A SPECTROSCOPIC STUDY OF THE ELECTRONIC STRUCTURE OF METALLIC POTASSIUM AND CALCIUM

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A SPECTROSCOPIC STUDY OF THE ELECTRONIC STRUCTURE
OF METALLIC POTASSIUM AND CALCIUM

R. H. Kingston

This report is essentially the same as a
doctoral thesis in the Department of Physics, M.I.T.

Abstract

The spectrograph used by O'Bryan and Skinner to study the emission bands of
metals has been modified for use with a photomultiplier detector in place of photographic
plates. The apparatus consists of a grazing incidence vacuum spectrograph, with a
movable photodetector which records photon counting rate as a function of wavelength in
the range 50 to 800 A. In a separate evacuated chamber, connected to the spectrograph
by the object slit, are an electron gun, evaporating furnace and target upon which a
sample metal may be placed for study. The sample is prepared by evaporation from the
furnace onto the target, and the radiation is produced by bombarding the target with
electrons of 300 to 500 ev energy, at currents of 2 to 6 ma. The radiation studied
in this report is produced by the transitions of the valence electrons into the ionized 3p
state of the atom. The limiting factor in the accuracy of the emission band obtained in
this way is the purity of the sample studied. As a result of the increased sensitivity of
the spectrograph a spectrum curve may be recorded in five minutes at bombarding power
approximately one one-hundredth as great as those required with photographic plates.
The emission bandwidths for potassium and calcium are found to be 1.9 and 3.0 ev
respectively, compared with 3.6 and 5.0 ev predicted from theoretical calculations. The
general results indicate that the present theories do not give an adequate picture of the
electronic structure of metals of the third period of the periodic table.
A SPECTROSCOPIC STUDY OF THE ELECTRONIC STRUCTURE OF METALLIC POTASSIUM AND CALCIUM

Introduction

In 1931 Houston (1) pointed out the possibility of studying the energy distribution of electrons in a solid by means of optical spectroscopy. No significant work was carried out along these lines until 1934 when O'Bryan and Skinner (2) set up a high-vacuum spectrograph for solid state studies in the wavelength region 50 to 500 A. From then until 1941 a complete study of the first two periods of the periodic table had been made, specifically lithium, beryllium, boron, carbon, sodium, magnesium, aluminum, silicon, phosphorous, and sulphur (3, 4, 5, 6). Other investigations have been made in the soft X-ray region (5 to 50A) but these are in general inferior as will be explained later.

One of the chief difficulties in the study of the emission bands of solids is the long exposure time necessary with photographic plates; thus, for a typical exposure, fifteen minutes to an hour may elapse, during which time the surface of the solid may become seriously altered by contamination. Although this may be alleviated by periodic evaporation of the specimen onto the target, it is never certain that the spectrum of the pure solid is obtained. This problem is enhanced in the particular region of the spectrum studied since the absorption coefficient for radiation of these wavelengths is exceedingly high. In addition to the contamination difficulty there is also the inconvenience of evacuating and reopening the large tank containing the spectrograph in order to change photographic plates. To overcome these difficulties Piore (7) suggested the use of a photomultiplier detection system to replace the photographic plate method. The advantages are immediately apparent. First, the radiated intensity as a function of wavelength can be measured directly with external pulse counting circuits, as the photomultiplier is mechanically driven along the focusing region of the spectrograph by an external mechanical drive. Second, the sensitivity of the photomultiplier not only reduces the observation time to roughly five minutes but also the necessary power input to the target by a ratio of 100 to 1. Generally these two effects mean a much lower contamination and also present the possibility of studying the gradual deterioration of the specimen by observing the intensity of radiation as a function of time as well as wavelength. Piore, Gyorgy, Kingston, and Harvey (8) have made this modification on the original spectrograph used by O'Bryan and Skinner and it is this apparatus which has been used in the research to be described.

After successful reproduction of several of the curves of previous workers a study was commenced on the transition metals of the third period or iron group, scandium through nickel. During the preliminary investigations the author received in manuscript form a paper by Professor Skinner giving the results he had obtained for these metals in both the L and M emission bands. After examining the curves, which showed only broad spectral distributions with emission edges that were not well defined, and comparing them with those of the lighter metals, we decided to concentrate on the two metals.
preceding the transition group, potassium and calcium. The reasons were twofold. First, if Skinner's curves are representative then there must be a point in the periodic table where the emission bands of metals lose the characteristic sharp edge at the high energy side of the band. For example, aluminum, the last metal in the table before potassium, has an edge which is sharp within a few hundredths of an electron-volt. Second, upon investigation of the literature no experimental work is found on either potassium or calcium with the exception of the calcium L band on the following page. Skinner also attempted to photograph the M emission band of calcium but the background caused by his high bombarding potential was too high for satisfactory results. As will be pointed out in the results of our work, it is very probable that the contamination of the target was also serious. It is hoped when a complete program of study on the transition metals is carried out, utilizing the newer techniques, more highly resolved bands may be observed. The reported curves for potassium and calcium and the additional advantage of a much lower bombarding potential and higher sensitivity than that used by Skinner are all encouraging signs.

This report will be composed of two main parts. The first two sections attempt to give a fairly complete description of the band emission process and its relation to the electronic structure and also a thorough description of the new spectrograph and its operation. The last two sections are devoted to the presentation of the results obtained for potassium and calcium with a discussion of their theoretical and experimental significance.

Part of the value of any technical report is its presentation of the results obtained by other workers in the field. For this reason there is included at the end of this work a complete bibliography of all the significant papers on electron energy bands, both theoretical and experimental. In addition there are also included those papers which are valuable in their contribution to the techniques of high-vacuum spectroscopy, and the experimental details which were necessary for the completion of this work.

I. The Band Emission Process and its Relation to the Electronic Structure

The Emission Process

In these studies the electron distribution in a conduction band is determined by observing the radiation caused by transitions of the valence electrons into a sharp atomic level of an individual atom. Experimentally this means that a sharp level of the atom is ionized, in this case, by electron bombardment, and the rate of production of photons determined as a function of the photon energy. Before discussing the exact relationship of the electron energy distribution to the observed radiation intensities it is necessary to investigate the experimental process more thoroughly.

In the spectrographic studies there are two major considerations affecting the validity of the data. Since we are bombarding and observing radiation from the surface of the specimen we must be sure that the electron transitions occur far enough below
this surface to represent the state of the electrons in a continuous medium. We must also consider the absorption of the photons leaving the metal to be sure that the observed radiation comes from the bulk of the material and not just from the surface. If we make the assumption that the surface effects are negligible at depths of about ten or more atomic diameters, we may then specify that the bombarding electrons should penetrate to this depth or deeper and that the radiation should be absorbed only slightly over a path of length 50 Å, since the interatomic spacing in potassium and calcium, for example, is about 5 Å. In the case of electron penetration there is little data for the bombarding potentials used. Compton and Allison (9) describe work done for energies of 10,000 volts and higher, but since extremely thin foils (of the order of 100 Å) would be necessary for penetration studies at 100 to 500 volts, little or no experimental work has been done along these lines. It might be possible to extrapolate the known results for high-energy electrons but it is not obvious that such extensions of the experimental data would be reliable. It has therefore been necessary to estimate the importance of the electron penetration by studying the data we can obtain from the spectrographic studies. Section III contains a discussion of the electron penetration based on results determined by taking emission-band curves at several values of bombardment potential. In general, the depth of penetration seems sufficient if this voltage is 300 volts or greater. As for the absorption of the radiated photons as they leave the metal, a substantial amount of information may be obtained by studying the data taken on absorption edges by Skinner and Johnston (10) and Johnston (11). If we define the absorption coefficient by the equation

\[ I = I_0 e^{-\mu t} \]

where \( \mu \) is the linear absorption coefficient and \( t \) is the thickness of the metal then we obtain the values given in Table 1. Here the maximum and minimum values of the coefficient have been taken at the absorption edge corresponding to the emission edge we would observe in the same spectral region. The values given are only approximate as they are averaged from data for samples of varying thickness and the separate values

<table>
<thead>
<tr>
<th>Metal</th>
<th>( \mu (\text{Å}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>3.0 - 4.0 \times 10^{-4}</td>
</tr>
<tr>
<td>Mg</td>
<td>3.8 - 5.2 \times 10^{-4}</td>
</tr>
<tr>
<td>Al</td>
<td>8.0 - 11.3 \times 10^{-4}</td>
</tr>
<tr>
<td>Cu</td>
<td>8.3 - 9.3 \times 10^{-4}</td>
</tr>
<tr>
<td>Zn</td>
<td>27.0 - 29.0 \times 10^{-4}</td>
</tr>
<tr>
<td>Ni</td>
<td>22.0 - 46.0 \times 10^{-4}</td>
</tr>
</tbody>
</table>
were not always in agreement. At any rate it may be seen that radiation absorption
would not be serious for any of the metals listed since it does not become substantial
until the thickness is 1000 A or greater. It seems justified to assume the same condi-
tions for potassium and calcium.

In the above discussion it has been tacitly assumed that the metal studied had a pure
uncontaminated surface. This, of course, is far from the case since even by evapora-
ting the metal onto the target at a pressure of $10^{-6}$ mm Hg a pure surface cannot be
maintained. The above arguments still hold if the estimated thickness of the contami-
nating layer is less than the 50 odd Angstroms established as necessary for a valid
study of the pure metal. The contamination effect varies markedly from one metal to
another and will be discussed in Sec. III.

Relation of Emission Curve to Electron Energy Distribution

The sharp atomic levels which might be used as the final state for transitions from
the conduction band of potassium and calcium are the 3s and 3p states, since both tran-
sitions would produce wavelengths of the order of 300 to 600 A. Unfortunately the 3s
transition is not observable spectroscopically because of an intermediate transition from
the 3p to the 3s level which occurs with much higher probability than the valence band
to 3s transition. This obstacle occurs throughout all the possible valence-band-to-sharp-
level transitions with the exception of those with a final state, 1s. This transition is at
much shorter wavelengths than are satisfactory for band emission curves, except for the
metals of the first period, and we are generally limited to transitions involving a final
p state only.

As a consequence of the type transition we must study, the band-emission curves
give information about the s-type and d-type electrons only. Specifically, referring to
the free atom, the possible transitions would be from the 4s and the 3d levels, the tran-
sition 4p to 3p being forbidden. Now in the solid the conduction electrons no longer can
be described by a simple s, p, or d wave function but must be considered to have wave
functions which are combinations of all of these types. Alternatively we may think of the
electrons in a small energy range as composed of three or more kinds, s electrons, p
electrons, etc. Using the former concept the radiation intensity may be written as fol-
lows

$$I \alpha \nu^2 (a_s^2 + a_d^2) \frac{dN}{dE}$$

where $dN/dE$ is the number of electrons per unit energy range. Here $I$ represents the
number of photons per unit time, thus explaining the $\nu^2$ term in the transition probability
rather than the more familiar $\nu^3$ term. The factor $a_s$ is of the order of unity and $a_s$ and
$a_d$ are defined by

$$\psi = a_s \psi_{4s} + a_p \psi_{4p} + a_d \psi_{3d} + \ldots$$

$$a_s^2 + a_p^2 + a_d^2 + \ldots = 1$$
where \( \psi \) is the wave function of the electron for a particular energy and \( \psi_{4s}, \psi_{4p}, \) etc. are the free atomic wave functions. The specific behavior of the wave functions for potassium and calcium will be left to Sec. IV, where the electronic structure of these metals is discussed in the light of the results.

In order to analyze the curves one more modification must be made, which is of spectroscopic origin. This is that the photomultiplier observes equal increments of wavelength rather than energy as determined by the width of the image slit. The intensity expression must therefore be modified so that it now reads

\[
I \propto \frac{E^4}{2} \left( a_s^2 + a_p^2 \right) \frac{dN}{dE}
\]

since

\[
d\nu = -\nu^2 \, d\lambda \quad \text{and} \quad E = h\nu
\]

The above treatment is based upon the work of Mott, Jones, and Skinner (12) who also give an approximate treatment of the behavior of the wave functions throughout the band. They have treated the case of metals such as Be and Mg where the lowest band is derived from an s function and the second band overlaps and is derived from a p state. Specifically they find that \( a_s \) is unity at the bottom of the lower band and decreases to zero at the top of this band. At the bottom of the second band \( a_s \) is again unity even though the band is derived from a p state, and again \( a_s \) decreases to zero with a corresponding increase in \( a_p \). The metals potassium and calcium are more complicated in this respect since the first band, derived from the 4s state, could overlap with two bands, those from the 3d and the 4p. It is not immediately obvious which band would come at the lower energy, although the behavior of the transition metals and calculations by Manning and Krutter (13) indicate that the 3d band is more probable. Even if this is the case there is still the uncertainty as to whether the electrons in the bottom of this 3d band have d-type wave functions or some other type, specifically s or p. A complete investigation of this problem is left to Sec. IV.

II. Experimental Equipment

High-Vacuum Spectrograph

Since the widths of the emission bands to be studied are of the order of a few electron volts it is advantageous to study them in a region of the spectrum where the electron transition from the band to a sharp level has an energy less than a hundred volts. In this way the width of the band in Angstrom units will be several percent of the average wavelength, thus enabling a resolution of the order of 0.01 to 0.1 volts, since spectroscopic resolutions are generally better than one part in ten thousand. Now the lowest energy transitions from the conduction band to a sharp level in a metal range from 15 to 100 volts so that they are the limiting factor in determining the electron transition which gives the highest band resolution. This corresponds to wavelengths which range from
100 A to 800 A, which radiation lies in a region of high optical absorption and thus necessitates the evacuation of the whole spectrograph system.

As mentioned previously the spectrograph used in this work is the same as that used by O'Bryan and Skinner except that the recording system is now a photomultiplier rather than a photographic plate. Where previous workers have taken a direct photograph of the spectrum and traced the curve with a microphotometer it is now possible to obtain a direct reading of intensity as a function of wavelength by scanning the focal region with a photosensitive electron multiplier. Figure 1 is the main platform of the spectrograph with the grating at the left and the photosensitive detector at the right. The grating has a radius of curvature of 2.00 meters and 30,000 lines per inch ruled on glass. Both this grating spacing and the critical angle of reflection for light of these wavelengths require that a grazing-incidence mounting be used; in this equipment the grazing angle is 5.4°. By the Rowland construction the diffracted radiation will focus on a circle of radius 1.0 meter, tangent to the centerpoint of the grating and passing through the object slit. The object slit cannot be seen in the photograph since it is to the left of the grating in the specimen chamber (See Fig. 4). The radiation transmitted by this slit enters the spectrograph through the small rectangular hole in the scattering shield at the extreme left of the spectrograph. The additional shields serve to control the effective width of the grating, prevent light from going directly to the photomultiplier from the object slit, and trap the zero-order reflection. The platform supporting all the equipment was especially cast and machined for use with the photomultiplier. It is cadmium plated cast iron and has a dovetail groove whose large radius is machined to 1.0 meters with a tolerance of 0.001 inch. The driving mechanism is built from a standard machinist’s lathe lead screw and is controlled externally. The large circular hole behind the lead screw coupling is the pumping port and leads to a liquid air trap, water cooled baffle and six-inch three-stage oil diffusion pump manufactured by Distillation Products, Inc. An external view of these units may be seen in Fig. 3. The spectrograph is enclosed in a cylindrical brass tank also shown in the latter figure.

Figure 2 is another view of the photomultiplier, showing the image slit which is usually adjusted to 0.2 to 1.0 mm width depending upon the resolution required. The electrical connections to the photomultiplier are made through phosphor bronze wipers which slide along the copper bus bars as the mounting is moved along the Rowland circle. The spectrograph was first focused by means of photographic plates in conjunction
with a high-vacuum spark (14, 15) and rough calibration points determined for several wavelengths. The photomultiplier was then installed and the slit accurately placed on the Rowland circle. For a final calibration, that is, wavelength as a function of lead screw rotation, we have used the sharp edges of the aluminum, magnesium and sodium bands determined by O'Bryan and Skinner (2). The Be-Cu photomultiplier has been described by Allen (16, 17) and has been used for optical detection by Moorish, Williams, and Darby (18). A special advantage of this type photomultiplier is the high work function of the Be-Cu surface, which is approximately 4.2 volts. This means that it is insensitive to light of wavelength greater than 3000 Å and thus is not affected by any visible light which might enter the spectrograph. The instrumentation for this unit is discussed in the section on the specimen chamber.

The Specimen Chamber

The specimen chamber, containing the target, electron gun, and object slit is seen at the right of Fig. 3. Also included in this chamber is an evaporating furnace for placing a pure coat of the sample metal on the target. The evacuating system for this part of the equipment is composed of a mechanical pump, a single-stage glass booster
pump, and a three-stage metal diffusion pump; the last two units may be seen in the figure. To prevent oil particles from entering the chamber and to further improve the vacuum there is also a water-cooled baffle and liquid air trap between the pumps and the chamber. Since the spectrograph is continually evacuated, and it is necessary to open the specimen chamber for each experimental run, the two systems are separated by a sliding-type high-vacuum valve. Part of the valve mechanism is shown in Fig. 4 to the right of the picture. While in operation the spectrograph is connected to the chamber by the slit only, thus enabling a vacuum of better than $10^{-6}$ mm Hg to be maintained in the chamber despite the value of $10^{-5}$ mm in the spectrograph.

Figure 4, a view of the chamber with the liquid-air trap removed, shows the orientation and mounting of the elements in the specimen chamber. At the center is the target, a hollow cylinder of oxygen-free copper with a flat surface in the direction of the slit and electron gun. At the upper left is the electron gun, and directly below it, the evaporating furnace. The distance from the center of the plane surface of the target to the object slit is approximately 1.5 inches. The target is rotated in its mounting so that electrons from the gun strike the flat surface at almost normal incidence, and radiation to the slit leaves the target at a grazing angle of approximately 5°. This has the advantage of presenting a large area of the target to the slit and also takes account of the fact that radiation of this type usually has a maximum of intensity at grazing angles with the surface. In addition, the normal incidence of the electron beam places less severe limits on its collimation and assures maximum penetration for any given bombardment potential. The electron gun is aimed so that no material evaporated from the cathode may deposit on the target. This is accomplished by bending the electron beam slightly as it leaves the gun. The horizontal tube at the left of the chamber (see also Fig. 3) contains a mechanical coupling unit which may be used either for external adjustment of the slit width or for control of any mechanical process in the vacuum such as scraping of the target to obtain a clean surface. It was not necessary to use this coupling unit in the work described.

Figure 5 shows the target in more detail. The bellows arrangement at the top is
used to adjust the position of the target in a horizontal plane, since the alignment at such small grazing angles of radiation is quite critical. The target is operated at 300-500 volts with respect to the surrounding chamber which necessitates the glass section in the middle of the unit. Only one of the three leads shown was used in this work. The other two may be connected to a thermocouple on the target if this is necessary. In this work the target temperature was not critical and was known to be between 25° and 100°C since water placed inside the assembly for cooling purposes did not boil during any of the experimental runs.

During the preliminary work extraneous radiation was observed to be coming from the object slit. This was found to be photon emission from the steel slit jaws produced by stray electrons which had been reflected from the target. For this reason the electrical connections to the electron gun and target were changed so that the cathode of the gun was at the potential of the chamber. Originally the connections placed the target at the chamber potential.

The electron gun in Fig. 6 was designed to produce a narrow beam approximately 1 cm high on the target. Since the gun was to be operated at voltages of 500 volts and lower, yet producing currents of the order of 5 ma, it was necessary to choose a high perveance electrode structure of the Pierce type. The design considerations are discussed fully in Pierce (Ref. 19, Chs. VII and X). The final gun produced a beam 2-3 mm wide and about 1.5 cm high at the target. One of the newer developments utilized in this gun is the cathode, which is sintered molybdenum and thorium oxide. Since it is necessary to open the system frequently, it is essential that the cathode be stable in air. For this reason tungsten was first chosen as the cathode material; however, the heat generated and the short life of the filament made necessary the choice of something with a lower operating temperature but still stable in air. Thoriated tungsten was considered, but since it requires reactivation after each exposure to the atmosphere, material was used similar to that recently developed by Goldberg (20). This material, 75 percent molybdenum and 25 percent thoria, is extremely stable and operates at approximately 1600°C as compared with tungsten at 2200-2400°C. The electrode design and power supply for this gun are described in the Appendix.
Dushman (21) has given the physical constants describing the evaporation process, and O'Bryan (22) has described the experimental techniques necessary for numerous metals. The required temperatures as determined from Dushman, for the evaporation of a coat about 1000 A thick onto the target from the cup shown in Fig. 7 are given in Table 2.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Temperature for Evaporation (°C)</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>207</td>
<td>64</td>
</tr>
<tr>
<td>Ca</td>
<td>605</td>
<td>810</td>
</tr>
<tr>
<td>Na</td>
<td>291</td>
<td>98</td>
</tr>
<tr>
<td>Mg</td>
<td>443</td>
<td>651</td>
</tr>
<tr>
<td>Al</td>
<td>996</td>
<td>660</td>
</tr>
</tbody>
</table>

This tabulation assumes that the evaporation should take place in a period of one minute. Note that calcium, as well as magnesium, both sublime from the solid state; this effect will be discussed in the experimental work on calcium. The furnace shown in the figure was designed for the evaporation of the above metals. All the metal parts are made of tantalum with the exception of two strips of molybdenum-thoria cathode material mounted inside the cylindrical shield, which serve to heat the tantalum cup by radiation and electron bombardment. The cup-holding electrode is insulated from the cathodes and the tantalum cylinder; the cup itself, spun from 0.015-inch tantalum, is one-fourth inch long and one-eighth inch inside diameter. For potassium, calcium, sodium and magnesium the heat radiated from the cathodes is sufficient to evaporate the metal; however, aluminum requires the additional heat obtained by placing 300 rms volts between the cup and the cathodes. The average electron bombardment current required is from 30 to 60 ma. This unit has been satisfactory for the above metals; however, metals with higher evaporating temperatures show poor results. A run with iron in the cup resulted in an alloying of the tantalum and iron with resultant erosion of the cup before any of the sample could be evaporated onto the target.

All metal-to-metal joints in the specimen chamber, as well as throughout the spectrograph, have been made vacuum-tight by means of one-eighth inch diameter "O" ring neoprene gaskets lubricated with high-vacuum grease. For rotating or sliding joints the Duplex V-2 Klozure manufactured by the Garlock Packing Company makes an excellent vacuum seal. These units are designed as oil retaining packings for rotating shafts but if
cleaned thoroughly with a volatile solvent and treated with high-vacuum grease they may be seated against an "O" ring gasket or soldered in place to make a tight seal.

General Instrumentation

The vacuum instrumentation consists of National Research Company thermocouple gauges for measuring the fore-vacuum (two of these may be seen projecting from the liquid air trap assemblies in Fig. 3) and standard ionization gauges, one on the specimen chamber (projecting below it in the figure) and one on the end of the cylinder containing the spectrograph. The measuring equipment is mounted below the spectrograph platform on the opposite side of the equipment from the rack panel.

At the left of the main body of the spectrograph may be seen the crank which rotates the lead screw on the spectrograph platform. This is coupled to an Esterline-Angus 0- to 1-ma recording meter. In front of the recording unit is a disengaging clutch so that the meter may be disconnected from the lead screw when necessary. The rotation of the driving crank is recorded by a small counter mounted on the head of the spectrograph and the recording meter is directly coupled to the counting-rate meter.

At the top of the rack panel is the electron gun power supply, below it a panel holding the voltage regulator tubes, and below them the counting-rate meter, the photomultiplier voltage supply, and the main pulse amplifier. To the left of the rack panel is an oscilloscope for observing the pulses produced by the photomultiplier. The bus bars inside the spectrograph are connected to three glass lead-through electrodes beneath the platform, which are in turn connected to the photomultiplier voltage supply and the pulse preamplifier. The copper box at the right of the large diffusion pump contains the preamplifier and this is connected by a cable to the main pulse amplifier in the rack panel. The amplifier system used is the model 500 described in Elmore and Sands (23). Sufficient gain, enough to produce 50-volt pulses at the counting-rate meter, was obtained with the main amplifier gain control in the number 2 position. The photomultiplier voltage was maintained at 4500 d-c volts, which, for the 16-stage multiplier, is approximately 300 volts per stage.

When the photomultiplier was first chosen as a detector for the radiation studied, there arose the question as to whether the radiation should be measured by metering the d-c output current from the unit or counting the number of pulses per unit time. Since measurements of small values of direct current require a sensitive galvanometer and usually a d-c amplifier, both of which are difficult to operate, the latter method was chosen. The amplifiers described above supply pulses of approximately 1 μsec duration to the counting-rate meter which is described in the Appendix. When using this type of meter it is important to realize that the accuracy of the reading is a direct function of the time of observation. Since the photons arrive at the detector in a time sequence known to be a Poisson distribution, it is possible to relate the statistical fluctuation of the counting rate to the time of observation of a specific average counting rate. Physically this means that if the average value of the counting rate is measured, then the
fluctuations of the meter reading about this average are greater as the response time is decreased. Table 3 gives the response time as a function of the full-scale counting rate of the meter for several values of rms deviation of the meter reading.

Table 3
Response Time of Counting-Rate Meter

<table>
<thead>
<tr>
<th>Counting Rate Full Scale (sec(^{-1}))</th>
<th>Response Time in Seconds for Deviations of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 percent</td>
</tr>
<tr>
<td>10</td>
<td>1760</td>
</tr>
<tr>
<td>20</td>
<td>880</td>
</tr>
<tr>
<td>50</td>
<td>350</td>
</tr>
<tr>
<td>100</td>
<td>176</td>
</tr>
<tr>
<td>200</td>
<td>88</td>
</tr>
<tr>
<td>500</td>
<td>35</td>
</tr>
<tr>
<td>1000</td>
<td>18</td>
</tr>
</tbody>
</table>

The response time is defined as the time required for the meter to attain a reading which is within \(p\Delta n\) of the actual value where \(p\) is the percent deviation at half-scale as used in the table and \(\Delta n\) is the change in the average counting rate. As an example if the average counting rate changes from 200 to 400 counts per second on the 500 scale, and the damping of the instrument is set at 2 percent deviation, then the meter will require 8.8 seconds to reach a value within \((0.02)(200)\) or 4 counts per second of the value 400. Note that the rms deviation of the meter reading about the value 400 will be 2 percent of 250 or 5 counts per second. This inaccuracy in the reading is not an attribute of the instrumentation but is a result of an uncertainty principle similar to the quantum-mechanical analog. This law, in effect, states that for a random occurrence of events in the time domain, the square of the fractional error in the measurement of rate of occurrence, multiplied by the observation time is inversely proportional to the average rate. This law will have a definite effect upon the accuracy of the curves to be presented, for it means that the spectrum must be scanned at a maximum speed determined by the required accuracy of the meter reading. Theoretically, for highest accuracy the counting-rate meter should be set to the lowest value of deviation and the spectrum traversed in a time long with respect to the response time. Unfortunately a compromise has to be attained in this process since the sample slowly becomes contaminated, thus placing an upper limit upon the time of observation. The above discussion is based upon the analysis of Schiff and Evans (24).

III. The Emission Bands of Potassium and Calcium

General Experimental Details

After a preliminary investigation to determine the approximate position of the bands
to be studied the experimental procedure is as follows. The tantalum evaporating cup is filled with a pure sample of the metal to be studied and the evaporating furnace placed in the specimen chamber. The target, chemically cleaned and degreased, is placed in position so that the flat surface is at a grazing angle of a few degrees with a line from the target to the slit. The actual grazing angle was determined by placing a light source in the spectrograph and observing the shadow of the slit on the target. After this determination the proper position was fixed by index marks on the top of the specimen chamber and the target assembly. The specimen chamber is then evacuated to better than $10^{-6}$ mm Hg and the electron gun turned on to outgas the electrodes and the target. The photomultiplier is meanwhile placed at a position on the Rowland circle corresponding to maximum intensity of the emission band and the target is adjusted in a horizontal plane until the photomultiplier output is a maximum. After the elements have been sufficiently outgassed the evaporating furnace is turned on and the applied voltage gradually increased. This is of necessity a slow process since this unit must be heated slowly to drive off the absorbed gases from the metal parts. As the tantalum cup becomes hot enough to evaporate the metal the photon counting rate gradually increases and when this rate reaches a steady maximum the position of the detector is changed to correspond to a wavelength slightly shorter than that of the high-energy edge of the emission band. Depending upon the metal studied the evaporating furnace is either left running or shut off and the emission-band curve taken by slowly driving the photodetector along the Rowland circle. The clutch mechanism between the recording meter and the lead screw drive may be engaged and disengaged as necessary so that the curve may be observed repeatedly.

Since it is desirable to record the curve in as short a time as possible, whereas the counting-rate meter has a finite response time, the speed of traversal must be adjusted to assure an accurate record of the curve. This is especially important at the high-energy edge of the band where the intensity rises abruptly as the band is approached from shorter wavelengths. By varying the speed of traversal to correspond with the rate of change of counting rate we have been able to obtain a satisfactory curve in approximately three minutes. The contamination will be discussed separately for potassium and calcium but in either case it was found necessary to record the data in this time in order to be assured of a representative curve. Since the counting rate averaged about 200-500 counts per second, the accuracy had to be limited to 1.5 percent. That is, the rms deviation of the meter reading was 1.5 percent of the full-scale meter deflection. This corresponds to response times of 15 to 40 seconds. The fluctuation in the meter reading actually had the advantage of overcoming the frictional drag of the recording pen. If the meter output was perfectly steady the pen often lagged behind the reading unless the recording meter was gently tapped.

During all the runs taken the object slit was set at 0.25 mm width and the image slit at 1.0 mm. This corresponds to a resolution of approximately 5 A in the region studied. The calibration of the spectrograph was made at this same slit setting so that the
wavelength of the emission edges should be accurate within 1 or 2 Å, if this value is measured at 50 percent of the maximum value of intensity at the emission edge. The calibrating edge was that of aluminum in the third and fourth order, corresponding to wavelengths of 510 and 680 Å.

The target temperature was somewhere between 25°C and 100°C since during all the experiments the copper target was filled with tap water. Since the input power to the target was of the order of 1.5 watts there was not enough heat to cause boiling so an accurate value of temperature was not obtained. It is important to realize that the temperature of the body of the target does not correspond to the temperature of the active surface. Actually the metal at the surface could theoretically be hot enough to melt. The only investigation of this problem has been made by Skinner (4), who made an accurate study of the width of the emission edge as a function of target temperature. By relating this width to the Fermi distribution theoretical width he concluded that the temperature of the active surface was close to the over-all temperature. Since Skinner's input power to the target was much higher than ours it is reasonable to assume that the temperature of the sample in our work was within a few degrees of the target temperature.

In the work to be described the bombardment potential was kept as low as possible to eliminate the high background which might be produced by excitation of higher energy states, specifically those in the 2s and 2p shells of the atom. As has been observed by other workers the conduction band-to-3s transition is not observed in these metals because of the high probability of an intermediate 3p-to-3s transition.

The Potassium Band

The observed band for potassium is shown in Fig. 8. The sample was reagent grade metal packed in kerosene. For evaporation purposes the metal was rinsed in toluene and cut in small pieces before being placed in the evaporating cup. In this way the surface of the potassium was not exposed to air at any time, since it was protected by the solvent until the evacuation process caused the toluene to evaporate, leaving the bare metal exposed only at a high vacuum. A total of a dozen curves was taken, with several values of bombarding voltage and varying evaporation cycles. The curve shown was taken several minutes after the metal had been evaporated onto the target and the furnace shut off. It is representative of all the curves taken within a few minutes of the evaporation. An interesting point is that at voltages of
300 volts and higher the curves reproduced well; however, if the voltage is decreased to 150 volts, a sharp peak no longer appears at the high-energy end of the band. The same results occur if the curve is taken ten or more minutes after the evaporation is stopped. This is interpreted as meaning that the penetration of the electrons is not sufficient at 150 volts to produce radiation representative of the pure bulk metal. In all probability the loss of the high-energy peak is a result of oxide forming on the surface of the specimen. The fact that this effect is observed at higher voltages if the target has had time to deteriorate would indicate a slow penetration of the contaminating atoms into the interior of the metal.

The Calcium Band

Much more difficulty was experienced in obtaining the calcium emission band as a result of the contamination of the sample. There are two reasons for this. First, as shown in Table 2, calcium does not melt before it reaches a temperature sufficient to evaporate metal onto the target; this means that an oxidized layer may easily form on the surface of the solid calcium, preventing the pure metal atoms from leaving the material. Second, calcium does not form a protective coat as do metals such as potassium and aluminum; instead of a thin layer of oxide forming on the surface and protecting the metal, the oxygen atoms seem to penetrate into the bulk of the metal in a matter of seconds. Because of this the curve shown in Fig. 9, one of approximately 30 curves, had to be taken with the evaporating furnace still running. The calcium on the target was thus being replenished continually with pure metal. To assure maximum purity the metal chips were first ground by means of a mortar and pestle to expose as much fresh surface as possible before being evaporated. Even with these precautions it was not possible to take more than one accurate curve for each filling of the evaporating cup. A second plot taken with the furnace still in operation produced a curve of the same general shape, but decreased in intensity by a factor of 50 to 75 percent. The behavior of the curve at the emission edge was checked carefully by starting the record at the peak of the edge, thus starting the curve only a few seconds from the time a satisfactory coat was on the target. In this way it was definitely established that the rising intensity with increasing wavelength was an accurate observation. If the evaporating furnace is shut off before the curve is started the result is a band-emission curve which looks like a decreasing exponential, since the decrease in intensity as a function of time because of contamination completely masks the true shape of the
emission band. This same effect may be observed if the photomultiplier is set at the peak of the emission band and the intensity of radiation as a function of time is studied at the one particular wavelength. The time required for the intensity to drop to one-half of its maximum value is about 30 seconds for calcium while it is closer to ten minutes for potassium. On the whole this seems to indicate that the behavior of metallic surfaces is not simply related to the activity of the free atom. These effects should certainly be considered in any future work on the band emission of solids.

A curve of a contaminated sample of calcium is shown in Fig. 10. Note how the intensity has fallen to almost half its value and the maximum has shifted to longer wavelengths. This particular curve was run ten minutes after the evaporating furnace had been turned on. Although the coat was being slowly replenished, oxidation of the metal in the cup and on the target caused a high percentage of impurities in the target. As was observed in potassium it was impossible to obtain any representative curve at all at 150 volts bombardment potential, even though the record was started at the beginning of the evaporation cycle.

IV. Discussion and Interpretation of the Experimental Data

Theoretical Considerations

The curves in the previous section may be modified to represent the density, $dN/dE$, of the s-type and d-type electrons according to the method outlined in Sec. I. The background is first subtracted from the emission curve and then the resultant distribution replotted as a function of quantum energy, with the modification by the factor $E^4$ included. The final curve then represents the density of electrons weighted according to their particular wave function. For example, if the wave function of electrons at some specific point in the band is composed of s and p functions, the resultant plot will give only the contribution of the s part of the function. For simplicity the emission edge has been sharpened to correspond to the shape of the theoretical edge obtained from the Fermi statistics at the temperature used. This is not a strictly accurate interpretation since it cannot be said definitely that the edge would be this sharp if the spectrograph were operated at its limiting resolution. The width of the edge, however, as measured on the experimental curves corresponds to the calculated resolution of the spectrograph and it is therefore assumed that the above alteration is reasonable. The energy at the emission edge was determined by a direct comparison with higher orders of the
aluminum edge obtained by Skinner. The cross calibration was made at the midpoint of
the experimental edge.

Before presenting the modified curves it is necessary to review the theoretical
treatments of the electron band structure. These are composed of three types: the
Sommerfeld free-electron approximation, the Bloch perturbation method, and the cellular
method of Wigner and Seitz as modified by Slater and others. A complete survey of
papers on these methods is given in the bibliography.

The Sommerfeld method consists of treating the electrons as if they moved in a
potential well with constant potential energy. The resultant distribution of the electrons
in energy space is thus the familiar Fermi-Dirac distribution as applied to particles
whose energy is given by

\[ E = E_o + \frac{p^2}{2m} \]

The density of electrons is then

\[ \frac{dN}{dE} = \frac{4\pi V(2m)^{\frac{3}{2}}}{\hbar^3} \frac{1}{(E - E_o)^{\frac{1}{2}}} F(E - E_o) \]

where \( F(E - E_o) \) is the Fermi-Dirac distribution factor

\[ F(E - E_o) = \frac{1}{(E - E_o) - \epsilon_0' + \frac{kT}{\epsilon_0}} - 1 \]

The width of the band will then be

\[ \epsilon_0' = \frac{\hbar^2}{2m} \left( \frac{3N}{8\pi V} \right)^{\frac{2}{3}} \]

where \( N \) is the total number of valence electrons in a crystal of volume \( V \). This approximation of constant potential only applies to an ideal metal; however, the energy may be written as

\[ E = E_o + \frac{\hbar^2 k^2}{2m^*} \]

where \( k \) is the quantum mechanical wave vector. The free electron distribution may then be applied, where \( m^* \) is now an effective mass not necessarily equal to the true electron mass. This approximation holds only when the energy can be written accurately in the above form, thus limiting it to cases where the band is only about half full or specifically to monovalent metals, since at the top of the Brillouin zone the parabolic approximation of \( E \) against \( k \) may be shown to be no longer valid.

The Bloch perturbation method of obtaining the wave functions and the energy as a
function of \( k \) consists of taking the electron wave function as

\[
\psi_{nk} = \sum_m a_{mk} \sum_g e^{ikr_g} \psi_m(\bar{r} - \bar{r}_g)
\]

where \( r_g \) is the radius vector from the origin to the \( g^{th} \) nucleus. The \( \psi_m \)'s are the free atomic wave functions \( \psi_s, \psi_p, \) etc. The energy, as a function of \( k \), and the coefficients of the free atomic wave functions are then determined by solving the secular determinant obtained by use of the Hamiltonian

\[
H = - \left( \frac{\hbar^2}{8\pi^2 m} \right) \nabla^2 + \sum_g V(\bar{r} - \bar{r}_g)
\]

In most calculations of this type the interactions of nearest neighbors only are considered, that is, the only off-diagonal elements used in the determinant are those involving \( r_g \)'s connecting nearest neighbors. Any higher-order terms produce calculations of extreme complexity.

The final method, that of Wigner and Seitz, as modified by Slater, consists of setting up a wave function for the electron composed of \( s, p \) and \( d \) functions which satisfy the boundary conditions on the faces of a unit cell about each ion. The boundary conditions are determined by the Bloch modulation factor and the wave functions are no longer the free atomic functions but those obtained by numerical integration of the radial-dependent Schrödinger equation. The absolute values and slopes of these functions must satisfactorily meet the prescribed boundary conditions. For example the lowest energy wave function is obtained by numerically integrating the Schrödinger equation containing the ion-core potential so that the slope of the \( s \) function is zero at the boundary of the cell. The major difference between this and the preceding method is the treatment of nearest neighbor interactions. In the Bloch perturbation scheme the potential seen by the electron is that produced by the ion cores of all the atoms in the lattice. In the cellular method, however, the potential of the ion in one cell only is considered and neighboring ions are considered to contribute no potential field as a result of the neutralizing effect of the electrons in each cell. Actually the true potential acting upon an electron probably lies somewhere between these two extremes. In addition to the different potential seen by the electron there also seems to be a better treatment of exchange interactions in the Bloch approximation.

Electronic Structure of Potassium

Since potassium is a monovalent metal, it is quite well described by the Sommerfeld free-electron approximation. Figure 11 shows the distribution of electrons as a function of energy as determined from the experimental curves. The dotted line at the low energy end of the curve shows the probable position of the bottom of the Brillouin zone.
The low energy "tail" on the curve is a common characteristic of emission bands and has been discussed by Skinner (4) and Seitz (25). There are several explanations for the effect. Skinner concludes that it is a result of Auger transitions during the radiative process while Seitz attributes it to either contamination or the vestiges of excited states formed below the band. A detailed analysis applied to sodium is given by Landsberg (26).

In this curve and the curve for calcium a parabola has been fitted to the bottom of the band since it is known that electrons in this region behave according to the free electron theory. The position of the estimated limit of the band cannot be determined accurately because of this phenomenon, but a reasonable value of the bandwidth is $1.9 \pm 0.2$ electron volts. It is of interest to note that the Sommerfeld approximation gives 2.1 volts for this value, while a Wigner-Seitz calculation of the effective mass of the electrons at the bottom of the zone gives a bandwidth of 3.6 volts (27). Evidently the wave functions of the electrons in the potassium band are predominantly of the s-type, since the overall curve is a good representation of the parabolic distribution which would be expected in this case. The ordinate of the curve gives the value of the energy of transition when an electron falls from the valence band into an ionized 3p state. Additional information about the electronic structure may be obtained if this transition energy is compared with that corresponding to the equivalent free atomic transition $3p^5 4s$ to $3p^6$. This will be discussed in the Conclusion.

Electronic Structure of Calcium

The calcium conduction band shows a shape much different than the free electron theory would predict. Figure 12 indicates that the first Brillouin zone is nearly filled,
since the density of states falls off well before the high-energy edge. As was discussed in the first section, the second zone must necessarily overlap with the first since the metal is a conductor; however there is an uncertainty as to the wave functions at the bottom of this excited band. There is certainly no definite indication of an overlapping curve such as may be seen in Fig. 13, taken from data obtained for aluminum. Even though calcium has two valence electrons, compared with three for aluminum, Skinner's curves (4) for magnesium indicate that even in the divalent case an overlap should be observed. There are two possible explanations for the lack of structure in the calcium case. First, it is possible that the wave functions at the bottom of the second band are p-type, therefore not observable in a transition to the 3p state; or second, the excited band rises so slowly that it would not produce any observable inflection in the curve. Manning and Krutter's calculations (13) indicate a d band as the overlapping zone; however, examination of their predicted curve in Fig. 14 shows that the calculations cannot be too sound since the bandwidths are in very poor agreement. The observed bandwidth is 3.0 ± 0.2 volts, Manning and Krutter's value, 5.0 volts and the free-electron determination, 4.3 volts. It is not possible to determine from the above authors' calculations whether the electrons in the bottom of the d band are s-, p-, or d-type. If the band is as sharp as their calculations would indicate then p-type functions would be expected since a sharp rise is not visible in the experimental
curve; however, there is the possibility that an overlap into the 4p-derived band exists, in which case it would most likely be fairly broad and would therefore not be obvious in the curves. The peak of the density curve does not necessarily correspond to the maximum number of electrons per unit energy range since, as discussed in Sec. I, there is every indication that the electron wave function changes from s to either p or d as the eigenvalue increases in magnitude. Nevertheless it may certainly be stated that the degeneracy at the top of the band is as high if not higher than the observed curve indicates contrary to the theory. A survey of the literature indicates that there are no data on the Hall coefficient for calcium. When such measurements are made, it should prove instructive to ascertain the relation of this coefficient to the filling of the first Brillouin zone. Since this zone is almost completely full it is highly probable that the coefficient would have the anomalous sign, that is, the negative mass effect in the quantum mechanical treatment would cause the current carriers to appear as positive charges.

The above observations point out the inadequacy of the present methods of calculation for the electronic structure of calcium. It would be interesting to attempt a Bloch perturbation calculation for calcium, since, as will be pointed out in the Conclusion, an over-all analysis of the emission bands of metals indicates that this method is perhaps superior to the cellular approach.

Conclusion

The experimental work described has definitely established the fact that the emission edges of the metals potassium and calcium are sharp as has been observed in aluminum and the preceding conductors in the periodic table. On the basis of these results it seems possible that the proposed work on the transition metals, which is to be carried out on the equipment described, will produce similar sharp edges. A study of the absorption coefficients of metals for radiation of the wavelengths used has shown that the important factor in determining the reliability of the observed band emission curves is the depth of penetration of the bombarding electrons. For the metals described in this report the necessary bombarding potential has been found to be 300 volts or higher. There is of course the possibility that the metals which have d band structure may have higher electron absorption, in which case the voltage should be raised to take this into account. A thorough study of electron penetrations at voltages of 100 to 1000

Fig. 14
Manning and Krutter's calculated distribution curve.
volts would be an extremely valuable addition to the literature, as well as further studies on photon absorption in the 100 to 800 Å range.

Another important result of the work is the observation that the chemical activity of a metal is not a decisive factor in determining its resistance to oxide contamination. Before intensive studies of the transition metals are taken up it seems advisable that the protective layer effect as observed in potassium should be investigated more thoroughly, probably by a survey of the metallurgical literature.

The use of the photomultiplier in place of photographic plates has added another variable to the experimental observations. This is the possibility of studying time-dependence of the radiation from the sample. The high sensitivity and the above effect suggest possible studies of surface effects in metals and nonconductors.

The experimental results for potassium and calcium are summarized in Table 4, and an over-all survey of the relation of the theory of the electronic structure to the experimental results is given in the following section.

Table 4
Summary of Experimental Results for Potassium and Calcium

<table>
<thead>
<tr>
<th></th>
<th>Bandwidth (ev)</th>
<th>Emission Edge Wavelength (Å)</th>
<th>Energy (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium</td>
<td>1.9 ± 0.2</td>
<td>675 ± 2</td>
<td>18.4 ± 0.1</td>
</tr>
<tr>
<td>Calcium</td>
<td>3.0 ± 0.2</td>
<td>500 ± 2</td>
<td>24.8 ± 0.1</td>
</tr>
</tbody>
</table>

Table 5 is a survey of the theoretical and experimental results obtained for the electronic structure of metals from lithium to zinc in the periodic table. The values of the observed bandwidth for titanium through zinc are taken from Skinner's curves shown in the Introduction and are not considered too reliable, since the emission edges are not at all sharp. The free-electron bandwidths for the transition metals have not been calculated since the value obtained would be in complete disagreement with the actual bandwidths since the d electrons are known to be tightly bound. The cellular calculations for the transition metals are also unreliable since they are only qualitative values obtained by Slater by extrapolating Krutter's results for copper. The lithium value has been recalculated by Silverman (28, 29) giving a value of effective mass in closer correspondence with the observed bandwidth.

The calculations show generally good agreement for the first two periods of the table; however, the potassium and calcium bandwidths are closer to the free electron value than that of the Wigner-Seitz calculation, and the work on the transition metals is too sketchy to make any generalizations. It is interesting that the Fletcher and Wohlfarth calculation for nickel gives a bandwidth just one-half the value of that obtained by Slater using the cellular method. If similar results were to be expected for potassium and calcium using the Bloch perturbation method the bandwidths would correspond much more closely with the experimental values. It is not immediately obvious why the Bloch
Table 5
Summary of Band Emission Data and Theoretical Calculations
(All energies given in electron volts.)

<table>
<thead>
<tr>
<th>Metal</th>
<th>No. of Valence Electrons</th>
<th>Free Electrons</th>
<th>Bloch Pert.</th>
<th>Bandwidth Cellular</th>
<th>Obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1</td>
<td>4.7</td>
<td>-</td>
<td>3.1a</td>
<td>3.7 ± 0.5</td>
</tr>
<tr>
<td>Be</td>
<td>2</td>
<td>14.3</td>
<td>-</td>
<td>11.8b</td>
<td>13.8 ± 1.0</td>
</tr>
<tr>
<td>Na</td>
<td>1</td>
<td>3.2</td>
<td>-</td>
<td>3.2c</td>
<td>2.5 ± 0.3</td>
</tr>
<tr>
<td>Mg</td>
<td>2</td>
<td>7.2</td>
<td>-</td>
<td>-</td>
<td>6.2 ± 0.3</td>
</tr>
<tr>
<td>Al</td>
<td>3</td>
<td>11.7</td>
<td>13.0</td>
<td>-</td>
<td>11.8 ± 0.5</td>
</tr>
<tr>
<td>K</td>
<td>1</td>
<td>2.1</td>
<td>-</td>
<td>3.6a</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>Ca</td>
<td>2</td>
<td>4.3</td>
<td>-</td>
<td>5.0e</td>
<td>3.0 ± 0.2</td>
</tr>
<tr>
<td>Ti</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>1.8f</td>
<td>5.6 ± 0.5</td>
</tr>
<tr>
<td>Va</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>2.5f</td>
<td>5.6 ± 0.5</td>
</tr>
<tr>
<td>Cr</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>3.1f</td>
<td>6.3 ± 0.5</td>
</tr>
<tr>
<td>Mn</td>
<td>7</td>
<td>-</td>
<td>-</td>
<td>3.7f</td>
<td>6.0 ± 0.5</td>
</tr>
<tr>
<td>Fe</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>4.3f</td>
<td>4.4 ± 0.5</td>
</tr>
<tr>
<td>Co</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>4.6f</td>
<td>5.8 ± 0.5</td>
</tr>
<tr>
<td>Ni</td>
<td>10</td>
<td>-</td>
<td>2.4g</td>
<td>4.9f</td>
<td>4.7 ± 0.5</td>
</tr>
<tr>
<td>Cu</td>
<td>1 (?)</td>
<td>7.1</td>
<td>-</td>
<td>7.3h</td>
<td>7.0 ± 0.5</td>
</tr>
<tr>
<td>Zn</td>
<td>2 (?)</td>
<td>9.5</td>
<td>-</td>
<td>-</td>
<td>11.0 ± 0.5</td>
</tr>
</tbody>
</table>

Note: Observed bandwidths are taken from Skinner: Phil. Trans. Roy. Soc. A239, 95, 1940 for Li to Al; from this report, for K and Ca; and the remainder from the Skinner manuscript.

c. J. C. Slater, Phys. Rev. 45, 794, 1934
d. M. F. Manning, H. M. Krutter, Phys. Rev. 51, 761, 1937
g. G. C. Fletcher, E. P. Wohlfarth, Phil. Mag. 42, 106, 1951

calculation gives a bandwidth corresponding to much tighter binding than the cellular method. It may be that the presence of a 3d level with energy very close to the 4s energy, and yet a mean radius corresponding to that of the 3p level, introduces
complications not taken into full account in the cellular method. As mentioned in the analysis of Sec. IV the Bloch scheme seems to take a much more accurate account of exchange interactions. Slater (30) has proposed an intermediate method of calculating the interaction potentials and a trial calculation is being carried out by R. H. Parmenter to determine the validity of this approach. The idea is to modify the Hartree-Fock equations in such a way that the potential seen by the electron is somewhere between the extreme of the Bloch method where neighboring cells are assumed to contain no valence electrons and the cellular method where the neighboring cells are treated as electrically neutral.

Appendix

Supplementary Instrument Information

a. Electron Gun and Power Supply: Figure A1 is a construction drawing for the electron gun. The electrodes numbered 1 and 2 are shaped to correspond to the calculated curves given by Pierce (Ref. 20, p. 171). The cathode is mounted according to a technique described by Stone (31). The method consists of platinum welding a narrow strip of tantalum to each end of the cathode strip. The material used in this work was obtained from the Raytheon Manufacturing Company.

Fig. A1
Electrode design for electron gun.
Figure A2 is the power supply for the electron gun. For optimum focusing with this electrode configuration it was found that the focusing electrode P₂ should be operated at approximately three times the bombardment potential. A typical set of values for satisfactory focus was found to be P₁, -90 volts; K, 0; P₃, D⁺ and D⁻, 300; and P₂, 900 volts. The target current could be varied from 0 to 8 ma for these values of voltage. Since the intensity of radiation is an extremely sensitive function of the bombardment voltage, it was found necessary to incorporate the bank of voltage regulator tubes shown in the schematic. The switches served to short out specific tubes so that the target potential could be varied from 75 to 575 volts in steps of approximately 25 volts.

b. Photomultiplier Circuits: The high voltage supply for the photomultiplier is a standard half-wave rectifier with RC filtering. In this equipment the negative side of the supply, which is connected to the photosensitive cathode, is grounded to the apparatus. The counting-rate meter is shown schematically in Fig. A3. The terminal marked EA is the connector for the Esterline-Angus Recording Milliammeter. This unit was designed by Mr. Emil DeAgazio of the Laboratory for Nuclear Science and Engineering at M.I.T. The details of its operation are given in Elmore and Sands (24).

Figure A2
Electron gun power supply.

Figure A3
Schematic diagram: counting-rate meter.
Acknowledgment

The work described in this report was given its original stimulus and guidance by Dr. E. R. Piore while on leave of absence from the Office of Naval Research, and the original design and initial construction of the spectrograph were undertaken by him and the staff of the Research Laboratory of Electronics at M.I.T. The author is also grateful to Professor G. G. Harvey, who supervised the research program; E. M. Gyorgy, who assisted in the experimental work; and Professors J. C. Slater and L. Tisza who, with the members of the solid state theory group in the Physics Department, contributed many helpful ideas and suggestions.

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17. J. S. Allen: R.S.I. 18, 739, 1947
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Z. Matyas: The Energies of Electrons in Aluminum, Phil. Mag. 39, 429, 1948
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-28-
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