THE K–CHARACTERISTIC ABSORPTION FREQUENCIES FOR THE CHEMICAL ELEMENTS MAGNESIUM TO CHROMIUM.

BY HUGO FRICKE.

SYNOPSIS.

Absorption of X-Rays.—This paper contains an account of an experimental investigation concerning the discontinuity in the *X*-ray absorption corresponding to the K-series for the chemical elements from magnesium to chromium inclusively. The method followed was the same as that devised and employed by de Broglie. A specially designed vacuum spectrograph was used.

Fine Structure of Absorption.—The spectrograms show that the discontinuity has a rather *complex structure*, a result in advance of those obtained by earlier investigators. A *photometric study* of the plates was made in order to obtain a more accurate knowledge of the detailed structure of the absorption limits.

Results. These are recorded in tables which give for each element the wave-lengths of the different remarkable points in the structure of the discontinuities. The theoretical bearing of the new observations is briefly discussed.

DURING the last few years, an accurate method for determining the longer wave-lengths of X-rays has been worked out by M. Siegbahn and his assistants, employing a vacuum spectrograph designed by him.[1] An interesting feature of the method is that the wave-length differences which can be determined correspond to an amount of energy of the order of 1 volt times the charge on the electron, that is of the same order as arises in processes performed in the exterior of the atom. For the frequency ν, the potential E, and the glancing angle ϕ, we find

$$\frac{\Delta\nu}{\nu} = \frac{\Delta E}{E} = \frac{\Delta\phi}{\tan\phi}.$$

$\Delta\phi$ can be determined by Siegbahn's method and apparatus to within 10^{-4}. For the longest waves with which one can work, E is about 1,000 volts, that is $\Delta E < 1$ volt. It may therefore be expected that Siegbahn's method will lead to the detection of many effects which are caused by the action of the outermost electrons from which effects a calculation of the arrangement of the electrons can be made. For instance, it may be found that the position of certain lines of the X-ray

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[1] M. Siegbahn, Phil. Mag. (37), p. 601, 1919, and Ann. d. Phys. (4), 59, p. 56, 1919. W. Stenström, Ann. d. Phys. (4), 57, p. 347, 1918 and Diss. Lund., 1919.

spectrum of a given substance depends on the chemical combination of the radiating atom. It is also to be expected that the variation in the wave-lengths of a given line for the different elements in the periodic table will not be continuous, but a little irregular, corresponding to the discontinuities in the arrangement of the outermost electrons as we progress in the periodic table. Effects of these sorts ought to be most strongly pronounced for the limiting frequencies of the series, because one of the two energies, on the difference of which the frequency depends, is directly associated with the conditions in the outermost part of the atom.

Up to the present time measurements of the longer wave-lengths with the precision stated above have been made for only a few lines.[1]

The following is a contribution to the completion of this work. It consists of a series of measurements of the limiting frequencies in the K-series for the chemical elements from magnesium to chromium. As will be seen a rather complex structure of the limit is found.

The measurements were all performed in 1918 at the physical laboratory of the University of Lund (Sweden), using the vacuum spectrograph of M. Siegbahn. It gives me great pleasure to express here my gratitude to Prof. M. Siegbahn for putting at my disposal the vacuum spectrograph and the other resources of his X-ray laboratory, and for the interest he has taken in my work.

As regards the construction and operation of the vacuum spectrograph the reader is referred to the above cited papers of M. Siegbahn and W. Stenström.

The method of investigation is that first employed by de Broglie.[1] A suitable part of the continuous X-ray spectrum from the target in an X-ray tube, with an absorbing substance introduced in the path of the rays, is photographed.

Care must be taken to use the proper quantity of absorbing substance. Too great or too small a quantity effaces the details of the structure of the limit.

The quantity should be so chosen that the ratio between the intensities of the emergent rays on opposite sides of the limiting frequency has a convenient value which is neither too great nor too small.

Glocker[2] has given two simple formulas, which express the absorption coefficient of the X-rays for the two sides of the limit as a function of the wave-lengths of the absorbed radiation and the atomic number of the absorbing substance. Using these formulæ the quantities of the sub-

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[1] M. de Broglie, C. R., 158, p. 1493, 1914.

[2] Glocker, Phys. Zeits., 19, p. 66, 1918.

stances to be investigated were calculated so that the ratio in question was about 1 : 6.

For most substances the pure element or one of its salts was spread in a thin layer upon a thin sheet of paper. This was placed between the slit and the crystal.

Argon was procured from the air by absorption of the oxygen and nitrogen. This was done by the well known method of leading the air over glowing copper and magnesium. Most of the oxygen was previously absorbed by pyrogallol. The argon was drawn at a pressure of 6 cm. of mercury into a container. This was made of a brass tube 8 cm. long closed at both ends with plates, which, to allow for the passage of the X-rays, were provided with slits closed with gold-beater's skin. A test before filling the tube showed that it could support a vacuum sufficiently well. The tube when under exposure, was placed between the slit and the crystal.

In the case of chlorine, since in this work rock-salt was used as the crystal, no particular absorbing substance was needed.

In the case of aluminium and magnesium some difficulties were encountered, owing to the fact that the absorption of organic substances for the long wave-lengths here employed is very considerable. The proper quantities of Al and Mg to be used are about 0.25 mg. per cm.^{2} (or foils about 1 μ thick). The most convenient manner of manipulating such small quantities would be perhaps to employ the same method as is used for most of the other substances (see above), that is to spread suitable salts of Mg and Al (MgO, Al_2O_3) in a thin layer on a thin sheet of paper. As stated in the cited papers of M. Siegbahn and W. Stenström, it is necessary to place a suitable foil in the slit in order to attain the high vacuum in the discharge tube; the best method for that purpose would then be to use gold-beater's skin in the case of Al and a thin foil of Al in the case of Mg (the limiting wave-length of Mg being longer than the limiting wave-length of Al, its absorption in this substance will be comparatively small). This arrangement will, however, owing to the great absorption of the gold-beater's skin, and of the paper demand too long a time of exposure. For this reason it was decided to employ another method. Thin foils of Al and Mg were placed over the slit, acting both to seal the tube and to absorb the rays. Owing to the comparatively small absorption of these substances for wave-lengths longer than the limiting ones, we can with this arrangement reduce the time of exposure very considerably, but in employing this method it is necessary to use fairly thick foils, and therefore we will find only the sudden change in the absorption. No details of the limit can be found. The Al foil had a thickness of 7 μ, the Mg foil 10 μ. The latter was made from ordinary mg. wire by rolling. Foil as thin as 6 μ could be made in this way. This thin foil was found, however, to be unable to maintain the high vacuum in the X-ray tube, because of small holes which could not be avoided at these small thicknesses; nothing thinner than 10 μ was found adequate for the purpose. Calculation shows that these two foils absorb practically all the radiation of a wave-length smaller than the limiting one; in accordance with this, the plates for Mg and Al, as we shall see, do not show any structure of the limit.

The discharge tube is a metal one of the Coolidge type. This is a great advantage in this work, owing to the fact that the potential can immediately be given the desired value. This is important because it is necessary, especially for the longest wave-lengths, to be able to use such a low potential that the spectra of higher orders are not produced. Otherwise these spectra, their smaller absorption compensating for their smaller reflection from the crystal, will be strong enough to mask completely the structure of the limit. Care of this must especially be taken when working with sugar as a crystal, for here we have a third order spectrum which is just as strong as, or even stronger than, the 1st order. An unpleasant consequence of the low potential is the comparatively slight intensity of the radiation. For the lightest substances the low potential causes further difficulty, in that here the space charge prevents the passage through the tube of the great current usually used, and particularly desirable in this case. For magnesium, in order to obtain a current of the proper magnitude, it was necessary to use a potential rather greater than that indicated by the above-mentioned considerations; in consequence we have here a distinct superposition of the third order spectrum (see below). Tungsten was used for the anticathode. It gives a very strong continuous radiation, and allows the passage of a large current. The same metal was used for the incandescent spirals. The current through the tube was about 40 milliamperes, the time of exposure varying from 3 to 16 hours. Only one plate of each substance was taken; in order to get the right time of exposure at once, a rough calculation of the absorption of the wave-length in question was made before the exposure, and the time for this chosen in accordance with the result obtained. So far as possible the chemical compound of the absorbing substance was chosen so as to contain only very light atoms. This, however, was not always possible.

A sugar crystal was used for the lighter substances examined. For the others a rock salt crystal was employed. The reflecting power of both these crystals is very good. The grating constant used for sugar is

$$\log 2d = 1.32503$$

and for rock salt

$$\log 2d = 0.750354.$$

The first was determined by photographing the CuK_α line using for the wave-length of this line the value given by Siegbahn.[1] The second is the generally adopted value.

The width of the slit (between the anticathode and the crystal) was 0.10 mm.

Under exposure the crystal was turned through a certain angle so that a proper wave-length interval around the wave-length in question is obtained on the plate; this angle was 1°.5–2.°0.

For the calculation of the desired wave-lengths from the photographic plate, it is necessary to photograph a known spectral line on the same plate. For this purpose lines only are used on which precision measurements had already been made at Lund.[2]

To determine the different details in the limit a photometric investigation of the plates was made. The arrangement used for this was the following: Through a microscope objective a narrow ray of light (.02 mm. wide) from an incandescent lamp run by a storage battery, was thrown on the plate; after emerging it was suitably enlarged and thrown upon a thermopile; the deflection of a galvanometer connected to this gave a measure of the blackening of the plate. The plate was mounted on a slide; the galvanometer mirror formed an image of the filament of an incandescent lamp upon a photographic paper wrapped around a cylinder. Automatic registration could then be obtained by coupling (by toothed wheels) the cylinder and the slide. The slide was moved by a motor at a speed determined by the oscillation constants of the aperiodic system composed of the thermopile and the galvanometer. These constants were previously determined by a simple experiment.

The ratio between the distances on the plate and on the photographic paper must be determined for each plate, as the dimensions of the paper are altered slightly when it is developed. For this purpose, before the photometric investigation, two fine lines are drawn on each plate at a convenient distance from the limit. They are recorded very distinctly on the curve of blackening. By measuring their distance on this and on the plate the desired ratio can be obtained, and is found to be about 17.46 : 1. The measurement on the plate was made with a comparator with better than .01 mm. accuracy.

By means of a microscope the correct orientation of the light ray on

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[1] M. Siegbahn, loc. cit.

[2] M. Siegbahn, loc. cit.

the plate is obtained. Owing to the short length (1 mm.) of the ray three investigations are made, with the ray at the upper, middle and lower part of the plate.

Only the part of the plate around the limit is investigated; the distance of the reference line from one of the drawn lines is measured with the comparator with an accuracy of about .01 mm.

By the photometric method here described the position of the points on the photographic plates can be determined with an accuracy of a few hundredths of a mm. A difficulty encountered in this method is the above mentioned alteration of the photographic paper when developed; this is not always exactly the same in every part.

No limit was found for silicon. First a plate was taken with the above mentioned arrangement. As absorbing substance pure silicon was used, spread in a layer of .70 mg. per cm.^{2} on a sheet of paper. During the exposure the crystal was turned through an angle corresponding to the wave-length interval

$$\lambda = 6.46 - 7.09\text{Å} \ (\text{Si } K_{\beta 1}\lambda = 6.76).^1$$

No limit could be detected on the plate. The reason may be that the limit was covered by the $WM_{\beta 1}$, line; this has a wave-length of 6.75Å, and is recorded very strongly on the plate.

A new plate was taken with platinum as anticathode; this time J used 1.7 mg. of silicon per cm.^{2} and examined the wave-length interval $\lambda = 6.35$–7.09Å. No limit could be detected; still the $WM_{\beta 1}$ line was rather strong owing to the deposition of tungsten from the incandescent spiral on the target. Later, spirals of molybdenum were tried. These were found to be impracticable because of their great evaporation, which causes so poor a vacuum that a sufficiently strong current could not be obtained, and also causes the spiral to be rapidly consumed. Tantalum, which probably would have been found very suitable, was unfortunately not procurable.

As has already been mentioned above, the plates show that the limit is not, as has been commonly thought up to this time, a simple discontinuity in the blackening of the plate, which covers a wave-length interval equal to about the width of a spectralline; but it is found, that the limit presents a rather complex structure. As a rule we can state: we have on the plate two parts of uniform, but unequal blackenings; the limit is the transition between these two; the stronger of the two blackenings has always on the side of the shorter wave-lengths a very distinct boundary (Km), on the other side of this we have a very bright

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[1] M. Siegbahn and W. Stenström, Phys. Zeits., 15, 1916.

line or band (L); after this we frequently have a dark line and then again sometimes a bright band.

On the plates for chromium, vanadium and titanium, a characteristic narrow dark line is seen in the bright line *L* close up to the boundary Km; the phenomenon is most pronounced for chromium and vanadium; for titanium the fine bright boundary line between Km and the dark line is less distinct.

No structure is found for the limits of magnesium, aluminium and argon. As regards the first two substances, this was to be expected for the reason mentioned above. As regards argon the reason perhaps may be that the plate is rather underexposed.

In the following for each substance tables will be given containing the wave-length (λ, unit Å) of Km and the wave-length difference ($\Delta\lambda$, unit Å) between Km and the different remarkable points in the structure of the limit, also the distances (Δx unit mm.) on the photographic plate, the frequency differences (Δv unit : 10^{15}) and energy differences (Δe unit: volt times the charge of the electron) corresponding to the latter are given. $\Delta\lambda$ is determined by:

$$\Delta\lambda = \frac{\lambda}{2\gamma \tan \varphi} \Delta x,$$

λ : Wave-length of Km,

φ : glancing angle,

γ : Distance from the axis of the vacuum spectrograph to the photographic plate. In addition a description of each plate is given. Owing to different well known optical illusions, it is always specially emphasized when features observed in the plates are not shown in the photometric curves.

12 MAGNESIUM (FIG. 1).

Absorbing screen: pure Mg: 1.74 mg. per cm.^{2}; reference line:

$$\text{SnL}\alpha_1\ \lambda = 3.5929.$$

Crystal: Sugar.

Spectrum—1st order.

$$K_m : \lambda = 9.5112 \text{ Å.},$$

$$K_m - K_l : \Delta x = 0.26 \text{ mm.},$$

$$\Delta\lambda = 0.019 \text{ Å.},$$

$$\Delta\nu = 0.64 \times .10^{15},$$

$$\Delta\epsilon = 2.7 \text{ volt}.$$

Description of the plate: No structure of the limit is seen; this appears only as a distinct discontinuity $K_m - K_l$ in the blackening of the plate.

13 Aluminium (Fig. 1).

Absorbing screen: pure Al, 1.89 mg. per cm.^{2}; reference line:

$$\mathrm{WL}\alpha_1 : \lambda = 1.4735 \text{ and } \mathrm{SnL}\alpha_1 : \lambda = 3.5929.$$

Crystal: Sugar.
Spectrum: 1st order.

$$\begin{aligned} \mathrm{K}_m : \lambda &= 7.9470 \text{ Å.}, \\ \mathrm{K}_m - \mathrm{K}_l : \Delta x &= 0.32 \text{ mm.}, \\ \Delta\lambda &= 0.025 \text{ Å.}, \\ \Delta\nu &= 1.18 \times 10^{15}, \\ \Delta\epsilon &= 4.9 \text{ volt.} \end{aligned}$$

Description of the plate: What is stated for magnesium will apply here also.

15 Phosphorus (Fig. 2).

Absorbing screen: H_3PO_4, 0.80 mg. P per cm.^{2}; reference line:

$$\mathrm{Sn}\ \mathcal{L}\alpha_1\ \lambda = 3.5929.$$

Crystal: Sugar.
Spectrum: 3d order.

$$\mathrm{K}_m : \lambda = 5.7580 \text{ Å.}$$

	$\mathbf{K}_m - \mathcal{L}$.	$\mathbf{K}_m - \mathbf{K}_l$.
$\Delta\chi$	0.52 mm.	0.86 mm.
$\Delta\lambda$	0.0084 Å.	0.0139 Å.
$\Delta\nu$	$0.76.10^{15}$	$1.26.10^{15}$
$\Delta\epsilon$	3.16 volt	5.25 volt

Description of the plate: Two parts of unequal blackening ($\mathrm{I} - \mathrm{K}_m$ and $\mathrm{K}_l - \mathrm{II}$), separated by a bright line ($\mathrm{K}_m \mathcal{L} \mathrm{K}_l$).

16 Sulphur (Fig. 3 and Fig. 9).

Absorbing screen: S, 0.90 mg. per cm.^{2}; reference line:

$$\mathrm{Sn}\mathcal{L}\alpha_1\ \lambda = 3.5929.$$

Crystal: Sugar.
Spectrum: 3d order.

$$\mathrm{K}_m : \lambda = 5.0123 \text{ Å.}$$

	$\mathbf{K}_m - \mathcal{L}$.	$\mathbf{K}_m - \mathcal{M}$.	$\mathbf{K}_m - \mathbf{N}$.
$\Delta\chi$	0.23 mm.	0.64	1.29
$\Delta\lambda$	0.0045 Å.	0.0125	0.0253
$\Delta\nu$	$0.54.10^{15}$	1.49	3.02
$\Delta\epsilon$	2.3 volt	6.2	12.6

Description of the plate: Starting from the boundary (K_m) of the stronger uniform blackening ($I - K_m$), we have first a distinct bright line ($K_m\mathcal{L}\mathcal{M}$, 0.3 mm.), then a distinct dark line ($\mathcal{M}$) and then at last a very faint bright band (MN, 0.7 mm.), which, with an apparently distinct limit, borders on the fainter uniform blackening (N − II).

Whether there is in reality a distinct limit between the bright band (MN) and the uniform blackening (NII) cannot, owing to the faintness of the bright band, be decided with certainty from the photometric curves.

17 CHLORINE [FIG. 3].

No absorbing screen. Reference line: $ClK\alpha_1\ \lambda = 4.7187$.
Crystal: Rocksalt.
Spectrum: 1st order.

$$K_m = 4.3844.$$

	$K_m - \mathcal{L}$.	$K_m - \mathcal{M}$.
$\Delta\chi$	0.43 mm.	0.95 —
$\Delta\lambda$	0.0060 Å.	0.0132 —
$\Delta\nu$	$0.93.10^{15}$	2.06 —
$\Delta\epsilon$	3.9 volt	8.6 —

Description of the plate: Looks exactly like that for sulphur; the bright line apparently is 0.6 mm., the bright band 0.9 mm. wide.

18 ARGON (FIG. 1).

Absorbing substance: A., 1.5 mg. per cm.^{2}; reference line:

$$Sn\ \mathcal{L}\alpha_1\ \lambda = 3.5929.$$

Crystal: Sugar.
Spectrum: 3d order.

$$K_m\ \lambda = 3.8657.$$

	$K_m - K_l$
Δx	0/14 mm.
$\Delta\lambda$	0.0033 Å.
Δv	$0.67.10^{15}$
Δe	2.8 volt.

Description of the plate: The same as for those of magnesium and aluminium.

19 POTASSIUM (FIG. 4).

Absorbing substance: K_2CO_3, 2.00 mg. K per cm.^{2}; reference line:

$$Sn\mathcal{L}\alpha : \lambda = 3.5929.$$

Crystal: Sugar.

Spectrum: 1st order.

$$K_m : \lambda = 3.4345.$$

	$K_m - \mathcal{L}$.	$K_m - \mathcal{M}$.	$K_m - \mathcal{L}'$.
$\Delta\chi$	0.16 mm.	0.35 –	0.47 –
$\Delta\lambda$	0.013 Å.	0.027 –	0.039 –
$\Delta\nu$	$3.4.10^{15}$	6.9 –	9.9 –
$\Delta\epsilon$	14. volt	29. –	41. –

Description of the plate: Looks about the same as the plates for sulphur and chlorine; a bright line ($\mathcal{L}$), a dark line (M) and a fainter bright band ($\mathcal{L}'$); no distinct limit of this however can be seen here; still it must be remarked, that, Sn$\mathcal{L}\beta$, which is presented very strongly, perhaps covers the last part of the bright band.

The photometric curves seem to indicate the same structure for the bright band as for the bright line $\mathcal{L}$.

20 CALCIUM (FIG. 2).

Absorbing substance: $CaCO_3$, 1 mg. Ca. per cm.^{2}; reference line:

$$CuK\alpha_1 \ \lambda = 1.5374.$$
$$W\mathcal{L}\alpha_1 \ \lambda = 1.4735.$$

Crystal: Rocksalt.
Spectrum: 1st order.

$$K_m : \lambda = 3.0633 \text{ Å}.$$

	$K_m - \mathcal{L}$.	$K_m - K_l$.
$\Delta\chi$	0.41 mm.	1.2 –
$\Delta\lambda$	0.0078 Å.	0.023 –
$\Delta\nu$	$2.48.10^{15}$	7.4 –
$\Delta\epsilon$	10.3 volt	31 –

Description of the plate: Looks about the same as the plate for phosphorus.

21 SCANDIUM (FIG. 5.)

Absorbing substance: $Sc_2(SO_4)_3$, 1.7 mg. Sc. per cm.^{2}; reference line:

$$VK\alpha_1 \ \lambda = 2.4987 \text{ Å}.$$

Crystal: Rocksalt.
Spectrum: 1st order.

$$K_m : \lambda = 2.7517 \text{ Å}.$$

	$K_m - \mathcal{L}$.	$K_m - M$.	$K_m - N$.
$\Delta\chi$	0.47 mm.	1.14 –	2.30 –
$\Delta\lambda$	0.0091 Å.	0.0222 –	0.0446 –
$\Delta\nu$	$3.62.10^{15}$	8.79 –	17.67 –
$\Delta\epsilon$	15.1 volt	36.7 –	73.7 –

Description of the plate: Here and also on the following plates for titanium and vanadium two dark, rather broad and diffuse lines (M_1 and M_2) are seen in the fainter uniform blackening; their distances from K_m are about 1 and 3 mm.; the first is the stronger; it forms the boundary between $\mathscr{L}$ and the fainter uniform blackening. The existence of the second is perhaps questionable; it cannot be shown with certainty on the photometric curves.

22 TITANIUM (FIG. 6 and Fig. 10.)

Absorbing substance: TiO_2, 2.0 mg. Ti per cm.^{2}; reference line:

Cr $K\alpha_1$ $\lambda = 2.2852$.

Crystal: Rocksalt.
Spectrum: 1st order.

K_m, $\lambda = 2.4937$.

	$K_m-\mathscr{L}'$.	**[$K_m-\mathscr{L}''$].**	**K_m–m.**
$\Delta\chi$	0.63 mm.	1.07 –	0.14 –
$\Delta\lambda$	0.0124 Å.	0.0214 –	0.0028 –
$\Delta\nu$	$6.0.10^{15}$	10.3 –	1.3 –
$\Delta\epsilon$	25.0 volt	43.0 –	5.6 –

Description of the plate: M_1 (see under scandium) has here a very distinct boundary on the side toward the bright line $\mathscr{L}$; this has a very well defined breadth ($\mathscr{L}' - \mathscr{L}''$). In the middle of $\mathscr{L}$ is seen a very faint dark line M′; where this is shown on the photometric curves cannot with certainty be determined. As already mentioned above we have a very dark distinct line (here not so pronounced as in the case of vanadium and chromium) in $\mathscr{L}$ close up to K_m; it is shown in the photometric curves at *m*.

23 VANADIUM (FIG. 7).

Absorbing substance: V_2O_5, 2mg. V per cm.^{2}; reference line:

Fe $K\alpha_1$: $\lambda = 1.9324$.

Crsytal: Rocksalt.
Spectrum: 1st order.

K_m : $\lambda = 2.2653$.

	K_m – l.	**K_m – m.**	**$K_m - \mathscr{L}$.**	**K_m – M′.**	**K_m – M.**
$\Delta\chi$	0.17 mm.	0.26 –	0.60 –	1.18 –	1.60 –
$\Delta\lambda$	0.0035 Å.	0.0053 –	0.0123 –	0.0242 –	0.0327 –
$\Delta\nu$	$2.0.10^{15}$	3.1 –	7.2 –	14.2 –	19.1 –
$\Delta\epsilon$	8.5 volt	12.9 –	30.0 –	59.0 –	79.8 –

Physical Review, Vol. XVI., Second Series.
September, 1920.

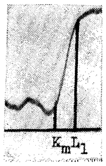

Fig. 1.

Aluminium.

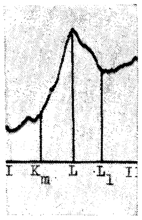

Fig. 2.

Phosphorus.

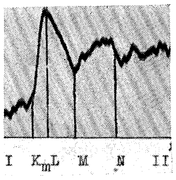

Fig. 3.

Sulphur.

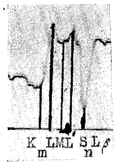

Fig. 4.

Potassium.

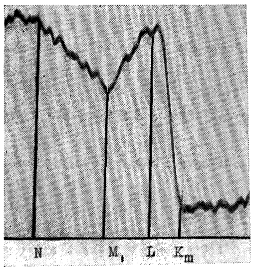

Fig. 5.

Scandium.

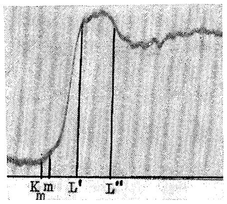

Fig. 6.

Titanium.

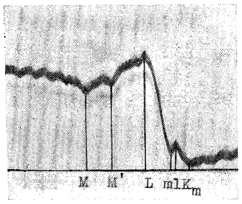

Fig. 7.

Vanadium.

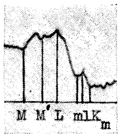

Fig. 8.

Chromium.

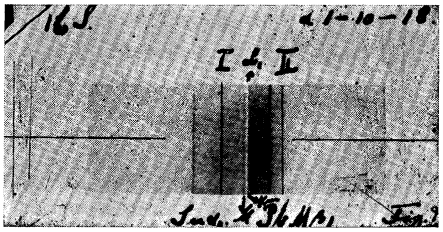

Fig. 9.

Sulphur.

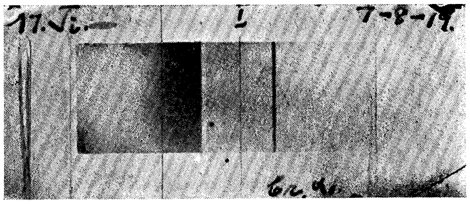

Fig. 10.

Titanium.

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Description of the plate: Like the plate for titanium; the dark line *m* close to K_m is here seen very distinctly; the bright line between *m* and K_m is shown on the photometric curves by l.

24 CHROMIUM (FIG. 8).

Absorbing substance: K_2CrO_4, 1 mg. Cr. per cm.[2]; reference line:

$W\mathcal{L}\alpha_1\ \lambda = 1.4735$.

Crystal: Rocksalt.
Spectrum: 1st order.

$K_m : \lambda = 2.0675$ Å.

	K_m – l.	K_m – m.	K_m – $\mathcal{L}$.	K_m – M′.	K_m – M.
$\Delta\chi$........	0.13 mm.	0.20 –	0.47 –	0.74 –	1.05 –
$\Delta\lambda$........	0.0026 Å.	0.0040 –	0.0098 –	0.0153 –	0.0218 –
$\Delta\nu$........	$1.8.10^{15}$	2.8 –	6.8 –	10.7 –	15.3 –
$\Delta\epsilon$........	7.6 volt	11.8 –	28.6 –	45.0 –	64.0 –

Description of the plate: The two dark lines M_1 and M_2 are not seen here; the bright line $\mathcal{L}$ has very distinct boundaries on both sides ($\mathcal{L}'$ and $\mathcal{L}''$); as in the case of titanium and vanadium a very faint dark line M′ is seen in the middle of $\mathcal{L}$. What is stated for vanadium about the dark line m will apply here also.

No satisfactory theory for the limiting frequency has as yet been published. Kossel,[1] on the basis of Bohr's theory, regards the limiting frequency of a certain series as corresponding to the passing of the electron from the ring in the atom, corresponding to this series, to the space outside all the rings of electrons in the atom. On the basis of this theory, a theory for the structure of the limit here discovered would be, that different orbits exist outside the atom, to all of which the electron (with different probabilities) can go starting from the K-ring. The different passages corresponding to these orbits will give a series of absorption lines. Further, the electron from the K-ring can pass to infinity with all kinds of velocities (still with a varying probability); this will give a broad absorption band succeeding the above-mentioned absorption lines. The last type of passage is used by Bohr[2] to explain the continuous absorption band, which is observed by R. W. Wood at the head of the principal series of sodium, extending to the extreme ultra-violet.

It ought, however, to be mentioned that this theory does not seem to explain the more special formation of the structure observed for the different substances.

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[1] W. Kossel, Verh. d. D. Phys. Ges. (16), p. 953, 1914.

[2] N. Bohr, Phil. Mag. (26), p. 17, 1913.

Table for K_m.

Atomic Number.	Element.	$K_m : \lambda$.	$\sqrt{\frac{1}{\lambda}}$.	Difference.
12	Mg	9.5112	0.32425	
				.3050
13	Al	7.9470	0.35475	
14	Si	———	———	(.6199)
15	P	5.7580	0.41674	
				.2992
16	S	5.0123	0.44666	
				.3093
17	Cl	4.3844	0.47759	
				.3102
18	A	3.8657	0.50861	
				.3099
19	K	3.4345	0.53960	
				.3175
20	Ca	3.0633	0.57135	
				.3149
21	Sc	2.7517	0.60284	
				.3042
22	Ti	2.4937	0.63326	
				.3116
23	V	2.2653	0.66442	
				.3105
24	Cr.	2.0675	0.69547	

For none of the substances, with the exception of Mg, are the wave-lengths of the limit found, with certainty, longer than any of the K-lines. For Mg the wave-length in question is found considerably longer than the wave-length of the $K_{\beta 1}$ line.[1] The reason for this perhaps may be illustrated by the following simple consideration: The K_β line corresponds to a transmission of the electron from one ring of electrons (the M-ring) to another ring situated nearer the nucleus (the K-ring). A simple calculation shows however, that more energy is not always required to move the electron from the innermost ring to infinity than to move it between two such rings. The latter passage can require the greater amount of energy if the M-ring is situated in the exterior of the atom.

Limiting frequencies have previously been determined by de Broglie,[2] Wagner[3] and Siegbahn-Jonsson[4] using the photographic method and by

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[1] M. Siegbahn and W. Stenström, loc. cit.

[2] M. de Broglie, C. R., 163, p. 87, 1916, and Jour. de Phys., 5, p. 161, 1916.

[3] E. Wagner, Bayr. Akad. d. Wiss., 1916.

[4] M. Siegbahn and E. Jonsson, Phys. Zeits., 20, p. 251, 1919.

Blake[1]-Duane, Duane[2]-Kang-Fuh-Hu and Duane-Takeo Shimizu[3] using the ionization method.[4]

No structure of the limit has been found by any of these authors. As regards the smaller wave-lengths the reason for that is certainly that the structure here covers so small an interval of wave-length, that it could not be observed with the accuracy obtainable in the investigations concerned; this agrees with the theory here given. As regards the longer wave-lengths, the reason may be that in order to get sufficiently high intensity and a distinct limit the investigators have used comparatively broad slits, high potentials and large quantities of the absorbing substances.[5]

Copenhagen, Denmark.

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[1] F. C. Blake and W. Duane, Phys. Rev., 10, p. 697, 1917.

[2] W. Duane and Kang-Fuh-Hu, Phys. Rev., 14, p. 516, 1919.

[3] W. Duane and Takeo Shimizu, Phys. Rev., 14, p. 522, 1919.

[4] After the completion of this work, W. Stenström (Diss. Lund. Sweden 1919), using the photographic method, has found three limits in the M-series. These present a structure about the same as is found here; however, the whole complex is, as to be expected, rather faint.

[5] Wagner[2] states, that in his investigation of the limit of Iron he has used a foil of Iron 0.02 mm. thick. A calculation shows that this foil will absorb practically the whole radiation of shorter wave-lengths than the limiting wave-length. Furthermore he has used a slit 0.4 mm. wide.

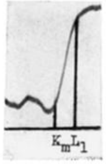

Fig. 1.

Aluminium.

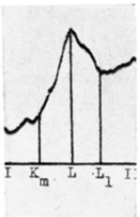

Fig. 2.

Phosphorus.

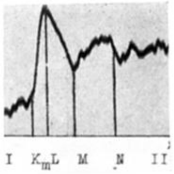

Fig. 3.

Sulphur.

Fig. 4.

Potassium.

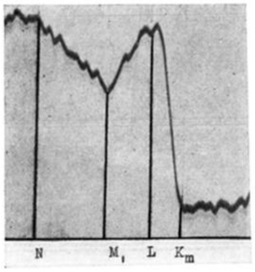

Fig. 5.

Scandium.

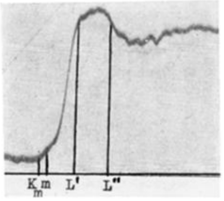

Fig. 6.

Titanium.

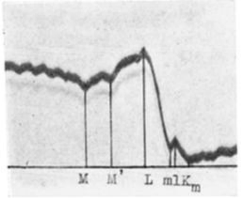

Fig. 7.

Vanadium.

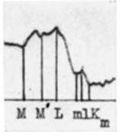

Fig. 8.

Chromium.

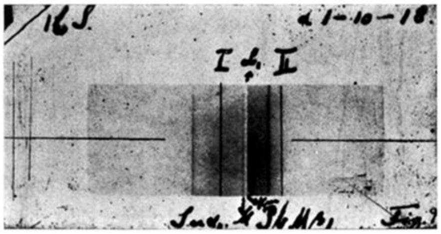

Fig. 9.

Sulphur.

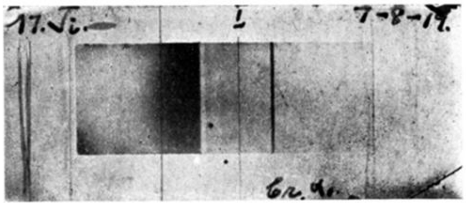

Fig. 10.

Titanium.