

## The X-Ray $K$ -Absorption Edge for Sodium and the Secondary Structure\* Accompanying the Edge for the Sodium Halides

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A high vacuum, curved-crystal spectrograph was constructed for study of the  $K$ -absorption edge and the accompanying secondary absorption structures for evaporated films of sodium metal and of the sodium halides. Comparison of the  $K\beta_x$  emission line and the  $K$ -absorption edge for metallic sodium indicates that the  $K\beta_x$  line is not semi-optical in origin, but represents a transition from the  $M_{II III}$  valence shell. The energies of the  $1s$ ,  $2p$ , and  $3p$  electron energy levels for metallic sodium are calculated. The energy difference between the  $K\beta_1$  emission line and the  $K$ -absorption edge for  $\text{Na}^+$  in  $\text{NaCl}$  is found to be 5 eV greater than the difference between the  $K\beta_x$  emission line and the  $K$ -absorption edge for  $\text{Cl}^-$  in  $\text{NaCl}$ . Strong secondary absorption patterns are found on the short wave-length side of the  $K$ -absorption edge for  $\text{Na}^+$  in the sodium halides. The distances from the various maxima and minima in the pattern to the main edges are correlated with the lattice distances and satisfactory agreement with Kronig's hypothesis is found except for the features near the main edge in the spectrum for  $\text{NaF}$ . Fair agreement is also found in comparison of these patterns with the patterns accompanying the  $K$ -absorption edge for  $\text{K}^+$  in the potassium halides, as determined by Brewington.

IN Kronig's<sup>1</sup> hypothesis of the origin of the secondary absorption structure which often appears on the short wave-length side of x-ray absorption edges of elements in crystal lattices, it is supposed that the final energies of the electrons ejected in any given direction through the lattice are restricted by the occurrence of Bragg-like reflections in the periodic potential field in the lattice. Owing to the overlapping of the effects of reflections from numerous sets of planes, actual calculations of secondary absorption patterns have not been carried out rigorously even for the simplest lattice types, although approximate calculations have been attempted.<sup>2</sup> A number of simple deductions from the theory have, however, been subjected to extensive experimental tests in which metals and binary alloys have been employed as absorbing media. Most of these experimental data have been found to be harmony with the theory,<sup>1-4</sup> but in the case of alloys the

crystal lattice is not always the decisive factor in determining the secondary structure.<sup>5</sup>

The most serious discrepancies with theory have been encountered in the case of absorption edges of elements in ionic lattices.<sup>6-8</sup> Since Kronig's theory applies only to the motion of a "free electron," discrepancies in the structure located within twenty-five or fifty electron volts from the edge can be attributed to effects of the field about the ion from whose x-ray level the electron is ejected. Stephenson<sup>9</sup> has found, however, that the ionic charge and the ionic group from which the electron is ejected affect the secondary structure at least as far as 100 eV from the edge.

It has been deduced from Kronig's theory that for an ion occurring in a succession of ionic lattices of a given type and varying lattice distances, the difference in energy between a given feature in the secondary absorption structure and the main edge should be inversely proportional to the square of the lattice distance. Since the

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<sup>1</sup> R. de L. Kronig, *Zeits. f. Physik* **70**, 317 (1931); D. Coster and J. Veldkamp, *Zeits. f. Physik* **74**, 191 (1932).

<sup>2</sup> R. de L. Kronig, *Zeits. f. Physik* **75**, 191 (1932); C. Kurylenko, *J. de phys. et rad.* **1**, 133 (1940).

<sup>3</sup> D. Coster and H. Levy, *Physica* **6**, 44 (1939).

<sup>4</sup> J. H. Munier, J. A. Bearden, and C. H. Shaw, *Phys. Rev.* **58**, 537 (1940).

<sup>5</sup> J. A. Bearden and H. Friedman, *Phys. Rev.* **58**, 387 (1940).

<sup>6</sup> Vola P. Barton and Geo. A. Lindsay, *Phys. Rev.* **46**, 362 (1934); S. Yoshida, *Sci. Papers Tokyo Inst. Phys.-Chem. Research* **38**, 272 (1941).

<sup>7</sup> D. Coster and G. H. Klamer, *Physica* **1**, 145 (1933).

<sup>8</sup> G. P. Brewington, *Phys. Rev.* **46**, 861 (1934).

<sup>9</sup> S. I. Stephenson, *Phys. Rev.* **58**, 873 (1941).

absolute separation depends only on the lattice and is independent of the energy of the main edge, it is evident that the relative separation of the secondary absorption structure from the main edge should be greatest for an edge of long

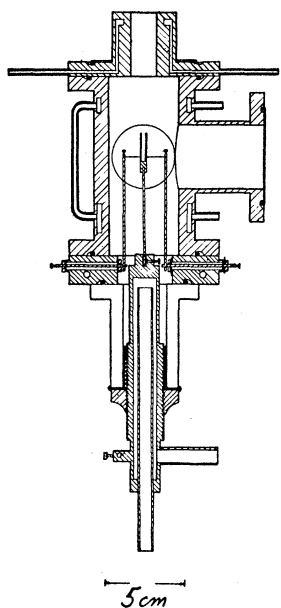


FIG. 1. Cross section of the cathode-ray oven.

wave-length. Previous experiments with ionic lattices as absorbing media have been confined to *K* and *L* edges of comparatively short wave-lengths. Early indications were that secondary absorption becomes weaker for elements of low atomic number,<sup>7</sup> but recent work has succeeded in bringing out the secondary structure in the *K* edges for metallic Al and Mg.<sup>4</sup> In view of the realizable gain in resolving power, it therefore seemed worth while to attempt to study the structure accompanying an edge at still longer wave-length, such as the *K* edge for Na in its halides. A second advantage in a study of the sodium halides is that the lattice constants increase as much as 1.4-fold from the fluoride to the iodide, a range which should make it possible to draw significant conclusions as to the correctness of Kronig's hypothesis in respect to dependence of the separation from the main edge on lattice distance.

Aside from the objective of studying the secondary absorption structure, a determination

of the wave-length of the main sodium edge, in which the various halides and also sodium metal were used as absorption films, was of interest in itself. The only previous determination found in the literature was an incidental measurement by Johnson,<sup>10</sup> who employed sodium chloride as the absorption film.

## EXPERIMENTAL

### Apparatus

The apparatus and technique employed were designed to avoid excessively long times of exposure in bringing out absorption edges and secondary absorption structure in the region of long wave-lengths. The curved-crystal type of spectrograph was therefore chosen. A further advantage of this instrument is that the edge and the absorption spectrum extending far out from the edge can be photographed on a single plate at one setting of the crystal. The high vacuum extended throughout the spectrograph so that no diaphragm was required over the mouth of the x-ray tube. Since thin, homogeneous absorption films would further contribute to lowering the exposure time, the films were formed by condensation on an aluminum foil of vapors produced by heating the materials in a cathode-ray oven. In order that films of metallic sodium as well as of the sodium halides could be deposited and employed without exposure to air, the cathode-ray oven was constructed as an integral part of the high vacuum spectrograph.

The cathode-ray oven, Fig. 1, was essentially a water-cooled, metal, x-ray tube mounted at the bottom of the crystal chamber. The anticathode was designed<sup>11</sup> to minimize loss of heat by radiation and was thimble-shaped in order to facilitate heat transfer to the material to be evaporated. A loop of tungsten wire at ground potential was the source of an electron beam of 1 to 200 milliamperes which served to maintain the crucible at 600 to 1400°C when a potential of 1 to 20 kv was applied to the anticathode. The oven was evacuated through a flexible metal tube connected directly to the oil-diffusion pump.

The x-ray tube was a water-cooled, metal tube which projected through the cover of the crystal

<sup>10</sup> Nils G. Johnson, Dissertation (Lund, 1939), p. 50.

<sup>11</sup> H. M. O'Bryan, Rev. Sci. Inst. 5, 125 (1934).

chamber, Fig. 2. Since a bent crystal requires a long focal spot, the cathode was a straight section of tungsten wire screened so as to produce a focal spot 18 mm long and 1 mm high. The aluminum foil, upon which the vapors were condensed to form the absorption film, was mounted so that it could be revolved about a vertical axis and stand either beside the mouth of the oven or in the path of the beam from the x-ray tube to the crystal. When the film was beside the mouth of the oven, it could be lowered over the oven by means of an arm attached to a ground metal joint mounted on the side of the crystal chamber. All other joints except the two for the manipulation of the film were flanged joints sealed by rubber-ring gaskets mounted in a groove in one of each pair of flanges.

The crystal holder and the cover carrying the x-ray tube could be rotated independently to give any glancing angle from  $15^\circ$  to  $80^\circ$ . The holder for the bent crystal was of the type designed by Haglund and described by Ohlin,<sup>12</sup> the opening in the front face being 1.5 mm by 20 mm.

The beam reflected by the crystal passed through a two-inch hole drilled through the cylindrical wall of the crystal chamber and through a cast-iron plate two inches thick and one foot square, to which the wall of the chamber was fastened. A shelf of cantilever construction was bolted to the other side of the cast-iron plate in order to support a track upon which the table bearing the plate holder moved. In order to protect the plate from visible light and scattered radiation, the plate holder was surrounded by an aluminum shield in which a window covered by two thicknesses of  $0.6\mu$  aluminum foil was provided for passage of the x-rays.

A flanged, steel pipe three feet long, ten inches in diameter, and blinded off at one end was mounted on a track to form the vacuum chamber for the plate holder when rolled forward to abut against the cast-iron plate. The degree of evacuation at any time could be determined by means of a Pirani tube and an ionization gauge, both permanently attached to the crystal chamber. The measuring circuit for these gauges was built according to the design of Sten v. Friesen.<sup>13</sup>

<sup>12</sup> Per Ohlin, Dissertation (Upsala, 1941), pp. 25, 26.

<sup>13</sup> Sten v. Friesen, Arkiv. f. Mat. Astronom. Fysik B27, No. 11 (1939).

### Operation

The process of forming the absorption film was not started until the spectrograph and cathode-ray oven had been evacuated to  $2 \times 10^{-4}$  mm of Hg or less. To produce films of sodium metal a reaction mixture of equal parts by weight of powdered zirconium and sodium molybdate was employed.<sup>14</sup> The films of sodium halides were produced by evaporating C. P. halides. The evaporation process was always carried out by increasing the strength of the cathode-ray current in small steps, with sufficient time between successive steps to reduce each temporary rise in pressure. Whether or not a deposit had been evenly formed on the aluminum foil could be determined by tilting up the film holder until the under side of the foil could be viewed through a glass window in the side wall of the crystal chamber. The approximate thickness of the deposit was determined, after recording the absorption spectrum, by weighing the film and the aluminum foil.

A tungsten anticathode was employed as the source of the continuous radiation since it produced no interfering lines in the region of the sodium edge. Because the rectifying equipment available, four tubes in Greinacher coupling without condensers, did not prevent a half-sine-wave fluctuation of voltage, the effective voltage had to be maintained at or below 1.6 kv to prevent higher orders of radiation from obscuring

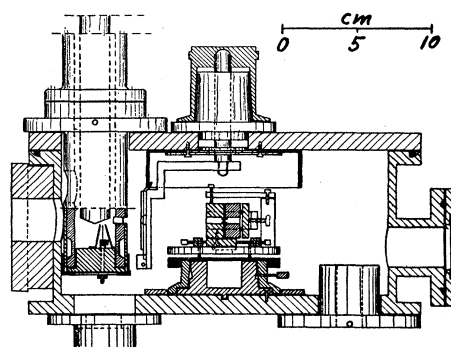


FIG. 2. Cross section of the crystal chamber.

<sup>14</sup> The use of this ratio was an oversight, since de Boer, Broos, and Emmens [Zeits. f. anorg. allgem. Chemie 191, 113 (1930)] state that the product evaporated from a 1 to 1 mixture is sodium metal containing some oxide, while a mixture of 1 part sodium molybdate to 4 parts zirconium gives the pure metal.

the absorption spectrum at 1.1 kv. The  $K\alpha_1$  line of sulfur always appeared on the plates, but not the  $K\alpha_1$  line of potassium, which indicated that some second-order, but no third-order radiation was excited. Agfa Isochrome Plates, 18/10 Din, were employed for recording the spectra although their large grain size set a low limit to the enlargement which could be employed in making photometer curves.

Reference lines were exposed on one-half of the photographic plate either before or after the absorption spectrum was recorded. KCl and ZnO powders on a copper base on the other half of the anticathode were the source of the reference lines, 19-K  $K\alpha_1$  at 3733.68 x.u. (effectively 11217.05 x.u. for a mica crystal in the third order) and 30-Zn  $K\alpha_1$  at 1432.17 x.u. (11474.56 x.u. for mica in the eighth order).<sup>15</sup>

#### Measurements and Errors

A scratch was made on each plate parallel to the absorption edge, and the distances from this scratch to the reference lines were measured on a comparator. All measurements of positions of the edges and secondary absorption structures were made on photometer curves with respect to the sharp peak produced by this scratch. An abscissa enlargement of three was found suitable, the exact enlargement always being determined by recording at the same time a photometer curve of two scratches on a plate, the distances between the scratches having been determined by means of the comparator. A millimeter netting was also copied onto the photometer curve in order to provide automatic correction for shrinkage of the paper during photographic development.

The position of the edge and other main features on the photometer curves could be measured to  $\pm 0.1$  mm, corresponding to  $\pm 0.03$  mm on the plate or to  $\pm 1.1$  x.u. The positions of the reference lines could, of course, be determined with greater precision, while the precision was much lower for the weaker features of the spectra.

A number of systematic errors in wave-length measurements arise when a bent-crystal spectrograph is employed and the spectrum is recorded on a plane plate tangent to the focusing circle.

Equations for calculating the various errors have been published by Sandstrom.<sup>16</sup> These errors arise from the geometry of the system even though the curved surface of the crystal is perfectly cylindrical. For the spectrograph employed in this work, the geometrical data required for Sandstrom's equations are: radius of the bent crystal 498 mm, crystal opening 20 mm  $\times$  1.5 mm, height of focal spot 1 mm, glancing angle  $35^\circ 49'$ , distance from focal spot to crystal 80 mm, and thickness of the photographic emulsion  $12\mu$ . Variations in temperature of the crystal are also a factor, and while the temperature of the crystal itself was not measured, the maximum temperature variation in the room during an exposure was  $3^\circ\text{C}$ .

At a crystal opening of 20 mm, which was that employed in obtaining most of the data, the largest error under these conditions is the focusing error, which arises because of the fact that the radius of curvature of the surface of the bent crystal is twice that of the focusing circle. When a crystal opening of 20 mm is employed, the focusing defect at a glancing angle of  $35^\circ$  should broaden a sharp line toward shorter wavelengths into a beam 4.7 x.u. wide. A reduction of the crystal opening to 8 mm would reduce the focusing defect to 1.1 x.u., which should be practically counterbalanced by other effects so as to produce symmetrical broadening. Comparison of the positions of the reference lines when recorded with 20-mm and 8-mm openings revealed a shift toward shorter wave-lengths of only 0.4 x.u. at the larger opening.

In addition to errors owing to geometry of the system, the possibility of lack of definition owing to imperfect bending of the crystal and inaccurate focusing of the apparatus must be considered. The radius of curvature of the crystal was determined by the standard methods employed at the Institute of Physics at Upsala, which involve observation of the points of focus of x-ray emission lines on a nearly horizontally inclined photographic plate. From the radius of curvature so determined the required distance from the crystal to the plate can be calculated for any glancing angle. In order to check the sharpness of focus,

<sup>15</sup> Manne Siegbahn, *Spektroskopie der Röntgenstrahlen* (Julius Springer, Berlin, 1931).

<sup>16</sup> Arne Sandstrom, *Zeits. f. Physik* **84**, 541 (1933); **92**, 622 (1934); Dissertation (Upsala, 1935), pp. 21-27; also H. H. Johann, *Zeits. f. Physik* **69**, 185 (1931).

TABLE I. Absorption films, exposure times, and individual measurements of the main edges.

Sub- stance	Absorption film		Hours at 60 ma	Exposure Crystal opening mm	Plate No.	Wave-lengths for the main edges x.u.			
	mg cm <sup>2</sup>	Film No.				K'	K <sub>1</sub>	K <sub>2</sub>	K <sub>3</sub>
Na	0.4*	24	12	20	24		11544.3		
	0.6*	35	16	20	35		11544.6		
	1.0*	37	27	20	37		11545.5		
	0.6*	39	12	20	39		11545.5		
Na <sub>2</sub> O	0.6	35	5	20	36			11507.4	
	1.0	37	31	20	38		11523.8	11509.4	11488.8
	0.6	39	15	20	40		11520.1	11507.1	11480.6
		39	12	20	45		11522.1	11506.5	11484.5
NaF	0.5	46	26	20	46		11498.9		
		46	10	20	47	11517.5	11502.3		
		46	20	8	48	11518.5	11498.9		
	0.6	49	14	8	49	11519.8	11501.2		
		49	7	20	50	11519.0	11500.6		
		49	6	20	51	11522.0	11503.1		
		49	12	8	52	11523.7	11503.1		
NaCl	0.5	22	9	20	22		11500.3		
	0.9	28	18	20	28		11502.6		
	0.4	30	25	20	30		11501.2		
		30	38	20	31		11502.3		
NaBr	0.3	53	15	20	53		11504.6		
	0.5	54	8	20	54		11505.1		
		54	12	20	55		11504.6		
NaI	0.6	56	16	20	56		11507.1		
	0.2	59	22	20	59		11502.9		

\* Weight given for oxidized film after removal from spectrograph.

estimates were made of the widths of emission lines exposed at large glancing angles with the full opening of the crystal. At a glancing angle of 58° the full width for 29-Cu  $K\alpha_1$  (eleventh order) was found to be 0.6 x.u. at half-maximum intensity, which is comparable with the widths observed in a double-crystal spectrometer.<sup>17</sup> It is evident that even with the full crystal opening no significant broadening occurred such as might be expected to result from imperfect bending of the crystal.

It can be concluded that the systematic errors

TABLE II. Average wave-length and energy values for the sodium  $K$ -absorption edge.

Absorbing material	Edge	Wave-length		Energy values		
		x.u.	Average deviation	$\nu/R$	ev	$\Delta$ ev
Na	$K_1$	11545.0	0.6	78.93 <sub>2</sub>	1071.4 <sub>8</sub>	—
NaF	$K'$	11520.1	1.6	79.10 <sub>3</sub>	1073.7 <sub>9</sub>	2.3 <sub>2</sub>
	$K_1$	11501.2	1.5	79.23 <sub>3</sub>	1075.5 <sub>6</sub>	4.0 <sub>9</sub>
NaCl	$K_1$	11501.6	0.9	79.22 <sub>9</sub>	1075.5 <sub>2</sub>	4.0 <sub>5</sub>
NaBr	$K_1$	11504.8	0.3	79.20 <sub>8</sub>	1075.2 <sub>2</sub>	3.7 <sub>5</sub>
NaI	$K_1$	11505.0	2.1	79.20 <sub>8</sub>	1075.2 <sub>0</sub>	3.7 <sub>3</sub>
Na <sub>2</sub> O	$K_1$	11522.0	1.3	79.09 <sub>6</sub>	1073.6 <sub>2</sub>	2.1 <sub>5</sub>
	$K_2$	11507.6	0.9	79.18 <sub>9</sub>	1074.9 <sub>6</sub>	3.4 <sub>9</sub>
	$K_3$	11484.6	2.8	79.34 <sub>7</sub>	1077.1 <sub>1</sub>	5.6 <sub>4</sub>

<sup>17</sup> Lyman G. Parratt, Phys. Rev. 50, 1-15 (1936).

are smaller than the accidental errors in determining the wave-lengths. However, repetition of the measurements at higher dispersion might reveal additional structure in the edges, in which case some of the wave-lengths obtained might differ appreciably from those reported here.

#### DATA

Table I lists each absorption film from which absorption spectra were obtained, together with the wave-length values found for each of the main edges. Table II gives the average value obtained for the wave-length of each edge and the corresponding average energy values, calculated from the relations  $\nu/R=10^{11}/109737\lambda$  and  $e\nu=12370.2\times 10^3/\lambda$ , where  $\lambda$  is in  $x$  units. Average wave-lengths for the edges and all reproducible features in the secondary absorption structures are listed in Table III. The figures in the third column of each compound in Table III indicate the average deviation of the individual measurements from the average, and the figures in the fourth column indicate the number of

TABLE III. Wave-length values for the features of the sodium *K*-absorption edge.

Feature	Av. $\lambda$ x.u.	Av. measure- dev.	No. of measure- ments	Feature	Av. $\lambda$ x.u.	Av. measure- dev.	No. of measure- ments
NaF				NaCl			
<i>K'</i>	11520.1	1.6	(6)	<i>K</i> <sub>1</sub>	11501.6	0.9	(4)
<i>K</i> <sub>1</sub>	11501.2	1.5	(7)	<i>A</i>	11492.6	0.5	(4)
<i>A</i>	11481.2	2.9	(7)	$\alpha$	11479.0	3.1	(4)
<i>a</i>	11447.3	3.5	(7)	<i>B</i>	11462.0	1.1	(4)
<i>b</i>	11435.8	5.3	(7)	<i>a</i>	11442.4	1.9	(3)
$\alpha$	11426.4	1.0	(7)	$\beta$	11424.6	1.1	(4)
<i>B</i>	11399.1	3.3	(7)	<i>C</i>	11412.1	2.5	(4)
<i>c</i>	11371.2	0.9	(3)	$\gamma$	11402.1	1.5	(4)
<i>d</i>	11353.1	1.6	(3)	<i>D</i>	11383.5	1.2	(4)
<i>C</i>	11347.5	5.5	(4)	$\delta$	11323.6	3.6	(4)
$\gamma$	11332.7	3.2	(4)	<i>E</i>	11286.3	4.3	(4)
<i>D</i>	11299.7	4.3	(7)	<i>F</i>	11216.9	6.0	(4)
$\delta$	11223.6	3.2	(7)	$\epsilon$	11164.5	9.0	(4)
<i>E</i>	11156.9	7.0	(7)	<i>G</i>	11094.5	5.2	(4)
<i>F</i>	11058.4	7.5	(6)	$\zeta$	10917.4	1.8	(2)
$\epsilon$	10974.7	9.1	(7)	<i>H</i>	10765.8	5.4	(2)
<i>G</i>	10869.1	8.7	(7)				
NaBr				Na <sub>2</sub> O*			
<i>K</i> <sub>1</sub>	11504.8	0.3	(3)	<i>K</i> <sub>1</sub>	11522.0	1.3	(3)
<i>A</i>	11495.4	0.5	(3)	<i>a</i>	11517.2	0.2	(2)
$\alpha$	11486.7	1.5	(3)	<i>K</i> <sub>2</sub>	11507.6	0.9	(4)
<i>a</i>	11479.6	1.9	(2)	<i>b</i>	11499.2	1.4	(2)
<i>B</i>	11468.9	0.8	(3)	<i>K</i> <sub>3</sub>	11484.6	2.8	(3)
<i>b</i>	11452.3	0	(2)	<i>A</i>	11464.2	0.8	(3)
$\beta$	11430.0	1.8	(3)	$\alpha$	11425.0	7.7	(2)
<i>C</i>	11421.8	1.1	(3)	<i>B</i>	11410.0	1.7	(2)
$\gamma$	11412.8	0.9	(3)	$\beta$	11247.7	7.4	(3)
<i>D</i>	11399.5	1.4	(3)	<i>C</i>	11093.7		(1)
$\delta$	11335.8	5.3	(3)	$\gamma$	10932.8		(1)
<i>E</i>	11298.2	7.9	(3)				
<i>F</i>	11244.8	3.3	(2)				
$\epsilon$	11198.5	9.7	(3)				
<i>G</i>	11032.7		(1)				
$\zeta$	10945.8	17	(2)				
NaI				Na			
<i>K</i> <sub>1</sub>	11505.0	2.1	(2)	<i>K</i> <sub>1</sub>	11545.0	0.6	(4)
<i>A</i>	11499.0	0.5	(2)	<i>K</i> <sub>2</sub>	11516.4	7.4	(4)
$\alpha$	11487.8	0.6	(2)	<i>K</i> <sub>3</sub>	11489.4	0.8	(4)
<i>a</i>	11481.2	0.5	(2)	<i>A</i>	11439.6	13	(4)
<i>B</i>	11471.8		(1)	$\alpha$	11266.4		(1)
<i>b</i>	11446.6		(1)	<i>B</i>	11114.7		(1)
$\beta$	11430.1		(1)	$\beta$	10958.2		(1)
<i>D</i>	11420.8		(1)	<i>C</i>	10677.6		(1)

\* Film of metallic sodium oxidized by exposure to air.

measurements (number of plates) entering into the determination of each average. Typical

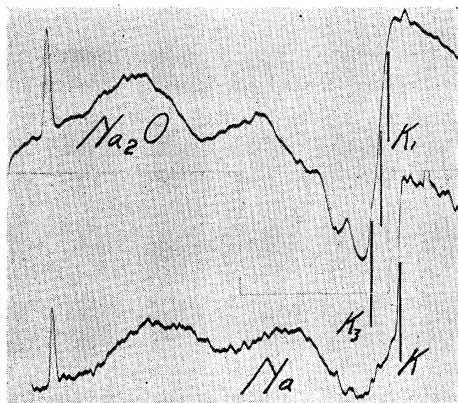


FIG. 3. Photometer curves of the edge for a film of sodium metal and for an air-oxidized film.

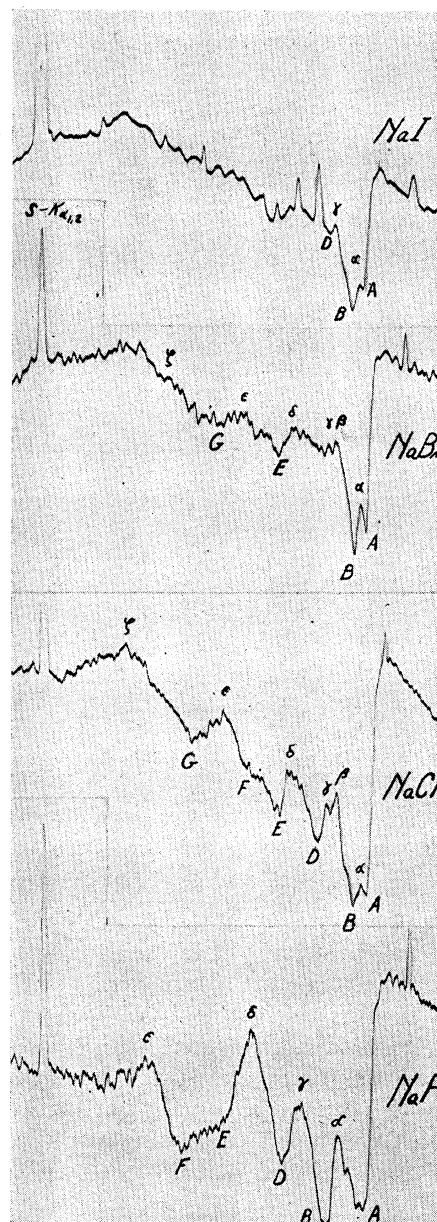


FIG. 4. Photometer curves of the edges for the sodium halides. Reading from top to bottom, the curves correspond to plates Nos. 59, 54, 28, and 49.

photometer curves are reproduced in Figs. 3 and 4.

In all tables the main edge is distinguished by *K*<sub>1</sub>, the minima on the photometer curves (i.e., maxima of absorption) are symbolized by Roman capitals, and the maxima on the photometer curves (minima of absorption) by Greek letters.

TABLE IV. The energy levels for sodium metal.

Level		ev	$\nu/R$
<i>K</i>	1 <i>s</i>	1071.5	78.93 <sub>2</sub>
<i>L</i> <sub>II III</sub>	2 <i>p</i>	30.7	2.26 <sub>9</sub>
<i>M</i> <sub>II III</sub>	3 <i>p</i>	0.64	0.04 <sub>8</sub>

These symbols have been written in on the photometer curves. The small Roman letters in Table III designate less conspicuous features, whose positions are not indicated in Figs. 3 and 4, but which can perhaps be discerned in relation to the designated maxima and minima.

In connection with the discussion to follow it should be noted that only those features which are similar in appearance (width, strength, and shape) as well as in relative position have received like designations in the photometer curves of the spectra for the several halides. The secondary structures for the spectra of sodium metal and sodium oxide are quite distinct from those of the halides, however. The features  $\alpha$ ,  $B$ ,  $\beta$ , and  $C$  in the spectrum for sodium metal and  $C$  and  $\gamma$  in the spectrum for sodium oxide appeared in each case on only one plate and may be fictitious.

## DISCUSSION

### (a) The Main Edges

The  $K\beta_x$  emission line for Na and Mg has been considered in the past<sup>18</sup> as representing a semi-optical transition since this line is assigned to the transition  $K-M_{II III}$ , and there should be no electrons in the  $M_{II III}$  shell for these elements. Wetterblad<sup>19</sup> plotted the wave-length differences between the  $K\alpha_{12}$  and the  $K\beta_x$  emission lines for the elements from 17-Cl to 11-Na and found that the curve changed sharply in slope at 12-Mg and 11-Na. A plot of the difference between the  $K$  edge and the  $K\beta_x$  line in terms of ev, Fig. 5, gives a smooth curve from Si through Na, however. The energies of the  $K$ -absorption edges also agree within 1 or 2 ev with the energies of the  $K\beta_x$  lines. Since the  $K\beta_x$  emission actually constitutes a band, careful determination of the short wave-length edges of these bands for the elements from 17-Cl to 11-Na would undoubtedly result in a

closer agreement with the  $K$ -absorption edges. It therefore appears unnecessary to consider the  $K\beta_x$  line as a semi-optical transition for Na and Mg, but as a transition from a valence shell, which may be designated  $M_{II III}$ . Farineau<sup>20</sup> has previously reached a similar conclusion as to the origin of this line in the case of Mg, Al, Si. With this assignment for the  $K\beta_x$  emission line, the wave-lengths for the  $K$ -absorption edge and the  $K\beta_x$  emission line,<sup>21</sup> together with the value of  $11.9093A=11885.2$  x.u. obtained by Tyrén<sup>22</sup> for the  $K\alpha_1$  line, can be used to calculate the energies of the 1*s*, 2*p*, and 3*p* levels for metallic sodium. The energy values obtained are shown in Table IV.

The main edge for sodium metal is followed by two very weak edges,  $K_2$  and  $K_3$ . Their wave-

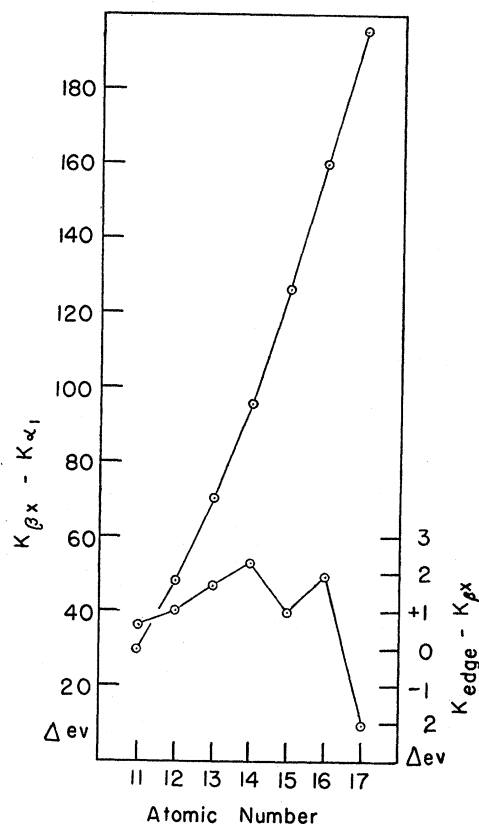


FIG. 5. Energy differences for  $K\beta_x - K\alpha_1$  and  $K$  edge -  $K\beta_x$ , for the elements sodium to chlorine.

<sup>18</sup> E. Bäcklin, M. Siegbahn, R. Thoraues, Phil. Mag. 49, 513 and 1326 (1925). Reference 15, p. 392.

<sup>19</sup> Thorsten Wetterblad, Zeits. f. Physik 42, 603 (1927).

<sup>20</sup> Jules Farineau, Comptes rendus 208, 1725 (1939).

<sup>21</sup> Reference 15, p. 165.

<sup>22</sup> Folke Tyrén, Nova Acta Reg. Soc. Sci. Upsala [IV], 12, 39 (1940).

TABLE V.

Compound	$K_1$ absorption edge		$K\beta_1$ emission line <sup>a</sup>	
	$\lambda$ , x.u.	ev	$\lambda$ , x.u.	ev
NaF	11501.2	1075.6	11637	1063.0
NaCl	11501.6	1075.5	11633	1063.4
NaI	11504.8	1075.2	11621	1064.5
NaBr	11505.0	1075.2	11614	1065.1

<sup>a</sup> See reference 19.

lengths correspond approximately to the average of the wave-lengths of the  $K_1$  and  $K_2$  edges and to the wave-length of the  $K_3$  edge of the oxide, respectively. As mentioned in the experimental section, there is reason to believe that the sodium film contained some oxide.

The main edge for the oxide lies 23 x.u. toward shorter wave-length, or 2.1<sub>5</sub> ev toward higher energies, than the edge for the metal. Furthermore, it no longer coincides with the  $K\beta_1$  emission line for the oxide, which is shifted 43 x.u. in the opposite direction as compared with the  $K\beta_x$  line for the metal.<sup>21</sup> The directions of these shifts are the same as are found in analogous cases for elements in higher series of the periodic system.<sup>23</sup>

The  $K$ -absorption edge for  $\text{Na}^+$  in its halides is shifted still farther than for the oxide toward shorter wave-lengths. The shift is some 40 x.u., or about 4 ev toward higher energies. From NaF to NaI the shift decreases from 4.0<sub>9</sub> to 3.7<sub>3</sub> ev, a shift which exceeds the probable error of the data. In terms of energy the shifts are somewhat larger than the corresponding shifts observed by Lindh<sup>24</sup> for the  $K$ -absorption edge for  $\text{K}^+$  in its

halides. Our result for the  $K$  edge for  $\text{Na}^+$  in NaCl can be compared with the value obtained by Johnson<sup>10</sup> in the course of a study of the effects of chemical combination on emission spectra. He found a wave-length of 11498 x.u., compared with the present result of 11501.6 x.u. In terms of energy the difference is 0.4 ev. Since Johnson's measurement was not intended to be a precision determination, the agreement between the two results is satisfactory.

In Table V the wave-lengths of the absorption edges for the halides are compared with Wetterblad's measurements of the  $K\beta_1$  line for  $\text{Na}^+$  in its halides. The energy for the  $K\beta_1$  emission line for  $\text{Na}^+$  in NaCl is 12.1 ev less than the energy for the absorption edge. Valasek<sup>25</sup> has plotted the separations in units of ev between the various  $K$ -emission lines and the  $K$ -absorption edge for  $\text{Cl}^-$  in NaCl. He predicted that if the difference between the  $K\beta_1$  line and the  $K$ -absorption edge for  $\text{Na}^+$  in NaCl were plotted in the same figure, the  $K\beta_1$  line for  $\text{Na}^+$  would coincide with the  $K\beta_1$  line for  $\text{Cl}^-$ , which lies 7.1 ev from the edge. The difference of 5.0 ev between the predicted and observed positions for the  $K\beta_1$  line for  $\text{Na}^+$  is fully an order of magnitude greater than the probable experimental errors. It seems necessary to conclude either that the  $K\beta_1$  line for  $\text{Na}^+$  in NaCl does not represent the  $\text{Na}^+ - 1s - \text{Cl}^- - 3p$  transition as predicted, or that the end levels for the  $K$ -absorption transitions for  $\text{Na}^+$  and  $\text{Cl}^-$  do not both begin at the  $\text{Cl}^-$  continuum as assumed. Different end levels might be attributed to different selection rules.<sup>7</sup>

<sup>23</sup> V. Hugo Sanner, Dissertation (Upsala, 1941), p. 93.

<sup>24</sup> Axel E. Lindh, Arkiv. f. Mat. Astronom. Fysik **18**, No. 14 (1924). See also reference 15, pp. 289-290.

<sup>25</sup> Joseph Valasek, Phys. Rev. **53**, 274 (1938).

TABLE VI. Distance of the secondary-structure features to the main edge, in x.u., ev, and  $a^2$  (ev).

Structure	NaF			NaCl			NaBr			NaI		
	x.u.	ev	$a^2 \text{ ev} \cdot 10^{16}$	x.u.	ev	$a^2 \text{ ev} \cdot 10^{16}$	x.u.	ev	$a^2 \text{ ev} \cdot 10^{16}$	x.u.	ev	$a^2 \text{ ev} \cdot 10^{16}$
<i>A</i>	20	1.9	40	8	0.9	29	10	0.9	32	6	0.6	29
$\alpha$	75	7.0	150	23	2.2	70	18	1.7	60	17	1.6	67
<i>B</i>	102	9.6	205	40	3.8	120	36	3.4	121	33	3.1	129
$\beta$				77	7.3	231	75	7.1	252			
$\gamma$	168	16.0	326	100	9.4	298	92	8.7	309	75	7.0	292
<i>D</i>	201	19.1	408	118	11.2	354	105	10.0	355	84	7.9	330
$\delta$	277	26.5	566	178	16.9	535	169	16.0	568			
<i>E</i>	344	33.1	706	215	20.5	649	207	19.7	700			
<i>F</i>	443	42.9	915	285	27.2	861	260	24.8	881			
$\epsilon$	526	51.4	1097	338	32.4	1025	307	29.4	1044			
<i>G</i>	632	62.4	1331	408	39.4	1248	472	45.9	1630			
$\zeta$				585	57.4	1817	559	54.8	1948			
<i>H</i>				735	73.3	2320						



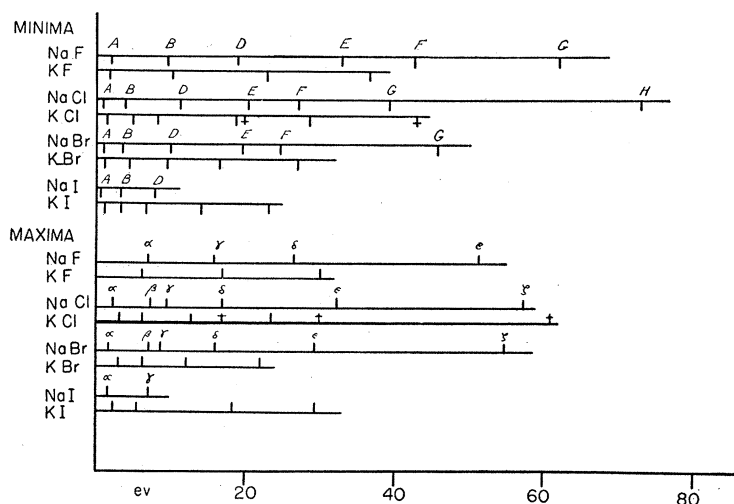


FIG. 6. Separation in electron volts between the secondary structure and the main edges for Na<sup>+</sup> and K<sup>+</sup>. + indicates data from Coster and Klamer (reference 7). Other data for K halides taken from Brewington (reference 8).

In the case of KCl, also, the coincidence between the  $K\beta_5$  line for K<sup>+</sup> and the  $K\beta_1$  line for Cl<sup>-</sup> is not perfect, the  $K\beta_5$  line for K<sup>+</sup> lying 1.2 eV farther out from the edge. Valasek attributed this discrepancy, however, to an error in Stelling's energy value<sup>26</sup> for the  $K$ -absorption edge for Cl<sup>-</sup> in KCl.

### (b) Secondary Absorption Structure for the Halides

As was mentioned in the introductory section, in view of the difficulties of carrying out detailed calculations of the shape of the secondary absorption pattern which should arise from the overlapping of the numerous forbidden energy zones predicted by Kronig's theory, the theory has usually been indirectly tested in case of ionic lattices by comparison of the secondary structures for a particular absorption edge for a series of similar lattices of varying lattice distances. For a cubic type of lattice the separation of the structure from the edge in terms of energy should be inversely proportional to the square of the lattice distance. Brewington<sup>8</sup> applied this criterion in the case of the secondary absorption patterns accompanying the  $K$ -absorption edges for K<sup>+</sup> and Cl<sup>-</sup> in the series of potassium halides

and alkali chlorides. He came to the conclusion that his data did not agree with the hypothesis. The same criterion will now be applied to the data given in Table III, and since the potassium and sodium halides belong to the same crystal type and the  $K$ -absorption edges for sodium and potassium should represent the same transition, the data in Table III will be compared directly with the available data for the  $K$  edge of K<sup>+</sup> in the potassium halides.

The separation of each feature of the secondary structure from the main edge has been calculated from Table III and is listed in Table VI for the absorption spectrum from each halide. The separations are expressed in x.u., electron volts, and in electron volts multiplied by the square of the lattice constant of the halide. The values employed for the squares of the lattice constants are 21.34, 31.65, 35.52, and 41.73  $\text{cm}^2 \times 10^{-16}$  for NaF, NaCl, NaBr, and NaI, respectively. In Fig. 6, the separations shown in Table VI in terms of electron volts are plotted together with similar data of Brewington<sup>8</sup> and of Coster and Klamer<sup>7</sup> for the secondary absorption structure accompanying the  $K$ -absorption edge for potassium in its halides. This comparison does not reveal very striking likenesses between the spectra for the different halides, except for the features close to the main edges. In Fig. 7, however, in which the

<sup>26</sup> Reference 15, p. 282.

abscissas represent separations multiplied by the squares of the lattice constants, the similarities are more marked. It is true that the positions of the first two maxima and minima for the other halides are not matched in the spectra for NaF and KF. On the other hand, considering the spectra for the sodium halides alone, the double minimum E-F is exceptionally strong for NaF, obvious for NaCl, and still apparent, though very weak, for NaBr, and they lie on a nearly vertical line in Fig. 7. Aside from the discrepancies mentioned for NaF and KF, even the differences between the patterns for the sodium and potassium halides are not very striking in view of the facts that the spectra were recorded in different laboratories and are based on measurements at two different wave-lengths in which the dispersions obtainable, in terms of energy units, differ greatly. With reservations, it can therefore be said that the pattern in Fig. 7 confirms the inverse proportionality with the squares of the lattice distances, as required by Kronig's hypothesis.

On the other hand, Brewington's data for the absorption structures accompanying the  $K$ -absorption edge for  $\text{Cl}^-$  in the various alkali chlorides show very significant variations from the relations predicted by Kronig's hypothesis. It is conceivable that there may be some principal

difference between the secondary structure accompanying absorption by anions as compared with cations, such as different selection rules for the electronic transitions.<sup>7</sup> The fact, discussed in the foregoing section, that the energy difference between presumably similar emission and absorption transitions is not the same for  $\text{Na}^+$  and  $\text{Cl}^-$  transitions in NaCl, or for  $\text{K}^+$  and  $\text{Cl}^-$  transitions in KCl, is in harmony with the supposition that electron transitions involving anions in ionic lattices obey different selection rules from those involving cations. Additional experimental data concerned with the secondary absorption structure accompanying absorption edges of anions would be desirable. It is suggested that a study of the secondary absorption patterns accompanying the  $K$ -absorption edge for fluorine in the series of alkali fluorides, whose lattice constants extend over a wide range, would serve to make any differences very evident when compared with the present patterns for the sodium halides.

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The author is pleased to acknowledge his deep indebtedness to Professor Axel H. Lindh, Director of the Institute of Physics of the University of Upsala, who, under the difficult conditions prevailing in a war-threatened country,

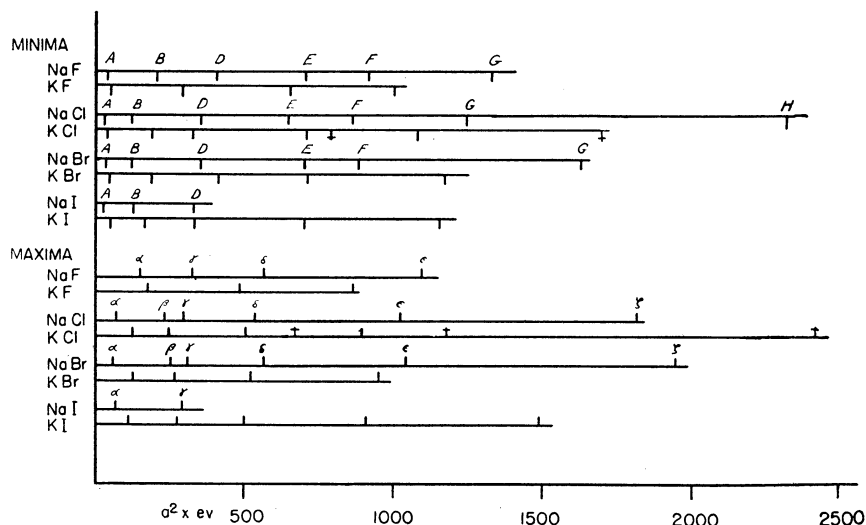


FIG. 7. Separation between the secondary structure and the main edges in  $a^2 \text{ ev} \cdot 10^{16}$ . + indicates data from Coster and Klamer (reference 7). Other data for K halides taken from Brewington (reference 8).

put material, skilled machinists, and a laboratory at the author's disposal during 1940 and 1941. He is also indebted to Mr. John Amberntson for skilled workmanship, to many Fellows of the Institute, including Åke Nilsson, Philip Haglund, Per Ohlin, and Harald Flemberg for advice, and to Professor Manne Siegbahn and Torsten

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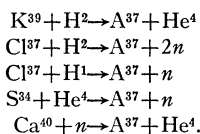
PHYSICAL REVIEW VOLUME 66, NUMBERS 7 AND 8 OCTOBER 1 AND 15, 1944

### K-Electron Capture in Radioactive Argon A<sup>37</sup>

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(Received May 14, 1942)

A radioactive gas possessing a half-life of  $34.1 \pm 0.3$  days has been produced by bombarding solid samples containing potassium, chlorine, calcium, or sulfur. The observed data require that this activity be assigned to A<sup>37</sup> in accord with the following reactions:



Alpha-bombardment of chlorine has failed to produce a measurable quantity of this activity by an ( $\alpha, d$ ) reaction. The detection of 4.72A Cl  $K\alpha$  x-rays by means of critical absorption measurements in gaseous compounds of chlorine and sulfur reveals that A<sup>37</sup> decays by  $K$ -electron capture. Cloud-chamber observations and aluminum absorption measurements indicate that  $K$ -electron capture accounts for more than 99.9 percent of the total number of disintegrations. The probability of the x-ray quantum being internally converted has been calculated to be  $0.96 \pm 0.03$ . No gamma-rays were observed.

#### INTRODUCTION

THE first radioactive argon to be reported<sup>1</sup> was produced by the bombardment of the gas itself with deuterons. This activity, which decayed with a half-life of 1.83 hours, was assigned to the isotope A<sup>41</sup>. The radiation emitted was found to consist of beta-rays<sup>2</sup> with a maximum energy of 1.5 Mev and of a gamma-ray<sup>3</sup> of 1.37 Mev. More recently, a 1.9-sec. radioactive argon A<sup>35</sup> has resulted from the bombardment of chlorine with protons<sup>4</sup> and of sulfur with alpha-

particles.<sup>5</sup> This isotope was found to emit positrons with a maximum energy of 4.38 Mev.

The stable isotopes of argon have the mass numbers 36, 38, and 40. The existence of isotopes A<sup>37</sup> and A<sup>39</sup> had never been proved although it is evident from the nuclear chart, shown in Fig. 1, that they might be produced by the bombardment of solid samples containing one of the neighboring elements. However, if an isotope of argon formed in this manner should decay entirely by  $K$  capture, then the resulting  $K\alpha$  x-rays of chlorine (4.72A) would be largely absorbed in the sample itself. It is well known that a sensitive means for detecting a soft radiation emitted by a radioactive gas is obtained by admitting the

<sup>1</sup> A. H. Snell, Phys. Rev. **49**, 555 (1936).

<sup>2</sup> F. N. D. Kurie, J. R. Richardson, and H. C. Paxton, Phys. Rev. **49**, 368 (1936).

<sup>3</sup> J. R. Richardson and F. N. D. Kurie, Phys. Rev. **50**, 999 (1936).

<sup>4</sup> M. G. White, E. C. Creutz, L. A. Delsasso, and R. R. Wilson, Phys. Rev. **59**, 63 (1941).

<sup>5</sup> L. D. P. King and D. R. Elliott, Phys. Rev. **59**, 108A (1941).

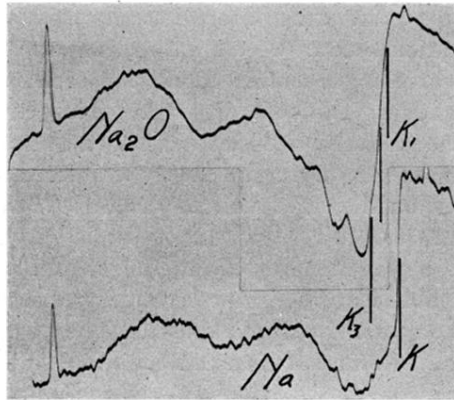


FIG. 3. Photometer curves of the edge for a film of sodium metal and for an air-oxidized film.

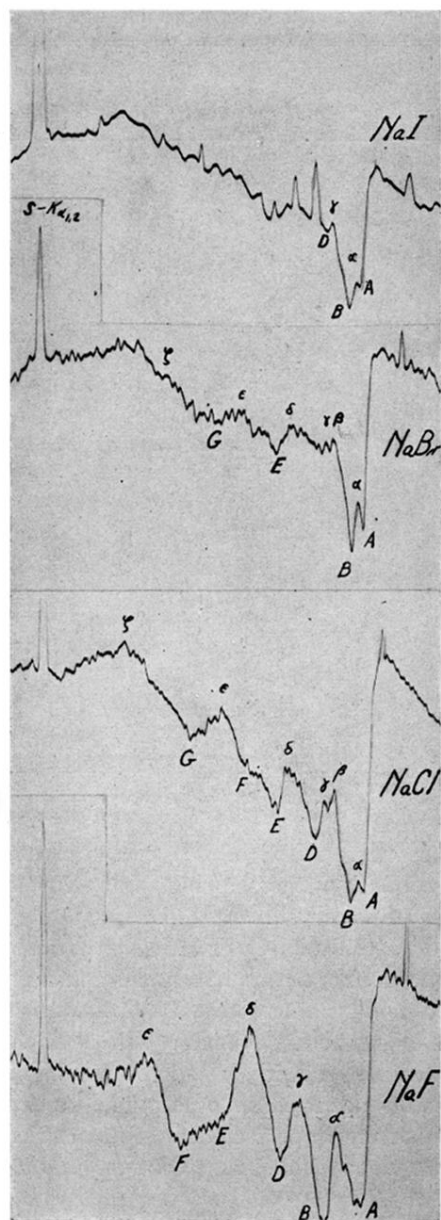


FIG. 4. Photometer curves of the edges for the sodium halides. Reading from top to bottom, the curves correspond to plates Nos. 59, 54, 28, and 49.