

Characteristic X-Rays from Metals in the Extreme Ultraviolet

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Soft x-ray bands in region 50–500Å from Li, Be, C, Na, Mg, Al, Si and Ba targets. A 2-meter grazing-incidence spectrograph was used. The bands (except those for Ba) correspond to transitions of outer (or conduction) electrons into a vacant *K*- or *L*-shell. The diffuseness of the bands is associated with the energy spread of the filled conduction electron levels. The Ba band is an *O*→*N* transition. The other metal bands extend over a fairly wide wave-length region and each has a sharp short wave-length edge which corresponds to the sharp "surface" of the filled conduction electron levels. The bands of C and Si have a more diffuse

head which is connected with their semiconducting property. The energy spread of the metal bands may be calculated approximately from the Sommerfeld theory of metals; this provides a method of determining uniquely the number of conduction-electrons per atom in a metal. But the explanation of the precise shapes of the bands will require a more detailed theory and in particular an investigation of the transition probability of a conduction electron into a *K*- or *L*-shell. Some discussion is added on the absolute energies involved in the transitions which give rise to the bands.

THE radiation emitted when free electrons in a metal make transitions into the relatively sharp *K*- or *L*-levels which have been ionized by electron impact furnishes one of the most direct sources of information about the energy states of conduction electrons in the unexcited metal. DuMond¹ has recently published results on the breadth of the Compton scattered band from beryllium and carbon and has been able to make inferences about the momentum of the electrons in the metal. However, since the electrons of even a free atom have a finite momentum spread, these results are not very sensitively affected by the actual lattice-binding. In working with the soft x-ray emission-bands, one has the advantage that the actual energy levels of the electrons in the metal are directly involved; and also the dispersion of the spectrograph used (in the region 50 to 500Å) is easily able to show fine details within the actual energy-spread of the conduction electrons (of the order of 10 volts). An attempt to use the *K*-band of beryllium, as measured by Söderman,² was made by Houston.³ He was led to the conclusion

that the conduction electrons were badly represented by a theory of the Sommerfeld type. In a recent note⁴ we have shown that this conclusion is not supported if our measured band of beryllium is used in place of Söderman's. The discrepancy between his result (and also that of Prins⁵) and ours may probably be traced to the question of cleanness of the beryllium surface. Simultaneously with our note, Osgood⁶ has published a photometer trace of the aluminum *L*-band; his result agrees fairly well with ours, except that he has missed an interesting structure effect. We have also observed the bands of lithium, magnesium and silicon, and rather inadequately, those of carbon and sodium. The carbon results agree reasonably with observations of Söderman⁷ and Renniger.⁸ Since our note, Siegbahn and Magnusson⁹ have published in a brief preliminary note the wave-lengths of the bands of Mg, Al and Si. These agree closely with our wave-lengths.

⁴ O'Bryan and Skinner, *Phys. Rev.* **44**, 602 (1933).

⁵ Prins, *Zeits. f. Physik* **69**, 618 (1931).

⁶ Osgood, *Phys. Rev.* **44**, 517 (1933).

⁷ Söderman, *Zeits. f. Physik* **52**, 795 (1929).

⁸ Renniger, *Zeits. f. Physik* **38**, 510 (1932).

⁹ Siegbahn and Magnusson, *Nature* **132**, 750 (1933).

¹ DuMond, *Rev. Mod. Phys.* **5**, 1 (1933).

² Söderman, *Zeits. f. Physik* **65**, 656 (1930).

³ Houston, *Phys. Rev.* **38**, 1791 (1931).

EXPERIMENTAL METHOD

The soft x-ray bands were photographed on a 2-meter glancing-incidence vacuum spectrograph of the same general construction as those used in Siegbahn's Laboratory. The glass grating ruled by Professor R. W. Wood with 30,000 lines per inch was lightly etched with hydrofluoric acid as previously described by O'Bryan.¹⁰ The extreme astigmatic property of the concave grating at angles near grazing incidence made possible a direct comparison of the spectra from narrow strips of the grating surface perpendicular to the ruled lines, and in this way it was shown that the first-order spectrum was increased in intensity at least twenty times by the proper amount of etching.

The incident radiation made a mean angle of about 6° with the grating surface. The slit-width was normally 0.3 mm but was reduced to 0.075 mm for certain exposures. A system of diaphragms was inserted between the grating and the slit to prevent scattered light or localized fogging of the plate. The light from the direct image was trapped effectively, and diffused light from the inside of the spectrograph was prevented as far as possible from reaching the plate.

The purity of the metal surface from which the radiation is emitted is of great importance, since metals have a high absorption coefficient both for radiation in this wave-length range (50 to 500A) and for the bombarding electrons (of 2000 volts energy). With the exception of carbon, all the elements we have tried were evaporated onto a copper anode in a high vacuum; the surface could thus be renewed at suitable intervals during the exposure. In this way, surfaces were obtained which we believe give x-rays characteristic of the pure metal and in fact in one case (beryllium) evidence will be given of the effect of the inevitable fouling of the surface after a period of electron bombardment. The carbon surface used was one produced accidentally by the decomposition of hydrocarbons in a good vacuum. From this surface seven orders of the carbon *K*-line were obtained on one plate. The absence of this line from all other plates is good evidence of freedom from other

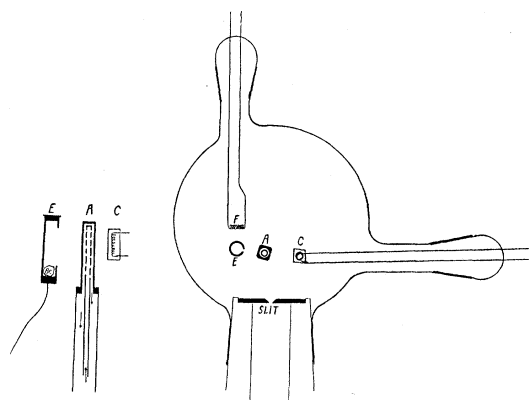


FIG. 1. X-ray tube and evaporating oven.

contaminations such as oxygen and nitrogen which are often present.

The x-ray tube was a one liter glass bulb fitted to a cone around the spectrograph slit as shown in Fig. 1. Into it are fitted, by means of cones in side tubes, the hot cathode *C*, the oven *E* used for evaporating the metals, the auxiliary filament *F* used for heating *E*, and the target *A*. The latter was a square sectioned copper rod about 6 mm thick, drilled for water cooling so that the minimum thickness of wall was about 1/10 mm. The rod was placed parallel to the slit (at about 2 cm from it) and was carefully lined up optically with the spectrograph by slight bending of the glass tube holding it. It could be rotated so that any of the four sides could be put in place for the exposure. The position chosen was one in which the radiation entering the spectrograph made an angle of about 10° with the surface. In this way, a fairly large area of the anode was effective in spite of the narrow angle (about 2°) taken in by the spectrograph. When the apparatus was satisfactorily evacuated, the anode was heated to a dull-red by discontinuing the water cooling and bombarding with electrons to free it as far as possible from gas. The cathode *C* was a dull-emitter consisting of a nickel box coated with barium oxide, indirectly heated by a tungsten filament. It was placed about 3 mm from the anode, and with a 2000 volt acceleration, a current of 500 m.a. was possible. A focussing cylinder (not shown in the diagram) was mounted around the filament. The evaporating oven *E* was a hollow molybdenum cylinder

¹⁰ O'Bryan, Phys. Rev. 38, 32 (1931).

closed at the ends with a slit in the side which faces the anode. It was heated to a suitable temperature by electron-bombardment from the filament *F*. To get a steady evaporation of clean metal, it was necessary to overheat *E* for some time to drive out the occluded gases. One side of *A* was sacrificed for this purpose. When all signs of gas discharge had ceased, a fresh side of *A* was turned towards the oven and a coating was slowly put on at a gas pressure of less than 10^{-5} mm. Generally all four sides of *A* were coated since this appeared to prevent gas-liberation by electrons which had strayed around the anode. This method of evaporation worked well even for a substance with so low a vapor pressure as silicon which required a temperature of at least 1500°C for evaporation. The temperature of the target surface under electron bombardment is rather difficult to estimate. For good heat conductors, it was probably less than 200°C ; but with carbon there were glowing particles visible on the surface.

The spectrograph was exhausted to a pressure of about 10^{-4} to 10^{-5} mm by continued pumping by a Gaede 4-stage steel mercury pump and liquid air trap. A fast multi-jet glass mercury pump kept the pressure in the x-ray tube down to 10^{-6} mm at which pressure exposures were made. The pressures were measured by ionization gauges. Liquid air traps were placed in the lines of both pumps and a glass bulb inside the body of the spectrograph was usually filled with liquid air to remove vapors. In this way the time necessary before the spectrograph vacuum was sufficiently good for use was considerably shortened. The good vacuum was required partly to prevent surface contamination of the anode and partly to increase the temperature efficiency of the dull-emitter. If the pressure were allowed to get high, it became necessary to overheat the filament to get sufficient electron current; then it was found that barium was distilled on to the target and barium lines appeared on the plate. In a bad case, the barium might mask the element to be investigated; but it was quite possible by paying attention to the vacuum to avoid the barium lines completely. The tube was kept free from carbon vapors by the use of a mixture of the low vapor-pressure Apiezon grease with powdered graphite on the cones. In fact the carbon *K*-line

only appeared on a single plate taken early in the series of exposures.

Eastman "Spectroscopic" plates were used coated with Apiezon oil. This combination was found fairly satisfactory for photometry provided the oil was carefully applied by a soft leather pad. With a beryllium target, a good exposure was taken in 15 minutes with an applied potential of 2000 volts and a current of 400 m.a. This represents the shortest exposure; often several hours were necessary. With lithium surfaces, for example, we had to work with a considerably lower current and to recoat frequently because of the tendency to melt and to acquire obvious contamination under the electron bombardment. With sodium, the metal tended to flow away from the spot bombarded leaving a very foul surface, and the problem was not adequately solved. For all the other metals, it was easy to keep the surface spotless during the course of the exposure by redistillation at about half-hourly intervals.

The standard voltage chosen was 2000 volts supplied by a 60 cycle transformer rectified by two 866 mercury vapor tubes. No smoothing was used. The power input was limited by the boiling of the water cooling. Spectra of beryllium were also taken with accelerating voltages of 700 volts and 10,000 volts. They showed no essential differences as far as the structure of the line was concerned but the general continuous background seemed to increase with the voltage. There was no evidence of any great alteration in the exposure time for different voltages with equal power input; but this could not be maintained at its maximum value for the lowest voltage.

The wave-lengths were determined by placing the spectrum of a vacuum hot spark on the same plate as the x-ray spectrum. Electrodes of aluminum and beryllium were used and the wave-lengths were taken from a paper by Soderquist and Edlen.¹¹ The metal spark chamber fitted on the cone around the spectrograph in the place usually occupied by the x-ray tube. It was necessary to admit air to the spectrograph during the change of sources but the photographic plate was not touched. The Be, Li, Mg and Ba wave-

¹¹ Soderquist and Edlen, *Zeits. f. Physik* **69**, 356 (1931).

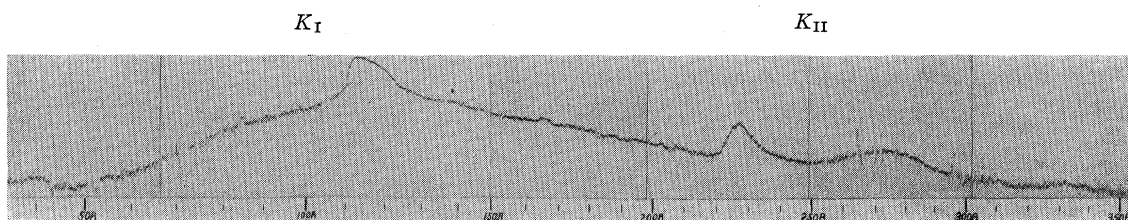


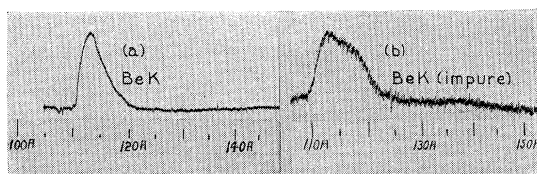
FIG. 2. Photometric curve of a heavy Be exposure.

lengths were compared directly with spark lines. The accuracy of measurement was limited entirely by the difficulty of fixing a definable characteristic of the radiation band; but a precision of a few tenths of an Angstrom could be attained. The other x-ray bands (of C, Al, Si) were determined by using these known x-ray bands as standards. Only for Si, which had no standard sufficiently near, was the loss in accuracy serious.

RESULTS

Fig. 2 shows a photometric curve of a heavy exposure with a beryllium target over an extended range of the spectrum. The humps near 115 and 230A are the Be K -radiation in the first and second orders. Besides these, there is a strong continuous background which is not due to scattered visible or near ultraviolet radiation. It is hard to be sure that it is a genuine continuous spectrum, but there was some indication from the intensity distribution that this is really the case. If so it may possibly be partly due to contamination. The faint broad band at about 137A is certainly due to contamination of the target; that at 270A is perhaps the second order of the other although its intensity seems at first sight too great.

Fig. 3 shows (a) a good Be exposure in the first order of suitable density for photometry. The slit width was 0.075 mm and the target was frequently recoated. Also (b) an exposure from a

FIG. 3. Structure of beryllium K .

target which had been run for two hours without recoating. There was an obvious brownish spot on the surface, almost certainly due to oxidation. Originally the surface had given a spectrum like (a), but the band has become broadened to the long wave-length side. The sharp edge of (a) is missing and two extra bands are to be seen, one at about 117A and the other at about 137A. The generally broadened band looks somewhat similar to those found by Söderman and Prins who worked at considerably higher gas-pressures than we have and without distillation. Some faint but (on the original plate) quite definite signs of structure are to be found even on (a) on the long wave-length side of the maximum. These are perhaps due to residual contamination.

Fig. 4 shows (a) a lithium exposure in which slight hump on the short wave-length side is probably genuinely present, if so it may be due to impurity; (b) a magnesium exposure in which the main features have been carefully verified, in particular the curious minimum and sudden rise near the head; (c) an aluminum exposure showing rather similar characteristics; (d) a silicon exposure in which the main feature is the unsharpness of the band-head; (e) a barium exposure showing a quite different form from the remaining bands.

To obtain the actual energy distribution of the emitted radiation, the plate was calibrated with a quartz spectrograph in the region below 3800A (the approximate region of the oil fluorescence under the action of soft x-rays). A series of photometric screens¹² was kindly lent by Professor Harrison. To obtain the energies, it is necessary to assume that the wave-lengths in a given band are equally efficient in producing fluorescence in the oil, but as the bands are not

¹² Harrison and Leighton, Phys. Rev. 38, 899 (1931).

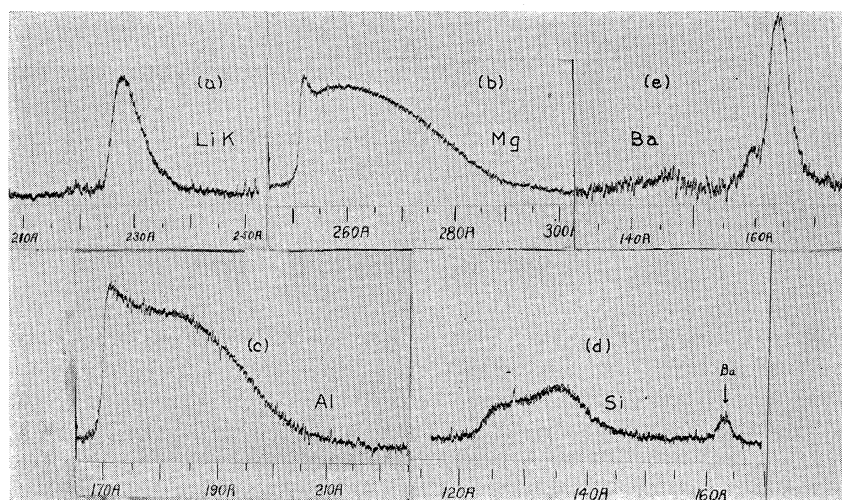


FIG. 4. Photometer curves of x-ray lines.

very wide compared with their absolute frequency, this is probably legitimate. Corrected curves of the intensity of the radiation (on an arbitrary scale) plotted against the energy of the quanta (in volts) are shown in Fig. 5 for the elements Li, Be, Mg and Al. It is worth noting that, besides characteristic differences in the forms of the curve near the band-head, there is a definite difference in the tail-shapes of the bands of Li and Be compared with those of Mg and Al.

In Table I, certain numerical characteristics of the bands are tabulated. The bands of C and Na were not satisfactorily investigated; only one plate of each was taken and these were not

suitable for photometry. The band of Na appeared to have a suggestion of a minimum of intensity in the middle, but this was possibly due to surface contamination of which there was a strong suspicion. The wave-lengths for Na and Si were not directly compared with standards and the possible error is difficult to assess.

TABLE I. Numerical characteristics of the bands. λ_0 is the wave-length of the band-head obtained by extrapolating the straight portion of the sudden fall in intensity to the level of the uniform background and applying a correction for slit width. V_0 is the voltage corresponding to λ_0 . δV is the voltage range from λ_0 to the maximum intensity of the band. ΔV is the total estimated width of the band.

Element	λ_0	V_0	δV	ΔV (exp.)	ΔV (theor.)
Li	225.3 ± 0.2	54.8	0.6	4.2 ± 0.6	4.6
Be	110.9 ± 0.2	111.2	2.7	13.5 ± 2.5	13.8
C*	45.4 ± 0.3	272	—	5	20.8(?)
Na	405 ± 2	30.5	—	3.5 ± 1	3.2
Mg	251.0 ± 0.2	49.2	0.6	9.0 ± 1.5	7.2
Al	169.8 ± 0.2	72.7	0.4	16.0 ± 2	12.0
Si	123 ± 1.5	100.3	5	19.2 ± 2.5	13
Ba*	164.6 ± 0.3	74.9	—	3.0 ± 0.3	—
Ba*	159 ± 0.5	77.6	—	—	—

* Measurement to the center of band.

IDENTIFICATION OF THE BANDS

For Li, Be and C, the observed bands are obviously *K*-bands. They represent transitions from the outermost (or conduction) levels into

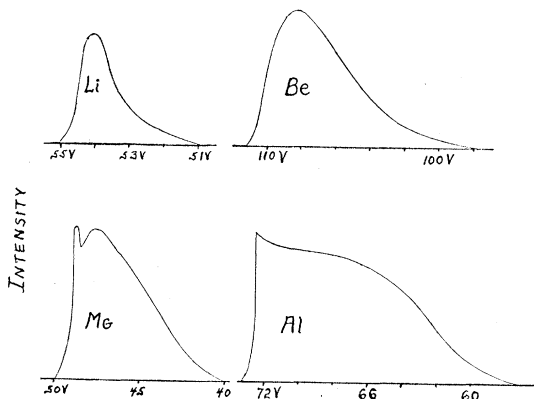


FIG. 5. Intensity against energy in electron-volts of soft x-ray emission.

the K -level. For Na, Mg, Al, Si the bands are L -bands. The question arises in the latter case which of the three L -levels is concerned.

The separations between the L -levels may be estimated from the laws of x-ray doublet separation. It is found that the $L_{II} - L_{III}$ ($2p_{\frac{1}{2}} - 2p_{\frac{3}{2}}$) separation is negligible for us; but that the $L_I - L_{II}$ ($2s - 2p$) separation is quite large. The $L_{II, III}$ term values for these elements are known within a few percent and tabulated.¹³ These are sufficient to determine the observed bands unambiguously as due to transitions into the $L_{II, III}$ levels. The agreement is as follows:

	Mg	Al	Si
V_0 (obs.)	49.2	72.8	101 (inaccurate)
V_0 (Siegbahn)	49.9	71.5	97.5

We are left to explain why there are not two bands instead of only one. Evidently the transitions (conduction $\rightarrow L_I$) do not occur with any probability. This at first sight is rather strange since they seem of the same type as the transitions (conduction $\rightarrow K$) which are found for Li and Be. But it may be that these (conduction $\rightarrow L_I$) transitions are extinguished through the higher probability of ($L_{II, III} \rightarrow L_I$) transitions. To obtain an estimate of the wave-length at which the radiation from these transitions should be found we have to make an extrapolation by the screening-doublet formula, since the energies of the L_I -levels have not been evaluated. We find in this way that the ($L_{II, III} \rightarrow L_I$) transitions should have been in the region of our observations; but the extrapolation necessary is very long, and we suggest that it would be worth while to look for them in the region above about 500A which was not covered in our experiments.

Finally there remains the interpretations of the barium bands (Fig. 4e). Their different form suggests immediately that they are not due to transition from conduction electron levels, but from underlying "atomic" levels. Actually these bands were observed by Osgood¹⁴ and were correctly assigned by him as $O \rightarrow N$ transitions. He did not make accurate wave-length determinations; also he reports the $\lambda 165$ band as a doublet and an extra line at a much shorter

wave-length, neither of which features we observed. Table II gives a comparison of our values of V_m , the mean voltage of the band and that calculated from x-ray data.¹³ (The last column can be neglected for the present.) The agreement is poor, and since our determination is

TABLE II. Observed and calculated values of V_m for Ba band.

Transition	V_m (obs.)	V_m (calc. 1)	V_m (calc. 2)
$O_{II, III} \rightarrow N_{IV}$	75	84	73
$O_{II, III} \rightarrow N_V$	77.6	88	77

accurate, an error in the x-ray data is suggested. The faint band of radiation visible on Fig. 4e at around 145A represents probably the transitions (conduction $\rightarrow N_{IV}$ and (conduction $\rightarrow N_V$), that is to say two broad superposed bands. If we assume a band-head at 145A, we are able to obtain a (ν/R) value for the $O_{II, III}$ level of Ba of 1.40 as compared with Siegbahn's value of 0.7. This value when used in conjunction with Siegbahn's values for N_{IV} and N_V gives a much better agreement with the values of V_m , as is shown by the last calculated column of Table II. This gives one confidence in the identifications. However, more experimental data on pure Barium targets are needed to complete these interpretations.

DISCUSSION OF BAND-FORMS

Except in the case of barium, the soft x-ray bands observed are all due to transitions from the filled outer (or conduction) electron levels into a vacant K - or L -shell. In the excited state, a K - or L -electron is missing but all the conduction levels are filled and thus the energy of the system is well defined. On the other hand, after the radiation has been emitted, we have a normal metal in which an arbitrary level of the conduction electron system lacks an electron. The structure of the filled conduction levels therefore plays an important part in determining the structure of the bands. If E is the energy, n_E the number of occupied conduction levels per unit energy range, and f_E the transition probability into a K - or L -shell of an electron from a level of energy E , the intensity distribution in the band is given by

$$I_E = n_E f_E. \quad (1)$$

¹³ Siegbahn, *Spektroskopie der Rontgenstrahlen*, p. 348 (1931).

¹⁴ Osgood, *Phys. Rev.* **30**, 567 (1927).

The form of f_E is indeterminate at present but some characteristics of the bands can be obtained from that of n_E .

It is well known that a good conductor of electricity is a substance for which there exist a large number of unoccupied levels within a small energy range above the highest occupied level. A rough sketch of some possible curves of n_E for metals, semiconductors and insulators is given in Fig. 6, in which the unoccupied levels

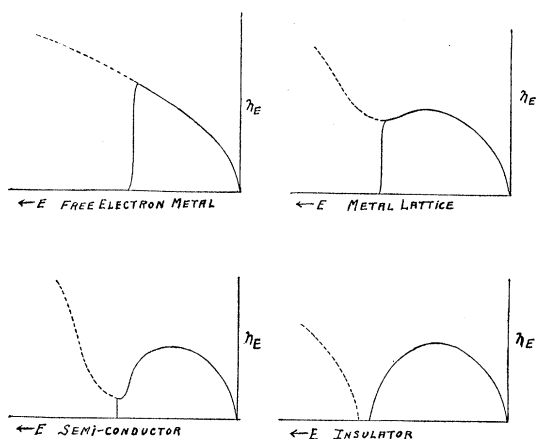


FIG. 6. Energy states in solids.

are represented by dotted curves. It follows that, for metals, I_E must drop suddenly to zero from some finite value; and so the bands must have a high-energy head, just as is observed (Fig. 4a, b and c). For insulators, on the other hand, no sharp edge is to be expected. We have no observations for such substances but the case is actually exemplified by the Ba $O \rightarrow N$ band, since the O -levels are certainly nonconducting. We find a band which is symmetrical about its center (Fig. 4e). It is also interesting that the bands of the semiconductors C and Si (Fig. 4d) do not show any appreciable sharp edge, thus demonstrating that the valence-electrons in these substances form almost self-contained groups, as might be expected.

The actual energy range δV (in volts) of the intensity drop from a maximum to zero for the metals has been given in Table I. Apparently this should be dead sharp except for the obvious temperature-diffusion (of the order of 1/10 volt) of the "surface" of the filled conduction electron levels. Actually we have to take into account the

finite slit-width which increases in effect for decreasing wave-length. This would account for an unsharpness of about 0.3 volt for Li and Mg and 0.4 volt for Al. These are certainly smaller than the observed values δV but the difference can probably be accounted for by photographic spreading of the image. The case of Be is exceptional; the apparent diffusion of the edge is much more than could be accounted for. But a close examination of the Be curve (Fig. 3a) suggests that I_E is beginning to diminish before the edge is reached.¹⁵

An elementary conclusion from (1) is that the energy-spread of the bands is equal to the energy spread of the filled conduction electron levels. If we adopt the Sommerfeld (or free-electron) model of the metal, this spread ΔE is calculated in terms of the number of atoms per cc ρ and the number of electrons per atom N is

$$\Delta E = (h^2/2m)(3\rho N/8\pi)^{2/3}. \quad (2)$$

On the assumption that N is 1 for Li and Na, 2 for Be and Mg, 3 for Al, and 4 for C and Si, the result of the calculation of the corresponding voltage-range ΔV is given in Table I, and may be compared with the experimental values. The agreement for the true metals is good, and, in spite of the fact that the discrepancy for Al seems to be outside the limits of error, one is able to determine unambiguously in all cases the number of conduction electrons per atom. For C and Si one could not expect the Sommerfeld theory to hold; but the great breadth of the Si band is perhaps unexpected. For Ba, the relative sharpness of the $O \rightarrow N$ bands is due to the sharpness of the O -level which lies at about 20 volts below the surface of the conduction electron levels.

Even for metals, the formula (2) involves all the consequences of the elementary theory which neglects completely the lattice-structure of the metals. We know that in fact n_E does not increase continuously as $E^{3/2}$ as would be required; the curve of n_E against E breaks up into separate zones which, for metals with two conduction electrons must overlap somewhat. This is probably unimportant in the case of alkali-metals with only one conduction electron per atom, and in fact no evident breach of the theory

¹⁵ Jones, Mott and Skinner, Phys. Rev. 45, 379 (1934).

occurs for Li. Preliminary calculations by means of Bragg's law for the de Broglie wave-lengths reflected by the metallic lattice give fair agreement with the most obvious structures noted in the photometer curves shown in Fig. 4. These are the breadth of the short wave-length edge of Be, the minima of intensity near the short wave-length edge of the Mg band and possibly a similar effect for Al but not as close to the edge. To discuss the meaning of the curious shapes of these bands involves a detailed and much more careful consideration of the functions f_E and n_E which will be left to a subsequent paper.¹⁵ But here we may note that there is a certain similarity between the shapes of the K -bands of Li and Be (Fig. 5) when compared with the L -bands of Mg and Al. This may be ascribed to the fact that the first are transitions into an s -level, while the second are transitions into a p -level.

We may sum up in saying that the characteristic properties of metals, semiconductors and insulators are reflected in the sharpness of the soft x-ray band-heads and that the breadths of the bands allow one to fix the number of free electrons per atom in a metal.

COMPARISON WITH CRITICAL POTENTIAL MEASUREMENTS

In two recent papers,¹⁶ Skinner has described photoelectric measurements of the intensity distribution in the K -bands of Li and Be, using an exciting voltage of 300. These agree as well as could be expected with the results of the present experiments; the band-heads were found correctly to within one volt. In the same papers, direct measurements were also described of the K -excitation voltages. The method employed was to vary the energy of the bombarding electrons and measure photoelectrically the intensity of the radiation emitted. Thus curves were obtained showing breaks when the region of K -excitation is reached. In this way, the values 53.7 and 92 volts were obtained for the minimum K -excitation potentials of Li and Be metals. It follows from what has been said that the minimum K -excitation voltage must be equal to the voltage V_0 of radiation corresponding to the

band-head. From Table I values of V_0 of 54.9 and 110.3 volts for Li and Be are obtained. The agreement for Li is fair; but there is no agreement for Be. However, the voltage 92 agrees reasonably with the limit of the faint band at about 140A (Fig. 3b) which has been definitely ascribed to contamination of the surface. A further strong break at 107 volts appears to correspond with the hump at 117A which also appears with an impure surface. One seems therefore to be forced to the conclusion that the results of the excitation-potential measurements were spoiled by surface contamination.¹⁷ This was in spite of great precaution taken to ensure purity. It is possible that a very slight contamination will have a serious effect for electrons with energy of the order of 100 volts; the results of experiments using higher exciting voltages will be much less sensitively affected. It is hoped to investigate this question further.

It is of some interest to compare the energy corresponding to the radiation emitted with the energy values for $L \rightarrow K$ transitions in the corresponding free atoms. The energy difference between $\text{Li}(1s \cdot 2s^2)$ and the normal atom, $\text{Li}(1s^2 \cdot 2s)$, may be obtained from the experimental value of the energy¹⁸ of $\text{Li}^+(1a \cdot 2s)$ by subtracting a rough estimated value of 7.5 volts for the work gained in replacing the second $2s$ electrons. The value for $\text{Be}(1s \cdot 2s^2 \cdot 2p)$ was similarly found from a calculated value for $\text{Be}^+(1s \cdot 2s^2)$ kindly supplied by Professor P. M. Morse. The values so obtained are better than those given previously by Skinner.¹⁶ The following table shows (a) the maximum energy V_0 of the radiation emitted from the metals, (b) an approximate estimate of the mean energy V_m of the radiation bands and (c) the energy V_a for the $L \rightarrow K$ transition in the free atom.

	V_0	V_m	V_a
Li	54.9	53	56.6 ± 1
Be	111.2	105	117.5 ± 4

It is seen that, as might be expected, the metallic binding has the effect of depressing the value of V .

¹⁷ We are indebted to Dr. D. R. Bhawalkar for the information that he has obtained by a similar method the low value of 63 volts for Al. The value of V_0 from Table I is 72.8 volts.

¹⁸ Bacher and Goudsmit, *Atomic Energy States*.

¹⁶ Skinner, Proc. Roy. Soc. A135, 84 (1932); and A140, 277 (1933).

The value of 170.5Å for the L absorption edge given by Siegbahn¹⁹ agrees well with our measurement of the short wave-length edge of the conduction band for aluminum. The experiments of R. W. Wood²⁰ on the absorption in the near ultraviolet and those²¹ started at this laboratory should add much information about the filled levels and the transition probabilities to the empty levels in solids.

The experiments were carried out during the tenure by one of us (H.W.B.S.) of a Rockefeller Fellowship at the Massachusetts Institute of Technology. A grant by the Rumford Committee made possible the construction of the vacuum spectrograph.

Note added in proof. More recently we have photographed the boron K line at 67.5Å emitted by bombardment of an evaporated surface. In a recent report (Siegbahn, Proc. Phys. Soc. **45**, 689, 1933) on some of the same elements from Siegbahn's laboratory there are a few differences which are worthy of comment.

Our curves (Fig. 3) for beryllium show the vast differences which a slight contamination may produce. Hence their curves (Fig. 3) for this

element are probably not characteristic of the pure metal since nearly all spectra and photometer curves in this and a preceding article (Siegbahn and Magnusson, Zeits. f. Physik **87**, 291, 1934) show intense carbon lines and even oxygen and nitrogen lines. The carbon lines were present only on one of our plates and yet plates which showed no trace of this commonest of contaminations gave spurious structure when the target surface was not renewed frequently. The surfaces prepared and recoated frequently by evaporation in high vacuum are the most satisfactory, for these lines are due to transitions from the conduction electron states which are very sensitive to the effect of chemical combination.

The boron line is almost symmetrical with a width at half-maximum intensity of 7.8 volts. The wave-length is that reported by Siegbahn and Magnusson but the shape more symmetrical. The boron shape resembles what is expected of semiconductors on the short wave-length side of the line. The edge at 169.9Å due to the $Al L_{II}$ level is not as distinct in our Fig. 4c as in theirs. There is an indication of a similar structure for Mg in our Fig. 4b. Their photometer curve Fig. 6 for aluminum shows structure at 212.4Å and 198.5 obviously due to Al_2O_3 present in the target.

¹⁹ Siegbahn, Proc. Phys. Soc. **45**, 689 (1933).

²⁰ Wood, Phys. Rev. **44**, 353 (1933).

²¹ Liben and O'Bryan, Phys. Rev. **44**, 952A (1933).

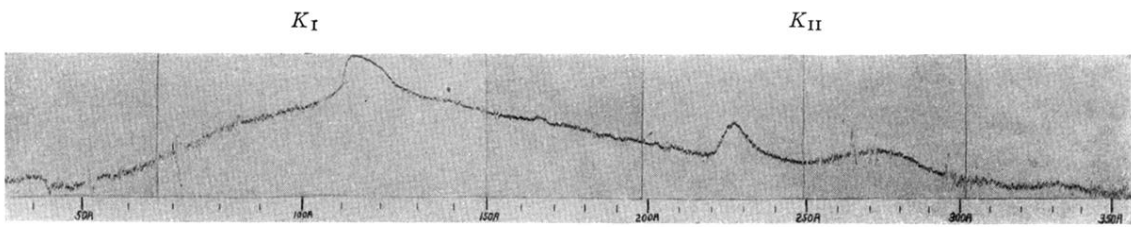


FIG. 2. Photometric curve of a heavy Be exposure.

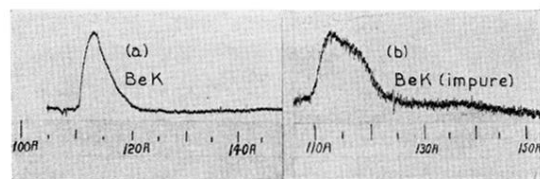


FIG. 3. Structure of beryllium K.

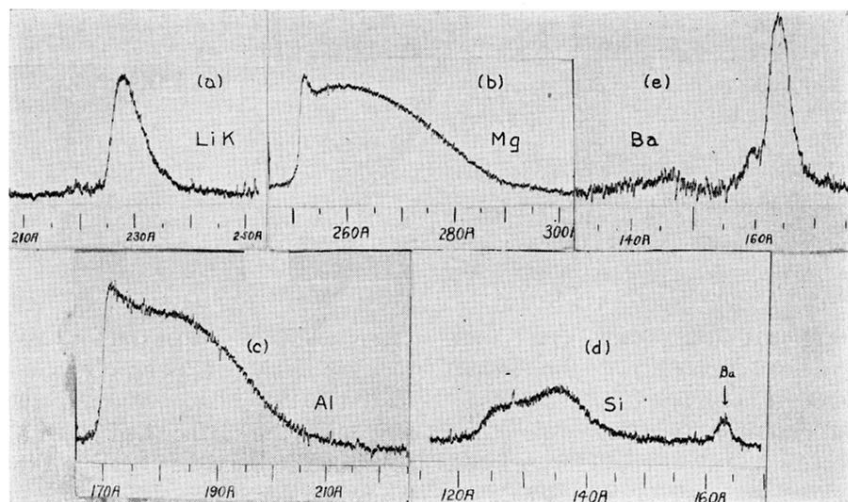


FIG. 4. Photometer curves of x-ray lines.