MAY, 1928 *PHYSICAL REVIEW* *VOLUME 31*

THE APPLICATION OF THE X-RAY LAWS TO OPTICAL SPECTRA OF HIGHER RANK, AND THE CLASSIFICATION OF GA IV AND GE V

By J. E. Mack, Otto Laporte, and R. J. Lang

Abstract

Spectra of Ga IV and Ge V.—By application of the Moseley law and the two doublet laws of x-ray spectroscopy, the $(3d^94s)$ and $(3d^94p)$ levels of Ga IV and Ge V and a tentative $(3d^{10})$ level for Ga IV, have been found. The levels formerly classified as $^3D_1$, $^1P_1(3d^94p)$ of Zn III have been interchanged.

Correlation of inverted multiplet levels to series limits.—On the hypothesis that as the nuclear charge increases the levels of an isoelectronic sequence tend to cluster relatively into groups forecasting the next higher ion due to a transition from *ls*- to *jj*-coupling, evidence is adduced to show that of the ^3D, $^1D(d^9s)$, the $^3D_2$ level approaches the limit $^2D_3(d^9)$, contrary to the theory of Hund. The case is analogous to that of Ne, in whose empirical series $^3P_1(2p^53s)$ approaches $^2P_2(2p^5)$.

Distinctions between x-ray and optical spectra, in application of the x-ray laws.—(1) Exact representation of isoelectronic optical spectra on a Moseley diagram generally requires knowledge of series limit correlations of individual levels; the problem is close to that of general term-representation. (2) X-ray energy levels are ionization energies of neutral atoms, whereas in isoelectronic spectra the net charge increases with the atomic number Z; the first order screening number σ_1 increases with Z in x-ray spectra, but decreases to an asymptote in isoelectronic spectra. The difference might be explained by outer screening.

Shape of the σ_1 curve for isoelectronic spectra.—If σ_1 is plotted as a function of Z, the initial slope of the curve depends upon the n- and l-values of the added electron but changes only slowly with the total number of electrons, and substantially not at all with the ion configuration for a given number of electrons; this rule implies that the lines on the Moseley diagram, representing the addition of a given n_l electron to different isoelectronic sequences containing nearly the same number of electrons, are parallel, to a second approximation.

The irregular doublet law applied to isoelectronic sequences in the neighborhood of a closed d-shell (d^{10}), is valid for $(p)^{1/2}-(s)^{1/2}$ but not for $(d)^{1/2}-(p)^{1/2}$ or $(f)^{1/2}-(d)^{1/2}$.

I. Introduction

The work of Millikan and Bowen[1] extended the application of the following three laws of x-ray spectra into the field of optical spectroscopy:

The Moseley law[2]

$$\nu^{1/2} = \text{a linear function of } Z \tag{1}$$

where ν is the energy value of a level referred to the next higher ion, and Z is the atomic number.

The Sommerfeld law of regular or relativistic doublets[2]

$$\Delta\nu = \frac{\alpha^2 R(Z-\sigma_2)^4}{n^3 l(l+1)} \tag{2}$$

---

[1] R. A. Millikan and I. S. Bowen, many papers, especially in Phys. Rev., 1924–1927.

[2] The higher degree terms in α^2 that enter into the exact infinite series expressions are extremely small in optical spectra and are omitted in Eqs. (1) to (3).

between two levels of equal n and equal l but different j; where α and R are universal constants and σ_2 is independent of Z.

The irregular or screening doublet law[2] of Hertz

$$\Delta(\nu^{1/2}) \text{ is independent of } Z \tag{3a}$$

or

$$\Delta\nu = \text{a linear function of } Z \tag{3b}$$

between two levels of equal n but different l.

Since the early work of Millikan and Bowen, these laws have been used extensively in the classification of optical spectra, and the doublet laws have been extended in some cases to apply to terms of higher multiplicity. In the first long period, in particular, Gibbs and White[3] and Russell[4] and Lang have applied them to the frequencies of the lines of combination between low terms in systems of several electrons, especially in the first part of the period.* Laporte and Lang[5] have applied them at the other end of the period in the classification of Zn III, by extrapolation from the classifications of the spectra of Ni I[6] and Cu II.[7] In this paper it is shown that these laws may still be used most succesfully in cases where the spectra are of higher rank, i.e., lacking that multiplet structure characteristic of "normal" spectra. They are applied to higher spark spectra at the end of the iron group, isoelectronic with Ni I; namely to Ga IV and Ge V.

While the x-ray laws are used in this investigation in the simple forms expressed in Eqs. (1) to (3), it is shown in Chapter VIII that it is impossible to apply them in general to the optical region, except in the first approximation; and the distinctions between the x-ray region and the optical region from the viewpoint of the applicability of these laws, are examined.

The ten-electron systems are an especially appropriate subject for investigation of higher coupling, since, being at the end of a period, they are a true analogue of neon, the first spectrum where the breakdown of the Russell-Saunders coupling was noticed and other coupling schemes were tested. The similarity between the energy diagrams of the spectra under consideration here, and that of neon, is discussed in Chapter VII.

II. Experimental Procedure

The vacuum-spark between electrodes of pure metallic germanium and aluminum cored with pure metallic gallium was photographed on the two-meter grating as previously described for zinc.[5] The aluminum was of exceptional purity; it was generously supplied by the research department of the Aluminum Company of America.

---

* See note added to proof, at the end of the paper.

[3] R. C. Gibbs and H. E. White, Natl. Acad. Sci. Proc. **13**, 525 (1927).

[4] H. N. Russell and R. J. Lang, Astroph. Jour. **66**, 13 (1927); H. N. Russell, Astroph. Jour., **66**, 233 (1927); **66**, 347 (1927).

[5] O. Laporte and R. J. Lang, Phys. Rev. **30**, 378 (1927).

[6] K. Bechert and L. A. Sommer, Ann. d. Physik **77**, 351 (1925); K. Bechert, Ann. d. Physik **77**, 537 (1925).

[7] A. G. Shenstone, Phys. Rev. **29**, 380 (1927).

The source of excitation was a large x-ray coil, the primary of which was joined, through suitable resistance, to the 110-volt A.C. 60 cycle mains. To the secondary of the coil two spark-gaps were joined in series, one in vacuum and the other in air. The latter was between brass spheres about one cm in diameter and the gap width varied between one and two cms. Across this circuit, in parallel with the secondary of the coil, sufficient capacity in the form of glass plate condensers was used to give an approximately resonant circuit.

TABLE I. *Classification of lines of Ga IV (see footnote 12).*

$(3d^94s)$ / $(3d^94p)$			$^3D_3$ 0		$^3D_2$ 1455		$^3D_1$ 3575		$^1D_2$ 6512
				1455		*2120*		*2937*	
$^3P_2$	74730		74730 (15) 0		73281 (1) 6		71146 (0) −9		68216 (1) −2
		3081							
$^3P_1$	77811				76356 (9) 0		74239 (3) 3		71291 (2) −8
		1820							
$^3P_0$	79631						76056 (5) 0		
		−187							
$^3F_4$	79444		79444 (15) 0						
		−1271							
$^3F_3$	78172		78172 (10) 0		76718 (15) 1				71658 (4) −2
		2358							
$^3F_2$	80530		80533 (1) 3		79076 (10) 1		76954 (15) −1		74018 (0) 0
		3148							
$^3D_3$	83678		83678 (10) 0		82224 (00) 1				77166 (15) 0
		636							
$^3D_2$	84314		84313 (0) −1		82857 (10) −2		80740 (5) 1		77804 (12) 2
		3080							
$^3D_1$	87394				85938 (3) −1		83820 (9) 1		80881 (3) −1
		−1968							
$^1F_3$	85426		85427 (10) 1		83970 (9) −1				78920 (18-Ga III) 4
		1375							
$^1P_1$	86801				85344 (0) −2		83225 (4) −1		80289 (12) 0
		1144							
$^1D_2$	87945		87947 (1) 2		86489 (5) −1		84370 (8) 0		81434 (10) 1

Very considerable difficulty had been encountered in the past in getting intense spectrograms owing to a fogging effect in the vacuum chamber which caused the Schumann plates to blacken uniformly over the whole film surface very shortly after being placed in the developer. That this was not due to stray light was evident at once because of the absence of shadows. It was therefore attributed to fluorescence of the residual gases in the vacuum chamber, to ions formed from the gases in the vacuum chamber, or to ions formed from the gases in the spark. Following the advice of Dr. I. S.

Bowen, an attempt was made to obtain a higher vacuum. This was done by covering the end castings of the instrument with heavy coats of enamel paint and attaching an all metal "Kaye" diffusion pump to the main body of the spectrograph. These changes resulted in a great improvement in the intensity and contrast of the plates. The absence of a supply of liquid air has been a very great handicap in the successful operation of the instruments.

TABLE II. *Wave-length list of Ga IV (see footnote 12).*

Weinberg		Carroll		This investigation			
λ vac. I. A.	Int.	λ vac. I. A.	Int.	λ vac. I. A.	Int.	ν	desgination $(d^9s)-(d^9p)$
1465.7	4	1466.0	1	1465.93	1	68216	$^1D_2-{}^3P_2$
				1405.55	0	71146	$^3D_1-{}^3P_2$
		1402.88	3	1402.70	2	71291	$^1D_2-{}^3P_1$
		1395.58	3	1395.51	4	71658	$^1D_2-{}^3F_3$
		1364.73	3	1364.60	1	73281	$^3D_2-{}^3P_2$
		1351.2	2	1351.03	2	74018	$^1D_2-{}^3F_2$
		1347.09	3	1346.99	3	74239	$^3D_1-{}^3P_1$
1338.0	8	1338.15	6	1338.15	15	74730	$^3D_3-{}^3P_2$
1314.8	6	1314.86	4	1314.81	5	76056	$^3D_1-{}^3P_0$
1309.7	9	1309.73	5	1309.65	10	76356	$^3D_2-{}^3P_1$
1303.5	11	1303.56	6δ	1303.48	15	76718	$^3D_2-{}^3F_3$
1299.5	9	1299.49	6	1299.48	15	76954	$^3D_1-{}^3F_2$
1295.9	10	1295.91	6	1295.90	15	77166	$^1D_2-{}^3F_3$
1285.2	9	1285.39	5	1285.28	12	77804	$^1D_2-{}^3D_2$
1279.2	9	1279.30	5	1279.23	10	78172	$^3D_3-{}^3F_3$
1267.0	9	1267.19	6	1267.11	18*a*	78920	$^1D_2-{}^1F_3$
1264.5	8	1264.64	4	1264.60	10	79076	$^3D_2-{}^3F_2$
1258.8	10	1258.81	7	1258.75	15	79444	$^3D_3-{}^3F_4$
1245.4	7	1245.56	4	1245.50	12	80289	$^1D_2-{}^1P_1$
		1241.6	0	1241.73	1	80533	$^3D_3-{}^3F_2$
1238.4	7	1238.58	3	1238.54	5	80740	$^3D_1-{}^3D_2$
		1236.40	3	1236.38	3	80881	$^1D_2-{}^3D_1$
1228.0	9	1228.01	6	1227.98	10	81434	$^1D_2-{}^1D_2$
				1216.19	00	82224	$^3D_2-{}^3D_3$
		1206.9	4δ	1206.89	10	82857	$^3D_2-{}^3D_2$
1201.4	7	1201.55	3	1201.56	4	83225	$^3D_1-{}^1P_1$
1195.0	8	1195.02	4	1195.05	10	83678	$^3D_3-{}^3D_3$
1192.9	8	1192.99	4	1193.02	9	83820	$^3D_1-{}^3D_1$
1190.7	7	1190.81	4	1190.90	9	83970	$^3D_2-{}^1F_3$
				1186.06	0	84313	$^3D_3-{}^3D_2$
		1185.20	4	1185.25	8	84370	$^3D_1-{}^1D_2$
				1171.73	0	85344	$^3D_2-{}^1P_1$
1170.3	13	1170.57	5	1170.59	10	85427	$^3D_3-{}^1F_3$
1163.4	9	1163.58	4	1163.63	3	85938	$^3D_2-{}^3D_1$
1156.0	10	1156.3	4δ	1156.21	5	86489	$^3D_2-{}^1D_2$
1136.9	8	1136.99	2	1137.05	1	87947	$^3D_3-{}^1D_2$

δ Diffuse.
a Also classified in Ga III: $4^2P_1-4^2D_2$.

The degree of ionization attained by the metallic atoms in the source depends on many factors; one of the most important, after the actual potential of the coil, is the width of the spark-gaps, especially the external gap. In spite of the fact that the potential attained is estimated to be between 50,000 and 100,000 volts it was found impossible with the present apparatus to excite the spectrum of Ge V. This failure was perhaps the more unexpected owing to the fact that the lines of the less-ionized Ge spectra seem to be rather more easily excited than one might expect. For example, several lines identified as belonging to Ge III appear in the spectrum from a Geissler tube containing $GeCl_4$.[8] On the other hand, the present apparatus brings out but faintly the lines of V V and Cr VI.

III. THE CLASSIFICATION OF GA IV AND GE V

The classification of Ga IV is given in Tables I and II, and that of Ge V in Tables III and IV. The data of Table I are all original with this investigation; in Table II, wave-lengths and intensities are repeated from Miss Weinberg's[9] table, which extends to 157A, and Carroll's.[10] All the experimental data on germanium are from Carroll's[10] table. Both Carroll's tables extend to 600A.

TABLE III. *Classification of lines of Ge V.*

($3d^94p$)		($3d^94s$)	$^3D_3$ 0		$^3D_2$ 1740		$^3D_1$ 4536		$^1D_2$ 7716	
				1740		*2796*		*3180*		
$^3P_2$	89541		89542 1	(6)	87796 −5	(0)	85012 7	(0)	81806 −19	(0)
		4083								
$^3P_1$	93624				91886 2	(8-Ge III)	89095 7	(1)	85896 −12	(4)
		2487								
$^3P_0$	96111						91575 0	(5)		
		−463								
$^3F_4$	95648		95648 0	(7)						
		−2113								
$^3F_3$	93535		93537 2	(5)	91794 −1	(5)			85815 −4	(0)
		3039								
$^3F_2$	96574				94832 −2	(4)	92039 1	(5)	88865 7	(0)
		4382								
$^3D_3$	100956		100959 3	(5)	99206 −10	(0)			93240 0	(6)
		362								
$^3D_2$	101318				99582 4	(6)	96768 −14	(3)	93607 5	(5)
		4005								
$^3D_1$	105323				103584 1	(2)	100786 −1	(4)	97618 11	(0)
		−2362								
$^1F_3$	102961		102955 −6	(6)	101225 4	(5)			95247 2	(5)
		1063								
$^1P_1$	104024						99483 −5	(1)	96311 3	(4)
		2056								
$^1D_2$	106080		106078 −2	(2)	104341 1	(3)	101544 0	(4)	98377 13	(8δ)

δ Diffuse.

---

[8] J. Lunt, Roy. Astr. Soc., M. N. **85,** 1 (1924).

[9] M. Weinberg, Roy. Soc. Proc., **A107,** 138 (1925).

[10] J. A. Carroll, Phil. Trans. Roy. Soc., **A225,** 357 (1925).

TABLE IV. *Wave-length list of Ge V.* (Carroll)

λ vac. I. A.	Int.	ν	designation $(d^9s)-(d^9p)$	λ vac. I. A.	Int.	ν	designation $(d^9s)-(d^9p)$
1222.4	0	81806	$^1D_2-{}^3P_2$	1045.5	7	95648	$^3D_3-{}^3F_4$
1176.3	0	85012	$^3D_1-{}^3P_2$	1038.3	4	96311	$^1D_2-{}^1P_1$
1165.3	0	85815	$^1D_2-{}^3F_3$	1033.4	3	96768	$^3D_1-{}^3D_2$
1164.2	4	85896	$^1D_2-{}^3P_1$	1024.4	0	97618	$^1D_2-{}^3D_1$
1139.0	0	87796	$^3D_2-{}^3P_2$	1016.5	8δ	98377	$^1D_2-{}^1D_2$
1125.3	0	88865	$^1D_2-{}^3F_2$	1008.0	0	99206	$^3D_2-{}^3D_3$
1122.4	1	89095	$^3D_1-{}^3P_1$	1005.2	1	99483	$^3D_1-{}^1P_1$
1116.8	6	89542	$^3D_3-{}^3P_2$	1004.2	6	99582	$^3D_2-{}^3D_2$
1092.0	5	91575	$^3D_1-{}^3P_0$	992.2	4	100786	$^3D_1-{}^3D_1$
1089.4	5	91794	$^3D_2-{}^3F_3$	990.5	5	100959	$^3D_3-{}^3D_3$
1088.3	8a	91886	$^3D_2-{}^3P_1$	987.9	5	101225	$^3D_2-{}^3F_3$
1086.5	5	92039	$^3D_1-{}^3F_2$	984.8	4	101544	$^3D_1-{}^1D_2$
1072.5	6	93240	$^1D_2-{}^3D_3$	971.3	6	102955	$^3D_3-{}^1F_3$
1069.1	5	93537	$^3D_3-{}^3F_3$	965.4	2	103584	$^3D_2-{}^3D_1$
1068.3	5	93607	$^1D_2-{}^3D_2$	958.4	3	104341	$^3D_2-{}^1D_2$
1054.5	4	94832	$^3D_2-{}^3F_2$	942.7	2	106078	$^3D_3-{}^1D_2$
1049.9	5	95247	$^1D_2-{}^3F_3$				

δ Diffuse
a Also classified in Ge III: $4^1S_0-4^1P_1$.

In Tables I and III the levels are designated at the heads of the columns and rows, with their values referred to $^3D_3(3d^94s)$; in the body of the tables are the wave numbers of the lines, followed in parentheses by their intensities. Below each wave number is the discrepancy (observed value minus calculated value) between the observed wave number and the wave number calculated from the positions assigned to the levels.

Tables II and IV are lists of the lines of Ga IV and Ge V classified in this investigation.

It will be noticed that all permitted combinations between the configurations (d^9p) and (d^9s) are found in Ga IV and all except three in Ge V, each of which would have been expected to be missing or at any rate very weak. The anomalous absence of $^3D_2(d^9s)-{}^3D_3(d^9p)$, was noted for Cu II and Zn III. This transition is recorded for Ga IV on the evidence of a mere trace found upon close re-examination of the plate, and for Ge V on the basis of a line which shows a deviation considerably greater than the probable error.

The simple average of the deviations in wave-numbers is 1.6 for Ga IV, and 4.6 for Ge V.

It will be seen that for both spectra the intensity relationships for combinations (except the $^3D_2-{}^3D_3$) between terms of the same multiplicity, are qualitatively in agreement with the intensity rules. This regularity persists from Ni I to Ge V. The intercombination intensities, in Ga IV and Ge V, which are anomalous, might have been extrapolated qualitatively from those of the previous spectra.

Table V shows the intensity of each line as a function of the nuclear charge. The levels are designated at the heads of the rows and columns. In the body of the table there appears in each space the intensity of the corresponding line for each of the five isoelectronic spectra. The table gives a survey of the relative change in intensity of the transitions with increasing nuclear charge; of course the intensity standards are different for the different spectra. As the nuclear charge increases, there is a considerable increase in the intensities of intercombinations relative to those of the singlet-singlet and triplet-triplet combinations; this relative increase is perhaps most marked in the *D-D* intercombinations.

TABLE V. *Intensities of lines in the spectra isolectronic with Ni I.*

		$(d^9p)^1P_1$	$^1D_2$	$^1F_3$	$^3P_0$	$^3P_1$	$^3P_2$	$^3D_1$	$^3D_2$	$^3D_3$	$^3F_2$	$^3F_3$	$^3F_4$
(d^9s)	Ni I		5	25R			200R		8	100R	8	70R	150R
	Cu II		2	7			10		1	8	3	4	10
D_3	Zn III		5	8			9		2	8	x	8	15
	Ga IV		1	10			15		0	10	1	10	15
	Ge V		2	6			6		—	5	—	5	7
	Ni I	20R	10	30R		150R	60R	5	100R	70R	20R	150R	
	Cu II	1	2	6		8	5	2	8	—	4	10	
$^3D_2$	Zn III	4	8	6		10	6	5	8	—	10	10	
	Ga IV	0	5	9		9	1	3	10	00	10	15	
	Ge V	—	3	5		8c	0	2	6	0	4	5	
	Ni I	10r	6		80R	50R	15	50R	20r		125R		
	Cu II	1	5		5	5	2	7	3		8		
$^3D_1$	Zn III	6	7		8	7	3	5	7−x		10		
	Ga IV	4	8		5	3	0	9	5		15		
	Ge V	1	4		5	1	0	4	3		5		
	Ni I	80R	100	150R		20	25	12	30r	35r	15	40r	
	Cu II	5	5	6		2	7	4	7	9	0	6	
$^1D_2$	Zn III	9	7	9		7	4	7b	8	10	3	9	
	Ga IV	12	10	18a		2	1	3	12	15	0	4	
	Ge V	4	8δ	5		4	0	0	5	6	0	0	

R, r Reversed.
δ Diffuse.
— Missing.
x, 7−x Intensities of an unresolved pair.
a Includes intensity of a Ga III line.
b Includes intensity of a carbon line.
c Includes intensity of a Ge III line.

IV. GENERAL SURVEY OF THE NICKEL-LIKE SPECTRA

The most stable terms arising from the grouping of twenty-eight electrons can be derived easily from the theory of Hund; they have been discussed in previous papers. [5,7] Based upon the next higher ion ($3d^9$), the important electron configurations in the spark spectra of this sequence, in the order of decreasing stability, and the terms arising from them are:

Configuration	Terms	Spectra
$3d^{10}$	^1S	I II III (IV?)[11]
$3d^94s$	$^3D\,^1D$	I II III IV V
$3d^94p$	$^3F\,^3D\,^3P\,^1F\,^1D\,^1P$	I II III IV V
$3d^94d$	$^3G\,^3F\,^3D\,^3P\,^3S\,^1G\,^1F\,^1D\,^1P\,^1S$	

and so on. The Roman numerals indicate the spectra among those in the isoelectronic sequence Ni I, Cu II, Zn III, for which the terms of a given configuration have been found previously, and Ga IV, Ge V, for which they are reported in this paper. A higher series member ($3d^9,5s$) in Ni I and Cu II, and a number of multiplets in Ni I arising from the addition of an electron to the ion configuration ($3d^84s$), complete the list of known terms for this sequence. Nickel is the only element in this period in whose arc spectrum a term arising from the configuration (d^z) has been identified among the low terms.

[11] See footnote 12.

The failure to establish the ^1S term in the high spark spectra is not surprising in view of the relative faintness which appears to be a general characteristic of spark lines involving (d^z) configurations; Shenstone[7] has mentioned this faintness in the cases of Cu II (d^{10}) and Ni II (d^9). It will be seen below (from Table VI) that the $(d^{10})-(d^9p)$ lines may be expected at about 425A for Ga IV and at about 310A for Ge V[12].

The $(d^9,5s)$ terms would be expected to be absent due to the usual sharp intensity decrease in lines from higher series members, especially where the excitation energy is extremely high as in this case. The $(d^9p)-(d^9,5s)$ lines would lie at about 860A for Ga IV and 610A for Ge V.

TABLE VI. *Approximate[13] ionizing potentials of configurations, referred to the limit configuration* $(3d^9)$.

Spectrum	$(3d^{10})$		$(3d^94s)$			$(3d^94p)$		$(3d^95s)$	
	volts	$(\nu/R)^{1/2}$	volts	$(\nu/R)^{1/2}$	n_{eff}	volts	$(\nu/R)^{1/2}$	volts	$(\nu/R)^{1/2}$
Ni I	6.1	.67	7.7	.75	1.33	4.1	.55	2.5	.44
Cu II	20.4	1.23	17.7	1.14	1.77	12.0	.94	7.2	.73
Zn III	40.4	1.73	30.5	1.50	2.00	22.7	1.30	(13.6)b	1.00
Ga IV	63.9	2.17	45.5	1.83	2.18	35.6	1.62	(21.3)b	1.25
Ge V	(90)	2.58	62.1	2.14	2.28	50.3	1.93	(30.0)b	1.49

b. Extrapolation of the (d^9,s) values by the usual optical method, using a Rydberg table and the n_{eff} values of the (d^9s) configuration, would yield (13.6) volts for Zn III, (21.4) volts for Ga IV, and (31.5) volts for Ge V.

Table VI gives the approximate[13] energy values (recorded in terms of ionizing potentials, 1 volt $=8100$ cm^{-1}) of the levels of the Ga IV and Ge V, referred to the most stable configuration (d^9) of the next higher ion. It includes, for completeness, the values of some of the important configurations in the other spectra of this isoelectronic sequence, together with the Moseley ordinates $(\nu/R)^{1/2}$, and the effective quantum numbers n_{eff} of the (d^9s) levels. Predicted values of levels not yet observed, are enclosed in parentheses.

With the aid of Shenstone's[7] determinations of the series limits of Ni I and Cu II, the (d^9s) values were obtained for each successive atomic number by linear extrapolation of the Moseley diagram, Eq. (1), slightly modified by a consideration of the first order screening numbers, fully discussed

---

[12] *Note added to proof, March, 1928.* The original draft of this article contained, in a footnote, a tentative assignment of the normal level $^1S_0(d^{10})$ of Ga IV. The spectrum of gallium below 1000A has now been rephotographed with the aid of a new grating, and the level established at -149298. The $(3d^{10})-(3d^94p)$ lines are:

λ	Int.	ν	designation	obs. − calc.
440.27	1	227133	$^1S_0-{}^3P_1$	24
423.59	5	236077	$^1S_0-{}^1P_1$	−22
422.49	4	236692	$^1S_0-{}^3D_1$	0

All the tables except I and II have been revised, where necessary, to incorporate the new data.

[13] Russell's consideration (l.c., p. 320) of the errors arising in certain cases in the prediction of series limits from only two members, indicates that the values shown for the ionizing potentials in Table VI may be 1 or 2 percent too high.

in Chapter VIII. The values of the other terms already observed were calculated from those of the (d^9s) configuration by subtraction, and the values in parentheses were extrapolated by the method described in Chapter VIII.

In Table VI, as elsewhere in this discussion where a value depending upon a configuration (that is, upon the n- and l-values of the individual electrons) is used, the value is chosen at the centroid of the configuration, with each level given its quantum statistical weight $2j+1$; not on account of any great significance to be attached to the centroid, but because for the application of the Moseley law in the form of Eq. (1), some representative point for the configuration must be chosen,[14] and the centroid appears to be the most satisfactory.[15]

Chapters V, VI, and VII will be devoted chiefly to a discussion of the (d^9s) and (d^9p) levels, which have all been identified in all the five spectra of the sequence.

V. Application of the Doublet Laws

In addition to the constancy of the frequency differences between the classified lines, and the satisfactory intensity relationships, the validity of the classifications of Ga IV and Ge V presented here rests upon the following three regularities:

1. The total separation of the $^3D(d^9s)$ term is in each case exactly in agreement with that demanded by the regular doublet law, Eq. (2); indeed, the separation was actually predicted in each case within 2 units, by extrapolation of the screening number. The term $^2D(d^9)$ upon which the ten electron system is built, is in one sense[14] identical with the regular x-ray doublet M_{33}, M_{32}. The doublet is inverted; its separation is given by Eq. (2). As Goudsmit and Back[16] have shown in the case of (ps) or (p^5s), if one or two s-electrons are added to the nearly complete shell (d^9), then the total separation of the resulting (d^9s) triplet or (d^9s^2) doublet is independent of the coupling and the same as that of the (d^9) doublet, and the new screening number $\sigma_2(d^9s)$ or $\sigma_2(d^9s^2)$ is equal to the one characteristic of the higher ion (d^9).

Table VII gives the screening numbers calculated from the $^2D(d^9s^2)$ and $^3D(d^9s)$ separations, with the corresponding x-ray screening number for comparison. The numbers are calculated to a higher degree of accuracy than the certainty of α allows ($\alpha^2=5.315\times10^{-5}$); but that fact has no effect

---

[14] See Chapter VIII.

[15] Table VIII, for instance, shows a much more satisfactory set of second differences than if the strongest line were chosen to represent the transition. Also, in the Gibbs-White graph,[3] where the transition $(d^{z-1}s)-(d^{z-1}p)$ plotted against Z for atoms in a given state of ionization is supposed to have a slope independent of the state of ionization, it is found that between the ten- and the eleven-electron spectra the slope varies from 1508 for Cu I – Ni I to 4660 for Ge IV – Ga IV if the lines $^3D_3-^3F_4$ and $^2S_1-^2P_2$ are used; while if the centroids are used, the variation is only about half that amount: from 1951 for Cu I – Ni I to 3595 for Ge IV – Ga IV.

[16] S. Goudsmit and E. Back, Zeits. f. Physik **40**, 530 (1926).

TABLE VII. *Relativistic screening number* $\sigma_2(3d^9)$.

Element	spectrum	Screening number ${}^3D(d^9s)$	${}^2D(d^9s^2)$	${}^2D(d^9s^2p^6\cdots)$
28 Ni	I	13.693		
29 Cu	I		13.566	
	II	13.516		
30 Zn	II		13.422	
	III	13.370		
31 Ga	IV	13.249		
32 Ge	V	13.161		
41 etc.	x-rays			13.0

Note added to proof. We can now add in a new row and a new column for 27 Co I ${}^2D(d^9)$, $\sigma_2=13.398$ (M. A. Catalán, Zeits. f. Physik. **47,** 89 (1928)). If all the values in the table are correct, there is a sharp break in the values of $\sigma_2(3d^9)$ for the successive arc spectra Co I, Ni I, Cu I.

on the differences. The second differences of the numbers in the third column are successively 0.031, 0.025, 0.033. This remarkable regularity indicates the accuracy with which the doublet separations can be predicted by the extension of this table, and by similar ones.[17]

2. The irregular doublet law, Eq. (3b), may be applied to the transition $(d^9s)-(d^9p)$. Table VIII shows the distance between the centroids of the two configurations, for the sequence of isoelectronic spectra; together with the differences Δ_1 between the frequencies in successive stages of ionization, and the second differences Δ_2. One would expect the differences Δ_1 to approach a constant for high stages of ionization; which in fact they do as the decrease in the absolute value of Δ_2 shows. The approximate linearity of the curves in Fig. 1, discussed in the next paragraph, shows that this linear dependence of the distance between the centroids upon atomic number implies a like linearity for the individual levels.

TABLE VIII. *Dependence of* $(d^9s)-(d^9p)$ *upon nuclear charge.*

Spectrum	Frequency	Δ_1	Δ_2
Ni I	28740		
		17965	
Cu II	46705		-1423
		16542	
Zn III	63247		-330
		16212	
Ga IV	79459		-119
		16091	
Ge V	95550		

3. The differences between corresponding levels within each of the two groups due to the configurations $(3d^94s)$ and $(3d^94p)$ respectively, may be

---

[17] Table VII was calculated from Eq. (2), for convenience in extrapolation. A more accurate equation (A. Sommerfeld, "Atombau und Spektrallinien," 4. Aufl., p. 450, Eq. (14)) taking higher terms into account, yields only slightly higher values for σ_2; the correction in σ_2 ranges from 0.007 for Ni I to 0.014 for Ge V.

represented by smooth, nearly linear curves. These curves[18] are given in Fig. 1; against nuclear charge as abscissa, are plotted the values of the levels composing the (d^9s) and (d^9p) configurations, referred to their respective centroids. The two horizontal center lines are the centroids; the distance between them in the figure was chosen arbitrarily.

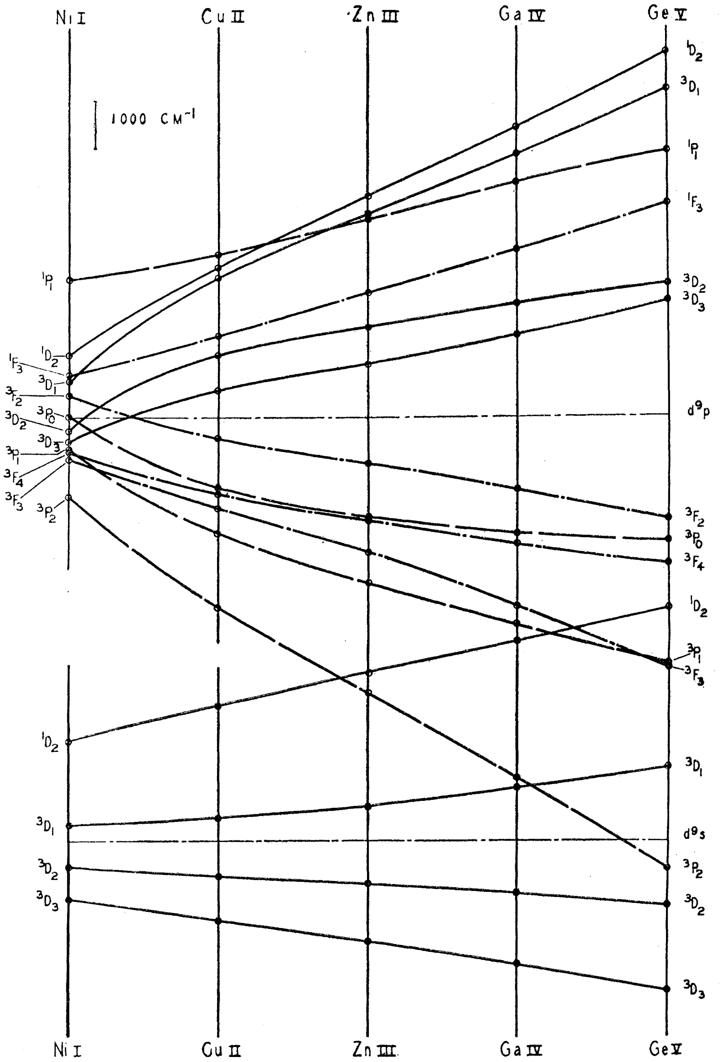

Fig. 1. The $(3d^94s)$ and $(3d^94p)$ configurations of the nickel-like spectra.

In the (d^9p) group, by far the greatest curvature occurs between the arc and the first spark spectra, as might have been expected. For higher ioniza-

---

[18] Although continuous smooth curves are drawn and their curvature is discussed, of course no points of any of them have any meaning except the intersections with the vertical lines.

tions, the levels with a given inner quantum number are so far apart and the curvature is so slight that no doubt can be entertained as to the connection of the points; with a single exception in the case of the Zn III levels designated as $^3D_1$, $^1P_1(d^9p)$. In this case the two levels, lying almost at the intersection of the lines, are separated by only 72 cm^{-1}. In an earlier assignment[5] of these levels, made on the basis of an extrapolation from Ni I and Cu II, the lines were not crossed between Cu II and Zn III. The evidence of the higher spark spectra, however, clearly favors the interchange of the two points. Neither assignment is especially favored against the other by the intensities (Table V).

Two of the curves, $^3F_4$ and $^3P_0$, had to be drawn from the evidence of a single transition in each spectrum: but all serious doubt of their reality is removed by the support of the intensities and the smoothness of the curves; together with the fact that in zinc, no line of intensity greater than 3 remains unclassified within 4000 cm^{-1} of either of the ones assigned to these levels. With the curves thus carried through Zn III, there is no choice of points in Ga IV and Ge V.

VI. ASSIGNMENT OF l AND s

We come now to a field in which we must proceed most cautiously: namely, the assignment of values to the multiplicities and orbital angular momenta of the several terms.

Goudsmit and Uhlenbeck[19] have shown that the interaction between an outer electron and its ion, depending upon the relative magnitudes of the interaction energies between their several momenta, may be represented by any of several symbolic coupling equations, of which we need consider here only the following: the extreme Russell-Saunders coupling:

$$((l_1l_2)(s_1s_2)) = (ls) = j \tag{4}$$

and the opposite extreme:

$$((l_1s_1)(l_2s_2)) = (j_1j_2) = j \tag{5}$$

where the subscripts 1 and 2 refer to the ion and the electron, respectively, and letters without subscripts indicate momenta of the configuration as a whole. Close coupling or association within a bracket indicates relatively large interaction energy. Eq. (4) shows that the atom as a whole would be characterized by values of l and s only in the ideal case of simple Russell-Saunders coupling.

The interaction energies in the spectra under consideration can be represented by no such pure coupling scheme. According to the usual practice, then, each level is given a symbol intended to indicate the spin and orbital angular momenta that would be expected to result for that level in the case of a continuous change (if that were possible) of the charges and orbital elements of the system until complete Russell-Saunders coupling should occur. The necessity of postulating such an imaginary continuous transi-

---

[19] S. Goudsmit and G. E. Uhlenbeck, Zeits. f. Physik 35, 618 (1925).

tion in order to justify our notation, is evidence of the formal nature of the assignment of "multiplicity" and "total orbital angular momentum" to "multiplet" levels where we are not justified in speaking of the quantization of l and s.

Ni I and Cu II having been already classified with the aid of criteria not available for the higher spark spectra, it was found possible on the basis of the Ni I and Cu II assignments to assign l- and s-values unambiguously (with the unimportant exception mentioned above for Zn III $^3D_1$, $^1P_1(d^9p)$) in agreement with the following three plausible rules:

(a) Homologous levels, when plotted with reference to each other or to the centroid of the configuration (Fig. 1) lie on smooth, nearly linear curves.

(b) The intensity rules hold qualitatively (Table V) among the singlet-singlet and triplet-triplet combinations.

(c) Interval ratios are not greatly altered, as the atomic number increases; in particular, there is no crossing of lines with the same l-value, at least for stages of ionization of the order of magnitude of those considered here.

A striking characteristic of the curves drawn according to these rules is that in spite of the departure from the normal, indicated by the non-applicability of the interval rules, the (d^9p) levels are sharply separated by their curvatures in the region of greatest curvature, into three groups, agreeing exactly with their grouping by l-values. The $^{3,1}D$ curves are all sharply concave downward and the $^{3,1}P$ somewhat less sharply concave upward, between Ni I and Cu II; while the $^{3,1}F$ levels show only a slight upward concavity. This similarity of curvature might almost be used as a criterion in similar cases, to associate the singlet levels with their triplets: but more material would be necessary to establish such a criterion.*

Since the assignments, made (except for the levels $^3D_3$, $^3D_1(d^9s)$) chiefly upon the basis of (a), depend for their validity directly upon that of the Ni I and Cu II levels, it is necessary to examine critically the classifications of these two spectra.

Bechert and Sommer were aided in the classification of Ni I by the evidence offered by many combinations with higher lying multiplets. The relative positions of the terms, and the intensity ratios, are quite convincing. Of the two overlapping ^3F terms due to (d^9p) and (d^8sp), the one chosen[5] was selected by rule (c); Russell's[20] recent assignment of this term on the basis of the relative positions of corresponding levels in neighboring arc spectra, confirms this choice.

Shenstone's classification of Cu II was based largely on a Zeeman effect analysis. His g-values from triplet blends are in good agreement with those which would be expected in the case of Russell-Saunders coupling; except in the case of $^1F_3$ and $^3D_3(d^9p)$, which share their g-sum but show a wide departure from normal g-values. The only basis for the present choice (which is in accord with Shenstone's) in the spectra from Cu II to Ge V,

---

* See note added to proof, at the end of the paper.

[20] H. N. Russell, Astroph. Jour. **66**, 184 (1927).

is the one advanced by Shenstone; the relative positions of the terms, in particular the inversion of the ^3D in agreement with rule (c). On the other hand, the intensity criterion now slightly favors the opposite assignment; and the absence of the intercombination $^3D_2-{}^1F_3$ would be less perplexing than that of $^3D_2-{}^3D_3$, especially in the face of the irregular intensity relationships among the intercombination lines in this isoelectronic sequence, compared with the good agreement among all the other triplet combinations. It must be remembered that although the assignment of *l*- and *s*-values on the basis of *g*-values, appears to have led here to results that are quite satisfactory, such an assignment has not the finality[21] in cases of complex coupling like the present one, that it has in cases of practically pure coupling of one type or another, such as is exemplified in Eqs. (4) and (5).

VII. Coordination of Levels to Series Limits

There are three familiar ways of tracing the dependence of the coupling schemes of similar configurations, upon the nuclear charge and the total quantum numbers of the electrons:

First, by considering an increase in the total quantum number of the added electron, only. Although the lower members of a series may consist of normal terms, the higher members always show the *jj*-coupling of Eq. (5). Specifically, for higher series members all the other interaction energies are small compared with that of the ion, a fact which may be represented as a special case of Eq. (5) by the scheme

$$((l_1s_1),l_2,s_2)=(j_1,l_2,s_2),=j \tag{6}$$

where a comma between two momenta indicates that their coupling is negligible.

Second, by comparison of corresponding levels in the arc spectra of elements in the same column of the periodic table; where increasing nuclear charge is accompanied by increasing total quantum numbers. Goudsmit and Back[16] have shown, for instance, that in the case of the configuration (*ps*) there is a complete change from Russell-Saunders coupling, Eq. (4), for the triplet and singlet $^3P,{}^1P(2p3s)$ of carbon, to the opposite extreme, Eq. (5), for the Pb levels designated $^3P,{}^1P(6p7s)$, which lie in two close pairs.

Third, by comparing regular x-ray doublets with the terms arising from the corresponding optical configurations, as (d^9x) and (p^5x), where the x within the symbol for the configuration stands for any outer electron or electrons. In the transition to the x-ray region, the magnitude of the nuclear charge effective upon the inner orbits (whose total quantum number is the same as in the corresponding optical orbits) is greatly increased; and the total quantum numbers of the outer electrons are greatest for the heaviest atoms. In this case again, the coupling is represented by Eq. (6) (except that

---

[21] See, for instance, Hund's reassignment ("Linienspektren und Periodisches System der Elemente," p. 200, 1925) of certain of the neon *p*-lines previously classified by Goudsmit (Zeits. f. Physik **32**, 794, 1925) on the basis of the Zeeman effect.

the pair l_2,s_2 must be replaced by l_2,s_2,l_3,s_3 . . . ; as many pairs as there are outer electrons in the configuration); the case is discussed further in Chapter VIII.

From the similar behavior of the couplings in these three cases, one would expect to find the same trend in a fourth one, in which only the nuclear charge is altered. This is exactly the case of the isoelectronic sequence under our consideration. We expect, then, that for extremely high ionizations, the (d^9s) and (d^9p) configurations will eventually be split into two subgroups

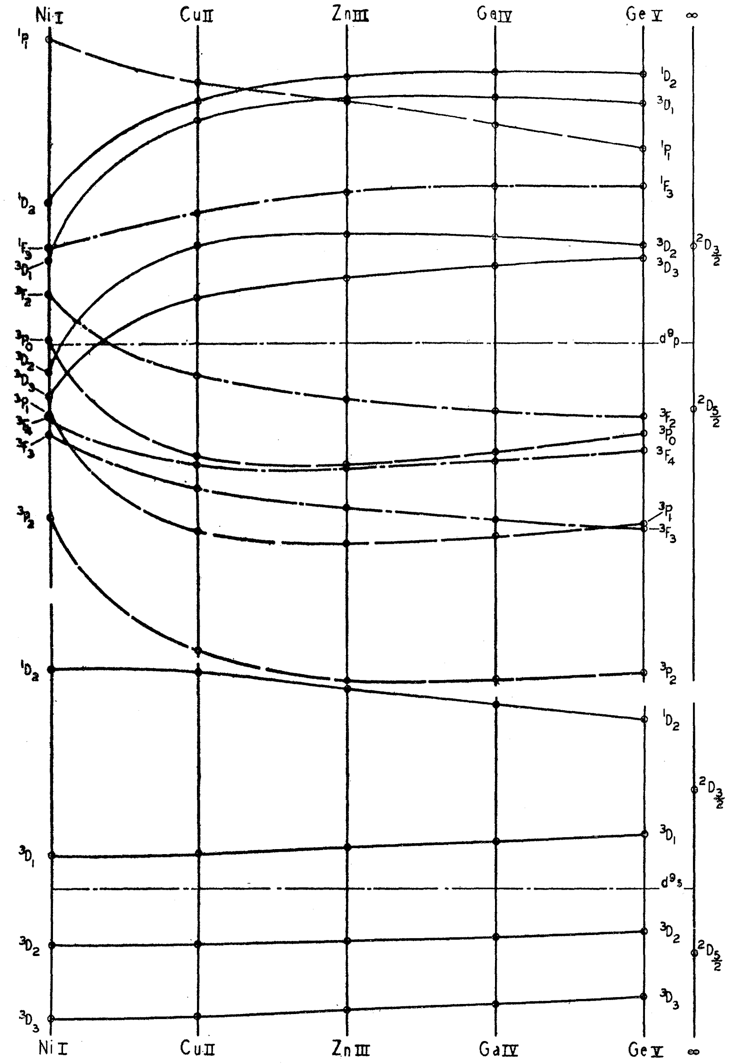

Fig. 2. The $(3d^94s)$ and $(3d^94p)$ configurations of the nickel-like spectra in terms of the regular doublet $(3d^9)$.

separated by the difference of the doublet $^2D(d^9)$ of the ion (although this splitting into subgroups may occur much less rapidly with increasing nuclear charge than in the x-ray case, where the total quantum numbers of the outer electrons increase).

Fig. 2 differs from Fig. 1 only in that its ordinates, measured from the centroid for each configuration, are in terms of the relativistic doublet distance $^3D_1-^3D_3(d^9s)$ as a unit, instead of in cm^{-1}; and that there is added at the side on a vertical line labelled "∞", the doublet separation about which the levels of the subgroups must cluster with extremly high ionization if the prediction of the paragraph above is correct.

The order of magnitude of the separations for each configuration, is in agreement with the prediction; but the grouping of the levels demands special consideration in the case of each of the two configurations:

1. The method of Hund[22] yields the following correlation between the levels of a (d^9s) or (ds) configuration and the levels of the ion (d^9) or (d):

$$^3D_3, {}^1D_2 \rightarrow {}^2D_{5/2}$$

$$^3D_2, {}^3D_1 \rightarrow {}^2D_{3/2}$$

Upon the postulate that the levels tend to cluster about the relativistic doublet as the nuclear charge increases, the evidence of Fig. 2 indicates that the limits for the levels $^1D_2$ and $^3D_2$ should be interchanged. The ratio:

$$^3D_2-{}^3D_3:{}^3D_1-{}^3D_3$$

in each of the spectra of the nickel-like sequence, as well as in each of the other known (d^9s) configurations, is given in Table IX. The progressive decrease of this ratio for the successive isoelectronic spectra from Ni I to Ge V, and the marked decrease in the columns representing the first three stages of ionization, are evidences against Hund's correlation. But the complexity of the progress of the coupling is exemplified by the fact that the ratio is greater for Ag II than for Pd I, in contrast with its decrease in the first row.

TABLE IX. *Ratio of the separations* $^3D_2-{}^3D_3:{}^3D_1-{}^3D_3$, ($d^9s$).

($3d^94s$)	Ni I 0.448	Cu II 0.444	Zn III 0.428	Ga IV 0.407	Ge V 0.384
($4d^95s$)	Pd I[23] 0.337	Ag II[24] 0.345	Cd III 0.330*	In IV 0.309*	
($5d^96s$)	Pt. I[25] 0.077a				

a. New assignment of term formerly designated $^1D_2$; the only other possible ratio on the basis of the existing data is .648.

* See note added to proof, at the end of the paper.

---

[22] F. Hund, Zeits. f. Physik **34,** 296 (1925).

[23] K. Bechert and M. A. Catalan, Zeits. f. Physik **35,** 449 (1925).

[24] A. G. Shenstone, Phys. Rev. **31,** 317 (1928).

[25] W. F. Meggers and O. Laporte, Phys. Rev. **28,** 642 (1926).

Shenstone [7,24] has already pointed out exactly this disagreement with Hund's correlation in the case of the series limits extrapolated from the first two numbers of the (d^9,ms) series in every case where the second member is known: namely, in Ni I, Cu II, Pd I, and Ag II. Shenstone's assignments of multiplicity values to the ${}^1D_2$ and ${}^3D_2$ levels of these terms was on the unequivocal evidence of relative positions, separations, intensities, and in the case of Cu II, Zeeman effect.

Indeed, Hund[26] himself would have been confronted with a disagreement in neon strictly analogous with this, had he not rearranged the (p^5,ms) series by interchanging s_2 and s_4 in the higher members of the first subordinate series, arranged by Paschen.[27] The levels of the lowest member ${}^3P_{210}\ {}^1P_1(2p^53s)$ of this series have been determined unambiguously by their relative positions and their Zeeman patterns to be respectively the levels $1s_5$, $1s_4$, $1s_3$, $1s_2$ of Paschen. But Paschen's s_2 and s_3 series approach the upper, and his s_4 and s_5 the lower of the levels of his doublet series limit, the inverted ${}^2P(p^5)$; giving directly the correlation

$$ {}^3P_2, {}^3P_1 \rightarrow {}^2P_{3/2} $$
$$ {}^3P_0, {}^1P_1 \rightarrow {}^2P_{1/2} $$

in agreement with the findings

$$ {}^3D_3, {}^3D_2 \rightarrow {}^2D_{5/2} $$
$$ {}^3D_1, {}^1D_2 \rightarrow {}^2D_{3/2} $$

of Shenstone and of this investigation, but contrary to the theory.

2. The grouping of the observed (d^9p) levels in Zn III, Ga IV, and Ge V, by j-values can be represented by the following qualitative scheme, where the levels are listed in order of decreasing stability and the larger intervals are represented by commas:

$$ 2,\ 1\,3\,4\,0\,2,\ 3\,2\,3\,1\,1\,2. $$

The normal grouping pattern from Eq. (4) is

$$ 4\,3\,2,\ 3\,2\,1,\ 2\,1\,0,\ 3,\ 2,\ 1 $$

and the opposite extreme, from Eq. (5), is

$$ 4\,3\,2\,1,\ 3\,2,\ 3\,2\,1\,0,\ 2\,1. $$

The order of the groups here, or of the numbers within a group, is not intended to have any significance. From Eq. (6) we may derive the series limit grouping:

$$ 4\,3\,3\,2\,2\,1 \rightarrow 5/2 $$
$$ 3\,2\,2\,1\,1\,0 \rightarrow 3/2 $$

---

[26] F. Hund, "Linienspektren und Periodisches System der Elemente," p. 198 (1925).

[27] F. Paschen und R. Götze, "Seriengesetze der Linienspektren," p. 30, 1922.

independent of any complete theory, such as Hund's, for the approach of Russell-Saunders levels to their series limits. The irreconcilability of the observed grouping with the series limit grouping expected asymptotically for high nuclear charge, is best shown by the fact that the levels 0 and 4 are close companions from Cu II to Ge V. The coupling scheme must be, then, of an intermediate sort. As an example of the grouping patterns that may be expected from such intermediate coupling schemes, we may consider the coupling equations

$$(((l_2s_2)s_1)l_1)=((j_2s_1)l_1)=j \tag{7}$$

and

$$(((s_1s_2)l_2)l_1)=((sl_2)l_1)=j \tag{8}$$

These yield the same pattern,[28] which in our case becomes

43210, 321, 321, 2

This grouping with its isolated 2 and its grouped 43210, appears to be more nearly in agreement with the observations than any of the other calculated groupings. Of course such a coupling, if it actually occurs, must, like the Russell-Saunders, be considered transient; it is to be expected that for higher ionization it will give way to the j_1j_2 scheme.

Comparison of our (d^9p) with the analogous neon configuration is not as simple as in the case where the added electron was an s-electron. The observed $(2p^53p)$ grouping in neon is

1, 32121201, 0.

The Russell-Saunders scheme, Eq. (4), yields

321, 210, 1, 2, 1, 0

the intermediate Eq. (7) or Eq. (8)

321, 210, 210, 1

and the j_1j_2 coupling Eq. (5)

3210, 21, 21, 10.

It may be observed that corresponding to ${}^3P_2$ in the structural scheme $(d^9)+(p)={}^3F{}^3D{}^3P{}^1F{}^1D{}^1P$, the neon level is ${}^3S_1$; these, ${}^3P_2$ and ${}^3S_1$, are the strikingly isolated low levels of our spectra from Ni I to Ge V, and of Ne, respectively.

---

[28] Where the added electron is an s-electron, as in 1 above, Eqs. (4), (7), and (8) degenerate into the same form $((s_1s_2)l_1)=(sl_1)=j$; the atom may be considered both for Ne and for all our isoelectronic spectra, to be already in the intermediate coupling state. The (d^9s) configuration might be expected, then, to show earlier and more simply than the (d^9p) configuration, the influence of j_1j_2 coupling. Regarding the plausibility of Eq. (7) and Eq. (8), it must be remarked that the occurrence of l_2 deeper within the brackets than l_1 is less satisfactory in the present case than in the analogous case of neon, where the electrons all have the same l-value, and the subscripts are interchangeable.

VIII. APPLICATION OF THE X-RAY LAWS TO OPTICAL SPECTRA, IN GENERAL

Sommerfeld [29] points out in the fourth edition of his book, that in contrast with the situation in x-ray spectroscopy, in the optical region we are far (except in the case of hydrogen) from the achievement of a truly rational term representation.

We shall consider now, more generally than in the previous chapters, the applicability of the x-ray laws, Eqs. (1) to (3), to sequences of isoelectronic optical spectra. Between the x-ray field and the optical field there may be pointed out two[30] distinctions in the application of the laws, which are closely related to the differences in aspect between the fields from the viewpoint of term representation.

First, *in the usual optical Moseley diagram the axis of ordinates represents a manifold of levels, in contrast with the "closed shell" singlet of the x-ray diagram.* In the x-ray diagram the squares of the ordinates represent, in effect, a one-electron configuration (doublet) minus a closed shell (singlet); for the energy differences among the several possible levels of the outer configuration are negligible compared with the energy required to remove an electron from an *inner* closed shell (compare Eq. (6)). The differences within the outer configuration are not negligible compared with the energy required to remove an *outer* electron; so that, strictly, an optical Moseley diagram requires as many graphs (or as many zero points) as there are levels in the higher ion, and, moreover, requires a knowledge of the correlation of the levels to those of the ion. For example, in the case of the nickel-like sequence, the plotting of the (d^9s) levels on the basis of the (d^9) ion requires two zero points, $^2D_{5/2}$ and $^2D_{3/2}$. The ordinates $(^3D_3-{}^2D_{5/2})^{1/2}$ and $(^3D_1-{}^2D_{3/2})^{1/2}$ are (neglecting the minute change in screening number between d^9 and d^9s) exactly the same, and $^3D_2$ lies a little lower (or, according to Hund's correlation, a little higher). This exact representation has in this case the advantage that it attributes the difference $^3D_3-{}^3D_1$ to the ion (d^9) where it belongs and not to the optical electron; this regular doublet difference is easily expressible in the usual doublet term formula built upon the single state (d^{10}). The differences $^3D_3-{}^3D_2$ and $^3D_1-{}^1D_2$ (or from Hund's viewpoint, $^3D_3-{}^1D_2$ and $^3D_2-{}^3D_1$) due to the difference in orientation of the s electron's spin vector, might perhaps be represented with the aid of another screening number as a new function of Z; although obviously not depending in the same way upon Z as the regular doublet, because for high

---

[29] A. Sommerfeld, "Atombau und Spektrallinien," p. 460, 1924: "Das Problem der Termdarstellung hat also im Röntgengebiet ein ganz anderes Gesicht als im sichtbaren Gebiet. Dort genügen für jedes Element wenige Parameter $\mathfrak{s}$, um mit ihrer Hilfe sämtliche Terme darzustellen durch Formeln, welche sonst nur ganze Zahlen und universelle Konstante, z.B. unser α, enthalten. Hier dagegen ist—ausser im Wasserstoffspektrum —jeder Term letzten Endes empirischen Ursprungs. Eine wirkliche rationelle Termdarstellung liegt für das sichtbare Gebiet noch in unabsehbarer Ferne. Im Röntgengebiet scheinen wir dicht davor zu stehen."

[30] A third distinction, the well-known difference of sign in the Moseley diagrams, need not be discussed here.

values of Z these differences are expected to vanish in comparison with the (d^9) doublet difference, as Chapter VII shows.

The paragraph above concerns exact energy values of levels. In the paragraph below, the complex structure, in the energy diagram, of each configuration, must be neglected. A representative point must be chosen for each configuration, analogous to the ν_{red} of an x-ray term, which for a given value of Z depends only upon the missing electron (that is, upon the n and l of that electron), and which consists only of the member free from α^2 in the infinite series term formula. Since we do not know the laws of the optical fine structure, the centroid is chosen as the best point available to represent the configuration;[15] the members in α^2 would be expected to represent relatively less energy in optical spectra than in x-ray spectra.

Second, *whereas the optical spectra of a given isoelectronic sequence increase in ionization with increasing Z, all the ordinary x-ray levels represent ionizing potentials of the neutral atom.* Let the first order screening number σ_1, be defined by the relation

$$(\nu/R)^{1/2}=(Z-\sigma_1)/n, \text{ or } \sigma_1=Z-n(\nu/R)^{1/2} \qquad (9)$$

where ν is the value representative of a given configuration, referred to any one of its next higher ions (that is, the ion made by removing any one of its electrons) and n is the total quantum number of the removed electron. To every configuration for a given Z there correspond as many values of σ_1, as there are different n_l electrons in the configuration. The x-ray first order screening numbers are derived from Eq. (9) by considering the removal of an inner electron. As a result of the second distinction between x-ray and isoelectronic optical spectra it is found that whereas for x-rays, σ_1 is an increasing function of Z, for isoelectronic spectra it is a decreasing function, approaching an asymptotic value for large Z (see below, Fig. 6).

Fig. 3 is a Moseley diagram for the optical sequence of one-electron copper-like spectra[31] built upon the closed shell ($3d^{10}$); the absolute values are established for the earlier spectra by several series, and for the later ones by the non-penetration of the hydrogen-like ($4f$) and ($5g$) orgits. Fig. 4 is a similar diagram for the ten-electron nickel-like sequence, built upon ($3d^9$); it contains the same material as Table VI. From the data used in Fig. 3 and Fig. 4, it was possible to construct a third Moseley diagram, Fig. 5, for the eleven-electron copper-like spectra built upon the configuration ($3d^94s$); it should be noted that the $3d$-curve of Fig. 5 represents *exactly the same* configuration as the $4s$-curve of Fig. 3.

Now from Eq. (9) and the data of these Moseley diagrams, a screening number curve may be drawn corresponding to each of the Moseley curves. These numbers are shown in Fig. 6, in which the first order screening number is plotted against the atomic number. Since the absolute term values are usually only approximately established, caution must be used in comparing

---

[31] Cu I: A. G. Shenstone, Phys. Rev. **28,** 449 (1926); Zn II: G. v. Salis, Ann. d. Physik **76,** 145 (1925); Ga III, Ge IV: R. J. Lang, Phys. Rev., **30,** 762 (1927).

the ordinates (this is true to a less extent, of the slopes) of Fig. 6 in cases of configurations built upon different ions. The dotted lines in Fig. 4 and Fig. 6 are the mean values obtained by application of the Moseley law,

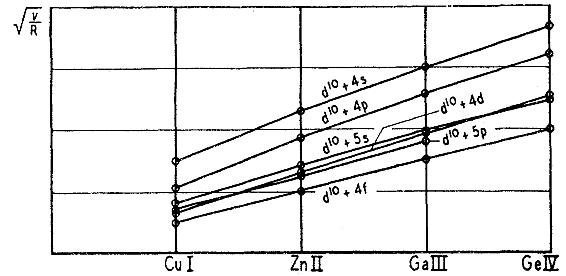

Fig. 3. Moseley diagram, based upon the configuration ($3d^{10}$).

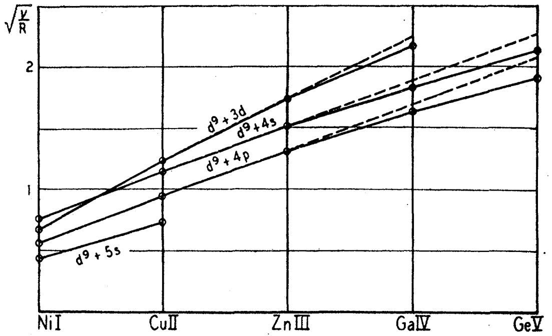

Fig. 4. Moseley diagram, based upon the configuration ($3d^9$).

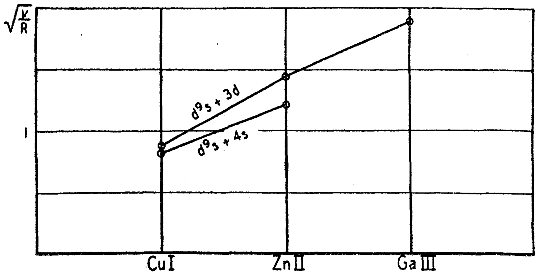

Fig. 5. Moseley diagram, based upon the configuration ($3d^94s$).

Eq. (1), and the irregular doublet law, Eq. (3a), to the configurations (d^9s) and (d^9p). All the other curves tend to approach horizontal asymptotes; with increasing ionization, their slopes decrease approximately in geometric progression like those of exponential curves.

First order screening number curves, plotted for sequences of isoelectronic optical spectra, appear quite generally to possess this property of decreasing downward slope.[32] (For the hydrogen-like orbits this slope is zero). Moreover, it appears to be a rule that among the curves associated with *the addition of a given electron* to different ion configurations: *The shapes of the curves change quite slowly with changing total number of electrons; and for a given total number of electrons, the shape of the curves is approximately the same for all configurations.*

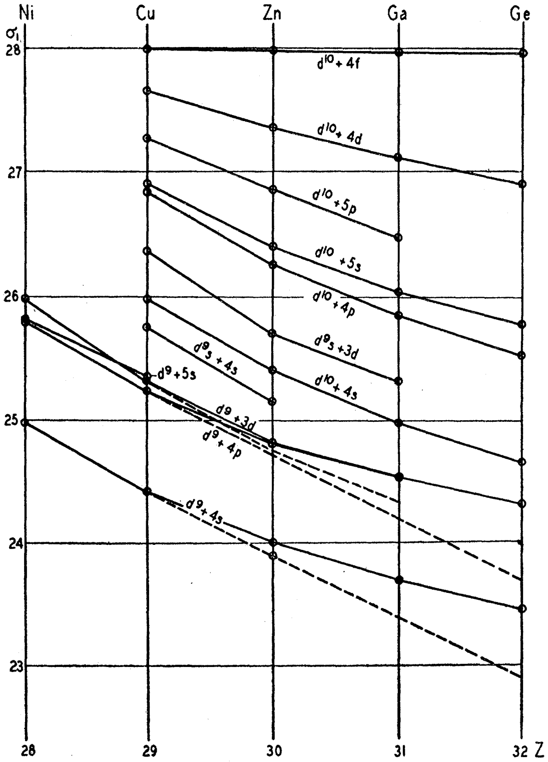

Fig. 6. The first-term screening numbers σ_1 from nickel-like and copper-like spectra.

Table X gives several examples of this rule, chosen from isoelectronic sequences in the neighborhood of closed shells. In each example several ion configurations are listed. The fourth column gives the values of σ_1 for the arc spectrum, calculated from Eq. (9), and the following columns show the negative slopes of the σ_1 curves between the arc and the first spark spectra, the first and second spark spectra, etc. The rule is verified by the slow increase of the values in each column after the fourth for increasing total number of electrons, and the approximate constancy of the values in in the neighborhood of a given total number of electrons. The rule was used

---

[32] An exponential curve is uniquely determined by the position, slope, and curvature at one point. In the following sentences we shall for convenience speak of the slope and curvature at the initial point (the point representing σ_1 for the arc spectrum) of the exponential curve which most nearly fits the empirical points, as the "shape" of the σ_1 curve.

in determining the values of σ_1 and consequently the absolute energy values in the higher spark spectra of the nickel-like sequence, as follows (so the regularity of the italicized numbers may not be considered a verification of the rule): The italicized numbers in the row representing the addition of a $4s$-electron to the ion configuration ($3d^9$), were chosen to be equal to the corresponding numbers in the ($3d^{10}$) row; and the numbers in parentheses were derived from those in italics. For Ge V it was necessary to extrapolate the slope. The solid lines departing from the dotted ones in Fig. 4 and Fig. 6, are derived from the numbers in italics and in parentheses in Table X.

TABLE X. *Slopes of first order screening number curves.*

Added electron	Ion configuration	Total number of electrons in ion	I	I–II	II–III	III–IV	IV–V
$3d$	$2p^6$	10[1]	10.00	.02	.03	.04	.03
	$3p^6$	18[1]	17.95	.55	.45	.30	
	$3d^9$	27	25.99	.67	(.50)	(.33)	
	$3d^9 4s$	28[31]	26.37	.67	.38		
$4s$	$2p^6$	10	9.49	.23	.14	.10	.08
	$3s^2$	12	11.17	.28	.17	.12	
	$3p^6$	18	16.74	.48	.30	.20	
	$3d^9$	27	24.99	.57	*.42*	*.32*	*.24*
	$3d^{10}$	28	25.98	.58	.42	.32	
	$3d^9 4s$	28	25.75	.60			
$4p$	$2p^6$	10	9.72	.15	.11	.07	.05
	$3s^2$	12	11.50	.22	.14	.10	
	$3p^6$	18	17.21	.41	.28	.19	
	$3d^9$	27	25.79	.55	(.42)	(.30)	(.22)
	$3d^{10}$	28	26.85	.59	.41	.32	
$5s$	$2p^6$	10	9.63	.18	.11	.08	.06
	$3s^2$	12	11.45	.23	.14	.10	
	$3p^6$	18	17.22	.37	.25	.18	
	$3d^9$	27	25.82	.46			
	$3d^{10}$	28	26.91	.50	.37	.32	
	$4d^9$	45[23,24]	42.25	.83			
	$4d^{10}$	46[33]	43.28	.85	.60	.46	.49

The effect on Table VI, of the adoption of the solid lines instead of the dotted ones in Fig. 6, was to lower the ionizing potentials for the (d^9s) and (d^9p) configurations by 1 volt for Zn III, 3 volts for Ga IV, and 8 volts for Ge V; and to decrease the other values accordingly.

If we call M the slope of a curve in the Moseley diagram, then we may see from the definition Eq. (9) that the slope of σ_1 as a function of Z is $1-nM$; and the rule that the screening numbers for a given electron are approximately parallel functions of the state of ionization, implies that in the neighborhood of any atomic number the initial slopes of the lines in the Moseley diagram depend only upon the added electron. Russell[34] has already pointed out several instances of this property of the Moseley diagram. The upward curvature of $\sigma_1(Z)$ as it approaches its asymptotic value,

---

[33] R. J. Lang, Natl. Acad. Sci. Proc., **13**, **341** (1927).

[34] H. N. Russell, l.c., p. 325, p. 434.

may be seen in the downward curvature of $(\nu/R)^{1/2}$ in the Moseley graph, its slope approaching $1/n$ for high stages of ionization.

The rule concerning the parallelism of the curves representing the addition of a given electron to each of several configurations, is distinct, of course, from the irregular doublet law, which concerns the addition of different electrons to the same ion.

For high values of Z, the x-ray screening number $\sigma_1(M_{32}\, M_{33})$ is a quite accurately known function of Z; but as Z decreases to nearly 28 the first distinction pointed out above, between the x-ray and the optical field, becomes invalid. For instance, the "x-ray $M_{32}\, M_{33}$ doublet" of Ge consists of the totality of the twenty-eight levels arising from the improbable configuration $(3d^9 4s^2 4p^2)$. But in the ${}^2D(3d^9)$ of Ni II, the x-ray doublet and the optical doublet become identical. The value, at Ni, of the σ_1 curve labeled d^9+3d is in the strictest sense the x-ray $M_{32}\, M_{33}$ screening number of nickel. It would have been just as proper to label the point $3d^{10}-3d$, as $3d^9+3d$, considering the differences in sign in the two fields. The value of σ_1 at this point is 25.99. Since this is very near the value obtained by extrapolating the x-ray screening number down to $Z=28$, and since the x-ray screening number increases and the optical one decreases with increasing atomic number, we see that there is a progressive difference between the optical and the x-ray screening numbers, which might well be accounted for by the outer screening in the x-ray spectra, due to the electrons which are missing in the isoelectronic sequences.

For a given total quantum number, both penetrating and non-penetrating orbits occur; and for non-penetrating orbits, as we have seen, the initial negative slope is zero. But from Eq. (3a) and Eq. (9) we can see that the irregular doublet law, applied as usual to isoelectronic sequences, requires that all the σ_1 curves representing the addition of electrons of a given total quantum number to a given configuration, be parallel. Therefore the irregular doublet law cannot be valid for all the added electrons with a given n-value, in general. This invalidity may be seen at once from the divergence of the lines $3d^{10}+4s$, $3d^{10}+4p$, $3d^{10}+4d$, and $3d^{10}+4f$ in Fig. 6, for instance.

TABLE XI. *Differences among the first order screening numbers σ_1, as functions of Z.*

Ion configuration	Added electrons	Spectrum	I	II	III	IV	V
$3d^9$	$4p-4s$		0.80	0.82	0.82	0.81	0.84
$3d^{10}$	$4p-4s$		.87	.86	.87	.87	
	$4d-4p$		.81	1.10	1.27	1.38	
	$4f-4d$		.34	.63	.86	1.06	
	$5p-5s$		.37	.45	.44		
	$5d-5p$		.46	.66			
	$5f-5d$		.26	.47			
$4d^{10}$	$5p-5s$		1.06	1.03	1.03	1.04	
	$5d-5p$		.98	1.28	1.44	1.58	
	$5f-5d$		.42	.73	.90	1.08	

In the neighborhood of a closed d-shell the parallelism between the s- and the p-curves appears to hold to a much higher order of accuracy than in the case of higher l-values. Table XI illustrates this fact by recording in rows labeled $p-s$, $d-p$, etc., the values $\sigma_1(p)-\sigma_1(s)$, $\sigma_1(d)-\sigma_1(p)$, etc., as a function of the ionization for each of several ion configurations; the values in the rows $p-s$ remain nearly constant, while the others show large increases. For some of the lighter atoms $\sigma_1(p)-\sigma_1(s)$ appears to show an appreciable increase with increasing ionization, though not as great relatively as $\sigma_1(d)-\sigma_1(p)$. Wentzel[35] has secured, on the basis of the Bohr atom-model, an asymptotic expression for the distance $\Delta(\nu/R)^{1/2}$ between the Moseley ordinates, which he has applied not only to x-ray terms but also to some optical sequences.

In conclusion, the authors wish to express their appreciation to Dr. S. Goudsmit for the valuable advice and criticism they sought and received from him, in the preparation of this paper. Mr. Lang acknowledges gratefully a grant from the Research Council of Canada, to aid him in carrying on this work.

Department of Physics,
University of Michigan (J. E. M., O. L.)

University of Alberta,
Edmonton, Canada (R. J. L.)
February, 1928.

Note added to proof. Gibbs and White (Amer. Phys. Soc. Bull., **3**, 12 (1928) abstract) have identified the levels of the configurations ($4d^{10}$), ($4d^9 5s$), ($4d^9 5p$) of the palladium-like spectra Cd III and In IV. Three characteristics of the curves which might be drawn for the palladium-like spectra, corresponding to our Figs. 1 and 2, deserve special notice here:

1. The behavior of the curves is in several respects like that which we would expect for high ionizations in the case of the nickel-like spectra if our Figs. 1 and 2 could be extended to the right. The curvature is much less than in the case of our figures; the sharp curvature near spectrum I, especially, is missing. Several pairs of curves which in Fig. 1 appear to be about to cross, occur in opposite order in the palladium-like sequence; $^3D_2(d^9p)$ is more stable than $^3D_3$ in Pd I, for instance, and its relative stability increases with increasing ionization.

This behavior of the palladium-like sequence as though it were an extension of the nickel-like sequence might be expected from the considerations at the beginning of Chapter VII; it should prove valuable in the classification of the platinum-like spectra.

2. Although the regularities in the l- and s-values, set down in Chapter VI, are for the most part verified in the palladium-like sequence, an exception occurs in the case of the curvature. For each triplet all the levels show similar curvature; but the singlets may no longer be associated with their triplets by the curvature criterion.

3. The ratio of the separations of the $^3D(d^9s)$ term, recorded in Table IX, progresses in the expected direction; in fact, the values in the ($4d^9 5s$) row run almost exactly parallel to those in the ($3d^9 4s$) row.

---

[35] G. Wentzel, Ann. d. Physik **76,** 803 (1925).