SPECTRAL SERIES IN THE SOFT X-RAY REGION

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Abstract

Critical radiation potentials for iron, determined photo-electrically.—Electrons were accelerated from a filament heated by a constant current, to an iron plate, and the photo-electric effect of the radiation excited on a plate carefully shielded from stray electrons, was measured. All surfaces exposed to the radiation were of metal and were maintained at definite potentials, and the tube after thorough baking was maintained at a pressure of 10^{-6} mm or less during measurements. (1) *M series, 40 to 175 volts.* Nine critical potentials were observed, the corresponding ν/R values being 3.46, 6.03, 7.05, 8.21, 9.63, 10.40, 10.88, 11.33 and 11.83, where R is the Rydberg frequency. The first and third are interpreted as resonance potentials of the M_3, M_4 series, the others as belonging to the M_5 series. The difference in ν/R for the two levels comes out 2.58. (2) *L series, 600 to 700 volts.* The three points observed correspond to Sommerfeld's L_ϵ, L_η and L_α, the ν/R values being 45.5, 47.0, and 51.5. These agree well with x-ray data.

Ionizing potentials for iron. The convergence limit of M_5 series is $\nu/R = 13.1$ which should correspond to an ionizing potential for that level. For the L series, the value for L_1 comes out $\nu/R = 59.0$.

Extreme ultra-violet spectrum of iron, 1188 to 18 A.—The critical potentials are interpreted as corresponding to emission lines of wave-length 264, 151, 129.6, 111.0. 94.6, 87.8, 83.9, 80.5 and 77.0 A. Differences between various pairs of the ν/R values correspond closely with eleven wave-lengths, from 294 to 1188 A, measured by Millikan, indicating that these belong to combination series. The L potentials correspond to 20.0, 19.4 and 17.7 A.

During the past two years a number of investigators have reported attempts to study the portion of the spectrum lying between the Millikan region and the x-rays by means of the photo-electric action of the radiation.[1-7] The general method used was to generate the radiation by electronic bombardment and study the total photo-electric effect as a function of the accelerating potential applied to the electrons producing the radiation. A discontinuity in the rate of increase of the photo-electric current was interpreted as indicating the excitation of characteristic radiation. In the earlier work this method gave only one

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[1] Richardson and Bazzoni, Phil. Mag. **42**, 1015 (1921)

[2] Kurth, Phys. Rev. **18**, 461 (1921)

[3] Hughes, Phil. Mag. **43**, (1922)

[4] Mohler and Foote, J. Wash. Acad. Sci. **11**, 273 (1921)

[5] Holweck, Ann. de Phys. (9) **17**, 5 (1922)

[6] Holtsmark, Phys. Z., **23**, 252 (1922)

[7] McLennan and Clark, Proc. Roy. Soc., A **102**, 389 (1923)

discontinuity for each spectral series in the region under investigation. These points have been interpreted as corresponding to the x-ray absorption limits, i.e., to the energy necessary to remove an electron from its normal position to infinity. Now in the ordinary x-ray region the absorption limits have been found to possess a fine structure on the high frequency side of the main absorption limit. The explanation which Kossel[8] has advanced for this is that the first absorption observed corresponds to the energy necessary to remove an electron from its normal energy level to the first incomplete electron shell and the other lines represent the energies necessary to eject the electron to the virtual orbits in the exterior of the atom. If this explanation is correct then a similar phenomenon should be observed in the soft x-ray region and therefore we should expect to find not one break in the photo-electric current but several for each x-ray series. This has now been observed, and this paper deals with the experimental procedure followed and the interpretation of the results.

Apparatus

The apparatus used is shown in Fig. 1. The radiation was generated by bombarding the solid target 1 with electrons from the hot tungsten filament 2, the accelerating potential being applied from the negative end of the filament to the target by means of a battery composed of small

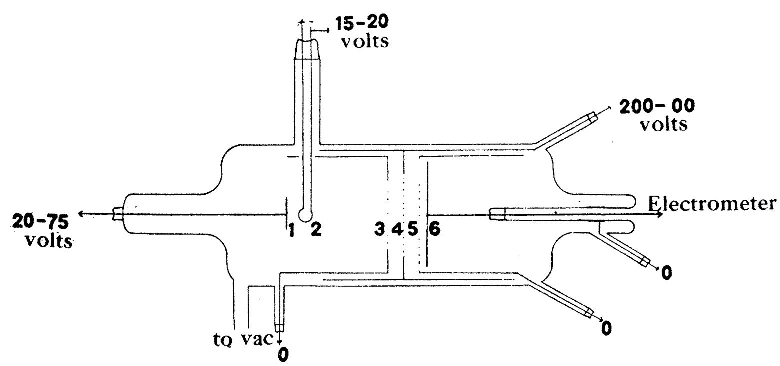

Fig. 1*

lead storage cells. The radiation fell upon the platinum plate 6 producing a photo-electric current which was measured by means of a Compton electrometer using the constant deflection method. The gauze 5 acted as a receiver for the photo-electrons. The gauze 4 was maintained at a potential at least 75 volts higher than 1 so as to keep positive ions from

[8] Kossel, Z. für Physik **1**, 124 (1920)

* The potentials on *1* should read 20-750 volts and on 4 should read 200-1000 volts.

reaching the photo-electric plate. Gauze 3 was kept at a potential 15–20 volts lower than the negative and of the filament, thus stopping electrons. The gauzes 3 and 4 were constructed in such a manner that they shielded the parts of the tube around the photo-electric plate from the direct action of the radiation. It is to be noted also that the tube was constructed so that all the surfaces exposed to the action either of the direct radiation from the target or of that reflected from 6 were of metal and were maintained at definite potentials.

Before any measurements were made the tube was thoroughly evacuated by means of a mercury vapor pump backed up by an oil pump. During the evacuation the tube was heated to about 500°C and the target bombarded with electrons from the hot filament. The vacuum obtained in this way was such that during the experiments the pressure did not register on a McLeod gauge sensitive to a pressure of 10^{-5} mm. Mercury and other condensible vapors were frozen out in a liquid air trap. It was found impossible to obtain reproducible results if this high vacuum was not maintained.

As it is desirable to keep the initial conditions as nearly constant as possible the filament temperature was not changed during a run. The exciting current therefore, increased as the accelerating voltage was increased in the low voltage range. At high voltages a saturation current was obtained, so the exciting current was maintained at a constant value by slight alterations in the rheostat controlling the filament current whenever necessary. The electron current used ranged from 1 to 2.5 milli-amperes. This required a potential drop of 3–5 volts across the filament.

After running for some time it was found necessary to remove the target and free the surface from the tungsten which had been deposited. On replacing the target in the tube after such treatment and re-evacuating, the same breaks were always obtained.

Experimental Results

The method of experimentation was developed using an iron target. From the x-ray data on iron, it was estimated that some members of the M series should be found in the range of 50–100 volts. With this in view the region from 30–185 volts was studied first. The ratio of the photo-electric current to the exciting current was plotted along one axis and the accelerating voltage on the other. Fig. 2 shows one of the curves obtained. It is to be observed that the form of the curve is similar to that obtained by Franck and Einsporn[9] for mercury at lower voltages.

[9] Franck and Einsporn, Z. für Physik, **2,** 18 (1920)

The breaks, while small, are very definite and can be reproduced, although some of the fainter breaks do not appear in all the curves. Table I gives a complete list of the points obtained in this range. Curves 1–4 were run first, then the target was cleaned and the remaining curves

TABLE I

Critical points for iron at low voltages

Curve	1	2	3	4	5	6	7	8	9
1	47.2	82.5	96.4	......	129.9	140.2	......	......	......
2	46.9	......	......	111.7	......	143.6	......	152.0	......
3	48.2	82.2	94.9	110.8	131.0	139.9	......	153.7	......
4	48.7	81.2	91.9	111.4	129.7	......	......	153.7	......
5	45.7	83.0	96.3	112.0	......	140.4	No readings above 155 volts		
6	46.2	80.5	94.1	112.0	......	142.0	" " " " "		
7	46.3	81.3	96.8	112.8	......	......	148.7	......	160.5
8	46.2	82.2	95.4	110.2	......	......	146.2	......	160.7
9	46.2	81.9	93.7	108.7	130.7	......	146.4	......	159.0
10	46.7	80.2	95.5	111.4	129.9	140.1	......	153.7	......
11	47.1	81.8	97.1	111.2	131.4	140.7	......	153.9	......
Av.	46.8	81.7	95.4	111.2	130.4	140.9	147.1	153.4	160.1
ν/R	3.46	6.03	7.05	8.21	9.63	10.40	10.88	11.33	11.83
λ	264	151	129.6	111.0	94.6	87.8	83.9	80.5	77.0

obtained. The values for the individual curves are given in volts; the values ν/R are the ratios of the frequencies to the Rydberg frequency; the wave-lengths λ are given in angstrom units. The relative intensities of the breaks are indicated fairly well by the number of times they were found.

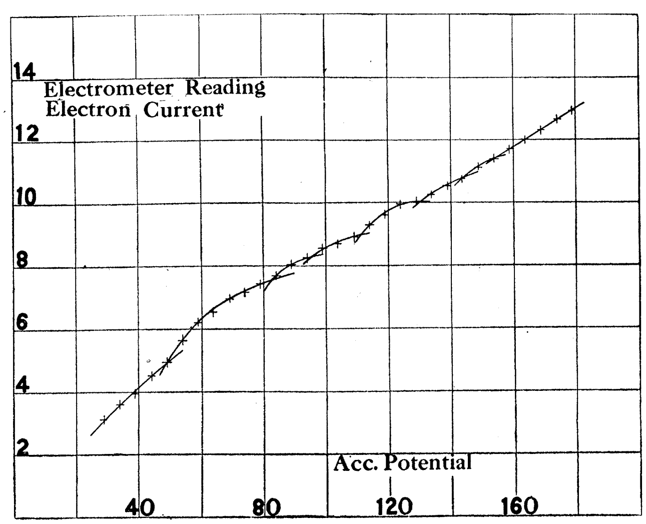

Fig. 2

A number of experiments were also carried on at higher and lower accelerating voltages. In the low voltage range the electrometer readings were too small to attain very high accuracy. The radiation was found to begin at 13–14 volts and rather definite breaks occurred at 20 and 26 volts. In this range readings were taken every two volts.

At high voltages some measurements have been made on the softer L lines. Readings were taken at ten volt intervals in this range so the values given are not as accurate as those for the M series. The breaks were found at 618, 637 and 697 volts; the corresponding wave lengths are 20.0, 19.4 and 17.7 angstrom units; the ν/R values are 45.5, 47.0 and 51.5.

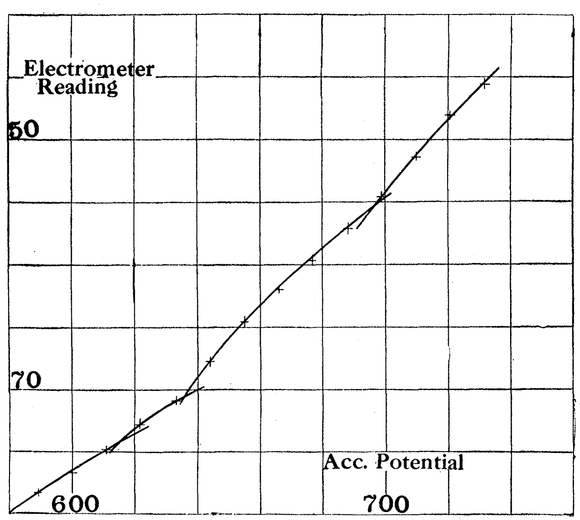

Fig. 3

One of the curves obtained is shown in Fig. 3. In this high voltage range the reason that only three lines were observed is probably because it was necessary to decrease the sensitivity of the electrometer considerably in order to handle the currents which were obtained; also, with the experimental arrangement used, it was necessary to take the points farther apart than at low voltages.

The experimental errors involved in making the measurements of the photo-electric and exciting currents were such that the points used in plotting the curves are accurate to about 0.5 per cent below 200 volts and 0.5 to 1 per cent in the higher range. In some runs, however, the readings were so large that the errors were even less. It is, therefore, evident that the breaks observed are considerably larger than the experimental errors.

Discussion of Results

The experimental procedure described in this paper is the same in principle as that employed by Franck and Einsporn[9] to study critical potentials in mercury vapor and by Olson and Glockler[10] to obtain the critical potentials in hydrogen. In their experiments gas molecules were bombarded with electrons, the radiation produced fell upon a metal plate and produced a photo-electric current which was measured by an electrometer. A sudden increase in the photo-electric current was found every time the energy of the bombarding electrons became great enough to remove an electron from its normal position in the atom or molecule struck to one of the orbits of higher quantic number. For example three of the critical potentials found by Franck and Einsporn for mercury correspond to the energy differences $1S-2P$, $1S-3P$, and $1S-4P$ (Sommerfeld notation) which had been determined previously from spectral data.[11] In my experiments a solid has been bombarded instead of a gas and higher voltages have been applied to the electrons. The critical potentials observed may be interpreted, by analogy to the above cases, as corresponding to differences between energy levels in the atom but these levels are so deep in the atom that the spectral lines corresponding to the same differences have not been observed up to the present time. It is possible however, to calculate some of these differences by applying the combination principle to the available x-ray data and thus test the interpretation given to the critical potentials.

Before proceeding with such calculations, the reasons will be given for interpreting the critical potentials reported in this paper as resonance potentials instead of following the policy of the earlier workers in this field who have classed all their values as ionizing potentials. The latter viewpoint is carried over from the x-ray theory which has interpreted the characteristic x-ray absorption limits as corresponding to the ionizing potentials of the various electron orbits within the atom. Some doubt has been cast upon the accuracy of this interpretation by the experiments of Stenstrom, Hertz, and Fricke on the M, L, and K limits respectively, who found a number of maxima in the absorption on the short wave-length side of the main absorption limit. In explanation of the maxima for the K-series—and a similar explanation can be given for the other series—Kossel suggested that "the principal limit corresponds to the energy which is necessary to remove an electron from the K shell to

[10] Olson and Glockler, Proc. Nat. Acad. **9**, 122 (1923)

[11] For a more detailed discussion of the interpretation of critical potentials at low voltages the reader is referred to the third section of the sixth chapter in Sommerfeld's "Atombau und Spektrallinien" 3rd ed.

the periphery of the atom; the following maxima correspond to the transition of a K-electron to certain virtual quantic orbits which are distributed outside the atom."*

Carrying this viewpoint over into the soft x-ray region, the first critical potential for a given energy level should correspond to the removal of an electron from that level to the "periphery" of the atom. Whether this means to the outside of the valence shell, to the valence shell, or to one of the other shells which does not possess enough electrons to form a stable group of 4, 6, or 8 can not be determined from the x-ray measurements which have been made. We know from the work which has been done on resonance potentials that critical potentials are found corresponding to transitions in which the electron is transferred to one of the quantic orbits which lie beyond the valence shell, and from x-ray data we know that no such potentials are found corresponding to the transfer of an electron from an x-ray level to a completed shell of higher quantic number, but there is no theoretical or experimental basis for saying that such a transition can not terminate in one of the incomplete shells lying within the valence shell. In the following paragraphs we shall see that some of the critical potentials observed correspond to transitions of the latter type. The notation used in designating energy levels and in referring to spectral lines is the same as that used by Sommerfeld in the third edition of "Atombau und Spektrallinien." In general the critical potentials have been identified with emission lines although these lines have not been detected by ordinary spectroscopic methods; this practise, however, is in accord with that followed in the study of resonance potentials at low voltages in which case such a relationship has been found to exist.

The M-series of the heavy elements consists of five groups of lines, the classification being based on the M level into which the electron fal s. For elements of as low atomic number as that of iron, two pairs of the M levels are so close together in energy value that they can not be distinguished experimentally; hence the M-series appears to exist of only three groups of lines.[12] First, we have the lines due to the electrons falling into the M_1 and M_2 levels (in this discussion pairs of levels which differ only by the relativity separation will be considered as single levels since the separation for such elements as iron is too small to be detected in these experiments), then a higher frequency group corresponding to M_3 or M_4 as the final state, and finally a still higher frequency group

*The quotation is taken from Sommerfeld "Atombau and Spektrallinien" 3rd ed. p. 233.

[12] The evidence for this statement is given in an article by Bohr and Coster, Z. f. Physik **12**, 342 (1923).

corresponding to the transitions ending in M_5. From the known x-ray spectrum of iron we can calculate only one of the lines of the M_3-M_4 group. The $K\beta$ line corresponds to the transition $M_3 \rightarrow K$ and the K_γ line to $N_5 \rightarrow K$ therefore the difference between the two corresponds to the transition from N_5-N_6 to M_3-M_4. The most recent values for the $K\beta$ and K_γ lines are those given by Siegbahn,[13] the ν/R values (519.83 and 523.54) giving 3.71 for the difference. Older data give 519.55[14] and 523.1,[15] the difference being 3.55. Whichever value is used the agreement with the value 3.46 obtained for the first point in Table I is fairly good, especially since uncertain initial conditions make this point the least accurate. This point must therefore represent the first line of the M_3-M_4 group.

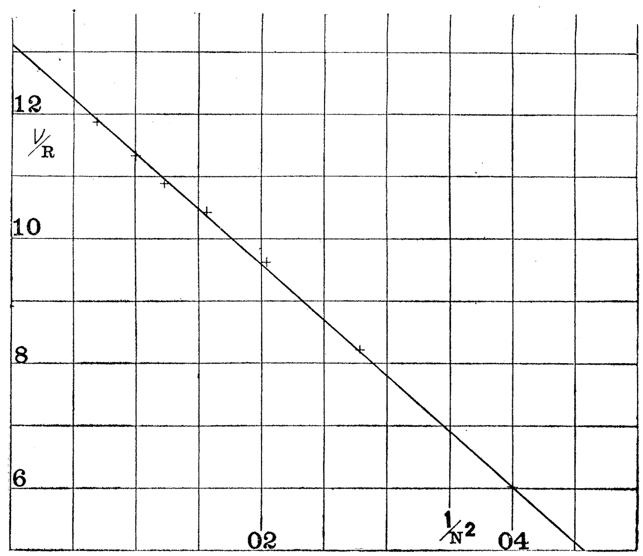

Fig. 4

In the iron atom we have electrons in the K, L and M levels and possibly one or two in the N but none farther out. It is to be expected, therefore, that the energies of the orbits of higher quantic number having the same azimuthal quantum number should be proportional to $1/N^2$ where N is the principal quantum number. The values of ν/R given in Table I were plotted against various values of $1/N^2$ to see if any such relationship could be found. On using 5, 6, 7, 8, 9, 10 and 12 for N it was found that the points numbered 2, 4, 5, 6, 7, 8, 9 in Table I would fall on a straight

[13] Siegbahn and Dolejsek, Z. f. Physik **10**, 159 (1922)
[14] Siegbahn, Ann. der Phys. **59**, 56 (1919)
[15] Siegbahn and Stenstrom, Phys. Z. **17**, pp. 48 and 318 (1916)

line as shown in Fig. 4, with an average deviation in terms of ν/R of .041, while omitting the point corresponding to $N=7$, the average deviation is .028. The points 1 and 3 are decidedly off this line and this is taken as an indication that they belong to another series. Now 1 has already been identified as corresponding to N_5-$N_6 \rightarrow M_3$-M_4 and therefore 1 and 3 are believed to be lines of the M_3-M_4 series and the others can be considered as the M_5 series, i.e. they correspond to transitions from levels having effective quantum numbers equal to the values used for N in the plot to the M_5 level.

The difference in the ν/R values of the points 1 and 2 is 2.57 and of 3 and 5 is 2.58; a point differing from 4 by a similar amount would fall too close to 2 to be detected with the apparatus used. This constant difference may be due to the fact that the points correspond to the ejection of electrons from the M_3-M_4 and M_5 levels to the same final levels. This may be tested by measurements on the L-series. The softest line in the L series corresponds to the transition from M_5 to L_1. From Siegbahn's[13] measurements on the K lines of iron we find the ν/R for $K\alpha$, corresponding to $L_1 \rightarrow K$ is 471.60 and for $K\beta$ corresponding to $M_3 \rightarrow K$, is 519.83, giving a difference of 48.23 for $M_3 \rightarrow L_1$. The difference between M_3 and M_5 has been given above as 2.58. Subtracting this we obtain 45.65 for $M_5 \rightarrow L_1$. Experimentally, the first line of the L series was found at 45.5 which is a very satisfactory check and confirms the interpretation of the M lines. The points 1 and 3 in Table I are, therefore, the first and third lines of the M_3-M_4 series and the others are the M_5 series. The second line in the M_3-M_4 series falls too close to the first line of the M_5 series to be separated from that line with the apparatus used.

By extending the straight line shown in Fig. 4 the convergence limit of the M_5 series is found to be 13.1. From the known separation between the M_5 and M_3-M_4 levels we obtain 10.5 for the M_3-M_4 and combining the values for M_5 and $M_5 \rightarrow L_1$, 59.0 is obtained for L_1. These values differ considerably from those given by Sommerfeld[16] or by Bohr and Coster[17], but this is due to the values selected for reference levels by these authors. For the elements of atomic number 12 to 31 the K absorption limit has been chosen as the reference level. Now for the light elements Fricke[18] has shown that the K limit is not a single discontinuity in the absorption but consists of a number of such discontinuities, the first of which is the most pronounced, the others being less marked and finally merging into the continuous band. The first discontinuity is the one which has been

[16] Sommerfeld, Atombau und Spektrallinien, 3rd Edition, p. 630
[17] Bohr and Coster, Z. f. Physik **12**, 342 (1923)
[18] Fricke, Phys. Rev. **16**, 202 (1920)

used as the K limit. If Kossel's explanation[8] of this fine structure is correct then the value selected as the absorption limit does not correspond to the energy necessary to remove an electron from the K level to infinity but only to that necessary to take an electron from the K level to the "periphery" of the atom. The energy necessary for the ionization is represented more accurately by the beginning of the continuous band. The difference between these values as found by Fricke varies considerably with the different atoms, amounting to as much as 80 volts in some cases. This is of the same order of magnitude as the difference between the first line and convergence frequency of the M_5 series as given in this paper. Therefore, we may suppose that the values which have been derived in this paper are the true values for the removal of an electron to infinity.

The results may be further tested by applying the combination principle to calculate some lines in the Millikan region. The values given by Millikan[19] have been changed over to volts for convenience in comparison. They are given in the following table. The numbers in the column headed "combination" refer to the numbering of the points as given in Table I. No values lower than ten volts are given as at such voltages there are so many lines that the comparison has no significance.

TABLE II

Combination	G.K.R.	Millikan	Intensity
8–4	42.2	42.0	2
7–4	35.9	36.9	1
6–4	29.2	28.9	3
5–4	19.2	19.1	1
9–5	29.7	29.6	4
8–5	23.0	22.4	7
7–5	16.7	16.9	3
6–5	10.5	10.4	2
9–6	19.2	19.1	1
8–6	12.5	12.56	3
9–7	13.0	13.0	1
4–2	29.5	29.25	3

The three L lines which have been obtained are probably those corresponding to the transitions $M_5 \rightarrow L_1$, $M_5 \rightarrow L_2$, and $M_1 \rightarrow L_1$. The argument in favor of the first of these has been given in the discussion of the M lines. A similar calculation confirms the second line, as the only difference between the two is the difference between L_1 and L_2 which is known from the values of $K\alpha$ and $K\alpha'$. The observed and calculated values are 47.0 and 46.7 respectively. The third line is the $L\alpha$ line and this can be checked by extrapolating the Moseley curve for $L\alpha$. The extra-

[19] Millikan, Astrophysical J. **53**, 157 (1921)

polated value for $\sqrt{\nu/R}$ is 7.22 and the experimental value is 7.18, a very satisfactory agreement. According to the nomenclature used by Sommerfeld the lines are Lϵ, Lη and Lα respectively.

It is rather difficult to account for the failure of other investigators to obtain breaks such as those described in this paper since the information contained in the published reports is not sufficiently detailed. In some preliminary experiments with different tubes the writer found that one of the most important factors affecting the accurate measurement of the radiation effects was the control of the potential of every surface in the vicinity of the measuring plate. This is one thing which apparently has been neglected by most workers in this field as nearly all the published diagrams of apparatus show exposed glass surfaces near the photoelectric plate. Now under the conditions prevailing in an x-ray tube a glass surface cannot be said to be at a known or even constant potential and variations in the potential of such surfaces will materially affect the accuracy of the work. Another factor which must be considered is the potential drop across the filament, which must be small.

Summary

It has been found that spectral lines can be detected in the soft x-ray region by studying the total photo-electric effect produced by the radiation as a function of the accelerating voltage applied to the electrons producing the radiation. This method has been used to measure the wave-lengths of nine M lines of iron between $\lambda = 264$A and $\lambda = 77$A, and three L lines $\lambda = 20.0$, 19.4 and 17.7A. These measurements show that the method is capable of filling in the gap in the spectrum between the ultra-violet and the x-ray regions. By applying the combination principle it has been shown that the results obtained are in accord with Millikan's measurements in the extreme ultra-violet spectrum of iron and also with Siegbahn's measurements on the K-series of iron.

In conclusion the writer wishes to express his thanks to Professor G. N. Lewis for the aid and encouragement he has extended during the progress of this research.

Department of Chemistry,
University of California,
May 20, 1923.