scribed here was carried out, to Dr. Harry M. Day, of the Research Laboratories of the General Electric Company, who prepared all of the crystals and performed the heat treatments, to Professors Frederick Seitz and Enos Witmer for their valuable discussions; and to the workers of WPA Project No. 21637 for assistance.

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The *L*-Emission Bands of Sodium, Magnesium and Aluminum

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The radiation emitted when conduction electrons fill vacancies in the *L* shell is spread over a band whose shape represents the energy distribution of the conduction electrons. This band has been studied spectrophotometrically for pure sodium, magnesium and aluminum. The observed shapes are in general agreement with theoretical predictions and confirm the results of previous experimental studies. In each case a "tail" has been observed at the low frequency end of the band, for which alternative explanations are offered. With the x-ray continuum as a standard of intensity, the total intensity of the *L* band increases nineteen-fold from sodium to aluminum.

THE electronic structure of a metal can be investigated by a study of the x-radiation emitted by the metal when one of its conduction electrons falls into a vacancy in an inner shell. Since the conduction electrons have energies throughout a range of several electron volts, this x-radiation is a band of corresponding width. The distribution in energy of the intensity in this band is related to the distribution in energy of the conduction electrons; thus the definite upper limit of the energy of the conduction electrons is evidenced by the fact that the x-ray emission band is sharply bounded at its high frequency end.

X-ray bands of this origin have been observed repeatedly. The recent work of Bearden and collaborators[1] provides examples in the region of 1.5A. In principle, it is preferable to observe the structure of the bands emitted in the ultra-soft x-ray region ($\lambda > 10$A), for here the frequency of the radiation is not large in comparison with the frequency spread of the emission band and high resolution technique is not necessary. Of several reports of bands emitted in this region, those of O'Bryan and Skinner[2] and of Skinner[3] are outstanding in that they present and discuss reliable photometric descriptions of the radiation from very clean surfaces of certain metals. In the emission of ultra-soft x-rays, the surface of the target must be extremely clean, since all photons except those from the surface are absorbed in the target. Foreign elements on the target not only introduce their own characteristic spectra, but also affect the characteristic radiation of the target element itself. The numerous reports of ultra-soft x-rays by Siegbahn and Magnusson[4] and others at Uppsala must be regarded as qualitative, since their targets were admittedly contaminated with carbon, nitrogen and oxygen.

The present work was undertaken as an attempt to confirm and extend previous work in the photometry of the band of radiation emitted as conduction electrons fall to L_{II} or L_{III} levels made vacant by electron bombardment.

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[1] H. Friedman and W. W. Beeman, Phys. Rev. **58**, 400 (1940).

[2] H. M. O'Bryan and H. W. B. Skinner, Phys. Rev. **45**, 370 (1934).

[3] H. W. B. Skinner, Prog. Rep. Phys. Soc. **5**, 257 (1939).

[4] M. Siegbahn and T. Magnusson, Zeits. f. Physik **62**, 435 (1930); **87**, 291 (1934); **88**, 559 (1934); **95**, 133 (1935).

EXPERIMENTAL

The vacuum spectrograph comprised a glass grating of radius of curvature about 1.5 meters and effective width 2.5 cm, ruled with 30,000 lines per inch and adjusted for about 5.7° grazing angle of incidence; a vertical slit, made of two fragments of a razor blade; and a plateholder, embracing the wave-length range from zero to about 740A, which could be raised or lowered without breaking the vacuum. (This motion of the plateholder caused no wave-length displacement of spectrum lines, within the wave-length accuracy demanded in the present work.) A horizontal slot before the plate made it possible successively to bring adjacent zones of the plate into the same part of the x-ray beam, and an externally controlled shutter was used to begin and end the exposures. The dispersion varied from about 1.0A/mm at 100A to 2.2A/mm at 740A.

The x-ray tube was similar to that of O'Bryan and Skinner.[2] It consisted of a 2-liter Pyrex bulb having arms with tapers into which were inserted the filament and target assemblies. The x-ray filament was a tungsten helix, 2 cm long, wound on a 60-mil mandrel out of 10-mil wire 40 cm in length. The filament was partly surrounded by a tantalum shield to prevent direct illumination of the slit by the filament. An evaporator for aluminum, inserted in a third sidearm, consisted of a 20-mil tungsten filament in the form of a helix, the coils of which were charged with small loops of aluminum wire; magnesium was evapoated from tungsten baskets, while in the case of sodium a special distilling furnace was employed. The metals used in coating the target were of high purity. In no case was the impurity content greater than 0.1 percent.

The target was a thin-walled copper tube of square section. It was free to rotate so that any one of the four faces could be placed in position for the exposure, the target being so turned that the radiation entering the slit made an angle of 45° with the normal to the face in use. The target was placed at 6 mm from the filament and 14 cm from the spectrograph slit, which was protected by a "fore-slit." None of the grease (Apiezon *L*) used to lubricate the tapers at the three arms was nearer than 15 cm from the target; therefore the grease was not appreciably warmed by the heat of the filament. During all aluminum and magnesium runs the target was water cooled.

In the case of sodium it was necessary to keep the target temperature below 0°C in order to prevent the sodium from melting. This was accomplished by circulating a liquid (alcohol), cooled in passing through a copper coil surrounded by solid carbon dioxide and alcohol. The circulation was maintained by a gear pump. The temperature of the alcohol leaving the target assembly was about −45°C. Provision was made for keeping the greased taper of the target near room temperature in order to prevent "freezing" of the metal to the glass.

PROCEDURE

The x-ray exposures were so planned that the relative intensity could be found as a function of the distance along the length of the spectrogram. The target was bombarded for a couple of hours to outgas it, the shutter being closed; two or three times during this conditioning the target was coated by heating the evaporator. When the ionization gauge read about 4×10^{-6} mm Hg, the target was recoated and the shutter opened to begin the exposure. During the exposure, the tube was connected directly to a transformer giving 1450 volts, r.m.s.; by adjustment of the filament current (about 5.4 amp. a.c.) the d.c. milliammeter in series with the target was held at 200 ma.

In the case of aluminum, the exposure time was 50 minutes with the plateholder up, and 100 minutes with the plateholder down; for an additional 50 minutes the plateholder was up and the target potential was off, to equalize the slight light fog from the x-ray filament upon the two zones of the plate. There was no visible fouling of the target, but to insure ideal surface conditions the target was recoated at 5-minute intervals. (It was found that aging the aluminum target for 10 minutes gave a general reduction of the intensity by a few percent, with no obvious change in the wave-length distribution of relative intensity.) Since during the exposures the pressure fell typically from 4×10^{-6} to 1×10^{-6} mm Hg, it was considered necessary to break up the total of 200 minutes of exposure into ten

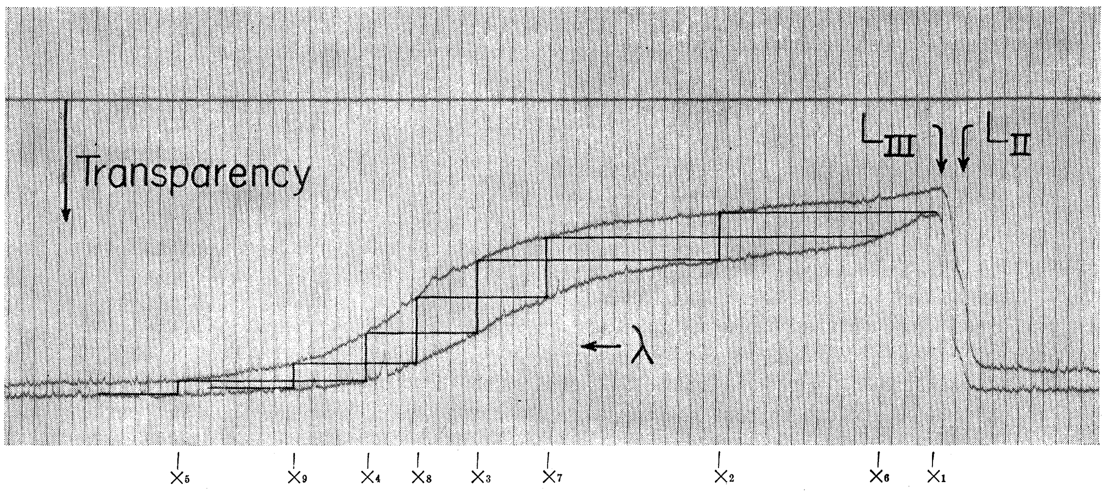

FIG. 1. Densitometer curves of a one-hour and a two-hour exposure of the aluminum L band on the same plate, illustrating the sensitometric method. The wave-length range is 162 to 218A.

cycles to prevent favoring either the "up" or the "down" portions. During each cycle the plateholder was up (with x-rays turned on) for 5 minutes, up (with x-rays off) for 5 minutes, and down (with x-rays on) for 10 minutes. This routine, here described for aluminum, provides two juxtaposed exposures which have had the same treatment as regards light fog, and which differ only in respect to their x-ray illumination. Two good aluminum plates were made in this way.

The seven good magnesium plates were exposed by a routine similar to the above, but there were six cycles of 4 times 10 minutes each, giving x-ray exposure times of 60 and 120 minutes; the target was recoated at 10-minute intervals. For sodium, all four faces were simultaneously coated at hourly intervals, so that each face was used for 15 minutes before recoating; there were eight one-hour cycles, and the four target faces were in each cycle used in sequence, permuted variously to avoid beginning each cycle with the same face. Thus on each sodium plate the x-ray exposure times were 120 and 240 minutes; two plates were so made, the tube current being limited to 100 ma to prevent the coating of sodium from melting.

The respective slit widths for sodium, magnesium and aluminum were roughly 0.32 mm, 0.12 mm, 0.08 mm. The wave-length at the peak of the sodium band was determined by comparison with the line spectrum of air from a disruptive capillary discharge to which the plate was exposed after the x-ray tube had been removed. Ilford QI plates were used in all photometric runs. These seem nearly as sensitive as Schumann plates, and their sensitivity is fairly free of local irregularities.

The photometric process by which the intensity distribution in the band was determined from the spectrogram is reminiscent of a method used by Skinner and Johnston[5] for comparing spectrum line intensities. The process depends on the assumption that the plate sensitivity is independent of wave-length throughout the band and also that the reciprocity law is valid. No assumption need be made as to the characteristic curve of the plate; in fact, the characteristic curve is deduced in the course of this process.

Densitometer curves from the two exposures on the same plate are recorded together as in Fig. 1. Since the exposures stand in the ratio 2:1, it may be seen that the intensity at the point x_2 on the faint trace is half the intensity at x_1, that the intensity at x_3 is half the intensity at x_2, etc. On the basis of these observations a preliminary characteristic curve may be sketched, showing the relation between the intensity and the transparency of the fainter exposure. (For convenience the deflection of the densitometer galvanometer

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[5] H. W. B. Skinner and J. E. Johnston, Proc. Roy. Soc. **A161**, 420 (1937).

may be used in place of transparency.) A second preliminary characteristic curve may similarly be obtained from the points x_6, x_7, etc., x_6 being arbitrarily chosen. The final characteristic curve may then be obtained by superposing two or more such preliminary curves. The galvanometer deflection is now tabulated as a function of distance along the plate; with the aid of the characteristic curve these data now yield values of $I(x)$, the relative intensity per unit distance along the plate.[6] The values of $I(x)$ when multiplied by dx/dV give $I(V)$; here V is the energy in electron volts of the photons incident at any position x on the plate and $I(V)$ is the relative intensity of the radiation in the band per electron-volt interval. The quantity dx/dV is related to the dispersion of the spectrograph. It must be pointed out that this scheme of photometry gives results which represent the x-radiation only and are not influenced by uniform light fogging.

TABLE I. *Intensity distribution in the L bands.*

SODIUM V	$\nu^{-3}I(V)$	MAGNESIUM V	$\nu^{-3}I(V)$	ALUMINUM V	$\nu^{-3}I(V)$
25.00	1.6	39.5	1.1	58.0	4
25.50	2.4	40.0	1.3	59.0	6
25.75	5.6	40.5	2.0	60.0	9
26.00	7.5	41.0	4.2	61.0	13
26.25	9.4	41.5	6.6	62.0	21
26.50	12	42.0	10	63.0	33
26.75	14	42.5	17	64.0	48
27.00	18	43.0	27	65.0	60
27.25	21	43.5	39	66.0	67
27.50	28	44.0	52	67.0	71
27.75	41	44.5	65	68.0	71
28.00	53	45.0	75	69.0	69
28.25	64	45.5	81	70.0	67
28.50	74	46.0	86	70.5	68
28.75	81	46.5	89	71.0	71
29.00	87	47.0	91	71.5	82
29.25	94	47.5	91	72.0	100
29.50	97	48.0	89	72.2	97
29.75	100	48.4	85	72.4	73
30.10	97	48.8	87	72.6	29
30.20	93	48.9	92	72.8	12
30.25	79	49.0	97	73.0	2
30.30	61	49.1	100	73.5	1
30.35	40	49.2	83	74.0	0
30.40	25	49.3	43		
30.45	17	49.4	15		
30.50	11	49.5	7.3		
30.55	6.1	49.6	3.9		
30.70	3.7	50.0	1.1		
31.25	1.9	50.4	0.4		
31.75	0.8	51.0	0.4		

RESULTS

For each element there has been observed a characteristic band superimposed on a continuous background. (This background is assumed to be the true x-ray continuum, although it may be due in part to x-rays scattered from the grating.) The results on these spectra, averaged for each element, are presented in Tables I and II and Fig. 2. Table I gives, for several values of V, the intensity distribution as $\nu^{-3}I(V)$ where ν is the frequency of the L radiation; the continuous spectrum, evident on both sides of the L band, has been subtracted off. From the work of Jones, Mott and Skinner[7] and Skinner,[3] it is expected that the curve $\nu^{-3}I(V)$ *vs.* V for an $L_{\mathrm{II\ III}}$ band will be parabolic near the low frequency end of the band. These curves are shown for sodium, magnesium and aluminum in Fig. 2, together with the parabolas that best fit them. The curves resemble those of Skinner.[3]

Certain numerical characteristics are compiled in Table II. For sodium, λ(peak) is the wave-length for the greatest value of $I(\lambda)$, which is the relative intensity per unit wave-length interval; while the quantity designated as V(peak) is the photon energy when $I(V)$ is maximum. For the remaining elements V(peak) is calculated directly from the published values of λ(grenze) which are here listed as λ(peak). "Maximum V, extrapolated" is the intercept of the steepest tangent to the high V end of the $\nu^{-3}I(V)$ curve. "Band width" is defined as the separation between this intercept and the foot of the "best parabola." For comparison, there are also listed the data of O'Bryan and Skinner[2] as

TABLE II. *Summary of results.*

		SODIUM	MAGNESIUM	ALUMINUM
λ (peak)	(A)	407.6 ± 0.4	250.20*	170.49**
V (peak)	(ev)	29.9	49.1	72.0
Maximum V, extrapolated	(ev)	30.4	49.4	72.8
V at foot of best parabola	(ev)	27.3_5	43.0	62.2
λ at tip of tail	(A)	487	307	212+
V at tip of tail	(ev)	$25._2$	40	58−
Band width (observed)	(ev)	3.05 ± 0.10	6.4	10.6
Band width (Skinner)(3)	(ev)	3.0 ± 0.2	7.6 ± 0.3	13.2 ± 0.5
Sommerfeld band width(3)	(ev)	3.2	7.3	11.9
Area ratio (tail to total band)		0.10_4	0.06_5	0.07_3
Intensity ratio (peak to continuum)		1.7	7	11
Intensity ratio (total band to continuum)		4.2	34	78

* M. Siegbahn and T. Magnusson, Zeits. f. Physik **87**, 291 (1934).
** M. Siegbahn, Ergeb. d. exakt. Naturwiss. **16**, 123 (1937).

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[6] This "staircase" method, originated by Professor L. G. Parratt for a somewhat different purpose, is described by him in a paper now in preparation.

[7] Jones, Mott and Skinner, Phys. Rev. **45**, 379 (1934).

recalculated by Skinner,[3] and band width predictions on the basis of the Sommerfeld free electron model.

The tail at the low energy end of the bands, reported also by O'Bryan and Skinner, is interesting. Table II gives a comparison of the area, (measured on the $\nu^{-3}I(V)$ graph, between the curve and the best parabola) of the tail with the total area under the $\nu^{-3}I(V)$ curve. This ratio of areas is roughly independent of atomic number. The origin of the tails is uncertain. Skinner[3] suggests that they are caused by a softening of the radiation in the band, as by the Raman effect. Seitz[8] attributes them to "excitation levels," i.e., to extra levels below the valence band, that occur wherever a completed shell of an atom has been ionized; since this is, of course, the case at each point in the lattice where a photon is produced, the excitation states might affect the emission band.

It may be pointed out that thermal fluctuations in the lattice constant might, according to the Sommerfeld theory, cause a diffuseness at the foot of the parabola, observed as a tail. Alternatively one may propose a double jump hypothesis to account for the tails: that as one conduction electron falls to the ionized L shell a second conduction electron jumps into an unoccupied conduction level; in this "semi-Auger" process a photon is emitted, of which the energy is less than the energy loss of the first electron.*

The bands have very unequal intensities for the different elements. A convenient measure for the relative intensities of the bands is afforded by the continuous spectrum, since the continuum is not expected to vary greatly among the present three elements. The maximum $I(V)$ is seen in Table II to increase rapidly in relation to the continuum, with increasing atomic number. It is, perhaps, of theoretical interest to compare, for each element, the total band intensity $\int I(V)dV$ with the intensity per volt of the continuous spectrum. This ratio is also seen to increase greatly with atomic number. This increase is to be expected; in fact a semiquantitative calculation involving the radiative transition probability, Auger effect and ionization probability affords a prediction that the foregoing ratio shall, between sodium and aluminum, show a 12-fold increase.

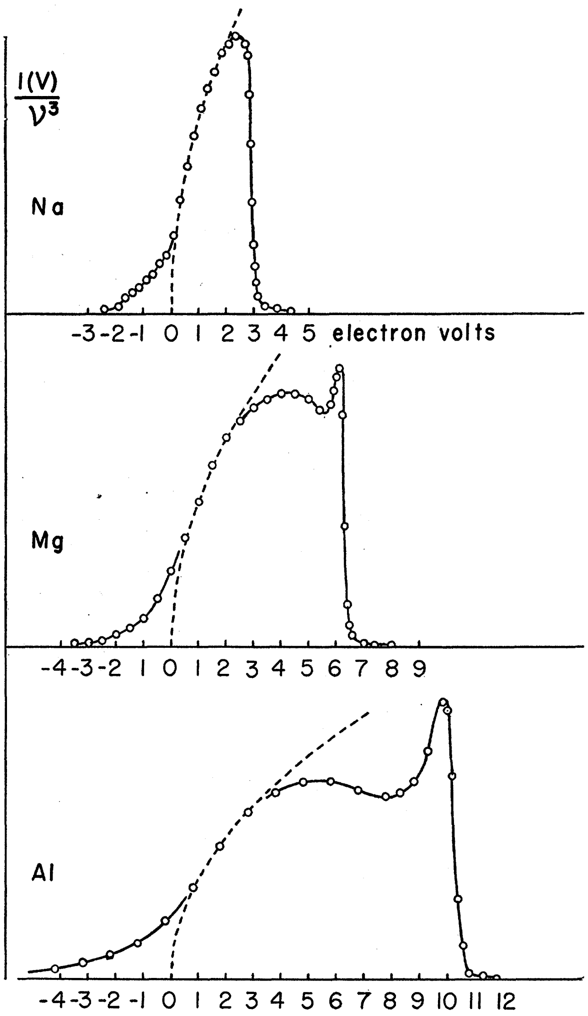

FIG. 2. Intensity distribution in the L bands corrected for continuum, divided by ν^3. The dotted curves are the parabolas which best fit the data. The zero of the energy scale is at the foot of the parabolas.

It is a pleasure to acknowledge helpful conversations with Professor Debye and Professor Parratt, and the assistance generously given by Professor Bethe in the interpretation of the bands. The design and operation of the x-ray tube were influenced by the good advice of Professor H. M. O'Bryan of Georgetown University.

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[8] F. Seitz, *Modern Theory of Solids* (McGraw Hill, 1940), p. 438.

* *Note added in proof.*—A semi-Auger process, independently considered by Skinner and the authors, (H. W. B. Skinner, Phil. Trans. Roy. Soc. **A239**, 95 (1940)) (above) as resulting in the tails that appear on the low energy side of the emission bands, is rejected by Skinner in favor of an alternative hypothesis on the ground that this process would produce tails at both sides of the bands. This rejection is however invalid: the semi-Auger process can decrease but never increase the energy of an emitted photon.

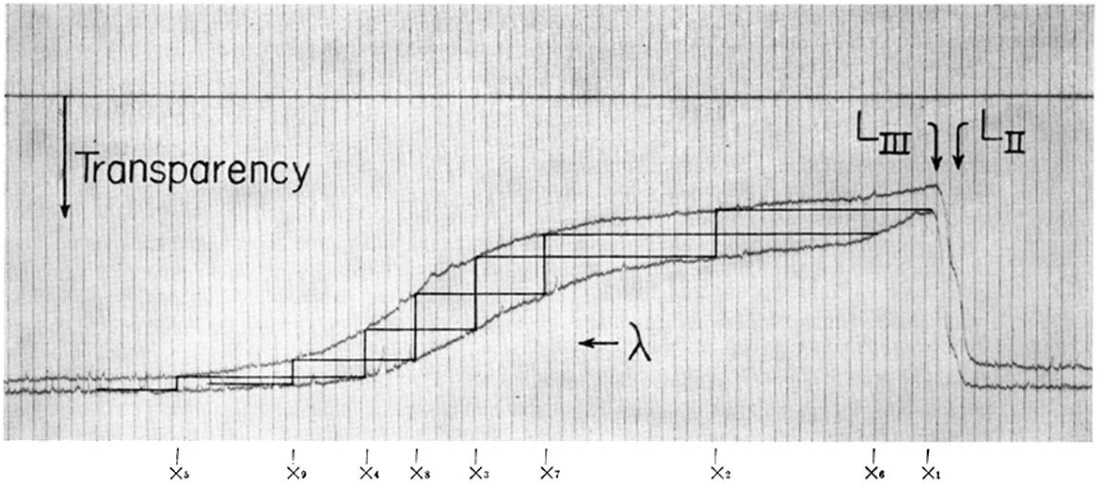

FIG. 1. Densitometer curves of a one-hour and a two-hour exposure of the aluminum *L* band on the same plate, illustrating the sensitometric method. The wave-length range is 162 to 218A.