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FINE STRUCTURE IN THE X-RAY ABSORPTION SPECTRA OF THE *K* SERIES OF THE ELEMENTS CALCIUM TO GALLIUM

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Abstract

The *K* x-ray absorption spectra of the free elements Ca, Cr, Mn, Co, Ni, Cu and Zn have been photographed and for each of these elements an extended fine structure has been obtained. The fine structure, consisting of six or seven secondary edges, extends over an energy range of more than 200 volts. In every instance the element was used as the absorbing screen except Mn where it was present in the alloy manganin. No detectable difference was found in the absorption spectrum of copper between that obtained with a brass screen and that with the element alone. An attempt was made to show more definitely the relation of the $K\beta_2$ emission line to the principal *K* absorption limit for Fe, Co, Ni and Cu. Indications are that the main edge is produced by the ejection of a *K* electron to an optical level rather than to infinity. It is shown that the Kossel theory alone is quite inadequate to explain all the secondary edges. On the basis of multiple ionization the probable electron transitions have been determined and tabulated to account for the observed separations of the various secondary edges from the principal *K* edge. The methods employed herein to account for probable electron transitions, when applied to the transitions proposed by Ray, in his treatment of the fine structure in *K* and Ca, give very different energy values from those which he has computed.

Introduction

THE more or less complicated appearance of absorption spectra which is often found on the short wave-length side of the edge is known as absorption fine-structure. Stenstrom,[1] Fricke,[2] Hertz[3] and Lindh[4] were among those who made the earlier investigations. The latter made an extensive study of the *K* absorption spectra of the elements P(15) to Fe(26) and found as many as three white lines on the plates i.e., in addition to the ordinary absorption discontinuity there appeared lighter and darker regions on the short wave-length side. Coster and van der Tuuk[5] found a very limited fine structure associated with the *K* edge of argon. An extended fine structure of the edge was found by Lindsay and Van Dyke[6] in the *K* absorption of calcium, where the element was present in the crystals used as reflectors and served also in the capacity of absorbing material. Nuttall's[7] investiga-

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[1] W. Stenstrom, Diss. Lund, 1919.
[2] H. Fricke, Phys. Rev. **16**, 202 (1920).
[3] G. Hertz, Zeits. f. Physik **3**, 19 (1920).
[4] A. E. Lindh, Diss. Lund, 1923.
[5] D. Coster, and J. H. van der Tuuk, Zeits. f. Physik **37**, 367 (1926).
[6] G. A. Lindsay and G. Van Dyke, Phys. Rev. **27**, 508 (1926).
[7] J. M. Nuttall, Phys. Rev. **31**, 742 (1928).

tion of the *K* edges of potassium and chlorine in compounds showed as many as five secondary edges. Voorhees and one of the authors[8] have shown that the multiple structure for iron, both as a metal and in compounds, extends over a range considerably greater than that of any fine structure previously reported. They found that the outstanding features for the element alone were in the structure which was apparent in the main edge itself, the absence of the intense white-line absorption, the increase in extent or range of the secondary edges, and verified the fact that the free element has the principal absorption edge of longest wave-length[9] which should therefore be more characteristic of the substance.

Since metallic iron afforded such an excellent fine-structure it was felt that other neighboring elements in the free state might also under suitable conditions, give an extended structure of the *K* absorption edge. Besides it was hoped that with information regarding the secondary edges of a considerable number of adjacent elements, it might be possible to arrive more readily at a satisfactory explanation for the observed phenomena. It was with such aims in view that the present work was undertaken. The general method employed was that of placing films of the absorbing metal in the path of the x-ray beam and obtaining photographic records of the absorption spectrum by reflection of the radiation from a sylvite or a calcite crystal.

Apparatus and Experimental Procedure

A Siegbahn precision vacuum spectrograph was used for obtaining photographs of the absorption edges. For absorption spectra of all the elements investigated a natural potassium chloride crystal served as the reflector. The dispersion with this crystal varied from about 15 X.U. per mm for Ca to about 17 X.U. per mm in the case of zinc. Since the secondary edges become more crowded together with increasing atomic number it was necessary to increase the dispersion for Cu and Zn in order to obtain plates showing the fine structure which could be measured with a fair degree of accuracy. Accordingly, a calcite crystal was ground parallel to the (111) planes and mounted in the usual manner. This provided a dispersion of about 7 X.U. per mm.

Proper screens are one of the most essential requirements necessary to insure success in obtaining fine structure in the absorption edges. One must have uniformity as well as optimum thickness and both of these are troublesome factors in many cases. An excellent principal edge can be produced with screens which are either too thick or too thin to show the secondary edges. The surest method of determining the proper thickness is by trial.

Using such a trial method it was found that a nickel film about 0.007 mm thick gave excellent fine structure. This nickel had been prepared electrolytically and annealed in hydrogen. The copper, brass and zinc screens were prepared simply by carefully rolling out the metals to suitable thicknesses. It may be pointed out here that the results obtained for copper in

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[8] G. A. Lindsay and H. R. Voorhees, Phil. Mag. **6,** 910 (1928).

[9] Kath. Chamberlain, Nature **114,** 500 (1924), Phys. Rev. **26,** 525 (1925).

brass showed no measurable deviations from that obtained when copper screens were used.

Considering the results obtained with brass screens for copper fine structure it was thought permissible to use an alloy of manganese as an absorber. Manganin, a copper-manganese alloy containing 15% manganese, was used since it could be easily rolled to the proper thickness and also because the manganese content is high in this alloy.

The preparation of cobalt screens presented no difficulties. The metal was deposited electrolytically on chromium plated electrodes from which it was then easily removed. The chromium screens required a different procedure. Due to its extreme hardness and brittleness rolling was out of the question. A layer of Cr about 0.003 mm thick was plated on a thin steel electrode. Then a thin coating of paraffin was applied over the Cr to strengthen the film, this added support being necessary during the following chemical process. HCl was used to etch away the iron from a small area leaving the Cr film which was supported by the remainder of the steel.

Calcium screens required extra precautions due to the rapid oxidation. Pure Ca was rolled out to the desired thickness and immediately given a thin coating of paraffin. In this manner Ca films could be used for a hundred or more hours.

Although no very definite results were obtained for gallium (31) and selenium (34), as far as fine structure is concerned, the preparation of these screens is described. Ga melts at 30.1°C. Like Hg in the liquid state its surface tension is great. Fortunately one is able to spread it out into a thin layer when applied on aluminum. If the Al is used in the form of thin foil there will be only a very slight amount of absorption due to this element since the wave-length of the K edge of Ga is below 1.2A. Selenium screens were made by heating the element somewhat above its melting point and then when temperature conditions were just right it was possible to spread out the substance on thin pieces of paper. Here again the amount of absorption by the supporting material was negligible.

Measurements on all plates were made on a comparator having a least count of 0.005 mm. In making settings on the various edges the cross-hair of the instrument was brought across the blackening to such a position that it was possible just to see no falling off in the intensity on the long wavelength side of the cross-hair. Settings were also made on any good emission lines, if they were present on the plate, since they served as convenient reference lines to determine the wave-length of the principal edge and also permitted a check on the dispersion for the adjacent regions. The photometric curves incorporated in this paper were made on a Moll microphotometer. Duplicate runs over different portions of the plate gave curves which were essentially the same.

To aid in the interpretation of the fine structure data additional plates were made to show more definitely the location of the KB_2 line of an element with respect to the principal K absorption limit of the same substance. Copper, nickel, iron and cobalt were studied. The method employed was to photograph on a plate the main K edge and any suitable reference line so that the distance between these two could be measured on the comparator. On another plate the emission spectrum of the element was obtained in which the $K\beta_2$ line was sufficiently prominent to be measured. The same reference line was photographed with the $K\beta_2$ line and therefore the distance between the lines could be determined. In each case of absorption the screens were of the free element, no attempt being made to obtain fine structure. For copper absorption the continuous spectrum came from a molybdenum target while in the other three cases a copper anode was employed. This procedure prevented the appearance of the $K\beta_2$ line in the absorption spectrum and therefore aided in making more reliable settings on the main edge. For the emission spectra targets of these various metals were used. At least two plates of each type for each element were obtained and measured.

In every case the value used in the computation of the wave-length of edge or line was the mean value of ten settings on the comparator. The general method used was that of reference measurements. Since the wave-length of the principal absorption edge depends upon the chemical combination of the absorber it was desirable to determine the wave-length of the absorption limits for each of the free elements studied. Having determined the wave-lengths of the main K edge for each element the wave-lengths of the secondary edges were computed by multiplying each linear separation, from the principal edge to the secondary edge, by the proper dispersion factor and subtracting each product from the known absorption limit. The reciprocal of the wave-length gives the frequency ν in cm^{-1} and division by the Rydberg constant 109737 gives ν/R for each edge. The separation $\Delta\nu/R$ of any secondary edge from the main edge may then be expressed in equivalent volts by multiplying the by the factor 13.56.

DATA AND RESULTS

I. Wave-Length determinations of principal K absorption limits.

In Table I have been recorded the mean values, expressed to the nearest 0.1 X.U., of the principal K absorption limits. The value of iron is included, this result having been taken from the work of Voorhees and one of the authors.[8]

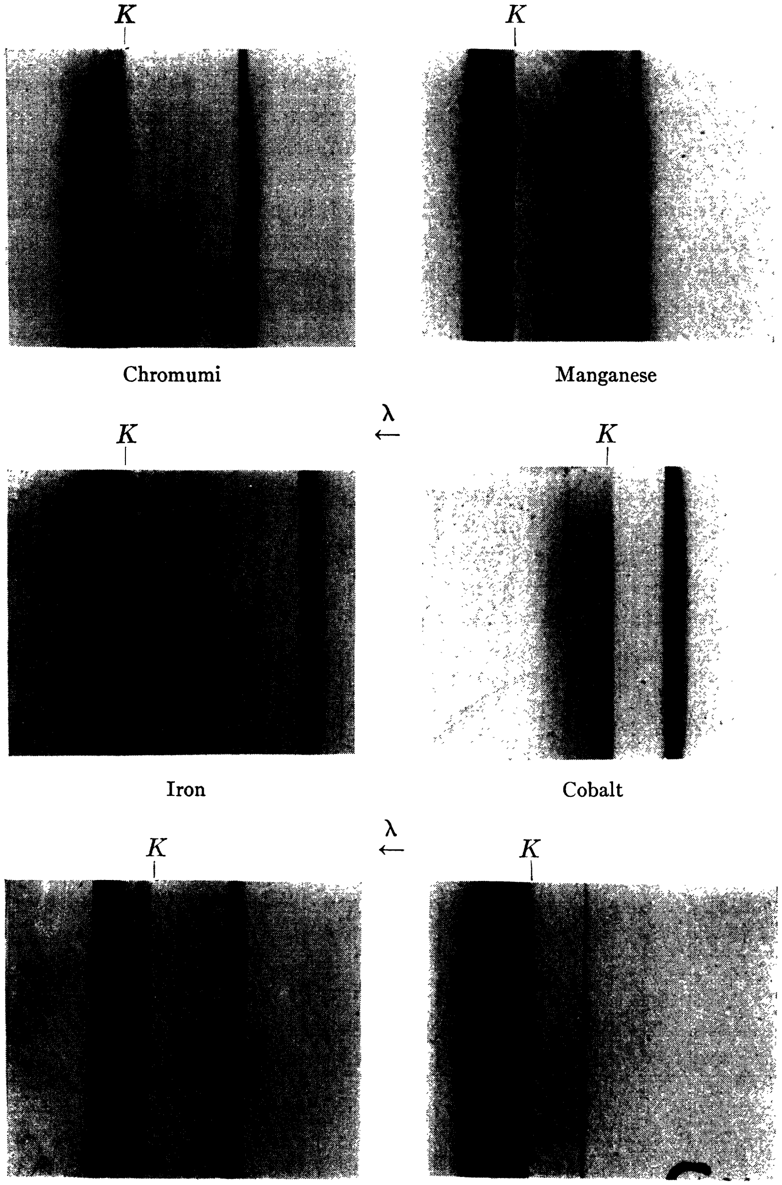
TABLE I. *Wave-lengths of the K absorption limits.* λ *in X.U.*

Element	λ	Element	λ
20 Ca	3063.9	28 Ni	1484.6
24 Cr	2066.1	29 Cu	1377.8
25 Mn	1891.3	30 Zn	1280.8
26 Fe	1739.3*	31 Ga	1192.9
27 Co	1604.3	34 Se	977.8

* Lindsay and Voorhees.[8]

II. Absorption fine structure.

The general appearance of the plates showing absorption spectra in which the principal edges are accompanied by several secondary edges may be seen in Fig. 1. The micro-photograms are reproduced in Fig. 2. The discontinuity designated by "K" marks the location of the main edge



Chromumi Manganese

Iron Cobalt

Nickel Copper

Fig. 1. Fine structure in the absorption spectra of the K series of several elements.

and it is in the lighter region to the short wave-length side of this edge that one observes the fine structure, whose general appearence is that of a series of alternately light and dark regions. The "white lines" are not of the same width, nor of the same intensity, neither are they equally spaced on the plate but appear farther and farther apart as one proceeds to shorter wave-lengths. In the discussion below an attempt is made to trace the most intense white line, or better, the adjacent secondary edge, through the various elements.

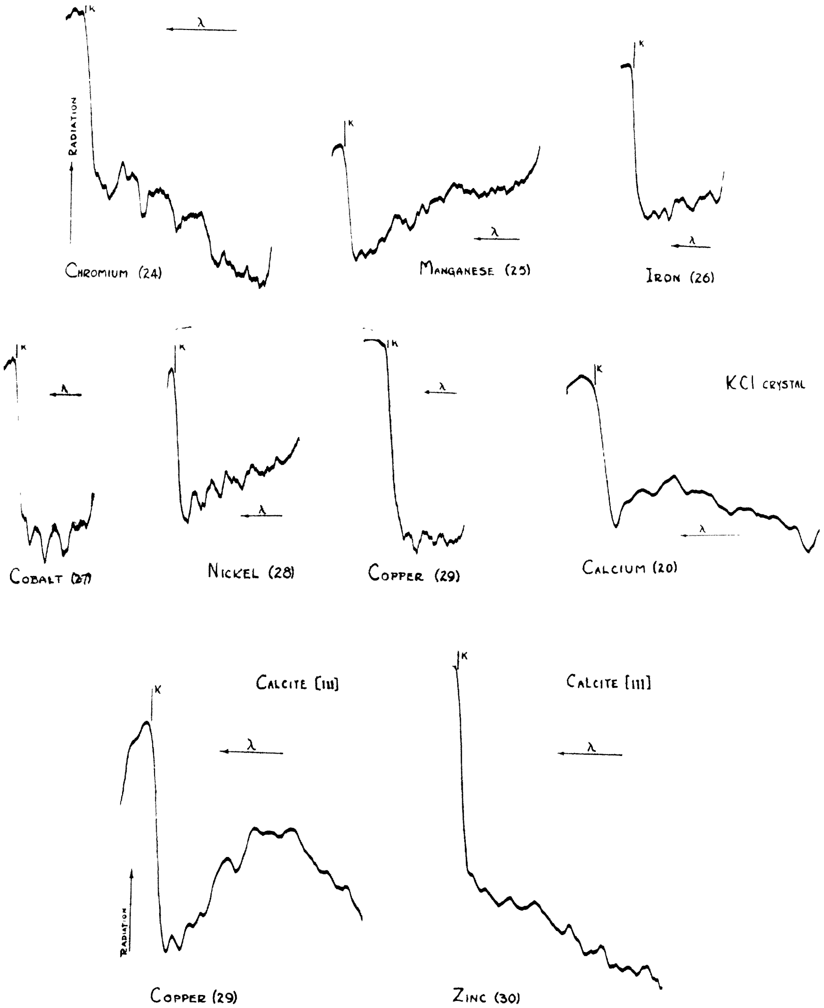


Fig. 2. Photometric records of K x-ray absorption spectra.

The results obtained from data on each element for which fine structure was observed and measured have been collected in Table II. In this table are given the mean values of the wave-lengths of the secondary edges, expressed to 0.1 X.U. together with the separations of these edges from the

Table II. *Secondary absorption edges.*

		λ—Wave-length in X. U.								$\Delta(\nu/R)$ ΔV (volts)	Separation from Principal Edge			
		K												
Ca	λ	3063.9	3059.0	3048.5	3041.8	3034.7	3014.2	2987.3	2959.9					
	$\Delta(\nu/R)$		.48	1.50	2.16	2.87	4.90	6.93	10.45					
	ΔV		6.5	20.2	29.3	38.9	66.4	94.0	142.					
Cr	λ	2066.1	2060.5	2049.1	2040.0	2030.5	2019.9	2009.3	1984.9	1958.6				
	$\Delta(\nu/R)$		1.19	3.67	5.66	7.73	10.1	12.48	18.08	24.23				
	ΔV		16.2	49.8	76.7	105.	137.	169.	245.	329				
Mn	λ	1891.3	1886.8	1880.6	1876.6	1870.4	1867.6	1857.6	1850.7	1842.3	1838.1	1827.4	1811.2	1787.0
	$\Delta(\nu/R)$		1.13	2.73	3.77	5.38	6.10	8.74	10.23	12.81	13.95	16.85	21.3	28.1
	ΔV		15.4	37.1	51.	73.	83.	118.	139.	174.	189.	228.	289.	381.
Fe	λ	1739.3	1737.1	1731.4	1726.7	1721.1	1715.2	1706.9	1701.3	1690 9	1683.4	1663.0 *		
	$\Delta(\nu/R)$		.67	2.39	3.82	5.54	7.36	9.90	11.7	14.9	17 4	24.0		
	ΔV		9.1	32.4	51.8	75.	100.	134.	159.	202.	236.	325.		
Co	λ	1604.3	1601.9	1595.4	1586.6	1573.3	1557.0							
	$\Delta(\nu/R)$		.86	3.17	6.32	11.2	17.25							
	ΔV		11.6	43.	86.	152.	234.							
Ni	λ	1484.6	1483.0	1478.3	1471.0	1458.2	1449.4	1442.7	1431.3	1413.0				
	$\Delta(\nu/R)$		.69	2.61	5.65	11.14	14.97	17.86	22.95	31.2				
	ΔV		9.3	35.3	77.	151.	203.	242.	311.	423.				
Cu	λ	1377.8	1375.8	1374.2	1372.4	1365.3	1363.2	1357.0	1354.1	1349.5	1348.0	1342.2	1337.0	1329.1
	$\Delta(\nu/R)$		.96	1.74	2.64	6.06	7.09	10.11	11.56	13.9	14.6	17.5	20.2	24.3
	ΔV		13.0	23.6	36.	82.	96.	137.	157.	188.	191.	238.	273.	330.
Zn	λ	1280.8	1278.7	1277.2	1275.6	1273.7	1270.6	1265.6	1261.5	1258.4	1253.5	1249.5	1238.9	
	$\Delta(\nu/R)$		1.15	2.0	2.88	3.95	5.71	8.46	10.85	12.63	15.48	17.75	24.0	
	ΔV		15.6	27.	39.	54.	77.	115.	147.	171.	209.	241.	326.	

* Lindsay & Voorhees.[8]

principal edge. The separations are tabulated in ν/R units as well as in equivalent volts. The values for iron were taken from the results of Lindsay and Voorhees[8] and were incorporated in order to have a complete sequence from Cr to Zn.

III. Relation between the $K\beta_2$ line and the principal K edge for the elements Fe, Co, Ni and Cu.

In the discussion of possible electron transitions corresponding to secondary edges it is evidently necessary to know as much as possible of the transition related to the principal edge. It has been rather assumed that the K electron goes to infinity. Now the $K\beta_2$ line represents a transition from the $N_{\mathrm{II,III}}$ level to the K level, and if the K electron in absorption goes to infinity we should have for the elements here considered a difference between the K edge and the $K\mathrm{B}_2$ line about equal to the first ionization potential.

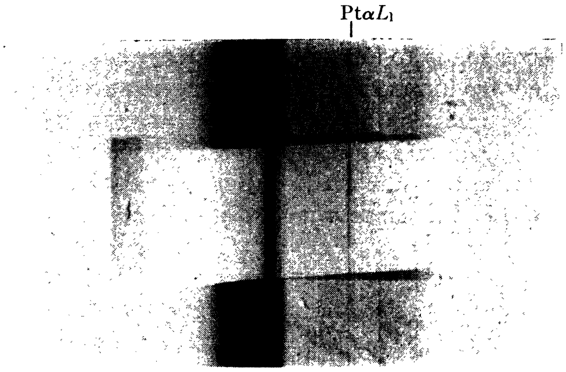


Fig. 3. K absorption and emission spectrum of copper.

Measurements from a number of plates of the relative positions of the K edge and the $K\beta_2$ line with respect to a chosen reference line show a separation smaller than that of the ionizing potential. The difference also varies with different elements. In fact, for nickel, what we have been accustomed to take as the position of the K edge is slightly longer in wave-length than the $K\beta_2$ line, while for Cu the two are sensibly the same. Fig. 3 shows the K absorption spectrum and the $K\beta_1$ and $K\beta_2$ emission lines for Cu photographed on the same plate. The reference lines is $\mathrm{Pt}L\alpha_1$.

THEORETICAL ASPECTS OF THE PROBLEM

Several hypotheses have been set forth to account for the observed structure of x-ray absorption edges. Since in this investigation free elements were used as absorbers there was no possibility of observing the white line absorption on the long wave-length side of the principal edge, similar to that found by Coster[10] and by Lindh,[11] resulting from reduction of the com-

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[10] D. Coster, Zeits. f. Physik **25,** 83 (1924).

[11] A. E. Lindh, Zeits. f. Physik **31,** 210 (1925).

pounds in the screen by the x-ray beam thus producing some of the free element. It has been demonstrated that the free element has its principal absorption limit at a longer wave-length than any of the ionized forms.

According to Kossel's[12] viewpoint, published in 1920, the principal K absorption limit corresponds to the absorption of a quantum of energy sufficient to eject a K electron to the first permissible, unoccupied orbit. For the elements studied in this investigation this would mean a transition from the K level to the N_{II} level, or what is the same, from a $1s$ to a $4p$ state. That many atoms are excited to this state by the absorption of energy, is evidenced by the fact that the $K\beta_2$ line is emitted with considerable intensity by these elements. Thus one may conclude, as did Kossel, that the probability of a K electron stopping in the first unoccupied orbit is large. However, it is very likely that in many atoms the K electron would be ejected to the $5p$ or $6p$ level if the atom absorbed a quantum sufficient for such a jump. One would therefore expect absorption limits corresponding to these various transitions. The limiting position for these secondary edges would be that which corresponds to absorption of energy sufficient to remove a K electron completely from an atom. The energy required would be in excess of that for the principal edge by an amount corresponding approximately to the first ionization potential of an atom of atomic number one greater. The first ionization potentials for the elements under consideration are 6 to 9 volts. Edges within this small range are hardly to be detected although results indicate that the separation of the first secondary edge corresponds to the limiting value, that is, to the energy of ionization. Coster and Van der Tuuk in their study of the K edge of argon found a secondary edge at 1.7 volts from the main edge. They attributed this to the absorption of energy sufficient to eject a K electron to one of the optical levels of the atom.

There is rather convincing evidence that the main edge results from absorption of energy which will remove a K electron to an outer orbit rather than from that which would completely remove the K electron from the atom. As stated under Part III, the principal edge, at least for iron, cobalt, nickel and copper, has a separation from the $K\beta_2$ line which is never more than about half the ionizing potential. The $K\beta_2$ line is ascribed to the transition of an electron from the N_{II} level to the K level. To exactly what orbit the K electron goes in the absorption process is difficult to say, although the results would indicate an excitation to a higher optical level in the cases of cobalt, iron and copper than in nickel. Allowance for this condition was made in the determination to account for the secondary edges.

The extent of absorption fine structure such as that observed by Lindsay and VanDyke for calcium in calcium compounds, by Nuttall for potassium and for chlorine in compounds of those elements, by Lindsay and Voorhees for iron (free and in combinations), by Coster[13] for copper and that by the authors has all been such that Kossel's theory, which he himself

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[12] W. Kossel, Zeits. f. Physik **1**, 119 (1920).

[13] D. Coster, Nature **124**, 652 (1929).

pointed out would explain only a small range of fine structure, would alone be quite inadequate to account for it. Secondary edges occur whose separations from the main edge are much greater than that which one could ascribe to an amount of energy of the order of the first ionization potentials. Thus one is led immediately to the supposition that a multiple ionization may result from the absorption of a single quantum of energy. It was this idea of multiple ionization that Wentzel[14] proposed to account for the so-called "spark lines" or non-diagram lines which were found in x-ray emission spectra.

If Wentzel's hypothesis is a valid one to account for the emission of the "spark" lines then the atoms must absorb energy sufficient to excite them to the states which would give rise to such lines and one ought to be able to obtain absorption edges for the corresponding states. Lindsay and Voorhees, in their work on the K absorption in iron and iron compounds sought to locate an edge which would result when the incident quantum of energy ejected an L electron with a K electron. This edge would have a separation of about 750 volts from the principal edge. The indications of such an edge were too feeble to furnish any conclusive evidence for this double ionization. Likewise, no one has reported absorption edges to confirm a double ionization of the K state. However, this does not lead to the conclusion that simultaneous multiple ionization is improbable. Ionizations involving K and M or N electrons may occur and edges corresponding to these have been found by several investigators.

To calculate the energy difference in states represented by the separation of any secondary edge from the main edge one must know, or determine, or possibly assume, the electron transition which resulted from absorption of energy to produce the main edge. It was by means of measurements on the K edge and $K\beta_2$ line for several elements that one could say with some degree of assurance to which orbit the K electron went in the case of the main edge.

Consider first the zinc absorption spectrum. Zinc, atomic number 30, has the normal configuration of electrons $3d^{10}\ 4s^2$, and all the inner orbits are filled. To excite the atom to the K state means that a K electron must be ejected at least to an N_{II} level, i.e., to a $4p$ orbit. This will be designated by $(K \rightarrow N_{\mathrm{II}})$. The ejected electron cannot stop in an inner orbit since there are no vacant ones in the neutral zinc atom. If this be the case then the wave-length for the main edge would correspond exactly to the wave-length of the $K\beta_2$ line. Although this was not verified for zinc in a manner similar to that for iron, nickel, cobalt and copper, there are other reasons to believe that one should attribute the main K edge to the transition $K \rightarrow N_{\mathrm{II}}$ as recorded in Table III under zinc. In the first place it seems reasonable to assume that when one K electron is missing, then to an outer electron the nucleus and remaining K shell together, or the core of the atom, is very much like the central portion of the element with atomic number one

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[14] G. Wentzel, Ann. d. Physik **66**, 437 (1921)

greater. Thus the nucleus and K shell of neutral zinc taken as a unit acts like a charge of 30–2 or 28 to an outer electron. This assumes that the K electrons have a complete screening effect. But with one K electron gone the effective charge would be 29. This is just the value of the charge of the

TABLE III. *Probable multiple ionizations for secondary absorption edges.*

Edge	Electron transitions	Separation from K edge in ν/R units	
		Calculated	Observed
	Calcium		
K	$(K\rightarrow M_{\mathrm{IV}})$	0.00	0.00
1	$(K\rightarrow M_{\mathrm{IV}})+(N_{\mathrm{I}}\rightarrow\infty)$	0.48	0.48
2	$(K\rightarrow M_{\mathrm{IV}})+(N_{\mathrm{I}}\rightarrow\infty)+(N_{\mathrm{I}}\rightarrow\infty)$	1.43	1.50
3	$(K\rightarrow M_{\mathrm{IV}})+(M_{\mathrm{III}}\rightarrow\infty)$	2.70	2.87
4	$(K\rightarrow M_{\mathrm{IV}})+(M_{\mathrm{I}}\rightarrow\infty)$	4.70	4.90
5	$(K\rightarrow M_{\mathrm{IV}})+(M_{\mathrm{I}}\rightarrow N_{\mathrm{II}})+(M_{\mathrm{II\,III}}\rightarrow N_{\mathrm{IV}})$	6.90	6.93
6	$(K\rightarrow M_{\mathrm{IV}})+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow\infty)$	10.20	10.45
	Chromium		
K	$(K\rightarrow N_{\mathrm{II}})$	0.00	0.00
1	$(K\rightarrow\infty)+(N_{\mathrm{I}}\rightarrow O_{\mathrm{II}})$	1.0	1.19
2	$(K\rightarrow N_{\mathrm{II}})+(M_{\mathrm{II}}\rightarrow N_{\mathrm{I}})$	3.5	3.67
3	$(K\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow\infty)+(M_{\mathrm{IV}}\rightarrow N_{\mathrm{II}})$	5.3	5.66
4	$(K\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow\infty)$	7.55	7.73
5	$(K\rightarrow N_{\mathrm{II}})+(M_{\mathrm{I}}\rightarrow M_{\mathrm{IV}})+(M_{\mathrm{II}}\rightarrow N_{\mathrm{I}})$	10.1	10.1
6	$(K\rightarrow N_{\mathrm{II}})+(M_{\mathrm{I}}\rightarrow N_{\mathrm{II}})+(M_{\mathrm{I}}\rightarrow M_{\mathrm{IV}})$	12.7	12.48
7	$(K\rightarrow N_{\mathrm{II}})+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow N_{\mathrm{IV}})$	18.2	18.08
8	$(K\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow N_{\mathrm{IV}})+(M_{\mathrm{II}}\rightarrow N_{\mathrm{IV}})$	24.1	24.23
	Manganese		
K	$(K\rightarrow N_{\mathrm{II}})+(N_{\mathrm{I}}\rightarrow M_{\mathrm{IV}})$	0.00	0.00
1	$(K\rightarrow N_{\mathrm{II}})+(M_{\mathrm{IV}}\rightarrow N_{\mathrm{II}}+(M_{\mathrm{IV}}\rightarrow N_{\mathrm{II}})$	1.2	1.13
2	$(K\rightarrow\infty)+(N_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{IV}}\rightarrow N_{\mathrm{II}})$	2.8	2.73
3	$(K\rightarrow\infty)+(N_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{IV}}\rightarrow\infty)$	3.71	3.77
4	$(K\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow\infty)$	5.3	5.38
5	$(K\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow\infty)+(M_{\mathrm{IV}}\rightarrow N_{\mathrm{II}})$	5.9	6.10
6	$(K\rightarrow N_{\mathrm{II}})+(M_{\mathrm{II}}\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow N_{\mathrm{I}})$	8.9	8.74
7	$(K\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow N_{\mathrm{IV}})$	10.1	10.23
8	$(K\rightarrow N_{\mathrm{II}})+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow\infty)$	12.6	12.80
9	$(K\rightarrow N_{\mathrm{II}})+(M_{\mathrm{II}}\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow\infty)+(M_{\mathrm{III}}\rightarrow N_{\mathrm{I}})$	13.9	13.95
10	$(K\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow N_{\mathrm{I}})+(M_{\mathrm{II}}\rightarrow N_{\mathrm{IV}})$	17.1	16.85
11	$(K\rightarrow N_{\mathrm{II}})+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow\infty)$	21.6	21.30
12	$(K\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow N_{\mathrm{I}})$	27.9	28.10
	Iron		
K	$(K\rightarrow N_{\mathrm{II}})+(N_{\mathrm{I}}\rightarrow M_{\mathrm{IV}})$	0.00	0.00
1	$(K\rightarrow\infty)+(N_{\mathrm{I}}\rightarrow N_{\mathrm{II}})$	0.72	0.67
2	$(K\rightarrow\infty)+(N_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{IV}}\rightarrow N_{\mathrm{II}})$	2.4	2.39
3	$(K\rightarrow\infty)+(N_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{IV}}\rightarrow\infty)$	3.73	3.82
4	$(K\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow\infty)$	5.8	5.54
5	$(K\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow M_{\mathrm{IV}})$	7.4	7.36
7	$(K\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow N_{\mathrm{I}})+(M_{\mathrm{II}}\rightarrow N_{\mathrm{IV}})$	9.9	9.90
7	$(K\rightarrow N_{\mathrm{II}})+(M_{\mathrm{I}}\rightarrow N_{\mathrm{II}})+(M_{\mathrm{II}}\rightarrow M_{\mathrm{IV}})$	11.9	11.70
8	$(K\rightarrow N_{\mathrm{II}})+(M_{\mathrm{I}}\rightarrow M_{\mathrm{IV}})+(M_{\mathrm{I}}\rightarrow N_{\mathrm{III}})$	15.0	14.90
9	$(K\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow N_{\mathrm{II}})+(M_{\mathrm{IV}}\rightarrow N_{\mathrm{II}})$	17.4	17.40
10	$(K\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow N_{\mathrm{I}})+(M_{\mathrm{II}}\rightarrow N_{\mathrm{IV}})+(M_{\mathrm{II}}\rightarrow N_{\mathrm{IV}})$	24.2	24.00
	Cobalt		
K	$(K\rightarrow\infty)+(N_{\mathrm{I}}\rightarrow M_{\mathrm{IV}})$	0.00	0.00
1	$(K\rightarrow\infty)+(N_{\mathrm{I}}\rightarrow O_{\mathrm{II}})$	0.86	0.86
2	$(K\rightarrow\infty)+(N_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{IV}}\rightarrow O_{\mathrm{II}})$	3.1	3.17
3	$(K\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow\infty)$	6.33	6.32
4	$(K\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow\infty)+(M_{\mathrm{II}}\rightarrow M_{\mathrm{IV}})$	11.23	11.14
5	$(K\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow\infty)+(M_{\mathrm{I}}\rightarrow M_{\mathrm{IV}})$	17.0	17.25

TABLE III. *(Continued)*

Edge	Electron transitions	Separation from K edge in ν/R units	
	Nickel	Calculated	Observed
K	$(K\to M_{\mathrm{IV}})+(N_{\mathrm{I}}\to M_{\mathrm{IV}})$	0.00	0.00
1	$(K\to M_{\mathrm{IV}})+(N_{\mathrm{I}}\to\infty)$	0.57	0.69
	$(K\to\infty)$	0.79	0.69
2	$(K\to\infty)+(N_{\mathrm{I}}\to\infty)+(M_{\mathrm{IV}}\to N_{\mathrm{I}})$	2.6	2.61
3	$(K\to M_{\mathrm{IV}})+(M_{\mathrm{II}}\to N_{\mathrm{IV}})$	5.7	5.65
4	$(K\to M_{\mathrm{IV}})+(M_{\mathrm{II}}\to N_{\mathrm{IV}})+(M_{\mathrm{II}}\to N_{\mathrm{I}})$	11.3	11.14
5	$(K\to M_{\mathrm{IV}})+(M_{\mathrm{I}}\to N_{\mathrm{II}})+(M_{\mathrm{II}}\to\infty)$	15.0	14.97
6	$(K\to M_{\mathrm{IV}})+(M_{\mathrm{I}}\to N_{\mathrm{II}})+(M_{\mathrm{I}}\to N_{\mathrm{III}})$	18.0	17.86
7	$(K\to\infty)+(M_{\mathrm{I}}\to\infty)+(M_{\mathrm{I}}\to\infty)+(M_{\mathrm{IV}}\to N_{\mathrm{II}})$	22.7	22.95
8	$(K\to\infty)+(M_{\mathrm{I}}\to\infty)+(M_{\mathrm{I}}\to\infty)+(M_{\mathrm{II}}\to\infty)$	31.2	31.20
	Copper		
K	$(K\to N_{\mathrm{II}})$	0.00	0.00
1	$(K\to\infty)+(N_{\mathrm{I}}\to N_{\mathrm{II}})$	.86	.96
2	$(K\to\infty)+(N_{\mathrm{I}}\to\infty)$	1.72	1.74
3	$(K\to\infty)+(M_{\mathrm{IV}}\to\infty)$	2.45	2.64
4	$(K\to N_{\mathrm{II}})+(M_{\mathrm{II}}\to N_{\mathrm{I}})$	6.50	6.06
5	$(K\to N_{\mathrm{II}})+(M_{\mathrm{II}}\to\infty)$	7.20	7.09
6	$(K\to N_{\mathrm{II}})+(M_{\mathrm{I}}\to N_{\mathrm{II}})$	10.10	10.11
7	$(K\to N_{\mathrm{II}})+(M_{\mathrm{I}}\to N_{\mathrm{II}})+(M_{\mathrm{IV}}\to\infty)$	11.7	11.56
8	$(K\to N_{\mathrm{II}})+(M_{\mathrm{II}}\to\infty)+(M_{\mathrm{II}}\to N_{\mathrm{I}})$	13.9	13.89
9	$(K\to N_{\mathrm{II}})+(M_{\mathrm{II}}\to\infty)+(M_{\mathrm{II}}\to N_{\mathrm{IV}})$	14.5	14.60
10	$(K\to N_{\mathrm{II}})+(M_{\mathrm{I}}\to\infty)+(M_{\mathrm{II}}\to N_{\mathrm{IV}})$	17.8	17.50
11	$(K\to N_{\mathrm{II}})+(M_{\mathrm{I}}\to N_{\mathrm{II}})+(M_{\mathrm{I}}\to N_{\mathrm{III}})$	20.7	20.20
12	$(K\to N_{\mathrm{II}})+(M_{\mathrm{I}}\to N_{\mathrm{II}})+(M_{\mathrm{II}}\to N_{\mathrm{IV}})+(M_{\mathrm{II}}\to N_{\mathrm{I}})$	24.3	24.30
	Zinc		
K	$(K\to N_{\mathrm{II}})$	0.00	0.00
1	$(K\to\infty)+(N_{\mathrm{I}}\to N_{\mathrm{II}})$	1.11	1.15
2	$(K\to\infty)+(N_{\mathrm{I}}\to\infty)$	1.95	2.00
3	$(K\to\infty)+(M_{\mathrm{IV}}\to\infty)$	2.88	2.88
4	$(K\to N_{\mathrm{II}})+(M_{\mathrm{IV}}\to\infty)+(N_{\mathrm{IV}}\to N_{\mathrm{II}})$	3.95	3.95
5	$(K\to\infty)+(N_{\mathrm{I}}\to\infty)+(M_{\mathrm{IV}}\to\infty)$	5.75	5.71
6	$(K\to N_{\mathrm{II}})+(M_{\mathrm{II}}\to\infty)$	8.24	8.46
7	$(K\to N_{\mathrm{II}})+(M_{\mathrm{II}}\to\infty)+(M_{\mathrm{IV}}\to\infty)$	11.0	10.85
8	$(K\to\infty)+(M_{\mathrm{I}}\to\infty)$	12.88	12.63
9	$(K\to\infty)+(N_{\mathrm{I}}\to\infty)+(M_{\mathrm{I}}\to\infty)$	15.35	15.48
10	$(K\to N_{\mathrm{II}})+(M_{\mathrm{II}}\to\infty)+(M_{\mathrm{II}}\to\infty)$	17.3	17.75
11	$(K\to N_{\mathrm{II}})+(M_{\mathrm{I}}\to\infty)+(M_{\mathrm{I}}\to N_{\mathrm{II}})$	24.14	24.00

core of neutral gallium. The electron configuration for gallium is $3d^{10}4s^24p$. Hence the K electron of zinc in being ejected by the absorption of energy sufficient to excite the K state would probably stop in the $4p$ orbit so as to give an outer configuration like gallium, and there would now be 29 electrons outside the K shell just as there are in neutral gallium.

Further evidence that this assumption is valid comes from the results expressed in Table III for the energy separations of the secondary edges in the zinc absorption spectrum. By taking the K electron to an N_{II} level for the main edge remarkably good agreement has been obtained between calculated and observed values for the energy separations of secondary edges from the K edge. The method employed in calculating these energy separations follows.

Column one in Table III lists the edges in order of decreasing wave-length beginning with the main edge (which has the longest wave-length) marked

"K". In the second column appear the probable electron transitions which involve absorptions of energy of sufficient amounts to account for the observed edges. Calculated and observed values (expressed in the customary ν/R units) of the energy differences which correspond to the separations of the main and secondary edges are given in the last two columns.

Confining attention to the tabulation on zinc, one notes that the K edge has been recorded as resulting from the transition $K \rightarrow N_{\text{II}}$ as mentioned above. The first secondary edge, might arise from the transitions:

$$(K \rightarrow \infty) + (N_{\text{I}} \rightarrow N_{\text{II}})$$

which may also be written as: $(K \rightarrow N_{\text{II}}) + (N_{\text{I}} \rightarrow \infty)$ although the former is easier to compute. The additional energy involved here, above that for $(K \rightarrow N_{\text{II}})$, may be determined since it amounts to:

$$(N_{\text{II}} \rightarrow \infty) + (N_{\text{I}} \rightarrow N_{\text{II}}).$$

Keeping in mind that the configuration after $(K \rightarrow N_{\text{II}})$ is $3d^{10}4s^24p$, it is evident that the term $(N_{\text{II}} \rightarrow \infty)$ requires energy measured by the first ionization potential for gallium which is 5.97 volts or 0.44 in ν/R units. One must then add to this the energy to excite a gallium ion from a $4s^2$ state to a $4s\,4p$ state. From Ga II, as given by Sawyer and Lang[15], the separation of these states is about 0.67 in ν/R. Hence the total separation of the first secondary edge from the K edge is $0.44+0.67=1.11$ whereas the observed value is 1.15.

For edge #2 we have written:

$$(K \rightarrow \infty) + (N_{\text{I}} \rightarrow \infty)$$

and since we are interested in the separation from the K edge we may write:

$$(N_{\text{II}} \rightarrow \infty) + (N_{\text{I}} \rightarrow \infty).$$

The first term as before is the energy to ionize the gallium atom once leaving the configuration $4s^2$, and the second term is the energy to remove the second ion after the first one is gone or, in other words, the second ionization potential which one obtains from the Ga II spectrum. Its value is 20.45 volts or 1.51 in ν/R. Thus the energy difference is computed to be: $0.44+1.51=1.95$. This corresponds favorably with the observed value of 2.0.

The next edge involves changes in the atom whereby two electrons, a K electron and an M_{IV} electron, are ejected from the atom. The transitions are given by:

$$(K \rightarrow \infty) + (M_{\text{IV}} \rightarrow \infty)$$

Similar to the preceding case the first term requires 0.44 in ν/R units to ionize the atom once. With the values of the energy levels as given in the thesis of F.P. Mulder,[16] the energy to remove an M_{IV} electron to an N_{II} level is found to be 1.6. But to remove the M_{IV} electron completely from

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[15] R. A. Sawyer and R. J. Lang, Phys. Rev. **34,** 712 (1929).

[16] F. P. Mulder, Diss. Groningen, 1927.

the atom will take more than that amount. In the computation for the first secondary edge it was seen that ($N_{\mathrm{I}} \rightarrow N_{\mathrm{II}}$) required 0.67 providing the K electron was ejected to infinity, while in #2 the energy was the second ionization potential if ($N_{\mathrm{I}} \rightarrow \infty$). Hence to take the M_{IV} electron out completely would require $1.51-0.67$ or 0.84 in addition to that necessary to eject it from an M_{IV} level to the N_{II} level. This gives as the total energy of separation of the third edge from the main edge:

$$0.44 + (1.6 + 0.84) = 2.88.$$

The observed value for this edge is also equal to 2.88.

Edge #4 may be accounted for by the transitions:

$$(K \rightarrow N_{\mathrm{II}}) + (M_{\mathrm{IV}} \rightarrow \infty) + (M_{\mathrm{IV}} \rightarrow N_{\mathrm{II}})$$

and for the separation value we need consider just the last two terms. With the K electron stopping in the N_{II} orbit the atom is much like neutral gallium. We need therefore 1.6 in ν/R to take an M_{IV} electron to the N_{II} orbit but this time only 0.44 more to remove it entirely from the atom since this amounts to the first ionization. Hence the term ($M_{\mathrm{IV}} \rightarrow \infty$) requires $1.6+0.44=2.04$. The next step necessitates the excitation of a second M_{IV} electron to the N_{II} level. Since one electron has already been taken from this group it should require more than 1.6 for the second M_{IV} electron. In order to estimate what increase ought to be made one needs to consider the value of the screening constant for the $M_{\mathrm{IV},\mathrm{V}}$ levels, which Sommerfeld[17] gives as 13.0. This means that the average screening effect for each electron is not more than about one half so that it seems reasonable to assume the value of the M_{IV} level to be increased by approximately one third the amount that the germanium M_{IV} level exceeds the gallium M_{IV} level. Thus the term ($M_{\mathrm{IV}} \rightarrow N_{\mathrm{II}}$) requires 1.9 and the total amount of energy that corresponds to the separation of edge #4 from the K edge is:

$$1.6 + 0.44 + 1.9 = 3.94.$$

Experimentally the separation was found to be 3.95.

The fifth secondary edge is associated with the following changes in electron configuration:

$$(K \rightarrow \infty) + (N_{\mathrm{I}} \rightarrow \infty) + (M_{\mathrm{IV}} \rightarrow \infty)$$

which may be written:

$$(K \rightarrow \infty) + (N_{\mathrm{I}} \rightarrow \infty) + (N_{\mathrm{I}} \rightarrow \infty) + (M_{\mathrm{IV}} \rightarrow N_{\mathrm{I}})$$

since in both the resulting configuration is the same, and the latter form lends itself more readily to computation. Considering again only the energy corresponding to the separation of the secondary edge and the K edge we may write:

$$(N_{\mathrm{II}} \rightarrow \infty) + (N_{\mathrm{I}} \rightarrow \infty) + (N_{\mathrm{I}} \rightarrow \infty) + (M_{\mathrm{IV}} \rightarrow N_{\mathrm{I}})$$

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[17] A. Sommerfeld, "Atomic Structure and Spectral Lines," Methuen, London.

and recalling that the configuration after $(K \rightarrow N_{\mathrm{II}})$ is $3d^{10}4s^2\,4p$ we see that the first, second and third terms require energy equal to the first, second and third ionization potentials of gallium respectively. The last term amounts to the excitation of a Ga^{+++} ion from a $3d^{10}$ state to a $3d^94s$ state. From the Ga IV spectrum as reported by Mack, LaPorte and Lang,[18] the separation of the terms $3d^{10}$ and $3d^9\,4s$ is approximately 1.3. The four terms above give then:

$$0.44 + 1.51 + 2.5 + 1.3 = 5.75$$

compared with 5.71 which is the observed value for the separation in energy of the fifth secondary edge from the K edge.

In quite an analogous manner one can account for the other observed secondary edges. For each case one must choose those transitions such that the energy involved will correspond as nearly as possible to the observed values. This has been done for six more edges in zinc as well as for those found for the other elements studied. In most cases the agreement is good.

The question naturally arises as to the uniqueness of the transitions involved. Are there other possible combinations of transitions that will serve equally well to account for any given edge? In most instances the answer would probably be in the negative. One exception has been recorded in Table III for edge #1 in nickel. For the first few edges in each spectrum one must restrict the choice of electron transitions to those involving only the outer or valence electrons, since levels inside $M_{\mathrm{IV,V}}$ are already too deep. In contrast with this one has difficulty (especially with the lighter elements studied) in finding transitions which involve enough energy to account for the shortest wave-length secondary edges. As mentioned above, changes calling for transitions from the L levels do not aid in this situation since one change such as $(L \rightarrow M)$ would involve too much energy to account for any observed secondary edge.

The predominating factors which governed the choice of transitions to account for a given separation (other than that the total energy be correct) were:

(1) the electron configuration corresponding to the K edge
(2) minimum number of electron transitions.

The first of these had been discussed at length under the calculations of the various secondary edges. Some verification of the second is shown by the fact that the most prominent secondary edges seem to be associated with those changes in which the K electron and only one other (usually an M_{I} or an M_{II}) electron are excited. Thus two electron jumps seem more probable than those involving three or more, which is to be expected.

In connection with this characteristic feature concerning the excitation of M electrons with K electron it has been mentioned above that Coster has observed a fine structure in copper that is in good agreement with the results herein reported for that element. However, he obtained no secondary

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[18] J. E. Mack, Otto Laporte and R. J. Lang, Phys. Rev. **31**, 748 (1928).

edges in zinc and attributed this negative result to the fact that in zinc (normal configuration $3d^{10}4s^2$) the $3d$ group of electrons is completely filled, so that it would be much more difficult to break into this configuration than it would be in the case of let us say—iron, nickel or even copper. A glance at Table III will indicate, however, that transitions of M electrons enter into practically every computation for zinc secondary edges.

When one compares the general method of computing the energy separations of the secondary edges from the K edge as outlined and applied in this investigation with the method used by Ray[19] for potassium, calcium and chlorine, it is very evident that there will be wide deviations in the results. One or two specific calculations will be given to confirm this statement.

Ray has used the experimental data of Nuttall[7] for potassium in various compounds, and also the data of Lindsay and Van Dyke[6] for calcium in calcium compounds. The normal configuration of potassium is $2p^64s$. The K edge, according to Ray, is associated with the transition ($K\rightarrow\infty$). The first secondary edge is related to the change:

$$(K \rightarrow \infty) + (N_{\mathrm{I}} \rightarrow \infty)$$

so that the separation of this edge from the main edge is due to the term ($N_{\mathrm{I}}\rightarrow\infty$) which Ray gives as the first inoization potential of potassium or 4.1 volts. The observed value for the separation varies from 2.8 to 4.9 volts in different compounds. Several objections to this treatment may be noted.

In the first place, when the K electron is ejected either to an outer orbit or to infinity it seems more reasonable to assume that to an outer electron, such as an N_{I} electron, the core of the atom should be more like calcium than potassium. If the K electron remained in the outer portion of the atom then the transition ($N_{\mathrm{I}}\rightarrow\infty$) ought to correspond to the first ionization potential of calcium (6.09 volts), instead of to that for potassium (4.3 volts). But with the assumption that the K electron is ejected to infinity one ought therefore to regard ($N_{\mathrm{I}}\rightarrow\infty$) as requiring energy equal to the second ionization potential of calcium which is 11.8 volts rather than 4.1 volts. A further objection arises since the potassium is present as an ion and not as an atom in the free state. In the ionic state there might not even be an N electron which could be ejected. The calculations on subsequent edges for potassium are also open to quite similar objections.

Ray's treatment of the calcium edges seems equally unsatisfactory. The normal configuration is $2p^64s^2$ and for the K edge he has assigned the transition ($K\rightarrow\infty$). For the first edge he gives as the electron jumps:

$$(K \rightarrow \infty) + 2(N_{\mathrm{I}} \rightarrow \infty)$$

so that the latter term involves the energy which corresponds to the separation of this edge from the main edge. This he gives as twice the first ioniza-

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[19] B. B. Ray, Zeits. f. Physik **55**, 119 (1929).

tion potential for calcium (6.1 volts) or 12.2 volts, as compared with the observed value of 13.3 to 16.0 volts.

Neglecting the fact that the calcium is in a compound, the following interpretation of the transitions:

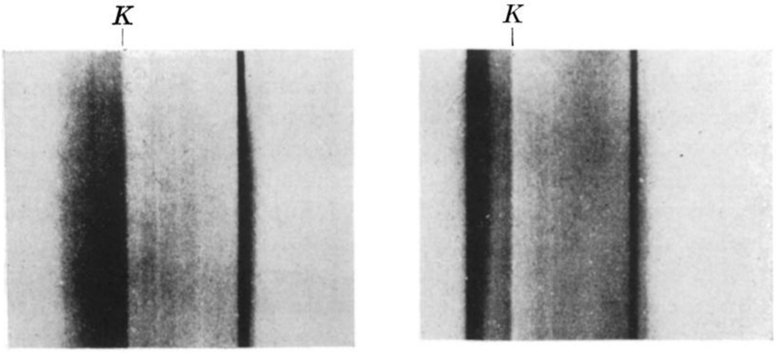
$$(K \rightarrow \infty) + 2(N_{\mathrm{I}} \rightarrow \infty)$$

seems more preferable:

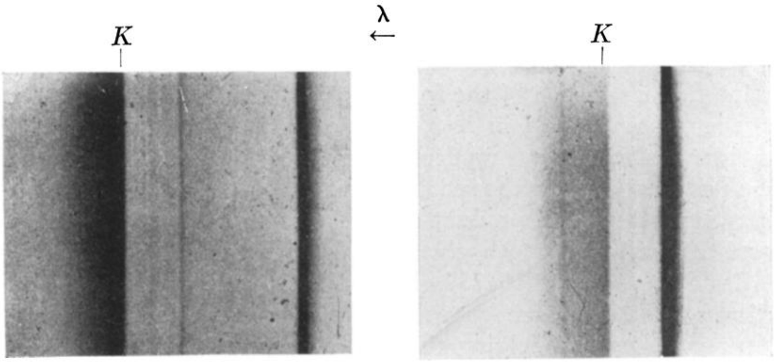
Since the K electron is completely ejected the atom is now much like ionized scandium (Sc^+). Removing one of the N_{I} electrons would require energy equal to the second ionization potential of scandium which is 12.8 volts. To remove the second N_{I} electron ought to take an amount of energy equal to the third ionization potential which is about 25 volts. Thus the total energy separation would be approximately 38 volts instead of 12.2. volts as given by Ray. The value for the next secondary edge in calcium is about 31 volts. Thus the transitions:

$$(K \rightarrow \infty) + 2(N_{\mathrm{I}} \rightarrow \infty)$$

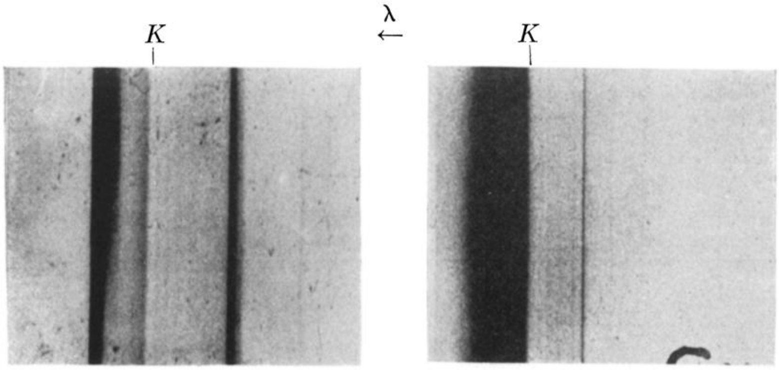
as chosen by Ray, which under our interpretation given above corresponds to an energy separation from the K edge of 38 volts, represent not only a great deal in excess of the 15 volts demanded for the first edge, but even too much to account for the separation of the second secondary edge from the main edge.



Chromumi Manganese



Iron Cobalt



Nickel Copper

Fig. 1. Fine structure in the absorption spectra of the K series of several elements.

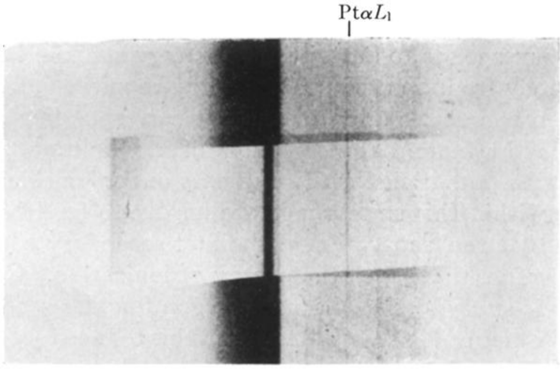


Fig. 3. *K* absorption and emission spectrum of copper.