.910	12s	1s	0	1546.7	8.432
		3	7171.3	3.912	11d	1D	2	1419.3	8.793

TABLE II E (Continued)

Config	Symbol	J	Term Value (CM ⁻¹) $= \frac{T}{Z^2}$ q	n *	Config	Symbol	J	Term Value (CM ⁻¹) $= \frac{T}{Z^2}$ q	n *
7p	1p ^o	1	7044.6	3.947	12p	1p ^o	1	1380.9	8.915
4f	3f ^o	2,3,4	6957.1	3.972	11d	3D	2	1379.3	8.920
8s	3S	1	5857.3	4.328	13s	3S	1	1257.0	9.343
8s	1S	0	5634.1	4.413	13s	1S	0	1239.8	9.408
8p	3p ^o	0	4709.2	4.827	12d	3D	2	1114.3	9.924
7d	1D	2	4701.7	4.831	14s	3S	1	1023.2	10.356
8p	3p ^o	1	4696.7	4.834	14s	1S	0	1010.8	10.419
		2	4663.6	4.851	13d	1D	2	942.5	10.790
7d	3D	1	4549.9	4.911	13d	3D	2	920.3	10.920
		2	4546.3	4.913	15s	3S	1	849.2	11.368
		3	4541.3	4.916	15s	1S	0	846.4	11.386
8p	1p ^o	1	4483.4	4.947	14d	1D	2	782.7	11.841
5f	2f ^o	2,3,4	4445.1	4.969	14d	3D	2	771.6	11.926
9s	3S	1	3856.6	5.335	15d	1D	2	669.6	12.802
9s	1S	0	3739.2	5.417	15d	3D	2	658.1	12.913
					16d	3D	2	566.7	13.916
					17d	3D	2	492.1	14.933
					18d	3D	2	430.6	15.964
					19d	3D	2	383.1	16.925

THE ELECTRODELESS DISCHARGE



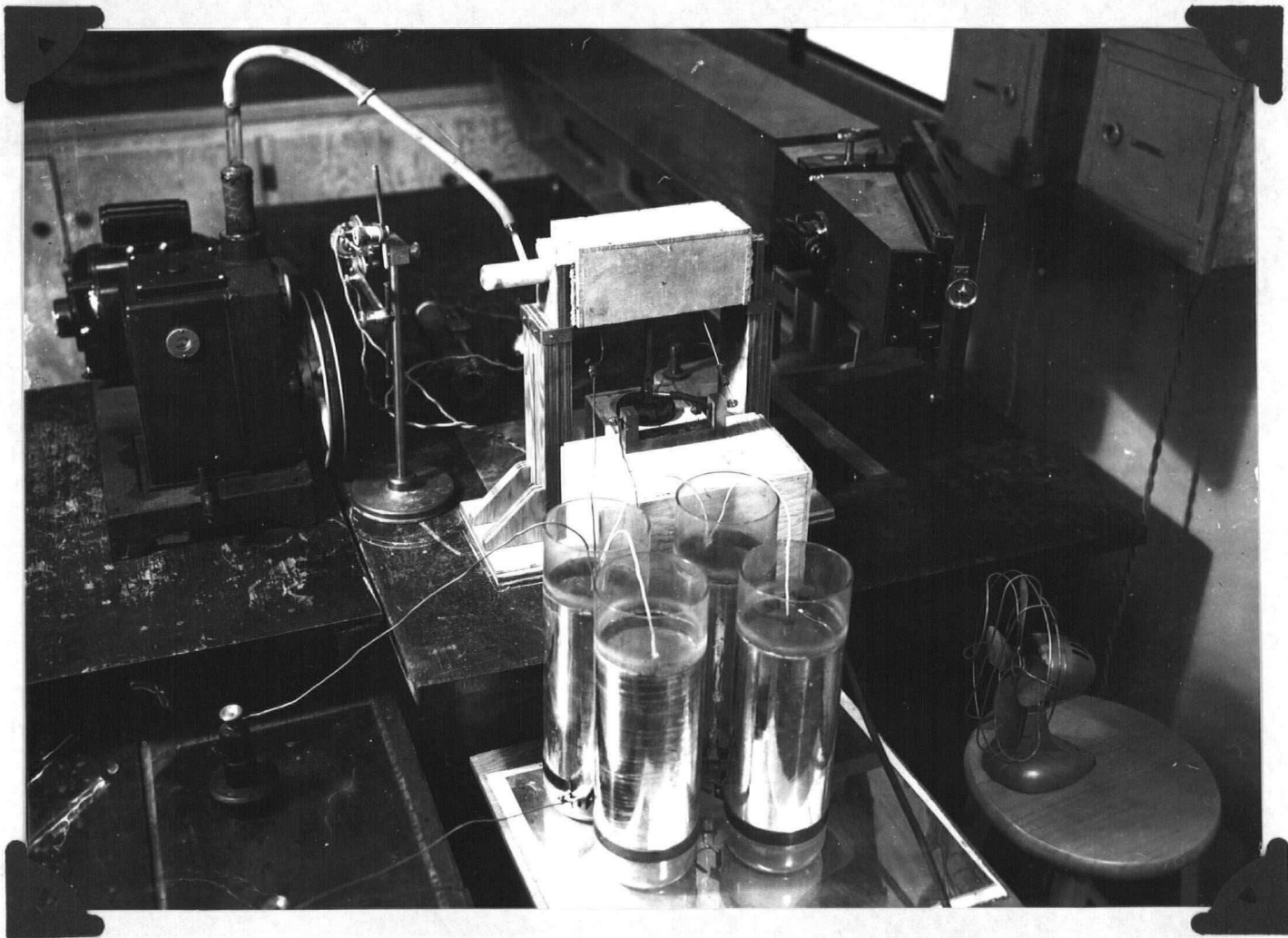


PLATE II

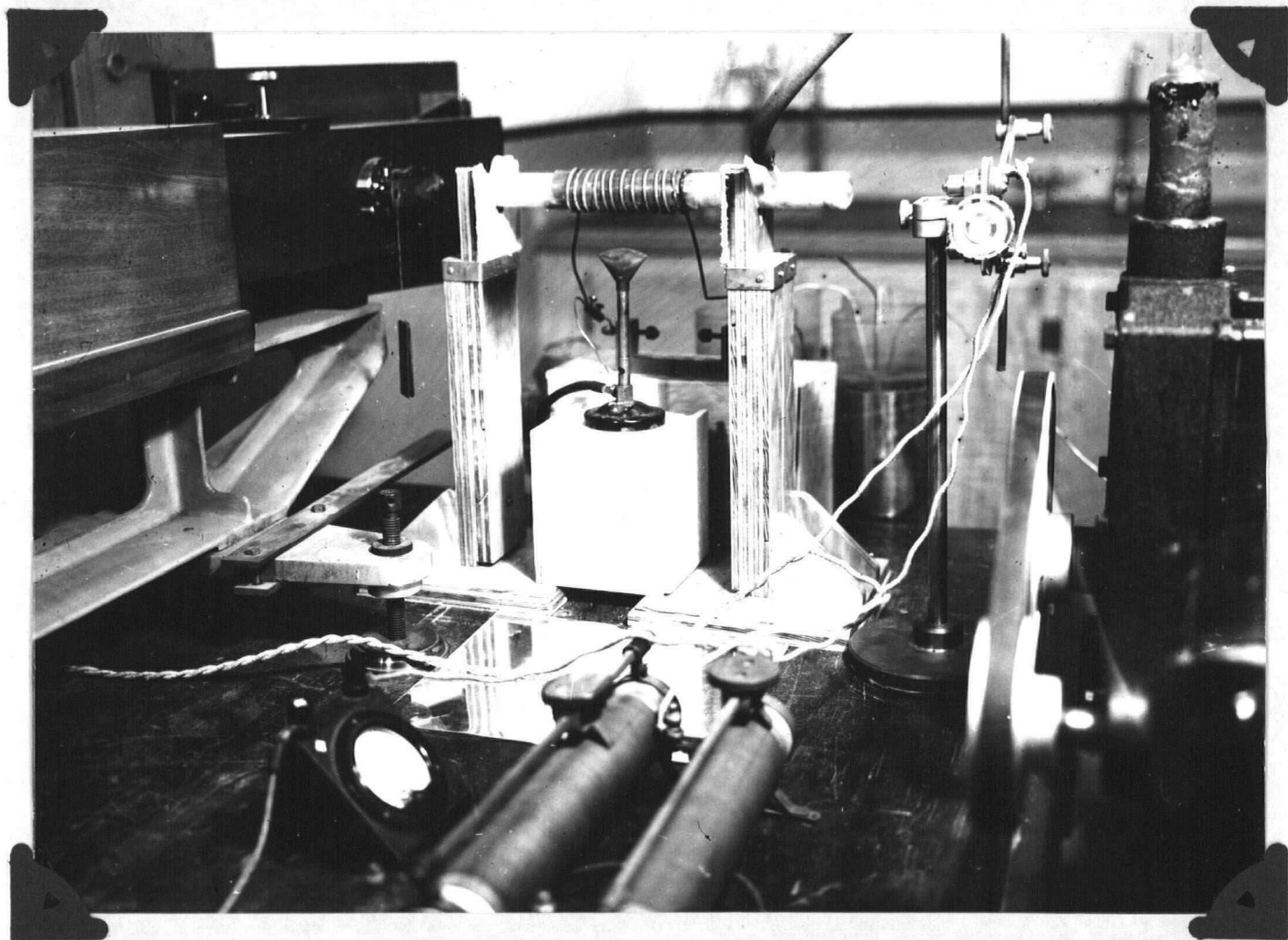


PLATE III

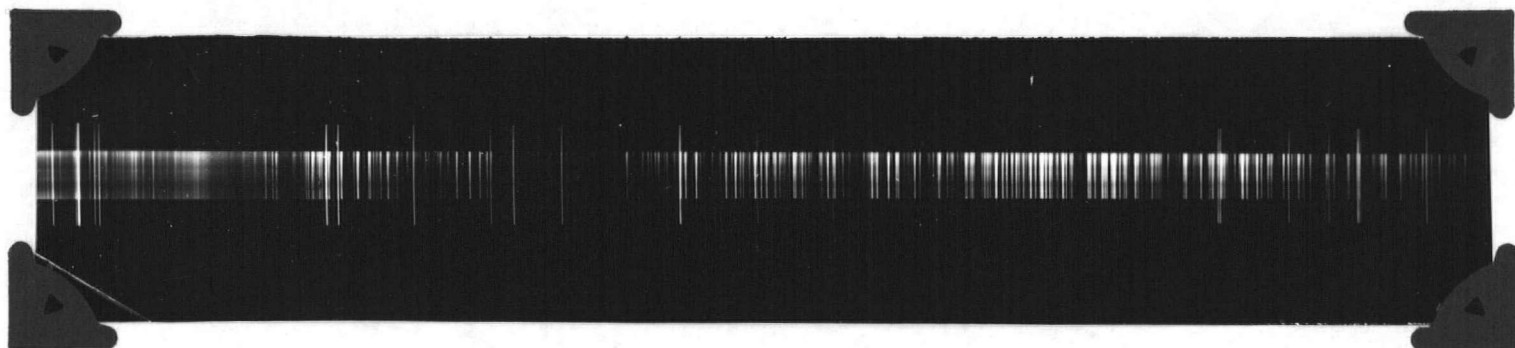
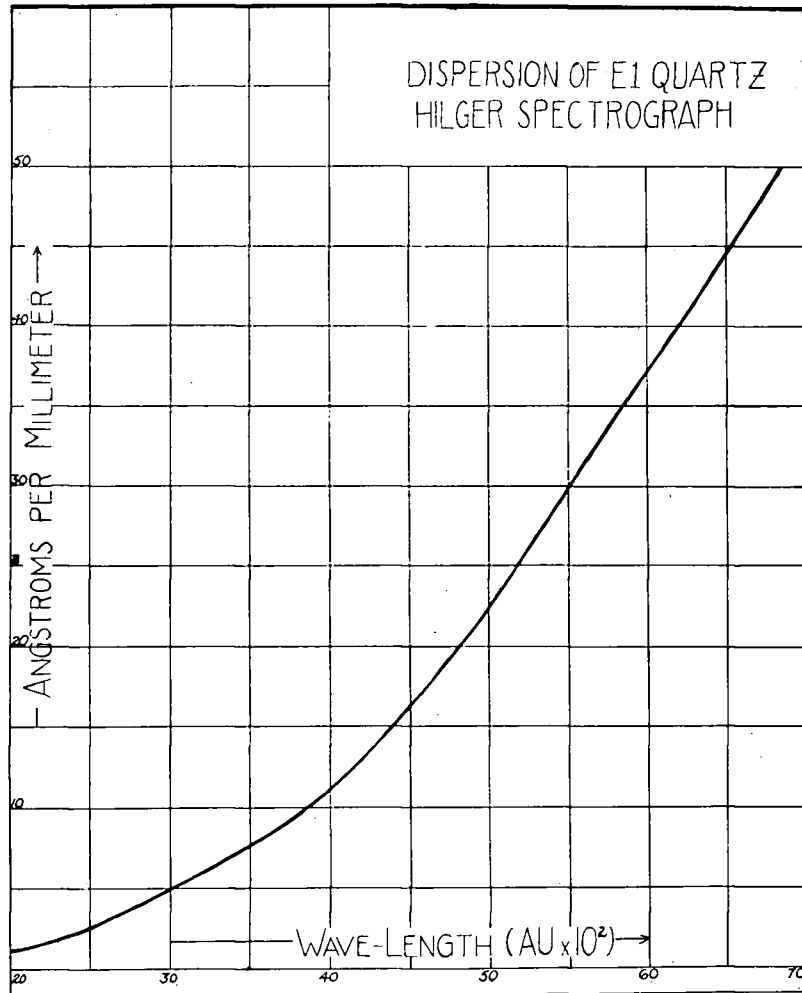


PLATE IV

CADMIUM SPECTRUM : REGION 6800\AA - 3300\AA .

Iron Arc Comparison in Centre.

PLATE V



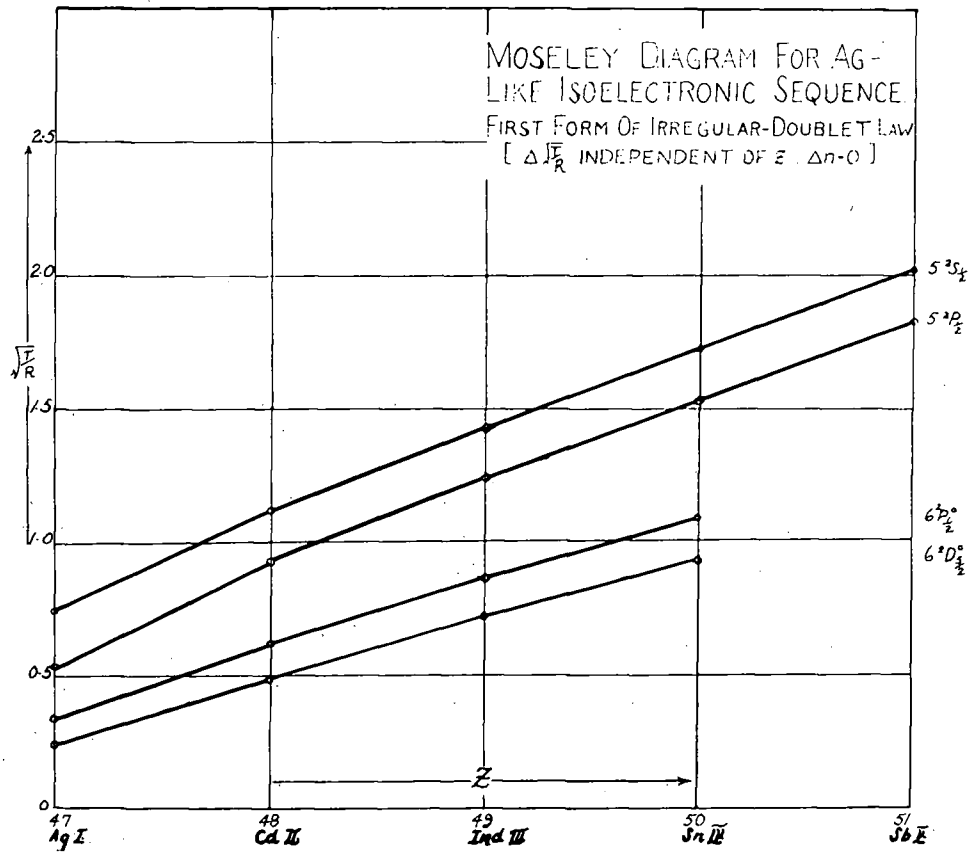


PLATE VII

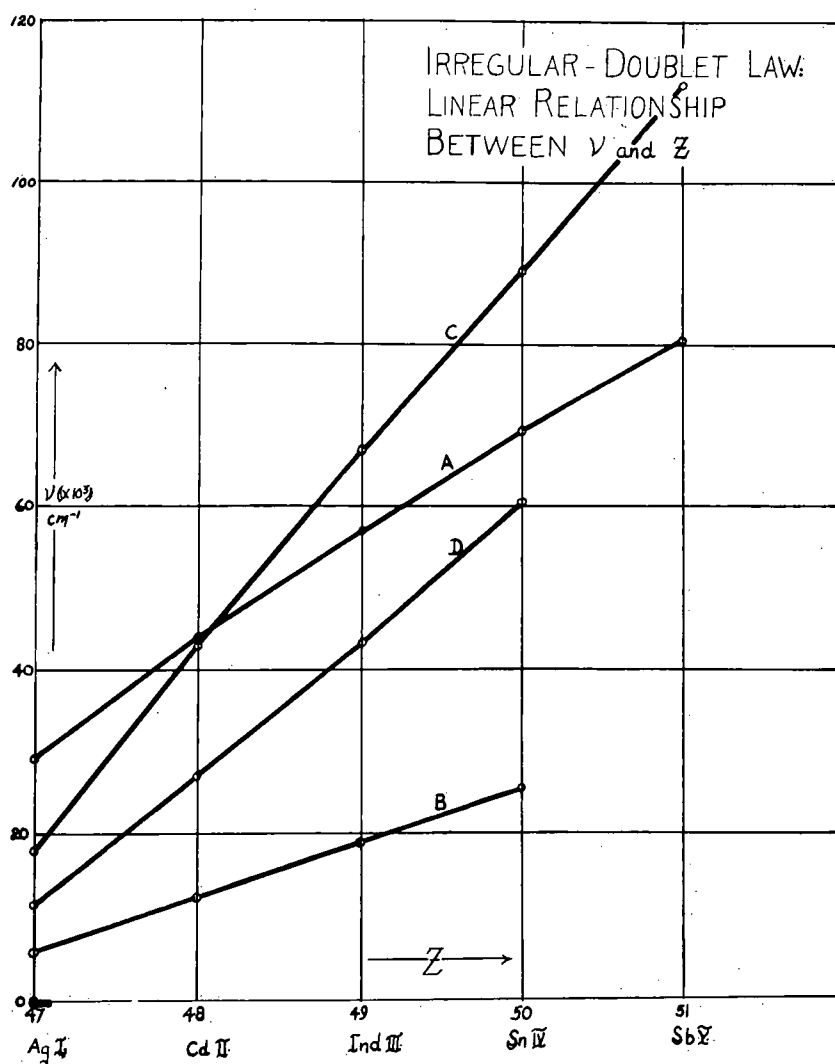
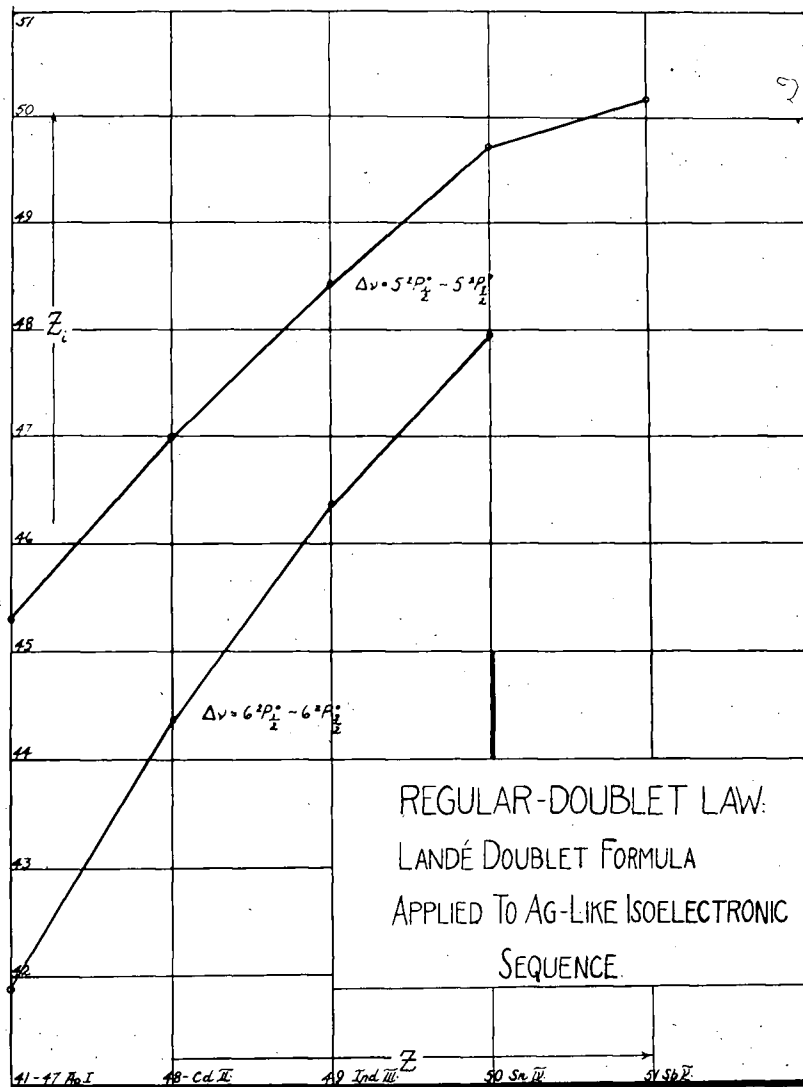
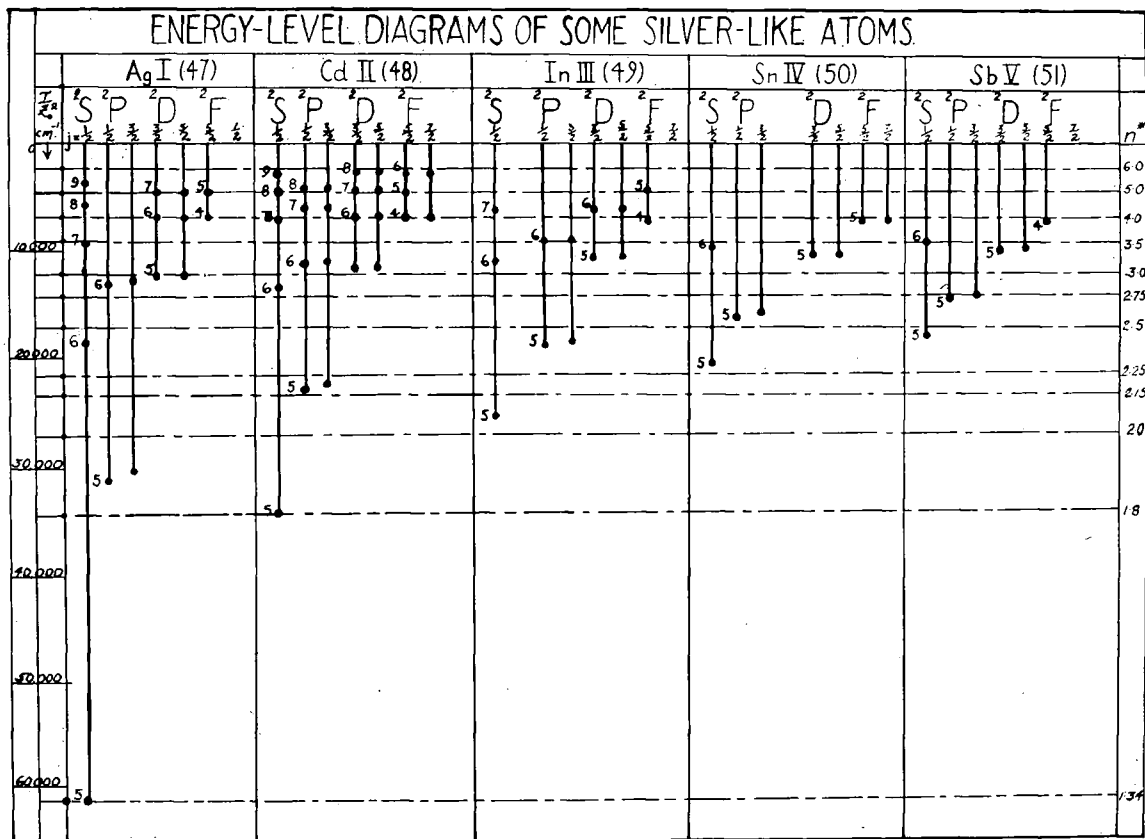


PLATE VIII



ENERGY-LEVEL DIAGRAMS OF SOME SILVER-LIKE ATOMS.



MODIFIED MOSELEY DIAGRAM OF AN AG-LIKE ISOELECTRONIC SEQUENCE

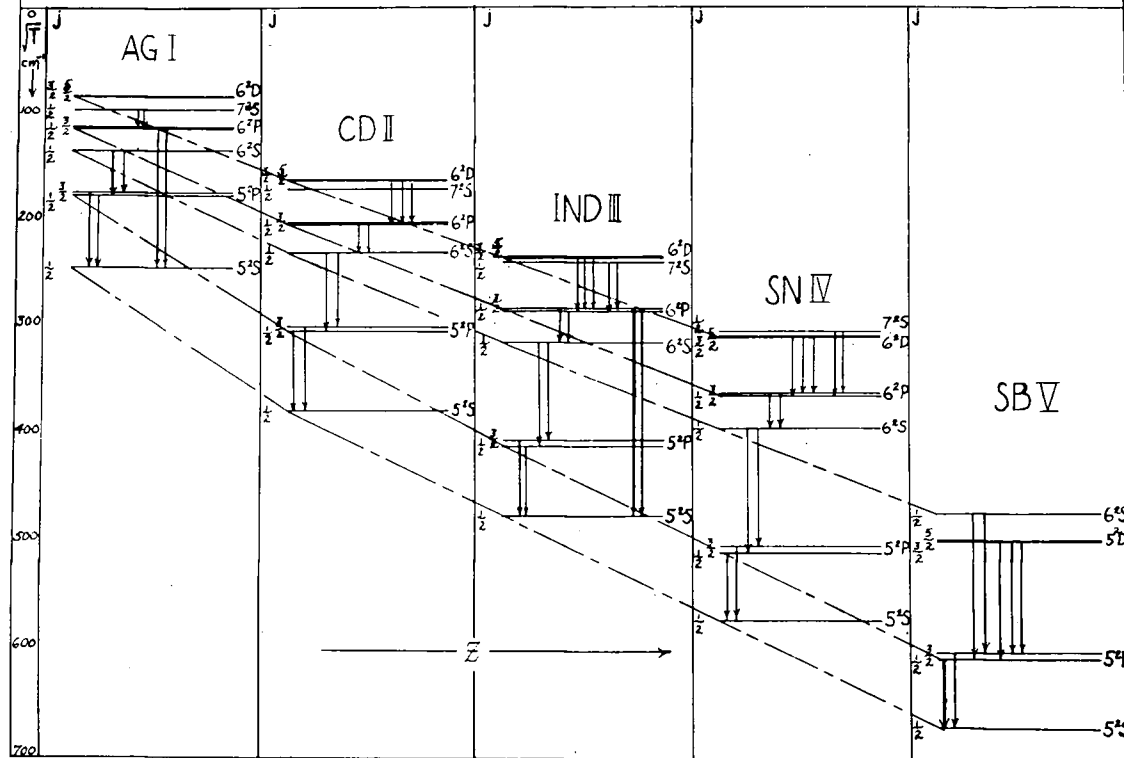
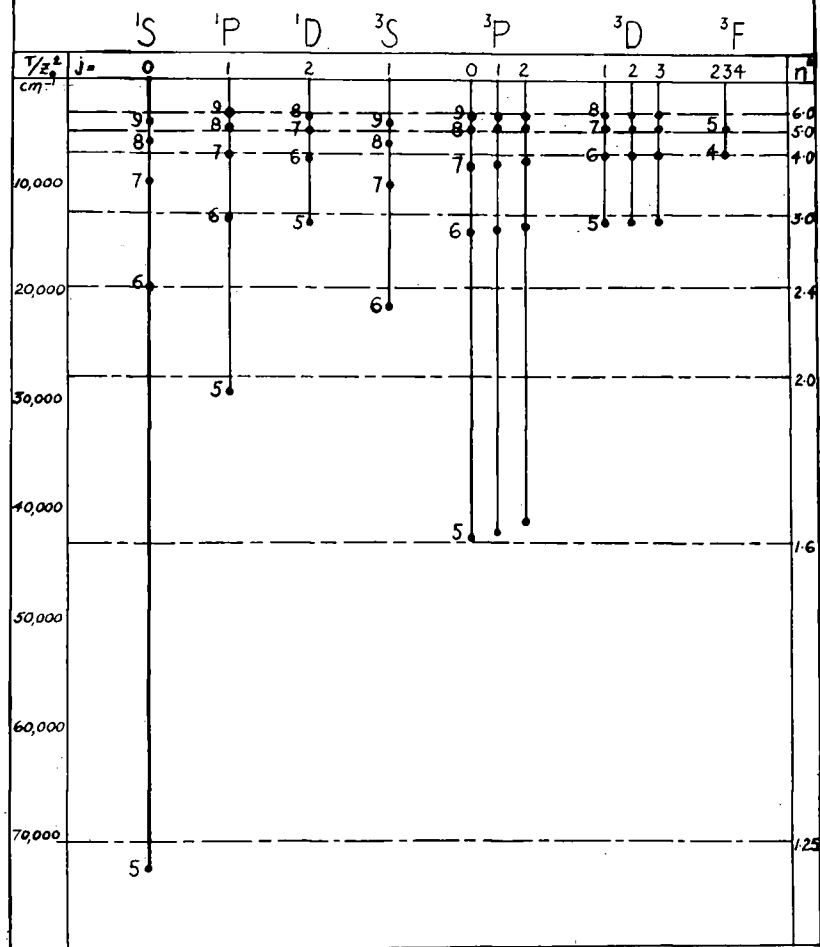


PLATE XI

ENERGY LEVEL DIAGRAM OF CADMIUM I



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