

## The Energy Distribution of Secondary Electrons from Molybdenum

LELAND J. HAWORTH, *Department of Physics, University of Wisconsin*

(Received April 15, 1935)

Energy distribution curves of secondary electrons from a thoroughly outgassed molybdenum target have been obtained by magnetic analysis with primary electron energies up to 150 volts. In addition to the usual sharp "elastically reflected" peak and the broad, low energy maximum, other maxima and irregularities appear which may be classified as follows: (1) peaks at energies 10.6, 22 and 48 volts less than the primary energy which are due to critical energy losses among the inelastically scattered electrons; (2) "humps" in the curves at secondary energies

of 11, 24 and 35 volts, independent of the primary energy. The number of elastically reflected electrons is plotted as a function of primary energy. This curve exhibits several maxima, some of which are correlated with the "critical potentials" giving rise to the peaks of type (1). Others are due to electron diffraction. A discussion of possible applications of modern metallic theories to the present results is given. Two of the peaks of type (1) and all of those of type (2) are tentatively accounted for.

NUMEROUS investigators<sup>1-6</sup> have studied the distribution in energy of secondary electrons emitted by a metal surface when bombarded by a narrow, homogeneous beam of primary electrons. In many of these experiments, however, the specimen did not receive the rigorous heat treatment which photoelectric and thermionic studies indicate is necessary to obtain a comparatively clean surface. For this reason and others the present investigation was undertaken with the intention of studying a metal as free from gas and other impurities as modern vacuum technique will allow.

The energy distribution of secondary electrons from numerous samples of thoroughly outgassed molybdenum was determined by the method of magnetic analysis. The targets used were arranged so that it was possible to make observations with the specimen at high temperatures, the assumption being made that under such conditions the surface would be relatively cleaner than at room temperature. This rendered the use of single crystals not feasible.

The molybdenum used was obtained from two sources, the Elkton Company and the Fansteel Products Company, and in both cases was stated to be extremely pure. No essential differences were detected in the results obtained from samples from the two sources.

<sup>1</sup> H. E. Farnsworth, *Phys. Rev.* **25**, 41 (1925); **31**, 405 (1928).

<sup>2</sup> C. F. Sharman, *Proc. Camb. Phil. Soc.* **23**, 523 (1927); **23**, 922 (1927).

<sup>3</sup> E. Rudberg, *Proc. Roy. Soc.* **A127**, 111 (1930).

<sup>4</sup> T. Soller, *Phys. Rev.* **36**, 1212 (1930).

<sup>5</sup> J. B. Brinsmade, *Phys. Rev.* **30**, 494 (1927).

<sup>6</sup> P. Tartakowsky and W. Kudrjawzewa, *Zeits. f. Physik* **75**, 137 (1932).

### APPARATUS AND PROCEDURE

Primary electrons from the oxide coated filament  $F_1$  (Fig. 1a) traversed the slits of the electron gun and were incident at a  $45^\circ$  angle on the target  $T$ . Secondary electrons in the direction of specular reflection passed through the narrow slit  $S_5$  and, under the influence of a uniform magnetic field furnished by a large pair of Helmholtz coils, those of the desired velocity traversed the analyzer  $A$  (Fig. 1b) and passed into the Faraday collector  $C$ . As the path of the primary electrons was along the axis of the field they were undeflected. Primary electrons not striking the target were trapped in the grounded cylinder  $W$ .

The electron gun was adapted from a model described by Farnsworth<sup>7</sup> and was in three sections for reasons to be discussed later. A magnetically operated shutter  $L$  could be placed in front of  $F_1$  when not actually making observations in order to reduce possible contamination of the target from this source, particularly during the early heating of  $F_1$ . It might be mentioned in this connection that on two occasions tungsten filaments were used in place of the oxide coated type with no apparent change in the results obtained.

The analyzer, remodelled from the one previously used by Soller,<sup>4</sup> was of such dimensions as to give a high resolving power ( $dV=0.006 V$ ).

Most of the targets used were heated by conduction. They consisted of strips of molybdenum 2.5 mm wide and 0.03 mm in thickness bent into hairpin form and held in position at the bent end by a slight tension provided by a weak tungsten

<sup>7</sup> H. E. Farnsworth, *J.O.S.A. and R.S.I.* **15**, 290 (1927).

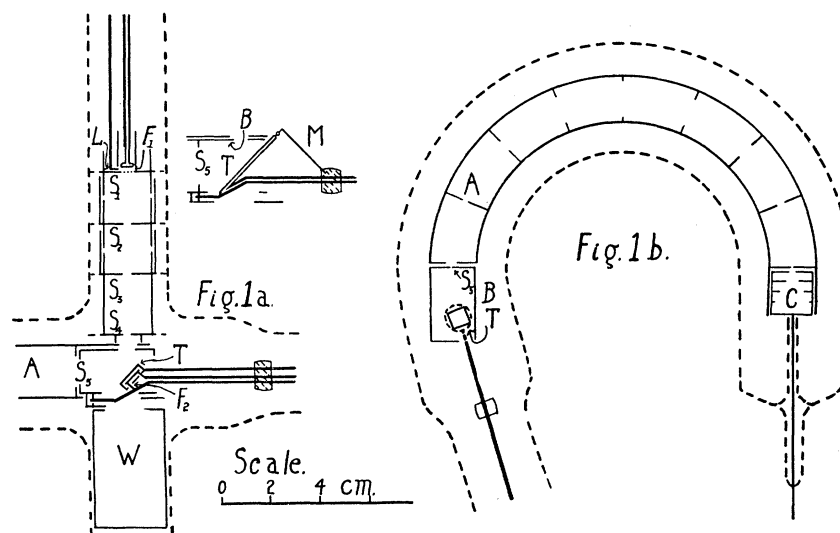


FIG. 1. Experimental apparatus.

spring  $M$  (Fig. 1a, inset). Considerable difficulty was experienced from breaking of these filaments at high temperatures because of the tension necessary for exact alignment.

A later and more satisfactory form of target (subsequently referred to as "heater target") consisted of a small cylinder of sheet molybdenum enclosing a non-magnetic pancake filament  $F_2$  of tungsten. The target proper was a thin foil (0.03 mm) of molybdenum mounted on the end of the cylinder and backed by a heavier piece of the same material. The target could be maintained at a temperature of 1400°K by radiation alone during the making of observations and could be heated to any desired temperature by electron bombardment for outgassing purposes. It was found experimentally that the use of alternating current eliminated (by an averaging process) the effect of the very slight magnetic field.

All metal parts of the apparatus were of molybdenum and tungsten with the exception of the small iron armature controlling  $L$ . They were enclosed in a Pyrex tube of the shape indicated by the dashed lines of Fig. 1.

The pumping system consisted of a water-cooled mercury diffusion pump backed by a Cenco Hyvac. Two liquid air traps were placed in series between the research tube proper and the diffusion pump, and a third between the latter

and the Hyvac. Pressures were measured by a McLeod gauge and an ionization gauge of sensitivity  $4 \times 10^{-9}$  mm Hg per mm deflection of the accompanying galvanometer.

Electrical connections were as follows. The target, the box  $B$  surrounding the target, and the analyzer were grounded through a galvanometer, thus affording a measure of the primary current. Switches were so arranged that the current to each could be measured separately. The primary filament was maintained at a negative potential determined by the desired energy of the primary electrons. The grid  $S_1$  was 4.5 volts positive with respect to this filament;  $S_3S_4$  was grounded; and  $S_2$  was held at that potential, usually ground, which gave the maximum current to the target. This arrangement served to give a quite homogeneous beam, which was due in part to the elimination of secondary electrons from the first grid, and in part to a narrower thermal distribution than would have been the case had the entire accelerating potential been applied to this grid. The focusing action of the field between  $S_1$  and  $S_2$  helped compensate for a loss of intensity because of space charge saturation in the region of the cathode. By means of a two-position switch a retarding potential could be applied to  $S_2$ , completely stopping the primary beam and affording a method of obtaining the zeros of the various indicating instruments.

Currents to the collector  $C$  were amplified by an FP54 vacuum tube circuit of maximum sensitivity  $2.5 \times 10^{-16}$  amperes per mm deflection of the indicating galvanometer.

After assembly the tube was baked at a temperature of  $500^\circ\text{C}$  for more than 500 hours, the process being repeated whenever it was necessary to admit air into the system. The furnaces were then removed and special heat treatment of the target begun, the temperature being raised as rapidly as possible without allowing the pressure to rise to too high values. Ultimate outgassing temperatures varied for different specimens. In the case of the heater target the degassing period extended over 3500 hours, the greater part of the last 1000 hours of heating being at temperatures well in excess of  $2100^\circ\text{K}$ . On removal the target was found to be firmly welded to its molybdenum backing. Pressures at the end of the degassing period were of the order  $2 \times 10^{-8}$  mm Hg when the specimen was cold and  $3$  to  $4 \times 10^{-8}$  mm Hg when it was hot. From the behavior on heating and cooling it is believed that the difference was due to gas evolved from the surrounding metal parts (which achieved a bright red temperature) rather than from the target itself.

An analysis of the thermions emitted when the specimen was hot placed the contact potential between a clean target and the analyzer at about 0.8 volt. Application of this correction to the secondary energies just sufficed to make the distribution curves pass through the origin. This contact potential apparently increased by about one volt when the target was exposed to residual gas for a few hours (Fig. 4, curve  $e$ ).

### RESULTS

Typical distribution curves for three different primary energies are shown in Fig. 2, curves  $a$ ,  $b$  and  $c$ . Abscissae are secondary energies in volts and ordinates are  $(K \cdot I_s)/(I_p \cdot E_s)$ , where  $K$  is a constant,  $I_s$  is current to the collector  $C$ ,  $I_p$  is the primary current, and  $E_s$  is the secondary energy. Division by  $E_s$  is necessary to correct for variable dispersion across the analyzer slits. These results were obtained (as were those of Figs. 3, 4, 5) at the end of the 3500 hour degassing period, the target being at a temperature of  $1400^\circ\text{K}$ . Results obtained before outgassing were somewhat similar but the secondary currents were much larger,

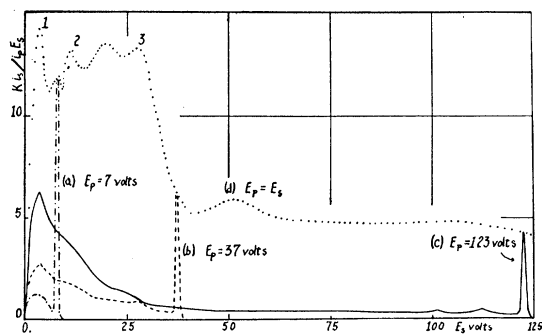


FIG. 2.  $a$ ,  $b$ ,  $c$ , typical distribution curves.  $d$ , full velocity curve. Experimental points are indicated in curve  $d$ .

particularly at very low secondary energies. The general form of the curves of Fig. 2 agrees with the results of other observers.

The high, sharp peak at the high energy end of each distribution curve is due to the so-called "full velocity" or "elastically reflected" electrons, the latter name being given in recognition of the generally accepted belief that they are primary electrons which have been reflected from the target without appreciable loss of energy. Secondary electrons of lower energies are generally assumed to be of two types; "inelastically reflected" electrons; and "true secondary" or "emitted" electrons, i.e. metallic electrons which have received sufficient energy from the primary beam to allow them to escape. The existence of the latter type is proved by the fact that at sufficiently high primary energies the total number of secondaries exceeds that of the primaries.<sup>8</sup> It is generally believed that the large group of secondaries at low energies is composed principally of emitted electrons; that electrons of energies slightly less than the primary energy are mostly inelastically reflected electrons; and that both types are present at intermediate energies.

As previously reported by the author,<sup>9</sup> the distribution curves exhibit a certain fine structure which may be classified under two main headings.

<sup>8</sup> See, for example, P. L. Copeland, Phys. Rev. **46**, 167 (1934).

<sup>9</sup> L. J. Haworth, Phys. Rev. **37**, 93 (1931); **42**, 906 (1932). Later work has somewhat modified the results reported in the first of these two references. The discrete loss peak then found at a loss of 4.7 volts was made to disappear with further outgassing. The positions of the remainder have been more exactly determined. The absence of very low energy secondaries when the target was cold was found to be due to a charging up of the slits of the analyzer. Soller's results<sup>4</sup> were also in error at low energies for this reason.

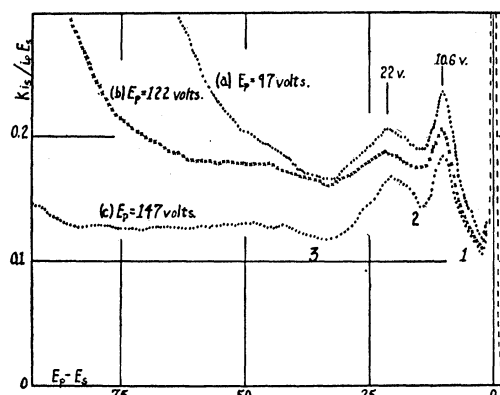


FIG. 3. Discrete loss peaks. Experimental points are indicated.

(1) In all cases of sufficiently high primary energy, peaks were present in the distribution curves at energies 10.6, 22 and (approximately) 48 volts less than that of the primary electrons (Fig. 3). The first two covered relatively narrow ranges of energy but the third formed part of a wide band extending from an energy about 36 volts less than the primary energy down to a point somewhere near half of the latter. Although these maxima were not at all marked before outgassing the specimen, a hundred or so hours of heat treatment were sufficient to bring them to almost their full prominence. Additional slight "humps" sometimes appeared at energies approximately 17, 31, 43, 66 and 76 volts less than the primary energy but the evidence on this point is not conclusive.

Peaks similar to those just discussed have been observed by Rudberg<sup>3</sup> for various metals. As he has pointed out, they are undoubtedly due to the presence of groups of inelastically reflected electrons which have suffered discrete losses of energy in the process of reflection.

(2) Irregularities in the curves indicate the presence at low secondary energies of a selective emission which is independent of the primary energy. This type of fine structure is illustrated by Fig. 4, in which the scales of ordinates of curves *b*, *c* and *d* have been multiplied by the proper factors to make these curves coincide with curve *a* at a secondary energy of 4 volts. In the energy regions centering about 11, 24 and 35 volts the number of secondaries is abnormally large. This phenomenon was not apparent before several hundred hours of outgassing and in all cases dis-

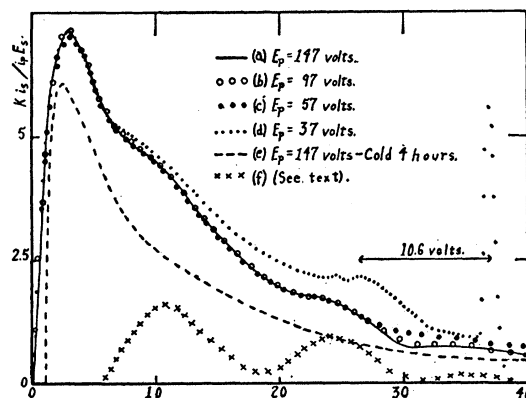


FIG. 4. Low energy secondaries. Ordinates of *b*, *c*, *d*, multiplied by factor to give coincidence with *a* at a secondary energy of 4 volts. *f* represents difference between *a* and extrapolated background. Experimental points are indicated in curves *b*, *c*, *d*, *f*.

appeared entirely after a few hours exposure to residual gas (Fig. 4, curve *e*). As is shown by the near coincidence of curves *a*, *b* and *c* the positions and relative magnitudes of these irregularities are practically independent of the primary energy, provided the latter is sufficiently high. In order to study the effect more closely the background of a given distribution curve was extrapolated through the energy ranges of the irregularities and the differences in ordinates between this curve and the experimental curve were plotted on a much larger scale of ordinates. Curve *f*, Fig. 4 was obtained from curve *a* in this manner.

This type of selective emission has not, to the author's knowledge, been previously observed.

It is seen that the distribution curves of Fig. 4 practically coincide over the range of secondary energies from zero to 25 volts for all primary energies of 60 volts or more. The coincidence of the curves for high primary energies in a measure justifies the assumption that the low energy group of secondaries is in such cases made up almost entirely of emitted electrons. As the primary energy is decreased, however, the successive curves are no longer coincident, but diverge rapidly at the higher secondary energies. This is undoubtedly due to the presence of relatively larger numbers of inelastically reflected secondaries of low energies as the primary energy is decreased. For example, the 10.6-volt discrete loss peak is distinctly observable at 26.4 volts in curve *d*.

As molybdenum apparently adsorbs residual gas very quickly even at relatively high tempera-

tures it was felt that perhaps the temperature at which most of the observations were taken (1400°K) was not high enough to assure an absolutely clean surface. For this reason much data was taken under the following conditions. Before each observation the heater target was heated by electron bombardment to a temperature of about 2200°K over a period of 30 seconds. The bombarding potential was then removed, the filament remaining hot, and an observation taken 15 seconds later. That the target was still much above 1400°K was shown by the larger number of thermions being emitted than was the case at that temperature. 15 seconds more were required to obtain instrument zeros, after which bombardment in preparation for the next observation was begun.

Results obtained in this way were not essentially different from those obtained by the usual method. The secondaries were somewhat more numerous and on some occasions the discrete loss peaks were slightly more prominent. The curves were rather irregular because of the rapidly changing conditions under which observations were taken. Curve *a*, Fig. 3, and curve *a* Fig. 4, were obtained in this manner.

### Full velocity secondaries

A careful study of a number of the full velocity peaks was made. From their form, together with the calculated slit dispersion, second order dispersion corrections were worked out so that it was possible to compute the area under any peak and hence the number of full velocity secondaries from the observed maximum current to the collector. Observations of this type were taken at close intervals of primary energy from zero to 120 volts, the results for the heater specimen being plotted in curve *d*, Fig. 2.

The principal features of this curve are the relative scarcity of full velocity secondaries at primary energies just greater than zero and the great decrease in their number as the primary energy is increased beyond 30 volts. In addition a number of maxima and minima are present. The positions of the maxima were in approximate agreement for the various specimens, although one or two were sometimes missing. The energies and relative magnitudes of the various maxima are summarized in Table I, the data being from the three most completely outgassed specimens.

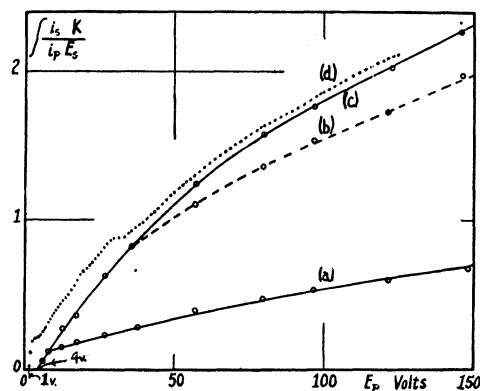


FIG. 5. Integration of distribution curves as functions of primary energy. Curve *a*, integration limits zero to 10 volts (secondary energy); curve *b*, zero to 35 volts; curve *c*, zero to  $E_p - 4$  volts; curve *d*, all secondaries included.

TABLE I. Energies and relative magnitudes of the various maxima. Intensities *I* range from 5 (very strong) to 1 (very weak). Specimen No. 1, outgassed 1000 hrs.; No. 2, 2500 hrs.; No. 3, 3400 hrs. Average values of  $E_p$  are weighted.

	$E_p$	<i>I</i>	$E_p$	<i>I</i>	$E_p$	<i>I</i>	$E_p$	<i>I</i>	$E_p$	<i>I</i>	$E_p$	<i>I</i>	$E_p$	<i>I</i>
No. 1	3.3	5	14.5	3	21.5	3	29.5	3	51.5	2	No data taken			
No. 2	3.8	3	7.8	2	13.0	4	21.5	2	28.5	1	50.0	2	78.5	2
No. 3	3.5	3	7.5	2	11.5	3	20.0	3	28.5	2	51.0	4	101	1
Aver.	3.6		7.6		12.0		20.8		28.8		50.7		78.5	101

### Integration of distribution curves

The total number of secondary electrons (per primary electron) in any given range of energy could be determined by measurements of the areas under the distribution curves. The results of such integrations are plotted as functions of primary energy in Fig. 5, the various curves representing integrations over different ranges of secondary energy.

No secondary electrons of any energy were observed when the primary energy was less than one volt. For primary energies less than 4 volts\* only full velocity secondaries appeared. At higher primary energies the secondaries covered the whole energy range from zero up to the energy of the primaries. The number of secondaries in each energy range increased steadily with increasing primary energy, the greatest increase being at low secondary energies. That curves *c* and *d* rise

\* Throughout this paper the primary energies given have been corrected for the contact potential between the cathode and the target. This correction amounted to three volts so that, for example, the value of four volts at which slow secondaries first appeared corresponded to a reading of seven volts on the voltmeter indicating the primary energy.

more rapidly than  $b$  is because of their wider integration limits. The general form of curve  $d$  is similar to that given by Petry<sup>10</sup> and others who have plotted the (total secondary)/(total primary) ratio, including all directions of emergence. The irregularities are not, however, of the same nature. This may be because of their integration over all directions. A more likely explanation is, however, the fact that only a few primary energies were used in obtaining curve  $c$  and that curve  $d$  was built from curve  $c$  by adding the areas of many full velocity peaks to the ordinates of a smooth curve drawn through the few experimental points of curve  $c$ . Thus the fine structure of curve  $d$  is not necessarily correct.

#### DISCUSSION

Various theoretical studies<sup>11</sup> have shown that in a metal lattice the tightly bound "atomic" electrons behave almost identically as in an isolated atom but that the energy spectrum at the higher energies characteristic of the "valence" or "free" electrons is markedly different. For a given direction of motion in the crystal the allowed states lie in bands with forbidden intervals between. When all directions of motion are considered the bands overlap so that no energies are absolutely forbidden but, as Kronig<sup>12</sup> has shown, certain energies are much more probable than others.

The situation in an ideal one-dimensional crystal is shown in Fig. 6. The dashed lines represent the potential field which approaches the value indicated by the line  $AA$  at an infinite distance from the crystal. The "conduction" or "free" electrons distribute themselves among the lower states of band 1 in accordance with a normal Fermi distribution so that, since there are two allowed states per atom in each band, half of the states in the first band will be occupied in a monovalent metal. The energy spread  $W_i$  among the filled levels at 0°K is given by a well-known formula of Sommerfeld. The situation in molybdenum is somewhat complicated by the fact that in the free atom there is not a closed shell inside the valence shell so that the number of "free" electrons is not definitely known. If, however, we

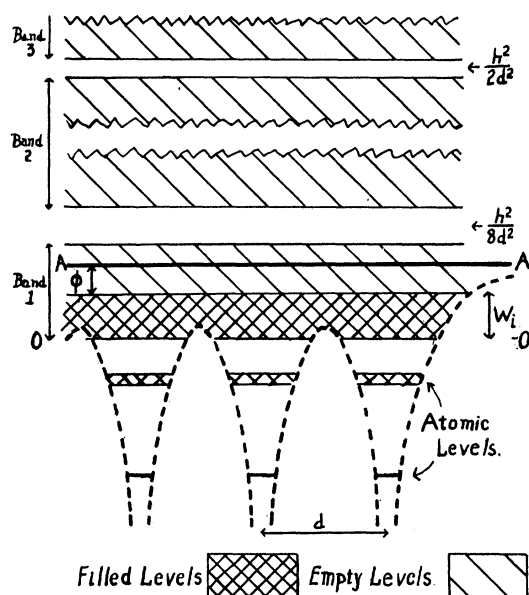


FIG. 6. Energy levels in an idealized crystal.  $d$  is the spacing between atoms.

assume one such per atom we get  $W_i = 5.9$  volts. The additional energy necessary to allow the highest energy conduction electron to escape from the metal is the thermionic work function  $\phi$ . According to DuBridge<sup>13</sup>  $\phi = 4.15$  volts for molybdenum.

Three types of secondary electrons are possible in addition to the elastically reflected primaries. They are: (1) inelastically reflected primaries; (2) emitted "free" or "conduction" electrons; and (3) emitted atomic electrons. We are thus interested on the one hand in the processes by which the primary electrons may lose energy and on the other hand in the processes by which electrons within the metal may absorb sufficient energy to escape.

#### Elastically and inelastically reflected electrons

Primary electrons may lose energy to either the atomic or the free electrons. Energy absorbed by an atomic electron will result in its ejection from the atom, giving rise to the excitation of soft x-rays. The energy transferred in such a process must be not less than that necessary to enable the ejected electron to occupy the lowest vacant conduction level. Froehlich<sup>14</sup> has studied the excitation of free electrons by primary electrons

<sup>10</sup> R. L. Petry, Phys. Rev. **26**, 346 (1925).

<sup>11</sup> See J. C. Slater, Rev. Mod. Phys. **6**, 209 (1934) for a complete bibliography.

<sup>12</sup> R. de L. Kronig, Zeits. f. Physik **75**, 191 (1932).

<sup>13</sup> L. A. DuBridge, Phys. Rev. **42**, 52 (1932).

<sup>14</sup> H. Froehlich, Ann. d. Physik **13**, 229 (1932).

for a rather simple model. He has found that certain selection rules require that the excited electron be lifted to at least the second allowed energy band and that the most probable transitions are those to the second band. Kronig and Penney<sup>15</sup> have obtained the same result in the case of excitation by radiation. Thus there seems to be a minimum to the energy which one of these electrons may absorb, but on the other hand few of them have very high energies after excitation.

Whatever the process, then, there is apparently a more or less definite lower limit (call it  $W_{\min}$ ) to the energy which a primary electron can lose, so that no inelastically reflected secondaries should appear at energies greater than  $E_p - W_{\min}$ . This probably accounts for the sharp minimum just before the full velocity peak in the curves of Fig. 3.

The sharpness of the discrete loss peaks indicates that the banded structure of the upper energy levels is playing an important role. Excitation of the conduction electrons could give rise to such peaks only if some sort of selection rules or discontinuous transition probabilities such as those of Froehlich govern the process. Furthermore the ejection of atomic electrons would account for sharp edges only on the low loss sides of the discrete loss peaks unless transitions to the upper conduction levels are somewhat discontinuous. Kronig<sup>12</sup> has explained the fine structure of x-ray absorption spectra by assuming that this is the case.

A definite relationship exists between the irregularities of Fig. 3 and certain of those of the full velocity curve ( $d$  of Fig. 2). This is to be expected. As the primary energy is increased from zero the number of elastically reflected electrons should suffer sharp decreases at energies just sufficient to give rise to the processes responsible for the discrete loss peaks. That is, there should be a sort of critical potential effect. A primary electron may surrender up to  $E_p + \phi$  volts of energy and still be able to occupy one of the unfilled conduction levels. In Table II values for this expression corresponding to various points  $E_c$  at which curve  $d$ , Fig. 1, "breaks" downward are listed together with the lowest energy losses  $E_1$  found in the different discrete loss peaks. In

<sup>15</sup> R. de L. Kronig and W. G. Penney, Proc. Roy. Soc. **A133**, 255 (1931).

TABLE II.

	1	2	3
$E_c$	3.6	12.0	28.8
$E_c + \phi$	7.8	16.1	33.0
$E_1$	7.5	17.0	35.0
$E_{x\text{-ray}}$	$\left\{ \begin{array}{l} 4.5(N_{IV, v}) \\ 5.5(Y_{II}) \end{array} \right\}$	23.3( $Y_I$ )	38.2( $N_{II, III}$ )

computing the latter account was taken of the nonhomogeneity of the primary beam and the imperfect resolving power of the analyzer. The term values of the lowest x-ray states are listed in line 4 for comparison. These are taken from Siegbahn<sup>16</sup> and were determined from measurements of the  $L$  and  $M$  emission spectra. The  $Y_I$  and  $Y_{II}$  term values probably represent multiple excitations. The  $N_{IV, v}$  and  $Y_{II}$  values seem too low to be consistent with our calculated value of  $W_i$  but this may arise from inaccuracies in their determination because of the rather indirect way in which they were measured. It is seen that the agreement between  $E_c + \phi$  and  $E_1$  is good and that in cases one and three the x-ray term values are sufficiently close to the experimental values to make it seem likely that it is the excitation of these levels which is responsible for the irregularities in question. Thus the large decrease in the number of elastically reflected electrons as the primary energy is increased beyond 30 volts seems to represent a sort of absorption edge for the  $N_{II, III}$  x-ray states.

The phenomenon of electron diffraction may also enter into the results represented by the full velocity curve. This is merely another way of saying that when a primary electron has a momentum component perpendicular to some set of net planes of a crystal of such a value that the corresponding energy falls in one of the forbidden bands, the electron will be specularly reflected from that set of net planes. Simple assumptions indicate that in the present case maxima arising from this cause should appear in the full velocity curve at energies given by

$$E_{p(\max)} = (75 n^2/d^2) - 2W_a$$

where  $n$  is an integer,  $d$  is the spacing between Bragg planes and  $W_a + E_p$  is the energy which the electron possesses within the crystal. Calculated values for this expression are listed in the first

<sup>16</sup> M. Siegbahn, Zeits. f. Physik **88**, 559 (1934).

TABLE III.

$E_{\text{theor.}}$	10.1	25.4	40.6	55.8	86.0	101.3
$E_{\text{exp.}}$	7.6	20.2	—	50.7	78.5	101
Difference	2.5	5.2		5.1	7.5	0.3

line of Table III, where we have assumed a value for  $W_a$  given by  $W_a = \phi + W_i = 10.05$  volts. In the second line are listed values from Table I which seem to correspond. If this interpretation is correct our value for  $W_a$  seems somewhat too small.

It is probable that both "critical potential" and electron diffraction effects influence the number of full velocity secondaries but whether or not the assignments we have made are correct is problematical.

### Emitted electrons

The emitted electrons may receive their energy directly from the primary electrons or there may be some intermediate process such as the photoelectric action of soft x-rays. In either case it is to be expected on general grounds that the energies of most of the emitted electrons will be low. This is true in the case of electrons ejected from isolated atoms by either electrons or radiation and the results of Froehlich<sup>14</sup> and Kronig and Penney<sup>15</sup> indicate that fairly low energies are most probable among excited conduction electrons.

The large, low energy group of emitted electrons covers a range of energies which is approximately the same as the range of energy which includes most of those electrons which can with certainty be classed as inelastically reflected. This would seem to indicate that most of the emitted electrons originated in the conduction levels as somewhat greater energy transfers would be necessary to give rise to emitted atomic electrons.

The relative scarcity of secondaries at energies just above zero may be the result of a high internal reflection coefficient for very slow electrons; or it may be possible that such energies are improbable because of the banded structure of the allowed states.

Fig. 5 shows that when the primary energy is less than about 4 volts, only elastically reflected secondaries are observed. This may be explained as follows. We have seen that most inelastically reflected electrons have lost at least 7.5 volts of energy. Thus they cannot escape unless the pri-

mary energy is greater than this value. Furthermore, in order to have appreciable excitation it is necessary that the primary energy available for that purpose be greater than  $W_{\text{min}} = 7.5$  volts. Thus, in order to have any emitted electrons it is necessary that  $E_p + \phi \geq 7.5$  volts, or  $E_p \geq 3.35$  volts, not far from the experimental value mentioned above.

The fixed energy groups may be a result of the irregular density of the allowed energy states above the filled conduction levels. That is, if the number of states is particularly large in a certain energy range, one should expect a large number of secondaries at the corresponding energies. Measurements by Zinn<sup>17</sup> on the fine structure of x-ray absorption spectra for molybdenum indicate, according to Kronig's<sup>12</sup> interpretation, that transitions to states in the regions near 14, 41 and 79 volts above the highest unoccupied conduction level are unusually numerous. Measured from the same origin our first and third fixed energy groups would be centered around 15 and 39 volts, in good agreement with two of Zinn's values. The presence of the discrete loss groups precluded the possibility of determining whether an additional fixed energy group existed in the neighborhood of 79 volts.

It is possible to account for the 24-volt fixed energy group by an entirely different process. We have seen that it seems likely that the  $N_{\text{II, III}}$  x-ray levels are strongly excited. Transitions of the type  $N_{\text{IV, V}} \rightarrow N_{\text{II, III}}$  would give rise to x-rays of energy 33.7 volts (or somewhat less if, as previously suggested, the  $N_{\text{IV, V}}$  term value listed is too low). Photoelectrons ejected by this radiation would have energies between  $33.7 - (\phi + W_i)$  and  $33.7 - \phi$  or, roughly, between 23.5 and 29.5 volts, thus accounting, perhaps, for the 24-volt fixed energy group.

It is thus possible to find reasonable explanations for most of the experimental results. However, both theory and experiment are as yet too incomplete to render these explanations anything but tentative. The experimental work is being continued on other metals.

It is a pleasure to express my sincere thanks to Professor C. E. Mendenhall who suggested the problem and who has given generously of his time during the progress of the work.

<sup>17</sup> W. H. Zinn, Phys. Rev. **46**, 659 (1934).